

Hierarchically Porous Bio-inspired Films by combining “Breath Figure” Templating and selectively Degradable Block Copolymer Directed self-assembly.

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Materials

D,L-lactide was purchased from Alfa Aesar and used as received. All other reagents were purchased from Aldrich and used as received unless otherwise stated. Styrene was passed through a basic alumina column to remove the inhibitor. Dichloromethane was dried over 4 Å molecular sieves. Copper (I) bromide was purified by sequential washing with glacial acetic acid, ethanol and diethylether as reported elsewhere.¹

Characterization

¹H NMR spectra were recorded on a Bruker 400MHz spectrometer at 25°C using CDCl₃ as solvent. Polymers were analyzed with a Steric Exclusion Chromatography (SEC) apparatus running in THF at 30°C (flow rate: 1 mL.min⁻¹) equipped with a Viscotek VE 5200 automatic injector, a pre-column and two columns (Styragels HR 5E and 4E), a Viscotek VE3580 refractive index detector, and a Wyatt Heleos II MALLS detector. The thickness of continuous thin films was measured by ellipsometry. Atomic Force Microscopy (AFM) was performed on a Bruker Nanoscope III Multimode in PeakForce QNM mode, using Bruker ScanAssyst probes. Optical microscope pictures were taken in reflection with a Leica DM/LM microscope equipped with a Leica DFC280 video camera. Scanning electron microscopy (SEM) images were obtained with a Hitachi JEOL 6700F FEG-SEM using a 1 kV accelerating voltage. SEM samples were metallized with about 1 nm of gold-palladium using a vacuum sputter coater. DSC

Synthesis of hydroxyl-terminated polylactide(PLA-OH)

PLA-OH was prepared by ring-opening transesterification polymerization of D,L-lactide catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), using benzyl alcohol as initiator. In a glovebox, anhydrous benzyl alcohol was dissolved in a 50 mL round-bottom flask containing 30 mL of anhydrous dichloromethane and a stir bar. DBU then D,L-lactide were then added and the

reaction mixture was stirred at room temperature for 1h40 h. After quenching the polymerization with a spatula tip of benzoic acid, the reaction mixture was precipitated twice in cold methanol, and dried overnight at 40 °C. To remove undesired traces of methanol, the polymer was finally precipitated in *n*-hexane and dried 24 h at 40 °C under vacuum.

Synthesis of PLA macroinitiator (PLA-Br)

In a 50 mL round-bottom flask, PLA-OH was dissolved in 20 mL of dry dichloromethane under inert atmosphere. Triethylamine was added and the flask was cooled to 0 °C using an ice bath. 2-bromopropionyl bromide in dry dichloromethane was then added dropwise over 15min under stirring. The ice bath was then removed and the reaction mixture was further stirred at room temperature overnight. The reaction mixture was washed with distilled water (200 mL, 2X) and the organic layer was collected and concentrated with a rotary evaporator. The polymer was isolated by precipitating twice in cold methanol and was finally dried 48 h at room temperature under vacuum.

Synthesis of polylactide-*block*-polystyrene block copolymer (PLA-*b*-PS)

A well-defined PLA-*b*-PS diblock copolymer was obtained by a combination of ring-opening polymerization (ROP) and atom transfer radical polymerization (ATRP) (Fig. S1).

