Polymerization

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Semi-Crystalline Polar Polyethylene: Ester-Functionalized Linear Polyolefins Enabled by a Functional-Group-Tolerant, Cationic Nickel Catalyst

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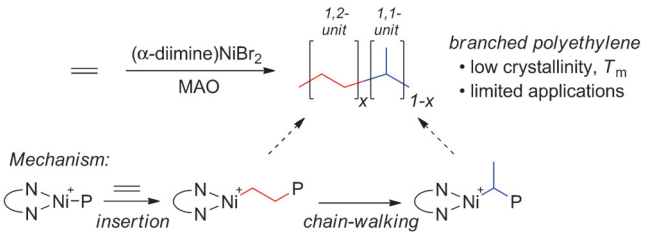
Abstract: *A dibenzobarrelene-bridged, α-diimine Ni^{II} catalyst (rac-**3**) was synthesized and shown to have exceptional behavior for the polymerization of ethylene. The catalyst afforded high molecular weight polyethylenes with narrow dispersities and degrees of branching much lower than those made by related α-diimine nickel catalysts. Catalyst rac-**3** demonstrated living behavior at room temperature, produced linear polyethylene ($T_m = 135\,°C$) at −20 °C, and, most importantly, was able to copolymerize ethylene with the biorenewable polar monomer methyl 10-undecenoate to yield highly linear ester-functionalized polyethylene.*

Linear polyethylene (PE) is the most abundantly produced plastic owing to its inexpensive monomer, thermoplastic properties, and semi-crystalline nature. The hydrocarbon composition of PE imparts hydrophobic character to the material, a feature that dictates the surface properties (for example, adhesion and wettability), permeability, and rheology.[1] One strategy for tuning these properties is to introduce functional groups along the PE backbone through either post-polymerization modification[2] such as surface treatments,[3] oxidation,[4] "click" reactions,[5] and C–H activation,[6] or by copolymerization of ethylene with functional vinyl monomers.[7] While the latter has been achieved with free radical polymerization of ethylene, the high temperatures and pressures required result in a highly branched amorphous PE material lacking the desired semi-crystalline properties of linear PE.[8] Ring-opening metathesis (ROMP)[9] and acyclic diene metathesis (ADMET)[10] polymerizations have both functional group tolerance and afford linear polymers, but require several steps for monomer synthesis. Alternatively, traditional ethylene polymerization catalysts, such as Ziegler–Natta and group IV metallocenes, produce linear semi-crystalline PE backbones, but suffer from high oxophilicity and are therefore often poisoned by the polar co-monomers.[11–14]

In contrast, late transition metal complexes pioneered by Brookhart and co-workers in the late 1990's[15] display enhanced stability toward polar functional monomers and can produce high molecular weight polymers in a controlled/living manner.[16–18] However, the ethylene polymers formed by these late transition metal catalysts are typically branched owing to the propensity of the metal to undergo consecutive β-hydride eliminations and re-insertions ("chain-walking" mechanism: Scheme 1). This process yields branched PE materials with lower crystallinity and melting temperatures, ultimately limiting their utility as semi-crystalline thermoplastics.[19]



Scheme 1. Chain walking of α-diimine Ni Catalysts.

Although chain-walking can be mitigated through the use of high ethylene pressures or sterically unhindered metal centers,[15e] the co-monomer incorporation or molecular weights suffer, respectively. These observations suggest that the controlled polymerization of ethylene with polar co-monomers to yield semi-crystalline copolymers remains a long-standing challenge for the field.[20] Recent advances in catalysts capable of incorporating polar monomers into linear PE have been made, most notably in the form of neutral late transition metal catalysts, such as Drent-type Pd phosphino-sulfonates[21] and Grubbs-type Ni salicylaldiminato complexes,[22,23] however these neutral catalysts often exhibit lower activities than cationic Brookhart-type α-diimine Ni/Pd catalysts. Nozaki and co-workers recently reported an exciting class of neutral nickel catalysts bearing chelating aryloxy-carbene ligands that incorporate functional monomers, and also exhibit excellent activities for alkene polymerization.[24]

Our work takes advantage of the functional group tolerance and high activity of cationic α-diimine Ni catalysts, but is distinct in suppressing chain-walking at low pressures (< 7 atm), thereby preserving the linear PE backbone while simultaneously incorporating functionalized α-olefins. We have synthesized and characterized a Ni^{II} α-diimine catalyst based upon a bulky dibenzobarrelene (DBB) ligand[17g] backbone (*rac*-**3**) and studied its ability to produce linear PE homopolymers and, more importantly, polar copolymers.

