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Phosphine/Benzocyclone-based Neutral Nickel Catalysts for Ethylene Polymerization and Copolymerization with Polar Monomers

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Electronic Supplementary Information

Abstract The efficient copolymerization of olefin with polar monomers using nickel-based catalysts presents a longstanding challenge. In this contribution, three phosphine-benzocyclone ligands and corresponding neutral nickel catalysts (**Ni1**: Ar = Ph; **Ni2**: Ar = 2-(C_6H_5)C_6H_4; **Ni3**: Ar = 2-[2',6'-$(MeO)_2$-C_6H_3]C_6H_4) were prepared and applied for the ethylene polymerization and copolymerization with polar monomers without any cocatalyst. The bulky substituent groups in complexes **Ni2** and **Ni3** contributed to high catalytic activities (up to 7.24×10^6 and 9.04×10^6 g·mol_{Ni}^{-1}·h^{-1}, respectively), and produced high-molecular-weight polyethylene (M_w up to 545.7 kDa). Complex **Ni3** exhibited high activities for ethylene polymerization at the level of 10^6 g·mol_{Ni}^{-1}·h^{-1} across a wide range from 30 °C to 120 °C, exhibiting excellent high temperature tolerance. These nickel complexes were also effectively employed in the copolymerization of ethylene with methyl acrylate, ethyl acrylate, butyl acrylate and lauryl acrylate, producing copolymers with high molecular weights (M_w up to 80.5 kDa) and high polar monomer incorporation (up to 8.2 mol%). Microstructure analyses revealed that the introduction of large sterically hindered substituents facilitated the incorporation of polar functional units into the polymer backbone. This study demonstrates the potential of these nickel-based catalysts for efficient copolymerization of olefin with polar monomers.

Keywords Neutral nickel catalyst; Ethylene polymerization; Copolymerization; Polar acrylate monomers

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INTRODUCTION

Direct introducing polar functional groups into polyolefin chains composed of saturated carbon chains to improve the functional properties of polyolefin, such as adhesion, printability, dyeing, rheology, barrier, degradability, compatibility with other polymer materials, blending, *etc*., has been an extremely important and challenging topic in the field of olefin polymerization for a long time.[1–5] Despite the widespread use of early transition metal catalysts in industrial production, their high oxygen affinity poses toxic effects to the catalytic center in copolymerization of ethylene with polar monomers.[6–8] This toxicity can be caused by direct coordination poisoning of the polar monomer with the metal center, formation of stable chelates, or deactivation of the catalyst because of elimination reactions of β-X (X = heteroatom) after polar monomer insertion.[9–11] In contrast, late transition metal catalysts with weak oxygen affinity facilitate the direct copolymerization of olefins and polar monomers.[3,5,11–18] Over the past few decades, palladium catalysts have made remarkable advancements in copolymerizing ethylene with abundant of challenging polar monomers, and extensive research has been carried out on the underlying mechanisms[19–24] after Brookhart *et al*.'s[25] groundbreaking discover in 1996 that α-diimine palladium complexes could catalyze the copolymerization of ethylene and acrylate monomer. However, the high cost and relatively low activity of palladium catalysts limit their wide application. In contrast, the late transition metal nickel, owing to its natural abundance, low price, and good water and oxygen resistance, has emerged as a competitive alternative in the field of polyolefin catalysis and has garnered increasing attention.[16,26,27] Meanwhile, despite ongoing efforts, compared with palladium-based catalysts, the development of corresponding cationic nickel catalysts has still remained a longstanding challenge because of their intrinsically high oxophilicity nature, which manifests in poor temperature tolerance, the lower molecular weight of the resulting (co)polymers, and greater susceptibility to suppression by polar monomers. These limitations significantly diminish the development and application of cationic nickel catalysts.

Compared with commonly used cationic catalyst, neutral

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nickel catalyst possess relatively weaker oxophilicity nature.[28,29] Recently, several neutral nickel catalysts featuring diverse ligand structures, including phosphine sulfonates,[30–32] *N*-heterocyclic carbene,[33] salicylaldimine,[34] six-membered aniline-anthraquinone,[35,36] heterogeneous naphthoquinone-based[37] and other specially designed structures,[38–40] have been reported for their efficacy in facilitating the copolymerization of ethylene with polar monomers (Chart 1, I–IX). Building upon salicylaldimine Ni catalytic systems[34,41] (Chart 1, I) have been reported with optimized substitutions with different steric and electronic effects and/or backbone structures for the copolymerization of ethylene with polar monomers. In order to improve the stability of the catalyst, our group designed and synthesized phenoxyiminato (Chart 1, II) and β-ketiminato (Chart 1, III) neutral nickel complexes.[42] The β-ketiminato complexes catalyzed ethylene polymerization to obtain higher molecular weight polyethylene due to a lower ethylene insertion energy and a higher β-H transfer energy barrier. However, the range of polar monomers is mostly limited to the those bearing multiple methylene groups between the double bond and functional group, which also applies to the diverse phosphine-sulfonate Ni catalysts[31,32,43,44] (Chart 1, IV). Nozaki *et al.*[33] reported a series of *N*-heterocyclic carbene-based nickel complexes (Chart 1, V) that were successfully applied to the copolymerization of ethylene with allyl monomers, leading to the production of corresponding copolymers. Additionally, the first nickel-catalyzed copolymerization of ethylene with allyl ether monomers was achieved. Cai *et al.*[35,36] revealed a high-performance anilinoanthraquinone-based neutral nickel catalyst promoted ethylene copolymerization and norbornene copolymerization with polar monomers such as 5-hexenyl-acetate and 10-undecen-1-ol with high activity and good thermal stability (Chart 1, VI). Considering heterogeneous catalysts as the primary choice for industry olefin polymerization processes,[45] Chen and Cai collaborated together to develop a heterogeneous naphthoquinone-based nickel (Ni/SiO_2) used in the copolymerization of ethylene with 5-hexene-1-yl-acetete, exhibiting high activity and moderate comonomer incorporation of 2.8 mol% (Chart 1, VII).[46] Similarly, this nickel system does not seem to copolymerize ethylene with fundamental polar monomer which as the most challenging monomer. Of the various nickel catalysts available, [P,O]-type nickel catalysts[47–56] exhibited notable thermal stability and exceptional activity levels. Our group recently designed a series of nickel methyl complexes bearing bulky phosphine-phenolate chelate ligands[52,53] (Chart 1, VIII), exhibiting exceptional tolerance towards polar functional groups in the copolymerization of ethylene with polar monomers. Impressively, they employed in ethylene/MA copolymerization to obtain the corresponding copolymer with M_n over 100 kDa. Compared with the benzene ring framework, a stronger electron-withdrawing effect of naphthalene ring framework on neutral nickel catalyst, facilitated the chain transfer of β-H elimination, thus leading to a significant decrease for molecular weight of the (co)polymer, which is a critical parameter that determines the properties of a polyolefin material (Chart 1, IX).[55,56]

