Development of Nanostructured Water Treatment Membranes Based on Thermotropic Liquid Crystals: Molecular Design of Sub-Nanoporous Materials

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Supply of safe fresh water is currently one of the most important global issues. Membranes technologies are essential to treat water efficiently with low costs and energy consumption. Here, the development of self-organized nanostructured water treatment membranes based on ionic liquid crystals composed of ammonium, imidazolium, and pyridinium moieties is reported. Membranes with preserved 1D or 3D self-organized sub-nanopores are obtained by photopolymerization of ionic columnar or bicontinuous cubic liquid crystals. These membranes show salt rejection ability, ion selectivity, and excellent water permeability. The relationships between the structures and the transport properties of water molecules and ionic solutes in the sub-nanopores in the membranes are examined by molecular dynamics simulations. The results suggest that the volume of vacant space in the nano-channel greatly affects the water and ion permeability.

1. Introduction

An inadequate supply of safe fresh water is one of the most important global issues of our time. Water purification with polymer membranes is a promising method because high-grade drinking water can be obtained with low energy consumption at a low cost. Current commercial membrane materials are cross-linked polyamides and cellulose derivatives. However, it is difficult to obtain ordered sub-nanopores with uniform diameters in these conventional membranes. New materials such as carbon-based materials, synthetic or recombinant channel peptides, and block copolymers have been developed as components for water treatment membranes. These materials can be used to prepare membranes with ordered nanopores and sub-nanopores. Self-assembly of polymerizable liquid-crystalline (LC) molecules and block copolymers has attracted attention for the preparation of stable functional materials thin films because these materials offer uniformly sized nanopores and sub-nanopores. In addition, the alignment of channels within these materials is expected to be easier than that for membranes consisting of carbon nanotubes. The structures and sizes of the self-assembled channels are dependent on the molecular structures and intermolecular interactions. 1D, 2D, and 3D nanochannels are obtained from LC materials that exhibit columnar (Col), smectic (Sm), and bicontinuous cubic (Cubii) phases, respectively. These LC nanoporous and sub-nanoporous materials have been applied as water treatment membranes, ion conductors and organic molecular sieves. For block copolymers, self-assembly of cylinder, lamellar, and gyroid structures leads to formation of 1D, 2D, and 3D nanoporous membranes, respectively. Pore diameters range from 0.5 to 2 nm for LC materials and 5 to 50 nm for block copolymers. The sizes of the channels in LC materials are in range required for reverse osmosis (RO) and nanofiltration (NF) membranes stopping small molecules and ions, whereas porous films prepared from block copolymers can function as ultrafiltration (UF) or microfiltration membranes rejecting larger solutes.

The ionic sub-nanopores of thermotropic ionic LC materials have excellent potential for use as membranes for selective rejection of salts or hazardous substances from seawater or brackish water. These membranes have sub-nanopores with uniform...
diameters, which form by self-organization of the liquid crystals. The moieties on the inside walls of the sub-nanopores can be changed. Moreover, these membranes may have fewer defects than commercial membranes because LC fluid states of monomeric compounds are used before photopolymerization in the membrane preparation process. Lyotropic liquid crystals are of interest and were used in an earlier study to prepare polymer membranes with Cubbi structures for water treatment.[14–18]

The aim of this study was to develop water purification materials based on nanostructured ionic polymer membranes with preserved thermotropic LC nanostructures. Wedge-shaped ionic LC compounds containing hydrophobic polymerizable moieties (1(n)–5(n), Figure 1) were designed and prepared. The water treatment properties of the nanostructured membranes with thermotropic hexagonal columnar (Colh) and Cubbi LC structures were studied. Molecular dynamics (MD) simulations of water molecules and ionic solutes in the ionic nanochannels of the LC materials were examined to understand transport properties of water molecules and the rejection of ionic solutes in the sub-nanoporous LC membranes.

2. Results and Discussion

2.1. Molecular Design and Thermotropic LC Properties of the Ionic Monomers

The principles of the molecular design for development of the thermotropic liquid crystals in this work are shown in Figures 1 and 2.

