Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Nanoporous Polysulfones with *In Situ* PEGylated Surfaces by A Simple Swelling Strategy Using Paired Solvents

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Experimental Procedures

Materials. The PSF-*b*-PEG block copolymer was obtained from Nanjing Bangding. According to the manufacturer, the weight average molecular weight (M_w) of the copolymer is 79.1 kDa and the polydispersity index (PDI) is 2.00, while the molecular weight of the PEG block ~20 kDa with a weight ratio of ~21% in the copolymer. PSF homopolymer (Solvay P3500) and PEG homopolymer (molecular weight = 20000 Da) were obtained from Solvay and Sigma, respectively. Analytically pure organic solvents including acetone, ethanol, hexanol, and chloroform were purchased from local suppliers and used without further purification. Osmium tetroxide (OsO_4) was provided by Nanjing Dong Rui Platinum Co., Ltd. and was used as the staining agent. Bovine serum albumin (BSA) with a molecular weight 67 kDa and monodispersed SiO_2 nanospheres with a diameter of 22 nm were purchased from Sigma-Aldrich.

Preparation of nanoporous PSF-*b*-PEG materials. PSF-*b*-PEG was dissolved in chloroform with a typical concentration of 2 wt%. The solutions were then spin-coated on silicon wafers to produce thin films with a thickness of ~253 nm (2000 rpm, 30 s). The films were soaked in solvent pairs or single solvents at a pre-set temperature for different durations. Subsequently, the films were removed from the solvent and dried in air at room temperature. The flat-sheet films of PSF-*b*-PEG with a thickness of ~ 60 μm were processed in a twin-screw extruder (Nanjing Juli Chemical Machinery Co., Ltd), and the extruded films were soaked in the hexanol/acetone solvent pair with $\Phi_{acetone}$ = 20% at 60 °C for 6 h and then air dried at room temperature. PSF-*b*-PEG monoliths were injection moulded and soaked under the same conditions as

the extruded films but with an extended duration of 12 h.

Characterizations. Field-emission scanning electron microscopy (Hitachi, S4800) was used to view the surfaces and cross sections of samples at a voltage of 5 kV. Before SEM examination, the samples were sputter coated with a thin layer of Au/Pd alloy. A transmission electron microscope (TEM) was used to determine the distribution of PSF and PEG phases in the films before and after swelling. Ultrathin (< 200 nm) PSF-*b*-PEG films were produced on silicon wafers with ~ 1-μm-thick SiO_2 layer by spin coating, and soaked in the ethanol/acetone solvent pair with $\Phi_{acetone}$ = 20% at 70 °C for 5 h. The PSF-*b*-PEG films deposited on the silicon substrates were immersed in a dilute HF solution to exfoliate the films from the substrate by dissolving the SiO_2 sacrificial layers. The films floating on water were then carefully collected on copper grids and exposed to OsO_4 vapour at 30 °C for 12 h to selectively stain the PEG phases. TEM was conducted with a Philips Tecnai 12 transmission electron microscope operated at 120 kV. The thicknesses of the PSF-*b*-PEG films spin coated on silicon wafers were measured using a spectroscopic ellipsometer (M-2000U, J.A. Woollam. Co. Inc.) at an incidence angle of 65° in the wavelength range of 246.1-999.8 nm. The refractive indexes were acquired simultaneously at the wavelength of 632.8 nm. The surface wettability of the PSF-*b*-PEG films was analysed by a contact angle goniometer (DropMeter A100, Maist), and the measurements were performed on at least three different positions and the averaged values were reported. The swelling tests for the PSF and PEG homopolymers were carried out at 70°C. For the PEG homopolymers, the as-received granules were immersed in ethanol and acetone, respectively, to observe whether the polymer can be

