NOTE

Preparation of robust RO membranes for water desalination by interfacial copolymerization of bis[(triethoxysilyl)propyl]amine and bis(triethoxysilyl)ethane

Dian Zhang[1] · Joji Ohshita [1]

Introduction

Water scarcity has been discussed as a global issue, and the development of an efficient strategy for water purification is needed [1, 2]. Reverse osmosis (RO) membranes are widely used and efficient for water purification in a variety of applications. At present, the most common desalination membranes are polyamide membranes. Polyamide membranes show favorable RO performance with excellent water permeability and salt rejection. However, they usually show low resistance to chlorine, which is often used to clean up biofouling on the membrane surface, and chemical reactions with chlorine result in membrane failure, although several approaches have been examined to improve stability [3–5]. In addition to the issue of chlorine resistance, polyamide membranes show low thermal stability, meaning they can be used only at temperatures lower than 45 °C.

In contrast, organically bridged polysilsesquioxane (PSQ) membranes have great potential with high thermal stability and chlorine resistance [6–8]. Findings on bridged PSQ membranes prepared from bis(triethoxysilyl)ethane (**BTESE**, in Fig. 1) have shown excellent stability during hydrothermal treatment and favorable resistance to chlorine [7]. Similar studies concerning bridged PSQ membranes have been carried out [9–12]. However, **BTESE**-based membranes showed lower water permeability, on the order of 10^{-13} m^3/m^2·s·Pa, in RO experiments using 2000 ppm NaCl solution compared with polyamide membranes, which showed a water permeance

(L_p) of 10^{-12}–10^{-11} m^2·s·Pa, although NaCl rejection (R) was sufficiently high (97–99%) [7].

In previous experiments, the sol–gel process with the hydrolysis/condensation of bridged alkoxysilanes has been employed to prepare bridged PSQ membranes. This is a multistep process including the preparation of precursor sols under careful control of the sol particle size and coating of the sols on a porous support, followed by calcination of the sol film again under careful control of the conditions (temperature and reaction period) to form fine gel membranes without defects. Recently, we introduced interfacial polymerization as an alternative method to provide fine PSQ membranes [13]. Interfacial polymerization could be performed simply by pouring a monomer solution onto a wet polymeric porous support, followed by calcination of the resultant polymer film, and has been proven to be more efficient and time-saving than the sol–gel process. Interfacial polymerization, however, presents some problems. For example, only certain kinds of precursors, such as **BTESPA** (structure shown in Fig. 1), that have an amine unit that works as a self-catalyst for polymerization can be used. In fact, a **BTESE** membrane prepared by interfacial polymerization demonstrated a low R of 57.3%, much lower than that of a **BTESE** membrane prepared by the sol–gel process [13]. **BTESPA** membranes have been prepared by interfacial polymerization and show good RO performance similar to that of membranes prepared by the sol–gel process [14]; however, these membranes still show rather low water permeability.

One approach to improve L_p involves the use of a rigid structure as a comonomer. For example, copolymerization of POSS-based alkoxysilane (**TESE-POSS**) with **BTESE** improved the water permeability by approximately two times relative to that of a homopolymer membrane of **TESE-POSS** [15]. Copolymerization of the acetoxy-containing monomer **BTESEAc** with **BTESE** also improved L_p without changing R [16].

✉ Joji Ohshita
   jo@hiroshima-u.ac.jp

1   Department of Applied Chemistry, Graduate School of
    Engineering, Hiroshima University, Higashi-Hiroshima 739-8527,
    Japan

Fig. 1 Structures of precursors of bridged PSQ membranes

BTESE

BTESPA

BTESEAc

TESE-POSS

(R = $(H_3CH_2CO)_3SiCH_2CH_2/CH_2=CH = 7/3$)

In this work, we studied the interfacial copolymerization of **BTESPA** and **BTESE** to enhance the water permeability. As expected, the copolymerization resulted in an ~10 times higher L_p than that of the **BTESPA** homopolymer membrane, while R was kept at nearly the same level.

