

Electronic Supplementary Information

Asymmetric block copolymer membranes with ultrahigh porosity and hierarchical pore structure by plain solvent evaporation

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1. Hansen solubility parameter

The following Hansen solubility parameters^[1] are reported for dioxane and the polymer blocks under consideration here:

Table S1. Hansen solubility parameters

	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
Polystyrene (PS)	21.3	5.8	4.3
Styrene (S)	18.6	1.0	4.1
Acrylic acid (AA)	17.7	6.4	14.9
1,4-Dioxane	19.0	1.8	7.4

d, p and h: dispersive, polar and h-bond contributions to solubility parameters (δ)

2. Grazing Incidence Small-Angle X-Ray Scattering (GISAXS) and Small-Angle X-Ray Scattering (SAXS)

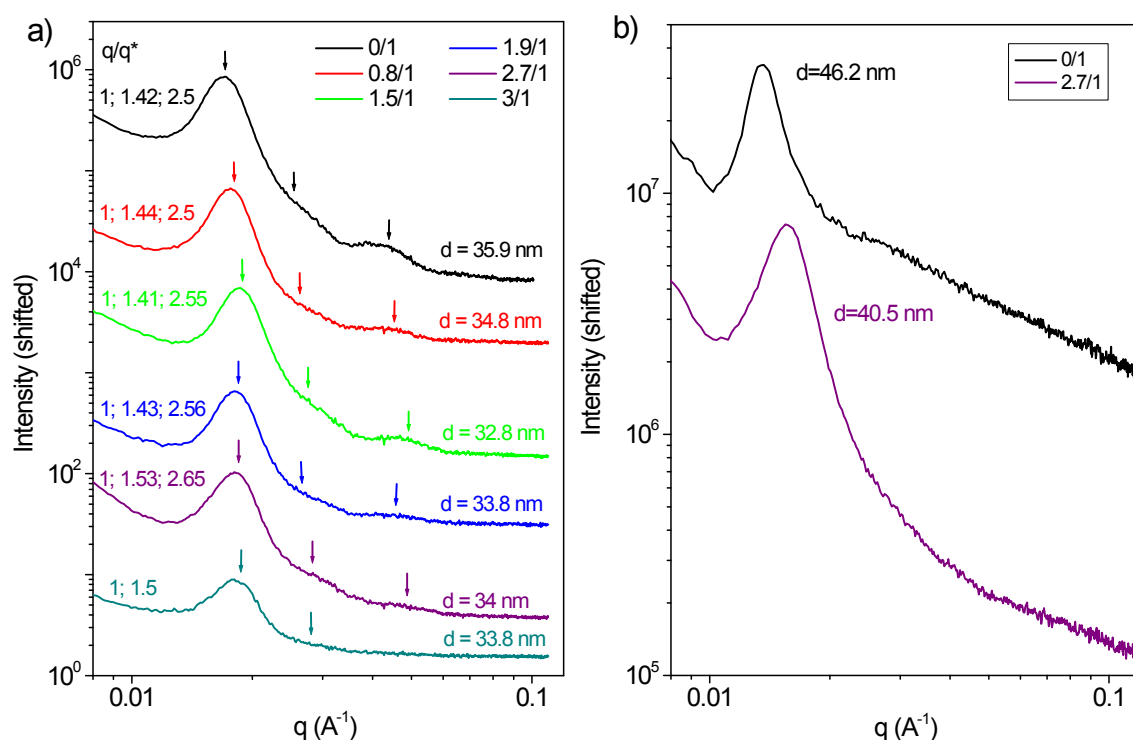


Figure S1. (a) In plane GISAXS data for casted membranes with different PS₁₄₄-*b*-PAA₂₂ / PS₆₇₈-*b*-PAA₁₈₀ ratio after 5 min solvent evaporation time. (b) SAXS data for solution pure PS₆₇₈-*b*-PAA₁₈₀ and PS₁₄₄-*b*-PAA₂₂ / PS₆₇₈-*b*-PAA₁₈₀ blend with a 2.7 / 1 molar ratio.

