Styrene-containing Phosphine-sulfonate Ligands for Nickel- and Palladium-catalyzed Ethylene Polymerization

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\section*{INTRODUCTION}

Late transition metal catalysts have been playing increasingly important roles in the field of olefin polymerization\textsuperscript{[1–15]} Nickel compounds were initially known as a "poison" for olefin polymerization, since the famous nickel effect was observed by Ziegler and co-workers\textsuperscript{[16]}. Now, the situation has changed dramatically\textsuperscript{[17]}, since many nickel catalysts have been developed for producing high molecular weight polyethylenes, such as \(\alpha\)-diimine\textsuperscript{[1,18–32]} (Chart 1, I), salicyaldimine\textsuperscript{[33–36]} (Chart 1, II), pyridine-imine\textsuperscript{[37–39]} (Chart 1, III), 2-iminopyridine-N-oxide\textsuperscript{[40]} (Chart 1, IV) and \(\alpha\)-iminoketone\textsuperscript{[41]} (Chart 1, V) nickel catalysts. Moreover, some phosphine-ligand-based nickel catalysts exhibit the capabilities of producing high molecular weight polyethylenes, including tri-1-adamantylphosphine\textsuperscript{[42]} (Chart 1, VI) and some SHOP (shell higher olefin process) type\textsuperscript{[43–46]} (Chart 1, VII) nickel catalysts.

To improve catalytic performances of catalysts, many efforts have been directed towards modifying ligand structures by introducing various substituents. Many systematic researches on either steric or electronic effects of substituents have been reported\textsuperscript{[3–3,9–15]}. For instance, the dicyclohexyl-substituted phosphine-sulfonate nickel catalyst can only produce oligomers of ethylene (\(M_n<10^3\) g·mol\(^{-1}\)) at 30 °C\textsuperscript{[47]} (Chart 1, VIII). In contrast, sterically bulky biaryl based phosphine-sulfonate nickel catalysts can generate high molecular weight polyethylenes at 25 °C (\(M_n\) up to 4.05×10\(^5\) g·mol\(^{-1}\))\textsuperscript{[48–54]} (Chart 1, IX). It was indicated that the sterically bulky substituent at the axial position with respect to the nickel center is essential, since the steric effect could suppress \(\beta\)-H elimination. However, most of these catalysts generated moderate molecular weight polyethylenes (\(M_n\) up to 1.03×10\(^5\) g·mol\(^{-1}\), typically <10\(^4\) g·mol\(^{-1}\)) at 80 °C, making them not suitable for industrially used gas-phase ethylene polymerization conditions (80–100 °C). Jian and co-workers reported a series of asymmetrically methyl/biaryl-substituted phosphine-sulfonate nickel catalysts\textsuperscript{[55]}. These catalysts can generate moderate molecular weight polyethylenes at 90 °C (\(M_n\) up to 8.8×10\(^3\) g·mol\(^{-1}\)). It is possible that phosphine-sulfonate nickel catalysts bearing sterically even bulkier substituent might generate polyethylenes with higher molecular weight. However, the strategy based on endless exploration on substitute effects poses formidable challenges on ligand syntheses.

In this contribution, we wish to explore an alternative strategy by introducing a polymerizable moiety to the ligand structure. This way, a polymeric substituent could be generated \textit{in situ} during polymerization and significantly alters ligand and steric effects. A series of phosphine-sulfonate ligands bearing 2-, 3- and 4-vinylphenyl groups on the phosphorus
atom (Chart 1, X) (Scheme 1) were designed, synthesized, characterized and investigated in Ni- and Pd-catalyzed ethylene polymerization. These phosphine-sulfonate nickel and palladium catalysts are well-defined single component catalysts. For the nickel catalysts, the dissociated ligand PPh$_3$ was used. For the palladium catalysts, the dissociated ligand DMSO (dimethylsulfoxide) was used. It is hypothesized that the copolymerization of the 2-vinyl group on ligand with ethylene can generate a bulky polymer substituent on ligand\[45,56–63\] associated with enhanced steric effect. Consequently, the catalyst bearing 2-vinylphenyl group might result in increased molecular weight of polyethylene product compared with the catalysts bearing 3- or 4-vinylphenyl groups.

**EXPERIMENTAL**

**General**

All experiments were carried out under dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. $^1$H-, $^{13}$C- and $^{31}$P-NMR spectra were recorded on a Bruker AscendTm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the $^1$H- and $^{13}$C-NMR spectra were referenced to tetramethylsilane; the $^{31}$P-NMR spectra were referenced to an external 85% H$_3$PO$_4$ solution. Coupling constants are in Hz. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray diffraction data were collected at 298 (2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda$=0.071073 nm). The molecular weights and molecular weight distributions of the polymers were determined using gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using trichlorobenzene as a solvent. The calibration curve was constructed from polystyrene standards and was corrected for linear polyethylene by universal calibration using the Mark-Houwink parameters of Rudin: $K$=5.90×10$^{-2}$ cm$^2$g$^{-1}$ and $\alpha$ = 0.69 for polyethylene. Dichloromethane, THF, and hexanes were purified by solvent purification systems.

