Effect of Primary Structure on Permselectivity of Ultrathin Semipermeable Polybenzimidazole Membrane

Motohiro Aiba,[1] Takahiro Tokuyama,[2] Hidetoshi Matsumoto,[1] Hiroki Tomioka,[2] Tomoya Higashihara,[3] Mitsuru Ueda[3]

[1]Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152–8552, Japan
[2]Toray Industries Inc., Otsu, Shiga 520-0842, Japan
[3]Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa City, Yamagata 992–8510, Japan
Correspondence to: M. Ueda (E-mail: ueda.m.ad@m.titech.ac.jp)

ABSTRACT: A series of polybenzimidazoles (PBIs) with different main chains and sulfonated PBI were successfully synthesized from the corresponding dicarboxylic acids and 3,3'-diaminobenzidine for the formation of ultrathin, single-component, and semipermeable membranes. Furthermore, the covalently crosslinked PBI membrane was prepared by the reaction of sulfonated PBI with divinyl sulfone. Their water transport properties were evaluated under a reverse osmosis mode and compared with the primary structure based on the water permeability (A) and salt permeability (B) values normalized by the membrane thickness. It was found that the A and B values of the PBIs were improved with increasing the weight ratio of the imidazole rings per repeating unit, the introduction of sulfonate group as the hydrophilic group to the PBI was an effective way to enhance the A value, and the crosslinked structure enhanced the salt rejection rate (R) value while maintaining the water flux. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41531.

INTRODUCTION

The separation of water from aqueous solutions using semipermeable membranes has been studied over the past half century.[1,2] During this time, a pressure-driven membrane separation, such as nanofiltration (NF) and reverse osmosis (RO), has become popular for removing undesired solutes from aqueous solutions.[3,4] These purification systems have been employed in the field of water treatment, namely for filtration and desalination. However, the pressure-driven process, especially in the RO desalination, requires a significant hydraulic pressure to overcome the osmotic pressure of the source waters. This leads to their high operating cost, which is the main drawback of the pressure-driven membrane process. On the other hand, the forward osmosis (FO) is an osmotic-driven process based on an osmotic pressure difference across semipermeable membranes, in which a water molecule permeates through the membrane from a low-concentration solution to a high-concentration solution. Using the FO membrane application, pure water can also be easily obtained from a diluted solution by separation of the dissolved solute.[5,6] It was noted that an FO membrane can also be applied to an energy recovery system

known as pressure retarded osmosis (PRO) suggested by Loeb.[7] Thus, the studies to develop FO membranes with a high water transport property have been widely conducted.[8–12] All of the membrane applications require a high water flux and salt rejection to improve their efficiency.

Many studies concerned with semipermeable membranes focused on the cellulose triacetate (CTA) asymmetric membrane and the crosslinked polyamide (PA) thin-film composite membrane. However, the CTA membrane has a relatively low water permeability and salt rejection in addition to a biodegradability, which limits its use for membrane applications.[13] On the other hand, crosslinked PA membranes showed better transport properties and more stable to microbiological attack than the CTA ones. However, the main obstacle to using the crosslinked PA thin-film composite membrane is its chlorine instability, which leads to an irreversible performance loss over time.[3,14,15] Chlorine is the most widely used oxidizing biocide in water treatment because of its low price and high effectiveness. Thus, when the crosslinked PA thin-film composite membrane is used for the desalination process, it requires expensive dechlorination and rechlorination treatment steps. To overcome this severe
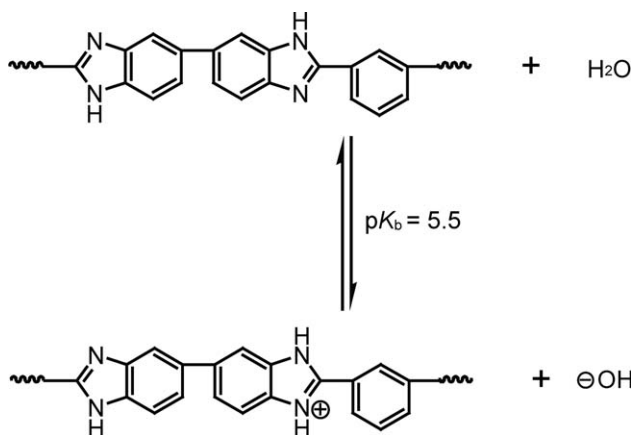
Figure 1. Charge property of PBI in an aqueous environment.

