## **Supporting Information**

## End-Capped Poly(benzyl ethers): Acid and Base Stable Polymers That Depolymerize Rapidly from Head-to-Tail in Response to Specific Applied Signals

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#### I. Materials and Methods

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or cannula. Organic solutions were concentrated by rotary evaporation at ambient temperature under reduced pressure. Reagents were purchased commercially and were used as received unless otherwise noted. Dichloromethane (DCM), diethyl ether, N,N-dimethylformamide (DMF), toluene, and tetrahydrofuran (THF) were purified by the method of Pangborn et al.<sup>1</sup> Methanol (MeOH) was dried over activated 3Å molecular sieves for 24 h and then distilled from fresh activated 3Å molecular sieves. Pvridine was distilled from ninhydrin, dried over activated 5Å molecular sieves for 24 h, and then redistilled from fresh activated 5Å molecular sieves. Isopropanol (*i*PrOH) was distilled from calcium hydride and stored over  $3\text{\AA}$  molecular sieves. 1-tert-Butyl-2,2,4,4,4-pentakis(dimethylamino)-2 $\lambda$ 5,4 $\lambda$ 5-catenadi(phosphazene) (P<sub>2</sub>-t-Bu base) (2.0 M solution in THF) was purchased and stored in a glove box under a N<sub>2</sub> atmosphere. 1-[[(Chlorocarbonyl)oxy]methyl]-4,5-dimethoxy-2-nitrobenzene was synthesized as described by Katrizky et al.<sup>2</sup> Flash column chromatography was performed as described by Still, Kahn, and Mitra,<sup>3</sup> employing silica gel (60 Å pore size,  $32-63 \mu m$ , standard grade, Dynamic Adsorbents). Thin-layer chromatography was carried out on Dynamic Adsorbents silica gel TLC ( $20 \times 20$  w/h, F-254, 250  $\mu$ m). Deionized water was purified using a Millipore purification system (Barnstead EASYpure II UV/UF).

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded at 25 °C. Proton chemical shifts are expressed in parts per million (ppm,  $\delta$  scale) and are referenced to the residual protium in the solvent (CHCl<sub>3</sub>, 7.27 ppm; CH<sub>2</sub>Cl<sub>2</sub>, 5.32 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br s = broad singlet), integration, and coupling constant (*J*) in hertz. Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) were recorded at 25 °C. Carbon chemical shifts are expressed in parts per million (ppm,  $\delta$  scale) and are referenced to the carbon resonances of the NMR solvent (CDCl<sub>3</sub>,77.0 ppm; CH<sub>2</sub>Cl<sub>2</sub>, 54.0 ppm).

Number-average molecular weight (Mn), weight-average molecular weight (Mw), and polydispersity (Mw/Mn) values were determined by size exclusion chromatography (SEC) using an Agilent Technologies 1260 Infinity GPC system equipped with a refractive index detector, a Malvern Viscotek model 270 Dual Detector with right and low-angle light scattering, and either a Viscotek T-column (300 mm  $\times$  7.8 mm, CLM3012) and Agilent Resipore column (300 mm  $\times$  7.5 mm) in series or a single Agilent Resipore column (300 mm  $\times$ 7.5 mm) using THF (dn/dc = 0.185) or DMF (dn/dc = 0.159) as the mobile phase (flow rate: 1 ml/min, 25 °C).

#### Synthesis of Monomer 5:

Synthesis of 3,5-dimethyl-4-hydroxybenzophenone (3). Benzoyl chloride (9.5 mL, 82 mmol, 1 equiv) was added dropwise to a solution of 2,6-dimethylphenol (10 g, 82 mmol, 1 equiv) in pyridine (30 mL) at 0 °C. The reaction mixture was allowed to warm to 23 °C and stirred for 2 h. Ethyl acetate (100 mL) was added to the reaction mixture, and the resulting solution was washed with water ( $2 \times 100$  mL). The organic layer was dried over sodium sulfate, the solids were removed by filtration, and the solution was concentrated by rotary evaporation. Trifluoromethanesulfonic acid (25 mL) was added in one portion to the resulting solid at 0 °C and the flask was purged with argon. The reaction mixture was heated to 60 °C and stirred for 16 h. The reaction mixture was cooled to 23 °C and then poured into ice water (100 mL). The resulting solution was extracted with ethyl acetate (100 mL) and the aqueous later was neutralized with saturated aqueous sodium bicarbonate. The aqueous layer was extracted with ethyl acetate ( $2 \times 100$ mL) and the combined organic layers were dried over sodium sulfate. The solids were removed by filtration, the solution was concentrated by rotary evaporation, and the residue was purified by silica gel flash column chromatography (100% hexanes increasing to 30% ethyl acetate in hexanes) to afford compound **3** as a peach, amorphous solid (17.4 g, 76.7 mmol, 90% over two steps).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) & 7.76–7.74 (m, 2H), 7.59–7.55 (m, 1H), 7.52 (s, 2H), 7.52–7.45 (m, 2H), 5.95 (s, 1H), 2.29 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz) δ 196.6, 157.0, 138.4, 132.0, 131.8, 129.9, 129.4, 128.3, 123.2, 16.1. The NMR data matches the known spectra for this compound.<sup>4,5</sup>

