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Supplementary Materials for

Artificial 3D hierarchical and isotropic porous polymeric materials

Stefan Chisca, Valentina-Elena Musteata, Rachid Sougrat, Ali Reza Behzad, Suzana P. Nunes

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Supplementary text on Flory-Huggins parameter estimation

The Flory-Huggins interaction parameters (χ) between PS-*b*-PtBA and the solvent mixture were estimated from Hansen solubility values, δ, values

$$\chi_{PS} = \frac{V A_{PS}}{RT} \quad (1)$$

where *V* is the solvent molar volume; and *A* was calculated from the weight average of the different δ contributions

$$A_{PS} = (\delta_{DS} - \delta_{DP})^2 + 0.25(\delta_{PS} - \delta_{PP})^2 + 0.25(\delta_{HS} - \delta_{HP})^2 \quad (2)$$

where δ_{iS} and δ_{iP} are Hansen solubility parameters for the solvents and PS-*b*-PtBA, respectively.

table S1. Flory-Huggins interaction parameters (χ) between copolymer blocks and the solvent mixture.

	δ_D ($MPa^{1/2}$)	δ_P ($MPa^{1/2}$)	δ_H ($MPa^{1/2}$)	χ_{SPS}	χ_{SPtBA}
PS	18.5	4.5	2.9		
PtBA	16	2.3	3.1		
THF:DMF (1:3)	17.2	11.6	10.4	0.90	1.16
DOX:DMF (1:3)	17.4	10.9	10.8	0.86	1.13
DMF	17.4	13.7	11.3	1.25	1.60
THF	16.8	5.7	8	0.32	0.31
DOX	17.5	1.8	9	0.42	0.38

