Unusual Flexibility of Transparent Poly(methylsilsesquioxane) Aerogels by Surfactant-Induced Mesoscopic Fiber Assembly

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Abstract: We report a new synthetic strategy to realize highly transparent aerogels with outstanding bending flexibility. Taking poly(methylsilsesquioxane) (PMSQ) aerogels as an example, surfactant-induced fiber-like mesoscopic assembly of PMSQ and poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-b-PPO-b-PEO, so-called Pluronics) has been demonstrated. The obtained PMSQ aerogels possessed a characteristic branched fibrous structure in the mesoscale. With employing various kinds of PEO-b-PPO-b-PEO as the structure determining agent, optimization of the mesoscale structure of PMSQ gels has realized highly transparent aerogels with outstanding bendability compared to those reported in previous works. This approach provides a novel way to thermally superinsulating flexible devices with glasslike transparency.

Introduction

Transparent aerogels, which show ultralow thermal conductivity (down to 12 mW m\(^{-1}\) K\(^{-1}\)) with low bulk density (typically 0.001–0.2 g cm\(^{-3}\)), are sol–gel materials with a mesoscale homogeneous porous structure.\(^1,2\) These unique features of visible transparency and low thermal conductivity make aerogels an ideal material for thermally superinsulating devices including windows for efficient energy savings.\(^3-5\) Aerogels are, however, mechanically weak materials due to their weakly linked skeletons and high porosity. To
improve their mechanical strength, many efforts have been devoted by controlling the molecular-scale network \textsuperscript{6} and forming composite with mechanically more reliable materials such as organic polymers and glass fibers.\textsuperscript{7-9} However, such structural controls and modifications while maintaining visible transparency have been challenging due to the lack of knowledge in structurization in the mesoscale in high-porosity materials.

Fundamental studies on influences of the macroscale (\textit{e.g.}, in micrometer scales) porous structure on their mechanical properties have been intensively studied through experimental and simulation approaches, in which it has been found architectural features, in addition to the chemical structure of the network, influence their mechanical strength and flexibility.\textsuperscript{10-12} When looking at the mesoscale (\textit{e.g.}, in nanometer scales) porous structure in aerogels, the fundamental knowledge of the relationship between the porous structure and their mechanical properties would give an opportunity to realize highly flexible aerogels through the control over the mesoscale porous structure. In particular, three-dimensional (3D) branched fibrous architecture can be considered as a promising way to realize high flexibility due to the absence of the “necks” where stress would be accumulated. As demonstrated in nanofiber-based aerogels such as cellulose/chitosan nanofiber aerogels and carbon nanotube (CNT) aerogels, designing a 3D fibrous structure brings out high flexibility in aerogels.\textsuperscript{13-15} However, the optimized mesoscale fibrous structure which realizes both high flexibility and transparency is still unclear due to the difficulty in designing the mesoscale fibrous structure built up with a well-controlled molecular-scale network.

Here, we demonstrate a new synthetic strategy to realize highly transparent aerogels with outstanding flexibility through the optimization of the mesoscale porous structure by surfactant-induced mesoscopic fiber assembly. We employed poly(methylsilsesquioxane) (PMSQ, CH\textsubscript{3}SiO\textsubscript{3/2}) aerogels\textsuperscript{16,17} as an example. Transparent PMSQ aerogels have been prepared by hydrolysis and polycondensation of methyltrimethoxysilane (MTMS, CH\textsubscript{3}Si(OCH\textsubscript{3})\textsubscript{3}), in the presence of surfactant as a phase separation suppressor. Formally, the PMSQ network can be prepared by the following two-step acid-base process in these examples:

1. Acid-catalyzed hydrolysis

   \[ \text{CH}_3\text{Si(OCH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{CH}_3\text{Si(OH)}_3 + 3\text{CH}_3\text{OH} \]

2. Base-catalyzed polycondensation

   \[ \text{CH}_3\text{Si(OH)}_3 \rightarrow \text{CH}_3\text{SiO}_{3/2} + 3/2\text{H}_2\text{O} \]
Although some research has been demonstrated their high transparency and the compression and spring-back behavior derived from the organic-inorganic hybrid network with high hydrophobicity \textsuperscript{16-18}, there is no report on the strategic synthesis of the mesoscale branched fibrous structure toward their mechanical flexibility. The key to our approach toward fibrous structured PMSQ aerogels is a use of nonionic surfactant PEO-\textit{b}-PPO-\textit{b}-PEO (known as Pluronics) as the structure determining agent. According to the literature \textsuperscript{19,20}, the hydrophobic network of PMSQ showed high tendency of macroscopic phase separation (spinodal decomposition) in aqueous media. Although a sol-gel system with high concentrations (\textit{e.g.}, 0.1 g mL\textsuperscript{-1} or more) of surfactant Pluronic F127 (properties of Pluronic surfactants are listed in \textbf{Table S1}) was found to moderately suppress the macroscopic phase separation and resulted in translucent ($T_{550}$ ~ 60\%, transmittance at 550 nm through a 10-mm-thick specimen) PMSQ aerogels, no aerogels with high transparency (> 90\%) have been reported.\textsuperscript{21} Inspired by these results, we came up with an idea that this structural diversity of PMSQ gels prepared in the presence of the Pluronics surfactant would provide an opportunity to obtain PMSQ aerogels with mesoscale branched fibrous structures.

