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Supporting Information for

Polymerization of Alkyl Diazoacetates Initiated with Amidinate/Pd System: Efficient Synthesis of High Molecular Weight Poly(alkoxycarbonylmethylene)s with Moderate Stereoregularity

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Scheme S1. Generation of (A) amidinate/Pd and (B) *n*BuLi/Pd(OAc)$_2$ systems

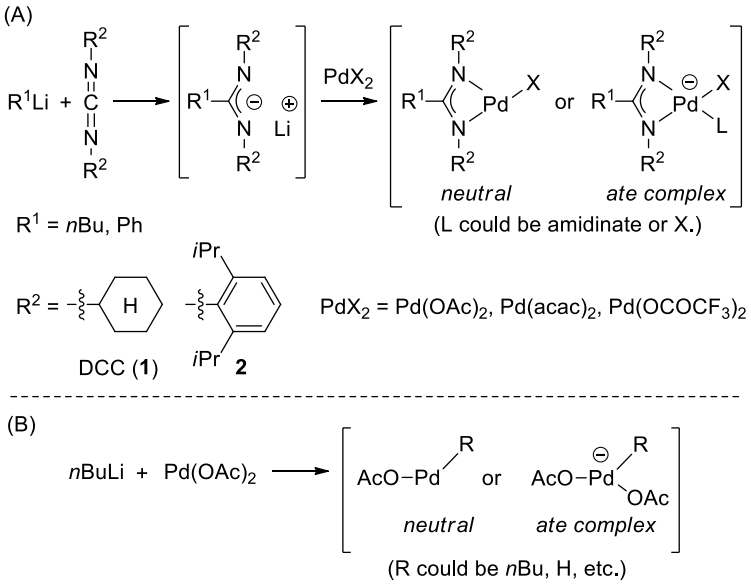
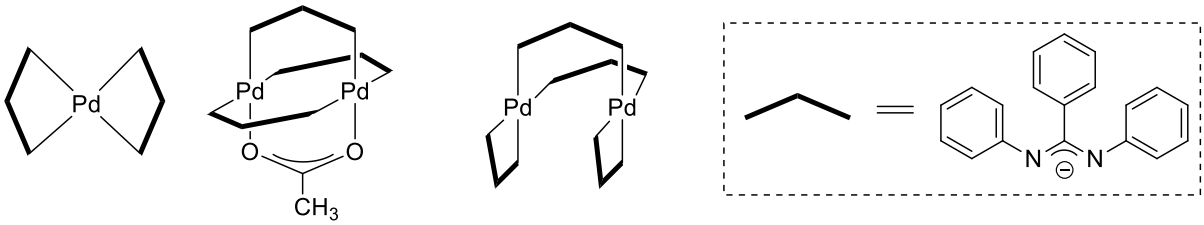


Table S1. Polymerization of **EDA** initiated with isolated Pd complexes[a]



Pd(DPhBz)$_2$ Pd$_2$(DPhBz)$_3$(OAc) β-Pd$_2$(DPhBz)$_2$(η^2-DPhBz)$_2$

run	Pd complex	organolithium	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	Pd(DPhBz)$_2$	none	0	-	-
2	Pd$_2$(DPhBz)$_3$(OAc)	none	0	-	-
3	β-Pd$_2$(DPhBz)$_2$(η^2-DPhBz)$_2$	none	0	-	-
4[d]	Pd(DPhBz)$_2$	*n*BuLi	7	50800	1.34
5[d]	Pd$_2$(DPhBz)$_3$(OAc)	*n*BuLi	19	50200	1.41

[a][Pd] =1.1-1.2 mM, [Pd]/[**EDA**] = 1/100, in THF at room temperature. **EDA** was used as a CH_2Cl_2 solution with a concentration of 2.3-2.4 M. [b]After purification with preparative SEC. [c]Determined by SEC. [d][*n*BuLi]/[Pd] = 1/1.

