Electronic **S**upplementary **I**nformation for:

Macroscopic samples of polystyrene with ordered three-dimensional nanochannels

Huiming Mao and Marc A. Hillmyer*
Department of Chemistry
University of Minnesota
Minneapolis, MN 55455-0431, USA

* To whom correspondence should be addressed (e-mail: hillmyer@chem.umn.edu)

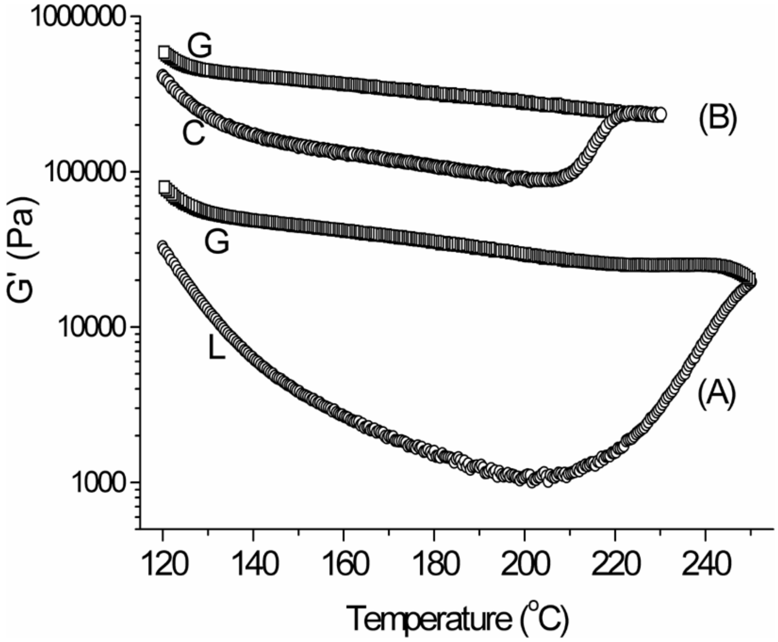

Figure S1. Isochronal heating (open circle) and cooling (open square) elastic modulus results for PS-PLA (A) and PS-PEO (B). The PS-PEO data were shifted vertically by a factor of 10. The T_{OOT} is 211 °C for PS-PLA, and 208 °C for PS-PEO as determined from the heating scan. The high temperature morphologies of these two samples are "trapped" during cooling scan and are confirmed as the G morphology by SAXS at 25 °C.

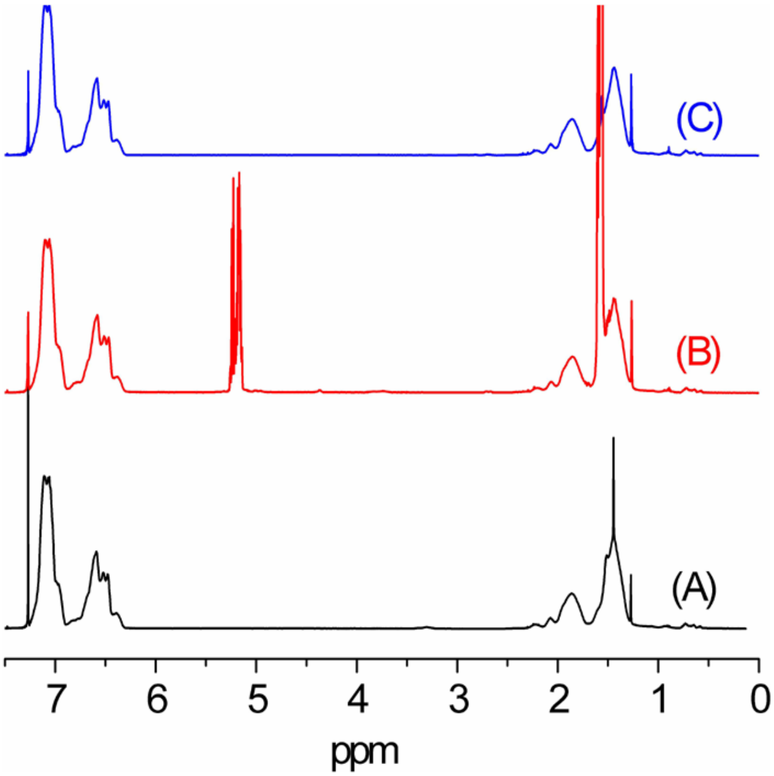

Figure S2. ^{1}H NMR spectra of (A) the starting block PS-OH, (B) the diblock copolymer PS-PLA, and (C) d-PS-PLA from the HI etching process.

