

## Supporting Information for

### Binary Breath Figures for Straightforward and Controllable Self-Assembly of Microspherical Caps

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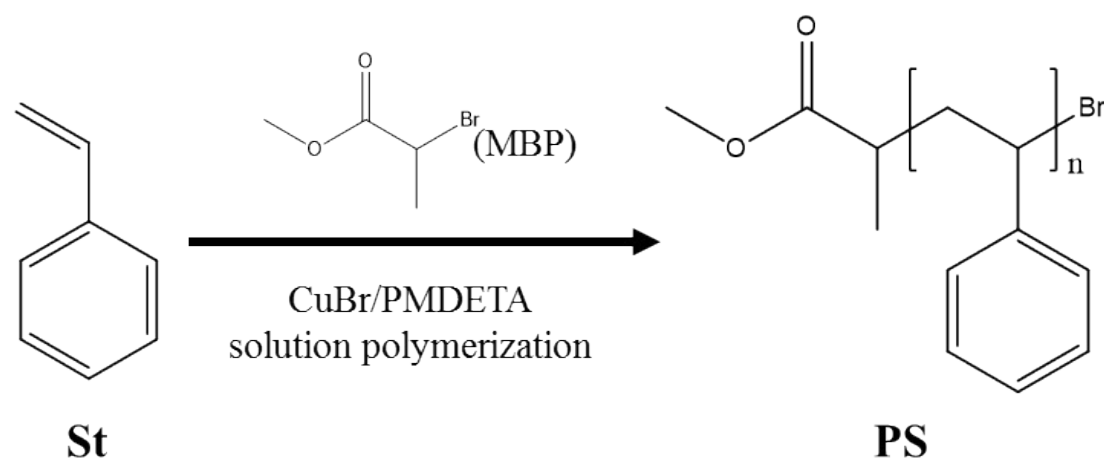


Fig. S1 Scheme of synthesizing PS by ATRP.

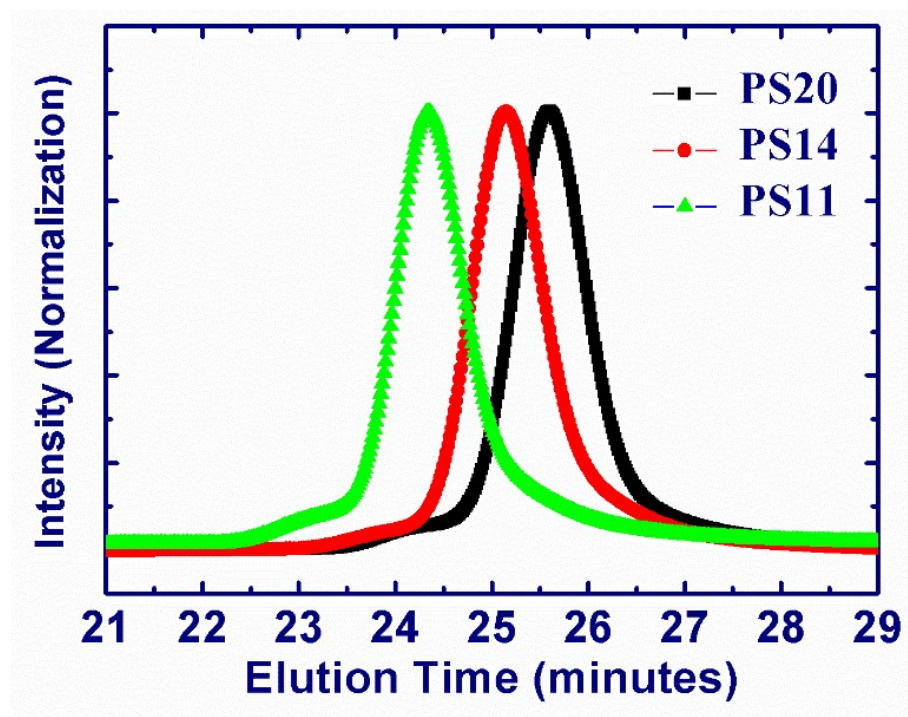


Fig. S2 GPC traces of PS-11, PS-14 and PS-20 homopolymers.

