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Ethylene Polymerization and Copolymerization with Polar Monomers by Benzothiophene-bridged BPMPD-Pd Catalysts

Hong-Liang Mu, Jun-Hao Ye, Guang-Lin Zhou, Kang-Kang Li, and Zhong-Bao Jian*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Electronic Supplementary Information

Abstract A series of new bisphosphine-monoxide (BPMPD) ligands based on benzothiophene backbone and the corresponding palladium complexes $\{K^+2-P(O)(Ph)_2-3-PR^1R^2-C_6H_4S\}PdMeCl$ (**2a**: $R^1 = R^2 = Ph$; **2b**: $R^1 = R^2 = 2-OMe-Ph$; **2c**: $R^1 = R^2 = 2-CF_3-Ph$; **2d**: $R^1 = Ph$, $R^2 = 2-(2',6'-(OMe)_2C_6H_3)-C_6H_4$) were synthesized and fully characterized by ^1H -, ^{13}C -, ^{31}P -, and 2D-NMR spectroscopy and single-crystal X-ray diffraction. In the presence of $Na^+B[3,5-(CF_3)_2C_6H_3]_4^-$ (NaBARF), these complexes showed very high activities (up to 2.0×10^7 g·mol $^{-1}$ ·h $^{-1}$) for ethylene polymerization. More significantly, these catalysts enabled the copolymerization of ethylene with a broad scope of commercially available polar comonomers such as acrylates, acrylic acid, acrylonitrile, vinyltrialkoxysilane, allyl acetate, and long-chain 6-chloro-1-hexene to give functionalized polyethylene with reasonable catalytic activities (up to 10^6 g·mol $^{-1}$ ·h $^{-1}$) and incorporations (up to 5.3 mol%). This contribution suggests that, besides the modulation of conventionally steric and electronic factors, the connectivity (at different linking positions) of BPMPD (P,O) donors to the heteroaryl backbone also greatly influences the catalyst properties in terms of catalytic activity, polymer branching content, comonomer scope, and comonomer incorporation.

Keywords Olefin polymerization; Bisphosphine monoxide; Palladium; Polar monomers; Heteroaryl backbone

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INTRODUCTION

Transition-metal-catalyzed insertion copolymerization of commercially available polar vinyl monomers with olefins represents the most straightforward method for the precise preparation of functionalized polyolefins.^[1–9] In these reactions, the choice of catalytic system is of crucial importance because the polar functional groups adjacent to the double bond tend to poison most organometallic catalysts. As a milestone, α -diimine palladium and nickel catalysts reported by Brookhart copolymerized olefins with acrylates,^[10,11] silyl vinyl ether,^[12] and vinylalkoxysilanes,^[13] giving branched functional polyolefins and could be also used to prepare polymers with versatile topologies.^[14–16] Further modification to these catalysts by Guan,^[17] Sun,^[18] Long,^[19] Gao,^[20,21] and Chen^[22–24] led to enhanced catalytic properties including higher thermal stability and the production of semicrystalline copolymers. As another seminal breakthrough, phosphine-sulfonate palladium catalysts reported by Drent^[25] (**Chart 1, A**) represented the most thoroughly studied system due to the excellent catalytic properties for a broad scope of polar vinyl comonomers.^[2,26] The asymmetric combination of strong (P) and weak (O) σ -donors is

considered to be crucial. Thus, Shimizu^[27] and Li^[28,29] separately described that phosphino-phenolate nickel complexes (**B**) were efficient catalysts for the copolymerization of ethylene with acrylates, affording high molecular weight linear functionalized polyethylenes. As an important extension, Nozaki designed cationic (not neutral) bisphosphine monoxide (BPMPD) palladium system^[30] (**C**) that could also copolymerize ethylene with a broad family of polar vinyl monomers. After that, great efforts have been devoted to the modification of this system (**C** and **D**).^[31–38] Notably, the optimization of catalysts mostly relied on altering steric and electronic effects of P,O donor substituents, with very few studies focusing on the modifications of the ligand backbone, let alone on the change of the connectivity (different linking positions) of P,O donors. In fact, the connectivity of P,O donors to the ligand backbone could also significantly influence the catalyst properties. For instance, it has been reported that ferrocene-bridged phosphine sulfonate palladium catalysts (**E**) polymerized ethylene to semicrystalline polyethylenes.^[39] Using the same backbone, however, if phosphine and sulfonate moieties are located at different cyclopentadienyl rings (**F**), these palladium catalysts only dimerized ethylene.^[40] More relevantly, Chen recently investigated the influence of connectivity of phosphine-sulfonate donors to naphthalene backbone on catalytic behavior (**G**,^[41] **H**^[42]). Very recently, we first developed a new series of BPMPD-Pd catalysts

