Electronic Supplementary Information (ESI)

Synthesis of Core Cross-linked Star Polystyrene with Functional End Groups and the Self-assemblies Templated by Breath Figures

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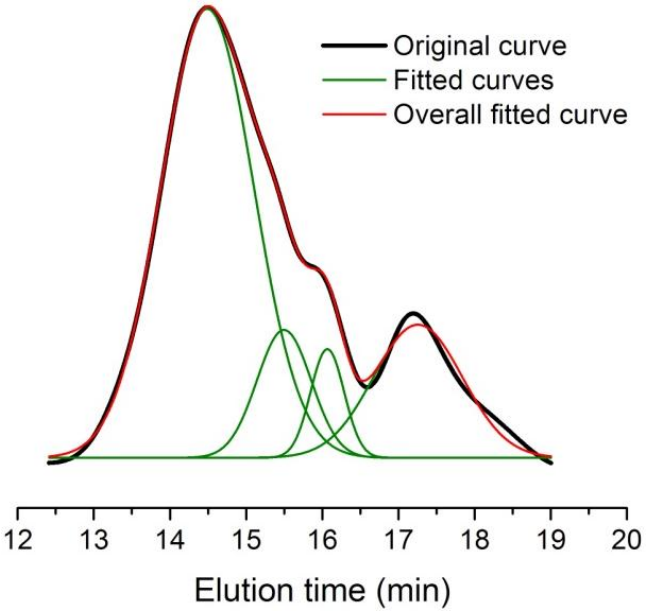

Fig. S1 Original and fitted GPC curves of CCS-$(PS)_4$-cyl.

Synthesis of PS with a Cyclic End Group (PS–cyl) by ATRP

The procedure used for synthesizing linear PS with five membered lactone end group, PS–cyl, is as follows. ATRP of styrene was performed with a ratio of St/**I**/CuBr/PMDETA = 360/1/1/2. A 50 mL Schlenk flask was added with α-bromo-γ-butyrolactone (1.63×10^{-4} mol, 15 μL), PMDETA (3.26×10^{-4} mol, 67.9 μL), and St (5.87×10^{-2} mol, 6.75 mL) under a nitrogen atmosphere. The solution was degassed by three freeze–pump–thaw cycles. Then CuBr (1.63×10^{-4} mmol, 23.38 mg) was added, and another three freeze–pump–thaw cycles were performed. The polymerization was allowed to proceed at a preheated 110 °C oil bath. After 4.8 h, the flask was quenched in liquid nitrogen to stop the polymerization. Then, the reaction mixture was dissolved with a small amount of tetrahydrofuran (THF), precipitated in methanol, and repeated three times. The obtained product was dried in a vacuum overnight and the molecular weight reaches 28900 g/mol.

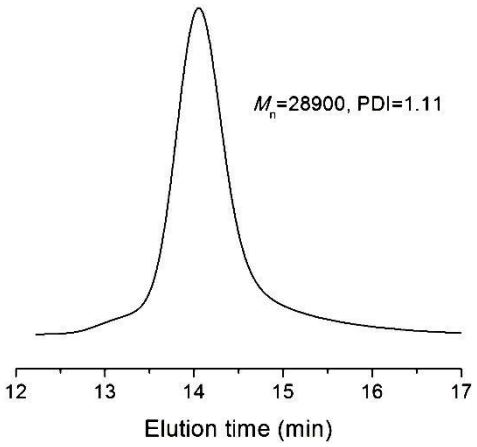

Fig. S2 GPC curve of linear PS-cyl.

Synthesis of PS with an Ionized End Group (PS–ion) via Hydrolysis of PS–cyl

In a typical hydrolysis reaction, 600 mg of PS–cyl in 20 mL of THF and 2 g of NaOH (50 mmol) in water (4 mL) were added into a 250 mL round-bottomed flask. The mixture was refluxed for 24 h and then precipitated in methanol. The precipitation procedure was performed three times. The obtained product was dried in a vacuum oven overnight to achieve the final product. Please note that PS-ion has a hydroxyl end group (–OH) adjacent to the ionized carboxyl (–COONa).

Synthesis of PS with a Neutralized End Group (PS–neu) via Acidification of PS–ion

The procedure of acidification was performed as follows. PS–ion (200 mg) was dissolved in 11 mL of THF/methanol mixture (10/1, v/v) in a 50 mL round-bottomed flask. Then, 2 mL of hydrochloric acid was added, and the reaction proceeded at ambient temperature for 1 h. The raw product was precipitated in methanol, repeated three times, and then dried in a vacuum oven overnight to achieve the final product. Please note that PS-neu has a hydroxyl end group (–OH) adjacent to the neutralized carboxyl (–COOH).

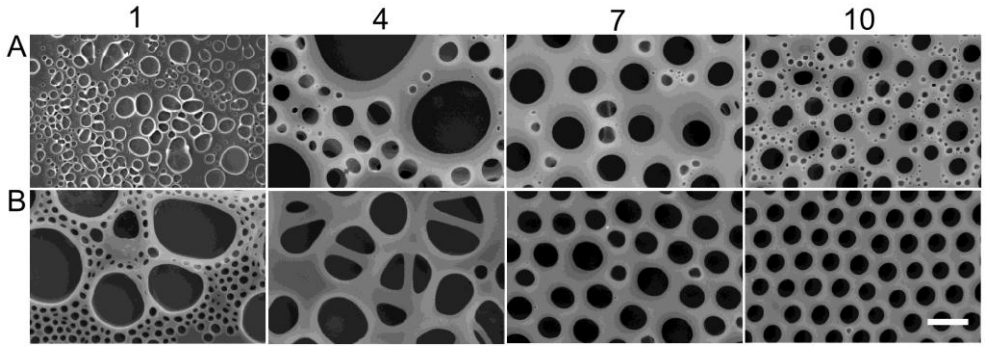

Fig. S3 SEM images of honeycomb films prepared from linear (A) PS-cyl and (B) PS-neu with M_n = 28900 g/mol at different concentrations of 1, 4, 7, and 10 mg/mL. Scale bar is 5 μm.