Supporting Information

Selective Scission of Pyridine–Boronium Complexes: Mechanical Generation of Brønsted Bases and Polymerization Catalysts

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1. General Considerations

Materials and Methods. Bis(pentafluorophenyl)boron chloride (**1–**Cl),[1] 4-pyridinyl-2-bromo-isobutyrate (**PyI**),[2] 4-pyridinyl pivalate (**PyPiv**),[3] and all $\mathbf{PyP_M}$ polymers (where M = M_n in kDa)[2] were prepared according to literature procedures. Methyl acrylate (MA) was purified by distillation under an inert atmosphere. All other chemical reagents were purchased from commercial sources and used without additional purification. All syntheses were performed under an inert N_2 atmosphere using standard Schlenk or glovebox techniques. Solvents were dried by molecular sieves (3 Å) or Al_2O_3 and deoxygenated using a Vacuum Atmospheres Company solvent purification system, and then subsequently stored over molecular sieves (3 Å) in a drybox. ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded using a Varian 300 or 400 MHz spectrometer. Chemical shifts δ (in ppm) for ^{1}H and ^{13}C NMR are referenced to $SiMe_4$ using the residual solvent as an internal standard ($CDCl_3$; ^{1}H NMR δ = 7.24 ppm; and ^{13}C NMR δ = 77.0 ppm). Chemical shifts for ^{19}F NMR and ^{11}B NMR are referenced to external standards ($CFCl_3$, δ = 0 ppm for ^{19}F NMR and $BF_3{\cdot}Et_2O$, δ = 0 ppm for ^{11}B NMR). Coupling constants (*J*) are expressed in hertz (Hz). Thermogravimetric analyses (TGA) were performed using a Mettler-Toledo TGA/SDTA851e under an atmosphere of N_2 at a temperature scan rate of 10 °C min^{-1}. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E instrument (ESI or CI). Elemental analyses were performed at Midwest Microlab, LLC (Indianapolis, IN).

Macromolecular Characterization. Gel permeation chromatography (GPC) was performed on a Waters HPLC system consisting of three Viscotek I-series columns (2 × GMHHRH and 1 × G3000HHR) arranged in series and thermostated to 40 °C, a 1515 isocratic pump, and a 2414 refractive index (RI) detector. Molecular weight and polydispersity data are reported relative to polystyrene standards in dimethylformamide (DMF, 0.1 M LiBr). For the fluorinated polymers

(i.e., **p(4)**), absolute molecular weight and polydispersity were determined in acetone using a Viscotek system equipped with a VE 1122 pump, a VE 7510 degasser, two fluorinated polystyrene columns (I-MBHW-3078 and I-MBLMW-3078) thermostated to 30 °C (using a ELDEX CH 150 column heater) and arranged in series, a Viscotek 270 Dual Detector (light scattering detector and differential viscometer), and a VE 3580 refractive index detector.

General Sonication Conditions. The sonication experiments were performed under an argon atmosphere using a Sonics & Materials VC-505 Liquid Cell Ultrasonic processor operating at 20 kHz equipped with a 12.8 mm replaceable titanium probe tip. Custom Suslick cells[4] were fabricated in house. An argon line was threaded through a septum attached to one cell side-arm and placed in solution, ensuring no contact with the probe. Prior to each experiment, 30 min of equilibration at 4 °C under an argon purge was performed. Pulsed ultrasound (1.0 s on, 1.0 s off) was supplied at 23% power (10.1 W cm^{-2}) for 4 h. All sonications were performed on solutions with a final volume of 10 mL in a Suslick cell under a positive pressure of argon. The external temperature was maintained at 4 °C by the use of a cold room and ice-water bath. The internal temperature was monitored over the course of the experiment via a thermocouple and was measured to be ≤ 9 °C.

2. Syntheses and Characterization Data

[(1)(PyPiv)$_2$][Cl]. In a nitrogen filled glovebox, **PyPiv** (0.094 g 0.526 mmol) was added to a stirred solution of **1**–Cl (0.100 g 0.263 mmol) in CH_2Cl_2 (10 mL). After stirring the resulting solution for 12 h at room temperature, the residual solvent was removed under reduced pressure. The resulting residue was taken up in a minimal amount of CH_2Cl_2 (1 mL) and added slowly to rapidly stirred hexanes (20 mL) which resulted in the precipitation of a white solid. The solution

