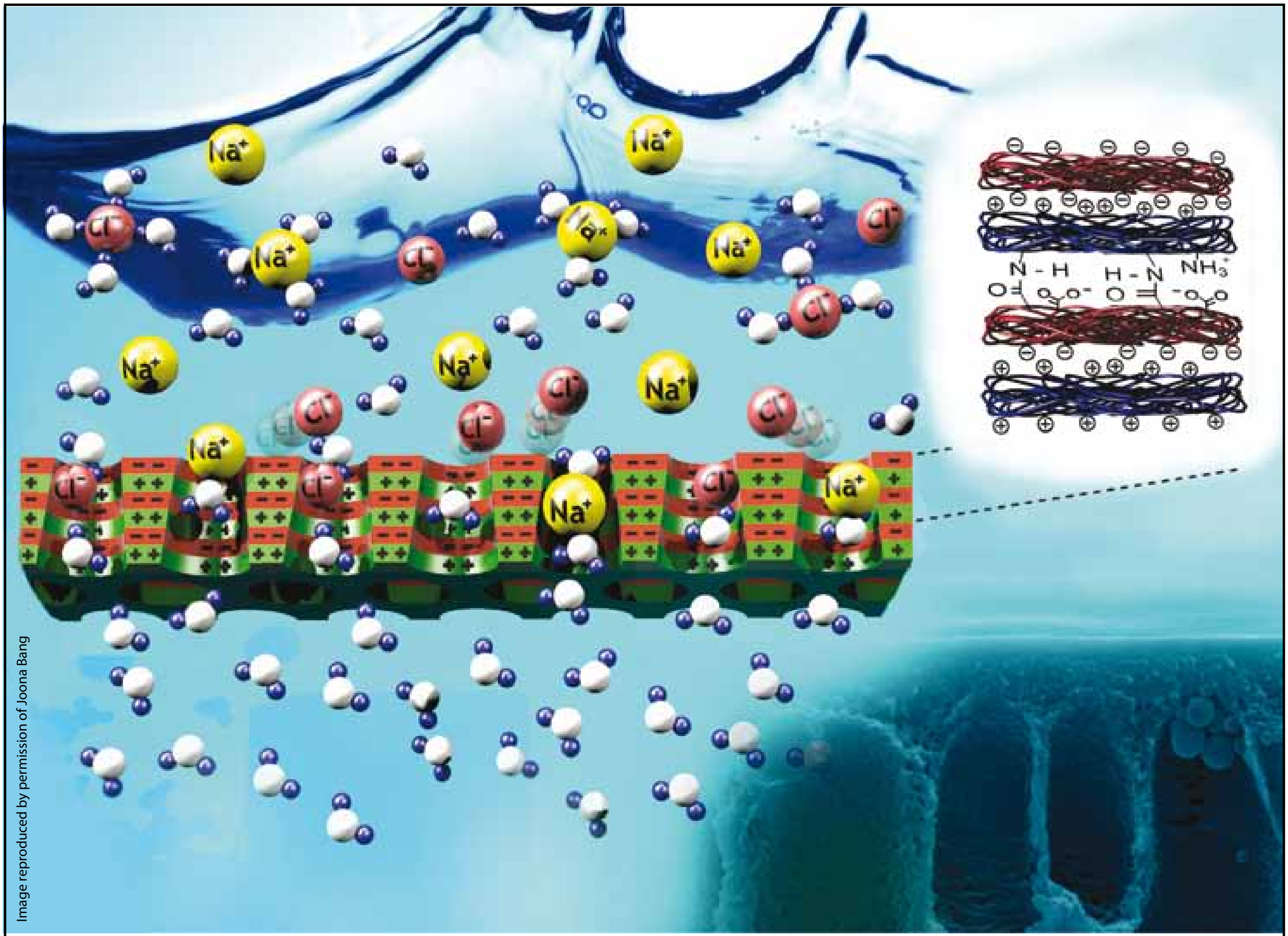

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Showcasing collaborative research from the Bang and Cho research labs, Korea University and Kookmin University, respectively.

Title: Desalination Membranes from pH-Controlled and Thermally-Crosslinked Layer-by-Layer Assembled Multilayers

Desalination membranes were fabricated by layer-by-layer assembly of polyelectrolytes and the effects of pH condition during deposition and thermal-crosslinking of multilayers on the desalination performance were systematically investigated. This approach provides an important basis for designing highly efficient RO membranes.

