Polymersomes-based high-performance reverse osmosis membrane for desalination

Qi, Saren; Fang, Wangxi; Siti, Winna; Widjajanti, Wentalia; Hu, Xiao; Wang, Rong

2018

Qi, S., Fang, W., Siti, W., Widjajanti, W., Hu, X., & Wang, R. (2018). Polymersomes-based high-performance reverse osmosis membrane for desalination. *Journal of Membrane Science*, 555, 177-184. doi:10.1016/j.memsci.2018.03.052

<https://hdl.handle.net/10356/85199>

<https://doi.org/10.1016/j.memsci.2018.03.052>

© 2018 Elsevier B.V. All rights reserved. This paper was published in *Journal of Membrane Science* and is made available with permission of Elsevier B.V.

Downloaded on 26 Apr 2023 19:24:21 SGT

Polymersomes-based high-performance reverse osmosis membrane for desalination

Saren Qi^{1†}, Wangxi Fang^{1†}, Winna Siti¹, Wentalia Widjajanti¹, Xiao Hu^{1,3}, Rong Wang^{1,2*}

1. Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141

2. School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

3. School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

**Corresponding author: rwang@ntu.edu.sg*

† The authors contributed equally

Abstract

Polymersomes-based reverse osmosis (RO) membrane (PBM) for desalination was reported for the first time. An amphiphilic tri-block copolymer, PMOXA₆-PDMS₃₅-PMOXA₆ (ABA), was self-assembled to form polymersomes with spherical nanostructure. The polymersomes were then immobilized into a polyamide network via an interfacial polymerization reaction on top of polysulfone membrane substrate. Under a moderate salinity condition, the PBM presented almost doubled water permeability and higher salt rejection than the control membrane without polymersomes in the polyamide network. Based on the results of a series of characterization the better water permeation of the PBM is believed to result from larger globular features containing highly water permeable polymersomes, which created a higher void fraction in the selective layer, whereas the highly cross-linked polyamide selective layer as well as the polymersome bilayer's impermeability to NaCl may led to the enhanced salt rejection. Surprisingly, at an elevated NaCl concentration up to 32,000 ppm, the PBM exhibited ~ 60% water flux enhancement and even better NaCl rejection as compared with commercial seawater RO membranes. In general, the PBM presented a water flux similar to the RO membranes with loose polyamide matrix (BW30), but a rejection behavior close to the dense RO membranes (SW30). This study provides a paradigm shift in developing new-generation RO membranes for energy and cost-effective desalination process.

Keywords: polymersome; reverse osmosis; seawater desalination; interfacial polymerization; high water flux.

Graphic abstract

Research highlights

- Polymersomes-based RO membrane (PBM) for desalination was firstly reported
- Polymersomes were immobilized into an interfacially polymerized polyamide layer
- Large globular features surrounded by the polyamide matrix were observed
- Superior performance than SW30 in desalination of 32,000 ppm NaCl feed solution

1. Introduction

Freshwater shortage is becoming a global issue due to rapidly multiplying population and severe environmental contamination [1, 2]. To address this worldwide challenge, reverse osmosis (RO) membranes are utilized to [extract](#) clean water from wastewater and seawater, which have been continuously developed for over 40 years [3, 4]. [The most commonly used commercial RO membranes are the thin-film composite \(TFC\) membranes](#), which consist of a [thin](#) polyamide selective layer, [an intermediate](#) porous polymeric substrate, [and](#) an additional woven/nonwoven mechanical [support](#) [5]. The polyamide selective layer, [synthesized](#) via the interfacial polymerization [technique](#), is the critical barrier for separation [6]. The high performance of the selective layer, in terms of water permeability, salt rejection and fouling resistance, is desirable to reduce the operational energy, chemical consumption, maintenance cost, and footprint of the RO membrane [7-9].

With the advancement of nanotechnology, thin-film nanocomposite (TFN) membranes were proposed by incorporating nanomaterials into the membrane selective layer [10-12]. Most nanomaterials used for TFN membrane preparation are inorganic nano-fillers, such as zeolites [13], silica [8], silver [14], titanium dioxide [15], and metal organic frameworks [16]. Few nanomaterials are organic nano-fillers such as protein water channels [17-19]. The TFN membranes are expected to exhibit high water permeability, high membrane selectivity or better antifouling properties. However, to date, most TFN membranes were evaluated and used under low salinity conditions, which are only suitable for the treatment of low salinity water streams like brackish water, wastewater, or meant for nanofiltration applications [11, 20]. The relatively poor compatibility between inorganic nanomaterials and polymeric materials may result in [a defective](#) selective layer in [micro-scales](#), deteriorating the rejection

at high salinity conditions [20, 21]. Moreover, due to the fact that the severity of concentration polarization is exponentially related to the salt concentration [22], concentrated feed would induce more severe concentration polarization and worsen the membrane rejection, particularly for a defective membrane. Therefore, a defect-free selective barrier with good water/salt selectivity is crucial for the successful adoption of the RO membrane in high salinity conditions [23].

