

## Supporting information

### **Telechelic PMMA Containing Two OH Groups at The Same Chain End Prepared by 8-Boraindane/Oxygen Initiator**

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#### Experimental

All manipulations were carried out under inert atmosphere or by using standard Schlenk technique.  $^1\text{H}$  and  $^{13}\text{C}$  NMR was measured on a Bruker AM-300 or WM-360 spectrometer with DISNMR software. The measurements were usually taken at room temperature using as solvent. The molecular weight and molecular weight distribution of the polymers were determined by Gel Permeation Chromatography (GPC) using a Waters with a refractive index (RI) detector. The measurements were taken at 35 °C using tetrahydrofuran (THF) as solvent and a mobile phase of 0.7 ml/min flow rate. Narrow molecular weight polystyrene samples were used as standards for calibration.

#### Synthesis of 1,3,7-octatriene

1,3,7-Octatriene was synthesized via dimerization of butadiene aided by phenol in the presence of a Pd catalyst. Under an argon (Ar) atmosphere, to a 1 liter flask equipped with a magnetic stirrer was added 100 g (1.06 mol) of phenol, 4.64 g (0.004 mol) of sodium phenoxide, 0.25 g of  $\pi$ -allylpalladium chloride and 400 ml of chloroform. After the flask was cooled down to -80° C, it was charged with 150 g of butadiene. The solution was gradually warmed up to room temperature within 1 hour. The stirring was continued overnight. Chloroform was then removed completely under vacuum at room temperature resulting in a pale suspension. To this suspension was added 8.0 g (0.03 mol) of triphenylphosphine followed by stirring at 100° C for 1 hour. About 76 g of 1,3,7-octatriene was then carefully distilled from the mixture by fractional distillation at about 120°C to 125°C.

#### Synthesis of 8-boraindane

Under Ar atmosphere at 0° C, 21.6 g (0.2 mol) of 1,3,7-octatriene in 50 ml of THF solution was added dropwise with 200 ml (1.0 M) of borane THF complex in THF solution. After the addition was complete, stirring continued for 1 hour at 0° C. Then the mixture was refluxed for 1 hour before THF was removed completely under vacuum at room temperature. The attained white solid was heated to 210°C for 3 hours then 9.6 g of 9-bora-indane (yield: 41%) was distilled from the mixture at about 50 °C to 60 °C (0.3 mmHg). The spectra data were as follows:  $^1\text{H}$ -NMR (25° C in  $\text{CDCl}_3$ )  $\delta$  .08~1.6 ppm (m);  $^{11}\text{B}$ -NMR(25°C in  $\text{CDCl}_3$ )  $\delta$  91.14 ppm (s);  $^{13}\text{C}$ -NMR (25°C in  $\text{CDCl}_3$ )  $\delta$  21.9 ppm (b,  $\text{CH}_2\text{-B}$ ),  $\delta$  25.6 ppm (s,  $\text{CH}_2$ ),  $\delta$  26.3 ppm (s,  $\text{CH}_2$ ),  $\delta$  27.4 ppm (b,  $\text{CH}_2\text{-B}$ ),  $\delta$  28.4 ppm (s,  $\text{CH}_2$ ),  $\delta$  31.6 ppm (s,  $\text{CH}_2$ ),  $\delta$  34.4 ppm (s,  $\text{CH}_2$ ),  $\delta$  42.4 ppm (b,  $\text{CH-B}$ ).

