

Synergistic Effect and Fluorination Effect in Ethylene Polymerization by Nickel Phenoxyiminato Catalysts

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Electronic Supplementary Information

Abstract A series of binuclear nickel phenoxyiminato catalysts with different linkers and fluorine substituents were efficiently synthesized. Binuclear nickel catalysts with rigid linkers showed higher catalytic activity and thermal stability in ethylene polymerization and produced polymers with higher molecular weight possibly due to the larger steric hindrance and metal-metal synergistic effect. The introduction of fluorine atoms on the *N*-terphenyl moiety also enhanced polymerization activity and molecular weight of polymer due to the electronic effect of fluorine atoms.

Keywords Nickel phenoxyiminato catalysts; Fluorination effect; Synergistic effect; Bimetallic catalysts

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INTRODUCTION

Late-transition-metal catalysts have attracted more and more attention due to their tremendous potential for olefin and polar monomers copolymerization^[1–6]. These catalysts can produce polyethylene with highly branched structure and poly(α -olefins) with linear structure through a process termed as “chain walking”^[7–12]. Many design strategies have been explored to modify catalytic properties including adjusting steric and electronic effects^[13–21], fluorine substitution on the ligands^[22–24], redox-controlled polymerization^[25, 26], introducing interactions of ligand with metal center or substrate^[27–30], and bimetallic synergistic effect^[31, 32]. Bulky groups blocking the axial coordination sites tend to promote chain propagation over chain transfer^[33], which usually yield high or ultra-high molecular weight polymers. The molecular weight and microstructure of polyethylene could be adjusted by the electronic nature of ligands^[34, 35]. Mecking *et al.* reported a series of active *N*-terphenyl phenoxyiminato nickel catalysts for ethylene polymerization^[13, 19, 36–38]. Branch density and molecular weight of polymers are mainly controlled by remote electron-withdrawing or electron-donating groups attached on the terphenyl moiety. Among those catalysts, fluorinated catalysts displayed extremely high activity and produced polyethylenes with high molecular weight and low branch density. Actually, special effect of fluorine

substituents have been reported in many early and late transition metal catalysts^[22, 39–43]. In fields of group IV catalysts, weak fluorine bonding has been proposed as explanations for living polymerization^[44]. In late transition metal catalysts, suitably-positioned fluorine substituents can stabilize active sites through M...F or C—H...F interactions, which lead to improved molecular weight, enhanced thermal stability and reduction in branching^[22, 23]. In our previous work^[24], a series of nickel phenoxyiminato catalysts with fluorine atoms at different positions on the *N*-terphenyl moiety were synthesized. We found that microstructure of polyethylene mainly depended on the electronic effect of fluorine atoms. The *ortho* fluorine substituents that significantly influenced the conformation of the catalysts and formed weak hydrogen bonds in transition state, favored to lower migratory insertion barriers, thus resulting in higher activity. Therefore, fluorine substituent could be used as an effective tool to control catalytic behavior.

On the other hand, the bioinspired bimetallic approach has attracted enormous attention due to specially cooperative effects between two metal sites^[31, 45, 46]. The bimetallic catalysts with two metal centers held together by a flexible or rigid tether display different polymerization behaviors^[46–53] (Chart 1). For example, Mecking *et al.*^[54] reported the binuclear nickel catalysts with flexible or unrestricted-rotation linkers (Chart 1a), showing higher activity than the mononuclear analogue. Osakada *et al.*^[55] reported a double-decker binuclear nickel catalyst that supported by cyclic xanthene skeleton (Chart 1b), and it achieved copolymerizations of ethylene with unsaturated

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esters or terminal dienes. In addition, binuclear nickel catalysts with different Ni-Ni distances should enable selective copolymerization of ethylene and bifunctional co-monomers with different lengths. Our group^[32] also reported a series of binuclear nickel phenoxyiminato catalysts with rigid linkers of different lengths (Chart 1c). Such catalysts showed higher activity and polyethylenes of higher molecular weight with reduced nickel-nickel distances were produced. In addition, these catalysts displayed better polar monomer tolerance due to the enhanced bimetallic effect.

