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Enhancing Suppression of Chain Transfer via Catalyst Structural Evolution in Ethylene (Co)Polymerization

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December 28, 2022

Abstract

Usually, the aniline-based late-transition-metal catalysts often require bulky steric substituents on both sides of the ortho-aryl position to achieve efficient suppression of chain transfer in ethylene polymerization. In this contribution, we demonstrated that α-diimine catalysts based on naphthylamine with only one bulky ortho-aryl substituent also demonstrated excellent capabilities to suppress the chain transfer. Firstly, a class of α-diimine nickel and palladium complexes with only one o-aryl-dibenzhydryl or o-aryl-dibenzosuberyl substituent were synthesized and characterized. Secondly, the as-prepared naphthylamine-based nickel catalysts demonstrated outstanding activities and yielded lightly branched (16-40/1000C) polyethylenes with very high molecular weights (445.8-854.3 kg/mol) in ethylene polymerization. In comparison, the corresponding palladium catalysts showed moderate activities, generating moderately branched polyethylenes with moderate molecular weights (21.6-82.0 kg/mol). Moreover, the palladium catalysts could also copolymerize ethylene and methyl acrylate (MA), albeit in low activity (level of 103 g·mol-1·h-1),providing E-MA copolymers with low to moderate molecular weight (1.4-16.3 kg/mol) and a moderate level of incorporation ratio (2.4-7.4 mol%) and branching density. As compared with aniline-based nickel and palladium catalysts, the naphthylamine-based catalysts displayed a superior ability to suppress the chain transfer reactions and could give access to (co)polymers with orders of magnitude higher molecular weight in ethylene (co)polymerization.

Cite this paper: *Chin. J. Chem.* **2022** , *40* , XXX—XXX.

DOI: 10.1002/cjoc.202200XXX

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Comprehensive Summary

Usually, the aniline-based late-transition-metal catalysts often require bulky steric substituents on both sides of the *ortho*-a

Keywords

α-diimine catalysts | chain transfer | high molecular weight | naphthylamine-based catalysts | ethylene (co)polymerization

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Introduction

Suppression of the synergistic chain transfer from the growing polyethylene chain to ethylene monomer is crucial for achieving high-molecular-weight polyethylene products in late-transition metal-catalyzed polymerization of ethylene. [1-3]To this end, tremendous efforts have been devoted to designing novel ligands containing multiple sterically bulky substituents, as these bulky substituents have been found to facilitate the suppression of chain transfer.[4-26] In the case of imine-based late-transition-metal catalysts, the evolution of *o* -aryl substituents has endowed this type of catalysts with the capability to produce high molecular weight and even UHMWPE (ultra-high molecular weight polyethylene) (**Chart 1**). Taking salicylaldimine Ni(II) system as an example, replacing the *o* -aryl-*iso* propyl moieties in the nickel complex with bulkier *o* -aryl-dibenzhydryl or *o* -aryl-dibenzosuberyl substituents provides gradually improved molecular weights of the resulting polyethylenes (**Scheme 1**).[22]

Scheme 1 The ascending trend in molecular weights of polyethylenes generated by salicylaldimine Ni(II) catalysts bearing*o* -aryl-isopropyl, *o* -aryl-dibenzhydryl or *o* -aryl- dibenzosuberyl substituent.

Along with enhanced chain transfer suppression, catalyst stability, especially thermal stability, can be also improved with the evolution of substituents. [12-15] In most cases, these aniline-based catalysts often require symmetrical bulky steric substituents in the both *ortho* -positions of the aniline unit to achieve an axial shielding of the metal center, which promotes the efficient inhibition of chain transfer and good thermal stability. As a comparison, the catalysts composed of the ortho-monosubstituted bulky aniline often fail to retard chain transfer during the polymerization process, thus yielding polyethylene or copolymers with low molecular weights. [27]

Chart 1 (a) Representative imine-based nickel and palladium catalytic systems; **(b)** typical evolution of*o* -aryl anilines with bulky substituents; **(c)** this work.

