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Robust Bulky [P,O] Neutral Nickel Catalysts for Copolymerization of Ethylene with Polar Vinyl Monomers

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Abstract: Several nickel complexes bearing sterically bulky phosphino-phenolate ([P,O]) ligands were synthesized and explored as catalysts for olefin (co)polymerization. In the absence of an activator, the complexes showed very high catalytic activities (up to $10^7 \text{ g} \cdot \text{mol}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$) for ethylene polymerization even at 90 °C or with the addition of a large amount of a polar additive (such as ethyl alcohol, diethyl ether, acetone, or even water), affording linear polymers with high molecular weights (up to 6.53×10^5). In contrast, most of the previously reported nickel catalysts suffer from severe activity suppression at elevated temperature. It is rare that a catalyst owns so many good performances simultaneously, such as high catalytic activity, good tolerance for polar group, strong thermal stability, and yielding linear polyethylene with high-molecular-weight. Most importantly, these bulky nickel complexes used in this study also effectively copolymerized of ethylene with challenging polar vinyl monomers, including commercially available acrylates and an acrylamide. As we expected, introducing a bulky substituent group on the phosphorus atom of the complex was vital for enhanced catalytic activity and the formation of high-molecular-weight linear copolymers. Microstructure analyses revealed that the polar functional units were mainly incorporated into the polymer main chain and also located at the chain end, with insertion percentages of up to 7.4 mol %. The bulky [P,O] neutral nickel complexes reported herein are promising alternatives to the well-established palladium catalysts for direct copolymerization of olefins with commercially available polar vinyl comonomers.

Keywords: neutral nickel catalyst, bulky substituent, ethylene polymerization, copolymerization, polar vinyl monomer.

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1. Introduction

Introducing polar groups into the polymer chain of polyolefins is an effective strategy for improving their surface properties, such as wettability, adhesion, printability, and compatibility.^{1,2} The most straightforward method for this purpose is the direct coordination-insertion copolymerization of olefins with polar monomers by means of single-site organometallic catalysts.² Because early-transition-metal catalysts are highly oxophilic and easily deactivated by polar functional groups, late-transition-metal catalysts, especially palladium catalysts, are extensively used for copolymerization of ethylene with industrially relevant polar monomers, including acrylates,³ acrylonitrile,⁴ vinyl acetate,⁵ vinyl fluoride,⁶ and vinyl ethers,⁷ as well as others.^{8,9} Nevertheless, the high cost and relatively low activity of palladium catalysts limit their practical utility; and their replacement with less expensive catalysts, such as nickel catalysts, would therefore be highly desirable. In fact, numerous nickel complexes have been developed to catalyze (co)polymerization reactions, but these complexes are active mainly toward ethylene and norbornene (co)polymerization.^{10,11} In addition to their relatively poor thermal stability,¹¹ most of the nickel catalysts reported to date suffer from severe activity suppression by polar monomers and can produce only copolymers with low molecular weights (MWs) or with negligible polar comonomer incorporation.^{12,13} Although some nickel complexes have been reported to copolymerize ethylene with vinyl polar comonomers that have a relatively long spacer between the C=C bond and the polar functional group,¹² attempts at nickel-catalyzed copolymerization of olefins with commercially available polar vinyl monomers to yield semi-crystalline high-MW polymers with well-controlled composition have met with only limited success.¹³

The reasons for this limited success have been explored. For example, a mechanistic investigation about ethylene/methyl acrylate copolymerization achieved by neutral nickel salicylaldimine ([N,O]) catalysts revealed that 2,1-insertion of methyl acrylate (MA) into the Ni–C bond does occur, but the insertion products readily undergo bimolecular deactivation with nickel hydride complexes derived from β -H elimination.^{13b} In addition, the formation of a carbonyl chelate complex (the O atom of the carbonyl group interaction with the Ni center) leads to difficulty in chain initiation and propagation (Scheme 1). ACS Paragon Plus Environment

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Similar to [N,O] (e.g., salicylaldimine) neutral nickel catalysts, Shell Higher Olefin Process (SHOP) catalysts and some [P,O] (e.g., phosphine-sulfonate) neutral nickel catalysts generated in situ have been found to be inactive for ethylene/MA copolymerization.^{12a,d} In addition to showing poor tolerance to polar comonomers, nickel catalysts such as SHOP catalysts and α -diimine nickel catalysts usually produce higher α -olefins or highly branched polyethylenes (PEs) because of incidental β -H elimination reactions and "chain walking" processes.^{2c} Recently, making use of interactions between nickel centers and other atoms such as nitrogen atom or oxygen atom *via* transient interaction with metal center has been proved to be an effective strategy for the ethylene/MA copolymerization by the Mitsubishi team and the Chen group,^{13g,h} a strategy that is likely to retard β -H elimination reactions. Moreover, as shown in Scheme 2, introduction of a sterically bulky group oriented axially with respect to the nickel center also suppresses associative chain transfer or chain transfer to monomer, because the resting and terminating states are sharply destabilized, whereas the insertion state is stabilized.^{9f,11a,14}



Scheme 1. Deactivation of [N,O] Nickel Complexes in the Case of Methyl Acrylate (MA).



Scheme 2. Suppression of Chain Transfer by Introduction of an Axially Oriented Bulky Group.

Recently, we have been developing several well-defined phosphino-phenolate ([P,O]) neutral nickel catalysts based on SHOP catalysts because of their good tolerance for polar functional groups. Encouraged by the effect of an axial bulky group, we expected that the introduction of bulky substituents to shield the vacant p_z orbital would effectively suppress the chelating interaction and β -H elimination, as well as would hinder the coordination of a monomer approaching from the direction

perpendicular to the nickel coordination plane to produce high-MW polymers. In addition, a sterically hindered environment around the nickel center would help to reduce the possibility of bimolecular deactivation reactions. In this study, we strategically tune the steric hindrance at the axial direction of the nickel active site and evaluated the effects of bulky substituent group on the phosphorus atom.

2. Results and Discussion

2.1 Synthesis and Characterization of [P,O] Neutral Nickel Complexes

To evaluate the effects of steric hindrance at the axial position, we used commercially available chlorodiphenylphosphine (P1) as a small phosphine chloride, and we also designed and synthesized three additional diaromatic phosphine chlorides of different sizes: (2',6'-dimethoxybiphenyl-2-yl)phenylphosphine chloride (P2), (biphenyl-2-yl)phenylphosphine chloride (P3), and bis(biphenyl-2-yl)phosphine chloride (P4). P2-P4 were synthesized as described in Supporting Information, and were used for ligand synthesis without purification. Ligands 1a-1d, which bear substituents with different steric bulk, were synthesized as shown in Scheme 3. Briefly, 2-(2-(tert-butyl)phenoxy)tetrahydro-2H-pyran was lithiated with n-BuLi, and the prepared lithium salt was allowed to react with P1, P2, P3, or P4. The tetrahydro-2*H*-pyran protecting group was easily removed by reaction with hydrochloric acid and quenching with aqueous NaHCO₃ to afford ligands 1a-1d. [P,O] neutral nickel complexes 2a-2d were obtained in high yields (>76%) by addition of the corresponding ligands (1a-1d, respectively) to a stirred solution of Pv₂NiMe₂ in dry toluene. In order to explore the difference between Mitsubishi catalysts and these bulky [P,O] neutral catalysts, we also synthesized complex 2e according the literature for comparision.^{13g} It was found that complex 2e was not very stable in toluene or benzene, as nickel black could be obviously observed in about 5 hours, while no nickel black was not detectable for complexes 2a-2d even after 48 hours. This difference might be ascribed to the weaker coordination of labile ligand 1.5-Cyclooctadiene (COD).



Scheme 3. Synthesis of [P,O] Neutral Nickel Complexes 2a–2d.