In this work, as a proof of concept, we tried to control the mesoscopic assembly of the PMSQ network by employing several kinds of the Pluronics-type triblock copolymer both as phase separation suppressor and structural determining agent. In addition, an organic strong base, tetramethylammonium hydroxide (TMAOH), was employed as a polycondensation catalyst, which is effective for equilibration of polysiloxanes.\textsuperscript{22,23} By identifying and optimizing the synthesis parameters such as starting composition, PMSQ aerogels with both high transparency and outstanding bending flexibility have been demonstrated.

\textbf{Results and Discussion}

\textbf{Identifying appropriate synthetic parameters of the PMSQ aerogels with fibrous structure}

The typical procedure to prepare the PMSQ aerogels is as follows: (1) MTMS was hydrolyzed in 5 mM acetic acid; (2) a given amount of surfactant and water were subsequently added to the solution to obtain the homogeneous sol; (3) a given amount of aqueous TMAOH was added into the sol at 0 °C for polycondensation of hydrolyzed MTMS to form a wet gel; and (4) the obtained gel was washed with water, methanol, and 2-propanol in sequence, and then the washed alcogel was supercritically dried from carbon dioxide at 80 °C under 14 MPa.
The microstructure of the PMSQ aerogels depends mainly on the ratio of surfactant to MTMS and the concentrations of surfactant and MTMS in the starting solution. In our previous studies, several kinds of nonionic\textsuperscript{21} and cationic surfactants\textsuperscript{24} have been shown to suppress the macroscopic phase separation to lead to the mesoporous structure. Figure S1 and S2 demonstrate that the finer porous structure is obtained with increasing amount of F127 and n-hexadecyltrimethylammonium chloride (CTAC), respectively. Without surfactant, a high phase separation tendency between hydrophobic PMSQ polymer and water-based solvent resulted in the macroporous structure with spheroidized skeletons\textsuperscript{25} (Figure S1a). The transient co-continuous macroporous structure of phase separation, which was solidified by the sol-gel transition, has been observed in the case of F127 as phase separation suppressor (Figure S1b–c). On the other hand, when CTAC was employed as the phase separation suppressor, the transient structure of spinodal decomposition has not been observed, and pore skeletons with aggregated particles have been observed instead (Figure S2b).

To identify the suitable synthetic process which realizes both high transparency and high flexibility, we explored the starting composition to form the mesoscale branched fibrous structure by using several kinds of PEO-\textit{b}-PPO-\textit{b}-PEO-type triblock copolymers. As mentioned above, the co-continuous structure, which are derived from the spinodal decomposition in the micrometer scale, were formed in the presence of F127, while the presence of CTAC resulted in the macroporous structure with aggregated particles in the case of moderate phase separation tendency. We assumed that the mesoscale branched fibrous structure would be isotopically extended with a lower concentration of MTMS. We therefore decreased the concentration of MTMS from 5 mL (35 mmol) in 7 mL of water to 5 mL in 12 mL of the same.

The phase separation tendency between MTMS-derived methylsilsesquioxane (MSQ) condensates and water-based solvent is dominated mainly by the concentration and kinds of base catalyst and surfactant, which influences the molecular weight of MSQ and affinity between the gelling phase and the solvent-based phase. First, we discuss the effect of base catalyst. Figure S3 shows the influences of the base catalyst on the transparency of the PMSQ aerogels in the system containing surfactant F127. In the case of urea used in the previous studies, hydrolysis of urea generates ammonia as the polycondensation catalyst, and the solution pH gradually increases to 7–9. In the case of TMAOH, the solution pH rapidly increases to higher values (from ~12 (0.010 M) to ~14.3 (2 M)) because a strong base TMAOH is separately added after the hydrolysis of MTMS. The obtained PMSQ aerogels
prepared with TMAOH had higher transparency (except for the case of 0.010 M TMAOH) than that of the PMSQ aerogels prepared with urea as the base source. As discussed in the silicate system, it is reasonable to speculate that TMAOH more effectively suppresses the phase separation tendency, because the MSQ species ionically bound with the TMA$^+$ cations increase their affinity in the water-methanol solution.\textsuperscript{26,27} By varying the concentration of TMAOH, transparency of the PMSQ aerogels has been controlled and shown maximum (83 \%) at 0.50 M (Figure S3). The field-emission scanning electron microscopy (FE-SEM) images in Figure S4 show that the porous structure is composed of branched fibrous skeletons of \(~ 10 \text{nm}\) thickness and becomes finer with the increasing concentration of TMAOH.