Compared to the related and more typical acenaphthene backbone (Figure 1), the steric bulk of the DBB substituent

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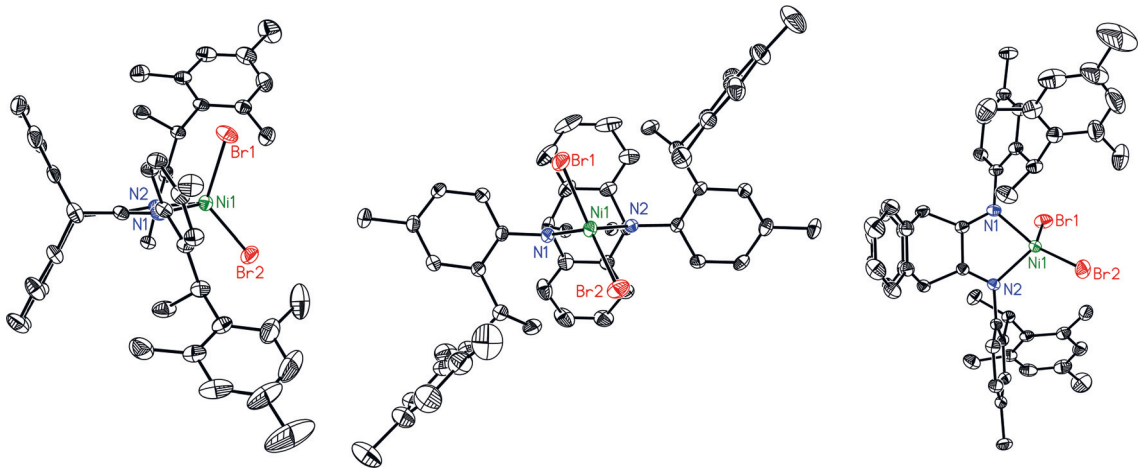
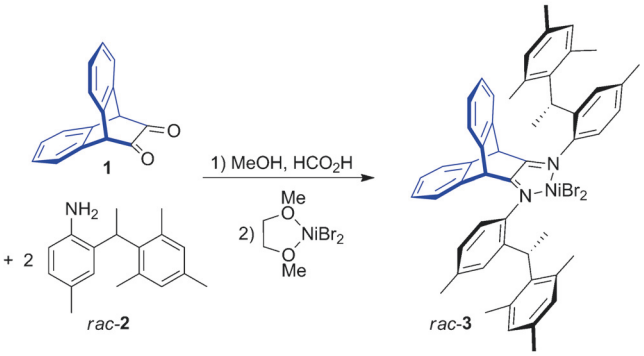


Figure 1. Three views of the molecular structure of *rac*-**3** determined by single-crystal X-ray diffraction. Atoms are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

(*rac*-**3**) was predicted to force the aryl groups closer to the reactive metal center, a feature linked to living character and decreased chain-walking.[19a,b] The DBB-based α-diimine ligand was synthesized through condensation of dione **1** with two equivalents of *rac*-4-methyl-2-(1-(2,4,6-trimethylphenyl)ethyl)aniline (*rac*-**2**, Scheme 2). The ligand was obtained as a non-statistical stereochemical mixture predominately composed of the racemic ligand isomer. Similar results have been observed with related diimines.[17c] Metalation with (dimethoxyethane)$NiBr_2$ resulted in the corresponding Ni^{II} diastereomerically-pure metal complex, *rac*-**3**.



Scheme 2. Synthesis of a dibenzobarrelene-based Ni complex, *rac*-**3**.

