Electronic Supplementary Information

Robust Porous Polymers Enabled by a Fast Trifluoroacetic Acid Etch with Improved Selectivity for Polylactide

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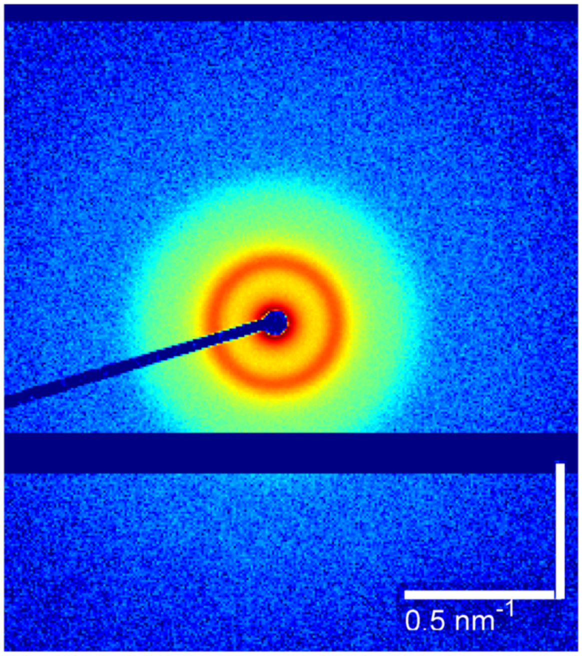

Fig. S1 The **as-made PS-*b*-PLA** 2D SAXS pattern consisting of isotropic rings. Color scale corresponds to the log of the X-ray intensity.

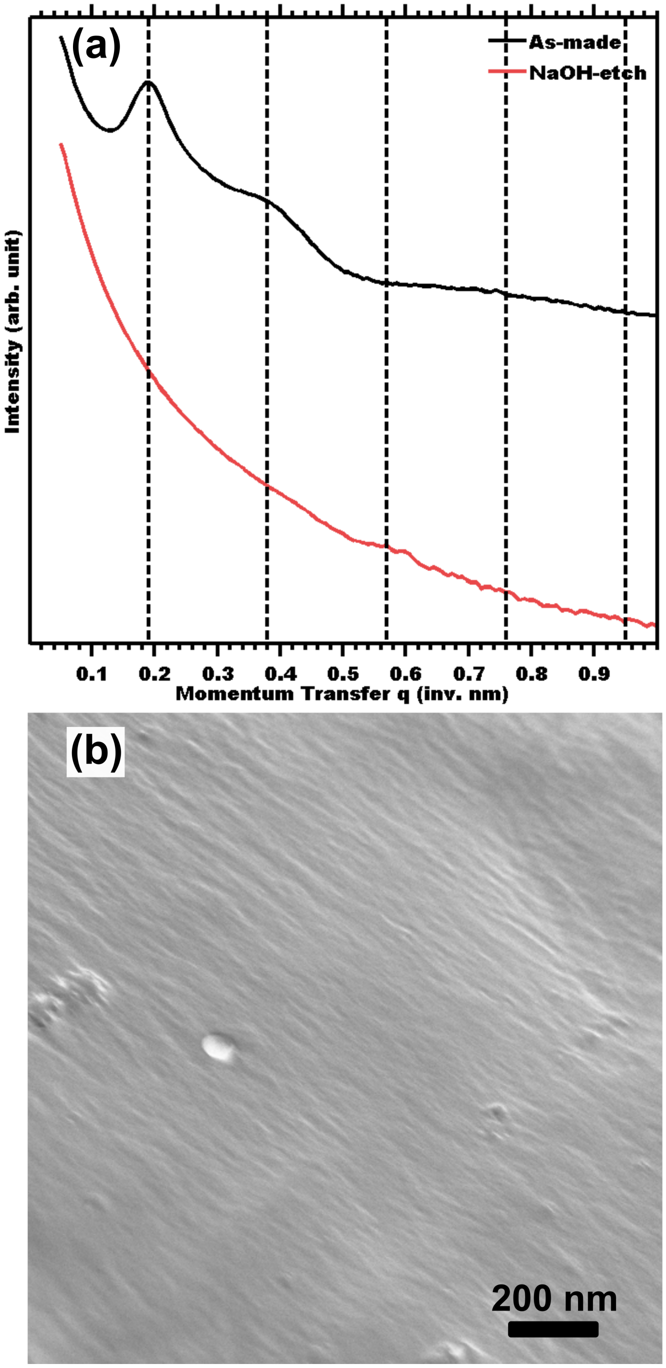

Fig. S2 (a) SAXS of **as-made** (2 mm thick) as compared to **NaOH-etch** (2mm thick) PS-*b*-PLA film. The samples were indexed for LAM symmetry with peaks indicated at q/q*=1, 2, 3, 4, and 5. The scattering data were offset vertically for clarity. (b) Top-view SEM image of sample **NaOH-etch**.