In addition to the optimization of the TMAOH concentration, we identified the appropriate amount of the surfactant toward the maximization of transparency. The details of the starting compositions are summarized in Table S2. We first focus on two types of PEO-$b$-PPO-$b$-PEO surfactant, F127 and P105. The molecular structures of F127 and P105 are expressed as EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106} ($M_w = 12\,600$) and EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37} ($M_w = 6\,500$), respectively (Table S1).\textsuperscript{28} The hydrophile-lipophile balance (HLB) values of F127 and P105 are 18-23 and 12-18, respectively.

**Physical features of the PMSQ aerogels with fibrous structure**

Figure 1a shows macro-/mesoscopic physical features of the PMSQ aerogels with the mesoscale branched fibrous structure prepared in the presence of F127 and P105. In the optimized starting compositions to maximize the transparency, light transmittance at 550 nm through a 10-mm equivalent specimen ($T_{550}$) of the PMSQ aerogels (denoted as PMSQ-F127 and PMSQ-P105) reached 83 \% and 90 \%, respectively (Figure 1b). These values are among the highest compared to the PMSQ aerogels reported in previous works.\textsuperscript{16,21} The skeletal features observed by transmission electron microscopy (TEM) and FE-SEM of PMSQ-F127 and PMSQ-P105 are shown in Figure 1c-d and Figure 1e-f, respectively. The pore structures are constructed with fibrous skeletons of approximately 6–8 nm thickness with branches (nodes). The size parameters of the structure are discussed later in Table S3. Because the material shape of the PMSQ aerogels depends on the shape of the vessel used in the sol-gel synthesis, the PMSQ aerogels can be prepared in different forms; for examples, plate (Figure 1b) and string (Figure 1g). Taking the PMSQ-F127 aerogel as an example, one unique
feature we found in the PMSQ aerogels with the branched fibrous skeletons is the extraordinarily high flexibility like a silicone wire or tube as shown in Figure 1g.

**Figure 1.** Macro-/mesoscopic physical features of the flexible and transparent PMSQ aerogels prepared with two types of surfactants. (a) The starting compositions were optimized to prepare highly transparent PMSQ aerogels with the mesoscale fibrous structure. (b) Appearance of the PMSQ aerogels prepared with the different surfactant, F127 and P105. (c,d) FE-SEM images of the samples PMSQ-F127 and PMSQ-P105, respectively. (e,f) TEM images of the samples PMSQ-F127 and PMSQ-P105, respectively. (g) A photograph of the string-shaped sample of PMSQ-F127, demonstrating high flexibility like a silicone tube.

**Effect of the fibrous structure in PMSQ aerogels on the mechanical properties**

To investigate the structural effect on the mechanical properties, we prepared the PMSQ aerogels while controlling the following characters: bulk density, transparency, and the material shape. Bulk density is related to porosity, which influences the mechanical properties, while transparency is related to the size and homogeneity of the porous structure. While the film-shaped PMSQ aerogels show bending flexibility (Figure S5), which has also been reported in our recent work in the polyvinyl-polysiloxane system, it should be emphasized here that the monolithic samples in a cylindrical shape show large bending
deformations (Figure 2). Thin materials such as glass sheets can be more bendable compared to bulky counterparts because of the decreased section modulus. In the present case, however, the monolithic samples with ca. 10-mm diameter show excellent bendability as shown in Figure 2c (span = 20 mm) and 2d (span = 60 mm), which is the first observation in a low-density, transparent aerogel. Movies S1-2 demonstrate the superbendability of PMSQ-P105 and -F127, respectively.

**Figure 2. Mechanical properties of the flexible and transparent PMSQ aerogels prepared in different conditions.** (a,b) Stress-strain curves obtained from three-point bending of the PMSQ samples with a span length of 20 mm (a) and 60 mm (b). (c,d) Photographs showing the bendability of the PMSQ samples PMSQ-P105 (span 20 mm) and PMSQ-F127 (span 60 mm).

