Electronic Supplementary Information

A Ligand Exchange Strategy for One-Pot Sequential Synthesis of (Hyperbranched Polyethylene)-*b*-(Linear Polyketone) Block Polymers

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Materials

The cationic Pd-diimine complex **1** was synthesized according to the literature procedure[1] and was structurally characterized with ^{1}H NMR in $CDCl_3$. (COD)PdMeCl was synthesized according to a literature procedure.[2] Ultra-high purity N_2 (99.97%) and polymer-grade ethylene (both from Praxair) were purified by passing through 3Å/5Å molecular sieve and Oxiclear columns to remove moisture and oxygen, respectively, before use. Carbon monoxide (99.5%) was purchased from Praxair and was used as received. 4-*Tert*-butylstyrene (TBS, 93%, Aldrich) was used as received. Chlorobenzene (HPLC grade, Fisher Scientific) and dichloromethane (HPLC grade, Fisher Scientific) were dried with a solvent purification system (Innovative Technology). Other chemicals, including $AgSbF_6$ (98%, Aldrich), methanol (ACS reagent grade, Fisher Scientific), and tetrahydrofuran (ACS reagent and HPLC grades, Fisher Scientific), were all used as received. All the manipulations involving air- and/or moisture-sensitive compounds were conducted using standard Schlenk techniques or in a glovebox filled with dry N_2.

Characterizations and Measurements

All proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Gemini 2000 200 MHz spectrometer at ambient temperature using $CDCl_3$ as solvent. Polymer characterization with differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 DSC equipped with a refrigerated cooling system (RCS) under a N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. A N_2 purging flow of 50 mL/min was used. Samples (~ 5 mg) were heated from room temperature to 180 ºC at 10 ºC /min and cooled to –90 ºC at 5 ºC /min, and the data were then collected on the second heating ramp from –90 ºC to 180 ºC at 10 ºC/min.

Polymer characterization with gel permeation chromatography (GPC) was carried out on a Polymer Laboratories PL-GPC220 system equipped with a triple-detection array comprised of a differential refractive index (DRI) detector (from Polymer Laboratories), a three-angle (45, 90, and 135°) miniDAWN light scattering (LS) detector (from Wyatt Technology) at a laser wavelength of 687 nm, and a four-bridge capillary viscosity detector (from Polymer Laboratories). One guard column (PL# 1110−1120) and three 30 cm columns (PLgel 10 μm MIXED-B 300 × 7.5 mm) were used for polymer fractionation. HPLC-grade THF was used as the mobile phase at a flow rate of 1.0 mL/min. The whole GPC system, including columns and detectors, was maintained at 33 °C. Polymers solutions at a concentration between 1-3 mg/mL were injected into the columns at an injection volume of 200 μL. Astra software from Wyatt Technology was used to collect and analyze the data from all three detectors. Two polystyrene narrow standards (from Pressure Chemicals) with a weight-average molecular weight (M_w) of 30 and 200 kg/mol, respectively, were used for the normalization of LS signals from three detecting angles, and for the determination of interdetector delay volume and band broadening, respectively. The DRI increment (d*n*/d*c*) value of the polyketone was determined to be of 0.151 mL/g with an on-line method. The values of 0.078 and 0.185 mL/g were used for hyperbranched polyethylenes and polystyrenes,[3] respectively. For each block copolymer synthesized through sequential polymerization with ligand exchange, the *dn/dc* value was calculated from the mass content of polyethylene (x_{PE}) according to the following equation:

$$(dn/dc)_{block\ polymer} = (dn/dc)_{PE} \times x_{PE} + (dn/dc)_{PK} \times (1 - x_{PE})$$

in which $(dn/dc)_{PE}$ = 0.078 mL/g, $(dn/dc)_{PK}$ = 0.151 mL/g, and x_{PE} was calculated from the ^{1}H NMR spectrum of the copolymer.

Synthesis of 2,2'-bipyridine-PdMeCl (2)

A literature procedure was used for the synthesis.[4] 2,2'-Bipyridine (1.64 g, 10.5 mmol) in 10 mL of toluene was added dropwise into a flask containing (COD)PdMeCl (2.65 g, 10 mmol) in toluene (25 mL) under the protection of N_2 to form yellow suspension. After being stirred for 1 h, the suspension was concentrated to 10 mL, followed with the addition of anhydrous diethyl ether (50 mL) to precipitate out the product. The supernatant was then removed and the solids were washed by diethyl ether for 3 times and dried overnight under vacuum at room temperature. ^{1}H NMR (25 °C, $CDCl_3$, 200 MHz): δ = 9.20 (d, 2 H, J = 2 Hz), 8.69 (d, 2 H, J = 2 Hz), 8.06 (m, 4 H), 7.55 (m, 2H), 1.03 (s, 3H) ppm.