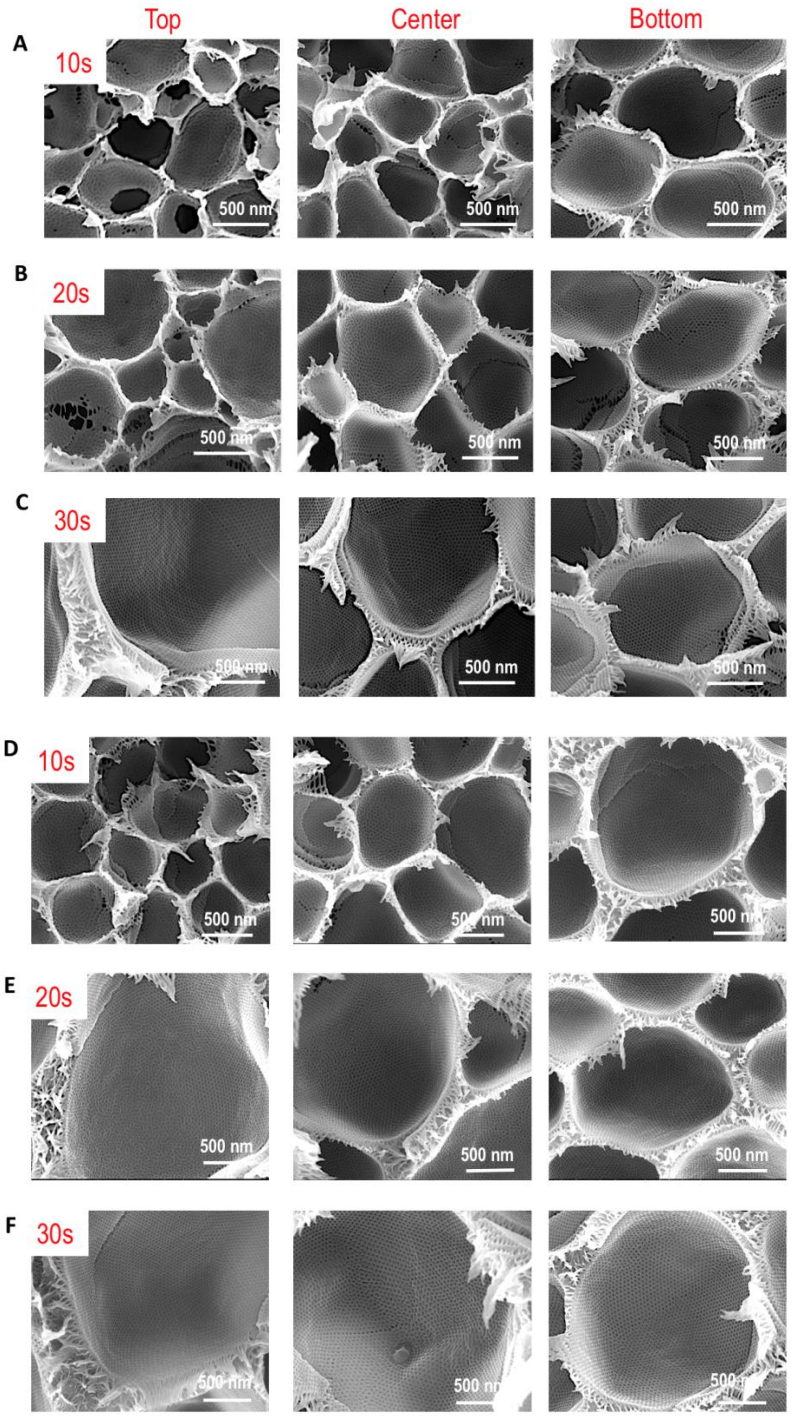

fig. S1. Hierarchical structure of PS_{636}-*b*-$PtBA_{250}$ films obtained after evaporation times varying from 10 to 30 s, before immersion in the nonsolvent bath. (**A-C**) Bulk SEM images of films obtained from 20 wt% block copolymer dissolved in 1:3 (wt%) THF/DMF; (D-E) analogous solutions with 6 wt% β-CD. Images are taken from different areas of the film (top, center, and bottom).