**Origin of the mechanical flexibility of the PMSQ aerogels with fibrous structure**

As a reference, we also prepared a PMSQ aerogel sample from a starting composition reported in our previous work (see Methods for details). This reference sample was prepared in the presence of a cationic surfactant CTAC and the base source urea, and is denoted as PMSQ-prev. This sample possesses a porous structure of aggregated colloidal particles, which is more like the microstructure of the standard silica aerogels with mass fractals (Figure 3a).\(^{32,33}\) The stress-strain curves of the three-point bending test are shown on the PMSQ aerogels; PMSQ-F127, -P105, and -prev with different span lengths, 20 mm (Figure 2a) and 60 mm (Figure 2b). The maximum bending strain at failure with the span length of 20 mm was 51 % and 75 % in PMSQ-F127 and -P105, respectively (Figure 2a). These maximum bending strains are much higher than that of the PMSQ-prev, 30 % (Figure 2a), and polymer-crosslinked silica aerogels (~ 40 %) with as high density as 0.63 g cm\(^{-3}\),\(^{34}\) while density of PMSQ-F127 and -P105 are 0.13 and 0.12 g cm\(^{-3}\), respectively, as mentioned below. It is
worth noting that the short span length (20 mm) did not show a natural curvature in the samples, which means the differences in these samples are not clearly expressed. The PMSQ-P105 aerogel showed much higher bending performance than PMSQ-F127 in the short span length test (20 mm). On the other hand, with the longer span length (60 mm), both PMSQ-F127 and -P105 aerogels showed natural curvature and almost the similar maximum bending strain 19 %, which is much higher than that of PMSQ-prev, 9 % (Figure 2b).

Figure 3. Control of the mesoscale structure of the PMSQ aerogel, and properties of the PMSQ samples with different mesoscale structures. (a) Schematic for controlling the mesoscale structure. (b) $^{29}$Si CP/MAS NMR spectra of the PMSQ samples magnified in the $T^2$ region. Note that the spectra are normalized by the $T^3$ peak intensities. (c) Stress-strain curves obtained from three-point bending of the PMSQ samples with the span length of 20 mm. (d) Obtained properties of the PMSQ samples. [a] Light transmittance at 550 nm through 10-mm equivalent specimen. [b] Maximum strain at failure of the three-point bending of the PMSQ samples with the span length of 20 mm. [c] Bulk density.

The shape of the pore skeletons naturally influences the mechanical properties of porous materials as deeply studied in the cellular solids. To discuss the effect of the mesoscale porous structure on their mechanical properties, we prepared a PMSQ aerogel with different skeletal structures by replacing a part of the solvent (water) with $N,N$-dimethylformamide (DMF) in the PMSQ-P105 system. Since the polarity of DMF is lower than that of water and
specific hydrogen bonding can be formed with silanol groups, the phase separation tendency of the MTMS-derived hydrophobic condensates varied in the additional presence of DMF. The PMSQ-P105 aerogel obtained in the presence of DMF (denoted as PMSQ-P105DMF) showed a typical particle aggregated porous structure (Figure 3a, Figure S6b,d). Figure S7 shows the comparison of solid-state $^{29}$Si cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectra on the aerogels with branched fibrous skeletons (PMSQ-F127, and -P105) and particle aggregated skeletons (PMSQ-prev and -P105DMF). Peaks around −67 ppm and −57 ppm correspond to fully condensed (CH$_3$Si(OSi)$_3$, T$^3$) and doubly condensed (CH$_3$Si(OSi)$_2$(OH/CH$_3$), T$^2$) silicon species, respectively. The NMR spectra magnified in the T$^2$ region is shown in Figure 3b. Although there is only negligible difference in the peak shape among these aerogels, the condensation degree values, (T$^3$+2/3T$^2$)/(T$^3$+T$^2$), calculated from the peak areas, are slightly different. The condensation degree is 97.4 %, 98.3 %, 97.7 %, and 97.6 % for PMSQ-F127, -P105, -prev, and -P105DMF systems, respectively. Note that we have confirmed that there is only negligible difference between CP/MAS and single-pulse measurements in the PMSQ system. It is reported that in the system using F127 and urea as the base source, the condensation degree was 95.0 % (calculated from the data in ref. 21). Comparison between these two cases using urea and TMAOH in the F127 system, the improvement of condensation degree can be attributed to the higher pH (~13.7 in 0.50 M TMAOH) during polycondensation. Polycondensation is promoted in such a higher pH condition compared to the weakly basic condition in the case of urea as the base source (pH reaches 7−9). Generally, from the viewpoint of molecular-level structure, the lower condensation degree or cross-linking density would lead to lower modulus and higher bendability. In the case starting from trifunctional MTMS, elasticity or resilience may be sacrificed due to the more remaining alkoxy/hydroxy groups in the less cross-linked network. In the present case, however, there is no clear correlation between the bending flexibility and cross-linking density; more flexible PMSQ-P105 has higher cross-linking density compared to PMSQ-prev and PMSQ-P105DMF with aggregated colloidal skeletons and with similar bulk density and transmittance (Figure 3c,d). In addition, no remaining surfactant, which may influence the mechanical properties, was detected in all the samples including PMSQ-P105 and -P105DMF by $^{13}$C NMR and TG-DTA measurements as presented in Figure S8a and S8b, respectively. Based on the above results, we conclude that the mesoscale branched fibrous porous structure gives a considerable improvement in the bending flexibility.
Classifying the 3D porous structure of PMSQ aerogels