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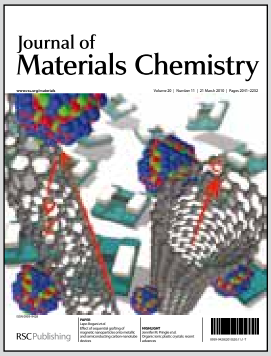

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Desalination membranes from pH-controlled and thermally-crosslinked layer-by-layer assembled multilayers

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We introduce a novel and facile approach to improve the desalination performance of pressure-driven layer-by-layer (LbL) assembled membranes. Electrostatic LbL multilayers composed of weak polyelectrolytes (PEs), *e.g.*, cationic poly(allylamine hydrochloride) (PAH) and anionic poly(acrylic acid) (PAA), were prepared on commercial polysulfone substrates. In order to measure the ion rejection and permeate flux of these membranes, the ionic concentration of the feed solution and operating pressure were fixed at 2000 ppm NaCl and 20 bar, respectively. It was observed that the crosslinked (PAH pH 7.5/PAA pH 3.5)$_{n=10,20}$ multilayers, which were assembled at the pH conditions allowing a low charge density of the respective PEs, show relatively high ion rejection compared to other multilayers. This result suggests that the optimal structures for desalination membranes should contain a large amount of freely charged groups with densely-packed structures *via* crosslinking. Finally, the recycling process was employed to further improve the desalination performance. In this case the (PAH pH 7.5/PAA pH 3.5)$_{n=10,20}$ multilayers exhibited the ion rejection up to 99.8%. This pH-controlled and thermal crosslinking method suggests a new route for the design of well-defined desalination reverse osmosis membranes based on LbL multilayers.

Introduction

Reverse osmosis (RO) and nanofiltration (NF) membranes for seawater desalination have attracted considerable attention due to the significant water-shortage in many countries where clean water supplies are unavailable.[1–8] Generally, the commercialized membranes are composed of a top selective layer, a few hundred nanometres in thickness, a microporous polysulfone support layer and a non-woven fabric layer for mechanical stability. In particular, the top selective layer is very important because the permeate flux and salt rejection in desalination membranes strongly depends on the physiochemical properties (*e.g.*, surface charge, surface roughness, selectivity and permeability) of the selective layer. Although it was reported that a variety of functional materials such as nanoporous polymers,[5] graphene,[6] carbon nanotube,[7] or cellulose[8] could be used as a top selective layer of desalination membranes, such approaches have much difficulty in producing large-area membranes at low cost with a simplified manufacturing process. At present, the selective layers in many commercial practices are formed by interfacial crosslinking polymerization between the amine monomers (such as 1,3-benzenediamine) and aromatic acyl chloride monomers (such as trimesoyl chloride). However, the resulting polyamide layer typically exhibits a rough surface showing peak-to-valley structures in the order of a few hundreds nanometres and, furthermore, it is very difficult to control the surface charge of selective layers in the conventional interfacial polymerization.

As an alternative, it was demonstrated that the layer-by-layer (LbL) assembly method based on solution dipping process and complementary interactions (*e.g.*, electrostatic, hydrogen-bonding or covalent bonding) is quite useful for preparing nanocomposite films with tailored physiochemical properties and thickness control in the nanometre range on substrates with different size and shape.[9–19] This technique allows the functional properties of the films to be adjusted through the deposition of multiple layers with the desired properties. This is in contrast to the other films, which only use a single layer. In the case of electrostatic LbL assembly, poly(acrylic acid) (PAA) with anionic carboxylic acid (–COO$^-$) groups and poly(allylamine hydrochloride) (PAH) containing cationic amine (–NH$_3^+$) groups have a pH-dependent charge density as a characteristic of weak polyelectrolytes (weak PEs).[12] Furthermore, the thermal treatment of PAA/PAH multilayers formed in the controlled pH range can form stable films *via* a crosslinking reaction between the carboxylic acid and amine groups.[20–22]

Based on previous reports, a number of ion-selective membrane films using LbL assembly have been demonstrated by many research groups. For example, Park *et al.* reported that pH-sensitive bipolar ion-permselective films could be prepared by photo-crosslinkable PAA/PAH multilayers.[23] They found that at low pH, cations such as $Ru(NH_3)_6^{3+}$ are excluded from the films but anions penetrate easily, while the opposite behavior is obtained at high pH. Stair *et al.* also reported that the LbL deposition of 1–3 bilayer (PAA/PAH) films on (poly(4-styrenesulfonate) (PSS)/PAH)$_5$ multilayers on porous alumina supports is a convenient method for producing ultrathin membranes.[22] They also demonstrated that the heat-induced

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crosslinking of PAA/PAH surface bilayers could enhance the Cl^-/SO_4^{2-} selectivity *via* the Donnan exclusion effect. Although aforementioned ion-selective membranes have potential as desalination membranes, a few issues need to be considered. First, LbL multilayered films should be prepared on mechanically strong and flexible substrates, because in the commercial RO process they are rolled up into the wound module and operated under high pressure conditions. Also, the permeate flux and rejection of total ions are very important factors in desalination RO membranes.[24] Therefore, the selective layers from LbL multilayers should be able to allow water to permeate through the membrane with high flux while repelling charged ion molecules. Furthermore, the degree of ionization within desalination RO membranes has a significant effect on ion rejection. Accordingly, desalination membranes should be designed such that the degree of ionization within membranes is high when the pH of the feed solution is adjusted to that of seawater.