The structure of *rac*-**3** was determined by single-crystal X-ray diffraction (Figure 1). Complex *rac*-**3** exhibits pseudo C_2-symmetry, and the sterically demanding mesityl moieties are positioned away from the bulky DBB backbone, in stark contrast to the previously reported π-stacked acenaphthene system.[17c] Additionally, the front views of the crystal structures show the plane of the mesityl groups and the Ni center rotate significantly with the introduction of the DBB backbone. Although it is unclear how these complexes might exist in solution or as propagating Ni cations, these structures suggest a dramatic alteration in the steric environment by introduction of the DBB backbone relative to the related acenaphthene ligand-based complex.[17c]

Polymerization temperatures were screened from 60 °C to −20 °C at 1 atm pressure of ethylene (Table 1, entries 1–5). As expected, branching content was found to decrease as temperature was decreased, yielding highly linear PE with only 6 branches/1000 carbons at −20 °C, as can be determined

Table 1: Polymerization of ethylene using *rac*-**3**.[a]

Entry	Catalyst loading [μmoles]	Ethylene pressure [atm]	T_{rxn} [°C]	Yield [g]	TOF[b] [h^{-1}]	M_n[c] [kg/mol]	$Đ$[c]	Branches/ 1000 carbons[d]	T_m[e] [°C]
1	10	1	60	1.010	7200	82	1.35	63	71
2	10	1	40	1.039	7400	87	1.18	55	78
3	10	1	20	1.842	13 000	128	1.25	45	85, 112[f]
4	10	1	0	2.320	17 000	157	1.59	36	106, 116[f]
5	10	1	−20	2.004	14 000	288	1.70	6	125
6	2.5	4	−20	0.472	13 000	639	1.39	4	132
7	0.5	7	−20	0.487	70 000	712	1.34	<1	135

[a] Polymerization conditions: 300 equiv. MAO, toluene (100 mL), 30 min. [b] Turnover frequency (TOF) = mol ethylene/(mol cat h). [c] Determined using gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene vs. polyethylene standards. [d] Determined by ^{1}H NMR spectroscopy. [e] Determined by differential scanning calorimetry, second heat. [f] Both a broad lower temperature and sharp high temperature endotherm were observed (See the Supporting Information).

from the ^{1}H NMR spectra (Supporting Information). The degree of branching was further reduced by increasing ethylene pressures to 4 or 7 atm, thereby favoring ethylene coordination and insertion over chain-walking. At −20 °C and 7 atm of ethylene (entry 7), highly linear PE could be obtained (T_m = 135 °C, < 1 branch/1000 carbons). For *rac*-**3**, narrow dispersity ($Đ$) values were observed at 20 and 40 °C, indicating that polymerizations using *rac*-**3** may be controlled/living at these temperatures. To investigate this, ethylene polymerizations were conducted at 20 °C using *rac*-**3** and monitored over a period of 2 h (Figure 2). During this time,

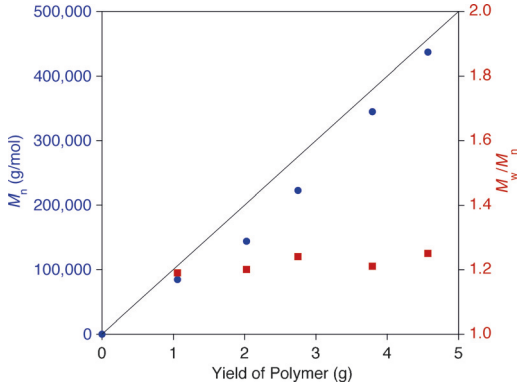
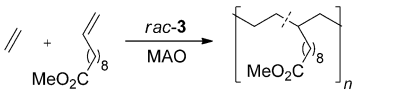


Figure 2. Molecular weight and dispersity as a function of polymer yield (T_{rxn} = 20 °C, 10 μmol *rac*-**3**, monitored over 2 h).

molecular weights increased linearly with conversion, $Đ$ values remained consistently low ($Đ$ = 1.25), and number average molecular weights (M_n) approached 500 kDa, which was in good agreement with theoretical values. It should be noted that the increased $Đ$ values observed as polymerization temperature was decreased (entries 4 and 5) were most likely due to the deleterious effect of polymer precipitation from solution at those temperatures. Comparing the ethylene polymerization activity of *rac*-**3** to other α-diimine nickel catalysts under identical conditions revealed that the activity was comparable to the complex derived from *rac*-**2** and an acenaphthene linker,[17c] but half as active as the prototypical Brookhart catalyst derived from 2,6-diisopropylaniline and an acenaphthene linker (Supporting Information).[15]

