JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Bimetallic Effects on Ethylene Polymerization in the Presence of Amines: Inhibition of the Deactivation by Lewis Bases

Madalyn R. Radlauer, Michael W. Day, and Theodor Agapie*

Department of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, MC 127-72, Pasadena, California 91125, United States

Supporting Information

ABSTRACT: Dinickel complexes supported by terphenyl ligands appended with phenoxy and imine donors were synthesized. Full substitution of the central arene blocks rotation around the aryl−aryl bond and allows for the isolation of atropisomers. The reported complexes perform ethylene polymerization in the presence of amines. The inhibiting effect of polar additives is up to 250 times lower for the syn isomer than the anti isomer. Comparisons with mononuclear systems indicate that the proximity of the metal centers leads to the observed inhibitory effect on the deactivation of the catalysts.

In recent years, a bioinspired strategy has been used for the design of multimetallic olefin polymerization catalysts in which the proximity of the active nuclei is intended to facilitate catalysis similar to the effects seen in many metalloproteins.[1,2] A wide variety of multimetallic olefin polymerization catalysts have been reported, with a broad range of distances between the metal centers and varying degrees of flexibility of the ancillary ligand.[3−9] In comparison with their monometallic counterparts, some bimetallic early transition metal catalysts have been reported to incorporate more comonomer and bulkier olefins in copolymerizations with ethylene.[9−14] Enhanced stability and activity have been reported as well.[1,2] Bimetallic catalysts based on late metals have been shown to increase the incorporation of olefins displaying polar moieties in copolymers with ethylene.[15] Although the nature of monomer interactions with bimetallic catalysts has been investigated in a few cases, studies of the effect of ligand rigidity and metal−metal distance on the polymerization outcome have been hindered by the scarcity of architectures in which these parameters can be controlled. Furthermore, the development of olefin polymerization catalysts that are not significantly affected by the presence of polar groups or that can incorporate polar monomers is of interest. Herein we report a series of bi- and monometallic nickel polymerization catalysts with rigid geometries and restricted intermetal distances. The dinickel catalyst with the metal centers found in proximity shows less inhibition of catalysis by amines, a favorable consequence of the bimetallic effect.

In the design of a ligand for bimetallic catalysts, a 1,4-terphenyl moiety bearing four methyl substitutents on the central ring and one ortho oxygen substitutent on each peripheral aryl ring was chosen as a suitably rigid backbone with restricted rotation around the aryl−aryl bonds. In the present work, salicylaldimine motifs were used as metal-binding sites on the outer aryl rings. For comparison, both bimetallic (**1-s** and **1-a**) and monometallic (**2-s** and **2-a**) species were prepared (Figure 1). Separation and purification of the atropisomers were achieved during the ligand synthesis. The nickel complexes were synthesized by reacting the phenols with $NiMe_2$(tmeda) (tmeda = tetramethylethylenediamine) in the presence of pyridine. Structural assignment of each atropisomer was accomplished on the basis of single-crystal X-ray diffraction studies for the bimetallic systems (Figure 2) and $^1H-^1H$ nuclear Overhauser effect NMR spectroscopy (NOESY) experiments for the monometallic systems.[16]

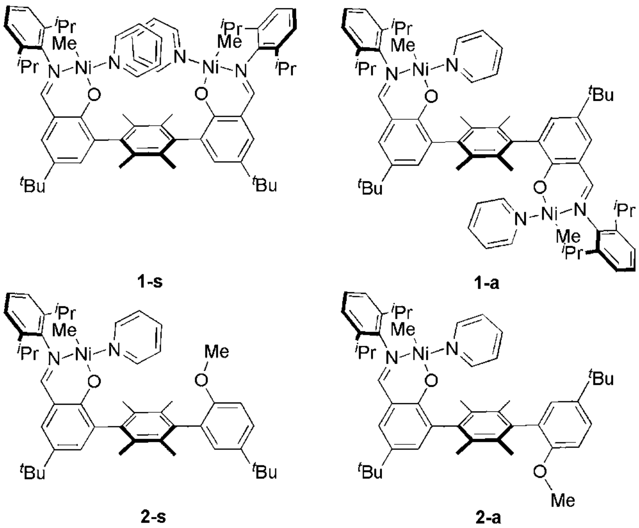

Figure 1. Mono- and bimetallic catalysts for the polymerization of ethylene.

