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## Synthesis of high molecular weight polyethylene using iminopyridyl nickel catalysts<sup>†</sup>

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A series of iminopyridyl Ni(n) catalysts containing both the dibenzhydryl and the naphthyl moieties can polymerize ethylene with high activity and high thermal stability, generating polyethylene with a molecular weight of up to one million. In  $\alpha$ -olefin polymerization, semicrystalline polymers with high melting temperatures are generated.

Since the Nobel Prize winning discovery of Ziegler and Natta catalysts in the 1950s, tremendous efforts have been dedicated to the development of olefin polymerization catalysts. Originally, the metal nickel found its way into this field as a "poison". The famous "nickel effect" was discovered by Ziegler in 1952, who found that ethylene was converted exclusively to 1-butene using aluminium alkyls in the presence of nickel salts.<sup>1</sup> The scenario has changed dramatically after decades of research. Recently, numerous Ni( $\pi$ ) based catalysts have been developed that are capable of generating high molecular weight polyolefin materials, including some SHOP-type catalysts (Scheme 1, **I**; SHOP = Shell Higher Olefin Process),<sup>2</sup>  $\alpha$ -diimine based Ni( $\pi$ ) catalysts (Scheme 1, **II**),<sup>5</sup> and some phosphine–sulfonate Ni( $\pi$ ) catalysts (Scheme 1, **IV**).<sup>6</sup>

Some interesting results have been reported for iminopyridyl based Ni(II) catalysts.<sup>7</sup> A series of dimeric iminopyridyl Ni(II) catalysts (Scheme 1, **V**) have been shown to be active in ethylene polymerization, generating polyethylene with  $M_n$  of less than 3500 at temperatures higher than 20 °C ( $M_n < 20\,000$  at 0 °C).<sup>8</sup> By utilizing a sterically bulky dibenzhydryl group, Sun *et al.* showed that the resulting Ni(II) catalysts (Scheme 1, **VI**) were highly active in ethylene polymerization with activities of up to  $10^7$  g (PE) mol<sup>-1</sup> (Ni) h<sup>-1.9</sup> However, the increase in steric bulkiness led to the reduction in polyethylene molecular weight



**Scheme 1** Previously reported nickel based ethylene polymerization catalysts (**I–IV**) and iminopyridyl complexes (**V–XI**; R = Me, <sup>i</sup>Pr; X = CI, Br; these complexes are usually in dimeric forms).

for these catalysts ( $M_n < 1000$ ) compared with the original iminopyridyl Ni(II) catalysts (Scheme 1, V). By increasing the steric bulkiness on the other side of the iminopyridyl ligand, only ethylene oligomerization Ni(II) catalysts could be obtained (Scheme 1, VII and VIII).<sup>10</sup> The Ni(II) catalysts with a fused iminopyridyl structure (Scheme 1, IX) led to the formation of polyethylene with a similar molecular weight to those generated by the original iminopyridyl Ni(II) catalysts (Scheme 1, V).<sup>11</sup> Similar to the cases in VII and VIII, the installation of substituents on the other side of the iminopyridyl ligand led to ethylene oligomerization using Ni(II) catalysts (Scheme 1, X). Sun *et al.* also studied a series of naphthylamine based iminopyridyl ligands (Scheme 1, XI). These Ni(II) catalysts were highly active in ethylene polymerization, affording very low molecular weight

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polyethylene  $(M_n < 500)$ .<sup>12</sup> Two conclusions can be drawn from these studies: (i) iminopyridyl Ni(n) catalysts are capable of only oligomerizing ethylene or generating low molecular weight polyethylene; (ii) the polyethylene molecular weight is not sensitive to ligand sterics in this system.

