Copolymerization of Ethylene with Methyl Methacrylate with Neutral Nickel(II) Complexes Bearing *β*-Ketoiminato Chelate Ligands

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New neutral nickel(II) complexes bearing asymmetric *β*-ketoiminato (N,O) ligands (**5a**−**c**), [(2,6-$^{i}Pr_2C_6H_3$)NC(R_2)C(H)C(R_1)O]Ni(Ph)(PPh_3), have been synthesized. X-ray crystal structures reveal that each of complexes **5a**−**c** adopts a near square-planar coordination geometry and the triphenylphosphine group is always trans to the arylamine group. With modified methylaluminoxane (MMAO) as a cocatalyst, complexes **5a**−**c** can promote the polymerization of methyl methacrylate (MMA) in excellent yields (>98%), producing syndiotactic-rich PMMAs (*rr* around 70%). It is very exciting that the **5a**−**c**/MMAO catalyst systems exhibit highly catalytic activities for the copolymerization of ethylene with MMA, producing high molecular weight functionalized polyethylenes with up to 16.7 mol % of methacrylate units built into the moderately branched polyethylene backbone. Further mechanistic studies have shown that PMMAs and copolymers obtained using these complexes possibly arise from a coordination−insertion mechanism rather than a radical mechanism.

Introduction

Functionalized polyolefins, obtained by the copolymerization of hydrocarbon monomers such as ethylene and propylene with readily available polar monomers such as methyl methacrylate (MMA), acrylates, and vinyl acetate, are excellent polymeric materials in which polar groups exercise control over important properties such as toughness, barrier properties, surface properties, etc.[1] At present, several approaches have been applied to synthesize functionalized polyolefins, while as one of the most appealing targets, obtaining functionalized polyolefins under moderate conditions is never successfully reached by industrial chemical processes.[2] In recent years, the increased interest in development of novel well-defined catalysts capable of copolymerizing hydrocarbon monomers with polar monomers under mild conditions has centered on late transition metal complexes.[3−9] Brookhart and co-workers discovered that α-diimine palladium catalysts can copolymerize ethylene or propylene with methyl acrylate, yielding highly branched copolymers in which the acrylate units are at the branch ends.[10] Grubbs and colleagues subsequently reported the use of neutral salicylaldimine nickel complexes for the copolymerization of ethylene with functionalized norbornene; however, the polar functionality is remote from the vinyl group.[11] Gibson and co-workers described the use of [P,O] nickel catalysts, formed in situ, to produce low molecular weight MMA-terminated polyethylenes.[12] Pugh et al. reported that neutral palladium catalysts, formed in situ, can promote the copolymerization of ethylene with acrylates, yielding copolymers in which the acrylate units are built into the linear polyethylene chain.[13] Carlini et al. introduced nickel salicylaldiminate catalysts, formed in situ, which can copolymerize ethylene with MMA, producing high molecular weight linear copolymers.[2]

Recently we described a series of titanium complexes bearing two asymmetric *β*-ketoiminato (N,O) ligands used as catalysts for the living ethylene polymerization and the living copolymerization of ethylene with norbornene.[14] Using this type of asymmetric *β*-ketoiminato (N,O) ligands, herein we report the synthesis and

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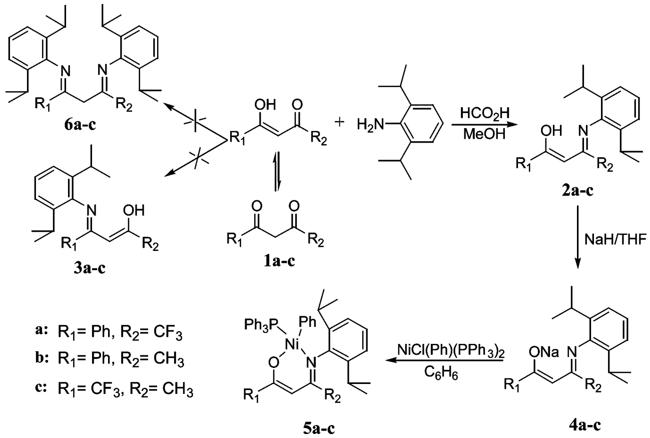
Scheme 1. Synthesis of Neutral Nickel(II) Complexes 5a−c



characterization of the new neutral nickel(II) complexes and their application as efficient catalysts for the polymerization of MMA and the copolymerization of ethylene with MMA under mild conditions in the presence of MMAO.

Results and Discussion

Synthesis and Structure of Neutral Nickel(ii) Complexes Bearing β-Ketoiminato Chelate Ligands. A general synthetic route for the neutral nickel(II) complexes with asymmetric bidentate β-ketoiminato as the ligands used in this study is shown in Scheme 1. The β-ketoimines **2a**−**c** were prepared in good yields (**2a**, 75.6%; **2b**, 92.5%; **2c**, 72.1%) by the condensation of the corresponding β-diketones **1a**−**c** with 2,6-diisopropylaniline in methanol containing a little formic acid as the catalyst. The reasons why the isomeric β-ketoiminates **3a**−**c** cannot be formed may lie in the steric bulk effect between R_1 and the bulky substitute on the N atom in the β-ketoimines **2a**−**c** or the great electron-drawing effect of R_1 (representing an aryl or a trifluoromethyl group), which increases the enol percentage in the β-diketones **1a**−**c**. In the way, the attempt to synthesize β-diimines **6a**−**c** has not succeeded under the same conditions. The sodium salts **4a**−**c** were obtained by the deprotonation of β-ketoimines **2a**−**c** with NaH in tetrahydrofuran (THF). The neutral nickel(II) complexes **5a**−**c** were obtained as dark red solids in good yields (**5a**, 83%; **5b**, 78%, **5c**, 80%) by the corresponding reactions of the sodium salts **4a**−**c** with *trans*-[NiCl(Ph)(PPh_3)$_2$].

According to the ^1H, ^{13}C, and ^{31}P NMR spectra, the neutral nickel(II) complexes with β-ketoiminato ligands (**5a**−**c**), similar to those neutral nickel(II) complexes bearing salicylaldiminate ligands, are diamagnetic and adopt square-planar geometry.[15] The signals of the triphenylphosphine ligands in the ^{31}P NMR spectra of complexes **5a**−**c** were observed between 20.5 and 22.4 ppm.

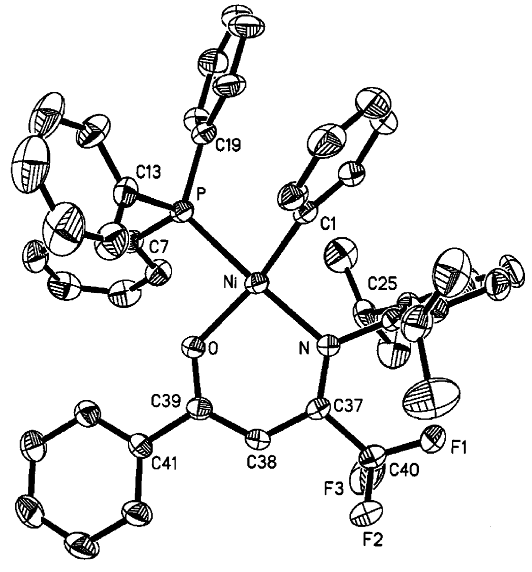


Figure 1. ORTEP drawing of the molecular structure of **5a** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Key atoms are labeled.

