Dynamic spring-back behavior in evaporative drying of polymethylsilsesquioxane monolithic gels for low-density transparent thermal superinsulators

Gen Hayase,^{†§} Kazuyoshi Kanamori,^{*†} Ayaka Maeno,[‡] Hironori Kaji,[‡] Kazuki Nakanishi[†]

[†] Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan

[‡] Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

[§] Present address: Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Aramaki aza Aoba 6-3, Aoba-ku, Sendai 980-8578, Japan

*Corresponding author: kanamori@kuchem.kyoto-u.ac.jp

ABSTRACT: Ambient pressure drying of polymethylsilsesquioxane gels via dynamic shrinkage-reexpansion has been investigated for preparation of aerogel-like xerogels and their application to thermal superinsulators. An extended aging of wet gels in aqueous solution containing precursor-derived species is found to be crucial in obtaining crack-free, monolithic xerogels with sufficiently low thermal conductivity ($13.7 \text{ mW m}^{-1} \text{ K}^{-1}$) at bulk density of 0.140 g cm^{-3} (porosity ~90 %).

Keywords: sol-gel; aerogels; xerogels; spring-back behavior; ambient pressure drying; thermal insulators

1. Introduction

Aerogels are low-density porous materials obtained via the sol-gel process and supercritical drying [1]. The chemical compositions of aerogels have virtually no restrictions; aerogels with a variety of compositions can be obtained as far as a wet gel can be prepared and the pore solvent can be removed without serious contraction by supercritical drying [2]. Various types of aerogels are therefore synthesized ranging from inorganic oxides [4-7], organic-inorganic hybrids [8-11], organic polymers [12-14] and to biomaterials [15-19] for many purposes. Silica aerogel is the most studied one due to the unique properties such as high visible-light transmittance and very low thermal conductivity [4,20]. Since the microstructure comprising solid skeletons, composed of silica nanoparticles with ca. 10 nm in diameter and pores with several tens nanometer, is finer than the visible-light wavelengths and mean free path of the molecules in air, properties like visible-light transparency and low thermal conductivity are resulted. Aerogels are expected to be a superior substitution of existing thermal insulators, and transparent insulating window systems can be designed by sandwiching aerogels between glazing materials [21]. However, fatal mechanical friability, derived from the solid skeletons with weakly connected silica nanoparticles and high porosity, and necessity of the supercritical drying process under high pressure hinder massive industrial productions and practical uses of silica aerogels.

Recent years, there are some reports on organic-inorganic hybrid aerogels of silica and organic polymers [11,22-25]. Those monolithic aerogels show higher mechanical properties such as compressibility and bendability, but often suffer from higher thermal conductivity and lower visible-light transmittance due to increased density and coarsened microstructure. Our group has been investigating polymethylsilsesquioxane

(PMSQ, $\text{CH}_3\text{SiO}_{1.5}$) aerogels derived from methyltrimethoxysilane (MTMS) and reported transparent monolithic aerogel-like xerogels via evaporative drying [26,27]. In comparison to silica, PMSQ has fewer siloxane bonds per each silicon, which is attached to one methyl group instead, resulting in the increased flexibility. In addition, the presence of hydrophobic methyl groups causes repulsion when compressed, and the low residual silanol density suppresses irreversible shrinkage. These improved structural and mechanical features enable ambient pressure drying without collapsing the delicate pore structure to obtain aerogel-like xerogels if processed under optimized conditions. Xerogels with no significant difference in bulk density, visible-light transmittance and thermal conductivity ($\sim 15 \text{ mW m}^{-1} \text{ K}^{-1}$ or less) have been obtained [28,29]. However, there are still only a few systematic studies on the process of evaporative drying of low-density gels under an ambient condition [30-32]. In the limiting case of transparent monolithic aerogels, there is no report as far as we know, though focusing the drying process is a necessary step toward further improvement of the microstructure for the practical use of aerogel-like xerogel-based transparent thermal superinsulators.

In the present paper, we synthesized PMSQ gels with different density under the presence of a cationic surfactant *n*-hexadecyltrimethylammonium chloride (CTAC) and observed a shrinkage-reexpansion (spring-back) behavior [30-32] in the course of evaporative drying. In addition, extended aging processes have been examined to reduce irreversible shrinkage and cracking of PMSQ gels during drying to achieve lower bulk density and higher thermal insulation.

