Journal of Sol-Gel Science and Technology (2022) 104:588–598
https://doi.org/10.1007/s10971-022-05821-0

INVITED PAPER: NANO-STRUCTURED MATERIALS (PARTICLES, FIBERS, COLLOIDS, COMPOSITES, ETC.)

Superacid-catalyzed preparation of ionic polyhedral oligomeric silsesquioxanes and their properties, polymerization, and hybridization

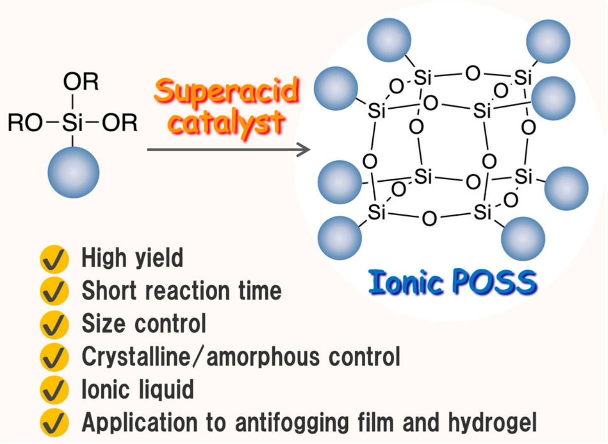
Yoshiro Kaneko[1]

Received: 1 March 2022 / Accepted: 20 April 2022 / Published online: 6 May 2022

Abstract

This paper provides a comprehensive review of recent studies on the superacid-catalyzed preparation of ionic polyhedral oligomeric silsesquioxanes (POSSs) and their properties, polymerization, and hybridization, that have been developed by the author and co-workers so far. Octameric POSSs (T_8-POSS) containing ammonium side-chain groups as the main products can be obtained at a high yield within a short reaction time by dissolving amino group-containing organotrialkoxysilanes in an aqueous superacid (e.g., trifluoromethanesulfonic acid) solution, followed by hydrolytic condensation by heating in an open system to evaporate the solvents. When these reactions were performed in a hydrophobic alcohol, such as 1-hexanol, a POSS mixture with a high proportion of decameric POSS (T_{10}-POSS) was obtained. It was found that the proportion of T_{10}-POSS can be increased by properly controlling the reaction conditions (temperature, pressure, and solvent evaporation time) using a Kugelrohr apparatus during POSS preparation in an aqueous superacid solution. Furthermore, a low-crystalline POSS and ionic liquids containing POSS components can be obtained by the superacid-catalyzed hydrolytic condensation of the mixtures of two types of organotrialkoxysilanes containing functional groups, which can be converted into ionic groups. This superacid-catalyzed hydrolytic condensation can be applied to the preparation of carboxyl-functionalized POSSs and an ammonium-functionalized specific cyclotetrasiloxane isomer. An antifogging film with a hard-coating property comprising polyamide obtained by the polycondensation of ammonium- and carboxyl-functionalized POSSs was developed as an ionic POSS application. Furthermore, using an ionic POSS and cyclotetrasiloxane as crosslinking agents, polyacrylamide hydrogels exhibiting extremely flexible and irrefrangible properties can be obtained.

Graphical abstract



✉ Yoshiro Kaneko
ykaneko@eng.kagoshima-u.ac.jp

[1] Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

Keywords Polyhedral oligomeric silsesquioxane (POSS) · Superacid · Hydrolytic condensation · Ionic liquid · Antifogging film · Hydrogel

Highlights

- Ionic POSSs can be obtained at a high yield within a short reaction time using superacid catalysts.
- The POSS size can be controlled by properly selecting the solvent type and reaction conditions.
- Low-crystalline ionic POSS can be obtained from a mixture of two types of organotrialkoxysilanes.
- Ionic liquids containing POSS components can be obtained from the mixture of two types of organotrialkoxysilanes.
- An antifogging film and hydrogel with flexible and irrefrangible properties were developed using ionic POSSs.

1 Introduction

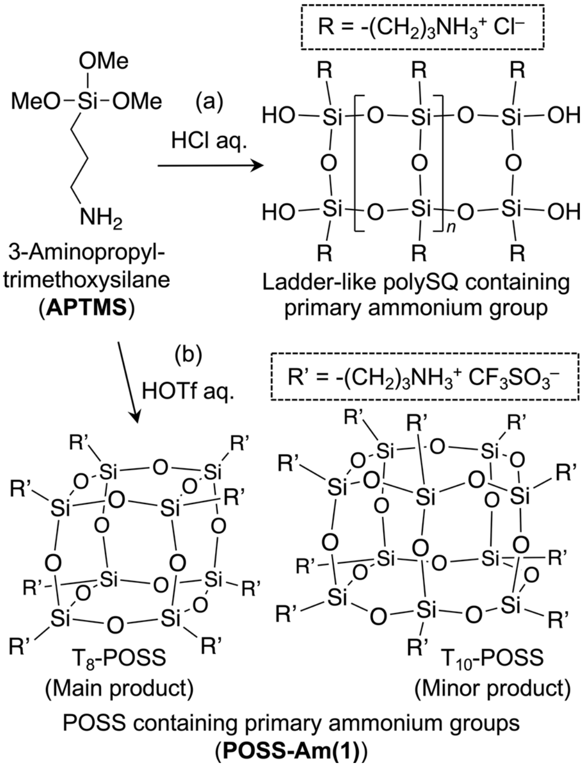
Silsesquioxanes (SQs) are represented by a repeating structure of $RSiO_{1.5}$, where R is organic groups or hydrogen; they are prepared by the hydrolysis of organotrialkoxysilanes or organotrichlorosilanes and a subsequent condensation reaction. They exhibit thermal, mechanical, and chemical stabilities derived from siloxane bond frameworks. In addition, they can be imparted with various properties through the introduction of functional groups into the side-chains (R) [1–4]. Therefore, SQs have recently attracted considerable attention. Among them, polyhedral oligomeric SQs (POSSs) are siloxane compounds with cage structures and excellent dispersibility in various media; they have been widely studied in the field of organic-inorganic hybrids [5–17]. Although POSSs containing various side-chain groups have been reported to date [18], there have been limitations, such as low yield, long reaction time, and difficulty regarding the material application because of the powdered oligomer.

To date, the author and co-workers have discovered methods for synthesizing POSSs containing ionic side-chain groups (ammonium, imidazolium, and carboxyl groups) at a high yield, short reaction time, and good reproducibility using superacid catalysts. In addition, methods for controlling the size and crystalline/amorphous structures of POSSs have been developed, as well as the preparation of ionic liquids containing POSS components. Furthermore, as ionic POSS applications, characteristic materials (an antifogging film and hydrogel) were prepared by polymerization and hybridization using ionic POSSs. This is a comprehensive paper on the superacid-catalyzed preparation of ionic POSSs and their properties, polymerization, and hybridization, which have recently been studied.

