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Synthesis of silanol-rich long-life polysilsesquioxane liquids by cosolvent-free hydrolytic polycondensation of organotrimethoxysilanes followed by aging

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Polysilsesquioxane (PSQ) liquids have been prepared from propyltrimethoxysilane–water and trimethoxy(3-sulfanylpropyl)silane–water binary systems without the use of organic solvents through hydrolytic polycondensation followed by aging. By introducing the aging step, the viscosity of as-prepared PSQ liquid is decreased by more than an order of magnitude, and the long-term viscosity stability is improved considearbly. These variations are mainly attributed to the modification of the topology of the Si–O–Si network because the crosslinking density was influenced little by the aging. The viscosity of PSQ liquids obtained via aging at 80°C was ~4–5×10^3 mPa s and the viscosity increase was less than 25% after storage for 2 months at room temperature despite the many unreacted silanol (SiOH) groups present in the liquid.

Introduction

Organic–inorganic hybrid materials have attracted attention because they may exhibit unique properties that are not realised by organic or inorganic materials alone.[1–3] Polysilsesquioxanes (PSQs) are typical organic–inorganic hybrids consisting of silsesquioxane (SQ) building blocks with general chemical formula of $RSiO_{3/2}$, where R is an organic functional group.[4,5] The properties of PSQs depend strongly on the manufacturing process because the structure can be widely varied from amorphous[6–11] to ordered structures, such as polyhedral cages[12–17] and ladder-like polymers.[18–22] They are typically solid or highly viscous at room temperature. Liquid PSQs are useful in casting, coating, and mixing with other reagents, and would be suitable for the processing of functional materials and devices. Modification of cage-like and cyclic PSQs with large, specifically-designed R groups affords various functional PSQ liquids[23–32] including liquid crystals,[23–26] curable liquids,[27,28] and ionic liquids.[29–31] However, amorphous PSQ liquids have attracted less attention and the successful preparation[33,34] has hardly been reported particularly for relatively small R groups.

Hydrolytic polycondensation of organotrialkoxysilanes is an important synthetic route for PSQs, and is usually performed in the presence of cosolvents such as alcohols and other organic solvents in order to homogenise the reaction mixture. However, these cosolvents are usually removed during processing and therefore absent in the final products. Thus,

cosolvent (or solvent)-free processes[6,35–45] are promising for reducing the use of reagents and simplifying synthetic routes. Silica gels[35–38] and PSQ gels[6,39,40] have been prepared via hydrolytic polycondensation from alkoxide-water binary systems. Non-hydrolytic sol-gel process utilizing reactions between organotrialkoxysilanes and organotrichlorosilanes enables solvent-free synthesis of PSQs.[41–43] However, cosolvent-free synthesis of PSQ liquids from organotrialkoxysilane-water binary systems has not been explored. We have recently developed cosolvent-free processes to synthesize PSQ liquids from organotrimethoxysilane–water binary systems via hydrolytic polycondensation, followed by aging in a closed container.[44,45] The resultant PSQs, including PSQ liquids, are utilised to prepare PSQ monoliths with deep-ultraviolet (DUV, wavelength ≲300 nm) transparency[44] and photocurable PSQ organic-inorganic hybrids.[45]

In this article, we demonstrate the importance of the aging step in obtaining PSQ liquids from organotrialkoxysilane–water binary systems by employing n-propyl (Pr) and 3-sulfanylpropyl (3-SP) groups as model organic functional groups.

Experimental procedure

100 mmol of n-propyltrimethoxysilane (PrTMS, Shin-Etsu Chemical) or trimethoxy(3-sulfanylpropyl)silane (3-SPTMS, Shin-Etsu Chemical) was mixed with a dilute aqueous solution of nitric acid (~0.037 mol L^{-1}) at an alkoxide : H_2O : HNO_3 molar ratio of 1 : 3 : 0.002 and the mixture was stirred for 3 h at 20°C in a sealed container. The solution was aged for 1 d at room temperature (RT) or 80°C. Then the container was opened and the top layer of the biphasic solution was discarded by

