論文の要旨

題　目　Synthesis of polysilsesquioxanes for water desalination and functionalized polydimethylsiloxanes

（海水淡水化用ポリシルセスキオキサンと官能基化ポリジメチルシロキサンの合成）

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Part 1 describes *Development of organosilica reverse osmosis (RO) membranes for water desalination.* The reverse osmosis membranes are widely used to produced fresh water to solve the shortage of water in the world. Organosilica membranes have shown great advantages compared with the commercial polyamide RO membrane, which is sensitive to chlorine. This part focuses on the improvement of the properties of the organosilica membranes especially the water permeability.

Chapter 1 describes *Introduction*. The issue of water shortage in the world and the reverse osmosis technology to solve the problem is introduced. Commercially used RO membranes including polymeric membranes such as cellulose acetate (CA) and polyamide (PA) membranes and some novel RO membranes are introduced with respect to fabrication and advantages and disadvantages for the use.

Chapter 2 describes *Preparation of bridged silica RO membranes from copolymerization of bis(triethoxysilyl)ethene/(hydroxymethyl)triethoxysilane. Effects of ethenylene-bridge enhancing water permeability.* Copolymerization of bis(triethoxysilyl)ethene (**BTESE2**) and hydroxymethyl(triethoxy)silane (**HMTES**) was carried out to prepare new bridged silica membranes containing C-O-Si linkages. The membranes were examined for reverse osmosis (RO) to evaluate the water desalination properties. It was found that the hydrolysis of C-O-Si bonds occurred during the RO experiments to generate hydrophilic alcohol (C-OH) and silanol (Si-OH) units, thereby increasing the water permeability of the bridged silica membranes. Similar phenomenon was already reported for copolymer membranes prepared from bis(triethoxysilyl)ethane (**BTESE1**) and **HMTES**. However, the present membranes showed improved performance with higher water permeance by 4-14 times when compared to the previous BTESE1/HMTES-based membranes, although NaCl rejection was slightly lowered.

Chapter 3 describes *Preparation of bridged organosilica reverse osmosis membrane* *by interfacial polymerization of bis[(triethoxysilyl)propyl]amine*. Interfacial polymerization was applied to the preparation of bridged organosilica membranes with bis[3-(triethoxysilyl)propyl]amine (**BTESPA**) and (trimethoxysilyl)propyl]amine (**BTMSPA**) as monomers. The **BTESPA** membrane exhibited reverse osmosis (RO) performance with favorable water permeance (1.41×10^{-13} m^3/ ($m^2\cdot$ s· Pa)) and salt rejection (93.6%), similar to those of membranes prepared by the sol-gel process. The **BTMSPA** membrane showed improved water permeance (3.11×10^{-13} m^3/ ($m^2\cdot$ s· Pa)) and salt rejection (97.4%). The interfacial polymerization provides a much simpler method than commonly used sol-gel process to prepare organosilica RO membrane.

Part 2 describes *Synthesis of polydimethylsiloxanes with functional end groups and their applications.* This research is focusing on the functionalization and applications of poly(dimethylsiloxane) (PDMS). The PDMS is prepared by ring-opening polymerization of hexamethylcyclotrisiloxane (D3) with different organolithium reagents that work as initiators and also as the functional terminal groups. The reactions are quenched by chlorosilanes to produce Si-H bond in the other end. Further functionalization is conducted at the Si-H ends based on the nucleophilic substitution reaction with palladium as the catalysts. The applications of PDMS are based on the functional groups.

Chapter 1 describes *Introduction*. The properties and application of PDMS are introduced. The anionic ring-opening polymerization to synthesize the PDMS and the problems in the reaction is introduced.

Chapter 2 describes *Preparation of polydimethylsiloxane with amino end group via Pd-catalyzed dehydrogenative coupling of terminal hydrosilyl unit and amine.* Ring-opening polymerization of hexamethylcyclotrisiloxane (D3) with organolithium reagents (R^1Li) followed by quenching the resulting anions with chlorodimethylsilane yielded the corresponding polysiloxanes with R^1 and $SiMe^2H$ groups at each end. The hydrosilyl end groups readily underwent palladium-catalyzed dehydrogenative amination reactions with secondary amines ($R^2{}_2NH$) to produce polysiloxanes with amino end groups, $R^1(SiMe_2O)_nSiMe_2NR^2{}_2$. The aminopolysiloxanes were applied as hydrophobic modifiers of glass surface and treatment of glass plates with THF solutions of the aminopolysiloxanes increased the water contact angles of the glass surface from

5° to 22°-65°, depending on the aminopolysiloxane structures and reaction conditions.

Chapter 3 describes *Palladium-catalyzed synthesis of poly(bromo/iodoalkoxy- and bromo/iodoalkanoyloxy- siloxane)s from functionalized polydimethylsiloxanes.* Anionic ring-opening polymerization of hexamethylcyclotrisiloxane (D3) with a catalytic amount of lithium initiators (R^1-Li, R^1 were *n*-butyllithium and phenyllithium) gives rise to an R^1 group in one end. The siloxy lithium unit at the other end was quenched with $ClSiCH_3R^2H$ providing a functional Si-H bond, thus yielding the *n*-butyl- and phenyl-terminated polydimethylsiloxane (PDMS) (**BuPDMSH**, **PhPDMSH** and **BuPhPDMSH**) with an SiH end group. The functionalized hydro-poly(dimethylsiloxane)s were conducted to the ring-opening of cyclic ethers and a lactone with MeI or allylBr in the presence of a catalyst $PdCl_2$. Compared with the previously prepared PDMS containing haloalkoxy or haloalkanoyloxy units in both ends, this project provided a method to functionalize only one end group. The products maybe potentially used as the macromonomers and coupling reagents with a variety of functional groups.