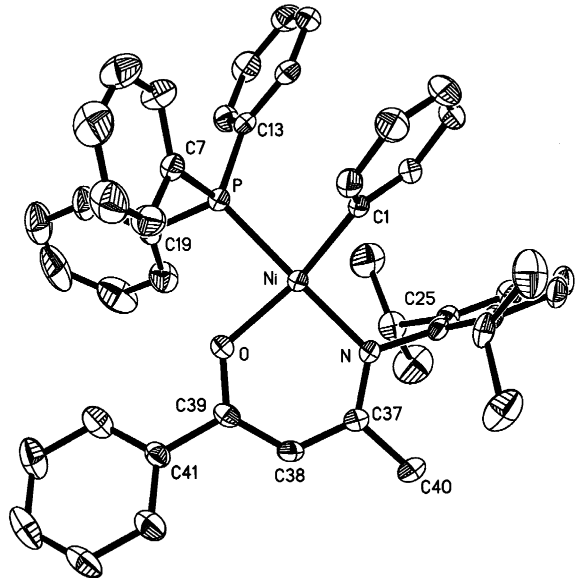


Figure 2. ORTEP drawing of the molecular structure of **5b** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Key atoms are labeled.

The single-crystal X-ray analyses have confirmed the structures of complexes **5a**−**c** (Figures 1−3). The data collection and the refinement data of the analyses are summarized in Table 1, and selected bond lengths and bond angles are listed in Table 2. In the solid state, each of complexes **5a**−**c** adopts a near square-planar coordination geometry, and the triphenylphosphine group is always trans to the arylamine group, just as the Grubbs' catalysts, because of the steric effect of N-aryl and triphenylphosphine groups. The difference among the Ni−C1 bond lengths of the neutral nickel(II) complexes (**5a**, 1.910(3), **5b**, 1.908(3), and **5c**, 1.913(6) Å, respectively) is very small. Analogously, the difference among the Ni−O bond lengths (**5a**, 1.906(2), **5b**, 1.896(2), and **5c**, 1.898(4) Å, respectively) is also small. Oppositely, the difference among the Ni−N bond lengths or the Ni−P bond lengths of complexes **5a**−**c** is relatively big. Of the three complexes, **5b** possesses the shortest Ni−N bond length (1.938(2) Å), and **5a** and **5c** display almost the same Ni−N bond lengths (**5a**, 1.957(2), and **5c**, 1.951(4) Å). While **5c** possesses the shortest

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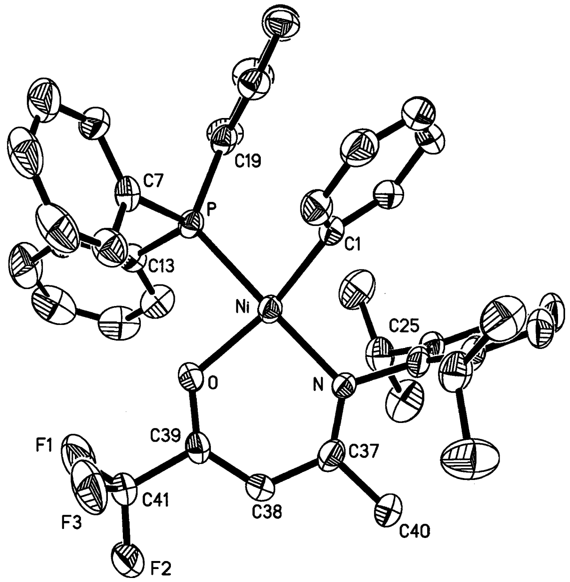

Figure 3. ORTEP drawing of the molecular structure of **5c** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Key atoms are labeled.

Ni–P bond length (2.180(15) Å), **5a** and **5b** show almost the same Ni–P bond lengths (**5a**, 2.198(10), and **5b**, 2.194(12) Å). It is worthy of note that the Ni–P bond lengths of complexes **5a–c** are longer than that of the neutral salicylaldiminato Ni(II) complex (2.172(2) Å).[15]

It is seen from the data listed in Table 2 that the complexes **5a–c** display similar O–Ni–N angles, C1–Ni–N angles, O–Ni–P angles, and C1–Ni–P angles. For example, the C1–Ni–P angles of the complexes **5a–c** are 86.4(9)°, 86.8(9)°, and 86.8(16)°, respectively. However, the great differences among the O–Ni–C1 and N–Ni–P angles of complexes **5a–c** are observed. Of the three complexes, **5a** displays the largest O–Ni–C1 angle (163.2(12)°), **5c** exhibits the smallest O–Ni–C1 angle (158.4(2)°), and **5b** possesses an O–Ni–C1 angle of 159.0(12)°. Similarly, **5a** exhibits the largest N–Ni–P angle (168.3(7)°), **5c** displays the smallest N–Ni–P angle (164.0(12)°), and **5b** has an O–Ni–C1 angle of 165.6(8)°. The torsion angles of the planes (C1, Ni, P) and (N, Ni, O) of the complexes are 18.6° (**5a**), 23.8° (**5b**), and 24.8° (**5c**), respectively, and those of the planes (P, Ni, N) and (O, Ni, C1) are 88.2 (**5a**), 89.3 (**5b**) and 87.9° (**5c**), respectively.

Ethylene Polymerization with Nickel(II) Complexes 5a–c. In contrast to Grubbs' catalysts, the neutral nickel(II) complexes **5a–c**, due to the lack of enough steric hindrance to promote PPh_3 dissociation, exhibit only low activities (ca. 1.0 kg PE/mol_{Ni}·h) for the polymerization of ethylene observed at 20 atm in the absence of cocatalysts such as MAO, $Ni(COD)_2$, or $B(C_6F_5)_3$. However, in the presence of $Ni(COD)_2$, complexes **5a–c** are active catalysts for the polymerization of ethylene at 60 °C. Polymerizations with complexes **5a** and **5c** occur with a relatively long induction period because the ligands in both **5a** and **5c** have strongly electron-withdrawing CF_3 groups, which make it very hard to abstract PPh_3 from the Ni(II) center. The results of several representative polymerizations are summarized in Table 3. The data of entries 1, 3, and 4 demonstrate that the change of substituents R_1 or/and R_2 affects significantly the catalytic activity and the property of the polymers obtained. With an electron-withdrawing trifluoromethyl group at the R_2 position, complex **5a** (R_1 = Ph) displayed the highest turnover of 80 kg PE/mol_{Ni}·h and produced low molecular weight PE with a highly branched structure (125 branches per 1000 carbon atoms, entry 1). In contrast, the replacement of the phenyl group at the R_1 position with a trifluoromethyl group, complex **5c** ($R_2 = CH_3$), displayed a turnover of 40.7 kg PE/mol_{Ni}·h, yielding low molecular weight PE with a moderately branched structure (67 branches per 1000 carbon atoms, entry 4). However, without the presence of a trifluoromethyl group, complex **5b** (R_1 = Ph, $R_2 = CH_3$) decreased the turnover to 2.7 kg PE/mol_{Ni}·h under similar conditions, and high molecular weight PE with about 21 branches per 1000 carbon atoms was obtained (entry 3). These results indicate that the introduction of an electron-withdrawing group at the R_1 or/and R_2 position can considerably increase the catalytic activity and the branching number of PEs, as well as decrease the molecular weight of PEs. In addition, the data of entries 2 and 3 indicate that reaction temperature also affects both the catalytic activity and the property of PEs obtained. The isolated PEs were analyzed by ^1H NMR spectroscopy, which revealed that in all cases, in addition to the resonance of methylene (δ 1.35 ppm), resonances at δ 1.21, 0.92 ppm can be assigned to methine and methyl protons, respectively. In fact, the methyl resonance (δ = 0.92 ppm) split into doublets, indicating that the branches in these PEs are mainly CH_3 branches.[16]