Based on previous studies, sterically bulky ligands are usually required to afford Ni(II) catalysts capable of generating high molecular weight polymers. For example, Long et al. showed that some sterically bulky  $\alpha$ -diimine Ni(II) complexes bearing a dibenzhydryl moiety (Scheme 1, XII) were highly active in ethylene polymerization, generating polyethylene with high molecular weight  $(M_n > 10^5)$ .<sup>13</sup> Also, our group showed that the dibenzhydryl moiety could lead to highly stable and active  $\alpha$ -diimine Pd(II) catalysts, generating semicrystalline polyethylene and ethylene-methyl acrylate copolymers with high molecular weight.<sup>14</sup> Recently, Brookhart, Coates, Daugulis et al. studied the olefin polymerization properties of some arylnaphthylamine derived  $\alpha$ -diimine and salicylaldimine Ni(II) catalysts (Scheme 1, XIII).<sup>15</sup> Inspired by these studies, we herein report the synthesis and olefin polymerization studies of a series of iminopyridyl Ni(II) catalysts bearing both the dibenzhydryl and the arylnaphthyl moieties. These Ni(II) complexes are highly active in ethylene polymerization when activated with aluminium cocatalysts. Most surprisingly, these catalysts could generate polyethylene with a molecular weight on the order of millions, about two orders of magnitude higher than all of the previously reported iminopyridyl  $Ni(\pi)$  catalysts. This is a very good demonstration of the power of the ligand structures to influence the polymerization processes.

8-(4-R-phenyl)-naphthalen-1-amine (R = H, Me, Ph) was easily synthesized using the literature procedure (Scheme 2).<sup>15a,16</sup> Subsequently, the reaction with two equiv. of Ph<sub>2</sub>CHOH led to the formation of anilines in 93–96% yields. The condensation reaction with picolinaldehyde afforded the desired iminopyridine ligands L1–L3 in 76–87% yields. All of these organic compounds were characterized by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy and mass spectrometry. The Ni(II) complexes (1–3) were generated in 92–96% yields by the reaction of the ligands with 1 equiv. of (DME)NiBr<sub>2</sub> (DME = ethylene glycol dimethyl ether) and were characterized by mass spectrometry and elemental analysis.

The molecular structure of L3 was determined by X-ray diffraction analysis (Fig. 1). Based on the structural analysis, the phenyl substituent on the naphthyl moiety would be able to block the axial position of the Ni center in the metal complexes.



Fig. 1 Molecular structure of L3. Hydrogen atoms have been omitted for clarity. Atoms are drawn at a 30% probability level. Selected bond lengths (Å) and angles (deg): C1-C2 = 1.467(3), N1-C1 = 1.261(2), N1-C7 = 1.420(2); C2-C1-N1 = 123.59(18), C1-N1-C7 = 117.41(15).

Multiple attempts to determine the molecular structure of the  $Ni(\pi)$  complexes failed due to their instability. A dimeric structure may be present in the solid state similar to those previously reported iminopyridyl  $Ni(\pi)$  catalysts shown in Scheme 1.

Upon activation with methylaluminoxane (MAO) or Et<sub>2</sub>AlCl, complexes 1-3 become highly active in ethylene polymerization (Table 1). Complex 1 was used to screen the influence of polymerization conditions. When the temperature was increased from 20 °C to 50 °C and 80 °C, both the activity and the polyethylene molecular weight decreased dramatically (Table 1, entries 1-3). The branching density increased. The melting temperature of the resulting polyethylene also significantly decreased. Some exciting results were obtained when the polymerization was carried out at 5 °C (Table 1, entries 4 and 5). By decreasing the temperature from 50 °C to 20 °C, M<sub>n</sub> of polyethylene increased from 5.2  $\times$  10<sup>4</sup> to 14.1  $\times$  10<sup>4</sup>. By decreasing the temperature from 20 °C to 5 °C,  $M_{\rm n}$  increased from 14.1 imes $10^4$  to  $44.6 \times 10^4$ . The difference between *M*<sub>n</sub>'s at 5 °C and 20 °C seems to be large. However, this actually agrees very well with previous reports. In ref. 8a, Mn of the polyethylene generated by catalyst V with the Pr substituent (Scheme 1) increased from

Table 1	Ethvlene	polymerization	mediated	by Ni(II)	complexes	1–3 <sup>a</sup>
	Lanyterie	potymenzation	mediated	<i>by</i> 11(1)	complexes	