More seriously, the presence of *cis*- and *trans*- isomers of the *ortho* -monosubstituted aniline-based catalysts often lead to bimodal or broad molecular weight distributions of polyethylenes.[27-28] In this contribution, we have found that α-diimine catalysts based on dibenzhydryl or dibenzosuberyl*ortho* -monosubstituted naphthylamines exhibit excellent ability to retard the chain transfer reactions in ethylene (co)polymerization (**Chart 1c**). Moreover, the dibenzosuberyl substituent displays excellent capability to retard the chain transfer than the dibenzhydryl substituent.

Results and Discussion

Synthesis of α-Diimine Ni(II) and Pd(II) Catalysts Based on Naphthylamine

Scheme 2 Synthesis of α-diimine ligands based on naphthylamine and the corresponding Ni(II) and Pd(II) catalysts.

Starting from 1-naphthylamine and diarylmethanols, 2,4-bis(diarylmethyl)naphthylamines **A1-A3** were synthesized in 63-81% yields via Friedel-Crafts alkylation (**Scheme 2**).**A1-A2** are known compounds from the literature[29-30], and the new compound **A3** is characterized by ^{1}H, ^{13}C NMR and high resolution mass spectrometry (HRMS) (cf. ESI, **Figure S1-2** ,**S11**). The PTSA-catalyzed condensation of naphthylamines**A1-A3** with 2, 3-butanedione in refluxing toluene provided the α-diimine ligands **L1-L3** in 56-71% yields (**Scheme 2**). Among them, the ligands **L1-L2** directly precipitated from the hot toluene solution during preparation and satisfactory NMR spectra of**L1-L2** could not be obtained due to their very poor solubility in common solvents (such as $CDCl_3$, CD_2Cl_2, d^6-benzene, CD_3OD, d^6-DMSO). Fortunately,**L1-L2**

could be identified by HRMS (cf. ESI, **Figure S12-13**) and X-ray single crystal diffraction (cf. ESI, **Table S2-3** ; **Figure 1**). The ligand **L3** was comprehensively characterized by ^{1}H and ^{13}C NMR, along with HRMS (cf. ESI, **Figure S3-4** and **S14**). Subsequently, treating **L1-L3** with 1 equivalent of (DME)$NiBr_2$ (DME=1, 2-dimethoxyethane) in CH_2Cl_2 at room temperature rendered**Ni1-Ni3** in 72-84% yields (**Scheme 2**). These α-diimine Ni(II) catalysts were confirmed and identified by analysis of elements and single-crystal X-ray diffraction (cf. ESI, **Table S4-5** ;**Figure 2a-b**). Likewise, reactions of (COD)PdMeCl (COD =1, 5-cyclooctandiene) with **L1-L3** afforded **Pd1-Pd3** with yields of 62-78% (**Scheme 2**). These Pd(II) catalysts were characterized by ^{1}H and ^{13}C NMR, analysis of elements, and single-crystal X-ray diffraction (cf. ESI,**Figure S5-10** , **Table S6-7** ; **Figure 2c-d**).**Ni4** and **Pd4** were also preparation as reference catalysts according to the previously reported literature.[27]

The single crystals of **Ni1** , **Ni3** , **Pd1** and**Pd3** were obtained by layering their CH_2Cl_2 solution with hexanes in a glove box at ambient temperature. As shown in **Figure 2** , **Ni1** ,**Ni3** , **Pd1,** and **Pd3** in solid state present in an *anti-* form where the bulky *ortho* -Ar substituents are located in the axial position of the metal coordination plane. The aryl groups in the diarylmethyl moiety are almost parallel to the five-membered coordination plane of the metal center, forming a cap blocking the axial space of the metal center. Moreover, it appears that the blocking effect stemming from dibenzosuberyl moieties is more prominent than that of dibenzhydryl groups due to the distortion of dibenzoheptad ring. In addition, **Ni1** and **Ni3**(**Figure 2a-b**) adopt a twisted tetrahedral geometry around the Ni center while **Pd1** and **Pd3** (**Figure 2c-d**) present an approximate square-planar geometry at the Pd center. The single crystals of **L1** and **L2** were also accidentally obtained by layering the CH_2Cl_2 solution of the corresponding nickel complexes with hexanes at ambient temperature when the water content in the glove box is abnormal (**Figure 1**). It is worth noting that the two C=N-Ar substituents are in the trans-position, which is the opposite of the situation when the metal is coordinated.