completely dissolved. For the PSF homopolymers, they were pressed into films at 210°C and the films were soaked in ethanol or acetone. 5 h later, the PSF films were removed from the solvent and were gently wiped with tissue paper to remove the solvent adhering on the surfaces. The swelling ratio (r) was obtained by comparing the weight of the PSF film before and after soaking in the solvent (m_0 and m_1, respectively): $r = (m_1-m_0)/m_0*100\%$. N_2 adsorption-desorption isotherms were obtained using a surface area and porosity analyser (Micromeritics, ASAP-2020) at 77 K. Before taking the measurements, the nanoporous PSF-*b*-PEG thick films were degassed in vacuum at 80 °C for 24 h. Specific surface areas (S_{BET}) were derived from the Brunauer−Emmett-Teller (BET) method using the adsorption data at p/p_0 = 0−1.0. Pore size distributions (PSD) and the pore volumes (V_{meso}) were derived from the adsorption branch by using the Barrett−Joyner−Halenda (BJH) model. The mechanical properties of the extruded films after soaking were measured on an electronic tensile tester (CMT-6203, Shenzhen Sans Test Machine Co.) at a crosshead speed of 5 mm/min using samples with dimension of 40 mm × 8 mm.

Filtration tests of the nanoporous PSF-*b*-PEG membranes. Flux experiments were performed on a Millipore test cell (Amicon 8010, Millipore Co.) at a stirring speed of 600 rpm and a pressure of 0.4 bar at room temperature. Before the flux test, pre-compaction was carried out at 0.4 bar for 10 min to obtain a stable water flux. BSA was dissolved in phosphate buffer (pH = 7.4) at a concentration of 0.5 g/L and was used to probe the retentions of the nanoporous films. The BSA concentrations in the feeds and filtrates were monitored using a UV-vis absorption spectrometer (NanoDrop

2000c, Thermo) and were compared to determine the retention rate of BSA for each sample. Aqueous solutions of silica particles (22 nm) with a concentration of 45 wt% were diluted 10,000 times and used as feed solutions after sonication under 60 W for 10 min, and concentrations of silicon in the feed and filtrate solutions were measured via inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7000DV, Perkin Elmer).

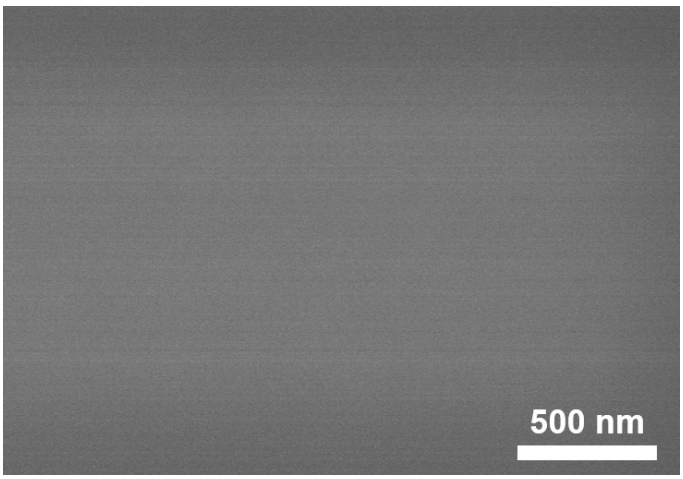

Fig. S1 The surface SEM micrograph of the PSF-*b*-PEG film spincoated on the silicon wafer before soaking treatment.