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extraction. In some samples the aging and extraction steps were skipped in order to examine the effects of these steps on the properties of PSQ. Either the bottom layer of the aged samples or the unaged monophasic mixture was dried under vacuum for 1 d at 80°C. Typically, samples were simultaneously prepared in 4–5 containers and finally mixed to provide sufficient quantity of samples for measurements. The resultant samples were characterized by an NMR spectrometer (JNM-ECS300, JEOL), a viscometer (LVT, Brookfield), and a Fourier transform infrared (IR) spectrometer (FT/IR-6100). The ^{29}Si single-pulse NMR spectra were taken with a 30° pulse and a 20 s relaxation delay. The viscosity was measured at 30°C. Gel permeation chromatography (GPC) using a Shodex KF-804L column and a refractive index detector (RID-10A, Shimadzu), employing tetrahydrofuran as the eluent (flow rate, 1.0 mL min^{-1}) was preformed to determine the number- and weight-average molecular weights (M_n and M_w, respectively) of PSQs. The molecular weights were estimated by comparing the retention times to those of standard polystyrene samples. IR spectra were measured for a liquid PSQ film formed between SiOH-free silica glass plates separated by 75 μm-thick spacers. The density of PSQ liquid was evaluated by measuring the weight of liquid in a container with a definite volume. Contact angle was observed by placing a droplet on a silica glass plate (20 × 20 × 1 mm^3) cleaned with dilute aqueous hydrofluoric acid. The samples were stored in a closed container for ~2 months at RT and variation of the properties over time was examined.

Results

The solution obtained by mixing PrTMS or 3-SPTMS with dilute aqueous nitric acid was homogeneous and transparent. However, it underwent liquid–liquid phase separation during aging[38,39] at RT or 80°C. Fig. 1a shows photograph of a solution derived from PrTMS and aged for 1 d at 80°C. The fractions of SQ units and methanol distributed in the bottom layer of the biphasic solutions were evaluated by ^{1}H NMR following the procedure described in refs.[38,39], and the results are listed in Table 1. The bottom layer consisted mainly of methanol and PSQ, and the yield of PSQ in the bottom layer was increased by increasing the aging temperature.

Table 1. Fractions of SQ units and methanol distributed in the bottom layer of the biphasic solutions obtained after aging at RT or 80°C.

R	Aging temp.	SQ unit	Methanol
Pr	RT	0.62	0.25
	80°C	0.92	0.14
3-SP	RT	0.78	0.39
	80°C	0.93	0.20

After vacuum drying for 1 d at 80°C, colourless and transparent PSQs were obtained. Figs. 1b-d show PSQs derived from PrTMS and Fig. 2 shows the ^{1}H NMR spectra of PSQs prepared in this study. The sharp signal arising from residual

methanol (peak f) was relatively small in all the samples. The mole fraction with respect to methoxy groups in the reagents (organotrimethoxysilanes) was ≲0.006 and the effects of residual solvent on the properties of PSQ were negligible. The mole fraction of residual methoxy groups (peak e), f_{SiOMe}, was ~0.02–0.05 and increased on introduction of the aging step. Fig. 3 shows ^{29}Si NMR spectra. Each spectrum exhibited peaks corresponding to the T^1, T^2, and T^3 SQ units, where the number in superscript denotes the number of bridging oxygen atoms bonded to the central Si atom. In addition to the broad signals, several sharp peaks were observed at −56.3, −59.9, and −65.8 ppm for poly(Pr-SQ)s, and −56.3, −60.2, and −65.8 ppm for poly(3-SP-SQ)s. The average number of bridging oxygen atoms per Si, <m>, was derived by <m> = $f_{T1} + 2f_{T2} + 3f_{T3}$, where f_{T1}, f_{T2}, and f_{T3} denote the fractions of the T^1, T^2, and T^3 units ($f_{T1} + f_{T2} + f_{T3}$ = 1), respectively. The fraction of residual SiOH groups, f_{SiOH}, was evaluated on the assumption that the nonbridging oxygen atoms belong to either methoxy or SiOH groups (<m>/3 + f_{SiOMe} + f_{SiOH} = 1). These values are summarised in Table 2. The values of <m>, f_{SiOMe}, and f_{SiOH} were relatively similar to each other; <m> was ~2.2–2.4 and the main origin of the nonbridging oxygen was SiOH groups (f_{SiOH} ≃ 0.2) rather than methoxy groups. However, aging significantly altered the appearance of PSQs; PSQs prepared via aging were liquid (Figs. 2b and c), whereas those prepared without aging were highly viscous (Fig. 2d).
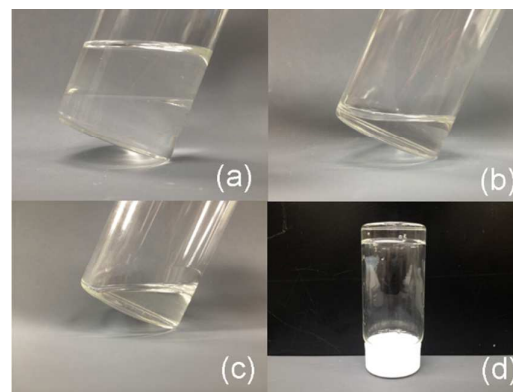