MMA Polymerization Behavior of 5a–c/MMAO Systems. It is well known that bis(β-diketonato) nickel(II) complexes can promote methacrylate polymerization, in the presence of MAO.[17] Moreover, recently, Carlini and co-workers found that bis(salicylaldiminate) nickel(II) complexes activated with MAO are active toward MMA polymerization.[18] This urges us to investigate if neutral nickel(II) complexes **5a–c** are capable of catalyzing MMA polymerization. Preliminary experiments indicated that the neutral nickel(II) complexes **5a–c**, without any cocatalysts, show only very low activities for the polymerization of MMA. Lenz and coworker[19] reported that alkylalumoxane alone is capable of polymerizing MMA, but we found that commercial MMAO itself exhibited a low activity for the polymerization of MMA (2.5% PMMA obtained after polymerization for 24 h). However, when MMAO was used as cocatalyst, the complexes **5a–c** exhibited high activities for the polymerization of MMA under mild conditions.

The results of polymerization of MMA are summarized in Table 4. The data indicate that the structure of the neutral nickel(II) complexes affects considerably the catalytic activity. Under the same experimental conditions, complex **5b** exhibited the highest yield (98.7%, entry 12), followed by complexes **5a** and **5c** (84.5

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Table 1. Crystal Data and Structure Refinements for Complexes 5a−c

	5a	**5b**	**5c**
empirical formula	$C_{46}H_{43}F_3NNiOP$	$C_{46}H_{46}NNiOP$	$C_{41}H_{41}F_3NNiOP$
fw, g	772.49	718.52	710.43
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
unit cell dimens			
a (Å)	12.611 (3)	10.782 (3)	9.299 (3)
b (Å)	12.665 (2)	38.013 (11)	21.609 (6)
c (Å)	14.887 (2)	10.424 (3)	18.370 (13)
volume, Å^3	2035.8 (6)	3897.5 (19)	3666.0 (3)
Z	2	4	4
density(calc), Mg/cm^3	1.260	1.225	1.287
abs coeff, mm^{-1}	0.564	0.574	0.620
F(000)	808	1520	1488
cryst size, mm	0.520.360.28	0.500.360.28	0.550.510.23
θ range, deg	1.77 to 24.98	2.07 to 25.98	1.46 to 24.99
indep rflns	7098 (R_{int} = 0.0251)	7656 (R_{int} = 0.0277)	6407 (R_{int} = 0.0377)
absorp correc	psi-scan	psi-scan	psi-scan
max. & min. transmn	0.54954 and 0.49629	0.7205 and 0.5631	0.5419 and 0.4412
data/restraints/params	7098/0/482	7656/0/456	6407/0/438
goodness-of-fit on F^2	0.872	0.915	1.020
final *R* indices [$I > 2\sigma(I)$]			
R1	0.0405	0.0438	0.0677
wR2	0.0643	0.0723	0.1763
largest diff peak and hole, e/Å^3	0.198 and −0.222	0.223 and −0.377	0.653 and −0.737

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complexes 5a−c

	5a	**5b**	**5c**
Ni−C(1)	1.910(3)	1.906(3)	1.913(6)
Ni−N	1.957(2)	1.938(2)	1.951(4)
Ni−O	1.908(2)	1.896(2)	1.898(4)
Ni−P	2.198(10)	2.194(12)	2.180(15)
N−C37	1,335(4)	1.325(3)	1.293(7)
O−C39	1.280(3)	1.293(3)	1.274(6)
C37−C38	1.399(4)	1.404(4)	1.431(8)
C38−C39	1.373(4)	1.379(4)	1.348(7)
N−C25	1.454(4)	1.440(4)	1.466(6)
C39−C41	1.495(4)	1.497(4)	1.529(7)
O−Ni−C1	163.2(12)	159.0(12)	158.4(2)
O−Ni−N	93.5(9)	94.1(9)	93.9(17)
C1−Ni−N	96.2(11)	96.5(11)	97.8(2)
O−Ni−P	87.0(7)	87.5(7)	86.9(12)
C1−Ni−P	86.4(9)	86.8(9)	86.8(16)
N−Ni−P	168.3(7)	165.6(8)	164.0(12)
N−C37−C38	125.9(3)	124.3(3)	123.1(1)
O−C39−C38	123.1(3)	123.5(3)	128.2(5)
C37−C38−C39	125.6(3)	125.8(3)	124.3(5)

and 77.3%, respectively, entries 5 and 13). This shows that in the complexes **5a−c**, the electronic effect influences considerably the catalytic activity toward MMA polymerization. CF_3, as the strongly electron-withdrawing group, decreases the catalytic activity of MMA polymerization. The variation of the reaction time (entries 1−6), the Al/Ni molar ratio (entries 4, 7−9), and the monomer concentration (entries 3, 10−13) affects significantly the polymer yields, tacticities, and molecular weights of PMMAs. The optimal Al/Ni molar ratio seems to be equal to 150, and the optimal MMA/Ni molar ratio is equal to 750 for the catalytic systems. The resulting polymers show high molecular weights ($\bar{M}_v$ about 400 kg/mol) calculated according to the Mark−Houwink equation.[20] These polymers have rather high degrees of syndiotacticity, *rr* triads being almost 70%, determined by means of ^{1}H NMR spectroscopy. Moreover, it is noteworthy that the syndiotactic degree of the polymers decreased gradually from 71.8% to 44.1%, when the Al/Ni ratio increased from 100 to 500. DSC measurements reveal that the glass transition temperatures (T_g's) of PMMAs are around 118 °C.