-								
Ent.	Cat.	Cocat.	$T(^{\circ}C)$	Yield (	g) Act. <sup>b</sup>	$M_n^c$ (×	$10^{-4}$ ) PDI <sup>c</sup> B <sup>d</sup>	$T_{\rm m}^{\ \ e} (^{\circ} {\rm C})$
1	1	MAO	20	0.76	7.6	14.1	1.77 49	74.0
2	1	MAO	50	0.35	3.5	5.2	1.86 66	58.4
3	1	MAO	80	0.21	2.1	4.8	2.00 71	44.8
4	1	MAO	5	1.42	14.2	44.6	2.00 25	105.2
$5^{f}$	1	MAO	5	3.32	8.30	101.2	1.83 26	112.3
6	1	MAO	-20	2.21	22.1	72.5	1.38 24	111.3
$7^f$	1	MAO	-20	6.41	16.0	142.5	1.43 25	115.5
8	2	MAO	20	0.61	6.1	13.5	1.47 58	71.4
9	3	MAO	20	0.56	5.6	21.1	2.10 52	83.6
10	1	Et <sub>2</sub> AlCl	20	4.30	43.0	8.3	1.78 - g	67.8
11	1	Et <sub>2</sub> AlCl	80	2.29	22.9	2.8	2.10 - g	h
12	2	Et <sub>2</sub> AlCl	20	2.63	26.3	8.1	2.01 - g	70.1
13	2	Et <sub>2</sub> AlCl	80	1.68	16.8	2.1	2.13 - g	h
14	3	Et <sub>2</sub> AlCl	20	3.23	32.3	9.9	$1.96 - g^{g}$	69.8
15	3	$Et_2AlCl$	80	2.52	25.2	2.4	1.97 - g	h

<sup>*a*</sup> Conditions: 2 μmol pre-catalyst, 1000 eq. cocatalyst, 5 mL CHCl<sub>3</sub>, 45 mL toluene, 8 atm, 30 min. <sup>*b*</sup> Activity (Act.) =  $10^5$  g (mol Ni h)<sup>-1</sup>. <sup>*c*</sup> Molecular weight was determined by GPC using polystyrene standards. <sup>*d*</sup> *B* = branches per 1000 carbon atoms, determined by <sup>1</sup>H NMR analysis. <sup>*e*</sup> Determined by differential scanning calorimetry (DSC). <sup>*f*</sup> Polymerization for 2 h. <sup>*g*</sup> Not determined. <sup>*h*</sup> Less than 25 °C.

 $3.5 \times 10^3$  to  $20 \times 10^3$  when the polymerization temperature was decreased from 20 °C to 0 °C. In ref. 8*b*,  $M_n$  of the polyethylene generated by catalyst **V** with the Me substituent (Scheme 1) increased from  $2.5 \times 10^3$  to  $14 \times 10^3$  when the polymerization temperature was decreased from 20 °C to 0 °C. At 5 °C and 2 h of polymerization time,  $M_n$  could reach  $101.2 \times 10^4$ . Meanwhile, the branching density was dramatically decreased to *ca.* 25/1000C, along with the dramatically increased polymer melting temperature. When the temperature was further decreased to -20 °C, the activity further increased, along with increased polyethylene molecular weight ( $M_n = 142.5 \times 10^4$ ) and melting temperatures (Table 1, entries 6 and 7).

When the activator was changed from MAO to Et<sub>2</sub>AlCl, the catalytic activity increased by 5 to 10 times (Table 1, entries 8–15). However, the polyethylene molecular weight and the melting temperature decreased. The catalyst system is more stable with Et<sub>2</sub>AlCl as the activator compared with MAO, maintaining very high activity even at 80 °C. For catalyst 1/Et<sub>2</sub>AlCl at 80 °C, the polyethylene yield increased from 2.29 g to 3.32 g and 3.50 g (Table S1, ESI<sup>†</sup>), when the time was increased from 30 min to 1 h and 2 h. This suggested that significant decomposition of the catalyst occurred after 30 min. It should be noted that the sterically bulky  $\alpha$ -diimine Ni(n) complexes bearing a dibenzhydryl moiety (Scheme 1, **XII**) reported by Long *et al.* were only shown to be stable on the time scale of 30 min.<sup>13</sup>

The microstructure of the polyethylene was analysed by  $^{13}$ C NMR (Table S2, ESI<sup>†</sup>).<sup>17</sup> For the polyethylene obtained using 1/MAO at 80 °C (Table 1, entry 3),  $^{13}$ C NMR analysis (Fig. 2) indicates a branching density of 77/1000C (agrees well with that determined by <sup>1</sup>H NMR) including methyl (60.2%), ethyl (6.4%), propyl (2.9%), butyl (6.3%), *sec*-butyl (6.4%) and long chain (17.8%) branches. For the polyethylene generated at lower temperatures (Table 1, entries 1 and 2 at 20 and 50 °C), fewer percentages of long chain branches and more percentages of methyl branches were observed.