Fig. 1 Photograph of samples derived from PrTMS. Biphasic solution obtained after aging at 80°C (a), poly(Pr-SQ) liquids prepared via aging at 80°C (b) and RT (c), and poly(Pr-SQ) obtained without aging (d).
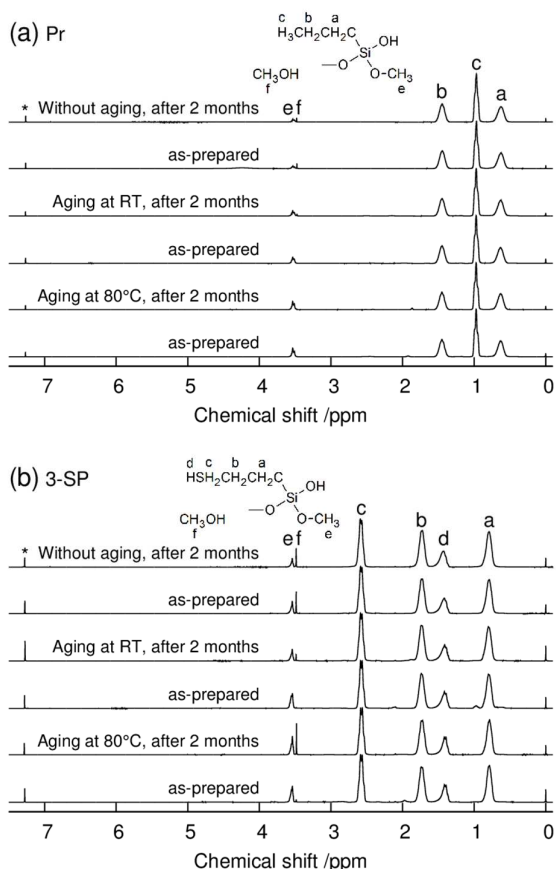
(a) Pr

(b) 3-SP

Fig. 2 ^{1}H NMR spectra of poly(Pr-SQ) (a) or poly(3-SP-SQ) (b) prepared via aging at 80°C or RT, or without aging (300 MHz, CDCl$_3$). Spectra of as-prepared samples and those after storage for ~2 months are shown. The asterisk at ~7.3 ppm indicates the solvent residual peak.
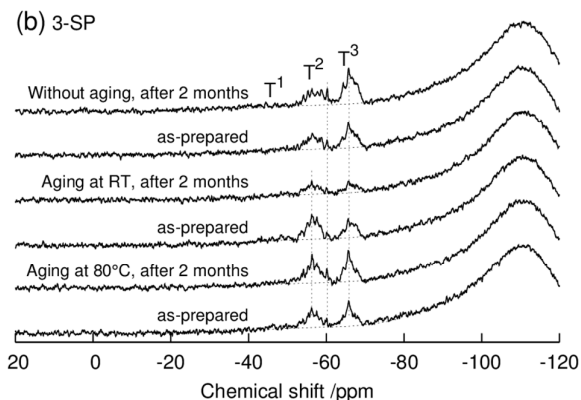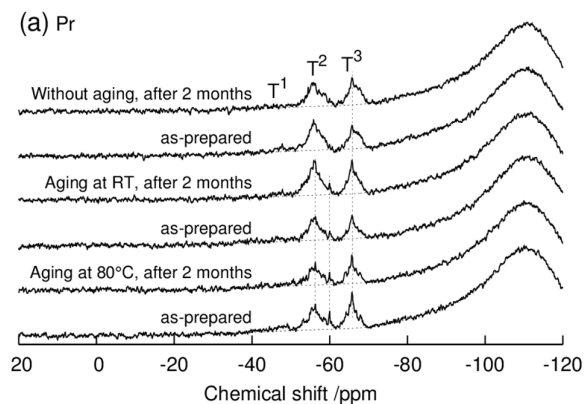
(a) Pr