Copolymerizations of ethylene and methyl 10-undecenoate[12,14,23] (both biorenewable monomers)[25] were conducted using *rac*-**3** (Scheme 3; Table 2). It was found that as methyl 10-undecenoate concentration was increased from 0.022 to 0.088 M, a corresponding increase in co-monomer incorporation was observed, with 1 mol% methyl 10-undecenoate incorporated into the polymer at higher concentrations (entry 3). Further decreasing temperature and ethylene pressure led to highly linear polymers with T_m values of 128 °C and up to 1 mol% co-monomer incorporation (entries 4 and 5). In the presence of ester functional groups, the activity of the polymerization dropped by an order of magnitude, presumably owing to the reversible coordination of the polar co-monomer with the cationic metal center (Supporting Information). For comparison, a cationic Ni complex bearing a P,O-chelating ligand showed 0.6–4.8 mol% incorporation for the copolymerization of ethylene and methyl 10-undecenoate;[23b] however, the polymers produced by *rac*-**3** showed much higher molecular weights (27–105 kg mol^{-1} vs. 3.4–4.5 kg mol^{-1}).



Ester-functionalized linear PE
T_m up to 128 °C

Scheme 3. Copolymerization of ethylene and methyl 10-undecenoate using *rac*-**3**.

In conclusion, a dibenzobarrelene-derived, α-diimine Ni complex (*rac*-**3**) was synthesized and tested for ethylene polymerization. It was found to be highly active, exhibiting living polymerization behavior for ethylene at room temperature while producing linear polyethylene (T_m = 135 °C) at a polymerization temperature of −20 °C. We propose that the DBB-bridged α-diimine backbone creates a steric environment around the cationic Ni center that decreases catalyst deactivation and chain walking, thereby producing highly linear PE under mild conditions. In addition, *rac*-**3** demonstrated the ability to incorporate polar functionality into highly linear PE backbones. This result lends promise toward the ability to fine-tune the material properties of polyethylene prepared using Ni-based, single-site catalysts. Future work is focused on maintaining linear backbones at higher temperatures and with higher activity through further catalyst optimization.

Table 2: Copolymerization of ethylene and methyl 10-undecenoate using *rac*-3.[a]

Entry	Toluene [mL]	[Methyl 10-undecenoate] [M]	Ethylene pressure [atm]	T_{rxn} [°C]	Yield [g]	M_n[b] [kg mol^{-1}]	$Đ$[b]	Comonomer incorp.[c] [mol%]	T_m [°C][d]
1	100	0.022	1.7	20	0.376	105	1.62	0.6	101
2	50	0.044	1.7	20	0.250	74	1.45	0.7	100
3	25	0.088	1.7	20	0.130	62	1.58	1.0	97
4[e]	25	0.088	1.7	−20	0.363	41	2.26	0.3	128
5[f]	25	0.088	0.7	−20	0.528	27	2.83	1.0	128

[a] Polymerization conditions: 10 μmol *rac*-**3**, 300 equiv. MAO, 1 h. [b] Determined using gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene vs. polyethylene standards. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by differential scanning calorimetry, second heat. [e] Polymerization time = 3 h. [f] Polymerization time = 14 h.

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[1] a) A. R. Padwa, *Prog. Polym. Sci.* **1989**, *14*, 811–833; b) *Functional Polymers*: *Modern Synthetic Methods and Novel Structures*, *ACS Symposium Series 704* (Eds.: A. O. Patil, D. N. Schulz, B. M. Novak), American Chemical Society, Washington, DC, **1998**.

[2] a) N. K. Boaen, M. A. Hillmyer, *Chem. Soc. Rev.* **2005**, *34*, 267–275; b) M. J. Yanjarappa, S. Sivaram, *Prog. Polym. Sci.* **2002**, *27*, 1347–1398.

[3] S. M. Desai, R. P. Singh, *Adv. Polym. Sci.* **2004**, *169*, 231–293.

[4] a) T. C. Chung, H. L. Lu, C. L. Li, *Macromolecules* **1994**, *27*, 7533–7537; b) T. C. Chung, W. Janvikul, *J. Organomet. Chem.* **1999**, *581*, 176–187.

[5] a) M. Hong, J.-Y. Liu, B.-X. Li, Y.-S. Li, *Macromolecules* **2011**, *44*, 5659–5665; b) M. Hong, S.-R. Liu, B.-X. Li, Y.-S. Li, *J. Polym. Sci. Part A* **2012**, *50*, 2499–2506.

[6] C. Bae, J. F. Hartwig, H. Chung, N. K. Harris, K. A. Switek, M. A. Hillmyer, *Angew. Chem. Int. Ed.* **2005**, *44*, 6410–6413; *Angew. Chem.* **2005**, *117*, 6568–6571.

