

## Supporting Information

### Polymerization-Induced Self-Assembly based on ATRP in Supercritical Carbon Dioxide

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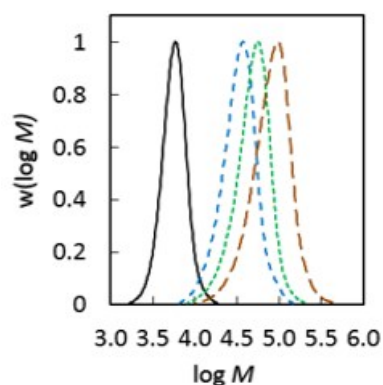
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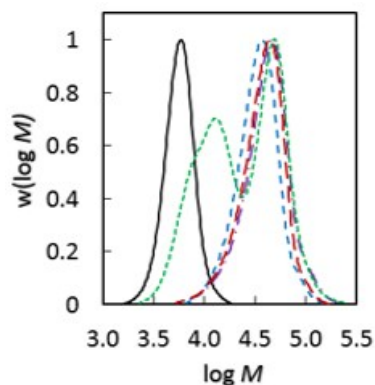
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**Figure S1:** Optical image (Samsung Galaxy A5 2016) of the dry PDMS-*b*-PBzMA<sub>138</sub> powder after purification using scCO<sub>2</sub>.

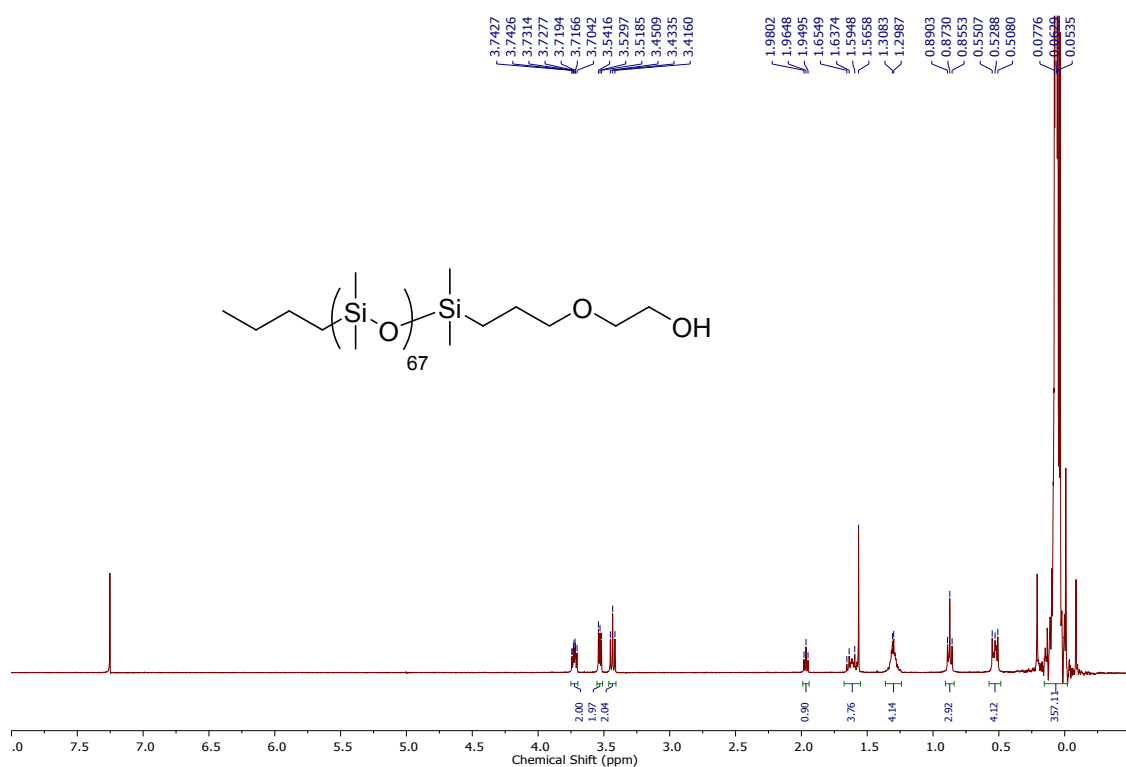


**Figure S2.** MWDs for ATRP dispersion polymerization of 35 v/v(%) BzMA in scCO<sub>2</sub> at 80 °C and 30 MPa corresponding to PDMS-Br macroinitiator (black), Run 3 (blue); Run 4 (green) and Run 2 (brown). See Table 1 for details.