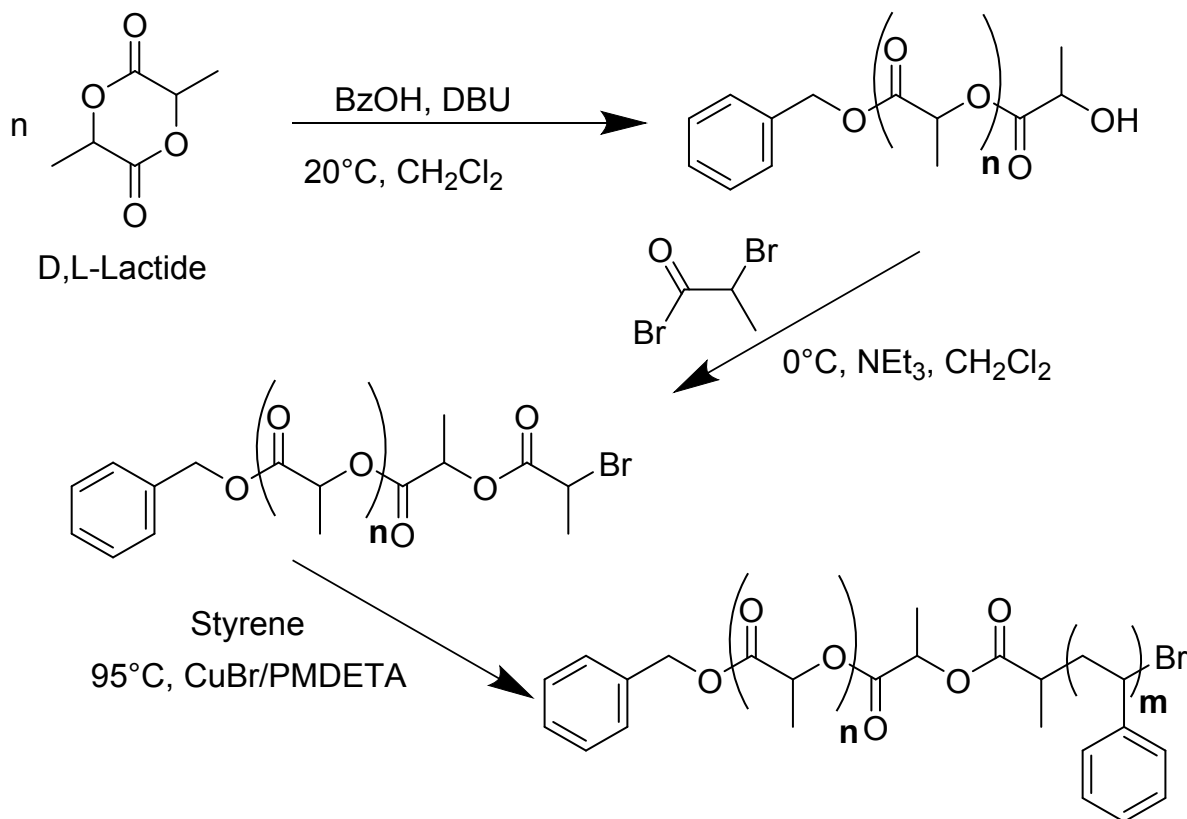


Fig. S1 Schematic representation of PLA-PS synthesis.

PLA-Br was used as macroinitiator for the ATRP polymerization of styrene in bulk, using CuBr /Pentamethyldiethylenetriamine (PMDETA) as catalytic system. In a 50 mL Schlenk flask, PLA-Br was dissolved in 4.55 g of styrene (43.7 mmol) and the mixture was degassed by bubbling nitrogen for 45 min. The catalytic system was prepared separately by adding a degassed solution of PMDETA in styrene into a nitrogen-purged flask contained CuBr . A 0.5 mL aliquot (styrene: 0.45 g, 4.3 mmol; CuBr : 4.6 mg, $3.2 \cdot 10^{-2}$ mmol; PMDETA 5.6 mg, $3.2 \cdot 10^{-2}$ mmol) was then transferred into the Schlenk flask using a nitrogen-purged syringe. The reaction mixture was further degassed by five freeze-pump-thaw cycles followed by nitrogen back-filling, and the Schlenk flask was immersed in an oil bath at 95°C equipped with magnetic stirring. The reaction was stopped after 28.5 h by plunging the flask into liquid nitrogen and opening to air. The

conversion (0.27) was calculated by ^1H NMR through relative integration of the styrene vinyl protons with the aromatic protons of both the monomer and the polymer. The polymer was diluted in THF and passed through a neutral alumina column to remove the copper catalyst. The PLA-*b*-PS copolymer was finally isolated by precipitating twice in methanol and dried 16 h at 40 °C under vacuum.

The molar masses for the PLA and PS blocks were determined to be 15.2 kg.mol $^{-1}$ and 43.6 kg.mol $^{-1}$, respectively, by ^1H NMR spectroscopy. Based on the calculated PLA volume fraction (0.23), a microstructure composed of PLA cylinders in a PS matrix is expected.¹⁷ The good initiation efficiency of the PLA macroinitiator was confirmed by SEC through the shift of the polymer peak after the chain extension, along with the narrow size distribution of the PLA-*b*-PS diblock copolymer ($D=1.01$, $M_{n(\text{PLA-PS})} = 51.6$ kg.mol $^{-1}$) (Fig. S2)

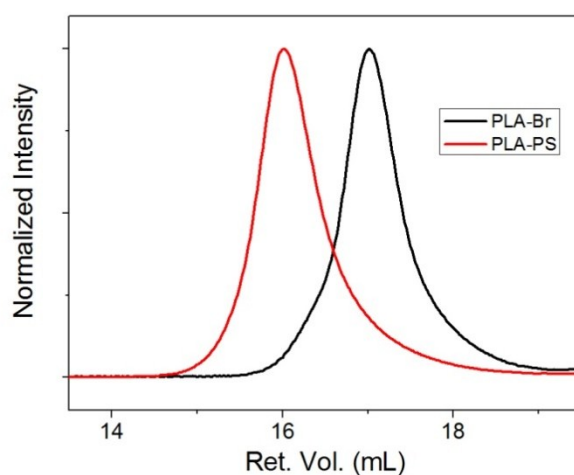


Fig. S2 SEC traces of PLA-Br macro-initiator and PLA-*b*-PS diblock copolymer.