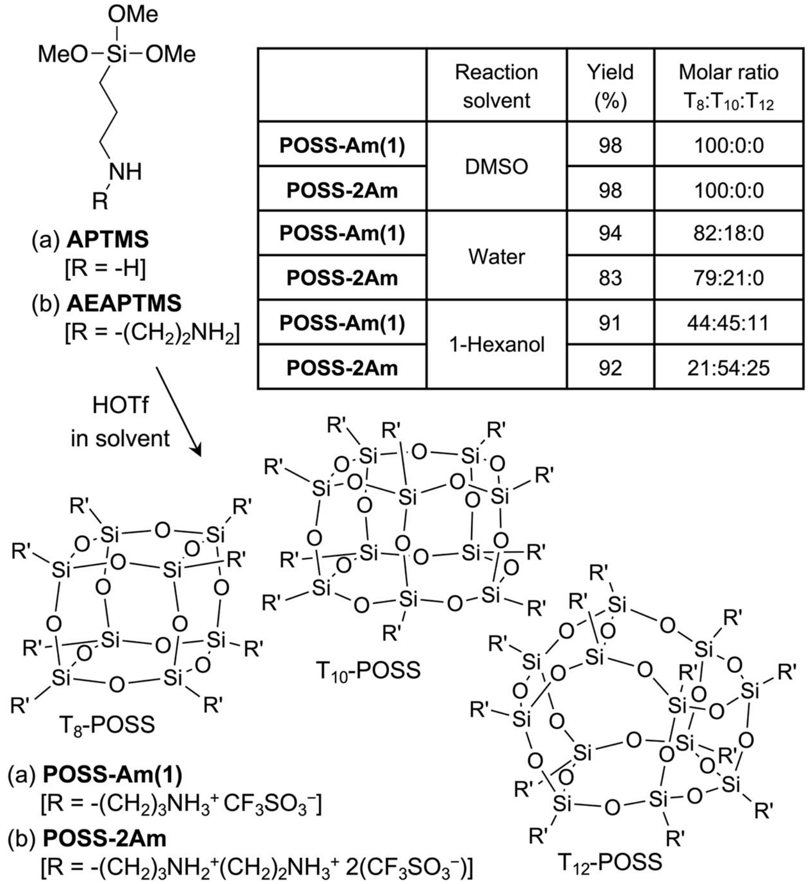
2 Preparation of ammonium-functionalized POSS at a high yield within a short reaction time

Reactive group-containing POSSs have attracted attention because they can be hybridized with various organic compounds by covalent bonds. For example, a primary ammonium group-containing POSS, **POSS-Am(1)**, is well-known and widely used [19]. This POSS is obtained by the hydrolytic condensation of 3-aminopropyltrialkoxysilane. It is typically prepared using a method in which 3-aminopropyltrialkoxysilane is reacted in a dilute alcohol solution in the presence of hydrochloric acid (HCl) under mild conditions to suppress the reaction between multiple molecules, and the gradually precipitating product is recovered. Therefore, although a long-time reaction is generally required for the preparation of **POSS-Am(1)**, the yield is relatively low (*ca.* 30%).

The author and co-workers reported that rod-like and ladder-like polySQ containing ammonium side-chain groups could be



Scheme 1 Preparation of (**a**) ladder-like polySQ and (**b**) POSS (**POSS-Am(1)**) containing primary ammonium groups



Scheme 2 Hydrolytic condensation of **a** APTMS and **b** AEAPTMS using a HOTf catalyst in various solvents. Correlation between reaction solvent and POSS size

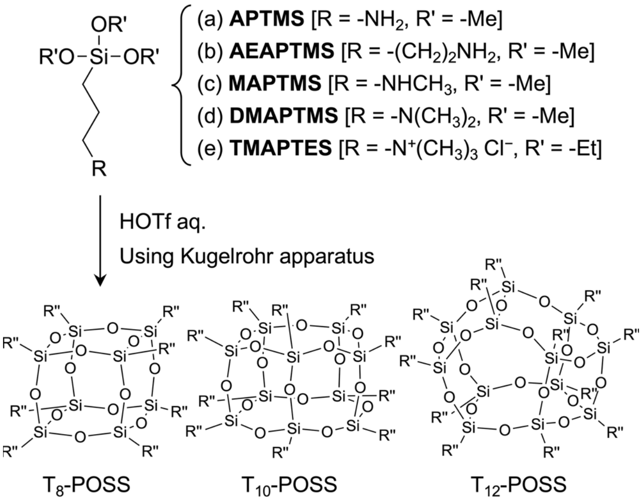
	Reaction solvent	Yield (%)	Molar ratio T_8:T_{10}:T_{12}
POSS-Am(1)	DMSO	98	100:0:0
POSS-2Am		98	100:0:0
POSS-Am(1)	Water	94	82:18:0
POSS-2Am		83	79:21:0
POSS-Am(1)	1-Hexanol	91	44:45:11
POSS-2Am		92	21:54:25

obtained by dissolving 3-aminopropyltrimethoxysilane (APTMS) in an aqueous HCl solution (working as a catalyst and solvent), followed by hydrolytic condensation by heating in an open system to evaporate the solvent (Scheme 1a) [20]. Meanwhile, when this catalyst/solvent (aqueous HCl solution) was replaced with an aqueous superacid trifluoromethanesulfonic acid (HOTf) solution and the solution was similarly heated in an open system to evaporate the solvent, **POSS-Am(1)** was obtained at a high yield (93%) within a short reaction time (total reaction time, *ca.* 5–6 h) (Scheme 1b) [21]. Octameric POSS (T_8-POSS) was the main product, with a small amount of decameric POSS (T_{10}-POSS) (T_8:T_{10} = 82:18) [22].

The following mechanism is considered as the reason POSS is formed without gelation or polymerization although the condensation reaction is performed using the heat concentration method. The amino group of APTMS was protonated to form an ammonium cation using a superacid, such as HOTf, which is prone to proton dissociation. Therefore, considering that the condensation reaction proceeded while electrostatic repulsion occurred between the side-chains, it was presumed that a POSS structure with a long distance between the side-chains was formed. In this method, since the reaction was accelerated by concentration, the condensation reaction occurred in a concentrated solution. Under these conditions, the protons in strong acids (e.g., HCl) do not completely dissociate. Based on these differences in acids, it is considered that POSS can not be formed using a strong acid but can be formed using a superacid in the heat concentration method.