**Synthesis of Ligands and Catalysts**

**Synthesis of L1**

At 0 °C, $^n$BuLi (2.5 g·mol$^{-1}$, 16 mL, 40 mmol) was added slowly to a solution of benzenesulfonic acid (3.16 g, 20 mmol) in THF (50 mL). The suspension was stirred for 1 h and added to a solution of dichlorocyclohexyl-phosphine (3.68 mL, 20 mmol) in THF (30 mL) at −78 °C. The mixture was stirred for another 12 h at room temperature to yield lithium [chloro(cyclohexyl)-phosphino]benzenesulfonate. In a separate Schlenk flask, 4-bromostyrene (3.66 g, 20 mmol) was dissolved in dry THF (100 mL) under nitrogen and cooled to −78 °C. $^n$BuLi (2.5
The solvent was removed under reduced pressure, the resulting solid Pd1 (203 mg, 67%). 1H-NMR (400 MHz, d6-DMSO, δ ppm): 7.96 (s, 1H), 7.78–7.70 (m, 2H), 7.58 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 7.3 Hz, 1H), 7.45–7.40 (m, 1H), 7.32 (t, J = 8.3 Hz, 1H), 6.75 (dd, J = 17.0, 11.2 Hz, 1H), 5.93 (d, J = 17.7 Hz, 1H), 5.36 (d, J = 10.6 Hz, 1H), 2.82 (s, 1H), 2.54 (s, 6H, DMSO), 2.07 (s, 1H), 1.76 (s, 1H), 1.67 (s, 2H), 1.45 (br, 4H), 1.30 (s, 1H), 1.21 (s, 1H), 0.20 (s, 3H, Phd-Me). 31P-NMR (162 MHz, d6-DMSO, δ ppm): 32.93 (s). 13C-NMR (101 MHz, d6-DMSO, δ ppm): 149.43 (d, J = 125 Hz), 139.15 (d, J = 2.1 Hz), 137.51 (s), 134.33 (s), 132.89 (d, J = 10.9 Hz), 130.98 (s), 130.35 (s), 130.20 (d, J = 5.9 Hz), 129.84 (s), 127.28 (s), 127.18 (d, J = 7.4 Hz), 126.87 (s), 126.48 (d, J = 10.7 Hz), 116.72 (s), 104.3 (s, DMSO), 36.17 (d, J = 30.6 Hz), 30.07 (d, J = 3.5 Hz), 28.26 (s), 26.02 (d, J = 21.0 Hz), 26.01 (d, J = 5.9 Hz), 25.64 (s), 0.27 (s, Phd-Me).

Synthesis of Pd2
Similar procedure was employed to catalyst Pd1 except L2 (200 mg, 0.53 mmol) was used. Pd2 was obtained as a gray solid (221 mg, 73%). 1H-NMR (400 MHz, d6-DMSO, δ ppm): 7.96 (s, 1H), 7.80 (d, J = 10.3 Hz, 1H), 7.69 (br, 1H), 7.61 (br, 1H), 7.54 (br, 1H), 7.47 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 7.3 Hz, 1H), 6.88–6.71 (m, 1H), 5.89 (d, J = 17.1 Hz, 1H), 5.34 (d, J = 10.4 Hz, 1H), 2.91 (br, 1H), 2.54 (s, 6H, DMSO), 2.08 (br, 1H), 1.78 (br, 1H), 1.69 (br, 2H), 1.45 (br, 4H), 1.33 (br, 1H), 1.22 (br, 1H), 0.19 (s, 3H, Phd-Me). 31P-NMR (162 MHz, d6-DMSO, δ ppm): 33.65 (s). 13C-NMR (101 MHz, d6-DMSO, δ ppm): 149.43 (d, J = 125 Hz), 137.55 (d, J = 10.2 Hz), 135.87 (s), 134.27 (s), 132.12 (d, J = 11.0 Hz), 131.63 (s), 131.02 (d, J = 3.1 Hz), 130.18 (s), 129.21 (d, J = 11.1 Hz), 127.87 (d, J = 14.3 Hz), 126.77 (s), 115.92 (s), 40.43 (s, DMSO), 36.04 (d, J = 20.8 Hz), 30.10 (d, J = 28.7 Hz), 28.28 (s), 26.03 (d, J = 60.3 Hz), 25.90 (d, J = 4.5 Hz), 25.65 (s), 0.27 (s, Phd-Me). Anal. Calcd. for C25H18O2.Pd (ΔPd): C, 48.21; H, 5.45. Found: C, 48.39; H, 5.19.

Synthesis of Pd3
Similar procedure was employed to catalyst Pd1 except L3 (200 mg, 0.53 mmol) was used. Pd3 was obtained as a gray solid (201 mg, 66%). 1H-NMR (400 MHz, d6-DMSO, δ ppm): 8.33 (s, 1H), 7.75 (s, 2H), 7.55 (s, 1H), 7.41 (d, J = 18.9 Hz, 4H), 4.33 (s, 1H, CH2), 2.98 (s, 1H, PCH), 2.82 (s, 6H, DMSO), 2.16 (s, 1H), 1.96 (s, 2H, CH2), 1.66 (s, 4H), 1.46–1.21 (m, 4H), 1.07 (s, 1H), 0.93 (s, 1H), 0.70 (s, 3H, CH3). 13C-NMR (162 MHz, d6-DMSO, δ ppm): 58.99 (s).