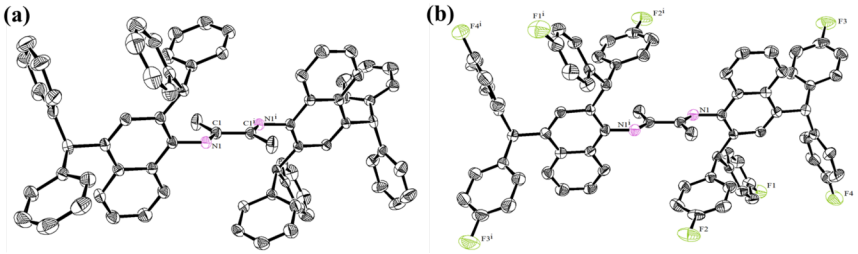

Figure 1 Solid-state molecular structures of **L1**(2211451) and **L2** (2211452) with 30% probability level. The H atoms have been omitted for clarity.

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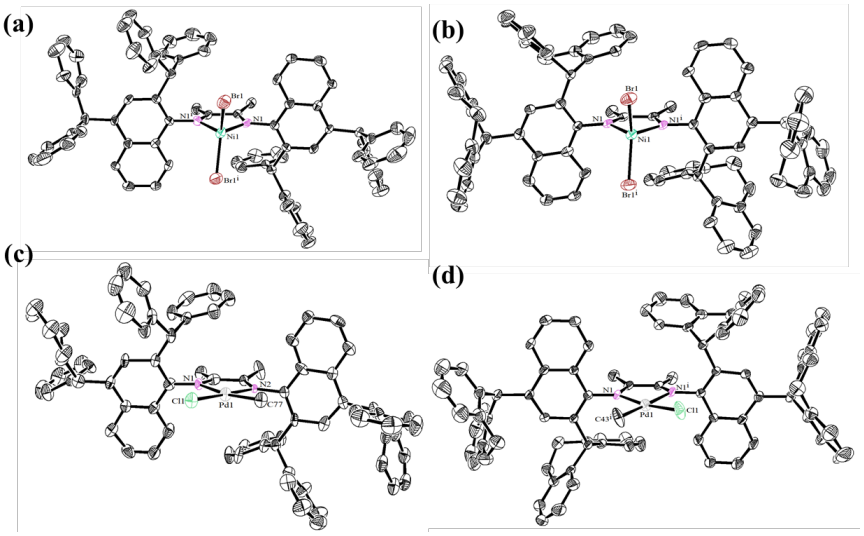

Figure 2 Solid-state molecular structures of **Ni1**(2211453), **Ni3** (2211454), **Pd1** (2211455) and**Pd3** (2211456) with 30% probability level. The H atoms have been omitted for clarity.

Ni(II)-Catalyzed Ethylene Polymerization

Table 1 Ethylene polymerization with Ni(II) catalysts.[a]

Ent.	Cat.	T/°C	Yield/g	Act.[b]	M_n[c]	M_w/M_n[c]	B[d]	T_m/[e]
1	**Ni1**	30	1.51	9.06	69.01	1.79	21	105
2	**Ni1**	50	1.48	8.88	58.93	1.80	22	94
3	**Ni1**	70	1.05	6.30	48.25	1.84	39	93
4	**Ni2**	30	2.17	13.02	63.18	1.80	16	111
5	**Ni2**	50	1.89	11.34	56.89	1.76	17	103
6	**Ni2**	70	1.44	8.64	44.58	1.84	26	97
7	**Ni3**	30	1.92	11.52	85.43	1.81	34	87,106
8	**Ni3**	50	1.57	9.42	72.40	2.09	36	81,103
9	**Ni3**	70	1.32	7.92	52.45	2.03	40	96
10	**Ni4**	30	1.96	11.76	0.23	5.8	40	95
11	**Ni4**	50	1.02	6.12	0.16	4.9	46	wax
12	**Ni4**	70	0.96	5.76	0.14	4.3	56	oil

