## Longstanding living polymerization of ethylene: substituent effect on bridging carbon of 2-pyridinemethanamine nickel catalysts †

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Bulky 2-pyridinemethanamine nickel complex activated by MAO was used as a catalyst to conduct longstanding living ethylene polymerization under atmospheric pressure to produce branched polyethylene.

Living alkene polymerizations have been paid special attention in the last ten years because these reactions allow for the synthesis of polyolefins with precise architectures, such as monodisperse polymers, block copolymers and end-functionalized materials, and improved physical properties.<sup>1</sup> Many early transition metal catalysts have been reported to catalyze living ethylene polymerization to produce linear polyethylene.<sup>2</sup> However, most of the living polymerizations last only a very short time. As compared to early transition metal catalysts, there are much fewer late transition metal catalysts that have been reported to catalyze living ethylene polymerization. A crucial reason is that  $\beta$ -H transfer can rapidly happen for late transition metal catalysts,3 and C-H activation through a free rotation C-NAr bond was also proposed as one potential deactivation pathway.<sup>4</sup> One noteworthy example is the cationic α-diimine palladium catalyst that can produce branched polyethylene with living behavior.<sup>5</sup> Although several catalysts based on nickel can produce polyethylenes with narrow polydispersities within short polymerization time, the living properties are not adequately explored.<sup>6</sup> An  $\alpha$ -keto- $\beta$ -diimine nickel catalyst for living ethylene polymerization within 60 min was recently reported.<sup>7</sup> Despite all the work mentioned, long lifetime living polymerization of ethylene by late-transition metals remains a challenge.

On the other hand, pyridylaniline ligands have been developed for Zr, Ti, Hf, and Pd based catalysts for olefin polymerizations due to their rich variation and potential for the control in olefin catalysis.8 Recently, a new type of nickel catalysts bearing 2-pyridinemethanamine ligands was also explored for ethylene polymerization by our group. Without a substituent on the bridging methane of the complexes, branched polymers with a high molecular weight as well as

short-chain oligomers were simultaneously produced, which can be attributed to different catalytic species yielded from isomerization equilibrium by the rotation of the amino-aryl bond.9 Based on a strategy of suppressing the rotation of the amino-aryl bond by increasing the steric hindrance of the bridge joining the pyridine and aniline moieties, 2-pyridinemethanamine nickel complexes 1 and 2 (Scheme 1) with substituents of different sizes on the bridging carbon were synthesized. Herein, we report the substituent effect on the bridging carbon of 2-pyridinemethanamine nickel catalysts for long-lifetime living polymerization of ethylene under atmospheric pressure.

Ligands were prepared by a reduction reaction of imine with trimethylaluminium or Grignard reagent, and nickel complexes 1 and 2 were obtained in high yield by the addition of ligands to a stirring suspension of (DME)NiBr<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.<sup>10</sup> Single crystals of complexes 1 and 2. H<sub>2</sub>O suitable for X-ray diffraction analysis were obtained from dichloromethane solutions layered with hexane.<sup>‡</sup> Because of a reaction with moisture during crystallization, the single crystal obtained from complex 2 contains a  $H_2O$ molecule coordinated to the nickel metal. Repeated efforts to obtain a single crystal of complex 2 without H<sub>2</sub>O were not successful. As shown in Fig. 1, complex 1 exists as a bimolecular structure bridging by Br atoms, while complex  $2 \cdot H_2 O$  is of a monomolecular structure. The aniline moieties of both complexes are roughly perpendicular to the five-membered planes (N1-C5-C6-N2-Ni1), and the isopropyl substituents on the aryls are positioned at the axial directions of the nickel centers. In the case of complex  $2 \cdot H_2O$ , the 2,4,6-trimethylphenyl plane (C7-C15) is also perpendicular to the fivemembered plane (87.3°), and leans toward the aniline moiety with an angle of 56.67°. It is obvious that the 2.4.6-trimethylphenyl group of complex 2 introduces much bulkier steric hindrance to the rotation of the aniline moiety than the methyl of complex 1, which should make the isopropyl substituents on the aryl group blocking the axial sites of the metal more effective at preventing  $\beta$ -H elimination and chain transfer.4,11



Scheme 1 Complexes 1 and 2.

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Fig. 1 Molecular structures of complex 1 (a) and complex  $2 \cdot H_2 O$  (b). Both depicted with 30% thermal ellipsoids. Hydrogen atoms and the uncoordinated CH<sub>2</sub>Cl<sub>2</sub> molecules have been omitted for clarity.