Experimental section

Interfacial polymerization

The process of interfacial polymerization has been reported in the literature [13]. A support membrane (NTR-7430, pore size: 2 nm, Nitto Denko Corporation, Osaka, Japan) was washed with ethanol and dried in a 60 °C oven for 10 min. Then, a 0.15 wt% sodium dodecyl sulfate (SDS) aqueous solution was poured onto the support surface. After 5 min at room temperature to allow permeation of the SDS aqueous solution, the excess SDS aqueous solution on the surface was removed, and a 5 wt% hexane solution of two copolymerization precursors with a specified proportion was poured onto the wet support surface, which was then allowed to stand for 5 min at room temperature. The excess monomer solution was removed, and the membrane was calcined at 150 °C for 10 min for further polymerization. After cooling to room temperature, the membrane was washed with distilled water and used for subsequent RO experiments. The starting monomers **BTESPA** and **BTESE** were obtained from Fujifilm Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), respectively.

RO experiments

The RO experiments were performed using the device shown in Fig. 2. The RO device works by attaching a high-pressure pump on top of the device to apply feed pressure.

Fig. 2 Schematic diagram of the RO experimental device

A 2000 ppm NaCl aqueous solution was placed in the device at room temperature, and the amount of permeated liquid was noted. The salt concentrations of the feed and permeate were determined by measuring their conductivities by a conductivity meter (HORIBA ES-51). L_p and R were calculated as shown in Eqs. (1) and (2), respectively, where ΔP and $\Delta \pi$ are the differences in applied pressure and osmotic pressure, respectively, J_v is the permeate water flux, and C_f and C_p are the NaCl concentrations of the feed and permeate, respectively.

$$L_p = J_v/(\Delta P - \Delta pi) \tag{1}$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

Table 1 Summary of RO performance of interfacial polymerization membranes

Monomer		Molar ratio a/b	Method[a]	L_p [m^3/m^2·s·Pa]	R [%]
a	b				
BTESPA	**BTESE**	1/1	I	5.61×10^{-13}	92.0
		1/3	I	1.29×10^{-12}	91.9
		1/5	I	2.40×10^{-12}	88.3
BTESPA[b]	None		I	1.14×10^{-13}	93.6
BTESE[b]	None		I	6.61×10^{-12}	57.3
BTESPA[c]	None		S	1.1×10^{-13}	96

[a]Polymerization method. I: interfacial polymerization, S: sol–gel process

[b]Data from literature [13]

[c]Data from literature [14]

The chlorine resistance of the membranes was evaluated by immersing a membrane in a 100 ppm NaOCl aqueous solution at room temperature in a covered beaker at room temperature. After every 25 h, the membrane RO performance was evaluated as mentioned above. To avoid decreases in NaOCl concentration, the solution was replaced by a new one every 25 h. Membrane thermal stability was investigated by raising the feed solution temperature.

Results and discussion

Interfacial copolymerization and RO performance

In previous research, **BTESE** could not be used alone for interfacial polymerization, and the **BTESE** membrane showed a lower R (57.3%) than the **BTESPA** membrane but a higher L_p [13]. However, copolymerization with **BTESPA** proceeded smoothly to provide good RO membranes. Compared with **BTESPA** homopolymerization, the copolymerization of **BTESPA** and **BTESE** resulted in an increase in L_p in RO experiments, but R was decreased only slightly (Table 1). When the **BTESPA/BTESE** ratio was 1, L_p was increased by five times, but R decreased by 1.6% relative to that of the **BTESPA** homopolymer membrane. When the monomer ratio was dropped to 1/3, L_p was further enhanced by two times without decreasing R. With a ratio of 1/5, L_p was again improved by approximately two times; however, R was suppressed from 93.6 to 88.3%. The best data for the copolymerization membrane made from **BTESPA/BTESE** = 1/3 were comparable to those of sol–gel membranes, with a three to five times higher L_p but a lower R by ~5%. These results indicate that **BTESPA** can be copolymerized with **BTESE** to provide good RO membranes for water desalination.
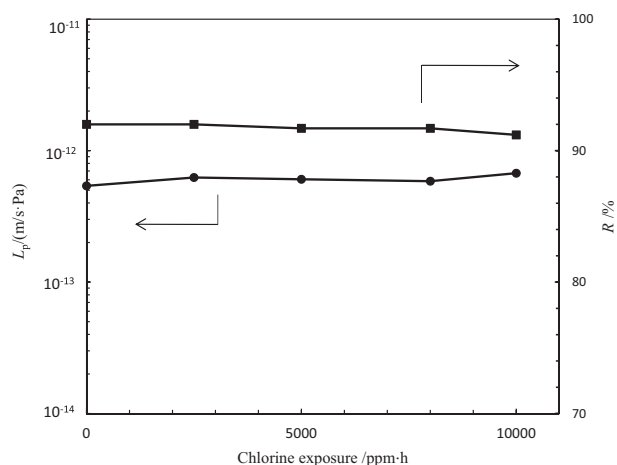

