



Semipermeable membranes based on polybenzimidazole: Simultaneous improvement in water flux and salt rejection by facile cross-linking



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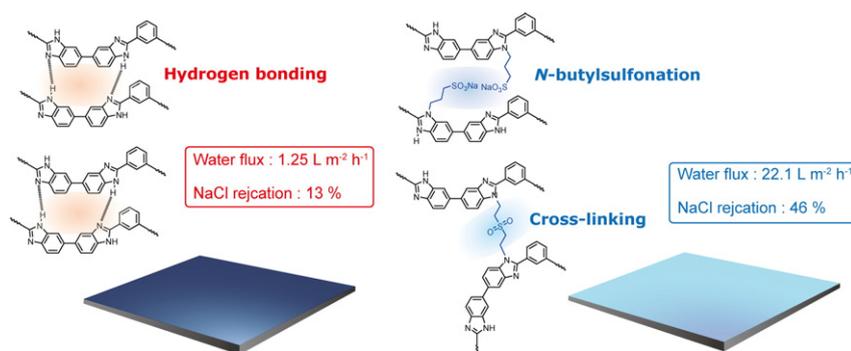
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HIGHLIGHTS

- Semipermeable membranes based on polybenzimidazoles (PBIs).
- Cross-linking and *N*-substitution induced the suppression of the hydrogen bondings.
- Facile thermal cross-linking of PBI membranes improved their water flux and salt rejection.

GRAPHICAL ABSTRACT



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ABSTRACT

To develop next-generation high-performance semipermeable membranes, novel semipermeable membranes based on the cross-linked polybenzimidazole have been synthesized and characterized. Polybenzimidazole with *N*-butylsulfonate (BSPBI) was prepared by the two steps, that is, deprotonation of PBI using lithium hydride, followed by treatment with 1,4-butanediol sulfonate. FTIR measurements showed that the *N*-substitution and cross-linking suppressed the hydrogen bonding. WAXD analyses also revealed that polymer packing was disrupted by the *N*-substitution and cross-linking. These results clearly indicate that the suppression of hydrogen bonding induced by the *N*-substitution and the cross-linking cause disruption of the polymer packing. The cross-linking reaction of BSPBI with divinyl sulfone led to the change of the pore size distribution, where the selective permeation of water molecule was successfully achieved. As a result, simultaneous improvement in water flux and salt rejection was achieved by the facile cross-linking reaction. The cross-linking of BSPBI simultaneously improved both water flux and salt rejection (water flux: 22.1 L m⁻² h⁻¹ and NaCl rejection: 46%) compared to those of non-cross-linked BSPBI (water flux: 1.88 L m⁻² h⁻¹ and NaCl rejection: 11%). These findings should contribute to develop high-performance semipermeable membranes for water treatment including reverse osmosis (RO), forward osmosis (FO), and pressure retarded osmosis (PRO).

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1. Introduction

Pressure retarded osmosis (PRO) is expected to be one of the energy recovery systems in conjunction with a seawater desalination plant [1–3], energy generation system [4], and so forth. Up to the present, two kinds of basic polymers have been used as PRO membrane materials, such as cross-linked aromatic polyamides (PA) and cellulose triacetates (CA) [5,6]. However, these membranes have the following problems when used in the PRO process.

Although the cross-linked PA flat sheet membrane shows a relatively high water flux and NaCl rejection, the internal concentration polarization (ICP), which is due to the dense and thick support layer, significantly reduces the available osmotic driving force and depresses the water flux across the membrane in the PRO process. Moreover, it is difficult to address this problem due to the structural problem of a spiral element, in which the feed water cannot be forced to flow inside the envelope composed of flat sheet membranes for reducing the ICP [7]. On the other hand, the CA hollow fiber membrane module allows the feed water and draw solution to flow on both sides of the membrane, thus there is no need for a thick support layer. These features are favorable for reducing the ICP and more practical in the PRO process. Actually, the TOYOBO CA hollow fiber membrane module shows higher results than the cross-linked PA flat sheet membrane in the energy recovery system used in the “Mega-ton Water System” project [8]. However, its result was not sufficient enough to realize an energy generation system due to the low water flux of the CA hollow fiber. Therefore, a new material, which has a higher water flux than CA, is needed. In the present study, alternative membrane materials for water treatment, including not only PRO process but also reverse osmosis (RO) and forward osmosis (FO) processes, have been investigated.

Polybenzimidazole (PBI) is expected to be one of novel membrane materials because of its high water absorbability, mechanical properties, thermal stability, and chemical stability over a wide range of pH values. Additionally, PBIs having a strong basic constant ($pK_b = 5.5$) become self-charged in an aqueous environment, because an adjacent benzene ring delocalizes the proton of the imidazole group [9]. Meanwhile, the hydrogen bonding between the imidazole rings is so strong that the PBI membranes become dense and produce low water transport properties [10]. Therefore, it is necessary to suppress the polymer/polymer interaction and to disrupt the polymer chain packing for the enhancement of the water flux of the PBI membranes [11]. It is well known that suppression of the hydrogen bonding in the amide linkage of aromatic condensation polymers affects the interplanar spacing, crystallinity, solubility, and transport properties [12–15]. Our previous study revealed that incorporation of the *N*-methyl amide linkage into the aromatic PA membranes suppressed the hydrogen bonding, prevented the polymer chain packing, and increased the water flux while decreasing the salt rejection [12]. In the case of PBI, Kharul et al. reported that the *N*-substitution of the PBI designed for suppressing the hydrogen bonding and for inhibiting the polymer chain packing enhanced the permeability for various gases because of the increase in diffusivity [16]. Therefore, the *N*-substitution of PBI would be an effective way to increase the water flux.

