Supporting Information

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Chain-growth Polymerization of Aryl Grignards Initiated by a Stabilized NHC-Pd Precatalyst

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Contents **Page**

I. Materials

Flash chromatography was performed on SiliCycle silica gel (40-63 μm) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F254. *i*-PrMgCl (2 M in THF) was purchased in 100 mL quantities from Aldrich. [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride was purchased from Aldrich. All other reagent grade materials and solvents were purchased from Aldrich, Acros, EMD, or Fisher and used without further purification unless otherwise noted. THF was dried and deoxygenated using an Innovative Technology (IT) solvent purification system composed of activated alumina, copper catalyst, and molecular sieves. All glassware was oven dried at 120 °C for at least 1 h before use. Compounds **S1**[1] and **S2**[2] were prepared according to literature procedures.

II. General Experimental

NMR Spectroscopy: ^{1}H NMR spectra for all compounds were acquired at rt in $CDCl_3$ on a Varian vnmrs 500 operating at 500 MHz. For ^{1}H NMR spectra in deuterated solvents, the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. Multiplicities are reported as follows: singlet (s), multiplet (m), pentet (p), and broad resonance (br).

MALDI-TOF MS: MALDI-TOF mass spectra were recorded using Waters Tofspec-2E in reflectron mode at a unit mass resolution of 4000. The matrix, α-cyano-4-hydroxy-cinnamic acid (CHCA), was prepared at a concentration of 10 mg/mL in a solution of 50/50 (v/v) CH_3CN/EtOH. The instrument was mass calibrated with a mixture of peptides in the CHCA matrix. The polymer sample was dissolved in CH_2Cl_2 to obtain a ~1 mg/mL solution. A 3 μL aliquot of the polymer solution was mixed with 3 μL of the matrix solution. 1 μL of this mixture was placed on the target plate and then air-dried.

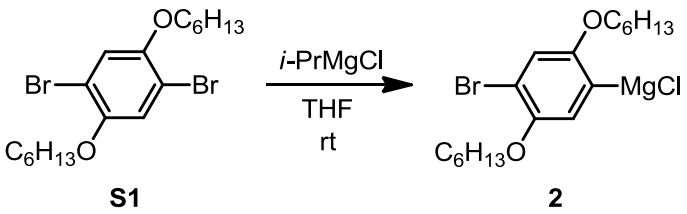
Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed with Waters 2487 dual absorbance detector (254 nm). Samples were dissolved in THF (with mild heating) and passed through a 0.2 μm PTFE filter prior to analysis.

Titrations of the Grignard Reagents: An accurately weighed sample of salicylaldehyde phenylhydrazone (typically between 290-310 mg) was dissolved in 5.00 mL of THF. A 0.50 mL aliquot of this solution was stirred at rt while ArMgCl was added dropwise using a 500 μL syringe. The initial solution is yellow and turns bright orange at the end-point.[3]

Gas Chromatography: Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHRX5 (crossbound 5% diphenyl – 95% dimethyl polysiloxane; 15 m 0.25 mm ID, 0.25 μm df) column.

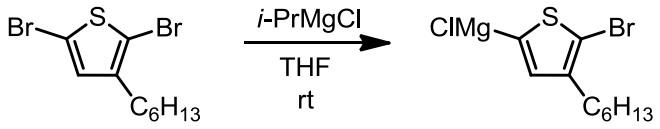
IR Spectroscopy: Samples were recorded using a Mettler Toledo ReactIR iC10 fitted with a Mercury Cadmium Telluride (MCT) detector, and AgX probe (9.5 mm x 1.5 mm) with a SiComp tip. The spectra were processed using icIR 4.0 software and raw absorbances were exported into Microsoft Excel or Sigma Plot 10 for analysis.

III. Synthetic Procedures



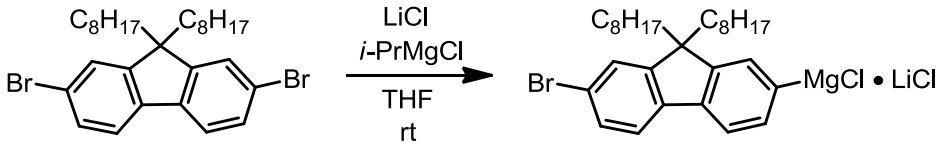
S1 **2**

2. In the glovebox, **S1** (1.025 g, 2.350 mmol, 1.0 equiv) was dissolved in THF (2.5 mL) in a 20 mL vial equipped with a stir bar. Then, *i*-PrMgCl (1.07 mL, 2.12 mmol, 0.9 equiv) was added via syringe, the vial was capped, and the reaction was stirred overnight at rt.



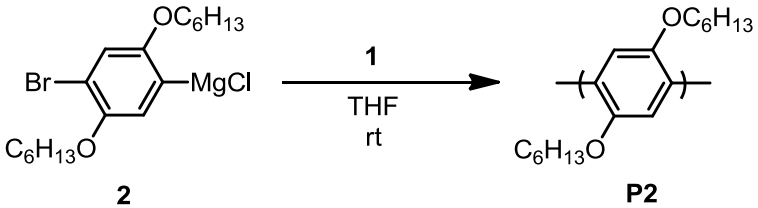
S2 **3**

3. In the glovebox, **S2** (0.424 g, 1.30 mmol, 1.0 equiv) was dissolved in THF (3.5 mL) in a 20 mL vial equipped with a stir bar. Then, *i*-PrMgCl (0.59 mL, 1.2 mmol, 0.9 equiv) was added via syringe, the vial was capped, and the reaction was stirred for 30 min at rt.



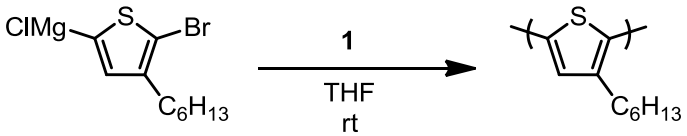
S3 **4**

4. In the glovebox, 9,9-dioctyl-2,7-dibromofluorene (2.742 g, 5.000 mmol, 1.0 equiv) and lithium chloride (0.463 g, 5.00 mmol, 1.0 equiv) was dissolved in THF (5.0 mL) in a 20 mL vial equipped with a stir bar. Then, *i*-PrMgCl (2.25 mL, 4.50 mmol, 0.9 equiv) was added via syringe, the vial was capped, and the reaction was stirred overnight at rt.



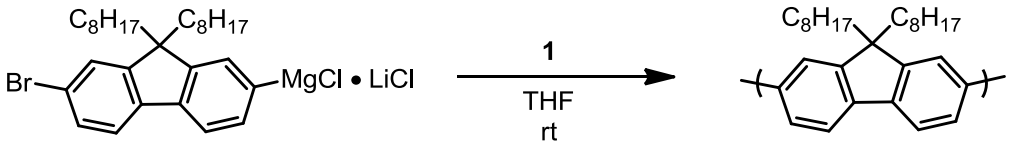
2 **P2**

P2. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (7.75 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **2** (2.25 mL, 0.466 M, 1.01 mmol, 67 equiv) was then added via syringe and stirred for 90 min at rt. The reaction was quenched with aq. HCl (5 M, 10 mL), extracted with CH_2Cl_2 (3 x 10 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting white solid was then washed with MeOH, and dried under vacuum (209 mg, 75% yield) M_n = 28.2 kDa, PDI = 1.19.



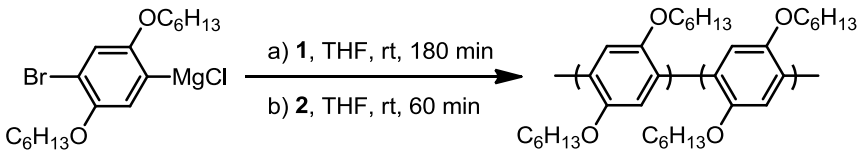
3 **P3**

P3. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (8.07 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **3** (1.93 mL, 0.466 M, 0.900 mmol, 60 equiv) was then added via syringe and stirred for 90 min at rt. The reaction was quenched with aq. HCl (5 M, 10 mL), extracted with $CHCl_3$ (3 x 10 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting purple solid was then dissolved in a minimum amount of $CHCl_3$ and precipitated into MeOH. The precipitate was collected and dried under vacuum (130 mg, 87% yield) M_n = 18.1 kDa, PDI = 1.19.



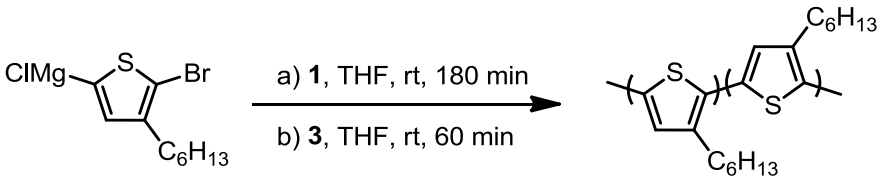
4 **P4**

P4. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (6.33 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **4** (3.67 mL, 0.286 M, 1.01 mmol, 67 equiv) was then added via syringe and stirred for 60 min at rt. The reaction was quenched with aq. HCl (5 M, 10 mL), extracted with $CHCl_3$ (3 x 10 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting yellow solid was then washed with acetone, and dried under vacuum. (246 mg, 63% yield) M_n = 7.2 kDa, PDI = 1.73.



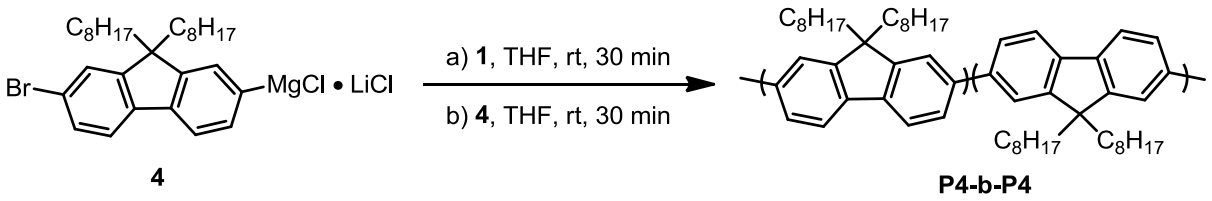
2 **P2-b-P2**

P2-b-P2. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (4.6 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **2** (2.70 mL, 0.210 M, 0.567 mmol, 38 equiv) was then added via syringe and stirred for 180 min at rt. After 180 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Monomer **2** (2.70 mL, 0.210 M, 0.567 mmol, 38 equiv) was then added via syringe and stirred for 60 min at rt. After 60 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with CH_2Cl_2 (3 x 1 mL) with mild heating, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting solid was then dissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis. Block 1: M_n = 13.8 kDa, PDI = 1.13, Block 2: M_n = 21.8 kDa, PDI = 1.18.