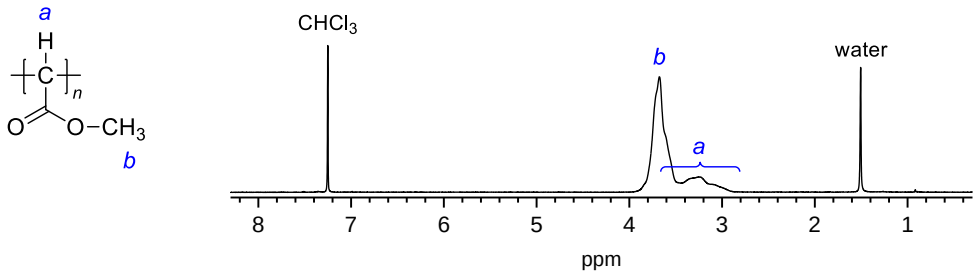


Figure S1. ^{1}H NMR spectrum of the polymer obtained from **MDA** (run 1 in Table 2).

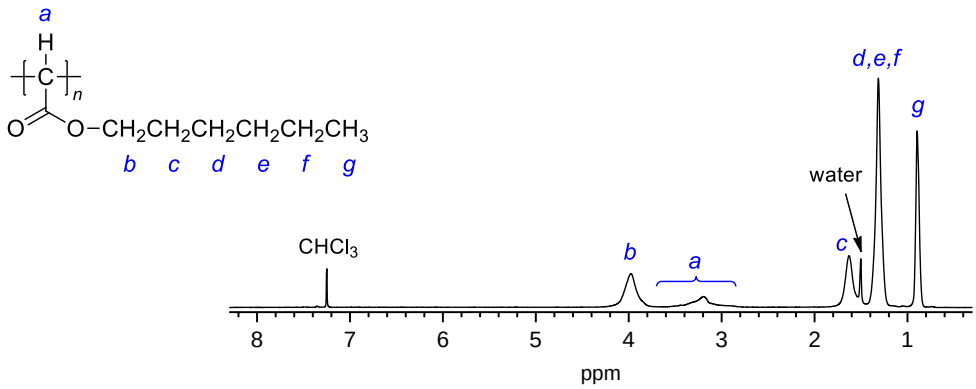


Figure S2. ^{1}H NMR spectrum of the polymer obtained from **nHDA** (run 3 in Table 2).

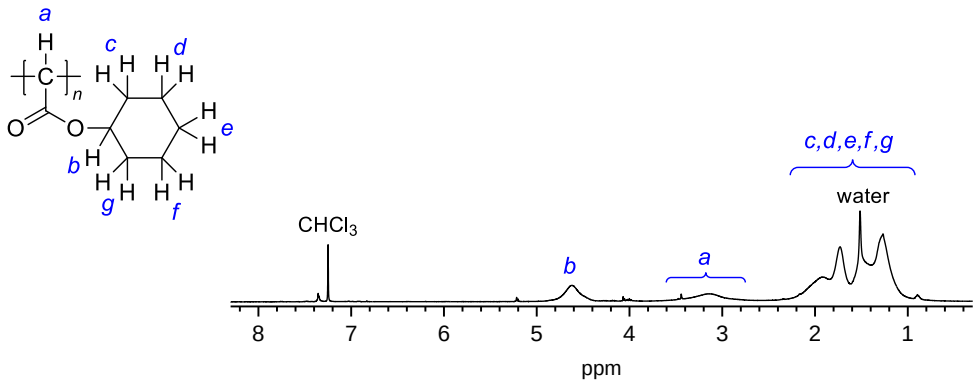


Figure S3. ^{1}H NMR spectrum of the polymer obtained from **cHDA** (run 5 in Table 2).