Because of the highly unsymmetric feature of the ligand structure, the performance of complexes 1–3 in  $\alpha$ -olefin polymerization was also investigated (Table 2). 1,2- or 2,1-insertion could occur during  $\alpha$ -olefin polymerization. For chain walking olefin polymerization catalysts, 1, $\omega$ -enchainment could occur from 2,1-monomer insertion followed by chain walking, and

βB

2B-

 $\beta B_2 / \beta B_3$ 

2B

3B3

βB1 1B3

ßB.

3B4

1B

sBu-Me-

1B<sub>1</sub>

sBu-Et-2

4B<sub>n</sub>

1B4

18

2B.

sBu-Et-2

4B4

2B4



(Table 1, entry 3).

aB2 YB

ßB

YB

2B

 $\gamma B_2 / \gamma B_3$ 

1B<sub>2</sub>

aB, brB1

βΒ

1B

brB

brB,

brB

Table 2 Polymerization of  $\alpha$ -olefins by Ni(II) complexes **1–3**<sup>a</sup>

Ent.	Cat.	Cocat.	$\alpha$ -Olefin <sup>b</sup>	Yield (mg)	Act. <sup>c</sup>	${M_{ m n}}^d \ \left( imes 10^{-4} ight)$	$PDI^d$	$B^e$	$T_{\rm m}^{f}(^{\circ}{\rm C})$
1	1	MAO	C6	291	9.7	2.1	1.61	69	44.9
2	1	Et <sub>2</sub> AlCl	C6	587	19.6	1.7	1.78	64	49.7
3	1	Et <sub>2</sub> AlCl	C8	372	12.4	1.4	1.73	46	70
4	1	Et <sub>2</sub> AlCl	C10	430	14.3	2.1	1.61	32	89
5	2	Et <sub>2</sub> AlCl	C6	171	5.7	3.6	2.01	75	39.3
6	3	Et <sub>2</sub> AlCl	C6	291	9.7	1	1.76	70	56.5
$7^g$	1	Et <sub>2</sub> AlCl	C10	64	0.26	1.4	1.52	29	97.9
$8^g$	3	Et <sub>2</sub> AlCl	C10	45	0.19	1.3	1.49	26	105.5
<sup><i>a</i></sup> Conditions: 10 μmol pre-catalyst, 200 eq. cocatalyst, 1.0 M α-olefin.									

2 mL CHCl<sub>3</sub>, total volume 20 mL, 3 h.  ${}^{b}$  C6 = 1-hexene, C8 = 1-octene, C10 = 1-decene.  ${}^{c}$  Activity (Act.) = 10<sup>3</sup> g (mol Ni h)<sup>-1</sup>.  ${}^{d}$  Molecular weight was determined by GPC using polystyrene standards.  ${}^{e}$  B = branches per 1000 carbon atoms, determined by <sup>1</sup>H NMR analysis.  ${}^{f}$  Determined by DSC.  ${}^{g}$  0.1 M C10 for 24 h.

2,ω-enchainment could occur from 1,2-monomer insertion followed by chain walking.<sup>4</sup> Recently, Coates *et al.* showed that semicrystalline polymers ( $T_{\rm m} > 100$  °C) could be obtained in a sandwich type α-diimine Ni(II) catalyzed α-olefin polymerization.<sup>15b</sup> This was attributed to the combination of regioselective 2,1-monomer insertion and precision chain walking events. A similar phenomenon was reported by Wu *et al.* in an amineimine Ni(II) system.<sup>18</sup> Herein, we report another example of such a kind of precision α-olefin polymerization using iminopyridyl Ni(II) catalysts.

Compared with cocatalyst MAO, Et<sub>2</sub>AlCl led to a catalyst system with much higher activity, slightly lower molecular weight, lower branching density and higher melting point in complex **1** initiated 1-hexene polymerization (Table 2, entries 1 and 2). Therefore, the Et<sub>2</sub>AlCl cocatalyst was used for the  $\alpha$ -olefin polymerization studies. When 1-octene and 1-decene were used, a similar polymer molecular weight, lower branching density and higher melting temperatures were observed (Table 2, entries 3 and 4). In terms of polymerization selectivity and correspondingly the polymer melting points, complex **3** showed better properties than complexes **1** and **2** (Table 2, entries 5 and 6). At lower concentration of 1-decene, much lower polymer branching density and much higher polymer melting points were observed (Table 2, entries 7 and 8).