The solid-state structures of **1-s** and **1-a** revealed that the distance between the two metal centers is 7.1 Å in the syn isomer (averaged over the two molecules in the asymmetric unit) and 11.1 Å in the anti isomer (Figure 2). The coordination environment around each metal is similar to that in previously reported nickel−phenoxyiminato complexes.[3−9,17] A slight distortion of the square-planar geometry is notable in **1-s**; the pyridine ligands extend toward the other metal center and bend away from each other as a result of steric

Received: November 22, 2011
Published: January 6, 2012

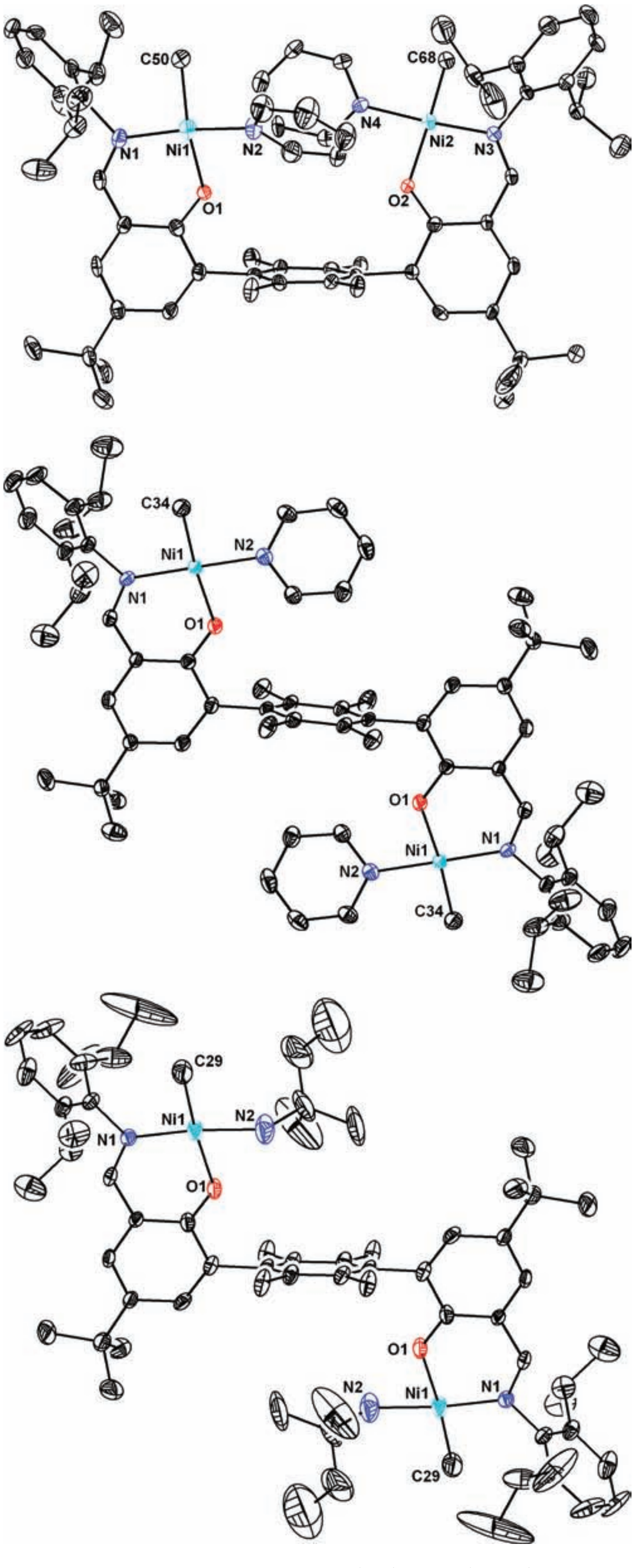

Figure 2. Solid-state structures of (top) **1-s**, (center) **1-a**, and (bottom) **1-a**-(1,1-dimethylpropylamine)$_2$. Solvent molecules and H atoms have been omitted for clarity.

repulsion. The structure of **1-a** forbids cooperative reactivity because the two nickel centers are on opposite faces of the central arene. The monometallic analogues **2-s** and **2-a** emulate the steric effect of the terphenyl backbone without the presence of a second metal center. No interconversion of the syn and anti isomers of either the di- or mononickel complexes was observed over 13 h at 50 °C.