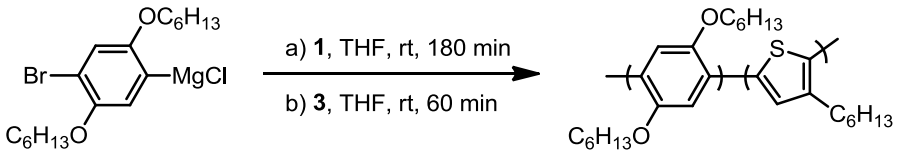
3 **P3-b-P3**

P3-b-P3. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (7.8 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **3** (1.06 mL, 0.525 M, 0.557 mmol, 37 equiv) was then added via syringe and stirred for 180 min at rt. After 180 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Monomer **3** (1.06 mL, 0.525 M, 0.557 mmol, 37 equiv) was then added via syringe and stirred for 60 min at rt. After 60 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with $CHCl_3$ (3 x 1 mL) with mild heating, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting solid was then dissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis. Block 1: M_n = 11.2 kDa, PDI = 1.22, Block 2: M_n = 17.8 kDa, PDI = 1.35.



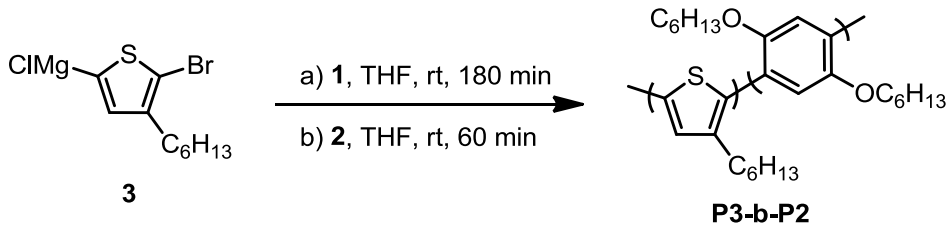
4 **P4-b-P4**

P4-b-P4. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (6.48 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **3** (1.76 mL, 0.286 M, 0.503 mmol, 35 equiv) was then added via syringe and stirred for 30 min at rt. After 30 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Monomer **3** (1.76 mL, 0.286 M, 0.503 mmol, 35 equiv) was then added via syringe and stirred for 30 min at rt. After 30 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with $CHCl_3$ (3 x 1 mL) with mild heating, dried over $MgSO_4$, filtered and concentrated in vacuo. The resulting solid was then dissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis. Block 1: M_n = 7.0 kDa, PDI = 1.97, Block 2: M_n = 7.3 kDa, PDI = 2.04.



2 **P2-b-P3**

P2-b-P3. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (7.11 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **2** (0.96 mL, 0.52 M, 0.50 mmol, 33 equiv) was then added via syringe and stirred for 180 min at rt. After 180 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Monomer **3** (1.93 mL, 0.466 M, 0.900 mmol, 60 equiv) was then added via syringe and stirred for 60 min at rt. After 60 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). The aliquots were extracted with $CHCl_3$ (3 x 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$. The organic phase was then concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis (Block 1: M_n = 9.2 kDa, PDI = 1.24, Block 2: M_n = 17.8 kDa, PDI = 1.32). The reaction was quenched with aq. HCl (5 M, 10 mL), extracted with $CHCl_3$ (3 x 10 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting purple solid was then dissolved in a minimum amount of $CHCl_3$ and precipitated into MeOH. The precipitate was collected and dried under vacuum (223 mg, 78% yield).



3 **P3-b-P2**

P3-b-P2. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (7.11 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **3** (1.93 mL, 0.466 M, 0.900 mmol, 60 equiv) was then added via syringe and stirred for 180 min at rt. After 180 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Monomer **2** (0.96 mL, 0.52 M, 0.50 mmol, 33 equiv) was then added via syringe and stirred for 60 min at rt. After 60 min, an aliquot was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). The aliquots were extracted with $CHCl_3$ (3 x 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$. The organic phase was then concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis (Block 1: M_n = 8.8 kDa, PDI = 1.26, Block 2: M_n = 15.8 kDa, PDI = 1.35). The reaction was quenched with aq. HCl (5 M, 10 mL), extracted with $CHCl_3$ (3 x 10 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting purple solid was then dissolved in a minimum amount of $CHCl_3$ and precipitated into MeOH. The precipitate was collected and dried under vacuum (238 mg, 83% yield).

IV. ^{1}H NMR Spectra

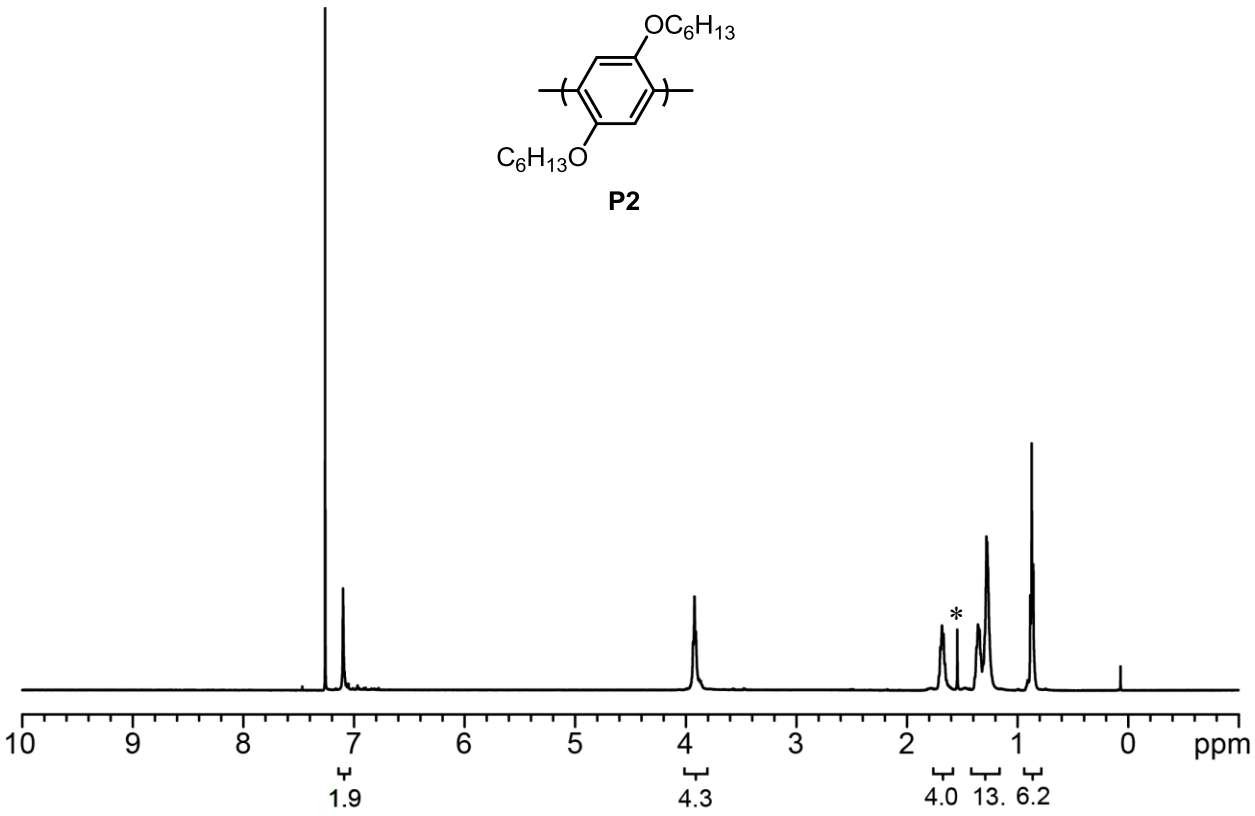


Figure S1. ^{1}H NMR spectrum for **P2**.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (br s, 2H), 3.92 (br m, 4H), 1.68 (br m, 4H) 1.40-1.21 (br m, 12H), 0.87 (br m, 6H). * indicates residual H_2O

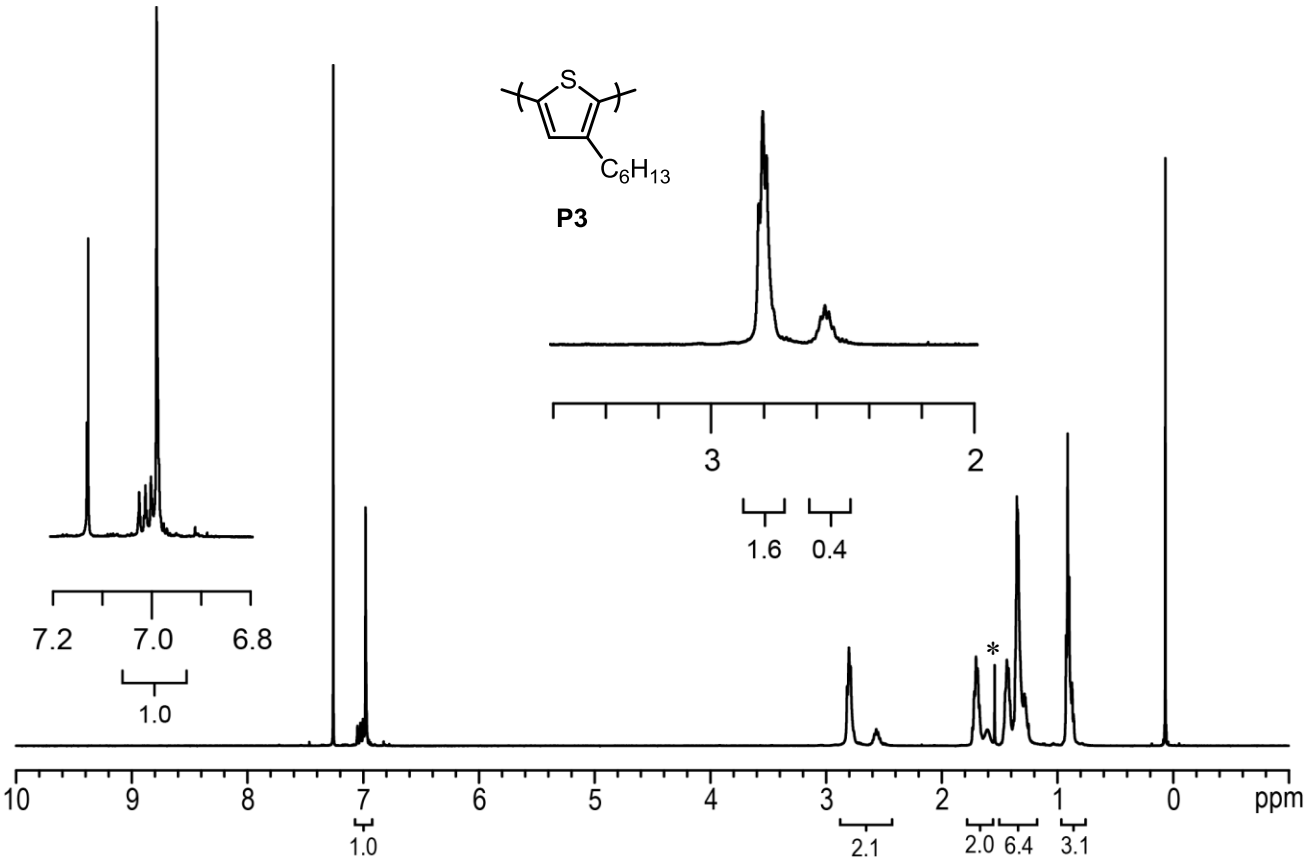


Figure S2. ^{1}H NMR spectrum for **P3**.
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 1H), 2.83-2.50 (br m, 2H), 1.74-1.57 (m, 2H) 1.47-1.24 (br m, 6H), 0.91 (br m, 3H). * indicates residual H_2O