Molecules 1(n)–5(n) were designed as ionic liquid crystals with ammonium, imidazolium, and pyridinium moieties. The cationic moieties for 1(n), 2(n), and 3(n) are quaternary ammonium cations with various short alkyl chains. It has been reported that the size of an ionic moiety affects the assembled structure.[44,45] Compounds 4(n) and 5(n) contain N-methylimidazolium and pyridinium moieties as their cationic groups, respectively. Compounds 1(n)–5(n) also contain a tris(alkoxy)phenyl group with 1,3-diene tails as polymerizable groups. These compounds were expected to exhibit thermotropic Colh or Cubbi phases with 1D or 3D uniform sub-nanopores in the membranes.[44–48]

We previously reported on water treatment with self-organized sub-nanoporous membranes prepared by photopolymerization of the triethylammonium molecule 1(12) in the Cubbi phase (Figure 1).[19] The Cubbi membrane showed selective permeation for the sulfate ion in addition to a NaCl rejection rate and water permeability that were comparable to those of commercial NF membranes. Recently, we have achieved highly efficient virus rejection using nanoporous membranes based on Cubbi LC compound 1(14).[20]

The LC properties of compounds 1(n)–5(n) are summarized in Table 1. For compounds 1(n) and 2(n), the lengths of the alkyl chains on the 4-position of the benzene ring was different. In our previous studies, compound 1(12) was used to prepare an ion-conducting film[46] and a water treatment membrane.[19] However, the LC isotropic transition temperature of 1(12) is below room temperature. Compound 1(14) was designed and obtained as a Cubbi material with a higher LC isotropic transition temperature than that of 1(12). A higher isotropic transition...
temperature makes preparation process of the membranes easier. Compound 1(10) was not mesomorphic (Figure S1, Supporting Information). Compounds 2(12)–5(12) formed Colh phases (Figures S2–S11, Supporting Information). It is notable that only replacement of one ethyl group with a methyl group changed the mesophase of the wedge-shaped compound from Cubbi phase to Col phase.

For the compounds 1(12), 2(12), and 3(12), those with smaller alkylammonium moieties showed higher isotropization temperatures. The higher isotropization temperatures of these compounds were partly attributed to stronger electrostatic interactions between the smaller cationic moiety and the anion in the ionic domain compared with compounds with a larger cationic moiety.[44,45] The LC phases of compounds 4(12) and 5(12) were stable over 100 °C. Ionic and π–π interactions may contribute to thermal stabilization of the Col phases. These monomers spontaneously polymerized because of thermal effects at temperatures over 100 °C.

2.2. Water Treatment with the LC Membranes

Composite membranes for water treatment were prepared from the LC monomers 1(n)–5(n) using the transcription method as previously reported (Figure 3).[19,20] The LC polymer films were prepared by spin-coating and subsequent photopolymerization, and were about 100 nm thick. The nanostructured LC polymer layer was supported by porous substrates of polysulfone and nonwoven polyester. The polysulfone and polyester layers were about 40 and 90 µm thick, respectively. These supporting layers can be used as ultrafiltration membranes having nanopores smaller than 10 nm[29] and they give the composite membranes mechanical toughness.

The water treatment properties of the composite membranes were examined using stainless steel cross-flow filtration cells with an applied pressure of 0.75 MPa following established methods.[19] The membranes were tested using aqueous solutions of NaCl and MgSO4 (Table 2). The solution fluxes and rejection

Table 1. Thermal properties of ammonium compounds 1(n)–5(n).

| Compound | Ionic moiety | Phase transition behaviora) | Transition temperature (°C) | Enthalpy change (kJ mol⁻¹) |
|----------|--------------|-----------------------------|-----------------------------|---------------------------|
| 1(10)    | Triethylammonium-BF₄ | Cr                          | <−50                        |                          |
| 1(12)    | Triethylammonium-BF₄ | Cr                          | −5 (4.3)                   | 19 (0.07)                 |
| 1(14)    | Triethylammonium-BF₄ | Cubbi                       | 15 (2.4)                   | 28 (0.49)                 |
| 2(10)    | Diethyl-methylammonium-BF₄ | Cr                          | −5 (19)                    | 55 (0.59)                 |
| 2(12)    | Diethyl-methylammonium-BF₄ | Cr                          | 8 (23.7)                   | 62 (0.58)                 |
| 3(12)    | Trimethylammonium-BF₄ | Cr                          | 37                         |                          |
| 4(12)    | N-Methylimidazolium-BF₄ | Cr                          | 42                         |                          |
| 5(12)    | Pyridinium-BF₄     | Cr                          | 40                         |                          |

a)Cr, crystalline; Cubbi, bicontinuous cubic; Colh, hexagonal columnar; Iso, isotropic; Polym, polymerization occurs in the LC phase. Transition temperatures (°C) and enthalpy changes (kJ mol⁻¹) were determined by differential scanning calorimetry on the second heating cycle; b)Compound 1(10) did not show a phase transition above −50 °C; c)Ref. [36]; d)Transition behavior in the first heating cycle.