[7] a) L. S. Boffa, B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479–1493; b) J.-Y. Dong, Y. Hu, *Coord. Chem. Rev.* **2006**, *250*, 47–65; c) E. Y. X. Chen, *Chem. Rev.* **2009**, *109*, 5157–5214; d) A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.* **2009**, *109*, 5215–5244; e) B. P. Carrow, K. Nozaki, *Macromolecules* **2014**, *47*, 2541–2555; f) "Functional Polyolefins from the Coordination Copolymerization of Vinyl Monomers": F. Di Lena, J. A. S. Bomfim in *Synthesis and Applications of Copolymers* (Ed.: A. Parthiban), Wiley, Hoboken, **2014**, pp. 29–53.

[8] a) A. L. Logothetis, J. M. McKenna, *J. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 1431–1439; b) S. Liu, S. Elyashiv, A. Sen, *J. Am. Chem. Soc.* **2001**, *123*, 12738–12739; c) M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009**, *109*, 4963–5050.

[9] a) M. A. Hillmyer, W. R. Laredo, R. H. Grubbs, *Macromolecules* **1995**, *28*, 6311–6316; b) H. Martinez, J. Zhang, S. Kobayashi, Y. Xu, L. M. Pitet, M. E. Matta, M. A. Hillmyer, *Appl. Petrochem. Res.* **2015**, *5*, 19–25.

[10] a) D. J. Valenti, K. B. Wagener, *Macromolecules* **1998**, *31*, 2764–2773; b) M. D. Watson, K. B. Wagener, *Macromolecules* **2000**, *33*, 8963–8970; c) M. D. Watson, K. B. Wagener, *Macromolecules* **2000**, *33*, 5411–5417; d) A. Rybak, M. A. R. Meier, *ChemSusChem* **2008**, *1*, 542–547.

[11] a) U. Giannini, G. Brückner, E. Pellino, A. Cassata, *J. Polym. Sci. Part B* **1967**, *5*, 527–533; b) U. Giannini, G. Brückner, E. Pellino, A. Cassata, *J. Polym. Sci. Part C* **1968**, *22*, 157–175; c) M. D. Purgett, O. Vogl, *J. Polym. Sci. Part A* **1989**, *27*, 2051–2063; d) P. Aaltonen, B. Löfgren, *Eur. Polym. J.* **1997**, *33*, 1187–1190; e) L. Ahjopalo, B. Löfgren, K. Hakala, L.-O. Pietilä, *Eur. Polym. J.* **1999**, *35*, 1519–1528; f) H. Terao, S. Ishii, M. Mitani, H. Tanaka, T. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 17636–17637.

[12] Z. Yinghuai, X. Shiwei, V. R. Vangala, S. C. Chia, A. Cheong, O. N. Qin, N. S. Hosmane, *J. Organomet. Chem.* **2012**, *721–722*, 119–123.

[13] a) P. Aaltonen, G. Fink, B. Löfgren, J. Seppälä, *Macromolecules* **1996**, *29*, 5255–5260; b) M. M. Marques, S. G. Correia, J. R. Ascenso, A. F. G. Ribeiro, P. T. Gomes, A. R. Dias, P. Foster, M. D. Rausch, J. C. W. Chien, *J. Polym. Sci. Part A* **1999**, *37*, 2457–2469; c) K. Hakala, T. Helaja, B. Löfgren, *J. Polym. Sci. Part A* **2000**, *38*, 1966–1971; d) H. Hagihara, M. Murata, T. Uozumi, *Macromol. Rapid Commun.* **2001**, *22*, 353–357; e) N. Kashiwa, T. Matsugi, S.-I. Kojoh, H. Kaneko, N. Kawahara, S. Matsuo, T. Nobori, J.-I. Imuta, *J. Polym. Sci. Part A* **2003**, *41*, 3657–3666; f) N. Kawahara, S.-I. Kojoh, S. Matsuo, H. Kaneko, T. Matsugi, N. Kashiwa, *J. Mol. Catal. A* **2005**, *241*, 156–161; g) X. Zhang, S. Chen, H. Li, Z. Zhang, Y. Lu, C. Wu, Y. Hu, *J. Polym. Sci. Part A* **2007**, *45*, 59–68; h) M. T. Expósito, J. F. Vega, J. Ramos, J. Osío-Barcina, A. García-Martínez, C. Martín, J. Martínez-Salazar, *J. Appl. Polym. Sci.* **2008**, *109*, 1529–1534.