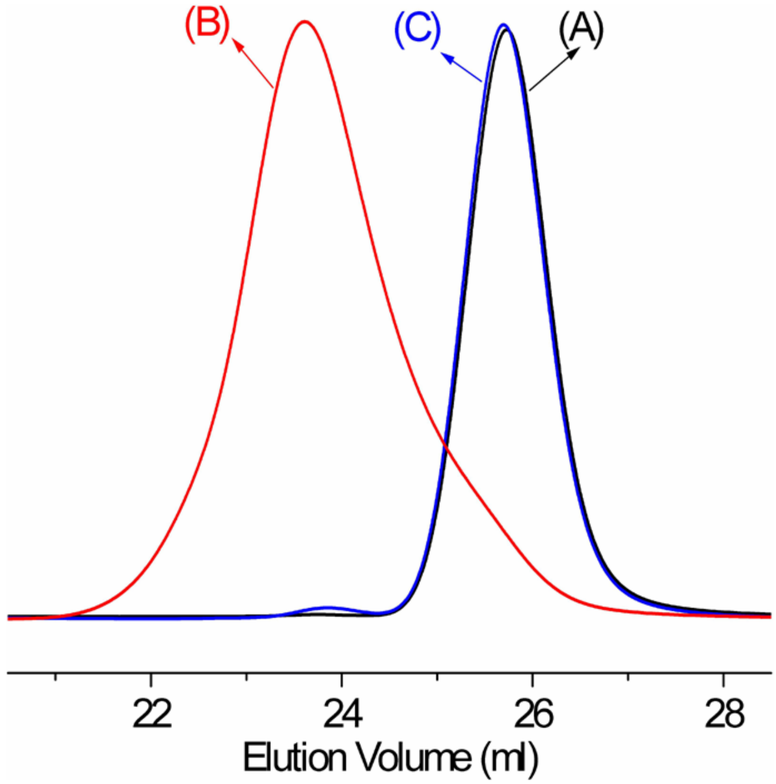

Figure S3. SEC traces for (A) the starting block PS-OH, (B) the diblock copolymer PS-PLA, and (C) d-PS-PLA from the HI etching process.

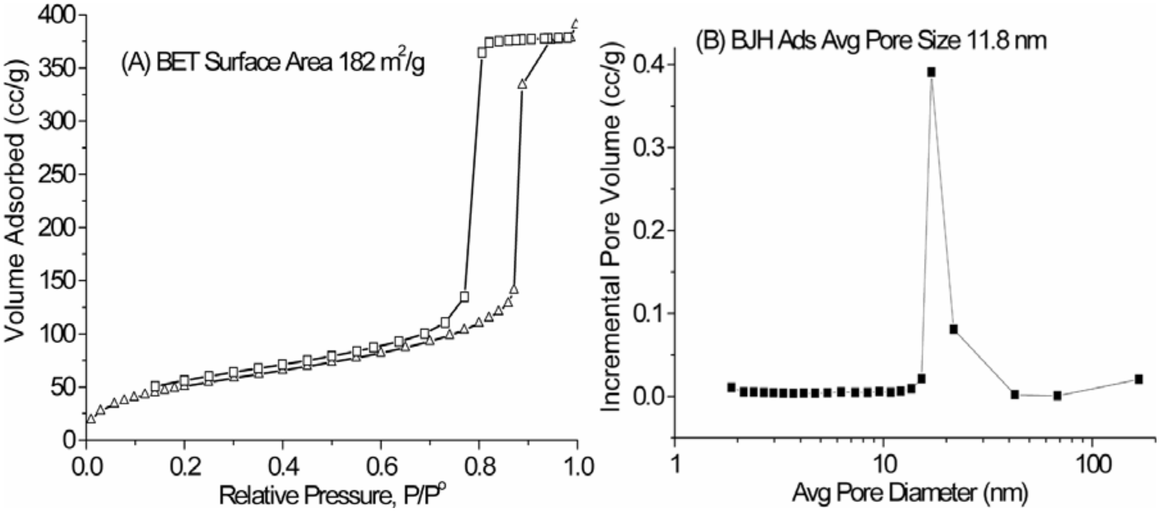

Figure S4. (A): N_2 adsorption of a HI etched d-PS-PLA (triangles = adsorption branch, squares = desorption branch). (B): Pore size distribution by the BJH method using the adsorption branch.