problem, new synthetic polymers designed to have a high tolerance to chlorine should be used as desalination membranes in order to remove the additional costly processes and to increase in membrane lifetime. McGrath et al. revealed that sulfonated poly(ether sulfone)s exhibited a high chlorine resistance due to the absence of amide linkages which are easily attacked by aqueous chlorine.[16] That is, polymers as membrane materials should not possess the vulnerable amide linkage. In addition, it has become obvious that the influence of the polymer structural characteristics on its transport properties should be studied to design alternative membrane materials for the CTA and crosslinked PA. An aromatic polybenzimidazole (PBI) without amide linkages in a polymer backbone is expected to be one of the strong candidates for highly chlorine-tolerant semipermeable membranes because of its high water absorptivity (absorbing water up to 13 wt %), thermal stability, excellent mechanical properties, and chemical stability over a wide pH range.[17,18] In the basic imidazole group of PBI molecules, the N-H unit acts as a hydrogen donor while the nitrogen with a lone pair behaves as a proton acceptor. In addition, PBIs have a strong basic constant ($pK_b = 5.5$) and may become self-charged in an aqueous environment because an adjacent benzene ring delocalizes the positive charge of the imidazole group as shown in Figure 1.[19] The charged property is expected to provide a high water transport property with its high hydrophilicity being preferable for antifouling. Based on such advantages, many papers have reported membranes based on PBIs, such as NF, FO, and PRO membranes.[20–24] The recent study by Wang et al. revealed that the chemical crosslinking of the –NH- group in the imidazole ring with p-xylene dichloride is an effective way to adjust the mean pore size and pore size distribution in a PBI asymmetric membrane.[22] They also reported that NaCl rejection depended on the pH due to the charge property of PBI. Escobar et al. studied the effect on the transport properties of the chemical modification of the –NH- group on the surface of FO asymmetric membrane using several different agents.[21,22] However, these studies were conducted using not the symmetric, but the asymmetric membranes prepared by the non-solvent induced phase separation method. Thus, there remains the issue to clarify the relationship between the primary structure of PBIs and transport properties of ultrathin semipermeable membranes based on the PBIs.

In this paper, we report in detail the relationship between the primary structure of the PBIs and the water and salt transport properties, by changing the polymer backbones, and introducing hydrophilic groups and crosslinked structures in order to establish the concept for designing the primary structure that would be useful in a variety of membrane applications.

EXPERIMENTAL

Materials

Isophthalic acid, 4,4′-dicarboxydiphenyl ether, 4,4′-dicarboxydiphenyl sulfone, 2,2-bis(4-carboxyphenyl)hexafluoropropane, hydroquinone, 4-fluorobenzonitrile, ethylene glycol, sulfuric acid, and divinyl sulfone, were purchased from TCI, Japan. N,N-Dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), acetone, hydrochloric acid, potassium carbonate, and sodium bicarbonate were purchased from Wako Pure Chemical Industries. Polyphosphoric acid was purchased from Sigma-Aldrich. 1,4-Bis(4-carboxyphenoxy)benzene and sodium 1,4-bis(4-carboxyphenoxy)-2-benzene sulfonate were prepared according to the previous report.[25] Phosphorus pentoxide/methanesulfonic acid (PPMA) was prepared according to the reported procedure.[18]

Synthesis of Polybenzimidazoles Having Various Repeating Units

Various polybenzimidazoles (**PBI1**, **PBI2**, **PBI3**, **PBI4**, and **PBI5**) having different repeating units were prepared by polycondensation between dicarboxylic acid including isophthalic acid, 4,4′-dicarboxydiphenyl ether, 4,4′-dicarboxydiphenyl sulfone, 2,2-bis(4-carboxyphenyl)hexafluoropropane, or, 1,4-bis(4-carboxyphenoxy)benzene, and 3,3′-diaminobenzidine, which is described in detail for PBI1 as a typical procedure. To a two-necked flask, isophthalic acid (1.66 g, 10.0 mmol) and polyphosphoric acid (74.5 g) were added under a nitrogen atomosphere. The flask was immersed in an oil bath and heated at 150°C with stirring. After complete dissolution of isophthalic acid, 3,3'-diaminobenzidine (2.14 g, 10.0 mmol) was added and the temperature was raised to 200°C. The solution was stirred for 24 h and then poured into water to obtain brown noodle-like polymer. The resulting polymer was filtered off, washed thoroughly with water and dipped in NaHCO3 aqueous solution for 24 h. Then, the polymer was filtered off and washed with water and dried in a vacuum oven for 24 h at 120°C.