**Figure S3.** MWDs assessing the influence of monomer (BzMA) loading on the ATRP dispersion polymerization in scCO<sub>2</sub> at 80 °C and 30 MPa after 24 h using [BzMA]:[PDMS-Br]:[CuBr]:[HMTETA] = 168:1:1.5:1.5. The MWDs correspond to PDMS-Br (black solid line), and polymerizations at 20 v/v(%) BzMA loading at 13% conversion (green square dotted line), 35 v/v(%) BzMA loadings at 88% conversion (Run 3, blue dashed line), 50 v/v(%) BzMA loadings at 94% conversion (Run 5, purple long dash dotted line), and 65 v/v(%) BzMA loadings at 89% conversion (Run 6, red long dashed line).

(a)



(b)

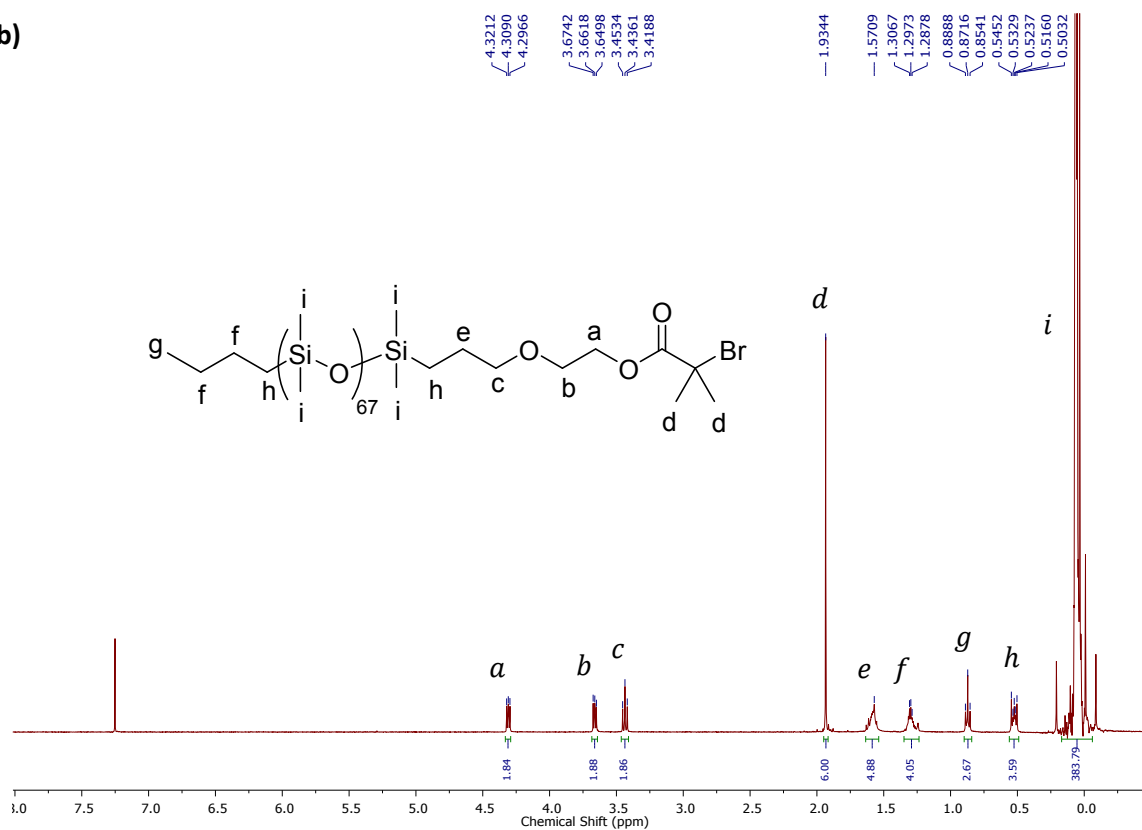
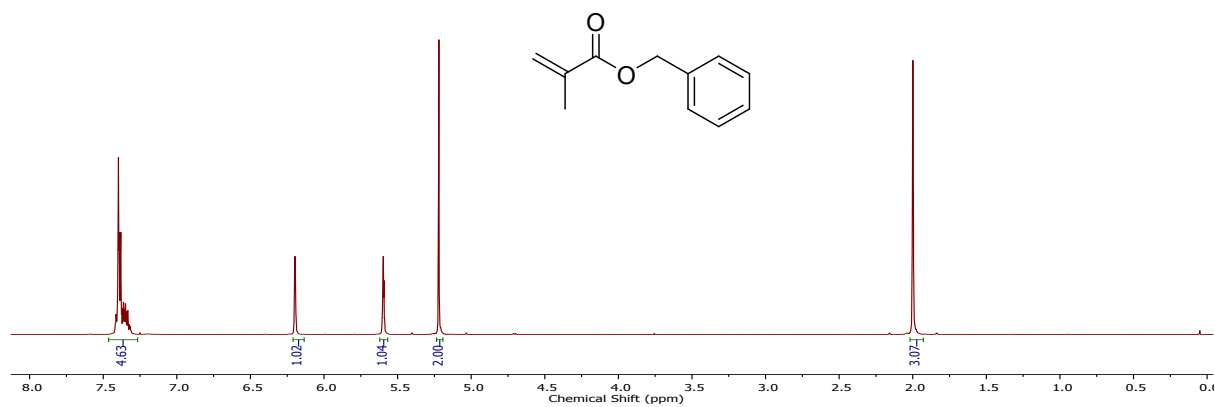
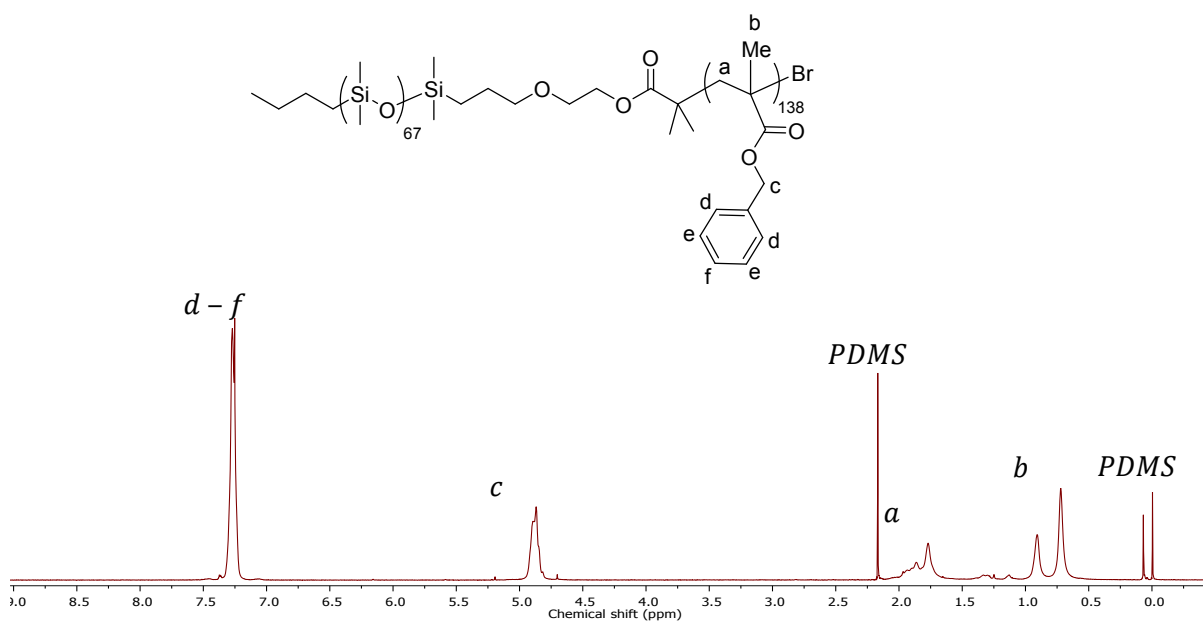


Figure S4: <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 400 MHz) of (a) PDMS-OH and (b) PDMS-Br.

(a)



(b)



**Figure S5:** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 400 MHz) of (a) BzMA monomer and (b) PDMS-*b*-PBzMA<sub>138</sub>.