In addition, it is generally accepted that the chemical cross-linking usually induces an enhancement of the salt rejection and a decrease in the water flux [17,18]. For example, Wang et al. reported that the cross-linking of PBI membranes by *p*-xylylene dichloride improved the NaCl rejection while decreasing the water flux due to the formation of smaller pores induced by the high cross-linking density [19]. However, this expectation is not always acceptable and there would be an improvement in the salt rejection without a reduced water flux. Indeed, the cross-linking of some polyimides used for gas permeable membranes can increase in the permeability without sacrificing the selectivity [20,21]. As has been discussed in a previous report by Lee et al., the improvement of the gas permeability with maintaining the gas selectivity was achieved in the cross-linked and thermally-rearranged

poly(benzoxazole-co-imide) membranes, wherein the increase in the pore radius (from 0.82 to 0.97 nm) was induced by the elimination of the hydrogen bonding among the cross-linked polymer chains [22]. Thus, we expected that the introduction of the cross-linked structure into PBI membranes would improve the salt rejection without decreasing the water flux by formation of appropriate water channels along with reduction of the hydrogen bonding. Thus, 50% of the $-NH-$ groups in the imidazole rings of PBI were substituted to butyl or butylsulfonate groups to suppress the hydrogen bonding and to compare the effects of the hydrophilicity on water and NaCl transport properties with the pristine PBI. Furthermore, the PBI was cross-linked with divinyl sulfone by thermal treatment, which is expected to make the polymer/polymer interaction looser.

Herein, we report the development of an ultrathin membrane based on the cross-linked PBI. In addition, the effects of the *N*-substitution as well as cross-linking of PBI on the water flux and NaCl rejection are described in detail. The cross-linking reaction of the *N*-substituted PBI led to a change in the pore size distribution from unimodal (0.25–0.33 nm) to bimodal (0.15–0.24 nm and 0.25–0.37 nm) in which the selective permeation of water molecules was successfully achieved.

2. Experiment

2.1. Materials

Isophthalic acid, 1,4-propanesultone, 1-bromobutane, and divinyl sulfone were purchased from TCI, Japan. *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), acetone, hydrochloric acid, sodium bicarbonate, and lithium hydride were purchased from Wako Pure Chemical Industries. Polyphosphoric acid (PPA) was purchased from Sigma-Aldrich. Poly(*p*-phenylenebenzimidazole) (PBI) was synthesized by the polycondensation of 3,3'-diaminobenzidine and isophthalic acid in PPA according to the reported procedure [23,24].

2.2. Synthesis of *N*-butylsulfonated PBI (BSPBI)

A 200 mL two-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with PBI (5.05 g, 16.4 mmol) and DMAc (80.0 mL) under a nitrogen atmosphere. The flask was immersed into an oil bath and the mixture was heated at 85 °C. After dissolution of the PBI, lithium hydride (1.29 g, 163 mmol) was added and the solution was stirred for 3 h. 1,4-butanediol (2.23 g, 16.4 mmol) was added to this solution and the solution was stirred for 24 h at 85 °C. Then, the solution was poured into a large amount of acetone to yield the brown fibrous polymer. The obtained polymer was filtered off, washed thoroughly with acetone, and dipped in a 10 wt% NaHCO_3 aqueous solution for 24 h. Then, the polymer was filtered off, washed with water, and dried in vacuum oven for 24 h at 120 °C.

Yield: 7.32 g (96%). $^1\text{H NMR}$ (300 MHz, $\text{DMSO}-d_6$, δ , 40 °C): 9.13–7.72 (m, 10H), 4.46 (s, 2H), 1.95 (s, 4H), 1.68 (s, 2H). IR (Film), ν (cm^{-1}): 1631 (C=N stretching), 1182 ($-\text{SO}_3\text{Na}$ asymmetric stretching), 1043 ($-\text{SO}_3\text{Na}$ symmetric stretching).

2.3. Synthesis of *N*-butylated PBI (BPBI)

The title compound, BPBI, was synthesized by the same procedure as the BSPBI performed with lithium hydride (1.29 g, 163 mmol), DMAc (80 mL), 1-bromobutane (2.23 g, 16.3 mmol). Yield: 5.91 g (99%). $^1\text{H NMR}$ (300 MHz, $\text{DMSO}-d_6$, δ , 40 °C): 9.18–7.58 (m, 10H), 4.32 (s, 2H), 1.74 (s, 2H), 1.20 (s, 2H), 0.78 (s, 3H). IR (Film), ν (cm^{-1}): 2959 (alkyl C–H stretching), 1620 (C=N stretching).

2.4. Preparation of non-cross-linked PBI membranes

10 wt% solutions of the PBIs were prepared in DMSO by heating at 180 °C for 6 h. Then, the polymer solutions were filtered with a

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