For X-ray diffraction analysis, we obtained single crystals of **2b–2d** by slowly diffusing *n*-hexane into solutions of the complexes in dry toluene. X-ray diffraction analysis for all single crystals revealed that these nickel complexes exhibited a square planar geometry around the nickel center, and labile ligand pyridine located *trans* to the phosphorus atom (Figures 1, 2, S97, and S98). The differences in Ni–N bond length between the complexes were negligible. Inspection of space-filling diagrams of **2b–2d** clearly indicates that the bulky 2-(2,6-(OCH₃)₂C₆H₃)C₆H₄– or 2-(C₆H₅)C₆H₄– group effectively shielded the vacant p_z orbital of the dsp²-hybridized nickel center (Figure 2). The C(1)–P(1)–C(3) angle in **2a** was 108.71°,¹²ⁱ and the corresponding angles were slightly smaller in the other three complexes: 107.67° in **2b** (C(6)–P(1)–C(17)), 107.21° in **2c** (C(2)–P(1)–C(17)), and 105.08° in **2d** (C(30)–P(1)–C(18)), respectively. This difference suggests a more sterically crowded environment in **2b–2d** than in **2a**. Moreover, the dihedral angles between the bulky phenyl-substituted planar group at the axial direction and the nickel coordination plane (21.22, 24.43, and 18.76° in **2b–2d**, respectively), as well as the distances from the nickel center to the axial phenyl ring (3.221, 3.238, and 2.824 Å in complexes **2b–2d**, ACS Paragon Plus Environment

respectively), reflected greater steric hindrance. Notably, the space-filling diagram of **2d** shows two pseudo-axial phenyl rings perpendicular to the coordination plane, and these rings jointly shield the vacant p_z orbital from above and below. The steric bulk of these complexes clearly increased in the order **2a** < **2c** < **2b** < **2d**. Note also that the Ni(1)–O(3) and Ni(1)–O(2) distances in **2b** were 3.556 and 4.557 Å, respectively, both of which are longer than the sum of the van der Waals radii between Ni atom and O atom (3.15 Å).^{13b} This distance indicates that the interaction between the –OMe group and the nickel center was negligible.



Figure 1. ORTEP plot of complex **2b**. Ellipsoids are shown with 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–C(36) 1.931(3), Ni(1)–O(1) 1.9330(19), Ni(1)–N(1) 1.950(2), Ni(1)–P(1) 2.0981(7), Ni(1)–O(3) 3.556 , Ni(1)–O(2) 4.557; C(36)–Ni(1)–O(1) 174.64(11), C(36)–Ni(1)–N(1) 92.86(12), O(1)–Ni(1)–N(1) 89.18(9), C(36)–Ni(1)–P(1) 90.85(9), O(1)–Ni(1)–P(1) 87.08(6), N(1)–Ni(1)–P(1) 176.25(8), C(6)–P(1)–C(17) 107.67(11).



Figure 2. Space-filling diagrams of complexes **2a–2d**, respectively. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for complex **2c**: Ni(1)–C(34) 1.943(3), Ni(1)–O(1) 1.9358(18), Ni(1)–N(1) 1.956(2), Ni(1)–P(1) 2.1090(7); O(1)–Ni(1)–C(34) 177.57(11), O(1)–Ni(1)–N(1) 90.03(8), C(34)–Ni(1)–N(1) 91.48(11), O(1)–Ni(1)–P(1) 86.78(5), C(34)–Ni(1)–P(1) 91.84(9), N(1)–Ni(1)–P(1) 174.87(6).

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C(2)–P(1)–C(17) 107.21(11). Selected bond lengths (Å) and angles (°) for complex 2d: Ni(1)–C(40) 1.927(3), Ni(1)–O(1) 1.9227(15), Ni(1)–N(1) 1.9507(18), Ni(1)–P(1) 2.1015(6); O(1)–Ni(1)–C(40) 177.75(10), O(1)–Ni(1)–N(1) 89.30(7), C(40)–Ni(1)–N(1) 91.74(10), O(1)–Ni(1)–P(1) 87.36(5), C(40)–Ni(1)–P(1) 91.35(8), N(1)–Ni(1)–P(1) 171.88(6), C(30)–P(1)–C(18) 105.08(10).

2.2 Ethylene Polymerization

We began by investigating the catalytic performances of neutral nickel complexes 2a-2d in ethylene polymerization; representative results are listed in Table 1. Without an activator, all four complexes were highly active for ethylene polymerization. Complex 2a, which has the smallest phosphorus ligand (-PPh₂), displayed a catalytic activity of 210×10^3 g·mol_{Ni}⁻¹·h⁻¹ at 70 °C (entry 1); whereas at a lower reaction temperature, this complex did not initiate ethylene polymerization (data of 30 and 50 °C was not shown). When the catalyst concentration and the reaction temperature were increased, the catalytic activity increased remarkably (up to ca. 10^7 g·mol_{Ni}⁻¹·h⁻¹; entry 2).^{11,14a}

In sharp contrast, complexes **2b** and **2c**, which have bulkier phosphorus ligands perpendicular to the coordination plane, produced PEs with higher MWs (up to 653×10^3 for **2b** and up to 613×10^3 for **2c**). Additionally, the catalytic activities of **2b** and **2c** were nearly 2 orders of magnitude higher than that of **2a** under the same conditions (compare entries 6 and 10 with entry 1). These results are consistent with our initial hypothesis that the axially oriented bulky phosphino-phenolate ligands would prevent chain transfer to an incoming monomer, leading to the formation of high-MW polymers. Note that although the difference between the catalytic activities of **2b** and **2c** for ethylene polymerization was not large, the activity of **2b** was slightly higher. Such slight difference indicates that there was no transient coordination of the apical –OMe group with Ni center in complex **2b**, a result that differs from previously reported results.^{3c,13g} Unexpectedly, the performance of the complex with a single bulky substituent (**2c**), in terms of both catalytic activity and polymer MW (Table 1, compare entries 8 and 11). This result suggests that steric hindrance around the active site of **2d** may have slowed ethylene coordination or insertion. Besides, there was no big difference between **2a** and Mitsubishi catalyst **2e** in

catalytic activity, and MW of polymer synthesized by these two complex is also very similar.

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Entry	Cat.	Temp (°C)	Yield (g)	TOF ^b	Activity ^c	$\frac{M_{\rm n}^{\ d}}{(10^3)}$	$M_{\rm w}^{\ d}$ (10^3)	$M_{ m w}/M_{ m n}^{\ d}$	$T_{\rm m}^{\ e}$ (°C)
1	2a	70	0.35	7.5	210	5.6	11.5	2.0	130
2^{f}	2a	90	32.6	350	9780	3.9	7.8	2.0	126
3	2b	10	0.34	7.3	204	90	124	1.4	136
4	2b	30	4.9	105	2940	480	653	1.4	136
5	2b	50	10.9	233	6540	241	458	1.9	136
6	2b	70	18.5	396	11100	146	219	1.5	131
7	2b	90	16.7	359	10020	9.4	25.5	2.7	129
8	2c	30	3.5	75	2100	398	613	1.5	137
9	2c	50	8.8	189	5280	206	390	1.9	136
10	2c	70	14	300	8400	59	126	2.1	134
11	2d	30	1.1	24	660	183	238	1.3	136
12 ^g	2a	70	9.6	206	5760	3.8	8.4	2.2	126
13 ^g	2e	70	11.4	245	6840	3.1	7.7	2.5	125

 Table 1. Ethylene Polymerization Catalyzed by Complexes 2a–2d.^a

^{*a*} Reaction conditions, unless otherwise noted: 5 µmol of catalyst; 100 mL of toluene; ethylene pressure, 10 bar; 20 min. ^{*b*} TOF, turnover frequency. In units of 10³ mol_E·mol_{Ni}⁻¹·h⁻¹, E, ethylene. ^{*c*} In units of 10³ g·mol_{Ni}⁻¹·h⁻¹. ^{*d*} Determined by gel permeation chromatography (GPC) at 150 °C vs narrow polystyrene standard in 1,2,4-trichlorobenzene. ^{*e*} Determined by differential scanning calorimetry (DSC), 20 °C·min⁻¹, second heating curve. ^{*f*} Reaction carried out with 10 µmol of catalyst. ^{*g*} Reaction carried out with 5 µmol of catalyst, 50 mL of toluene.