Ethylene polymerization trials were performed with the isolated nickel complexes in toluene at 25 °C (Table 1). The present catalysts performed ethylene polymerization with activities similar to those of previously reported pyridine-ligated nickel−phenoxyiminato systems.[17,18] These experiments generated polyethylene with methyl branches (4−20 branches per 1000 C atoms).[19] Of the studied complexes, catalysis with **1-s** was the slowest by a factor of 5, likely because of the increased steric bulk at the active site in comparison with the other systems. The neutral ligands coordinated to the nickel centers in **1-s** reach toward the other metal and hinder coordination of the olefin. This proposal is supported by the distortion observed in the solid-state structure of **1-s**. Although the methoxy substitutent is located syn with respect to nickel, the steric bulk in **2-s** is likely not as large as that caused by the pyridine ligand bound to the second metal in the bimetallic system.

Ethylene polymerization trials in the presence of excess primary, secondary, and tertiary amines showed distinct inhibition trends (Tables 1 and 2). Complexes **1-a**, **2-a**, and **2-s** were inhibited by 2 orders of magnitude upon the addition of *N*,*N*-dimethylbutylamine, although the difference between **1-a** and **2-a** is not well understood in light of the similar steric environments (Table 2). This deactivation effect in the presence of added amines is similar to that reported previously for related mononickel systems.[20] In contrast, **1-s** was inhibited by only 1 order of magnitude. Consequently, in some cases (Table 1, entries 7, 8, and 11−17), addition of a tertiary amine afforded a syn catalyst that was more productive than the anti analogue. The inhibition of the deactivation by amines observed only with **1-s** is hereafter termed the bimetallic effect. The ratio of the deactivations for **1-a** versus **1-s** (*R*, Table 1) provides a quantitative measure of this effect. Relative to **1-s**, catalyst **1-a** was inhibited 10−25 times more by triethylamine, *N*-methyldipropylamine, and *N*,*N*-dimethylbutylamine and up to 270 times more by tripropylamine. Differential inhibition by triethylamine at a shorter polymerization time that resulted in lower polymer yields for both **1-s** and **1-a** was also observed, indicating that the calculated *R* is not due to decomposition of the catalysts at different rates (Table 1, entries 7 and 8). The use of secondary or primary amines resulted in greater inhibition than the use of tertiary amines and, in all cases that yielded polymer, also displayed greater inhibition of **1-a** than **1-s** (Table 1, entries 23 and 25−28). Relative to **1-s**, catalyst **1-a** was inhibited ca. 10 times more with diisopropylamine and 70−140 times more with 1,1-dimethylpropylamine and 1,1,3,3-tetramethylbutylamine (Table 1, entries 23 and 25−28).

The effect of amines on **1-s** and **1-a** was studied by ^{1}H NMR spectroscopy. New Ni−CH_3 peaks were observed upon addition of 1 equiv of 1,1-dimethylpropylamine or of a large excess (≥100 equiv) of *N*,*N*-dimethylbutylamine or *N*,*N*-dimethylethylamine to **1-a** and **1-s**, indicating competitive substitution of pyridine. *N*,*N*-Dimethylbenzylamine did not displace pyridine even upon addition of 100 equiv. All of the investigated amines displaced more pyridine from **1-a** than from **1-s**. Qualitatively, the binding ability was found to vary in the following order: pyridine ≈ 1,1-dimethylpropylamine ≫ *N*,*N*-dimethylbutylamine > *N*,*N*-dimethylethylamine ≫ *N*,*N*-dimethylbenzylamine (additional analysis is included in the Supporting Information). This trend mirrors the degree of