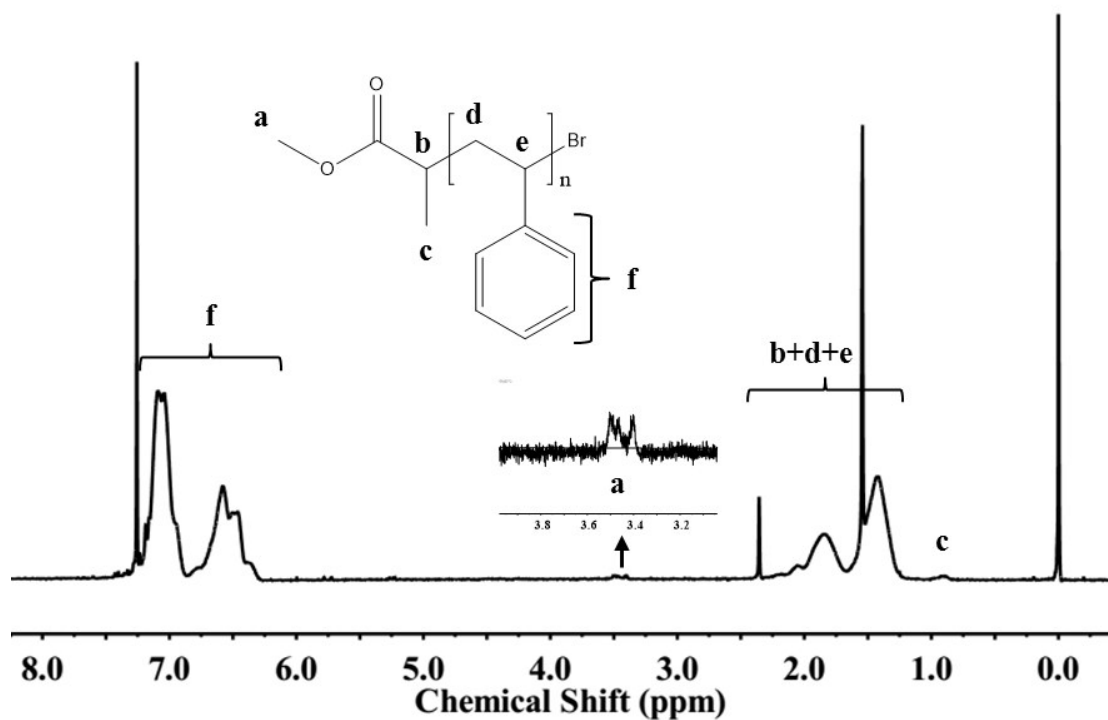
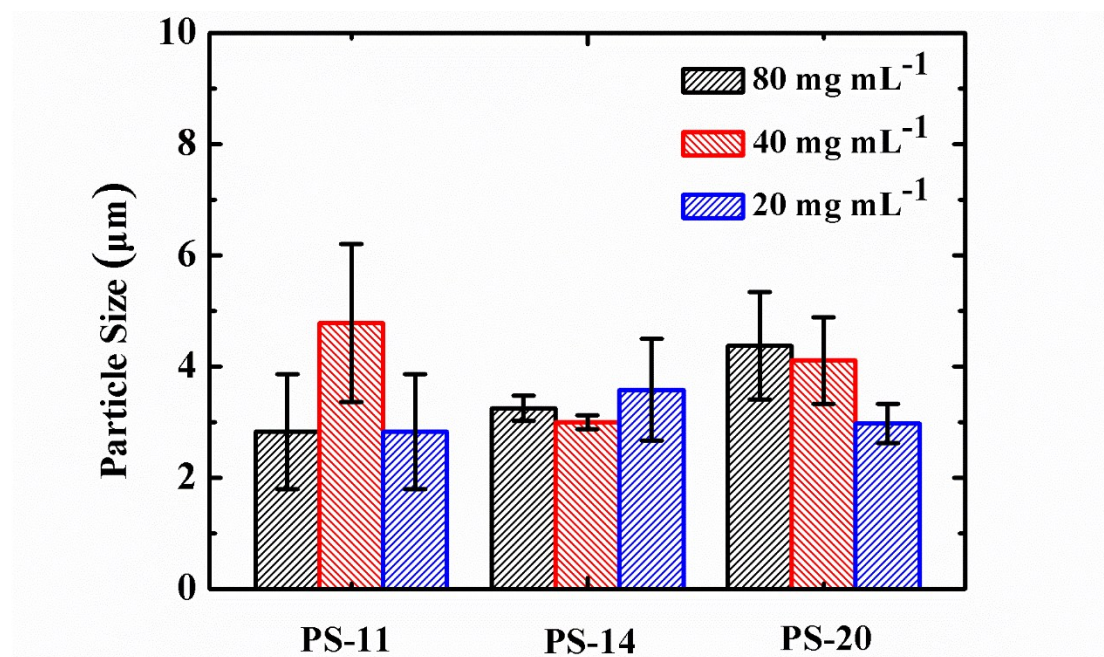
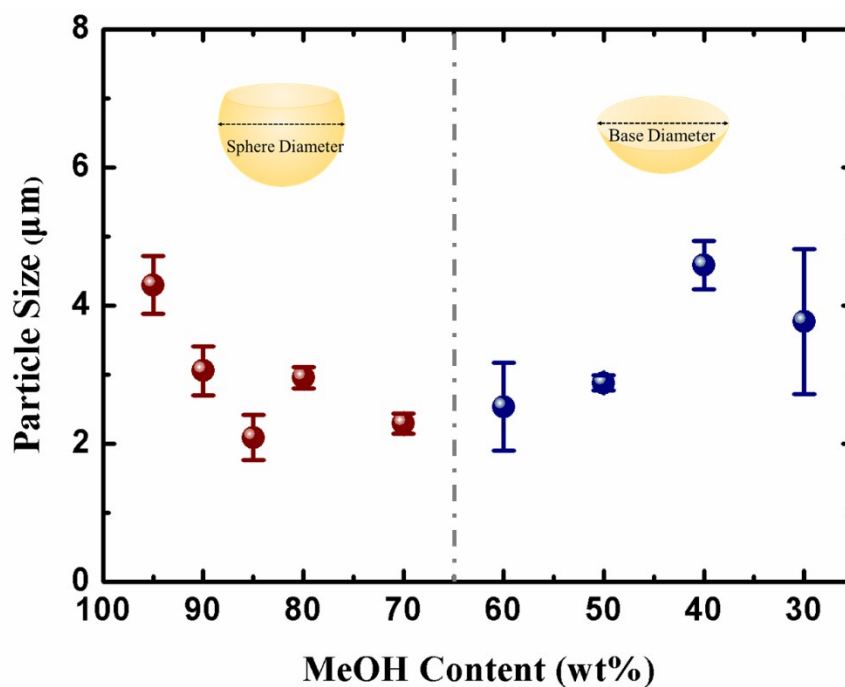


