Supplementary information

A hypercrosslinking-induced self-assembly strategy for preparation of advanced hierarchical porous polymers with customizable functional components

Hongji Xu,^{‡a} Jinlun Wu,^{‡a} Bingna Zheng,^a Weicong Mai,^a Fei Xu,^a Luyi Chen,^a Hao Liu,^a Ruowen Fu,^a Dingcai Wu^{*a} and Krzysztof Matyjaszewski^{*b}

^a Materials Science Institute, PCFM Lab and GDHPRC Lab, School of Chemistry,

Sun Yat-sen University, Guangzhou 510275, P. R. China.

E-mail: wudc@mail.sysu.edu.cn

^b Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA.

E-mail: km3b@andrew.cmu.edu

[‡]These authors contributed equally to this work.

Experimental Section

Materials: Methyl methacrylate and styrene were passed through an alkaline alumina column before polymerization. CuBr was purified by stirring in glacial acetic acid, followed by filtration and washing of the solid three times with ethanol and drying under N_2 flow overnight. The other chemicals were of analytical grade and used as received without further purification.

Synthesis of PEO-b-PS: PEO₁₁₆-*b*-PS₃₆₂ was synthesized by two steps, including preparation of a PEO₁₁₆-Br macroinitiator followed by chain extension polymerization of styrene. 20.0 g monomethoxy PEO (molecular weight 5000) was dissolved in 60 mL dichloromethane, and then 2.0 mL triethylamine was added. After a 30 min gentle N₂ purge, 3.0 mL 2-bromoisobutyryl bromide was slowly added with micro-injection pump under stirring within 30 min in ice-water bath. The reaction mixture was taken out from the ice-water bath after 3 h and the reaction was continued at room temperature for another 20 h under stirring. The resulting mixture was filtered to remove the insoluble by-product triethylamine salt. Then the resulting filtrate was added to 500 mL diethyl ether to precipitate the crude PEO₁₁₆-Br product that was filtrated. The crude product was washed with 100 mL diethyl ether twice, followed by drying at 30 °C for 24 h, leading to formation of the target macromolecular initiator PEO₁₁₆-Br.

ATRP was used for the chain extension polymerization of styrene. 1.0 g PEO_{116} -Br was dissolved in 10 mL styrene, followed by addition of 0.042 mL of the *N*,*N*,*N*',*N*',*N*''-pentamethyldiethylenetriamine (PMDETA) ligand. After 30 min under

gentle N₂ purge, 0.028 g CuBr was added rapidly under N₂ flow. The N₂ purge was continued for another 30 min to completely remove any air. Then the flask was sealed and put into an oil bath set at 110 °C. The reaction was stopped by opening the flask and exposing the catalyst to air. A moderate amount of tetrahydrofuran (THF) was added to reduce the viscosity, and the resulting mixture was passed through a column of neutral alumina before precipitating the block copolymer by addition of the solution to 500 mL methanol. After filtration and vacuum-drying at 30 °C for 24 h, the PEO₁₁₆-*b*-PS₃₆₂ was collected. PEO₁₁₆-*b*-PS₆₃₅ and PEO₁₁₆-*b*-PS₇₁₈ were synthesized by varying the polymerization time for the styrene segment.

Synthesis of AHPPs: 0.3 g PEO₁₁₆-*b*-PS₃₆₂ was completely dissolved in 30 mL CCl₄ in a three-necked flask equipped with reflux condenser and heated to 75 °C, and then 0.72 g AlCl₃ was added quickly to start the Friedel-Crafts hypercrosslinking reaction. The reaction mixture was kept at 75 °C for 24 h under stirring, and then terminated by slowly adding a mixture of acetone and 3.7% hydrochloric acid (v/v=3:1) (acetone/HCl). The product was filtered off, washed by stirring with acetone/HCl three times (6 h per time) and finally ethanol, followed by drying at 80 °C for 12 h, leading to the formation of AHPP-PEO₁₁₆-*b*-PS₃₆₂.

Other AHPPs were also prepared according to the above method under the same conditions, unless changes were mentioned. PEO_{116} -*b*-PS₆₃₅ and PEO_{113} -*b*-PS₇₁₈ were used to prepare AHPP-PEO₁₁₆-*b*-PS₆₃₅ and AHPP-PEO₁₁₆-*b*-PS₇₁₈, respectively. PEO_{116} -*b*-PS₆₃₅ was used to prepare AHPP-PEO₁₁₆-*b*-PS₆₃₅-C1, AHPP-PEO₁₁₆-*b*-PS₆₃₅-C2 and AHPP-PEO₁₁₆-*b*-PS₆₃₅-C3 with the catalyst amount of 0.18, 0.42 and

1.20 g, respectively. PEO_{116} -b- PS_{635} was used to prepare AHPP-PEO_{116}-b- PS_{635} -T1 and AHPP-PEO_{116}-b- PS_{635} -T2 by conducting the hypercrosslinking reaction at 45 °C and 60 °C, respectively.