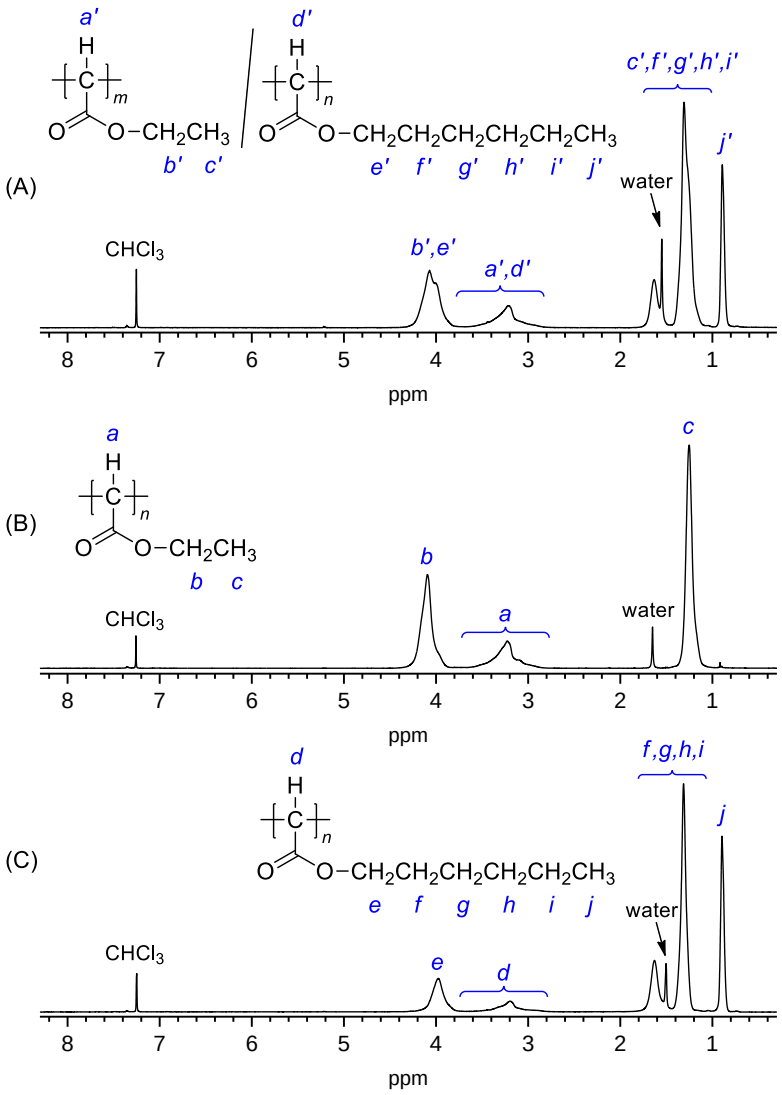


Figure S4. ^{1}H NMR spectra of homopolymers and copolymer from **EDA** and **nHDA**; (A) copolymer from **EDA** and **nHDA** (run 1 in Table 3), (B) homopolymer from **EDA** (run 1 in Table 1), and (C) homopolymer from **nHDA** (run 3 in Table 2).

