Supporting Information

Translocation across a self-healing block copolymer membrane

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1. Experimental section

1.1) Synthesis protocols

a) Materials

Polyethylene glycol 35000 (stabilised with 2-tert-butyl-4-methoxyphenol), triethylamine (\geq 99%), tetrahydrofuran, acryloyl chloride (\geq 97%), dichloromethane, N,N-dimethylformamide, styrene (\geq 99%, containing 4-tert-butylcatechol as stabilizer), acrylonitrile (\geq 99%, containing 35-45 ppm monomethyl ether hydroquinone as inhibitor), toluene, tetraethyl orthosilicate (\geq 99.0%), ammonium hydroxide (NH3, 25%), isopropanol, bovine serum albumin (\geq 96%), poly(ethylene oxide) (average Mv 100,000, 200 000 and 300 000, powder), monodisperse polystyrene nanoparticles (2% (solids), 0.2 µm std dev <0.03 µm and 0.1 µm std dev <0.03 µm) were purchased from Sigma-Aldrich and were used as received. Monomers were passed through basic alumina prior to use. Water (>18 MΩ) was obtained from a Milli-Q water purification system.

b) Synthesis of ABA triblock copolymer

PSAN-*b*-PEO-*b*-PSAN triblock copolymer has been prepared according to previous work [1] involving first the preparation of PEO macroalkoxyamine followed by styrene and acrylonitrile copolymerization (Scheme S1). The copolymer characteristics are: PEO sequence ($\bar{M}_n = 35000$ g.mol⁻¹, 27.1 wt %), PS sequence ($\bar{M}_n = 66400$ g.mol⁻¹, 51.4 wt %) and PAN sequence ($\bar{M}_n = 27800$ g.mol⁻¹, 21.5 wt %), P(Sty₃₁₉-*co*-AN₂₆₂)-*b*-PEO₇₉₅-*b*-P(Sty₃₁₉-*co*-AN₂₆₂), $\bar{D}=1.35$.

c) Preparation of self-healing membranes

Membranes were prepared according to previous work [2] from a 100 mg.mL⁻¹ solution of the triblock copolymer P(Sty₃₁₉-*co*-AN₂₆₂)-*b*-PEO₇₉₅-*b*-P(Sty₃₁₉-*co*-AN₂₆₂) in DMF/toluene (1:1 vol.). After 12h of magnetic stirring, the polymer solution was spin-coated onto 25 cm² silicon wafers (2000 rpm for 60 s with a speed ramp of 50 rpm.s⁻¹). Polymer films were then kept under vacuum for 1 day in order to complete the drying process. The coated Si wafers were then dipped into distilled water at 25°C. After 24 h, membranes were found to be detached from Si wafers and were taken out onto a non-woven polyester fabric. The film thickness is 1.3 μ m and the water flux is dependent to the pressure drop (see Figure S2 for more details). As previously described in literature, the pore size is dependent to the filtration pressure due to the reversible compaction of the PEO micelle shell, going from about 8 nm at 0.2 bar to about 1 nm at 2.5 bar [2].

d) Synthesis of silica nanoparticles

Two series of silica nanoparticles (SP1 and SP2) were prepared using a modified Stöber process [3]. The synthesis was carried out in isopropanol at 20°C with the concentrations of various reactants following $[NH_3] = 0.81[TEOS]$ and $[H_2O] = 6.25[TEOS]$ with [TEOS] = 0.22 M. The particle size was measured from SEM image using image J software (Table S1)

1.2) Methods

a) Atomic force microscopy (AFM)

AFM images were obtained with a Pico SPM II provided by Molecular Imaging. The imagery was controlled by the PicoView 1.10 software. The experiments were all carried out in tapping mode. The types of tips used were PPS-FMR purchased from Nanosensors with a frequency resonance between 45-115 kHz and a force constant between 0.5-9.5 N/m. Gwyddion[®] v2.25 software was used to treat the images.

b) Scanning Electron Microscopy (SEM)

SEM analyses were conducted using a Hitachi S-4500 instrument operating at spatial resolution of 1.50 nm at 15 kV energy. The samples were dried and coated with an ultrathin layer of electrically conducting Platinum deposited by high-vacuum evaporation. A careful freeze-fracturing process was carried out to preserve the membrane cross-section morphology. For that, the material was frozen in liquid nitrogen for 15 min and then cracked while still remaining in liquid nitrogen. After a filtration experiment, the non-woven polyester fabric could be removed easily before the freeze fracture to observe the membrane in SEM.

c) Photon Cross-Correlation Spectroscopy (PCCS)

The particle size and size distribution have been measured by Photon Cross-Correlation Spectroscopy (Nanophox – Sympatec). After a filtration experiment, the feed solution, the permeate and the retentate (dead-end filtration mode) were analyzed in PCCS. For each solution, the density distribution $q_3(x_{i,m})$ was plotted with small size intervals (x_{i-1},x_i) as a results of an average of 3 concordant measurements.