[a] Reaction conditions: Ni(II) catalyst (1μ mol), 300 eq. Et_2AlCl, CH_2Cl_2 (1 mL), toluene (20 mL), polymerization time (10 min), ethylene (6 atm).[b] Activity = 10^6 g/(mol Ni·h).[c]M_n is in unit of 10^4 g·mol^{-1}, determined by size exclusion chromatography (SEC) at 150 °C in trichlorobenzene vs. polystyrene standards. [d]B= branches per 1000 carbons, determined by ^{1}H NMR spectroscopy at 100 °C in d^8-toluene, B = 1000 x 2(I_{CH3})/3(I_{CH2+CH} + I_{CH3}). [e] Determined by differential scanning calorimetry (DSC), broad peak.

The ethylene polymerization catalyzed by **Ni1-4** at various temperatures was investigated and the results are listed in**Table 1** . In the presence of 300 equivalents of Et_2AlCl as an activator, the naphthylamine-based catalysts **Ni1-3** showed exceptionally high catalytic activity (up to 1.30x10^{7}g/(mol Ni*h)) for ethylene polymerization. High molecular weight (446-854 kg/mol) semi-crystalline polyethylenes with modest branching densities (16-40/1000C) and narrow molecular weight distributions (1.76-2.09) were synthesized using these α-diimine Ni(II) catalysts. Notably, compared to the reference catalyst**Ni4** , the naphthylamine-based

catalysts **Ni1-3** generated two orders of magnitude higher molecular weight polyethylene with lower branching density in a similar polymerization activity (**Figure 3**). The sharp increase in molecular weight of the polyethylene generated by **Ni1-3** indicates that the naphthyl moiety is fundamentally more effective than the phenyl frames in preventing chain transfer for this α-diimine Ni(II) system. Besides, the effect of the naphthyl group being more electron-withdrawing than the corresponding phenyl group may also contribute to the synthesis of high molecular weight polyethylene. Moreover, polyethylenes generated with naphthylamine-based **Ni1-3** possess unimodal molecular weight distributions while those generated with aniline-based **Ni4** have bimodal or broad molecular weight distributions. This is probably due to the fact that the naphthalene-based catalysts exist only in*anti*- form in polymerization solution as they exist in the solid state, while the aniline-based **Ni4** presents in both *syn*-and *anti*- isomers. DSC tests showed that all the obtained polyethylenes possessed high melting points, reflecting the low branching density feature of the polymers. The ultra-high chain growth rate may be the main factor depressing the ratio of chain walking relative to chain growth in this system, which is the main reason for the low branching of the resulting polyethylene.[31] In general, as the polymerization temperature was increased, the polymerization activity and the resulting polyethylene molecular weight gradually decreased while the corresponding polyethylene branching density gradually increased, which is consistent with most of the previously reported α-diimine nickel systems (**Figure 3**). [13, 18-20] Compared to **Ni1** , **Ni2** with remote non-conjugated electron-withdrawing substituent (F) exhibited higher catalytic activity and yielded lower molecular weight polyethylene with lower branching density under identical conditions (**Figure 3**). Weaker aryl-metal interactions may be responsible for the above experimental results. [32-34] As anticipated, in comparison with **Ni1** , **Ni3** containing restricted dibenzosuberyl moieties displayed superior activity, affording higher molecular weight polyethylenes with higher branching density (**Figure 3**). This is mainly attributed to the fact that the dibenzosuberyl group improves the thermal stability of the catalyst and suppresses chain transfer during the polymerization process more than the dibenzhydryl substituent, consistent with previously reported effects. [3, 21-23, 28] The sandwich-like structure formed by the dibenzosuberyl group is widely demonstrated to efficiently suppress chain transfer in ethylene polymerization. [35-38] The higher branching density may also be ascribed to its sandwich-like structure.[26]