In this contribution, several neutral nickel catalysts based on phosphine-benzocyclone framework were designed and synthesized (Chart 1). We adopt the strategy of replacing the reported phosphine-naphtholate[55,56] with an electron-donating effect phosphine-benzocyclone framework may provide a less electron deficient nickel center to reduce the rate of chain transfer, thereby increasing the molecular weight of the polymers.[42] Meanwhile, the introduction of bulky substituents on the phosphorus moiety would serve to reduce intermolecular interactions and suppress β-H elimination by increasing hindered environment around the nickel center.[52]

EXPERIMENTAL

General Procedures and Materials

All syntheses and manipulations of air- and moisture-sensitive compounds were carried out using the standard Schlenk technique or in an Etelux Lab 2000 type glovebox under a nitrogen atmosphere, unless otherwise noted. Commercially available reagents, including methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*BA) and lauryl acrylate (LA) stabilized

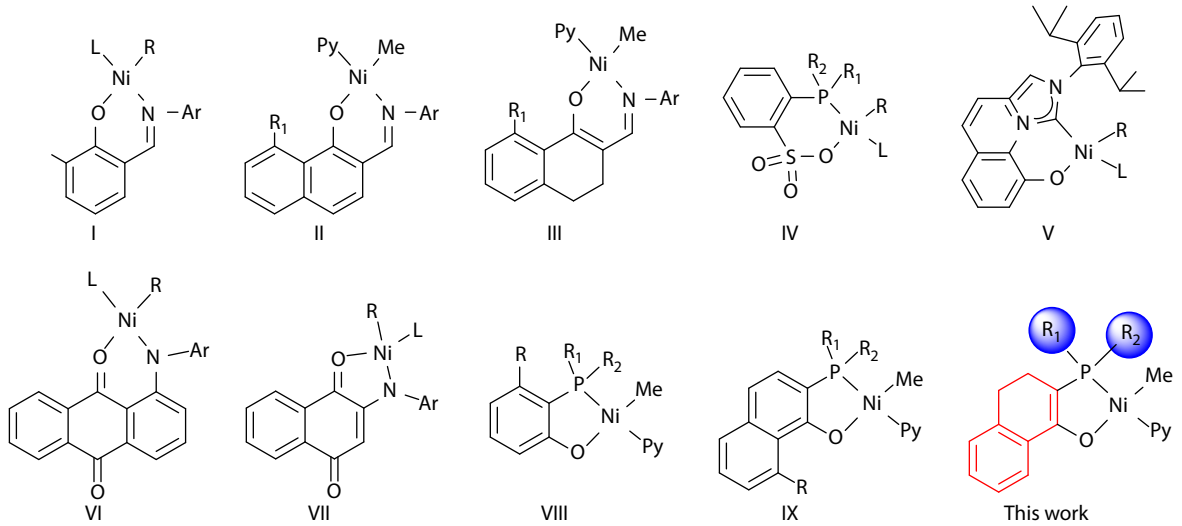

Chart 1 Nickel catalysts with different ligands for ethylene and polar monomer copolymersization.

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with MEHQ were purchased from Innochem and were further subjected to overnight drying over calcium hydride (CaH_2), followed by purification through reduced pressure distillation. The purification of toluene, *n*-hexane and diethyl ether was performed with an MBraun SPS solvent purification system. Characterization and analytical measurements of obtained (co)polymers and complexes are presented in detail in the electronic supplementary information (ESI).

Syntheses of Complexes Ni1–Ni3

*Synthesis of complex **Ni1***

The synthesis of ligands could be found detailly in the electronic supplementary information (ESI). In a nitrogen-filled glovebox, Ligand **L1** (0.330 g, 1 mmol) and metal source Py_2NiMe_2 (0.294 g, 1.2 mmol) were dissolved in 10 mL of dried toluene respectively. Then the toluene solution of ligand **L1** was added dropwise to the toluene solution of metal source under agitation. After reacting for 6 h at room temperature, the nickel black was filtered off through Celite. The filtrate was concentrated to about 2 mL under reduced pressure and the pure complex **Ni1** was obtained by crystallization (*n*-hexane/toluene=5/1) at −30 °C as a yellow solid (0.284 g, 59%). ^{1}H-NMR (400 MHz, C_6D_6, δ, ppm): 7.94–7.89 (m, 4H), 7.66–7.64 (d, *J*=7.4 Hz, 1H), 7.31–7.26 (m,2H), 7.09–7.06 (m, 7H), 7.04 (3H), 3.24 (2H), −0.41 (d, *J*=4.3Hz, 3H, Ni-CH_3). ^{13}C-NMR (101 MHz, C_6D_6, δ, ppm): 176.12, 138.31, 137.88, 133.93, 133.43, 130.06, 129.31, 128.83, 128.55, 125.68, 125.31, 124.04, 114.45, 114.38, 109.21, 108.69, 21.40, −12.88 (d, *J*=35.8 Hz, Ni-CH_3). ^{31}P-NMR (162 MHz, C_6D_6, δ, ppm): 21.50. Anal. Calcd. for $C_{28}H_{26}NNiOP$: C, 69.75; H, 5.44; N, 2.90. Found: C, 69.55; H, 5.50; N, 2.92.

*Synthesis of complex **Ni2***

The procedure of preparing complex **Ni2** (0.352 g, 63%) was the same as that of complex **Ni1** except that ligand **L2** is used instead of ligand **L1**. ^{1}H-NMR (400 MHz, C_6D_6, δ, ppm): 8.42 (s, 2H), 8.0 (d, *J*=7.4 Hz, 1H), 7.65–7.57 (m,3H), 7.44–7.32 (2H), 7.17 (2H), 7.06–6.92 (d, 7H), 6.72 (2H), 6.56 (1H), 6.43–6.34 (2H), 6.29–6.13 (1H), 3.36 (2H), 3.06(2H), −0.79 (d, *J*=4.8 Hz, 3H, Ni-CH_3). ^{13}C-NMR (101 MHz, C_6D_6, δ, ppm): 177.20, 150.41, 146.97, 142.12, 140.30, 138.26, 136.48, 136.07, 134.40, 134.07, 133.96, 130.45, 130.04, 129.70, 129.50, 127.39, 126.72, 126.45, 126.06, 124.49, 115.31, 111.62, 111.09, 21.81, −11.78(d, *J*=36.5 Hz, Ni-CH_3). ^{31}P-NMR (162 MHz, C_6D_6, δ, ppm): 23.03. Anal. Calcd. for $C_{34}H_{30}NNiOP$: C, 73.15; H, 5.42; N, 2.51. Found: C, 73.11; H, 5.48; N, 2.56.