was filtered off and the solid was washed with hexanes (3 × 10 mL) followed by drying under reduced pressure to afford the desired product as a white crystalline solid (0.165 g, 85% yield). T_d = 306.7 °C. ^{1}H NMR ($CDCl_3$, 400.27 MHz): δ 1.38 (s, 18H), 7.59 (d, ^3J = 7.2 Hz, 4H), 8.89 (d, ^3J = 6.8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 27.02, 40.15, 118.56, 139.03, 146.45, 148.15, 149.61, 162.85, 174.44, 180.77. ^{19}F NMR ($CDCl_3$, 282.41 MHz): δ –163.24 (td, ^3J = 8.84 Hz, 4F), –155.61 (t, ^3J = 13.6 Hz, 2F), –132.80 (dd, ^3J = 7.97 Hz, 4F). ^{11}B NMR ($CDCl_3$, 96.22 MHz): δ 1.48 (s). HRMS: $[M]^+$ calcd. for $C_{32}H_{26}B\ N_2O_4F_{10}$: 703.18259. Found: 703.18145. Anal. Calcd. for $C_{32}H_{26}N_2O_4F_{10}BCl$: C, 52.02; H, 3.55; N, 3.79; Found: C, 52.37; H, 3.61; N, 3.82.

Representative Procedure for [(1)(PyP$_M$)$_2$][Cl] (M = 2, 7, 11, 21, 25 and 66): Synthesis of [(1)(PyP$_{66}$)$_2$][Cl]. In a nitrogen filled glovebox, **1**–Cl (0.62 mg, 1.67 μmol) from a 2.68 mM stock solution in CH_2Cl_2 was added to a viscous solution of **PyP$_{66}$** (200 mg, 3.33 μmol) in CH_2Cl_2 (5 mL), and the resulting solution was stirred at room temperature for 12 h. The resulting viscous solution was then slowly added to excess methanol (50 mL) which caused a polymeric material to precipitate as a gummy solid. After decanting the supernatant, the residual polymer was washed with methanol (5 × 20 mL), collected via filtration, and then dried under vacuum to afford the desired polymer [(**1**)(**PyP$_{66}$**)$_2$][Cl] (199 mg, 96% yield). GPC (DMF, 0.1 M LiBr): M_n = 120 kDa, PDI = 1.3. Yields and molecular weight determinations for M = 7, 11, 21 and 25 prepared by this method are summarized in Table S1.

[(1)(PyP$_2$)$_2$]. In a nitrogen filled glovebox, **1**–Cl (1.4 mL, 15 μmol) from a 0.01 M stock solution in $CDCl_3$ was added to a viscous solution of **PyP$_2$** (50 mg, 29 μmol) in $CDCl_3$ (2 mL), and the resulting solution was stirred at room temperature for 12 h. The resulting polymer was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 8.89 (d, ^3J = 6.9 Hz),

7.54 (d, ^3J = 6.9 Hz), 3.61 (br s, 80H), 2.26 (br m, 30H), 1.91 (br m, 15H), 1.63 (br s, 30H), 1.45 (br m, 9H), 1.24 (s, 12H). ^{19}F NMR ($CDCl_3$, 282.41 MHz): δ –163.31 (td, ^3J = 8.84 Hz, 4F), –155.56 (t, ^3J = 13.6 Hz, 2F), –132.02 (dd, ^3J = 7.97 Hz, 4F). ^{11}B NMR ($CDCl_3$, 96.22 MHz): δ 1.48 (s).

[(2)(PyP$_{110}$)]. In a nitrogen filled glovebox, tris(pentafluorophenyl)boron (**2**) (0.1 mL, 0.01 M in CH_2Cl_2, 0.47 mg, 9.1 × 10^{-4} mmol) was added to a viscous solution of **PyP$_{110}$** (100 mg, 9.1 × 10^{-4} mmol) in CH_2Cl_2 (5 mL), and the resulting solution was stirred at room temperature for 12 h. The resulting viscous solution was then slowly added to excess methanol (50 mL) which caused a polymeric material to precipitate as a gummy solid. After decanting the supernatant, the residual polymer was washed with methanol (5 × 20 mL), collected via filtration, and then dried under vacuum to afford the desired polymer [(**2**)(**PyP$_{110}$**)] (88 mg, 88% yield). GPC (DMF, 0.1 M LiBr): M_n = 110 kDa, PDI = 1.3.