3. Experimental Details

3.1. Membrane Preparation

Polystyrene-*b*-poly(acrylic acid) block copolymers (PS₁₄₄-*b*-PAA₂₂, $M_n = 16,600$ g mol⁻¹ and PS₆₇₈-*b*-PAA₁₈₀, $M_n = 83,500$ g mol⁻¹) were purchased from Polymer Source, Inc., Canada. The subscripts indicate the number of repeat units of the blocks. Dioxane was supplied by Aldrich. The BCP membranes with two mixed molecular weights were cast from a polymer solution mixture of PS₁₄₄-*b*-PAA₂₂ and PS₆₇₈-*b*-PAA₁₈₀/dioxane on a Hirose TH100 polyester support, using casting blades with 200 μm air gap. The PS₆₇₈-*b*-PAA₁₈₀/dioxane composition was kept constant, *i.e.*, 18.7 wt % copolymer, 81.3 wt % dioxane, while the molar ratio of PS₁₄₄-*b*-PAA₂₂ to PS₆₇₈-*b*-PAA₁₈₀ varied from 0.8:1 to 3:1 in the preparation of different

membranes. The solvent was allowed to evaporate completely at room temperature in the fume hood. To study the kinetics of membrane surface phase transition the membranes were dried for different time at room temperature and then immersed in a non-solvent bath (Milli-Q water, 18.2 M Ω).

3.2. Electron Microscopy and Zeta Potential Measurement

Field emission scanning electron microscopy (FESEM) images were obtained using a FEI Quanta 600 series microscope at 5kV with a working distance of 10 mm. Cryo-field emission scanning electron microscopy (Cryo-FESEM) experiments were carried out using a Quorum PP2000T cryo-transfer system (Quorum Technologies, Newhaven, U.K.) that was fitted to an FEI Nova Nano630 FESEM with a field-emission electron source and through-lens electron detectors. A small amount of block copolymer blends was dropped on the specimen holder. The sample holder, attached to a transfer rod, was rapidly plunged into liquid-nitrogen slush, transferred under vacuum to the preparation chamber precooled to -180 °C, and allowed to equilibrate for 10 min. The sample temperature was raised to -160 °C. To avoid charging, the sample temperature was then reduced to -135 °C and the sample was sputter coated with gold-palladium for 90 s at a 5 mA current in an argon atmosphere. Then the sample was transferred to a FESEM cryo stage, which was held at -140 °C. The membrane surface zeta potential was tested using SurPASS electrokinetic analyzer (Anton Paar, Austria) with background of 10 mM NaCl solution around neutral pH.

3.3. Flux and Rejection Measurements

The membranes (diameter 2.2 cm) were tested in a stirred Amicon cell at a pressure of 1.38 bar until 3 ml of a 6 ml starting sample passed through the membranes. The rejection of the proteins was monitored by a NanoDrop 2000/2000c spectrophotometer (Thermo Fisher Scientific). Globulin- γ (IgG, 150 kDa), Bovine serum albumin (BSA, 66 kDa), Ovalbumin (OVA, 45 kDa), Myoglobin (MB, 17 kDa), protoporphyrin IX (PpIX, 562 g/mol) and vitamin B12 (VB12, 1355 g/mol) are from Sigma Co., and no further purification was carried out.

Transport of VB12 was carried out using a diffusion cell (PermGear, Inc) with two compartments (left and right chambers). The membrane was placed between the two chambers with the ordered top layer toward left side containing the VB12. The effective permeation area of the membrane was 1.77 cm². All permeate samples were collected from the right chamber and the concentration was determined by a NanoDrop 2000/2000c spectrophotometer.