*Synthesis of complex **Ni3***

The procedure of preparing complex **Ni3** (0.346 g, 55%) was the same as that of complex **Ni1** except that ligand **L3** is used instead of ligand **L1**. ^{1}H-NMR (400 MHz, C_6D_6, δ, ppm): 8.71 (s, 2H), 7.86–7.94 (m, 4H), 7.64 (s, 1H), 7.34–7.25 (m, 3H), 7.20 (m, 2H), 7.07–7.02 (m, 6H), 6.98–6.94 (d, 2H), 3.64 (m, 2H), 3.41 (s, 3H), 3.11 (m, 2H), 2.97 (s, 3H), −0.32 (d, *J*=4.5 Hz, 3H, Ni-CH_3). ^{13}C-NMR (101 MHz, C_6D_6, δ, ppm): 178.42, 148.36, 143.70, 141.55, 139.52, 136.44, 135.70, 135.36, 135.25, 131.65, 130.96, 130.63, 130.42, 130.32, 130.19, 129.03, 128.39, 127.88, 127.77, 116.65, 112.71, 111.98, 54,67, 53.14, 23.02, −10.53 (d, *J*=36.1 Hz, Ni-CH_3). ^{31}P-NMR (162 MHz, C_6D_6, δ, ppm): 24.80. Anal. Calcd. for $C_{36}H_{34}NNiO_3P$: C, 69.93; H, 5.54; N, 2.27. Found: C, 69.85; H, 5.56; N, 2.21.

Ethylene Polymerization Using Phosphine/Benzocyclone-based Neutral Nickel Catalysts

The polymerization is carried out in an autoclave reactor with anhydrous and anoxic conditions. Under a fixed ethylene pressure, a defined volume of anhydrous toluene was added into the autoclave reactor through glass injectors, followed by a toluene solution with a certain amount of catalyst, while keeping the total volume of the polymerization medium the same. The reaction proceeded under strict magnetic stirring at the predefined polymerization temperature. After the prescribed polymerization time elapsed, the pressure reactor was depressurized and the reaction was promptly terminated. The obtained copolymer was then readily precipitated from toluene by introducing methanol, followed by either centrifugation or precipitation from methanol. The resulting copolymer underwent multiple acetone washings before being dried in a vacuum oven at 70 °C for 6 h.

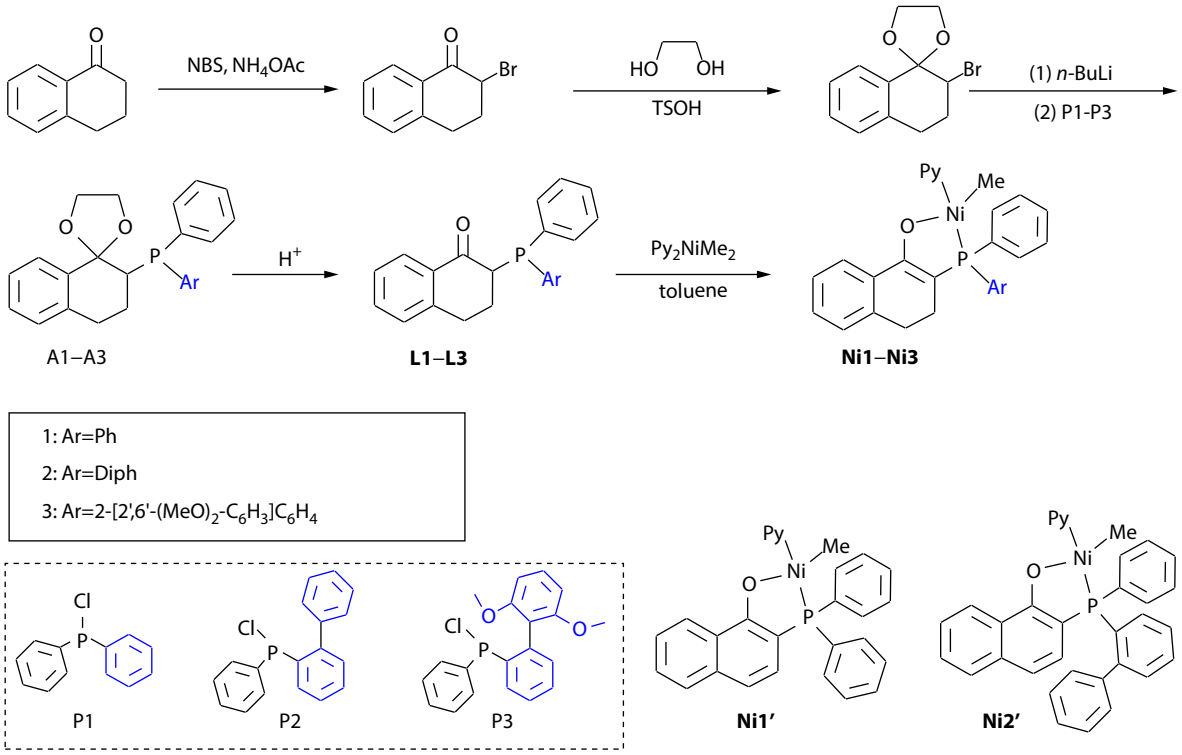
Ethylene Copolymerization with Polar Monomers Using Phosphine/Benzocyclone-based Neutral Nickel Catalysts

The polymerization is carried out in an autoclave reactor with anhydrous and anoxic conditions. Under a fixed ethylene pressure, a defined volume of anhydrous toluene was added into the autoclave reactor through glass injectors, followed by a toluene solution with a certain amount of catalyst, while keeping the total volume of the polymerization medium the same. The reaction proceeded under strict magnetic stirring at the predefined polymerization temperature. After the prescribed polymerization time elapsed, the pressure reactor was depressurized and the reaction was promptly terminated. The obtained copolymer was then readily precipitated from toluene by introducing methanol, followed by either centrifugation or precipitation from methanol. The resulting copolymer underwent multiple acetone washings before being dried in a vacuum oven at 70 °C for 6 h.