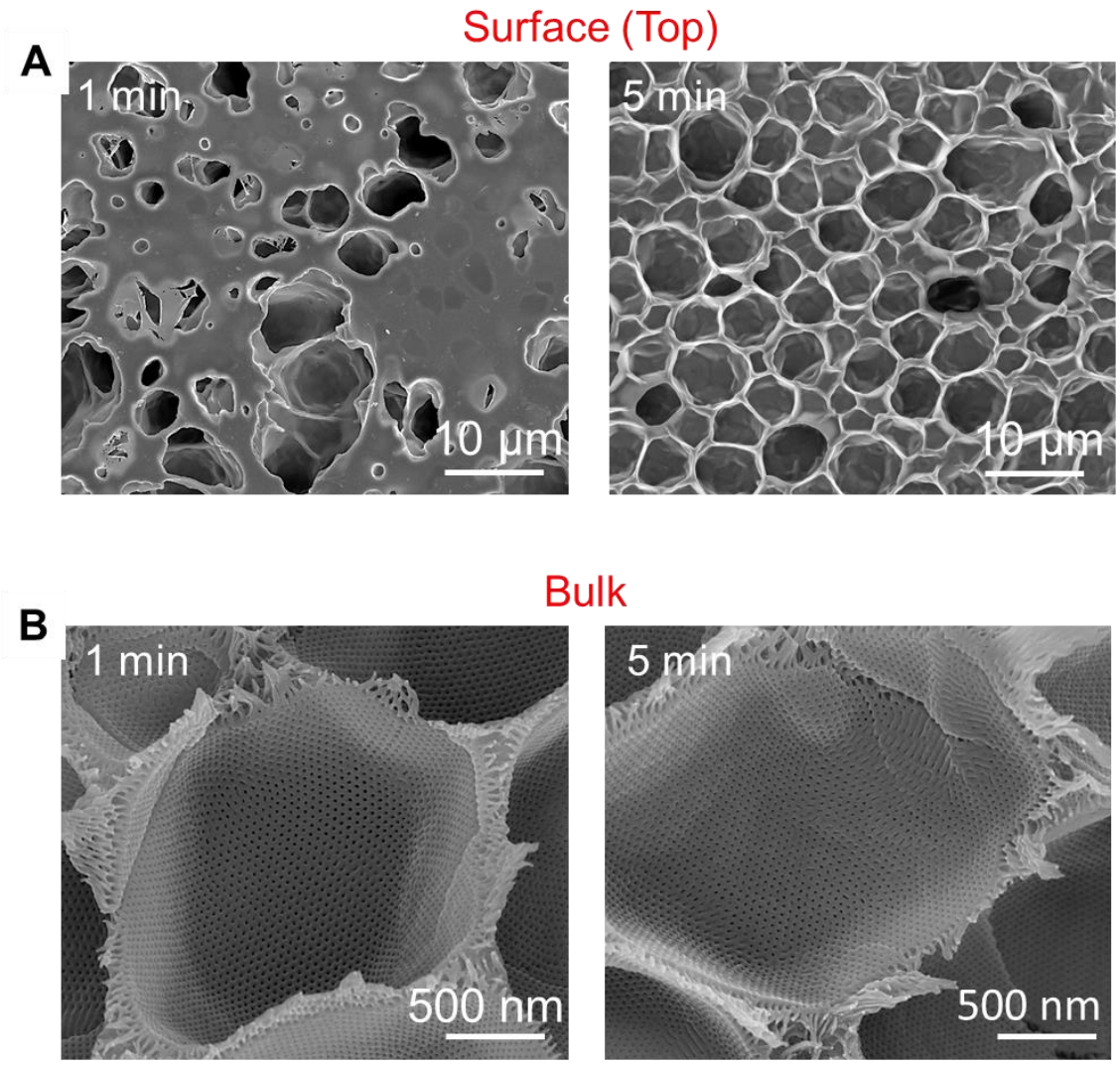

fig. S2. Hierarchical structure of PS_{636}-*b*-$PtBA_{250}$ films after long evaporation times. (**A**) Surface and (**B**) bulk SEM images of films obtained from 20 wt% block copolymer dissolved in 1:3 (wt%) THF/DMF.