Synthesis of Ni1
A suspension of L1 (200 mg, 0.53 mmol) and Na2CO3 (169 mg, 1.53 mmol) in 15 mL of dichloromethane was stirred for 6 h at room temperature. trans-(PPh2)3NiCl(CPh) (368 mg, 0.53 mmol) was added in small portions. Dichloromethane was added until the volume of the solution reached 20 mL, and the reaction mixture was stirred for 24 h at room temperature. The resulting yellow-orange mixture was filtered over Celite and the volatiles

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were removed under vacuum. Toluene (3 mL) was added to the orange residue to afford a slurry, then hexane (5 mL) was added and the mixture was stirred for 5 min. The precipitate was recovered by filtration, washed with hexane (3×10 mL) and dried for 20 h under dynamic vacuum to yield a yellow solid Ni1 (245 mg, 60%). 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.11 (dd, J = 7.3, 4.1 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.40–7.32 (m, 12H), 7.29 (d, J = 7.0 Hz, 2H), 7.23 (d, J = 7.3 Hz, 4H), 7.03 (t, J = 8.8 Hz, 3H), 6.80–6.71 (m, 1H), 6.59–6.51 (m, 2H), 6.25 (t, J = 8.1 Hz, 1H), 5.87 (d, J = 17.6 Hz, 1H), 5.79 (d, J = 7.7 Hz, 1H), 5.39 (d, J = 10.9 Hz, 1H), 3.23–3.13 (m, 1H), 1.93–1.78 (m, 2H), 1.61 (d, J = 19.8 Hz, 2H), 1.47 (s, 1H), 1.29 (d, J = 13.0 Hz, 1H), 1.16 (d, J = 13.2 Hz, 1H), 1.05 (d, J = 7.7 Hz, 3H). 31P-NMR (162 MHz, CDCl3, δ, ppm): 17.16 (d, J = 276.9 Hz), 4.07 (d, J = 276.9 Hz). Anal. Calcd. for C34H32NiO2P2S: C, 68.50; H, 5.49. Found: C, 68.70; H, 5.64.

**Synthesis of Ni2**

Similar procedure was employed to catalyst Ni1 except L2 (200 mg, 0.53 mmol) was used. Ni2 was obtained as a yellow powder (258 mg, 63%). 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.10 (s, 1H), 7.47 (s, 3H), 7.34 (d, J = 8.7 Hz, 12H), 7.23 (d, J = 8.1 Hz, 5H), 7.06 (s, 2H), 6.94 (s, 1H), 6.65 (dd, J = 17.0, 11.1 Hz, 1H), 6.55 (s, 2H), 6.23 (s, 1H), 5.70 (dd, J = 20.0, 12.5 Hz, 2H), 5.29 (d, J = 10.6 Hz, 1H), 3.18 (s, 1H), 1.85 (d, J = 19.2 Hz, 2H), 1.67–1.44 (m, 4H), 1.29 (d, J = 11.5 Hz, 1H), 1.17 (d, J = 9.8 Hz, 1H), 1.04 (s, 2H). 31P-NMR (162 MHz, CDCl3, δ, ppm): 17.35 (d, J = 276.1 Hz), 4.38 (d, J = 276.1 Hz). 13C-NMR (101 MHz, CDCl3, δ, ppm): 149.94 (d, J = 13.0 Hz, 141.07 (s), 140.74 (s), 140.41 (s), 137.64 (s), 137.15 (d, J = 9.1 Hz, 136.48 (d, J = 30.8 Hz), 135.85 (s), 134.08 (d, J = 10.7 Hz), 132.00 (d, J = 7.9 Hz, 130.71 (s), 129.79 (s), 129.15 (d, J = 5.4 Hz), 128.77 (s), 128.32 (s), 127.94 (d, J = 9.5 Hz), 127.10 (d, J = 6.1 Hz), 126.94 (s), 125.82 (d, J = 12.1 Hz), 124.81 (d, J = 26.9 Hz), 121.79 (s), 115.00 (s), 32.48 (d, J = 25.6 Hz), 29.56 (d, J = 6.2 Hz), 27.27 (d, J = 7.7 Hz), 27.08 (d, J = 17.5 Hz), 26.83 (d, J = 7.5 Hz), 25.73 (s). Anal. Calcd. for C47H40NiO2P2S: C, 68.50; H, 5.49. Found: C, 68.34; H, 5.16.

**Synthesis of Ni3**

Similar procedure was employed to catalyst Ni1 except L3 (200 mg, 0.53 mmol) was used. Ni3 was obtained as a yellow powder (267 mg, 65%). 31P-NMR (162 MHz, CDCl3, δ, ppm): 16.74 (d, J = 274.8 Hz), 1.03 (d, J = 274.8 Hz). Anal. Calcd. for C34H32NiO2P2S: C, 68.50; H, 5.49. Found: C, 69.10; H, 5.94.