3.4. SAXS and GISAXS Measurements

In-situ Grazing Incidence Small Angle X-Ray Scattering (GISAXS) experiments were performed at D1 beamline of the Cornell High Energy Synchrotron Source (CHESS). The operating parameters were: a wavelength of the X-ray beam of 0.1162 nm, a sample-to-detector distance of 1.82 m and a corresponding beam energy of 10.67 keV. Membranes were casted on a microscope glass slide as support using *in-situ* doctor blading system existent at the beam-line. A gap of 200 μm was used to cast the membranes. The data were taken immediately after casting at every 3.3 s. The time interval corresponds to 0.3 s exposure and 3 s detector readout time. A pre-alignment of height and incident angle of the beam with the substrate was performed. An incidence angle of 0.13 degrees was used, which is below the critical angle of the substrate and above the critical angle of the polymer film. 2D GISAXS pattern were recorded with a MedOptics CCD camera with a pixel size of (46.9 μm)² and 1024² pixels. The GISAXS images were analyzed using Igor Pro 6.3 software by taking a horizontal cut that contains details of the size distribution parallel to the sample surface. Using the same software, the position of the peaks was determined by fitting the obtained data with two or three Lorentz functions.

Small angle X-ray scattering (SAXS) measurements were performed at the SAXS1 beamline of the Brazilian Synchrotron facility (LNLS), which works at fixed energy of 8.0 keV. The solution was injected with syringe in a vacuum cell with mica windows. The X-ray wavelength was 1.764 Å and the sample to detector distance was 1 m. The detector used was

PILATUS with a pixel size of $(172 \text{ }\mu\text{m})^2$. The beam area on the sample was 1 mm^2 and a number of 20 frames each with 30 s exposure time were performed. Data was obtained as the average of the integrated 2D patterns, after normalization to the intensity of incident beam and subtraction of background.

4. Permeance and Rejection Results

Figure S2a and S2c show both the zeta potential and the water flux of the membrane decreased as the pH increased. The effect of pH on the water flux is mainly due to the change in the swelling and electrostatic repulsion generated by ionization of the PAA blocks. PAA is a weak polyelectrolyte and the amount of charged groups is a function of pH. The carboxylic acid groups were deprotonated at high pH and the PAA segments stretched to minimize the charge repulsion, transforming the pore into a pH-sensitive gate without affecting the overall ordered structure of the membrane. The effect is opposite to that observed in stimuli-responsive PS-*b*-P4VP isoporous membranes prepared by combining self-assembly with non-solvent-induced phase separation. Figure S2b shows the cut-off curve of the membrane at different pH, evaluated by filtering biomolecules with sizes ranging from *ca.* 1.5 to 14 nm in diameter. The effective pore radius of the membrane evaluated from the rejection experiment is *ca.* 10 nm at pH 3.0 and *ca.* 2 nm at pH 7.4. The water permeation of the membranes was measured for one day before and after immersion in water, which showed no big difference indicating the stability of the membrane. The pH responsive membrane with tunable nanopores can be used as a sensitive gate controlled by pH without any modification. To evaluate the controlled transport behavior of the membrane, vitamin B12 (VB12) was selected as a model substance. The transport rate of VB12 could be controlled by changing pH values at 37 °C. At a pH of 7.4 in phosphate-buffered saline (PBS) solution, VB12 was released in a very slow fashion in one day (Figure S2d). When the environmental pH was changed from pH

7.4 to pH 3.0, the pores of the membrane change from “closed” to “open”, due to the conformational change of the PAA chains. Therefore, the diffusion channels for the VB12 solutes become wider leading to an abrupt release.