3 Preparation of size-controlled ammonium-functionalized POSS

The focus of POSS research is T_8-POSS, and there is only a limited number of studies on preferential preparation of POSSs with larger structures than that of T_8-POSS. In particular, for ammonium-functionalized POSSs, T_8-POSS is formed as the main product, as previously described. Meanwhile, the hydrolytic condensation was investigated on APTMS and 3-(2-aminoethyl)aminopropyltrimethoxysilane (AEAPTMS) using the HOTf catalyst in various solvents other than water. It was found that T_8-POSS is selectively formed in dimethylsulfoxide (DMSO), a highly polar organic solvent [23], while a mixture of POSSs with a high proportion of T_{10}-POSS (*ca.* 50%) was obtained when a hydrophobic alcohol, such as 1-hexanol, was used as a



Ammonium-functionalized POSSs

(a) **POSS-Am(1)** [R'' = $-(CH_2)_3NH_3^+\ CF_3SO_3^-$]
(b) **POSS-2Am** [R'' = $-(CH_2)_3NH_2^+(CH_2)_2NH_3^+\ 2(CF_3SO_3^-)$]
(c) **POSS-Am(2)** [R'' = $-(CH_2)_3NH_2^+CH_3\ CF_3SO_3^-$]
(d) **POSS-Am(3)** [R'' = $-(CH_2)_3NH^+(CH_3)_2\ CF_3SO_3^-$]
(e) **POSS-Am(4)** [R'' = $-(CH_2)_3N^+(CH_3)_3\ CF_3SO_3^-$]

	Setting temperature / Solvent evaporation time (Setting pressure)	Molar ratio T_8:T_{10}:T_{12}
POSS-Am(1)	60 °C / 2 h (10 hPa)	80:20:0
	120 °C / 6 h (700 hPa)	42:58:0
POSS-2Am	60 °C / 2.5 h (10 hPa)	85:15:0
	120 °C / 6 h (700 hPa)	25:60:15
POSS-Am(2)	60 °C / 2 h (10 hPa)	79:21:0
	120 °C / 6 h (700 hPa)	20:68:12
POSS-Am(3)	60 °C / 2 h (10 hPa)	70:30:0
	120 °C / 6 h (700 hPa)	21:59:20
POSS-Am(4)	60 °C / 2 h (10 hPa)	89:11:0
	120 °C / 6 h (700 hPa)	31:49:20

Scheme 3 Correlation between reaction conditions (temperature and solvent evaporation time) and POSS size during the preparation of ammonium-functionalized POSSs, **a POSS-Am(1)**, **b POSS-2Am**, **c POSS-Am(2)**, **d POSS-Am(3)**, and **e POSS-Am(4)**, using an aqueous HOTf solution

solvent (Scheme 2) [22]. Although the mechanism is unknown, it was considered that the aforementioned electrostatic repulsion in the mechanism of **POSS-Am(1)** formation was weakened in a hydrophobic alcohol, such as 1-hexanol. Consequently, it was believed that T_{10}-POSS, in which the distance between the side-chains was shorter than that in T_8-POSS, was more preferentially formed. Presently, it is difficult to selectively prepare T_{10}-POSS using this method; however, a mixture of T_8-, T_{10}-, and T_{12}-POSSs could be separated into T_8-POSS and other POSSs using a simple method that uses their differences in solubility in various alcohols [22].

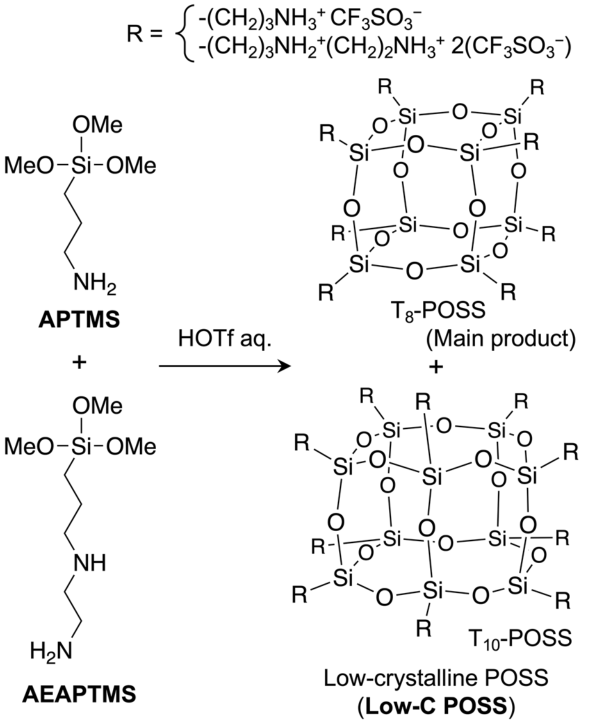
As previously mentioned, the hydrolytic condensation of APTMS and AEAPTMS in an aqueous HOTf solution yields T_8-POSS as the main product. To investigate this reaction in detail, the reaction was performed by changing the temperature, pressure, and solvent evaporation time using a Kugelrohr apparatus. At a relatively low setting temperature of a Kugelrohr apparatus, such as 60 °C, T_8-POSS was the main product regardless of the pressure and solvent evaporation time. It was observed that the ratio of T_{10}-POSS increased (*ca.* 60% in molar ratio) when the solvent was slowly evaporated over 6 h without considerably reducing the pressure at relatively high setting temperatures, such as 100–120 °C (Scheme 3a, b) [24]. The same tendency was observed during the preparation of POSSs containing secondary, tertiary, and quaternary ammonium side-chain groups (**POSS-Am(2)**, **POSS-Am(3)**, and **POSS-Am(4)**, respectively) using a similar method, i.e., the ratio of T_{10}-POSS increased (over 60% in molar ratio) when the solvent was slowly evaporated without significantly lowering the pressure at relatively high setting temperatures (Scheme 3c–e) [25]. Although the correlation between the reaction conditions (temperature, pressure, and solvent evaporation time) and POSS size has been clarified, the mechanism remains unknown.

4 Preparation of low-crystalline POSS with two types of ionic side-chain groups

Considering that POSS (particularly T_8-POSS), which is symmetrical, exhibits high crystallinity and typically exists in powder form, it is difficult to produce optically transparent films using only POSS. Oppositely, when a mixture of two types of amino group-containing organotrialkoxysilanes (APTMS and AEAPTMS) was used as a starting material and subjected to hydrolytic condensation in an aqueous HOTf solution, a low-crystalline POSS (**Low-C POSS**) capable of forming a transparent cast film was obtained (Scheme 4) [26]. The reason for the low crystallinity of **Low-C POSS** was that the symmetry of the molecule was reduced by randomly arranging two types of substituents on the side-chains of POSS. Therefore, the **Low-C POSS** film became transparent because there were virtually no crystal domains in the film sufficiently large to scatter visible light.

5 Preparation and properties of ionic liquids containing POSS components

Compounds that completely comprise ions and exist as a liquid below *ca.* 100 °C (also defined as below *ca.* 150 °C)



Scheme 4 Preparation of low-crystalline POSS (**Low-C POSS**) by the hydrolytic condensation of a mixture of APTMS and AEAPTMS in an aqueous HOTf solution

are called ionic liquids. Ionic liquids exhibit high ionic conductivity, flame retardancy, and nonvolatility and have recently attracted considerable attention [27–29]. Many ionic liquids comprise organic cations, anions, or both, while there are few reports of ionic liquids containing inorganic components, such as siloxane frameworks. Ionic liquids containing more inorganic components are expected to further improve heat resistance and flame retardancy and function as safe electrolytes and green solvents.