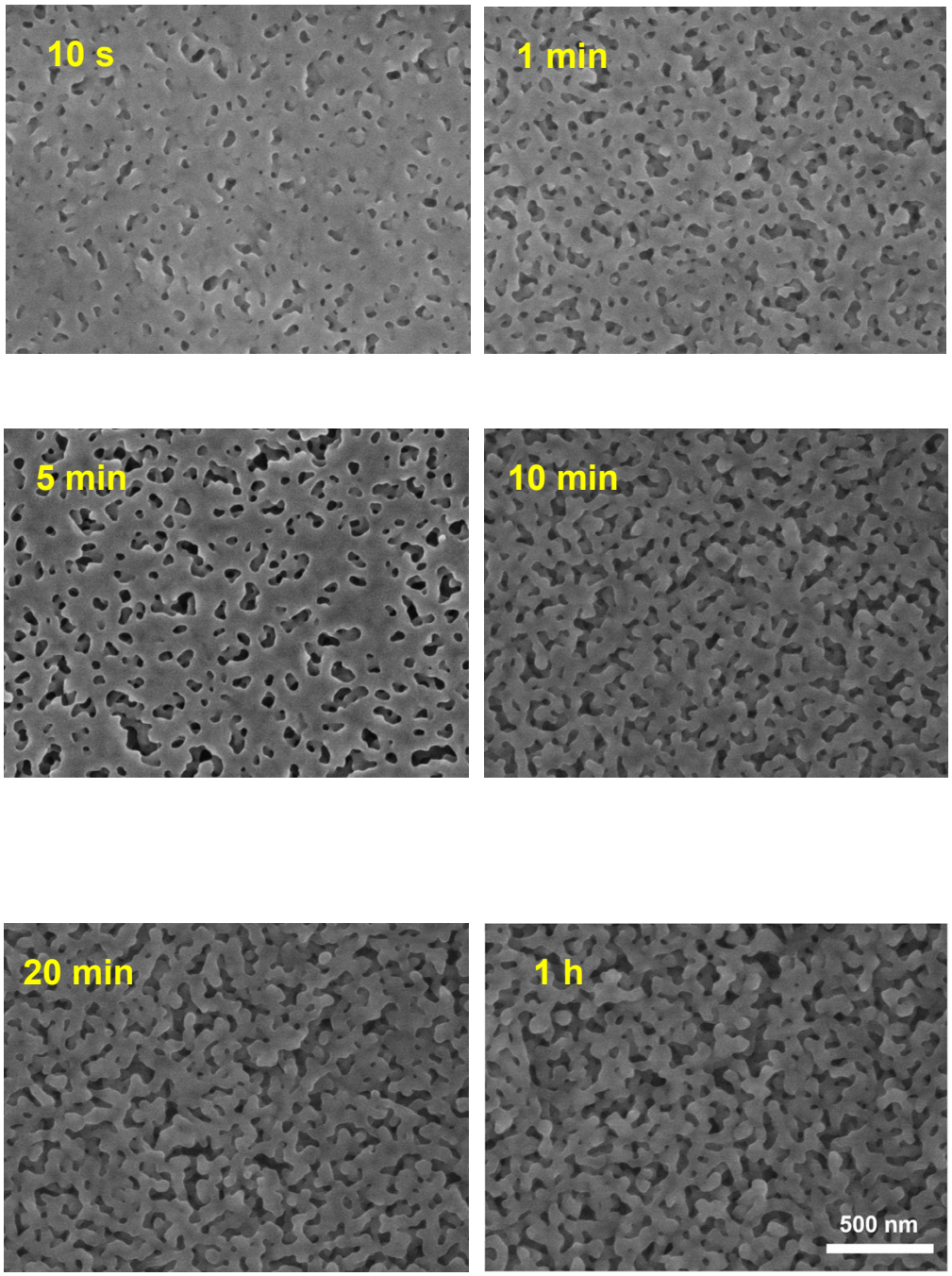

Fig. S2 The surface SEM micrographs of the PSF-*b*-PEG film after swelling in ethanol/acetone pair with Φacetone=20 % at 70 ºC for different durations. All the images have the same magnification and the scale bar is shown in the last

panel of the figure.

Tab. S1 The solubility parameters of PSF and PEG and organic solvents used in this work.

Polymer or solvent	PSf	PEG	Acetone	Ethanol	Hexanol
Solubility Parameter/ $MPa^{1/2}$	22.9	27.4	19.9	27.4	21.0

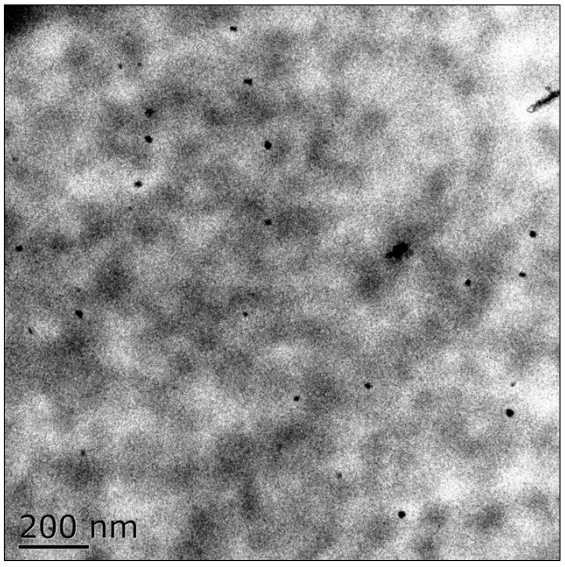

Fig. S3 The TEM micrograph of the as-coated PSF-*b*-PEG film before soaking treatment. The film was stained with OsO4 and the PEG phases appeared darker because of selective enrichment of OsO4.

