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Suppression of Chain Transfer in Catalytic Acrylate Polymerization via Rapid and Selective Secondary Insertion

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Supporting Information

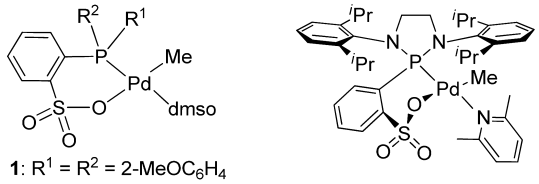
ABSTRACT: In catalytic copolymerization, undesired chain transfer after incorporation of a polar vinyl monomer is a fundamental problem. We show an approach to overcome this problem by a fast consecutive insertion. The second double bond of acrylic anhydride rapidly inserts intramolecularly to regio- and stereoselectively form a cyclic repeat unit and a primary alkyl favorable for chain growth (>96%). This results in significantly enhanced copolymer molecular weights vs monofunctional acrylate monomers.

Catalytic polymerizations of ethylene or propylene are among the largest scale synthetic chemical reactions performed today. By contrast, insertion (co)polymerization of polar vinyl monomers remains a long-standing challenge. The first significant breakthrough was made 40 years after Ziegler's and Natta's seminal discoveries, with the copolymerization of ethylene and acrylates to highly branched products.[1] More recently, the scope of polar monomers amenable to incorporation into linear polyethylene[2] has been expanded significantly, even to such difficult candidates as acrylonitrile, vinyl acetate, and acrylic acid.[3,4] Fundamental limitations and problems of these reactions can be understood from their mechanisms.[5]

Thus, low molecular weights of copolymers are a significant issue. The electron-poor polar α-olefins insert in a 2,1-fashion into the growing chain preferentially. The resulting secondary electron-withdrawing-group-substituted alkyls insert the next olefinic monomer only sluggishly. Additionally, they are particularly prone to chain transfer by β-hydride elimination. Indeed, copolymers contain an overly proportional amount of unsaturated end groups originating from chain transfer after incorporation of a polar vinyl monomer unit. Consequently, copolymer molecular weights are usually much lower than those of ethylene homopolymers, and they decrease with increasing polar monomer incorporation.

We now report how this issue can be approached by promoting a rapid second insertion after incorporation of a polar vinyl monomer, which at the same time generates a more favorable primary alkyl. This is brought about by a second electron-poor vinyl moiety in the copolymer, which is arranged in a favorable fashion by the first insertion.

The copolymerization of ethylene (E) with acrylic anhydride (AA) was studied with various catalyst precursors **1**−**3**, known to differ in their insertion regioselectivity and chemoselectivity



1: $R^1 = R^2 = 2\text{-MeOC}_6H_4$
2: $R^1 = {}^t\text{Bu}$; $R^2 = 2,4,6\text{-(MeO)}_3C_6H_2$
3

in methyl acrylate (MA) copolymerizations.[4,6,7] Under pressure-reactor conditions, exposure of **1** to 5 bar of E and 0.3 M of AA at 95 °C resulted in the formation of a copolymer with a high AA incorporation of 11.9 mol % (Table 1, entry 5). As expected, at a given E pressure, the incorporation of AA in the copolymers increases with increasing concentration of the co-monomer in the reaction mixture to reach 25.1 mol % at an initial concentration [AA] = 1.2 mol L^{-1} (Table 1, entries 4−7). Productivities decrease with increasing AA incorporation due to generally slower insertion into substituted alkyls formed by co-monomer incorporation compared to the reactivity of unsubstituted alkyls Pd-CH_2CH_2R from E. Under otherwise identical conditions, a lower polymerization temperature results in a slightly decreased incorporation of AA (Table 1, entries 1, 2, and 5). Importantly, prolonged reaction time resulted in a further increase of polymer yield and monomer conversion, demonstrating that catalyst activity is retained for more than an hour under polymerization condition (Table 1, entries 2 vs 3). With **2** as a catalyst precursor, both a lower catalytic activity and a slightly lower AA incorporation were observed (Table 1, entries 8 and 9). In line with the known copolymerization behavior toward MA,[7] a drastically lower activity (and AA incorporation) was found with **3** as a catalyst precursor, which is known to favor 1,2-incorporation of acrylate over the common 2,1-incorporation mode (Table 1, entries 11 vs 1).[7] Copolymers with AA incorporations of more than 7.5 mol % completely dissolved in tetrahydrofuran at 25 °C, indicating the absence of cross-linking.