Herein, we introduce a novel and facile approach to improve the desalination performance of LbL-assembled membranes. This study focuses on the rejection of monovalent ions, such as Na^+ and Cl^-, because divalent ions can be rejected more easily by the strong interaction (or repulsion) between divalent ions and charged membranes than monovalent ions. For this approach, thermally crosslinked $(\mathrm{PAH\ pH\ 7.5/PAA\ pH\ 3.5})_n$ multilayers on polysulfone supports were prepared as RO membranes. The surface morphology of resulting LbL membranes was remarkably homogeneous compared to conventional RO membranes. To enhance the ion rejection rate of these membranes, the recycling process was combined with this RO membrane process. As a result, LbL-assembled RO membranes exhibited an ion rejection rate >99% at a concentrated feed solution (2000 ppm NaCl aqueous solution) and a pressure of 20 bar. In addition, we fabricated the $(\mathrm{PAH/PAA})_n$ multilayers under different pH conditions to systematically investigate the effect of membrane structures on the ion rejection during the RO process. Although a large proportion of the carboxylic acid groups in the PAA embedded in this system is uncharged and unbounded at the deposition conditions of pH 3.5, we found that unbound –COOH groups within the PAA layers can be readily converted to $-COO^-$ groups at the seawater condition of pH 8.1. In addition, the amine groups of the PAH layers can contain the cationic charge density of approximately 50% (pK_a of PAH $\approx$ 9.5). Therefore, we conclude that the switching phenomena of the charge density within membranes can improve the ion rejection rate. This approach can provide a basis for designing highly efficient RO membranes *via* LbL assembly method.

Experimental section

Materials

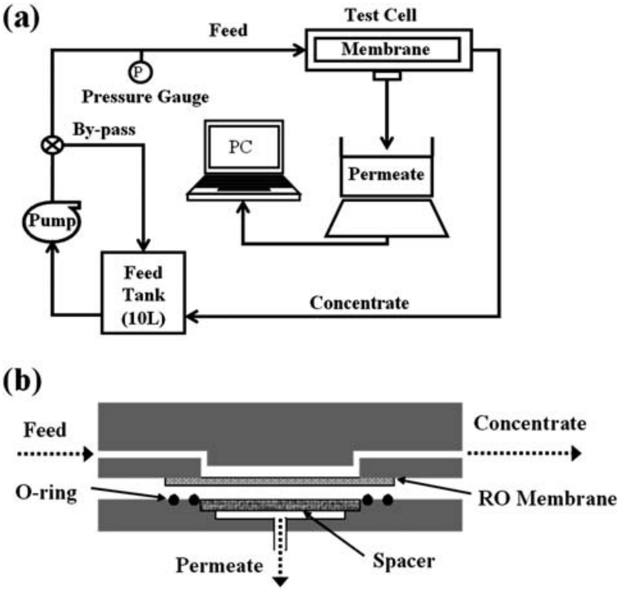
Poly(sodium 4-styrenesulfonate) (PSS) (Aldrich, $M_w = 70\,000$ g mol^{-1}) and poly(acrylic acid) (PAA) (Polysciences, $M_w = 100\,000$ g mol^{-1}) were used as anionic polyelectrolytes (PEs). On the other hand, poly(allylamine hydrochloride) (PAH) (Aldrich, $M_n = 56\,000$ g mol^{-1}) and poly(diallyldimethylammonium chloride) (PDAD) (Aldrich, $M_w = 200\,000$–$350\,000$ g mol^{-1}) were used as cationic PEs. As with commerical RO membrane, polysulfone (PSf) support film (Trisep Corp., UE50, 100 000 g mol^{-1}) was used as a substrate to construct the LbL multilayers.

Build-up of multilayers

The solution concentration of PAH, PAA, PDAD and PSS was adjusted to 1 mg mL^{-1}. The pH of the PAA and PAH solutions was controlled by 0.1 M HCl and NaOH without addition of ionic salts. For deposition of LbL-assembled multilayer films onto the PSf films, negatively charged PSf substrates were prepared by a treatment with a H_2SO_4 solution at 80 °C for 30 min. The substrates were first dipped in the cationic PE (PAH or PDAD) solution for 10 min, washed twice in deionized water for 1 min each, and air-dried with a gentle stream of nitrogen. The anionic PEs were then deposited onto the cationic PE-coated substrates by adsorption for 10 min, washed in deionized water, and dried. This process was repeated until the desired number of layers had been deposited. To impose the chemical crosslinking between PAH and PAA layers, the $(\mathrm{PAH/PAA})_n$ multilayer membranes were heated to 180 °C for 1 h under vacuo.