PBI1: Yield 93%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, 40°C): 13.16 (s, -NH, 2H), 9.14 (s, ArH, 1H), 8.32 (d, $J = 7.4$ Hz, ArH, 2H), 7.91-7.61 (m, ArH, 7H).

PBI2: Yield 99%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, 40°C): 12.87 (s, -NH, 2H), 8.28 (d, $J = 8.5$ Hz, ArH, 4H), 7.95-7.57 (m, ArH, 6H), 7.30 (d, $J = 8.3$ Hz, ArH, 4H).

PBI3: Yield 93%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, 40°C): 8.44 (d, $J = 8.1$ Hz, ArH, 4H), 8.19 (d, $J = 8.1$ Hz, ArH, 4H), 7.87-7.57 (m, ArH, 6H).

PBI4: Yield 97%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, 40°C): 8.40 (d, $J = 7.9$ Hz, ArH, 4H), 7.93-7.62 (m, ArH, 10H).

PBI5: Yield 91%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, 40°C): 8.24 (d, $J = 8.6$ Hz, ArH, 4H), 7.84-7.54 (m, ArH, 6H), 7.34-7.21 (m, ArH, 8H).

Synthesis of Polybenzimidazoles with Sodium Sulfonate Group

A series of polybenzimidazoles with sodium sulfonate group (**PBI6-20**, where 20 means the feed molar percent of sodium 1,4-bis(4-carboxyphenoxy)-2-benzenesulfonate in dicarboxylic acid monomers) were synthesized by polycondensation from sodium 1,4-bis(4-carboxyphenoxy)-2-benzenesulfonate, 4,4'-oxybis(benzoic acid), and 3,3'-diaminobenzidine by controlling the molar ratio of dicarboxylic acid monomers. To a two-necked flask, sodium 1,4-bis(4-carboxyphenoxy)-2-benzene sulfonate (0.562 g, 1.25 mmol), 4,4'-oxybis(benzoic acid) (1.28 g, 5.00 mmol) and PPMA (60.7 g) were added under a nitrogen atomosphere. The flask was immersed into oil bath and heated at 120°C with stirring for 2 h. After completely dissolution of dicarboxylic acids, 3,3'-diaminobenzidine (1.35 g, 6.25 mmol) was added and the temperature was raised to 140°C. The solution was stirred for 4 h and then poured into water to obtain brown noodle-like polymer. The obtained polymer was filtered off, washed thoroughly with water and dipped in NaHCO$_3$ aqueous solution for 24 h. Then, the polymer was filtered off and washed with water and dried in a vacuum oven for 24 h at 120°C.

Yield: 97%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, 40°C): 8.30-8.27 (m, ArH, 3.6H), 8.18 (d, J = 8.2 Hz, ArH, 0.4H), 7.80-7.46 (m, ArH, 6.2H), 7.31 (d, J = 7.89 Hz, ArH, 0.2H), 7.24 (d, J = 8.1 Hz, ArH, 3.6H), 7.18-7.05 (m, ArH, 1.0H).

Preparation of Polybenzimidazole Membranes

10 wt % solutions of the obtained polybenzimidazoles were prepared in DMAc (for **PBI1**, **PBI2**, **PBI3**, **PBI4**, and **PBI5**) or DMSO (for **PBI6-20**) and stirred by a magnetic stirrer with heating until the homogeneous polymer solutions were obtained. After cooling to the room temperature, the polymer solutions were filtered with a 0.45 μm poly(vinylidene fluoride) membrane filter. Then, the polymer solutions were spin-coated onto a clean glass substrate to form as-cast membranes with <2.0 μm thickness. Subsequently, the as-cast membranes were heated at 70°C for 30 min and at 200°C for 1 h, immersed into water to be peeled off from the glass substrate, and stored in water. Finally, the obtained membranes were immersed into 10 wt % isopropanol aqueous solution for 15 min and into water for 15 min before evaluating their membrane intrinsic separation properties.

