

## Supporting Information for:

# Large Pore Size Nanoporous Materials From the Self-Assembly of Asymmetric Bottlebrush Block Copolymers

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## Experimental Section

**Materials.** Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol, DL-lactide was recrystallized from ethyl acetate, and DMF was dried using a commercial solvent purification system (Innovative). Styrene was passed through basic alumina prior to polymerization to remove any inhibitors. 2-Cyanoisopropyl 4-cyanodithiobenzoate (CTB),<sup>1</sup> 2-(bromoisobutyryl)ethyl methacrylate (BIEM)<sup>2</sup> and solketal methacrylate (SM)<sup>3</sup> were prepared according to literature procedures.

**Poly(solketal methacrylate) (PSM).** Solketal methacrylate (1.540 g, 7.7 mmol) and CTB (9.47 mg, 38.5  $\mu$ mol) were dissolved in a reaction flask equipped with a stir bar. A solution (0.180 mL, 3.85  $\mu$ mol) of AIBN (3.5 mg/mL) in toluene was then added. The flask was subsequently degassed by three cycles of freeze-pump-thaw, sealed and placed in an oil bath at 65 °C. After 6.5 hrs, the flask was cooled in a water bath to room temperature, then diluted with dichloromethane, and the polymer was precipitated twice in petroleum ether. The polymer was filtered and dried in a vacuum oven overnight to yield 0.93 g of pink powder. GPC (light scattering detector):  $M_n$  = 39.9 kg/mol,  $M_w/M_n$  = 1.02.

**Poly(solketal methacrylate-*b*-2-(bromoisobutyryl)ethyl methacrylate) (PSM-*b*-PBIEM).** PSM (150.0 mg, 3.76  $\mu$ mol) was dissolved in (0.527 g, 1.88 mmol) of BIEM and 125  $\mu$ L of toluene in a reaction flask equipped with a stir bar. This mixture was allowed to stir approximately 30 min until the solids were completely dissolved. Subsequently, a mixture (41.2  $\mu$ L, 0.376  $\mu$ mol) of AIBN (1.5 mg/mL) in toluene was added. The flask was then degassed by three cycles of freeze-pump-thaw, and placed in an oil bath at 65 °C. After 11 hrs, the flask was cooled in a water bath to room temp, diluted with dichloromethane and precipitated twice in methanol. The polymer was then centrifuged, decanted and dried overnight in a vacuum oven to yield 0.25 g of slightly pink powder. GPC (PS standards):  $M_n$  = 89.7 kg/mol,  $M_w/M_n$  = 1.16.

**Grafting polystyrene from PSM-*b*-PBIEM.** In a dry 50 mL Schlenk flask equipped with a stir bar, CuBr (28.62 mg, 199  $\mu$ mol), CuBr<sub>2</sub> (6.68 mg, 29.9  $\mu$ mol) and 4,4'-Dinonyl-2,2'-bipyridine (187.60 mg, 459.0  $\mu$ mol) were subjected to three vacuum/N<sub>2</sub> fill cycles. Then, 4 mL of styrene that was previously sparged with N<sub>2</sub> for 20 min, was added. The catalyst was allowed to stir for 2 hours, with solution color turning dark red. In a separate reaction tube equipped with a stir bar, the PSM-PBIEM diblock copolymer (50.0 mg, 99.6  $\mu$ mol of Br) was dissolved in styrene (5.86 mL, 51.1 mmol). After the polymer completely dissolved, the flask was degassed by three cycles of freeze-pump-thaw. Under heavy N<sub>2</sub> flow, 1.00 mL of the catalyst solution was injected into the reaction flask, the flask was sealed and placed in an oil bath at 90 °C. After 28 hrs, the flask was cooled in a water bath, and the polymer was precipitated twice in methanol. The polymer was then centrifuged, decanted and dried overnight in a vacuum oven to yield 0.46 g of white powder. <sup>1</sup>H NMR:  $M_n$  (PS branch) = 4.8 kg/mol, GPC (PS standards):  $M_w/M_n$  = 1.18

**Solketal deprotection of PSM-*b*-(PBIEM-*g*-PS).** In a 20 dram vial equipped with a stirbar, PSM-*b*-(PBIEM-*g*-PS) (350 mg, 0.369  $\mu$ mol) was dissolved in 10 mL of THF. Subsequently, 25 drops of 1.0 M HCl was added and allowed to stir overnight at room temp. The mixture was then precipitated in salty methanol, dissolved in dichloromethane and then precipitated again in salty methanol, decanted and dried overnight in a vacuum oven to yield 0.17 g of white powder.