Amphiphilic block copolymers consist of two or more chemically distinct blocks, which could self-assemble to form various nanoscale structures, like vesicles, cylinders, micelles, and lamellae, depending on the composition and chain architecture of the block copolymers [24-26]. In previous studies, self-assembled block copolymers were made into thin-film ultrafiltration or nanofiltration membranes [27-30]. However, to the best of our knowledge, no RO membrane has yet to be made by block copolymers via self-assembling approach.

Herein, a triblock copolymer composed of poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) (PMOXA₆-PDMS₃₅-PMOXA₆, labeled as ABA) was used for self-assembling to form spherical nanostructures in an aqueous phase. The nano-spheres were then immobilized into a polyamide network via interfacial polymerization (IP) to form a selective layer of RO membrane. Good compatibility between ABA and polyamide is expected to produce a defect-free selective layer. In addition, the nano-channels for water in the ABA are envisaged to improve the membrane's intrinsic parameters, such as water permeability and water/salt selectivity [26].

As illustrated in Scheme 1, the ABA was self-assembled to spherical hollow structure (polymersomes) in the aqueous solution, and the polymersomes were then mixed with m-

phenylene diamine (MPD) solution. The mixture solution was subsequently applied to the polysulfone substrate surface. After removing the excess mixture using N₂ gas, the residual MPD/polymersomes impregnated membrane surface was brought to contact with the trimesoyl chloride (TMC) hexane solution to form a polyamide layer in which polymersomes were immobilized. The resultant membrane was labelled as polymersomes-based membranes (PBM). For comparison, the same procedure was taken for making the control membrane without polymersomes in the MPD solution. The membrane formation process is explained in the subsequent section.

Scheme 1. Procedure illustration of the synthesis of PBMs via interfacial polymerization

2. Experimental

2.1 Materials and chemicals

Milli-Q[®] deionized (DI) water (Millipore, integrated ultrapure water system, 18.2 MΩ·cm) was used for the preparation of solution. Polysulfone (PSf, Molecular weight (MW) 75,000-81,000 Da, Solvay), Polyethylene glycol (PEG, MW 200, Merck Chemicals, Singapore) and

N-Methyl-2-pyrrolidone (NMP, >99.5 %, Merck Chemicals, Singapore) were used as polymer materials, additives and solvents, respectively. Poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) triblock copolymer (PMOXA₆-PDMS₃₅-PMOXA₆ labeled as ABA, Polymer Source Inc.) was used to form polymersomes. M-Phenylenediamine (MPD, ≥ 99 %, Sigma Aldrich) and trimesoyl chloride (TMC, ≥ 99 %, Sigma Aldrich) were used as the monomers in the interfacial polymerization process. Brackish water membrane (BW30) and seawater membrane (SW30) were the two commercial membranes which are free samples from Dow Filmtec (USA). The feed solution used for evaluating reverse osmosis performance was prepared by sodium chloride (NaCl, analytical grade > 99 %, Merck). All chemicals were used without further purification.

2.2 Polymersome preparation

Polymersomes were prepared using a film rehydration [approach](#) [31]. First, 20 mg of ABA polymer was dissolved in 1 mL of chloroform. The solvent was removed using a rotavapor apparatus and dried under a high pump for 4 hours, leading to a polymer thin film. Next, [DI](#) water (2 mL) was added to rehydrate the polymer film with moderate agitation, followed by stirring at room temperature for 72 hours to form [vesicle solutions](#). Finally, the vesicle solutions were extruded through 400 nm and 200 nm pore size polycarbonate filters (Whatman, USA), respectively, for 21 times each using Avestin extruder (Canada) to form polymersomes with uniform size distributions.