Based on the aforementioned background, an ionic liquid containing a POSS component as an inorganic framework was reported for the first time by Tanaka et al. [30]. The POSS containing carboxylate anions in the side-chains and imidazolium cations as counterions was observed to exhibit properties of an ionic liquid with a melting point (T_m) at 23 °C. This ionic liquid had a rigid POSS framework; as a result, the thermal decomposition temperature was higher than that of an ionic liquid (without the POSS structure) having the same structure as the side-chain of this POSS.

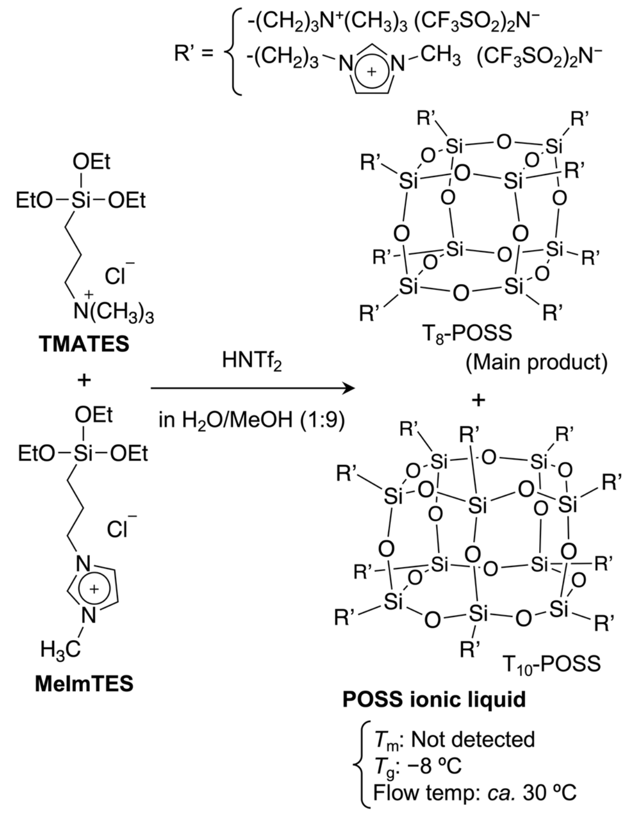
Meanwhile, the author and co-workers have reported that random oligoSQs, which exhibit ionic liquid properties, could be obtained by the hydrolytic condensation of organotriethoxysilanes containing quaternary ammonium groups and methyl imidazolium groups (TMATES and MeImTES, respectively) as starting materials, using an aqueous superacid bis(trifluoromethanesulfonyl)imide ($HNTf_2$) solution [31, 32]. The glass transition point (T_g) and actual flowing temperature were *ca.* 15 °C and 40 °C, respectively, for the quaternary ammonium-salt type and *ca.* −25 °C and 0 °C, respectively, for the imidazolium-salt type, indicating that they were room temperature ionic liquids. Although they were oligomers with a relatively large number of silanol (Si–OH) groups, the condensation between the Si–OH groups did not occur anymore, and the compounds were stable. X-ray diffraction and differential scanning calorimetry (DSC) measurements revealed that they were amorphous.

The author and co-workers discovered that crystalline POSSs could be easily obtained when a similar reaction was performed in a water/methanol (1:19, v/v) mixed solvent instead of only water [31, 32]. However, these crystalline POSSs did not exhibit fluidity unless they were heated to near T_m (quaternary ammonium-salt type, 172 °C; imidazolium-salt type, 106 °C), and these temperatures were higher than those of the aforementioned random oligoSQs. Considering the long-term stability, ionic liquids containing POSS structures (in which Si–OH groups do not exist) are considered to be more advantageous than random oligoSQs (in which Si–OH groups exist). However, high crystallinities of POSS cause high flow temperature and have constituted problems during the preparation of POSS ionic liquids containing quaternary ammonium and imidazolium groups.

Therefore, it was investigated the preparation of POSS ionic liquids with randomly arranging two types of substituents on the side-chains, which exhibit fluidity around room temperature, referring to the aforementioned preparation method for **Low-C POSS**. When a mixture of TMATES and MeImTES was used as a starting material and the hydrolytic condensation of this mixture was performed using an $HNTf_2$ catalyst in a water/methanol mixed solvent, POSSs containing two types of side-chain groups, which exhibit ionic liquid properties at room temperature, were obtained (Scheme 5) [33]. Based on the DSC measurement, no endothermic peak due to T_m was observed; T_g was −8 °C, and the visually observed flow temperature was *ca.* 30 °C.

In addition, POSSs containing the side-chain combinations of primary and tertiary (**POSS-Am(1,3)**), primary and quaternary (**POSS-Am(1,4)**), and secondary and quaternary (**POSS-Am(2,4)**) ammonium groups were amorphous and existed as ionic liquids flowing at relatively low temperatures (Fig. 1) [34]. When the structures of the two side-chain groups of POSS greatly differ, i.e., when the number of methyl groups adjacent to the N atom of the ammonium group differs by more than two, the symmetry of POSS is considered to be reduced, resulting in the formation of an amorphous POSS structure.

Regarding the imidazolium group-containing POSSs, when the substituents R of the POSS shown in Scheme 6 were methyl



Scheme 5 Preparation of POSS ionic liquid by the hydrolytic condensation of a mixture of TMATES and MeImTES in a water/methanol (1:9 v/v) mixed solution of $HNTf_2$ and its thermal properties

(a) and ethyl (b) groups, they were crystalline POSSs, and the T_m values were 106 °C and 59 °C, respectively. They did not flow unless heated up to T_m. However, when the substituents R were *n*-propyl (c) and *n*-butyl (d) groups, they did not have a T_m and were amorphous POSSs. The T_g values were −32 °C and −33 °C, respectively, and the flow temperatures were *ca.* 10 °C and 5 °C, respectively, indicating a room temperature ionic liquid [35]. These results clarified that the amorphous structure was important for obtaining POSSs, which exhibit the properties of ionic liquids at room temperature.