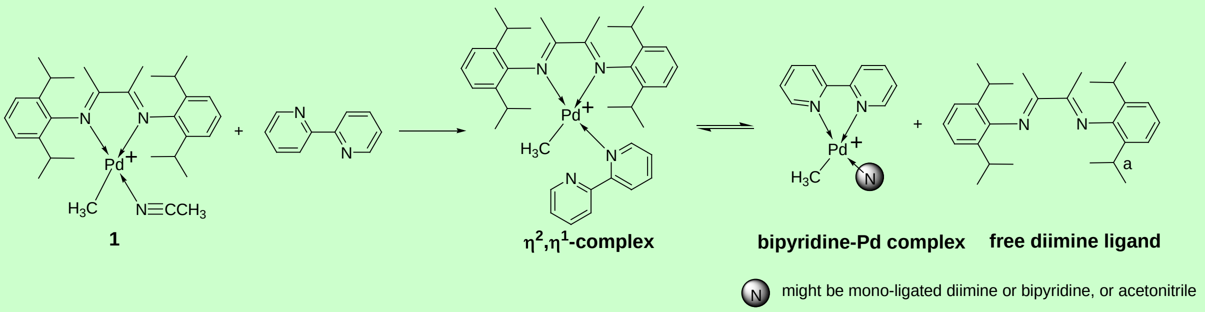
Alternating Polymerization of TBS and CO with 1/bipyridine or 2/AgSbF$_6$

A typical polymerization procedure is as follows. Inside a glove box, complex **1** (80.2 mg, 0.1 mmol) or **2** (31.3 mg, 0.1 mmol) was added into a 250 mL round-bottom flask. The flask was sealed and taken out of the glove box. It was then vacuumed and filled with CO at 1 atm. Anhydrous chlorobenzene (40 mL) was injected into the flask. Subsequently, a chlorobenzene solution (10 mL) containing TBS (4.0 g, 25 mmol) and a prescribed amount of bipyridine (at 1, 2, or 4 equiv., respectively) in the case with **1** or $AgSbF_6$ in the case with **2** (37.8 mg, 0.11 mmol, 1.1 equiv.) was injected into the flask to start the polymerization. During the course of polymerization, CO pressure was maintained at 1 atm by continuous feed from a cylinder and the polymerization temperature was maintained at 25 °C with a water circulator. Samples were taken periodically from the polymerization solution to monitor TBS conversion (by ^{1}H NMR) and polymer molecular weight development (by GPC). For each sampled solution, the polymer was obtained by precipitation in acidified methanol. It was redissolved in THF and precipitated again in methanol. Subsequently, it was dried overnight under vacuum at room temperature and was characterized with GPC.

Table S1 lists TBS conversion and polymer molecular weight data at different polymerization time in each run conducted with **1**/bipyridine or **2**/$AgSbF_6$. Figure S1 shows the ^{1}H NMR spectrum of a representative copolymer obtained in the run with **1**/bipyridine (1:1) at a polymerization time of 2 h. The NMR signals confirm that it is a polyketone with the exclusive presene of alternating TBS/CO structures. Figure S2 plots the kinetic curves (–ln(1–conv.) vs. time) of these runs. Figure S3 shows the GPC elution curves of the polyketones produced with both **1**/bipyridine (1:1 ratio) and **2**/$AgSbF_6$ at different polymerization time.

In Situ ^{1}H NMR Study on Ligand Exchange Between 1 and 2,2'-Bipyridine in the Absence of TBS and CO