Characterization of membranes

The film thickness of the $(\mathrm{PAH/PAA})_n$ multilayers on silicon substrates was measured by ellipsometry (Gaertner Scientific Corp., L2W15S830) using 632.8 nm He–Ne laser light. To examine the functional groups within $(\mathrm{PAH/PAA})_n$ multilayers, FT-IR spectra were taken using a FT-IR-200 spectrometer (JASCO Corporation). For this measurement, $(\mathrm{PAH/PAA})_n$ multilayers were spin-cast onto CdSe substrates, and amide bonding and carboxylic acid groups within multilayers were then examined qualitatively using FT-IR after heat treatment of the multilayers at 180 °C for 1 h. The surface morphology of the LbL multilayers was examined by FE-SEM (Hitachi, S-4300).



Scheme 1 (a) Schematic diagram of the RO membrane test system. (b) Cross-section of the test cell.

Test cell for RO membranes

A homemade RO test system was fabricated as illustrated in Scheme 1. The RO membranes are placed in a pressure chamber (effective area for the membrane cell = 13.85 cm^2; pressure = 20 bar). The ionic salt (NaCl) concentration and flux in the feed water were fixed to 2000 ppm and 333 L m^{-2} h^{-1}, respectively, at room temperature. At the bottom, the cell was equipped with an outlet for the permeate solution. In this case, the ion concentration of permeate was measured using the ionic conductivity meter (EUTECH, PC650). In this system, the concentrate from the test cell is recycled back to the feed tank. However, it should be noted that the amount of the concentrate is very small and hence the feed concentration is not affected by the recycled concentrate.

Results and discussion

As shown in Fig. 1, the film thicknesses of the (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers on the silicon substrates increased significantly from 3 nm to approximately 250 nm with increasing bilayer number (n) from 1 to 10. The build-up of these multilayers follows a typical exponential growth pattern, which can be explained by an "in-and-out diffusion" mechanism of the polyelectrolytes (PEs) during deposition (*i.e.*, polycation diffuses into the film during deposition, then out of the film during rinsing, and further out during polyanion deposition).[25–27] Considering that the thickness formed from the out-diffusing PEs and incoming oppositely charged PEs is proportional to the amount of PEs that diffuse out of the film, the amount of unbound or non-ionized PEs with the coil, loop or entangle structure within the multilayers can have a significant effect on the exponential growth of the multilayers due to the facile diffusion of PEs out of the film surface.

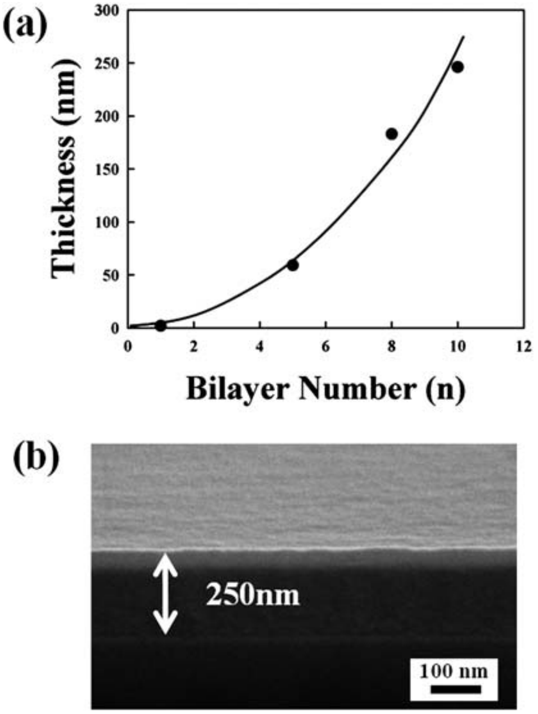


Fig. 1 (a) Film thickness of LbL assembled (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers measured using ellipsometry. (b) Cross-section SEM image of (PAH pH 7.5/PAA pH 3.5)$_{10}$ multilayers prepared on a silicon substrate.

LbL assembly under a condition of pH 7.5 for PAH and pH 3.5 for PAA can produce the thickest layers of all pH combinations. In a PAA solution at pH 3.5, weakly ionized PAA chains (pK_a of PAA ≈ about 4.5) with a number of loop and coil structures are deposited onto almost fully charged PAH layer (pK_a of PAH ≈ about 9.5). On the other hand, when the PAH chains are deposited onto the PAA-coated substrates at pH 7.5, the weakly ionized carboxylic acid groups of the adsorbed PAA are converted into highly ionized state. Therefore, a large amount of PAH with charged amine groups are required to neutralize the ionized PAA surface and achieve charge overcompensation for charge reversal.[23,28] In addition, these multilayers contain the partial hydrogen-bonding between the unionized amine and carboxylic acid groups.[20] Based on these phenomena and previously reported results, it is reasonable to conclude that the (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers have a number of unbound, non-ionized carboxylic acid or amine groups as well as a high degree of internal charge pairing within the multilayers assembled at pH 7.5/3.5, even though such functionalities could not be measured quantitatively. Recently, it was reported that the amine groups of PAH and the carboxylic acid groups of PAA could be chemically crosslinked through the formation of amide bonds after thermal treatment, which could induce the densely packed structures as well as the improved mechanical properties of the films.[20–22] Therefore, if the (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers containing unbound or slightly bound functionalities are crosslinked thermally, they will have an important advantage as seawater desalination membranes with efficient ion rejection properties and improved physical/chemical stability.