[(2)(PyP$_2$)]. In a nitrogen filled glovebox, tris(pentafluorophenyl)boron (**2**) (2.9 mL, 0.01 M in $CDCl_3$, 0.47 mg, 2.9 × 10^{-2} mmol) was added to a viscous solution of **PyP$_2$** (50 mg, 2.9 × 10^{-2} mmol) in $CDCl_3$ (2 mL), and the resulting solution was stirred at room temperature for 12 h. The resulting polymer was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 8.52 (d, ^3J = 6.9 Hz), 7.54 (d, ^3J = 6.9 Hz), 3.61 (br s, 40H), 2.26 (br m, 15H), 1.91 (br m, 7H), 1.63 (br s, 15H), 1.45 (br m, 5H), 1.24 (s, 6H). ^{19}F NMR ($CDCl_3$, 282.41 MHz): δ –163.17 (s, 6F), –156.56 (s, 3F), –131.88 (d, ^3J = 18.9 Hz, 6F). ^{11}B NMR ($CDCl_3$, 96.22 MHz): δ 1.8 (s).

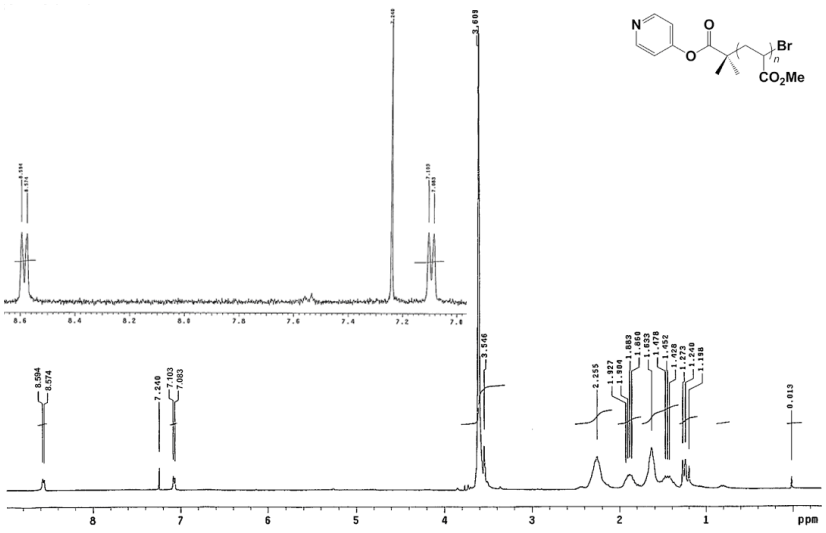

Figure S1. ^{1}H NMR spectrum of **PyP$_2$** ($CDCl_3$).

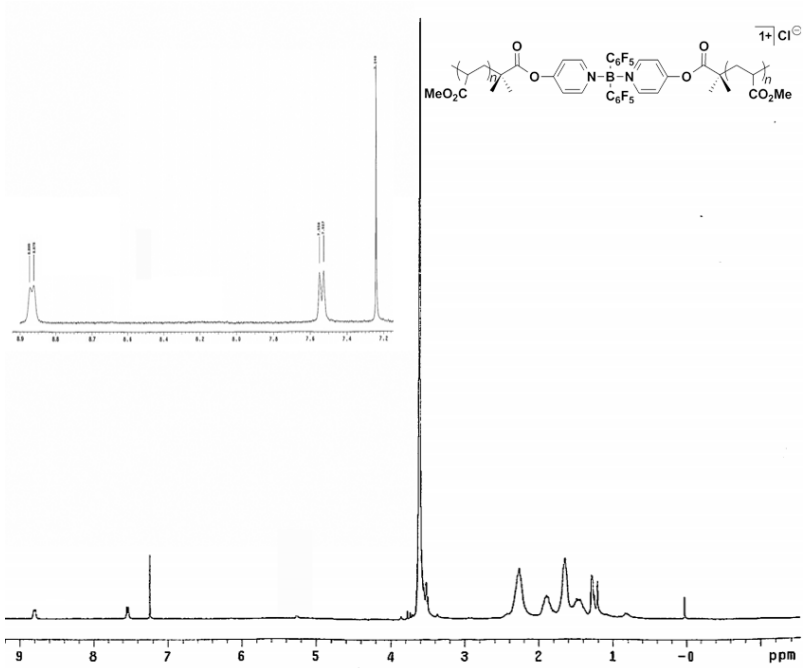

Figure S2. ^{1}H NMR spectrum of [(**1**)(**PyP$_2$**)$_2$][Cl] ($CDCl_3$).