In summary, we described the synthesis and characterization of some iminopyridyl Ni(II) catalysts containing both the dibenzhydryl and the naphthyl moieties. In ethylene polymerization, these complexes showed activities of above  $10^6$  g (mol Ni h)<sup>-1</sup>. With Et<sub>2</sub>AlCl as the cocatalyst, very high activity could be maintained up to 80 °C. Above 20 °C, polyethylene with a molecular weight ( $M_n$ ) of up to 2 × 10<sup>5</sup> could be generated. Moreover, a polymer with a molecular weight of up to 1 × 10<sup>6</sup> could be generated when the polymerization was carried out at 5 °C. This is *ca.* two orders of magnitude higher than all of the previously reported iminopyridyl Ni(II) catalysts. In  $\alpha$ -olefin polymerization, significant chain straightening was observed from the combination of 2,1-monomer insertion and precision chain walking. As a result, polymers with very high melting points ( $T_m$  up to 105.5 °C) were generated. This work was supported by the National Natural Science Foundation of China (NSFC, 21374108, 51522306), the Fundamental Research Funds for the Central Universities (WK3450000001), and the Recruitment Program of Global Experts. We thank Dr S. M. Zhou (HFNL, USTC) for the determination of the crystal structures.

## Notes and references

- 1 (a) K. Ziegler, Adv. Organomet. Chem., 1968, 6, 1; (b) L. Cerruti, HYLE, 1999, 5, 3; (c) F. M. McMillan, The Chain Straighteners, MacMillan Press, London, UK, 1979.
- 2 (a) W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, Angew. Chem., Int. Ed., 1978, 17, 466; (b) W. Keim, Angew. Chem., Int. Ed., 2013, 52, 12492.
- 3 (a) L. K. Johnson, C. M. Killian and M. Brookhart, J. Am. Chem. Soc., 1995, 117, 6414; (b) S. D. Ittel, L. K. Johnson and M. Brookhart, Chem. Rev., 2000, 100, 1169.
- 4 (a) A. Nakamura, S. Ito and K. Nozaki, Chem. Rev., 2009, 109, 5215;
  (b) E. Y. X. Chen, Chem. Rev., 2009, 109, 5157;
  (c) V. C. Gibson and S. K. Spitzmesser, Chem. Rev., 2003, 103, 283;
  (d) Z. Guan, Chem. Eur. J., 2002, 8, 3086;
  (e) Z. Guan, J. Polym. Sci., Part A: Polym. Chem., 2003, 41, 3680;
  (f) Z. Dong and Z. Ye, Polym. Chem., 2012, 3, 286;
  (g) D. Takeuchi, Macromol. Chem. Phys., 2011, 212, 1545;
  (h) Y. Chen, L. Wang, H. Yu, Y. Zhao, R. Sun, G. Jing, J. Huang, H. Khalid, N. M. Abbasi and M. Akram, Prog. Polym. Sci., 2015, 45, 23;
  (i) Z. Ye, L. Xu, Z. Dong and P. Xiang, Chem. Commun., 2013, 49, 6235;
  (j) D. Takeuchi, Macromol. Chem. Phys., 2011, 212, 1545;
  (k) D. Takeuchi, Polym. J., 2012, 44, 919;
  (l) L. H. Guo and C. L. Chen, Sci. China: Chem., 2015, 58, 1663;
  (m) L. H. Guo, S. Y. Dai, X. L. Sui and C. L. Chen, ACS Catal, 2016, 6, 428.
- 5 (a) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich,
  R. H. Grubbs and D. A. Bansleben, *Science*, 2000, 287, 460;
  (b) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs,
  D. A. Bansleben and M. W. Day, *Organometallics*, 1998, 17, 3149.
- 6 (a) X. Zhou, S. Bontemps and R. F. Jordan, Organometallics, 2008, 27, 4821; (b) D. Guironnet, T. Runzi, I. Gottker-Sechnetmann and S. Mecking, Chem. Commun., 2008, 4965; (c) S. Noda, T. Kochi and K. Nozaki, Organometallics, 2009, 28, 656; (d) P. Perrotin, J. S. J. McCahill, G. Wu and S. L. Scott, Chem. Commun., 2011, 47, 6948; (e) S. Ito, Y. Ota and K. Nozaki, Dalton Trans., 2012, 41, 13807; (f) M. Chen, W. P. Zou, Z. G. Cai and C. L. Chen, Polym. Chem., 2015, 6, 2669.