RESULTS AND DISCUSSION

Syntheses and Characterization of the Complexes

Phosphine-benzocyclone ligands **L1**–**L3** with different substituents bearing steric effects on the phosphorus moiety were synthesized as presented in Scheme 1. The precursors 2-bromo-1-tetralone were first prepared from the reaction of 1-tetralone and *N*-bromosuccinimide (NBS) catalyzed by NH_4OAc at 25 °C following the literature procedure.[57] Glycol-protected 2-bromo-3,4-dihydro-2*H*-spiro[naphthalene-1,2'-[1,3]dioxolane] compound was lithiated with *n*-BuLi, and after subsequent reaction with PArPhCl (P1 = Ph, P2 = Diph, P3 = 2-(2',6'-$(MeO)_2$-C_6H_3)-C_6H_4), compounds A1–A3 were obtained, respectively. Subsequently, ligands **L1**–**L3** were synthesized by adding drops of hydrochloric acid to move the glycol-protected group of compounds A1–A3. The reactions of **L1**–**L3** with Py_2NiMe_2 resulted in the formation of the neutral nickel complexes **Ni1**–**Ni3** based on the phosphine-benzocyclone framework in good yields (>55%) as depicted in Scheme 1. Phosphine-benzocyclone ligands **L1**–**L3** and corresponding neutral nickel complexes **Ni1**–**Ni3** were carefully characterized, respectively. Meanwhile, two nickel complexes with phosphino-naphtholate catalyst chelate ligands (**Ni1'** and **Ni2'** in Scheme 1) were used



Scheme 1 Syntheses of ligands **L1**–**L3** and corresponding nickel catalysts **Ni1**–**Ni3**.

for comparison.

Single crystal of complex **Ni1** was obtained by slowly diffusing *n*-hexane into a concentrated toluene solution of complex. The solid-state structure of complex was then determined by X-ray diffraction analysis (Fig. S1 in ESI). The nickel center adopts a slightly distorted square planar geometry where the leaving group pyridine and phosphorus atom occupy mutually *trans* dispositions owing to the strong *trans* effect of the phosphorus moiety. Additionally, the methyl group was found to be located in the trans position of the oxygen atom. The bond length Ni(1)-C(28) was different from that of the corresponding nickel complex previous reported,[55] indicating that the backbone of the ligand affects the electrical properties of the complex's nickel center.

Ethylene Polymerization

Firstly, the charge densities of the nickel metal centers of the two complexes were theoretically calculated based on density functional theory (DFT). Theoretical calculation result (Fig. S2 in ESI) showed that the charge density of the nickel atom center of complex **Ni1** was lower than that of complex **Ni1'** (+0.842 versus +0.844). Similarly, the charge density at the center of the nickel atom of complex **Ni2** with large sterically hindered substituents was also lower than that of the corresponding naphthalene ring framework complex **Ni2'** (+0.871 versus +0.875). This observation indicates that the introduction of a cyclic ketone framework with weak electron-withdrawing ability can reduce the charge density of the nickel atom center in the complex and the electron-deficient performance of the metal center.

Firstly, phosphine-benzocyclone-based nickel complexes **Ni1**–**Ni3** were examined as single-component catalyst for ethylene polymerization without the addition of any co-catalyst, respectively. As shown in Table 1, complex **Ni1** bearing less hindered phosphorus moiety (Ar = Ph) exhibits low activity (only 48×10^3 g·mol$_{Ni}^{-1}$·h^{-1}) at 50 °C and 10 bar of ethylene pressure, affording low-molecular-weight polyethylene (entry 1 in Table 1). In contrast, phosphino-naphtholate neutral complex **Ni1'** exhibits higher catalytic activity but produced polymer with lower molecular weight (20.2 versus 29.5 kDa), which strongly indicates that the benzocyclone framework with weaker electron-withdrawing ability can reduce the chain transfer rate, and increase polymer molecular weight. Further enhancement of temperature to 70 °C, the catalytic activity was improved to some extent, but at the expense of MW (entry 3 in Table 1). Similarly, in terms of complexes **Ni2** and **Ni2'** with large steric substituents on phosphine moiety, complex **Ni2** similarly produces higher molecular weight polyethylene (164.5 versus 91.3 kDa). Besides, complexes **Ni2** and **Ni3** which bear more bulkier substituents, give one order of magnitude higher catalytic activities and polymer molecular weights, indicating superior performance relative to the correspondingly complex **Ni1** bearing a relatively smaller phenyl substituent (compare entries 4 and 9 with entry 1 in Table 1). These results clearly suggest that the chain transfer reaction and β-H elimination could be effectively inhibited by the introduction of bulky steric substituent (see Figs. S23–S26 in ESI: the ^{1}H-NMR spectroscopy revealed the existence of vinyl end group formed by the β-H elimination reaction in the resulting polyethylene produced by complex **Ni1**, while it was not observed by complexes **Ni2** and **Ni3** bear bulky substituents). In addition, complex **Ni3** shows high catalytic activities at the level of 10^6 g·mol^{-1}·h^{-1} in a wide reaction temperature range from 30 °C to 120 °C.

On varying the reaction temperature from 50 °C to 90 °C,

Table 1 Ethylene polymerization with complexes **Ni1**–**Ni3**. [a]

Entry	Cat.	T (°C)	Yield (g)	TOF [b]	Act. [c]	M_w [d] (kDa)	M_w/M_n [d]	T_m [e] (°C)
1	**Ni1**	50	0.12	2	48	29.5	1.9	131
2	**Ni1'**	50	0.32	5	128	20.2	2.4	128
3	**Ni1**	70	1.48	21	592	12.6	2.1	136
4	**Ni2**	50	8.4	120	3360	311.7	1.9	137
5	**Ni2**	70	18.1	259	7240	164.5	2.4	136
6	**Ni2'**	70	27.6	460	11040	91.3	2.3	135
7	**Ni2**	90	14.3	204	5720	24.5	2.6	130
8	**Ni3**	30	5.8	83	2320	545.7	1.5	137
9	**Ni3**	50	12.2	174	4880	402.5	1.8	137
10	**Ni3**	70	22.6	323	9040	231.4	1.8	135
11	**Ni3**	90	17.9	256	7160	30.2	3.1	127
12 [f]	**Ni3**	120	9.3	133	3720	15.5	4.3	126

[a] Conditions: 5 μmol catalyst in 100 mL of toluene and under 1.0 MPa of ethylene, polymerization for 30 min; [b] Turnover frequency, in unit of 10^3 $mol_E \cdot mol_{Ni}^{-1} \cdot h^{-1}$; [c] Catalytic activity in unit of 10^3 $g_{PE} \cdot mol_{Ni}^{-1} \cdot h^{-1}$; [d] Determined by GPC at 150 °C with 1,2,4-trichlorobenzene as an eluent; [e] Determined by DSC; [f] Decalin as the solvent.

the catalytic activities of **Ni2** and **Ni3** in the ethylene polymerization increase first with their highest activities at 70 °C (up to 7.24×10^6 and 9.04×10^6 $g \cdot mol_{Ni}^{-1} \cdot h^{-1}$ correspond to entries 5 and 10 in Table 1, respectively). Complex **Ni3** still maintains relatively high catalytic activity up to 3.72×10^3 $g \cdot mol_{Ni}^{-1} \cdot h^{-1}$ at 120 °C with decalin as the solvent (entry 12 in Table 1), showing excellent stability under high temperature. However, the obtained polyethylene with a significantly decreased molecular weight and a broader molecular weight distribution (M_w=15.5 kDa, M_w/M_n=4.3) was observed, which could be ascribed to the enhanced chain-transfer rate with the temperature increases. Moreover, the melting temperatures (T_ms) of PEs by complexes **Ni2** and **Ni3** are beyond 130 °C (taken from the second heating curve), suggesting a characteristic of linear PE structure.