To our delight, the yields and MW of PE obtained with catalyst **2b** at 30 °C increased with increasing reaction time, and the catalytic activity ($4860 \times 10^3 \text{ g} \cdot \text{mol}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$) was still very high even after one hour (Table S1, entries S10–S13). In addition, **2a** and **2b** also showed strong thermal stability, retaining very high catalytic activity (up to $10^7 \text{ g} \cdot \text{mol}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$), and produced high-molecular-weight PE even at 90 °C (Table 1). As we know, it is a very good example that the catalytic activity value is among the highest activities of neutral nickel systems (e.g., SHOP catalyst, salicylaldiminato nickel systems, and phosphine sulfonate nickel system).¹⁵ The catalytic activities of catalyst **2b** and **2c** clearly increased as the temperature was raised from 30 to 70 °C, but the MWs of the resulting PEs decreased owing to acceleration of chain transfer reactions.

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As we have mentioned, tolerance to polar reagents is essential for copolymerization of olefins with polar monomers. In order to explore the polar additives effects on catalytic activity, we carried out ethylene polymerization by using complex 2c in the presence of the following saturated polar additives (Table 2): acetonitrile, dimethyl formamide, ethyl alcohol, diethyl ether, ethyl acetate, acetone, dichloromethane, and water. We found that although the inhibitory effects of acetonitrile and dimethyl formamide on the catalyst activity were relatively strong because these compounds can coordinate readily with the nickel center, the catalytic activity of 2c still remained as high as approximately 10^6 $g \cdot mol_{Ni}^{-1} \cdot h^{-1}$ even in the presence of these additives (Table 2, entries 8 and 9). To our surprise, 2c still showed good tolerance to ethyl alcohol and diethyl ether; the catalytic activity of 2c barely decreased in the presence of either of these polar solvents at a concentration of 2 M (40,000 equiv relative to the catalyst, entries 2 and 3). In addition, only a slight decrease in catalytic activity was observed after addition of ethyl acetate or acetone, indicating that the carbonyl group of these compounds coordinated only weakly, if at all, to the nickel center. Complex **2c** also exhibited high activity (3480 kg·mol_{Ni}⁻¹·h⁻¹) with the addition of alkyl halide dichloromethane. We were surprised to find that the activity of 2c was only moderately decreased with addition of 40,000 equiv of water. To our knowledge, this complex is one of the most robust catalysts reported to date for ethylene polymerization in the presence of water.¹⁶ As shown in Figure 3, the catalytic activities of ethylene polymerization decreased in the order ethanol < diethyl ether < acetone < ethyl acetate < water < dichloromethane < acetonitrile < dimethyl formamide. Taken together, these results indicate that 2c shows good tolerance to various polar additives, retaining remarkably high catalytic activity for ethylene polymerization with the addition of the tested additives: whereas most of the previously reported catalysts show severely decreased activity under similar conditions, especially in the presence of water.^{8h,16c–e} More interestingly, although abundant polar additives has been added, the MW and polydispersity index (PDI) of the obtained PE was not affected a lot, except for that when large amount of acetonitrile (MW decreased to 120000 and PDI is about 3.9) or dimethyl formamide (MW decreased to 307000) was added.

Entry	Catalyst	Additive	Yiled	Activity ^b	$M_{\rm w}^{\rm c}$	PDI ^c	$T_{\rm m}^{\ \rm d}$
	(µmol)	$(mol L^{-1})$	(g)		(10^{5})		(°C)
1	2c (2.5)	No additive	4.5	5400	467	1.9	138
2	2c (2.5)	Ethanol (2)	4.3	5160	437	2.0	137
3	2c (2.5)	Diethyl ether (2)	4.2	5040	502	2.0	137
4	2c (2.5)	Acetone (2)	3.9	3900	456	1.9	138
5	2c (2.5)	Ethyl acetate (2)	3.7	4440	478	1.9	136
6 ^{<i>e</i>}	2c (2.5)	Water (2)	3.1	3720	552	1.9	136
7	2c (2.5)	Dichloromethane (2)	2.9	3480	698	1.8	138
8	2c (2.5)	Acetonitrile (2)	0.9	960	120	3.9	135
9	2c (2.5)	Dimethyl formamide (2)	0.6	720	307	1.8	134

 Table 2. Representative Data for Ethylene Polymerization with the Addition of Polar Additives

 using complex 2c.^a

^a Reaction conditions, unless otherwise noted: ethylene 10 atm, toluene, 50 mL. ^b In 10^3 g·mol_{Ni}⁻¹·h⁻¹. ^cDetermined by GPC at 150 °C *vs* narrow polystyrene standard in 1,2,4-trichlorobenzene. ^d Measured by DSC, 20 °C min⁻¹. ^e Addition of 0.3 g SDS (sodium dodecyl sulfate).



Figure 3. Ethylene polymerization with the addition of various polar additives. Reaction conditions: 2.5 µmol of catalyst **2c**, 50 °C, 20 min, 10 bar, total volume 50 mL, 2 M additive. Control, no additive; DMF, dimethyl formamide; AcN, acetonitrile; DCM, dichloromethane; EA, ethyl acetate; ACE, acetone; DE, diethyl ether.

2.3 Copolymerization of Ethylene with Polar Vinyl Monomers

As shown in Figure 2, the bulky group 2,6-(OCH₃)₂C₆H₃C₆H₄- and C₆H₅C₆H₄- of complexes **2b**-**2d** effectively shielded the vacant p_z orbital of the dsp²-hybridized nickel center. Furthermore, these groups prevented monomer access to the metal center from the axial direction relative to the coordination plane, ACS Paragon Plus Environment Page 11 of 35

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thus reducing the chain transfer rate and favoring the formation of high-MW polymers. Because these nickel complexes displayed impressive catalytic performance for ethylene polymerization and good tolerance to various polar additives, we expected that introduction of a bulky axial substituent could facilitate copolymerization of ethylene with challenging polar vinyl monomers. Therefore, we conducted a detailed investigation of the catalytic performance of 2a-2d in the copolymerizations of ethylene with MA, a commercially available polar monomer (Table 3). We found that 2a gave unsatisfactory results under mild conditions: only tiny amounts of solid products were obtained even at a high catalyst loading (entry 1). In sharp contrast, 2b and 2c, which have bulkier phosphorus substituents, exhibited much higher catalytic activity and afforded much higher-MW copolymers (entries 3 and 4, respectively), suggesting that the bulky axial substituents not only retarded associative chain transfer and chain transfer to monomer but also prevented deactivation reactions such as bimolecular deactivation by means of chelating interaction between the ester group (-C(O)OMe) and the nickel center. Among the four complexes, 2d, which has the bulkiest substituents, displayed the highest catalytic activity (up to $10^5 \text{ g} \cdot \text{mol}_{Ni}^{-1} \cdot h^{-1}$) under similar conditions (entry 5). All in all, these neutral nickel catalysts displayed impressive catalytic activity for the copolymerization and produced high-MW copolymers (MW up to 108.0×10^3); MA incorporation percentages as high as 5.4 mol % could be easily achieved under mild conditions without requiring a large amount of MA.

Notably, all the copolymerizations described in this study were carried out with single-component nickel catalysts in the absence of any activators or additives that might generate radicals.¹⁷ In order to understand the catalytic copolymerization thoroughly, we also conducted the ethylene/MA copolymerization in the presence of butylated hydroxytoluene, a radical trap (Table 3, entry 7). Although the productivity decreased slightly (compare entries 6 and 7)—as was observed for ethylene polymerization in the presence of butylated hydroxytoluene (Table S1, compare entries S4 and S5)—similar MA incorporation was achieved. This result confirmed that all the copolymerizations catalyzed by **2a–2d** *via* a coordination–insertion mechanism.