Fig. 3 Effects of exposure to 100 ppm NaOCl aqueous solution on L_p and R of copolymer (**BTESPA/BTESE** = 1/3) membranes

Chlorine resistance

The **BTESPA** homomembrane prepared by the interfacial polymerization process showed low chlorine resistance. Exposure of the **BTESPA** membrane to 100 ppm chlorine in water for 10 h decreased R by ~3%. Hoping that the rigidity of **BTESE** would increase the chlorine resistance of **BTESPA**-based RO membranes, we examined the chlorine resistance of the copolymer membrane. A membrane prepared from **BTESPA/BTESE** = 1/3 was immersed in a 100 ppm NaOCl aqueous solution, and the RO performance was examined every 20 h. As shown in Fig. 3, no evident changes in RO performance were observed even after an exposure time of up to 100 h (chlorine exposure = 10,000 ppm h), indicating the high resistance of the membranes toward chlorine exposure.

Thermal stability

The **BTESPA** homomembrane showed low thermostability: R decreased from 93 to 89% when the temperature was raised to 80 °C, and upon returning to room temperature, R could not recover. The thermal stability of copolymer membranes was investigated to determine the effects of **BTESE** units on membrane thermal stability. RO experiments were carried out using heated NaCl solution (2000 ppm), and the results are shown in Fig. 4. As the temperature was elevated, L_p increased to 2.37×10^{-12} m/s·Pa, which is approximately five times higher than the value at room temperature, likely due to the activated vibration of the PSQ network. When the solution was cooled to room temperature, the original L_p was almost recovered, indicating the high thermal stability of the copolymer membrane. During all heating and cooling processes, R had no significant change.

Fig. 4 Plots of L_p and R of copolymer (**BTESPA/BTESE** = 1/3) membranes using 2000 ppm NaCl solution at 25–80 °C
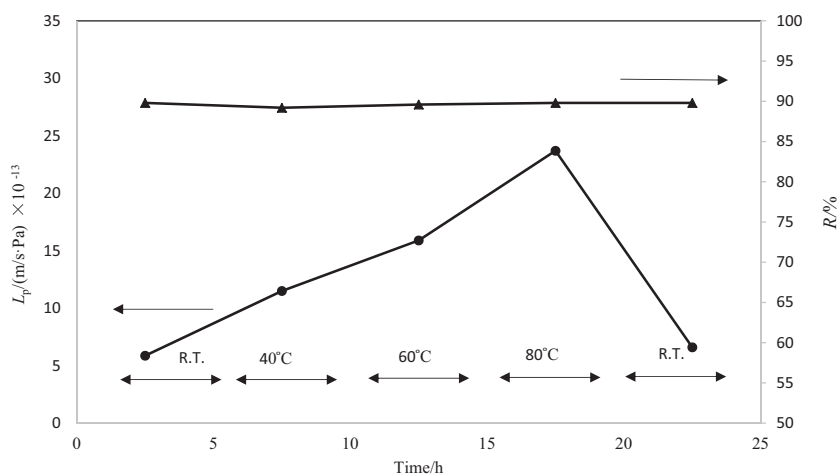
Conclusion

In conclusion, we copolymerized **BTESE** with nitrogen-containing **BTESPA**. Copolymerization with **BTESE** can remarkably increase L_p but slightly decreases R. It is speculated that **BTESE** may influence the degree of reaction and the pore size, which becomes larger as the **BTESE** ratio increases, resulting in an increase in L_p and a decrease in R. **BTESPA/BTESE** copolymerized membranes showed excellent resistance to chorine exposure at 10,000 ppm·h, and the RO performance had no obvious change. Good thermostability was also demonstrated during all processes of heating to 80 °C and cooling to room temperature, with no significant change in R. These results are indicative of the high potential of interfacial polymerization for the preparation of RO membranes for water desalination.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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