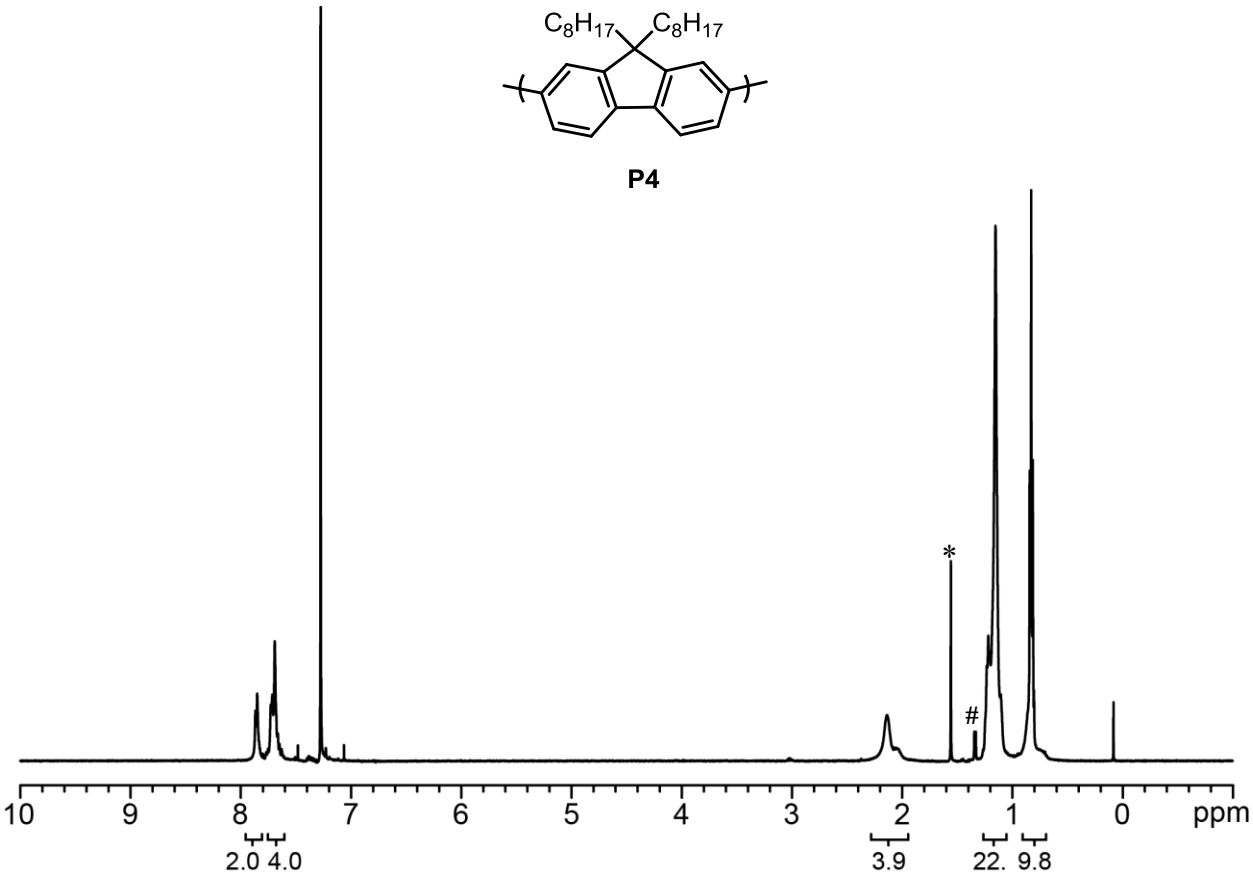


Figure S3. ^{1}H NMR spectrum for **P4**.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (br m, 2H), 7.69 (br m, 4H), 2.22-1.89 (br m, 4H), 1.27-1.06 (br m, 20H), 0.90-0.71 (br m, 10H). * indicates residual H_2O, # indicates iPr end groups

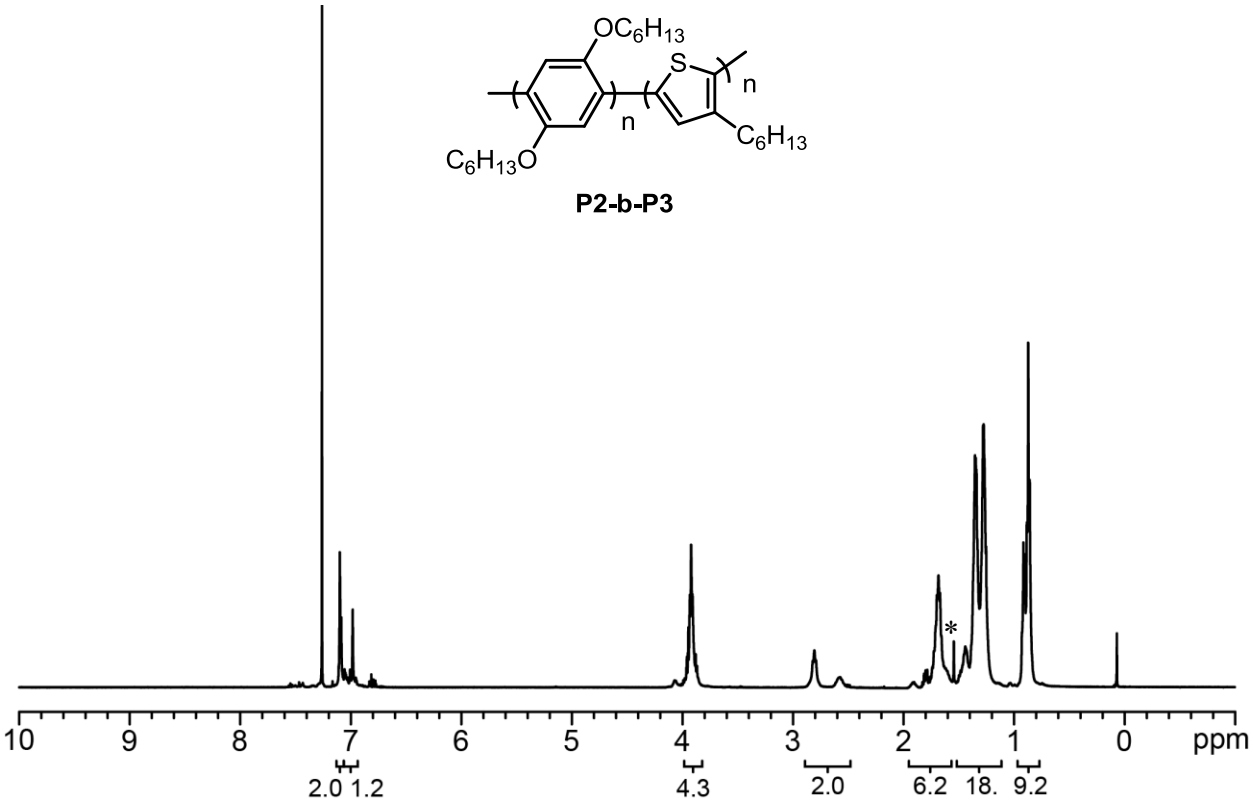


Figure S4. ^{1}H NMR spectrum for **P2-b-P3**.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (br s, 2H), 6.98 (s, 1H), 4.09-3.84 (br m, 4H), 2.83-2.50 (br m, 2H), 1.74-1.57 (br m, 6H) 1.47-1.24 (br m, 18H), 0.94-0.84 (br m, 9H). * indicates residual H_2O