In order to demonstrate this possibility, the formation of chemical crosslinking between PAH and PAA after a thermal treatment at 180 °C for 1 h was first investigated. As shown in

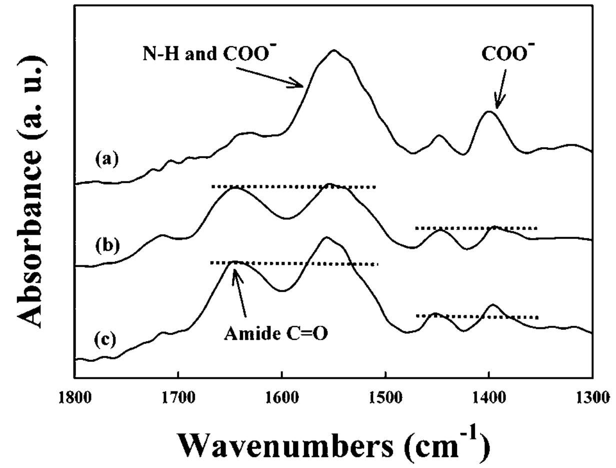


Fig. 2 FT-IR spectra of (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers prepared on CdSe substrates. (a) before heating, (b) after heating to 180 °C for 1 h, and (c) after immersing in an aqueous solution of pH 8.1 for 1 h. The dashed lines are to compare the relative intensity of –COO$^-$ peaks in (b) and (c).

Fig. 2, the FT-IR spectra of PAH/PAA multilayers before the thermal treatment revealed the presence of –COOH (carbonyl peak at 1710 cm^{-1}), $–COO^-$ (carboxylate peak at 1570 and 1400 cm^{-1}) and $–NH_3^+$ (symmetric and antisymmetric NH_3^+ deformation between 1625 and 1400 cm^{-1}). However, the NH_2 peak at 3000–3500 cm^{-1} was not observed due to an overlap with the –OH peak in the carboxylic acid groups at 2500 $\sim$ 3400 cm^{-1} (data not shown). When the films were thermally annealed at 180 °C, the intensity of the strong amide peak at 1650 and 1560 cm^{-1} indicating the formation of cross-linkage had significantly increased (the N–H peak of amide groups was overlapped with that of $–COO^-$ groups) with two different absorption peaks originating from –COOH and $–COO^-$ groups. These films were then immersed in an aqueous solution of pH 8.1 for 1 h to examine the film structures under the RO operation conditions. In this case, we observed that the intensity of $–COO^-$ groups at 1570 cm^{-1} was significantly pronounced with a concomitant decrease in –COOH peak intensity. This strongly suggests that the –COOH groups formed from the deposition of a PAA layer at pH 3.5 had almost completely converted to $–COO^-$ groups. Therefore, when (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers are used as a desalination membrane in seawater condition at pH 8.1, these films can maintain a highly charged state, and repel the various ions in seawater.

As a first step, (PAH pH 7.5/PAA pH 3.5)$_n$ multilayer films were prepared on the negatively charged polysulfone substrates that were treated with sulfuric acid (Fig. 3). After desired (PAH/PAA)$_n$ multilayers were deposited, the membranes were annealed at 180 °C for 1 h to induce the amide crosslinking

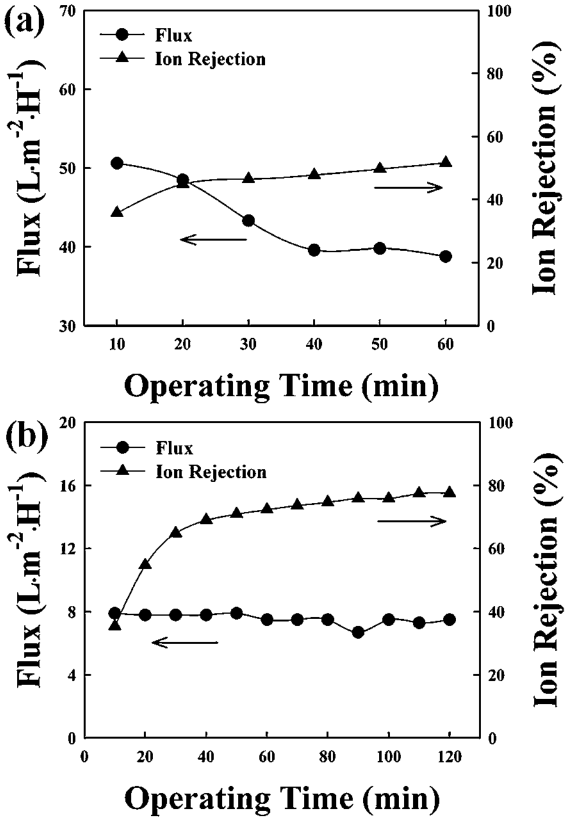


Fig. 4 Plot of permeation flux and ion rejection as a function of operation time for (PAH pH 7.5/PAA pH 3.5)$_{10}$ multilayers (a) before thermal annealing and (b) after thermal annealing at 180 °C for 1 h.