To a NMR tube containing **1** (16.0 mg, 0.02 mmol) in 0.3 mL anhydrous $CDCl_3$ was added 0.2 mL of $CDCl_3$ solution containing 0.02 mmol bipyridine (1 equiv.) under nitrogen protection. The ^{1}H NMR spectra were subsequently taken *in situ* after different reaction time at room temperature. Upon the addition of bipyridine, the solution color changed immediately from orange to brown. Figure S4 shows the *in situ* NMR spectra taken at different reaction time, along with the spectra of complexes **1** and **2**, and free diimine ligand for comparison. At 1 min (Figure S4d), a new signal (a_4 at 3.20 ppm) for the CH proton of the isopropyl groups on the diimine ligand appeared while the signal (a_3) for the same proton in **1** was still present at 2.98 ppm. Meanwhile, four additional new peaks (b_4 centered at 1.06 ppm, c_4 at 2.35 ppm, d_4 at –0.21 ppm, and free acetonitrile at 2.03 ppm), not present in **1**, also appeared. The new signals indicate the formation of a new Pd complex. With the increase of reaction time, the intensity of these new peaks increased while the intensity of the peaks for **1** decreased accordingly (see Figure S4e,f). At ca. 15 min, the signals for **1** nearly diminished. The new signals are proposed to result from a η^2,η^1-complex (see reaction equation below), with the diimine ligand being η^2-ligated and pyridine being η^1-ligated. The diimine ligand appears to be dual-ligated in the new complex since only one isopropyl CH signal (a_4 at 3.20 ppm) is present in the spectra. If it was mono-ligated, two signals would be expected to appear. Meanwhile, acetonitrile should be dissociated and replaced with bipyridine given the presence of the free acetonitrile signal at 2.03 ppm. The formation of similar η^2,η^1-complexes has been reported by Brookhart in their study on ligand exchange involving bis-oxazoline Pd catalysts.[5]



Ⓝ might be mono-ligated diimine or bipyridine, or acetonitrile

The concentration of the η^2,η^1-complex increased from 0 to 60 min on the basis of its increasing peak intensities. Afterwards, its concentration decreased indicating it underwent further reaction. At 60 min, dissociated free diimine ligand was released and its concentration increased on the basis of its signals (a_2 at 2.73 ppm, b_2 centered at 2.13 ppm, and c_2 at 2.09 ppm, see Figure S4e,f) of increasing intensity from 60 to 125 min. Concurrently with signals of the η^2,η^1-complex, new signals attributable to the dual-ligated bipyridine (f_5–g_5, f_5'–g_5') and a new methyl proton signal (d_5 at 0.77 ppm, see Figure S4e,f) in the Pd-Me bond also appeared at ca. 1 min and gained intensity over time. The signal was assigned to the Pd-bipyridine complex (see above reaction equation) probably generated from the η^2,η^1-complex following the dissociation and release of the diimine ligand. In addition to the dual-ligated bipyridine ligand, a mono-ligation of either the diimine or pyridine or ligation of acetonitrile may be possible in the Pd-bipyridine complex. The formation of the Pd-bipyridine complex and the dissociation of the diimine ligand confirm the occurrence of the proposed ligand exchange. Further extension of the reaction to 38 h only led to marginal changes in the NMR signals.

Sequential Ethylene "Living" Polymerization and "Living" Alternating Polymerization of TBS and CO via Ligand Exchange

A typical procedure for the sequential polymerization is as follows. An oven-dried round bottom jacketed flask was sealed with a rubber septum. It was vacuumed and filled with ethylene at 1 atm. Chlorobenzene (40 mL) was injected into the flask and the temperature was controlled at 15 °C by a water circulator. After thermal equilibrium for ca. 10 min, a solution of **1** (80.2 mg, 0.1 mmol) in chlorobenzene (10 mL) was injected into the flask to start ethylene polymerization under magnetic stirring. During the polymerization, ethylene pressure was maintained constant at 1 atm and the temperature was controlled at 15 °C. At the end of ethylene polymerization (0.5, 1, or 2 h), a polymerization solution (5 mL) was sampled for the determination of the molecular weight of the polyethylene. Meanwhile, the flask was vacuumed and purged with dry N_2 for 4 cycles to remove residual ethylene, and the flask temperature was reset at 25 °C. The flask was then filled with CO at 1 atm. Subsequently, bipyridine (15.6 mg, 0.1 mmol, 1.1 equiv. of **1**) and TBS (4.0 g, 25 mmol) in chlorobenzene (0.57 mL) were injected into the flask to have the ligand exchange and to start the alternating polymerization of TBS and CO. During the course of the alternating polymerization, CO pressure was maintained at 1 atm and the temperature was maintained at 25 °C. The polymerization solution was sampled periodically to monitor TBS conversion (by ^{1}H NMR) and the molecular weight development of the block copolymer (by GPC). For each sampled solution, the polymer was obtained by precipitation in acidified methanol. It was redissolved in THF and precipitated again in methanol. Subsequently, it was dried overnight under vacuum at room temperature and was characterized with GPC.

