Supporting Information

Membranes Prepared by Self-assembly and Chelation Assisted Phase Inversion

Yihui Xie, Burhannudin Sutisna and Suzana P. Nunes*

King Abdullah University of Science and Technology (KAUST), Biological and Environmental Science and Engineering Division (BESE), 23955-6900 Thuwal, Saudi Arabia.

*suzana.nunes@kaust.edu.sa

Experimental Section

Materials

Poly(*tert*-butyl acrylate)-*b*-polysulfone-*b*-poly(*tert*-butyl acrylate) (P*t*BA$_{30k}$-PSU$_{14k}$-P*t*BA$_{30k}$) copolymers (PDI = 1.4) was synthesized according to the method we reported before.[2] Dichloromethane (DCM, ≥ 99.9%, Aldrich), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich), diethyl ether (for HPLC, VWR), trifluoroacetic acid (TFA, 99%), tetrahydrofuran (THF, anhydrous, ≥99.9%, Sigma-Aldrich), acetone (for HPLC, VWR) methanol (≥ 99%, Fisher), copper(II) sulfate pentahydrate (98-102%, Fisher), 0.1 M silver nitrate solution (Fluka) and sodium borohydride ($NaBH_4$, ≥96%, Aldrich) were used as received without further purification.

Synthesis of Poly(acrylic acid)-*b*-Polusulfone-*b*-Poly(acrylic acid)

3 g P*t*BA-PSU-P*t*BA ($M_{n,NMR}$ = 75 kg mol^{-1}, PDI = 1.4, 19 mmol of *tert*-butyl group) was dissolved in 50 mL dichloromethane and 14.6 mL trifluoroacetic acid (10 equiv to *tert*-butyl) was added. The reaction mixture was stirred at room temperature for 24 h under nitrogen. Then, the solution was concentrated by rotavapor and precipitated into diethyl ether. The solids were collected by filtration, dissolved in DMF and reprecipitated in ether (3 times). The final product PAA$_{17k}$-PSU$_{14k}$-PAA$_{17k}$ as a white powder was obtained by drying in vacuum oven at 60 °C.

Polymer Characterization

^{1}H and ^{13}C NMR spectra of polymers were recorded with a Bruker AVANCE-III spectrometer at a frequency of 600 MHz at room temperature and deuterated solvents containing tetramethylsilane $Si(CH_3)_4$ as an internal standard. Polymer molecular weight and distribution were determined by triple detection gel permeation chromatography (GPC) from Viscotek using a GPCmax module (model VE-2001) and a GPC-TDA 305 system equipped with two columns (LT4000L, Mixed, Low Org. 300 mm X 8.0 mm) eluted at 1.0 mL min^{-1} in stabilized THF at 35 °C. Three detectors are light scattering (RALS and LALS), refractive index, and viscometer. Absolute molecular weights were determined using polystyrene standards for calibration. Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra were recorded at room temperature on a Thermo Nicolet iS10. Solid membrane was placed over the ATR crystal and maximum pressure was applied using the slip-clutch mechanism. Thermogravimetric analysis (TGA) was conducted using a TGA Q50 (TA instruments) with a heating rate of 10 °C min^{-1} under nitrogen flow from 25 to 800 °C. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC 204 F1 NETZSCH under nitrogen flow. The heating rate was 10 °C min^{-1} and the cooling rate was 5 °C min^{-1} in the range of temperature from -50 to 180 °C. The glass transition temperature (T_g) was taken from the second heating scan.

Preparation of PAA-PSU-PAA Thin Film

3 wt% PAA-PSU-PAA solution was prepared by dissolving the as-synthesized triblock copolymer in anhydrous THF and filtered using 0.45 µm syringe filter prior to coating. The spin-coated thin film was obtained by dropping this solution onto the clean silicon wafer, following by spinning at 2000 rpm for one minute. For thermal annealing, the as-coated membrane was placed in a 180 °C oven for five days under vacuum. The samples were then abruptly brought from the oven to room temperature.

Preparation of PAA-PSU-PAA Membranes *via* SCNIPS Process

The membrane fabrication procedure with self-assembly and chelation assisted non-solvent induced phase separation (SCNIPS) is the following. The casting solution from 20 wt % PAA_{17k}-PSU_{14k}-PAA_{17k} in a solvent mixture (DMF/THF/Acetone = 10/45/45) was stirred for 12 h to obtain a homogeneous solution and kept still for another 12 h to release bubbles. This viscous solution was cast onto a polyester nonwoven support by a doctor blade with 250 µm gap. After an evaporation time of 5 min , the membrane was then immersed quickly and smoothly into the coagulation bath of 0.1 M $CuSO_4$ or $AgNO_3$ solution at room temperature and kept overnight for exhaustive extraction of solvent. Then it was transferred to a water bath and to remove excess metallic salt solution for 30 min. Fresh water in the bath was changed for several times. The silver-containing membrane was immersed in 0.2 mM $NaBH_4$ solution for 30 min and washed with water afterwards. The final membranes were freeze-dried for microscopic characterizations.

The combination of dip coating and SCNIPS method was also used to prepare a thinner membrane. A polyacrylonitrile membrane support (GMT Membrantechnik GmbH; Germany) was immersed in a 3 wt % PAA_{17k}-PSU_{14k}-PAA_{17k} solution in THF. After 1 min of immersion, the membrane was withdrawn slowly and then kept vertically for 1 min to drain the excess solution and evaporate the solvent. The membrane was then immersed into a coagulation bath of 0.1 M $CuSO_4$ overnight. The membrane was cleaned with water and immersed in a water bath for at least 30 min before filtration tests. The final membrane was also freeze-dried prior to microscopic characterization.