* Corresponding author, E-mail: zbjian@ciac.ac.cn

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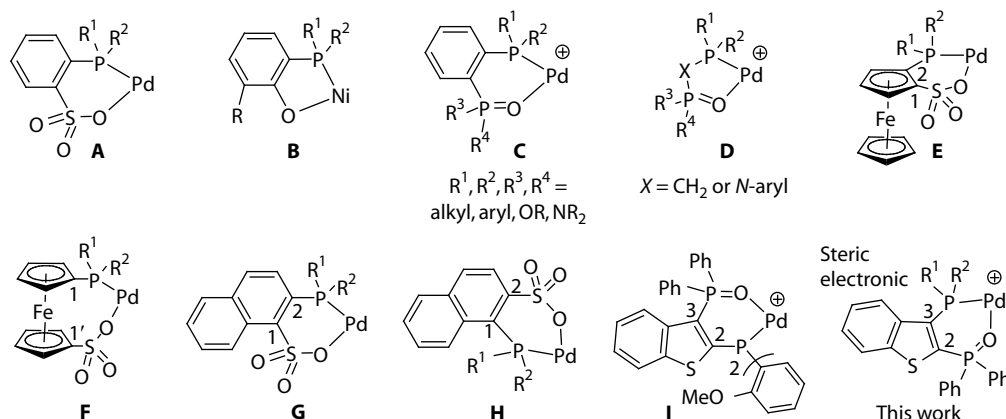


Chart 1 Late transition metal catalysts used for the copolymerization of ethylene with polar monomers.

(I) based on heteroaryl backbones, which were highly active for ethylene polymerization and copolymerization with various fundamental polar vinyl monomers.^[43] Differed from the conventional and symmetric benzene backbone group, heteroaryl backbone has different environment on the 2,3-positions, thus we envisioned that introducing P,O donors into different positions of heteroaryl backbone would lead to different catalytic properties due to the differed steric and electronic environment. In this contribution, we now report a family of new Pd catalysts bearing benzothiophene skeleton with the P,O donor fragments locating at the opposite position of our previously reported catalyst I. Catalysts with the modulation of steric and electronic effects in this case were even more active than the prototype catalyst I for ethylene polymerization. Most interestingly, the scope of polar comonomers applied to the copolymerizations was broadened.

EXPERIMENTAL

General Considerations

All moisture/oxygen sensitive reactions were performed using standard glove box or Schlenk techniques under a N_2 atmosphere. THF, n -hexane, CH_2Cl_2 , and Et_2O were purified by the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on Bruker AV400 (^1H : 400 MHz, ^{13}C : 100 MHz, ^{31}P : 162 MHz) or Bruker AV500 (^1H : 500 MHz, ^{13}C : 125 MHz, ^{31}P : 202 MHz) spectrometers. ^1H and ^{13}C chemical shifts are internally referenced to residual ^1H and ^{13}C solvent resonances. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4 (δ 0.0). NMR assignments were confirmed by ^1H - ^1H COSY, ^1H - ^{13}C HSQC, and ^1H - ^{13}C HMBC experiments when necessary. The molecular weights and molecular weight distributions (M_w/M_n) of polyethylenes and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 $^\circ C$. Melting points (T_m) of polyethylenes and copolymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 $^\circ C \cdot min^{-1}$ (temperature range: 20–160 $^\circ C$). Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry.

Synthesis of the Representative Compounds

Synthesis of ligand 1b

n -BuLi (0.9 mL, 1.6 mol·L⁻¹ in hexane, 1.44 mmol, 1.03 equiv.) was slowly added to a solution of 3-(dianisylphosphanyl)-benzo[*b*]thiophene (0.53 mg, 1.4 mmol, 1.0 equiv.) in the mixed solvent Et_2O (50 mL)/THF (10 mL) at -78 $^\circ C$. The mixture was stirred for 2 h at -78 $^\circ C$ and then $ClP(O)Ph_2$ was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed and the residue was extracted with CH_2Cl_2 /water. After dried with Na_2SO_4 , the solution was concentrated to a small volume, and precipitated in hexane. 0.31 g of pure ligand **1b** was obtained (total yield, 30%). ^1H -NMR (500 MHz, 298 K, CD_2Cl_2 , 5.32 ppm, δ): 7.91 (d, $J = 8.2$ Hz, 1H), 7.86 (br, 4H), 7.43 (t, $J = 7.0$ Hz, 2H), 7.34–7.24 (m, 7H), 7.04 (d, $J = 8.4$ Hz, 1H), 6.94 (t, $J = 7.7$ Hz, 1H), 6.82–6.67 (m, 6H), 3.46 (s, 1H). ^{13}C -NMR(^1H) (125 MHz, 298 K, $CDCl_3$, 77.16 ppm, δ): 161.05, 145.36 (dd, $J = 106.5$, 47.6 Hz), 143.58 (dd, $J = 13.2$, 4.2 Hz), 143.53 (d, $J = 6.1$ Hz), 137.39 (dd, $J = 27.3$, 9.5 Hz), 133.32, 132.59 (dd, $J = 10.7$, 4.7 Hz), 131.75 (d, $J = 3.0$ Hz), 130.04, 127.88 (d, $J = 12.9$ Hz), 125.55 (d, $J = 14.5$ Hz), 124.21, 122.63, 120.98, 110.33, 55.29. ^{31}P { ^1H }-NMR (202 MHz, CD_2Cl_2 , δ): 22.72 (d, $J = 15.3$ Hz), -40.80 (d, $J = 15.3$ Hz). Elemental analysis: Calcd. for $C_{34}H_{28}O_3P_2S$ (578.60 g·mol⁻¹): C, 70.58; H, 4.88. Found: C, 70.78; H, 4.78.