2.3 Membrane synthesis

Phase inversion method was adapted to fabricate the membrane substrate according to the previous study [17]. Briefly, a polymer mixture solution containing 20 wt% polysulfone (PSf), 5 wt% PEG and 75 wt% NMP was fully dissolved at 70° C. [The polymer dope](#)

solution was then cooled down and cast with a film applicator (Elcometer model 4340, Elcometer Asia) with a slot height of 150 μm . The polymer dope solution was spread evenly on the top of a nonwoven support, which had been fixed onto a clean glass plate. Then the cast film was immersed into a tap water coagulation bath (25 ± 1 °C) for phase inversion. After membrane substrate was solidified, the substrates were kept in DI water for further modification.

The polyamide layer was then formed on top of the membrane substrate using interfacial polymerization technique [17]. In aqueous solution, dilute MPD solution was mixed with a 5 mg/ml polymersome solution to obtain a final mixture solution containing 1 wt% of MPD and 0.016 wt% of polymersomes. The mixture solution was exposed to the substrate surface for 20 mins. After removing the excess mixture solution by using N_2 gas at 1 bar, the substrate surface was contacted with a 0.1 % TMC solution for 3 mins. Finally, the membrane was cured in a 70 °C DI water bath for 10 mins. The resultant membrane was labeled as PBM. For comparison, a control membrane was fabricated by the same procedures with the absence of polymersome in the MPD solution. All the membranes were preserved in 4° C DI water.

2.4 Polymersome characterization

The size distribution of the polymersomes was determined using a Zetasizer (NanoZS, Malvern Instruments Limited, UK) at 22°C, with a sample concentration of about 1 mg/mL in a disposable PMMA micro-cuvette. The structure of the polymersomes was characterized using transmission electron microscope (TEM, JEOL JEM-1400 Plus Electron Microscope, USA). For sample preparation, about 10 μL of polymersome sample was dropped on the Cu grid (Formvar Carbon 200 mesh, EMS, USA) for 10 mins, followed by removing the liquid

using filter paper (Whatman, USA). After 1 hour of drying inside a desiccator, the samples were ready to be imaged under TEM.

The permeability of vesicles was investigated using a Stopped-Flow Spectrometer (SX20, Applied Photophysics, UK), with a concentration of NaCl solutions of 0.3 M. The operation procedure is similar to that reported in Ref [18]. In brief, polymersomes were vigorously mixed with a hyper-osmolar solution. Due to the osmolarity difference between the intravesicular and extravesicular solutions, the vesicle shrinks. The shrinkage rates of vesicles were monitored by light scattering method. The final single curve was averaged from eight independent scattering traces from the stopped-flow measurements. The initial rising rate ($k=693\pm73\text{ s}^{-1}$ based on Figure 1c) was calculated by fitting the averaged curve with double order exponential. The water permeability of the polymersomes, P_f (m/s), was calculated as follows:

$$P_f = \frac{k}{S/V \times V_w \times \Delta_{osm}} \quad (1)$$

Where Δ_{osm} (osmol/L) represents the osmolarity difference between the intravesicular and extravesicular solutions, S/V represents the ratio of the initial surface area to the volume of vesicles, and V_w represents the partial molar volume of water (0.018 L/mol).

2.5 Membrane characterization

All membrane samples were dehydrated for 12 hours in freeze-dryer and preserved in vacuum desiccators for at least 24 hours prior to characterization. The membrane surface and cross-section morphologies were characterized by a Field-emission Scanning Electron Microscopy (FESEM, JSM-7600F, JEOL, Japan) following similar sample-preparation procedures by Qi et al. [32]. The membrane was snapped in liquid N_2 to expose the membrane cross-section.

The membrane surface roughness was evaluated by an atomic force microscope (AFM, Park XE-100) based on the parameters in literature [33-35]. $5 \times 5 \mu\text{m}^2$ area was measured by AFM under non-contact mode.

X-ray photoelectron spectroscopy (XPS) was performed on clean membranes using a PHI Quantera II with Al K α radiation as X-ray source (1486.6 eV) with a spot size of 200 x 200 μm according to the reference [36]. Briefly, ten survey scans sweeping over 0-1K eV electron binding energy with a resolution of 1 eV were averaged for each surface measurement. The elemental composition of C, N, O, S and Si were calculated from the integrated intensities of the C1s, N1s, O1s S2p and Si2p peaks. Depth profiles are recorded by continuously etching the sample until an estimated depth of 0.5 μm was reached. The etching rate was 5 nm per minute based on SiO₂ calibration and with a take-off angle of 45°. It should be noted that the depth in the XPS is an approximate value which depended on the calibration materials used [36].