Morphological Characterization

The surface and cross-section morphologies of the membranes were observed by field emission scanning electron microscopy (FESEM) in a FEI Nova Nano SEM. For surface imaging, a small piece of membrane sample was mounted on a flat aluminum stub, fixed by aluminum conductive tapes. For cross-section, the membrane sample was freeze-fractured in liquid nitrogen, and mounted on a 90° aluminum stub vertically with tapes. The samples were sputter-coated with 2 nm iridium nanoparticles to prevent electron charging using Quorum Q150T before imaging.

Topography and phase images of the PAA-*b*-PSU-*b*-PAA thin films were obtained using Agilent 5500 AFM in tapping (ACAFM) mode. The measurements were performed using silicon cantilevers with 76-263 kHz resonance frequency and 1.2-29 Nm^{-1} force constant. PicoView 1.8 software was used to control the measurement and the acquired data were post-processed using Gwyddion software.

Transmission electron microscopy (TEM) images of the membranes and micelles in the diluted casting solution were acquired using FEI Tecnai 12 microscope with an accelerating voltage of 120 kV. The membranes were embedded in an epoxy resin (EMS Embed 812) and cured in an oven at 60 °C for 24 h. The cured blocks were trimmed using Leica EM TRIM2 to remove the resin excess before sectioning into ultrathin slices with 60 nm thickness using ultra microtome (Leica EM UC6) with a diamond knife. The thin slices were placed on a 300-mesh copper grid before imaging. The sample for micelle characterization was prepared by dissolving the copolymer in a solvent or mixture with a polymer concentration of 0.1 wt% followed by stirring overnight. A drop of the solution (1.5 µL) was placed onto a carbon-coated copper grid while the solvent was removed by blotting with a filter paper placed under the grid. The grid was further dried at room temperature before imaging.

Dynamic Light Scattering (DLS) measurements were performed using Malvern Zetasizer Nano ZS to analyze the micellar size distribution of the copolymer in a diluted solution (0.1 wt%) followed by stirring overnight. The solution was filtered through a 0.45 µm PTFE syringe filter before loading into a glass cuvette with square aperture. Three measurements were done for each sample with 16 runs per measurement.

Grazing Incident Small Angle X-Ray Scattering (GISAXS) measurements of the dry spin-coated thin films were performed at the D1 beam line of Cornell High Energy Synchrotron Source (CHESS). The beam energy used was 10.6 keV and X-ray wavelength was 1.166 Å. The sample was fixed on a precise goniometer with a sample-to-detector distance of 1.77 m. The X-ray beam grazed the thin film surface with an incident angle of 0.13°, which is between the critical angle of the substrate and the polymer. The 2D scattering patterns were acquired using a Pilatus 200k detector with an exposure time of 1 s. The scattered intensity for horizontal projections of the 2D patterns were obtained using Fit2D software. The spacing between the repeating domain (d-spacing) was calculated as 2π/q*, where q* corresponds to the position of the first peak.

Membrane Filtration Test

Membrane filtration experiments were conducted using a dead-end magnetically stirred homemade stainless steel cell with an effective membrane area of 1.04 cm^2 to evaluate the membrane performance at an operation pressure of 8 bar. Water flux experiments were performed for at least 3 hours and the the rejection experiments were conducted for more than 12 hours per measurement. The stable pure water permeance J_w was calculated by using the following equation,

$$J_w = V/tS\Delta P$$

where V and t are the volume of the permeate and the time to collect it, respectively; S is the effective membrane area; ΔP is the transmembrane pressure. Afterwards the feed solution was replaced by 2000 ppm sodium chloride (NaCl) or magnesium chloride ($MgCl_2$) solution. Samples of the feed solution and permeate were collected after the filtration test in the same manner. The rejection ratio of salts R, was calculated according to the equation,

$$R = (1 - C_p/C_f) \times 100\ \%$$

where C_p and C_f are the concentrations of salts in the permeate and feed solution, measured by conductivity meter. Rejection of neutral solutes, poly(ethylene glycol) (PEG), was measured using 200; 3,000; 10,000; 35,000 and 100,000 g mol^{-1} PEG with a concentration of 0.1 wt% each. The measurements for PEG 200 – 3000 and PEG 10,000-100,000 were performed separately. Gel permeation chromatography (1260 infinity GPC/SEC, Agilent technologies) with two columns in series (PL aquagel-OH 40 and 60) and a refractive index detector was used to analyze PEG concentration in the feed and permeate. The molecular weight cut-off (MWCO) was estimated as the PEG molecular weight with 90% rejection.

The mean pore size of the membrane was estimated from the solute rejection and diameter by ignoring the interaction between solute and membrane pores.[3] The PEG diameter was calculated using the Stokes radius equation:[3, 4]

$$a = 16.73 \times 10^{-10} M^{0.557}$$

where a is the Stokes radius (cm) and M is the PEG molecular weight (g mol^{-1}). The mean pore size (μ_p) was estimated as the PEG size ($d_p = 2a$) at 50% rejection and the geometric standard deviation (σ_p) was determined as the ratio of the PEG diameter (d_p) at 84.13% rejection over the PEG diameter (d_p) at 50% rejection. Based on μ_p and σ_p, the pore size distribution of the membrane can be expressed by the probability density function as follows:[5]

$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} exp\left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2}\right]$$