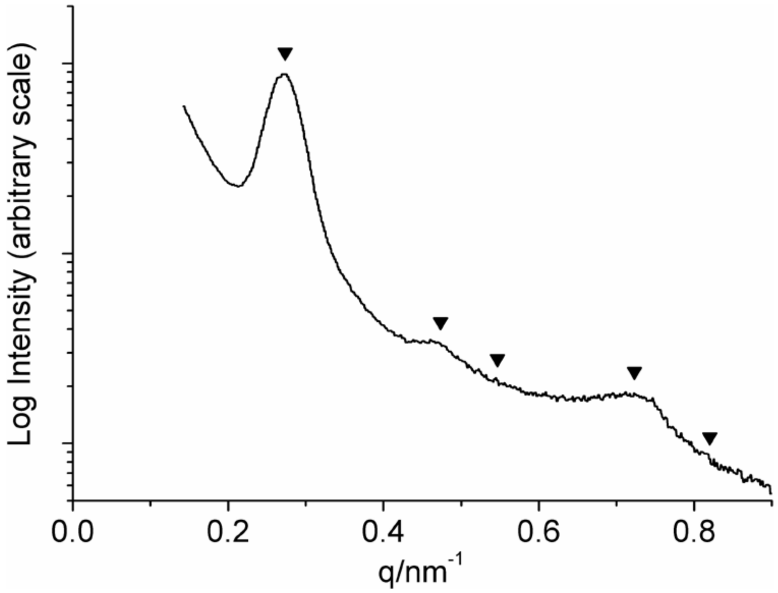

Figure S5. 1D SAXS profile of PS-PEO at RT after channel die alignment at 150 °C. The expected reflections for a cylindrical microstructure are marked by triangles (√1:√3:√4:√7:√9).

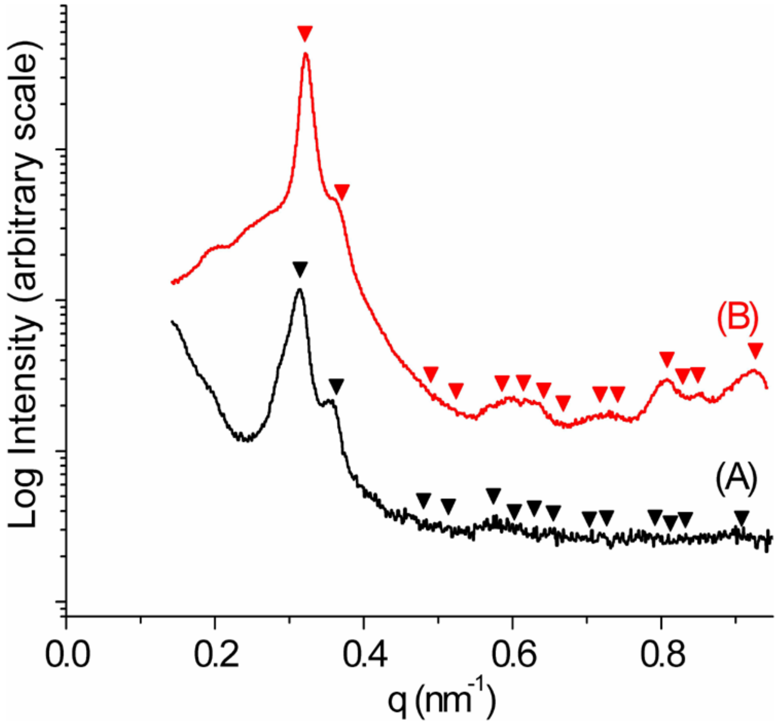

Figure S6. 1D SAXS profiles of the PS-PLA/polysytrene-poly(ethylene oxide) blend described in the text before (A) and after (B) degradation. The expected reflections for a gyroid microstructure are marked by triangles (√6:√8:√14:√16:√20:√22:√24:√26:√30:√32:√38: √40:√42:√50).