Relative to previous studies of the insertion copolymerization of E and MA with **1**,[4i,6] the co-monomer incorporations are comparable. (Note that incorporations are given on the basis of molecules of AA incorporated, that is, the amount of vinyl moieties incorporated is twice as high due to the difunctional character of AA.) However, molecular weights of the obtained copolymers are higher by up to an order of magnitude vs the low molecular weight E−MA copolymers. For example, a

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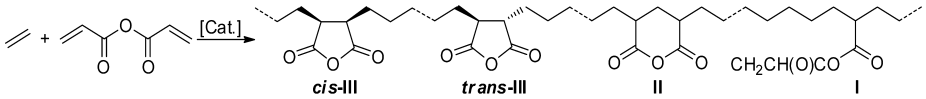
Table 1. Copolymerization of Ethylene with Acrylic Anhydride[a]



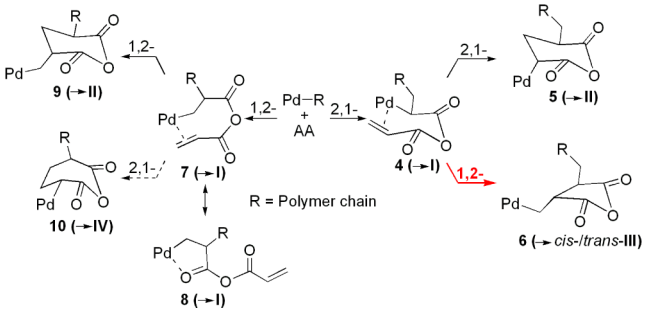
entry	cat.	conc (mol L^{-1})	T (°C)	t (min)	yield (mg)	TOF[b] E	TOF[b] AA	AA conv (%)	incorp[c] (mol %)	microstructure[c] (%) I	II	cis-III	trans-III	M_n[d]	M_w/M_n[d]
1	**1**	0.3	65	60	300	357	40	5.3	9.9	4.6	4.6	3.5	87.3	27.3	2.2
2	**1**	0.3	80	60	430	486	63	8.4	11.4	4.3	4.3	4.3	87.1	26.8	2.2
3	**1**	0.3	80	300	880	205	24	16.2	10.6	4.8	2.6	4.6	88.0	23.4	1.8
4	**1**	0.15	95	60	540	705	58	15.5	7.5	3.7	2.4	4.9	89.0	20.8	1.8
5	**1**	0.3	95	60	400	443	60	8.0	11.9	4.0	4.6	4.7	86.7	23.5	2.0
6	**1**	0.6	95	90	380	238	48	4.8	16.8	5.3	5.3	4.8	84.7	23.4	1.9
7	**1**	1.2	95	120	130	46	16	1.1	25.1	6.4	9.4	5.1	79.1	18.4	1.6
8	**2**	0.3	95	120	280	177	16	4.3	8.4	19.6	2.7	6.8	70.9	23.7	2.5
9	**2**	0.6	95	120	160	90	12	1.6	13.1	21.4	5.0	6.2	67.4	23.4	2.7
10[e]	**2**	0.2	80	60	900	1600	13	2.6	0.8	29.8	<0.1	3.8	66.4	38.5	1.7
11[f]	**3**	0.3	65	240	20	4	–	–	3.7	99.0	<0.1	<0.2	0.8	0.8	1.1
12[g]	**1**	0.6	95	90	70	78	1[h]	–	1.7	–	–	99.0	–	3.5	1.7

[a]Reaction conditions: toluene + monomer, 50 mL; catalyst precursor, 20 μmol; butylated hydroxytoluene (BHT), 200 mg; ethylene, 5 bar; 1000 rpm (unless stated otherwise). [b]In mol mol$_{Pd}^{-1}$ h^{-1}. [c]Determined by ^{1}H NMR in $CDCl_3$ at 25 °C for entries 1−9 and by ^{1}H NMR in $C_2D_2Cl_4$ at 90−120 °C for entries 10−12. [d]In kg mol^{-1}. Determined by GPC in THF at 40 °C vs linear polystyrene for entries 1−9 and by GPC in 1,2,4-trichlorobenzene at 160 °C vs linear polyethylene for entries 10−12. [e]Ethylene, 40 bar. [f]Catalyst **3**, 40 μmol. [g]Co-monomer, maleic anhydride, without BHT. [h]TOF for maleic anhydride.