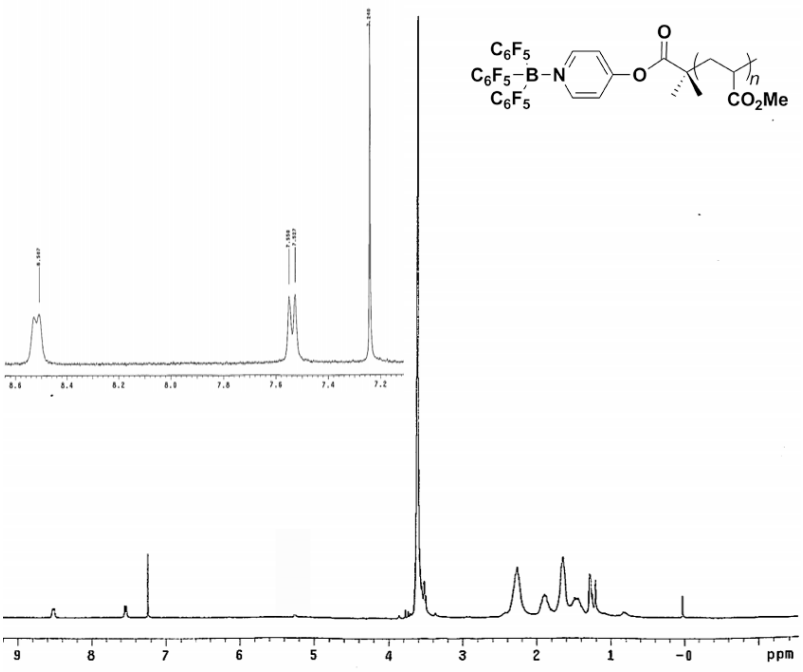

Figure S3. ^{1}H NMR spectrum of [(**2**)(**PyP$_2$**)] ($CDCl_3$).

Table S1. Selected Yield and Molecular Weight Data.[a]

	Pre-Coupled Polymers			Post-Coupled Polymers			
	Yield	M_n [kDa]	PDI	Product	Yield	M_n [kDa]	PDI
PyP$_2$	51%	1.7 [b]	—	[(**1**)(**PyP$_2$**)$_2$][Cl] [c]	—	1.7[b]	—
				* [(**2**)(**PyP$_2$**)] [c,d]	—	3.4[b]	—
PyP$_7$	72%	6.8	1.2	[(**1**)(**PyP$_7$**)$_2$][Cl]	92%	13	1.2
PyP$_{11}$	79%	11	1.2	[(**1**)(**PyP$_{11}$**)$_2$][Cl]	94%	23	1.1
PyP$_{21}$	89%	21	1.2	[(**1**)(**PyP$_{21}$**)$_2$][Cl]	89%	41	1.2
PyP$_{25}$	92%	25	1.4	[(**1**)(**PyP$_{25}$**)$_2$][Cl]	97%	48	1.3
PyP$_{66}$	83%	66	1.4	[(**1**)(**PyP$_{66}$**)$_2$][Cl]	96%	120	1.3
PyP$_{110}$	94%	110	1.3	* [(**2**)(**PyP$_{110}$**)] [d]	88%	110	1.3

[a] Pre- and post-coupled polymers refer to **PyP$_M$** before and after coupling with **1**–Cl or **2**. Number- and weight-averaged molecular weights (M_n and M_w, respectively) were determined by GPC (eluent = DMF, 0.1 M LiBr) and are reported relative to polystyrene standards. Polydispersity indices (PDIs) were calculated using the equation PDI = M_w / M_n. [b] Determined by ^{1}H NMR spectroscopy in $CDCl_3$. [c] Coupling reaction was monitored via integration of the ^{1}H NMR signals attributed to the *meta*-positions in the pyridine moiety in free **PyP$_2$** (δ = 7.08 ppm) versus its boron-coordinated derivative (δ = 7.55 ppm) (in $CDCl_3$). [d] The asterisk (*) is used to visually distinguish the entries for the end-capped polymers [(**2**)(**PyP$_M$**)].