Synthesis of complex 2b

A mixture of ligand **1b** (100 mg, 0.17 mmol) and (COD)PdMeCl (47 mg, 0.18 mmol) was dissolved in 15 mL of CH_2Cl_2 and stirred at room temperature for 12 h. Following filtration, the target complex was obtained as a white solid powder (105 mg, 84%). ^1H -NMR (500 MHz, 298 K, $CDCl_3$, 7.26 ppm, δ): 7.74 (d, $J = 8.2$ Hz, 1H, H_7), 7.69 (dd, $J = 12.7$, 7.9 Hz, 4H, H_{16}), 7.51 (t, $J = 7.3$ Hz, 2H, H_{18}), 7.44–7.34 (m, 8H, H_{12} , H_{14} , H_{17}), 7.31 (t, $J = 7.2$ Hz, 1H, H_6), 7.09–7.01 (m, 2H, H_4 , H_5), 6.85–6.72 (m, 4H, H_{11} , H_{13}), 3.36 (s, 6H, H_{19}), 0.43 (d, $J = 4.1$ Hz, 3H, H_{20}). ^{13}C { ^1H }-NMR (125 MHz, 298 K, $CDCl_3$, 77.16 ppm, δ): 160.6 (C_{10}), 142.3 (d, $J = 12.2$ Hz, C_3), 142.1 (t, $J = 7.2$ Hz, C_8), 139.6 (dd, $J = 103.3$, 25.4 Hz, C_1), 136.7 (d, $J = 12.7$ Hz, C_{14}), 136.1 (dd, $J = 36.8$, 6.4 Hz, C_2), 132.7 (d, $J = 10.9$ Hz, C_{16}), 130.3 (d, $J = 112.7$ Hz, C_{15}), 128.6 (d, $J = 12.7$ Hz, C_{17}), 126.6 (C_5), 126.2 (C_6), 124.5 (C_4), 121.9 (C_7), 120.9 (d, $J = 11.8$ Hz, C_{13}), 116.5 (d, $J = 52.8$ Hz, C_9), 111.2 (C_{11}), 55.4 (C_{19}), 1.2 (C_{20}). ^{31}P { ^1H }-NMR (202 MHz, $CDCl_3$, δ): 30.84 (d, $J = 17.7$ Hz), 9.38 (d,

$J = 17.6$ Hz). Elemental analysis: Calcd. for $C_{35}H_{31}ClO_3P_2PdS$ (734.02 g·mol $^{-1}$): C, 57.15; H, 4.25; Found: C, 56.95; H, 4.40.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes **2a–2d**

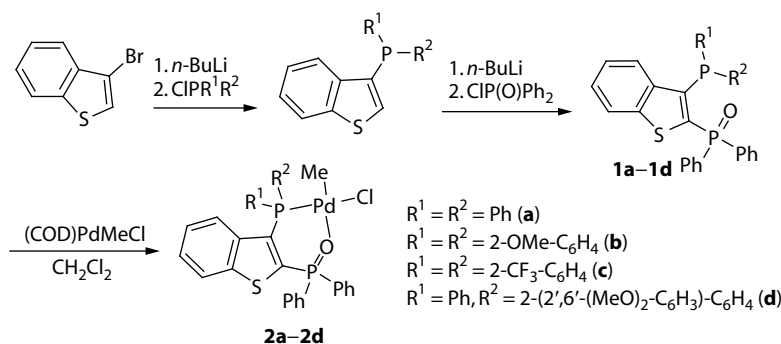
Benzothiophene-containing BPMP ligands **1a–1d** were facilely synthesized *via* a two-step method (Scheme 1). 3-Bromobenzothiophene was lithiated with *n*-BuLi at -78 °C before reacting with electrophile chlorophosphines to give 3-phosphinobenzothiophene in moderate yields. Ligands **1b–1d** were obtained from reaction of ClP(O)Ph $_2$ with the lithium salts of 3-phosphinobenzothiophenes. All four ligands were fully characterized by ^1H -, ^{13}C -, and ^{31}P -NMR spectroscopy and elemental analysis.