Figure 3. Schematic illustration for the preparation of the composite membranes from LC monomers.
values for NaCl and MgSO₄ with the membranes were measured, and Figure 4 shows the maximum flux recorded for each membrane. These membranes showed stable performance during the permeation test for tens of hours.

The membranes prepared from Cubₐ₁ compound 1(14) and Col₉ compounds 2(10), 2(12), 3(12), and 4(12) exhibited over 60% rejection of NaCl, and their results were comparable to that of Cubₐ₁ 1(12). These membranes are the first examples of Col membranes based on thermotropic liquid crystals that exhibit the same level of NaCl rejection with commercial NF membrane. Compared with these membranes, the Col₉ membrane prepared from compound 5(12) had a lower NaCl rejection rate.

The rejection rates for MgSO₄ with the LC 1(14) and 2(n)—5(12) membranes were lower than those of NaCl with the same membranes (Figure 4b). This behavior was similar to that of the Cubₐ₁ 1(12) membrane, which shows selective permeation of sulfate salts.[19] However, this is an interesting result because polymer NF membranes usually reject sulfonate salts more efficiently than chloride salts, as observed with the commercial NF membrane UTC-60.[50] This value is approximately twice that through the Cubₐ₁ 1(12) membrane.[19] We suppose that the membranes of polymerized Cubₐ₁ 1(14) formed more ordered and defectless structures than Cubₐ₁ 1(12). The decrease of defect and interruption in the sub-nanopores might induce higher water flux.

The structures of the LC monomers also greatly affected the water permeability performances of the membranes. Notably, the maximum flux through the Cubₐ₁ 1(14) membrane during water treatment for NaCl rejection was above 120 L m⁻² h⁻¹ (Figure 4a). This value is approximately twice that through the Cubₐ₁ 1(12) membrane.[19] We suppose that the membranes of polymerized Cubₐ₁ 1(14) formed more ordered and defectless structures than Cubₐ₁ 1(12). The decrease of defect and interruption in the sub-nanopores might induce higher water flux. The fluxes through the Col₉ membranes prepared from diethylmethylammonium compounds 2(12) and 2(10), and imidazolium compound 4(12) were comparable to that through the commercial UTC-60 membrane (Figure 4a). By contrast, the

Figure 4. Rejection rates and fluxes through the composite membranes for aqueous solutions of a) NaCl and b) MgSO₄. The maximum flux recorded for each membrane and rejection rate of the membrane are plotted. Conditions: operating pressure, 0.75 MPa; solution pH, 6.5; solution temperature, 25 °C; feeding rate, 3.5 L min⁻¹; NaCl concentration, 500 ppm; MgSO₄ concentration, 1500 ppm. a)Ref. [19]; b)Refs. [49] and [50].
Colh membranes prepared from trimethylammonium compound 3(12) and pyridinium compound 5(12) showed lower solution permeability than the Colh 2(12) membrane. The NaCl rejection with the Colh 3(12) membrane was similar to that of the Colh 2(2n) membrane, and NaCl rejection with the 5(12) membrane was lower than for these two membranes. These results suggest that the repulsion against NaCl and the affinity with water molecules of the Colh 5(12) membrane are weaker than those of the other LC materials used in the present study. The delocalized charge of pyridinium rings in the sub-nanopores may cause this lower repulsion against NaCl. The differences of the water permeability of the LC membranes indicated that the water permeation through inside of the ionic pores overwhelmed the permeation through the hydrophobic part.