3. Polymer Chain Scission Experiments: Kinetic Analyses

General Procedure. For each experiment, a Suslick cell was charged with a 10 mL solution of CH_3CN containing [(**1**)(**PyP$_M$**)$_2$][Cl] (10 mg) and 20 equiv of HBF_4. A 0.40 mL aliquot was withdrawn (t = 0) and sonication was then initiated. At timed intervals (t), sonication was stopped, a 0.40 mL aliquot was withdrawn, and the sonication was restarted. In this manner, 0.40 mL aliquots were withdrawn at t = 4, 8, 16, 30, 60, 120, 180 and 240 min. Each aliquot was concentrated to dryness under high vacuum. The resulting residues were then dissolved in DMF (0.10 mL) and analyzed by GPC (see Tables S1 and S2 and Figures S4–S6).

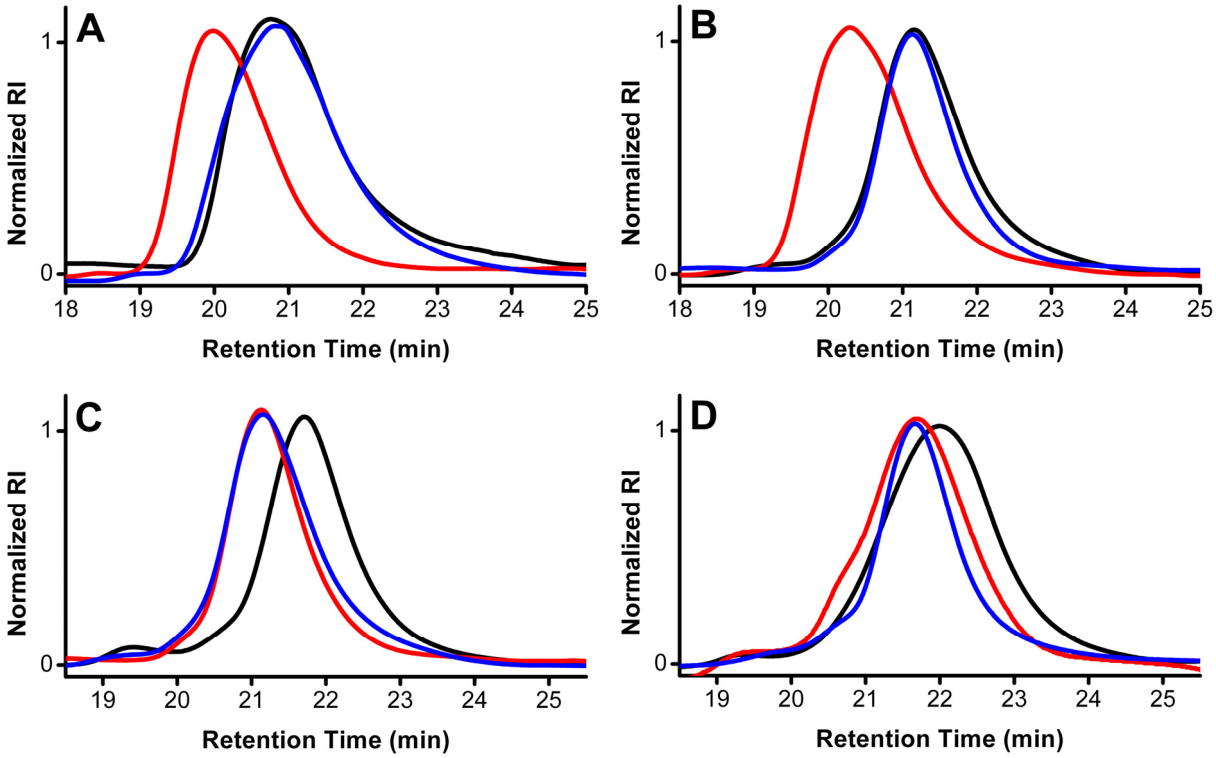

Figure S4. Gel permeation chromatograms of [(**1**)(**PyP$_M$**)$_2$][Cl] before and after sonication for 4 h at 4 °C (red and blue, respectively) overlaid with **PyP$_M$** for comparison (black). For [(**1**)(**PyP$_{25}$**)$_2$][Cl] (**A**) and [(**1**)(**PyP$_{21}$**)$_2$][Cl] (**B**), the observed M_n decreased from 48 to 24 kDa and from 41 to 21 kDa, respectively, following sonication. For [(**1**)(**PyP$_{11}$**)$_2$][Cl] (**C**) and [(**1**)(**PyP$_7$**)$_2$][Cl] (**D**), no significant change in M_n was observed.