Complexes 1 and 2 were used as catalyst precursors for ethylene polymerization under 1.2 atm ethylene pressure (Table 1). As compared with complex 1, complex 2 activated by methylaluminoxane (MAO) at 0 °C shows a more than 1-fold increase in activity, and produces a polymer with much higher  $M_{\rm n}$  (increase by one order of magnitude) and a much narrower PDI value (1.27 vs. 1.98). At -10 and -20 °C, complex 2 produces PEs with a narrow PDI value of 1.19, suggesting living polymerizations. However, even at -20 °C, complex 1 produces a relatively wide molecular weight distribution PE. These results provide a demonstration that 2,4,6-trimethylphenyl on the bridge backbone plays a dominant role in resisting the rotation of the CAr-N bond to eliminate chain transfer, while methyl substituent on the bridging carbon is not bulky enough to resist the rotation effectively. With an elevated temperature, complex 2 exhibited the highest activity for ethylene polymerization at 20 °C, and an obvious decrease in molecular weight at 40 °C. AlEt<sub>2</sub>Cl can also serve as an activator with the same activity and a slightly boarder PDI value (1.25), while using AlEt<sub>3</sub> as an activator leads to a board PDI value (1.75) and a dramatic decrease of activity. The PEs obtained by these catalytic systems are branched polymers mainly containing methyl branches as revealed by <sup>13</sup>C NMR spectra. The branch densities are around 60–90 branches/1000 C, indicating a "chain walking" process of the catalysts.<sup>12</sup> As shown in Table 1 (entry 4 and 10), there is little difference between the polymerizations catalyzed separately by complex 2 and  $2 \cdot H_2 O$  under the same conditions, suggesting that the coordinated water in  $2 \cdot H_2 O$  can be removed by excessive MAO.

Living polymerization of ethylene using catalyst 2/MAO was carried out in toluene at -10 °C under 1.2 atm of ethylene and quenched with ethanol after desired time. The results are summarized in Table 2, and a plot of  $M_n$  and  $M_w/M_n$  as a function of polymerization time and the GPC traces are shown in Fig. 2. The  $M_n$  value increases linearly with the polymerization time, and the  $M_w/M_n$  value can be maintained in 1.15–1.21 for 6 h. Although the  $M_w/M_n$  values are a little higher than that produced by an  $\alpha$ -diimine palladium catalyst,<sup>5</sup> the stable linear increase of the  $M_n$  value indicates a long-lifetime living polymerization. To the best of our knowledge, this is the first report of a nickel complex to catalyze long-standing living ethylene polymerization. Longstanding living ethylene polymerization metals has been achieved only in rare instances.<sup>5a</sup>

Table 1 Results of ethylene polymerization initiated by 1, 2,  $2 \cdot H_2 O^a$ 

Entry	Cat.	$T_p/^{\circ}C$	Yield/g	Act. <sup>b</sup>	$M_{\rm n}^{\ c}  [\times 10^4]$	PDI	$T_g/^{\circ}\mathrm{C}$	br <sup>d</sup>
1	1	-20	0.270	1.35	1.08	2.21	-37.3	82
2	1	0	0.192	0.96	0.13	1.98	-59.2	93
3	2	-20	0.194	0.97	0.94.	1.19	-29.3	57
4	2	-10	0.424	2.12	1.72	1.19	-35.2	66
5	2	0	0.438	2.19	1.75	1.27	-42.0	67
5	2	20	0.626	3.13	1.71	1.49	-46.0	68
7	2	40	0.258	1.29	0.81	1.56	-56.8	75
8	2	-10	0.431	2.16	1.88	1.25	-31.2	80
9	2	-10	0.050	0.25	0.37	1.75	-45.2	78
10	$2 \cdot H_2O$	-10	0.410	2.05	1.78	1.19	-36.2	68

<sup>*a*</sup> Polymerization conditions:  $2 \times 10^{-5}$  mol nickel complexes, 800 equiv. activator (MAO: entries 1–7 and 10; AlEt<sub>2</sub>Cl: entry 8; AlMe<sub>3</sub>: entry 9), 1.2 atm ethylene pressure, 40 mL toluene, 1 h. <sup>*b*</sup> Activity, 10<sup>4</sup> g PE/[mol·Ni·h]. <sup>*c*</sup>  $M_n$  [g mol<sup>-1</sup>] measured by GPC *vs.* linear polyethylene standards. <sup>*d*</sup> Branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.



Fig. 2 (a) Plot of  $M_n$  ( $\blacksquare$ ) and  $M_w/M_n$  ( $\blacktriangledown$ ) as a function of polymerization time at -10 °C under 1.2 atm of ethylene; catalyst 2/MAO. (b) GPC traces.