2. Experimental Procedure

The sample notations are defined as Ax and Xx, where A and X mean “aerogels” obtained via supercritical drying and “xerogel” via ambient pressure drying, respectively, and x denotes volume of acetic acid aqueous solution in the starting composition. At the starting composition of Ax/Xx, x mL of 5 mM aqueous acetic acid (Kishida Chemical Ltd., Japan), $0.3 \times x$ g of urea (Hayashi Pure Chemical Ind., Ltd., Japan), and 0.40 g of surfactant CTAC (Tokyo Chemical Ind. Co., Ltd., Japan) were dissolved in a glass sample tube, and then 5.0 mL of MTMS (Shin-Etsu Chemical Co., Ltd., Japan) was added under vigorous stirring. The mixed solution was continuously stirred for 30 min at room temperature for acid-catalyzed hydrolysis, followed by base-catalyzed gelation and aging at 60 °C in a closed vessel for 4 d. The gelation time was about 3 h in the case of A10/X10. Some of the samples were further processed by additional aging, in which wet gels were directly soaked in an “aging sol” at 80 °C for 1 d. The aging sol was prepared by the following process; (1) stirring 100 mL of 5 mM aqueous acetic acid and 3 mL of MTMS in a glass bottle for 30 min at room temperature, (2) adding 900 mL of distilled water and 5 g of urea into the bottle, and then keeping the solution at 80 °C for 24 h. The obtained gels both with and without the extended aging were then washed in a sufficient amount of methanol (Kishida Chemical Ltd.), which was exchanged with fresh one three times (at least 8 h for each duration of washing), and then in 2-propanol (Kishida Chemical Ltd.) three times in the same way to remove CTAC and other unreacted reagents. To obtain aerogels via supercritical drying, alcogels obtained in this way were dried from supercritical carbon dioxide at 80 °C, 14.0 MPa for 10 h in a custom-built

autoclave (Mitsubishi Materials Corp., Japan). For evaporative drying to obtain xerogels, the alcogels were subjected to solvent exchange with *n*-heptane (Kishida Chemical Ltd.) three times, and heptane was slowly removed by evaporation at room temperature for 1 d. After drying, all aerogel and xerogel samples were heated at 110 °C for 4 h to allow further spring-back by enhancing relaxation of the deformed PMSQ network.

Bulk density was obtained by measuring the volume and weight of a carved gel. Bulk density has been measured on 3-5 samples with estimated errors of 2 % (all aerogels), 4 % (xerogels X8, X10 and X20) and 10 % (X50 and X100). Thermal conductivity was measured with HFM 436 Lambda (Netzsch GmbH (Germany)) by measuring heat flow at the center part of the specimen with estimated error of 3-5 % (including systematic error of the device). To observe shrinkage-reexpansion behaviours during the evaporative drying process, digital photos were automatically taken at intervals of 25 s. To assess the molecular-level structure of obtained siloxane networks, ^{29}Si solid-state cross-polarization magic angle spinning (CPMAS) 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 ^1H - ^{29}Si cross-polarization was fixed at 5.5 ms and the rate of sample spinning was 15 kHz. The ^{29}Si chemical shift was expressed relative to tetramethylsilane (Me_4Si) by using the resonance line at -9.66 ppm for hexamethylcyclotrisiloxane crystals as an external reference. The same equipment with a probe for liquid samples was used for ^{29}Si liquid-state NMR measurements of the aging sol prepared in deuterated water (Tokyo Chemical Ind. Co., Ltd.). The relaxation delay was set to 10 s. Fourier transform infrared spectroscopy (FTIR, FT/IR-6100TY, JASCO

(Japan)) was employed to investigate the molecular-level structures of the aerogel/xerogel and aging sol samples with an ATR attachment (ATR PRO470-H). For microstructure observations, a field emission-type scanning electron microscope (JSM-6700F, JEOL, Japan) was employed.

3. Results and Discussion

Wet gels were synthesized with different ratios of the precursor methyltrimethoxysilane (MTMS) to aqueous acetic acid-urea solvent [33] in order to change density of obtained dried gels. During the observation of evaporative drying of 5 samples (Xx) with different concentrations of MTMS in the starting composition (Table 1), all samples showed three drying stages as follows (Fig. 1, and Movie S1-S5, Supplementary Material) [34,35]: (1) the whole gel shrinks by the capillary pressure on evaporation of the solvent; (2) the shrinkage rate becomes low and the gel shows critical opalescence; (3) the gel turns to transparent again and starts expanding. Fig. 2(a) displays the changes in diameter of the gels during evaporative drying, where T shows the normalized time when the diameter of the gel becomes minimum during shrinkage (*i.e.* the critical point). The shrinkage from the original shape was smaller when the gel has higher density, which is simply because the gel with higher density deforms less, given the compressive force applied by the capillary pressure is similar, *i.e.* the pore size is similar. Bulk density of each aerogel and xerogel is shown in Table 1. All xerogels obtained via evaporative drying does not have internal cracks (Fig. 2(b)) but have higher density than aerogels due to incomplete recovering without extended aging processes described below.