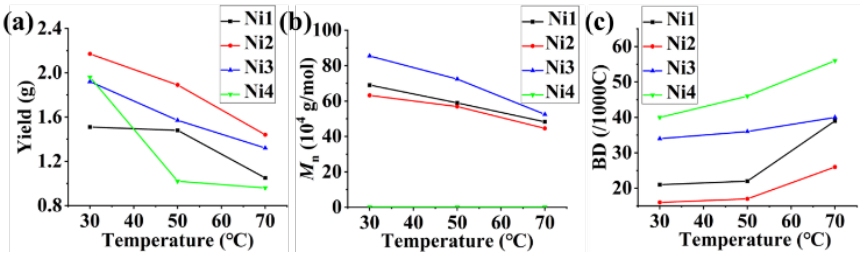

Figure 3 Comparisons on yield (**a**), molecular weight (**b**), and branching density (**c**) of polyethylene generated with **Ni1** -**4** from 30 °C to 70 °C.

It is known that the ratio between the chain growth rate and the chain walking rate is responsible for the microstructure of the polyethylene materials in α-diimine nickel/palladium catalyzed ethylene polymerization, which ultimately determines their mechanical properties.[13, 16, 20, 39] The mechanical properties of the resultant semi-crystalline polyethylenes were evaluated by tensile testing (**Figure 4, Table S1**). The branched polyethylenes generated by **Ni1-3** exhibited high stress at break values (12.0-33.1 MPa) and high strain at break values (392-1150%), manifesting the typical features of thermoplastics. In contrast, the polyethylenes generated by **Ni4** could not be used in tensile tests due to their very low molecular weight. Overall, the polyethylene which was generated at a higher polymerization temperature showed a lower Young's modulus (**Figure 4**). This can be attributed to the increase of branching density with temperature, which lowers the crystallinity of the generated polyethylene.

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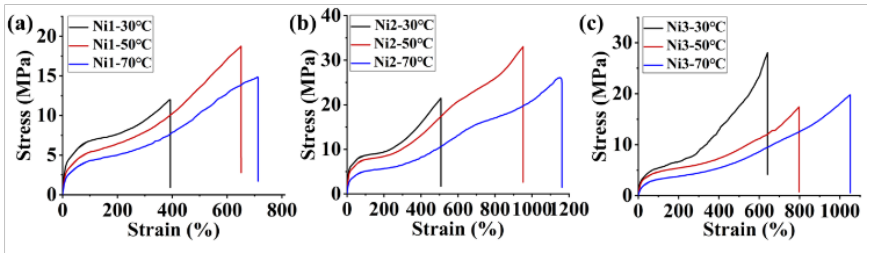

Figure 4 Stress–strain curves for polyethylene generated with (a) **Ni1** , (b) **Ni2** , and (c) **Ni3** at 30 to 70 °C.

Pd(II)-Catalyzed Ethylene (Co)Polymerization

Table 2 Ethylene polymerization with Pd(II) catalysts[a]

Ent.	Cat.	T (°C)	Yield (g)	Act. [b]	M_n [c]	M_w/M_n [c]	B[d]
1	**Pd1**	30	0.37	3.7	41.1	1.63	51
2	**Pd1**	50	1.08	10.8	46.6	1.98	55
3	**Pd1**	70	2.23	22.3	21.6	1.61	62
4	**Pd2**	30	0.65	6.5	67.0	1.43	47
5	**Pd2**	50	1.22	12.2	46.3	1.63	51
6	**Pd2**	70	0.85	8.5	26.5	1.60	55
7	**Pd3**	30	0.49	4.9	82.0	2.29	70
8	**Pd3**	50	1.92	19.2	73.7	1.83	76
9	**Pd3**	70	2.51	25.1	42.4	1.94	78
10	**Pd4**	30	0.33	3.3	3.8	1.50	58
11	**Pd4**	50	0.68	6.8	2.6	1.40	58
12	**Pd4**	70	0.73	7.3	2.2	1.33	59

[a] Reaction conditions: Pd catalyst (10μ mol), NaBArF (2.0 equiv.), ethylene (4 atm), toluene (20 mL), polymerization time (1 h). [b] Activity is in unit of 10^4 g mol^{-1}h^{-1}. [c] M_n is in unit of kg mol^{-1}. Determined by GPC in THF at 40 °C vs. polystyrene standards. [d] B = Number of branches per 1000C, as determined by ^{1}H NMR spectroscopy. Branching numbers for low molecular weight samples (M_n < 5 kg/mol) were corrected for end groups.