The data in Table 2 clearly indicate that the polymerization reaction allows growth of multiple polyethylene chains per catalyst molecule. Comparing entries 1 and 2, entries 5 and 6, it can be found that the benzocyclone framework complexes exhibited about several times lower catalytic efficiency than the corresponding naphthalene framework complexes under the same conditions (**Ni1** versus **Ni1'**, **Ni2** versus **Ni2'**), which indicates that the introduction of the benzocyclone framework makes the metal nickel center less electron-deficient that would rate lower of chain transfer reaction, and enhance the molecular weight of the polymers.

We selected **Ni3** to disclose the change of catalytic performance with reaction time, and the results were presented in Table 3. At 10 °C, an extension in reaction time led to a noticeable increase in polymer yield, while no significant alterations in catalytic activity and molecular weight with reaction time (entries 1 and 2 in Table 3), which may be attributed to the difficult dissociation of coordination group at low temperature. In order to obtain better catalytic properties, the polymerization temperature was further increased to 50 °C. Compared with that at 10 °C, catalytic activity increased by an order of magnitude (Comparing entries 1 with 4, entries 2 with 5 in Table 3). Additionally, it was noted that both polymer yield and catalytic activity increased as the time prolong from 5 min to 30 min, as well as the catalytic efficiency of **Ni3** gradually increased with the increase of reaction time. At 30 min, the catalytic activity remained relatively high at

Table 2 Differences in resulting polyethylene and catalytic efficiency of phosphino-naphtholate and phosphine-benzocyclone neutral nickel complexes for ethylene polymerization. [a]

Entry[a]	Cat.	Yield (g)	M_w (kDa)	M_w/M_n	N/Ni [b]
1	**Ni1**	0.12	29.5	1.9	2
2	**Ni1'**	0.32	20.2	2.4	8
5	**Ni2**	18.1	164.5	2.4	53
6	**Ni2'**	27.6	91.3	2.3	139

[a] Entry number corresponds to the entry number in Table 1; [b] Calculation formulas: $(M\text{-}R)_{extended} = yield_{polymer}/M_n$, $Chains_{initiated} = (M\text{-}R)_{extended}/moles_{catalyst}$.

Table 3 Effect of reaction time on ethylene polymerization with **Ni3**. [a]

Entry	T (°C)	Time (min)	Yield (g)	TOF [b]	Act [c]	M_w [d] (kDa)	M_w/M_n [d]	T_m [e] (°C)	N/Ni [f]
1	10	10	0.034	1	41	28.5	2.0	134	5
2	10	20	0.076	1	46	32.5	2.1	134	10
3	50	5	0.30	26	712	95.4	1.9	134	12
4	50	10	0.68	29	816	120.9	1.9	135	21
5	50	20	1.94	42	1164	143.5	2.0	135	54
6	50	30	3.42	49	1368	177.6	2.1	136	81

[a] Conditions: 5 μmol **Ni3** in 50 mL of toluene and under 0.5 MPa of ethylene; [b] Turnover frequency, in unit of 10^3 $mol_E \cdot mol_{Ni}^{-1} \cdot h^{-1}$; [c] Catalytic activity, in unit of 10^3 $g_{polymer} \cdot mol_{Ni}^{-1} \cdot h^{-1}$; [d] Determined by GPC at 150 °C with 1,2,4-trichlorobenzene as an eluent; [e] Determined by DSC. [f] Calculation formulas: $(M\text{-}R)_{extended} = yield_{polymer}/M_n$, $Chains_{initiated} = (M\text{-}R)_{extended}/moles_{catalyst}$.

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1.368×10^6 g·mol$_{Ni}^{-1}$·h^{-1}, highlighting the long lifetime of catalyst **Ni3** (Fig. 1). Interestingly, a rise in the molecular weight of polyethylene was observed with increasing reaction time (Fig. 1), suggesting the somewhat quasi-living polymerization characteristics of the polymerization system. Moreover, the unimodal GPC elution curves and relatively narrow molecular distributions of the obtained polyethylenes provided evidence of the presence of single-site active species in the ethylene polymerization process.

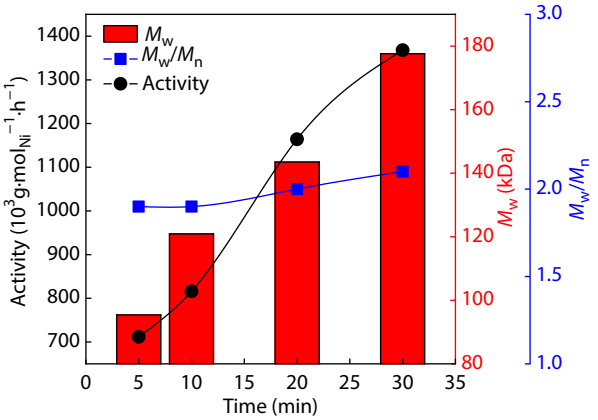


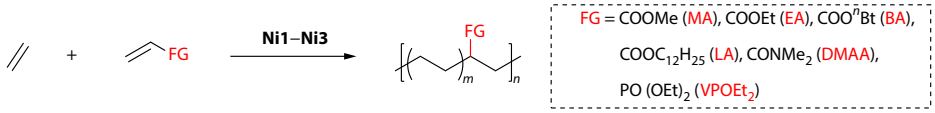
Fig. 1 Catalytic activity, molecular weight and molecular weight distribution of polymers obtained at 50 °C for **Ni3**-catalyzed ethylene polymerization.