The cross-section sample of the membrane for Transmission Electron Microscopy (TEM) characterization was prepared by Focus Ion Beam (FIB) in a PEI Helios 600i machine with a 30 kV ion beam voltage according to the reference [37, 38]. Briefly, before cutting, platinum (Pt) line was deposited on the area of interest to protect the top portion of the specimen and to mark the position of the target area (Figure 1a). After cutting two deep trenches (Figure 1b and c), the target lamella was removed from the trench by using micromanipulator, and further polished until a desired thickness (Figure 1d). Finally, the thin lamella was transferred to a TEM half-gird via an internal nano-manipulator inside the FIB chamber. After transferring the TEM half-gird to the TEM chamber, the cross-section images were observed under the TEM mode (FEI Tecnai F20) with different magnifications.

Figure 1. The cross-section sample preparation procedure via FIB technology

2.6 Membrane Separation Properties

Reverse Osmosis (RO) performance of the PBMs, control, and commercial membranes were tested using a customized cross-flow membrane filtration equipment with four parallelly-positioned permeation cells (CF42 Membrane Cell, Sterlitech, effective filtration area of 42 cm² each). The detailed process was described in detail elsewhere [17, 39]. In short, membrane coupons were installed in the cell with the polyamide layer facing the feed solution, and diamond-shape spacers were used to minimize the external concentration polarization. Membranes were first pressurized with pure water at 40 bars before testing until a consistent water flux was reached. After compaction, the pressure was reduced to 35 bars for water flux and conductivity measurements. Two concentrations of feed solution were used (i.e., 2,000 ppm and 32,000 ppm) to evaluate the membrane separation properties and the

desalination performance, respectively. A constant CFV of ~ 0.2 m/s was maintained at the operation temperature of 25 ± 2 °C for all measurements throughout the entire testing period.

The water flux (J_v) was calculated from the weight of the collected permeate per period of time and converted to liters per square meter per hour (L/m²h). The water permeability (A) and the salt rejection (R) were obtained according to the following equation:

$$A = J_v / (\Delta P - \Delta \pi) \quad (2)$$

$$R(\%) = \left(1 - C_p / C_f\right) \times 100\% \quad (3)$$

where J_v is the gravimetric water flux, ΔP is the applied pressure and $\Delta \pi$ is osmotic pressure difference between the feed and permeate solutions. In equation 3, the concentration of the permeate (C_p) and the concentration of the feed solution (C_f) were determined using a conductivity meter (Ultrameter II, Myron L Company, Carlsbad, CA). Furthermore, the value of the solute permeability (B) was obtained by fitting the RO filtration experimental results with the formula:

$$B = J_v \exp\left(-J_v / k\right) (1 - R) / R \quad (4)$$

where k is the mass transfer coefficient in the boundary layer near the membrane surface. In the case when concentration polarization is negligible, the value of $\exp(-J_v/k)$ nearly equals to 1, thus equation (4) can be simplified to:

$$B = A(\Delta P - \Delta \pi) (1/R - 1) \quad (5)$$

Further, the ratio of water permeability and solute permeability (A/B) characterize the selectivity of a membrane.

3. Results and discussion

3.1 Characteristics of polymersomes

Figure 2a shows the hydrodynamic diameter of polymersomes measured using dynamic light scattering (DLS). The polymersomes have an average diameter of ~ 200 nm and a good polydispersity index (PDI) of ~ 0.3 . A transmission electron microscope (TEM) image (Figure 1b) displays the morphology of dry polymersomes. Spherical hollow structures were successfully self-assembled with an average size around 100 nm. The polymersomes presented by TEM have a smaller size as compared to their hydrodynamic diameter as the vesicular structures contracted when the aqueous medium was removed [40].

Figure 2. (a) DLS results of the polymersome solution; (b) TEM image of dry polymersomes; (c) Stopped flow results of polymersome

Moreover, the water transportation feature was measured by the stopped-flow instrument (Figure 2c). A high water permeability P_f of 0.0023 m/s was obtained based on the stopped-flow results, which is believed to result from the nano-channels in vesicles [41]. Additionally, such results reveal the capability of the polymersome for effective NaCl rejection. Since the osmolarity of the experiment was provided by 0.3 M NaCl, the occurrence of osmosis indicated that the polymersome bilayer efficiently rejected the NaCl from entering the vesicles. Such impermeability to salt could boost the salt rejection of the resultant RO membranes, which will be demonstrated in the subsequent sections.