Thermal conductivity of a porous material consists of three components; heat transfer by the gas phase, solid phase and radiation, and shows the minimum at certain density, because the contribution of the gas phase becomes higher and that of the solid phase lower with decreasing density [36,37]. In the case of PMSQ aerogels Ax, the minimum thermal conductivity was found at around bulk density of *ca.* 0.14 g cm^{-3} (A10, Fig. 3). Based on this data, we tried to prepare PMSQ xerogels with density *ca.* 0.14 g cm^{-3} via evaporative drying. However, it was hard to obtain such optimized aerogels due to the irreversible shrinkage as mentioned above.

To solve this problem, we developed an aging process in aqueous conditions. In the case of porous silica materials, the hydrothermal treatment in basic solution is effective to improve the mechanical strength by the Ostwald ripening [38]. Through this treatment, the neck part of the colloid-aggregated silica microstructure grows by the dissolution-reprecipitation process, and the strength and stiffness of the network are improved [39]. In addition, aging in alkoxysilanes monomer or oligomer solution was found to further improves the mechanical properties and monolithicity [40,41]. We applied this process to PMSQ wet gels with an expectation for the same effect, though the solubility of the PMSQ network would be lower as compared to silica because of the higher electron density at silicon and hydrophobicity. In the first experiment, we simply immersed the gels in distilled water for 24 h for extended aging. After washing, solvent exchange and evaporative drying, irreversible shrinkage was drastically decreased, but many cracks formed on the gel surface and we could not obtain intact monolithic xerogels. The cracks are deduced to be derived from surface defects or “flaws”, which can be an origin of the cracks, at an atomic or molecular scale. We next tried to use

an aqueous solution (sol) containing a small amount of hydrolyzed and oligomerized MTMS during the aging process instead of pure distilled water to enhance the reprecipitation process. This “aging sol” has been prepared from a dilute aqueous solution of MTMS by an acid-base two-step process (see Experimental Procedure for details), and contains mainly hydrolyzed monomeric (T^0 , $\text{CH}_3\text{Si}(\text{OH}/\text{CH}_3)_3$) and dimeric (T^1 - T^1 , $(\text{OH}/\text{CH}_3)_2\text{CH}_3\text{SiOSiCH}_3(\text{OH}/\text{CH}_3)_2$) species judging from data of FTIR, ^{29}Si NMR (both in Fig. S1, Supplementary Material) and mass spectroscopy.

After many trials, we succeeded to obtain crack-free monolithic gels with using the aging sol via evaporative drying (Movie S6, Supplementary Material). Bulk density of xerogels prepared by the extended aging treatment with the aging sol (X10a, 0.140 g cm^{-3}) is found to be almost the same with that of corresponding aerogel (A10, 0.138 g cm^{-3}) from supercritical drying. Figs. 4(a) and (b) are the results of ^{29}Si solid-state CPMAS NMR and FTIR, showing the molecular-level structure change by the aging process. The width and relative intensity of the T^2 ($\text{CH}_3\text{Si}(\text{OSi})_2(\text{OH}/\text{CH}_3)$) peak in the NMR spectrum of X10a are broadened and decreased, respectively, as compared to X10, and absorption band at 920 cm^{-1} in FTIR is also decreased. These results mean that unreacted silanol groups in the PMSQ network are effectively reduced. In addition, the T^2 peak shows an upfield shift in the NMR spectrum, which can be attributed to the decrease of the cyclic components that consist of strained cyclosiloxane units [42,43]. These changes are rational when considering that the rearrangement of the network occurs to decrease the strained cyclosiloxanes during the Ostwald ripening process, and hydrolyzed monomeric and dimeric species in the aging sol attached to the

network, filling the defects or flaws. The decreases in the strained cyclosiloxane rings and silanol groups contribute to the improved mechanical properties.