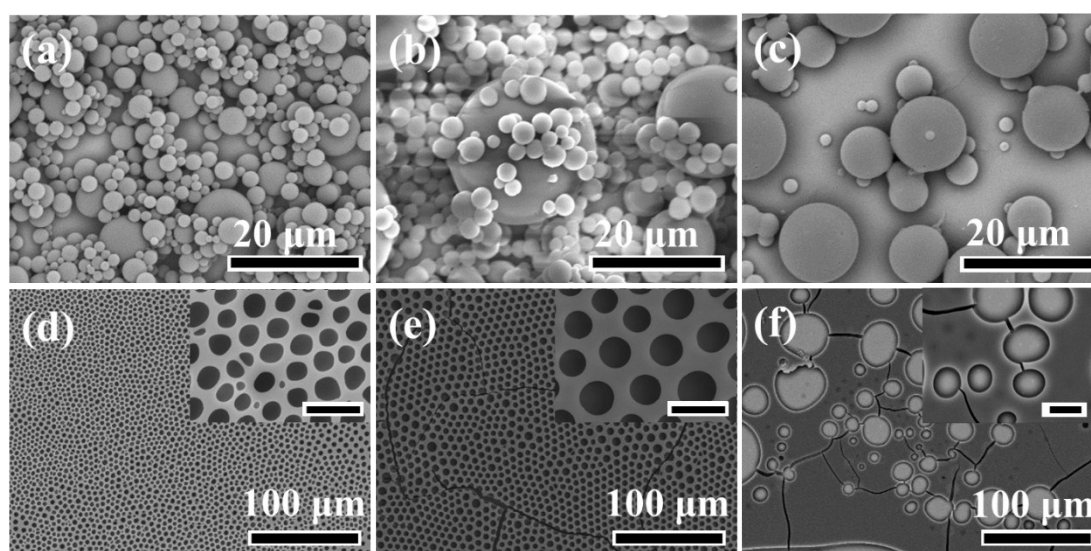
Fig. S3 A typical  $^1\text{H}$  NMR spectrum of PS homopolymer with  $\text{CDCl}_3$  as solvent.