The possible mechanism for the nickel-mediated polymerization of acrylates is radical and coordination insertion, etc. Recently, MA homopolymerizations have been reported using neutral palladium catalysts by Novak[21] and by Sen.[22] For the neutral palladium catalysts, Novak reported that an efficient radical inhibitor, galvinoxyl, can completely inhibit the process of the polymerization and no polymer was obtained, suggesting that the polymerization occurs via a radical mechanism.[21] To perform mechanistic studies on the neutral nickel(II) catalysts, we evaluated the effect of radical inhibitor on the polymerization of MMA. Under standard reaction conditions, and adding 5 equiv (per nickel) of galvinoxyl as a free radical inhibitor, polymer yield and catalyst productivity remained substantially the same, thus strongly suggesting that the polymerization of MMA catalyzed by the neutral nickel(II) complexes did not occur via a radical mechanism.

Ethylene/MMA Copolymerizations with the Nickel Complexes 5a−c/MMAO Systems. The neutral nickel(II) complexes **5a−c** are capable of promoting the polymerization of both ethylene and MMA, which motivates us to examine if they can also catalyze the copolymerization of ethylene with MMA. Before copolymerization tests, we investigated the ethylene polymerization promoted by the complexes **5a−c** in the presence of MMAO. Under the optimal conditions of MMA polymerization (Al/Ni molar ratio equal to 150), a great deal of α-olefins (mostly butenes) and only traces of PE (ca. 3% of ethylene consumed) were obtained, which may be caused by the rapid β-hydrogen elimination of the ethylene chain. Analyses of ^{1}H NMR spectra indicate that the PEs display modestly branched structures (e.g., the PE obtained by the complex **5b**/MMAO system, in Figure 5). In fact, the methyl resonance (δ = 0.92 ppm) splits into doublets, indicating that the

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Table 3. Polymerization of Ethylene by 5a−c/Ni(COD)$_2$ Systems[a]

entry	cat. (μmol)	T (°C)	polymer yield (g)	$\bar{M}_w$[b] (kg /mol)	$\bar{M}_w/\bar{M}_n$[b]	branches/1000C[c]	TON[d]
1	**5a** (10)	60	0.80	3.40	2.5	125	80.0
2	**5b** (75)	30	1.76	103.0	3.9	7	23.5
3	**5b** (75)	60	0.2	130.0	8.5	21	2.7
4	**5c** (75)	60	3.05	5.80	2.3	67	40.7

[a] Polymerization conditions: 60 mL of toluene, cat./Ni(COD)$_2$ molar ratio = 4:1, 15 bar of ethylene pressure, 2 h. [b] $\bar{M}_w$ and $\bar{M}_w$ values were determined by GPC. [c] Branching number was determined by ^{1}H NMR. [d] kg PE/mol$_{Ni}$.

Table 4. Polymerization of Methyl Methacrylate by 5a−c/MMAO Systems[a]

entry	catalyst	Al/Ni (molar ratio)	MMA/Ni (molar ratio)	time (h)	polymer (g)	yield (%)	$\bar{M}_v$[b] (kg/mol)	tacticity[c] *mm*	*mr*	*rr*	T_g[d] (°C)
1	**5a**	150	750	1	0.050	13.3	nd	nd	nd	nd	nd
2	**5a**	150	750	3	0.190	32.1	350	9.1	24.2	66.7	122.4
3	**5a**	150	750	5	0.200	50.0	360	8.8	22.7	68.5	118.9
4	**5a**	150	750	8	0.310	72.1	310	8.0	26.8	65.2	116.1
5	**5a**	150	750	12	0.318	84.5	410	7.0	21.8	71.2	121.0
6	**5a**	150	750	24	0.370	98.7	300	7.7	25.7	66.6	117.8
7	**5a**	100	750	8	0.230	61.3	380	8.2	20.0	71.8	122.8
8	**5a**	300	750	8	0.190	50.7	190	11.4	20.0	63.9	118.2
9	**5a**	500	750	8	0.091	24.0	nd	26.2	29.7	44.1	108.5
10	**5a**	150	500	5	0.090	35.8	nd	9.0	21.8	69.2	116.5
11	**5a**	150	1000	5	0.228	45.5	380	8.4	22.0	69.6	117.4
12	**5b**	150	750	12	0.370	98.7	470	7.9	26.9	65.2	121.8
13	**5c**	150	750	12	0.290	77.3	390	7.4	22.6	70.0	116.6

[a] Polymerization conditions: 5 μmol of nickel complex, 1.5 mL of toluene, 30 °C. [b] The viscosity-average molecular weight calculated from the intrinsic viscosity (determined in CHCl$_3$ and at 30 °C) by using the Mark−Houwink coefficients: $\alpha = 0.80$, $K = 4.3 \times 10^{-5}$ dL/g.[24] [c] Determined by means of ^{1}H NMR analysis. [d] Determined by means of DSC.

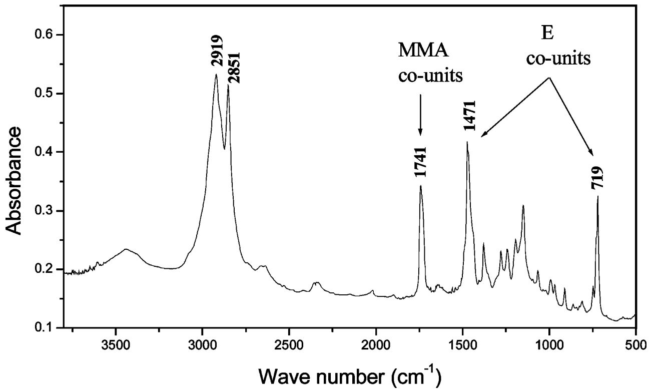


Figure 4. FTIR spectrum of typical ethylene/MMA copolymer (entry 6, Table 5).

branches in these polyethylenes are mainly CH$_3$ branches (90 branches per 1000 carbons atoms).[16]

It is very exciting that the **5a−c**/MMAO catalytic systems can promote the copolymerization of ethylene with MMA under mild conditions by adopting the optimal Al/Ni molar ratio in the polymerization of MMA. Surprisingly, no oligomeric products were detected, although the systems in the absence of MMA behaved substantially as ethylene oligomerization catalysts and produced only traces of PEs. At the end of each copolymerization, the resulting polymers were dissolved in 1,2,4-trichlorobenzene at 120 °C for 3 h, then the mixture solution was poured into cold THF and the polymers were precipitated again from tetrahydrofuran according to the literature reported by Gibson.[12] This procedure was repeated twice to remove any trace of PMMA.