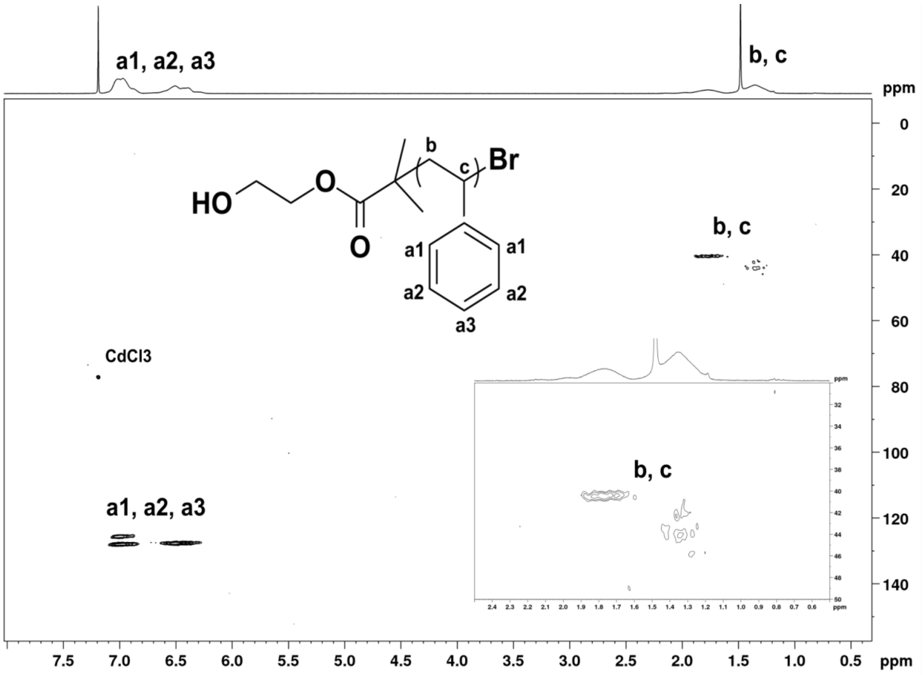

Fig. S3 Heteronuclear single quantum coherence spectroscopy of sample **TFA-etch**.

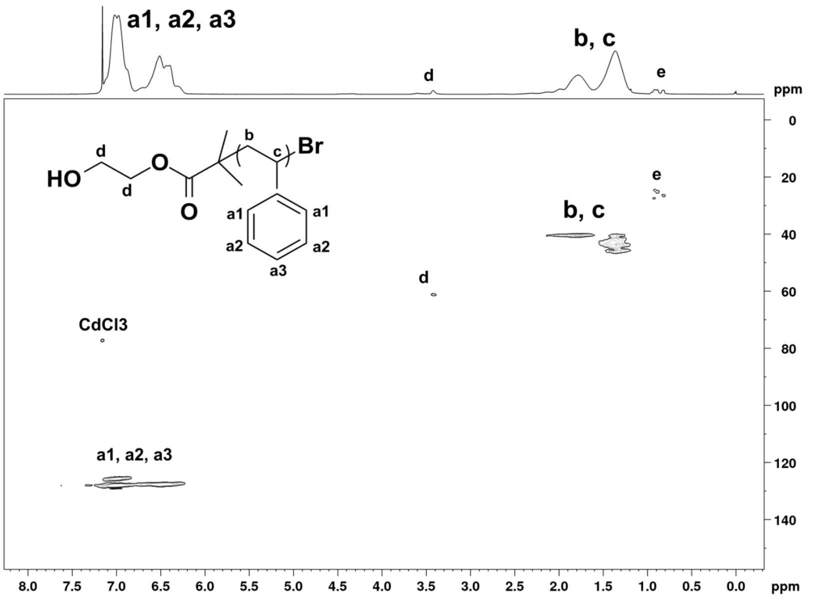

Fig. S4 Heteronuclear single quantum coherence spectroscopy of **PS-OH** macroinitiator.

