Sol–gel synthesis, porous structure, and mechanical property of polymethylsilsesquioxane aerogels

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Organic-inorganic hybrid aerogels with polymethylsilsesquioxane (PMSQ, CH₃SiO₁.₅) composition have been synthesized by a modified two-step sol–gel process. The precursor alkoxy silane is hydrolyzed in a weakly acidic condition, and subsequently allowed to undergo polycondensation in a weakly basic condition which is brought up by the hydrolysis of urea. Two kinds of surfactant (nonionic and cationic) have been utilized to suppress macroscopic phase separation. The resultant porous morphology could be modified by the kind of surfactant used. Small angle X-ray scattering (SAXS) and nitrogen adsorption have been employed to assess the porous morphology and it is found that the obtained PMSQ aerogels consist of aggregated particles and each particle contains micropores. Compressive mechanical properties have also been discussed based on the obtained information on porous morphology.

Key-words : Sol–gel, Aerogels, Organic-inorganic hybrid, Porous structure, Mechanical property, Nitrogen adsorption, Small angle X-ray scattering (SAXS)

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1. Introduction
Aerogels are a particular class of porous solids which are differentiated from other porous materials by high porosity (~90%) and fine porous structures (~50 nm). Typical silica aerogels are characterized by high transparency to the visible light (~90%), as well as by extremely low refractive index and low dielectric constant correlated with their low density (~0.1 g cm⁻³ (~90%), as well as by extremely low refractive index and low bulk density are lost in exchange with the improved mechanical properties while preserving other excellent properties has been made. In particular, the transparency and low bulk density are lost in exchange with the improved mechanical properties in the case of hybridization. However, all these efforts work well to a limited extent and no critical improvement of mechanical properties while preserving other excellent properties has been made. In particular, the transparency and low bulk density are lost in exchange with the improved mechanical properties in the case of hybridization.

We have reported the preparation of transparent polymethylsilsesquioxane (PMSQ, CH₃SiO₁.₅) aerogels using methyltrimethoxysilane (MTMS) as a single precursor by sol–gel. A modified 2-step acid/base sol–gel process utilizing hydrolysis of urea enhances the homogeneous gelation of MTMS. Additionally, an adequate surfactant is employed to suppress macroscopic phase separation which otherwise would develop in the micrometer scale and eliminate transparency. A significantly improved mechanical property (reversible compression-reexpansion process termed as “spring-back”) has also been reported. In the present study, we characterize the porous structure in detail and discuss the relationship between porous morphology and the mechanical properties to enable the better design of the porous morphology required to further improve the properties of aerogels.

2. Experimental
2.1 Chemicals
Acetic acid, distilled water, urea, methanol, and 2-propanol were purchased from Hayashi Pure Chemical Ind., Ltd. Surfactant n-hexadecyltrimethylammonium bromide and chloride (CTAB and CTAC, respectively), and poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide) (EO₁₀₆PO₇₀EO₁₀₆, Pluronic F127) were from Tokyo Chemical Ind. Co., Ltd., and BASF (Germany), respectively. Methyltrimethoxysilane (MTMS) was obtained from Shin-ETSu Chemical Co., Ltd. All reagents were used as received.

2.2 Synthesis procedures
A flow diagram of the experimental procedures is shown in Fig. 1. In a glass sample tube, 20 mL of aqueous acetic acid (1 and 5 mM for CTAB/CTAC and F127 systems, respectively), surfactant (0.80 g of CTAB/CTAC or 2.0 g of F127) and 6.0 g of urea were dissolved, and then 9.51 g of MTMS was added under vigorous stirring. The molar ratios are MTMS:water:acetic acid:urea = 1:15.9:0.0172 (1 mM) or 0.0860 (5 mM):1.43. The mixed solution was continuously stirred for 30 min at room temperature, followed by gelation and aging in a closed vessel at 60°C in an air-circulating oven for 3 d. For supercritical drying,
the resultant wet gels were solvent-exchanged with methanol for 3 times at 60°C (each for more than 8 h) and then 2-propanol in the same way as methanol. Alcogels obtained in this way were dried from supercritical carbon dioxide at 80°C, 14.0 MPa in a custom-built autoclave (Mitsubishi Materials Co.) to obtain aerogels.