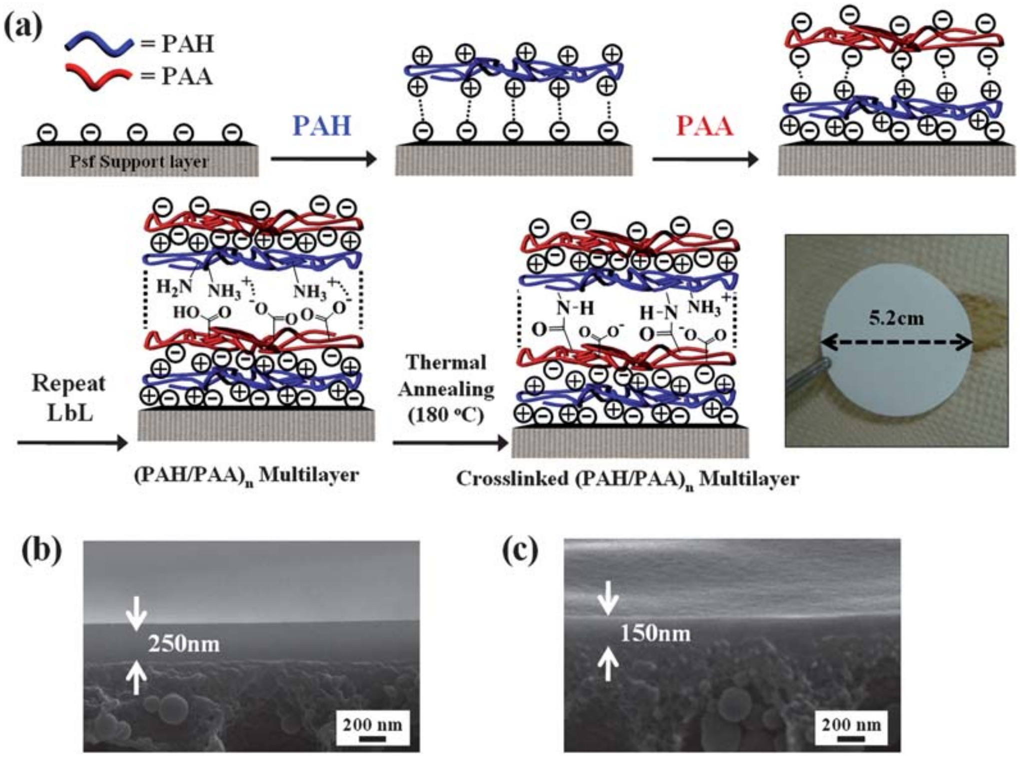


Fig. 3 (a) Schematic illustration of the fabrication of (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers on polysulfone substrate. The photograph is the resulting RO membrane adjusted to the size of the test cell in Scheme 1. (b) and (c) correspond to cross-section SEM images of (PAH pH 7.5/PAA pH 3.5)$_{10}$ multilayers prepared on polysulfone substrate before and after thermal annealing, respectively.

between PAH/PAA layers. As shown in Fig. 3b and Fig. 3c, the thickness of multilayers significantly decreases, *e.g.*, from 250 nm to 150 nm for (PAH pH 7.5/PAA pH 3.5)$_{10}$ multilayer, indicating that the crosslinking results in the densely packed structure. These membranes were then tested using a homemade RO test system, as shown in Scheme 1. To assess the desalination performance, highly ionic concentrated water (*i.e.*, NaCl concentration of 2000 ppm) at pH 8.1 was used as the feed solution at 20 bar.

As shown in Fig. 4a, the permeate flux and ion rejection of (PAH pH 7.5/PAA pH 3.5)$_{10}$ multilayers before thermal annealing were approximately 38 L m^{-2} h^{-1} and 54%, respectively (after operating time of 1 h). However, the thermally annealed films increased the ion rejection rate to approximately 80% with a 75% decrease in permeate flux (Fig. 4b). These notable differences in desalination performance before and after thermal annealing can be attributed to the formation of a dense structure through crosslinking (*i.e.*, amide bonding) in highly ionized films. In particular, the crosslinked films can effectively decrease a degree of swelling from the feed solution and thus decrease the permeate flux. In view of ion rejection, the highly ionized groups (*i.e.*, $-COO^-$ groups of PAA and $-NH_3^+$ group of PAH) in multilayers can reject the same charged ions or trap the oppositely charged ions of the feed solutions. Therefore, it can be deduced that crosslinked structures containing highly ionized groups are effective in rejecting ion molecules in feed solution. This result also suggests that the thickness of the (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers has a significant effect on the fluxes and ion rejection. To examine this, crosslinked (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers were prepared with increasing bilayer number (n) from 5 to 20. In this case, the permeate fluxes and ion rejections were 20 L m^{-2} h^{-1} and 21% for $n = 5$, 8 L m^{-2} h^{-1} and 78% for $n = 10$ and 7 L m^{-2} h^{-1} and 81% for $n = 20$, respectively (Fig. 4b and Fig. 5).