**Procedure for Ethylene Polymerization**

In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 20 mL of toluene and a magnetic stir bar under an inert atmosphere. The vessel was pressurized with ethylene gas with stirring. Then catalyst (in 1 mL of CH2Cl2) was injected to initiate polymerization and stirred continuously for the desired time. The polymerization was quenched by adding ethanol (30 mL) and the polymer was precipitated and dried overnight in vacuum at 50°C.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Ligands and Pd, Ni Complexes**

The phosphine-sulfonate ligands (L1, L2 and L3) bearing 2-, 3- and 4-vinylphenyl groups were prepared through the sequential reactions of CyPCL with lithiated benzenesulfonic acid and lithiated bromostyrenes (Scheme 1). The syntheses of these ligands were easier than those of the previously reported phosphine-sulfonate ligands bearing bulky biaryl or menthyl groups, since the synthetic routes were shorter and all the starting materials, including benzenesulfonic acid, dichlorocyclohexyl-phosphine, bromostyrenes and butyl lithium, are commercially available. The nickel complexes (Ni1, Ni2 and Ni3) were synthesized through the reactions between the ligands and trans-[(PPh3)2NiCl(P)]52. The reactions of the phosphine-sulfonate ligands with (TMEDA)PdMe2 (TMEDA = N,N,N’,N’-tetramethylethylenediamine) and DMSO (dimethyl sulfoxide) resulted in the palladium complexes Pd1, Pd2 and Pd3. The ligands were characterized by NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The nickel and palladium complexes were characterized by NMR spectroscopy and elemental analysis. The structure of the complex Pd3 bearing 2-vinylphenyl on the palladium atom showed the 2,1-insertion for the 2-vinyl group, indicating the 2-vinyl group would be a polymerizable moiety during coordination-insertion polymerization. The nickel complex Ni1 was characterized by X-ray crystallographic analysis (Fig. 1) (CCDC number: 1528274). The observed bond lengths are typical for phosphine-sulfonate nickel complexes.47–54 The Ni center exhibited square planar geometry.

![Fig. 1](https://doi.org/10.1007/s10118-021-2509-z)
symmetrical dicyclohexyl- or diphenyl-substituted phosphine-sulfonate based Pd catalysts.\[^{[64]}\] Catalyst \textbf{Pd1} resulted in higher molecular weight of polyethylene compared with \textbf{Pd2}, which could be due to the electronic effects. 3-Vinyl group is more electron-withdrawing than 4-vinyl group (\(\sigma_p\) of vinyl is 0.06 and \(\sigma_p\) of vinyl is −0.04),\[^{[65]}\] resulting in reduced electron density of vinyl is −0.04),\[^{[65]}\] which could be due to the electronic effects (for vinyl, \(\sigma_m > \sigma_p\)).\[^{[66]}\] Catalyst \textbf{Ni1} resulted in higher molecular weight of polyethylene compared with \textbf{Ni2}, which could be due to the electronic effects (for vinyl, \(\sigma_m > \sigma_p\)).\[^{[66]}\] Catalyst \textbf{Ni2} resulted in low-melting branched polyethylenes (Table 1, entries 5 and 8). For the formation of the branched polyethylenes, the exact mechanism is currently unknown. Generally, the electronically unsymmetrical nature of phosphine-sulfonate ligands was believed to inhibit \(\beta\)-H (X) elimination, resulting in the formation of highly linear polyethylenes.\[^{[16]}\] 3-Vinyl group is a more electron-withdrawing group compared with 4-vinyl group (\(\sigma_m\) of vinyl is 0.06 and \(\sigma_m\) of vinyl is −0.04).\[^{[66]}\] Consequently, the 3-vinyl group may alleviate the electronic unsymmetry in the ligand, resulting in the formation of branched polyethylene.\[^{[52]}\] The catalytic activities of the nickel catalysts increased significantly with increasing temperature, while the polyethylene molecular weight decreased (Table 1, entries 7–9). Catalysts \textbf{Ni1} and \textbf{Ni2} showed moderate catalytic activities and generated low molecular weight polyethylene products (\(M_n<1500\) g·mol\(^{-1}\)) at 80 °C (Table 1, entries 7 and 8), indicating the \(\beta\)-H elimination was accelerated significantly with increasing temperature. Remarkably, catalyst \textbf{Ni3} bearing 2-vinylphenyl exhibited high catalytic activity (activity=3.4×10\(^4\) g·mol\(^{-1}\)·h\(^{-1}\)) and resulted in much higher molecular weight of polyethylene (\(M_n=3.69×10^4\) g·mol\(^{-1}\), \(M_w=1.38×10^5\) g·mol\(^{-1}\)) (Table 1, entry 9) compared with \textbf{Ni1} and \textbf{Ni2}, indicating it is potentially suitable for industrially used gas-phase ethylene polymerization conditions (80–100 °C).\[^{[21,29]}\] The polyethylenes’ molecular weights declined more than 2 orders of magnitude for \textbf{Ni1} and \textbf{Ni2} with increasing temperature. In contrast, the polyethylenes molecular weight was decreased less than 7 times for \textbf{Ni3} (Table 1, entries 4 versus 8, 7 versus 5, 9 versus 6), demonstrating the great thermal stability of \textbf{Ni3}.

We do not currently fully understand the effect of the 2-vinyl group in this system. Nevertheless, there are several possible explanations on the good catalytic performance of \textbf{Ni3}. First, the 2-vinyl group is more sterically hindered compared with 3- and 4-vinyl groups. However, \textbf{Ni3} resulted in much higher molecular weight compared with the phosphine-sulfonate nickel catalysts bearing bulkier biaryl groups at 80 °C (Scheme 2).