[14] a) W. Zuo, M. Zhang, W.-H. Sun, *J. Polym. Sci. Part A* **2009**, *47*, 357–372; b) Z. Chen, J.-F. Li, W.-J. Tao, X.-L. Sun, X.-H. Yang, Y. Tang, *Macromolecules* **2013**, *46*, 2870–2875; c) P. Hu, Z. Li, G. Jin, *Sci. China Chem.* **2014**, *57*, 1137–1143.

[15] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415; b) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268; c) C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664–11665; d) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888–899; e) D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromolecules* **2000**, *33*, 2320–2334.

[16] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203; b) G. J. Domski, J. M. Rose, G. W. Coates, A. D. Bolig, M. Brookhart, *Prog. Polym. Sci.* **2007**, *32*, 30–92; c) D. H. Camacho, Z. Guan, *Chem. Commun.* **2010**, *46*, 7879–7893; d) L. Guo, C. Chen, *Sci. China Chem.* **2015**, *58*, 1663–1673.

[17] a) S. Fernandes, M. M. Marques, S. G. Correia, J. Mano, J. C. W. Chien, *Macromol. Chem. Phys.* **2000**, *201*, 2566–2572; b) J. C. W. Chien, S. Fernandes, S. G. Correia, M. D. Rausch, L. C. Dickson, M. M. Marques, *Polym. Int.* **2002**, *51*, 729–737; c) A. E. Cherian, J. M. Rose, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2005**, *127*, 13770–13771; d) D. Meinhard, M. Wegner, G. Kipiani, A. Hearley, P. Reuter, S. Fischer, O. Marti, B. Rieger, *J. Am. Chem. Soc.* **2007**, *129*, 9182–9191; e) J. M. Rose, F. Deplace, N. A. Lynd, Z. Wang, A. Hotta, E. B. Lobkovsky, E. J. Kramer, G. W. Coates, *Macromolecules* **2008**, *41*, 9548–9555; f) F.-S. Liu, H.-B. Hu, Y. Xu, L.-H. Guo, S.-B. Zai, K.-M. Song, H.-Y. Gao, L. Zhang, F.-M. Zhu, Q. Wu, *Macromolecules* **2009**, *42*, 7789–7796; g) P. Huo, W. Liu, X. He, H. Wang, Y. Chen, *Organometallics* **2013**, *32*, 2291–2299.

[18] a) S. P. Meneghetti, J. Kress, P. Lutz, *J. Macromol. Chem. Phys.* **2000**, *201*, 1823–1832; b) M. Schmid, R. Eberhardt, M. Klinga, M. Leskelae, B. Rieger, *Organometallics* **2001**, *20*, 2321–2330; c) G. Chen, X. S. Ma, Z. Guan, *J. Am. Chem. Soc.* **2003**, *125*, 6697–6704; d) C. S. Popeney, D. H. Camacho, Z. Guan, *J. Am. Chem. Soc.* **2007**, *129*, 10062–10063; e) C. S. Popeney, Z. Guan, *J. Am. Chem. Soc.* **2009**, *131*, 12384–12393; f) C. S. Popeney, Z. Guan, *Macromolecules* **2010**, *43*, 4091–4097; g) H. Pan, L. Zhu, J. Li, D. Zang, Z. Fu, Z. Fan, *J. Mol. Catal. A* **2014**, *390*, 76–82; h) S. Dai, X. Sui, C. Chen, *Angew. Chem. Int. Ed.* **2015**, *54*, 9948–9953; *Angew. Chem.* **2015**, *127*, 10086–10091.