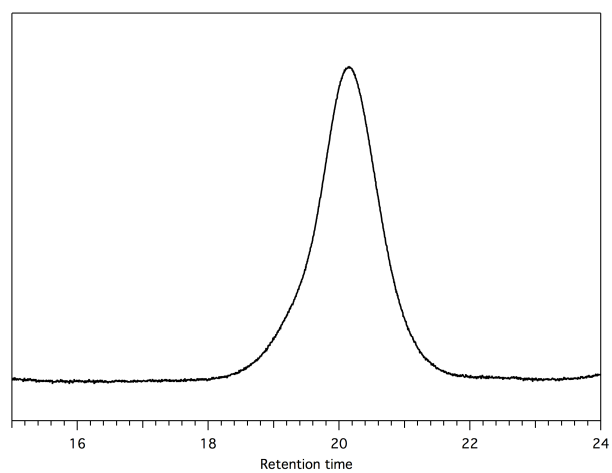
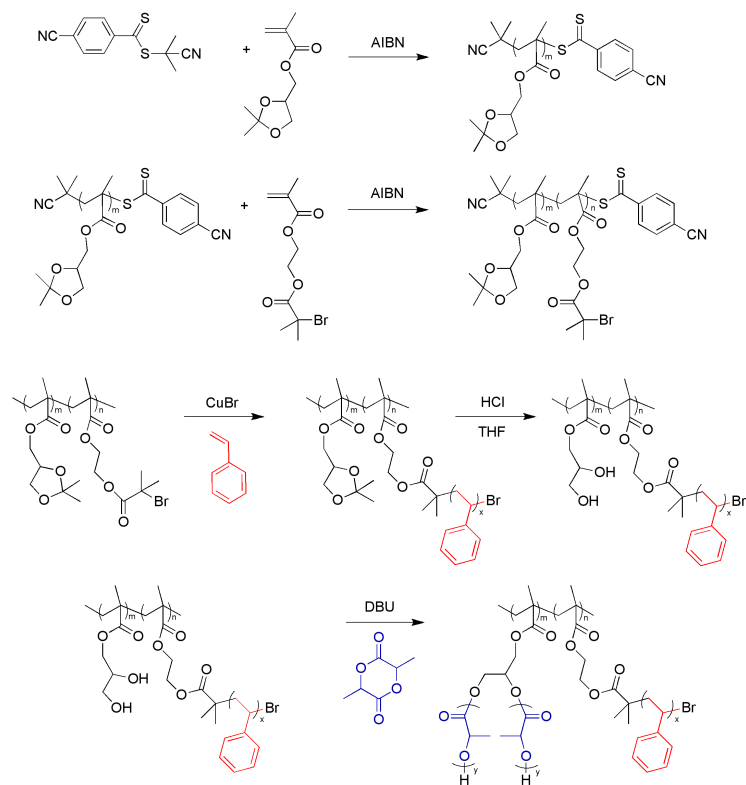
**Grafting PLA from PSM-*b*-(PBIEM-*g*-PS).** In a dry 5 mL round bottom flask equipped with a stir bar, deprotected polymer (130 mg, 54.8  $\mu\text{mol}$  of hydroxyls) and D,L-lactide (71 mg, 493.1  $\mu\text{mol}$ ) were dissolved in 1.48 mL of dry DMF. DBU (2.21  $\mu\text{L}$ , 14.8  $\mu\text{mol}$ ) was injected and allowed to stir for two hours at room temperature, at which time the flask was diluted with dichloromethane, and the polymer was precipitated twice in methanol. The polymer was then centrifuged, decanted and dried overnight in a vacuum oven to yield 0.18 g of white powder.  $^1\text{H}$  NMR:  $M_n$  (PLA branch) = 1.0 kg/mol, grafting density = 84%, GPC (PS standards):  $M_w/M_n$  = 1.29.