Therefore, the superior catalytic performance of \textbf{Ni3} cannot solely be explained by the steric hindrance of the 2-vinyl group. Second, the 2-vinyl group on ligand could be copolymerized with ethylene via nickel catalyzed polymerization, resulting in the formation of a bulky polymer substituent (Scheme 3a) associated with the enhanced steric effect. This was reported by literature evidences that some nickel complexes can efficiently catalyze co-polymerization of ethylene with styrene.\[^{[57–59]}\] As a result, \textbf{Ni3} can generate high molecular weight polyethylene at 80 °C, since the sterically bulky polymer substituent at the axial position with respect to the nickel center suppressed \(\beta\)-H elimination during ethylene polymerization. The significantly increased PDI value also supported this hypothesis (Table 1, entry 9). Third, the 2-vinyl substituent at the axial position might form a secondary interaction with the nickel center (Scheme 3b), preventing ethylene coordination and subsequently chain transfer to monomer.\[^{[2,3,10,50,70–72]}\]
In summary, a series of phosphine-sulfonate ligands containing styrene moieties (L1, L2 and L3) and the corresponding nickel (Ni1, Ni2 and Ni3) and palladium (Pd1, Pd2 and Pd3) catalysts have been synthesized, characterized and investigated in ethylene polymerization. The syntheses of the ligands were easier than the traditional phosphine-sulfonate ligands bearing bulky biaryl or methyl groups. Catalysts Ni1 and Pd1 bearing 4-vinyl group led to polyethylenes with higher molecular weights than those from Ni2 and Pd2 bearing 3-vinyl group, which could be due to the electronic effects (for vinyl, \(\sigma_+ > \sigma_\text{P} \)). The more electron-withdrawing 3-vinyl group resulted in reduced electron density from the metal center, resulting in decreased molecular weight of polyethylene. Pd3 bearing 2-vinylphenyl showed 2,1-insertion for the 2-vinyl group, indicating that the 2-vinyl group was a polymerizable moiety during coordination-insertion polymerization. Catalyst Pd3 possesses no catalytic activity in ethylene polymerization, which could be due to the formation of the stable five-membered ring in the structure of Pd3. Catalyst Ni3 bearing 2-vinylphenyl resulted in higher activity and much higher polyethylene molecular weight (Mn = 3.69 x 10^5 g mol\(^{-1}\), Mw = 1.38 x 10^6 g mol\(^{-1}\)) compared with Ni1, Ni2 as well as previously reported nickel catalysts bearing bulky biaryl groups (Mn up to 1.03 x 10^5 g mol\(^{-1}\), typically <10^5 g mol\(^{-1}\)) at 80 °C. Some possible explanations on the superior catalytic performance of Ni3 have been discussed. It is envisaged that vinyl-containing ligands will be applicable to other catalytic systems for olefin polymerization and other types of organic transformations.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2509-z.

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REFERENCES

1. Chen, Z.; Brookhart, M. Exploring ethylene/polar vinyl monomer copolymerizations using Ni and Pd \(\alpha\)-diimine catalysts. Acc. Chem. Res. 2018, 51, 1831–1839.
2. Walsh, D. J.; Hyatt, M. G.; Miller, S. A.; Guironnet, D. Recent trends in catalytic polymerizations. ACS Catal. 2019, 9, 11153–11188.
3. Tan, C.; Chen, C. Emerging palladium and nickel catalysts for copolymerization of olefins with polar monomers. Angew. Chem. Int. Ed. 2019, 58, 7192–7200.
4. Chen, M.; Chen, C. Direct and tandem routes for the copolymerization of ethylene with polar functionalized internal olefins. Angew. Chem. Int. Ed. 2020, 59, 1206–1210.
5. Zou, C.; Chen, C. Polar-functionalized, crosslinkable, self-healing and photoresponsive polyolefins. Angew. Chem. Int. Ed. 2020, 59, 395–402.
6. Dai, S.; Chen, C. A self-supporting strategy for gas-phase and slurry-phase ethylene polymerization using late-transition-metal catalysts. Angew. Chem. Int. Ed. 2020, 59, 14884–14890.
7. Na, Y.; Chen, C. Catechol functionalized polyolefins. Angew. Chem. Int. Ed. 2020, 59, 7953–7959.
8. Keyes, A.; Basbug, A. H.; Ordonez, E.; Ha, U.; Beezer, D. B.; Dau, H.; Liu, Y. S.; Tsogtgerel, E.; Jones, G. B.; Harth, E. Olefins and vinyl polar monomers: bridging the gap for next generation materials. Angew. Chem. Int. Ed. 2019, 58, 12370–12391.
9. Takeuchi, D.; Osakada, K. Controlled isomerization polymerization of olefins, cycloolefins, and dienes. Polymer 2016, 82, 392–405.
10. Dai, S.; Li, S.; Xu, G.; Chen, C. Direct synthesis of polar functionalized polyethylene thermoplastic elastomer. Macromolecules 2020, 53, 2539–2546.
11. Nishiura, M.; Guo, F.; Hou, Z. Half-sandwich rare-earth-catalyzed olefin polymerization, carbometalation, and hydroarylation. Acc. Chem. Res. 2015, 48, 2220–2220.
12. Chen, M.; Chen, C. L. Polar functionalized polyolefins: new catalysts, new modulation strategies and new materials. Acta Polymerica Sinica (in Chinese) 2018, 11, 1372–1384.
13. Carrow, B. P.; Nozaki, K. Transition-metal-catalyzed functional polyolefin synthesis: effecting control through chelating ancillary ligand design and mechanistic insights. Macromolecules 2014, 47, 2541–2555.
14. Nakamura, A.; Anselment, T. M.; Claverie, J. P.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. Ortho-phosphinobenzenesulfonate: a superb ligand for palladium-catalyzed coordination-insertion copolymerization of polar vinyl monomers. Acc. Chem. Res. 2013, 46, 1438–1449.
15. Nakamura, A.; Ito, S.; Nozaki, K. Coordination-insertion copolymerization of fundamental polar monomers. Chem. Rev. 2009, 109, 5215–5244.
16. Wilke, G. Fifty years of ziegler catalysts: consequences and development of an invention. Angew. Chem. Int. Ed. 2003, 42, 5000–5008.
17. Tan, C.; Chen, C. Nickel catalysts for the synthesis of ultra-high molecular weight polyethylene. Sci. Bull. 2020, 65, 1137–1138.
18. Johnson, L. K.; Killian, C. M.; Brookhart, M. New Pd(III) and Ni(II)-based catalysts for polymerization of ethylene and \(\alpha\)-olefins. J. Am. Chem. Soc. 1995, 117, 6414–6415.
19. Muhammad, Q.; Tan, C.; Chen, C. Concerted steric and electronic effects on \(\alpha\)-dimine nickel- and palladium-catalyzed ethylene polymerization and copolymerization. Sci. Bull. 2020, 65, 300–307.
20. Wang, F.; Chen, C. A continuing legend: the Brookhart-type \(\alpha\)-
diimine nickel and palladium catalysts. *Polym. Chem.* **2019**, *10*, 2354−2369.