In our goal to study synergistic effect and fluorination effect in nickel catalysts, a series of mono- and binuclear nickel catalysts with different substituents and linkers were designed and synthesized (Chart 2). In our previous work^[24],

we have studied fluorine effect in mononuclear nickel phenoxyiminato catalysts systematically. Herein, we would like to introduce bimetallic synergistic effect into the neutrally charged nickel phenoxyiminato catalysts with fluorine atoms at different positions on the *N*-terphenyl moiety (catalysts **4a–4c** in comparison to **5a–5c**). The combination of bimetallic synergistic effect and fluorination effect in catalysts is expected to improve catalytic performance in ethylene polymerization with higher activity and PEs of higher molecular weight. Binuclear catalysts with flexible or rigid linkers of different connected positions (Chart 2, catalysts **2**, **3**, **4**) were designed to study the influence of metal-metal position on olefin polymerization.

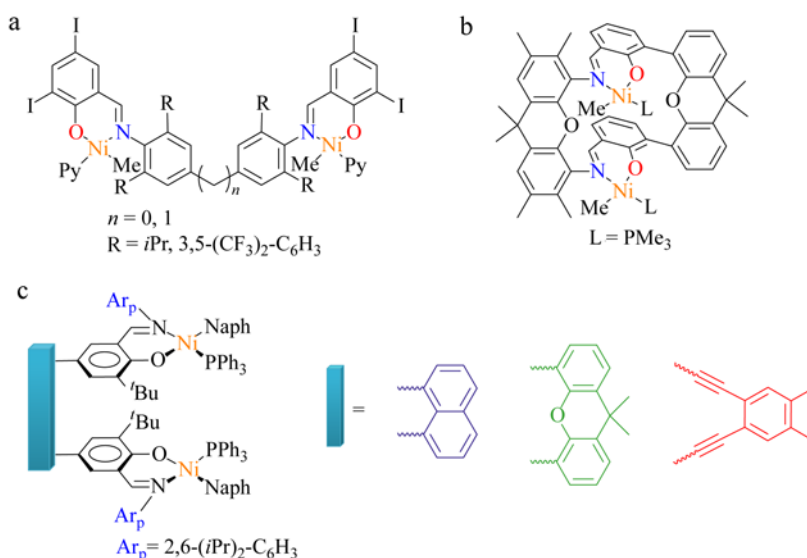


Chart 1 Structures of bridged nickel(II) phenoxyiminato catalysts

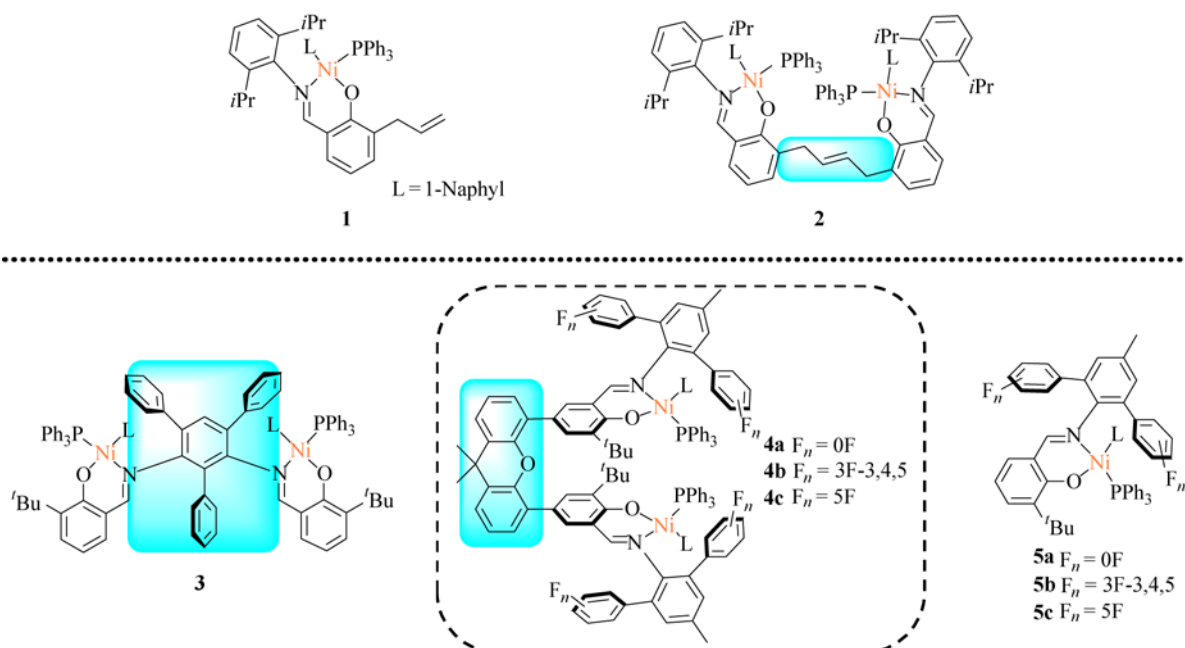


Chart 2 Design and structures of mono- and binuclear nickel phenoxyiminato catalysts for olefin polymerization