**Synthesis of 2,6-dimethyl-4-benzylphenol (4).** Palladium (10% by weight on carbon powder) (0.87 g, 5% by weight of compound **3**) was added in one portion to a solution of compound **3** (17.4 g, 75.8 mmol, 1.0 equiv) in ethanol (250 mL) under a N<sub>2</sub> atmosphere. The flask was evacuated and purged three times with H<sub>2</sub> gas. The reaction mixture was stirred vigorously for 3 h at 23 °C under an atmosphere of H<sub>2</sub> (balloon). The flask was evacuated, purged with argon, and the reaction mixture was filtered through a pad of celite. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (5% ethyl acetate in hexanes, increasing to 10% ethyl acetate in hexanes) to afford compound **4** as a white, amorphous solid (15.3 g, 72.0 mmol, 95%).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.99–7.88 (m, 5H), 7.51 (s, 2H), 4.52 (s, 2H), 2.88 (s, 6H) ;<sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  151.0, 142.6, 133.3, 129.3, 129.1, 128.8, 126.2, 123.5, 41.5, 16.1. The NMR data matches the known spectra for this compound.<sup>4,5</sup>

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**Synthesis of 2,6-dimethyl-7-phenyl-1,4-benzoquinone methide (5).** Potassium ferricyanide (25.0 g, 75.9 mmol, 4 equiv) and potassium hydroxide (4.5 g, 80.0 mmol, 4.2 equiv) in deionized water (100 mL) was added in one portion to a solution of compound **4** (4.0 g, 19.0 mmol, 1 equiv) in hexanes (500 mL) under an N<sub>2</sub> atmosphere. The reaction mixture was stirred vigorously for 1 h at 23 °C. The aqueous layer was separated and extracted with hexanes (200 mL). The combined organic layers were washed with brine (200 mL) and dried over sodium sulfate. The solids were removed by filtration and the solution was concentrated by rotary evaporation. The resulting crude orange oil was dissolved in pentane (1.0 L) and filtered to remove insoluble orange impurities. The solution was concentrated by rotary evaporation (3 x) from cyclohexane at 55 °C to afford compound **5** as yellow needles (3.15 g, 15.0 mmol, 79%). Compound **5** was dried in a schlenk flask at 1.1 mmHg for 36 h. The flask was back-filled with an N<sub>2</sub> atmosphere and stored in a glove box. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  187.75, 143.1, 139.3, 138.0, 136.2, 136.0, 132.2, 131.8, 130.9, 129.7, 129.2, 17.3, 16.7. The NMR data matches the known spectra for this compound.<sup>4,5</sup> Monomer **5** was also prepared using silver(I) oxide as described by Lin et al. in a 82% yield.<sup>4</sup>

#### Synthesis of End-capped Polymers 6–11:

#### **Polymerization Procedure A corresponding to Figure 2:**

A 10 mL round bottom flask and stir bar were flame dried under vacuum (1.1 mmHg) and backfilled with an Ar atmosphere. To the flask was added compound **5** (0.210 g, 1.00 mmol), dry THF (1.16 mL), and freshly distilled isopropanol (38.0  $\mu$ L, 0.500 mmol). The solution was then chilled to -10 °C using an isopropanol bath and recirculating chiller for 10 min. To the solution was added a 2.0 M P<sub>2</sub>-*t*-Bu phosphazene base solution in THF (25.0  $\mu$ L, 0.050 mmol) at a rate of 1 drop/sec. After 1 h, the endcapping reagent (0.1 equiv) and base (0.1 equiv) were added to the solution. The solution was stirred at – 10 °C for 1 h and then at rt for 12 h. The polymer was precipitated by addition to MeOH (40 mL) at –10 °C. The solvent was drained using a polymer washer,<sup>6</sup> redissolved in THF (4.0 mL), and precipitated again with MeOH (40 mL). N<sub>2</sub> was bubbled through this solution for 15 min and the solvent was drained. Acetonitrile was added (40 mL), N<sub>2</sub> was bubbled through this solution for 15 min, and the solvent was drained. This process (starting from redissolution) was repeated twice more. The resulting polymer was dried under vacuum (1.1 mmHg) for 12 h. Synthesis of polymer 6 (5.1 kDa,  $M_n$ ). Following general polymerization procedure A, the reaction mixture was quenched by end-capping with glacial acetic acid (50 µL) to yield polymer 6 as a white solid (0.088 g, 42%).  $M_n$ = 5.1 kDa,  $M_w$  = 8.2 kDa, PDI = 1.6.

Synthesis of polymer 6 (72.1 kDa,  $M_n$ ). Following general polymerization procedure A with the following quantities of reagents: Compound 5 (2.0 g, 9.5 mmol), THF (11.9 mL), *i*PrOH (36 µL), P<sub>2</sub>-*t*-Bu base (0.24 mL), HCl (1.14 mL of a 1.25 M solution in MeOH) to give polymer 6 as a white solid (1.64 g, 82%).  $M_n = 72.1$  kDa,  $M_w = 78.0$  kDa, PDI = 1.08.

Synthesis of polymer 7 (9.3 kDa,  $M_n$ ). Following general polymerization procedure A, the reaction mixture was quenched by end-capping with *tert*-butyldimethylsilyl chloride (0.18 g, 1.2 mmol) and imidazole (0.082 g, 1.2 mmol) to yield polymer 7 as a white solid (0.14 g, 56%).  $M_n = 9.3$  kDa,  $M_w = 11.3$  kDa, PDI = 1.2.

Synthesis of polymer 7 (164.5 kDa,  $M_n$ ). Following general polymerization procedure A with the following quantities of reagents: Compound 5 (0.5 g, 2.38 mmol), THF (2.86 mL), *i*PrOH (9.0 µL, 0.119 mmol), and P<sub>2</sub>-*t*-Bu base (60.0 µL, 0.119 mmol). The reaction mixture was quenched by end-capping with *tert*-butyldimethylsilyl chloride (0.036 g, 0.24 mmol) and imidazole (0.016 g, 0.24 mmol) to yield polymer 7 as a white solid (0.344 g, 69%).  $M_n = 164.5$  kDa,  $M_w = 78.0$  kDa, PDI = 1.08.