Table S2 lists TBS conversion and polymer molecular weight data at different polymerization time in each sequential copolymerization. Figure S5 plots the kinetic curves (–ln(1–conv.) vs. time) in the second-step TBS/CO alternating polymerization of these runs. Representatively, Figure S6 shows the GPC elution curves of the polymers (HBPE homopolymer and the block copolymers) obtained at different polymerization time in run 1 with the first-step ethylene polymerization for 0.5 h. Representatively, Figure S7 shows the ^{1}H NMR spectrum of the block copolymer obtained in run 2 at $t_{TBS/CO}$ = 32 h. The presence of the PK block in the copolymer is confirmed on the basis of the signals *b* (7.01, 6.59 ppm), *c* (4.11 ppm), and *d* (2.98, 2.63 ppm) in the figure, while the methyl signals (*a* at 1.26 ppm) on the *t*-butyl groups overlap with those of the methylene and methine groups in the HBPE block. Figure S8 shows the DSC thermograms for some selected polymers.

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Table S1. Alternating copolymerization of TBS and CO with **1**/bipyridine or **2**/$AgSbF_6$ [a]

Catalyst	Time (h)	TBS Conv.[b] (%)	M_n [c] (kg/mol)	PDI [d]
1	20	0		
2/$AgSbF_6$ (1:1.1)	2	11	6.4	1.15
	4	18	10.7	1.16
	8	35	14.8	1.20
	20	59	23.5	1.25
	32	77	26.2	1.27
	48	83	30.6	1.28
1/bipyridine (1:1)	2	12	5.9	1.12
	4	18	10.1	1.12
	8	30	17.2	1.13
	20	53	27.5	1.17
	32	70	37.4	1.22
	48	80	49.3	1.24
1/bipyridine (1:2)	2	11	5.3	1.12
	4	17	8.6	1.12
	8	24	13.3	1.13
	20	38	22.1	1.17
	32	44	24.0	1.18
	48	51	28.8	1.23
1/bipyridine (1:4)	2	7	3.8	1.12
	4	12	6.4	1.12
	8	21	11.6	1.12
	20	34	18.2	1.15
	32	42	23.0	1.16
	48	48	26.4	1.18

[a] Polymerization conditions: 0.1 mmol Pd complex, TBS at 0.5 M, CO at 1 atm, 50 mL of chlorobenzene as solvent, 25 ºC. [b] Conversion of TBS was calculated from the ^1H NMR spectrum for each sample. [c] The number-average molecular weight (M_n) is absolute value determined with the light scattering detector in triple-detection GPC measurement. [d] polydispersity index (PDI) is determined by RI detector against polystyrene standards.

Table S2. Sequential block copolymerizations of ethylene and TBS/CO through ligand exchange [a]

Run	Ethylene polymn time [b] t_{C2H4} (h)	TBS/CO polymn time [c] $t_{TBS/CO}$ (h)	TBS Conv.[d] (%)	M_n [e] (kg/mol)	PDI [f]
1	0.5	0	0	6.4	1.07
		2	4	12.6	1.09
		4	11	16.5	1.17
		8	24	23.6	1.14
		20	51	32.8	1.18
		32	60	42.0	1.20
		48	72	46.2	1.22
2	1	0	0	10.9	1.14
		2	9	17.5	1.16
		4	15	20.9	1.17
		8	29	27.0	1.17
		20	53	41.1	1.21
		32	62	48.3	1.25
		48	69	49.8	1.34
3	2	0	0	20.6	1.10
		2	7	26.3	1.11
		4	11	30.4	1.21
		8	21	33.6	1.21
		20	40	47.0	1.24
		32	49	52.1	1.29
		48	57	57.9	1.29

[a] Polymerization condition: 0.1 mmol Pd-diimine complex **1**, 50 mL of chlorobenzene as solvent, 15 ºC for first-step ethylene polymerization, 25 ºC for second-step TBS/CO alternating polymerization, TBS at 0.5 M and CO at 1 atm in the second step, 1.1 equiv. bipyridine for ligand exchange. [b] Time for the first-step ethylene polymerization. [c] Time for the second-step TBS/CO alternating polymerization. [d] Conversion of TBS was calculated from the ^{1}H NMR spectrum for each sample. [e] M_n is absolute value determined with the light scattering detector in triple-detection GPC characterization. [f] PDI is determined by RI detector.