EXPERIMENTAL

Chemicals and Methods

All manipulations of air- and/or water- sensitive compounds were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled mBraun glovebox with a high capacity recirculator (< 5 ppm of O_2/H_2O). All solvents for high-vacuum line manipulations were purified by passing through the mBraun solvent purification system and stored under nitrogen over activated 4Å molecular sieves in resealable flasks. Commercial ethylene was used directly for polymerization without further purification. All the other reagents were purchased and used as received.

Physical and Analytical Measurements

^1H -, ^{13}C -, ^{19}F -, and ^{31}P -nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-400 (400 MHz) and a Bruker-500 (500 MHz) spectrometer using $CDCl_3$ (1,1,2,2-tetrachloroethane- d_2 for polymer characterization) as solvent. Chemical shifts are reported in parts per million (ppm), and coupling constants are reported in hertz (Hz). ^1H -NMR chemical shifts were referenced versus internal tetramethylsilane (0 ppm), ^{13}C -NMR chemical shifts were referenced versus chloroform- d (77.0 ppm) or 1,1,2,2-tetrachloroethane- d_2 (73.80 ppm), and ^{31}P -NMR spectra chemical shifts were referenced to 85% H_3PO_4 as an external standard (0 ppm). ^{19}F -NMR spectra chemical shifts were referenced versus a CF_3CO_2H external standard (0 ppm). Mass spectra were recorded on a VG ZAB-HS mass spectrometer. Single crystal X-ray diffraction data were collected with a NONIUS Kappa CCD diffractometer, with graphite monochromator and Mo $K\alpha$ radiation [$\lambda(Mo K\alpha) = 0.71073$ Å]. Structures were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXS-97. Polymer melting points were measured by differential scanning calorimetry (DSC) using a TA DSC Q100 instrument, and data were collected from the second heating run at a heating rate of 10 K/min. High temperature gel permeation chromatography (GPC) was performed on Agilent PL-GPC 220 equipped with a refractive index (RI) detector. GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) at 150 °C with a rate of 1.0 mL/min. GPC data calibration was done with unimodal polystyrene standards and corrected by universal calibration using the Mark-Houwink parameters: $K = 4.06 \times 10^{-2} \text{ cm}^3/\text{g}$ and $\alpha = 0.727$ for polyethylene.

Synthesis of the Complexes

Nickel catalyst 1: To a Schlenk flask containing **L1** (1 mmol) and THF (1 mL), KH (1.5 mmol) was added under a nitrogen atmosphere. After stirring for 1 h, the mixture was evaporated under vacuum to afford potassium salts of **L1**. The toluene solution of potassium salts was added dropwise to a toluene (5 mL) solution of *trans*-[Ni(PPh_3) $_2$ (Naph)Cl] (0.95 mmol) at room temperature. After stirring for 24 h, the dark red mixture was filtered through celite and evaporated under vacuum. The corresponding residue was then recrystallized from toluene/hexane to remove the *trans*-[Ni(PPh_3) $_2$ (Naph)Cl], yielding **1** as orange-yellow powder (85%): ^1H -NMR (400 MHz, $CDCl_3$, δ , ppm): 10.10 (d, $J = 8.2$ Hz, 1H), 7.94 (d,