Synthesis of polymer 8 (6.4 kDa,  $M_n$ ).Following general polymerization procedure A, the reaction mixture was quenched by end-capping with1-[[(chlorocarbonyl)oxy]methyl]-4,5-dimethoxy-2-nitrobenzene (0.33 g, 1.2 mmol) and 4-(dimethylamino)pyridine (0.15 g, 1.2 mmol) to yield polymer 8 as a white solid (0.11 g, 45%).  $M_n = 6.4$  kDa,  $M_w = 8.1$  kDa, PDI = 1.3.

Synthesis of polymer 9 (3.6 kDa,  $M_n$ ). Following general polymerization procedure A, the reaction mixture was quenched by end-capping with allyl chloroformate (0.13 mL, 1.2 mmol) and 4-(dimethylamino)-pyridine (0.15 g, 1.2 mmol) to yield polymer 9 as a white solid (0.20 g, 80%).  $M_n = 3.6$  kDa,  $M_w = 4.3$  kDa, PDI = 1.2.

Synthesis of polymer 10 (6.5 kDa,  $M_n$ ). Following general polymerization procedure A, the reaction mixture was quenched by end-capping with fluorenylmethyloxycarbonyl chloride (0.31 g, 1.2 mmol) and 4-(dimethylamino)pyridine (0.15 g, 1.2 mmol) to yield polymer 10 as a white solid (0.10 g, 41%).  $M_n$  = 6.5 kDa,  $M_w$  = 8.9 kDa, PDI = 1.4.

Synthesis of polymer 11 (3.9 kDa,  $M_n$ ). Following general polymerization procedure A, the reaction mixture was quenched by end-capping with methyl iodide (0.075 mL, 1.2 mmol) and pyridine (0.097 mL, 1.2 mmol) to yield polymer 11 as a white solid (0.15 g, 60%).  $M_n = 3.9$  kDa,  $M_w = 4.8$  kDa, PDI = 1.2.

Synthesis of polymer 11 (27.6 kDa,  $M_n$ ). Following general polymerization procedure A with the following quantities of reagents: Compound 5 (0.5 g, 2.4 mmol), THF (2.76 mL), *i*PrOH (18.0 µL, 0.24 mmol), and P<sub>2</sub>-*t*-Bu base (60.0 µL, 0.119 mmol). The reaction mixture was quenched by end-capping with methyl iodide (0.15 mL, 2.4 mmol) and pyridine (0.2 mL, 2.4 mmol) to yield polymer 11 as a white solid (0.39 g, 80%).  $M_n = 27.6$  kDa,  $M_w = 53.1$  kDa, PDI = 1.9.









Figure S3. <sup>1</sup>H-NMR spectrum for polymer 9 (3.6 kDa, M<sub>n</sub>).







Figure S5. <sup>1</sup>H-NMR spectrum for polymer 11 (3.9 kDa, M<sub>n</sub>).



#### Molecular Weight Control Studies for Polymer 12 and synthesis of Polymer 13:

### **Polymerization Procedure B corresponding to Figure 4:**

A 10 mL round bottom flask and stir bar were flame dried under vacuum (1.1 mmHg) and then purged with dry  $N_2$ . In a glovebox, compound 5 (0.25 g, 1.2 mmol) was added to the flask, which was then backfilled with an Ar atmosphere. Anhydrous THF (1.4 mL) was added to the flask. The solution was degassed via the freeze-pump-thaw method three times, backfilling with Ar on the final cycle. The solution was allowed to equilibrate to the reaction temperature over 20 min stirring at 350 rpm using a hot oil bath for reactions at elevated temperatures and isopropanol bath with recirculating chiller for reactions below room temperature. A stock solution of freshly distilled MeOH in anhydrous THF (10.0 mL) was prepared and 100  $\mu$ L of this solution was added at a rate of 1 drop/s to the reaction mixture, immediately followed by addition of the 2.0 M P<sub>2</sub>-t-Bu phosphazene base solution in THF (30 µL, 0.06 mmol) at a rate of 1 drop/s. After 2 h, the reaction mixture was either quenched with glacial acetic acid (50  $\mu$ L) or the end-capping reagent (1 equiv) and base (1 equiv). The reaction mixture was allowed to warm to rt over 15 min and the polymer was precipitated into MeOH (40 mL) at -10 °C and allowed to sit for 5 min. The solvent was drained using a polymer washer,<sup>5</sup> dissolved in THF (4.0 mL), and precipitated again by addition to MeOH (40 mL). N<sub>2</sub> was bubbled through the solution for 15 min and the solvent was drained. Acetonitrile was added (40 mL), N<sub>2</sub> was bubbled through this solution for 15 min, and the solvent was drained. This process (starting from dissolution in THF) was repeated twice more. The resulting polymer was dried under vacuum (1.1 mmHg) for 12 h.