To extend this knowledge of the relationship between the mesoscale porous structure and mechanical properties toward the preparation of new PMSQ aerogels combining high transparency and high flexibility, optimization of the structural properties is important. The thin fibrous structure with long 1D-shaped skeletons with branches contributes to limited scattering of visible light, which is advantageous for improving the transparency. To obtain further insight of the skeleton shape, we classify the 3D porous structure by focusing on the structural units that comprise the 3D network. Scheme 1 shows schematics of the types of 3D mesoscale porous structure of PMSQ aerogels. The pore skeletons can be classified into (i) connected colloidal particles and (ii) branched 1D skeletons with nodes (the latter shown in Scheme 1a). When the porous structure is closer to the branched 1D skeletons (ii, to the right in Scheme 1b), the mesoscale porous structure can be identified as the fibrous structure that shows higher skeletal ratio and leads to higher bendability. On the other hand, when the porous structure is closer to the connected particles (i, to the left in Scheme 1b), the mesoscale porous structures can be identified as aggregated particles that shows lower skeletal ratio, and bendability becomes lower because the stress is accumulated in small neck parts.37-40

Scheme 1. Schematics of the relationship between the mesoscaled structures and bulk mechanical properties. (a) Schematic of the pore skeletons with 1D branched fibrous structure with nodes. (b) Schematic of the relationship between skeletal ratio and bendability. The fibrous structure that has higher skeletal ratio leads to higher bendability.

Optimization of the mesoscale porous structure of PMSQ aerogels toward thermally superinsulating materials with both high transparency and high flexibility
To demonstrate the optimization of mesoscale structure toward thermally superinsulating materials with both high transparency and high flexibility, we tried to identify the suitable starting composition using other PEO-\textit{b}-PPO-\textit{b}-PEO-type triblock copolymers as phase separation suppressor and structural determining agent (Table S1,2). When surfactant Pluronic P94 and L64, which have the similar HLB values (13.5 for P94 and 12-18 for L64) and lower molecular weight (ca. 5 000 for P94 and ca. 2 900 for L64) than those of P105 (HLB value: 12-18 and \( M_w \approx 6 500 \)) were used, aerogels with higher transmittance (denoted as PMSQ-P94, and PMSQ-L64, respectively) than PMSQ-P105 were obtained (Figure 4a,b). The light transmittance values \( T_{550} \) of the obtained aerogels are 96 % and 93 % for PMSQ-P94, and -L64, respectively, which are higher than those of the other aerogels. When surfactant F68 (HLB value: \( >24 \) and \( M_w \approx 8 400 \)) was used (denoted as PMSQ-F68), light transmittance is almost the same as that of PMSQ-F127 (\( T_{550} = 83 \) %, Figure 4b,e), and PMSQ-F68 has the similar branched fibrous structure, which shows higher bending flexibility than PMSQ-prev (Figure S9b,d,e, and Figure 4c,d).

**Figure 4.** Influence of the kind of Pluronic surfactant on transparency and mechanical flexibility. The starting compositions were optimized to prepare highly transparent PMSQ aerogels with the mesoscale fibrous structure. (a) Appearance of the PMSQ aerogels prepared with the different surfactants, P94, F68, and L64. (b) Spectra of the total transmittance of the PMSQ samples. The thickness of the samples is 5.0 mm. (c) Stress-strain curves obtained from three-point bending of the PMSQ samples with the span length of 60 mm. (d) Obtained properties of the PMSQ samples. [a] Light transmittance at 550 nm through 10-mm equivalent specimen. [b] Maximum strain at failure of
the three-point bending of the PMSQ samples with the span length of 60 mm. [c] Bulk density. (f) Total (solid lines) and diffuse (broken lines) transmittance of PMSQ-P94, a borosilicate glass, and a soda glass. Thickness of the three samples is 5.3, 5.0, and 4.8 mm, respectively.

Although it is difficult to compare the pore size by the gas sorption measurement due to their mechanically compliant nature, the visible light transparency of the aerogels is a guide to the sizes of skeletons and mesopores in the present samples. Table S3 compares the size parameters of the porous structure manually measured from high-resolution FE-SEM and TEM images (see also Scheme 1 for the parameter definitions). The mesopore size of the PMSQ aerogels is in the following order: PMSQ-P105 ~ -F127 > -F68 > -prev > -P94. The comparison of the skeleton sizes is rather complicated, but roughly correlated to the mesopore size. Although the BJH pore size distributions presented in Figure S10 show a somewhat different tendency because of possible deformations of these materials during measurement, correlation between the samples and the scale of mesoporosity can be understood as follows. As discussed above, the mesoscale structure of PMSQ aerogels is related to the phase separation tendency, which is strongly influenced by the kind of surfactant. In the present PMSQ system, the phase separation tendency between the PMSQ condensates and water-based solvent becomes lower by the triblock copolymer surfactant with lower molecular weight and moderate HLB value.