Under the *in-situ* activation with excess sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBArF), the naphthylamine-based **Pd1 -3** displayed moderate activities and yielded moderately branched (47-78/1000C) polyethylenes with high molecular weights (21.6-82.0 kg/mol), while the aniline-based**Pd4** showed inferior activity and provided polyethylenes with one order of magnitude lower molecular weight (entries 1-9 vs 10-12,**Table 2**). With the increase of polymerization temperature from 30 °C to 70 °C, the catalytic activities of these palladium catalysts also rose except for**Pd2** , which reached its highest activity at 50°C (**Figure 5**). Consistent with the above discussed Ni(II) systems, the molecular weights of the polyethylenes generated by **Pd2 -4** also gradually dropped when the temperature was raised (**Figure 5**). However, in the case of**Pd1** , polymers generated at 50 °C possessed higher molecular weight than those obtained at 30 or 70°C. Theoretically, increasing temperature not only lowers the energy barrier of ethylene insertion but also elevates the ratio between the chain transfer rate and the chain growth rate, the ethylene insertion barrier and the ratio collectively affect the polymer molecular weight. [12-13, 16] The branching densities of the generated polyethylenes were slightly elevated with increasing temperature (**Figure 5**). Compared to **Pd1** ,**Pd2** with remote F atoms exhibited higher catalytic activity at 30-50 °C, however, the situation flipped at 70°C. A plausible explanation is that the relatively weaker aryl-metal interactions originating

from F atoms favor the insertion of ethylene while the interactions reduce the catalyst stability especially at high temperatures. This is the reason why the activity of **Pd2** decreased at 70 °C, which is different from the activity-temperature relationship trend of the other catalysts. Moreover, **Pd2** produced higher molecular weight polyethylene with lower branching density than **Pd1** under identical conditions (**Figure 5**). As the restricted dibenzosuberyl **Pd3** was used as catalyst, higher molecular weight, higher activity and higher branching density were observed compared with **Pd1** (**Figure 5**), similar to those observed in the nickel-catalyzed ethylene polymerization (**Figure 3**).

Further, the microstructure of the selective polyethylene from entry 8,**Table 2** was revealed by ^{1}H and^{13}C NMR analysis, which is mainly composed of long-chain (C_{4+}) branching (52%), methyl (19%) and ethyl (20%) branching (**Figure 6**). Besides, the sec-butyl groups also account for 5%, representing the amount of branch-on-branch structure. This indicates that these palladium catalysts exhibited strong chain walking ability and are competent to yield more in-depth branched polyethylene.

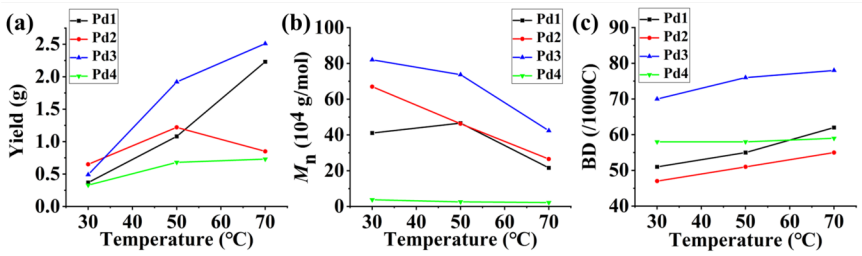

Figure 5 Comparisons on yield (**a**), molecular weight (**b**), and branching density (**c**) of polyethylene generated with **Pd1 -4** at 30-70 °C.