A xerogel panel based on X10a prepared via the aging sol process is expected to show excellent thermal insulation due to their fine and uniform porous structure (Fig. 4(c)). Thermal conductivity of X10a is $13.7 \text{ mW m}^{-1} \text{ K}^{-1}$, which is as low as the minimum value of PMSQ aerogels (Fig. 3) and standard silica aerogels with similar density. Besides, the visible-light transmittance of those xerogel panels is above 80 % (through 10 mm thickness at 550 nm), which is only a few percent lower than the aerogel counterpart.

4. Conclusions

Transparent wet gels of PMSQ have been synthesized with varied concentrations of MTMS in the starting composition. These gels show an incomplete spring-back behavior in the course of evaporative drying at ambient temperature and pressure, and xerogels with rather higher bulk density have been obtained without cracking. Reinforcing the network of PMSQ gels by an additional aging in aqueous solution containing a small amount of MTMS-derived monomers and oligomers leads to xerogels with only a negligible difference in bulk density, visible-light transmittance and thermal conductivity as compared to the supercritically dried aerogels derived from the identical starting composition. Although still there are technological issues to overcome, a high possibility is expected to bring PMSQ xerogels up toward practical transparent thermal superinsulators for the use in insulating window applications in the near future.

Acknowledgements

This study was carried out with the NMR spectrometer in the JURC at the Institute for Chemical Research, Kyoto University. Financial supports by a Grant-in-Aid for Scientific Research (No. 25·1089 and 24550253) administrated by the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Japan) are acknowledged. Also partially supported by Advanced Low Carbon Technology Research and Development Program (ALCA) administrated by Japan Science and Technology Agency (JST).

References

- [1] N. Hüsing, U. Schubert, Aerogels - airy materials: Chemistry, structure, and properties, *Angew. Chem., Int. Ed.*, 37, 23-45 (1998).
- [2] A.C. Pierre, G.M. Pajonk, Chemistry of aerogels and their applications, *Chem. Rev.* 102 (2002) 4243-4265.
- [3] M. Schneider, A. Baiker, Titania-based aerogels, *Catalysis Today* 35 (1997) 339-365.
- [4] L.W. Hrubesh, Aerogel applications, *J. Non-Cryst. Solids* 225 (1998) 335-342.
- [5] C.N. Sisk, L.J. Hope-Weeks, Copper(II) aerogels via 1,2-epoxide gelation, *J. Mater. Chem.* 18 (2008) 2607-2610.
- [6] F.J. Heiligt, W. Cheng, V.R. de Mendonça, M.J. Süess, K. Hametner, D. Günther, C. Ribeiro, M.

- Niederberger, Self-assembly of metal and metal oxide nanoparticles and nanowires into a macroscopic ternary aerogel monolith with tailored photocatalytic properties, *Chem. Mater.* 26 (2014) 5576-5584.
- [7] G. Hayase, K. Nonomura, G. Hasegawa, K. Kanamori, K. Nakanishi, Ultralow-density, transparent, superamphiphobic boehmite nanofiber aerogels and their alumina derivatives, *Chem. Mater.* 27 (2015) 3-5.
- [8] S.J. Kramer, F. Rubio-Alonso, J. D. MacKenzie, Organically modified silicate aerogels, “Aeromosils”, *Mater. Res. Soc. Symp. Proc.* 435 (1996) 295-300.
- [9] N. Hüsing, U. Schubert, Organofunctional silica aerogels, *J. Sol-Gel Sci. Technol.* 8 (1997) 807-812.
- [10] G. Zhang, A. Dass, A.-M.M. Rawashdeh, J. Thomas, J.A. Counsil, C. Sotiriou-Leventis, E.F. Fabrizio, F. Ilhan, P. Vassilaras, D.A. Scheiman, L. McCorkle, A. Palczar, J.C. Johnston, M.A. Meador, N. Leventis, Isocyanate-crosslinked silica aerogel monoliths: preparation and characterization, *J. Non-Cryst. Solids* 350 (2004) 152-164.
- [11] M.A.B. Meador, E.F. Fabrizio, F. Ilhan, A. Dass, G. Zhang, P. Vassilaras, J.C. Johnston, N. Leventis, Cross-linking amine-modified silica aerogels with epoxies: Mechanically strong lightweight porous materials, *Chem. Mater.* 17 (2005) 1085-1098.
- [12] R.W. Pekala, Organic aerogels from the polycondensation of resorcinol with formaldehyde, *J. Mater. Sci.* 24 (1989) 3221-3227.
- [13] A. Rigacci, J.C. Marechal, M. Repoux, M. Moreno, P. Achard, Preparation of polyurethane-based aerogels and xerogels for thermal superinsulation, *J. Non-Cryst. Solids* 350 (2004) 372-378.