Table 1. Ethylene Polymerization Trials with 1-s and 1-a and Polar Additives[a]

			yield (g)		TOF[b]		
entry	additive	equiv	**1-s**	**1-a**	**1-s**	**1-a**	R[c]
1	none	n/a	0.574	3.415	341	2029	–
2	none	n/a	0.894	1.893[d]	531	2250[d]	–
3	NMe$_2$Et	500	0.150	1.440	89	856	0.5
4	NMe$_2$Et	500	0.148	1.032	88	613	0.7
5	NMe$_2$Et	5000	0.068	0.103	41	61	3.3
6	NMeEt$_2$	500	0.128	0.181	76	108	3.5
7	NEt$_3$	500	0.039	0.016	23	9	12.2
8	NEt$_3$	500	0.010[d]	0.006[d]	12[d]	7[d]	8.0
9	NMe$_2$R^1 [e,f]	225	0.058	0.071	103	126	4.0
10	NMe$_2$R^1 [e]	500	0.062	0.111	36	66	2.7
11	NMe$_2$^{n}Pr	500	0.036	0.025	21	15	7.2
12	NMe^{n}Pr$_2$	500	0.070	0.019	41	11	18.4
13	N^{n}Pr$_3$	500	0.055	0.001	33	1	269
14	NMe$_2$^{n}Bu	500	0.047	0.019	25	10	12.1
15	NMe$_2$^{n}Bu	500	0.066[i]	0.028[i]	39[i]	17[i]	11.6
16	NMe^{n}Bu$_2$	500	0.012	0.009	7	5	6.3
17	N^{n}Bu$_3$	500	0.003	–[j]	2	–[j]	–
18	NMe$_2$Ph	500	0.619	2.867	367	1703	1.1
19	NMe$_2$Bz	500	0.252	1.330	150	790	0.9
20	HN^{n}Pr$_2$	20	–[j]	–[j]	–[j]	–[j]	–
21	HNMe^{n}Bu	20	–[j]	–[j]	–[j]	–[j]	–
22	HN^{n}Bu$_2$	20	–[j]	–[j]	–[j]	–[j]	–
23	HN^{i}Pr$_2$	20	0.299	0.149	178	88	9.9
24	H$_2$N^{n}Bu	5	–[j]	–[j]	–[j]	–[j]	–
25	H$_2$NR^2 [g]	50	0.011	–[j]	7	–[j]	–
26	H$_2$NR^2 [g]	20	0.022	–[j]	13	–[j]	–
27	H$_2$NR^2 [g]	5	0.080	0.003	48	2	136
28	H$_2$NR^3 [h]	5	0.086	0.006	51	4	69.4
29	pyridine	10	–[j]	–[j]	–[j]	–[j]	–

[a] All polymerizations were run for 3 h at 25 °C under ethylene at 100 psig in 25 mL of toluene with 10 μmol of dinickel complex. The number of equivalents of base listed is the number of equivalents per nickel. [b] TOF = turnover frequency in units of (mol of C_2H_4) (mol of Ni)$^{-1}$ h^{-1}. [c] R = [(TOF for **1-a** with no additive)/(TOF for **1-a** with additive)]/[(TOF for **1-s** with no additive)/(TOF for **1-s** with additive)]. [d] Polymerization was run for 1.5 h. [e] R^1 = allyl. [f] Polymerization was run for 1 h. [g] R^2 = 1,1-dimethylpropyl. [h] R^3 = 1,1,3,3-tetramethylbutyl. [i] Different catalyst batches than in entry 14. [j] Insufficient product for accurate determination of the mass (<1 mg).

Table 2. Ethylene Polymerization Trials with 500 equiv of *N*,*N*-Dimethylbutylamine per Ni[a]

entry	complex	yield (g)	TOF[b]	R_a[c]
1	**1-s**	0.047	28	15
2	**1-s**	0.066	39	11
3	**1-a**	0.019	11	190
4	**1-a**	0.028	17	130
5	**2-s**	0.012	7	105
6	**2-s**	0.010	6	121
7	**2-a**	0.053	31	57
8	**2-a**	0.048	29	62

[a] All polymerizations were run for 3 h at 25 °C under ethylene at 100 psig in 25 mL of toluene with 20 μmol of nickel. [b] TOF = turnover frequency in units of (mol of C_2H_4) (mol of Ni)$^{-1}$ h^{-1}. [c] R_a = (TOF with no additive)/(TOF with additive).

inhibition recorded in ethylene polymerizations (Table 1, entries 4, 14, 19, 27, and 29). The correlation suggests that stronger amine binding to nickel increases the bimetallic effect.