Copolymerization of Ethylene and Acrylate Monomers

Ethylene/acrylate copolymerization of is widely used to evaluate the properties of new catalysts for ethylene/polar monomer. Considering high catalytic activity and high thermal stability of phosphine-benzocyclone-based neutral nickel catalysts for ethylene polymerization, we further explored their catalytic performance towards copolymerization ethylene with acrylates. So copolymerization of ethylene with polar monomers such as methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*BA) and lauryl acrylate (LA) was investigated systematically with complexes **Ni1**–**Ni3**, respectively, and the representative results are summarized in Table 4. Notably, no extra activator has been added in the copolymerization system. The results provided an opportunity to evaluate the effect of substituent on the phosphorus moiety on catalytic performance in the copolymerization. Under the same reaction conditions, complex **Ni1** having less hindered phenyl substituent on the phosphorus moiety, gave low catalytic activity and molecular weight of E-MA copolymer (Act.=1.4×10^3 g·mol$_{Ni}^{-1}$·h^{-1}, M_w=9.8 kDa, entry 1 in Table 4). In the copolymerization of ethylene and MA, **Ni1'** and **Ni2'** exhibited higher activity but lower molecular weight (**Ni1'**: 4.0 kDa; **Ni2'** versus **Ni2**: 20.9 versus 33.3 kDa). Whereas complexes **Ni2** and **Ni3** having bulky substituents, were superior to that of the nickel complex with phenyl substituent (**Ni1**), gave an order of magnitude increase in catalytic activity and M_W of copolymer (entries 3 and 5 in Table 4). Among them, complex **Ni2** shows the highest activity while complex **Ni3** could obtain the highest molecular weight E-MA copolymer. It seemed to be that bulky aromatic substituents on the phosphorus moiety gave a better performance, taking into consideration in suppressing the chelating interaction and β-H elimination after polar monomer insertion by the axial protection formed by large steric substituents, similar to what was reported.[9,52] Meanwhile, introduction of a sterically bulky group could prevent the formation of a carbonyl chelate complex and reduce the possibility of bimolecular deactivation reactions. In contrast, complex **Ni1**, which has the smallest substituent group will lead to difficulty in chain propagation.

The MA incorporation and molecular weight of the copolymers could be tuned to a certain extent by changing polar monomer feeding concentration. **Ni3** was used to conduct a series of copolymerization of ethylene with MA in the gradient concentration range of MA. At MA of 0.1 mol/L, the cata-

Table 4 Copolymerization of ethylene with different acrylate monomers using complexes **Ni1**–**Ni3**. [a]



Entry	Cat.	Com.	[M] (mol/L)	Yield (mg)	Act. [b]	Incorp. [c] (mol%)	M_w [d] (kDa)	M_w/M_n [d]	T_m [e] (°C)
1 [f]	**Ni1**	MA	0.1	54	1.4	5.6	9.8	1.9	92
2 [f]	**Ni1'**	MA	0.1	161	4.0	4.7	4.0	2.0	85
3	**Ni2**	MA	0.1	721	36.1	2.2	33.3	1.9	118
4	**Ni2'**	MA	0.1	1640	82.0	2.0	20.9	2.1	116
5	**Ni3**	MA	0.1	508	25.4	1.5	35.8	2.1	120
6	**Ni3**	MA	0.2	387	19.4	3.3	30.6	2.0	114
7	**Ni3**	MA	0.4	173	8.7	5.4	21.7	2.2	108
8	**Ni3**	MA	0.8	59	3.0	8.2	11.8	2.2	87
9	**Ni3**	EA	0.2	623	31.2	2.8	48.5	2.1	120
10	**Ni3**	BA	0.2	696	34.8	2.6	61.6	2.2	119
11	**Ni3**	LA	0.2	401	20.1	2.0	33.6	2.1	118
12	**Ni3**	DMAA	0.2	130	6.5	2.5	17.3	1.8	118
13	**Ni3**	VPOEt$_2$	0.2	106	5.3	2.2	15.8	2.0	117

[a] Conditions: 10 μmol catalyst in 50 mL of toluene, at 50 °C and 1.0 MPa of ethylene, copolymerization for 2 h; [b] Catalytic activity in unit of 10^3 g·mol$_{Ni}^{-1}$·h^{-1}; [c] Determined by ^{1}H-NMR in 1,1,2,2-tetrachloroethane-d$_2$ at 120 °C; [d] Determined by GPC at 150 °C with 1,2,4-trichlorobenzene as an eluent; [e] Determined by DSC; [f] Catalyst, 20 μmol.

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lytic activity was 25.4×10³ g·mol$_{Ni}^{-1}$·h^{-1} (entry 5 in Table 4) with the incorporation of 1.5 mol%. Increasing the concentration of comonomer to 0.2 mol/L, the more than doubles incorporation of MA (3.3 mol% versus 1.5 mol%) was obtained, with the catalytic activity and molecular weight remaining above 10⁴ g·mol$_{Ni}^{-1}$·h^{-1} and 10 kDa, respectively. Increasing polar comonomer concentration from 0.2 mol/L through 0.4 mol/L to 0.8 mol/L, the MA incorporation increases from 3.3 mol% to 5.4 mol% and 8.2 mol% (entries 7 and 8 in Table 4), respectively. However, copolymerization activity and copolymer molecular weight decreased correspondingly decreased (Fig. 2a, the activities decreased from 19.4×10³ g·mol$_{Ni}^{-1}$·h^{-1} to 3.0×10³ g·mol$_{Ni}^{-1}$·h^{-1} and M_w decreased from 30.6 kDa to 11.8 kDa, respectively).

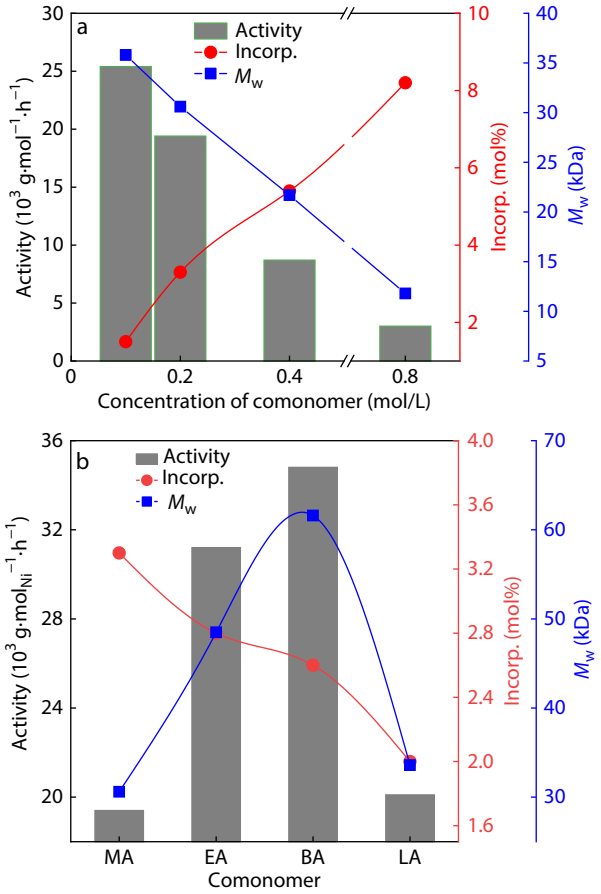


Fig. 2 The effect of (a) different MA concentrations, (b) the bulkiness of acrylate on polymerization performance for **Ni3**-catalyzed copolymerization of ethylene and acrylate monomers.