3.2 Characteristics of polymersomes-based membranes (PBM)

Representative cross-sectional TEM images and XPS elemental depth profiles are presented in Figure 3 for the PBM along with its control membrane. For both membranes, from the TEM images, well-defined globular features were observed near the interface of the polyamide and polysulfone layers, which were surrounded by the polyamide matrix. Bigger globules were shown for the PBM as compared to the control membrane, which is believed to be introduced by the presence of polymersomes. In previous studies, the globules have been identified as voids which commonly existed in commercial polyamide RO membranes [42, 43]. Significant amounts of voids are critical for effectively improved water permeability [42, 43]. Probably due to the excellent compatibility between the two polymeric materials, the boundaries between the polymersomes and polyamide are difficult to be distinguished in the TEM image. However, the evidence is provided in Figure 2b and 2d, where the XPS depth profiling (Figure 2d) showed that silicon (Si) was detected in the PBM, confirming the presence of polymersomes, while Si was absent in the control membrane (Figure 2b). Furthermore, the concentration of Si increased with an increase in depth and gradually reached a plateau at approximate 200 nm below the top surface. Sulphur (S) and

nitrogen (N) are presented for both the PBM and control membrane, which mainly came from the polysulfone substrate and polyamide layer, respectively.

Figure 3. Characterization of home-made membranes by TEM and XPS: (a-b) control membrane and (c-d) the PBM

Figure 4 presents the surface and cross-section FESEM images of the control and the PBM membranes. Both membrane surfaces (Figure 4a-b) exhibited the characteristic “ridge-and-valley” structure, which typically resulted from the reaction of aromatic acid chloride with aromatic diamines [6]. However, larger leaf-like micro-structures can be observed on the surface of the PBM as compared to the control membrane. From the cross-section morphologies (Figure 4c-d), a polyamide layer on the top of the porous polysulfone substrate, with thicknesses in the range of several-hundred nanometers, can be observed for both

membranes. However, the polyamide layer of the PBM presented thicker and larger protuberances in comparison with the control membrane, which resulted in a rougher surface. Based on the atomic force microscope (AFM) measurements shown in Figure 5, the average roughness is ~ 75 nm for the PBM, larger than that for the control membrane (~ 38 nm).

Figure 4. FESEM images of membrane surface: (a) control membrane and (b) the PBM;
FESEM images of membrane cross-section: (c) control membrane and (d) the PBM

Figure 5. AFM images of (a) control membrane and (b) the PBM.

3.3 Separation properties of PBM

Separation properties of the control and the PBM membranes were firstly evaluated under low salinity condition and the results are listed in Table 1. Water permeability (A) was measured by the gravimetric method, and NaCl rejection (R) was determined based on the conductivity of the feed and permeate, respectively. Compared with the control membrane, close to 100% improvement for A value and a significantly higher R were obtained for the PBM. Based on Figures 3 and 4, the improved void fractions and highly rough surface of the PBM are believed to be responsible for the improvement, due to the creation of shorter paths for water diffusion [43]. In addition, the highly water-permeable polymersomes are also believed to contribute to water permeation.

Table 1. Separation properties for the control, the PBM, commercial SW and BW membranes using 2,000 ppm NaCl as feed under an applied pressure of 35 bars at 25 °C.

Membrane*	A L/m ² .h.bar	R %	B L/m ² .h	Selectivity 1/bar
Control	1.3±0.1	93.7±0.5	3.0±0.5	0.4±0.1
PBM	2.4±0.2	99.6±0.1	0.4±0.1	6.7±0.4
SW30	1.2±0.1	99.3±0.2	0.3±0.1	3.3±0.2
BW30	2.6±0.3	97.6±0.2	2.2±0.4	1.2±0.1

*All the membranes were compacted under 40 bars until flux was stable and the applied pressure was then lowered to 35 bars to evaluate the separation properties. The CFV was maintained at 0.2 m/s during the tests. The standard deviations represented at least three independent membranes.

Meanwhile, as listed in Table 1, the PBM exhibited much lower solute permeability (B) and better membrane water/salt selectivity A/B . The commonly observed trade-off [relationship](#) between water permeability and water/salt selectivity (i.e., [membranes with](#) high A usually exhibited low A/B) didn't apply to the PBM [44, 45]. Based on the elemental composition and oxygen to nitrogen (O/N) ratio of the control and PBM membranes from the XPS analysis (Table 2 and Figure 6), the O/N ratio for the PBM is around 1, while the O/N ratio for the control membrane is around 1.3. Theoretically, if a polyamide layer is fully cross-linked, the value of O/N is 1, whereas the value of O/N is 2 if it is partially cross-linked [5]. This indicated that the PBM had a highly cross-linked polyamide [network](#) as compared with the control membrane, leading to a tighter polymer matrix for higher salt rejection. Besides, as revealed in Section 3.1, the polymersome bilayer's impermeability to NaCl would also add up to the better salt rejection of PBM.