Table 3. Representative Copolymerization of Ethylene and Polar Vinyl Monomers Using	
Complexes 2a–2d. ^a	

			// + //	<pre> FG FG </pre>	Catalysts 2a	-2d ┣		FG: OMe,	O ⁿ Bu, NN BA DM	le ₂ 4A		
-	Entry	Cat. (µmol)	Comon.	Temp. (°C)	[Comon.] (mol L-1)	Yield (mg)	Act. ^b	TOF ^c (E/Comon.)	Incorp. ^d (mol %)	$M_{\rm w}^{\ e}$ (10 ³)	PDI ^e	$T_{\rm m}^{f}$ (°C)
-	1	2a (20)	MA	70	0.1	64	3.2	100/6	5.4	1.2	1.3	92
	2	2b (10)	MA	70	0.2	257	25.7	823/30	3.7	9.4	2.0	112
	3	2b (10)	MA	50	0.2	263	26.3	882/20	2.2	22.6	2.0	117
	4	2c (10)	MA	50	0.2	493	49.3	1547/69	4.3	21.7	2.1	108
	5	2d (10)	MA	50	0.2	1000	100.0	3517/17	0.5	72.4	1.8	126
	6 ^{<i>g</i>}	2b (10)	MA	30	0.1	370	37.0	1301/7	0.5	108.0	1.6	131
	7^h	2b (10)	MA	30	0.1	240	24.0	844/4	0.5	64.4	1.7	129
	8^g	2a (30)	BA	70	0.2	84	2.8	73/6	7.7	1.6	1.3	$n.d.^{j}$
	9	2b (10)	BA	50	0.2	500	50.2	1646/32	1.9	45.3	2.6	120
	10	2c (10)	BA	50	0.2	402	40.2	1221/47	4.0	30.3	2.1	111
	11	2d (10)	BA	50	0.2	536	53.6	1947/14	0.7	95.8	1.8	125
	12 ^g	2a (30)	DMAA	70	0.1	3.6	1.2	37/2	3.3	3.2	2.7	113
	13	2b (10)	DMAA	50	0.2	89	8.9	301/4	1.2	16.3	1.7	126
	14	2c (10)	DMAA	50	0.2	111	11.1	386/3	0.7	23.4	1.8	127
	15	2d (10)	DMAA	50	0.2	202	20.2	710/(<4)	<0.5	63.2	2.2	129
	16	2e (10)	MA	50	0.1	trace	_	_	_	_	_	_
	17	2e (10)	MA	70	0.1	trace	_	_	_	_	_	_
	18 ⁱ	2e (20)	MA	70	0.1	46	2.3	55/9	13.6	_	_	n.d.

^{*a*} Reaction conditions, unless otherwise noted: 50 mL of toluene, ethylene pressure 10 bar, copolymerization for 60 min. MA, methyl acrylate; BA, *n*-butyl acrylate; DMAA, *N*,*N*-dimethylacrylamide. ^{*b*} In units of 10³ $g \cdot mol_{Ni}^{-1} \cdot h^{-1}$. ^{*c*} In units of $mol_{E} \cdot mol_{Ni}^{-1} \cdot h^{-1}/mol_{Comon}$. $mol_{Ni}^{-1} \cdot h^{-1}$. E, ethylene. ^{*d*} Determined by ¹H NMR spectroscopy at 120 °C. ^{*e*} PDI, polydispersity index; determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C vs narrow polystyrene standard. ^{*f*} Determined by differential scanning calorimetry. ^{*g*} Reaction carried out in 100 mL of toluene. ^{*h*} Reaction conducted in 100 mL of toluene in the presence of 200 mg of butylated hydroxytoluene. ^{*i*} Ethylene pressure 18 bar. ^{*j*} Not detected.

Moreover, these bulky nickel catalysts can be used to efficiently incorporate not only MA but also other polar vinyl monomers, specifically *n*-butyl acrylate (BA; Table 3, entries 8–11) and *N*,*N*-dimethylacrylamide (DMAA; entries 12–15, the first successful example *via* neutral nickel catalyst) into polymer chains. Specifically, **2a** afforded ethylene/BA copolymers containing up to 7.7 mol % BA

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and ethylene/DMAA copolymers containing up to 3.3 mol % DMAA, whereas 2d afforded copolymers with high MWs (BA, M_w up to 95.8 × 10³; DMAA, M_w up to 63.2 × 10³). The data in Table 3 indicates that the activities of the catalysts and the MWs of the copolymers increased upon introduction of bulky substituent group on the phosphorus atom of the nickel complexes. All the nickel catalysts showed better tolerance to a –C(O)OR group than to a –C(O)NMe group; that is, both catalytic activity for ethylene/acrylate copolymerization and –C(O)OR content in the ethylene/MA copolymer were much higher than the corresponding values in ethylene/acrylamide copolymerization.

Mitsubishi catalysts has only been reported to achieve the copolymerization of ethylene and MA under harsh reaction conditions (e.g., much higher ethylene pressure, 30 bar; a large amount of catalysts, $80 \mu mol$).^{13g} In this study, copolymerization of ethylene and MA promoted by Mitsubishi catalyst **2e** was also tried under milder reaction conditions. Unfortunately, there was hardly any polymers at 10 bar of ethylene pressure (Table 3, entries 16 and 17), or only discernible amount of polymers could be obtained even under 18 bar of ethylene pressure and larger dosage of **2e** was added (Table 3, entry 18).

The MWs of copolymers and the incorporation percentage of polar units in the copolymers could be controlled by tuning ethylene pressure, the concentration of polar comonomer in feed, and reaction temperature. In order to study the effect of different reaction parameter, we conducted the tunable ethylene/MA copolymerization by means of **2c**, and the results are summarized in Table 4. As ethylene pressure was increased from 5 to 20 bar, the catalytic activities $(11.4-185 \text{ kg} \cdot \text{mol}_{Ni}^{-1} \cdot \text{h}^{-1})$ and MWs $(10-79 \times 10^3)$ of the resulting copolymers dramatically increased, while the MA content (7.4–2.6 mol %) gradually decreased. In addition, reaction temperature was also intimately correlated with catalytic activity and copolymer structure. As the temperature was increased from 30 to 90 °C (Table 4, entries 1–4), catalytic activities and MWs of the copolymers decreased, whereas MA insertion percentage gradually increased, from 1.4 to 4.8 mol % (the data for reactions catalyzed by **2b** and **2d** at 70 °C are shown in Supporting Information). This observation is reasonable because the possible chain transfer reactions, like β -hydride elimination, were accelerated relative to chain propagation as reaction temperature increased. Compared with the palladium catalysts bearing classical phosphino-sulfonate

ligands, which work only at elevated temperature (>80 °C),³ the nickel complexes described herein can achieve the copolymerization of ethylene with MA in a wide temperature range (30–90 °C). Furthermore, **2c** exhibited impressive copolymerization ability: high MA incorporation percentages (up to 7.4 mol %) can be easily achieved without the need for a large amount of MA in feed.

Incorp.^d $M_{\rm w}^{\ e}$ TOF^{c} $T_{\rm m}^{f}$ Temp Comon. Р Yield Act.^b PDI^{e} Entry (10^3) $(^{\circ}C)$ $(mol L^{-1})$ (E/MA)(mol %)(°C) (bar) (mg)1 30 0.2 543 1858/26 107.4 2.0 10 54.3 1.4 127 493 21.7 2 50 0.2 10 49.3 1546/70 4.3 2.1 108 3 70 0.2 10 444 44.4 1379/68 4.7 13.5 2.0 108 27.1 6.7 4 90 0.2 10 271 843/35 4.8 2.1 101 5 50 0.2 5 114 11.4 7.4 96 329/26 10.0 1.7 6 50 0.2 20 185.0 6107/163 2.6 78.9 108 1850 1.8 7 50 10 5.8 12.3 1.9 97 0.4 137 13.7 411/25

Table 4. Tunable Copolymerization of Ethylene and Methyl Acrylate by Using Complex 2c.^a

^{*a*} Reaction conditions, unless otherwise noted: 50 mL of toluene, copolymerization for 60 min. ^{*b*} In units of $kg \cdot mol_{Ni}^{-1} \cdot h^{-1}$. ^{*c*} E, ethylene; in units of $mol_E \cdot mol_{Ni}^{-1} \cdot h^{-1}/mol_{MA} \cdot mol_{Ni}^{-1} \cdot h^{-1}$. ^{*d*} Determined by ¹H NMR spectroscopy at 120 °C. ^{*e*} PDI, polydispersity index; determined by gel permeation chromatography in 1,2,4-trichlorobenzene at 150 °C vs narrow polystyrene standard. ^{*f*} Determined by differential scanning calorimetry.

2.4 Characterization of Copolymers and Analysis of Their Microstructure

Differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) experiments showed that all the copolymers had relatively high MWs, unimodal MW distributions (M_w/M_n = 1.3–2.7), and high melting temperatures (92–131 °C), indicating their suitability for applications requiring functional semi-crystalline polymeric materials with homogeneous compositions. ¹H and ¹³C NMR analyses of the resultant copolymer microstructures (Supporting Information, Figures S23–S41) unambiguously confirmed successful insertion of polar units into the polymer backbone. All the collected characterization data (NMR, GPC and DSC) suggested that the comonomers were inserted both into the main chain and located at the chain end, as shown in Chart 1. The structure of the terminal polar unit of the copolymer indicates that the terminal polar monomer was inserted in a 2,1-fashion.