Synthesis of polymer 12 (484 kDa,  $M_n$ ). General polymerization procedure B was used with some modifications as follows: Compound 5 (0.5 g, 2.38 mmol), THF (1.60 mL), MeOH (0.48 µL, 11.9 µmol), and P<sub>2</sub>-*t*-Bu base (6.0 µL, 11.9 µmol). In another deviation from general polymerization procedure B, no freeze-pump-thaw degassing was performed on the monomer solution. Additionally, a 2.0 M solution of MeOH in THF (30 µL) was added to the 2.0 M solution of P<sub>2</sub>-*t*-Bu base in THF (30 µL) in a flame-dried vial under an Ar atmosphere at rt. After 15 min, 12 µL of this initiator-base solution was added to the chilled monomer solution at -20 °C. The reaction mixture was quenched with glacial acetic acid (100 µL) to give polymer 12 as a white solid (1.64 g, 82%). M<sub>n</sub> = 484.3 kDa, M<sub>w</sub> = 711.4 kDa, PDI = 1.5.

Synthesis of polymer 13 (7.1 kDa,  $M_n$ ). General polymerization procedure B was used with some modifications as follows: Compound 5 (0.25 g, 1.2 mmol), THF (1.5 mL), MeOH (1.2  $\mu$ L, 30  $\mu$ mol), and

P<sub>2</sub>-*t*-Bu base (30  $\mu$ L, 60  $\mu$ mol). The polymerization reaction was conducted at 0 °C. Allyl chloroformate (0.13 mL, 1.2 mmol) and 4-(dimethylamino)-pyridine (0.15 g, 1.2 mmol) were used to quench the reaction mixture and yielded polymer **13** as a white solid (0.20 g, 80%). M<sub>n</sub> = 7.1 kDa, M<sub>w</sub> = 10.3 kDa, PDI = 1.5.

Synthesis of polymer 14 (27 kDa,  $M_n$ ). General polymerization procedure B was used with some modifications as follows: Compound 5 (0.25 g, 1.2 mmol), THF (1.5 mL), MeOH (0.26 µL, 6.0 µmol), and P<sub>2</sub>-*t*-Bu base (3 µL, 6.0 µmol). All glassware was flame dried under vacuum (1.1 mmHg) and then purged with dry Ar. (10.0 mL) was prepared. In a glovebox, a 3 mL vial with stir bar was load with compound 5 (75.6 mg, 0.359 mmol). To this vial was added a 0.6 M stock solution of MeOH in THF (0.30 mL, 0.18 mmol MeOH) followed by THF (0.30 mL). The solution was degassed via the freeze-pump-thaw method three times, backfilling with Ar on the final cycle. To this solution was added the 2.0 M P<sub>2</sub>-*t*-Bu phosphazene base solution in THF (90 µL, 0.18 mmol) in a single portion at 20 °C. The solution was stirred for 45 min. A 20 µL aliquot of this initiator solution was added to a degassed solution of compound 5 (0.25 g, 1.2 mmol) in THF (1.5 mL), pre-chilled to -20 °C. The reaction mixture was quenched with glacial acetic acid (68 µL) to give polymer 14 as a white solid (0.16 g, 64%).  $M_n = 26.6$  kDa,  $M_w = 29.7$  kDa, PDI = 1.1.

Synthesis of polymer 15 (2.9 kDa,  $M_n$ ). General polymerization procedure B was used with some modifications as follows: Compound 5 (0.25 g, 1.2 mmol), THF (1.5 mL), MeOH (2.6 µL, 60.0 µmol), and P<sub>2</sub>-*t*-Bu base (30.0 µL, 60.0 µmol). The polymerization reaction was conducted at 20 °C. The reaction mixture was quenched with glacial acetic acid (68 µL) to give polymer 15 as a white solid (0.093 g, 37%). To test the effect of washing the polymer on the molecular weight and PDI, the polymer was analyzed by GPC directly after precipitating the reaction solution in MeOH (M<sub>n</sub> = 2.6 kDa, M<sub>w</sub> = 3.5 kDa, PDI = 1.3) and after the full washing procedure (M<sub>n</sub> = 2.9 kDa, M<sub>w</sub> = 3.7 kDa, PDI = 1.3).

## Effect of Polymerization Temperature on Polymer Molecular Weight:

The effect of polymerization temperature on the molecular weight of polymer **12** was investigated following general polymerization procedure B using 0.025 equiv MeOH (0.122 mL, 2.98 mmol in THF stock solution) and quenching with acetic acid as shown in Table S1:

Entry	Polymerization Temperature (°C)	M <sub>n</sub> (kDa)	M <sub>w</sub> (kDa)	PDI	% Yield
1	-20	15.1	26.2	1.73	38
2	-10	11.8	19.6	1.67	48
3	0	9.9	14.6	1.48	35
4	10	7.3	9.7	1.34	49
5	20	5.3	6.6	1.23	31

 Table S1. Effect of polymerization temperature on the synthesis of polymer 12.

## Effect of Equivalents of Initiator on Polymer Molecular Weight:

The effect of equivalents of initiator (MeOH) on the molecular weight of polymer 12 was investigated following general polymerization procedure B at 0  $^{\circ}$ C and quenching with acetic acid as shown in Table S2:

Entry	Equivalents of Initiator	M <sub>n</sub> (kDa)	M <sub>w</sub> (kDa)	PDI	% Yield
1	0.020	11.8	16.9	1.43	52
2	0.025	11.4	17.5	1.54	45
3	0.050	8.39	11.3	1.35	38
4	0.075	6.38	8.20	1.28	51
5	0.080	5.45	6.89	1.26	41

**Table S2.** Effect of the number of equivalents of initiator (MeOH) relative to monomer on the synthesisof polymer 12.

## **Procedure for Testing the Stability of the Proton End-Capped Poly(benzyl ether) backbone:**

A solution of proton end-capped polymer **6** (72 kDa,  $M_n$ ) in CH<sub>2</sub>Cl<sub>2</sub> (500 µL, 69 µM) was prepared at 18 °C in a sealed flask. A GPC trace was acquired for this solution at time 0 min to act as a reference, and then after 24 h to monitor for decomposition.