The typical results are summarized in Table 5. At first, the optimal MMA/Ni molar ratio equal to 750 was adopted in the polymerization of MMA. When the concentration of MMA was equal to 0.94 mol/L, complex **5b** showed the highest catalytic activity (17.7 kg polym/mol$_{Ni}$·h), affording the copolymer with the lowest content of MMA units (around 0.8%) incorporated into the polyethylene backbone (entry 3, Table 5), as determined by ^{1}H NMR analysis. In contrast, complexes **5a** and **5c** display moderate activities (7.2 and 2.8 kg polym/mol$_{Ni}$·h, respectively), while the related copolymers show high contents of MMA units (6.7 and 16.7%, respectively) (entries 1 and 7, Table 5). When the concentration of MMA was increased to 1.88 mol/L, the decrease in catalytic activity (from 7.2 to 4.5 kg polym/mol$_{Ni}$·h) and increase in polar comonomer incorporation (from 6.7 to 11.1 mol %) were obtained in the case of complex **5a** (entries 1 and 2, Table 5). However, as for complex **5b**, further increases in catalytic activity (from 17.7 to 38.3 kg polym/mol$_{Ni}$·h) and polar comonomer incorporation (from 0.8 to 2.6%) were obtained (entries 3 and 6, Table 5). Moreover, the data of entries 3−5 demonstrated that the change of MMA/Ni molar ratio from 750 to 2150 increased the catalytic activity of complex **5b** (from 17.7 to 53.1 kg polym/mol$_{Ni}$·h) and MMA incorporation (from 0.8 to 1.3%). To the best of our knowledge, this is the first example of highly active well-defined neutral nickel(II) catalysts that can promote both MMA homo- and copolymerization under moderate conditions.

Both the structures of the complexes **5a−c** and the conditions of polymerization reaction influence the molecular weights and molecular weight distributions of ethylene/MMA copolymers. Among three catalyst systems, the **5c**/MMAO system produces the highest molecular weight copolymer with broad molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 155 kg/mol, $\bar{M}_w/\bar{M}_n$ = 21.7, entry 7 in Table 5), and the **5a**/MMAO system affords the lowest molecular weight copolymer with moderate molecular weight distribution ($\bar{M}_w$ = 39.7 kg/mol, $\bar{M}_w/\bar{M}_n$ = 6.5, entry 1 in Table 5), while the **5b**/MMAO system yields the moderate molecular weight copolymer with narrow molecular weight distribution ($\bar{M}_w$ = 99 kg/mol, $\bar{M}_w/\bar{M}_n$ = 4.1, entry 3 in Table 5). The data of entries

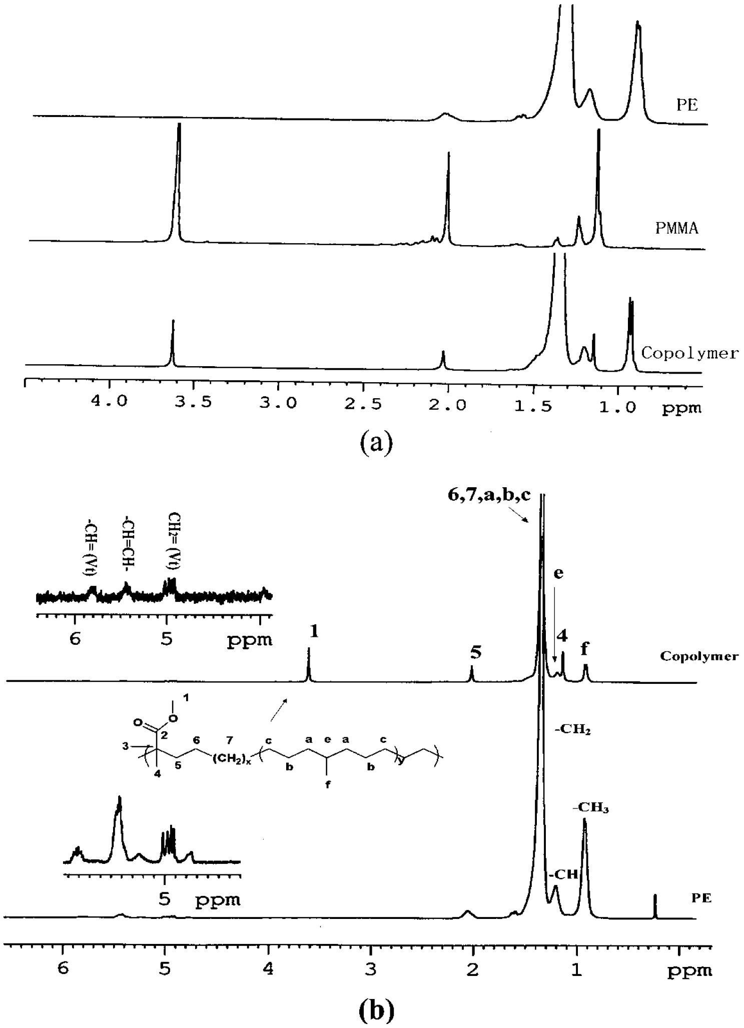


Figure 5. ^{1}H NMR spectrum of PE, PMMA (obtained by the **5b**/MMAO system), and typical ethylene/MMA copolymer (entry 6, Table 5).

Table 5. Copolymerization of Ethylene and MMA by 5a–c/MMAO Systems [a]

entry	catalyst (μmol)	MMA (mol/L)	MMA/Ni (molar ratio)	polymer (g)	activity (kg/mol$_{Ni}$·h)	MMA incorp[b] (mol %)	$\bar{M}_w$[c] (kg/mol)	$\bar{M}_w/\bar{M}_n$[c]	T_m[d] (°C)
1	**5a** (50)	0.94	750	0.72	7.2	6.7	39.7	6.5	119
2	**5a** (100)	1.88	750	0.90	4.5	11.1	300	39.0	118
3	**5b** (50)	0.94	750	1.77	17.7	0.8	99.0	4.1	123
4	**5b** (50)	1.88	1500	5.31	53.1	0.9	55.0	6.6	120
5	**5b** (50)	2.56	2150	2.12	21.2	1.3	45.0	7.1	120
6	**5b** (100)	1.88	750	7.66	38.3	2.6	18.9	7.6	120
7	**5c** (50)	0.94	750	0.28	2.8	16.7	155	21.7	115

[a] Conditions: Al/Ni molar ratio = 150, 20 atm of ethylene, 40 mL of toluene, 2 h, 25 °C. [b] Determined by means of high-temperature ^{1}H NMR analysis in 1,2,4-trichlorobenezene-d_3 in 120 °C. [c] Determined by GPC vs polystyrene standards, uncorrected. [d] Determined by means of DSC.

3–5 in Table 5 indicate that with an increase of the MMA/Ni molar ratio, the molecular weights of the copolymers decrease, while the molecular weight distributions of the copolymers increase, in the case of the **5b**/MMAO catalyst system. When the **5a**/MMAO catalyst system was used, the increase of the concentration of MMA resulted in the increase of both molecular weight and molecular weight distribution of the copolymer obtained (entries 1 and 2 in Table 5).