The rejection properties of nonionic solutes through the LC membranes were measured to examine the sizes of the sub-nanopores (Table 3). The rejection rate of glucose (monosaccharide) with the Cubbi and Col LC membranes was less than 40%, although the molecular radius of glucose (0.37 nm)[52,53] is larger than the hydrated radius of Cl− (0.33 nm) or Na+ (0.36 nm). The rejection rates of sucrose (disaccharide) and raffinose (trisaccharide), which have larger radii than glucose, were higher than that of glucose but lower than that of NaCl. These results indicated that the rejection of ionic species by the LC membranes was a result of interaction between the ionic sub-nanopores and solute, and the sizes of the ions compared with the vacant space in the sub-nanopores. This comparison among saccharides also revealed that the permeation/rejection of nonionic solutes by the LC membranes was dependent on the ionic moieties on the LC molecules. The ionic sub-nanopores of 3(12), which consist of smaller ammonium moieties, showed higher rejection ability than those of 1(12) and 2(12). These results indicate that the volume of vacant space in the ionic nanochannels of 3(12) is smaller than that in other materials.

The efficient permeation of water and the higher rejection rate of NaCl than MgSO4 with the Colh membranes, such as the Colh 2(10) membrane, indicates that a large fraction of ionic sub-nanopores in the Colh structures fully span the membrane and water is mainly transported through the sub-nanopores. Formation of sub-nanopores from Col phases without any specific processes required for their alignment control is important for preparation of separation membranes that can effectively transport molecules and ions. There is a wide range of possible molecular designs for Col LC structures, whereas the range for Cubbi LC structures is rather limited.[45] This wider range for Col LC materials could be used to prepare membranes that exhibit highly selective separation, which is currently an important target. It is likely that the thickness of the LC films (~100 nm) enabled more efficient transport of water molecules than a thicker membrane would. Thinner Col film provides shorter columnar sub-nanopores between their surfaces than thicker Col films, which may decrease the possibility of the nanopores being discontinuous. It has been reported that Col channels in thinner films more frequently spontaneously align vertically than in thicker films.[54,55]

The solution flux for the membranes is inversely proportional to the length of the pores and proportional to the number of pores. The path length for water molecules in the sub-nanopores of the Cubbi structures is about twice that in the vertically aligned straight pores of the Col membranes. In addition, rough estimation based on X-ray diffraction (XRD) measurements suggests that the number of ionic liquid crystalline pores in the Colh membranes would be similar to or slightly larger than in the Cubbi membranes (Table S1, Supporting Information). These results indicate that a higher solution flux though the Col membranes could be obtained if homeotropical alignment in the Col structure increased.

### Table 3. Rejection of nonionic solutes and NaCl by the LC composite membranes.

| Solutea) | Stokes radiusb) [nm] | Rejection rates with the LC membranes [%] |
|----------|----------------------|-----------------------------------------|
|          | 1(12) | 1(14) | 2(10) | 2(12) | 3(12) | 4(12) |
| glucoseb) | 0.37  | 17    | 7     | 12    | 18    | 34    | 19    |
| sucroseb) | 0.47  | 19    | 11    | 22    | 34    | 57    | 33    |
| raffinoseb) | 0.58  | 30    | 20    | 33    | 43    | 72    | 54    |
| NaCl (aq.) | Na+, 0.36 | 67  | 68    | 71    | 72    | 74    | 65    |
| Cl− (aq.) | 0.33 | 67    | 68    | 71    | 72    | 74    | 65    |

a)Glucose, sucrose, and raffinose were all used at 1000 ppm.
the transport of water molecules and ions in LC polymer membranes with sub-nanopores of uniform sizes and structures.

In this simulation, we focused on the stable structure of the assembled ammonium moieties forming the ionic nanopores and their effects on the transport properties of water molecules and ionic solutes. Triethylammonium (compounds 1(\(n\))), diethylmethyllummonium (compounds 2(\(n\))), and trimethylammonium (compound 3(\(n\))) moieties were examined for the LC monomers (Figure S12 and Table S2, Supporting Information). The alkoxy chains in the hydrophobic part of the LC monomers were eliminated and differences between 1(12) and 1(14) or 2(10) and 2(12) were not considered. The simulation method for stable structures of the ionic nanopores is described below and further details are given in the Supporting Information (Figure S13, Supporting Information). First, we supposed an LC tetramer layer was composed of four monomers, which were arranged radially in positions rotated by 90° so that their ammonium moieties were oriented toward the center of the layer. For simplicity, Cl\(^-\) was applied as an anion instead of BF\(_4^-\). Next, four of the LC tetramers were stacked in the direction normal to the layer (the z-axis direction) to construct an ionic nanopore. In the assembly, the second and forth layers were rotated by 45° around the center to form a close-packed structure. The distance between the layers was fixed at 0.45 nm, which corresponds to the alkyl chain spacing. Then, several assemblies with different pore sizes were prepared by changing the distance, \(R\), between the centers of the tetramer layer and the benzene ring of each LC monomer. Finally, an MD simulation for the energy minimization was performed for each assembly with 16 anions to obtain the stable structure of the nanopore at each \(R\). During the simulation, the benzene rings of the LC monomers were fixed at their initial positions.