**Figure S6.** Refractive index traces for the proton end-capped polymer **6** (72 kDa,  $M_n$ ) stability study. The orange trace represents the proton-end-capped polymer (69  $\mu$ M, 18 °C, peak area: 102) at time zero. The blue trace represents the proton-end-capped polymer (69  $\mu$ M, 18 °C, peak area: 112) after 24 h.

## Procedure for Measuring the Depolymerization of Poly(benzyl ether) 6 in the Presence of Base:

To a solution of proton end-capped polymer **6** (72 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub> (500 µL, 139 µM) was added 69 µL of 0.1 M anisole in CD<sub>2</sub>Cl<sub>2</sub>. A <sup>1</sup>H NMR spectrum was obtained to determine the peak ratio via integration values between the benzyl proton of the poly(benzyl ether) and the methyl ether peak of the anisole standard. A portion of 1.0 M DBU (69 µL, 1000 equiv) in CD<sub>2</sub>Cl<sub>2</sub> was added to the polymer solution and <sup>1</sup>H NMR spectra were obtained periodically over the period of 100 min. The ratio of the benzyl proton of the polymerization in DMF, THF, and toluene, a solution of 1.0 M DBU (140 µL, 1000 equiv) was added to a solution of polymer **6** (72 kDa,  $M_n$ ) (1.0 mL, 139 µM) in each respective solvent. Each solution was filtered through a 0.2 µm PTFE filter and analyzed by GPC every 30 min for 4 h and then every 24 h until no polymer peak was observed by refractive index.

Time			
(min)	Trial 1	Trial 2	Trial 3
0	1.11	0.96	1.12
2.5	0.87	0.82	0.95
10	0.63	0.69	0.74
20	0.53	0.52	0.54
30	0.40	0.40	0.40
40	0.29	0.31	0.28
50	0.21	0.24	0.19
60	0.15	0.19	0.16
70	0.11	0.15	—
80	0.08	0.09	_
90	0.06	0.07	0.07
100	0.05	0.05	0.04

Table S3. Ratio of the benzyl proton peak area to the peak area for the anisole standard.

## **Determining Clean Conversion of Polymer to Monomer:**

To a solution of proton end-capped polymer **6** (72 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub> (500 µL, 139 µM) was added a portion of 1M DBU (69 µL, 1000 equiv)) in CD<sub>2</sub>Cl<sub>2</sub> and <sup>1</sup>H NMR's were aquired periodically over the period of 180 min.



**Figure S7**. <sup>1</sup>H NMR spectrum of polymer **6** (72 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub> before addition of DBU.



Figure S8. <sup>1</sup>H NMR spectrum of 6 (72 kDa, M<sub>n</sub>) in CD<sub>2</sub>Cl<sub>2</sub> 30 min after addition of DBU.

**Figure S9.** <sup>1</sup>H NMR spectrum of **6** (72 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub> 3 h after addition of DBU.



### **Studies of the Selective Depolymerization of End-capped Polymers:**

# Procedure for Testing the Selective Depolymerization of End-capped Polymer in Response to Fluoride.

Stock solutions were prepared of (i) tetrabutylammonium fluoride (TBAF) (43.7 mg, 0.167 mmol) in THF (0.10 mL) and 1.25 mM pH 7.0 potassium phosphate buffer solution (0.200 mL) and (ii) tetrabutylammonium chloride (TBAC) (46.4 mg, 0.167 mmol) in THF (0.10 mL) and 1.25 mM pH 7.0 potassium phosphate buffer solution (0.200 mL). Stock solutions of TBS end-capped polymer **7** (165 kDa,  $M_n$ ), Alloc end-capped polymer **13** (7.1 kDa,  $M_n$ ), and methyl end-capped polymer **11** (28 kDa,  $M_n$ ) were prepared using THF (5.0 mL, 0.146 mM). To 0.985 mL of the polymer solution was added 15 µL of either the TBAF or TBAC solution at 18 °C under air in a plastic eppendorf tube. The reaction mixtures were vortexed for 30 seconds, filtered, and analyzed by GPC every 30 min for 2 h. As a control, 0.985 mL of each stock polymer solution were diluted with 15 µL of a 1:2 THF-deionized water solution, filtered and analyzed by GPC after 30 min.

# Procedure for Testing the Selective Depolymerization of End-capped Polymer in Response to Palladium.

Stock solutions were prepared of (i) DBU (0.14 mL, 0.95 mmol) and AcOH (27  $\mu$ L, 0.48 mmol) in DMF (10.0 mL) and (ii) Pd(0)(PPh<sub>3</sub>)<sub>4</sub> (6.6 mg, 5.7 mmol) in DMSO (10.0 mL). Stock solutions of TBS end-capped polymer **7** (165 kDa, M<sub>n</sub>), Alloc end-capped polymer **13** (7.1 kDa, M<sub>n</sub>), and methyl end-capped polymer **11** (28 kDa, M<sub>n</sub>) were prepared with the DBU–AcOH solution (3.0 mL, 0.57  $\mu$ M). To the polymer solution (0.90 mL) was added DMSO (0.199 mL) and the Pd(0)(PPh<sub>3</sub>)<sub>4</sub> solution (1  $\mu$ L). The reaction mixtures were vortexed for 30 seconds, filtered, and analyzed by GPC every 30 min for 2 h. As a control, 0.90 mL of each stock polymer solution was diluted with 0.10 mL DMSO, filtered and analyzed by GPC after 30 min.