Table 2. Elemental compositions and O/N ratios of the control and PBM membranes from XPS analysis

Membrane	XPS surface elemental analysis			
	O (%)	N (%)	C (%)	O/N ratio
Control	14.2±0.04	10.9±0.2	74.9±0.3	1.30
PBM	11.9±0.6	12.1±0.4	76.0±1.1	0.98

Figure 6. Elemental compositions of the surface for control membrane and the PBM from XPS analysis

Moreover, the separation properties of the PBM were also compared with the state-of-the-art commercial seawater RO membrane (SW30) and brackish water RO membrane (BW30) in Table 1. Higher A and better R were found for the PBM as compared to the SW30 membrane. On the other hand, a slightly lower A but the much higher selectivity of the PBM than the BW30 membrane resulted in a much higher R of the PBM.

3.4 Desalination performance of PBM

The PBM was also evaluated for high salinity application together with the commercial SW30 and BW30 membranes under the same testing conditions (Figure 7). All membranes performed a stable water flux and salt rejection during the period of the tests. **Over the whole testing period**, PBM exhibited nearly 60% higher water flux than the SW30 membrane with **slightly enhanced** rejection. Compared with the BW30 membrane, the PBM showed a similar

water flux but a much higher salt rejection of 98.9% in comparison with 94.6% for the BW30 membrane. More information is presented in Table 3. For both of the PBM and the SW30 membranes, around 0.7~0.8% decline in salt rejection was observed when the feed salt concentration increased from 2,000 ppm to 32,000 ppm (Table 1 and Table 3). In contrast, a significant deterioration in rejection (~2%) was found for the BW membrane with an elevated salt concentration of 32,000 ppm. At a higher salinity condition, more severe concentration polarization would occur when other operational conditions were maintained the same [46]. The severe concentration polarization tended to lead to a high degree of salt leakage for the membrane with loose polyamide matrix [20]. The PBM presented water flux similar to RO membranes with loose polyamide matrix like BW30, but rejection behavior close to the dense RO membranes like SW30.

Figure 7. Desalination performance of the PBM and commercial membranes. 32,000 ppm NaCl was used as feed solution. Applied pressure was 35 bars. Temperature was 25 °C. (All

membranes were compacted under 40 bars until flux was stable and the applied pressure was reduced to 35 bars to measure the [separation properties](#). The [CFV](#) was maintained at 0.2 m/s during the tests).

Table 3. Water flux and NaCl salt rejection for control, the PBM, commercial SW and BW membranes at 25 °C.

Membrane	J_v L/m ² .h	R %	C_f X 10 ³ ppm
Control	14.7±1.8	94.2±0.7	32
PBM	20.4±0.8	98.9±0.2	32
SW	12.8±1.9	98.5±0.1	32
BW	15.0±1.5	94.6±0.2	32

[*All the membranes were compacted under 40 bars until flux was stable and the applied pressure was reduced to 35 bars to measure the water flux and salt rejection. The standard deviations represented at least three independent membranes.](#)

4. Conclusions

In conclusion, the polymersomes-based RO membranes were successfully fabricated for the first time, which presented excellent water permeability and water/salt selectivity particularly under feed conditions with elevated salt concentrations. The performance of the PBM is superior to the state-of-the-art commercial seawater and brackish water RO membranes. More importantly, the special functionality of polymersomes, such as controllable size, excellent compatibility with polymer matrix, and the feasibility of blending with other functional nanomaterials, allows for further optimization of the PBMs. The current study provides a paradigm shift in developing new-generation RO membranes for energy and cost-effective desalination process. [Although we mainly discuss the successful incorporation of bio-inspired polymersomes into polyamide matrix, the general construction concept also shed light on the](#)

fabrication of copolymer-based biomimetic structures, such as artificial skin and organs, imbedded selective channels and so on, due to the high selectivity of the resultant films.