The presence of two doublets in the ^{31}P -NMR spectra of **1a–1d** was a diagnostic for the formation of bisphosphine monoxide compounds. The resultant BPMP ligands reacted with (COD)PdMeCl in dichloromethane at room temperature to yield white powder of the target palladium complexes followed by precipitation in hexane. Upon coordination to palladium, the ^{31}P chemical shifts of phosphine signals moved downfield as compared to the free ligands. The complete disappearance of P(III) signals and X-ray structure (see below) verified that the coordination mode was unique, excluding the possibility of [S, P=O] coordination, which was consistent with the expected weak donor ability of the sulfur atom of thiophene. The NMR chemical shifts for the newly formed Pd-Me groups of **2a–2c** in both ^1H - (0.58, 0.43, 0.68 ppm) and ^{13}C -NMR (2.16, 1.20, 2.64 ppm) spectra correlated with the or-

der of **2c** (CF_3) > **2a** (H) > **2b** (OMe), clearly reflecting the different shielding effects caused by the change in electronic density. The small coupling constants ($^3J_{PH} = 3.8$ –4.4 Hz) of Pd-Me doublets indicated a *cis* arrangement between methyl group and phosphine moiety in each case.

The solid-state structures of **2a–2c** were further confirmed by X-ray single crystal diffraction analysis (Fig. 1). In each case, a near-square-planar Pd(II) center is chelated by phosphorus and oxygen donor atoms with the chloride atom *cis* to the phosphine oxide moiety and the methyl group *cis* to the phosphine moiety, which is consistent with the $^3J_{PH}$ values observed. The bond lengths of Pd–C (**2a**: 2.039(3) Å, **2b**: 2.023(4) Å, **2c**: 2.047(3) Å) of these complexes are similar, and are also close to that of **1** (Pd–C: 2.047(3) Å).^[43] The bite angles (O–Pd–P) of **2b** (85.40(7)°) and **2c** (84.82(8)°) are close to that of **1** (85.23(6)°) but are much smaller than that of **2a** (98.12(5)°). The most prominently different structural feature for **2a–2c** and **1** lies in the angles between P–C–P and O–Pd–P planes. For less sterically demanding **2a**, this value is only 28.6°. As the steric bulk of the phosphine substituents increases, the angle reaches 50.32° for **2b** and 53.6° for **2c**, which is much larger than that in **1** (42.2°). The distortion causes the repulsion to varying degrees between the substituents and the backbone, leading to different influences on the metal center. These observations also indicate that both the position of P and P=O donors on the benzothiophene backbone and substituents on the donor fragments greatly influence the structure of the complexes, which would potentially lead to differed catalytic properties.

The solid-state structures of **2a–2c** were also analyzed by



Scheme 1 Synthesis of heteroaryl-bridged BPMP ligands and corresponding Pd complexes.

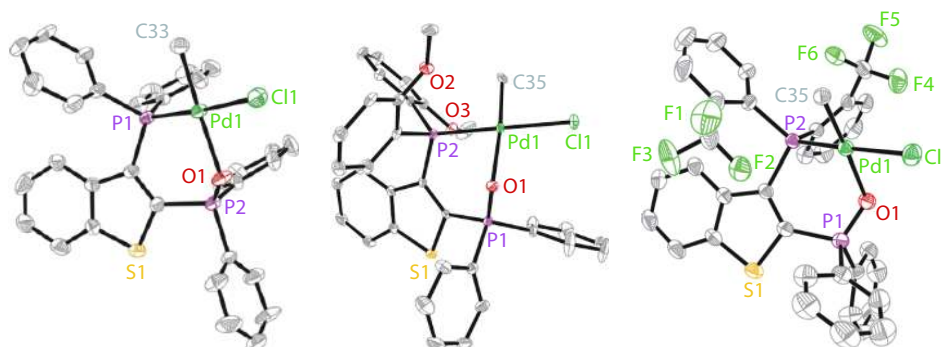


Fig. 1 ORTEP view of Pd(II) complexes **2a–2c** drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Cavallo's SambVca 2.0 program^[44] to visualize steric hindrance around the palladium center (Fig. 2). As expected, **2a** (H) shows widely open space in the northwest quadrants and a low percent buried volume (% V_{bur}) of 45.6. **2b** (OMe) shows an increased % V_{bur} of 48.2 that is also slightly higher than the counterpart **1** (% V_{bur} 46.8). Introducing two CF₃ groups to the phosphine moiety significantly increases the filled space (% V_{bur} 54.1) around the palladium center. Due to different folding direction, the less crowded quadrant for **2b** and **2c** is northwest and southwest, respectively. However, additional space is filled for **2c** in this area (Fig. 2, right versus middle) due to the presence of CF₃ group that is situated at the phenyl ring titling toward the coordination plane (Pd...F = 3.2 Å). In **2b** and **1**, the *o*-anisyl group is almost perpendicular

ular to the coordination plane, and the methoxy group thereon is far from the metal center (Pd...O > 3.3 Å). We believe that differences in the structure between **1** and the current catalysts come from the repulsion between the phosphine substituent and the backbone.