**Measurements.** GPC analysis was performed by using Viscotek's GPCMax and TDA302 Tetradelector Array system equipped with three Olexis columns (Polymer Laboratories, Varian Inc.) The detector unit contained a refractive index, UV viscosity, low ( $7^\circ$ ) and right angle light scattering modules. Tetrahydrofuran (30  $^\circ\text{C}$ , 1 mL/min) was used as a mobile phase. The system was calibrated with 10 polystyrene standards from  $1.2 \times 10^6$  to 500 g/mol. The refractive index increment ( $dn/dc$ ) for poly(SM) was measured to be 0.067 mL/g in THF (30  $^\circ\text{C}$ ,  $\lambda=630$  nm) and was used to determine absolute molecular weights of the homopolymer. Scanning electron microscopy (SEM) images were obtained by a Hitachi SU-70 using secondary electron detector at an acceleration voltage of 20.0 kV. SAXS data were obtained on a Rigaku S-Max 3000 High Brilliance 3 Pinhole SAXS System outfitted with a MicroMax-007HFM Rotating Anode ( $\text{CuK}\alpha$ ), Confocal Max-Flux<sup>TM</sup> Optics and Gabriel Multiwire Area Detector. Transmission electron microscopy was performed on JEOL-2010 instrument with an accelerating voltage of 200 kV. The samples were prepared by spin coating the block copolymer solution (3 wt%, 2,000 rpm) onto the carbon-coated copper grids, annealing (230  $^\circ\text{C}$ , 16 h) and staining with  $\text{RuO}_4$  (5 min).

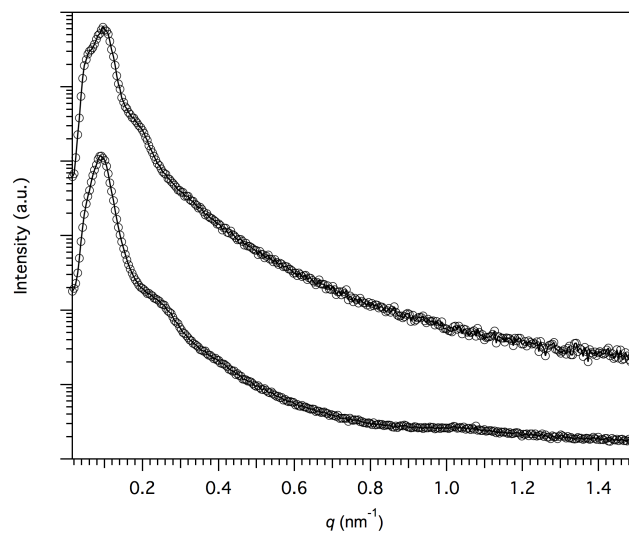
## References

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- (2) Venkatesh, R.; Yajjou, L.; Koning, C. E.; Klumperman, B. *Macromol. Chem. Phys.* **2004**, *205*, 2161.
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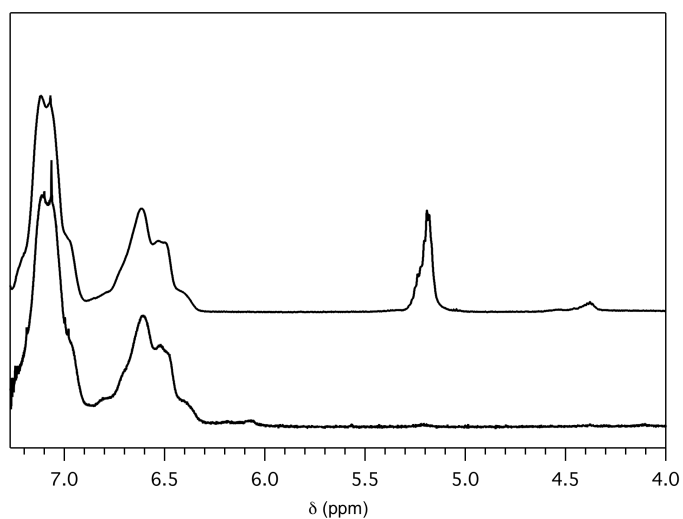
### Scheme S1