copolymer with M_n = 27.3 × 10^3 g mol^{-1} (9.9 mol % X_{AA}) compares to M_n = 2.5 × 10^3 g mol^{-1} (9.4 mol % X_{MA}). Catalyst **2** at a high E pressure of 40 bar yielded an E−AA copolymer with higher M_n = 38.4 × 10^3 g mol^{-1}. By contrast, a very low molecular weight E−AA copolymer (M_n = 0.8 × 10^3 g mol^{-1}) was formed with a very low activity with **3**.

To account for these observations, polymer microstructures were analyzed. In principle, incorporation of AA can occur in a noncyclic fashion (repeat unit **I**, arising from insertion into alkyls **4**, **7**, and **8** in Scheme 1) or yields cyclic[8,9] structures (**II**

Scheme 1. Possible Microstructures after Insertion of AA into Pd−R



from **5**, **9**; **III** from **6**; or **IV** from **10**). An ATR-IR spectrum of the E−AA copolymer (Table 1, entry 5) features strong characteristic bands at 1857 and 1776 cm^{-1}, assigned to ν(CO)$_{sym}$ and ν(CO)$_{asym}$ of the five-membered cyclic structure **III** (Supporting Information, Figure S44). For further unambiguous conformation, E and maleic anhydride were copolymerized. In agreement with Claverie's findings,[10] a low molecular weight copolymer (M_n = 3.5 × 10^3 g mol^{-1}) with a limited incorporation of 1.7 mol % was obtained with a low catalytic activity (Table 1, entry 12). ^{1}H NMR spectra (Figure S39) feature two characteristic resonances at δ = 3.08 and 1.73 ppm for the *cis*-**III** motif (cf. Figure 1b). To further illuminate

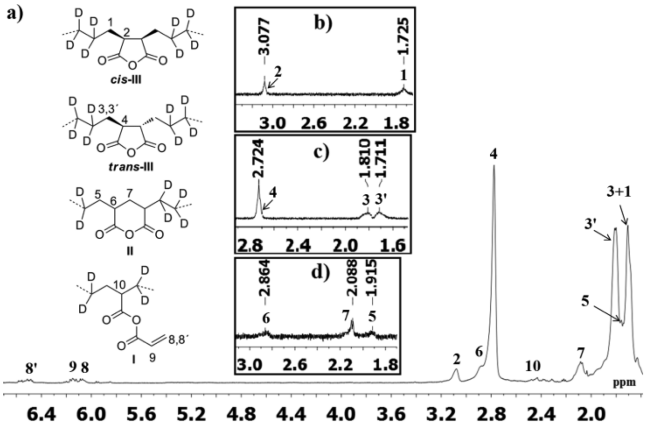


Figure 1. NMR spectra (600 MHz, 25 °C, $CDCl_3$) of an ethylene-d_4−AA copolymer obtained with **1**: (a) ^{1}H NMR spectrum, (b) TOCSY1D spectrum ($^3J_{H,H}$) with selective excitation at 3.08 ppm, (c) TOCSY1D spectrum ($^3J_{H,H}$) with selective excitation at 2.72 ppm, and (d) TOCSY1D spectrum ($^3J_{H,H}$ and $^4J_{H,H}$) with selective excitation at 2.09 ppm.

the regio- and stereochemistry, ethylene-d_4 and AA were copolymerized with **1**. The resulting copolymer features ^{1}H NMR resonances at δ = 2.72, 1.81, and 1.71 ppm with integral ratio of ca. 1:1:1, arising from *trans*-**III** units (Figures 1a and 1c). TOCSY1D experiments further confirm that resonances at δ = 2.86, 2.09, and 1.92 ppm originate from the six-membered cyclic structure **II** (Figure 1d). The noncyclic motif **I** gives rise to four identifiable multiplets at δ = 6.55, 6.21, 6.10, and 2.45 ppm, respectively. Seven-membered cycles (**IV**) were not found. 1D and 2D NMR analyses of all E−AA copolymers reveal a highly linear microstructure (ca. 1−2 methyl branches/1000 C) with cyclic and noncyclic structures incorporated in the main chain (Figures S34−S41).

