## **Supporting Information**

## Poly(*N*,*N*-diethylacrylamide)-Endowed Spontaneous Emulsification during the Breath Figure Process and the Formation of Membranes with Hierarchical Pores

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Fig. S1 Optical photographs of PDEAM/CS<sub>2</sub> solutions with concentrations of 4 and 8 mg mL<sup>-1</sup> at (a) 50 and (b) 25 °C.



**Fig. S2** Optical photograph of a vial containing PDEAM (4 mg) dissolved into CS<sub>2</sub> which is pre-saturated with water (2 mL) at 25 °C.



**Fig. S3** In-situ bright-field optical microscopic images of (a) pure  $CS_2$  and (b) PDEAM/ $CS_2$  solution (2 mg mL<sup>-1</sup>) locating in water with glass capillaries as the reservoir. All images share the same scale bar.



**Fig. S4** Optical photographs of different solutions at different time: (I) H<sub>2</sub>O–PDEAM/CS<sub>2</sub>; (II) H<sub>2</sub>O–PDEAM/CHCl<sub>3</sub>; (III) PDEAM/H<sub>2</sub>O–CHCl<sub>3</sub>. The concentration of each PDEAM-containing solution is 2 mg mL<sup>-1</sup>.



**Fig. S5** (a) Optical photograph of PDEAM (4 mg) and PNIPAM (4 mg) added with water which is pre-saturated with CHCl<sub>3</sub> (2 mL) at 25 °C. The photograph was taken after 12 h. (b, c) Optical photographs of pure CHCl<sub>3</sub> pendent droplets in (b) PDEAM/water and (c) PNIPAM/water solutions. (d, e) Optical photographs of upside-down water droplets in (d) PDEAM/CHCl<sub>3</sub> and (e) PNIPAM/CHCl<sub>3</sub> solutions. Concentrations of the solutions in (b–e) are 2 mg mL<sup>-1</sup>. All scale bars are 1 mm.



**Fig. S6** Optical photograph of benzene and toluene solutions dissolved with PDEAM (2 mg  $mL^{-1}$ , 1 mL) contacted with bottom water (1 mL). Photograph was taken after 1 h.



**Fig. S7** Optical photographs of different solutions at different time: (I) PDEAM/H<sub>2</sub>O–CS<sub>2</sub>; (II) H<sub>2</sub>O–PNIPAM/CHCl<sub>3</sub>; (III) PNIPAM/H<sub>2</sub>O–CHCl<sub>3</sub>. The concentration of PDEAM- or PNIPAM-containing solution is 2 mg mL<sup>-1</sup>.



**Fig. S8** (a) UV absorption spectra of PDEAM aqueous solutions at different concentrations. The lowest concentration is 0.0025 mg mL<sup>-1</sup>, and the concentration represented by each curve doubles gradually. Inset shows the corresponding concentration-dependent absorbance at 281 nm. (b) UV absorption spectra of water (1 mL) acquired 1 h after being contacted with pure CS<sub>2</sub> (1 mL) or PDEAM/CS<sub>2</sub> (1 mg mL<sup>-1</sup>, 1 mL) at 25 °C. No obvious peak at 281 nm was observed. The concentration of PDEAM in water can be estimated to be ~0.02 mg mL<sup>-1</sup> according to the increased absorption in 200–220 nm.



**Fig. S9** Optical photographs of PDEAM/CS<sub>2</sub> solution (1 mg mL<sup>-1</sup>, 1 mL) which is contacted with water (1 mL). The environmental temperature was switched between 40 °C and 25 °C.



**Fig. S10** Surface (upper row) and cross-sectional (bottom row) SEM images of porous films of PS-*b*-PDMAEMA/PDEAM with various concentrations by static breath figure method. Scale bar is 5 µm.



**Fig. S11** Optical photographs of water droplets in  $CS_2$  solutions at different time. The concentration of PS-*b*-PDMAEMA in the solutions is fixed at 4 mg mL<sup>-1</sup> and concentrations of PDEAM vary between 0~4 mg mL<sup>-1</sup>. Scale bars are 0.5 mm.



**Fig. S12** (a–d) Surface and (e–h) cross-sectional SEM images of PS-*b*-PDMAEMA/PDEAM (6/2 mg mL<sup>-1</sup>) porous films prepared by static breath figure method with different casting volumes. (a, e) 60  $\mu$ L; (b, f) 90  $\mu$ L; (c, g) 120  $\mu$ L; (d, h) 150  $\mu$ L. The same row shares the same magnification and the scale bars are 10  $\mu$ m.



**Fig. S13** Surface (upper row) and cross-sectional (bottom row) SEM images of porous films of PS-*b*-PDMAEMA/PDEAM (6/0.6 mg mL<sup>-1</sup>) by the dynamic breath figure method with different gas flow rates.



**Fig. S14** Surface (upper row) and cross-sectional (bottom row) SEM images of porous films of PS-*b*-PDMAEMA (10 mg mL<sup>-1</sup>) and PS-*b*-PDMAEMA/PDEAM (10/2 mg mL<sup>-1</sup>) by the static breath figure method with CHCl<sub>3</sub> as the solvent.