2. Results and Discussion of Polymer Characterizations

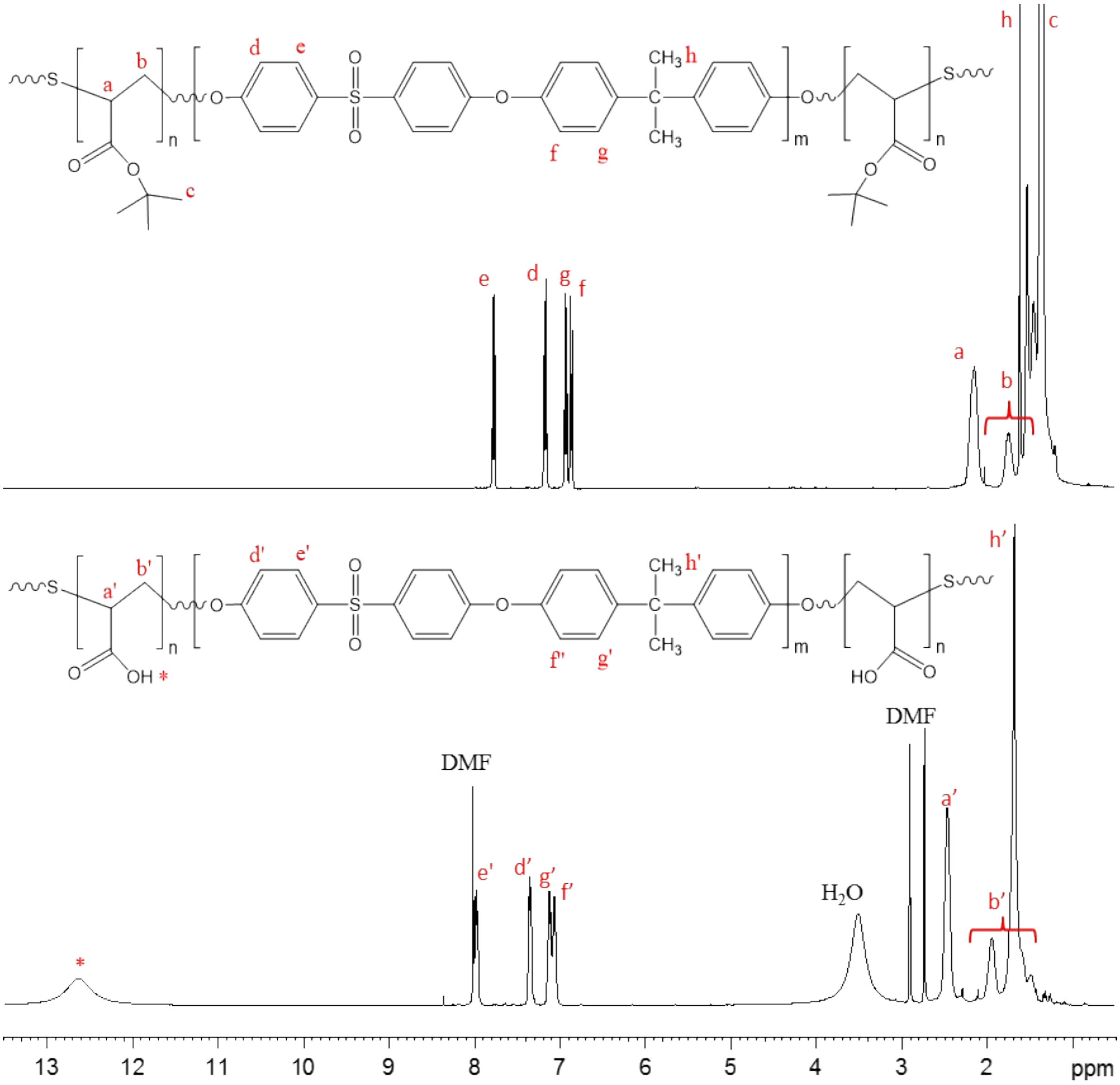

Figure S1. ^{1}H NMR spectra for P*t*BA-PSU-P*t*BA in $CDCl_3$ and PAA-PSU-PAA in DMF-d7.