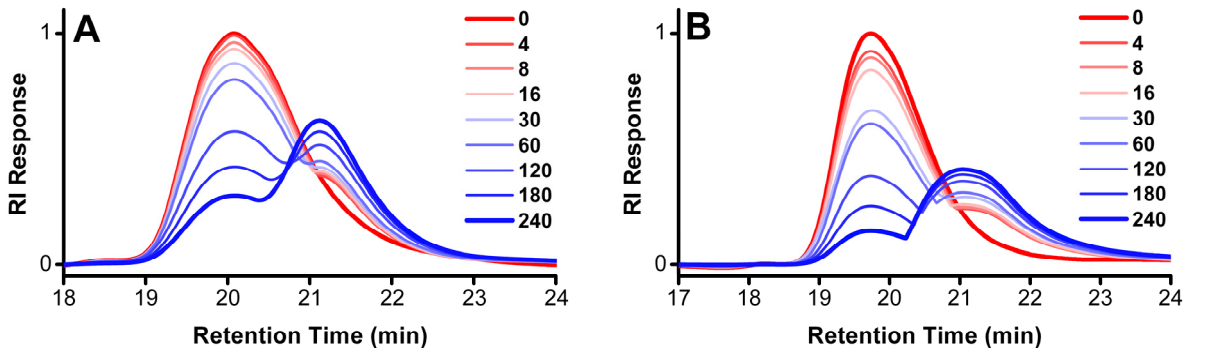

Figure S5. Gel permeation chromatograms acquired at timed intervals during the sonication of [(**1**)(**PyP$_{21}$**)$_2$][Cl] and [(**1**)(**PyP$_{25}$**)$_2$][Cl] (**A** and **B**, respectively; t = 0, topmost red). The gradual decrease in peak intensity observed at retention times = 20.29 and 20.01 min (**A** and **B**, respectively; t = 4–16 min, fading red) was accompanied by the appearance of a peak at retention times = 20.97 and 20.81 min over the course of 4 h (**A** and **B**, respectively; t = 30–240 min, darkening blue). All aliquots analyzed consisted of an initial polymer concentration of 4 mg/mL.

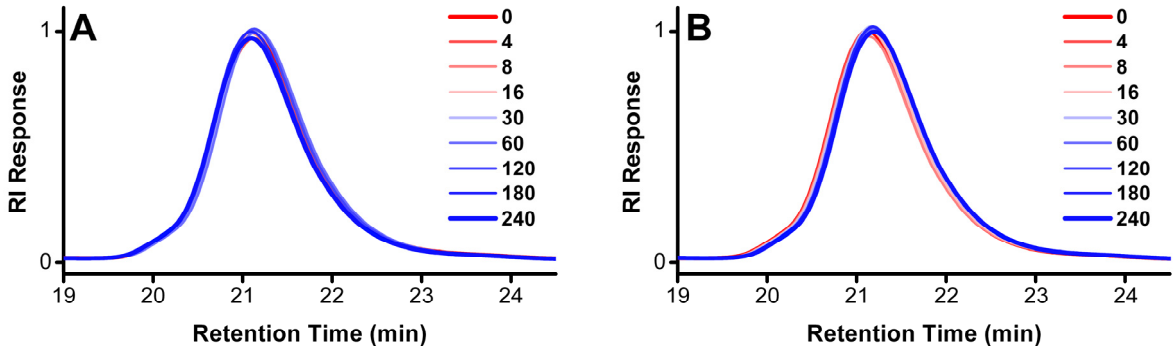

Figure S6. Gel permeation chromatograms acquired at timed intervals during the sonication of [(**1**)(**PyP$_{11}$**)$_2$][Cl] (retention time = 20.85 min) and [(**1**)(**PyP$_7$**)$_2$][Cl] (retention time = 21.09 min) (**A** and **B**, respectively; t = 0, topmost red). No change in peak intensities were observed for these materials. All aliquots analyzed consisted of an initial polymer concentration of 4 mg/mL.

Additional Evidence for Reversible Bond Dissociation. A Suslick cell was charged with a 10 mL solution of [(**1**)(**PyP$_M$**)$_2$] (10 mg) in CH_3CN and then subjected to sonication under the conditions described above. After 2 h, the solution was concentrated under reduced pressure, and the resulting residue was then dissolved in DMF (0.10 mL) and analyzed by GPC (e.g., Figure S7). No difference in molecular weight or polydispersity was observed in the GPC traces before and after sonication (see Table S2), indicating that polymer chains recombined upon concentration and that the boron-pyridine bond dissociation process was reversible.