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Chart 1. Microstructures of Copolymers and Chain-End Structure.

To shed some light on the microstructure of the produced copolymers, we measured the ¹³C NMR spectra of three lower-MW copolymer samples that were produced with catalyst 2a and that contained 5.4 mol % MA, 7.7 mol % BA, or 3.3 mol % DMAA (Table 3, entries 1, 8 and 12, respectively). In the ¹³C NMR spectrum of the ethylene/MA copolymer (Figure 4), the resonances at 176.3, 166.9, and 50.3 ppm were ascribed to the -C=O group of in-chain MA (2.0 mol %), the -C=O group of terminal MA (3.4 mol %), and the -OCH₃ group of MA units, respectively. Note that signals corresponding to MA-initiated structure were negligible. In addition to the unimodal MW distribution (as indicated by GPC, Figures S72–S78) and the single melting point (as indicated by DSC, Figures S50–S56) for ethylene/MA copolymers, the presence of resonances for -CH(COOCH₃)CH₂CH₂- and -CH(COOCH₃)CH₂CH₂- moieties at 32.1 and 27.4 ppm in the ¹³C NMR spectrum of the 5.4 mol % MA copolymer confirmed that true copolymers rather than a simple mixture of PE and a MA homopolymer had been produced. Quantitative analysis of the ¹³C NMR spectrum of the 7.7 mol % BA copolymer revealed that BA had been incorporated both into the polymer main chain and at the chain end (Figure S38). In the ¹H NMR spectra of the ethylene/DMAA copolymers (Figures S35–S37), we observed two resonances of $-N-(CH_3)_2$ at around 3.08 ppm, which resulted from the presence of in-chain DMAA and chain-end DMAA structure. In the ¹³C NMR spectrum of the 3.3 mol % DMAA copolymer (Figure 5), a broad signal at around 35.7 ppm, corresponding to -N-(CH₃)₂, was clearly observed. The carbonyl resonance at 166.0 ppm was ascribed to C=O carbon linked to a C=C bond. This C=C double bond was generated via β -H elimination process after 2.1-insertion of DMAA. The other two lower-field carbonyl signals, at 175.5 and 176.8 ppm, were ascribed to in-chain DMAA units and DMAA-initiated end groups, respectively.



Figure 4. The ¹³C NMR spectrum of an ethylene/methyl acrylate (MA) copolymer containing 5.4 mol % MA produced *via* catalyst **2a** at 70 °C (Entry 1 in Table 3).



Figure 5. The ¹³C NMR spectrum of an ethylene/*N*,*N*-dimethylacrylamide (DMAA) copolymer containing 3.3 mol % DMAA produced *via* catalyst **2a** at 70 °C (Table 3, entry 12).

Finally, we carried out ${}^{1}\text{H}{-}^{1}\text{H}$ correlation spectroscopy (COSY) to obtain additional information about the microstructure of the copolymers. In the ${}^{1}\text{H}{-}^{1}\text{H}$ COSY spectrum of the ethylene/MA copolymer containing 5.4 mol % MA (Figure 6), we observed a cross-peak (B, C; 7.04, 2.28 ppm) corresponding to correlation between the two protons of the C=C bond (CH₃OOCCH₂=CH–) of a terminal MA unit, along with cross-peaks (D, E) and (C, D), which we ascribed to correlation between the protons of the C=C of the terminal MA unit (CH₃OOCCH₂=CH–) and the protons of the adjacent methylene group (PE-CH₂). In addition, cross-peaks (3,4) and (4,5) illustrate the correlation between the protons of the in-chain MA unit (CH₃OOCCHCH₂–) and the protons of the methylene group (PE-CH₂). ACS Paragon Plus Environment

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The correlation between the vinyl chain-end proton and the protons of the PE- CH_2 group in the PE skeleton was too weak to be observed, whereas correlation between the methyl chain-end proton and the PE- CH_2 protons could be observed as cross-peak (a', b'). Taken together, the ¹³C NMR, ¹H–¹H COSY, FT-IR (Figures S88 and S89), and DSC data indicate definitively that the material was a true copolymer rather than a mixture of PE and poly(methyl acrylate).



Figure 6. ¹H–¹H correlation spectrum of an ethylene/methyl acrylate (MA) copolymer containing 5.4 mol % MA obtained *via* catalyst **2a** at 70 °C (Table 3, entry 1).

All the NMR data of the copolymers produced by the new neutral nickel catalysts indicate that (1) the polar monomer can be inserted both into the polymer main chain and at the chain end in isolation and (2) the copolymers were highly linear structures without side branches. To investigate how the bulky nickel catalysts influenced the microstructure of the copolymers, we also carried out an in-depth analysis of the ¹H NMR spectra of four ethylene/MA copolymers, which were designated **copolymer a–d**, and which were obtained with complexes **2a–2d**, respectively (Table 5 and Figure 7). We found that the percentage of terminal MA structure (signal A in Figure 7) considerably decreased from 3.4 mol % in **copolymer a** (obtained with **2a**) to <0.1 mol % in **copolymer d** (obtained with **2d**), and the proportion of in-chain MA structure in total MA structure (signal 1 in Figure 7) dramatically increased from 37% in **copolymer a** to > 93% in **copolymer d**. That is, a β -H elimination reaction after 2,1-insertion of MA was effectively inhibited. In addition, the vinyl end (CH₂=CH–) signal (signal a in Figure 7), which

originates from the product of β -H elimination after ethylene insertion, was observed only in the copolymer produced with **2a** at 70 °C, confirming the hypothesis that the β -H elimination reaction was inhibited by the bulky axial group.

Table 5. Structures of Ethylene/Methyl Acrylate (MA) Copolymers a-d Obtained with Catalysts2a-2d at 70 °C, respectively.

	Copolymer a	Copolymer b	Copolymer c	Copolymer d
Total MA (mol %)	5.4	3.7	4.7	1.4
In-chain MA (mol %)	2.0	2.8	4.0	>1.3
Terminal MA (mol %)	3.4	0.9	0.8	<0.1
In-chain/total (%)	37	76	85	>93
Vinyl end (mol %)	0.8	n.d. ^{<i>a</i>}	n.d. ^{<i>a</i>}	n.d. ^{<i>a</i>}

^{*a*} Not detected. The copolymerization data of **copolymer a-d** were found in Table 3, entry 1, Table 3, entry 2, Table 4, entry 3, and Table S2, entry 6, respectively.



Figure 7. ¹H NMR spectra of ethylene/methyl acrylate (MA) copolymers (**copolymer a–d**) produced with complexes **2a–2d**, respectively, at 70 °C. The copolymers contained 5.4 mol %, 3.7 mol %, 4.7 mol %, and 1.4 mol % MA, respectively.

In addition to the MW and the percentage incorporation of MA, the manner that MA was incorporated into polymer chain was also strongly influenced by the reaction temperature. Since the temperature was elevated from 30 to 90 °C, the proportion of in-chain MA structure decreased from 100% to 85% (Figure 8), owing to the acceleration of the β -hydride elimination reaction; nevertheless, the vinyl-end

structure (signal a in Figure 8) could not be clearly observed even at 90 °C because the structure corresponding to vinyl-end incorporation accounted for only 0.2 mol % of the obtained copolymer. In the ¹³C NMR spectrum of a copolymer obtained by complex **2c** at low temperature 30 °C (Figure 9), the signals of terminal MA (signal F in Figure 4) were very weak, and the isolated MA units (signal 6 in Figures 4 and 9) were present mainly in the polymer main chain.



Figure 8. Temperature dependence of the ¹H NMR spectra of ethylene/methyl acrylate (MA) copolymers produced by means of complex **2c** (Table 4, entry 1-4). The copolymers produced at 30, 50, 70, and 90 °C contained 1.4 mol %, 4.3 mol %, 4.7 mol %, and 4.8 mol % MA, respectively.



Figure 9. The ¹³C NMR spectrum of an ethylene/methyl acrylate (MA) copolymer produced by catalyst **2c** at 30 °C (Table 3, entry 1, 1.4 mol % of MA incorporation).