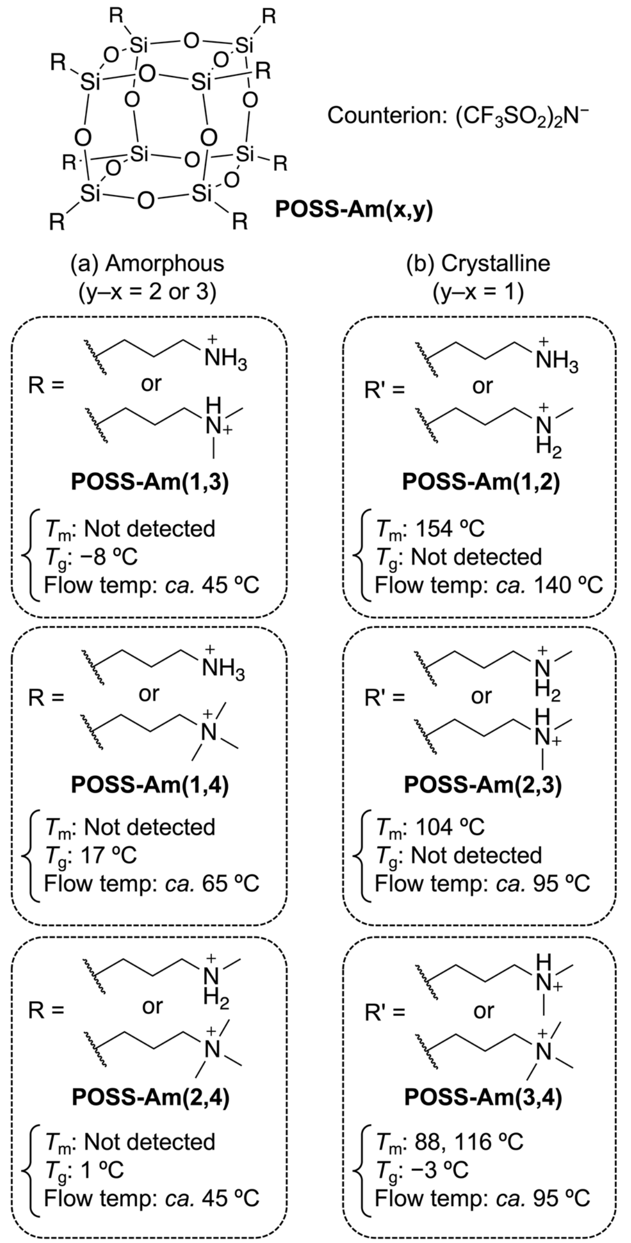
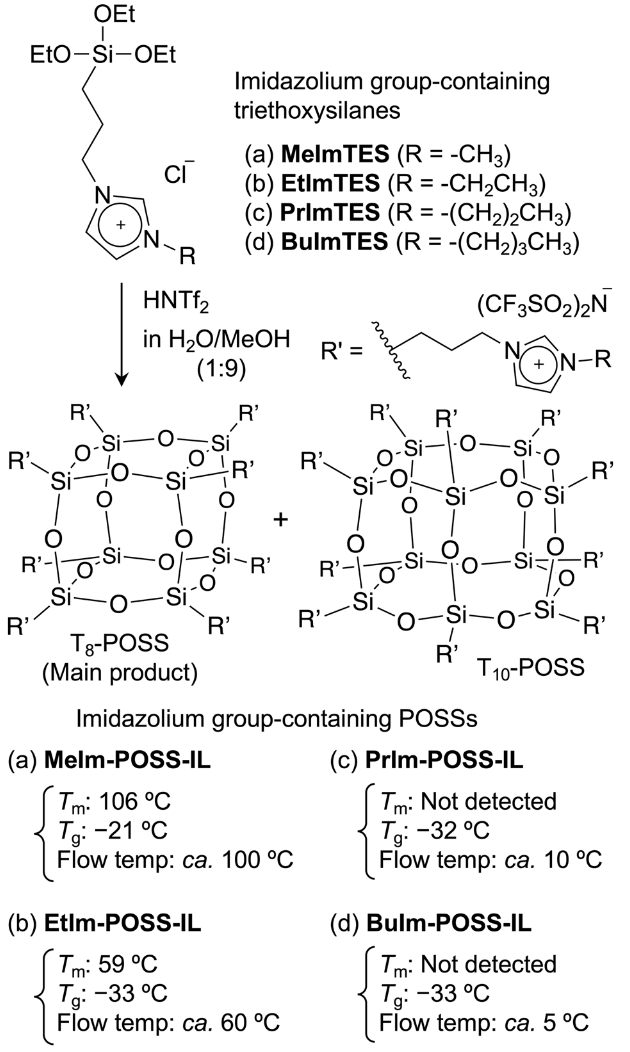


Fig. 1 Thermal properties of POSSs containing two types of ammonium side-chain groups (primary, secondary, tertiary, and quaternary ammonium groups) with (**a**) amorphous and (**b**) crystalline structures

6 Preparation of carboxyl-functionalized POSS

POSSs containing acidic side-chain groups, such as carboxyl groups, are difficult to directly prepare from organotrialkoxysilanes. This is because the carboxyl group-containing organotrialkoxysilane, which is a starting material, does not exist as a general reagent. The author and coworkers discovered that T_{10}-POSS (**POSS-2C-HOTf**) was mainly formed when 3-(triethoxysilyl)propylsuccinic anhydride (TESPSA) was used as a starting material to form carboxyl-functionalized POSSs using an aqueous HOTf solution (Scheme 7a) [36]. For catalysts other than HOTf, T_8-POSS (**POSS-2C-*n*Bu$_4$NOH**) was formed as the main product when an aqueous tetra-*n*-butylammonium hydroxide (nBu$_4$NOH) solution was used (Scheme 7b). PolySQs (**PolySQ-2C-HCl** and **PolySQ-2C-NaOH**) were obtained when aqueous HCl and NaOH solutions were used, respectively (Scheme 7c, d).

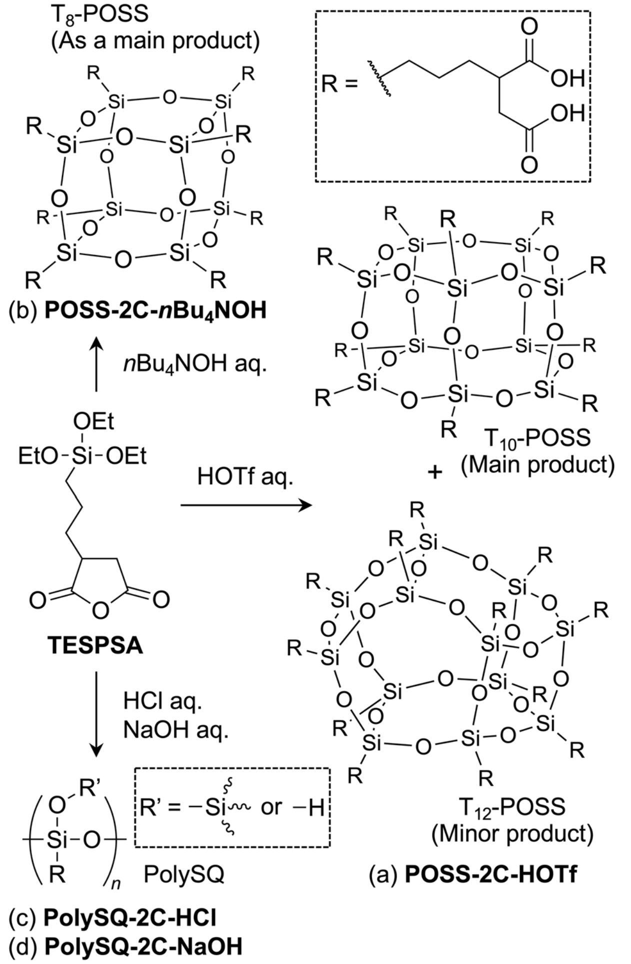
Furthermore, it was clarified that a carboxyl-functionalized POSS (**POSS-C**) could be obtained by



Scheme 6 Preparation of POSSs containing imidazolium groups in which the substituents R were **a** methyl (**MeIm-POSS-IL**), **b** ethyl (**EtIm-POSS-IL**), **c** *n*-propyl (**PrIm-POSS-IL**), and (**d**) *n*-butyl (**BuIm-POSS-IL**) groups, and their thermal properties

heat-treating a carboxyl group-containing rod-like/ladder-like polySQ, which was prepared by the hydrolytic polycondensation of 2-cyanoethyltriethoxysilane using an aqueous NaOH solution [37], in an aqueous HOTf solution and evaporating the solvent (Scheme 8) [38].

