

## 論文の要旨

題目 Development of Highly Water Permeable Robust PSQ-RO Membranes for Water Separation  
(高透水性有機シリカ逆浸透水分離膜の開発)

氏名 張典

The development of high-efficiency, low-cost seawater desalination technology is highly desired to resolve the problem of water scarcity. Water desalination by reverse osmosis (RO) membranes has been extensively studied and many types of membranes have been reported so far, including conventional polyamide membranes. Polyamide-based RO membranes are widely used in industry because of their excellent water permeability and high salt rejection. However, polyamide-RO membranes still have some problems including low resistance to chlorine and to high-temperature operation.

Organically bridged polysilsesquioxanes (PSQs) that can be easily prepared via the hydrolysis/condensation reaction (sol-gel (SG) process) of bridged alkoxysilanes have attracted much attention as robust organic-inorganic hybrid materials due to their three-dimensional thermally stable but flexible siloxane (Si-O-Si)-based frameworks. Organically bridged PSQs can be used as RO membrane materials with high stability to heat and chlorine treatment. In the previous work, it was demonstrated that organically bridged PSQ-RO membranes derived from the SG process using precursors such as bis(triethoxysilyl)ethane (BTESE) and bis(triethoxysilylpropyl)amine (BTESPA) exhibited excellent salt rejection, favorable thermal stability, and high chlorine resistance. However, these membranes present insufficient water permeability on the order of  $10^{-13}$  m<sup>3</sup>/m<sup>2</sup>sPa, which is more than 10 times lower than that of commercial polyamide-based RO membranes. Therefore, it is necessary to develop strategies to improve the water permeability of PSQ-RO membranes. In this work, four new strategies to improve the water permeability of PSQ-RO membranes were studied.

In Chapter 1, the author optimized the bridging structures of alkoxysilane monomers in the membranes. According to the previous work in the literature, rigid and polar organic bridging structures tend to increase water permeability. For example, membranes derived from bis(triethoxysilyl)ethene (BTESE2) and bis(triethoxysilyl)ethyne (BTESE3) exhibit higher water permeability than BTESE-based membranes. In the present work precursors with three reactive ethoxysilyl units: tris[(triethoxysilyl)propyl]amine (TTESPA), tris[(diethoxymethylsilyl)propyl]amine (TDEMSPA), and tris[(triethoxysilyl)methyl]amine (TTESMA) were prepared, as shown in Figure 1. It was anticipated

that these precursors with three reactive ethoxysilyl units would form dense RO membranes, thereby improving RO performance. In addition, the author prepared tris[(triethoxysilyl)propenyl]amine (TTESP2A) and tris[3-triethoxysilyl]prop-2-ynyl]amine (TTESP3A) as the precursors, in which rigid and polar ethenylene and ethynylene linkages were expected to improve RO performance of the resultant membranes.

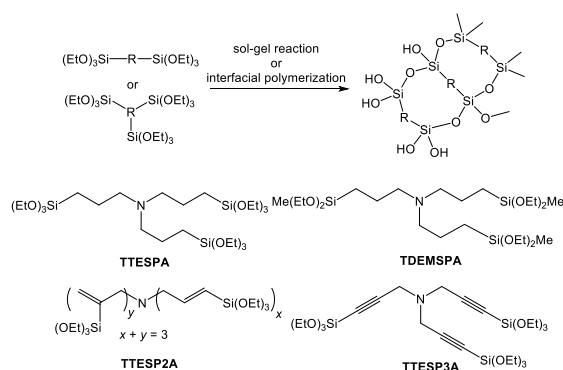


Figure 1. Organically bridged precursors for RO membrane preparation.

In Chapter 2, hydroxyl groups were successfully introduced into PSQ-RO membranes by copolymerizing BTESPA with triethoxy(3-glycidyloxypropyl)silane (TEGGS). It was demonstrated that epoxy groups in TEGGS underwent a ring-opening reaction by the nucleophilic attack of the amine unit of BTESPA to form hydroxy (C-OH) groups, which significantly improved the water permeability. The RO experiments by using a 2000 ppm NaCl aqueous solution clearly indicated that the use of epoxy-containing monomer TEGGS significantly improved RO performance, yielding water permeability of  $1 \times 10^{-12}$  m<sup>3</sup>/m<sup>2</sup>sPa and salt rejection of 98 %, approximately.

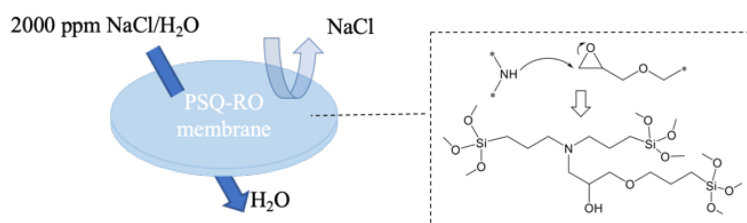


Figure 2. Schematic diagram of ring-opening reaction.

In Chapter 3, the author copolymerized BTESPA with *N*-(2-hydroxyethyl)-*N'*-[3-(triethoxysilyl)propyl]urea (HETESPU). The RO experiments of the copolymer membranes indicated that the water permeability was extremely improved approximately 19 times comparing to BTESPA homopolymer based membrane ( $1.86 \times 10^{-12}$  m<sup>3</sup>/m<sup>2</sup>sPa), with salt rejection remaining nearly unchanged (96%).

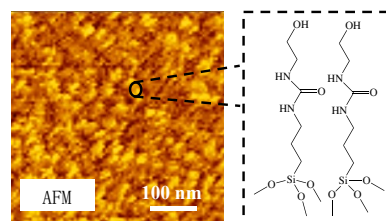


Figure 3. AFM image and the hydrophilic water channels formed by the aggregation through hydrogen bonding.

This is the highest water permeability so far obtained for PSQ membranes that show salt rejection higher than 90%. The extreme improvement of water permeability is likely due to the aggregation of hydroxyethylurea units through hydrogen bonding in the PSQ layer to form hydrophilic water channels.

In Chapter 4, mixed matrix membranes (MMMs) were prepared by the introduction of SiO<sub>2</sub> nanoparticles into the PSQ membranes. It was exhibited that the introduction of SiO<sub>2</sub> nanoparticles provided increased surface area and micropores in the PSQ membranes by the filler effects, thus enhancing the porosity and water permeability. It was also demonstrated that the thermal stability and chlorine resistance of SiO<sub>2</sub>

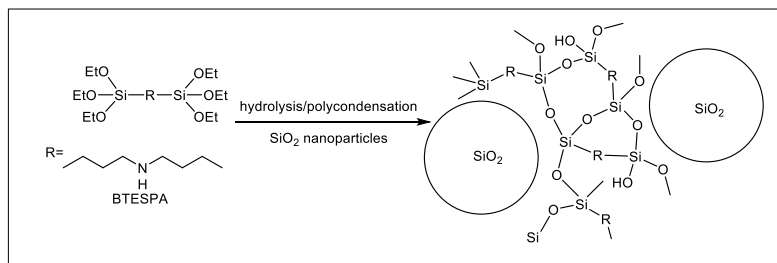


Figure 4. Preparation of PSQ-RO membranes modified by SiO<sub>2</sub> nanoparticles

nanoparticle-composite

membranes were also improved, which was probably due to the robust and rigid inorganic SiO<sub>2</sub> nanoparticles that stabilized the organically bridged PSQ structure by immobilization.