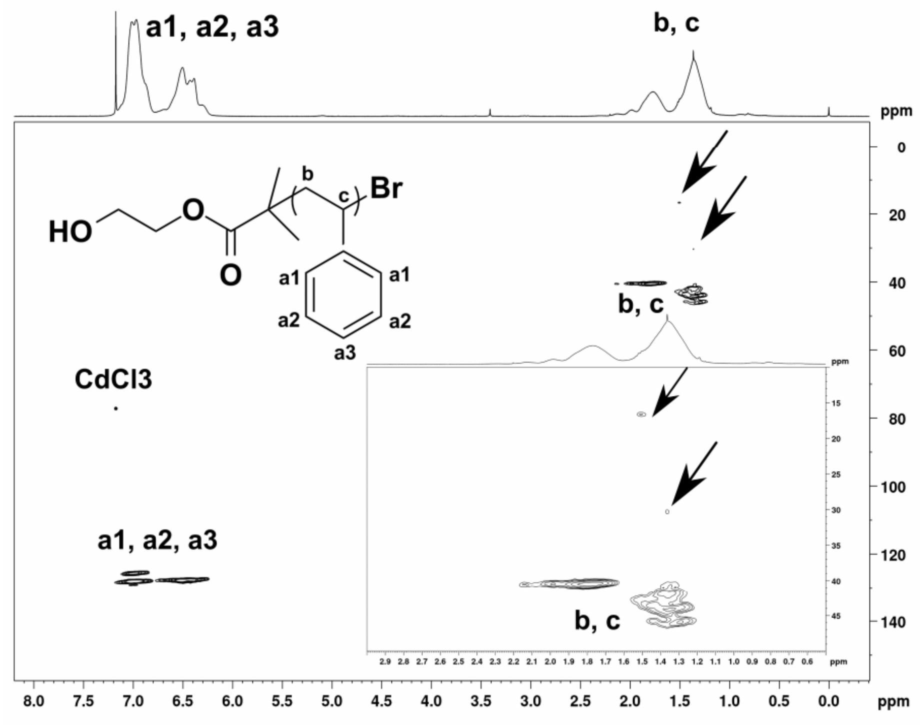

Fig. S5 Heteronuclear single quantum coherence spectroscopy of sample **NaOH-etch**. New and unidentified carbons resulting from the etch are indicated by arrows.

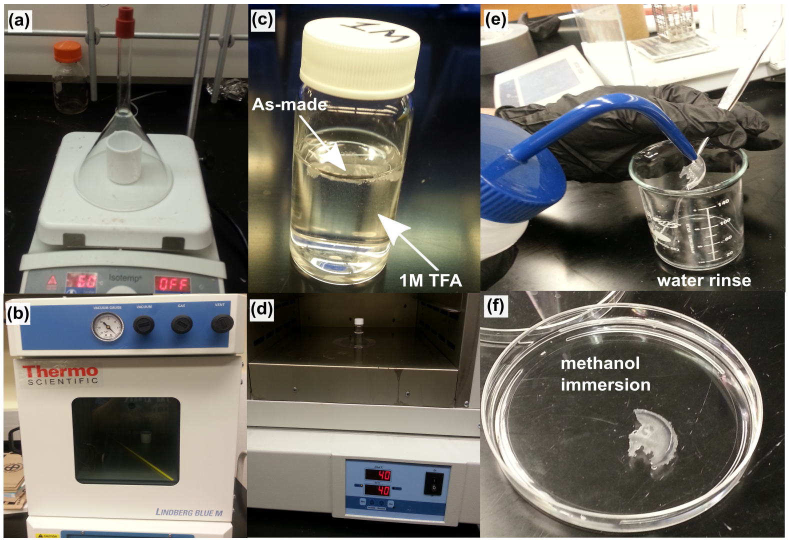

Fig. S6 The **as-made** samples resulted from a combination of solvent casting (a) and vacuum oven annealing (b). Samples were etched by immersion in a TFA solution (c) placed in an oven (d). The etched films were rinsed with water (e) and immersed in methanol (f) before drying in a vacuum oven.