- [14]M.A.B. Meador, E.J. Malow, R. Silva, S. Wright, D. Quade, S.L. Vivod, H. Guo, J. Guo, M. Cakmak, Mechanically strong, flexible polyimide aerogels cross-Linked with Aromatic triamine, ACS Appl. Mater. Interfaces 4 (2012) 536-544.
- [15]H. Jin, Y. Nishiyama, M. Wada, S. Kuga, Nanofibrillar cellulose aerogels, Colloids and Surf. A 240 (2004) 63-67.
- [16]F.O. Quignard, R. Valentin, F.D. Renzo, Aerogel materials from marine polysaccharides, New J. Chem. 32 (2008) 1300-1310.
- [17]A. Ricci, L. Bernardi, C. Gioia, S. Vierucci, M. Robitzer, F. Quignard, Chitosan aerogel: A recyclable, heterogeneous organocatalyst for the asymmetric direct aldol reaction in water, Chem. Commun. 46 (2008) 6288-6290.
- [18]C. Aulin, J. Netrval, L. Wågberg, T. Lindström, Aerogels from nanofibrillated cellulose with tunable oleophobicity, Soft Matter 6 (2010) 3298-3305.
- [19]Y. Kobayashi, T. Saito, A. Isogai, Aerogels with 3D ordered nanofiber skeletons of liquid-crystalline nanocellulose derivatives as tough and transparent insulators, Angew. Chem., Int. Ed. 53 (2014) 10394-10397.
- [20]J. Fricke, T. Tillotson, Aerogels: production, characterization, and applications, Thin Solid Films 297 (1997) 212-223.
- [21]K. I. Jensen, J. M. Schultz, F. H. Kristiansen, Development of windows based on highly insulating aerogel

- glazings, *J. Non-Cryst. Solids* 350 (2004) 351-357.
- [22] U.F. Ilhan, E.F. Fabrizio, L. McCorkle, D.A. Scheiman, A. Dass, A. Palczer, M.A.B. Meador, J.C. Johnston, N. Leventis, Hydrophobic monolithic aerogels by nanocasting polystyrene on amine-modified silica, *J. Mater. Chem.* 16 (2006) 3046-3054.
- [23] N. Leventis, Three-dimensional core-shell superstructures: Mechanically strong aerogels, *Acc. Chem. Res.* 40 (2007) 874-884.
- [24] A. Fidalgo, J.P.S. Farinha, J.M.G. Martinho, M.E. Rosa, L.M. Ilharco, Hybrid silica/polymer aerogels dried at ambient pressure, *Chem. Mater.* 19 (2007) 2603-2609.
- [25] T.-Y. Wei, S.-Y. Lu, Y.-C. Chang, Transparent, hydrophobic composite aerogels with high mechanical strength and low high-temperature thermal conductivities, *J. Phys. Chem. B* 112 (2008) 11881-11886.
- [26] K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada, New transparent methylsilsesquioxane aerogels and xerogels with improved mechanical properties, *Adv. Mater.* 19 (2007) 1589-1593.
- [27] K. Kanamori, M. Aizawa, K. Nakanishi, T. Hanada, Elastic organic-inorganic hybrid aerogels and xerogels, *J. Sol-Gel Sci. Technol.* 48 (2008) 172-181.
- [28] G. Hayase, K. Kugimiya, M. Ogawa, Y. Kodaera, K. Kanamori, K. Nakanishi, The thermal conductivity of polymethylsilsesquioxane aerogels and xerogels with varied pore sizes for practical application as thermal superinsulators, *J. Mater. Chem. A* 2 (2014) 6525-6531.
- [29] K. Kanamori, Monolithic silsesquioxane materials with well-defined pore structure, *J. Mater. Res.* 29

(2014) 2773-2786.

