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## Preparation of hydroxyl group containing bridged organosilica membranes for water desalination

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## ABSTRACT

Organosilica membranes were prepared by homo- and copolymerization of hydroxymethyl(triethoxy)silane (HMTES) for the first time, and applied to reverse osmosis (RO) to investigate the effects of the hydroxymethyl group. Fourier transform infrared (FT-IR) spectrometry, thermogravimetric analysis (TGA), and water contact angle measurements of the membrane surface indicated that the C–OH group of HMTES underwent a condensation reaction with Si–OH to form an Si–O–C bond during the calcination at 300 °C. Upon RO experiments using a NaCl aqueous solution, the HMTES membrane exhibited a significant increase of the liquid permeance and a decrease of the NaCl rejection during the measurement, which arose from the hydrolytic cleavage of the Si–O–C bond to form Si–OH and C–OH groups upon contact with water. On the other hand, for a membrane derived from the copolymerization of HMTES and bis(triethoxysilyl)ethane (BTESE) in the weight ratio of 1:1, liquid permeance was increased gradually to reach a steady state of  $3.4 \times 10^{-13} \text{ m}^3/(\text{m}^2 \text{ s Pa})$ , and NaCl rejection was maintained at a value as high as 95.5%. Thermal stability and chlorine resistance of the membranes were also studied.

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### 1. Introduction

Polymer and ceramic membranes for gas and liquid separation have seen a surge in popularity [1,2]. Reverse osmosis (RO) membranes have been applied to simple desalination processes that involve the removal of salt from brackish or sea water, and are recognized as one of the most efficient tools to solve the water shortage problem [3–5]. Studies on RO membranes have focused on achieving higher water flux and salt (NaCl, etc.) rejection since the 1960s. Currently, thin films of aromatic polyamide are widely used as RO membranes because of their high water flux ( $>0.1 \text{ m}^3/\text{m}^2 \text{ d}$ ) and salt rejection ( $>99\%$ ) [6–8]. However, the amide linkage is labile to chlorine, which is often employed to prevent biofouling of the membrane surface. In addition, the polyamide membranes must be used at temperatures lower than 45 °C due to the low thermal stability. To resolve those issues, various alternative materials, such as organic polymers including cellulose acetates [9,10] and modified polyamides [11,12], zeolites [13,14], silicates [15,16], and their composite membranes [17,18], have been studied.

Polysilsesquioxanes (PSQs), which can be readily synthesized by hydrolysis and polycondensation, the so-called sol–gel process

of trialkoxysilanes, have been extensively studied as organic-inorganic hybrid materials [19,20]. The inorganic Si–O–Si framework in those materials gives rise to the high thermal stability and structural rigidity of the materials. At the same time, the structure of organic bridge is responsible for the materials' flexibility and processability. PSQs have been also studied as RO materials [21–25]. Recently, bridged PSQ membranes prepared by the sol–gel process of organically bridged trialkoxysilanes,  $[(\text{R}'\text{O})_3\text{SiR}(\text{OR})_3]$ , have been reported as promising precursors of robust separation membranes. The bridged PSQ membranes usually show high permeability compared to silica or non-bridged PSQ membranes, because the organic bridges expand the siloxane network as a “spacer” to enhance porosity [21–26]. Previously, we reported that silica materials prepared from bis(triethoxysilyl)ethane (BTESE) could be used as robust RO membranes because of their high chlorine tolerance and thermal stability up to 90 °C [23,24]. However, the liquid permeability is much lower than that of commercially available polyamide membranes. In our efforts to improve the water permeability, we found that the introduction of ethylene and ethynylene units in place of the ethylene bridge increased the water permeability by increasing the rigidity and polarity of the bridges [21,22]. The rigidity expands the siloxane network to provide even higher porosity, while the higher polarity leads to the better water affinity of the membrane.

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In this study, hydroxymethyl(triethoxy)silane (HMTES in Chart 1), which is readily available from a commercial source, was employed as a new silica membrane precursor, in hopes that the high hydrophilicity of the hydroxymethyl group would lead to even higher water permeability. The sol–gel process of HMTES alone or HMTES/BTESE mixtures provided the corresponding membranes that showed separation properties. Unlike Si–OH bonds that readily undergo dehydro coupling to form thermally stable Si–O–Si bonds almost irreversibly under the sol–gel conditions, C–OH groups react with Si–OH to give less stable C–O–Si linkages in equilibrium. Therefore, it is required to monitor the behavior of the C–OH groups carefully during the curing process for membrane preparation and RO experiments with an aqueous NaCl solution. Interestingly, the C–O–Si bonds were hydrolyzed by contact with the aqueous solution to increase the hydrophilicity of the membranes. For mixed membranes of HMTES/BTESE, the present process improved the water permeability without suppressing the NaCl rejection. Usually, silica membranes that are prepared by calcination of silica sol-coated films are rather hydrophobic. The results clearly indicate that the post-treatment of HMTES-containing membranes with water offers a new convenient method to increase the hydrophilicity of the silica membranes. Although homo- and copolymerization of HMTES giving the polymer gels have been studied, their utilities as separation membranes and post-hydrolysis of the polymers tuning the hydrophilicity have not yet been reported to our knowledge [27–30].