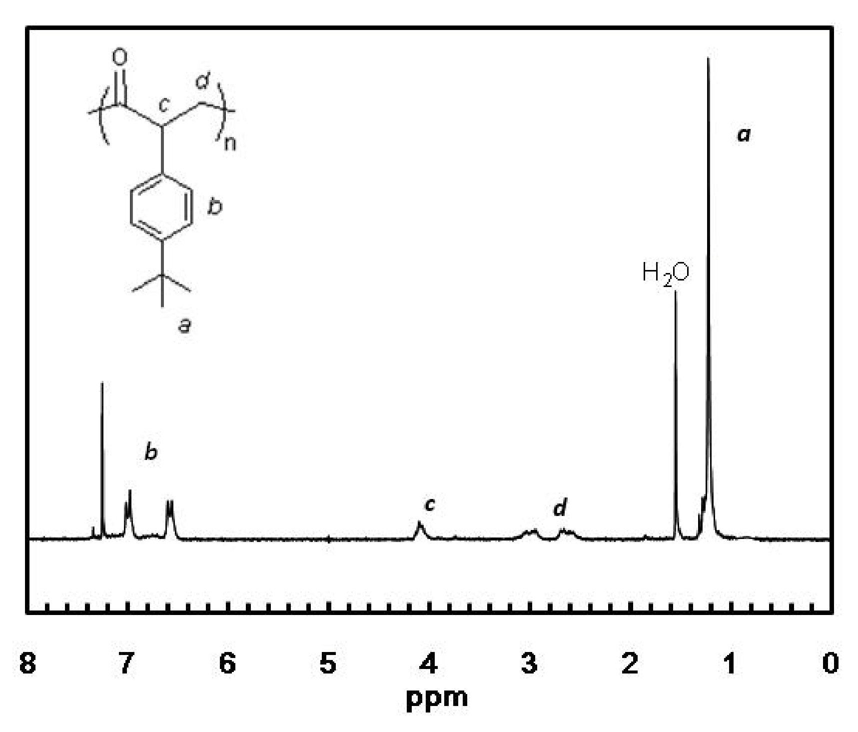

Figure S1. ^{1}H NMR spectrum of a representative TBS/CO alternating copolymer obtained in the run with **1**/bipyridine (1:1) at a polymerization time of 2 h.

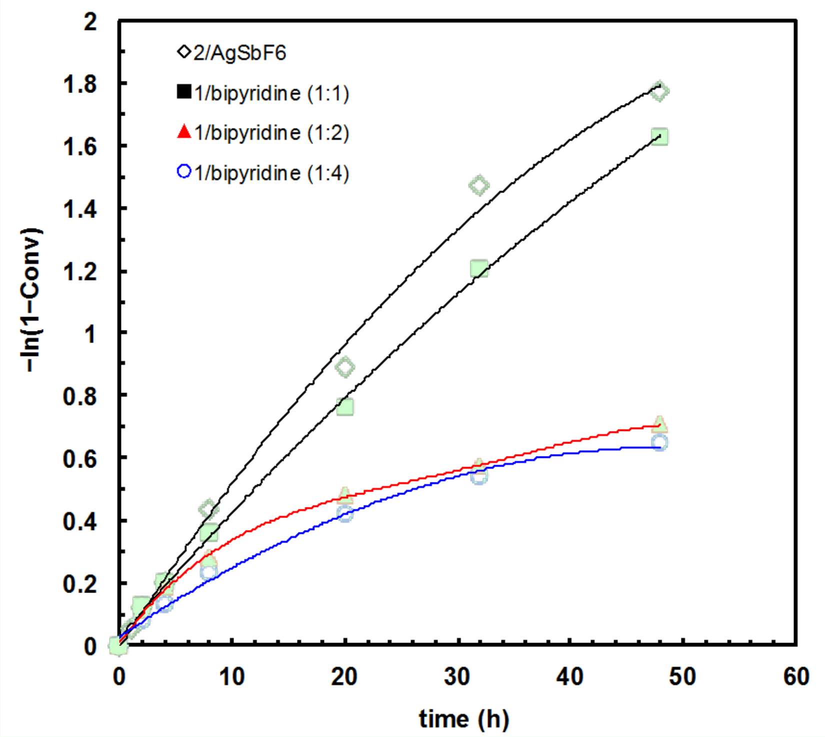

Figure S2. Kinetic curves (–ln(1–conv.) vs. time) of “living” polymerization of TBS and CO with **1**/bipyridine at different ratios and **2**/AgSbF$_6$. See Table S1 for polymerization conditions.