- [30]S.S. Prakash, C.J. Brinker, A.J. Hurd, S.M. Rao, Silica aerogel films prepared at ambient-pressure by using surface derivatization to induce reversible drying shrinkage, *Nature* 374 (1995) 439-443.
- [31]A. Bisson, E. Rodier, A. Rigacci, D. Lecomte, P. Achard, Study of evaporative drying of treated silica gels, *J. Non-Cryst. Solids* 350 (2004) 230-237.
- [32]A.V. Rao, N.D. Hegde, H. Hirashima, Absorption and desorption of organic liquids in elastic superhydrophobic silica aerogels, *J. Colloid Interface Sci.* 305 (2007) 124-132.
- [33]G. Hayase, K. Kanamori, K. Nakanishi, Structure and properties of polymethylsilsesquioxane aerogels synthesized with surfactant *n*-hexadecyltrimethylammonium chloride, *Microporous Mesoporous Mater.* 158 (2012) 247-252.
- [34]G.W. Scherer, Theory of drying, *J. Am. Ceram. Soc.* 73 (1990) 3-14.
- [35]C.J. Brinker, G.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processings*, Academic Press, San Diego, 1990, pp. 453-513.
- [36]M.G. Kaganer, *Thermal Insulation in Cryogenic Engineering*, Israel Program for Scientific Translations, Jerusalem, 1969.
- [37]X. Lu, M.C. Arduini-Schuster, J. Kuhn, O. Nilsson, J. Fricke, R.W. Pekala, Thermal conductivity of monolithic organic aerogels, *Science* 255 (1992) 971-972.
- [38]R.K. Iller, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and*

- Biochemistry of Silica, John Wiley & Sons, New York, 1979, pp. 3-94.
- [39]S. Hæreid, J. Anderson, M.A. Einarsrud, D.W. Hua, D. M. Smith, Thermal and temporal aging of TMOS-based aerogel precursors in water, *J. Non-Cryst. Solids* 185 (1995) 221-226.
- [40]M.-A. Einarsrud, E. Nilsen, Strengthening of water glass and colloidal sol based silica gels by aging in TEOS, *J. Non-Cryst. Solids* 226 (1998) 122-128.
- [41]A. Rigacci, M.-A. Einarsrud, E. Nilsen, R. Pirard, F. Ehrburger-Dolle, B. Chevalier, Improvement of the silica aerogel strengthening process for scaling-up monolithic tile production, *J. Non-Cryst. Solids* 350 (2004) 196-201.
- [42]R.B. Taylor, B. Parbhoo, D.M. Fillmore, Nuclear magnetic resonance spectroscopy, in: A.L. Smith (Ed), *The Analytical Chemistry of Silicones*, John Wiley & Sons, New York, 1991.
- [43]M. Itoh, F. Oka, M. Suto, S. D. Cook, N. Auner, Characterization and some insights into the reaction chemistry of polymethylsilsesquioxane or methyl silicone resins, *Int. J. Polym. Sci.* 2012 (2012) 526795.

Table 1. Starting compositions and properties of aerogels and xerogels obtained in the present study.

	5 mM HOAc	Urea	CTAC	MTMS	Bulk density	Thermal conductivity
	/mL	/g	/g	/g	/g cm ⁻³	/mW m ⁻¹ K ⁻¹
A8	8.0	2.4	0.40	4.8	0.167	15.3
A10	10	3.0	0.40	4.8	0.138	13.8
A20	20	6.0	0.40	4.8	0.084	15.1
A50	50	15	0.40	4.8	0.048	19.1
A100	100	30	0.40	4.8	0.040	22.4
X8	8.0	2.4	0.40	4.8	0.229	
X10	10	3.0	0.40	4.8	0.254	19.8
X20	20	6.0	0.40	4.8	0.288	
X50	50	15	0.40	4.8	0.345	
X100	100	30	0.40	4.8	0.374	
X10a	10	3.0	0.40	4.8	0.140	13.7

Fig. 1. Photographs of the PMSQ gel X10 during evaporative drying (left to right). The resultant dried gel did NOT fully recovered in this case without extended aging. (DOUBLE COLUMN)

Fig. 2. (a) Diameter change of the PMSQ gels during evaporative drying. The vertical axis shows linear shrinkage and T on the horizontal axis denotes the time when samples show maximum shrinkage. The shrinkage of X10a, which has undergone the extended aging in the “aging sol”, reached ca. 0 % (complete spring-back) after heat treatment at 110 °C as described later. The solid and broken lines are for the guide to

the eye. (b) The obtained xerogels; from upper left to lower right, X100, X50, X20, X10, and X8. The original shape of wet gels was the cylinder with 18.5 mm in diameter and 7 mm height. (SINGLE COLUMN)

Fig. 3. Relationship between bulk density and thermal conductivity of the obtained PMSQ aerogels (Ax) and xerogels (un-aged X10 and aged X10a). The solid line is for the guide to the eye. (SINGLE COLUMN)

Fig. 4. (a) ²⁹Si solid-state CPMAS NMR and (b) IR spectra of the PMSQ xerogels X10 and X10a. (c) FESEM image of the PMSQ xerogel X10a. (DOUBLE COLUMN)