$J = 8.8$ Hz, 1H), 7.56–7.38 (m, 5H), 7.25–6.98 (m, 16H), 6.81 (t, $J = 8.1$ Hz, 1H), 6.62 (d, $J = 8.1$ Hz, 1H), 6.51–6.46 (m, 2H), 6.39 (dd, $J = 7.6$, 1.2 Hz, 1H), 6.14 (t, $J = 7.2$ Hz, 1H), 5.58–5.36 (m, 1H), 4.78–4.68 (m, 2H), 4.63 (m, 1H), 2.71 (m, 1H), 2.23 (m, 2H), 1.68 (d, $J = 6.9$ Hz, 3H), 1.09 (d, $J = 6.8$ Hz, 3H), 0.83 (d, $J = 6.8$ Hz, 3H), –0.38 (d, $J = 6.7$ Hz, 3H). ^{13}C -NMR (100 MHz, $CDCl_3$, δ , ppm): 159.6, 147.3, 145.9, 138.1, 136.6, 136.4, 135.9, 132.41, 132.39, 132.37, 131.7, 131.0, 129.1, 129.0, 128.96, 128.93, 128.90, 128.88, 128.86, 128.84, 128.6, 128.1, 127.50, 127.47, 127.42, 126.7, 126.3, 126.1, 125.4, 125.1, 125.0, 124.5, 124.2, 113.2, 33.6, 28.7, 23.3. ^{31}P -NMR (202 MHz, $CDCl_3$, δ , ppm): 25.06. HRMS (ESI, m/z): Calculated for $C_{50}H_{48}NNiOP [(M+H)^+]$: 768.2796, Found 768.2798.

Other catalysts were synthesized according to the similar procedure as that of catalyst **1**.

Catalyst 2 (orange-yellow powder, 68%): ^1H -NMR (400 MHz, $CDCl_3$, δ , ppm): 10.12 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.48–6.39 (m, 52H), 6.14 (t, $J = 7.5$ Hz, 2H), 4.72 (d, $J = 4.5$ Hz, 4H), 2.73 (s, 2H), 2.12–1.90 (m, 4H), 1.69 (d, $J = 6.7$ Hz, 6H), 1.11 (d, $J = 6.6$ Hz, 6H), 0.83 (d, $J = 6.6$ Hz, 6H), –0.38 (d, $J = 6.5$ Hz, 6H). ^{13}C -NMR (100 MHz, $CDCl_3$, δ , ppm): 160.4, 160.1, 146.1, 146.0, 145.3, 145.2, 144.6, 138.2, 137.9, 136.9, 136.1, 133.6, 132.8, 131.6, 131.5, 131.1, 130.9, 130.3, 130.2, 130.1, 129.4, 129.3, 129.0, 128.7, 128.2, 127.8, 127.6, 127.5, 127.1, 126.9, 126.3, 126.0, 125.5, 125.0, 124.5, 124.4, 123.5, 123.4, 122.9, 33.1, 26.7, 22.2. ^{31}P -NMR (202 MHz, $CDCl_3$, δ , ppm): 24.94, 24.89. HRMS (ESI, m/z): Calculated for $C_{98}H_{92}N_2Ni_2O_2P_2 [(M+H)^+]$: 1507.5414, Found 1507.5412.

Catalyst 3 (orange-yellow solid, 62%): ^1H -NMR (400 MHz, $CDCl_3$, δ , ppm): 9.77 (d, $J = 7.5$ Hz, 1H), 9.67 (d, $J = 7.3$ Hz, 1H), 9.15 (d, $J = 7.8$ Hz, 1H), 9.02 (d, $J = 7.5$ Hz, 1H), 7.52–5.98 (m, 64H), 0.49 (s, 18H). ^{13}C -NMR (100 MHz, $CDCl_3$, δ , ppm): 161.9, 156.8, 152.1, 145.0, 144.6, 139.8, 138.7, 138.3, 138.0, 136.9, 135.2, 133.5, 131.7, 130.7, 130.2, 130.1, 129.0, 128.81, 128.79, 128.77, 127.9, 127.8, 127.77, 127.75, 127.6, 126.5, 126.3, 126.0, 125.9, 124.5, 124.2, 120.1, 33.1, 29.2. ^{31}P -NMR (162 MHz, $CDCl_3$, δ , ppm): 19.1. HRMS (ESI, m/z): Calculated for $C_{102}H_{86}N_2Ni_2O_2P_2 [(M+H)^+]$: 1549.4938, Found 1549.4941.