- 7 C. Bianchini, G. Giambastiani, L. Luconi and A. Meli, *Coord. Chem. Rev.*, 2010, **254**, 431.
- 8 (a) T. V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Löfgren and M. Leskelä, *Macromol. Rapid Commun.*, 1999, 20, 487; (b) T. V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola and M. Leskelä, *J. Organomet. Chem.*, 2000, 606, 112.
- 9 W.-H. Sun, S. Song, B. Li, C. Redshaw, X. Hao, Y. S. Li and F. Wang, Dalton Trans., 2012, **41**, 11999.
- 10 (a) S. Song, Y. Li, C. Redshaw, F. Wang and W.-H. Sun, J. Organomet. Chem., 2011, 696, 3772; (b) S. Song, T. Xiao, L. Wang, C. Redshaw, F. Wang and W.-H. Sun, J. Organomet. Chem., 2012, 699, 18; (c) T. Irrgang, S. Keller, H. Maisel, W. Kretschmer and R. Kempe, Eur. J. Inorg. Chem., 2007, 4221; (d) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen and W. Chen, J. Organomet. Chem., 2005, 690, 1570.
- 11 (a) J. Yu, Y. Zeng, W. Huang, X. Hao and W.-H. Sun, *Dalton Trans.*, 2011, 40, 8436; (b) L. Zhang, X. Hao, W.-H. Sun and C. Redshaw, *ACS Catal.*, 2011, 1, 1213; (c) X. H. Hou, Z. G. Cai, X. Chen, L. Wang, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2012, 41, 1617; (d) F. Huang, Z. L. Sun, S. Z. Du, E. L. Yue, J. J. Ba, X. Q. Hu, T. L. Liang, G. B. Gallandc and W.-H. Sun, *Dalton Trans.*, 2015, 44, 14281.
- 12 E. L. Yue, L. P. Zhang, Q. F. Xing, X.-P. Cao, X. Hao, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2014, **43**, 423.
- 13 (a) H. Liu and W.-H. Sun, Organometallics, 2011, 30, 2418;
  (b) S. Kong, K. Song, T. Liang, C. Y. Guo, W.-H. Sun and C. Redshaw, Dalton Trans., 2013, 42, 9176; (c) J. L. Rhinehart, L. A. Brown and B. K. Long, J. Am. Chem. Soc., 2013, 135, 16316;
  (d) J. L. Rhinehart, N. E. Mitchell and B. K. Long, ACS Catal., 2014, 4, 2501.
- 14 S. Y. Dai, X. L. Sui and C. L. Chen, Angew. Chem., Int. Ed., 2015, 54, 9948.
- (a) D. Zhang, E. T. Nadres, M. Brookhart and O. Daugulis, Organometallics, 2013, 32, 5136; (b) T. Vaidya, K. Klimovica, A. M. LaPointe, I. Keresztes, E. B. Lobkovsky, O. Daugulis and G. W. Coates, J. Am. Chem. Soc., 2014, 136, 7213; (c) Z. Chen, M. Mesgar, P. S. White, O. Daugulis and M. Brookhart, ACS Catal., 2014, 5, 631.
- 16 E. T. Nadres, G. I. F. Santos, D. Shabashov and O. Daugulis, J. Org. Chem., 2013, 78, 9689.
- (a) G. B. Galland, R. F. Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, 32, 1620; (b) E. F. McCord, S. J. McLain, L. T. J. Nelson, S. D. Arthur, E. B. Coughlin, S. D. Ittel, L. K. Johnson, D. Tempel, C. M. Killian and M. Brookhart, *Macromolecules*, 2001, 34, 362.
- 18 H. Hu, H. Gao, D. Chen, G. Li, Y. Tan, G. Liang, F. Zhu and Q. Wu, ACS Catal., 2015, 5, 122.