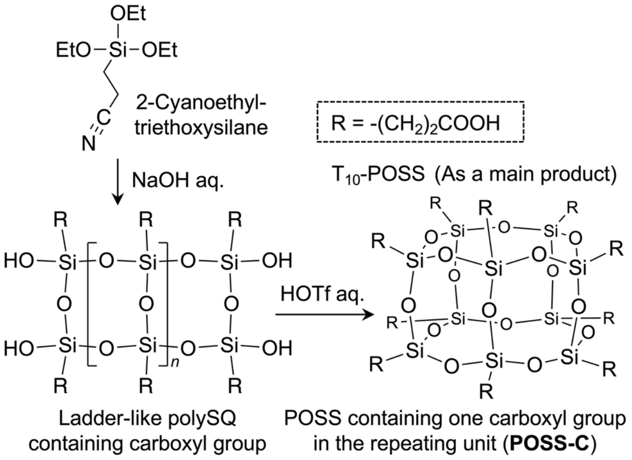
7 Preparation of ammonium-functionalized specific cyclotetrasiloxane isomer



Scheme 7 Preparation of POSSs and polySQs containing two carboxyl groups in the repeating unit by the hydrolytic condensation of TESPSA in aqueous **a** HOTf, **b** $n\mathrm{Bu_4NOH}$, **c** HCl, and **d** NaOH solutions

This section explains that the above method for preparing ammonium-functionalized POSS using superacids [21–26] can be applied in the preparation of a specific cyclotetrasiloxane isomer. Cyclosiloxanes are generally obtained by the hydrolytic condensation of bifunctional silane compounds and are used as raw materials for silicone preparation. Conventionally, the hydrolytic condensation of bifunctional silane compounds yields mixtures of cyclic and linear siloxanes of various molecular weights. In addition, cyclosiloxanes with the same molecular weight, in which two types of side-chain groups are bonded to one Si atom, possess isomers with different stereostructures. For example, a cyclotetrasiloxane possesses four isomers: all-*cis*, all-*trans*, *cis-trans-cis*, and *cis-cis-trans* [39], and it is difficult to selectively prepare one of them at a high yield in one step from a bifunctional silane compound. Therefore, the development of new techniques to prepare a specific cyclosiloxane isomer is extremely important in the academic and industrial fields.

As previously described, POSS can be obtained by the hydrolytic condensation of APTMS in an aqueous HOTf solution, while a rod-like/ladder-like PSQ can be obtained by a similar reaction in an aqueous HCl solution (Scheme 1). Therefore, it is expected that a cyclic compound would be preferentially formed over the polymeric



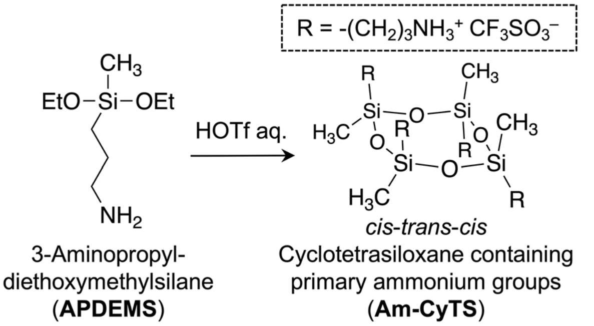
Scheme 8 Preparation of polySQ and POSS (**POSS-C**) containing one carboxyl group in a repeating unit

compound during the hydrolytic condensation of amino group-containing organoalkoxysilanes in an aqueous HOTf solution.

The hydrolytic condensation was investigated on 3-aminopropyldiethoxymethylsilane (APDEMS), which is a bifunctional organoalkoxysilane containing aminopropyl and methyl side-chain groups, in an aqueous HOTf solution. As expected, no polymer was formed, and only cyclosiloxane (**Am-CyTS**) was obtained. Unexpectedly, this compound exhibited a single structure (*cis-trans-cis* cyclotetramer only) (Scheme 9), which was clarified by ^{1}H NMR, ^{29}Si NMR, matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS), electrospray ionization (ESI) MS, and single-crystal X-ray structural analysis [40]. For the previously described POSS, it is expected that the *cis-trans-cis* structure was formed as a structure in which the distance between the side-chains was the longest by the electrostatic repulsion between the side-chains. Furthermore, single-crystal X-ray structural analysis showed that the *tert*-butoxycarbonyl (Boc)-protected product has a layered structure, in which hexagonal-arranged two-dimensional sheet-like aggregates are stacked.

8 Preparation of antifogging film using polyamide in which POSS-Am(1) and POSS-C are linked

Antifogging films are used in applications, which can be problematic if light passage or reflection is obstructed, e.g., show windows, goggles/helmets, greenhouses, automotive glass/mirrors, medical devices, and solar panels. For antifogging, two methods are used as follows: one in which the surface of a substrate is rendered water-repellent to prevent adhering water droplets [41–43] and another in which a thin continuous water film is formed by rendering the surface hydrophilic [44–49]. In particular, organic polymer coatings using the latter method are more mainstream [50–53]. However, the hardness of these organic polymers is insufficient, and the transparency and antifogging properties gradually decrease because of scratches and abrasion.

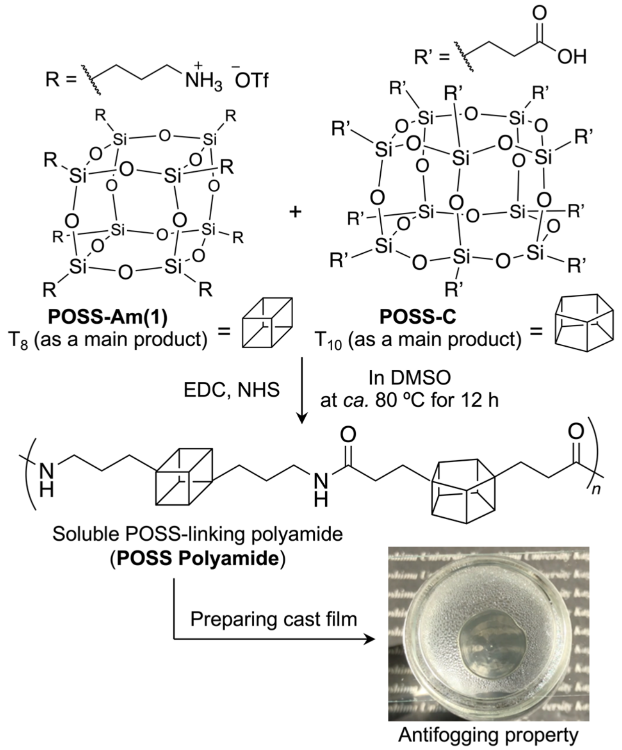


Scheme 9 Preparation of a *cis-trans-cis* cyclotetrasiloxane containing primary ammonium groups

A POSS-linked polyamide (**POSS Polyamide**) was prepared by the polycondensation of the aforementioned **POSS-Am(1)** and **POSS-C** as a material for an antifogging film with a hard-coating ability (Scheme 10) [54]. Specifically, **POSS-Am(1)** and **POSS-C** (molar ratio of units = 1:1) were stirred for 12 h at *ca*. 80 °C in dehydrated DMSO in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) as condensing agents. **POSS Polyamide** was soluble in polar solvents, such as water, DMSO, and methanol; therefore, it was presumed that the two POSSs were linearly linked without exhibiting a considerably branched structure.