With catalyst precursor **1**, copolymers with virtually exclusively cyclic units are accessible (>96%, Table 1, entry

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4). That is, an initial insertion of AA into the growing polymer chain is succeeded by a rapid insertion of the monomer's second double bond. Within this microstructure, *trans*-**III** predominates (89.0%). A similar pattern is formed with **2**, though not quite as selectively. By strong contrast, noncyclic incorporation **I** (99.0%) is found exclusively with catalyst precursor **3**, which is known to favor 1,2-insertion of acrylate. Note that the cyclic anhydride repeat units (**III**) in the E copolymers offer themselves for further post-polymerization modifications. This was exemplified by hydrolysis to linear polyethylenes with adjacently arranged carboxylic acid groups and cross-linking with amines (see Figure S33).

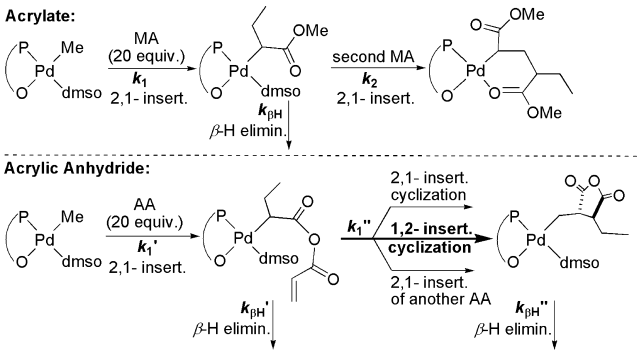
Notably, E-derived unsaturated end groups prevail over end groups (exocyclic methylidene, cf. Figure S34) formed from β-H elimination after cyclic co-monomer incorporation (ca. 2:1). This contrasts with low molecular weight E−MA copolymers,[4i,6] in which MA-derived end groups overwhelmingly prevail (>10:1) vs E-derived end groups. That is, the primary alkyl (**6**, Scheme 1) arising from consecutive 2,1−1,2-insertion has a low propensity for chain transfer, favorable for formation of higher molecular weight E−AA copolymers.

The underlying insertion events were elucidated by stoichiometric NMR studies (Figures S3−S14). Under pseudo-first-order conditions (excess monomer, ca. 20 equiv), insertion of MA into the Pd−Me bond of **1** or **2** at 25 °C predominantly yields the 2,1-insertion product with observed rate constants (k_1) of 7.1×10^{-4} and 3.1×10^{-4} s^{-1} (Table 2), respectively.[6] As expected, under otherwise identical conditions, insertion of AA into the Pd−Me bond of **1** or **2** at 25 °C also occurs in a 2,1-fashion exclusively (Table 2). The observed rate constants (k_1' = 8.9×10^{-4} and 2.1×10^{-4} s^{-1}) are comparable to the corresponding rate constants of MA. As a comparative measure of the further reactivity of these insertion products, the aforementioned MA 2,1-insertion product can insert another molecule of MA in a 2,1-mode (to form a six-membered chelate).[5c] In contrast, in the aforementioned AA insertion product, the remaining acrylic double bond inserts intramolecularly with a reversed 1,2-regioselectivity to form a five-membered cyclic repeat unit. The second MA insertion into the secondary carboxy-substituted alkyl is considerably slower (k_2 = 0.9×10^{-4} s^{-1}) than the first insertion into the Pd−Me bond of **1**. Thus, β-H elimination, which is only ca. 5-fold slower ($k_{\beta H}$ = 0.2×10^{-4} s^{-1}), is a relevant competitive reaction. By contrast, the intramolecular nature of the insertion of the second double bond of AA accelerates this insertion considerably even though it is forced into the less favorable 1,2-mode by the conformational constraint (k_1'' = 2.4×10^{-4} and 0.4×10^{-4} s^{-1} for **1** and **2**). In addition, β-H elimination from the first insertion product is negligible under these conditions (25 °C), and even at an elevated temperature of 90 °C ($k_1'' \gg k_{\beta H}'$). As expected,[7] the first insertion of AA into the Pd−Me bond of **3** at 25 °C selectively yields the 1,2-insertion product.[11] No obvious further insertion was observed in NMR scale experiments. This agrees with the noncyclic structure of AA-derived repeat units in the copolymer obtained by catalyst **3**.

