Supporting Information

Versatile Double-Cross-Linking Approach to Transparent, Machinable, Supercompressible, Highly Bendable Aerogel Thermal Superinsulators

Guoqing Zu,^{a,c,*} Kazuyoshi Kanamori,^{a,*} Taiyo Shimizu,^a Yang Zhu,^a Ayaka Maeno,^b Hironori Kaji,^b Kazuki Nakanishi,^a Jun Shen^c

^aDepartment of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan ^bInstitute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

^cShanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, Pohl

Institute of Solid State Physics, Tongji University, Shanghai 200092, P. R. China

E-mail: guoqingzu@yahoo.com (G. Zu), kanamori@kuchem.kyoto-u.ac.jp (K. Kanamori)

This PDF file includes:

Captions for Movies S1 to S4 Tables S1, S2 Figures S1 to S13

Other Supplementary Materials for this manuscript includes the following:

Movies S1 to S4

Movie list:

Movie S1. High compression flexibility of an ambient-dried PAPMS aerogel PAPMS1-X1.

Movie S2. High bending flexibility of a PAPMS aerogel PAPMS1 shown by hand bending.

Movie S3. High bending flexibility of a PVPMS aerogel PVPMS3 shown by hand bending.

Movie S4. High compression flexibility of an ambient-dried PVPMS aerogel PVPMS1-X2.

Tables

Table S1. Results on the radical polymerization of VTMS, ATMS, VMDMS, and AMDMS under the DTBP concentration of 1-20 mol%.

precursor	DTBP	Polymerization	$oldsymbol{M}_{\mathrm{w}}{}^{\mathrm{a})}$	Degree of	$M_{\rm w}/M_{\rm n}^{\rm b)}$	Conversion
	/mol%	time /h]	polymerization		/%
VTMS	20	48	22961	155	6.35	>99
ATMS	20	48	3510	22	1.78	97
VMDMS	1	48	5356	41	1.86	97
VMDMS	5	48	8998	68	2.57	>99
AMDMS	20	48	3399	23	1.95	91

^{a)} Weight-average molecular weight. ^{b)}Number-average molecular weight.

Table S2. Typical properties of PAPSQ aerogels with different DTBP concentrations (5, 10, and 20 mol %). A higher DTBP concentration is supposed to result in a higher degree of polymerization of PVTMS, PATMS, PVMDMS, and PAMDMS. ¹ The resulting PVTMS, PATMS, PVMDMS, and PAMDMS polymerized with a higher concentration of DTBP, therefore, possess more hydrolyzable groups in each molecule, which leads to higher crosslinking density and more homogenous gelation. As a result, in the case of PAPSQ aerogels, the bulk density increases and the pore size decreases with the increase of DTBP concentration in the range 5-20 mol %.

sample	DTBP	Density	S _{BET} a)	$d^{b)}$	$T^{c)}$
	/mol%	$/\mathrm{g}~\mathrm{cm}^{-3}$	$/{\rm m}^2 {\rm g}^{-1}$	/nm	/%
PAPSQ2-5%	5	0.14	905	77	53
PAPSQ2-10%	10	0.15	1088	58	74
PAPSQ2	20	0.18	1021	37	88

^{a)} SSA obtained from nitrogen adsorption measurement. ^{b)} Mean pore diameter. ^{c)} Visible-light transmittance at 550 nm for 2 mm thick aerogel.

Figures



Figure S1. Multiple peak fitting (Gaussian) on the solid-state NMR results of PVPSQ, PAPSQ, PVPMS, and PAPMS aerogels in Figure 2a.



Figure S2. Contact of PVPSQ, PAPSQ, PVPMS, and PAPMS aerogels with water. The PVPSQ aerogel (PVPSQ2) is hydrophilic and absorbs water quickly. The PAPSQ aerogel (PAPSQ1) is also hydrophilic but absorbs water slowly without fracture. It floats on top of water in the beginning, but sinks to the bottom after around 10 min. The PVPMS and PAPMS aerogels are hydrophobic and float on top of water for more than 6 months. The contact angle of water on PVPSQ2 and PAPSQ1 is lower than 40°, while that on PVPMS1 and PAPMS2 is around 130°.



Figure S3. TG curves of typical PVPSQ, PAPSQ, PVPMS, and PAPMS aerogels.



Figure S4. Morphology of typical aerogels. FESEM images of typical (a,b) PVPSQ aerogels, (c) PAPSQ aerogel, (d) ambient-dried PVPMS aerogel, and (e,f) ambient-dried and supercritical-dried PAPMS aerogels, showing highly porous nanostructure.



Figure S5. Porous structure of typical aerogels. N_2 adsorption/desorption isotherms and pore size distributions of typical (a) PVPSQ, (b) PAPSQ, (c) PVPMS, and (d) PAPMS aerogels. The type IV isotherms with distinct capillary condensation indicate the mesoporous structure of these four kinds of aerogels.²



Figure S6. Pore size distributions of PAPSQ aerogels with different DTBP concentrations (5, 10, and 20 mol %). The pore size distribution shifts to smaller pore size with the increase of DTBP concentration.



Figure S7. Light transmittance spectrum of typical 2 mm thick aerogels.



Figure S8. Photographs of a three-point bending test on PAPSQ2, showing high bending flexibility. The fixture span is 25 mm.



Figure S9. Photographs of a hand bending test on an ambient-dried PAPMS aerogel PAPMS1-X1, showing high bending flexibility.



Figure S10. Excellent machinability of typical (a) PVPSQ, (b) PAPSQ, (c) PVPMS, and (d) PAPMS aerogels shown by shaping with a knife.



Figure S11. Mechanical properties of a commercial thermal insulation materials—phenol foam. Stress-strain curves of (a) uniaxial compression-decompression and (b) three-point bending tests on a phenol foam with a density of around 0.030 g cm⁻³ and a thermal conductivity of around 20 mW m⁻¹ K⁻¹. (c) Photographs of a uniaxial compression-decompression test on the phenol foam. These data show the similar bending flexibility but much lower elasticity against compression and higher thermal conductivity compared to those of PVPMS aerogels in this work.



Figure S12. (a) Synthesis scheme and resultant PVPSQ aerogel from the precursor VTES *via* the double-cross-linking method. (b) Synthesis scheme and resultant PAPSQ aerogel from the precursor ATES *via* the double-cross-linking method.



Figure S13. Porous structure of typical PVPMS aerogels (PVPMS1-X2 and PVPMS2-X2) obtained via ultra-low-cost ambient pressure drying without any solvent exchange and modifications. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of PVPMS1-X2 and PVPMS2-X2.

References

(1) T. Gunji; Y. Kawaguchi; H. Okonogi; T. Sakan; K. Arimitsu; Y. Abe. Preparation and Properties of Organic-Inorganic Hybrid Gel Films Based on Polyvinylpolysilsesquioxane Synthesized from Trimethoxy(vinyl)silane, *J. Sol-Gel Sci. Technol.* **2005**, *33*, 9-13.

(2) M. Kruk; M. Jaroniec. Gas Adsorption Characterization of Ordered Organic-Inorganic Nanocomposite Materials, *Chem. Mater.* **2001**, *13*, 3169-3183.