Figure 5a shows the potential energy, \(U\), for the stable structure of the LC assembly as a function of \(R\) for 1(n)–3(n). The minimum \(U\) occurred at \(R = 1.0\) nm for 1(n), \(R = 0.95\) nm for 2(n), and \(R = 0.825\) nm for 3(n). Figure 5b shows the stable structures of the assemblies that provided the minimum energy structures. These results suggest that the centers of the ionic nanopores of compounds 1(n) and 2(n) have more vacant space than in compound 3(n).

For each of 1(n)–3(n), using the minimum energy structure of the assembly, an MD simulation was performed to examine the movement of water molecules and ions in the ionic sub-nanopores (for details see Section S5, Supporting Information). The MD simulation was performed for a system in which two copies of the assembly were stacked on the z-axis so that the length of the channel was twice that of a single assembly. Water molecules, Na\(^+\) ions, and Cl\(^-\) ions were put into the sub-nanopore. The number of water molecules in the pore was determined using a grand canonical Monte Carlo (GCMC) simulation. In the GCMC simulation, the chemical potential was set by assuming that a pressure of 1 atm was applied to the system. The mobilities of the water molecules and ions in the sub-nanopores were examined by analyzing the root-mean-square displacement, \(\langle \Delta r^2 \rangle\). The temperature was maintained at 298 K during the MD simulation.

Figure 5c shows the \(\langle \Delta r^2 \rangle\) as a function of time, \(t\) for water molecules, Na\(^+\) ions, and Cl\(^-\) ions. The increase in \(\langle \Delta r^2 \rangle\) with increasing \(t\) indicated that self-diffusion occurred, and the slope of the \(\langle \Delta r^2 \rangle\) function was proportional to the self-diffusion coefficient. The larger the self-diffusion coefficient of a species means the higher the mobility of the species. From the results (Figure 5c), it was obvious that the water molecules were more mobile than Na\(^+\) and Cl\(^-\) ions in the ionic sub-nanopores of 1(n)–3(n). Notably, the mobilities of water molecules and the ions were lower for 3(n) than for 1(n) and 2(n). These results are consistent with the NaCl rejection rates for the LC membranes prepared from 1(12)–3(12), and the lower water permeability of the Colh 3(12) membrane compared with the other LC membranes.

The different mobilities of ions and water molecules in the sub-nanopores of compounds 1(n), 2(n), and 3(n) could be caused by different volumes of vacant space in the pores and differences in the interactions between the solute ions and the ammonium moiety. In this simulation, the mobility of water molecules in the nanopores of compound 3(n) increased if \(R\) of the nanopores was changed to 0.875 nm (Figure S14, Supporting Information). This result suggests that the different mobilities of water molecules for compounds 1(n)–3(n) originated from the difference in the volume of vacant space in the nanopores. By contrast, the mobility of the ions did not change much even if \(R\) was changed to 0.875 nm. Thus, we speculate that the difference in the mobility of the ions for compounds 1(n), 2(n), and 3(n) originated from differences in the interactions between the ions and the ammonium moiety.

3. Conclusion

To develop efficient water treatment membranes, wedge-shaped ammonium, imidazolium, and pyridinium molecules containing polymerizable moieties were prepared. These organic ionic compounds form Cubh and Colh phases depending on the structure of the cationic moiety and the alkyl chain length. The LC states of these compounds are successfully preserved by photopolymerization. These membranes function as sub-nanoporous membranes for water treatment. Permeation tests using the composites membranes prepared from the LC monomers revealed that 3D interconnected sub-nanopores of the Cubh structures and 1D sub-nanopores of the Colh phase span the membranes, and no procedures are required for control of their alignment. Membranes prepared from monomers with smaller quaternary ammonium moieties show lower permeability to water molecules, ions, and saccharides than membranes prepared with larger ammonium moieties. The assembled structures of the LC compounds were examined using MD simulations. The simulation results indicate that the lower permeability of nanopores composed of smaller ammonium moieties is mainly caused by the smaller volume of vacant space in the ionic pores compared with that in membranes prepared with larger ammonium moieties.