**Figure S10.** Alloc end-capped polymer **13** (7.1 kDa, M<sub>n</sub>) exposed to TBAF (blue) and unexposed control (black).



Figure S11. TBS end-capped polymer 7 (165 kDa,  $M_n$ ) exposed to Pd(0) (blue) and unexposed control (black).



**Figure S12.** Methyl end-capped polymer **11** (28 kDa,  $M_n$ ) exposed to Pd(0) (blue) and unexposed control (black).



Figure S13. Methyl end-capped polymer 11 (28 kDa,  $M_n$ ) exposed to TBAF (blue) and unexposed control (black).

#### Procedure for Testing the Stability of the Poly(benzyl ether) Backbone.

Methyl end-capped polymer **11** (28 kDa,  $M_n$ ) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1.00 mL, 175  $\mu$ M). A GPC trace was obtained for the stock solution as a reference. To test the effect of acid, 69  $\mu$ L of 1.0 M acetic acid (~400 equiv) was added to the polymer solution (1.00 mL) at 18 °C. To test the effect of base, 69  $\mu$ L of 1 M DBU (~400 equiv) was added to the polymer solution (1.00 mL) at 18 °C. To test the effect of temperature, the polymer solution (1.00 mL) was transferred to a sealed reaction tube and heated to 40 °C. After 24 h, GPC traces were obtained for each reaction solution.



**Figure S14**. Refractive index traces for methyl end-capped polymer **11** (28 kDa,  $M_n$ ). The orange trace represents unexposed polymer **11** (175  $\mu$ M, 18 °C, peak area: 115). The green trace represents polymer **11** heated at 40 °C for 24 h (175  $\mu$ M, 40 °C, peak area: 109). The blue trace represents polymer **11** exposed to AcOH for 24 h (164  $\mu$ M, 18 °C, peak area: 103). The black trace represents polymer **11** exposed to DBU for 24 h (164  $\mu$ M, 18 °C, peak area: 109).



**Figure S15.** UV/Vis absorbance spectra for TBS end-capped polymer 7 (165 kDa,  $M_n$ ) (blue) and monomer 5 (black,  $\lambda_{max} = 346$  nm) in THF (0.238 mM).



Figure S16. <sup>1</sup>H NMR spectrum of compound 3 in CDCl<sub>3</sub>.



## Figure S17. <sup>13</sup>C NMR spectrum of compound 3 in CDCl<sub>3</sub>.



Figure S18. DEPT 45 NMR spectrum of compound 3 in CDCl<sub>3</sub>.



## Figure S19. <sup>1</sup>H NMR spectrum of compound 4 in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S20. <sup>13</sup>C NMR spectrum of compound 4 in CD<sub>2</sub>Cl<sub>2</sub>.

#### 10 NMR plot parameters CX 20.00 cm F1P 12.000 ppm F1 4801.56 H2 -1.000 ppm F2 -1.000 ppm F2 -0.65000 ppm/cm H2CM 260.08450 H2/cm = CHANNEL f1 ====== 1H 6.45 usec 0.00 dB 400.1324710 MHz B278.146 Hz 0.126314 Hz 3.9584243 sec 57 60.400 usec 6.00 usec 300.0 K 1.00000000 sec F2 - Processing parameters S1 32768 32768 442 MDW 400.1300056 442 NDW 00 130005 442 S58 00.00 Hz CB 0.00 Hz CB 0.00 Hz Current Data Parameters NAME 5-6-13MGONG3 EXPNO 1 PAOCNO 1 FIDRES P1 PL1 SF01 NUC1 ..... SN SS 비망 B AG TMS 9900.0--Fo - S.0489 8120.5 9**Þ**86 · G È∾ - 5.0560 4 110.7 7.04S6 و 44G1.7 7.3807 1385.7 1.0025 1166.7 1.0000 696E'L 4.9572 7.4025 0586.0 7.41SS 7814.7 8 7.4218 6664.7 1124.7 - 7.5062 6205.7 Me -9 Ο ŝ Re Edd

## Figure S21. <sup>1</sup>H NMR spectrum of compound 5 in CD<sub>2</sub>Cl<sub>2</sub>.

wdd

Integral



## **Figure S22.** <sup>13</sup>C NMR spectrum of compound **5** in $CD_2Cl_2$ .

## Figure S23. GPC trace of polymer 6 (5.1 kDa, $M_n$ ).











## Figure S25. GPC trace of polymer 7 (9.3 kDa, M<sub>n</sub>).



Figure S26. <sup>1</sup>H-NMR spectrum of polymer 7 (9.3 kDa, M<sub>n</sub>) in CD<sub>2</sub>Cl<sub>2</sub>.