21 Tan, C.; Pang, W.; Chen, C. A phenol-containing α-diimine ligand for nickel- and palladium-catalyzed ethylene polymerization. *Chinese J. Polym. Sci.* **2019**, *37*, 974−980.

22 Fang, J.; Sui, X.; Li, Y.; Chen, C. Synthesis of polyolefin elastomers from unsymmetrical α-diimine nickel catalyzed olefin polymerization. *Polym. Chem.* **2018**, *9*, 4143−4149.

23 Wang, F.; Tian, S.; Lia, R.; Li, W.; Chen, C. Ligand steric effects on naphthyl-α-diimine nickel catalyzed α-olefin polymerization. *Chinese J. Polym. Sci.* **2018**, *36*, 157−162.

24 Long, B. K.; Eagan, J. M.; Mulzer, M.; Coates, G. W. Semi-crystalline polar polyethylene: ester-functionalized linear polyolefins enabled by a functional-group-tolerant, cationic nickel catalyst. *Angew. Chem. Int. Ed.* **2016**, *55*, 7106−7110.

25 Padilla-Vélez, O.; O’Connor, K. S.; LaPointe, A. M.; MacMillan, S. N.; Coates, G. W. Switchable living nickel(III) α-diimine catalyst for ethylene polymerisation. *Chem. Commun.* **2019**, *55*, 7607−7610.

26 Vaccarello, D. N.; O'Connor, K. S.; Iacono, P.; Rose, J. M.; Cherian, A. E.; Coates, G. W. Synthesis of semicrystalline polyolefin materials: precision methyl branching via stereoretentive chain walking. *J. Am. Chem. Soc.* **2018**, *140*, 6208−6211.

27 Zhong, S.; Tan, Y.; Zhong, L.; Gao, J.; Liao, H.; Jiang, L.; Gao, H.; Wu, Q. Precision synthesis of ethylene and polar monomer copolymer by palladium-catalyzed living coordination copolymerization. *Macromolecules* **2017**, *50*, 5661−5669.

28 Zhong, L.; Li, G.; Liang, G.; Gao, H.; Wu, Q. Enhancing thermal stability and living fashion in α-diimine-catalyzed (co)polymerization of ethylene and polar monomer by increasing the steric bulk of ligand backbone. *Macromolecules* **2017**, *50*, 2675−2682.

29 Liao, G.; Xiao, Z.; Chen, X.; Du, C.; Zhong, L.; Cheung, C. S.; Gao, H. Fast and regioselective polymerization of para-alkoxyxystrene by palladium catalysts for precision production of high-molecular-weight polyethylene derivatives. *Macromolecules* **2020**, *53*, 256−266.

30 Zhong, L.; Du, C.; Liao, G.; Liao, H.; Zheng, H.; Wu, Q.; Gao, H. Effects of backbone substituent and intra-ligand hydrogen bonding interaction on ethylene polymerizations with α-diimine nickel catalysts. *J. Catal.* **2019**, *375*, 113−123.

31 Zhong, L.; Zheng, H.; Du, C.; Du, W.; Liao, G.; Cheung, C. S.; Gao, H. Thermally robust α-diimine nickel and palladium catalysts with constrained space for ethylene (co)polymerizations. *J. Catal.* **2020**, *384*, 208−217.