To verify that the hypercrosslinking-induced self-assembly led to generation of a nanosphere-interconnected nanonetwork structure, products were extracted at various Friedel-Crafts reaction times. 0.3 g PEO₁₁₆-*b*-PS₃₆₂ was completely dissolved in 30 mL CCl₄ in a three-necked flask equipped with reflux condenser and heated to 75 °C. Subsequently, 0.72 g AlCl₃ was added quickly to start the Friedel-Crafts reaction. 1 mL of reaction solution was sucked out rapidly at 30 s, 2 min, 8 min, 15 min, 30 min, 1 h, 3 h and 24 h, respectively, followed by quick refrigeration with ice-water bath. Subsequently, the solutions were promptly loaded on the copper foils for SEM analysis, or copper meshes for TEM analysis. After the CCl₄ was volatilized, the copper foil/mesh-loaded products were washed by mixture of methanol and concentrated hydrochloric acid (v/v=2:1) to remove AlCl₃, followed by drying at 45 °C for 24 h. Note that the methanol/HCl mixture cannot damage/modify the morphology of the products, considering that it is a non-solvent for PEO₁₁₆-*b*-PS₃₆₂.

Material characterizations: Molecular weight of PEO-Br and PEO-*b*-PS was obtained by analysis of the ¹H NMR spectra recorded on an INOVA500NB spectrometer (Varian) with tetramethylsilane as an internal standard and CDCl₃ as a solvent. The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM) and a FEI Tecnai G2 Spirit transmission electron microscope (TEM). 50 core-shell structured nanospheres in a TEM image of

corresponding AHPPs were picked at random for statistical analysis. Subsequently, a statistical analysis of the outer diameter and PEO core diameter distribution histograms of PEO@xPS nanosphere network units was carried out, and then the thickness of hypercrosslinked PS shell was correspondingly obtained. The analysis of the -CO- crosslinking bridges was performed on a Bruker EQUINOX 55 infrared spectrometer. A Micromeritics ASAP 2020 surface area and porosity analyzer was utilized to study the pore structure of the samples. The BET surface area (S_{BET}), micropore surface area (S_{mic}) and external surface area (S_{ext}) were analyzed by Brunauer-Emmett-Teller (BET) theory and t-plot method. The DFT pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. The total pore volume (V_1) was calculated according to the amount adsorbed at a relative pressure P/P₀ of about 0.99. Mercury porosimetry was used to further characterize the macroporosity.

Phenol adsorption measurement: The amount of phenol adsorption in AHPP-PEO₁₁₆-*b*-PS₇₁₈ and HPP-PS were obtained by measuring their concentrations before and after adsorption. 50 mg AHPP-PEO₁₁₆-*b*-PS₇₁₈ (or HPP-PS) powder was added into a conical flask, and then 50 mL phenol solution (250 mg/L) was added quickly. Then, this suspension was stirred at a rate of 150 rpm at 35 °C. At intervals, 0.3 mL of the supernate was taken out and diluted to 3 mL. The concentration of adsorbate was measured by UV-Vis spectra. The wavelength for phenol was 269.8 nm. The adsorption capacity (C) was calculated according to the equation $C = (c_0V_0-c_1V_1)/m$, where c_0 , V_0 , c_1 , V_1 and m represent the initial concentration, initial volume, concentration and volume after adsorption, and weight of the materials, respectively.

CO₂ adsorption measurement: CO₂ adsorption isotherms of AHPP-PEO₁₁₆-b-PS₇₁₈ and HPP-PS were obtained on a Micromeritics ASAP 2010 at 273 K. The test pressure was from 0 to 740 mmHg and balance time was 60 s. Each sample was degassed under vacuum for 6 h at 90 °C before conducting the adsorption characterization.



Fig. S1. ¹H NMR spectra of (A) PEO₁₁₆-Br and (B) PEO₁₁₆-b-PS₃₆₂.



Fig. S2. GPC traces of PEO₁₁₆-Br and PEO₁₁₆-b-PS₃₆₂.



Fig. S3. Digital photos of (A) solid PEO_{116} -*b*-PS₃₆₂ and (B) CCl₄ solvent (left) and CCl₄ solution (10 mg/mL) of PEO_{116} -*b*-PS₃₆₂ (right).