20.00 cm 20.00 ppm 18112.25 Hz -15.000 ppm -1132.01 Hz 12.75000 ppm/cm 12.75000 Hz/cm 18832.333 Hz 0.287360 Hz 1.7400308 sec 26.550 usec 6.00 usec 5.0000000 sec 0.0300000 sec 0.0300000 sec CHANNEL f2 ====== waltz16 11 110.00 d9 17.50 d8 17.50 d8 300.1312005 MHz 19 paramu. 32768 75,4677205 MHz EM - CHANNEL f1 ===== 13C 9.75 usec 75.4760200 MHz F2 - Acquisition Parameters Date\_\_\_\_\_\_20130219 Time\_\_\_\_\_\_18.50 Time\_\_\_\_\_\_18.50 Time\_\_\_\_\_\_18.50 PROBHD\_\_\_\_\_\_\_\_18.99330 PULPHOG\_\_\_\_\_\_\_299330 TID\_\_\_\_\_\_25536 SULVENT\_\_\_\_\_\_255212 NS\_\_\_\_\_\_500 F2 - Processing parameters SI 32768 32769 Mt2 MDW 5760 Mt2 MDW 64 100 H2 CB 1.00 H2 CB 1.00 H2 CB 1.40 Current Data Parameters NAME 21913M603-176 EXPNO 21913M603-176 PPOCNO 1 1D NMR plot parameters CX 20.00 F1P 240.000 SPDPRG2 FIDRES F1 F2P FPMCM HZCM CPD2 PL12 PL13 SF02 NUC1 SF01 200 2 2 AG d11 d12 d12 d12 55 SWH 0 778.71 -- 52.998 156.321 611.53  $CD_2CI_2$ 23.480 20 648.62 105.42 54.562 691.89 ≱Z1.88 — 100 157.265 962.7S1-127.742 \$£8.751 128.331 512.851-E78.1E1-970.7E1-150 -145.444 815.331-Me Me Polymer 7 (9.3 kDa, M<sub>n</sub>) ⊆ Me 200 Me Me fBu<sup>\_Si^</sup> mdd Me wdd

## Figure S27. <sup>13</sup>C-NMR spectrum of polymer 7 (9.3 kDa, $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S28. GPC trace of polymer 7 (164.5 kDa, M<sub>n</sub>).



## Figure S29. GPC trace of polymer 8 (6.4 kDa, M<sub>n</sub>).

 
 1D NMR plot parameters

 CX
 20.00 cm

 F1P
 12.000 ppm

 F1
 4801.56 Hz

 F2P
 -400.03 Hz

 F2P
 -400.13 Hz

 PPMCM
 0.55000 ppm/cm

 HZCM
 260.08450 Hz/cm

 F2 - Acquisition Parameters

 Date\_\_\_\_\_20130218

 Time
 22.15

 TSTRUM
 22.15

 INSTRUM
 22.15

 INSTRUM
 22.15

 INSTRUM
 22.33

 PULPROG
 5 mm BBI 14+

 PULPROG
 55536

 SOLVENT
 55534

 SOLVENT
 55534

 SOLVENT
 55534

 SOLVENT
 55534

 SOLVENT
 5534

 SOLVENT
 5534 = CHANNEL f1 ===== 1H 6.45 usec 0.00 dB 400.1324710 MHz 60.400 usec 6.00 usec 300.0 K Current Data Parameters NAME 021813MG03-177 EXPNO 21813MG03-177 PROCNO 1 P1 P1 PL1 SF01 ..... 0 ₽0175.1-0.2278 67867.1-9Se88.1 6.1485 -ru 1.95427 9914.0 ---2.27549 -3.72249 7520.0 6E197.E-0.3162 62026.5-4 97989.E-CD<sub>2</sub>Cl<sub>2</sub> -5.32109 S2E0.0 546443 8GÞÞZ'G 1.1510 5.80293 ۵ 79-93 Re \$9681 . T Me 2.0000 7.22444 3 0.2829 Ó 6418E.7-G109.2 ⊆ 10524.7-G180.0 080E8.7æ **8** (6.4 kDa, M<sub>n</sub>) Me C Me =0 10 ò o=t E dd wdd Integral Me Me

Figure S30. <sup>1</sup>H-NMR spectrum of polymer 8 (6.4 kDa,  $M_n$ ) in  $CD_2Cl_2$ .

10 NMR plot parameters CX 20.00 cm F1P 240.000 ppm F1 18112.25 Hz F2P -15.000 ppm F2 -15.01 Hz PPKCM 962.21338 Hz/cm HZCM 962.21338 Hz/cm 13C 9.75 usec 0.00 dB 75.4760200 MHz = CHANNEL f2 ====== waltz16 1H 110.00 usec 0.00 dB 17.50 dB 17.50 dB F2 - Acquisition Parameters Date\_\_\_\_\_20130219 Time 20130219 Time 20130219 Time 20130219 TINSFRUM spect FROBHO 5 mm Mutinu PULPROG 290330 13004 26.550 usec 6.00 usec 300.0 K 18832.393 Hz 0.287360 Hz 1.7400308 sec 2.0000000 sec 0.03000000 sec 0.00002000 sec Processing parameters 32768 75.4677228 MHz £ i Current Data Parameters NAME 21913MG03-177 EXPNO 2 PROCNO 1 mm Multinu zgpg30 65536 CO2C12 1.40 CHANNEL f1 400 Ð : TD SOLVENT ds Swh Fiores CPDPRG2 PCPD2 PL2 PL12 PL13 SF02 NUC1 P1 PL1 SF01 AG DW DF DF d11 d12 d12 -0 16.430 17.431 53.122 53.482  $CD_2CI_2$ 59.842 20 54.203 49<u>6</u>.42 56.720 56.763 86.230 100 127.300 127.623 £08.7St 127.884 158.564 ₹ 010.1E1-Me 311.751 145.485 150 ⊆ \$76.374 **8** (M<sub>n</sub> = 6.4 kDa) Me Ó Me 200 =0 0 0=z mdd wdd Me Me

**Figure S31.** <sup>13</sup>C-NMR spectrum of polymer **8** (6.4 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub>.