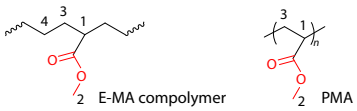
Next, we investigated the impact of the steric bulk of acrylate comonomer on polymerization performance using a range of alkyl acrylates including MA, EA, BA and LA as shown in Table 4. For the three monomers MA, EA, and BA, the results indicated that the copolymerization activity and MW increase whereas comonomer incorporation decreases with the bulkiness of alkyl acrylate, and molecular weight distribution (M_w/M_n) of the copolymers were always around 2 (entries 6, 9 and 10 in Table 4). This likely attributable to the increase of steric hindrance of the polar monomer, which is not conducive to the competitive coordination with ethylene, thus reducing the toxic effect of the polar monomer on the metal active center, resulting in the increase of polymerization activity and copolymer molecular weight. In addition, the decreased incorporation of polar monomers further confirmed the above speculation. Interestingly, we observed that the longer chain dodecyl acrylate monomer resulted in sharp decreases in catalytic activity and the molecular weight of the copolymer (20.1×10³ g·mol$_{Ni}^{-1}$·h^{-1} and 33.6 kDa, entry 11 in Table 4) due to greater steric hindrance (Fig. 2b), which is probably due to increased steric hindrance hindering the coordination of ethylene to the catalytic centers after insertion of polar monomers. Moreover, complex **Ni3** can be applied for efficiently copolymerization of ethylene with other polar vinyl monomers, such as *N*,*N*-dimethylacrylamide (DMAA; entry 12, Table 4) and diethyl vinylphosphonate (VPOEt$_2$; entry 13, Table 4). Complex **Ni3** afforded ethylene/DMAA copolymers containing up to 2.5 mol% DMAA and ethylene/VPOEt$_2$ copolymers containing up to 2.2 mol% VPOEt$_2$ with moderate molecular weights (DMAA, M_w up to 17.3×10³ kDa; VPOEt$_2$, M_w up to 15.8×10³ kDa), respectively. Comparing the copolymerization results of ethylene and methyl acrylate, complex **Ni3** displayed better tolerance to a —C(O)OR group than to —C(O)NMe$_2$ and —PO(OEt)$_2$ groups.

Microstructure of Ethylene/Methyl Acrylate Copolymer

To verify that the copolymerized products are neat E-MA copolymers without methyl acrylate homopolymer (PMA), the E-MA copolymers were carefully compared with PMA and their ^{13}C-NMR chemical shifts (Fig. S27 in ESI) are summarized in Table 5. The data in Table 5 shows that there is a big difference in the chemical shifts of the two polymers. The chemical shift of carbon 3 in the E-MA copolymers was observed at 31.91 ppm, which significantly differs from that of PMA at 35.01 ppm. The chemical shift of carbon 1 of methyne associated with an ester group in the E-MA copolymers was observed at 45.73 ppm, which also differed from that of PMA at 41.38 ppm. Similarly, the corresponding change in the chemical shifts of the carbonyl group and the methoxy group could also be observed (Carbonyl group: 176.49 versus 175.06 ppm; carbon 2: 31.91 versus 35.01 ppm). This indicated that MA unit was introduced in isolation into the polymer chain without successively multiple MA unit inserted into the main chain.

To evaluate the effect of the alkoxy phosphine catalysts on the microstructure of the copolymer, the copolymer chains

Table 5 Chemical shifts (ppm) in ^{13}C-NMR spectra of PMA and E-MA copolymers.



Sample	1	2	3	4	—C=O
E-MA Copolymer [a]	45.73	51.06	31.91	27.48	176.49
PMA [b]	41.38	52.08	35.01	–	175.06

[a] Obtained by entry 6 in Table 4; [b] Obtained by free radical polymerization.

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were elucidated by ^{1}H spectra at 120 °C in tetrachloroethane-d_2. The chain structure of the copolymers generated with **Ni1**–**Ni3** exhibited that: (i) the copolymers have highly linear structure without short-chain and long-chain branches connected to polymer backbones; (ii) isolated acrylate unit was introduced into the polymer chain without successively multiple acrylate unit inserted into the main chain. Here in, complex **Ni1** bearing small axial groups and **Ni3** bearing bulky axial groups were selected for comparison. Both the amount of MA unit inserted in the chain end (terminal MA) and the main chain (in-chain MA) were considerably influenced by the structure of aromatic substituent (Ar) on phosphorus. Fig. 3(a) shows the selected ^{1}H-NMR spectrum of E-MA copolymer prepared by **Ni1**. In addition to the resonances of unsaturated vinylic protons, two resonances centered at δ 3.76 and 3.81 ppm were detected in the region of methoxy protons, which were ascribed to the in-chain MA unit and the terminal MA unit, respectively. The proportion of in-chain MA to terminal MA can be calculated by the integrated area of the methyne (labeled as "1") and methylene (labeled as "C") signal peaks. Notably, the ratio of the amounts of terminal MA unit and in-chain MA unit is 100% (1.00/1):115.5% (2.31/2) as shown in Fig. 3(a), indicating that the content of terminal MA unit was higher than that of the in-chain MA unit, indicating that β-H elimination can easily occur after the insertion of acrylate monomer, similar to the situation reported.[54] Fig. 3(b) shows that the ^{1}H-NMR spectrum of E-MA copolymer prepared by **Ni3** bearing bulky axial groups, in which the proportion of the in-chain MA unit remarkably increase, in view of the ratio of the amounts of terminal MA unit and in-chain MA unit is 100% (1.00/1):9.5% (0.19/2). That was, **Ni3** can incorporate much more MA into the polymer chains than **Ni1**, but rarely at the end of chains. As already mentioned, the fact that the copolymer obtained by **Ni3** exhibited much higher MW than that by **Ni1** (entry 1 versus entry 6 in Table 4), it was likely that ethylene insertion after the insertion of MA was the rate-determining step in the copolymerization of ethylene and