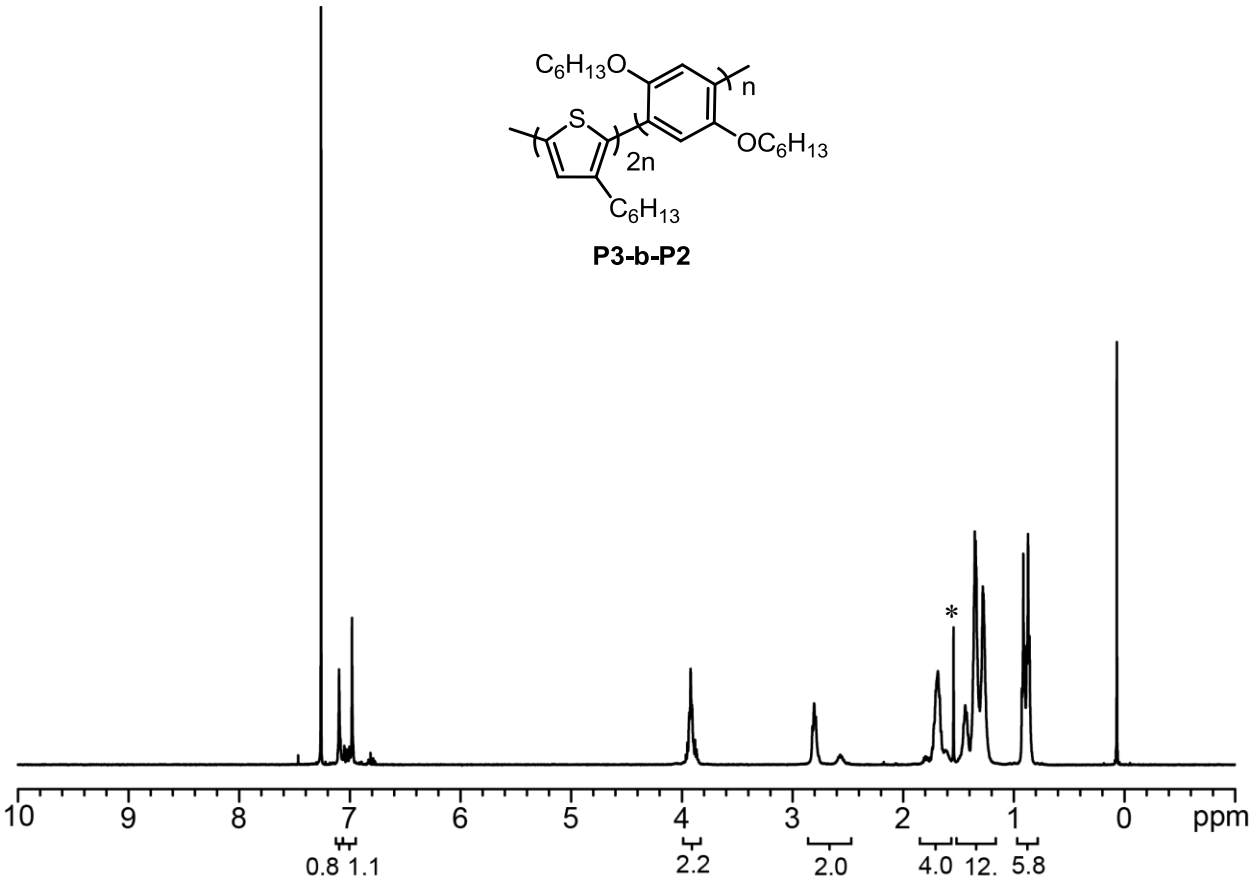


Figure S5. ^{1}H NMR spectrum for **P3-b-P2**
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (br s, 1H), 6.98 (m, 1H), 4.09-3.84 (br m, 2H), 2.83-2.50 (br m, 2H), 1.74-1.57 (br m, 4H) 1.47-1.24 (br m, 12H), 0.94-0.84 (br m, 6H). * indicates residual H_2O

V. M_n and PDI versus Conversion

Representative Procedure for M_n and PDI versus Conversion Studies utilizing GC analysis:
A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (7.75 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **2** (2.25 mL, 0.466 M, 1.01 mmol, 67 equiv), with docosane added (as an internal standard), was then added via syringe and stirred for 90 min at rt. Aliquots (~0.5 mL) were withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with CH_2Cl_2 (3 x 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$. To monitor conversion, GC samples were prepared by taking aliquots (~0.25 mL) of this organic phase and diluting with CH_2Cl_2 (~0.75 mL). Conversion was determined relative to the initial concentration, using the internal standard as a reference. To measure molecular weight and molecular weight distribution, the remaining organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

Note: nonadecane was used as internal standard with monomer **3**, docosane was used as internal standard with monomer **4**.

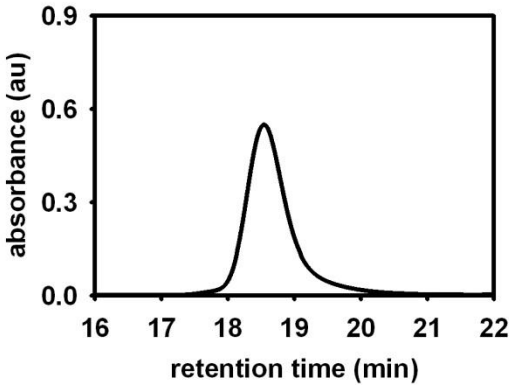


Figure S6. Representative GPC trace of **P2** at 60% conversion with precatalyst **1** (M_n: 22.5 kDa, PDI: 1.17).

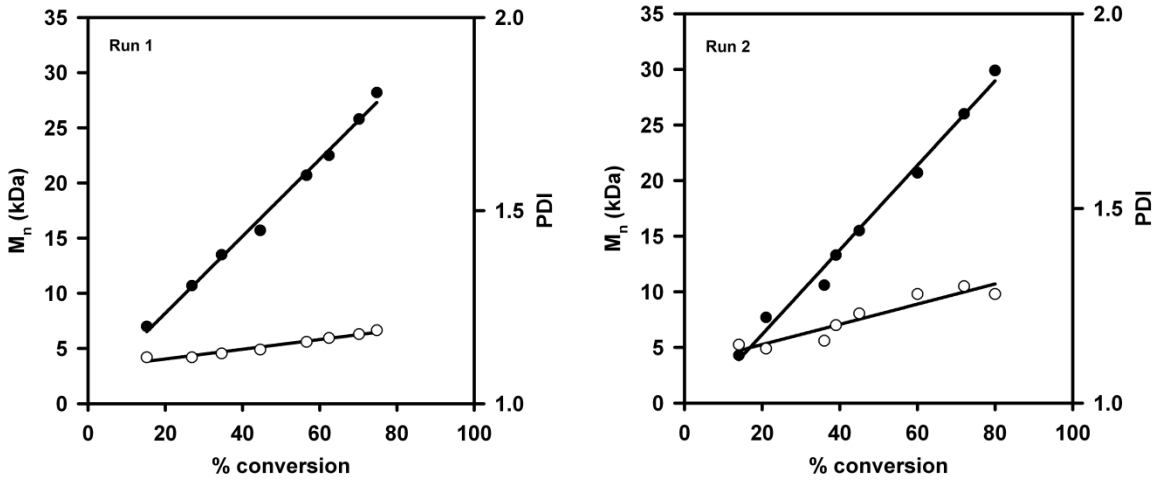


Figure S7. Plots of M_n (●) and PDI (○) versus conversion for the polymerization of monomer **2** using precatalyst **1** ([**1**] = 1.5 mM, [**2**] = 77 mM (run 1), 91 mM (run 2), 25 °C, THF).

Table S1. Data for the plot in Figure S7, run 1.

% Conversion	M_n (kDa)	PDI
15	7.0	1.12
27	10.7	1.12
35	13.5	1.13
45	15.7	1.14
57	20.7	1.16
62	22.5	1.17
70	25.8	1.18
75	28.2	1.19

Table S2. Data for the plot in Figure S7, run 2.

% Conversion	M_n (kDa)	PDI
14	4.3	1.15
21	7.7	1.14
36	10.6	1.16
39	13.3	1.20
45	15.5	1.23
60	20.7	1.28
72	26.0	1.30
80	29.9	1.28

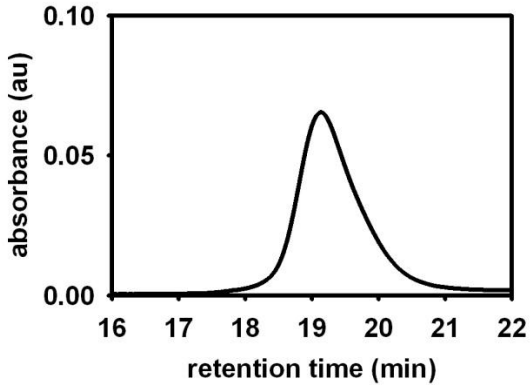


Figure S8. Representative GPC trace of **P3** at 60% conversion with precatalyst **1** (M_n: 11.5 kDa, PDI: 1.20).

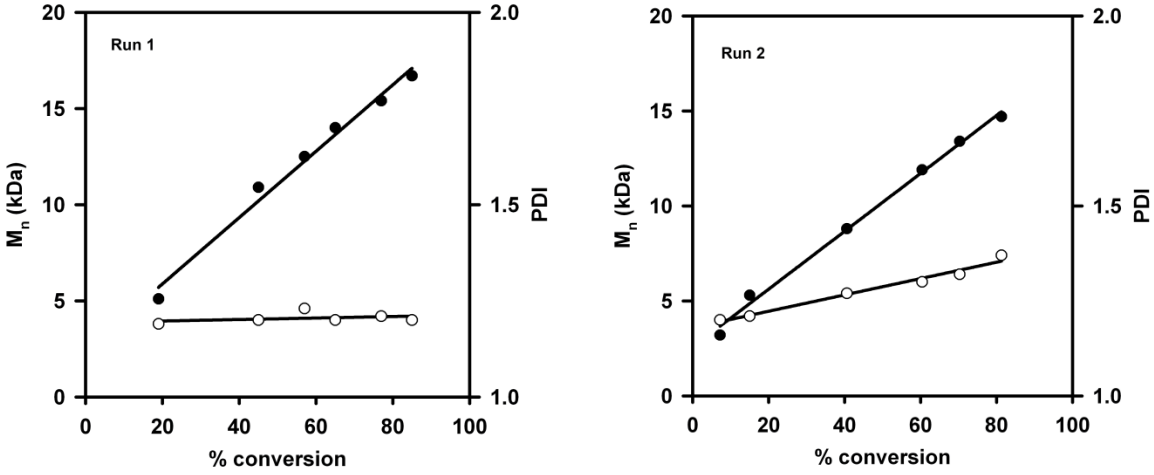


Figure S9. Plots of M_n (●) and PDI (○) versus conversion for the polymerization of monomer **3** using precatalyst **1** ([**1**] = 1.5 mM, [**3**] = 98 mM (run 1), 88 mM (run 2), 25 °C, THF).

Table S3. Data for the plot in Figure S9, run 1.

% Conversion	M_n (kDa)	PDI
19	5.1	1.19
45	10.9	1.20
57	12.5	1.23
65	14.0	1.20
77	15.4	1.21
85	16.7	1.20

Table S4. Data for the plot in Figure S9, run 2.

% Conversion	M_n (kDa)	PDI
7	3.2	1.20
15	5.3	1.21
41	8.8	1.27
60	11.9	1.30
70	13.4	1.32
81	14.7	1.37

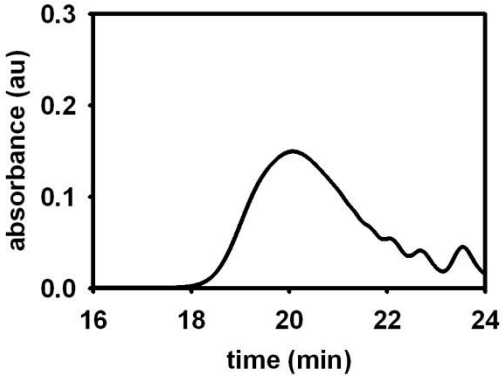


Figure S10. Representative GPC trace of **P4** at 60% conversion with precatalyst **1** (M_n: 4.3 kDa, PDI: 1.53).