The PMSQ-L64 sample was too fragile to obtain a crack-free monolith to perform the bending test accurately in this study, because the porous structure was too fine (Figure S9a,c). By comparing the mechanical properties except PMSQ-L64, bending flexibility was investigated (Figure 4c,d). The maximum bending strain at failure of PMSQ-P94 is slightly higher than that of PMSQ-prev, while much lower than that of PMSQ-F127 and -P105 (Figure 2b and 4c,d). Although the mesoscaled porous structure of PMSQ-P94 (Figure S11) with thinnest skeletons and a low skeletal ratio ([skeleton length]/[node size]) contributes to the higher transmittance than other samples (Figure 4b,d), the geometrical feature at the same time decreases the flexible response toward the bending deformation (Figure 4c,d). As mentioned above, the maximum bending strain of PMSQ-P94 is slightly higher than that of PMSQ-prev (PMSQ-P94: $\varepsilon_{\text{max,60}} = 10$ % and -prev: $\varepsilon_{\text{max,60}} = 9$ %, Figure 2b and Figure 4c,d), while transparency of PMSQ-P94 is much higher than that of PMSQ-prev (PMSQ-P94: $T_{550} = 96$ %, and -prev: $T_{550} = 90$ %) owing to the finer porous structure. The bending flexibility tends to be lower in finer pore structure due to the smaller thickness of the skeletons and higher number density of mechanically weaker unit (nodes). In other words, bending
flexibility and transparency are generally tradeoff. Here the PMSQ aerogel prepared in the presence of CTAC (PMSQ-prev) has the skeletons of aggregated colloids (Figure 3a), which is not advantageous in bending flexibility, while those prepared in the presence of the triblock copolymer surfactant has the branched fibrous skeletons with high connectivity. The sample PMSQ-P94 with the outstanding transparency therefore shows bending flexibility even higher than PMSQ-prev.

In addition, the maximum strain of PMSQ-F68 by three-point bending is lower than that of PMSQ-F127 (PMSQ-F68: \( \varepsilon_{\text{max,60}} = 15 \% \), and -F127: \( \varepsilon_{\text{max,60}} = 19 \% \), Figure 4c,d). The porous structure of PMSQ-F68 is finer with lower skeletal ratio (Table S3). In this case, it is plausible that the more coarsened fibrous feature of PMSQ-F127 resulted in higher bendability than that of PMSQ-F68. The same is true for the sample PMSQ-P105 with the more coarsened structure with higher skeletal ratio, which shows higher bending flexibility compared to PMSQ-F68. Transparency of PMSQ-F68 and -F127 is lower than that of -P105, which does not reflect the scale of the pore structure. However, this fact implies the surfactant with a higher HLB value not only shows lower ability in suppression of phase separation, but also decreases the structural homogeneity presumably by promoting excess aggregation of the condensates through hydrogen bonding between condensates and the EO unit of surfactant. Optimization of the pore size and skeletal shape of the PMSQ aerogels by employing adequate surfactant can lead to high transparency and high flexibility at the same time. The comparison of these samples in Figure 4d reinforces the idea that the scale of the pore structure strongly influences the macroscopic mechanical flexibility.

Here we stress again that this is the first report realizing a high-level combination of visible transparency and mechanical flexibility. In previous literature, silica aerogels derived from tetramethoxysilane (TMOS) and those from partially hydrolyzed tetraethoxysilane (TEOS) were reported to show comparably high transmittance, but no improvement of the mechanical properties are reported. Improvement of mechanical flexibility has been demonstrated in polymer-reinforced aerogels and other aerogels consisting of specific nanostructures (e.g., CNT aerogels and graphene aerogels); however, their visible transparency remains low (or zero). Transparent aerogels were prepared with TEMPO-oxidized cellulose nanofibers and chitosan nanofibers, while these are not mechanically resilient because of the weak cross-links and low cross-linking density between the fibers. In the present study, we report superflexible and resilient aerogels with glass-like transparency consisting of the mesoscale fibrous skeletons, which have been formed through
polycondensation under the interaction with hydrogen-bonding surfactant. It is known that one-dimensional self-assembly of silica nanoparticles occurs in the presence of Pluronic surfactants due to the difference of steric crowding by hydrogen-bonded surfactant molecules on the particles. In the present case, it can be deduced that polycondensation proceeds preferentially in 1D direction in a similar manner under an additional effect of asymmetric viscoelastic properties of gelling phase and solvent. Such network microstructures as the result of viscoelastic phase separation were shown to be advantageous in obtaining materials with low density and high mechanical strength.