We also prepared the multilayers composed of strong PEs (*i.e.*, PEs with a fixed charge density irrespective of the solution pH) using PDAD and PSS. In this case, it was observed that the (PDAD/PSS)$_n$ multilayers did not have the remarkable feature of ion rejection (38% and 130 L m^{-2} h^{-1} for $n = 10$, 44% and 105 L m^{-2} h^{-1} for $n = 20$) with increasing bilayer number from 10 to 20, although a relatively high permeate flux could be maintained (Fig. 6). It should be noted that the thermal annealing did not improve the performance of these membranes significantly, because there are no crosslinkable groups in PDAD and PSS (*i.e.*, the films structures did not change upon thermal annealing). This implies that the densely crosslinked structure is inevitable for desalination membrane to prevent the 'free-pass' of ion molecules through the membrane.

The presence of freely charged groups within the membrane is also an important factor in the desalination membrane. As mentioned earlier, the (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers have a large amount of unbound and uncharged groups, which can be easily converted to freely charged groups in a relatively high pH solution, such as seawater conditions. However, in the case of (PAH pH 4/PAA pH 6)$_{10}$ multilayers after thermal

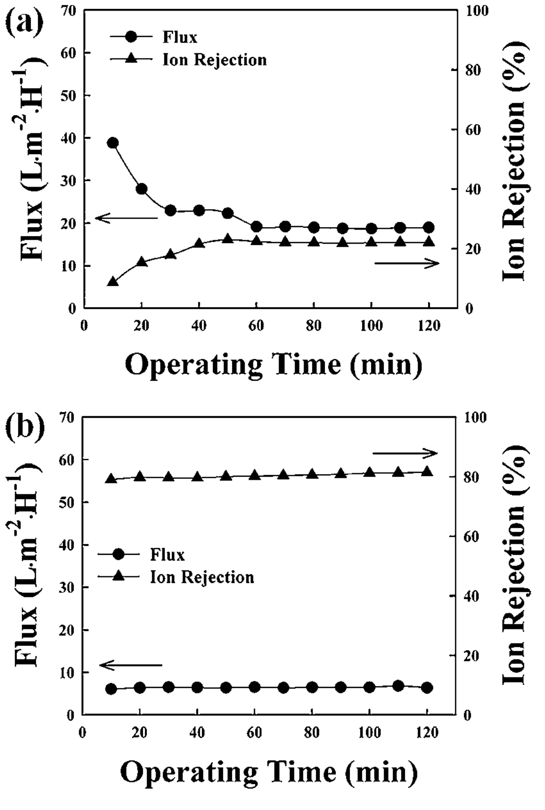


Fig. 5 Plot of permeation flux and ion rejection as a function of operation time for (a) (PAH pH 7.5/PAA pH 3.5)$_5$ multilayers and (b) (PAH pH 7.5/PAA pH 3.5)$_{20}$ multilayers after thermal annealing at 180 °C for 1 h.

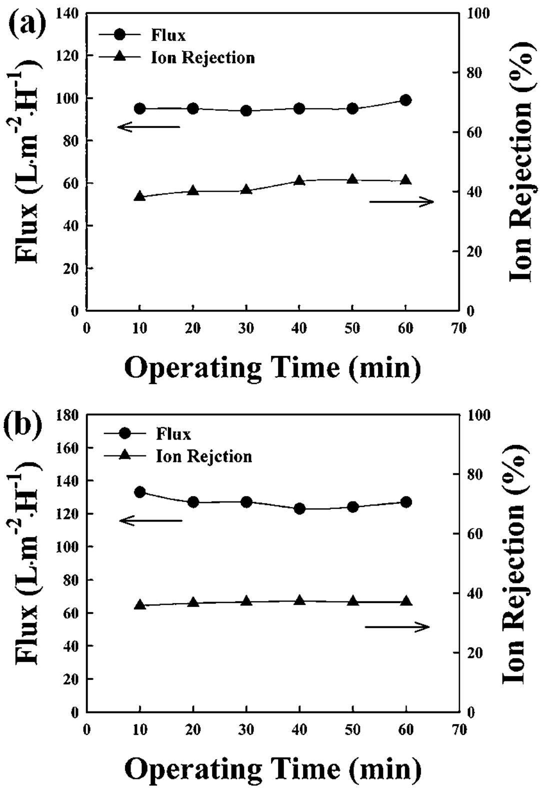


Fig. 6 Plot of permeation flux and ion rejection as a function of operation time for (a) (PDAD/PSS)$_{10}$ multilayers and (b) (PDAD/PSS)$_{20}$ multilayers after thermal annealing at 180 °C for 1 h.