32 Zhang, R. F.; Hou, Y. H.; Wei, X. L.; Zhao, D. D.; Cui, M. M.; Zhai, F. F.; Li, X. L.; Liu, B. Y.; Yang, M. Thermostable α-diimine nickel complexes with substituents onacenaphthquinone-backbone for ethylene polymerization. *Chinese J. Polym. Sci.* **2020**, *38*, 1214−1220.

33 Kenyon, P.; Mecking, S. Pentfluorosulfanyl substituents in polymerization catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 13786−13790.

34 Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S.; Grubbs, R. H.; Bansleben, D. A. Neutral, single-component nickel(II) polyolefin catalysts that tolerate heteroatoms. *Science* **2000**, *287*, 460−462.

35 Falivene, L.; Wiedemann, T.; Gottklerschettnet, I.; Caporaso, L.; Cavallo, L.; Mecking, S. Control of chain walking by weak neighboring group interactions in unsymmetrical catalysts. *J. Am. Chem. Soc.* **2017**, *140*, 1305−1312.

36 Kenyon, P.; Womar, M.; Mecking, S. Controlled polymerization in polar solvents to ultrahigh molecular weight polyethylene. *J. Am. Chem. Soc.* **2018**, *140*, 6685−6689.

37 Chen, Z.; Allen, K. E.; White, P. S.; Daugulis, O.; Brookhart, M. Synthesis of branched polyethylene with “half-sandwich” pyridine-imine nickel complexes. *Organometallics* **2016**, *35*, 1756−1760.

38 Dai, S.; Sui, X.; Chen, C. Synthesis of high molecular weight polyethylene using iminopyridyl nickel catalysts. *Chem. Commun.* **2016**, *52*, 9113−9116.

39 Chen, X. L.; Gao, J.; Liao, H.; Gao, H. Y.; Wu, Q. Synthesis, characterization, and catalytic ethylene oligomerization of pyridine-imine palladium complexes. *Chinese J. Polym. Sci.* **2018**, *36*, 176−184.

40 Zou, C.; Dai, S.; Chen, C. Ethylene PolymORIZATION and copolymerization using nickel 2-iminopyridine-N-oxide catalysts: modulation of polymer molecular weights and molecular-weight distributions. *Macromolecules* **2018**, *51*, 49−56.

41 Liang, T.; Goudard, S.; Chen, C. A simple and versatile nickel platform for the generation of branched high molecular weight polyolefins. *Nat. Commun.* **2020**, *11*, 372.

42 Kocen, A.; Brookhart, M.; Daugulis, O. A highly active Ni(II)-triamantylphosphine catalyst for ultra-high molecular-weight polyethylene synthesis. *Nat. Commun.* **2019**, *10*, 438.

43 Xin, B.; Sato, N.; Tanna, A.; Oishi, Y.; Konishi, Y.; Shimizu, F. Nickel catalyzed copolymerization of ethylene and alkyl acrylates. *J. Am. Chem. Soc.* **2017**, *139*, 3611−3614.

44 Zhang, Y.; Mu, H.; Pan, L.; Wang, X.; Li, Y. Robust bulky [P,O] neutral nickel catalysts for copolymerization of ethylene with polar vinyl monomers. *ACS Catal.* **2018**, *8*, 5963−5976.

45 Mu, H.; Pan, L.; Song, D.; Li, Y. Neutral nickel catalysts for olefin homo- and copolymerization: relationships between catalyst structures and catalytic properties. *Chem. Rev.* **2015**, *115*, 12091−12137.

46 Mu, H. L.; Ye, J. H.; Zhou, G. L.; Li, K. K.; Jian, Z. B. Ethylene polymerization and copolymerization with polar monomers by benzothiophene-bridged BPMO-Pd catalysts. *Chinese J. Polym. Sci.* **2020**, *38*, 579−586.

47 Ito, S.; Ota, Y.; Nozaki, K. Ethylene/allyl monomer cooigomerization with nickel/phosphine-sulfonate catalysts. *Dalton Trans.* **2012**, *41*, 13807−13809.

48 Chen, M.; Chen, C. Rational design of high-performance phosphine sulfonate nickel catalysts for ethylene polymerization and copolymerization with polar monomers. *ACS Catal.* **2017**, *7*, 1308−1312.

49 Liang, T.; Chen, C. Position makes the difference: electronic effects in nickel-catalyzed ethylene polymerizations and copolymerizations. *Inorg. Chem.* **2018**, *57*, 14913−14919.

50 Tan, C.; Qasim, M.; Pang, W.; Chen, C. Ligand-metal secondary interaction in phosphine-sulfonate palladium and nickel catalyzed ethylene (co)polymerization. *Polym. Chem.* **2020**, *11*, 411−416.

51 Song, G.; Pang, W.; Li, W.; Chen, M.; Chen, C. Phosphine sulfonate-based nickel catalysts: ethylene polymerization and copolymerization with polar-functionalized norbornenes. *Polym. Chem.* **2017**, *8*, 7400−7405.

52 Yang, B.; Xiong, S.; Chen, C. Manipulation of polymer branching density in phosphine-sulfonate palladium and nickel catalyzed ethylene polymerization. *Polym. Chem.* **2017**, *8*, 6272−6276.