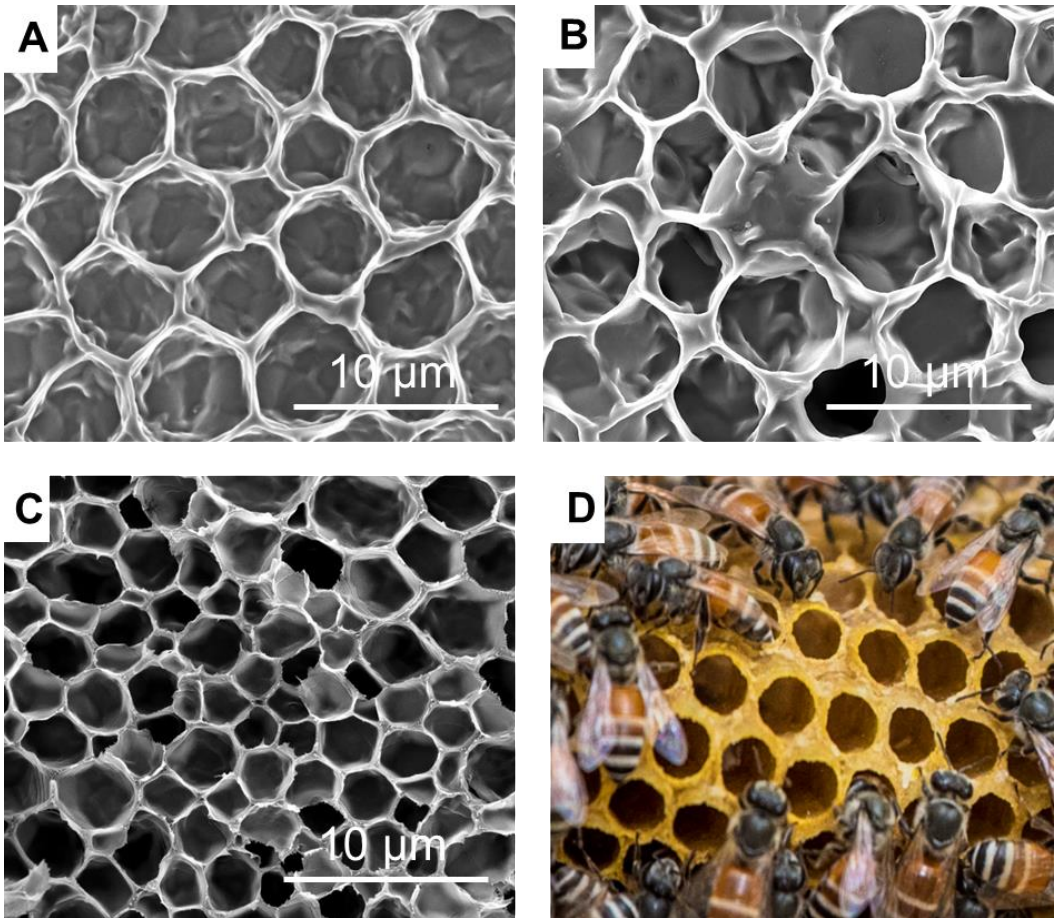

fig. S3. Influence of the addition of β-CD to the PS_{636}-*b*-$PtBA_{250}$/DOX/DMF system on the macroscale. (**A** and **B**) Surface SEM images of the film obtained from (A) plain and (B) with 6 wt% ß-CD solutions after 5 min evaporation. (**C**) Cross-section SEM image of the film obtained from plain solution. (**D**) Resembling a honeycomb architecture.