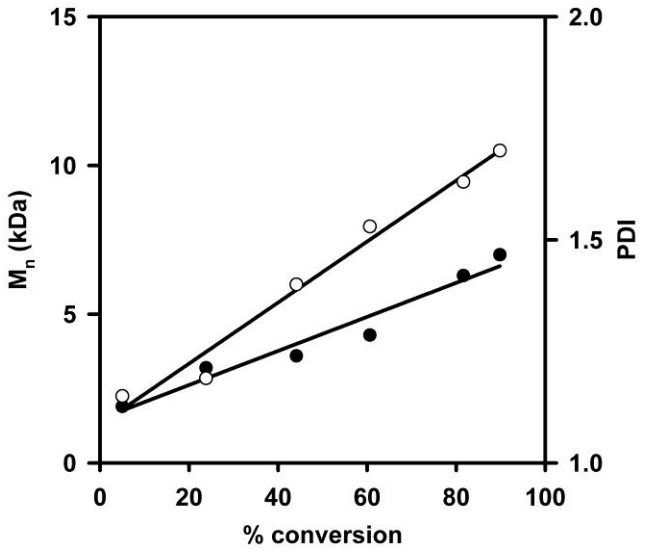


Figure S11. Plot of M_n (●) and PDI (○) versus conversion for the polymerization of monomer **4** using precatalyst **1** ([**1**] = 1.5 mM, [**2**] = 101 mM, 25 °C, THF).

Table S5. Data for the plot in Figure S11.

% Conversion	M_n (kDa)	PDI
5	1.9	1.15
24	3.2	1.19
44	3.6	1.40
61	4.3	1.53
82	6.3	1.63
90	7.0	1.70

VI. M_n and PDI versus [monomer]/[catalyst]

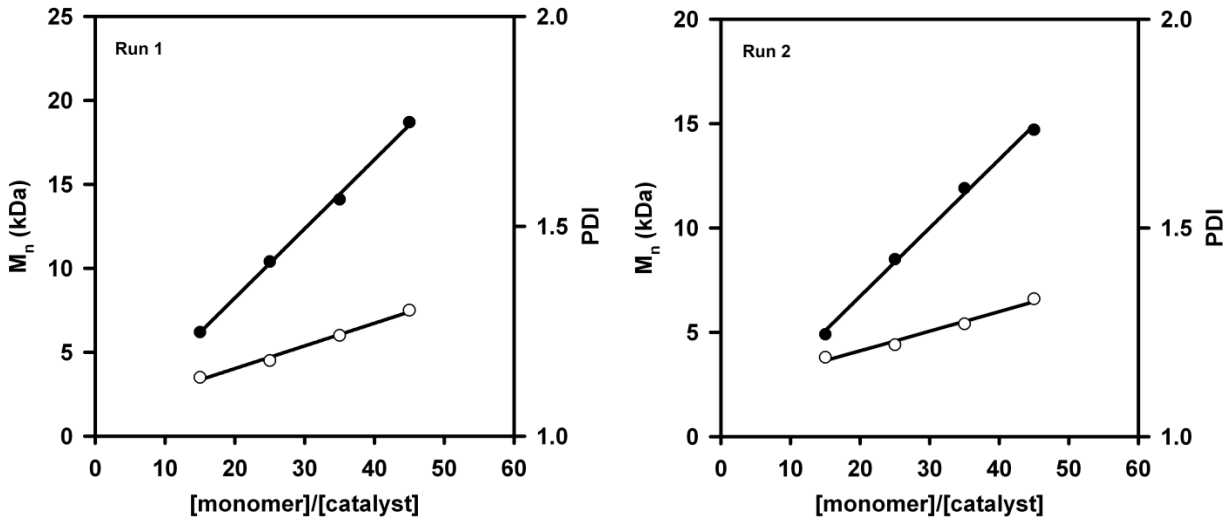


Figure S12. Plots of M_n (●) and PDI (○) versus [monomer]/[catalyst] for the polymerization of monomer **2** using precatalyst **1** ([**1**] = 1.5 mM, [**2**] = 23 mM, 38 mM, 53 mM, 68 mM, 25 °C, THF).

Table S6. Data for the plot in Figure S12, run 1.

[monomer]/[catalyst]	M_n (kDa)	PDI
15	6.2	1.14
25	10.4	1.18
35	14.1	1.24
45	18.7	1.30

Table S7. Data for the plot in Figure S12, run 2.

[monomer]/[catalyst]	M_n (kDa)	PDI
15	4.9	1.19
25	8.5	1.22
35	11.9	1.27
45	14.7	1.33

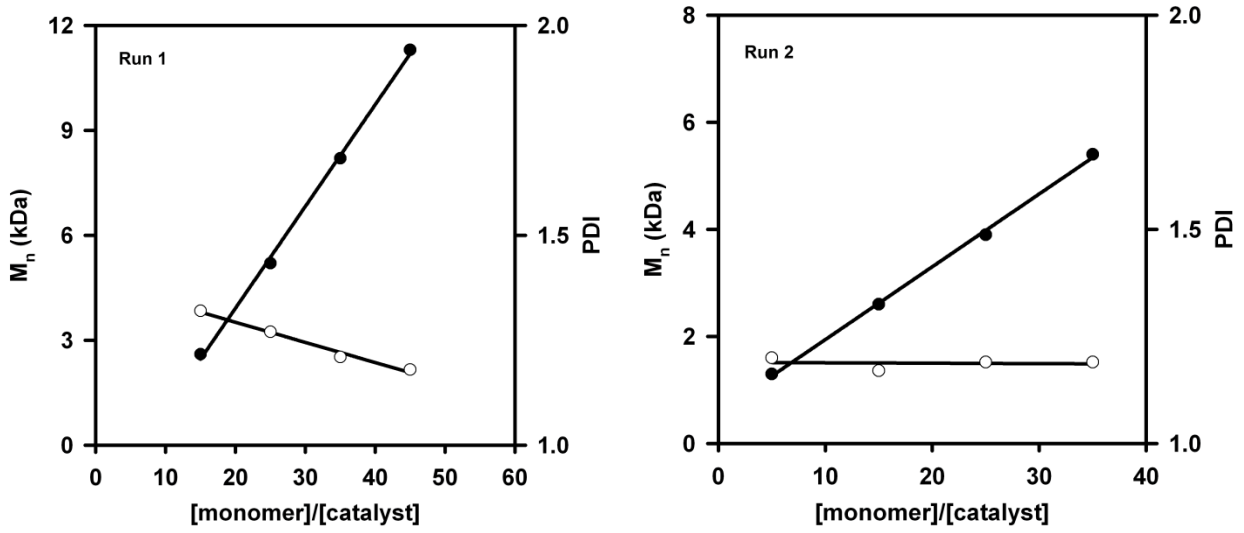


Figure S13. Plots of M_n (●) and PDI (○) versus [monomer]/[catalyst] for the polymerization of monomer **3** using precatalyst **1** ([**1**] = 1.5 mM, [**3**] = 23 mM, 38 mM, 53 mM, 68 mM (run 1), 8 mM, 23 mM, 38 mM, 53 mM (run 2), 25 °C, THF).

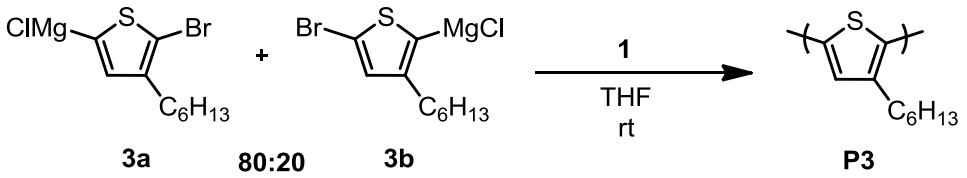
Table S8. Data for the plot in Figure S13, run 1.

[monomer]/[catalyst]	M_n (kDa)	PDI
15	2.6	1.37
25	5.2	1.27
35	8.2	1.21
45	11.3	1.18

Table S9. Data for the plot in Figure S13, run 2.

[monomer]/[catalyst]	M_n (kDa)	PDI
5	1.3	1.20
15	2.6	1.17
25	3.9	1.19
35	5.4	1.19

VII. Thiophene Regioregularity



P3. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (8.07 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **3** (1.93 mL, 0.466 M, 0.900 mmol, 60 equiv), with nonadecane added (as an internal standard), was then added via syringe and stirred for 90 min at rt. Aliquots (~0.5 mL) were withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with $CHCl_3$ (3 x 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$. To monitor conversion, GC samples were prepared by taking aliquots (~0.25 mL) of this organic phase and diluting with CH_2Cl_3 (~0.75 mL). Conversion was determined by sum of areas (**3a** + **3b**) relative to a nonadecane internal standard.

Table S10. Data for the consumption of thiophene regioisomers, run 1.

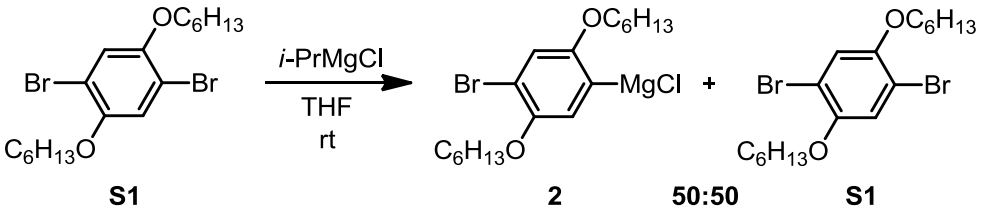
% Conversion (**3a**)	% Conversion (**3b**)	Total Conversion
20	0*	14
46	3	36
58	0	44
71	5	56
85	13	68
94	20	76
98	48	87
99	95	98

* Within range of intrinsic GC error

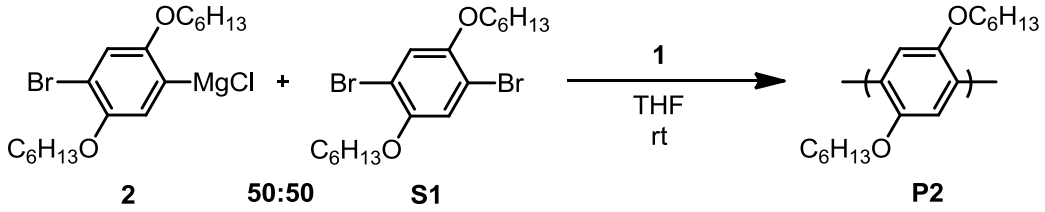
Table S11. Data for the consumption of thiophene regioisomers, run 2.

% Conversion (**3a**)	% Conversion (**3b**)	Total Conversion
22	0	17
39	2	31
46	1	36
63	9	51
79	18	65
90	28	76
98	42	86

VIII. Competition Experiment



2:S1 Mixture. In the glovebox, **S1** (3.00 g, 6.88 mmol, 1.0 equiv) was dissolved in THF (7.5 mL) in a 20 mL vial equipped with a stir bar. Then, *i*-PrMgCl (1.72 mL, 3.44 mmol, 0.5 equiv) was added via syringe, the vial was capped, and the reaction was stirred overnight at rt. Approximate ratio was confirmed via GC analysis.