### Synthesis of telechelic PMMA with two terminal OH groups

In a 100 ml flame-dried flask, 10.0 ml (100 mmol) of MMA (purified by distillation over  $\text{CaH}_2$ ) and 140 mg (1.2 mmol) of 8-bora-indane were introduced under argon. After injecting 10 ml of  $\text{O}_2$  (0.8 mmol), the solution was mixed by shaking the flask vigorously for about 5 minutes. The system was then kept at room temperature for another 60 min before adding 20 ml of acetone to reduce the solution viscosity. The solution was then poured into 200 ml of well stirred methanol to quench the polymerization and precipitate PMMA polymer. To assure complete oxidation of all borane moieties, the isolated PMMA polymer was then re-dissolved in 20 ml THF before adding 0.2 ml (6N) NaOH solution, followed by dropwise 0.4 ml, 33%  $\text{H}_2\text{O}_2$  at  $0^\circ\text{C}$ . The resulting mixture was heated up to  $50^\circ\text{C}$  for 1 hour to complete the oxidation. After cooling to room temperature, the solution was poured into 200 ml of well stirred methanol. The precipitated telechelic PMMA polymer was collected, washed, and dried in vacuum at  $60^\circ\text{C}$  for 2 days. The overall polymer yield was about 80%, and the polymers molecular weight determined by Gel Permeation Chromatography (GPC) was  $M_n = 20,300$  g/mole and  $M_w = 68,500$  g/mole. The terminal OH groups were examined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR-DEPT 135 spectra.

### Synthesis of telechelic PTFEA with two terminal OH groups

In a 150 ml flame-dried flask, 40 ml of THF, 5 ml of 2',2',2'-trifluoroethyl acrylate (TFEA) monomer, and 70 mg of 8-bora-indane were introduced under argon. After injecting 5 ml of  $\text{O}_2$ , the solution was mixed by shaking the flask vigorously for about 5 minutes. The solution was then kept at room temperature for various times (2 hr, 4 hr, 6 hr, 8 hr, and 10 hr, respectively) before exposing the solution to air that stops the reaction and oxidized all borane moieties. The polymer solution was then poured into 200 ml of well stirred methanol to precipitate the polymer. The precipitated telechelic poly(trifluoroethyl acrylate) was collected, washed, and dried in vacuum at  $60^\circ\text{C}$  for 2 days, then was characterized by Gel Permeation Chromatography (GPC) and  $^1\text{H}$  and  $^{13}\text{C}$  NMR-DEPT measurements. All the experimental results for the series of examples are summarized in the following table.

A summary of TFEA polymerization by 8-bora-indane/ $\text{O}_2$  in THF

| Reaction Time<br>(hr) | Conversion<br>(%) | $M_n$<br>(g/mole) | $M_w$<br>(g/mole) | PDI<br>( $M_w/M_n$ ) |
|-----------------------|-------------------|-------------------|-------------------|----------------------|
| 2.0                   | 12.0              | 7,000             | 14,000            | 2.0                  |
| 4.0                   | 19.0              |                   |                   |                      |
| 6.0                   | 40.0              | 25,000            | 49,000            | 1.9                  |
| 8.0                   | 52.0              |                   |                   |                      |
| 10                    | 60.0              | 33,000            | 56,000            | 1.6                  |

### Synthesis of poly(methyl methacrylate-*b*-trifluoroethyl acrylate) diblock copolymer

In a flame-dried 50 ml flask, 5.0 ml (50 mmol) of MMA and 70 mg (0.6 mmol) of 8-bora-indane were mixed under argon. To this mixture 5.0 ml of O<sub>2</sub> (0.2 mmol) was injected, following by vigorous shaking to assure complete mixing. The system was then kept at room temperature for 20 min, followed by removal of all the volatiles by vacuum distillation. About 5.0 ml of 2',2',2'-trifluoroethyl acrylate (TFEA) was subsequently injected into the system. The mixture was shaken vigorously to dissolve the solid as soon as possible. After complete dissolution, the solution was kept at room temperature for 1 hour before adding 10 ml of acetone to reduce the viscosity and then opening the system to air to oxidize all the borane moieties. The solution was then poured into 200 ml of well stirred methanol. The precipitated telechelic diblock polymer was collected, washed, and dried in vacuum at 60°C for 2 days. The resulting telechelic poly(methyl methacrylate-*b*-trifluoroethyl acrylate) diblock copolymer was characterized by Gel Permeation Chromatography (GPC) and <sup>1</sup>H and <sup>13</sup>C NMR-DEPT measurements.