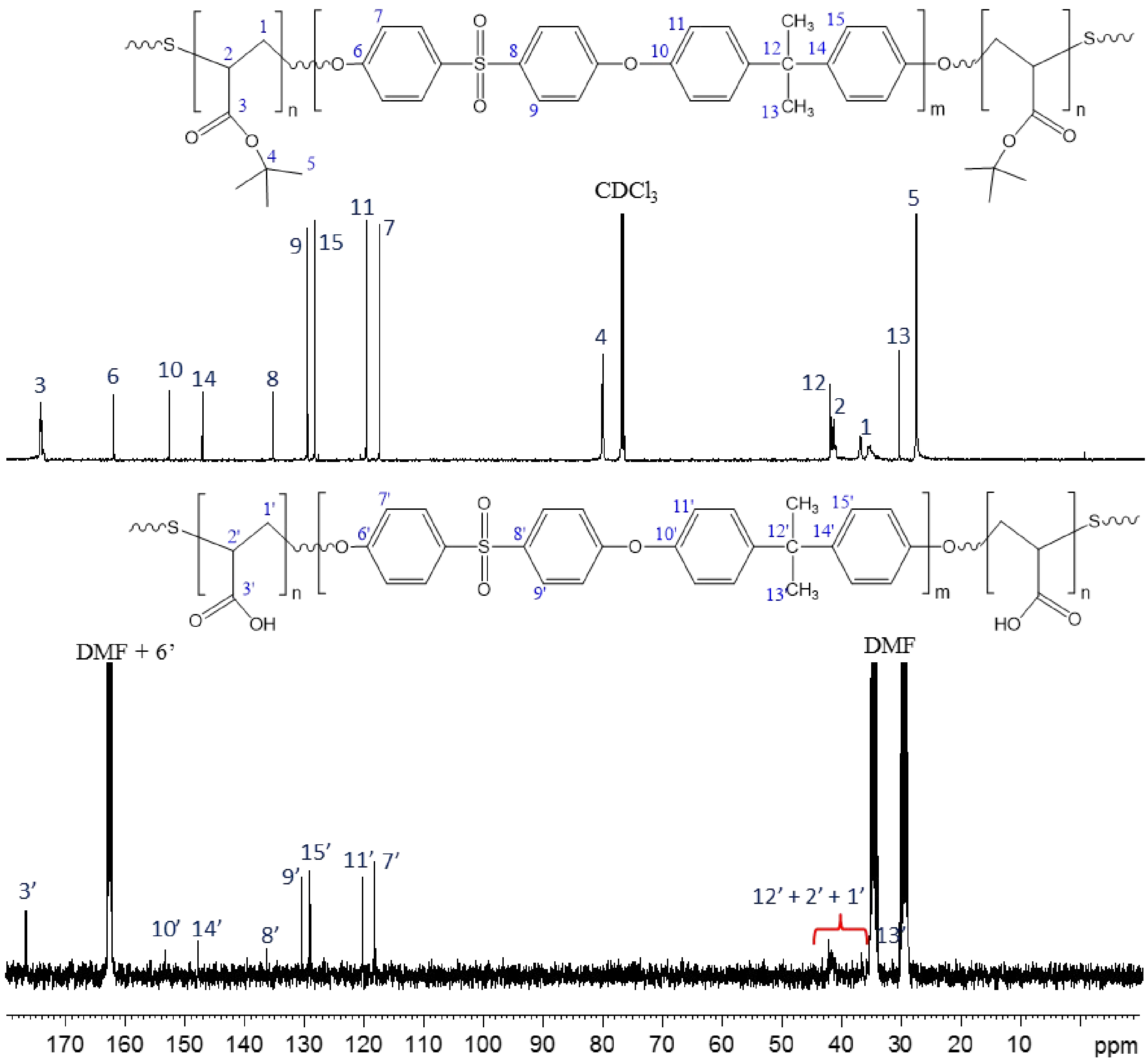

Figure S2. ^{13}C NMR spectra for P*t*BA-PSU-P*t*BA in CDCl$_3$ and PAA-PSU-PAA in DMF-d7.

From ^{1}H NMR, as shown in Figure S1, supporting information, the disappearance of the strong peak at 1.46 ppm (peak “c”) corresponding to the -C$\boldsymbol{H}_3$ protons of the *tert*-butyl group demonstrates the quantitative hydrolysis reaction.[6, 7] In addition, a new peak can be found at 12.63 ppm (peak “*”) after hydrolysis, which is attributed to the proton of -COO***H*** group.[8] The complete cleavage of *tert*-butyl group in P*t*BA block is also confirmed by ^{13}C NMR (Figure S2), where the signals from -***C***(CH$_3$) and -C(***C***H$_3$) previously at 80.4 (peak “4”) and 28.1 ppm (peak “5”), respectively, are absent from the spectrum of PAA-PSU-PAA.[8, 9] Furthermore, a new characteristic broad band of carboxylic acid O-H stretch around 2700-3500 cm^{-1} observed from FTIR spectrum for the hydrolysis product, clearly indicates the formation of PAA segment, as shown in Figure S3. Meanwhile, the peak of C=O carbonyl stretch shifts from 1724 to 1701 cm^{-1} due to the transformation of ester to its acid form.[7, 8]

The thermal properties of PAA-PSU-PAA were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA curve of PAA-PSU-PAA triblock under nitrogen (Figure S4) shows the first stage of decomposition

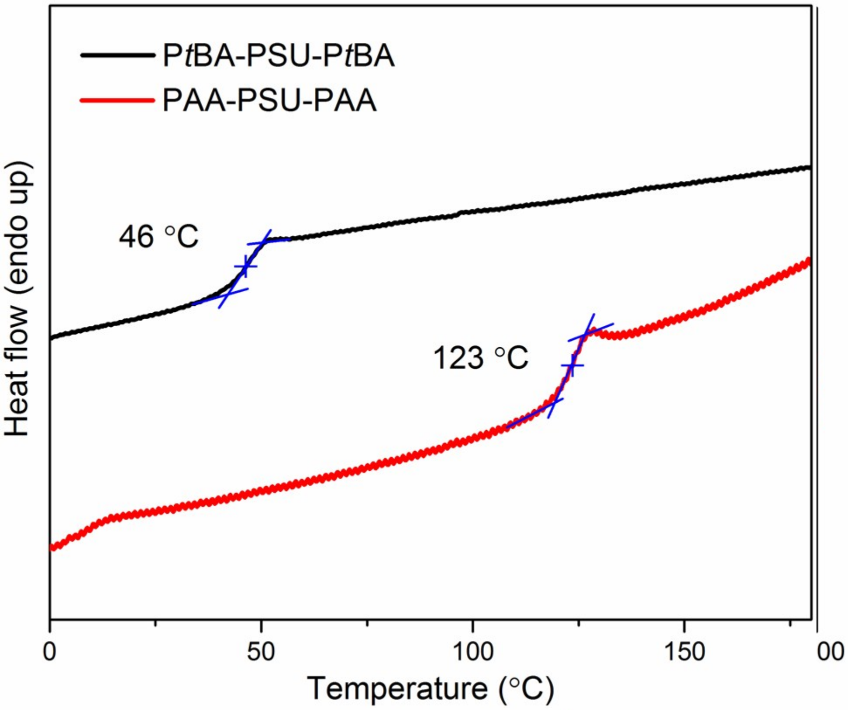

Figure S5. DSC curves for P*t*BA-PSU-P*t*BA and PAA-PSU-PAA under N_2.