Ethylene Polymerization Using Complexes 2a–2d

Complexes **2a–2d** were applied to ethylene polymerization at 80 °C under various ethylene pressures with NaBARf as the co-catalyst. All these complexes displayed very high activities (up to 2.0×10^7 g·mol^{−1}·h^{−1}) toward ethylene polymerization except **2c**. After 30 min, **2c** produced only 0.44 g of polyethylene with a higher melting point (Table 1, entries 1, 5, 9, and 13), indicating a lower branching density.^[45,46] However, when polymerizations were conducted at 60 °C, the activities raised to $2.7 \times$

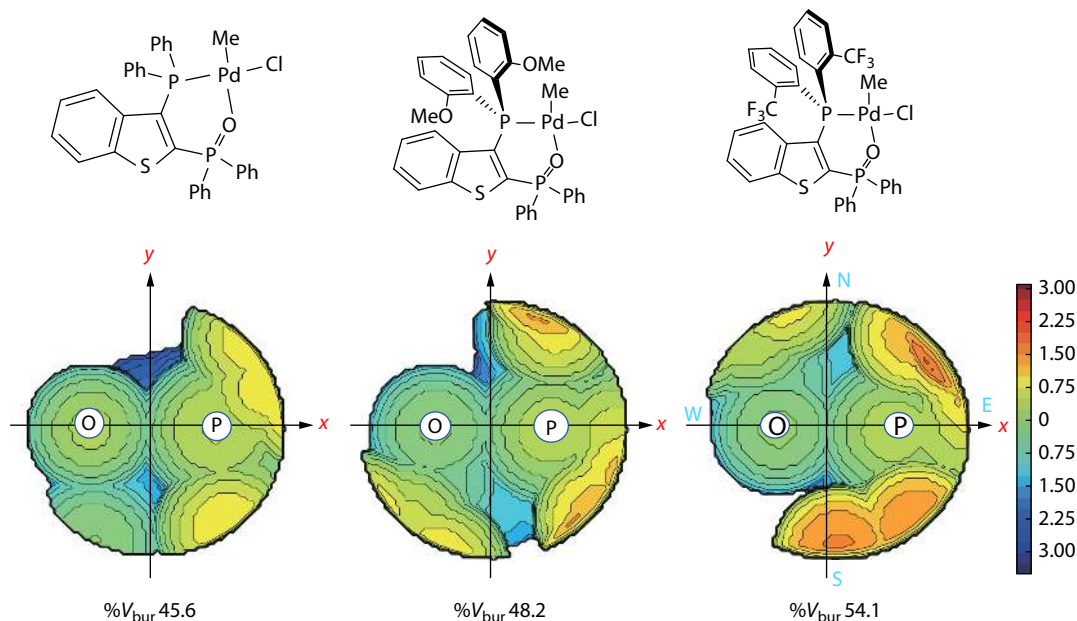


Fig. 2 Steric maps of palladium catalysts **2a–2c** based on heteroaryl BPMP ligands.

Table 1 Ethylene polymerization using catalysts **2a–2d**.^a

Entry	Cat.	<i>T</i> (°C)	<i>P</i> (bar)	Yield (g)	Activity ^b	<i>M_n</i> ^c × 10 ^{−3}	<i>M_w</i> / <i>M_n</i> ^c	<i>T_m</i> ^d (°C)	Brs ^e
1	2a	80	20	5.54	3.7	2.5	2.5	124.9	2
2	2a	80	10	5.32	3.5	2.4	2.5	123.7	2
3	2a	80	5	3.55	2.4	4.0	2.4	123.2	2
4	2a	60	5	0.71	1.1	3.7	2.3	127.5	1
5	2b	80	20	29.45	19.6	6.3	3.7	124.2	8
6	2b	80	10	22.32	14.9	6.7	2.8	120.0	10
7	2b	80	5	13.94	9.3	11.0	2.7	126.6	6
8	2b	60	5	5.09	3.4	19.2	2.3	134.8	1
9	2c	80	20	0.44	0.3	4.3	3.4	128.7	4
10	2c	60	20	3.98	2.7	10.5	2.7	132.3	1
11	2c	60	10	2.88	1.9	7.6	2.9	131.1	1
12	2c	60	5	2.72	1.8	14.2	2.9	130.8	1
13	2d	80	20	27.55	18.3	6.4	4.0	125.5	7
14	2d	80	10	18.75	12.5	8.1	2.8	124.1	7
15	2d	80	5	11.16	7.4	11.8	2.6	126.6	6
16	2d	60	5	2.41	1.6	38.5	1.9	135.8	<1