Preparation of Crosslinked Polybenzimidazole Membrane

10 wt % solution of **PBI6-20** was prepared in DMSO and stirred by a magnetic stirrer with heating until the homogeneous polymer solution was obtained. After cooling to the room temperature, divinyl sulfone (1.0 mol % to –NH- group in imidazole ring) was added to the polymer solutions and the obtained solution was filtered with a 0.45 μm poly(vinylidene fluoride) membrane filter. Then, the polymer solution was spin-coated onto a clean glass substrate to form as-cast membranes with <2.0 μm thickness. Subsequently, the as-cast membrane was heated at 70°C for 30 min and at 200°C for 1 h, immersed into water to be peeled off from the glass substrate, and stored in water. Finally, the obtained membrane was immersed into 10 wt % isopropanol aqueous solution for 15 min and into water

for 15 min before the evaluation of its membrane intrinsic separation properties.

Water Permeation Test

The procedure for water permeation tests of the membranes are described as follows. Membrane disks of 7 cm diameter were placed in the cross-flow filtration cells of custom-made equipment. Under an operating pressure of 0.75 MPa to perform membrane filtration, a 500 mg/L aqueous solution of NaCl was supplied to the membranes. The temperature and pH of the feed solution were maintained at 25°C and 6.5, respectively. Subsequently, the feed and permeate water were sampled after the operation had been continued for more than 3 h to stabilize the membrane performance. The salt rejection rate (R value) was calculated based on the electrical conductivities of the feed and permeate water measured by a WM-50EG pH/EC meter (DKK-TOA Corp.). The flow rate of the solution was 3.5 L/min. The water flux (Jw [m^3/m^2/day]), NaCl rejection (R [%]), water permeability (A value [μm^2/s/MPa]), and salt permeability (B value [μm^2/s]) are calculated using the following equations.

$$Jw = \frac{\Delta V}{S\Delta t}$$

$$R = \left(1 - \frac{C2}{C1}\right) \times 100$$

$$A = \frac{Jw \times l}{86400 \times (\Delta P - \Delta \pi)}$$

$$B = \frac{Jw \times l \times C2}{86400 \times (C1 - C2)} = \frac{Jw \times l \times (100 - R)}{86400 \times R}$$

where ΔV [m^3] is the volume of the permeate water, S [m^2] is the effective membrane area, Δt [day] is the time during water permeation, $C1$ is the salt concentration in the feed water, $C2$ is the salt concentration in the permeate water, l [μm] is the membrane thickness, ΔP [MPa] is the pressure difference across the membrane, and $\Delta \pi$ [MPa] is the osmotic pressure difference across the membrane. To clarify the relationships among the A value, B value, and R, R is also expressed by the following equation:[26]

$$R = 100 \times \left(1 + \frac{B}{A(\Delta P - \Delta \pi)}\right)^{-1}$$

Measurements

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker DPX300S spectrometer in DMSO-d_6 calibrated to tetramethylsilane as an internal standard (δ_H 0.00). FT-IR spectra were measured on a Horiba FT-720 spectrometer. Inherent viscosities were measured at 30°C in DMSO at a polymer concentration of 0.5 g/dL. The measurement of membrane thickness was performed using a Horiba spectroscopic ellipsometer. Dry densities of the dried membranes of PBI4 and PBI5 were measured on an Alfa Mirage SD-200L electronic densimeterat ambient temperature (24–25°C).