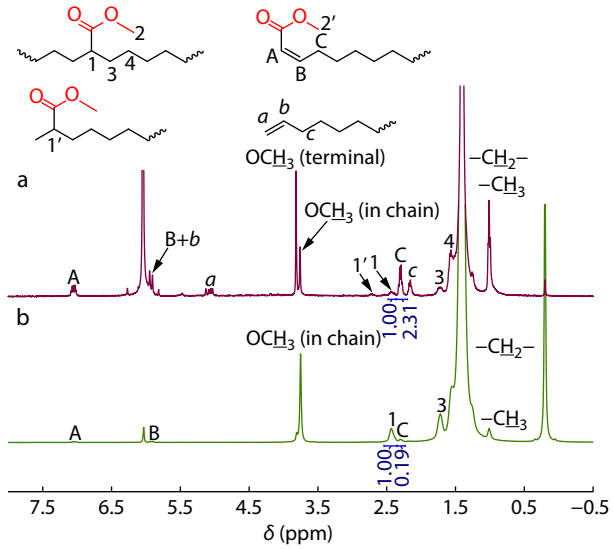

Fig. 3 ^{1}H-NMR spectra and the assignments of the E-MA copolymers obtained by **Ni1** (a, entry 1 in Table 4) and **Ni3** (b, entry 6 in Table 4).

MA, similar the case reported.[58] Furthermore, **Ni3** appeared to be at performing the ethylene insertion step compared with **Ni1**. This probably because the fact that larger steric hindrance of **Ni3** could effectively retard the β-H elimination reaction. In addition, the structure of terminal MA unit (Fig. 3) indicated that the insertion of terminal MA is *via* 2,1-fashion and the termination was β-H elimination from the last inserted MA, similar to what were reported.[54,59]

In order to further confirm the chain structure of the copolymer, we analyzed the ^{13}C- and ^{1}H-^{1}H COSY NMR spectra (Fig. S32 in ESI) of E-MA copolymer. Fig. 4 shows the ^{13}C-NMR spectrum of E-MA copolymer, and the relevant signals in the spectrum have been assigned in detail. The characteristic signal peaks of MA unit were observed at δ 176.5 ppm, 166.9 ppm and δ 50.9 ppm corresponding to the signal peaks of the carbonyl (—$COOCH_3$) and methoxy groups (—OCH_3), respectively. Further, a comparison of FTIR spectra (Fig. S40 in ESI) of these copolymers with neat PE also confirmed the incorporation of the alkacrylate monomer units in the polymer chain. For example, the bands at 1737.8 and 1735.9 cm^{-1} indicated the presence of carbonyl group exist in copolymer structures, respectively.

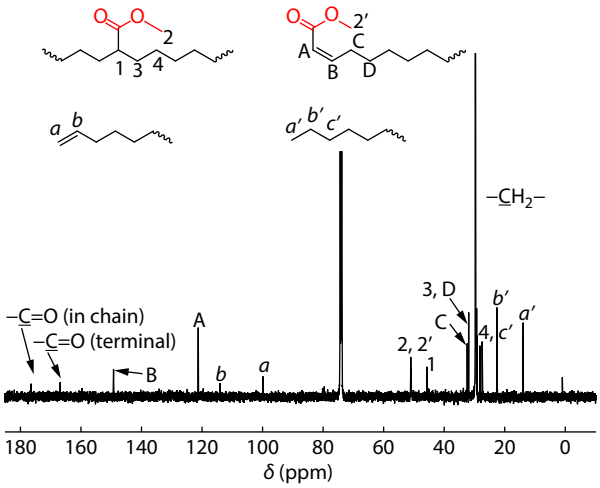

Fig. 4 ^{13}C-NMR spectrum and the assignments of E-MA copolymers obtained by **Ni1** (entry 1 in Table 4).

Surface Property of Copolymers

As discussed in the introduction, the introduction of a small number of polar groups can effectively alter the copolymer properties. Here, the surface properties of the copolymers obtained by copolymerization of ethylene with different alkyl acrylates were explored by measuring their water contact angles (WCAs). The results indicate that the incorporation of polar monomers could indeed improve the surface properties of the polyolefin materials (Fig. 5). As a comparison, the neat PE gave a WCA of 113.1°. For the MA monomer, the WCA decreased from 102.4° to 67.4° as incorporation of MA increases from 1.5 mol% to 8.2 mol%. Similarly, the incorporations of EA, BA and LA units can also effectively improve polymer hydrophilicity.

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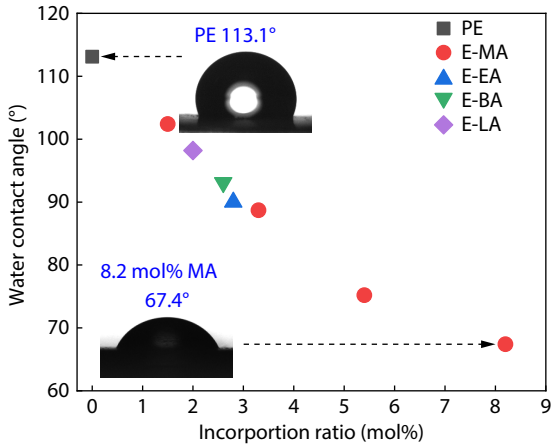

Fig. 5 Water contact angles of the polyethylene (sample from entry 9 in Table 1) and polar functionalized copolymer (samples from entries 5–11 in Table 4).

CONCLUSIONS

To summarize, a series of novel neutral nickel complexes (**Ni1**–**Ni3**) bearing based on phosphine-benzocyclone ligands were synthesized and characterized. These complexes possess bulky axial substituent groups on the phosphorus moiety displayed highly active (up to 9.04×10^6 g·mol$_{Ni}^{-1}$·h^{-1}) for ethylene polymerization in a wide temperature window (30–120 °C) and produced highly linear PE$_S$ with high polymer molecular weights (M_w up to 545.7 kDa). Furthermore, the highly efficient copolymerization of ethylene with other polat vinyl monomers such as *N*,*N*-dimethylacrylamide, diethyl vinylphosphonate and acrylate monomers with varying alkyl chain lengths was readily achieved with these complexes, gave high-molecular-weights copolymers with variable incorporation (1.5 mol%–8.2 mol%). NMR analyses of resulting copolymers revealed their high linearity and preferential incorporation of alkyl acrylate comonomers into the main chain. This study describes the preparation of highly active catalysts by the dual strategy of adjusting the ligand skeleton and introducing large steric substituents to yield high molecular weight (co)polymers, which inspires us to continue to explore modifications of the framework and expand the range of polar monomers in future work.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-023-3044-x.

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