2.5 Possible Deactivation Pathways for Reaction of Methyl Acrylate with [P,O] Nickel Catalysts

According to previous studies of ethylene/MA copolymerization.^{3c,2d} the desired chain propagation reaction may be accompanied by undesirable side reactions leading to the formation of an inactive metal center via the three pathways shown in Scheme 4: (a) formation of a stable σ -coordination complex by direct coordination of the ester group of free MA with the nickel center, resulting in loss of catalytic activity or even catalyst poisoning; (b) formation of a stable metal-carbonyl chelate after MA insertion through back-biting reaction of the carbonyl group; and (c) formation of a carbonyl chelate complex via coordination of the carbonyl group with the nickel center at the axial direction, which results in bimolecular deactivation.^{13b} These side reactions must be suppressed if effective chain propagation is to be achieved. The experimental results in this current study demonstrate that nickel catalysts with high activity for ethylene/MA copolymerization can be achieved by introducing a bulky group in the axial position relative to the nickel center. Compared with a small complex (2a), the nickel catalysts bearing bulkier axial groups exhibited much higher activities and produced copolymers with higher MWs. Therefore, we speculate that steric bulk in the axial position plays a vital role in the distinct differences between small complex 2a and bulkier complexes 2b-2d; that is, introduction of a bulky group in the axial position may partially or completely inhibit the abovementioned side reactions.



Scheme 4. Reaction Pathways during Ethylene/Methyl Acrylate Copolymerization in the Presence of [P,O] Neutral Nickel Catalysts.

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To further explore the effect of the bulky groups of these nickel complexes on the polymerization characteristics and the microstructure of the resultant polymers and, more importantly, to elucidate the possible mechanism of ethylene and MA copolymerization by these catalysts, we conducted real-time ¹H NMR spectroscopic monitoring of separate reactions of complex **2a** and **2b** with MA in the absence of ethylene in NMR tubes at ambient temperature (Supporting Information, Figures S92-S94). We observed that immediately upon addition of MA (60 equiv relative to the nickel complex) to a benzene- d_6 solution of complex 2a or 2b, the C=C double bond of MA inserted into the Ni(II)–CH₃ bond to afford a short-lived nickel species (not observed by ¹H NMR). Specifically, the resonance for Ni(II)-CH₃ decreased while the characteristic signals for MA insertion increased. The characteristic resonances of methyl butyrate, which forms readily via a bimolecular deactivation mechanism after 2,1-insertion of MA (Scheme 5, pathway a),^{13b} were clearly observed at 2.02 (t, ${}^{3}J_{H-H} = 7.3$ Hz), 1.63–1.26 (m), and 0.76 (t, ${}^{3}J_{H-H} = 7.4$ Hz) ppm. In addition, we observed the formation of methyl crotonate, a deactivation product generated by β -H elimination reaction after MA insertion into Ni(II)-CH₃ bond by 2,1-fashion (Scheme 5, pathway b; 1.37 and 3.44 ppm for CH₃CH=CH- and $-C(O)OCH_3$, respectively). Meanwhile, no distinct signal for the ultimate product formed via 1,2-insertion of MA was found in the ¹H NMR spectra, indicating that MA inserted into Ni(II)-C bond mainly via 2,1-fashion under these conditions. As revealed in Figures S95 and S96, the residual Ni-CH₃ content relative to the initial Ni–CH₃ content decreased over time, following first-order kinetics, and the rate for the reaction between MA and complex 2a ($2.36 \times 10^{-4} \text{ s}^{-1}$, Figure S95) was faster than the rate for complex **2b** $(9.97 \times 10^{-5} \text{ s}^{-1})$, Figure S96).



Scheme 5. Possible Pathways for Reaction of Methyl Acrylate with [P,O] Neutral Nickel Catalysts As Indicated by the NMR Monitoring at Ambient Temperature.

3. Summary and Conclusions

In conclusion, phosphino-phenolate nickel complexes with steric bulk were highly active for ethylene polymerization in a wide temperature window (10–90 °C); and produced highly linear, high-MW (M_w up to 6.53 × 10⁵) PEs. Furthermore, these nickel complexes displayed unexpectedly high catalytic activities for ethylene polymerization (up to ca. 10⁷ g·mol_{Ni}⁻¹·h⁻¹) even in the presence of large amounts of polar additives; and these values of catalytic activity among the highest catalytic activities by using neutral nickel catalysts. Moreover, highly efficient copolymerization between ethylene and commercially available polar vinyl monomers (MA, BA, and DMAA) was readily achieved with these complexes under mild conditions. High-molecular-weight (M_w up to 1.08 × 10⁵) copolymers, greatly improved catalytic activity, and good tolerance to polar solvents were simultaneously achieved by introducing bulky phosphorus substituents in the axial position. This paper describes a serious of unique single-component neutral nickel catalysts that showed unprecedentedly high catalytic activity and robust thermal stability to yield linear (co)polymers with high molecular weight, and also have potential utility for efficiently incorporating various challenging polar monomers (acrylates or an acrylamide) into linear polymer backbones. These phosphino-phenolate nickel catalysts may serve as economical alternatives to

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palladium catalysts for copolymerizing ethylene with challenging polar vinyl monomers. Future work will focus on exploring the effects of various bulky substituents on catalytic activity and copolymer MW, as well as on broadening the scope to other commercially available polar comonomers.

4. Experimental Section

Methods and Materials. All experiments and manipulations sensitive to moisture or air were performed in an MBraun glovebox or by means of standard Schlenk techniques, unless otherwise noted. Diethyl ether, *n*-hexane, dichloromethane, and toluene were purified by an MBraun solvent purification systems. Ethylene (99.9%) was purchased from BF Special Gas Limited Company without any purification. Compound 2-(diphenyphosphanyl)-6-*tert*-butylphenol (**1a**), complex [6-^{*t*}Bu-2-PPh₂-C₆H₃O]Ni(Me)(Py) (**2a**), Py₂Ni(CH₃)₂, and Py₄NiCl₂ were synthesized by literature procedure.¹²ⁱ NiCl₂·6H₂O was purchased from Chinese Medicine. Polar comonomers methyl acrylate (MA), *n*-butyl acrylate (BA), *N*,*N*-dimethylacrylamide (DMAA), and *n*-butyl acrylate (BA) were distillated over calcium hydride (CaH₂) prior to use.

Physical and Analytical measurements. The NMR spectra of obtained (co)polymers and complexes were recorded on a Bruker 400 MHz spectrometer at room temperature or 120 °C (¹H NMR: 400Hz, ³¹P NMR: 162 Hz, ¹³C NMR: 101 Hz). Chemical shift values for protons in all spectra are referenced to the residual proton resonance of chloroform-*d* (δ : 7.26), benzene-*d*₆ (δ : 7.16), 1,1,2,2-tetrachloroethane-*d*₂ (δ : 6.00) and *o*-dichlorobenzene-*d*₄ (δ : 7.14, 7.28, 7.41). Chemical shift values for carbons in all spectra are also referenced (δ : 77.16 for chloroform-*d*, δ : 128.62 for benzene-*d*₆, δ : 73.80 for 1,1,2,2-tetrachloroethane-*d*₂, (δ : 132.45, 129.86 (t), 126.86 (t) for *o*-dichlorobenzene-*d*₄). Gel permeation chromatography (GPC) analyses were performed at 150 °C on a high-temperature chromatograph (PL-GPC 220 type) equipped with three PLgel columns (10 µm Mixed-B LS type) using 1,2,4-trichlorobenzene as mobile phase at a rate of 1.0 mL·min⁻¹. Molecular weights were calculated according the calibration by the polystyrene standard EasiCal PS-1 (PL). DSC measurements were carried out with a differential scanning calorimeter (Q2000 V24.11 Build 124) under N₂ at a heating rate

of 20 °C·min⁻¹ from the second scan. X-ray data of crystals were collected on a Bruker Smart APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å) with CCD detector at 186 K with the ω scan mode. Elemental analyses were proceeded on an elemental Vario EL spectrometer. FT-IR data of polymer samples were collected on a Bio-Rad FTS-135 spectrometer (KBr pellet).