2.3 Characterizations

The porous morphology was observed under a field emission scanning electron microscope (FE-SEM) JSM-6700F (JEOL Ltd.). Bulk density \( \rho_b \) was obtained by measuring the volume and weight of a carved aerogel. Porosity \( \varepsilon \) in % was then determined by \( \varepsilon = (1 - \rho_b / \rho) \times 100 \), where \( \rho \) represents true density that was fixed to be 1.41 g cm\(^{-3}\) determined for dried MTMS-derived gels by helium pycnometry (Accupyc 1330, Micromeritics, USA). For light transmittance measurements, a UV-VIS spectrometer V–670 (JASCO Co.) 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 to 10 mm-thick samples using the Lambert-Beer equation. The normalized total transmittance is denoted as \( T \).

Small angle X-ray scattering (SAXS) has been employed to characterize the porous structure. The measurements were carried out with RINT-Ultima III (Rigaku Co.), equipped with a Cu K\( \alpha \) X-ray generator (2 kW, wavelength \( \lambda = 0.15418 \) nm). Scattering intensities from 0.07\(^\circ\) to 4.0\(^\circ\) were examined with an increment of 0.01\(^\circ\) and accumulation time of 100 s. After subtracting background, the silt-smearing effect was removed. The scattering profiles were plotted against scattering vector \( q \), which is related to the scattering angle \( 2\theta \) and the wavelength of the X-ray \( \lambda \) through \( q = 4\pi \lambda ^{-1} \sin \theta \).

Nitrogen adsorption measurements at 77 K by ASAP 2010 (Micromeritics, USA) were performed to obtain Brunauer–Emmett–Teller (BET) surface area and micropore character of the obtained aerogels. Bulk density \( \rho_b \) and porosity \( \varepsilon \) are strongly correlated with the shrinkage during aging and supercritical drying. Wet gels of CTAB–1 and CTAC–1 did not shrink during aging, which may result from the repulsion of ionic charge of CTAB or CTAC on the networks of the wet gels. This situation resembles the case where a small quantity of cationic silicon alkoxide is copolymerized with tetrafunctional one,\(^{20}\) in which positive surface charge prohibits the attraction of neighboring silanols and shrinkage during aging is significantly suppressed. In F127–1, a small shrinkage (1.2%) is observed during aging presumably because of the additional condensation of unreacted silanol groups. The unreacted silanols, which had been hindered by F127 through hydrogen bonding at the onset of gelation as described below in detail, cause the additional condensation during aging. High viscosity of the sol containing F127 may also lead more unreacted silanols due to the slow interdiffusion of the condensates. Light transmittance \( T \) at 550 nm is higher for cationic surfactant systems and reaches to ~90%.

![Fig. 1. Flow diagram of experimental procedure.](image1)

![Fig. 2. Appearance of three obtained aerogels. Aerogels prepared with CTAB and CTAC are more transparent.](image2)

### Table 1. Properties of Obtained PMSQ Aerogels

<table>
<thead>
<tr>
<th>Code</th>
<th>( \rho_b / g \ cm^{-3} )</th>
<th>( \varepsilon /% )</th>
<th>Aging shrinkage ( f_% )</th>
<th>Drying shrinkage ( f_% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB–1</td>
<td>0.13</td>
<td>90.6</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
<td>CTAC–1</td>
<td>0.14</td>
<td>90.0</td>
<td>0</td>
<td>1.8</td>
</tr>
<tr>
<td>F127–1</td>
<td>0.17</td>
<td>87.6</td>
<td>1.2</td>
<td>6.4</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Starting compositions are: MTMS 10 mL, aqueous acetic acid 20 mL, Urea 6.0 g and surfactant. The amounts of surfactant are: CTAB 0.80 g (CTAB–1), CTAC 0.80 g (CTAC–1) and F127 2.0 g (F127–1). Note that the concentration of acetic acid is 1 mM for CTAB–1 and CTAC–1, and 5 mM for F127–1.
with pore structures shown in Fig. 3 rationalizes the difference in \( T \). Pore structure of CTAB–1 consists of aggregated tiny particles, whereas that of F127–1 consists of fibrous networks. Note that pore structure of CTAC–1 is similar to that of CTAB–1. The domain size is apparently larger for F127–1 and which causes the more intense Mie scattering and results in lower visible light transmittance. In fact, these fibrous skeletons are made up with chains of tiny particles, which can be more clearly confirmed by the SAXS data. Thermal analysis by thermogravimetry (TG) combined with differential thermal analysis (DTA) in air proved that the thermal decomposition of methyl groups in obtained PMSQ aerogels gradually starts from 300°C and mainly proceeds from 400 to 500°C. Below 300°C and above 500°C, no change in the sample weight has been observed.