The observed catalytic behavior suggests a bimetallic effect on the extent of inhibition by added base. Polymer formation is dependent on coordination of olefin and turnover-limiting olefin insertion into the metal–polymeryl bond.[21,22] Lewis bases compete with olefin for coordination to the metal and decrease the overall polymerization rate and polymer yield.[23−26] While steric bulk from the ligand framework could cause a decrease in deactivation by hindering the binding of amine, the studied complexes showed similar inhibition profiles for **1-a**, **2-a**, and **2-s** in contrast to **1-s**. The proximal arrangement of the two metal centers in compound **1-s** is proposed to cause the difference in deactivation of **1-s** relative to **1-a**, **2-a**, or **2-s** (Figure 3). Simultaneous binding of a bulky base to each nickel center of **1-s** is expected to be sterically disfavored relative to binding of bases to all of the metal centers of **1-a**, **2-a**, or **2-s**. Hence, for **1-s**, ethylene may compete successfully with the amine for coordination to nickel. This has the net effect of inhibiting deactivation by the base for **1-s** relative to **1-a**, **2-a**, or **2-s**. Intriguingly, the proposed mechanism might also be relevant to the polymerization of olefins with binuclear cationic early transition metal catalysts, with the couteranions acting as inhibiting bases instead of amines.[11−14]

In agreement with the above mechanistic proposal, the extent of inhibition was found to be dependent on the nature of the amine. The smallest amines induced a smaller difference between **1-s** and **1-a**. Binding of a smaller amine to one of the nickel centers of **1-s** leaves space to bind a second amine to the other nickel center, thereby effecting inhibition similar to that

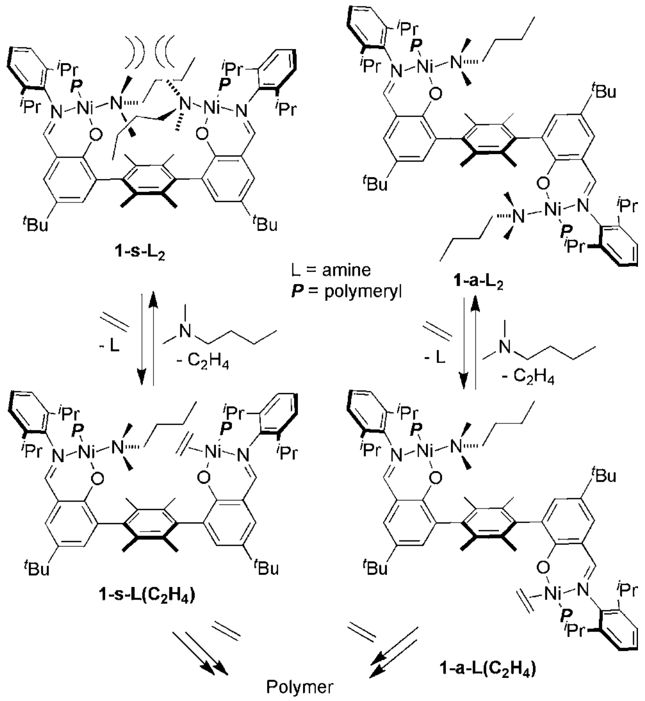

Figure 3. Competition between ethylene and amine for binding to nickel in bimetallic complexes.