P2. A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), and THF (6.25 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. A mixture of **2:S1** (~50:50) (3.75 mL, [**2**] = 0.268 M, 1.005 mmol, 67 equiv), with docosane added (as an internal standard), was then added via syringe and stirred for 90 min at rt. Aliquots (~0.5 mL) were withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with CH_2Cl_2 (3 x 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$. To monitor conversion, GC samples were prepared by taking aliquots (~0.25 mL) of this organic phase and diluting with CH_2Cl_2 (~0.75 mL). Conversion was determined relative to docosane internal standard. To measure molecular weight and molecular weight distribution, the remaining organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

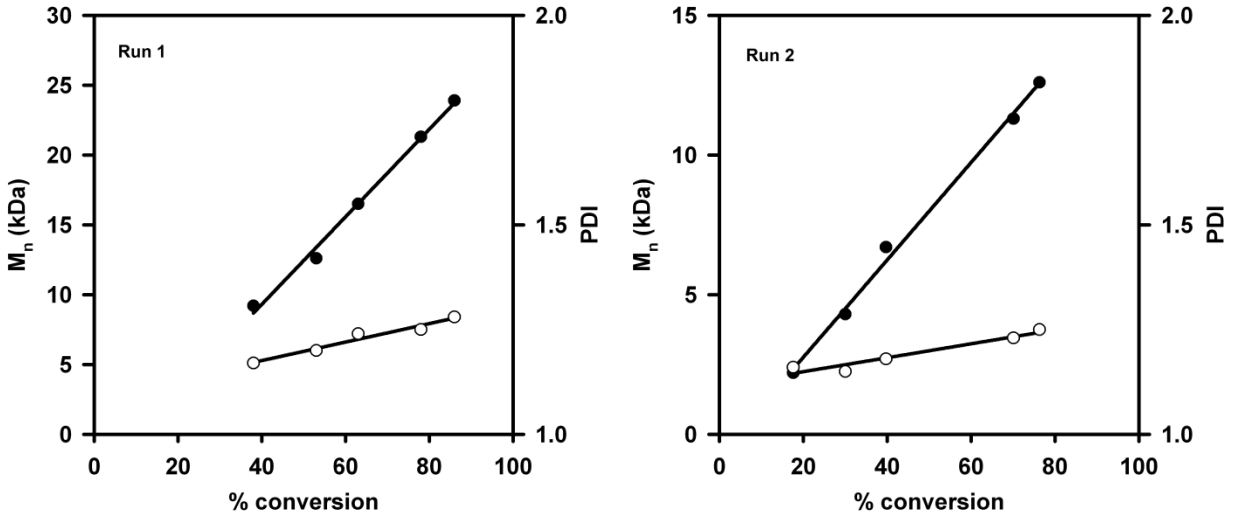


Figure S14. Plots of M_n (●) and PDI (○) versus conversion for the polymerization of monomer **2** with 50% **S1** using precatalyst **1** ([**1**] = 1.5 mM, [**2**] = 101 mM (run 1), 85 mM (run 2), 25 °C, THF).

Table S12. Data for the plot in Figure S14, run 1.

% Conversion (**2**)	% **S1**	M_n (kDa)	PDI
38	6	9.2	1.17
53	6	12.6	1.20
63	0*	16.5	1.24
78	1	21.3	1.25
86	7	23.9	1.28

* Within range of intrinsic GC error

Table S13. Data for the plot in Figure S14, run 2.

% Conversion (**2**)	% **S1**	M_n (kDa)	PDI
18	4	2.2	1.16
30	5	4.3	1.15
40	0*	6.7	1.18
70	1	11.3	1.23
76	0	12.6	1.25

* Within range of intrinsic GC error

IX. MALDI-TOF MS Data

Representative Procedure for Preparation of Oligomers for MALDI-TOF MS Studies:
All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, precatalyst **1** (10.2 mg, 0.0150 mmol, 1.0 equiv), THF (4.75 mL), and **2** (0.25 mL, 0.45 M, 0.11 mmol, 7.0 equiv) were added to the flask. After 1 h, the reaction was removed from the glovebox, and poured into aq. HCl (5 M, 5 mL). This mixture was then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting solid was washed with MeOH (50 mL) to give **P2** as an off-white solid: M_n: 2.04 kDa, PDI: 1.21 (GPC). For the MS sample, the polymer was dissolved in minimal $CHCl_3$ (~2 mL) and filtered through a pipet column of basic, acidic, and neutral alumina to remove Pd. The solution was then concentrated in vacuo. The general procedure was followed for MALDI-TOF MS sample preparation (see General Experimental pS2).

Figure S15. MALDI-TOF MS spectrum of **P2** initiated with precatalyst **1**.

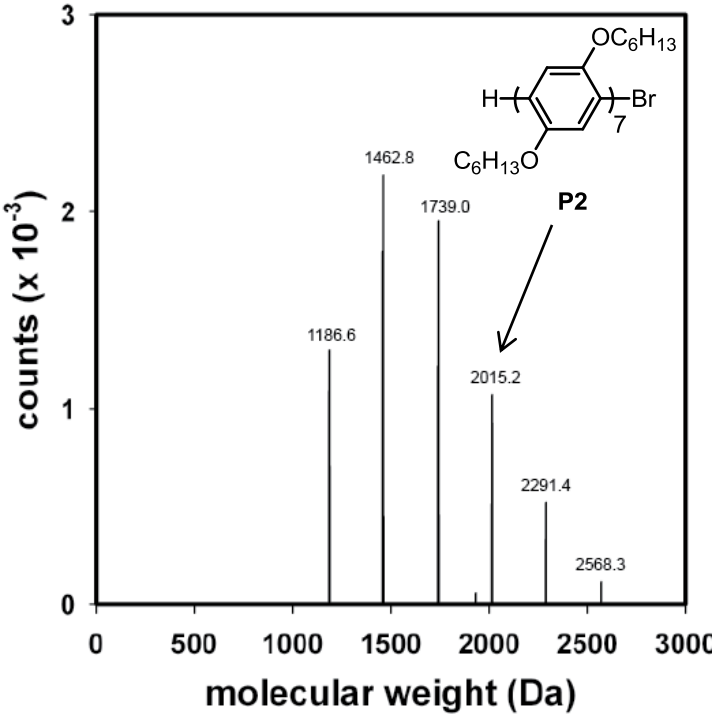


Figure S16. Expanded view of Figure S15.

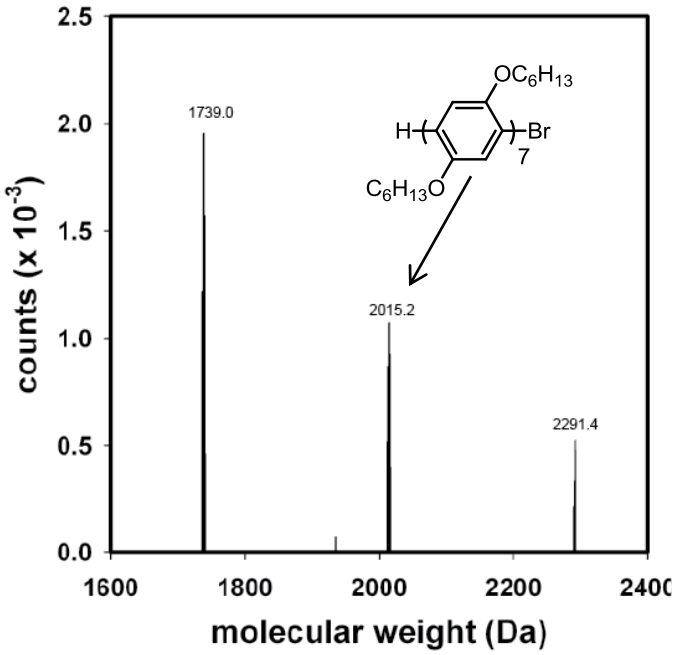


Figure S17. Expanded view of Figure S16.

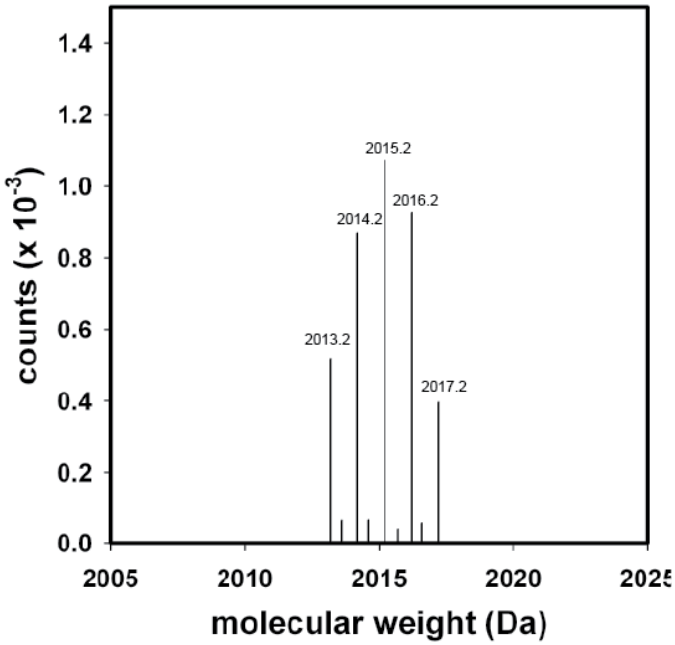


Figure S18. MALDI-TOF MS spectrum of **P3** initiated with precatalyst **1**.

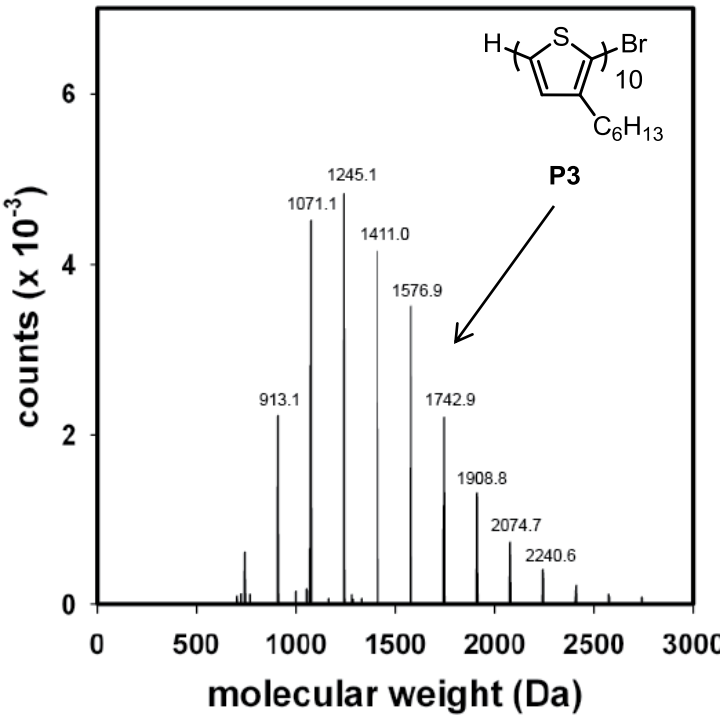


Figure S19. Expanded view of Figure S18.