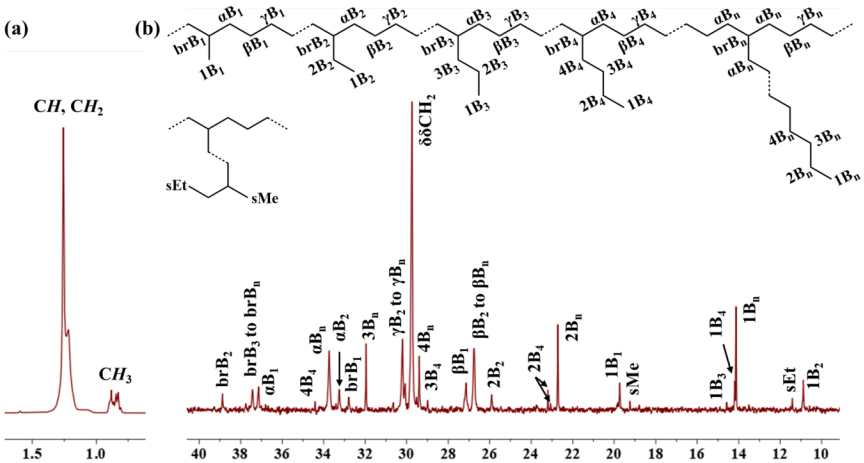

Figure 6 Detailed analysis of ^{1}H (**a**) and ^{13}C (**b**) NMR spectrum of the hyperbranched polyethylene obtained by using **Pd3** at 50 °C (**Table 2** , entry 8).

Table 3 Copolymerization of ethylene and MA with Pd(II) catalysts [a]

Ent.	Cat.	[MA] (M)	Yield (g)	Act. [b]	X_{MA} (mol %)[c]	M_n (kg/mol)[d]	M_w/M_n[d]	B[e]
1	**Pd1**	1	0.18	6.0	3.2	10.5	1.81	61
2	**Pd1**	2	0.07	2.3	4.9	3.9	1.25	66

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Ent.	Cat.	[MA] (M)	Yield (g)	Act. [b]	X_{MA} (mol %)[c]	M_n (kg/mol)[d]	M_w/M_n[d]	B[e]
3	**Pd2**	1	0.13	4.3	2.4	2.5	1.24	53
4	**Pd2**	2	0.05	1.7	5.6	1.4	1.02	68
5	**Pd3**	1	0.15	5.0	3.6	16.3	1.20	77
6	**Pd3**	2	0.08	2.7	7.4	7.9	1.13	84
7	**Pd4**	1	0.20	6.7	3.5	1.1	1.58	57
8	**Pd4**	2	0.08	2.7	7.1	0.5	1.57	59
8	**Pd4**	2	0.08	2.7	7.1	0.5	1.57	59

[a] General conditions: Pd catalyst (10μ mol), NaBArF (2.0 equiv.), ethylene (2 atm), polymerization time (3 h), total volume of CH_2Cl_2 and MA (20 mL), polymerization temperature (40 °C),[b] Activity is in unit of 10^3g·mol^{-1} h^{-1},[c]X_{MA} = Incorporation of MA, as determined by ^{1}H NMR spectroscopy.[d]M_n is in unit of kg·mol^{-1}. Determined by GPC in THF at 40 °C vs. polystyrene standards, [e] B = Number of branches per 1000C, as determined by ^{1}H NMR spectroscopy. Branching numbers for low molecular weight samples (M_n < 5 kg/mol) were corrected for end groups. The branches ending with functional groups are added to the total branches.

α-Diimine palladium catalysts are generally capable of catalyzing the copolymerization of ethylene with methyl acrylate (MA).[28, 35, 38, 40-42] In this study, the catalytic ability of **Pd1 -3** for E-MA copolymerization was also examined (**Table 3**). All the palladium catalysts displayed low activities (level of 10^3g·mol^{-1} h^{-1}), an order of magnitude lower than the corresponding ethylene homopolymerizations (**Table 3** vs **2**). Low to moderate molecular weight (1.4-16.3 kg/mol) E-MA copolymers with moderate incorporation ratios (2.4-7.4 mol%) were generated with **Pd1 -3** (**Figure 7**). All the resulting copolymers are highly branched polymers with ester groups located at the end of the branching. Generally, a higher MA concentration resulted in a higher incorporation ratio but significantly lower molecular weight and activity (**Figure 7**). Compared to**Pd1** , **Pd2** bearing remote F atoms exhibited modest copolymerization performance in terms of activity and molecular weight. Among these palladium catalysts, **Pd3** with the dibenzosuberyl substituents provided access to the E-MA copolymers with the highest molecular weights and incorporation ratios (**Figure 7**). This indicates that the dibenzosuberyl substituents are also beneficial for the E-MA copolymerization due to the sandwich-like structure formed by the dibenzosuberyl substituents, as discussed before.[3, 28]