3.2 Pore properties determined by SAXS and nitrogen adsorption

More detailed assessment of the porous structure has been carried out by SAXS and nitrogen adsorption at 77 K. Fig. 4(a) exhibits the SAXS profiles for CTAB–1 and F127–1 and part (b) depicts the corresponding Porod plots \((lq)q^2\) versus \(q\). Scattering curves from both samples do not contain a mass fractal power law regime, which is characteristic for typical silica aerogels.\(^{21,22}\) The curves show maxima corresponding to the length scale of \( A = 2\pi q_{\text{max}} = 35.9\) nm for CTAB–1 and 44.9 nm for F127–1, respectively, where \( q_{\text{max}}\) stands for the \( q\) value at the scattering peak. Haw et al. revealed that the small-angle peak is due to the periodic oscillation of density in diffusion-limited cluster-cluster aggregation (DLCCA) systems.\(^{23,24}\) The periodicity stems from the finite size of clusters surrounded by a depletion region. In the present system with smaller particles packing density, the cluster size can be regarded as the thickness of the strings of the linked particles. Judging from the FE–SEM images shown in Fig. 3, these values reflect the domain size of the structure, that is, pore size plus particle size.

The scattering in the lower \( q\) region is larger for F127–1 (compare with the decline of scattering intensity in the circled region in CTAB–1), which is consistent with the presence of larger structural units (>100 nm) in F127–1. Thus, in the case of F127–1, the typical structural length is ~45 nm but also contains the structures larger than ~100 nm, which reduces the light transmittance or transparency of F127–1. In the higher \( q\) region \((q > 1)\), the scatterings from the surfaces of particles do not follow the Porod’s law. In other words, the scattering fall in the higher \( q\) region is shallower than \( q^{-4}\) which suggests the existence of micropores as has widely been observed in organic aerogels.\(^{25–27}\) These slopes, \( -q^{-3.4}\) for CTAB–1 and \( -q^{-3.1}\) for F127–1, indicate fractally rough surfaces, that is, surface fractal dimensions are ~2.6 and ~2.9 for the respective samples.

From the Porod plots shown in part (b), particles diameter \( d\) can be roughly estimated by assuming the monodisperse spherical particles as

\[
d = 2 \times 2.74/q_{\text{max}},
\]

where \( q_{\text{max}}\) is the local maximum in the Porod plot. In the Porod plot of F127–1, since the local maximum is accompanied by a shoulder, it can be deduced that the F127–1 aerogel consists of two different sizes of particles. The values of correlation length and particles diameters are listed in Table 2 for three samples. Both length scales \((A\) and \(d\)) become larger in the order of CTAC–1 < CTAB–1 < F127–1.

Figure 5(a) displays nitrogen adsorption isotherms in the relative pressure range of \( 0 < p/p_0 < 0.9\). Although capillary condensation by the mesopores found in Fig. 3 can be observed at \( p/p_0 > 0.9\), we did not acquire adsorption data in that region because aerogel specimens are significantly contracted by the capillary force of the condensed nitrogen in the mesopores and fatal errors arise in estimating mesopore volume and size.\(^{28}\) The steep increase of adsorbed volume in the very low relative pressure region implies the presence of micropores and the continuous increase in the middle pressure region suggests the multilayer adsorption on the mesopore surfaces with high specific area. The \( \alpha_s\) plots of both samples shown in part (b) exhibit upward swing in the very small \( \alpha_s\) region such as \( \alpha_s < 0.1\). Note that the curve should run through the origin and be linear for nonporous samples. From the studies using carbon materials which contain considerable micropores, the upward swing in this region corresponds to the “f-swing”, suggesting the micropore filling by submonolayer adsorption in small micropores with ca. < 0.7 nm.\(^{29}\) As schematically shown in Fig. 6, the \( \alpha_s\) plots for

Table 2. Parameters Representing Pore Characters Obtained from SAXS and \( N_2\) Adsorption