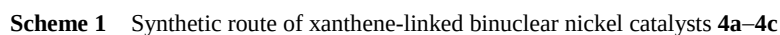
Catalyst 4a (yellow solid, 59%): ^1H -NMR (400 MHz, $CDCl_3$, δ , ppm): 10.79 (d, $J = 7.5$ Hz, 1H), 10.75 (d, $J = 7.8$ Hz, 1H), 8.15 (d, $J = 6.7$ Hz, 1H), 8.11 (d, $J = 6.5$ Hz, 1H), 7.93–5.96 (m, 76H), 2.19–2.15 (m, 6H), 1.72 (s, 6H), 0.55 (s, 9H), 0.52 (s, 9H). ^{13}C -NMR (100 MHz, $CDCl_3$, δ , ppm): 168.6, 151.0, 146.1, 145.9, 142.3, 140.3, 139.7, 138.8, 137.9, 137.6, 136.8, 133.7, 133.2, 132.0, 131.5, 130.9, 130.6, 128.9, 128.8, 128.6, 128.2, 127.8, 127.7, 127.6, 127.5, 125.9, 125.8, 125.5, 125.4, 125.3, 125.1, 125.0, 124.5, 122.9, 122.8, 33.5, 32.9, 32.2, 29.3, 19.9. ^{31}P -NMR (162 MHz, $CDCl_3$, δ , ppm): 22.9, 19.6. HRMS (ESI, m/z): Calculated for $C_{131}H_{110}N_2Ni_2O_3P_2 [(M+H)^+]$: 1937.6741, Found 1937.6753.

Catalyst 4b (yellow solid, 60%): ^1H -NMR (400 MHz, $CDCl_3$, δ , ppm): 10.83 (d, $J = 8.9$ Hz, 1H), 10.80 (d, $J = 8.7$ Hz, 1H), 8.11 (d, $J = 6.5$ Hz, 1H), 8.04 (d, $J = 6.7$ Hz, 1H), 7.96–5.89 (m, 64H), 2.16–2.13 (m, 6H), 1.72 (s, 6H), 0.56 (s, 9H), 0.54 (s, 9H). ^{13}C -NMR (100 MHz, $CDCl_3$, δ , ppm):

Catalyst **4c** (yellow solid, 66%): $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 11.90 (d, $J = 8.4$ Hz, 1H), 11.76 (d, $J = 8.6$ Hz, 1H), 8.09 (d, $J = 9.0$ Hz, 1H), 7.96 (d, $J = 8.7$ Hz, 1H), 7.88–6.03 (m, 56H), 2.18–2.16 (m, 6H), 1.73 (s, 6H), 0.58 (s, 9H), 0.53 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ , ppm): 169.4, 153.0, 146.3, 145.9, 142.4, 140.3, 140.2, 138.2, 138.3, 137.8, 137.2, 136.9, 133.8, 133.6, 132.0, 131.5, 130.9, 130.2, 128.9, 128.8, 127.8, 127.7, 127.6, 127.8, 125.9, 125.8, 125.7, 125.6, 125.5, 125.1, 125.0, 124.7, 122.9, 122.8, 120.2, 34.7, 34.3, 32.2, 30.5, 20.1. $^{19}\text{F-NMR}$ (282 MHz, CDCl_3 , δ , ppm): –56.2 (t, 2F), –57.4 (t, 2F), –57.9 (d, 1F), –58.3 (d, 1F), –59.0 (d, 1F), –59.2 (d, 1F), –75.6 (t, 1F), –76.1 (t, 1F), –77.5 (t, 1F), –77.9 (t, 1F), –81.2 (t, 1F), –81.4 (t, 1F), –82.3 (t, 1F), –82.5

In the glovebox, a 350 mL heavy-walled glass reactor (dried in a 120 °C oven overnight before usage) equipped with a stir bar was loaded with nickel complex, $\text{B}(\text{C}_6\text{F}_5)_3$, and toluene (25 mL). The glass reactor was then interfaced to a high-pressure line, and the solution was subjected to three freeze-pump-thaw cycles. The solution was then brought to the appropriate temperature using an oil bath. The reactor was pressured with ethylene to 90 psig. After the desired time, the reactor was vented and acidified methanol was syringed in. The precipitated polymer was stirred for 2 h, collected by filtration, washed with methanol, and dried under vacuum at 80 °C overnight.