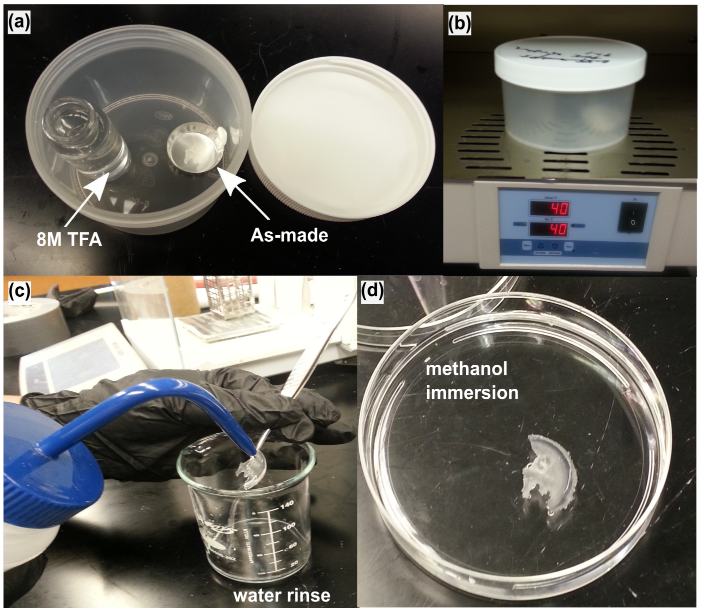

Fig. S7 TFA vapor etching was conducted with the **as-made** sample and etchant solution placed adjacent within a closed jar (a). The entire setup was placed within an oven (b). The etched film was rinsed with water (c) and immersed in methanol (d) before drying in vacuum oven.

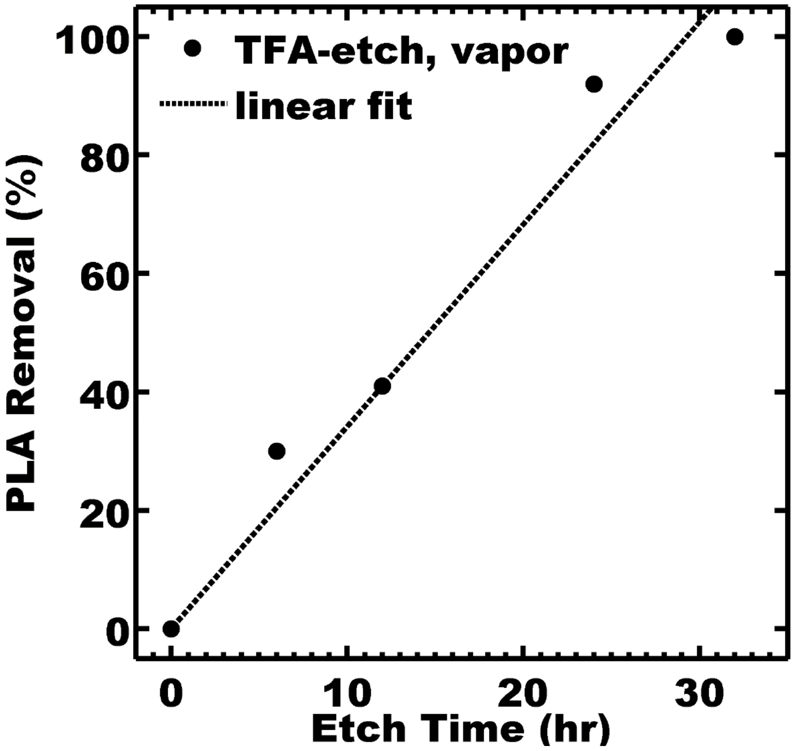

Fig. S8 PLA etch kinetics using the vapor from an 8M TFA solution.

PS-*b*-PLA2 Synthesis:

PS-*b*-PLA2 was synthesized following a similar procedure as PS-*b*-PLA. The PS-OH was synthesized using reagent ratio of [Styrene]:[Initiator]:[Me_6TREN]:[Cu(I)]:[Sn(II)] = 300:1:0.105:0.005:0.1. After 12 hrs of polymerization the PS-OH of 13.9 kg/mol and dispersity of 1.22 was obtained. The PS-*b*-PLA of 27.8 kg/mol with a molar mass dispersity (Đ) of 1.23 was obtained after 15 minutes of polymerization using a reagent ratio of [**PS-OH**]:[Lactide]:[DBU]:[Thiourea]=1:150:1.34:1.34. Sample **HEX-As-Made** was made using the already described annealing procedures. Sample **HEX-TFA-Etch** was prepared using immersion in 1M TFA solution for 27 hrs, following the already described procedures.

Table S1. **PS-*b*-PLA2 Characterization:**

Sample	**$M_{n, PS}$ (kg mol^{-1}) [a]**	**$M_{n, PLA}$ (kg mol^{-1}) [b]**	**Total M_n (kg mol^{-1}) [c]**	**Đ [a]**	**f^v_{PS} [d]**	**f^v_{PLA} [d]**	**Morphology [e]**
PS-*b*-PLA2	**13.9**	**13.9**	**27.8**	**1.23**	**0.54**	**0.46**	**HEX**

[a]obtained from GPC analysis, [b]obtained from ^{1}H NMR analysis, [c]obtained from a+b [d]volume fractions (f^v) calculated using densities[21,36] at 110˚C, PS= 1.02 g/cm^3, PLA = 1.18 g/cm^3 [e]Morphology determined by SAXS.