Table 2 Living ethylene polymerizations catalyzed by 2/MAO<sup>a</sup>

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66
66
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68
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<sup>*a*</sup> Polymerization conditions:  $2 \times 10^{-5}$  mol nickel complex, 800 equiv. MAO, -10 °C, 1.2 atm ethylene pressure, 40 mL toluene. <sup>*b*</sup>  $M_n$  [g mol<sup>-1</sup>] measured by GPC vs. linear polyethylene standards. <sup>*c*</sup> The theoretical number-average molecular weight. <sup>*d*</sup> Branches per 1000 C atoms determined by <sup>1</sup>H NMR spectroscopy.

As shown in Table 2, the number-average molecular weights of the polymers obtained at different polymerization time are basically consistent with the theoretical number-average molecular weights  $(M_{n,t})$  which is calculated gravimetrically on the basis of moles of catalyst employed and the weight of polymer produced, suggesting that all Ni metals have been successfully activated and each Ni metal center efficiently initiated the growth of one polymer chain.<sup>13</sup> A little lower values of  $M_n$  than the corresponding  $M_{n,t}$  can be attributed to the measurement of  $M_n$  by GPC with linear polyethylenes as standards. Because of the differences in the hydrodynamic volumes of these branched PEs and linear PEs standards, the  $M_n$  values determined for these polymers are smaller than the real number-average molecular weights.<sup>14</sup>



**Fig. 3** (a) Plot of  $M_n$  as a function of time for a postpolymerization at -10 °C under 1.2 atm of ethylene; catalyst 2/MAO. (b) GPC traces of PE and PE-*b*-PH.

A postpolymerization method was used to further test the stability of "living spots" in the absence of reacting monomer, which affects the application of the catalyst system to the preparation of block copolymers.<sup>2f</sup> After the polymerization was conducted for 1 h, ethylene was vented and the system was charged with N<sub>2</sub>. Ten hours later, the system was recharged with ethylene to continue the polymerization. As shown in Fig. 3a, the polymerization system still remains living, and the  $M_n$  value continues to increase linearly with the polymerization time after recharging ethylene monomer and the PDI values are around 1.2. Therefore, the longstanding living polymerization system should have a high potential for synthesis of ethylene-based block copolymers.

A further attempt at the synthesis of diblock copolymer polyethylene-*b*-poly(1-hexene) was made by catalyst 2/MAO at -10 °C. After polymerizing ethylene for 0.5 h, the ethylene monomer was removed, and then 5 mL 1-hexene was added and stirred for 5 h. As shown in GPC elution curves (Fig. 3b), the peak of polyethylene obtained at 0.5 h appears at a longer retention time ( $M_n = 0.88 \times 10^4$ ,  $M_w/M_n = 1.22$ ) and another peak of the final polyethylene-*b*-poly(1-hexene) copolymer shifts to the shorter retention time region ( $M_n = 2.14 \times 10^4$ ,  $M_w/M_n = 1.18$ ), indicating a successful preparation of an A–B diblock polymer under these conditions.

In conclusion, we have successfully developed a bulky 2-pyridinemethanamine nickel catalyst for longstanding living ethylene polymerization to yield branched polyethylene. Sufficiently bulky substitution on the bridging carbon of the complex plays a crucial role in resisting the rotation of the C<sub>Ar</sub>–N bond to prevent chain transfer reaction during the polymerization process. A diblock copolymer polyethylene*b*-poly(1-hexene) can also be synthesized by catalyst **2**/MAO. Further reports will address the influences of varied steric and electronic substituents and polymerizations with different monomers.

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## Notes and references

‡ Crystal data for complex **1**.  $C_{39}H_{54}Br_4Cl_2N_4Ni_2$ , M = 1086.82, monoclinic, a = 18.4583(17), b = 15.3616(14), c = 15.5084(14) Å, U = 4394.3(7) Å<sup>3</sup>, T = 173(2) K, space group  $P2_1/c$ , Z = 4, 29190. Reflections measured, 9553 unique ( $R_{int} = 0.0443$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.0769 (all data). Crystal data for complex **2**·**H**<sub>2</sub>**O**.  $C_{28}H_{38}Br_2Cl_2N_2NiO$ , M = 708.03, monoclinic,  $a = 13.4346(13), b = 13.4926(13), c = 17.6159(17) \text{ Å}, U = 3075.7(5) \text{ Å}^3, T = 173(2) \text{ K}$ , space group  $P2_1/c, Z = 4$ , 15490. Reflections measured, 6637 unique ( $R_{\text{int}} = 0.0358$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.1064 (all data).

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