<table>
<thead>
<tr>
<th>( d/\text{nm} )</th>
<th>( \lambda/\text{nm} )</th>
<th>( S_{\text{BET}}/\text{m}^2,\text{g}^{-1} )</th>
<th>( S_d/\text{m}^2,\text{g}^{-1} )</th>
<th>( W/\text{cm}^3,\text{g}^{-1} )</th>
<th>( V_b/\text{cm}^3,\text{g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB–1</td>
<td>11</td>
<td>35.9</td>
<td>601</td>
<td>148</td>
<td>0.080</td>
</tr>
<tr>
<td>CTAC–1</td>
<td>8</td>
<td>30.1</td>
<td>618</td>
<td>141</td>
<td>0.074</td>
</tr>
<tr>
<td>F127–1</td>
<td>15 and 21</td>
<td>44.9</td>
<td>528</td>
<td>220</td>
<td>0.113</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Total pore volume obtained from \( V_b = 1/\rho_s \), \( 1/\rho_s \), where \( \rho_s \) is true density (1.41 g cm\(^{-3}\)).
the PMSQ aerogels are the summation of the contributions from micropores \(V_{\text{amicro}}\) and mesopores \(V_{\text{ameso}}\). That is, \(V_{\text{amicro+meso}} = V_{\text{amicro}} + V_{\text{ameso}}\). Micropore volume \(W_0\) can be generally obtained as an intercept with the vertical axis of \(V_{\text{amicro}}\) in the case of microporous solids. In the case of our PMSQ aerogels, \(W_0\) is obtained by extrapolating the linear region in \(\alpha_S > 1\) because \(V_{\text{amicro}}\) can be regarded as being constant in that region. The total mesopore surface area (external area) \(S_{\text{ext}}\) is obtained from the slope \(s\) in \(V_{\text{ameso}}\) (indicated in Fig. 6) and micropore area \(S_m\) can be estimated as follows:

\[
S_{\text{ext}} = S^0 \times V_{\text{ext}}/V_{\text{ext}}^0 = S^0 \times s/s^0 = 2.91 \times s
\]

and

\[
S_m = S_{\text{ext}} - S_{\text{ext}}.
\]

Here, parameter \(V_{\text{ext}}^0\) stands for the adsorption volume at \(p/p_0 = 0.4\), and superscript “0” represents those of the standard adsorbent. Since, again, \(V_{\text{amicro}}\) is almost constant in \(\alpha_S > 1\), the slope \(s'\) in the experimental data in the region of \(\alpha_S > 1\) can be regarded as being close to \(s\) in \(V_{\text{ameso}}\) (see Fig. 6). The estimated \(W_0\) and \(S_m\) are listed in Table 2. The sample F127–1 has the larger micropore volume, which is consistent with the fractally rougher surface (larger surface fractal dimension) revealed by SAXS, and the contributions of micropore area to the total pore area are as large as 25, 23 and 42% for CTAB–1, CTAC–1, and F127–1, respectively.

Micropore size distributions of CTAB–1 calculated by the SF method are displayed in Fig. 7. The micropore size distribution of F127–1 has a peak at 0.68 nm and CTAB–1 shows the broader distribution. Above all, both distributions in the range of small pore diameters are close, but CTAB–1 contains the larger amount of micropores with \(D_m > 0.8\) nm. The higher micropore area \(S_m\) in F127–1 can be explained by the fact that F127–1 contains larger \(W_0\). Besides, the larger amount of smaller micropores more significantly contributes to the surface area.

The formation of micropores must be relevant to the polycondensation process and interactions between MTMS-derived condensates and surfactant. In the case of base-catalyzed polycondensation, highly branched particulates are formed in the course of polycondensation, which results in dense primary particles with mass fractal dimension of \(\sim 3.0\) (reaction-limited monomer-cluster aggregation, RLMCA). By contrast, in the acid-catalyzed polycondensation, less branched chain-like condensates are connected with each other to form the spanning cluster. The condensates possess loose and open networks, which contain a large amount of micropores as interstices, with the typical mass fractal dimension of \(\sim 2.1\) (reaction-limited cluster-cluster aggregation, RLCCA). From this viewpoint, pH of the reacting sol influences the formation of micropores. The situation is close to RLCCA in all systems described here because of the weakly acidic hydrolysis (at near the isoelectric point of MTMS where condensation rate is minimized) and basic condensation with the sufficiently large water/MTMS ratio (= 15.9)
throughout the reactions. However, there are slight variations in the aggregation behavior of clusters depending on the pH difference during condensation as follows. In CTAB or CTAC system, the solution pH becomes higher during the condensation step because more dilute (1 mM) acetic acid is used and surfactant to some extent raises the solution pH because of the strong basicity of dissociated quaternary ammonium anions. On the other hand, more concentrated acetic acid (5 mM) is used in F127 system in order to increase the reaction rate, and also, F127 somewhat lowers the solution pH by the dissociation of hydroxyl end groups.

The lower pH condition in F127 system should lead to the relatively less-branched and open networks with more interstices compared to CTAB/CTAC system. Interaction between MTMS-derived condensates and surfactant also influences the formation of micropores. In CTAB and CTAC systems, the surface of MTMS-derived condensates, which is highly hydrophobic due to the consumption of silanol groups and exposure of methyl groups, is considered to be contacted mainly by the alkyl chain of the surfactant. Two main reasons can be anticipated for this assumption. First, since only the small fraction of CTAB or CTAC molecules is dissociated in an aqueous solution, the negatively-charged MTMS-derived condensates and polar head groups of the surfactant hardly attractively interact in the form of Si–O–...X(CH3)3N+–R. Second, in the absence of interactions among polar parts of the solute molecules, hydrophobic interaction between MTMS-derived condensates and surfactant, which makes the surfaces of condensates hydrophilic, becomes dominant in the aqueous solution. Thus, the interaction between condensates and surfactant is relatively loose and polycondensation is not effectively hindered, leading to the denser condensates.