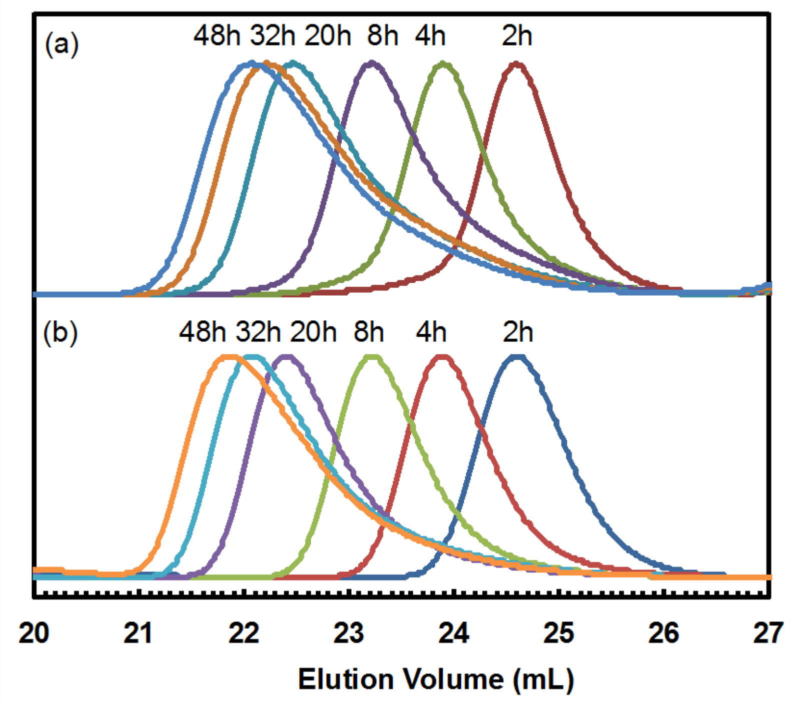

Figure S3. GPC elution curves (recorded from DRI detector) of polyketones obtained in “living” alternating polymerization of TBS and CO with (a) **2**/$AgSbF_6$ and (b) **1**/bipyridine (molar ratio, 1:1), respectively, at different polymerization time.