Key insertion products **11-dmso** and **12-dmso** from the reactions of MA or AA with **2** (Scheme 2) could be isolated, and fully characterized by NMR (Figures S20−S28). Solid-state structures of the pyridine and lutidine adducts **11-pyridine** and **12-lutidine**, respectively, further confirm that the incorporated molecule of AA forms a five-membered cyclic structure with C2 and C5 located *trans* to each other in **12-lutidine** (Figure 2). This fully agrees with the predominant *trans*-**III** microstructure in the E−AA copolymers.

As models of the growing chain after an incorporation of polar monomer, the reactivity of **11-dmso** and **12-dmso** for β-H elimination is of interest. At the temperature of pressure reactor copolymerization experiments (90 °C), elimination from **12-dmso** is significantly slower than **11-dmso** ($k_{\beta H}''$ = 0.7 $\times 10^{-4}$ s^{-1} vs $k_{\beta H}$ = 2.1×10^{-4} s^{-1}) (Figure 3). This agrees

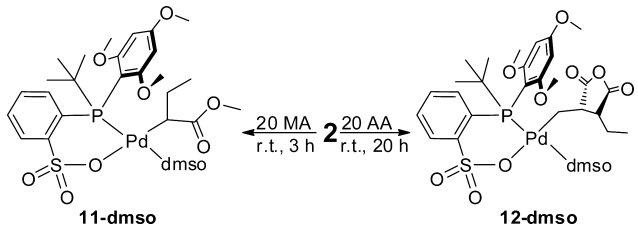
Table 2. Rate Constants of Insertion and Selectivity



	cat. **1**	cat. **2**
k_1 (25 °C), s^{-1}	7.1×10^{-4}	3.1×10^{-4}
2,1-:1,2-	>20:1	>20:1
$k_{\beta H}$ (25 °C), s^{-1}	0.2×10^{-4}	–[b]
k_1' (25 °C), s^{-1}	8.9×10^{-4}	2.1×10^{-4}
2,1-:1,2-	>20:1	>20:1
k_1'' (25 °C), s^{-1}	2.4×10^{-4}	0.4×10^{-4}
2,1-[a]:1,2-	<1:15	<1:15
$k_{\beta H}'$ (25 °C), s^{-1}	–[b]	–[b]

[a]2,1-regioselectivity includes 2,1-cyclization and 2,1-insertion of another molecule of AA. [b]No β-H elimination was observed in NMR scale experiments.

Scheme 2. Synthesis of Insertion Products



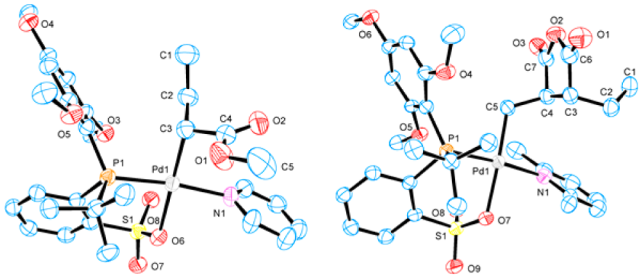


Figure 2. ORTEP plots of **11-pyridine** (left) and **12-lutidine** (right) drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

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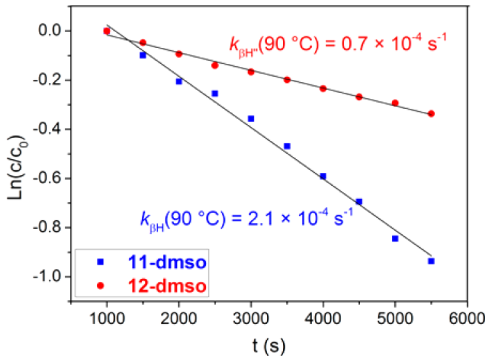

Figure 3. Observed rate constants of elimination of **11-dmso** and **12-dmso** ([Pd] = 0.025 mol L^{-1}, $C_2D_2Cl_4$). Data at 1000 s after addition of reagents to the NMR tube is taken as the initial concentration, [c_0].

qualitatively with the observed considerably higher molecular weights of AA copolymers and the minor portion of AA-derived end groups. Studies of the insertion of E into **11-dmso** (k_E') and **12-dmso** (k_E'') at 15 °C showed that insertion into the primary alkyl-Pd ($k_E'' = 3 \times 10^{-4}$ s^{-1}) is ca. 4-fold faster than into the secondary alkyl-Pd ($k_E' = 9 \times 10^{-5}$ s^{-1}).