seen for **1-a**. For several of the secondary and primary amines (dipropylamine, *N*-methylbutylamine, dibutylamine, and butylamine), tight coordination and insufficient bulk resulted in no polymerization (Table 1, entries 20–22 and 24). With intermediate-sized tertiary amines, as the size increased, the inhibition of **1-s** decreased relative to **1-a** (NMeEt$_2$ vs NEt$_3$ and NMe$_2$^{n}Bu vs NMe$_2$^{n}Pr vs NMe^{n}Pr$_2$ vs N^{n}Pr$_3$). This is consistent with the first coordinated amine hindering the binding of the second. Although X-ray-quality crystals of the corresponding syn isomer could not be obtained, the solid-state structure of the 1,1-dimethylpropylamine adduct of the bimetallic anti isomer highlights how the alkyl substituent of the primary amine extends toward the opposite aryl group, likely blocking the binding of a second amine in **1-s** (Figure 2). With larger amines (NMe^{n}Bu$_2$ and N^{n}Bu$_3$), it is proposed that binding of an amine at one nickel prevents the binding of ethylene at the second nickel of **1-s**; hence, the bimetallic effect is not apparent. Bulky and less basic *N*,*N*-dimethylbenzylamine and *N*,*N*-dimethylaniline likely show low inhibition because of weak binding to either isomer.

In summary, new mono- and dinickel ethylene polymerization catalysts have been reported. The supporting ligands based on atropisomers of a locked terphenyl backbone allow for control of the relative position of the two catalytic centers. The syn bimetallic isomer shows less inhibition by added amines relative to the anti bimetallic and monometallic catalysts. The bimetallic effect observed with **1-s** is proposed to arise from the close proximity of the nickels, which disfavors simultaneous ligation of base to both of the metal centers. This behavior is expected to have applications in the design of olefin polymerization catalysts with increased functional group tolerance and with potential for copolymerization of polar olefins by sterically favoring catalyst interactions with the olefin rather than the polar moiety. Future studies will explore these areas along with extending the terphenyl motif with restricted rotation to other multimetallic catalyst systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data, and crystallographic details for **1-s**, **1-a**, and **1-a**-(1,1-dimethylpropylamine)$_2$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

agapie@caltech.edu

■ ACKNOWLEDGMENTS

We thank Lawrence M. Henling for crystallographic assistance. We are grateful to Caltech and Dow Chemical for funding. The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF CRIF:MU award to Caltech (CHE-0639094). The 400 MHz NMR spectrometer was purchased via NIH Award RR027690.

■ REFERENCES

(1) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450.
(2) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363.
(3) Hu, T.; Li, Y. G.; Li, Y. S.; Hu, N. H. *J. Mol. Catal. A: Chem.* **2006**, *253*, 155.
(4) Na, S. J.; Joe, D. J.; Sujith, S.; Han, W. S.; Kang, S. O.; Lee, B. Y. *J. Organomet. Chem.* **2006**, *691*, 611.
(5) Sujith, S.; Joe, D. J.; Na, S. J.; Park, Y. W.; Chow, C. H.; Lee, B. Y. *Macromolecules* **2005**, *38*, 10027.
(6) Wang, W. H.; Jin, G. X. *Inorg. Chem. Commun.* **2006**, *9*, 548.
(7) Zhang, D.; Jin, G. X. *Inorg. Chem. Commun.* **2006**, *9*, 1322.
(8) Chen, Q.; Yu, J.; Huang, J. *Organometallics* **2007**, *26*, 617.
(9) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *Organometallics* **2008**, *27*, 2166.
(10) Salata, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *130*, 12.
(11) Li, H. B.; Li, L. T.; Schwartz, D. J.; Metz, M. V.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 14756.
(12) Li, H. B.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15295.
(13) Guo, N.; Li, L.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 6542.
(14) Guo, N.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 2246.
(15) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5902.
(16) Radlauer, M. R.; Day, M. W.; Agapie, T. *Organometallics* **2011**, submitted.
(17) Zuideveld, M. A.; Wehrmann, P.; Rohr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869.
(18) Wehrmann, P.; Zuideveld, M.; Thomann, R.; Mecking, S. *Macromolecules* **2006**, *39*, 5995.
(19) Crompton, T. R. *Analysis of Polymers: An Intoduction*; Pergamon Press: London, 1989.
(20) Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
(21) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
(22) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
(23) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827.
(24) Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 1841.
(25) Berkefeld, A.; Drexler, M.; Moàller, H. M.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 12613.
(26) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.