The present results demonstrate the synthetic strategy to optimize both transparency and bendability. For example, in developing a strategy toward highly transparent thermal insulating materials, the mesopore size should be smaller to decrease thermal conductivity, which in turn sacrifices the mechanical flexibility. By taking the synthetic route using PEO-\textsubscript{b}-PPO-\textsubscript{b}-PEO-type triblock copolymer as the phase separation suppressor and structural determining agent, the PMSQ aerogels with the mesoscale branched fibrous porous structure can be obtained. The most transparent sample PMSQ-P94 with the high visible light transparency comparable with conventional non-thermal insulating glass plates (Figure 4f and Figure 5) is one of the most transparent aerogels to the best of our knowledge. The low haze value (1.7 \% for PMSQ-P94), which is also comparable with the lowest value ever reported, is primarily due to the absence of aggregation in the scale of \( \sim \) 100 nm or larger.

Polycondensation under the high pH in the presence of high concentration of surfactant is considered to prevent excess aggregation due to a balanced polycondensation/hydrolysis equilibrium and moderately high viscosity. In addition, the Rayleigh scattering can be suppressed by the skeletons with small mean particle size. The low haze in the present samples is also attributed to the small size of the pore skeletons as shown in Table S3. In addition to the high transparency, PMSQ-P94 shows higher flexibility (Figure 2b and Figure 4c,d). Furthermore, thermal conductivity of PMSQ-P94 was 14.5 mW m\(^{-1}\) K\(^{-1}\), which is comparable with conventional silica aerogels and low enough for superinsulating window applications.

This study provides a new opportunity to realize thermal superinsulating flexible devices with high transparency through the control of the mesoscopic skeletal features and structural size, which influence the bending flexibility and transparency, respectively. In future studies, there is a high possibility to realize both mechanical flexibility and transparency at an even higher level by employing surfactant with optimized molecular structure.
Methods

Chemicals and Materials

Methyltrimethoxysilane (MTMS) was purchased from Shin-Etsu Chemical Co., Ltd. (Japan). Acetic acid (HOAc, ≥ 99.7 %), distilled water (H₂O), methanol (MeOH, ≥ 99.5 %), 2-propanol (IPA, ≥ 99.0 %), and N,N-dimethylformamide (DMF, ≥ 99.5 %) were purchased from Kishida Chemical Co., Ltd. (Japan). Aqueous tetramethylammonium hydroxide (TMAOH, ca. 25 %) and cationic surfactant n-hexadecyltrimethylammonium chloride (CTAC) were purchased from Tokyo Chemical Ind. Co., Ltd. (Japan). Urea was purchased from Hayashi Pure Chemical Ind., Ltd. (Japan). Nonionic surfactant Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆, M_w ≈ 12 600) and Pluronic L64 (EO₁₃PO₃₀EO₁₃, M_n ≈ 2 900) were purchased from Sigma-Aldrich Co., LLC (USA). Nonionic surfactant Synperonic P105 (EO₃₇PO₅₆EO₃₇, M_w ≈ 6 500) was kindly donated by Croda Japan K.K. Nonionic surfactant Pluronic P94 (EO₂₆PO₄₈EO₂₆, M_w ≈ 5 000) was purchased from BASF (Germany). Nonionic surfactant Pluronic F68 (EO₇₆PO₂₀EO₇₆, M_w ≈ 8 400) was kindly donated by ADEKA Co., Ltd. (Japan). Nonionic surfactant EH-208 (poly(oxyethylene) 2-ethylhexyl ether) was kindly donated by NOF Co., Ltd. (Japan). All reagents were used as received.

Materials Synthesis

The new PMSQ aerogels prepared by using nonionic surfactant and TMAOH
The starting compositions are listed in Table S2. In a glass tube, 5.0 mL of 5 mM HOAc and 5.0 mL of MTMS were mixed and continuously stirred for 15 min at room temperature for hydrolysis of MTMS. A given amount of surfactant and H_2O were subsequently added to the obtained homogeneous sol (in the case of PMSQ-P105DMF, a given amount of DMF was added instead of H_2O) and the solution was kept stirred until it became homogeneous (typically, for ~1 h) at room temperature. Then, the resulting sol was cooled in the reaction vessel in an ice bath for 30 min. Under moderate stirring to avoid a bubble formation in the ice bath, a given amount of TMAOH aq. was carefully added, and after stirring for 3 min, the mixture was transferred to an airtight container and allowed to gel and age at room temperature for 1 h. Gelation occurred in ~15 min. The obtained gel was kept at 60 °C for 3 d for further aging. The aged gel was soaked in solvents at 60 °C for at least 8 h for washing and solvent exchange. In order to prevent the gel from cracking due to osmotic pressure, the composition of the solvent was changed in the following order: H_2O:MeOH = 100:0, 90:10, 70:30, 50:50, 30:70, 10:90, 0:100 in volume ratio, and finally exchanged to IPA. In the case of the last two steps in pure MeOH and IPA, the solvent exchanging processes were repeated 5 times and 3 times, respectively. The obtained alcogel was supercritically dried at 80 °C under 14 MPa for 10 h with carbon dioxide.