In summary, our findings show that the concept of a second rapid intramolecular insertion can help to overcome fundamental issues of the insertion polymerization of electron-poor polar monomers. The product of polar monomer (2,1-) insertion, which is usually less reactive for chain growth but prone to β-H elimination and hereby limits molecular weights, is rapidly reacted before chain transfer occurs. At the same time, conformational constraints force this intramolecular insertion to occur in the electronically less favored 1,2-mode. This yields a primary alkyl, which is reactive for further chain growth and disfavors β-H elimination. This is reflected by significantly higher molecular weights. The resulting microstructures resemble linear ethylene−maleic anhydride copolymers. They are not accessible via maleic anhydride copolymerization due to poor incorporations. The anhydride repeat units render these novel polyethylenes reactive for various desirable post-polymerization reactions.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and product characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(2) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744.

(3) (a) Carrow, B. P.; Nozaki, K. *Macromolecules* **2014**, *47*, 2541. (b) Nakamura, A.; Anselment, T. M. J.; Claverie, J. P.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438. (c) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215. (d) Chen, E. Y. -X. *Chem. Rev.* **2009**, *109*, 5157. (e) Berkefeld, A.; Mecking, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2538. (f) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(4) (a) Ota, Y.; Ito, S.; Kuroda, J.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 11898. (b) Lanzinger, D.; Giuman, M. M.; Anselment, T. M. J.; Rieger, B. *ACS Macro Lett.* **2014**, *3*, 931. (c) Leicht, H.; Göttker-Schnetmann, I.; Mecking, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 3963. (d) Carrow, B. P.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 8802. (e) Piche, L.; Daigle, J.-C.; Rehse, G.; Claverie, J. P. *Chem.—Eur. J.* **2012**, *18*, 3277. (f) Ito, S.; Kanazawa, M.; Munakata, K.; Kuoda, J.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 1232. (g) Rünzi, T.; Fröhlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690. (h) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606. (i) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422. (j) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948. (k) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946. (l) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450.

(5) (a) Neuwald, B.; Caporaso, L.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2013**, *135*, 1026. (b) Friedberger, T.; Wucher, P.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 1010. (c) Guironnet, D.; Caporaso, L.; Neuwald, B.; Göttker-Schnetmann, I.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 4418. (d) Nozaki, K.; Kusumoto, S.; Noda, S.; Kochi, T.; Chung, L. W.; Morokuma, K. *J. Am. Chem. Soc.* **2010**, *132*, 16030. (e) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088.

(6) Wucher, P.; Goldbach, V.; Mecking, S. *Organometallics* **2013**, *32*, 4516.

(7) Wucher, P.; Caporaso, L.; Roesle, P.; Ragone, F.; Cavallo, L.; Mecking, S.; Göttker-Schnetmann, I. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 8955.

(8) For cyclopolymerizations of nonfunctionalized dienes cf.: (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (b) Shi, X.; Wang, Y.; Liu, J.; Cui, D.; Men, Y.; Li, Y. *Macromolecules* **2011**, *44*, 1062. (c) Crawford, K. E.; Sita, L. R. *J. Am. Chem. Soc.* **2013**, *135*, 8778. For reaction of ethylene with functionalized 1,6-dienes catalyzed by α-diimine Pd^{II} catalysts cf.: (d) Okada, T.; Park, S.; Takeuchi, D.; Osakada, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6141. (e) Park, S.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2006**, *128*, 3510.

(9) Copolymerization of ethylene with allyl acrylate by **1-pyridine** was shown to afford cyclic units (mixtures of five- and six-membered cycles) along with a similar amount of repeat units with a remaining intact double bond: Daigle, J.-C.; Piche, L.; Arnold, A.; Claverie, J. P. *ACS Macro Lett.* **2012**, *1*, 343. Note that allyl moieties generally incorporate less readily vs acrylates. Consequently, no clear effect on molecular weights was observed.

(10) Daigle, J.-C.; Piche, L.; Claverie, J. P. *Macromolecules* **2011**, *44*, 1760.

(11) Note that, due to the extreme slow rate of insertion of AA into lutidine-coordinated complex **3** at 25 °C, the alternative **3**-LiCl/$AgBF_4$ catalyst system was used for the kinetic insertion study. See ref 7.

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