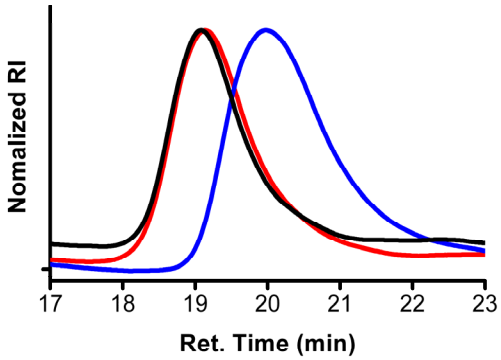

Figure S7. Gel permeation chromatograms of [(**1**)(**PyP$_{66}$**)$_2$] before (red) and after (black) sonication for 4 h at 4 °C in the absence of HBF_4 followed by concentration. The same experiment was also performed in the presence of 20 equiv. HBF_4 (blue).

Table S2. Retention Time and Molecular Weight Data.[a]

			[(**1**)(**PyP$_M$**)$_2$]			
	PyP$_M$		**Pre-Sonication**		**Post-Sonication**	
	Retention Time (min)[b]	M_p [kDa][c]	Retention Time (min)[b]	M_p [kDa][c]	Retention Time (min)[b]	M_p [kDa][c]
P$_7$	21.98	5.9	21.09	13	21.08	13
P$_{11}$	21.70	10	20.85	23	20.87	23
P$_{21}$	21.01	19	20.29	41	20.97	20
P$_{25}$	20.75	25	20.01	48	20.81	24
P$_{66}$	19.86	64	19.11	121	19.87	61

[a] Peak retention times by GPC analysis (eluent = DMF, 0.1 M LiBr). The RI intensity at these retention times was used to calculate the rate of bond scission (see text). [b] M_p refers to the molecular weight associated with the observed peak of the signal at the given retention time.

4. Colorimetric Indicator Experiments for Detecting Free Pyridine

General Procedure. To qualitatively confirm that $\mathbf{PyP_M}$ was generated upon sonication of [(**1**)($\mathbf{PyP_M}$)$_2$][Cl], a base-sensitive indicator ([**3**H][BF_4]) was employed to exhibit a colorimetric response from purple-to-yellow upon deprotonation. For each sonication experiment, a Suslick cell was charged with a 10 mL solution of CH_3CN containing 10 μM each of [**3**H][BF_4] and analyte (i.e. [(**1**)($\mathbf{PyP_M}$)$_2$][Cl], [(**2**)($\mathbf{PyP_{110}}$)] or [(**1**)(**PyPiv**)$_2$][Cl] + 90 kDa PMA). For experiments that afforded a purple-to-yellow color change, the integrity of the indicator was confirmed by subsequently adding 1 equiv of HBF_4 to restore the original purple color. For experiments that did not afford a color change, UV/vis spectra were acquired to confirm the observation (see Figure S8 for a representative example). Results are summarized in Figure 2 and Table S3.

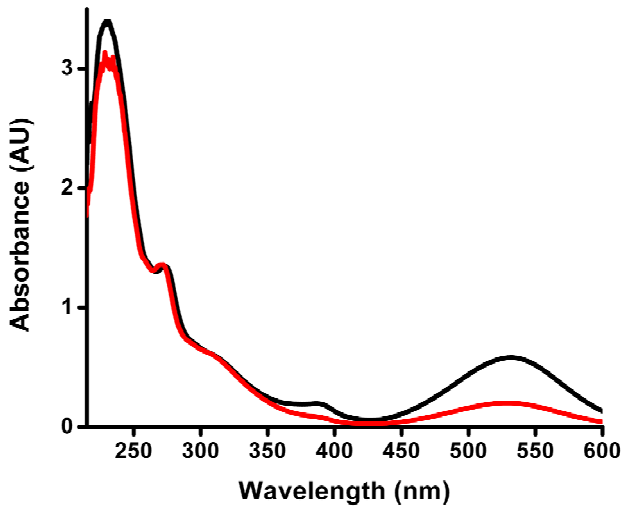

Figure S8. UV/vis spectra of CH_3CN solutions containing 10 μM [(**2**)($\mathbf{PyP_{110}}$)] and 10 μM [**3**H][BF_4] before (red) and after (black) sonication. The slight increase in absorbance at 230 and 540 nm (corresponding to polymer- and dye-based transitions, respectively) presumably arose from the loss of solvent during sonication, affording a more concentrated sample. The increased signal at 390 nm was assigned to solvent decomposition products that formed under sonication.