(b) 3-SP

Fig. 3 ^{29}Si single-pulse NMR spectra of poly(Pr-SQ) (a) and poly(3-SP-SQ) (b) prepared via aging at 80°C or RT, or without aging (59.6 MHz, CDCl$_3$). Spectra of as-prepared samples and those after storage for ~2 months are shown. The positions of the dotted lines are −56.3, −59.9, and −65.8 ppm for panel (a) and −56.3, −60.2, and −65.8 ppm for panel (b). The broad background signal peaking at ~−110 ppm originated from ^{29}Si in the sample tube.

Figure 4 shows the molecular weight distribution curves of PSQs measured by GPC. The aging considerably narrowed the molecular weight distribution and suppressed polycondensation during storage for ~2 months at RT. The GPC curves of the PSQs prepared via aging at 80°C exhibited two peaks, and the variation of the peak shape was quite small after storage for ~2 months. The peak positions expressed in the number of SQ units, n in (RSiO$_{3/2}$)$_n$, were $n_{GPC} \simeq 7.4$ and 12.2 for poly(Pr-SQ) and $n_{GPC} \simeq 7.0$ and 10.5 for poly(3-SP-SQ), respectively. A similar measurement of octamethyloctasilsesquioxane (CH$_3$SiO$_{3/2}$)$_8$, a cubic SQ octamer used as a reference sample, gave a single peak at $n_{GPC} \simeq 6.8$. The peak at $n_{GPC} \simeq 7$–8 was observed for all the samples. This peak was the most intense for the PSQ prepared via aging at 80°C, and the position and width were unchanged by the storage and aging conditions. In contrast, the peak at $n_{GPC} \simeq$ 10–12 became less distinct for the PSQs prepared without aging and via aging at RT, particularly after storage. Table 2 lists the M_n and M_w values calculated by simply integrating the curves shown in Fig. 4.
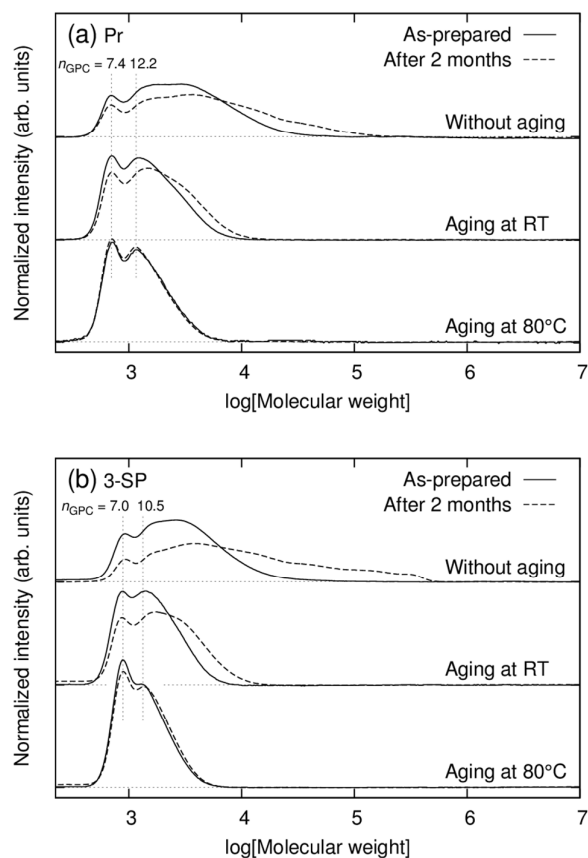
Fig. 4 Polystyrene-equivalent molecular weight distribution curves of poly(Pr-SQ) (a) and poly(3-SP-SQ) (b) evaluated by GPC. The numbers (n_{GPC}) denote molecular weights described by the number of SQ units, i.e., n in (RSiO$_{3/2}$)$_n$.