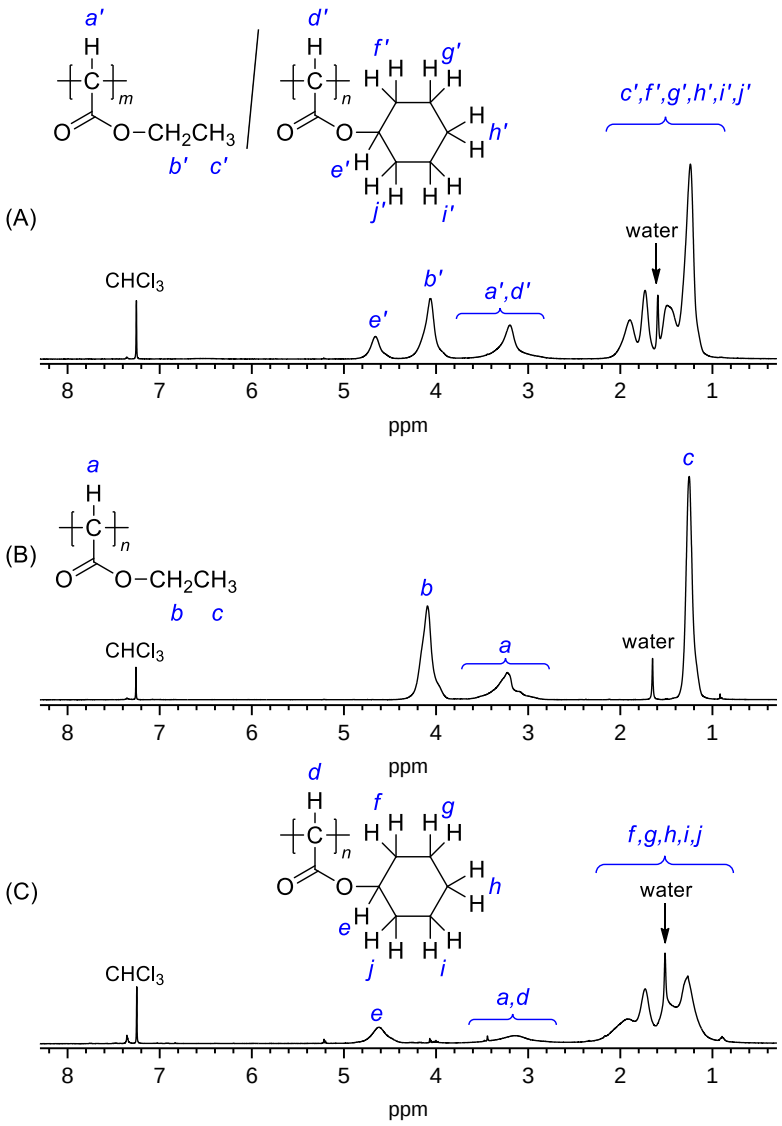


Figure S5. ^{1}H NMR spectra of homopolymers and copolymer from **EDA** and **cHDA**; (A) copolymer from **EDA** and **cHDA** (run 5 in Table 3), (B) homopolymer from **EDA** (run 1 in Table 1), and (C) homopolymer from **cHDA** (run 5 in Table 2).