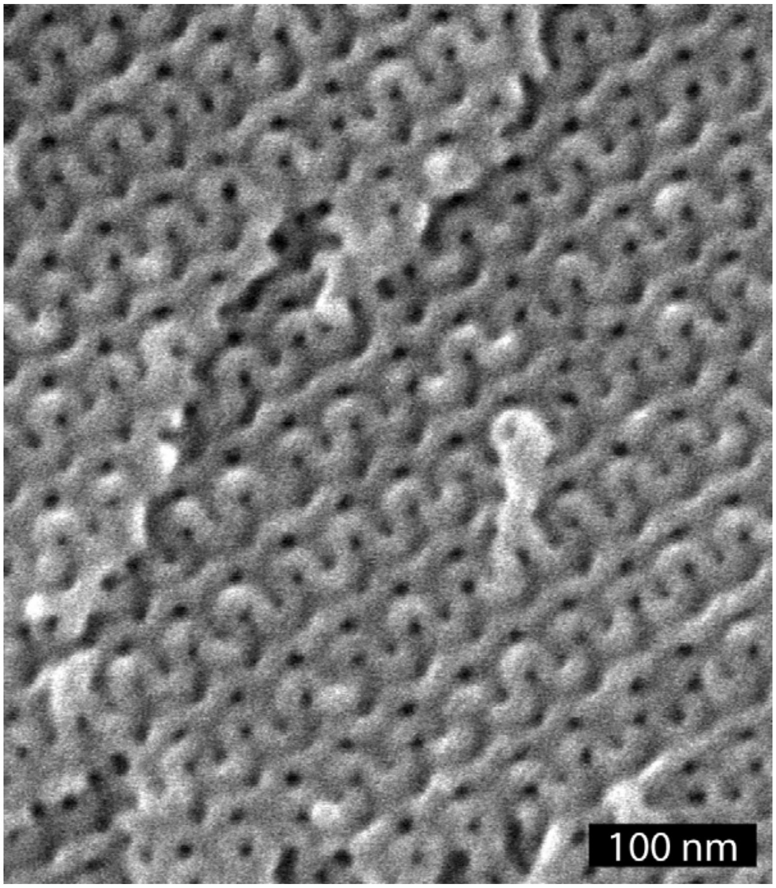

Figure S7. SEM image of the degraded blend described in the text.

Estimation of specific surface areas and pore sizes in nanoporous G samples

Method 1. Self-consistent mean field theory. We assume the degraded sample has the same surface area as the starting sample at 140 °C. The specific surface area and average pore diameter can be estimated from the self-consistent mean field theory using the following procedure. First, the average statistical segment length for PS-PLA (a_{SL}) and PS-PEO (a_{SO}) block copolymers were determined from $a_{12} = \left(\frac{f_1}{a_1^{\,2}} + \frac{f_2}{a_2^{\,2}} \right)^{-1/2}$ where f_1 and f_2 are volume fractions of each block. The statistical segment length a_{S} = 5.9 Å (Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* 1994, **27**, 4639), a_{L} = 7.0 Å (Anderson, K. A.; Hillmyer, M. A. *Macromolecules* 2004, **37**, 1857) and a_{O} = 7.1 Å (Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* 1994, **27**, 4639) were used after correction for a common reference volume of 118 Å^3. Thus a_{SL} = 6.3 Å and a_{SO} = 6.2 Å can be calculated. Degree of polymerization (N) was calculated from molecular weight, density at 140 °C and a common reference volume of 118 Å^3. Then, the D spacing of the undegraded samples at 140 °C were calculated from Figure 11 in Matsen, M. W.; Bates, F. S. *J. Chem. Phys.* 1997, **106**, 2436 using χN (PS-PLA) = 21.6 (Zalusky, A. S.; Olayo-Valles, R.; Wolf, J. H.; Hillmyer, M. A. *J. Am. Chem. Soc.* 2002, **124**, 12761) and χN (PS-PEO) = 21.1 (Cochran, E. W.; Morse, D. C.; Bates, F. S. *Macromolecules* 2003, **36**, 782) and these values agreed fairly well with experimental values. Next, the specific surface area (*S*) was determined from Figure 10 in Matsen, M. W.; Bates, F. S. *J. Chem. Phys.* 1997, **106**, 2436 using the appropriate χN and f values (Based on a private communication with Professor Matsen, the actual y-axial in Figure 10 in this reference should be $A\left(\overline{N}\right)^{1/2} / na^2N$ instead of A / na^2N) and corrected by the square of the ratio of the estimated D spacing (from Figure 11 in Matsen, M. W.; Bates, F. S. *J. Chem. Phys.* 1997, **106**, 2436) to the experimental D spacing at 140 °C and including the weight loss after degradation. Finally, the pore diameter (*d*) was estimated based on a cylindrical model from equation $d = \frac{4V}{S}$ where *V* is the specific pore volume (m^3 g^{-1}) of the sample. Using this method we calculate a pore diameter for d-PS-PLA of 11.5 nm.

Method 2. A simple cylindrical channel model. A simplified cylindrical channel model with the equivalent volume of cylindrical channels and three-dimensional channels was assumed. For the G morphology, the minor block forms two interpenetrating network structures on a cubic unit cell. These two channels can be disassembled into 24 equivalent basic rod structures. Each rod has a length of 0.301a (a is the unit cell length) and the total equivalent cylindrical channel length is 7.297a (Luzzati, V.; Spegt, P. A. *Nature* 1967, **215**, 701). The pore diameter can be calculated from equation $d = \sqrt{\frac{4a^2 f}{7.297\pi}}$ where f is the volume fraction of minority phase. And the specific surface area (*S*) can be estimated from the following equation assuming cylindrical model ($d = \frac{4V}{S}$) and $S = \frac{7.297\pi d}{a^2 f_{PS}\rho_{PS}}$. Using this method we calculate a pore diameter for d-PS-PLA of 12.8 nm.