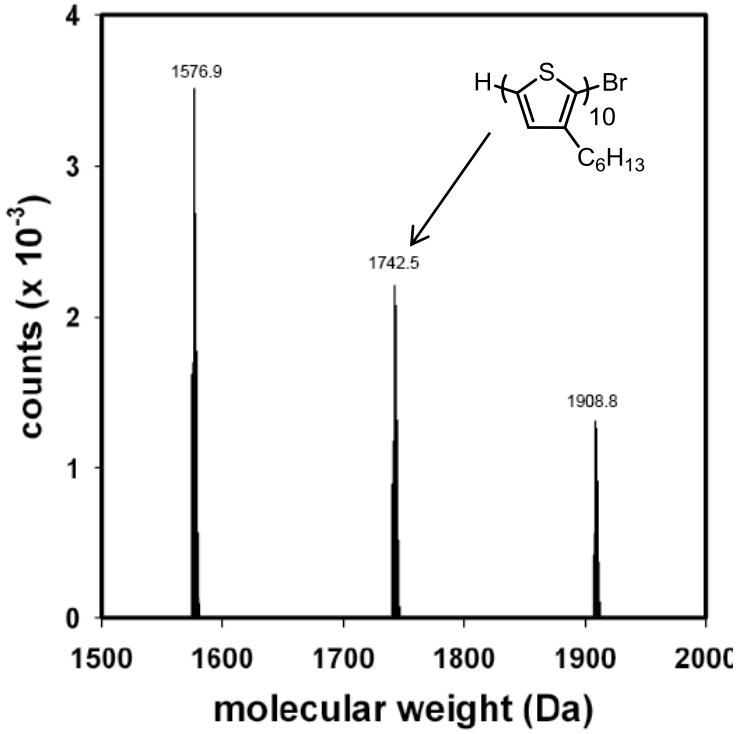


Figure S20. Expanded view of Figure S19.

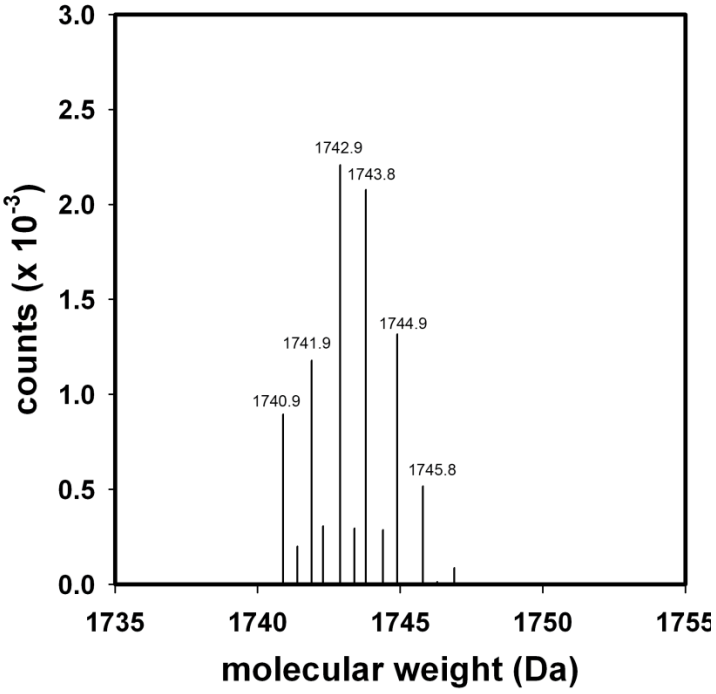


Figure S21. MALDI-TOF MS spectrum of **P4** initiated with precatalyst **1**.

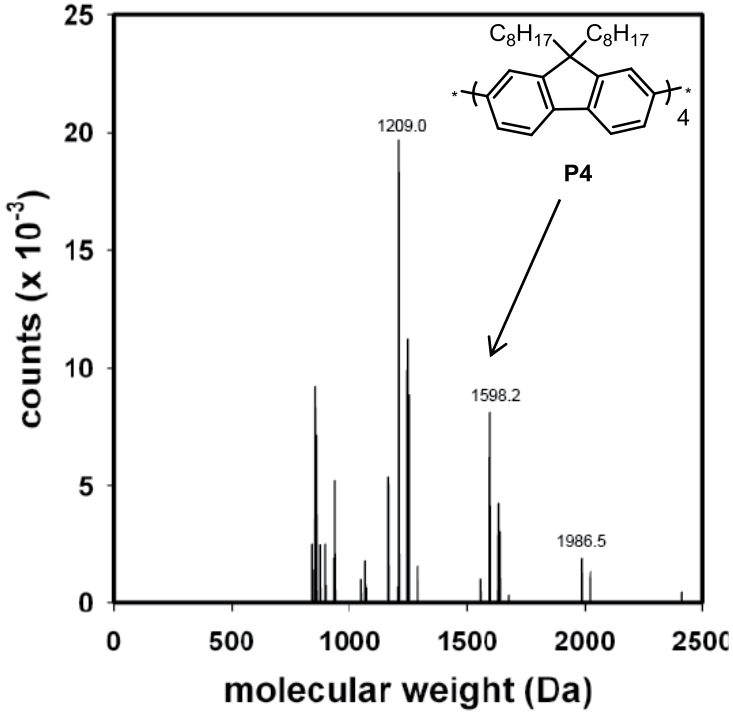


Figure S22. Expanded view of Figure S21.

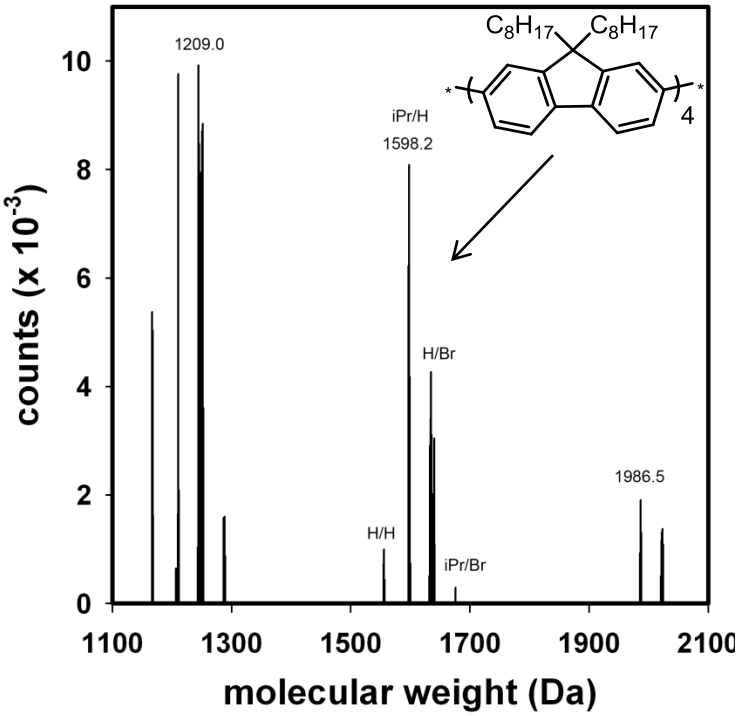
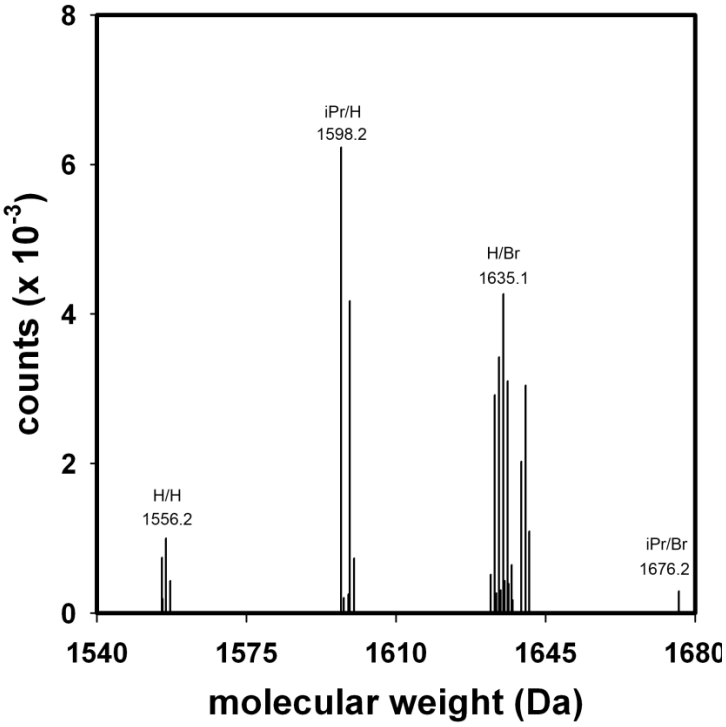


Figure S23. Expanded view of Figure S22.



X. Plot of $\ln([M]_0/[M])$ versus Time

Representative Procedure for studies utilizing react IR:

The IR probe was inserted through an O-ring sealed 14/20 ground glass adapter (custom-made) into an oven-dried 50 mL 2-neck flask equipped with a stir bar. The other neck was fitted with a two-way adapter fitted with a septum for injections/aliquot sampling and an N_2 line. The oven-dried flask was cooled under vacuum. The flask was then filled with N_2 and evacuated again for a total of three cycles. The flask was charged with THF (6.75 mL). After recording a background spectrum, monomer **2** (2.25 mL, 0.466 M, 1.01 mmol, 67 equiv) was added by syringe. Precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv), dissolved in THF (1 mL), was then injected and spectra were recorded every 30 s over the entire reaction. To account for mixing, spectra recorded in the first 60 s of the reaction were discarded. Aliquots (~0.5 mL) were withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). Each aliquot was then extracted with CH_2Cl_2 (3 x 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$. Conversion was determined by absorbance readings relative to starting concentration. To measure molecular weight and molecular weight distribution, the organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

Although linear plots of $\ln([M]_0/[M])$ have been used to provide evidence of a "living" polymerization,[4] this analysis assumes that the polymerization is first-order in monomer throughout the polymerization. If, on the other hand, the rate-determining step changes with conversion, then a non-linear plot can be observed, even under "living" conditions. Because the mechanism has not been established in this case, it is not possible to determine whether the observed non-linearity stems from chain termination pathways or a change in rate-determining step.