RESULTS AND DISCUSSION

Synthesis of Various Polybenzimidazoles

A series of PBIs with different repeating units (**PBI1**, **PBI2**, **PBI3**, **PBI4**, and **PBI5**), and the sulfonated random
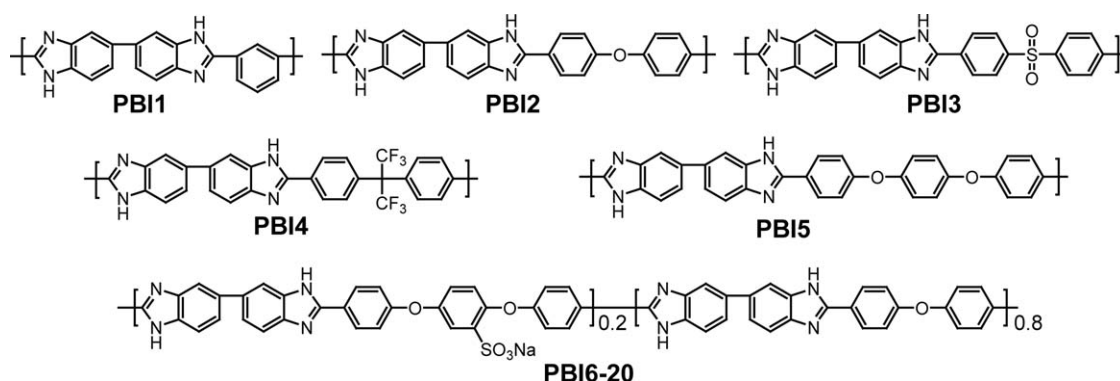
Figure 2. Chemical structures of **PBI1**, **PBI2**, **PBI3**, **PBI4**, **PBI5**, and **PBI6-20**.

copolybenzimidazole (**PBI6-20**) shown in Figure 2, were synthesized by the solution polycondensation of the corresponding dicarboxylic acids with 3,3'-diaminobenzidine. The chemical composition of **PBI6-20** was precisely controlled by the feed molar ratio of sodium 1,4-bis(4-carboxyphenoxy)−2-benzene sulfonate and 4,4'-oxybis(benzoic acid). The ^{1}H NMR spectrum shown in Figure 3 was employed to identify the molar ratio of the sodium 1,4-bis(4-carboxyphenoxy)-2-benzenesulfonate unit in the repeating unit for **PBI6-20**. In Figure 3, the integral ratio of the aromatic protons of sodium 1,4-bis(4-carboxyphenoxy)-2-benzenesulfonate unit and 4,4'-oxybis(benzoic acid) unit is in accordance with the expected chemical structure. The resulting PBIs were soluble in polar aprotic solvents, such as DMSO and DMAc, and had high molecular weights based on the measurement of inherent viscosity η_{inh} listed in Table I.

Effect of the Molecular Structure on the Water Transport Property

Previous our study revealed that ultrathin membranes (< 2 μm) based on wholly aromatic polyamides did not show water permeation phenomenon even if flexible ether linkage, bulky binaphthyl and fluorene units were introduced into the polymer backbones without hydrophilic substituents.[27] However, in the case of PBI ultrathin membrane, it is obvious that water permeation phenomenon was confirmed without introducing the hydrophilic groups into the polymer backbones (Table II). This result is probably due to the nature of the imidazole ring, which

makes PBI molecules self-charged in aqueous environment, resulting in the assistance for the formation of water transporting channels.[21] In order to compare water transport properties with primary PBI structures, the water permeability (A value) and salt permeability (B value) of all PBI membranes were normalized by membrane thickness. In spite of introducing flexible ether linkage into the polymer backbone, the A values of **PBI2** and **PBI5** were not improved and slightly decreased. Similarly, the A values of **PBI3** and **PBI4** were also lower than that of **PBI1**.

From the viewpoint of self-charged property, it can be expected that an increase in the weight ratio of the imidazole rings per a repeating unit leads to the increase in the number of the charged moiety. In the previous work, Escobar et al. have studied a difference of water permeability between PBI and N-substituted PBI.[21,24] Their observation revealed that the active proton in the imidazole ring mainly affected water flux, since the water flux of non-substituted PBI was higher than N-substituted PBIs under the pressure-driven nanofiltration process. Thus, the weight ratio of the imidazole rings per a repeating unit (WI) was calculated for each PBIs using the following equation:

$$ \text{WI } [\%] = \frac{Wi}{Wr} $$

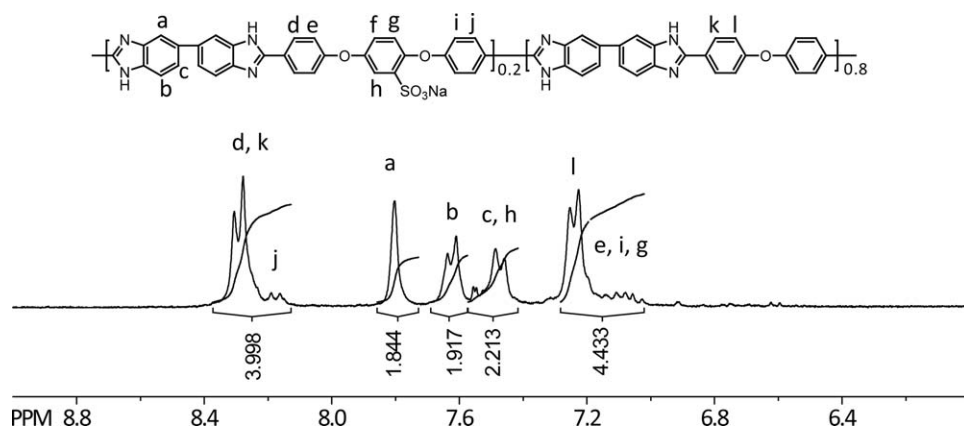where Wr and Wi are molecular weight of a repeating unit and imidazole rings in a repeating unit, respectively.

Figure 3. ^{1}H NMR spectrum of **PBI6-20**.

**Table I.** η_{inh} Values of Various PBIs

Polymer	PBI1	PBI2	PBI3	PBI4	PBI5	PBI6-20
η_{inh} (g/dL)	1.00	1.42	0.96	1.12	0.96	1.01

As shown in Figure 4, the both of A and B values increase with increasing the WI, which indicates that the active protons on the imidazole rings positively affect the water transport properties almost regardless of molecular rigidity and flexibility. In spite of the lowest WI value of **PBI4**, **PBI4** exceptionally showed the higher A value than **PBI5** probably due to the high free volume attributed to the steric hindrance of the hexafluoroisopropylidene diphenyl moiety. Indeed, **PBI4** shows lower dry density (1.22 g/cm^3) than that of **PBI5** (1.26 g/cm^3), which supports the high A value of **PBI4** is owing to its higher free volume than that of **PBI5**.

Effect of the Hydrophilic Group and Crosslinked Structure on Water Transport Properties

To further improve water permeability, the introduction of hydrophilic groups into the polymer backbone is one of the effective methods.[14,16,28–30] For example, thick single membranes (20–40 μm) based on disulfonated poly(arylene ether sulfone)[16,28,29] and sulfonated poly(arylene ether)[29] were previously studied and these membranes showed the improvement of water permeability according to the ratio of introducing hydrophilic groups into the polymer chains. These previous observations prompted us to study the effect of the hydrophilic group on water transport properties of PBI membranes. **PBI2** was selected as a polymer backbone due to its highest separation properties (see Table II). However, since the sulfonated **PBI2** prepared from 4,4′-oxybis(benzoic acid) and 4,4'dicarboxydiphenyl ether-2,2'-disulfonic acid disodium salt was known to yield insoluble gel due to the crosslinking between the sulfuric acid groups and the dicarboxylic moiety in the PBI.[31] Thus, sodium 1,4-bis(4-carboxyphenoxy)-2-benzenesulfonate was employed instead of 4,4'dicarboxydiphenyl ether-2,2'-disulfonic acid disodium salt to decrease the possibility of the crosslinking. **PBI6-20** was synthesized by the polycondensation of sodium 1,4-bis(4-carboxyphenoxy)-2-benzene sulfonated and 4,4'-oxybis(benzoic acid), with 3,3′-diaminobenzidine without gel formation.

Table III shows water transport properties of non-sulfonated polymer **PBI2** and sulfonated random copolymer **PBI6-20**, where 20 indicates the feed molar percent of sodium 1,4-bis(4-
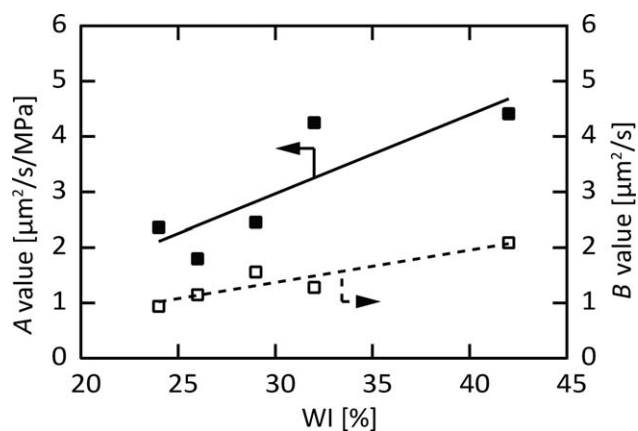
Figure 4. Effect of WI on A (left) and B (right) values.

carboxyphenoxy)−2-benzenesulfonate in dicarboxylic acid monomers). As expected, the improvement of water flux and the A value for **PBI6–20** is accomplished by the introduction of sulfonate group whereas the R and B values are depressed.