**Fig. S4** The pore size and size distribution of microspherical caps prepared from PS with different molecular weights and solution concentration. The sphere diameter of microspherical cap was measured for statistical analysis.

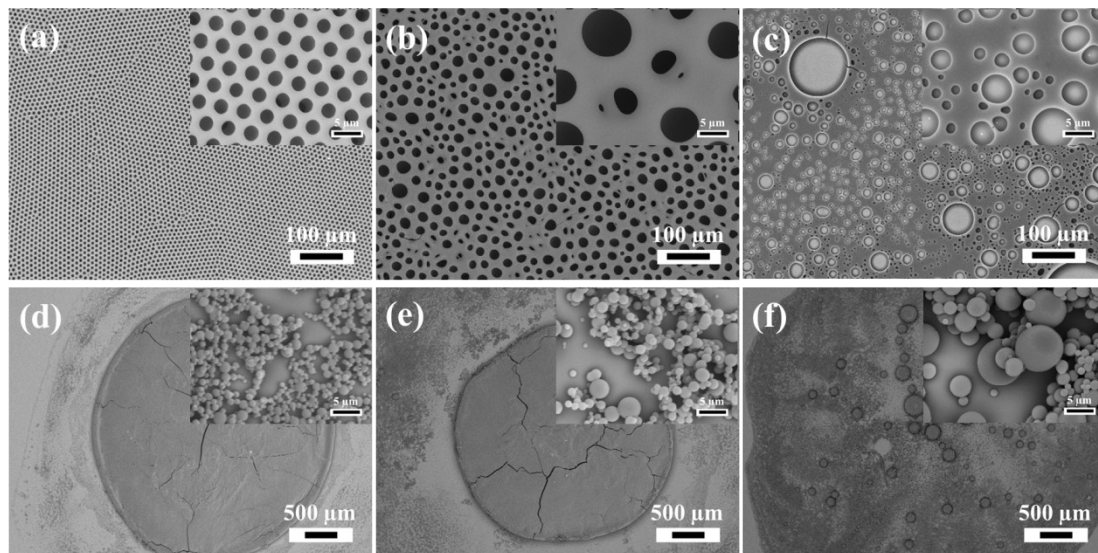


**Fig. S5** The particle size of microspherical caps plotted against on the MeOH contents. The scale bars indicate the particle size distribution. The sphere diameter of large-portion microspherical cap and the base diameter of small-portion microspherical cap were measured for statistical analysis, respectively.