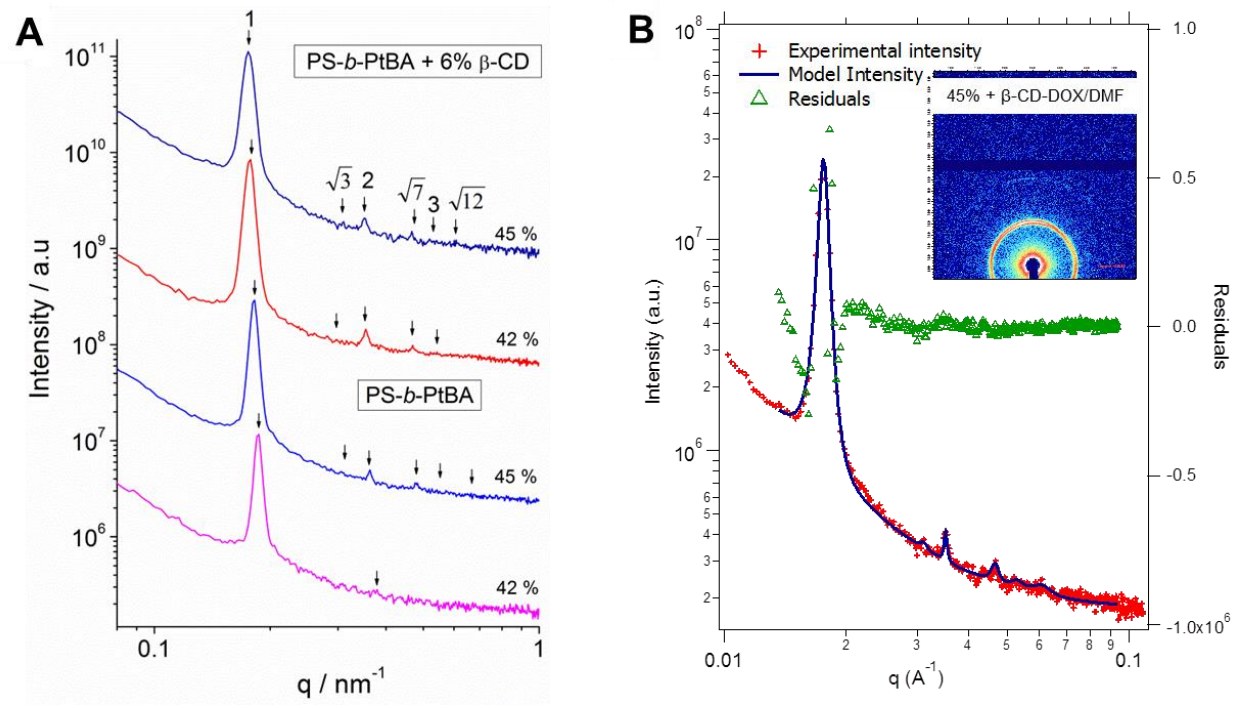

fig. S4. Influence of the addition of β-CD to the PS_{636}-*b*-$PtBA_{250}$/DOX/DMF system on the mesoscale. (**A**) SAXS patterns for 42 and 45 wt% PS_{636}–*b*–$PtBA_{250}$ plain and with 6 wt% ß-CD solutions. The peaks positions corresponding to *p6mm* symmetry are highlighted with arrows. (**B**) Scaterring profile of *I* vs. *q* for 45 % + 6% β-CD in DOX/DMF and the corresponding 2D scattering profile (inset). The relative position of the peaks are q/q* : 1, 1.77, 2.01, 2.66, 3.01, 3. 48, very close to 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$ which are characteristic to hexagonally packed cylinders, with domain spacing $d = 2\pi/q^*$ (where $q^*=q_1$ and represents the first scattering peak position) of 35.82 nm.

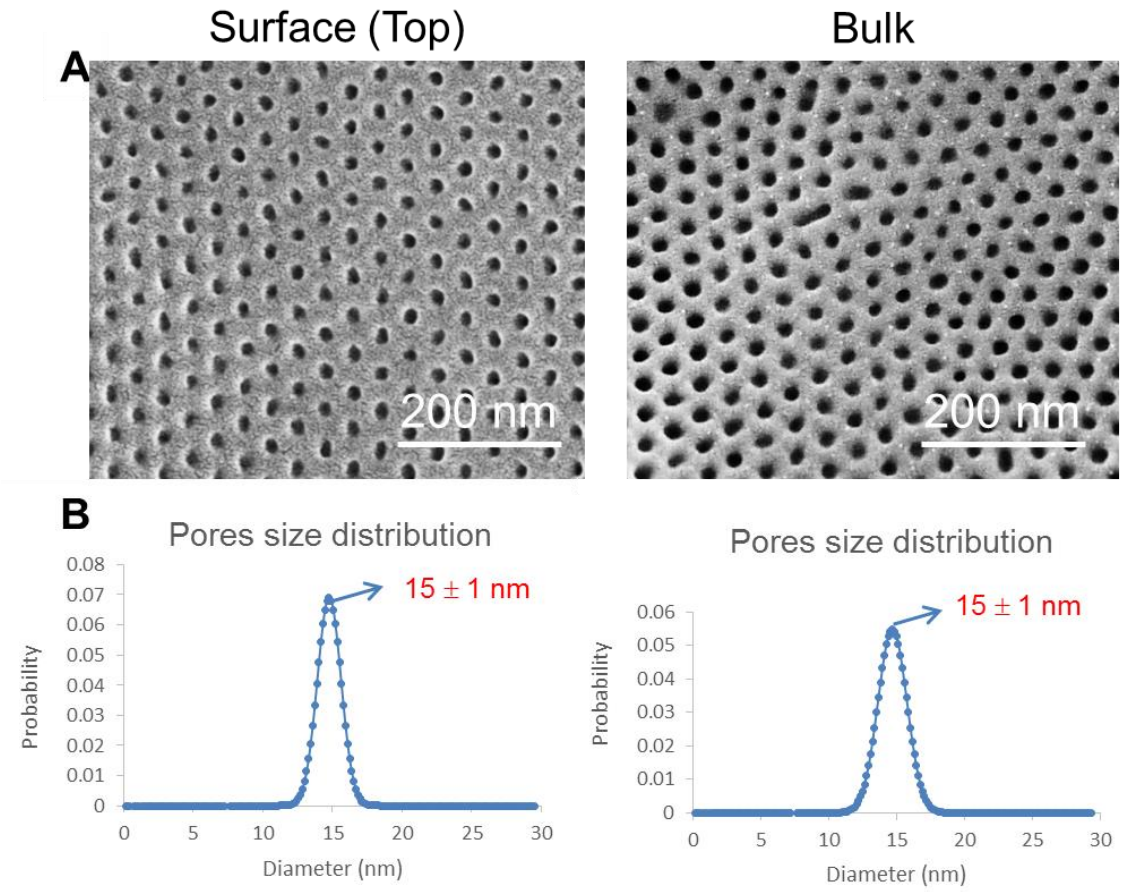

fig. S5. Mesopore dimensions of PS_{636}-*b*-$PtBA_{250}$ films prepared from solutions in 1:3 (wt %) DOX/DMF. (**A**) Surface (left) and bulk (right) SEM images of films obtained after 5 min evaporation. (**B**) Corresponding pore size distributions calculated from SEM images.