The isolated polymers were analyzed by FTIR and ^{1}H, ^{13}C NMR spectra, which revealed that in all cases, in addition to the signals for polyethylene, signals corresponding to the functional group of the comonomer were presented. FTIR spectra show that the band at 1741 cm^{-1} is connected with the stretching vibration of aliphatic ester groups in MMA co-units and bands at 1471 and 719 cm^{-1}are related to scissoring and rocking vibrations of methylene groups for E co-units (Figure 4).[2] NMR spectral analyses reveal that the polymers obtained in the copolymerization of ethylene with MMA are copolymers with long runs of ethylene and isolated MMA in the backbone. The ^{1}H NMR spectrum of a typical copolymer is also illustrated in Figure 5 (top). In addition to the resonances of polyethylene with methyl branches (δ 1.36, 1.20, 0.93 ppm), resonances at δ 3.63, 2.03, and 1.15 ppm can be assigned to methoxy, methylene, and methyl protons in MMA units on the basis of the ^{1}H NMR spectrum of the MMA

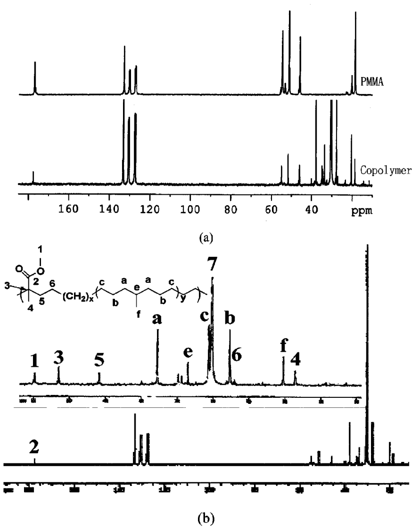
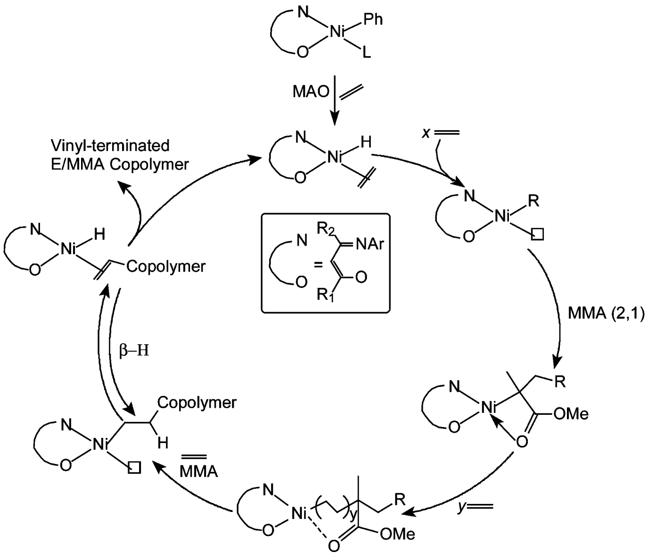


Figure 6. ^{13}C NMR spectra of PMMA and typical ethylene/MMA copolymer (entry 6, Table 5).

homopolymer (see Supporting Information). It is worth noting that the low field gives vinylidene end-groups, total internal $-HC{=}CH-$ double bonds ($CH_3-CH{=}CH-$), and terminal vinyl (V_t)($CH_2{=}CH-$), showing a predominance of ethylene-initiated/ethylene-terminated polymer. The ^{13}C NMR spectrum of the same polymer is much more definitive, as shown in Figure 6. The resonances for the methoxyl carbon, methylene carbon, and methyl carbon in MMA units are assigned on the basis of the ^{13}C NMR spectrum of the MMA homopolymer (see Supporting Information). In particular, the resonances at δ 37.8, 33.5, 30.6, 30.2, 27.7, and 20.2 ppm are attributable to typical sequences of E co-units with methyl branches,[21] while the resonances at δ 177.5, 54.9, 51.5, 45.9, 27.6, and 18.6 ppm confirm the presence of MMA co-units.[2] The fact that the absence of splitting of the signal arising from C=O (δ 177.5 ppm) in the copolymer differing from those for the carbonyl carbons (mainly at δ 176.7 ppm) in homo-PMMA indicates that MMA units are statistically incorporated into the copolymer chain backbone.[13] Moreover, as reported by Gibson, if the polyethylene chains possess a methylenoate end-group, resonances at δ 130 and 140 ppm are attributable to a double bond substituted by an ester functionality.[12] However, the absence of resonances at δ 120 and 140 ppm is evidence that a methylenoate end-group does not exist in the copolymer.

Recently, Novak and co-workers found that galvinoxyl did not affect the activity of Brookhart's cationic palladium catalyst toward ethylene polymerization, thus supporting the supposition that galvinoxyl will not inhibit or retard a polymerization proceeding through a coordination mechanism.[21] To evaluate the mechanism of the copolymerization of ethylene with MMA with the neutral nickel(II) catalysts, we evaluated the effect of radical inhibitor on the copolymerization. Under standard reaction conditions, the addition of 5 equiv (per nickel) of galvinoxyl as a free radical inhibitor, polymer yield and catalyst productivity remained substantially the same, thus strongly suggesting that the copolymerization of ethylene with MMA catalyzed by the neutral nickel(II) complexes did not occur via a radical mechanism.

Scheme 2. Proposed Mechanism for Copolymerization of Ethylene and MMA



It is well known that the relative reactivities of MA and ethylene are quite different in coordination and radical polymerization reactions. In coordination polymerizations catalyzed by cationic palladium catalysts reported by Brookhart,[10] the ethylene outcompetes the electron-deficient MA so that the MA incorporation in copolymers remains low even if an excess amount of MA is used in the reaction. The reactivity of MA is considerably higher than olefin in radical polymerization. The hexene/MA copolymers produced by the neutral palladium are richer in MA-enriched copolymers, in good agreement with the data reported in the literature for radical polymerization of the two monomers.[21,22] In contrast, as described above, the copolymers of ethylene and MMA produced by the **5a**−**c**/MMAO systems are ethylene-enriched, even in the cases where MMA was used in excess. All the evidence, taken together, appears to favor a coordination insertion pathway rather than a radical mechanism for polymerization of MMA catalyzed by the neutral nickel(II) complexes **5a**−**c**.

On the basis of the possible mechanism for the polymerization of MMA and the NMR spectra of the copolymers, a proposed mechanism for the dominant ethylene-initiated/MMA and ethylene-propagated/ethylene-terminated copolymer is shown in Scheme 2. With regard to initiation, we assume a [N,O] chelate Ni hydride active catalyst species, based on the observed copolymer end-groups, and thoroughly studied analogous neutral [P,O] Ni catalysts for ethylene oligomerization/polymerizaztion.[10b,12,13,24,25] Substitution of the donor ligand PPh_3 by ethylene followed by insertion of ethylene into the Ni−Ph bond of the catalyst forms an intermediate that undergoes β-hydrogen elimination to form a Ni−H species.[23] Further ethylene is inserted and polyethylene with methyl branches is formed. Then propagation occurs by insertion of MMA in a 2,1-mode to the growing polyethylene chain according to ^{1}H, ^{13}C NMR spectra. Followed by the formation of the oxo-chelate between Ni and acrylate, further ethylene and MMA inserting into the Ni-alkyl is presumably facili-

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[23] Schroder, D. L.; Keim, W.; Zuideveld, M. A.; Mecking, S. *Macromolecules* **2002**, *35*, 6071.

tated by destabilization of the oxo-chelate.[13] Termination in ethylene-MMA copolymerization occurs via β-hydrogen elimination from the last inserted ethylene unit to form, presumably, a Ni-H species coordinated by a vinyl-terminated polymer. Ethylene competes with this coordinated polymer, and as a result, the vinyl-terminated copolymer product is obtained and the purported Ni-H catalyst species is regenerated.[25]

Conclusion

A series of new neutral nickel(II) complexes bearing asymmetric β-ketoiminato (N,O) ligands (**5a**–**c**) has been synthesized and characterized. The β-ketoiminato nickel(II) complexes were the first example of highly active well-defined neutral nickel(II) catalysts for both MMA polymerization and ethylene/MMA copolymerization. MMA can be polymerized in excellent yields (>98%) by MMAO activated with these complexes. Likewise, ethylene and MMA have been successfully copolymerized, and the copolymers produced are generally ethylene-enriched. The mechanistic studies all support a coordination–insertion mechanism rather than a radical pathway for polymerization using these neutral nickel complexes. Moreover, the NMR data and FTIR spectra of the copolymers obtained are discussed and a copolymerization mechanism is proposed.