Fig. S4. FT-IR spectra of (A) PEO₁₁₆-*b*-PS₃₆₂ block copolymer and (B) AHPP-PEO₁₁₆-*b*-PS₃₆₂.



Fig. S5. (A) Outer diameter and (B) PEO core diameter distribution histograms of PEO@xPS nanosphere network units based on analysis of TEM image of AHPP-PEO₁₁₆-*b*-PS₃₆₂.



Fig. S6. TEM image of *x*PS.



Fig. S7. Pore size distribution of AHPP-PEO₁₁₆-b-PS₃₆₂ measured by mercury porosimetry.



Fig. S8. (A) TEM image of a microtomed and RuO_4 -stained polymer film of AHPP-PEO₁₁₆-*b*-PS₃₆₂; (B) diameter distribution histogram of the solid blackspots based on analysis of TEM image in Fig. 3A.



Fig. S9. SEM images of the products with various Friedel-Crafts reaction times: (A) 30 s, (B) 2 min, (C) 8 min, (D) 15 min, (E) 30 min, (F) 1 h, (G) 3 h and (H) 24 h.



Fig. S10. TEM images of the product after a reaction time of 30 min. The product was obtained according to the procedures in Fig. S9, except that the reaction solutions were promptly loaded in the copper meshes instead of the copper foils.



Fig. S11. ¹H NMR spectra of PEO-*b*-PS with different lengths of PS segment: (A) PEO₁₁₆-*b*-PS₆₃₅ and (B) PEO₁₁₆-*b*-PS₇₁₈.



Fig. S12. GPC traces of (A) PEO₁₁₆-*b*-PS₆₃₅ and (B) PEO₁₁₆-*b*-PS₇₁₈.



Fig. S13. SEM and TEM images of (A and B) AHPP-PEO₁₁₆-*b*-PS₆₃₅ and (C and D) AHPP-PEO₁₁₆-*b*-PS₇₁₈.



Fig. S14. (A) Outer diameter and (B) PEO core diameter distribution histograms of PEO@xPS nanosphere network units based on analysis of TEM image of AHPP-PEO₁₁₆-b-PS₆₃₅; (C) outer diameter and (D) PEO core diameter distribution histograms of PEO@xPS nanosphere network units based on analysis of TEM image of AHPP-PEO₁₁₆-b-PS₇₁₈.



Fig. S15. N₂ adsorption-desorption isotherms and DFT pore size distributions of (A, C) AHPP-PEO₁₁₆-*b*-PS₆₃₅ and (B, D) AHPP-PEO₁₁₆-*b*-PS₇₁₈.



Fig. S16. (A) Schematic illustration of the fabrication of hierarchical porous polymeric materials (HPP). (B) SEM image and (C) TEM image of HPP-PS. Fabrication of HPP-PS included preparation of PS-grafted SiO₂ nanoparticles by SI-ATRP, hypercrosslinking of PS-grafted SiO₂ nanoparticles via Friedel-Crafts reaction, and SiO₂ removal by HF etching.



Fig. S17. (A) Adsorption capacities of AHPP-PEO₁₁₆-b-PS₇₁₈ and HPP-PS toward phenol at 308 K. (B) CO₂ adsorption isotherms at 273 K for AHPP-PEO₁₁₆-b-PS₇₁₈ and HPP-PS.

Sample	$\frac{S_{BET}}{(m^2 g^{-1})}$	$\frac{S_{mic}}{(m^2 g^{-1})}$	$\frac{S_{ext}}{(m^2 g^{-1})}$	V_t (cm ³ g ⁻¹)
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₃₆₂	502	50	452	1.27
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₆₃₅	451	106	345	0.92
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₇₁₈	484	132	352	0.99

 Table S1. Pore structures of AHPPs from various diblock copolymers.

Table S2. Pore structures of AHPPs from PEO_{116} -*b*-PS₆₃₅ with various reaction conditions.

Sample	Catalyst Amount (g)	Reaction Temperatur e (°C)	S_{BET} (m ² g ⁻¹)	$\frac{S_{mic}}{(m^2 g^{-1})}$	$\frac{S_{ext}}{(m^2 g^{-1})}$	V _t (cm ³ g ⁻¹)
AHPP-PEO ₁₁₆ -b-PS ₆₃₅	0.72	75	451	106	345	0.92
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₆₃₅ - C1	0.18	75	188	6	182	0.53
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₆₃₅ - C2	0.42	75	412	60	350	0.73
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₆₃₅ - C3	1.20	75	506	121	385	1.07
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₆₃₅ -T1	0.72	45	210	10	200	0.41
AHPP-PEO ₁₁₆ - <i>b</i> -PS ₆₃₅ -T2	0.72	60	424	72	352	0.76