## Experimental

### Materials

Benzyl Methacrylate (BzMA, Sigma-Aldrich, 96%) was distilled *in vacuo* to remove radical inhibitor. Hydroxyl terminated poly(dimethylsiloxane) (PDMS-OH, Sigma-Aldrich, av.  $M_n \sim 4670 \text{ g mol}^{-1}$ ,  $M_n = 5150 \text{ g mol}^{-1}$  and  $D = 1.12$  determined by GPC, as described below), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Sigma-Aldrich, 97%), triethylamine (Sigma-Aldrich,  $\geq 99\%$ ), and 2-bromoisobutyl bromide (Sigma-Aldrich, 98%) were used as received. Tetrahydrofuran (THF, Sigma-Aldrich,  $\geq 99\%$ ) and diethyl ether ( $\text{Et}_2\text{O}$ , Sigma-Aldrich) were distilled over Na wire and benzophenone (Sigma-Aldrich, 95%).  $\text{Na}_2\text{CO}_3$  (Sigma-Aldrich,  $\geq 99\%$ ) and  $\text{MgSO}_4$  (Sigma-Aldrich,  $\geq 99.99\%$ ) were used as received.  $\text{CH}_2\text{Cl}_2$  (Sigma-Aldrich,  $\geq 99\%$ ),  $\text{CDCl}_3$  (Sigma-Aldrich, 99.8 atom%), glacial acetic acid (Sigma-Aldrich,  $\geq 99.5\%$ ), absolute ethanol (Sigma-Aldrich,  $\geq 99.5\%$ ), and  $\text{CO}_2$  (BOC, 99.8%) were used as received. CuBr (Acros Organics, 98%) was purified by washing slowly with glacial acetic acid (4 x 25 mL) followed by absolute ethanol (3 x 30 mL) and anhydrous  $\text{Et}_2\text{O}$  (6 x 15 mL).<sup>1</sup> CuBr was placed in a vacuum oven at  $\sim 75^\circ\text{C}$  for 25 mins and stored in an airtight container.

### Preparation of bromo-terminated PDMS-Br macroinitiator<sup>2</sup>

PDMS-OH (10.00 g, 2.20 mmol) and triethylamine (1.54 mL, 11.10 mmol) were dissolved in anhydrous THF (300 mL). 2-Bromoisobutyl bromide (1.28 g, 5.55 mmol) was added dropwise to the mixture whilst stirring. The solution was left overnight to stir at ambient temperature. The solution was filtered and evaporated to dryness.  $\text{CH}_2\text{Cl}_2$  (300 mL) was added to the yellow residue and washed with saturated  $\text{Na}_2\text{CO}_3$  solution (3 x 200 mL). The organic layer was separated, dried with  $\text{MgSO}_4$ , filtered, and the solvent evaporated to give the product as yellow oil (10.37 g, 92% yield,  $M_n = 5350 \text{ g mol}^{-1}$  and  $D = 1.12$ ).

PDMS-Br  $^1\text{H NMR}$   $\delta$ : 4.31 (t,  $J = 4.9 \text{ Hz}$ , 2H,  $\text{CH}_2\text{OCO}$ ), 3.66 (t,  $J = 4.9 \text{ Hz}$ , 2H), 3.44 (t,  $J = 6.9 \text{ Hz}$ , 2H), 1.93 (s, 6H) with the remaining spectrum presumably the PDMS block by comparison to the  $^1\text{H NMR}$  spectrum of PDMS-OH. In agreement with the literature spectrum.<sup>3</sup>

### Equipment

The solubility of BzMA monomer in supercritical carbon dioxide ( $\text{scCO}_2$ ) was visually inspected at 35 and 65 v/v(%) loadings, using a 100 ml stainless steel Thar reactor with  $180^\circ$  inline sapphire windows, and overhead Magdrive stirrer with maximum programmable operating pressure and temperature of 41.4 MPa and  $125^\circ\text{C}$ , respectively. The pressure was produced and maintained by a Thar P-50 series high pressure pump to within  $\pm 0.2 \text{ MPa}$ . The temperature was regulated by a Thar CN6 controller to within  $\pm 1^\circ\text{C}$ . The reactor is connected to a Thar Automated Back Pressure Regulator (ABPR, a computer controlled-needle valve) for controlled venting.