Figure 5 shows the variation of the viscosity of PSQs with the duration of the storage at RT. The viscosity of as-prepared PSQs obtained via aging was ~1–2 orders of magnitude smaller than that of PSQs prepared without aging, and the viscosity decreased when the aging temperature was increased from RT to 80°C. The viscosities of as-prepared poly(Pr-SQ) and poly(3-SP-SQ) obtained via aging at 80°C were ~4×10^3 and ~5×10^3 mPa s, respectively. In addition, the introduction of the aging step considerably suppressed the viscosity change during the storage, in agreement with the GPC data shown in Fig. 4. For samples aged at 80°C, the viscosity increase was quite small although they contained many SiOH groups; the average viscosity increase for 60 d storage was ~1% for poly(Pr-SQ) and ~24% for poly(3-SP-SQ). At all preparation conditions, the viscosity increase over 60 d was larger for poly(3-SP-SQ) than poly(Pr-SQ).
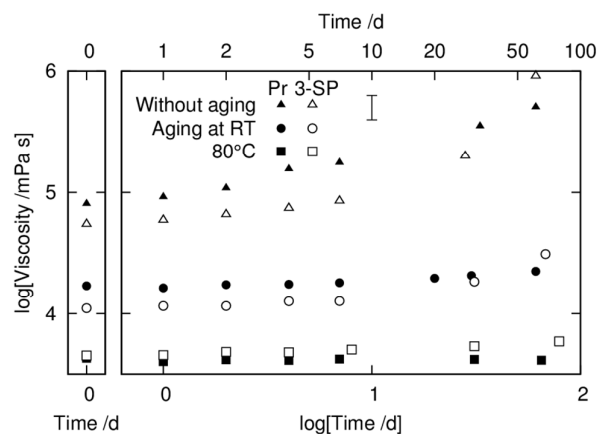

Fig. 5 Viscosity of poly(Pr-SQ) and poly(3-SP-SQ) measured at 30°C for as-prepared ones (left panel) and those stored up to ~2 months at RT. The error bar represents the experimental uncertainly.

Figure 6 shows IR spectra of PSQ liquids prepared via aging at 80°C. The stretching mode of O–H bond of SiOH groups was observed at ~3100–3700 cm^{-1}. The concentration of SiOH groups was evaluated on the assumption that the integrated absorption coefficient is identical to that of SiOH groups in silica glass (peak position ~3670 cm^{-1})[46] because reliable values of absorption coefficients of SiOH groups could not be found for other siloxane compounds. The concentration of SiOH groups and f_{SiOH} value evaluated from the intensity of the absorption band and the density (~1.15 g cm^{-3} for poly(Pr-SQ) and ~1.31 g cm^{-3} for poly(3-SP-SQ)) were ~3.9x10^{21} cm^{-3} and ~0.18, respectively, for poly(Pr-SQ) and ~3.5x10^{21} cm^{-3} and ~0.19, respectively, for poly(3-SP-SQ). These values were consistent with the f_{SiOH} value evaluated by NMR spectroscopy (~0.2) (Table 2).
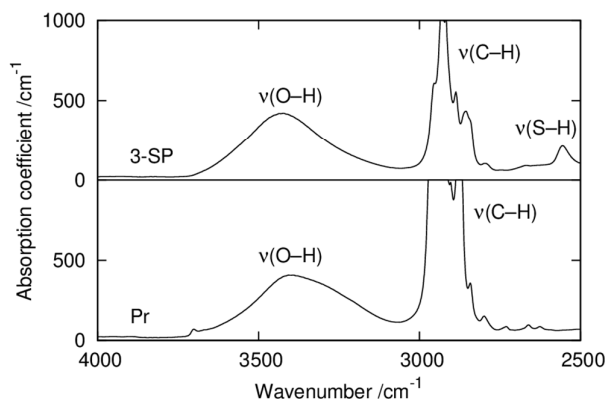

Fig. 6 IR spectra of poly(Pr-SQ) and poly(3-SP-SQ) prepared via aging at 80°C.