It is also well known that the introduction of the crosslinked structure into the polymer main chain affects the water permeability and salt permeability because the network structure of polymer chains suppress the transport of water molecules and salt through the membrane.[30,32] In this study, divinyl sulfone is employed as a crosslinker,[33] which can react with –NH- group of imidazole ring as shown in Figure 5 to produce the covalent bonds between the polymers unlike another crosslinking such as a hydrogen bonding and an ionic crosslinking. It is expected that the chemical modification of the N-H group in the imidazole ring may affect the self-charged property of PBI and thereby leads to a significant enhancement of water transport properties.[34,35] **PBI6-20** was chosen as a representative material due to the highest A value in this study.

Crosslinked PBI membrane was successfully prepared through the covalent crosslinking between divinyl sulfone and -NH-groups of imidazole rings. The obtained membrane was insoluble in DMSO, indicating that the crosslinking reaction successfully occurred. FT-IR spectra also supported the formation of covalent crosslinking. As shown in Figure 6, the absorption peaks at 1307 and 1130 cm^{-1}, assigned as the asymmetric and the symmetric stretchings of the sulfone (O=S=O), appear after the crosslinking reaction. In addition, the absorption peaks at 3421 and 3073 cm^{-1}, assigned to the stretching vibrations of the isolated N-H group and the hydrogen bonded N-H group,

Table II. Water Transport Properties of **PBI1**, **PBI2**, **PBI3**, **PBI4**, and **PBI5**

Polymer	WI (%)	l (μm)	Jw (m^3/m^2/day)	R (%)	A value (μm^2/s/MPa)	B value (μm^2/s)
PBI1	42	0.9	0.030	13	4.41×10^{-7}	2.09×10^{-6}
PBI2	32	1.3	0.020	19	4.25×10^{-7}	1.28×10^{-6}
PBI3	29	1.0	0.015	10	2.45×10^{-7}	1.56×10^{-6}
PBI4	24	1.2	0.012	15	2.36×10^{-7}	0.94×10^{-6}
PBI5	26	1.1	0.010	10	1.80×10^{-7}	1.15×10^{-6}

Table III. Water Transport Properties of PBI2, PBI6-20, and PBI6-20CL

polymer	l (μm)	Jw (m^3/m^2/day)	R (%)	A value (μm^2/s/MPa)	B value (μm^2/s)
PBI2	1.3	0.020	19	4.25×10^{-7}	1.28×10^{-6}
PBI6-20	0.8	0.045	8	5.89×10^{-7}	4.79×10^{-6}
PBI6-20CL	0.7	0.030	29	3.43×10^{-7}	0.60×10^{-6}

are intact after the crosslinking reaction. These observation indicates the hydrogen bonding between N-H groups does not become weak after the crosslinked reaction probably due to the low crosslinking density.[17,36] As described above, the protons located on the imidazole rings play an important role in the permeation of water. Thus, the effect of the protons in the imidazole rings on water transport properties would not be changed before and after the crosslinking reaction.

Table III shows the RO membrane performance of **PBI6-20** and **PBI6-20CL**. The crosslinked structure leads to the slightly decrease in the A value (3.27×10^{-7} μm^2/s/MPa) and large decrease in the B value (0.59×10^{-6} μm^2/s). Consequently, the enhancement of R value (29%) with maintaining the water flux (0.030 m^3/m^2/day) is achieved. Both of water and salt molecules are generally sensitive toward structural and conformational changes in the polymer by the crosslinking reaction due to the reduction of free volume. However, a salt molecule can be more restricted by crosslinked structure because a salt molecule is usually hydrated and shows larger the dynamic radius than water molecules.[28,37–39] Similar results have been previously reported by McGrath et al., where covalent crosslinking of disulfonated poly(arylene ether sulfone)s by the reaction of multifunctional epoxy agent with phenoxide end group improved R value while maintaining water permeability.[32]