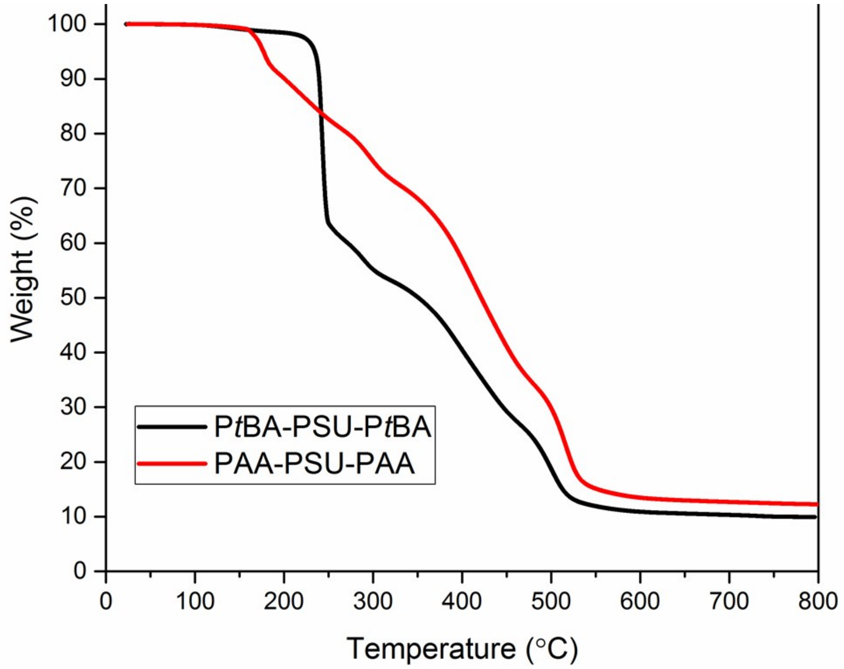

Figure S4. TGA curves for P*t*BA-PSU-P*t*BA and PAA-PSU-PAA under N_2.

accompanied by a small weight loss started from 160 °C, which is associated with the dehydration of carboxylic acid groups to form six-member cyclic anhydride structure and release of water.[10] The decarboxylation of the anhydride occurs from 190 °C to 350 °C, which broke the anhydride ring and released CO_2. When heated up to 350 °C, the PAA backbone underwent chain scission, followed by the decomposition of PSU mid-block above 400 °C.[11] As shown in Figure S5, DSC study reveals that the thermal transition peak centered at 46 °C in P*t*BA-PSU-P*t*BA curve corresponding to P*t*BA segment completely disappears after hydrolysis. The glass transition temperature (T_g) of the new copolymer increases to 123 °C, which is close to the T_g of poly(acrylic acid) homopolymer reported in the literature.[12]

3. Solubility Parameter of Polymers and Solvents

Table S1. Values of Hansen solubility parameter for polymer segments and solvents

	δa [MPa]$^{1/2}$				
	δ_D	δ_P	δ_H	δ_T	dielectric constant (ε)
PAA	17.3	12.2	18.6	28.2	--
PSU	16.6	6.0	6.6	18.8	--
THF	16.8	5.7	8.0	19.5	7.6
DMF	17.4	13.7	11.3	24.9	30.7
Acetone	15.5	10.4	7.0	19.9	20.7

[a]δ of PAA is calculated by HSPiP software 4th Edition, others are cited from Hansen [13], $\delta_T = (\delta_D^2 + \delta_H^2 + \delta_P^2)^{1/2}$

4. Supporting Electron Micrographs

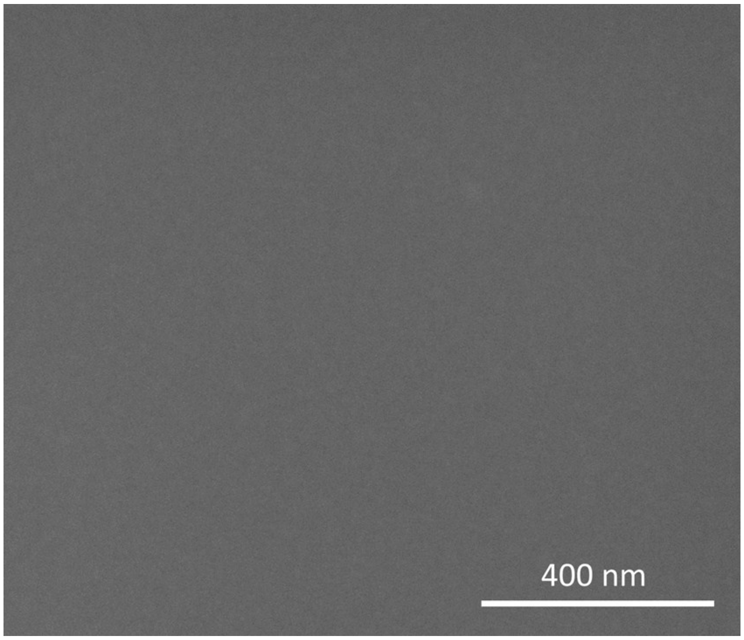

Figure S6. Surface SEM image of PAA-PSU-PAA thin film spin-coated on silicon wafer from 3 wt% solution in THF after thermal annealing.