Preparation and characterization of ligands and nickel complexes. The ligand **1a** and nickel complex **2a** were synthesized as our previous work,¹²ⁱ and all the other ligands (**1b–1d**) as well as nickel complexes (**2b–2d**) were prepared as following similar procedures:

Synthesis of 2-[(2',6'-dimethoxybiphenyl-2-yl)phenylphosphanyl]-6-tert-butylphenol (1b). A 100 mL vial was charged with 2-(2-tert-butylphenoxy)-tetrahydro-2H-pyran (2.34 g, 10 mmol) and 25 mL of diethyl ether. n-BuLi (4.6 mL, 11 mmol, 2.4 M in hexane) was slowly injected dropwise, and the reaction mixture was stirred for 6 h at 25 °C, yielding suspension A. Meanwhile, another vial was charged with of 2-bromo-2',6'-dimethoxybiphenyl (2.9 g, 10 mmol) and 30 mL of THF, and 1.1 equiv of *n*-BuLi (11 mmol, 2.4 M in *n*-hexane) was added under an ice bath. After stirring for 3 h, the resulting reaction mixture was slowly transferred to a solution of PPhCl₂ (10 mmol, 1.35 mL) in 10 mL of THF cooled in an ice bath, and then the suspension was stirred for 7 h at 25 °C, yielding reaction mixture **B**. Hereafter the suspension A was slowly transferred into B. After reaction for overnight, the solvent was removed under vacuum by means of a rotary evaporator, and the residue was purified by column chromatography. The resultant white solid was dissolved in degassed ethyl acetate and mixed with aqueous HCl. The solution was stirred at room temperature for 5 h before addition of aqueous NaHCO₃, and then extracted with ether. The pure target compound was obtained by column chromatography as a white solid (2.5 g, 53%). ¹H NMR (400 MHz, C₆D₆): δ 7.49 (dd, J = 7.6, 4.5 Hz, 1H), 7.32 (m, 3H), 7.25 (d, J = 7.7 Hz, 1H), 7.14–6.92 (m, 7H), 6.74 (t, J = 7.6 Hz, 1H), 6.32 (dd, J = 15.2, 8.4 Hz, 2H), 3.14 (d, J = 5.3 Hz, 6H, $-OCH_3$), 1.50 (s, 9H, t-Bu). ¹³C NMR (101 MHz, C₆D₆): δ 158.8, 158.6, 158.3 (d, J = 10.9 Hz), 142.4, 142.1, 136.3 (d, J = 5.5 Hz), 136.1, 135.8, 134.0, 133.9, 133.8, 133.0, 131.7 (d, J = 10.9 Hz), 142.4, 142.1, 136.3 (d, J = 5.5 Hz), 136.1, 135.8, 134.0, 133.9, 133.8, 133.0, 131.7 (d, J = 10.9 Hz), 136.1, 135.8, 134.0, 133.9, 133.8, 133.0, 131.7 (d, J = 10.9 Hz), 136.1, 1J = 6.6 Hz), 129.6, 128.7, 122.5 (d, J = 2.7 Hz), 120.5, 119.5 (d, J = 8.0 Hz), 104.1 (d, J = 4.7 Hz), 55.2 $(d, J = 12.1 \text{ Hz}, -OCH_3)$, 35.1 $(d, J = 19 \text{ Hz}, -C(CH_3)_3)$, 30.0 $(-C(CH_3)_3)$. ³¹P NMR (162 MHz, C₆D₆): δ ACS Paragon Plus Environment

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-26.53. Anal. Calcd for C₃₀H₃₁O₃P: C, 76.58; H, 6.64. Found: C, 76.79; H, 6.43.

Synthesis of 2-[(biphenyl-2-yl)phenylphosphanyl]-6-tert-butylphenol (1c). Into a 250 mL flask equipped with PPhCl₂ (1.85 g, 10 mmol) and 20 mL of dry THF, a solution of 2-biphenylmagnesiumbromide (0.5 M, 10 mmol, 20 mL) in diethyl ether was slowly transferred over 0.5 h at -78 °C. After stirring for 2 h at 25 °C, the resulting white suspension was slowly transferred into the suspension A (10 mmol, the same synthesis as that for compound 1b) at 0 °C, and then the mixture quickly became clear. After reaction for 6 h, all the solvents of resulting mixture were removed under vacuum, and the residue were dissolved in 40 mL of degassed ethyl acetate. After the addition of several drops aqueous HCl, the mixture was reaction for 5 h at room temperature until saturated aqueous NaHCO₃ added, and then extracted with ether. The organic phase was dried over Na₂SO₄, filtered, and concentrated under vacuum via a rotary evaporator. The ultimate pure target compound was obtained by column chromatography as a white solid (1.84 g, 45%). ¹H NMR (400 MHz, C_6D_6): δ 7.34 (dd, J = 6.8, 5.4 Hz, 1H), 7.30–7.22 (m, 3H), 7.18 (m, 3H), 7.14–7.03 (m, 5H), 6.95 (m, 5H), 6.72 (t, *J* = 7.6 Hz, 1H), 1.46 (s, 9H, $-C(CH_3)_3$). ¹³C NMR (101 MHz, C₆D₆): δ 158.8 (d, J = 15.1 Hz), 148.5, 148.3, 142.1 (d, J= 6.3 Hz), 136.4 (d, J = 0.9 Hz), 135.6 (d, J = 3.0 Hz), 135.3 (d, J = 4.9 Hz), 134.0, 133.9 (d, J = 1.5Hz), 133.5, 130.6, 130.5, 129.8 (d, J = 3.3 Hz), 129.3 (d, J = 5.3 Hz), 128.9, 128.8, 128.1, 127.7, 121.5, 120.9 (d, J = 1.8 Hz), 35.2 (d, J = 1.8 Hz, $-C(CH_3)_3$), 29.8 ($-C(CH_3)_3$). ³¹P NMR (162 MHz, C_6D_6): δ -29.03. Anal. Calcd for C₂₈H₂₇OP: C, 81.93; H, 6.63. Found: C, 81.83; H, 6.82.

Synthesis of 2-[bis(biphenyl-2-yl)phosphanyl]-6-tert-butylphenol (1d). In a 100 mL vial, 2-bromobiphenyl (4.66 g, 20 mmol) was dissolved in 40 mL of diethyl ether, and then *n*-BuLi (4.6 mL, 2.4 M in *n*-hexane, 11 mmol) was slowly added under a dry ice-acetone bathing. After reaction for further 2 h at room temperature, (Et₂N)PCl₂ (1.74 g, 10 mmol, 0.5 equiv) was added dropwise at that temperature, and then the reaction mixture was stirred for 5 h at -20 °C (slowly warm to -20 °C). Ethereal HCl (10 mL, 20 mmol, 2 M in diethyl ether) was slowly added, and the reaction mixture stirred for 6 h, and then the resulting precipitate was filtered off over Celite under N₂ atmosphere. The filtrate used as obtained as purification was slowly transferred into another vial charged with suspension **A** (10

mmol, the same synthesis as that for compound **1b**) at an ice bath, and then the resulting mixture was warm to 25 °C. After stirring for 10 h, all the solvents were removed under vacuum and the residue was redissolved in 50 mL of degassed ethyl acetate. After addition of 2 mL of aqueous HCl (5 M in diethyl ether), the mixture was stirred at ambient temperature for 6 h before aqueous NaHCO₃ added, and then extracted with ether. The organic phase was dried over Na₂SO₄, filtered and concentrated. Finally, the pure target compound was prepared by column chromatography as a white solid (2.08 g, 43%). ¹H NMR (400 MHz, C₆D₆): δ 7.38–7.32 (m, 2H), 7.25 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.10–6.98 (m, 14H), 6.95 (td, *J* = 7.4, 1.5 Hz, 2H), 6.90 (d, *J* = 12.1 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 1.47 (s, 9H). ¹³C NMR (101 MHz, C₆D₆): δ 159.1, 158.9, 148.3, 148.0, 142.1 (d, *J* = 6.0 Hz), 136.4 (d, *J* = 1.0 Hz), 135.0 (d, *J* = 3.7 Hz), 134.3, 134.3, 130.4 (d, *J* = 5.2 Hz, 1H), 129.9, 129.8, 129.3, 129.2, 128.0, 121.3, 120.9, 35.2 (d, *J* = 2.1 Hz, $-C(CH_3)_3$), 29.9 ($-C(CH_3)_3$). ³¹P NMR (162 MHz, C₆D₆): δ -50.14. Anal. Calcd for C₃₄H₃₁OP: C, 83.92; H, 6.42. Found: C, 84.01; H, 6.50.

