

Full Length Article

## Fabrication of hydrophobic polymethylsilsesquioxane aerogels by a surfactant-free method using alkoxysilane with ionic group

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### ABSTRACT

Phase separation control is an important factor to prepare a porous monolith by an aqueous sol–gel reaction. Here, we report a surfactant-free synthesis method to obtain hydrophobic polymethylsilsesquioxane aerogels by copolymerizing a cationic-functionalized alkoxysilane *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride. The resultant materials have low-density, high visible-light transmittance, and high thermal insulating equivalent to those of prepared under the presence of surfactant.

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## 1. Introduction

Transparent silica aerogels are expected to be used as the main component of daylighting windows with high thermal insulation [1–4]. Optical and thermal insulating properties of those porous materials are derived from a well-controlled microstructure with a typical length scale in a hundred nanometer or less. To achieve better performances, many researchers have been trying to tune the pore size and morphology of skeletal structures in a desired manner. Apart from the research to brush up the excellent physical properties for applications, there is another trend in silica aerogel research. Since the ultrafine structure of the silica aerogel is too friable and easily destroyed even by small mechanical shocks or deformations, the mechanical strength has to be improved. As a further disadvantage, the final drying process usually needs a supercritical liquid under a high pressure condition, because those sensitive microstructures are collapsed by the capillary force during evaporative drying [5]. These problems have been obstacles to the

massive industrial production and commercial use of transparent silica aerogels for a long time.

Up to now, various approaches have been proposed to improve the mechanical strength of silica aerogels. Aging processes after gelation and surface modification of the skeleton by organic polymers are the examples of effective techniques [6–10]. However, these methods deteriorate other properties such as visible-light transparency and thermal insulation due to morphological changes of the microstructure. There are also reports aerogels with non-silica compositions such as organic polymers, which have unique mechanical properties [11–14]. For example, polyurethane aerogels have flexibility against bending and thiol-ene network polymer aerogels show a thermoresponsive shape-memory effect. However, these aerogels do not have visible-light transmittance due to their relatively coarsened and less homogeneous microstructures compared to silica counterparts.

Our group also has been trying to increase the mechanical strength of aerogels mainly for the purpose of thermal insulation [15,16]. Instead of the silica composition, we found the polymethylsilsesquioxane (PMSQ) network gives transparent aerogels and drastically improves strength and flexibility [17,18]. Each silicon atom in the network not only has siloxane bonds but also one dangling methyl group, which results in flexibility of the polysiloxane network and elasticity due to a repulsive interaction between the methyl groups. This high strength and flexibility enables to obtaining aerogel-like xerogels as large as several hundred square

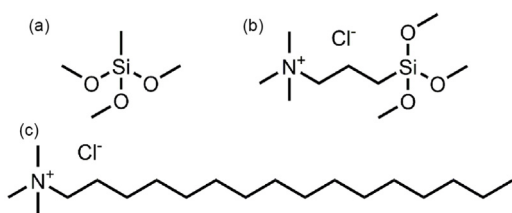
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**Fig. 1.** Chemical structure of (a) methyltrimethoxysilane (MTMS), (b) *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMAC), and (c) *n*-hexadecyltrimethylammonium chloride (CTAC).

centimeters in area with 10 cm in thickness via evaporative drying at ambient conditions thorough temporal shrinkage by the capillary force and subsequent spring-back [19]. However, such large PMSQ xerogel monoliths need careful and extended washing of surfactant that is used to control phase separation of the hydrophobic PMSQ network in the course of the aqueous sol–gel reaction, because the residual surfactant causes serious shrinkage and cracks in the monoliths during drying. For this reason, a surfactant-free synthesis process is desired. In the case of emulsion polymerization, there have been many reports on soap-free synthesis [20]. Among them, co-polymerization with a small amount of hydrophilic monomers is a simple and effective method in aqueous media.

In this paper, we report a surfactant-free synthesis of PMSQ aerogels using a hydrophilic alkoxy silane as the co-precursor for controlling the phase separation. We synthesized PMSQ aerogels by employing methyltrimethoxysilane (MTMS, Fig. 1(a)) under the presence of a small amount of *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMAC, Fig. 1(b)) with a quaternary ammonium salt site as one of the starting components, instead of surfactant *n*-hexadecyltrimethylammonium chloride (CTAC, Fig. 1(c)). The ionic sites introduced by TMAC are expected to give local hydrophilic portions into the hydrophobic PMSQ network, which contributes to the inhibition of macroscopic phase separation in aqueous sol–gel media and allows fabrication of monolithic gels with a homogeneous microstructure.