The hydrophilicity of PSQ liquids prepared via aging at 80°C was tested by placing a droplet on a hydrophilic substrate. Figure 7 shows photograph of a droplet of water, poly(Pr-SQ), and poly(3-SP-SQ) placed on a hydrophilic silica glass plate. The

contact angle of water was close to 0°. The contact angles of PSQ liquids were ~20–30° and they exhibited considerable hydrophilicity.

Fig. 7 Photograph of a droplet of water (a), poly(Pr-SQ) (b), and poly(3-SP-SQ) (c) on a hydrophilic silica glass plate. PSQ liquids were prepared via aging at 80°C.
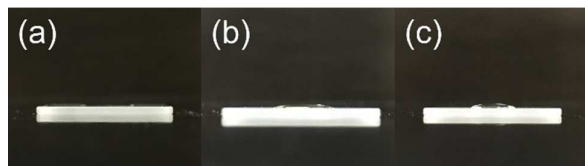
Table 2. Fractions of T^1, T^2, and T^3 units (f_{T1}, f_{T2}, and f_{T3}, respectively), average number of bridging oxygen atoms per Si ($<m>$), and fractions of residual methanol, methoxy groups, and SiOH groups (f_{MeOH}, f_{SiOMe}, and f_{SiOH}, respectively) evaluated by ^{1}H NMR and ^{29}Si NMR measurements, and number- and weight-average molecular weights (M_n and M_w, respectively) evaluated by GPC measurements for PSQ samples prepared in this study. For each sample, the upper and lower rows list the values for as-prepared samples and those stored for ~2 months, respectively.

R	Aging	Storage /month	f_{T1}[b]	f_{T2}[b]	f_{T3}[b]	$<m>$	f_{MeOH}	f_{SiOMe}	f_{SiOH}	M_n /10^3 g mol^{-1}	M_w /10^3 g mol^{-1}	M_w/M_n
Pr	No	No	0.10	0.55	0.35	2.25	0.002	0.02	0.23	1.8	4.5	2.4
		2	0.09	0.49	0.41	2.32	0.002	0.02	0.21	2.2	9.8	4.6
	RT	No	0.11	0.55	0.34	2.23	(a)	0.04	0.22	1.2	1.8	1.5
		2	0.08	0.56	0.36	2.27	0.001	0.03	0.21	1.4	2.3	1.6
	80°C	No	0.12	0.47	0.40	2.28	(a)	0.05	0.19	1.1	1.5	1.4
		2	0.12	0.49	0.39	2.27	(a)	0.05	0.20	1.1	1.5	1.4
3-SP	No	No	0.05	0.44	0.51	2.45	0.006	0.03	0.15	2.0	3.2	1.6
		2	0.05	0.38	0.57	2.52	0.006	0.02	0.14	3.8	32.6	8.7
	RT	No	0.07	0.58	0.36	2.29	(a)	0.05	0.19	1.3	1.7	1.3
		2	0.08	0.52	0.40	2.32	0.002	0.03	0.20	1.5	2.5	1.6
	80°C	No	0.11	0.46	0.43	2.32	0.001	0.04	0.18	1.3	1.6	1.2
		2	0.07	0.54	0.39	2.32	0.008	0.04	0.18	1.3	1.7	1.3

(a) Below limit of quantification: <0.001.
(b) Because of rounding, sum of individual items may not equal 1.