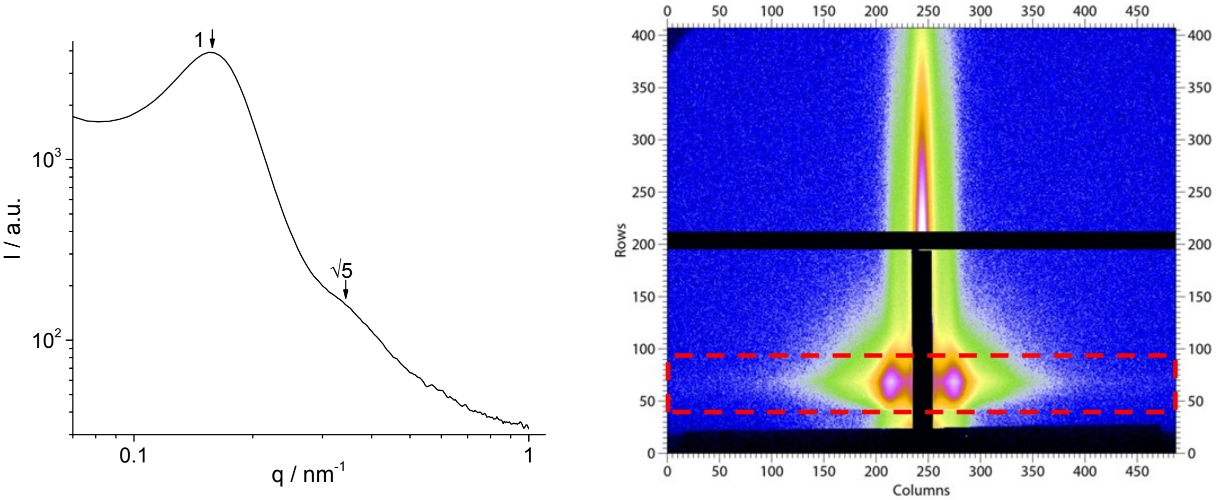

Figure S7. GISAXS of the annealed spin-coated PAA-PSU-PAA thin film; horizontal projection (left) of the area inside the red-dashed line of the 2D scattering pattern (right). A sharp principal peak was observed at q = 0.154 nm^{-1} which corresponds to the d-spacing of 40.7 nm. It is close to the distance between the center of the repeating domain measured from the AFM image, which is about 40 nm. The second peak of around $q/q^* = \sqrt{5}$ (one of the characteristic ratios of the body centered cubic structure)[1] was also observed, which shows that the equilibrium structure of the polymer is more cubical rather than hexagonal.

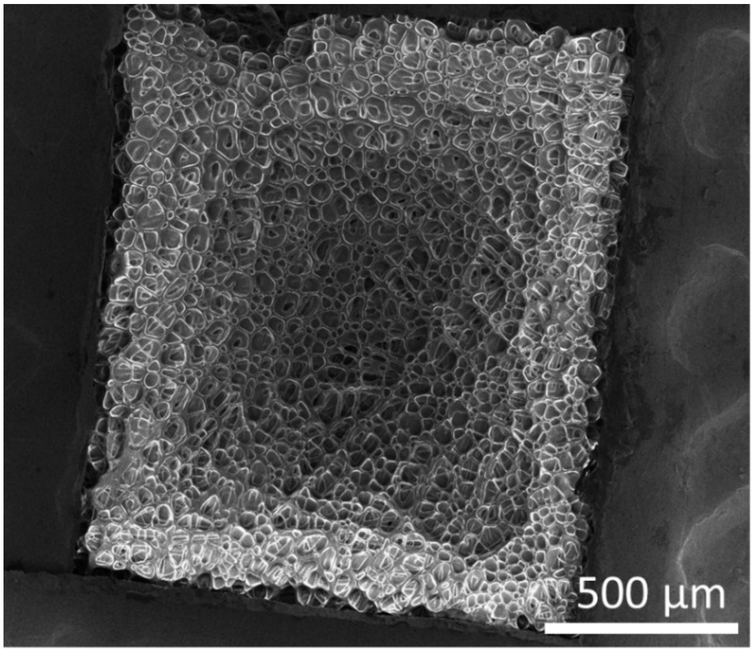

Figure S8. Surface SEM image of PAA-PSU-PAA membranes from 20 wt% polymer solution in DMF/THF/acetone solution (10/45/45) formed in a pure water coagulation bath.