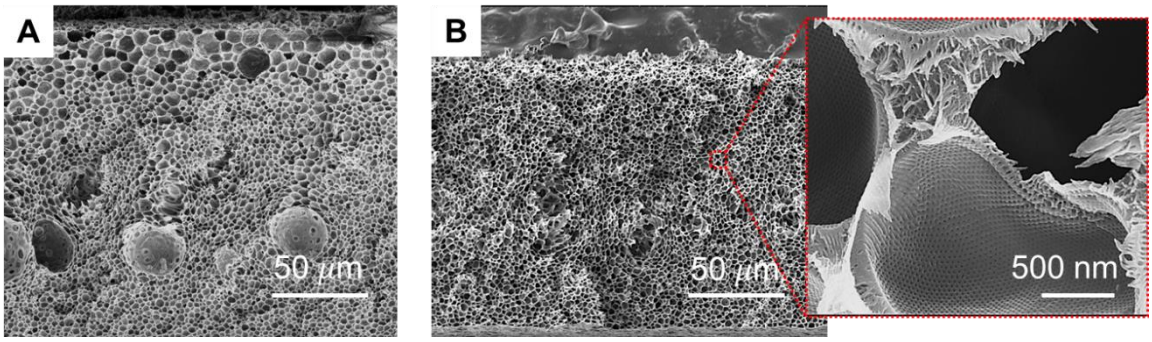

fig. S6. fig. S6. Effect of the relative humidity on the cross-section morphology of PS_{636}-*b*-$PtBA_{250}$ films obtained from solutions in 1:3 (wt %) DOX/DMF, after 5-min evaporation. Cross-section morphology of PS_{636}-*b*-$PtBA_{250}$ films obtained from solutions in 1:3 (wt%) DOX/DMF, after 5 min evaporation, under (**A**) 60% and (**B**) <20% relative humidity.

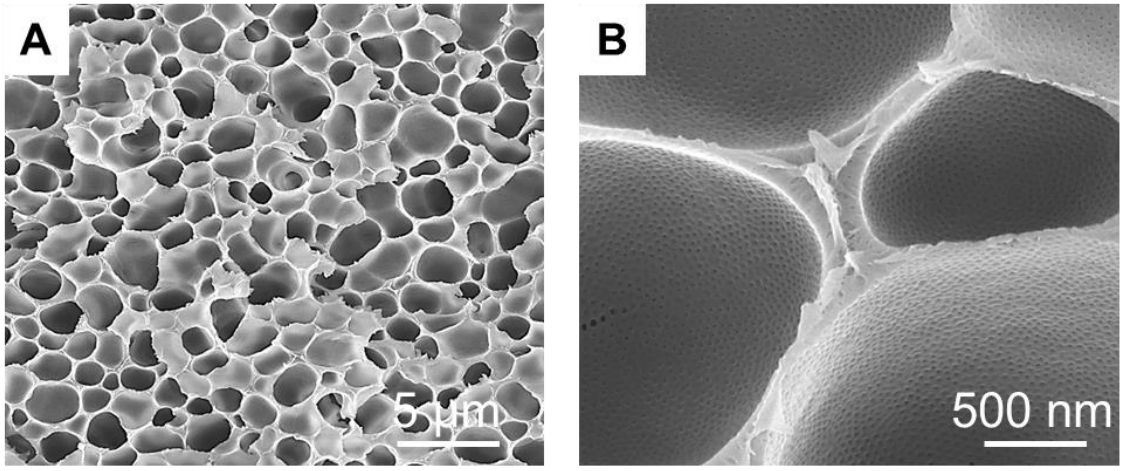

fig. S7. Hierarchical structure prepared from PS_{677}-*b*-$PtBA_{180}$ dissolved in 1:3 (wt %) DOX/DMF. The films were obtained after 5 min evaporation.