53 Wu, Z.; Hong, C.; Du, H.; Pang, W.; Chen, C. Influence of ligand backbone structure and connectivity on the properties of phosphine-sulfonate Pd(II)/Ni(II) catalysts. *Polymers* **2017**, *9*, 168.

54 Perrotin, P.; McCahill, J. S.; Wu, G.; Scott, S. L. Linear, high molecular weight polyethylene from a discrete, mononuclear phosphinoarenesulfonate complex of nickel(II). *Chem. Commun.* **2011**, *47*, 6948−6950.

55 Xia, J.; Zhang, Y.; Zhang, J.; Jian, J. High-performance neutral phosphine-sulfonate nickel(II) catalysts for efficient ethylene polymerization and copolymerization with polar monomers. *Organometallics* **2019**, *38*, 1118−1126.
56 Ohno, K.; Nagasawa, A.; Fujihara, T. Dinuclear nickel(II) complexes with 2,5-diamino-1,4-benzoquinonenediimine ligands as precatalysts for the polymerization of styrene: electronic and steric substituent effects. *Dalton Trans.* 2015, **44**, 368−376.

57 Zhao, C.; Yuan, Q. Catalytic copolymerization of styrene and ethylene by neutral nickel(II) complexes in emulsion. *Chinese J. Polym. Sci.* 2009, **27**, 667−674.

58 Zhang, D.; Jin, G. Radical co-polymerization of diiminedibromidenickel(II)-functionalized olefin with styrene: synthesis of polymer-incorporated nickel α-diamine catalysts for ethylene polymerization. *Appl. Catal. A: Gen.* 2004, **262**, 13−18.

59 Carlini, C.; Galletti, A. M.; Sbrana, G.; Caretti, D. Homo- and co-polymerization of styrene with ethylene by novel nickel catalysts. *Polymer* 2001, **42**, 5069−5078.

60 Borkar, S.; Newsham, D. K.; Sen, A. Copolymerization of ethene with styrene derivatives, vinyl ketone, and vinlylcyclohexane using a (phosphine-sulfonate)palladium(II) system: unusual functionality and solvent tolerance. *Organometallics* 2008, **27**, 3331−3334.

61 Cui, L.; Chen, M.; Chen, C.; Liu, D.; Jian, Z. Systematic studies on (co)polymerization of polar styrene monomers with palladium catalysts. *Macromolecules* 2019, **52**, 7197−7206.

62 Pellecchia, C.; Pappalardo, D.; D’Arc, M.; Zambelli, A. Alternating ethylene-styrene copolymerization with a methylaluminoxane-free half-titanocene catalyst. *Macromolecules* 1996, **29**, 1158−1162.

63 Guo, N.; Stern, C. L.; Marks, T. J. Binmetallic effects in homopolymerization of styrene and copolymerization of ethylene and styrenic comonomers: scope, kinetics, and mechanism. *J. Am. Chem. Soc.* 2008, **130**, 2246−2261.

64 Nakano, R.; Chung, L. W.; Watanabe Y.; Okuno, Y.; Okumura, Y.; Ito, S.; Morokuma, K.; Nozaki, K. Elucidating the key role of phosphine-sulfonate ligands in palladium-catalyzed ethylene polymerization: effect of ligand structure on the molecular weight and linearity of polyethylene. *ACS Catal.* 2016, **6**, 6101−6113.

65 Hansch, C.; Leo, A. J.; Taft, R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* 1991, **91**, 165−195.

66 Cai, Z.; Shen, Z.; Zhou, X.; Jordan, R. F. Enhancement of chain growth and chain transfer rates in ethylene polymerization by (phosphine-sulfonate)PdMe catalysts by binding of B(C₆F₅)₃ to the sulfonate group. *ACS Catal.* 2012, **2**, 1187−1195.

67 Chen, M.; Zou, W.; Cai, Z.; Chen, C. Norbornene homopolymerization and copolymerization with ethylene by phosphine-sulfonate nickel catalysts. *Polym. Chem.* 2015, **6**, 2669−2676.

68 Popeney, C. S.; Guan, Z. Effect of ligand electronics on the stability and chain transfer rates of substituted Pd(II) α-diamine catalysts. *Macromolecules* 2010, **43**, 4091−4097.

69 Rhinehart, J. L.; Brown, L. A.; Long, B. K. A robust Ni(II) α-diamine catalyst for high temperature ethylene polymerization. *J. Am. Chem. Soc.* 2013, **135**, 16316−16319.

70 Li, M.; Wang, X.; Luo, Y.; Chen, C. A second-coordination-sphere strategy to modulate nickel- and palladium-catalyzed olefin polymerization and copolymerization. *Angew. Chem. Int. Ed.* 2017, **56**, 11604−11609.

71 Zhang, D.; Chen, C. Influence of polyethylene glycol unit on palladium and nickel catalyzed ethylene polymerization and copolymerization. *Angew. Chem. Int. Ed.* 2017, **56**, 14672−14676.

72 Lian, K.; Zhu, Y.; Li, W.; Dai, S.; Chen, C. Direct synthesis of thermoplastic polyolefin elastomers from nickel catalyzed ethylene polymerization. *Macromolecules* 2017, **50**, 6074−6080.

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