Acknowledgements

The research is supported by the Singapore National Research Foundation and PUB, Singapore's National Water Agency (1301-IRIS-44). Funding support from the Singapore Economic Development Board to the Singapore Membrane Technology Centre is also gratefully acknowledged.

References

1. Elimelech, M. and W.A. Phillip, *The Future of Seawater Desalination: Energy, Technology, and the Environment*. Science, 2011. **333**(6043): p. 712-717.
2. Shannon, M.A., et al., *Science and technology for water purification in the coming decades*. Nature, 2008. **452**(7185): p. 301-310.
3. Greenlee, L.F., et al., *Reverse osmosis desalination: Water sources, technology, and today's challenges*. Water Research, 2009. **43**(9): p. 2317-2348.
4. Shi, L., et al., *Effect of substrate structure on the performance of thin-film composite forward osmosis hollow fiber membranes*. Journal of Membrane Science, 2011. **382**(1-2): p. 116-123.
5. Petersen, R.J., *Composite reverse osmosis and nanofiltration membranes*. Journal of Membrane Science, 1993. **83**(1): p. 81-150.
6. Tang, C.Y., Y.-N. Kwon, and J.O. Leckie, *Probing the nano- and micro-scales of reverse osmosis membranes—A comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements*. Journal of Membrane Science, 2007. **287**(1): p. 146-156.
7. Cohen-Tanugi, D., et al., *Quantifying the potential of ultra-permeable membranes for water desalination*. Energy and Environmental Science, 2014. **7**(3): p. 1134-1141.
8. Merkel, T.C., et al., *Ultrapervious, reverse-selective nanocomposite membranes*. Science, 2002. **296**(5567): p. 519-522.
9. Karan, S., Z. Jiang, and A.G. Livingston, *Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation*. Science, 2015. **348**(6241): p. 1347-1351.

10. Goh, P.S., A.F. Ismail, and N. Hilal, *Nano-enabled membranes technology: Sustainable and revolutionary solutions for membrane desalination?* Desalination, 2016. **380**: p. 100-104.
11. Yin, J. and B. Deng, *Polymer-matrix nanocomposite membranes for water treatment.* Journal of Membrane Science, 2015. **479**: p. 256-275.
12. Werber, J.R., C.O. Osuji, and M. Elimelech, *Materials for next-generation desalination and water purification membranes.* Nature Reviews Materials, 2016. **1**: p. 16018.
13. Jeong, B.-H., et al., *Interfacial polymerization of thin film nanocomposites: A new concept for reverse osmosis membranes.* Journal of Membrane Science, 2007. **294**(1–2): p. 1-7.
14. Geilich, B.M., et al., *Silver nanoparticle-embedded polymersome nanocarriers for the treatment of antibiotic-resistant infections.* Nanoscale, 2015. **7**(8): p. 3511-3519.
15. Pan, J.H., et al., *Self-Etching Reconstruction of Hierarchically Mesoporous F-TiO₂ Hollow Microspherical Photocatalyst for Concurrent Membrane Water Purifications.* Journal of the American Chemical Society, 2008. **130**(34): p. 11256-11257.
16. Liu, X., et al., *Highly Water-Stable Zirconium Metal–Organic Framework UiO-66 Membranes Supported on Alumina Hollow Fibers for Desalination.* Journal of the American Chemical Society, 2015. **137**(22): p. 6999-7002.
17. Qi, S., et al., *Aquaporin-based biomimetic reverse osmosis membranes: Stability and long term performance.* Journal of Membrane Science, 2016. **508**: p. 94-103.
18. Li, X., et al., *Nature gives the best solution for desalination: Aquaporin-based hollow fiber composite membrane with superior performance.* Journal of Membrane Science, 2015. **494**: p. 68-77.
19. Zhao, Y., et al., *Synthesis of robust and high-performance aquaporin-based biomimetic membranes by interfacial polymerization-membrane preparation and RO performance characterization.* Journal of Membrane Science, 2012. **423–424**(0): p. 422-428.