Polymerizations in  $\text{scCO}_2$  were conducted in a 25 mL stainless steel Parr reactor with maximum operating pressure and temperature of 40 MPa and  $130^\circ\text{C}$  respectively. The pressure was produced by a Thar P-50 series high pressure pump to within  $\pm 0.2 \text{ MPa}$ . Temperature was achieved with an oil bath and stirring was achieved using a magnetic stirring bar.

### Typical Polymerization Procedure (e.g. Runs 1 and 2)

Dispersion ATRP of BzMA ( $\sim 35 \text{ v/v(%)}$ ) in  $\text{scCO}_2$  was conducted in a 25 mL stainless steel reactor. BzMA (9.10 g, 0.052 mol), PDMS-Br (0.69 g, 0.129 mmol), CuBr (28.0 mg, 0.195 mmol) and HMTETA (44.9 mg, 0.195 mmol) were added to the reactor. The reaction mixture was purged for 20 min by passing gaseous  $\text{CO}_2$  through the mixture to remove oxygen.

Liquid CO<sub>2</sub> (~5 MPa) was added and the reactor immersed in an oil bath. The temperature was raised to the reaction temperature of 80 °C followed by the pressure to the reaction pressure of 30 MPa by addition of CO<sub>2</sub>. Separate reactions were quenched after 6, 12, 16, 24 and 36 h by submersion of the reactor into an ice-water bath. When at approximately room temperature, the CO<sub>2</sub> was vented slowly from the reactor into a conical flask to prevent loss of the polymer. For high conversion polymerizations (after 24 and 36 h), the light blue crystalline solid was washed three times using scCO<sub>2</sub> at 50 °C and 30 MPa in order to remove residual monomer. For all other polymerizations (taken to lower conversions), visible unreacted BzMA was removed by pipette, and the residue washed five times using scCO<sub>2</sub> at 50 °C and 30 MPa. <sup>1</sup>H NMR was used to confirm that the light blue polymer powders were free of BzMA monomer (Figure S5). Conversions in all cases were measured by gravimetry.

### Characterization

*Gel Permeation Chromatography (GPC).*  $M_n$  and dispersity ( $\mathcal{D}$ ) were measured using Agilent Technologies 1260 Infinity liquid chromatography system using a Polar Gel-M guard column (50 × 7.5 mm) and two Polar Gel-M columns (300 × 7.5 mm). Measurements were carried out at 50 °C at a flow rate of 1.0 mL min<sup>-1</sup> using THF as the eluent. The columns were calibrated using twelve polystyrene (PSt) standards (EasiVial PS-H 2 mL, Agilent) ( $M_n$  = 580-6,035,000 g mol<sup>-1</sup>).  $M_n$  is given in g mol<sup>-1</sup> throughout. All GPC corresponds to polymer before purification, unless otherwise stated. The use of PSt standards inevitably leads to error, however control/living character was assessed based on the shapes of molecular weight distributions (MWDs) and trends in  $M_n$  and  $\mathcal{D}$  versus conversion.

*Nuclear Magnetic Resonance (NMR) Spectroscopy.* <sup>1</sup>H NMR spectra were recorded using a Joel GXFT 400 MHz instrument equipped with a DEC AXP 300 computer workstation.

The theoretical number-average molecular weights ( $M_{n,th}$ ):

$$M_{n,th} = \left( \frac{[BzMA]_0}{[PDMS-Br]_0} \times MW_{BzMA} \times Conversion \right) + MW_{PDMS-Br} \quad (1)$$

where  $[BzMA]_0$  is the initial BzMA monomer concentration,  $[PDMS-Br]_0$  is the initial PDMS-Br concentration,  $MW_{BzMA}$  is the molecular weight of the monomer, and  $MW_{PDMS-Br}$  is the molecular weight of the macroinitiator (*PDMS-Br*) determined by GPC.

*Transmission Electron Microscopy (TEM).* TEM micrographs were obtained using a Transmission Electron Microscope at an accelerating voltage of either 100 keV (JEOL-1400) or 200 keV (FEI Tecnai G2 20). The samples were suspended in pentane, ultrasonicated for 10 minutes and then deposited onto carbon-coated copper grids (Ted Pella, Redding CA). Excess solvent was drained using filter paper. Images were recorded digitally using an Eagle 2k CCD camera (FEI) and Digital Micrograph (Gatan; FEI Tecani G2 20), and via the Gatan CCD imaging software (JEOL-1400).

## References

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