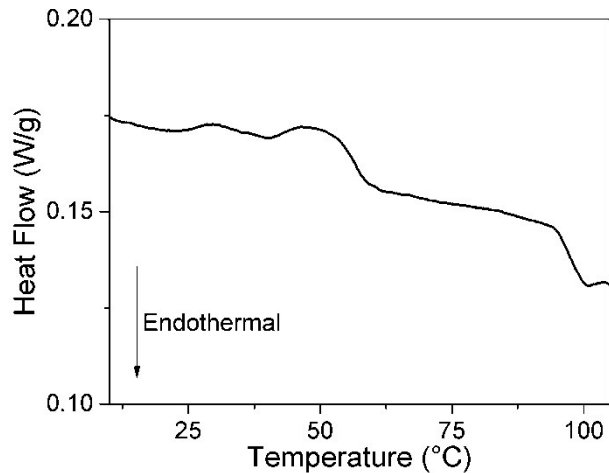


Fig. S3 DSC thermogram of PLA-*b*-PS diblock copolymer.

Film preparation

Continuous thin films from PLA-*b*-PS copolymer

Thin films (50 nm) of cylinder-forming polymers were obtained by spin-coating (3000 rpm, 60 s) from a toluene solution (20 g.L⁻¹), using silicon wafer as substrate. Their thickness was measured by ellipsometry. Films were subsequently annealed by THF vapors during 17h in a 1.5 L desiccator at room temperature containing a 10 mL reservoir to ensure a saturated atmosphere. Films were subsequently allowed to dry in a fumehood.

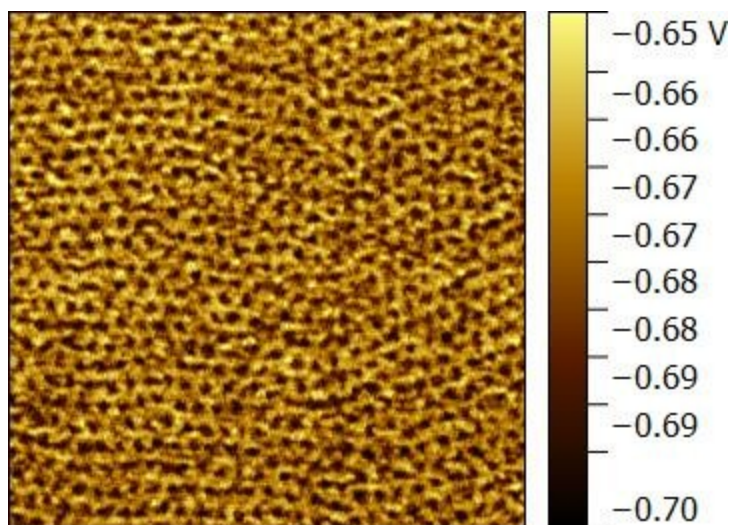


Fig. S4 AFM stiffness image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of PLA-*b*-PS thin films after annealing with THF vapors at r.t. during 17h, obtained in PeakForce™ mode (channel: Log DMT modulus)

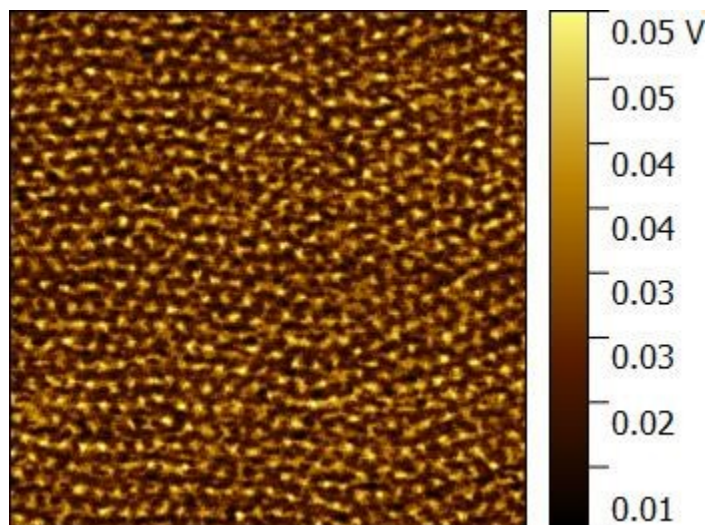


Fig. S5 AFM adhesion image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of PLA-*b*-PS thin films after annealing with THF vapors at r.t. during 17h, obtained in PeakForce™ mode.