The results obtained here suggest that the covalent crosslinking of sulfonated PBI is a promising method to prepare the
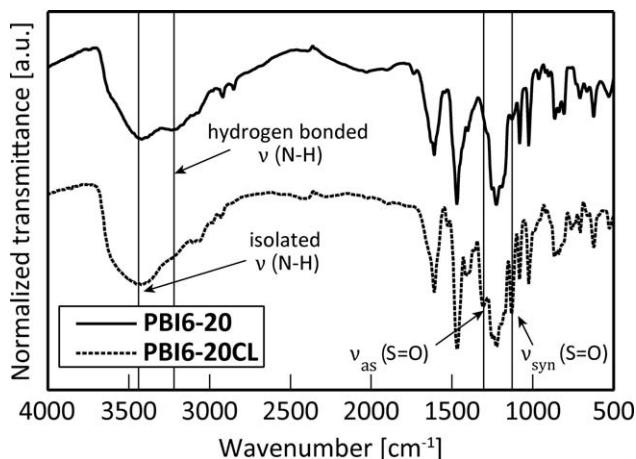
Figure 6. FT-IR spectra of **PBI6-20** and **PBI6-20CL**.

ultrathin semipermeable membrane with enhanced water transport properties.

CONCLUSIONS

The ultrathin membranes based on a series of PBIs (**PBI1**, **PBI2**, **PBI3**, **PBI4**, **PBI5**), and sulfonated PBI (**PBI6-20**) were prepared by the spin-coating method. Furthermore, covalently crosslinked PBI membrane (**PBI6-20CL**) was prepared by the reaction of **PBI6-20** with divinyl sulfone. Their water transport properties were evaluated under a reverse osmosis mode and compared with the primary structure using the A and B values normalized by membrane thickness. From the results of water permeation test, the relationship between water transport properties and primary molecular structure of PBI was concluded as follows. (1) The A and B values directly increased with increasing the weight ratio of the imidazole rings per a repeating unit. (2) The introduction of sulfonate group as the hydrophilic group into polymer backbone is effective way to enhance the A value. (3) The crosslinked structure led to the slightly decrease in the A value and large decrease in the B value, achieving the enhancement of the R value (29%) with maintaining the water flux (0.030 m^3/m^2/day).
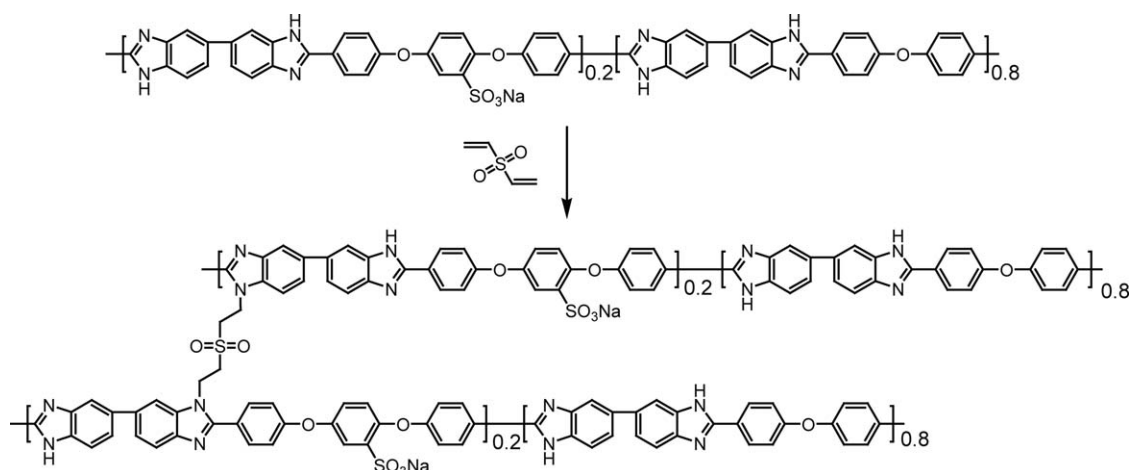
Figure 5. Crosslinking reaction of **PBI6-20** with divinyl sulfone.

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