**PMSQ aerogels prepared by following our previous research for testing the hypothesis of phase separation phenomenon**[^20] and for comparison with this work[^24,49]

In a glass tube, 6.0 mL of 5 mM HOAc, 0.50 g of urea, and a given amount of Pluronic F127 or CTAC were mixed and continuously stirred until the mixture became homogeneous (typically, for 30 min). Then, 5.0 mL of MTMS was added and the mixture was kept stirred at room temperature for 30 min to allow hydrolysis of MTMS. In another case for preparing the PMSQ aerogel with colloidal aggregate structure (PMSQ-prev), 12 mL of 5 mM HOAc, 3.0 g of urea, 0.40 g of CTAC, and 5.0 mL of MTMS were mixed in a similar way. The obtained homogeneous mixture was kept at 60 °C for 4 d for gelation and aging. The obtained gels were subjected to washing by solvent exchange using MeOH (for ≥ 8 h, each for 3–5 times) and IPA (for ≥ 8 h, each for 3 times). The resultant gels were then supercritically dried at 80 °C under 14 MPa for 10 h with carbon dioxide.

**Physical Characterizations**

Bulk density (ρ_b) of the obtained aerogels was determined by measuring the diameter, height, and weight of cylindrical samples. The spectral data of transmittance of the aerogels were obtained with a V-670 UV-vis-NIR spectrophotometer (JASCO Co., Japan) equipped
with an integrated sphere. The value of total transmittance at 550 nm wavelength was converted to the one in a 10 mm-thick sample according to the Lambert-Beer equation and denoted as total transmittance ($T_{550}$). The pore/skeletal structures of aerogels were observed under a field-emission scanning electron microscopy (FE-SEM: Regulus 8220, Hitachi High-Tech Co., Japan) and a scanning transmission electron microscopy (STEM: JEM-1400Plus, JEOL Co., Japan). Before observation, aerogels were gently crushed with an ultra-fine sandpaper and the crushed aerogels on the sandpaper were scattered on a carbon tape attached to a sample stage (FESEM) or a grid (STEM). All structural observations were performed without any conductive coatings to avoid influence on the microstructure. Pore structures of the samples were characterized from nitrogen isotherms at 77 K with BELSORP-max (MicrotracBEL Corp., Japan). The samples were degassed at 80 °C overnight prior to each measurement. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method and pore size distribution was by the Barrett-Joyner-Halenda (BJH) method from the adsorption branch.

The chemical structures were investigated by $^{29}$Si and $^{13}$C CP/MAS NMR experiments using an NMR spectrometer equipped with a double-resonance 4-mm MAS probe (Bruker Avance III 800US Plus, Germany, operated at 158.96 MHz, and 201.20 MHz for $^{29}$Si, and $^{13}$C, respectively). The measurements were carried out at room temperature at the MAS frequency of 12 kHz throughout the study. Hexamethyldisiloxane and hexamethylbenzene were used as external reference materials for $^{29}$Si, and $^{13}$C, respectively. Cross-polarization contact times were 5.5 ms for $^{29}$Si and 4.5 ms for $^{13}$C. The $^{29}$Si and $^{13}$C field strengths of 50 and 100 kHz were used during the CP period. The thermal properties of the samples were investigated by thermogravimetry-differential thermal analysis (TG-DTA: TG-DTA 8122, Rigaku Co., Japan). The samples were heated with a rate of 5 °C min$^{-1}$ in air supplied at ca. 100 mL min$^{-1}$. The mechanical properties of the aerogels were investigated by a material tester (AUTOGRAPH AG-X plus, Shimadzu Co., Japan). For three-point bending tests, cylindrical samples with diameter of about 9 mm and length of about 80 mm were used. The span length was fixed at 20 mm or 60 mm, and the cross-head speed was fixed at 0.5 mm min$^{-1}$.

The stress ($\sigma$) and bending strain ($\varepsilon$) were calculated from the following equations, in which $D$ is the diameter of a cylindrical sample, $L$ is span length, $\Delta l$ is displacement length, and $F$ is loaded force.
The thermal conductivity was determined by a heat flow meter (HFM 436 Lambda, Netzsch, Germany) at the mean temperature of 25 °C with a plate sample of 100 × 100 × 8 mm.

**Data availability**

Data discussed in this study are presented in the text and the Supplementary Information. Additional data can be obtained from the corresponding author upon reasonable request.
References


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**Author contributions**

R.U., K.K., and Y.H. designed the project. R.U. performed the experiments. Y.H. prepared the manuscript with input from all authors. A.M. and H.K. contributed to the NMR measurement. K.K. and K.N. provided the research facility of materials synthesis and characterization. K.K. supervised the project. All authors reviewed and commented on the manuscript.

**Competing interests**

The authors declare no competing interests.

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**Supplementary Information**

Supplementary Information

Supplementary Movie S1-2