## Figure S32. GPC trace of polymer 9 (3.6 kDa, M<sub>n</sub>).



Figure S33. <sup>1</sup>H-NMR spectrum of polymer 9 (3.6 kDa, M<sub>n</sub>) in CD<sub>2</sub>Cl<sub>2</sub>.

10 NMR plot parameters CX 20.00 cm F1P 240.000 ppm F1 18112.55 H2 F2P -1132.01 Ppm F2 -1132.01 H2 H2CM 962.21338 H2/cm F2 - Processing parameters SI 32768 SF 75.467711 MH2 MDW 0 SSB 1.00 H2 CB 1.00 H2 GB 1.00 H2 CB 1.40 = CHANNEL f2 ====== waltz15 11 110.00 dB 17.50 dB 17.50 dB 17.50 dB CHANNEL f1 =====
 13C
 9.75 usec
 0.00 dB
 75.4760200 MHz 11585.2 26.550 usec 6.00 usec 300.0 K 2.0000000 sec 0.0300000 sec 18832.393 Hz 0.287360 Hz 1.7400308 sec F2 - Acquisition Parameters Current Data Panameters NAME 22513MG03-183 EXPNO 3 PROCNO 1 i mm Multinu zgpg30 65536 CO2C12 800 20130225 18.19 spect ß Date\_ Time INSTRUM PROBHD PULPROG TD SOLVENT CPDPRG2 NS DS SWH FIDRES NUC2 PCPD2 PL2 PL12 PL13 SF02 NUC1 P1 PL1 SF01 ..... AG DW d11 d12 d12 0 795.31 114.71 69G.TI 52.412 25.564 53.122  $CD_2CI_2$ 20-23.482 53.842 54.203 Þ9G.ÞZ £45.63 G12.93 80.425 115.08 -100 965.911 127.288 713.751 387.7SF 127.863 785.851 128.547 130.566 E03.1E1-188.161-150 IOI.TEI Me 145.476 Re -122 323 ⊆ **9** (M<sub>n</sub> = 7.6 kDa) Me 200 Me =0 Ó mdd wdd



S40



Figure S35. GPC trace of polymer 10 (6.5 kDa, M<sub>n</sub>).



Figure S36. <sup>1</sup>H-NMR spectrum of polymer 10 (6.5 kDa, M<sub>n</sub>) in CD<sub>2</sub>Cl<sub>2</sub>.

Current Data Parameters NAME 22013MG03-105 EXPNO 22013MG03-12 PACCNO 1 PACCNO 1 F2 - Acquisition Parameters	Time concert concount INSTRUM spect PROBHO 5 mm Multinu PULPAOG 299330 TD 65555 SOLVENT CO2C12	NS 400 DS 5MH 18832.393 HZ FURES 18832.393 HZ FI 0.287360 HZ FI 1740308 SEC FI 15384 SEC FI 250 USEC DI 25.00 USEC DI 2.00000000 SEC d11 0.00000000 SEC d12 0.0000000 SEC	CHANNEL f1	CHANNEL F2 CPDRAR Maltz16 NUC2 110.00 Usec PL2 110.00 dB PL2 17.50 dB PL12 17.50 dB PL12 17.50 dB PL12 17.50 dB PL13 17.50 dB	F2 - Processing parameters SI 27268 SF 75.4671294 M+2 MOM EN EN SSB 0 0 LB 1.00 H2 GB 1.00 H2 GB 1.00 H2 CB 1.40	10 NMM plot parameters CX 20.00 cm F1 240.000 ppm F1 1812.25 H2 F2 112.25 H2 F2 -1132.00 ppm F2 -1132.00 ppm F2 -1132.00 ppm/cm H2CM 962.21338 H2/cm
16,133 16,133 17,000 12,000 17,0100 17,0100 17,010000000000						100
mqq		Me Me	<b>10</b> ( $M_n = 6.5 \text{ kDa}$ )			ppm 200 150 150

Figure S37. <sup>13</sup>C-NMR spectrum of polymer 10 (6.5 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub>.

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## Figure S38. GPC trace of polymer 11 (3.9 kDa, M<sub>n</sub>).







Figure S40. <sup>13</sup>C-NMR spectrum of polymer 11 (3.9 kDa,  $M_n$ ) in CD<sub>2</sub>Cl<sub>2</sub>.



## Figure S41. GPC trace of polymer 11 (27.6 kDa, M<sub>n</sub>).



Figure S42. GPC trace of polymer 12 (484.3 kDa, M<sub>n</sub>).



## Figure S43. GPC trace of polymer 13 (7.1 kDa, M<sub>n</sub>).



## Figure S44. GPC trace of polymer 12 (26.6 kDa, M<sub>n</sub>).



## Figure S45. GPC trace of polymer 12 (2.9 kDa, M<sub>n</sub>) before washing.



## Figure S46. GPC trace of polymer 12 (2.9 kDa, M<sub>n</sub>) after washing.



Figure S47. GPC trace of polymer 12 (table S1, entry 1).



## Figure S48. GPC trace of polymer 12 (table S1, entry 2).



## Figure S49. GPC trace of polymer 12 (table S1, entry 3).



## Figure S50. GPC trace of polymer 12 (table S1, entry 4).



Figure S51. GPC trace of polymer 12 (table S1, entry 5).



## Figure S52. GPC trace of polymer 12 (table S2, entry 1).



Figure S53. GPC trace of polymer 12 (table S2, entry 2).



## Figure S54. GPC trace of polymer 12 (table S2, entry 3).



## Figure S55. GPC trace of polymer 12 (table S2, entry 4).



Figure S56. GPC trace of polymer 12 (table S2, entry 5).

## References

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