Table S3. Colorimetric Responses to Sonication and Control Experiments.[a]

	Pre	Post
[(**1**)(**PyP$_{66}$**)$_2$][Cl]	Purple	Yellow
[(**1**)(**PyP$_{66}$**)$_2$][Cl] (no sonication)	Purple	Purple
[(**1**)(**PyP$_7$**)$_2$][Cl]	Purple	Purple
[(**2**)(**PyP$_{110}$**)]	Purple	Purple
[(**1**)(**PyPiv**)$_2$][Cl] + 90kDa PMA	Purple	Purple
Indicator only	Purple	Purple

[a] Color of the respective pre- and post-sonicated solution (indicated).

5. Pyridine-Catalyzed Anionic Polymerization Reactions

Formation of p(4) by Sonochemically-Liberated PyP$_M$. In a nitrogen filled drybox, a vial was charged with CH_3CN (7 mL), monomer **4** (3.0 mL, 3.8 mmol), and 1 μmol of a pyridine complex (i.e. [(**1**)(**PyP$_{66}$**)$_2$][Cl], [(**1**)(**PyP$_7$**)$_2$][Cl], [(**2**)(**PyP$_{110}$**)][Cl] or [(**1**)(**PyPiv**)$_2$][Cl] + 90 kDa PMA). The vial was then sealed with a Teflon-lined screw cap, removed from the drybox, and equilibrated at 4 °C for 30 min. The solution was subsequently transferred to a Suslick cell and then subjected to sonication (see general sonication procedure above). After 4 h, the solution was transferred from the Suslick cell to a vial under a cone of argon and then stirred for an additional 22 h at 4 °C. The reaction was then concentrated under reduced pressure (to remove unreacted **4**). The resulting residue was dissolved in minimal CH_3CN and then added to excess $CHCl_3$ to induce precipitation of **p(4)** (related Pd-derived polymers were previously determined to be insoluble in $CHCl_3$).[2] The precipitated solids were subsequently collected via filtration and dried under reduced pressure to afford **p(4)**. Spectral data were consistent with an authentic sample.[2] GPC (acetone): M_n = 21 kDa, PDI = 1.5.

Table S4. Polymerization of **4** to **p(4)** Under Various Conditions.[a]

	Monomer Consumption	M_n (kDa)	PDI	Yield [b]
[(**1**)(**PyP$_{66}$**)$_2$][Cl]	18%	21	1.5	49%
[(**1**)(**PyP$_{66}$**)$_2$][Cl] (no sonication)	< 1%	— [c]	— [c]	— [c]
[(**1**)(**PyP$_7$**)$_2$][Cl]	3%	— [c]	— [c]	— [c]
[(**2**)(**PyP$_{110}$**)]	3%	— [c]	— [c]	— [c]
[(**1**)(**PyPiv**)$_2$][Cl] + 90kDa PMA	2%	— [c]	— [c]	— [c]
monomer only (**4**)	2%	— [c]	— [c]	— [c]
PyP$_{66}$ (no sonication)	20%	30	1.3	50%

[a] Monomer concentration and consumption were measured by ^{1}H NMR spectroscopic analysis (THF-d_8) of aliquots removed before and after sonication by comparing the integrated signals assigned to CH_3CN to those assigned to **4**. Some monomer loss occurred in each sonication experiment due to the volatility of **4**. M_n and M_w refer to the absolute number-average and weight-average molecular weight, respectively, of the polymer as determined by triple detection GPC. The polydispersity index (PDI) was calculated using the equation PDI = M_w / M_n. [b] Percent yield determined relative to monomer consumption. [c] Polymer formation was not observed by GPC (acetone) or ^{1}H NMR spectroscopy (THF-d_8).

6. References

(1) D. J. Parks, W. E. Piers, S. P. A. Yap, *Organometallics* 1998, **17**, 5492.

(2) A. G. Tennyson, K. M. Wiggins, C. W. Bielawski, C. W. *J. Am. Chem. Soc.* 2010, **132**, 16631.

(3) F. Effenberger, A. O. Muck A. O. E. Hessey, *Chem. Ber*. 1980, **113**, 2086.

(4) K. S. Suslick, J. W. Goodale, P. F. Schubert, H. H. Wang, *J. Am. Chem. Soc.* 1983, **105**, 5781.