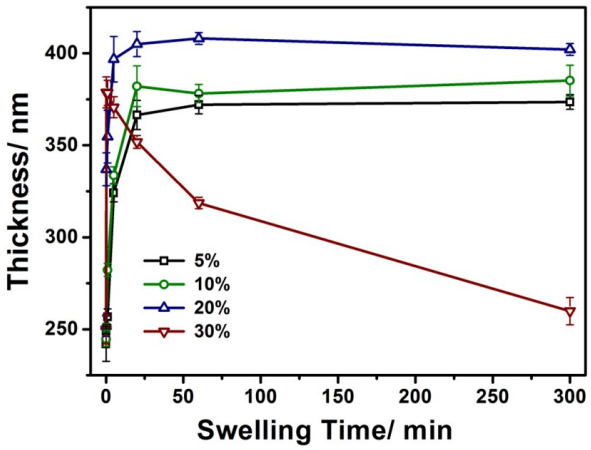

Fig. S4 The thicknesses of the PSF-*b*-PEG films after soaking in the ethanol/acetone pair with $\Phi_{acetone}$=5 %, 10%, 20%, and 30%, respectively at 70 °C for different durations.

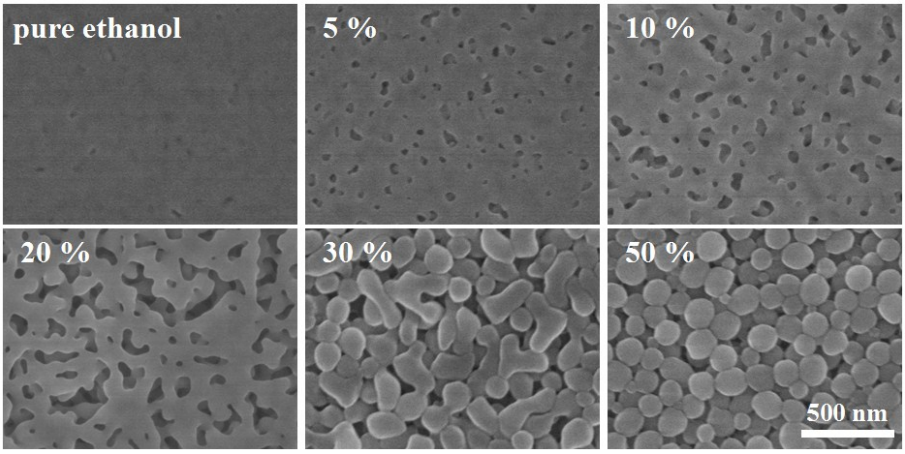

Fig. S5 The surface SEM micrograph showing the morphological evolution of PSF-*b*-PEG films soaked in the ethanol/acetone pair with Φacetone increasing from 0 (pure ethanol) to 50 % at 70 ºC for 5 h.

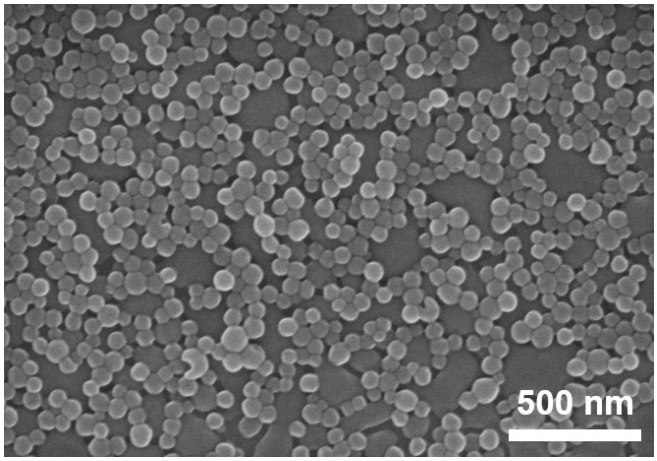

Fig. S6 The surface SEM micrograph of the PSF-*b*-PEG film after soaking in pure acetone at 50 ºC for 5 h.