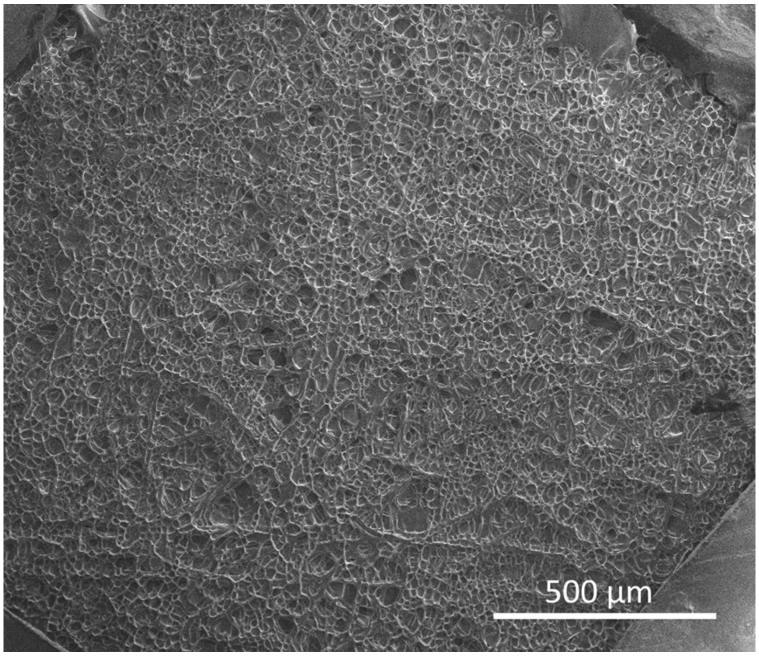

Figure S9. Surface SEM image of PAA-PSU-PAA membranes from 20 wt% polymer solution in DMF/THF/acetone solution (10/45/45) formed in a pure water coagulation bath then immersed in 0.1 M HCl aqueous solution.

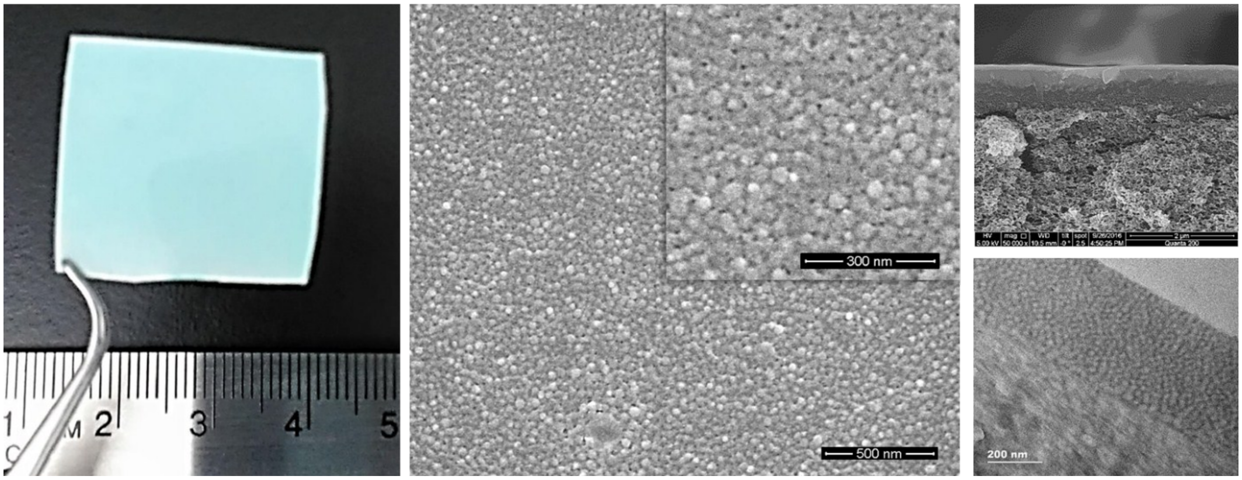

Figure S10. (a) Photograph, (b) surface and (c) cross-sectional SEM image, and (d) TEM image of PAA-PSU-PAA membrane from 3 wt% polymer solution in THF with 1 min evaporation time and 0.1 M $CuSO_4$ fabricated by dip-coating on PAN support.

Table S2. PEG rejection of the Cu-complexed PAA-PSU-PAA membrane prepared by dip-coating method

PEG Molecular Weight (g mol^{-1})	Rejection	d_p (nm)[a]
200	34±5%	0.6
3000	62±7%	2.9
10,000	99±1%	5.7
35,000	99±1%	11.4
100,000	100%	20.4

[a]Estimated from the Stokes radius equation

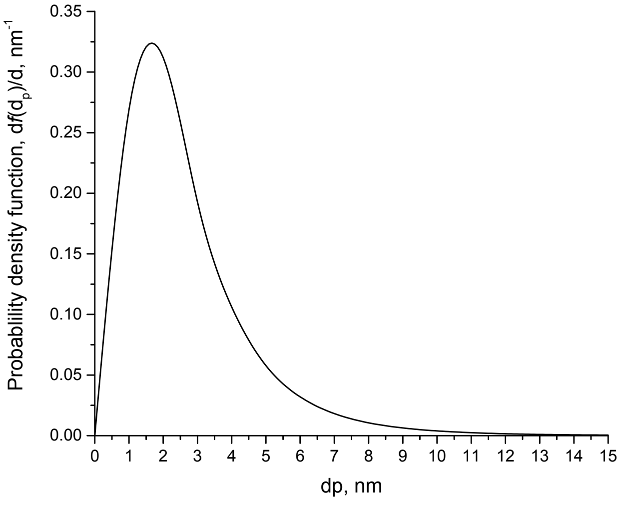

Figure S11. Pore size distribution of the Cu-complexed PAA-PSU-PAA membrane prepared by dip-coating.