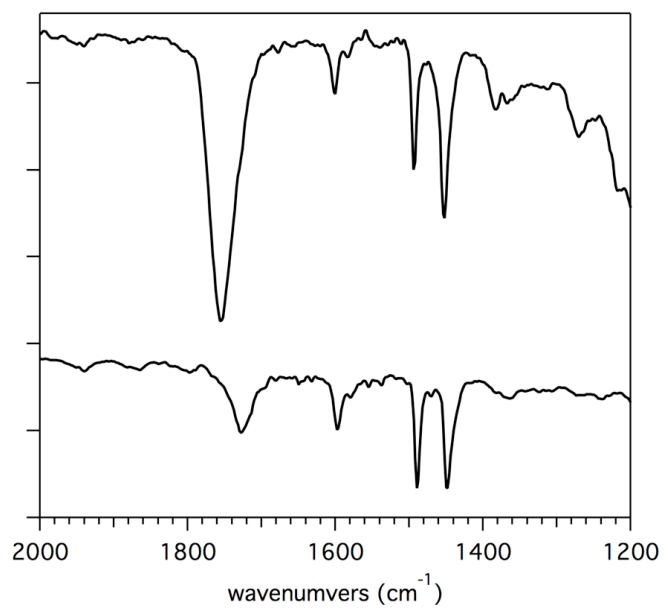
**Figure S1.** SEC analysis of the final PS-PLA bottlebrush block copolymer (RI signal).



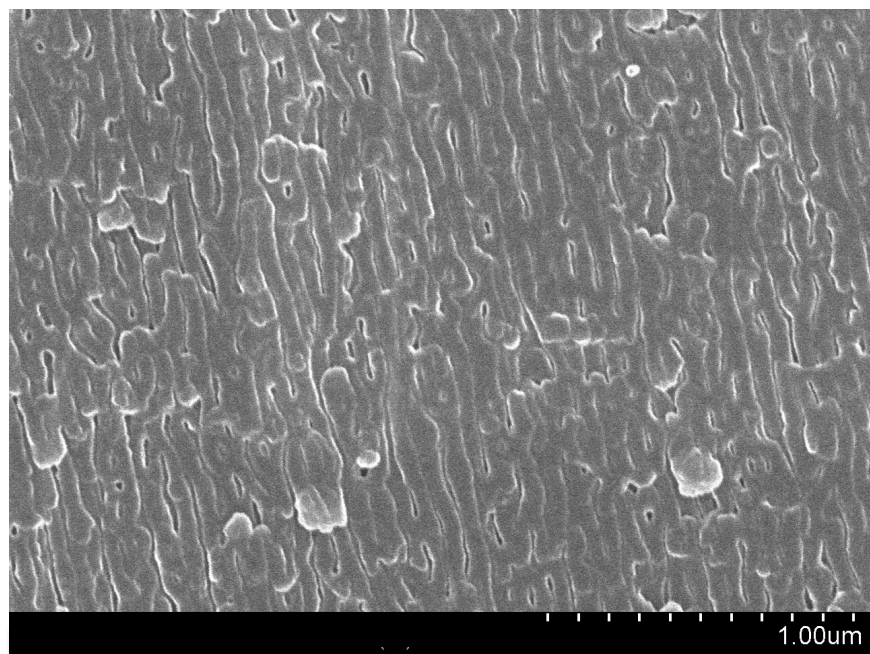
**Figure S2.** SAXS analysis of PS-PLA bottlebrush copolymer monoliths before (bottom) and after (top) PLA degradation.