^a Reaction conditions: catalyst (3 μmol), NaBARf (3.6 μmol), toluene/CH₂Cl₂ (96 mL/4 mL), time (0.5 h), 750 r·min^{−1}, unless noted otherwise; ^b Activity is in unit of 10⁶ g·mol^{−1}·h^{−1}; ^c Determined by GPC in 1,2,4-trichlorobenzene at 150 °C versus linear polystyrene standards, and corrected by universal calibration versus linear polyethylene via Mark-Houwink-Sakurada equation; ^d Determined by DSC (second heating); ^e Number of branches per 1000C, as determined by ¹H-NMR in C₂D₂Cl₄ at 110 °C.

$10^6 \text{ g}\cdot\text{mol}_{\text{Pd}}^{-1}\cdot\text{h}^{-1}$, indicating a less thermally stable nature of **2c** possibly caused by the electron-withdrawing CF_3 groups. It has been reported that the analogous phenylene-bridged BPMPD-Pd catalyst (**C**, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Ph}$) showed low activity ($6.4 \times 10^4 \text{ g}\cdot\text{mol}_{\text{Pd}}^{-1}\cdot\text{h}^{-1}$) and produced very low molecular weight polyethylene ($M_n = 800$).^[30] By comparison, the heteroaryl-bridged **2a** showed significantly higher activities ($> 2.4 \times 10^6 \text{ g}\cdot\text{mol}_{\text{Pd}}^{-1}\cdot\text{h}^{-1}$), but the molecular weight only increased by 3 times. Expectedly, both **2b** with electron-donating group and **2d** with bulkier group further enhanced the activities by 3–5 times and increased the molecular weight by 3 times (Table 1, entries 3, 7, and 15). Note that the activities markedly increased when ethylene pressure increased from 5 bar to 10 bar, but this trend was less prominent when ethylene pressure further elevated from 10 bar to 20 bar (Table 1, entries 5–7), suggesting that the active sites became saturated at higher ethylene concentration. In addition, the polymer molecular weights roughly decreased with increasing ethylene pressures, indicating the presence of serious chain transfer to ethylene monomer.

To investigate the effect of connectivity of P,O donors on catalytic behavior, **1** and **2b** were compared. **2b** displayed more than twice higher activity than **1** under otherwise identical conditions (e.g. 20 bar, 8.7×10^6 versus $2.0 \times 10^7 \text{ g}\cdot\text{mol}_{\text{Pd}}^{-1}\cdot\text{h}^{-1}$). These two catalysts produced polymers with substantially the same molecular weight under low ethylene pressure ($M_n = 11000$). The molecular weight of the polymer produced by **1** slightly altered with the increase of ethylene pressure, while the decrease of molecular weight for **2b** took place due to the more serious chain transfer to monomer (Table 1, entries 5–7). Moreover, the melting point of the polymers with the same molecular weight prepared by the two catalysts also differed, indicating that the two catalysts generated different branching densities. Calculation from ^1H -NMR spectra verified that the branching densities of the polymer produced by **2b** (6–10 brs/1000C) were higher than those by **1** (≤ 2 brs/1000C). Meanwhile, the polymer branching was sensitive to polymerization temperature, and highly linear polyethylene (< 1 brs/1000C) could be obtained at 60°C (Table 1, entries 8 and 16) with high T_m s. At the first glance, these results seem to be somewhat confusing, as catalysts with higher steric hindrance generally give higher molecular weight polymers with lower branching content. We thus believe that the small difference in steric hindrance ($\%V_{\text{bur}}$ 48.2 (**2b**) versus 46.8 (**1**)) does not cause a decisive influence, and that the difference between the chain transfer tendency and the aforementioned catalytic activity is more likely to be electronic reason due to the different connectivity (2,3- versus 3,2-).

Time-dependence ethylene polymerization studies using **2b** (80°C , 2 μmol cat., 1.2 equiv. NaBARf, ethylene = 5 bar, toluene = 96 mL, CH_2Cl_2 = 4 mL) showed no obvious attenuation in activity for this catalyst from 15 min to 60 min (Fig. 3), indicating that the catalyst has excellent thermal stability under high temperature. Catalyst **1** also showed good thermal stability under these conditions, but the catalytic activities were about half lower than those of **2b**.