Experimental Section

General Procedures and Materials. All the manipulations of air- and/or water-sensitive compounds were performed under a dry nitrogen atmosphere by means of standard Schlenk techniques. The NMR data of PMMAs were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, with $CDCl_3$ as the solvent. The NMR analyses of copolymers were performed on a Varian Unity 400 MHz spectrometer at 120 °C, with o-$C_6D_4Cl_2$ as the solvent. The other NMR data of the ligands and the complexes were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, with C_6D_6 or $CDCl_3$ as the solvent. The ^{31}P NMR spectra were referenced to that of external H_3PO_4. FTIR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. Viscosity-average molecular weights of PMMAs were calculated from the intrinsic viscosity at 30 °C by using the Mark–Houwink coefficients: $\alpha = 0.8$, $K = 4.3 \times 10^{-5}$ dL/g.[20] The molecular weights and the polydispersities of the copolymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

Anhydrous benzene, tetrahydrofuran, and toluene were refluxed and distilled from Na/benzophenone under dry nitrogen. Benzene-d_6 was dried over CaH_2, vacuum-transferred, degassed by repeated freeze–pump–thaw cycles, and stored over 4 Å molecular sieves. o-Dichlorobenzene-d_4 was obtained from Aldrich and used without further purification. MMA was dried over CaH_2 and purified by distillation under reduced pressure before use. Modified methylaluminoxane (MMAO, 2.0 M in heptane) was purchased from Akzo Nobel Chemical Inc. 2,6-Diisopropylaniline, 4,4,4-trifluoro-1-phenyl-1,3-butanedione, 1,1,1-trifluoro-2,4-pentanedione, and 1-benzoyl acetone were purchased from Aldrich.

Ligand and Complex Syntheses. (2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CF$_3$)C(H)C(Ph)OH (2a). To a stirred solution of 4,4,4-trifluoro-1-phenyl-1,3-butanedione (5 g, 23 mmol) in dried methanol (15 mL) was added 2,6-diisopropylaniline (8.5 mL, 46 mmol) and formic acid (1 mL) as catalyst. The reaction mixture was stirred and refluxed for 48 h. After having been cooled, the colorless precipitate was separated by filtration, washed with cold methanol, and then dried to afford **2a** as colorless crystals in 75.6% (6.5 g) yield. The other ligands **2b** and **2c** were prepared by the same procedure.

(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CF$_3$)C(H)C(Ph)OH (2a). ^{1}H NMR ($CDCl_3$): δ 12.07 (s, 1H, N-H), 7.99 (d, 2H, Ph-H), 7.58–7.48 (m, 3H, Ph-H), 7.34 (t, 1H, Ph-H), 7.19 (d, 2H, Ph-H), 6.45 (s, 1H, =CH), 3.11 (m, 2H, *i*Pr–CH), 1.26–1.13 (dd, 12H, *i*Pr-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 191.39 (N=C), 147.16, 138.67, 132.33, 132.19, 128.84, 127.47, 123.54 (Ph, CF$_3$), 90.31 (=C), 33.80 (^{i}Pr-CH), 25.31, 21.71 (^{i}Pr-CH$_3$). Anal. Calcd for $C_{22}H_{24}F_3NO$: C, 70.38; H, 6.44; N, 3.73; Found: C, 70.48; H, 6.37; N, 3.79.

(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CH$_3$)C(H)C(Ph)OH (2b). Yield: 92.5%. ^{1}H NMR ($CDCl_3$): δ 12.63 (s, 1H, N-H), 7.96 (d, 2H, Ph-H), 7.46–7.42 (m, 3H, Ph-H), 7.32 (t, 1H, Ph-H), 7.20 (d, 2H, Ph-H), 5.93 (s, 1H, =CH), 3.12–3.06 (m, 2H, ^{i}Pr-CH), 1.79 (s, 3H, CO-CH$_3$), 1.24–1.16 (dd, 12H, ^{i}Pr-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 188.28 (N=C), 164.98, 146.02, 139.93, 133.40, 130.61, 128.27, 128.09, 126.97, 123.48 (Ph), 92.05 (=C), 28.41 (^{i}Pr-CH), 24.49, 22.57 (^{i}Pr-CH$_3$), 19.58 (CH$_3$). Anal. Calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 82.09; H, 8.43; N, 4.40.

(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CH$_3$)C(H)C(CF$_3$)OH (2c). Yield: 72.1%. ^{1}H NMR ($CDCl_3$): δ 12.22 (s, 1H, N-H), 7.46 (t, 1H, Ph-H), 7.22 (d, 2H, Ph-H), 5.59 (s, 1H, =CH), 3.02–2.91 (m, 2H, ^{i}Pr-CH), 1.84 (s, 3H, CO-CH$_3$), 1.27–1.18 (dd, 12H, ^{i}Pr-CH$_3$). ^{13}C NMR ($CDCl_3$): δ 170.41 (N=C), 145.44, 132.02, 129.23, 123.53 (Ph, CF$_3$), 89.49 (=C), 28.58 (^{i}Pr-CH), 24.40, 22.53 (^{i}Pr-CH$_3$), 19.57 (CO-CH$_3$). Anal. Calcd for $C_{17}H_{22}F_3NO$: C, 65.16; H, 7.08; N, 4.47. Found: C, 65.28; H, 7.12; N, 4.51.

[(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CF$_3$)C(H)C(Ph)O]Ni(Ph)(PPh$_3$) (5a). A solution of ligand **2a** (0.50 g, 1.3 mmol) in THF (20 mL) was added to sodium hydride (70 mg, 2.8 mmol). The mixture was stirred at room temperature for 1 h, filtered, and evaporated. The solid residue was washed with pentane (20 mL) and dried in a vacuum. The sodium salt **4a** (0.4 g, 1 mmol) and *trans*-[NiCl(Ph)(PPh$_3$)$_2$] (0.55 g, 0.9 mmol) were put in a Schlenk flask and dissolved in benzene (20 mL) and stirred at room temperature for 12 h, and then the reaction mixture was filtered by cannula filtration and the filtrate was concentrated in vacuo to ca. 5 mL, to which pentane (30 mL) was added. Subsequently, a red crystal precipitated from the solution and was isolated by cannula filtration and washed several times by cold pentane to yield 0.58 g (83%) of **5a** as a red crystal. The other neutral nickel(II) complexes were prepared by the same procedure with similar yields.