According to the route as illustrated in Scheme 1, binuclear nickel catalysts (**4a–4c**) with rigid xanthene linked to



para-position of phenolic oxygen were synthesized. By following the procedures in our previous report^[24], we obtained a series of terphenylamines through Miyaura-Suzuki coupling reactions. Acid-catalyzed condensation of these terphenylamines with di-salicylaldehyde bridged by rigid xanthene linker afforded desired ligands **L4a–L4c** in high yields. The ligands were then converted to potassium salts by stirring with excess KH in THF at room temperature. All of these binuclear complexes were prepared by reaction of the corresponding potassium salts with 2.0 equiv. of NiCl(Naphthyl)(PPh₃)₂. Binuclear catalyst **2** with much more flexible allylic group linked to the position *ortho* to phenolic oxygen was synthesized through olefin metathesis reaction (Scheme S2 in electronic supplementary information, ESI). In addition, binuclear catalyst **3** with metal centers tethered together by rigid imine moiety was also synthesized (Scheme S3, ESI). These kinds of binuclear catalysts with various linkers and connected position would have different metal-metal distances and relative site orientations, thus leading to different catalytic properties. All catalysts and ligands were characterized by ¹H-, ¹³C-, ¹⁹F-, ³¹P-NMR spectra, and HRMS.

Crystal of **L4b** suitable for single-crystal X-ray diffraction analysis was obtained by slow diffusion of hexane into toluene solution at room temperature. The solid state structure (Fig. 1) revealed a C₂ symmetry, which was consistent with

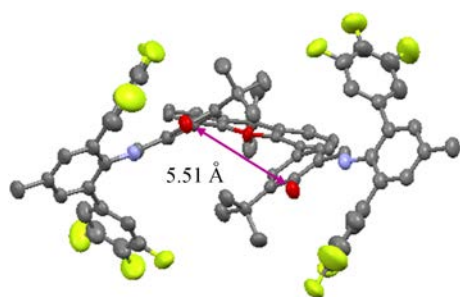


Fig. 1 Crystal structure of ligand **L4b**

Thermal ellipsoid are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Atoms are displayed in different color in the online version: fluorine (yellow); oxygen (red); nitrogen (blue); carbon (gray)

the results of ¹H-NMR and ¹³C-NMR spectra. The distance between two hydroxyl groups was about 5.51 Å, implying a short nickel-nickel distance in **4b**. The two coordination planes were linked to the rigid skeleton in an *anti* cofacial fashion due to the greater steric repulsion of *N*-terphenyl imine moiety. As seen from the ligand structure, bulky *N*-terphenyl moiety provided efficient steric hindrance for coordination center. In addition, the excess axial steric congestion from the other nickel coordination plane was expected in catalyst structure, thereby reducing the rate of chain transfer and catalyst deactivation, and resulting in polymers of higher molecular weight.

Ethylene Polymerizations

Ethylene homopolymerizations were performed using B(C₆F₅)₃ as a phosphine scavenger in toluene at a constant 90 psig ethylene pressure (Table 1). We quoted some polymerization data of corresponding mononuclear analogues (catalysts **5a–5c**) in literature under similar conditions for comparison (entries 8–10)^[16]. Mononuclear catalyst **1** with the allylic group *ortho* to the phenoxy oxygen showed very low activity in ethylene polymerization. This is mainly due to the insufficient steric hindrance of the *ortho* position, which would lead to the potential catalyst decomposition and chain transfer process^[1, 56, 57]. The same phenomenon was also observed in the binuclear nickel catalyst **2**. With flexible linker chains, catalyst **2** did not display improved polymerization behavior as expected. We speculated that the unrestricted conformation rotation caused by flexible linker weakened the metal-metal synergistic interaction and resulted in insignificant influence on polymerization behavior.

Binuclear nickel catalysts **3** and **4a–4c** with rigid linkers showed much higher activity in ethylene polymerization and produced PE of higher molecular weight. The results could be attributed to the increased steric hindrance around nickel centers and close proximity of metal-metal centers, which favor ethylene insertion into Ni–C bond more significantly^[32] compared with catalyst **2**. Rigid linker relative to flexible chains was prone to lock catalyst conformation, which strengthened synergistic effect in binuclear catalysts. In relative to mononuclear analogues, binuclear catalysts **4a** and **4c** showed higher activity in ethylene polymerization, which

Table 1 Ethylene polymerization results^a

Entry	Precat.	Yield (g)	TOF ^b	Branches ^c	<i>T</i> _m ^d (°C)	<i>M</i> _n ^e	<i>M</i> _w / <i>M</i> _n ^e
1	1	0.003	0.2	n.d. ^f	n.d. ^f	n.d. ^f	n.d. ^f
2	2	0.011	0.4	n.d. ^f	n.d. ^f	n.d. ^f	n.d. ^f
3	3	0.59	22	58	119.9	3.8	2.65
4	4a	0.40	15	60	121.4	4.1	3.98
5	4b	0.77	29	25	122.7	12.9	2.24
6	4c	8.05	302	36	125.9	39.7	3.72
7 ^{g, h}	4c	7.71	578	64	120.8	11.5	3.40
8 ⁱ	5a	0.10	7.6	59	–	3.7	3.3
9 ⁱ	5b	0.96	72	25	–	24.3	2.7
10 ⁱ	5c	2.93	220	14	–	61.7	2.57
11 ^g	5c	5.64	423	55	–	6.4	2.16