Honeycomb films from PLA-*b*-PS copolymer

The HC microporous films were prepared by the BF process in a closed chamber with a relative humidity between 40 and 55 % and a temperature between 21 °C and 23 °C. The copolymer was dissolved in dichloromethane (CH₂Cl₂) or carbon disulfide (CS₂) at a 5 mg/mL concentration and 300 μL were casted on a glass slide. A vertical stream of humid air (2 L.min⁻¹, 80-90 % humidity, obtained by bubbling air into water) was then applied through a hole in the on top of the chamber, right above the sample.

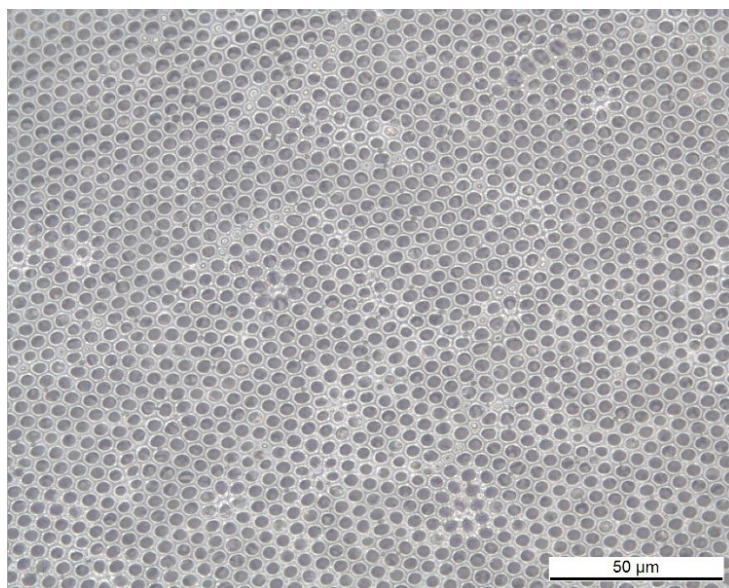


Fig. S6 Optical microscopy image of PLA-*b*-PS diblock copolymer honeycomb film

PLA hydrolysis

The PLA was selectively degraded by immersing the HC films into a basic hydroalcoholic solution (H₂O/MeOH 6/4, NaOH 0.5 M) at 65 °C for 40h. The films were then rinsed by immersing them into fresh basic solution for 15 min at r.t, then twice into neutral H₂O/MeOH for 15 h at r.t. The hydrolysis yield was estimated by ¹H NMR through relative integration of the styrene aromatic protons and lactide protons (O=C-CH-O) before and after hydrolysis.

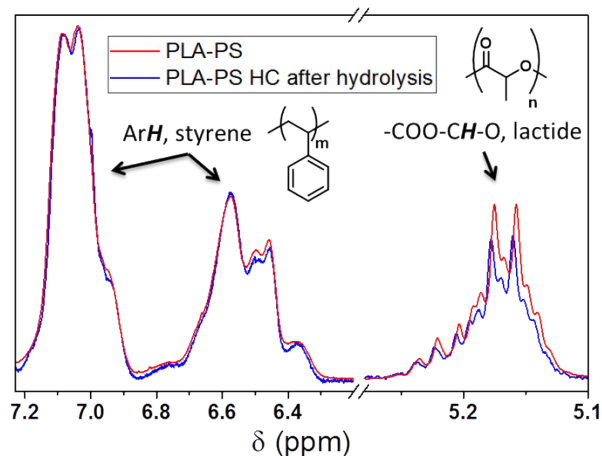


Fig. S7 ¹H NMR spectra of PLA-*b*-PS (red line) and PLA-*b*-PS HC film after hydrolysis (blue line).

The PS-PLA HC films tend to be teared and peeled off their substrate in the course of the hydrolysis, often yielding film fragment at the surface. Performing the hydrolysis with the HC/substrates stacks placed upside down in the hydrolytic solution solved this issue.

PLA degradation was evidenced by ¹H NMR (after dissolving entire HC films into CDCl₃) through the decrease in intensity of a peak attributed to lactide repeat units (-COO-CH-; δ = 5.1-5.3 ppm) relatively to a peak attributed to styrene units (ArH; δ = 5.75-7.25 ppm). The PLA loss was estimated to about 15% after 24h of hydrolysis. Performing the hydrolysis for longer time did not appreciably improve the degradation yield. It is likely that the PLA cylinders are still not spanning through the entire microporous film, thus a portion of the PLA remains inaccessible to the hydrolytic solution.

Reference

- 1 R. N. Keller, H. D. Wrcoff, L. E. Marchi, In *Inorganic Syntheses* John Wiley & Sons, Inc., 2007; pp 1