[(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CF$_3$)C(H)C(Ph)O]Ni(Ph)(PPh$_3$) (5a). ^{1}H NMR (C_6D_6): δ 7.62–6.40 (m, 39H, Ph-H and =CH), 3.85 (m, 2H, ^{i}Pr-CH), 1.49–1.16 (dd, 12H, ^{i}Pr-CH$_3$). ^{13}C NMR (C_6D_6): δ 174.91 (N=C), 140.87, 139.07, 137.78, 137.74, 134.73, 134.60, 131.73, 131.15, 130.22, 128.88, 128.50, 128.39, 128.24, 128.18, 127.86, 126.97, 125.98, 125.69, 123.33,122.10 (Ph, CF$_3$), 90.21 (=C), 29.20 (^{i}Pr-CH), 24.86, 24.72 (^{i}Pr-CH$_3$). ^{31}P NMR (C_6D_6): δ 20.52. Anal. Calcd for $C_{46}H_{43}F_3NNiOP$: C, 71.52; H, 5.61; N, 1.81. Found: C, 71.45; H, 5.48; N, 1.84.

[(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CH$_3$)C(H)C(Ph)O]Ni(Ph)(PPh$_3$) (5b). Yield: 78%. ^{1}H NMR (C_6D_6): δ 7.74–6.41 (m, 28H, Ph-H), 6.12 (s, 1H, =CH), 3.96–3.92 (m, 2H, ^{i}Pr-CH), 1.83 (s, 3H, CN-CH$_3$), 1.42–1.33 (dd, 12H, ^{i}Pr-CH$_3$). ^{13}C NMR (C_6D_6): δ 170.46 (N=C), 167.84, 148.55, 146.30, 145.79, 141.41, 140.36, 138.37, 135.04, 134.94, 132.61, 132.19, 130.12, 129.47, 128.95, 128.65,

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128.47, 128.40, 128.17, 127.11, 125.88, 125.66, 123.69, 121.73 (Ph), 96.03 (=C), 29.18 (^{i}Pr-CH), 26.48, 26.44 (N=C-CH_3), 25.07, 24.75 (^{i}Pr-CH_3). ^{31}P NMR (C_6D_6): δ 22.43. Anal. Calcd for $C_{46}H_{46}NNiOP$: C, 76.89; H, 6.45; N, 1.95. Found: C, 76.71; H, 5.40; N, 1.98.

[(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(CH$_3$)C(H)C(CF$_3$)O]Ni(Ph)(PPh$_3$) (5c). Yield: 80%. ^{1}H NMR (C_6D_6): δ 7.64−6.36 (m, 23H, Ph-H), 5.77 (s, 1H, =CH), 3.71−3.67 (m, 2H, ^{i}Pr-CH), 1.52 (s, 3H, CN-CH_3), 1.31−1.16 (dd, 12H, ^{i}Pr-CH_3). ^{13}C NMR (C_6D_6): δ 169.46 (N=C), 140.42, 137.84, 134.61, 134.48, 134.19, 131.75, 131.16, 130.07, 128.49, 128.17, 127.85, 126.84, 126.08, 125.61, 124.26, 123.58, 122.48, 121.85, 118.74, 115.93 (Ph, CF_3), 95.42 (=C), 28.94 (^{i}Pr-CH), 25.88 (N=C-CH_3), 24.32, 24.02 (^{i}Pr-CH_3). ^{31}P NMR (C_6D_6): δ 21.14. Anal. Calcd for $C_{41}H_{41}F_3NNiOP$: C, 69.32; H, 5.82; N, 1.97. Found: C, 69.21; H, 5.78; N, 1.99.

Crystallographic Studies. The X-ray crystallographic analyses were performed using crystals **5a**−**c** with sizes 0.52 × 0.36 × 0.28, 0.50 × 0.36 × 0.28, and 0.55 × 0.51 × 0.23 mm, obtained by recrystallization from toluene/hexane solution at room temperature. The intensity data were collected with the ω scan mode (293 K) on a Bruker Smart APEX diffractometer with a CCD detector using Mo Kα radiation (λ = 0.71073 Å). Lorentz and polarization factors were obtained for the intensity data, and absorption corrections were performed using the SADABS program.[26] The crystal structures were solved using the SHELXTL program and refined using full matrix least squares.[27] The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 211060−211062 for compounds **5a**−**c**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://ccdc.cam.ac.uk).

Polymerizations of MMA. A 100 mL Schlenk tube used for the polymerization was oven-dried for 24 h and flame-dried under vacuum and argon purge stream for 4 cycles. The total volume of the added liquid phase amounted to 1.5 mL. Measured amounts of a solution of catalysts (5 μmol cat. in 0.5 mL of toluene) and MMA were introduced into the reactor under argon atmosphere with a syringe in this order. Polymerizations were initiated by injecting a measured amount of MMAO at 30 °C and, after the reaction time, terminated by adding a large amount of acidic methanol. The resulting polymer was collected, filtered, washed with methanol, and dried under vacuum at 60 °C for 24 h.

Polymerizations of MMA Using Complex 5a and Galvinoxyl as Inhibitor. The reaction was conducted according to the above general procedure for the polymerization of MMA. Measured amounts of a solution of complex **5a** (5 μmol cat.), MMA, and galvinoxyl (25 μmol) were introduced into the reactor under argon atmosphere with a syringe in this order. Polymerizations were initiated by injecting a measured amount of MMAO at 30 °C and, after 8 h, terminated by adding a large amount of acidic methanol. The resulting polymer was collected, filtered, washed with methanol, and dried under vacuum at 60 °C for 24 h. Polymer yield and catalyst productivity remained substantially the same.

Copolymerizations of Ethylene with MMA. Copolymerizations of ethylene with MMA were performed at 25 °C in a mechanically stirred 100 mL pressure reactor. The total volume of the added liquid phase amounted to 40 mL. Toluene (20 mL) was introduced to the nitrogen-purged reactor and stirred at 600 rpm. Measured amounts of a solution of catalysts (10 μmol cat. in 10 mL of tolune) and MMA were introduced into the reactor in this order. The reactor was pressurized with ethylene (20 atm), and copolymerizations were initiated by injecting a measured amount of MMAO. The polymerization was quenched after the prescribed time by adding a large amount of acidic methanol. The resulting polymers were filtered and dried under reduced pressure. Then the polymers were dissolved in 1,2,4-trichlorobenzene at 120 °C for 3 h, and the mixture solution was poured into tetrahydrofuran. The polymers were precipitated again from tetrahydrofuran, filtered, and dried under reduced pressure. This procedure was repeated twice to remove any traces of PMMA.[12]

Acknowledgment. The authors are grateful for the financial support by the National Natural Science Foundation of China and SINOPEC (No. 20334030).

Supporting Information Available: Crystallographic data for **5a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049080W

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