## 2. Experimental

### 2.1. General

Precursors HMTES (50% ethanol solution) and BTESE were obtained from Gelest Inc. and used as received. Sol particle sizes were measured in 5 wt% ethanol solution by means of dynamic light scattering (DLS) on a Malvern Zetasizer Nano (Malvern, ZEN3600) analyzer. Fourier transform infrared (FT-IR) spectra were measured with a Shimadzu IRAffinity-1 spectrometer using coating films on silicon wafer. Thermogravimetric analysis (TGA) was carried out on a SII EXSTAR TG-DTA6200 thermal analyzer in the temperature range of 100–1000 °C after keeping the sample at 100 °C for 30 min to remove adsorbed water. Contact angle measurements of water drops on the silica surface were performed with a Kyowa DM300 contact angle meter using coating films on silicon wafer. Solution conductivities were measured using a HORIBA ES-51 conductivity meter. Mechanical strengths of the film surface were examined according to the ASTM Standard D 3363-92 [31], using a TQC Wolff-Wilborn tester (COTEC) with pencils varying in hardness from 6B to 6H.

### 2.2. Sol–gel process

To an ethanol (5 wt%) solution of HMTES or HMTES/BTESE (0.25 g) was slowly added an HCl (aq) as the acidic catalyst in the HCl/alkoxysilane/H<sub>2</sub>O molar ratio of 1/10/900. The mixture was stirred for 12 h at room temperature to produce the sol, the

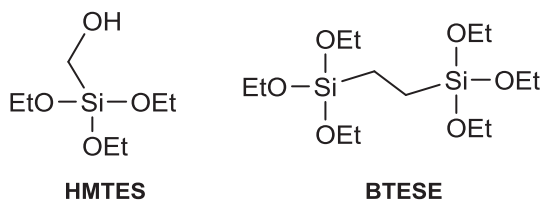


Chart 1. Chemical structures of alkoxysilanes investigated in this study.

size of which was measured by DLS, as presented in Fig. 1. The mixture was then diluted with ethanol to 0.25 wt% and preserved in a refrigerator until use. A gel powder was obtained by drying the sol at 60 °C in a glass vial, and a coating film was prepared by drop casting on silicon wafer. Then, the gel powder and the coating film were subjected to TGA, and IR spectrometry and water contact angle measurements, respectively.

A porous-alumina tubular support (NOK Corp., average pore size 150 nm, outer diameter 3 mm, length 50 mm) was coated five times with TiO<sub>2</sub> (ca. 30 nm average particle size, 0.72 wt% aqueous solution) and three times with SiO<sub>2</sub>–ZrO<sub>2</sub> (Si/Zr = 1, ca. 50 nm average particle size, 0.25 wt% aqueous solution). After each coating, the tubular support was heated at 550 °C for 15 min in air. At this stage, the average pore size distribution of the intermediate layer was evaluated to be less than 2 nm by nanoporometry [32,33]. The separation layer was prepared by coating the silica sol on the intermediate layer, followed by calcination at 300 °C in a nitrogen atmosphere.

### 2.3. Water permeability measurements

RO desalination measurements were performed using a 2000 ppm NaCl aqueous solution at 25 °C. The feed pressure of 1.0 MPa was applied with a plunger pump. Liquid permeance ( $L_p$ ) and NaCl rejection ( $R$ ) were calculated based on Eqs. (1) and (2), respectively, where  $\Delta P$  and  $\Delta\pi$ ,  $J_v$ , and  $C_f$  and  $C_p$  are, respectively, differences in applied pressure and osmotic pressure, permeate water flux, and NaCl concentrations of feed and permeate determined from their conductivities. Details of water permeability measurements are available in the literature [28].

$$L_p = J_v / (\Delta P - \Delta\pi) \quad (1)$$

$$R = (1 - C_p / C_f) \times 100 \quad (2)$$

### 2.4. Stability test of BT-HM50 membrane toward chlorine exposure

The chlorine stability of the membrane was evaluated with 10% NaClO (Aldrich). A chlorine solution was prepared at 100 ppm and pH was adjusted to 7 using a 0.2 M KH<sub>2</sub>PO<sub>4</sub> buffer solution. The membrane was periodically immersed in, and removed from, the chlorine solution, which was placed in a sealed, stirred, dark glass bottle. Their performance was then tested after a thorough rinse with deionized water.

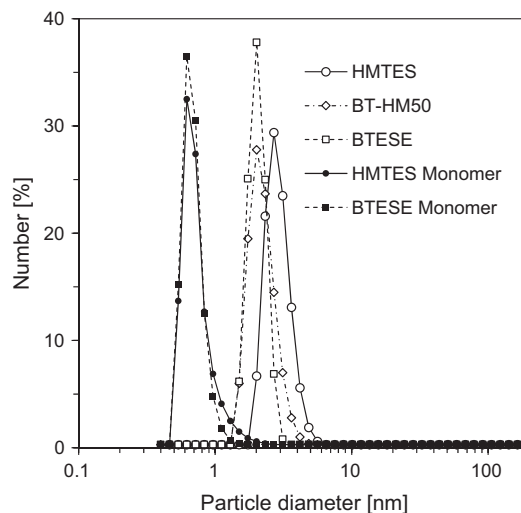


Fig. 1. Size distributions of monomers and sols determined by DLS.

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