In order to plot the sieving curves, the density distributions of the permeate and retentate were fitted so that their addition gives the density distribution obtained from the feed solution. A simple multiplication factor was applied to the whole density distribution curve to not alter the peak position. For each size interval (Δx_i), the retention rate was calculated by:

$$R = \frac{q_3(x_{i,m})_{retentate}}{q_3(x_{i,m})_{retentate} + q_3(x_{i,m})_{permeate}} \times 100$$

In addition, a global retention rate for each pressure drop was calculated by two ways. PCCS is using two separate beams thus giving two count rates. The global retention rate has been calculated by:

$$R = 1 - \frac{C_{permeate,i}}{C_{retentate,i}}$$

with C_i being the average count rate values for the permeate or the retentate.

The quality of the fitting step was further checked by recalculating the global retention rate with:

$$R = \frac{A_{retentate}}{A_{retentate} + A_{permeate}} \times 100$$

with A being the surface area of the density distribution curves for the retentate and the permeate after fitting. The global retention rate values were found to be very close with less than one percent of difference.

d) Filtration experiments

Ultra-pure water solutions of bovine serum albumin (Aldrich), poly(ethylene oxide) (Aldrich), polystyrene nanoparticles (Aldrich), or silica nanoparticles was prepared to study their translocation through the triblock copolymer membranes at a temperature of 25 ± 0.5 °C in a stirred ultrafiltration cell (Millipore). The effective membrane area was 4.1 cm² and the membrane was supported by a non-woven material (polyethylene terephthalate) to enhance the mechanical properties. The pressure was increased from 0 to 1.4 bars with pressure steps of 0.2 bar. For information, the pure water flux values as a function of the pressure drop is given in Figure S2. Empirical relationships between the size of PEG and PEO solutes expressed as the Stokes radii (r_s in nm) and their molecular weight was calculated from:

 $r_{S} = 0.01044 \times M_{w}^{0.587}$

2. Supplementary Scheme 1. Synthesis of PSAN-*b*-PEO-*b*-PSAN triblock copolymer



3. Supplementary Equation 1

The retention rate (R) of particles has been calculated from:

$$R = \left(1 - \frac{C_{\boxed{2}}}{C_{\boxed{2}}}\right) \times 100$$

where C_p is the concentration of particles in the permeate and C_r the concentration of particles in the retentate, as estimated from the count rate given in PCCS without any signal attenuation.

4. Supplementary Table 1

Table S1. Silica particle diameter, dispersity indices and relative % calculated from Scanning ElectronMicroscopy images. 200 particles were counted for each type of population.

Nanoparticles	Average Mean Diameter (D _a) (nm)	De Brouckere Mean Diameter (D _b) (nm)	Dispersity Index (D _b /D _a)	Percentage of Nanoparticles %
Silica SP1 – i	156	167	1.07	57
Silica SP1 – ii	279	293	1.05	43
Silica SP2 – i	88	94	1.07	61
Silica SP2 – ii	223	230	1.03	39

5. Supplementary Figures.



Figure S1. Schematic illustration showing the possible arrangements of triblock copolymer chains in the different observed cases. (a) The initial system composed of a percolating micellar network where block copolymer chains can adopt either a loop conformation with the two end blocks buried in the same micellar core, or a bridge conformation with the two end blocks pulled apart into different micellar cores. (b) During a translocation event, a particle is creating a transient pore by separating the constituting micelles. This pore is formed thanks to a structural reorganization of the micellar network. At this occasion, bridging copolymer chains are pulled out leading to "dangling" end-blocks. (c) Translocation of SP2 particles generates supplementary pressure on the membrane micelles pushing them closer to each other until complete fusion and irreversible deformation of the membrane.



Figure S2. Pure water flux values as a function of the pressure drop ($\Delta P=0.04-1.5$ bar) across the membrane, measured during 2h after a conditioning step (micelle compression) at the corresponding pressure during 8h.



Figure S3. Translocation of PEG. $\Delta P=0.2$ bar; [PEG]=0.75 g.l⁻¹; Filtration time of ~75 min (a) Size Exclusion Chromatograms of the retentate and the permeate showing that none of the 3 PEGs have translocated at 0.2 bar. (b) Evolution of the water flux at 0.2 bar overtime demonstrating a sharp flux decline due to clogging of the membrane pores.



Figure S4. Translocation of BSA. (a) Absorbance vs. concentration calibration curve obtained for BSA protein using UV-Vis. spectroscopy. (b) Amplitude (left) and phase (right) AFM images of the top surface of block copolymer membranes after BSA translocation at $\Delta P=0.2$ bar during 3h, for different concentrations of the feed solution ([BSA]=0.5, 1, and 1.5 g.l⁻¹).



Figure S5. Differential distribution curves obtained for feed, retentates and permeates obtained at different water pressures for PS_{100} using PCCS. [PS_{100}] =25.9 mg l⁻¹; Filtration time 3h.



Figure S6. Size distribution of PS_{100} in the feed and permeate solutions after 3h of translocation experiments at 1.4 bar. $[PS_{100}] = 25.9 \text{ mg } l^{-1}$.



Figure S7. SEM image of membrane top surface (a) and cross-section (b) after PS_{200} filtration at 0.8 bar for 3h. [PS_{200}] =5.12 mg l⁻¹.

6. References

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