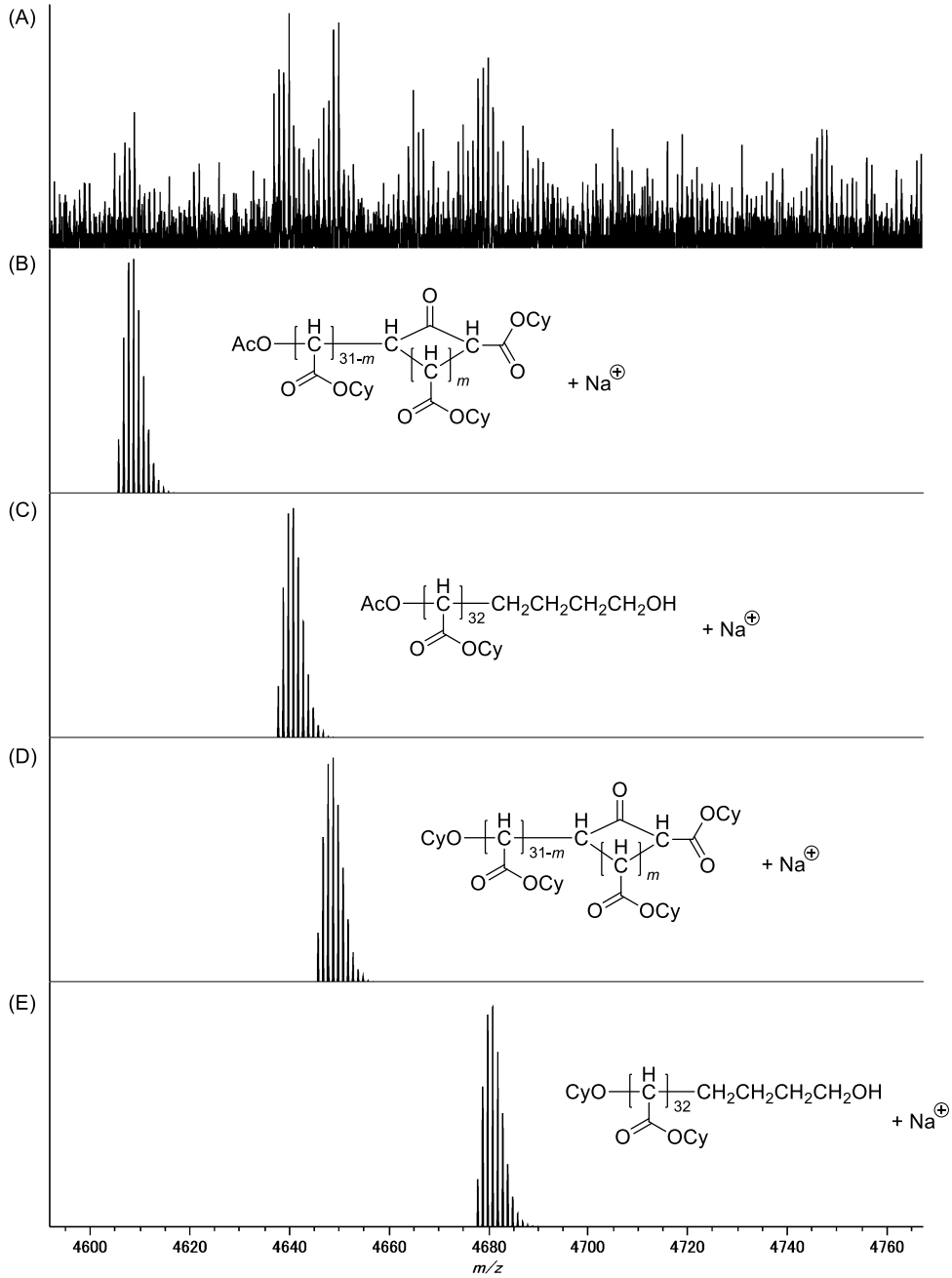


Figure S6. (A) Part of MALDI-TOF-MS spectrum of the polymer obtained from **cHDA** (run 5 in Table 2) and (B)-(E) the theoretical isotopic distributions of Na-adduct of polymers.