The pencil hardness of a cast film of **POSS Polyamide** was 5H. The reason for this relatively high hard-coating property might be that a crosslinked structure was formed by the dehydrating condensation of the ammonium and a carboxyl groups of the polymer side-chains during the cast film preparation by heating, in addition to the original hardness of the POSS components.

The antifogging property of the cast film was evaluated. When the aforementioned cast film was placed on 5 cm of hot water (*ca*. 80 °C) and exposed to water vapor, it did not fog at first and exhibited antifogging properties, but it became cloudy in the middle. Subsequently, it became transparent after further exposure to water vapor and finally exhibited antifogging properties (Scheme 10). After the heat treatment, the cast film exhibited a porous crosslinked structure probably due to the formation of new amide bonds. Upon exposure to water vapor, the water molecules infiltrated the porous structure as water vapor, and the water produced by cooling filled the pores. Thus, the hydrophilicity of the cast film surface increased, and it was



Scheme 10 Preparation of POSS-linked polyamide (**POSS Polyamide**) by the polycondensation of **POSS-Am(1)** and **POSS-C** and its antifogging property

considered that the antifogging property was exhibited by forming a continuous water film.

9 Preparation of hydrogels using ionic POSS and cyclotetrasiloxane as crosslinking agents and their mechanical properties

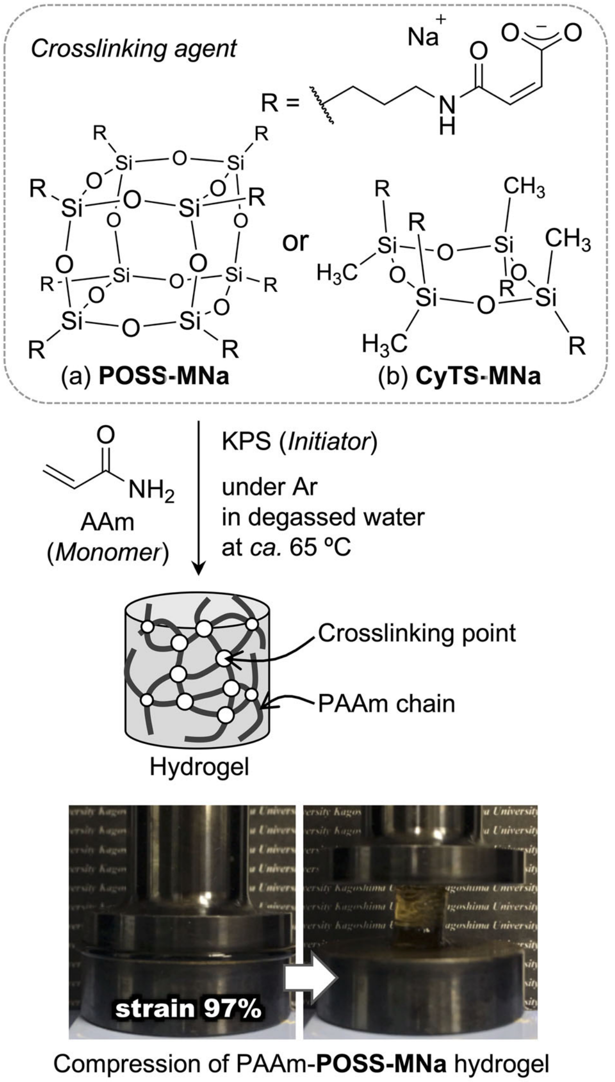
Hydrogel is a material that can contain a large amount of water in a network polymer and is widely used in a variety of applications, *e.g*., soft contact lenses and superabsorbent polymers. However, because general hydrogels are fragile, the development of durable hydrogels is important to expand the application range of hydrogels. Based on this, hydrogels with excellent mechanical properties, such as a topological [55], nanocomposite [56], double-network [57], and tetra-PEG gels [58] have been developed.

Crosslinking agents (**POSS-MNa** and **CyTS-MNa**) as shown in Scheme 11 for hydrogel preparation were prepared by introducing polymerizable groups via the reaction of maleic anhydride with **POSS-Am(1)** and **Am-CyTS**, and polyacrylamide hydrogels were prepared by the free-radical polymerization of an acrylamide monomer using the resulting crosslinking agents and potassium persulfate (KPS) as an initiator (Scheme 11a, b) [59]. These hydrogels were not destroyed even when compressed to a strain of 97%, and they exhibited extremely flexible and irrefrangible properties. For example, the state of compression of a hydrogel (PAAm-**POSS-MNa** hydrogel) obtained using **POSS-MNa** is shown in Scheme 11. It is considered that the occurrence of chemical and physical crosslinking due to the formation of aggregates of **POSS-MNa** and **CyTS-MNa** was important for these excellent mechanical properties.

10 Conclusion

This paper highlighted recent studies on the superacid-catalyzed preparation of ionic POSSs and their properties, polymerization, and hybridization, that have been developed by the author and co-workers so far. Ammonium-functionalized T_8-POSS, as the main product, can be prepared at a high yield within a short reaction time by the hydrolytic condensation of amino group-containing organotrialkoxysilanes in an aqueous superacid solution. When these reactions were performed in a hydrophobic alcohol, such as 1-hexanol, a POSS mixture with a high proportion of T_{10}-POSS was obtained. In addition, the proportion of T_{10}-POSS can be increased by properly controlling the reaction conditions (temperature, pressure, and solvent evaporation time) using a Kugelrohr apparatus in preparing POSSs in an aqueous superacid solution. Furthermore, a low-crystalline POSS and ionic liquids containing POSS components can be obtained by the superacid-catalyzed hydrolytic condensation of the mixtures of two types of organotrialkoxysilanes containing functional groups capable of converting to ionic groups. The superacid-catalyzed hydrolytic condensation was applicable to the preparation of carboxyl-functionalized POSSs and an ammonium-functionalized specific cyclotetrasiloxane isomer. As an application of an ionic POSS, an antifogging film with a hard-coating property can be prepared using polyamide obtained by the polycondensation of ammonium- and carboxyl-functionalized POSSs. Furthermore, it was possible to obtain a polyacrylamide hydrogel exhibiting extremely flexible and irrefrangible properties using an ionic POSS and cyclotetrasiloxane as crosslinking agents.