Synthesis of [6-*tert*-**Bu**-2-(2-(2',6'-(MeO)₂-C₆H₃)-C₆H₄)(Ph)P-C₆H₃O]Ni(Me)(Py) (2b). To a stirred solution of Py₂NiMe₂ (0.15 g, 0.6 mmol) in 10 mL of dry toluene, a solution of ligand **1b** (0.24 g, 0.5 mmol) in toluene (10 mL) at room temperature was added over 5 min. After reaction for 5 h, the resultant nickel black was filtered off through Celite and washed with 3 mL of toluene by two times. The filtrate was concentrated to about 2 mL, and crystallization by diffusion of *n*-hexane (15 mL) into the clear solution afforded yellowish brown crystals **2b** (0.24 g, 76%). ¹H NMR (400 MHz, C₆D₆): δ 8.50–8.12 (m, 2H), 7.76–7.54 (m, 3H), 7.48 (m, 1H), 7.30 (d, *J* = 6.5 Hz, 1H), 7.29–7.18 (m, 3H), 7.13–6.88 (m, 4H), 6.80 (m, 1H), 6.68–6.46 (m, 4H), 6.37 (d, *J* = 8.2 Hz, 1H), 3.37 (s, 3H, (–OCH₃), 2.97 (s, 3H, –OCH₃), 1.55 (s, 9H, –C(CH₃)₃), –0.71 (d, *J* = 4.9 Hz, 3H, Ni–CH₃). ¹³C NMR (101 MHz, C₆D₆): δ 174.9 (d, *J* = 20.8 Hz), 159.7, 158.2, 150.6, 137.4 (d, *J* = 8.8 Hz), 137.1, 136.6, 136.0, 134.9, 133.3 (d, *J* = 9.3 Hz), 132.4 (d, *J* = 9.6 Hz), 130.4, 130.4, 129.9, 129.19, 128.8, 128.6 (d, *J* = 1.7 Hz), 126.5 (d, *J* = 6.6 Hz), 54.6 (–OCH₃), 54.0 (–OCH₃), 35.0 (d, *J* = 1.7 Hz), -C(CH₃)₃), 29.5 (–C(CH₃)₃), 54.0 (–OCH₃), 35.0 (d, *J* = 1.7 Hz), -C(CH₃)₃), 29.5 (–C(CH₃)₃), 54.0 (–OCH₃), 35.0 (d, *J* = 1.7 Hz), -C(CH₃)₃), 29.5 (–C(CH₃)₃), 54.0 (–OCH₃), 55.0 (–C(CH₃)₃), 54.0 (–OCH₃), 55.0 (–C(CH₃)₃), 55.0 (

-14.6 (d, *J* = 40.0 Hz, Ni–*C*H₃). ³¹P NMR (162 MHz, C₆D₆): δ 21.47. Anal. Calcd for C₃₆H₃₈NNiO₃P: C, 69.59; H, 6.00; N, 2.25. Found: C, 69.43; H, 6.13; N, 2.19.

Synthesis of [6-*tert*-Bu-2-(2-C₆H₃-C₆H₄)(Ph)P-C₆H₃O]Ni(Me)(Py) (2c). Complex 2c was prepared in 86% yield analogously to the synthesis of complex 2b using ligand 1c instead of ligand 1b. ¹H NMR (400 MHz, C₆D₆): δ 8.43 – 8.29 (m, 2H), 7.78–7.65 (m, 4H), 7.62–7.49 (m, 1H), 7.43 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (ddd, *J* = 7.6, 4.5, 1.4 Hz, 1H), 7.08–6.98 (m, 3H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.73 (ddd, *J* = 9.2, 3.2, 1.6 Hz, 1H), 6.64 (td, *J* = 7.4, 2.1 Hz, 1H), 6.46–6.40 (m, 2H), 1.61 (s, 9H, –C(CH₃)₃), –0.84 (d, *J* = 4.9 Hz, 3H, Ni–CH₃). ¹³C NMR (101 MHz, C₆D₆): δ 175.0, 174.8, 150.9, 148.6, 148.5, 142.9 (d, *J* = 5.2 Hz), 139.1 (d, *J* = 8.8 Hz), 136.4, 135.7, 135.2, 135.0 (d, *J* = 1.2 Hz), 132.8, 132.7, 132.1, 132.0, 131.8, 131.3, 131.1, 131.0, 130.97, 130.4 (d, *J* = 2.2 Hz), 129.7 (d, *J* = 1.2 Hz), 129.3 (d, *J* = 1.9 Hz, –C(CH₃)₃), 29.9 (–C(CH₃)₃), –14.28 (d, *J* = 37.4 Hz, Ni–CH₃). ³¹P NMR (162 MHz, C₆D₆): δ 25.02. Anal. Calcd for C₃₄H₃₆NNiOP: C, 72.62; H, 6.09; N, 2.49. Found: C, 72.51; H, 5.97; N, 2.54.

Synthesis of [6-*tert*-Bu-2-(2-C₆H₃-C₆H₄)₂P-C₆H₃O]Ni(Me)(Py) (2d). Complex 2d was prepared in 84% yield analogously to the synthesis of complex 2b using ligand 1d instead of ligand 1b. ¹H NMR (400 MHz, C₆D₆): δ 8.59–8.49 (m, 2H), 7.87 (broad, 4H), 7.67–7.55 (m, 1H), 7.25–7.17 (m, 6H), 7.14–6.93 (m, 7H), 6.88–6.80 (m, 1H), 6.59–6.54 (m, 2H), 6.38 (td, *J* = 7.5, 2.2 Hz, 1H), 1.53 (s, 9H, -C(CH₃)₃), C1.04 (d, *J* = 5.2 Hz, 3H, Ni–CH₃). ¹³C NMR (101 MHz, C₆D₆): δ 172.6, 172.4, 150.6, 147.7, 147.5, 142.3 (d, *J* = 3.0 Hz), 137.5, 137.4, 136.1, 134.7 (d, *J* = 3.3 Hz), 133.4, 132.9, 131.9 (d, *J* = 7.8 Hz), 129.9, 129.7, 129.0, 126.7, 126.0 (d, *J* = 7.1 Hz), 122.7 (d, *J* = 1.4 Hz), 121.6, 121.1, 113.4 (d, *J* = 7.8 Hz), 34.8 (d, *J* = 1.9 Hz, -C(CH₃)₃), 29.5 (-C(CH₃)₃), -13.2 (d, *J* = 37.3 Hz, Ni–CH₃). ³¹P NMR (162 MHz, C₆D₆): δ 22.39. Anal. Calcd for C₄₀H₃₈NNiOP: C, 75.25; H, 6.00; N, 2.19. Found: C, 75.51; H, 5.87; N, 2.24.

Polymerization using well-defined neutral nickel catalysts. Polymerizations was performed in a 200 mL autoclave, which was heated under vacuum at 150 °C for 5 h, and then was cooled to the

required temperature. Into the autoclave equipped with a vigorous mechanical stirring motor, toluene was added under vacuum. A fresh toluene solution of certain amount of catalyst was injected into the autoclave by a dry syringe. The total volume of the polymerization medium was fixed at 100 mL or 50 mL. The polymerization apparatus was filled with ethylene rapidly to the prescribed pressure, and maintain at the desired constant pressure. For copolymerization trials, polymerization medium was pre-saturated with ethylene before catalysts added. Then, the comonomer solution was quickly injected into the autoclave, followed by quickly pressuring of ethylene. After a specified reaction time, the mechanical stirring motor was quickly stopped, and the remaining ethylene was evacuated. The solid polymer or copolymer was collected by filtration after precipitation from ethanol, except for ethylene/MA copolymer precipitation from methanol, washed with acetone, and dried in a vacuum drying oven at 60 °C.

ASSOCIATED CONTENT

Supporting Information

In the Supporting Information, details for the characterization of the compounds, representative NMR spectra, DSC traces, FT-IR spectra, and GPC traces of the polymers, and X-ray crystallography data are all supplied. It is available free of charge *via* the Internet at <u>http://pubs.acs.org.</u>

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