Discussion

This study demonstrates that aging is crucial in obtaining the liquids of poly(Pr-SQ) and poly(3-SP-SQ) by lowering the viscosity. It is not due to the decrease in the crosslinking density of the Si–O–Si network, because the average number of bridging oxygen atoms per Si, $<m>$, for PSQs obtained in this study was ~2.2−2.4 and clear correlation between the $<m>$ value and the aging conditions seems absent (Table 2). The variation in the $<m>$ value is probably due to uncontrolled experimental conditions and uncertainty of the estimation of the background ^{29}Si signal from the sample tube. Thus, the distinct narrowing of the molecular weight distribution (Fig. 4) and reduction of viscosity (Fig. 5) of PSQs prepared via aging is attributed to the modification of the topology of the Si–O–Si network of PSQ. The most probable mechanism of the lowering of molecular weight and viscosity is the formation of

"closed" SQ oligomers, where R groups orientate towards the outside and SiOH groups towards the inside.

In the aged biphasic solution, PSQ molecules are mainly distributed in the bottom layer with methanol (Table 1). Since the hydrophobicity of the bottom layer is higher, the organic functional groups in PSQs probably turn outward while orienting Si–O bonds and hydrophilic SiOH groups inward, resulting in the formation of PSQs with smaller molecular weights. Such reconstruction of the Si–O–Si network to form rather compact and ordered PSQ molecules would be enhanced at higher temperatures, consistent with the result that PSQs prepared via aging at higher temperatures have lower viscosities. Such reconstruction of the Si–O–Si network probably increases the fraction of SiOH groups orientated inward and inaccessible by other PSQ molecules, making it possible to improve the long-term stability of viscosity. The small increase in the fraction of residual SiOCH$_3$ groups in PSQs obtained via aging is explained by an enhancement of the

esterification (the back reaction of hydrolysis) due to the deficiency of water in the hydrophobic bottom layer.

The increase in viscosity during the storage was larger for poly(3-SP-SQ) than poly(Pr-SQ). However, polymerization with the formation of S–S bonds is unlikely because the number of SH groups evaluated by ^{1}H NMR remained unchanged before and after storage for ~2 months at RT. The viscosity increase may be attributable to the hydrophilicity of SH groups, which probably weaken the tendency to orientate the SiOH groups inward.

As shown in Fig. 4, the GPC curves exhibited two peaks at $n_{GPC} \simeq 7-8$ and $10-12$. We suggest that the peak at $n_{GPC} \simeq 7-8$ is due to the cubic octamer [$n = 8$ in $(RSiO_{3/2})_n$, T_8] for the following reasons. First, the peak position and width were unaffected by preparation conditions and long-term storage. These observations are consistent with the inertness of the cage structure, which does not have reactive SiOH and methoxy groups. Second, ^{29}Si NMR spectra exhibited a signal at −65.8 ppm, which is close to the peak position expected for the cubic octamer of poly(Pr-SQ) (−66.16,[14] −67.22,[15] and −66.93 ppm[47,48]) and poly(3-SP-SQ) (−66.16 ppm[14]). Third, the GPC signal of $(CH_3SiO_{3/2})_8$, employed as a reference compound, appeared at $n_{GPC} \simeq 6.8$. The systematic decrease of the n_{GPC} value compared with the ideal value 8 is due to the presence of heavy atoms, such as Si and S, which increase the average weight per atom with respect to the polystyrene used as the molecular weight standard. Indeed, the n_{GPC} value for this peak decreases in the order of poly(Pr-SQ) (~7.4), poly(3-SP-SQ) (~7.0), and $(CH_3SiO_{3/2})_8$ (~6.8), as the fraction of the heavy atoms increases. Thus, the most probable proportional factor to derive the true molecular weight from the GPC curve, n/n_{GPC}, where n is the true number of SQ unit, is ~8/7.4 = 1.08 for poly(Pr-SQ) and ~8/7.0 = 1.14 for poly(3-SP-SQ).