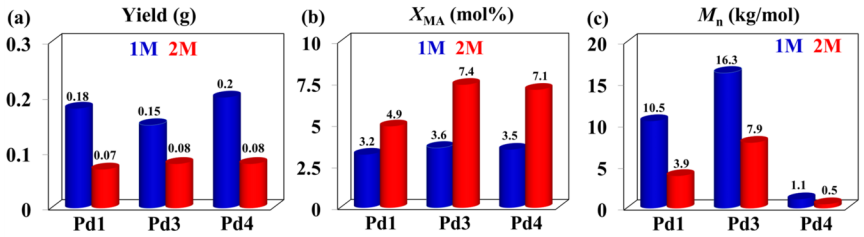

Figure 7 Comparisons on yield (**a**), incorporation ratio (**b**), and molecular weight (**c**) of ethylene-MA copolymer generated with **Pd1** , **Pd3** and **Pd4** at 1.0 M (blue), 2.0 M (red) MA concentration.

Conclusions

In summary, we prepared a class of sandwich-like naphthylamine-based α-diimine Ni(II) and Pd(II) complexes by combining bulky *o* -aryl dibenzhydryl and dibenzosuberyl substituent. The naphthyl Ni(II) catalysts exhibited exceptional high activities (well above 10^6 g·mol^{-1}·h^{-1}) and yielded lightly branched (16-40/1000C) polyethylenes with very high molecular weights (445.8-854.3 kg/mol) in ethylene polymerization. On the other hand, the corresponding naphthyl Pd(II) catalysts displayed moderate activities (10^4-10^5g·mol^{-1}·h^{-1}), producing moderately branched (47-78/1000C) polyethylenes with high molecular weights (21.6-82.0 kg/mol).

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Moreover, low to moderate molecular weight (1.4-16.3 kg/mol) E-MA copolymers with moderate incorporation ratios (2.4-7.4 mol%) and branching densities (53-84/1000C) could be generated by these Pd(II) catalysts, although in low activities (10^3g·mol^{-1}·h^{-1}). Compared with aniline-based Ni(II) and Pd(II) catalysts, the naphthylamine-based catalysts displayed a superior ability to suppress the chain transfer reactions, thus giving access to (co)polymers with 1-2 orders of magnitude higher molecular weights during ethylene (co)polymerization. The comparison between the catalytic performance of naphthylamine-based and aniline-based catalysts reveals that a minor evolution of the catalyst from aniline to naphthylamine can dramatically affect the level of chain transfer.

Experimental

Full experimental details for the synthetic procedures, materials, analytical methods, NMR and mass spectra of synthetic compounds, NMR, DSC and SEC curves of polymer and copolymer samples are placed in the supporting information. CCDC numbers of **L1** , **L3** ,**Ni1** , **Ni3** , **Pd1** and **Pd3** are 2211451-2211456. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via*www.ccdc.cam.ac.uk/data_request/cif*.

Supporting Information

The supporting information for this article is available on the WWW under*https://doi.org/10.1002/cjoc.2021xxxxx*.

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Notes

The authors declare no competing financial interests.

Acknowledgement

This work was supported by Natural Science Foundation of Anhui Province (2108085Y06). Anhui Provincial Key Laboratory Open Project Foundation (LCECSC-01).

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Manuscript received: XXXX, 2022 Manuscript revised: XXXX, 2022 Manuscript accepted: XXXX, 2022 Accepted manuscr

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Enhancing Suppression of Chain Transfer via Catalyst Structural Evolution in Ethylene (Co)Polymerizatio

The minor evolution of the catalyst from aniline to naphthylamine greatly contributed to the molecular weight of the result

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