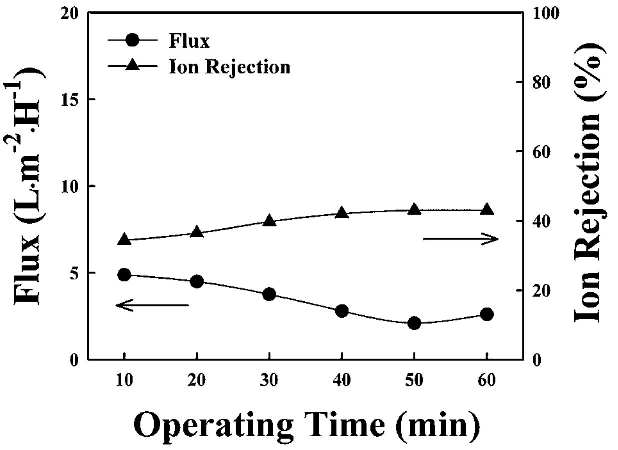


Fig. 7 Plot of permeation flux and ion rejection as a function of operation time for (PAH pH 4/PAA pH 6)$_{10}$ multilayers after thermal annealing at 180 °C for 1 h.

crosslinking, it was found that the permeate flux and ion rejection were only 5 L m^{-2} h^{-1} and 44%, respectively (Fig. 7). Under a deposition condition of pH 4 for PAH and pH 6 for PAA, these polymers have stiff or extended chain conformation with the highly ionized state. As a result, the LbL assembly between highly-charged PAH and PAA produces much thinner individual layers, because all charged amine and carboxylic acid groups will be coupled. Therefore, the low ion rejection rate for these membranes can be attributed to the lack of free functional groups within (PAH pH 4/PAA pH 6)$_{10}$ multilayers.

To further improve the ion rejection of (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers, a recycling process was employed. It was reported that an increase in salt concentration in the feed solution decreases the ion rejection of membranes significantly because the accumulation of the ion concentration within the membranes causes the shielding of PE-bound charges.[29] Therefore, recycling of the permeate is based on the concept that the ion rejection rate can be enhanced effectively by converting the high ion concentration of the feed solution into low concentrated solutions with a constant flux. Fig. 8 shows the ion rejection of (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers after the recycling process. The permeate fluxes after recycling was similar to those before recycling. Although the ion rejection of 5 bilayered films was approximately 52% even after recycling, it was found that 10 and 20 bilayered films exhibit high ion rejection (>99%), which is comparable to those of commercial RO membranes.

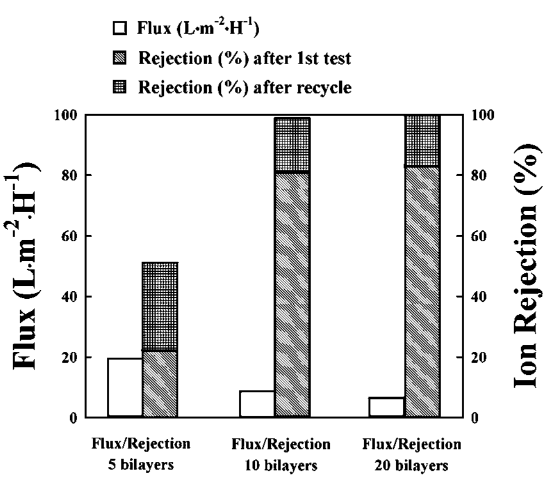


Fig. 8 Plot of permeation flux and ion rejection for (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers after recycle operation.

Conclusions

In this work, we demonstrated that thermally-crosslinked PE multilayers can be effectively used as desalination RO membranes. The (PAH pH 7.5/PAA pH 3.5)$_n$ multilayer membranes after thermal crosslinking showed an improved ion rejection rate and decreased permeate flux compared to those prepared with different deposition conditions and strong PEs. These results were attributed to the phenomena that the crosslinked (PAH pH 7.5/PAA pH 3.5)$_n$ multilayers increased their ionized state with restricted swelling in the feed solution at pH 8.1. Furthermore, the recycling process of the permeate through the crosslinked (PAH pH 7.5/PAA pH 3.5)$_{10,20}$ membranes showed an excellent ion rejection rate of ~99.8%. Although the ion rejection from this approach is comparable to that of commercial RO membrane, the flux needs to be further improved. Therefore, the future work will be focused on the development of RO membranes with both improved ion rejection and high permeate flux using a LbL assembly method. In this regards, various crosslinking agents will be explored to design well-defined crosslinked multilayers with different mesh size and stability.[30–34]

Acknowledgements

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