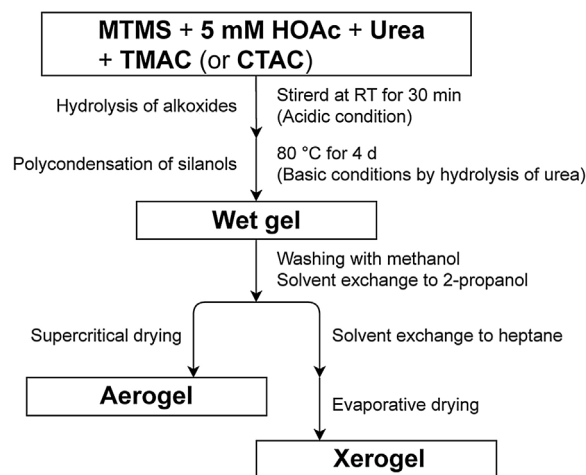
## 2. Experiment

### 2.1. Materials

Acetic acid, urea, methanol, and 2-propanol were purchased from Hayashi Pure Chemical Ind., Ltd., Japan. Methyltrimethoxysilane (MTMS) and *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMAC) in 50% methanol solution was obtained from Shin-Etsu Chemical Co., Ltd., Japan and Gelest, Inc., USA, respectively. Surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) was from Tokyo Chemical Ind. Co., Ltd., Japan. All reagents were used as received.

### 2.2. Sample preparation procedure

The outline of sample preparation is also shown in Scheme 1. A typical preparation procedure is as follows; 3 g of urea was dissolved in 10 mL of 5 mM acetic acid, and then 5 mL of MTMS and 1 mL of TMAC in 50% methanol solution were added and stirred at room temperature for 30 min to allow the hydrolysis of the alkoxy silanes. Subsequently, the resultant solution was transferred to a reaction vessel and allowed to gel in a closed condition at 60 °C. After gelation occurred in ~4 h under a raised pH by hydrolysis of urea, the gel was kept at the same temperature for 4 days for aging. The resulting wet gel was immersed in methanol for washing, and subsequently immersed in 2-propanol for solvent exchange. This alcogel was dried via a supercritical CO<sub>2</sub> drying process under the



**Scheme 1.** Preparation of PMSQ gels.

condition of 80 °C and 14 MPa for 10 h to obtain aerogels. For comparison, the same experiment was carried out with using 3 g of urea, 10 mL of 5 mM acetic acid, 5 mL of MTMS, and 0.4 g of CTAC as a starting composition. In these experiments, the starting compositions other than the amount of TMAC solution and CTAC were fixed.

### 2.3. Characterization

The pore structure was observed with an FE-SEM JSM-6700F (JEOL Ltd., Japan). Bulk density was obtained by measuring the volume and weight of a carved gel. For light transmittance measurements, a UV–vis spectrometer V-670 (JASCO Corp., Japan) equipped with an integrating sphere ISN-723 was employed. Direct-hemispherical transmittance was recorded, and obtained transmittance data at 550 nm were normalized into those corresponding the thickness of 10 mm using the Lambert–Beer equation. To assess the molecular structure of obtained PMSQ networks, solid-state NMR and Fourier transform infrared (FTIR) measurements were performed. <sup>29</sup>Si solid-state cross-polarization/magic angle spinning (CP/MAS) NMR measurements were performed on an NMR spectrometer Avance III 800 (Bruker Corp., Germany) operated under a static magnetic field of 18.8 T. The contact time for the <sup>1</sup>H–<sup>29</sup>Si cross-polarization was fixed at 5.5 ms and the rate of sample spinning was 15 kHz. The <sup>29</sup>Si chemical shift was expressed relative to tetramethylsilane (Me<sub>4</sub>Si) by using the resonance line at –9.66 ppm for hexamethylcyclotrisiloxane crystals as an external reference. For FTIR measurements, IRAffinity-1 (Shimadzu Corp., Japan) with an attenuated total reflection (ATR) attachment was used. A total of 100 scans were recorded with a resolution of 4 cm<sup>–1</sup>. Mechanical properties of aerogels were measured by a material tester EZGraph (Shimadzu Corp., Japan). Aerogel samples shaped into cuboid were compressed using a load cell of 5 kN. The uniaxial compression measurements were performed at a crosshead speed of 0.5 mm s<sup>–1</sup>. Young's modulus has been calculated using the slope of stress–strain curves between 0.1 and 0.2 MPa stress. Thermal conductivity was measured with HFM 436 Lambda (Netzsch GmbH, Germany) by measuring the heat flow at the central part of the specimen. Contact angle of water was measured with Drop Master DM-561Hi (Kyowa Interface Science Co., Ltd., Japan).

## 3. Results and discussion

Photographs of the gels obtained with TMAC or the surfactant CTAC in typical starting compositions (see Section 2) before and after supercritical drying and a micrograph by FESEM of the aero-

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