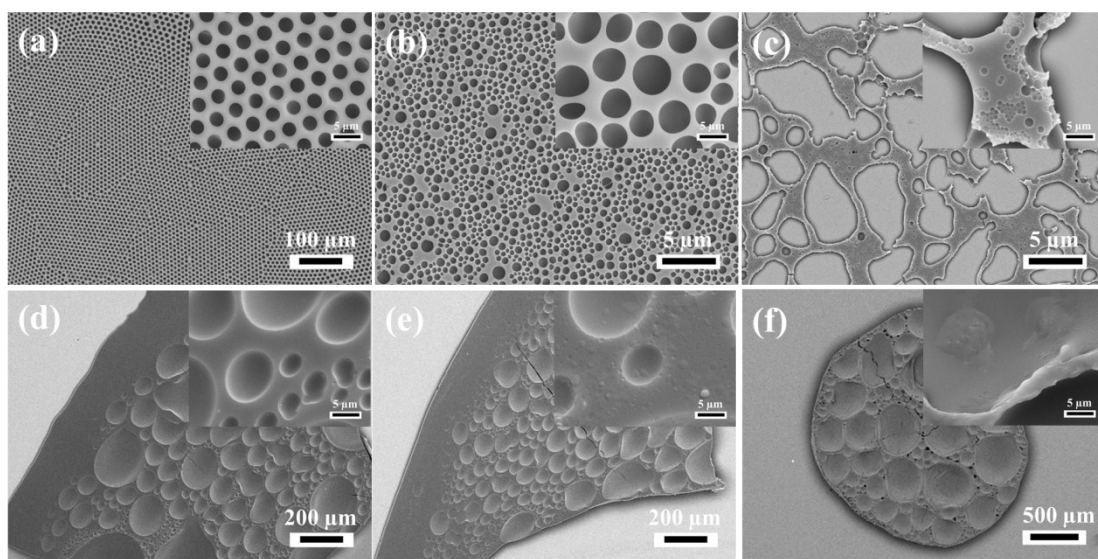


**Fig. S6** Microspheres formed in MeOH vapor (a-c) and porous microstructures prepared in water vapor (d-f) from PS-14/THF solution with different concentrations:

(a) and (d) 160 mg mL<sup>-1</sup>; (b) and (e) 80 mg mL<sup>-1</sup>; (c) and (f) 20 mg mL<sup>-1</sup>. The scale bars in the insets of (d-f) are 10  $\mu$ m.

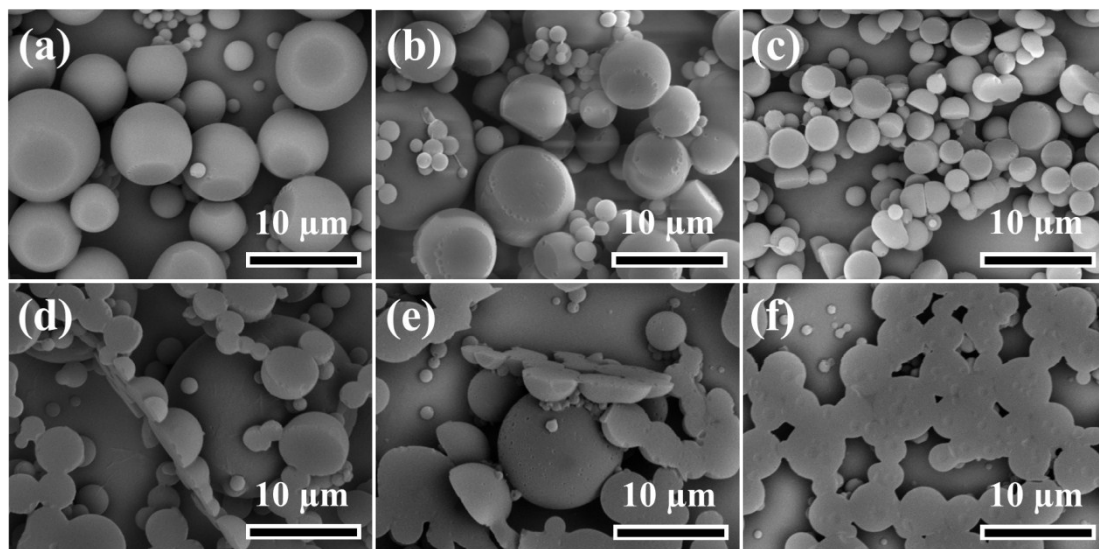


**Fig. S7** Porous microstructures prepared in water vapor (a-c) and microspheres formed in MeOH vapor (d-f) and from PS-14/CHCl<sub>3</sub> solution with different concentrations: (a) and (d) 160 mg mL<sup>-1</sup>; (b) and (e) 80 mg mL<sup>-1</sup>; (c) and (f) 20 mg mL<sup>-1</sup>.





**Fig. S8** Porous microstructures prepared in water vapor (a-c) and shrunk films with large pores formed in MeOH vapor (d-f) and from PS-14/CS<sub>2</sub> solution with different concentrations: (a) and (d) 160 mg mL<sup>-1</sup>; (b) and (e) 80 mg mL<sup>-1</sup>; (c) and (f) 20 mg mL<sup>-1</sup>.



**Fig. S9** Microspherical caps with tunable shapes prepared from evaporation of 20 mg mL<sup>-1</sup> PS-14/CHCl<sub>3</sub> solution in binary vapor generated by different MeOH/water weight ratios: (a) 95/5; (b) 90/10; (c) 85/15; (d) 80/20; (e) 70/30; (f) 60/40.