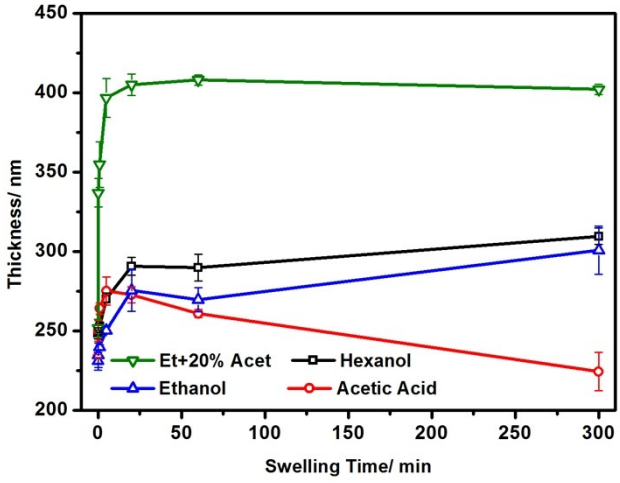

Fig. S7 Comparison of the thicknesses of PSF-*b*-PEG films after soaking in pure ethanol and in the ethanol/acetone pair with Φacetone= 20% at 70 ºC for different durations.

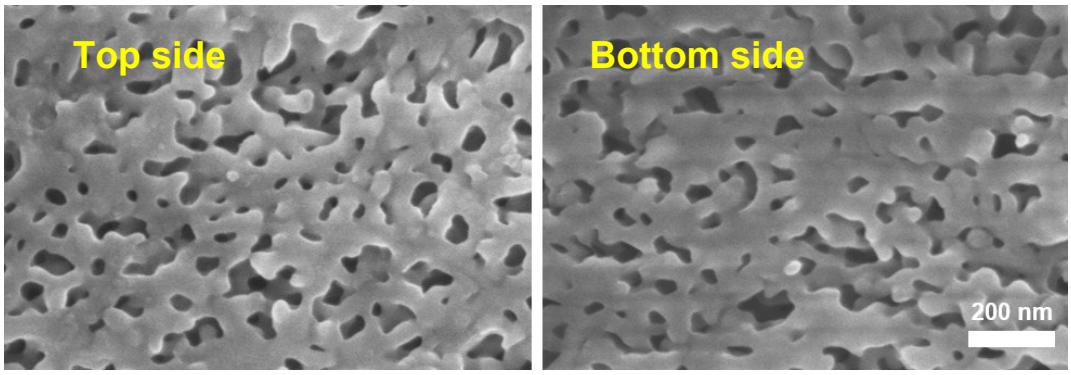

Fig. S8 The surface SEM micrographs of the two sides of the nanoporous PSF-*b*-PEG thick films soaked in the solvent pair of hexanol/acetone with Φacetone =20% at 60 ºC for 6 h.