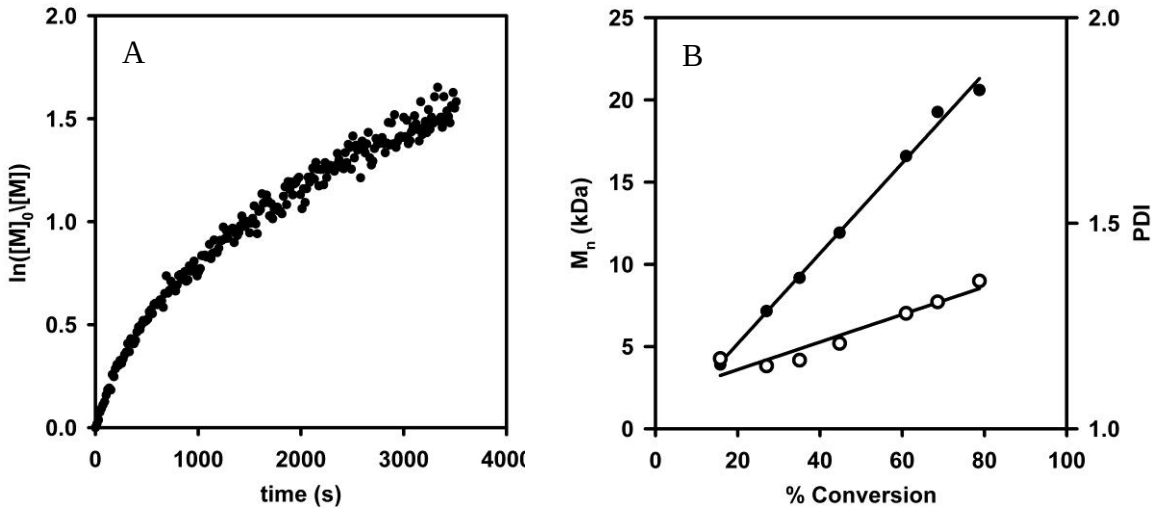


Figure S24. (A) Plot of $\ln([M]_0/[M])$ versus time for polymerization of **2** ([**1**] = 1.5 mM, [**2**] = 101 mM, 25 °C, THF). (B) Corresponding plot of M_n (●) and PDI (○) versus conversion for the polymerization of **2**.

XI. Summary of Homopolymerizations

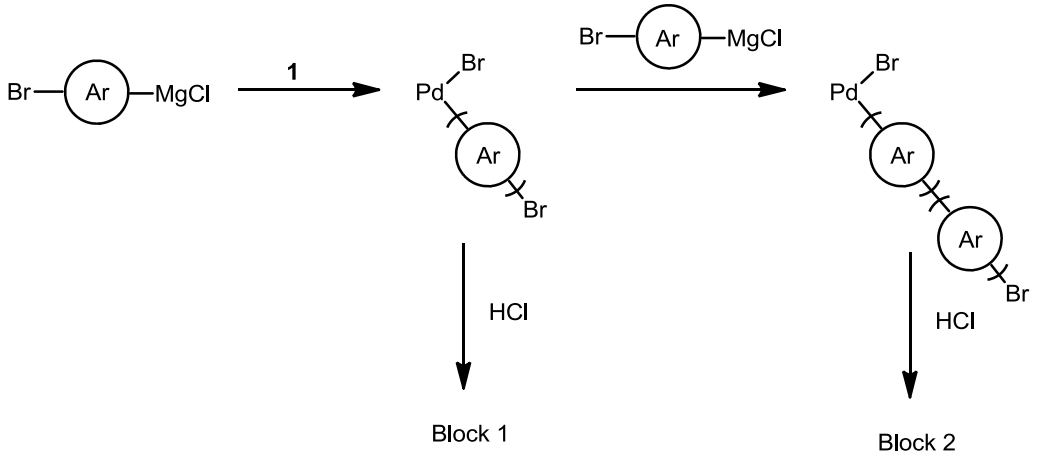


Table S14. Summary of GPC Data for Homopolymerizations (pgs S6 and S7).

Homopolymerization	M_n (kDa)	PDI
P2-b-P2 (Block 1)	13.8	1.13
P2-b-P2 (Block 2)	21.8	1.18
P3-b-P3 (Block 1)	11.2	1.22
P3-b-P3 (Block 2)	17.8	1.35
P4-b-P4 (Block 1)	7.0	1.97
P4-b-P4 (Block 2)	7.3	2.04

XII. Fluorene Side Reactions

(A) No consumption of *i*-PrBr was observed relative to internal standard (mesitylene), while complete consumption of *i*-PrMgCl was observed during polymerization of **4**.*

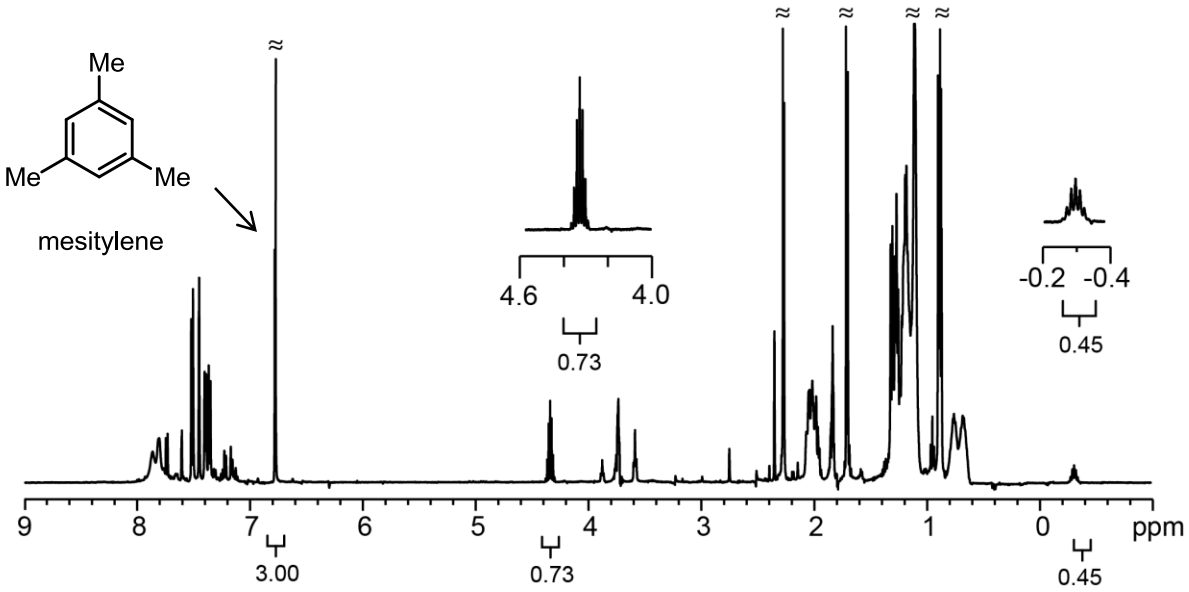


Figure S25. ^{1}H NMR spectrum for **4** (note: solvent suppresion was used). ^{1}H NMR (500 MHz, THF) δ 6.78 (s, 3H, Ar H), 4.36 (m, 1H, BrC*H*$(CH_3)_2$), -0.31 (m, 1H, ClMgC*H*$(CH_3)_2$).

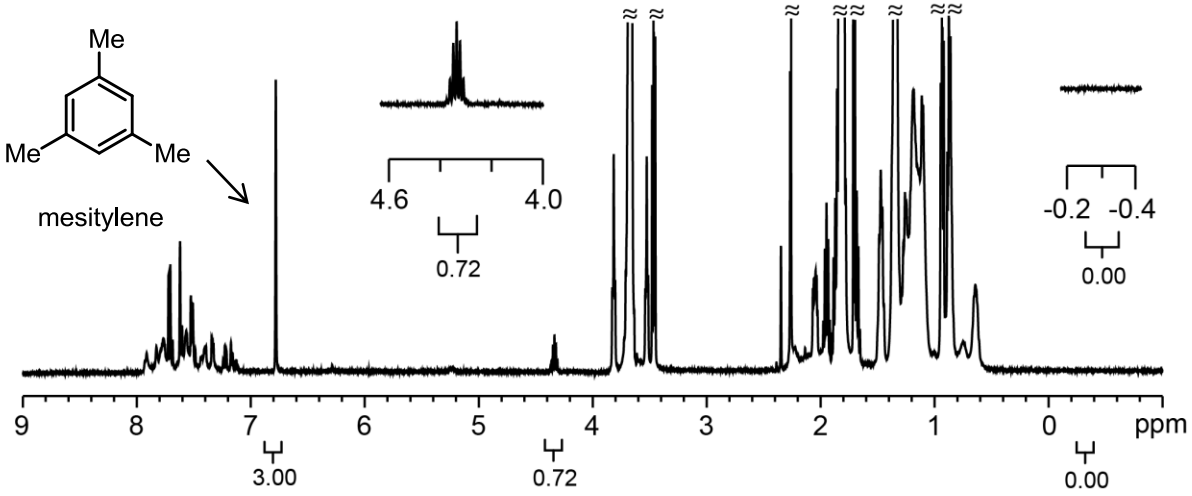


Figure S26. ^{1}H NMR spectrum for **P4** before quenching. ^{1}H NMR (500 MHz, THF) δ 6.78 (s, 3H, Ar H), 4.36 (m, 1H, BrC*H*$(CH_3)_2$), -0.31 (m, 1H, ClMgC*H*$(CH_3)_2$).

* These results are consistent with a control experiment wherein 1-bromodecane (20 equiv) was not consumed during the polymerization of **4** as evidenced by GC relative to internal standard.

(B) Consumption of the 2,7-dibromo-9,9-dioctylfluorene (**S3**) following Grignard metathesis was determined during the polymerization of **4**. Conversion was determined by GC relative to added internal standard (mesitylene).

Table S15. Conversion of 2,7-dibromo-9,9-dioctylfluorene (**S3**) during the polymerization of **4**.

Trial	% Conversion **S3**
Run 1	5
Run 2	10
Run 3	10
Run 4	11
Run 5	29

* All reactions showed > 85% monomer (**4**) conversion.

XII. References

[1] (a) E. L. Lanni, A. J. McNeil, *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579. (b) E. L. Lanni; A. J. McNeil, *Macromolecules* **2010**, *43*, 8039-8044.

[2] J. R. Locke, A. J. McNeil, *Macromolecules* **2010**, *43*, 8709-8710.

[3] B. D. Love, E. G. Jones, *J. Org. Chem.* **1999**, *64*, 3755-3756.

[4] S. Penczek, P. Kubisa, R. Szymanski, *Makromol. Chem., Rapid Commun.* **1991**, *12*, 77-80.