Ethylene Copolymerization with Polar Monomers

2a–2d/NaBARf were first used to copolymerize ethylene with

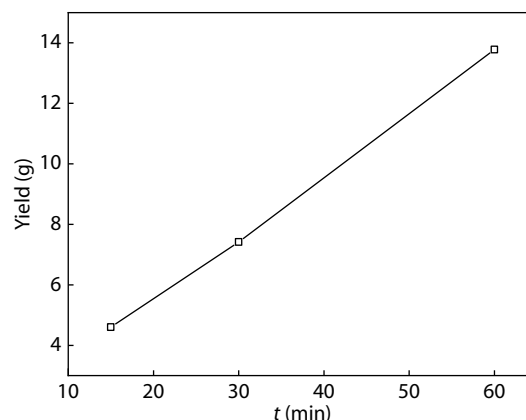


Fig. 3 Time-dependence curve of ethylene polymerization catalyzed by **2b**.

methyl acrylate (MA). Catalyst **2a** was completely deactivated in the presence of $1 \text{ mol}\cdot\text{L}^{-1}$ of MA (Table 2, entry 1), although it exhibited satisfactory activity for ethylene homopolymerization. Apart from the lower basic catalytic activity for ethylene, this may also originate from less protection due to the lack of steric hindrance around the metal center for **2a**. This phenomenon has been also observed in phosphine-sulfonate $\text{Pd}^{[47]}$ and phosphino-phenolate Ni catalysts,^[28] where $-\text{PPh}_2$ substituted catalysts performed poorly in the presence of polar monomers. However, **2b–2d** were active for these copolymerizations, giving highly linear ethylene/MA copolymers. The incorporation could be adjusted by changing the concentration of MA or the pressure of ethylene (Table 2, entries 2–4). Lowering temperature resulted in decrease of MA incorporation (Table 2, entry 4 versus 5). Considering the thermally less stable nature of **2c**, copolymerizations were carried out at 60°C . The MA incorporation was clearly lower than that using **2b** (Table 2, entry 5 mol% versus 7 mol%, 1.9 mol% versus 0.5 mol%), in line with the results reported by Nozaki.^[33] We believe that it can be partly attributed to the aforementioned crowded steric environment around metal center for **2c** besides the electronic effect. Considering the connectivity effect, under otherwise identical conditions, **2b** gave a lower MA incorporation than **1**, which may be related to a slightly higher $\%V_{\text{bur}}$ in **2b**. In addition, **2b** was better than bulkier **2d** (Table 2, entry 2 versus 8) in terms of both activity and MA incorporation. As anticipated, **2a** was also deactivated by $1 \text{ mol}\cdot\text{L}^{-1}$ of AA that has dual poisoning effects due to protonation and coordination (Table 2, entry 9). In contrast, **2b** showed good activity ($8.0 \times 10^4 \text{ g}\cdot\text{mol}_{\text{Pd}}^{-1}\cdot\text{h}^{-1}$) for the ethylene/AA copolymerization (Table 2, entry 10). The incorporation nearly doubled when the AA concentration was increased from $1 \text{ mol}\cdot\text{L}^{-1}$ to $2 \text{ mol}\cdot\text{L}^{-1}$ (Table 2, entry 10 versus 11), which could also be achieved by reducing ethylene pressure (Table 2, entry 10 versus 12). Compared to **1**,^[43] **2b** gave a slightly lower AA incorporation (3.9 mol% versus 2.4 mol%). Again, the electron-withdrawing **2c** and the bulkier **2d** showed very limited incorporation of AA (Table 2, entries 14–17), possibly due to more congested environment.

Since **2b–2d** exhibited satisfactorily catalytic activity and insertion ability in the copolymerization of ethylene with MA

Table 2 Ethylene copolymerization with polar monomers using catalysts **2a–2d**.^a