4. Experimental Section

Materials and Methods: Liquid-crystalline properties were examined by an Olympus BH-51 optical polarizing microscope equipped with a Mettler FP82HT hot-stage or a Linkam LTS150 hot-stage. Differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 Phoenix system at a cooling rate of 5 °C min\(^{-1}\). NMR
Figure 5. Simulation of ionic nanopores. 

a) Potential energy ($U$) for the stable structure of the assembly as a function of the distance between the centers of the tetramer layer and the benzene ring ($R$) for 1(n), 2(n), and 3(n). The vertical axis represents the potential energy difference $\Delta U = U - U_{\text{min}}$, which is the minimum $U$ estimated for each compound ($U$ at $R = 1.0$ nm for 1(n), $R = 0.95$ nm for 2(n), and $R = 0.825$ nm for 3(n)). 

b) The stable structures of the assemblies for 1(n)–3(n). The alkyl chains, and H atoms of the LC monomers are not shown. 

c) The root-mean-square displacement, $\langle dr^2 \rangle$, as a function of time, $t$, for water molecules, Na$^+$ ions, and Cl$^-$ ions in the ionic sub-nanopores of 1(n)–3(n).
spectra were recorded using a JEOL JNM-ECA400 at 400 MHz for $^1$H NMR and at 100 MHz for $^{13}$C NMR in CDCl$_3$. Chemical shifts of $^1$H and $^{13}$C NMR signals were quoted to internal standard Me$_4$Si ($\delta = 0.00$) and CDCl$_3$ ($\delta = 77.00$), respectively, and expressed by chemical shifts in ppm ($\delta$), multiplicity, coupling constant (Hz), and relative intensity. Elemental analyses were carried out on a CE-440 Elemental Analyser (Exeter Analytical Inc.). XRD patterns were obtained by a Rigaku RINT-2500 diffractometer with a heating stage using a Ni-filtered CuK$_\alpha$ radiation. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF-MS) were taken on a BRUKER autoflexTM speed spectrometer using dithranol as the matrix. UV irradiation was performed with a UV-LED CCS HLDL100U system or a high-pressure mercury lamp.

**Synthesis of LC Monomers and Preparation of Membranes:** Synthetic routes of the LC monomers and their details were described in Scheme S1 and the Supporting Information. All reagents of the highest quality were purchased from Aldrich, Kanto, Tokyo Kasei, or Wako, and were used as received.

The porous polysulfone layer and LC composite membranes were prepared using established methods.$^{[1-2,3]}$ For compounds 1(12), 1(14), and 2(10), the LC monomer on the polymer support was heated at a temperature 20 °C higher than the isotropization temperature of each compound, and then cooled to 10 °C. After cooling, UV light was irradiated to the LC monomer film on a polymer substrate using high-pressure mercury lamp or the CCS LED lamp at 30 °C for 10 min. For compounds 2(12) and 3(12)–5(12), the composite was heated at 80 °C and then cooled to room temperature. After cooling, UV light was irradiated at room temperature for 10 min.

**Performance Test:** Rejection/permeation performances of the composite membranes were tested as follows.$^{[19,20,22]}$ Membrane discs of 7 cm in diameter were set into cross-flow filtration cells of custom-made equipment. An aqueous solution of each solute was supplied to the membranes under an operating pressure 0.75 MPa to perform membrane filtration. The temperature and the pH of the feed solution were controlled to be 25 °C and 6.5, respectively. The feed and permeate water were sampled after the operation continued for more than 3 h for stabilizing membrane performance. This procedure using each solute was executed one by one. The salt rejection rate was calculated based on the electrical conductivity of the feed and permeate water, which was measured using pH/EC METER WM-50EC (DKK-TOA Corp.). Rejection rate of nonionic solute consisting of a single component was calculated from the concentrations in the feed and permeate water measured by differential refractometer (SHIMADZU RID-6A).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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