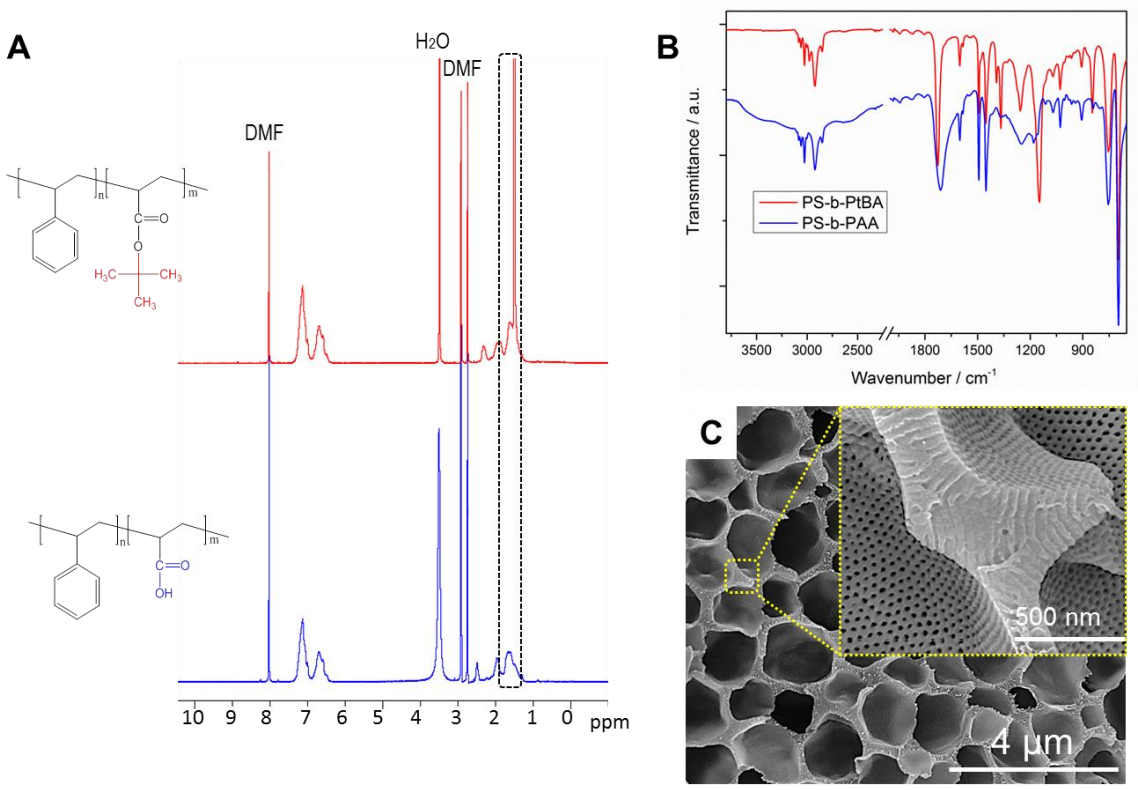

fig. S8. Hydrolysis of preformed hierarchical PS_{636}-*b*-$PtBA_{250}$ films to PS-*b*-PAA. (**A**) H-NMR spectra for PS-*b*-PtBA and PS-*b*-PAA. The absence of characteristic peak at $\delta = 1.45$ ppm, which corresponds to methyl protons from *tert*-butyl group, confirm that PtBA block was completely hydrolyzed into PAA. (**B**) FTIR spectra for PS-*b*-PtBA and PS-*b*-PAA. The presence of the broad peak at 2500 – 3600 cm^{-1} indicates the formation of carboxylic groups, as well as the shift of the C=O stretching band (1700 cm^{-1} region) to a lower wavenumber. (**C**) SEM images of the film after hydrolysis which proves that hierarchical structure is maintained after modification.