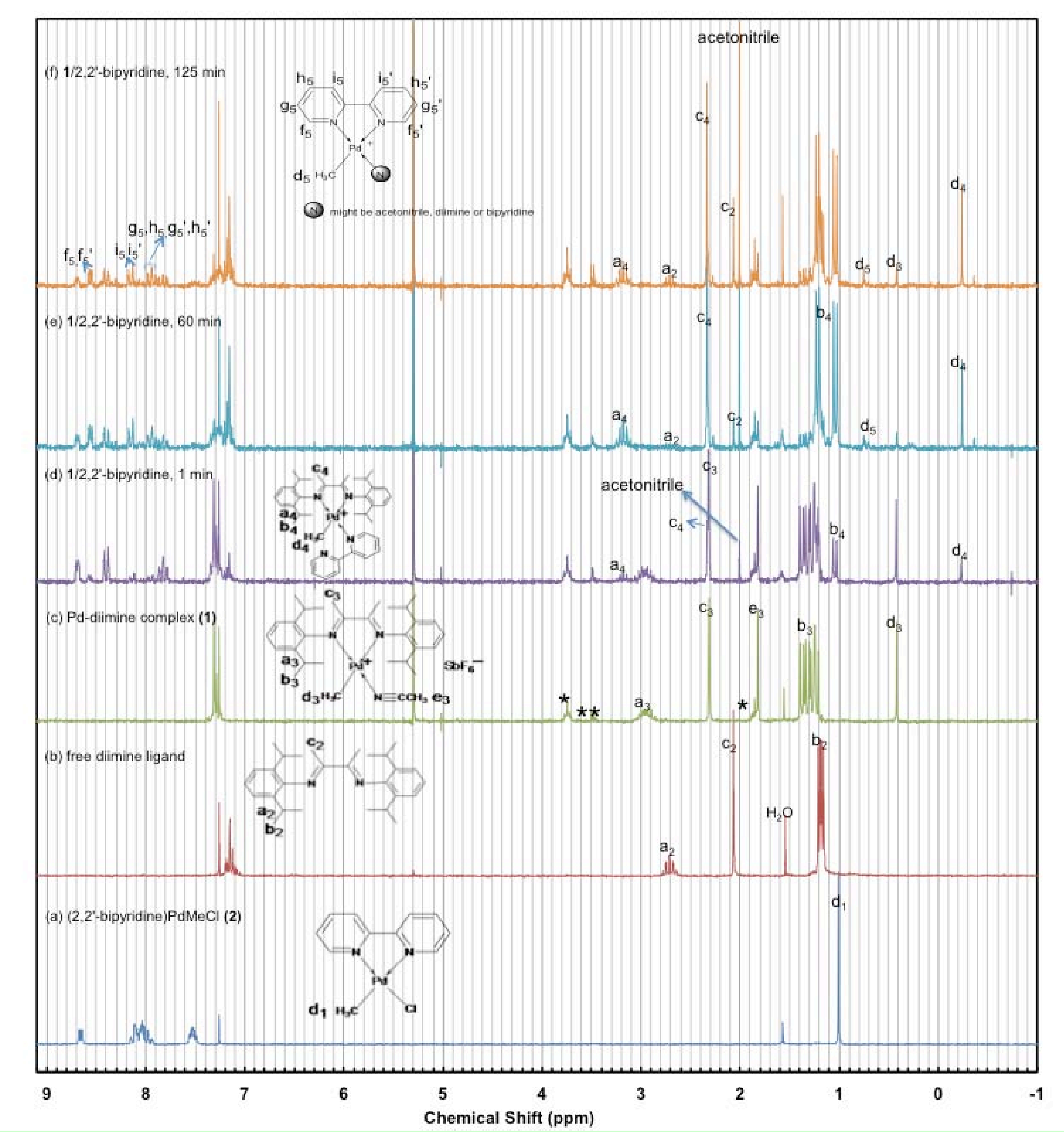

Figure S4. In situ ^{1}H NMR spectra (d–f) of the reaction mixture of Pd-diimine complex **1** and 2,2'-bipyridine (1:1 molar ratio) at different reaction time at room temperature. The spectra (a–c) for (2,2'-bipyridine)PdMeCl (**2**), free diimine ligand, and complex **1** are also included for comparison. The signals marked with an asterisk (*) result from trace tetrahydrofuran or methanol.

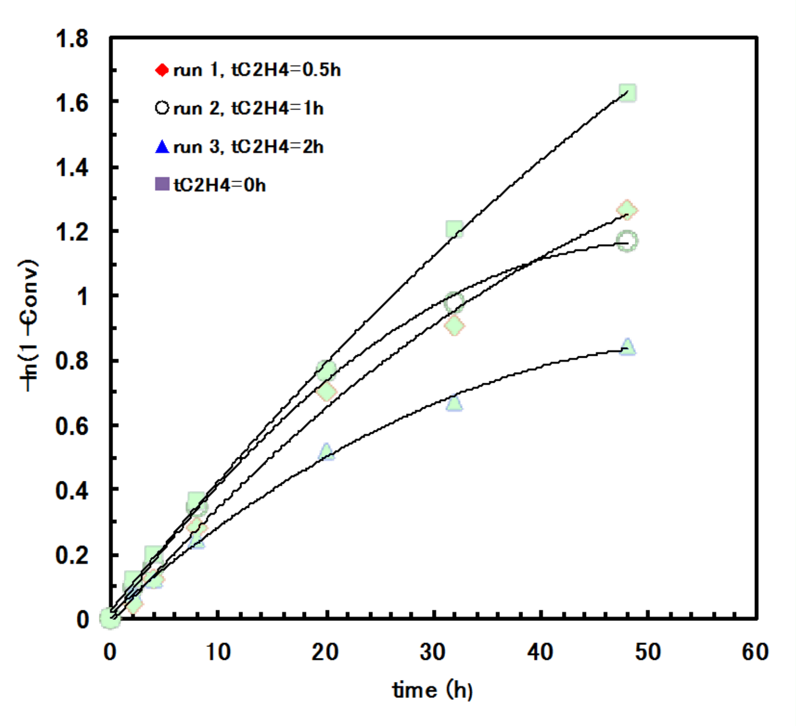

Figure S5. Kinetic curves (–ln(1–conv.) vs. time) of the second-step "living" alternating polymerization of TBS and CO in sequential block copolymerizations with different time (t_{C2H4}) for first-step ethylene polymerization. See Table S2 for polymerization conditions. The run with t_{C2H4} = 0 h is single-step TBS/CO copolymerization with **1**/bipyridine (1:1) shown in Table S1.

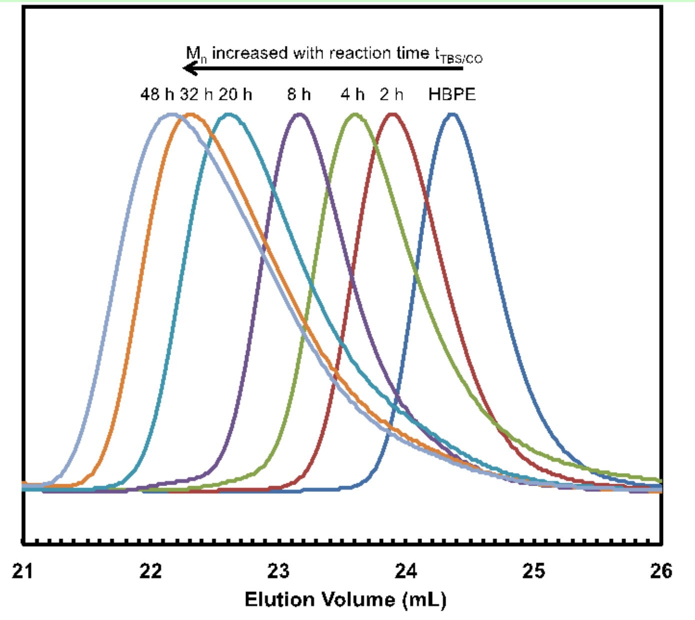

Figure S6. GPC elution curves (recorded from DRI detector) of the polymers obtained in run 1 (see Table S2) at different time in the sequential block copolymerization with the first-step ethylene polymerization for 0.5 h. See Table S2 for polymerization conditions.