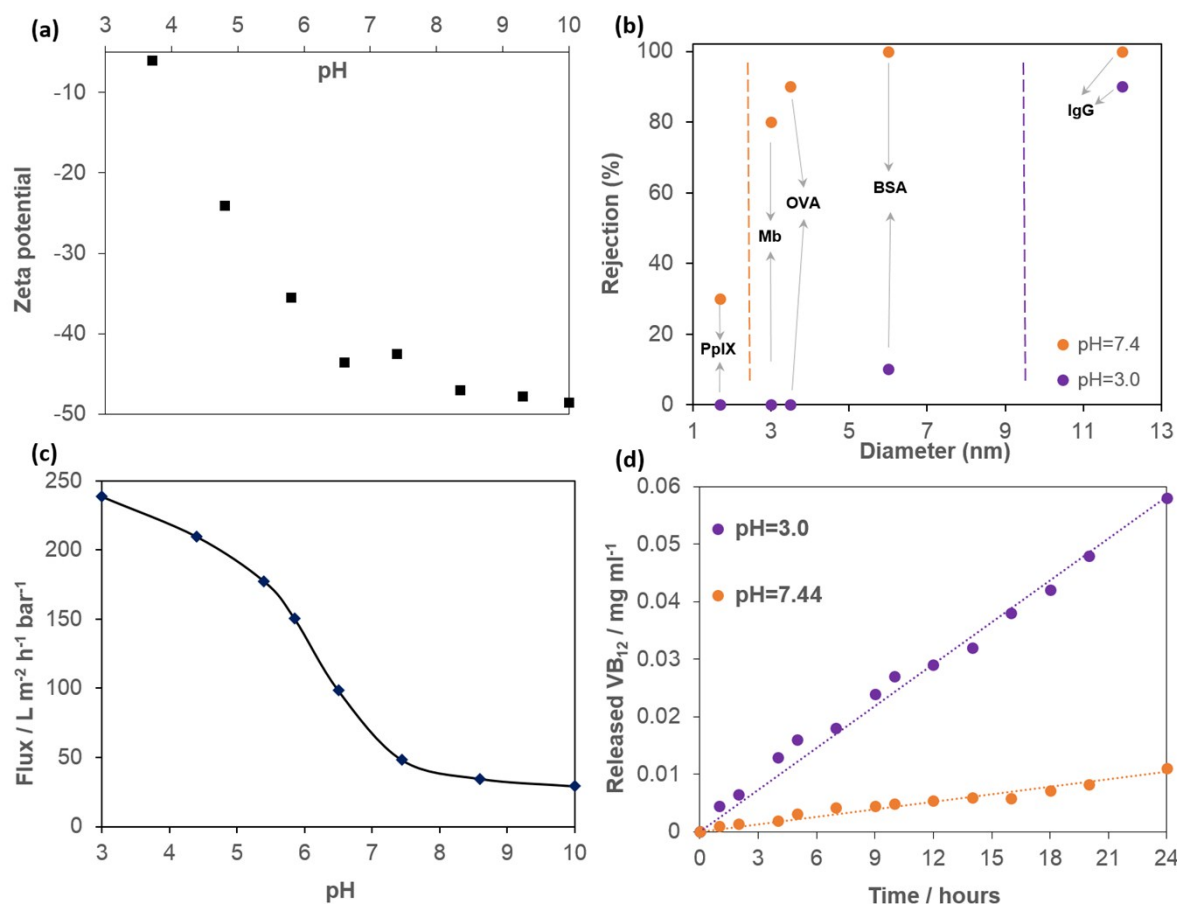


Figure S2. Performance of the blended membrane of PS₁₄₄-*b*-PAA₂₂ / PS₆₇₈-*b*-PAA₁₈₀ with a molar ratio 2.7/1: (a) zeta potential of this membrane as a function of pH; (b) filtration of biomolecules with sizes of 1.5-14 nm through this membrane; (c) water flux of this membrane as a function of the pH, measured at 1.38 bar feed pressure; (d) release of VB₁₂ at pH 3.0 and pH 7.4 using this membrane, respectively.

5. Supporting Reference

[1] C. M. Hansen, Hansen Solubility Parameters, a User's Handbook, CRC Press, Boca Raton, USA, 2000.