Apart from the cubic octamer, the cage-like decamer (T_{10}) and dodecamer (D_{2d}-T_{12}) are also polyhedral cages commonly formed by polycondensation of the SQ units.[13,15] However, the peak located at $n_{GPC} \simeq 10-12$ ($n \simeq 12-13$) is unlikely to be due to the cage-like dodecamer because a ^{29}Si NMR signal attributable to this structure (~70–72 ppm[15]) was absent. In addition, the GPC data shown in Fig. 4 suggest that the decamer, which usually coexists with the dodecamer, is not a major component. Thus, the $n_{GPC} \simeq 10-12$ peak probably originates from partially-ordered oligomers, whose n values are close to ~12. The destruction of the $n_{GPC} \simeq 10-12$ peak after the storage at RT is probably due to their further polycondensation. A typical precursor of such partially-ordered structures is a cyclic tetramer, $(RSiO(OH))_4$. It has four isomers[49–52] and only the all-cis variant can be a precursor of the cubic octamer. In the present method, all isomers of the tetramers can be formed because the stereochemistry is uncontrolled. Oligomers generated from isomers other than the all-cis tetramer inevitably contain SiOH groups that cannot participate in intramolecular dehydration because of geometrical restriction. The presence of such reactive ends explains the viscosity increase during the storage. On the other hand, these isomers can be isomerised under acid-catalyzed

conditions.[49,52] Thus, the main effect of the aging can be regarded as the enhancement of the formation of cis isomers.

The sharp peaks at −56.3, −59.9, and −60.2 ppm are probably attributed to T^2 units in such partially-ordered oligomers although the detailed structures are currently not known. The signals at −59.9 and −60.2 ppm may be originated from T^2 units consisting of four-membered rings because the chemical shift is close to that for $(iPrSiO(OH))_4$ (58.4–59.7 ppm[51,53]).

Conclusions

Cosolvent-free hydrolytic polycondensation of propyltrimethoxysilane and trimethoxy(3-sulfanylpropyl)silane followed by aging in a closed container causes liquid-liquid phase separation of the reaction mixture, and the vacuum drying of the silica-rich bottom phase yields silanol (SiOH)-rich polysilsesquioxane (PSQ) liquids. The aging step is crucial in decreasing the viscosity of the resultant PSQs. By increasing the aging temperature, both the viscosity and molecular weight distribution are decreased, and the long term stability of viscosity is significantly improved. The resultant PSQs contain many unreacted SiOH groups and the concentration is influenced little by the aging. Thus, the aging probably modifies the topology of the Si–O–Si network to form rather compact oligomers, where SiOH groups orientate inside and are therefore inaccessible by other oligomers. The residual SiOH groups can be utilised to impart partial hydrophilicity and to perform further chemical modification. The procedure developed in this study provides a unique opportunity for synthesising PSQ liquids in a simple and environmentally-friendly manner.

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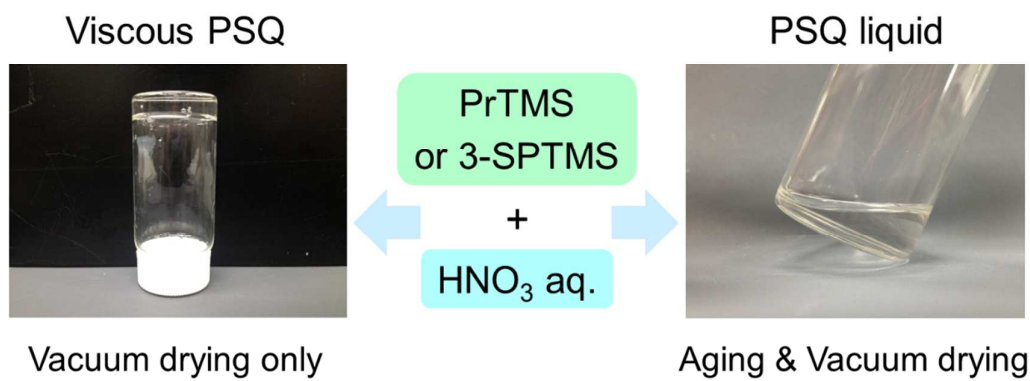
Silanol-rich polysilsesquioxane liquids with long-term viscosity stability are formed in a facile manner from organotrimethoxysilane-water binary systems via aging.