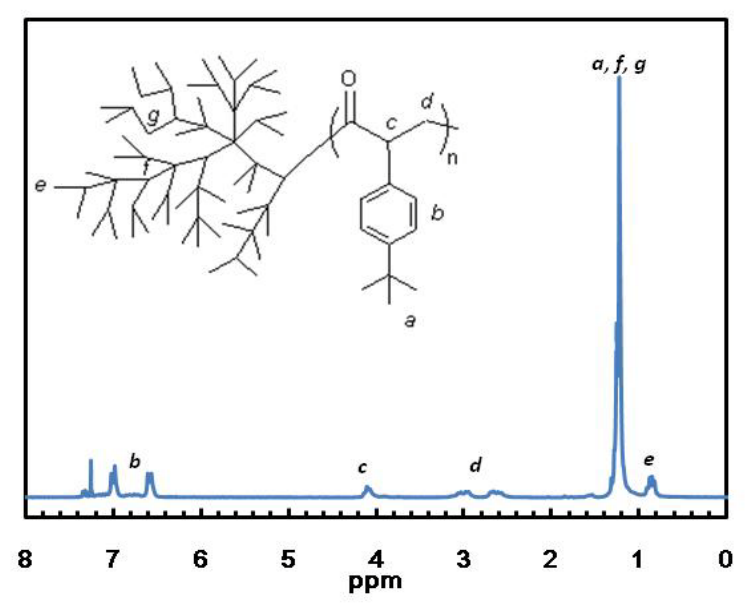

Figure S7. ^{1}H NMR spectrum of a representative HBPE-*b*-PK block copolymer (obtained in run 2 at $t_{TBS/CO}$ = 32 h, see Table S2). In the spectrum, peaks *a* (methyl protons in the *t*-butyl groups), *f* (methine protons in HBPE) and g (methylene protons in HBPE) overlap.

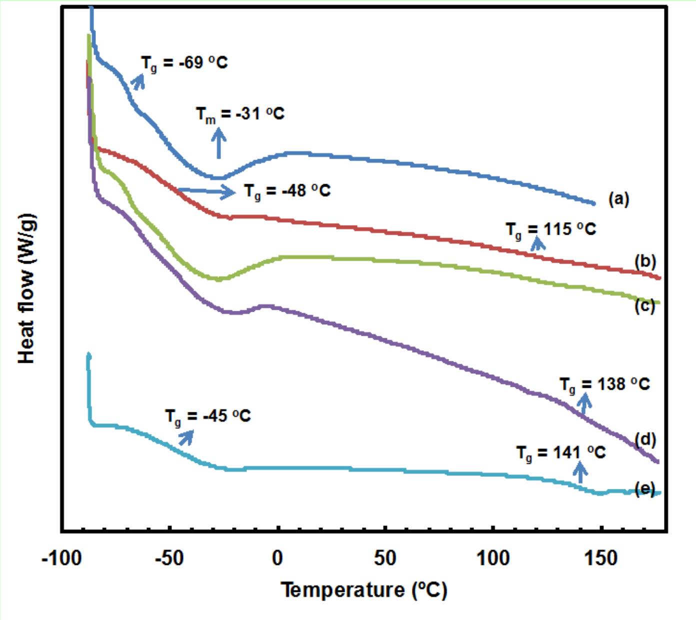

Figure S8. DSC thermograms of some selected polymers in Table S2: (a) run 1 HBPE homopolymer block ($t_{TBS/CO}$ = 0 h, M_n = 6.4 kg/mol); (b) run 1 block copolymer obtained at $t_{TBS/CO}$ of 4 h (M_n of PK block = 10 kg/mol); (c) run 2 HBPE homopolymer block ($t_{TBS/CO}$ = 0 h, M_n = 10.9 kg/mol); (d) run 2 block copolymer obtained at $t_{TBS/CO}$ of 2 h (M_n of PK block = 6.6 kg/mol); and (e) run 2 block copolymer obtained at $t_{TBS/CO}$ of 32 h (M_n of PK block = 37.4 kg/mol).