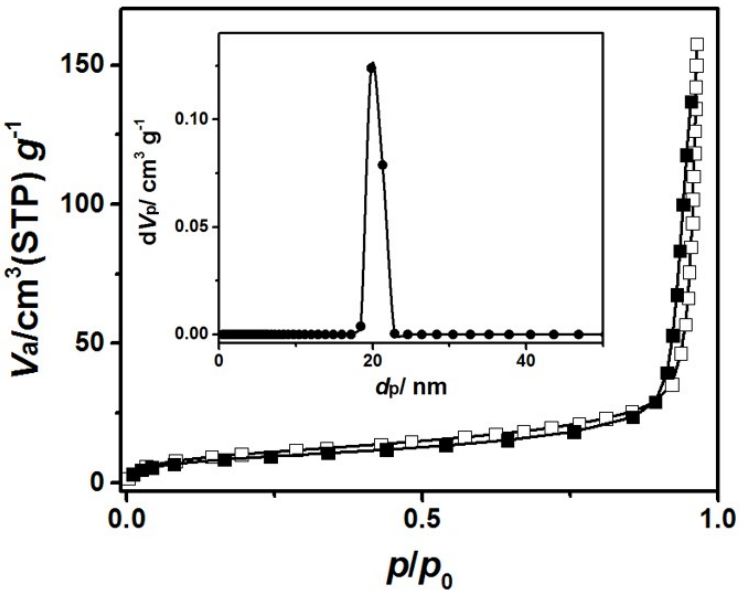

Fig. S9 Nitrogen adsorption-desorption isotherm (adsorption: open squares; desorption: solid squares) at 77 K and pore size distribution (inset) of the PSF-*b*-PEG film after soaking in the solvent pair of hexanol/acetone with

Φacetone =20% at 60 ºC for 6 h.

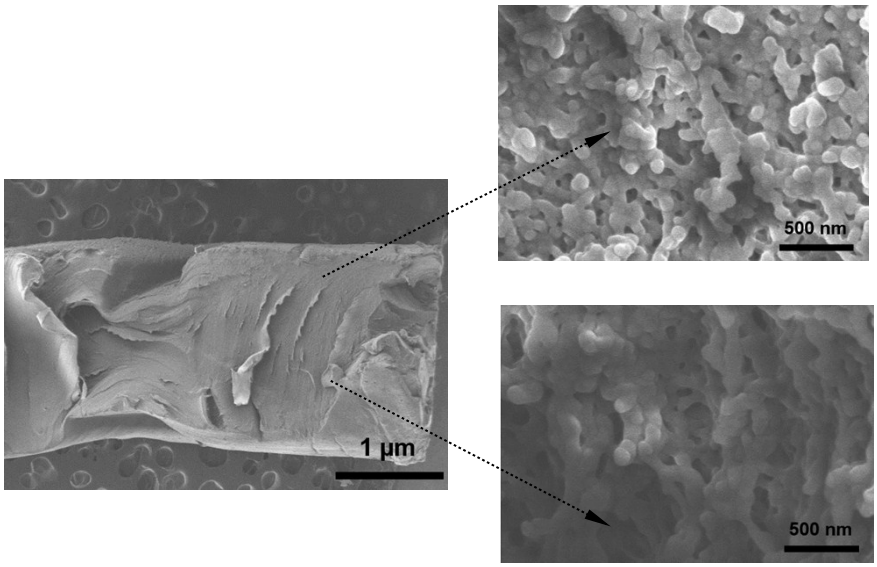

Fig. S10 The SEM micrographs exhibiting the cross-sectional morphology in different positions of the PSF-*b*-PEG monolith treated in the solvent pair of hexanol/acetone with Φacetone =20% at 60 ºC for 12 h.

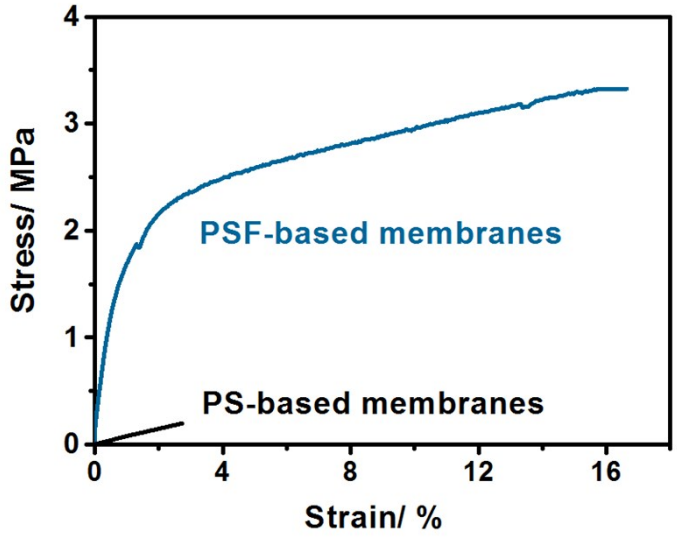

Fig. S11 The stress–strain curve of the nanoporous PSF-*b*-PEG films prepared by soaking in the solvent pair of hexanol/acetone with $\Phi_{acetone}$ =20% at 60 °C for 6 h. The stress–strain curve of a PS-based nanoporous

membrane was also given for comparison.