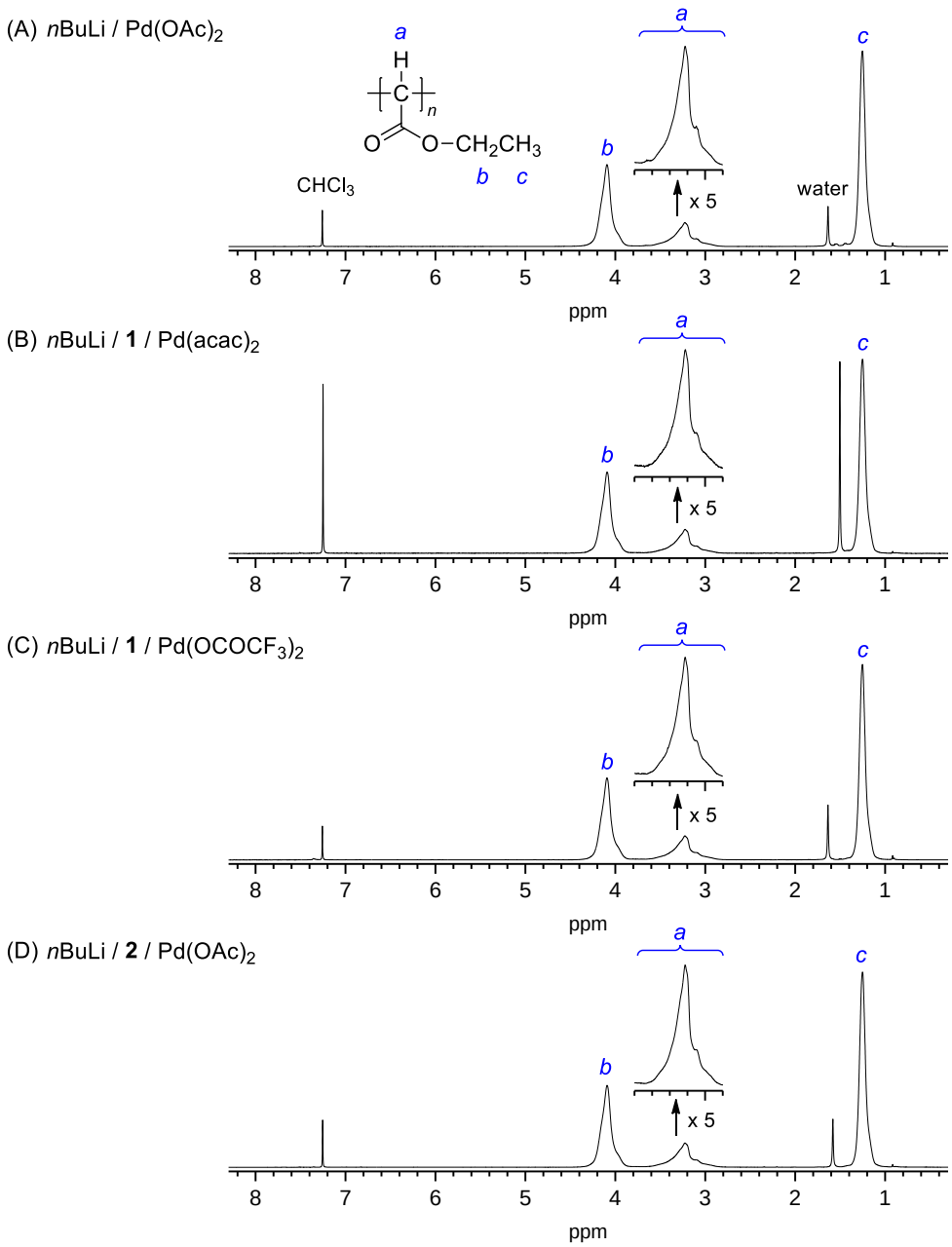


Figure S7. ^{1}H NMR spectra of the polymers obtained by polymerization of **EDA** using various initiating systems [(A) run 9 in Table 1, (B) run 12 in Table 1, (C) run 13 in Table 1, and (D) run 14 in Table 1].