In the case of F127 system, although the situation is somewhat complex, it can be roughly regarded as follows. Since the hydrophobic interaction between MTMS-derived condensates and F127 molecules works, MTMS-derived condensates mainly adsorb hydrophobic PPO units in polar solvent and the surfaces are made hydrophilic. However, since there exist small number of silanol sites available for the formation of hydrogen bonding and the interaction between the methylated silanol groups (= Si(CH3)(OH)) and the oxygen of PPO units are sterically difficult, hydrogen bonding is formed between PEO units and the MTMS-derived condensates. In particular, since less condensed MTMS-derived species possess more silanol groups and are more polar, hydrogen bonding between the PEO units and condensates begins to form at the early stage of polycondensation. As a result, the surfaces become only weakly hydrophilic due to the above-mentioned complicated adsorption mechanism. Polycondensation is to some extent hindered by the hydrogen-bonded F127 molecules and somewhat loose networks form. The remaining silanol density in F127 system observed by solid state 29Si NMR and FTIR supports this idea.

In summary, the relatively less-branched and open networks with more interstices (potential micropores) and with more remaining silanols are formed in F127 system. The remaining silanols are somewhat consumed in the aging and drying processes to allow larger shrinkage as shown in Table 1. Micropore size is thus smaller for F127–1 (Fig. 7), but larger micropore volume still remains in the siloxane networks in F127–1 as listed in Table 2.

### 3.3 Compressive mechanical properties

Stress (denoted as σ)-strain curves obtained by cyclic uniaxial compression tests are shown in Fig. 8, and obtained parameters are listed in Table 3. It is noteworthy that obtained aerogels are highly flexible to show ~75% recovery after 50% strain. By optimizing the starting composition and post treatments, recovery of almost 100% has been observed even after 80% compression as already reported. Here, we discuss the relationship between pore structures and mechanical properties using the data of the above three aerogel samples obtained from different compositions. From Fig. 8, it is noticed that stress becomes exponentially larger with increasing strain due to the densification of the aerogels, and that the aerogels become “softer” (more strain against fixed stress) in the order of F127–1 < CTAB–1 < CTAC–1. The “hardest” property of F127–1 is mainly attributed to the higher bulk density. The relatively large difference between CTAB–1 and CTAC–1 may reflect the difference in particles sizes. If we assume the point-contacts in-between constituent particles, probability density of deformation and breakage at the neck of the interparticles is larger for CTAC–1 because CTAC–1 consists of the smaller particles (higher neck density) as revealed by SAXS. The larger deformation at a fixed stress occurs in such a system. Considering the high recovery of CTAC–1, it is suggested that the neck structure in CTAC–1 is thicker and/or that density of remaining silanols are lower for CTAC–1 than CTAB–1. It is also noteworthy that no visible damage has been observed during the cyclic uniaxial compression tests of F127–1 while some cracks are evolved on the surfaces of CTAB–1 and CTAC–1. This apparently is due to the more continuous linkage (particles are contacted on larger area each other) of the particles with the smoother surfaces as observed in Fig. 3. Since the breakage of the networks is difficult, aerogels prepared by F127 system are more promising if remaining silanol groups are effectively reduced by, for example, post treatments of wet gels.
4. Conclusions

Synthesis, analysis of pore properties by SAXS and nitrogen adsorption, and examination of mechanical properties by uniaxial compression tests have been performed in the present study. The following conclusions are derived:

1. It is observed by FE–SEM that the aerogel obtained in the system containing CTAB or CTAC consists of aggregated particles, while that obtained in F127 system consists of continuous fibrous networks.

2. More transparent aerogels are obtained in CTAB or CTAC system than that obtained in F127 system due to the smaller and more homogeneous porous structure.

3. It is revealed by SAXS measurements that the obtained aerogels basically consist of particles aggregates, and small-angle peak suggests the domain size of the porous structure. Presence of micropores is also suggested.

4. Nitrogen adsorption measurements confirm the presence of micropores. The amount of micropores is larger for F127 system.

5. Compressive mechanical properties are related with particles diameter in CTAB and CTAC systems. Aerogels obtained in F127 system show no surface cracking and the further improvement of mechanical properties is expected.

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