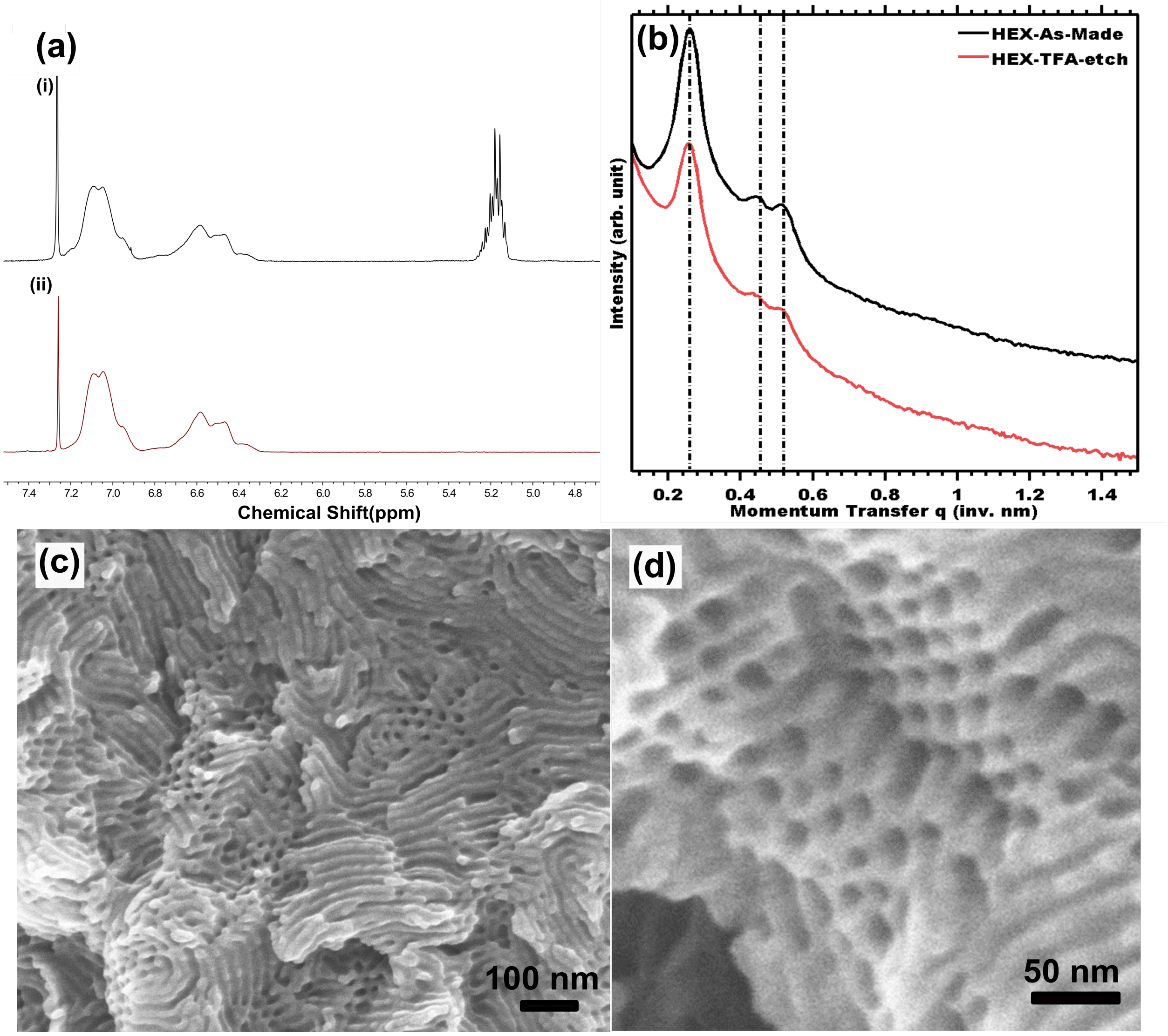

Fig. S9 (a) ^{1}H NMR spectra of (i) **HEX-As-Made** and (ii) **HEX-TFA-etch** dissolved in CDCl$_3$. 100% of PLA was removed selectively (PLA peak disappeared at 5.19 ppm) by immersion in 1M TFA solution for 26 hrs. (b) SAXS of **HEX-As-Made** and **HEX-TFA-etch** demonstrate preservation of a hexagonal morphology. The principal peak (q*) in both scattering profile is centered at 0.25 nm^{-1}. The samples were indexed for HEX symmetry with peaks indicated at q/q*=1, √3, and √4. The scattering data were offset vertically for clarity. (c-d) Top-view SEM images of sample **HEX-TFA-etch** with a measured pore size of 16.2 ±2.5 nm.