[19] a) L. Deng, P. Margl, T. Ziegler, *J. Am. Chem. Soc.* **1997**, *119*, 1094–1100; b) L. Deng, T. K. Woo, L. Cavallo, P. M. Margl, T. Ziegler, *J. Am. Chem. Soc.* **1997**, *119*, 6177–6186; c) Z. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science* **1999**, *283*, 2059–2062; d) 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, M. Brookhart, *Macromolecules* **2001**, *34*, 362–371; e) S. Mecking, *Angew. Chem. Int. Ed.* **2001**, *40*, 534–540; *Angew.*

Chem. **2001**, *113*, 550 – 557; f) Z. Guan, *Chem. Asian J.* **2010**, *5*, 1058 – 1070; g) D. Takeuchi, *Dalton Trans.* **2010**, *39*, 311 – 328.
[20] N. M. G. Franssen, J. N. H. Reek, B. de Bruin, *Chem. Soc. Rev.* **2013**, *42*, 5809 – 5832.
[21] a) E. Drent, R. van Dijk, R. van Ginkel, B. van Oort, R. I. Pugh, *Chem. Commun.* **2002**, 744 – 745; b) A. Nakamura, T. M. J. Anselment, J. Claverie, B. Goodall, R. F. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. Van Leeuwen, K. Nozaki, *Acc. Chem. Res.* **2013**, *46*, 1438 – 1449; c) T. Rünzi, D. Guironnet, I. Göttker-Schnetmann, S. Mecking, *J. Am. Chem. Soc.* **2010**, *132*, 16623 – 16630; d) A. Berkefeld, S. Mecking, *Angew. Chem. Int. Ed.* **2008**, *47*, 2538 – 2542; *Angew. Chem.* **2008**, *120*, 2572 – 2576; e) T. Rünzi, D. Fröhlich, S. Mecking, *J. Am. Chem. Soc.* **2010**, *132*, 17690 – 17691; f) S. Ito, M. Kanazawa, K. Munakata, J. Kuroda, Y. Okumura, K. Nozaki, *J. Am. Chem. Soc.* **2011**, *133*, 1232 – 1235; g) S. Ito, K. Munakata, A. Nakamura, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14606 – 14607; h) Z. Shen, R. F. Jordan, *J. Am. Chem. Soc.* **2010**, *132*, 52 – 53; i) Y. Ota, S. Ito, J. Kuroda, Y. Okumura, K. Nozaki, *J. Am. Chem. Soc.* **2014**, *136*, 11898 – 11901; j) K. M. Skupov, P. R. Marella, M. Simard, G. P. A. Yap, N. Allen, D. Conner, B. L. Goodall, J. P. Claverie, *Macromol. Rapid Commun.* **2007**, *28*, 2033 – 2038.
[22] a) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Freidrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460 – 462; b) V. C. Gibson, A. Tomov, *Chem. Commun.* **2001**, 1964 – 1965; c) S. J. Diamanti, P. Ghosh, F. Shimizu, G. C. Bazan, *Macromolecules* **2003**, *36*, 9731 – 9735; d) C. Carlini, V. De Luise, M. Martinelli, A. M. Raspolli Galletti, G. Sbrana, *J. Polym. Sci. Part A* **2006**, *44*, 620 – 633; e) X.-F. Li, Y.-G. Li, Y.-S. Li, Y.-X. Chen, N.-H. Hu, *Organometallics* **2005**, *24*, 2502 – 2510; f) B. M. Boardman, G. C. Bazan, *Acc. Chem. Res.* **2009**, *42*, 1597 – 1606; g) M. R. Radlauer, A. K. Buckley, L. M. Henling, T. Agapie, *J. Am. Chem. Soc.* **2013**, *135*, 3784 – 3787; h) S. Takeuchi, Y. Chiba, A. Takano, K. Osakada, *Angew. Chem. Int. Ed.* **2013**, *52*, 12536 – 12540; *Angew. Chem.* **2013**, *125*, 12768 – 12772; i) D. Y. Pong, S. Mandal, A. Sen, *Organometallics* **2014**, *33*, 7044 – 7051.
[23] a) J. Sun, Y. Shan, Y. Xu, Y. Cui, H. Schumann, M. Hummert, *J. Polym. Sci. Part A* **2004**, *42*, 6071 – 6080; b) W. Liu, J. M. Malinoski, M. Brookhart, *Organometallics* **2002**, *21*, 2836 – 2838.
[24] W.-J. Tao, R. Nakano, S. Ito, K. Nozaki, *Angew. Chem. Int. Ed.* **2016**, *55*, 2835 – 2839.
[25] a) T. Lebarbé, L. Maisonneuve, T. H. N. Nguyen, B. Gadenne, C. Alfos, H. Cramail, *Polym. Chem.* **2012**, *3*, 2842 – 2851; b) M. Zhang, Y. Yu, *Ind. Eng. Chem. Res.* **2013**, *52*, 9505 – 9514.

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