Entry	Cat.	T (°C)	P (bar)	Comono. (mol·L ⁻¹)	Yield (g)	Activity ^b	X ^c (mol%)	M _n ^d × 10 ⁻³	M _w /M _n ^d	T _m ^e (°C)	Brs ^f
1	2a	80	10	MA (1.0)	0	—	—	—	—	—	—
2	2b	80	10	MA (1.0)	0.54	5.4	2.3	6.3	2.0	116.2	<1
3	2b	80	10	MA (2.0)	0.27	2.7	3.6	3.3	2.2	108.9	1
4	2b	80	5	MA (1.0)	0.16	1.6	3.4	4.5	2.2	110.4	1
5	2b	60	5	MA (1.0)	0.13	1.3	1.9	8.5	1.9	117.1	<1
6	2c	60	10	MA (1.0)	1.66	16.6	0.3	5.3	2.2	129.0	<1
7	2c	60	5	MA (1.0)	0.57	5.7	0.5	4.6	2.1	127.1	<1
8	2d	80	10	MA (1.0)	0.12	1.2	0.9	3.9	2.0	124.7	2
9	2a	80	10	AA (1.0)	0	—	—	—	—	—	—
10	2b	80	10	AA (1.0)	0.80	8.0	1.3	4.2	2.1	123.9	<1
11	2b	80	10	AA (2.0)	0.32	3.2	2.4	1.6	3.0	109.5	<1
12	2b	80	5	AA (1.0)	0.24	2.4	2.6	1.9	3.1	115.8	1
13	2b	60	5	AA (1.0)	0.14	1.4	0.9	6.8	2.0	122.4	2
14	2c	60	10	AA (1.0)	2.29	22.9	n.d.	3.0	1.8	128.1	<1
15	2c	60	5	AA (1.0)	0.71	7.1	n.d.	2.4	1.8	126.3	<1
16	2c	60	5	AA (2.0)	0.13	1.3	0.3	0.9	2.2	111.1	1
17	2d	80	10	AA (1.0)	0.19	1.9	0.4	6.5	2.0	128.9	2
18 ^g	2b	80	10	VTMoS (1.0)	0.02	0.5	2.1	4.6	5.3	109.6	1
19 ^g	2b	80	10	AAc (1.0)	0.22	5.5	1.1	2.3	2.3	120.2	<1
20	2c	60	5	AAc (1.0)	0.09	9.0	0.8	1.8	2.1	121.8	2
21 ^g	2b	80	10	VAc (1.0)	0.09	2.3	0	3.7	2.4	129.1	1
22 ^g	2b	80	10	AN (1.0)	0.25	6.3	0.8	1.2	2.1	122.4	<1
23	2b	80	5	6-Cl-Hex (1.0)	10.10	101.0	5.3	2.9	2.8	103.5	2
24	2b	80	5	UA (1.0)	0.05	5.0	5.1	7.2	2.0	92.4	1

^a Reaction conditions: catalyst (10 μmol), NaBARf (1.2 equiv.), BHT (30 mg), toluene/CH₂Cl₂ (46 mL/4 mL), time (1.0 h), 750 r·min⁻¹, unless noted otherwise; ^b Activity is in unit of 10⁴ g·mol⁻¹·h⁻¹; ^c Determined by ¹H-NMR in C₂D₂Cl₄ at 110 °C; ^d Determined by GPC in 1,2,4-trichlorobenzene at 150 °C versus linear polystyrene standards, and corrected by universal calibration versus linear polyethylene via Mark-Houwink-Sakurada equation; ^e Determined by DSC (second heating); ^f Number of branches per 1000C, as determined by ¹H-NMR in C₂D₂Cl₄ at 110 °C; ^g Time, 4.0 h.

and AA, we further expanded the scope of polar monomers to which these catalysts are applied. Vinyl trimethoxysilane (VTMoS) was first tried for the copolymerization that was accessible using phosphine-sulfonate^[48,49] and α -diimine catalysts,^[13,50] although **1** was inactive and **2b** only displayed low catalytic activity (Table 2, entry 18). Furthermore, **2b** and **2c** were able to copolymerize ethylene with allyl acetate (AAc), but the copolymerization of ethylene with vinyl acetate (VAc) only generated polymer without VAc incorporation. We subsequently tried the more challenging polar comonomers acrylonitrile (AN) which could not be incorporated using **1**.^[43] By using **2b**, however, both end-capped and backbone comonomer signals were observed in ¹H-NMR spectrum of the copolymers, demonstrating the beneficial effects of P,O donor position on the catalytic performance. We also tried long chain polar monomers containing —Cl or —COOMe groups. In the presence of 1 mol·L⁻¹ of methyl 10-undecenoate (UA), the catalytic activity was greatly suppressed, with 5.1 mol% of the comonomer built into the polymer chain. However, it is worth noting that 6-chloro-1-hexene (6-Cl-Hex) was copolymerized with ethylene using **2b** with very high activity (1.0 × 10⁶ g·mol_{Pd}⁻¹·h⁻¹), giving linear copolymers with 5.3 mol% incorporation.

CONCLUSIONS

By altering the position of P,O donor fragments on the asymmetric benzothiophene backbone, a series of new BPMO-Pd complexes with different steric and electronic effects have been prepared and fully characterized. In the presence of NaBARf, these catalysts showed remarkably high activities for

ethylene polymerization. **2b** (2-P=O, 3-P) was more active than the counterpart **1** (2-P, 3-P=O), indicating the pivotal role of connectivity position of donors. Moreover, these catalysts were able to copolymerize ethylene with various challenging polar monomers with reasonable activities and incorporations to give functionalized linear copolymers. Compared to the counterpart **1**, a broader scope of polar comonomers including VTMoS, AN, 6-Cl-Hex, and UA could be applied to ethylene copolymerization using **2b**. This work suggests that installation of coordination groups at different positions of the backbone is a facile way to modulate the catalytic properties. The easily modified nature of asymmetric heterocyclic ligand backbones allows this method to avoid the tedious organic synthesis steps required for designing versatile phosphine(oxide) donors to some extent.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at

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