^a Catalyst: 20 μmol, co-cat.: B(C₆F₅)₃ (Ni:B 1:2), ethylene pressure: 90 psig, reaction temperature: 25 °C, toluene: 25 mL, reaction time: 40 min; ^b In 10³ g[PE]/(mol[Ni]·h); ^c Branching numbers per 1000 carbons were determined by ¹H-NMR spectroscopy; ^d Determined by differential scanning calorimetry; ^e In 10³ g/mol, obtained by GPC versus polystyrene standards; ^f n.d. = not detected; ^g Reaction temperature: 50 °C; ^h Catalyst: 10 μmol, B(C₆F₅)₃: 40 μmol, ethylene pressure: 90 psig, toluene: 25 mL, reaction time: 40 min; ⁱ Data taken from Ref. [24]

may indicate the existence of bimetallic cooperative effect. Furthermore, **4c** produced PE with higher branch density compared with **5c** (36 versus 14 branches/1000carbons). As we know, polymer branching is mainly caused by chain walking. It is reasonable to speculate that relatively faster chain walking occurred in binuclear catalyst **4c** due to the synergistic effect between metal centers^[33, 58]. Compared with the corresponding mononuclear catalyst **5c**, higher activity and polymer molecular weight were observed with binuclear catalyst **4c** at 50 °C (entry 7 versus 11), indicating that the binuclear structure possesses better thermal stability. In addition, the increase of degrees of branching and the decrease of molecular weights were due to the faster β -hydrogen elimination at higher temperature. Catalyst **4b** displayed lower activity and molecular weight compared with corresponding mononuclear catalyst **5b**. It might be associated with the differences in solubility of these two catalysts in toluene.

Among binuclear catalysts with different numbers of fluorine substituents (catalysts **4a–4c**), polymerization activity and molecular weight were improved dramatically as fluorine atoms increased. The trends matched well with the previous report^[24]. Especially, catalyst **4c** with *ortho*-fluorine substituents displayed a significant increase in activity and molecular weight, which could be ascribed to fluorine effect. Thus, the strategy of employing fluorine as substituents in catalyst structure was proved to significantly improve activity and molecular weight in olefin polymerization. In comparison to the other two catalysts, catalyst **4c** showed even higher branch density than catalyst **4b**, which was a deviation from the trend of fluorine effect. The presence of enhanced synergistic effect in catalyst **4c** may be a main origin.

For binuclear catalysts with metal centers of different relative locations (catalysts **3** and **4a**), polyethylene with similar branches and molecular weight were produced due to their similarly steric environment. Complex **3** showed slightly higher activity and produced PE with narrower PDI in comparison with catalyst **4a**. We speculated that the shorter linker minimized Ni–Ni distance, and inhibited conformation rotation and chain transfer, which provided efficient steric protection in complex **3**.

CONCLUSIONS

In summary, a series of mono- and binuclear nickel catalysts with different linkers and fluorine substituents were synthesized and characterized. Relative to flexible linker, catalysts with rigid linkers showed much higher activity in ethylene polymerization due to bulkier steric effect or potential synergistic effect. As to the catalysts **3** and **4a** with metal centers of different spatial arrangement, they produced polyethylene with similar molecular weight and branch density because of analogical site environment. Binuclear nickel catalysts **4a** and **4c** with xanthene linker showed higher activity and thermal stability than that of control catalysts, which may be attributed to the efficient axial steric hindrance provided by the other nickel center or potential synergistic effect. In binuclear catalysts **4a–4c**, different fluorinated aryl groups were applied to significantly influence activity and

molecular weight in ethylene polymerization. Fluorine substituents especially *ortho*-position fluorine could dramatically improve polymerization activity and molecular weight of polymers obtained. Further studies will explore the copolymerization of ethylene with α -olefin and other comonomers by binuclear catalysts.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2081-3>.

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