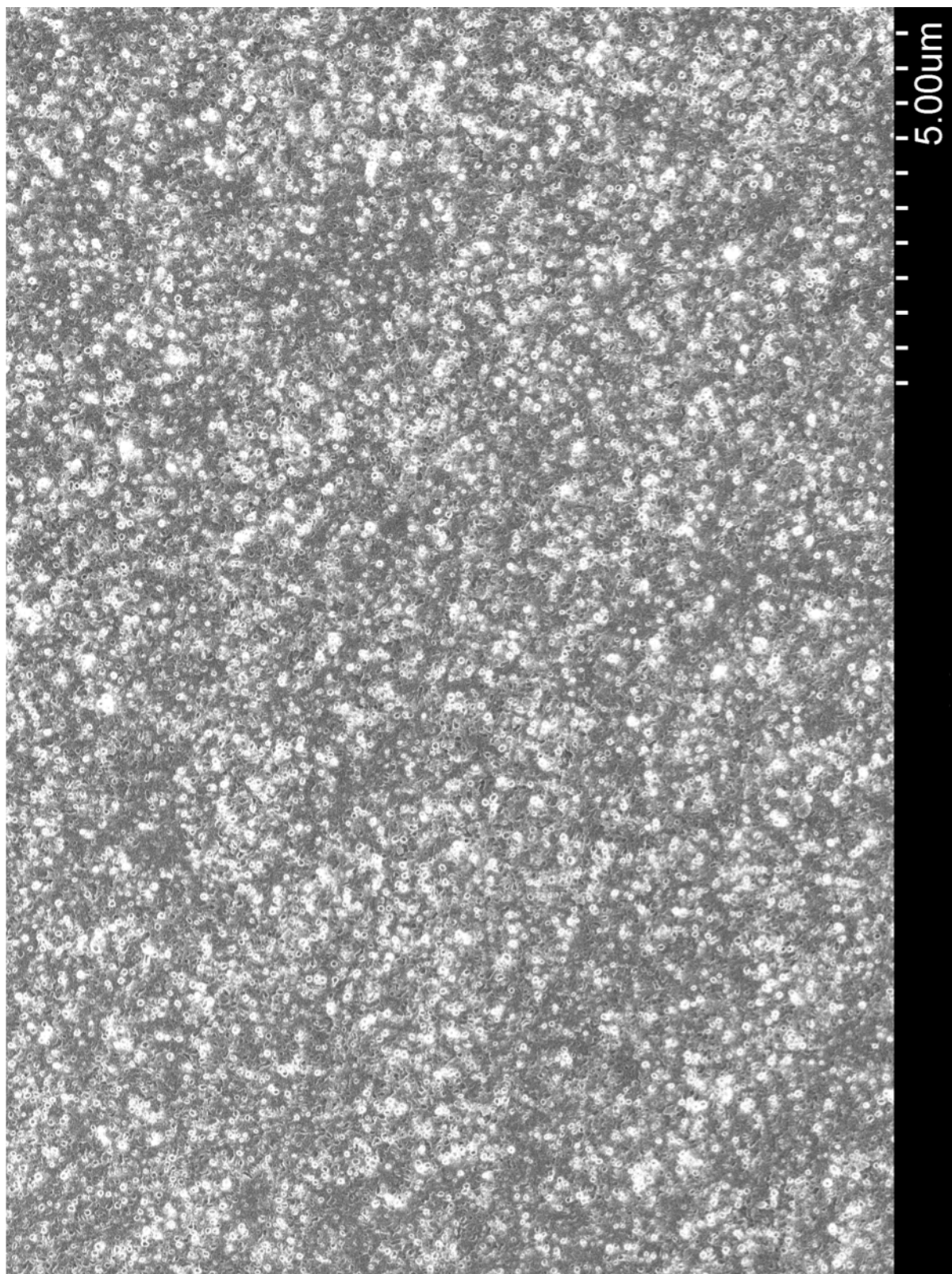
**Figure S3.**  $^1\text{H}$  NMR spectra of PS-PLA bottlebrush block copolymer before (top) and after (bottom) PLA degradation.



**Figure S4.** FTIR spectra of PS-PLA bottlebrush block copolymer before (top) and after (bottom) PLA degradation.



**Figure S5.** SEM analysis of nanoporous polymer monoliths fractured parallel to the direction of alignment.



**Figure S6.** Large area SEM image of a nanoporous monolith prepared from an asymmetric PS-PLA bottlebrush copolymer.