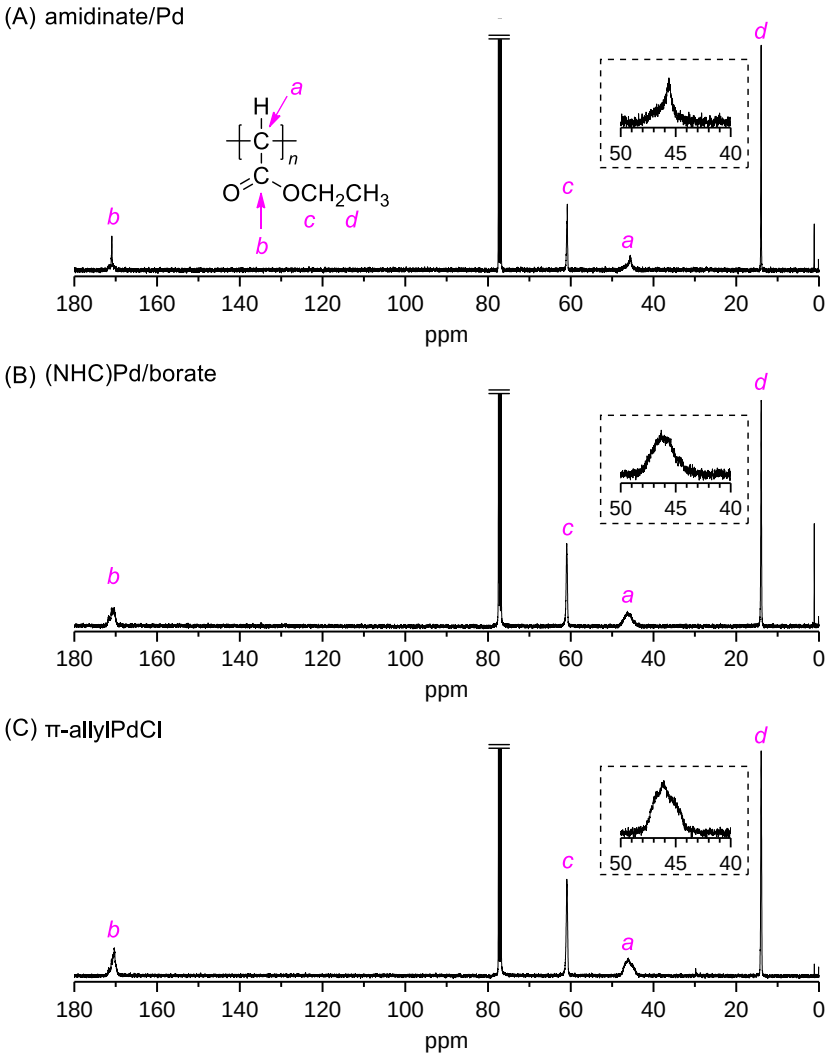


Figure S8. ^{13}C NMR spectra of polymers from **EDA** obtained with (A) amidinate/Pd (run 1 in Table 1), (B) (NHC)Pd/borate (run 2 in Table 1), and (C) π-allylPdCl (run 3 in Table 1).

Differential scanning calorimetry (DSC) measurements were carried out for polymers obtained with amidinate/Pd system (Figure S9). Glass transition temperatures (T_gs) for **EDA** and **BDA** polymers were observed at −19°C (M_n = 44,800, M_w/M_n = 2.28) and 23°C (M_n = 96,300, M_w/M_n = 2.00), respectively, which are lower than those of syndiotactic polymers obtained with a Rh(diene) initiator [**EDA** polymer: 22 °C (M_w = 150 kDa, M_w/M_n = 3.6) and **BDA** polymer: 52 °C (M_w = 370 kDa, M_w/M_n = 2.4)].[1] These comparisons of T_gs clearly show an effect of tacticity on the thermal behavior. On the other hand, T_gs of atactic **EDA** and **BDA** polymers obtained with (NHC)Pd/borate have been reported to be 6 °C (M_n = 19,300, M_w/M_n = 1.37) and 14 °C (M_n = 22,900, M_w/M_n = 1.60),[2] respectively, and thus the relationship of T_g and tacticity of the polymers is not fully understandable at present.

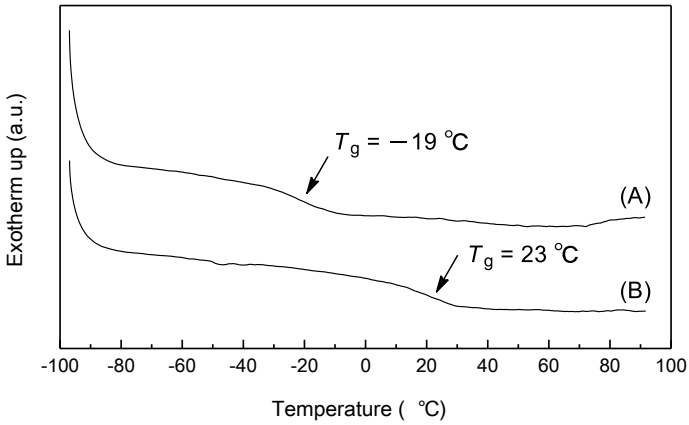


Figure S9. DSC curves of the polymers obtained from (A) **EDA** (M_n = 44,800, M_w/M_n = 2.28) and (B) **BDA** (M_n = 96,300, M_w/M_n = 2.00).

References

(1) E. Jellema, A. L. Jongerius, G. A. van Ekenstein, S. D. Mookhoek, T. J. Dingemans, E. M. Reingruber, A. Chojnacka, P. J. Schoenmakers, R. Sprenkels, E. R. H. van Eck, J. N. H. Reek and B. de Bruin, *Macromolecules*, 2010, **43**, 8892-8903.

(2) E. Ihara, H. Takahashi, M. Akazawa, T. Itoh and K. Inoue, *Macromolecules*, 2011, **44**, 3287-3292.