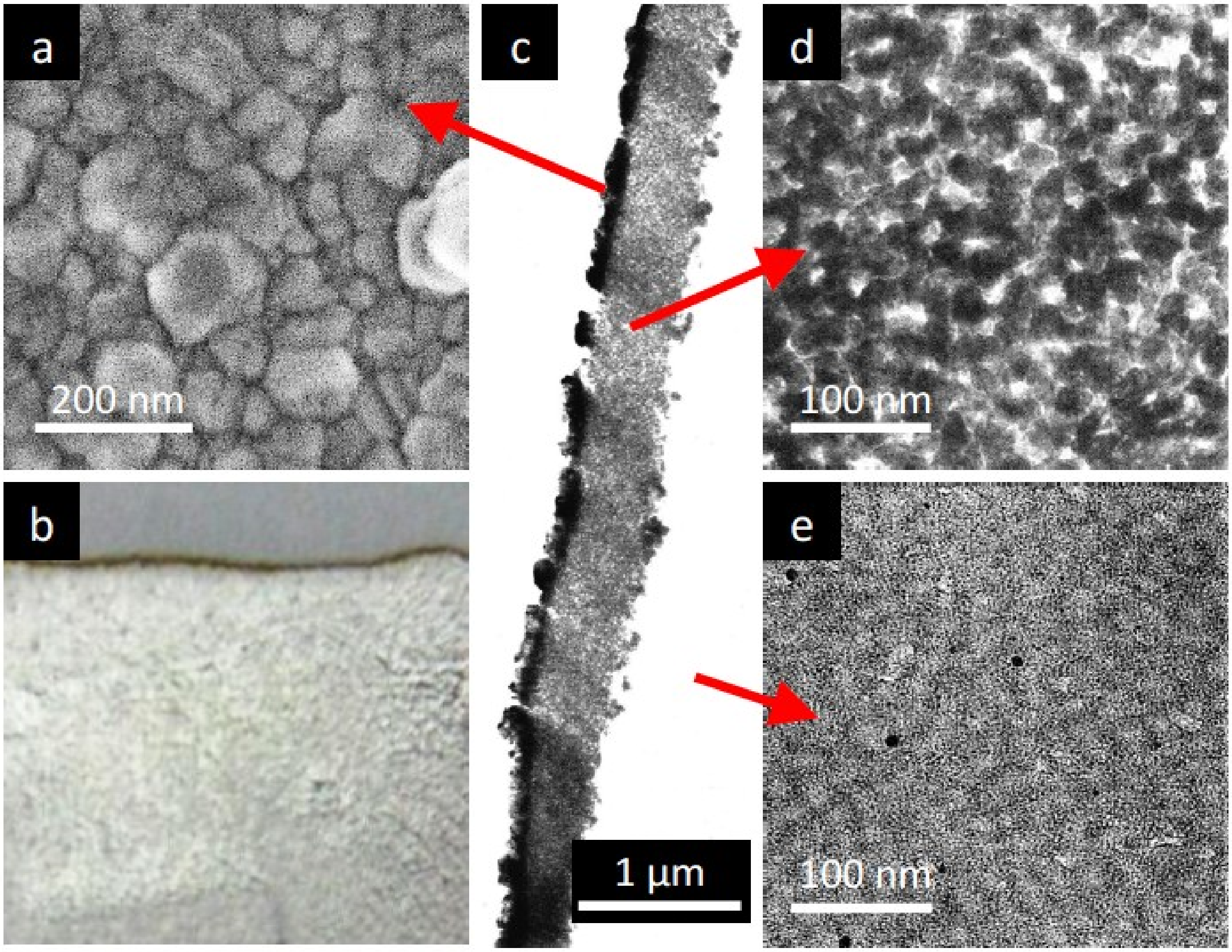

Figure S12. (a) FESEM image and (b) photograph of the surface of reduced silver-decorated PAA-PSU-PAA membranes prepared with Ag^+ coagulation bath; TEM images of (c) the entire membrane at low magnification, (d) the sublayer from 150 to 600 nm under the surface, and (e) the bottom layer of membrane.

Reference

(1) Hamley, I. W.; Castelletto, V. *Progress in polymer science* **2004,** 29, (9), 909-948.

(2) Xie, Y.; Moreno, N.; Calo, V. M.; Cheng, H.; Hong, P.-Y.; Sougrat, R.; Behzad, A. R.; Tayouo, R.; Nunes, S. P. *Polymer Chemistry* **2016,** 7, (18), 3076-3089.

(3) Singh, S.; Khulbe, K.; Matsuura, T.; Ramamurthy, P. *Journal of Membrane Science* **1998,** 142, (1), 111-127.

(4) Rahimpour, A.; Madaeni, S. S.; Mansourpanah, Y. *Journal of Membrane Science* **2010,** 364, (1), 380-388.

(5) Youm, K. H.; Kim, W. S. *Journal of chemical engineering of Japan* **1991,** 24, (1), 1-7.

(6) André, X.; Zhang, M.; Müller, A. H. E. *Macromolecular Rapid Communications* **2005,** 26, (7), 558-563.

(7) Greene, A. C.; Zhu, J.; Pochan, D. J.; Jia, X.; Kiick, K. L. *Macromolecules* **2011,** 44, (7), 1942-1951.

(8) Zhang, Y.; Shen, Z.; Yang, D.; Feng, C.; Hu, J.; Lu, G.; Huang, X. *Macromolecules* **2010,** 43, (1), 117-125.

(9) Colombani, O.; Ruppel, M.; Schubert, F.; Zettl, H.; Pergushov, D. V.; Müller, A. H. E. *Macromolecules* **2007,** 40, (12), 4338-4350.

(10) Dubinsky, S.; Grader, G. S.; Shter, G. E.; Silverstein, M. S. *Polymer Degradation and Stability* **2004,** 86, (1), 171-178.

(11) McNeill, I. C.; Sadeghi, S. M. T. *Polymer Degradation and Stability* **1990,** 29, (2), 233-246.

(12) Park, J.-K.; Kim, D.-W.; Kim, C.-H.; Maeng, K.-S.; Hwang, T.-S.; Kim, Y.-C. *Polymer Engineering & Science* **1991,** 31, (12), 867-872.

(13) Hansen, C. M., *Hansen solubility parameters: a user's handbook*. CRC press: 2007.