20. Lind, M.L., et al., *Tailoring the Structure of Thin Film Nanocomposite Membranes to Achieve Seawater RO Membrane Performance*. Environmental Science & Technology, 2010. **44**(21): p. 8230-8235.
21. Pendergast, M.M. and E.M.V. Hoek, *A review of water treatment membrane nanotechnologies*. Energy and Environmental Science, 2011. **4**(6): p. 1946-1971.
22. Sablani, S., et al., *Concentration polarization in ultrafiltration and reverse osmosis: A critical review*. Desalination, 2001. **141**(3): p. 269-289.
23. Werber, J.R., A. Deshmukh, and M. Elimelech, *The Critical Need for Increased Selectivity, Not Increased Water Permeability, for Desalination Membranes*. Environmental Science & Technology Letters, 2016. **3**(4): p. 112-120.
24. Discher, D.E. and F. Ahmed, *Polymersomes*, in *Annual Review of Biomedical Engineering*. 2006. p. 323-341.
25. Bang, J., et al., *Block Copolymer Nanolithography: Translation of Molecular Level Control to Nanoscale Patterns*. Advanced Materials, 2009. **21**(47): p. 4769-4792.
26. Hamley, I.W., *Ordering in thin films of block copolymers: Fundamentals to potential applications*. Progress in Polymer Science, 2009. **34**(11): p. 1161-1210.
27. Phillip, W.A., et al., *Self-assembled block copolymer thin films as water filtration membranes*. ACS Applied Materials and Interfaces, 2010. **2**(3): p. 847-853.
28. Nunes, S.P., et al., *Ultraporous films with uniform nanochannels by block copolymer micelles assembly*. Macromolecules, 2010. **43**(19): p. 8079-8085.
29. Li, X., et al., *Ordered nanoporous membranes based on diblock copolymers with high chemical stability and tunable separation properties*. Journal of Materials Chemistry, 2010. **20**(21): p. 4333-4339.
30. Jackson, E.A. and M.A. Hillmyer, *Nanoporous membranes derived from block copolymers: From drug delivery to water filtration*. ACS Nano, 2010. **4**(7): p. 3548-3553.

31. Zhu, Y., et al., *Polymer vesicles: Mechanism, preparation, application, and responsive behavior*. Progress in Polymer Science, 2016.
32. Saren, Q., C.Q. Qiu, and C.Y. Tang, *Synthesis and characterization of novel forward osmosis membranes based on layer-by-layer assembly*. Environmental Science and Technology, 2011. **45**(12): p. 5201-5208.
33. Qi, S., et al., *Influence of the properties of layer-by-layer active layers on forward osmosis performance*. Journal of Membrane Science, 2012. **423-424**: p. 536-542.
34. Qi, S., et al., *Double-skinned forward osmosis membranes based on layer-by-layer assembly-FO performance and fouling behavior*. Journal of Membrane Science, 2012. **405-406**: p. 20-29.
35. Tang, C.Y., Y.N. Kwon, and J.O. Leckie, *Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes. II. Membrane physiochemical properties and their dependence on polyamide and coating layers*. Desalination, 2009. **242**(1-3): p. 168-182.
36. György, E., et al., *Depth profiling characterisation of the surface layer obtained by pulsed Nd:YAG laser irradiation of titanium in nitrogen*. Surface and Coatings Technology, 2003. **173**(2-3): p. 265-270.
37. Mayer, J., et al., *TEM sample preparation and FIB-induced damage*. MRS Bulletin, 2007. **32**(5): p. 400-407.
38. Wirth, R., *Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale*. Chemical Geology, 2009. **261**(3-4): p. 217-229.
39. C. Y. Tang, et al., *Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration*. Journal of Membrane Science, 2010. **354**(1-2): p. 123-133.

40. Jaskiewicz, K., et al., *Mechanical properties of poly(dimethylsiloxane)-block-poly(2-methyloxazoline) polymersomes probed by atomic force Microscopy*. Langmuir, 2012. **28**(34): p. 12629-12636.
41. Kim, J.K., et al., *Functional nanomaterials based on block copolymer self-assembly*. Progress in Polymer Science, 2010. **35**(11): p. 1325-1349.
42. Lin, L., et al., *Investigating the void structure of the polyamide active layers of thin-film composite membranes*. Journal of Membrane Science, 2016. **497**: p. 365-376.
43. Wong, M.C.Y., et al., *Impact of liquid-filled voids within the active layer on transport through thin-film composite membranes*. Journal of Membrane Science, 2016. **500**: p. 124-135.
44. Geise, G.M., et al., *Water permeability and water/salt selectivity tradeoff in polymers for desalination*. Journal of Membrane Science, 2011. **369**(1-2): p. 130-138.
45. Geise, G.M., D.R. Paul, and B.D. Freeman, *Fundamental water and salt transport properties of polymeric materials*. Progress in Polymer Science, 2014. **39**(1): p. 1-24.
46. Baker, R.W., *Membrane Technology and Applications*. Membrane Technology and Applications. 2012.