Supporting Information for

Binary Breath Figures for Straightforward and Controllable Self-
Assembly of Meirospherical 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 $^1$H NMR spectrum of PS homopolymer with 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\(^{-1}\); (b) and (e) 80 mg mL\(^{-1}\); (c) and (f) 20 mg mL\(^{-1}\). The scale bars in the insets of (d-f) are 10 µm.

Fig. S7 Porous microstructures prepared in water vapor (a-c) and microspheres formed in MeOH vapor (d-f) and from PS-14/CHCl\(_3\) solution with different concentrations: (a) and (d) 160 mg mL\(^{-1}\); (b) and (e) 80 mg mL\(^{-1}\); (c) and (f) 20 mg mL\(^{-1}\).
**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$_2$ solution with different concentrations: (a) and (d) 160 mg mL$^{-1}$; (b) and (e) 80 mg mL$^{-1}$; (c) and (f) 20 mg mL$^{-1}$.

**Fig. S9** Microspherical caps with tunable shapes prepared from evaporation of 20 mg mL$^{-1}$ PS-14/CHCl$_3$ 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.