Studies on the applications of POSS as a material are expected to increase in industry and academia. To support these applications, basic research on the development of a facile preparation method, size control, and crystalline/amorphous structure control for ionic POSS is important. The author believes that applied research on the polymerization and hybridization of ionic POSS possesses potential and would like to continue studying POSSs from both basic and applied perspectives.



Scheme 11 Preparation of polyacrylamide hydrogels by the free-radical polymerization of acrylamide (AAm) using **a POSS-MNa** and **b CyTS-MNa** as crosslinking agents

Acknowledgements The author acknowledges to the co-workers, whose names are found in references from his papers, for their enthusiastic collaboration.

Compliance with ethical standards

Conflict of interest The author declares no competing interests.

References

1. Baney RH, Itoh M, Sakakibara A, Suzuki T (1995) Silsesquioxanes. Chem Rev 95:1409–1430
2. Loy DA, Baugher BM, Baugher CR, Schneider DA, Rahimian K (2000) Substituent effects on the sol–gel chemistry of organotrialkoxysilanes. Chem Mater 12:3624–3632
3. Kaneko Y, Coughlin EB, Gunji T, Itoh M, Matsukawa K, Naka K (2012) Silsesquioxanes: recent advancement and novel applications. Int J Polym Sci 453821
4. Kaneko Y (2018) Ionic silsesquioxanes: preparation, structure control, characterization, and applications. Polymer 144:205–224
5. Laine RM, Zhang C, Sellinger A, Viculis L (1998) Polyfunctional cubic silsesquioxanes as building blocks for organic/inorganic hybrids. Appl Organomet Chem 12:715–723
6. Choi J, Harcup J, Yee AF, Zhu Q, Laine RM (2001) Organic/inorganic hybrid composites from cubic silsesquioxanes. J Am Chem Soc 123:11420–11430
7. Kim KM, Chujo Y (2003) Organic–inorganic hybrid gels having functionalized silsesquioxanes. J Mater Chem 13:1384–1391
8. Tanaka K, Adachi S, Chujo Y (2009) Structure-property relationship of octa-substituted POSS in thermal and mechanical reinforcements of conventional polymers. J Polym Sci Part A: Polym Chem 47:5690–5697
9. Yu X, Zhong S, Li X, Tu Y, Yang S, Van Horn RM, Ni C, Pochan DJ, Quirk RP, Wesdemiotis C, Zhang WB, Cheng SZD (2010) A giant surfactant of polystyrene-(carboxylic acid-functionalized polyhedral oligomeric silsesquioxane) amphiphile with highly stretched polystyrene tails in micellar assemblies. J Am Chem Soc 132:16741–16744
10. Wang F, Lu X, He C (2011) Some recent developments of polyhedral oligomeric silsesquioxane (POSS)-based polymeric materials. J Mater Chem 21:2775–2782
11. Kuo SW, Chang FC (2011) POSS related polymer nanocomposites. Prog Polym Sci 36:1649–1696
12. Tanaka K, Chujo Y (2012) Advanced functional materials based on polyhedral oligomeric silsesquioxane (POSS). J Mater Chem 22:1733–1746
13. Sun J, Chen Y, Zhao L, Chen Y, Qi D, Choi KM, Shin DS, Jiang J (2013) Porphyrin-POSS molecular hybrids. Chem Eur J 19:12613–12618
14. Alves F, Nischang I (2013) Tailor-made hybrid organic–inorganic porous materials based on polyhedral oligomeric silsesquioxanes (POSS) by the step-growth mechanism of thiol-ene "click" chemistry. Chem Eur J 19:17310–17313
15. Guo M, David É, Fréchette M, Demarquette NR (2017) Polyethylene/polyhedral oligomeric silsesquioxanes composites: dielectric, thermal and rheological properties. Polymer 115:60–69
16. Li Y, Dong XH, Zou Y, Wang Z, Yue K, Huang M, Liu H, Feng X, Lin Z, Zhang W, Zhang WB, Cheng SZD (2017) Polyhedral oligomeric silsesquioxane meets "click" chemistry: rational design and facile preparation of functional hybrid materials. Polymer 125:303–329
17. Zhang W, Camino G, Yang R (2017) Polymer/polyhedral oligomeric silsesquioxane (POSS) nanocomposites: an overview of fire retardance. Prog Polym Sci 67:77–125
18. Cordes DB, Lickiss PD, Rataboul F (2010) Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes. Chem Rev 110:2081–2173
19. Feher FJ, Wyndham KD (1998) Amine and ester-substituted silsesquioxanes: synthesis, characterization and use as a core for starburst dendrimers. Chem Commun 323–324
20. Kaneko Y, Iyi N, Kurashima K, Matsumoto T, Fujita T, Kitamura K (2004) Hexagonal-structured polysiloxane material prepared by sol–gel reaction of aminoalkyltrialkoxysilane without using surfactants. Chem Mater 16:3417–3423
21. Kaneko Y, Shoiriki M, Mizumo T (2012) Preparation of cage-like octa(3-aminopropyl)silsesquioxane trifluoromethanesulfonate in higher yield with a shorter reaction time. J Mater Chem 22:14475–14478

22. Imai K, Kaneko Y (2017) Preparation of ammonium-functionalized polyhedral oligomeric silsesquioxanes with high proportions of cagelike decamer and their facile separation. Inorg Chem 56:4133–4140
23. Matsumoto T, Kaneko Y (2018) Selective and high-yielding preparation of ammonium-functionalized cage-like octa-silsesquioxanes using superacid catalyst in dimethyl sulfoxide. Chem lett 47:864–867
24. Matsumoto T, Kaneko Y (2019) Effect of reaction temperature and time on the preferential preparation of cage octamer and decamer of ammonium-functionalized POSSs. Bull Chem Soc Jpn 92:1060–1067
25. Matsumoto T, Kaneko Y (2020) Correlation between molecular structures and reaction conditions (temperature–pressure–time) in the preparation of secondary, tertiary, and quaternary ammonium-functionalized polyhedral oligomeric silsesquioxanes. J Sol-Gel Sci Technol 95:670–681
26. Tokunaga T, Shoiriki M, Mizumo T, Kaneko Y (2014) Preparation of low-crystalline POSS containing two types of alkylammonium groups and its optically transparent film. J Mater Chem C 2:2496–2501
27. Welton T (1999) Room-temperature ionic liquids. solvents for synthesis and catalysis. Chem Rev 99:2071–2084
28. Hallett JP, Welton T (2011) Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. Chem Rev 111:3508–3576
29. Kaneko Y, Harada A, Kubo T, Ishii T (2017) In: Handy S (ed) Progress and developments in ionic liquids. InTech, London.
30. Tanaka K, Ishiguro F, Chujo Y (2010) POSS ionic liquid. J Am Chem Soc 132:17649–17651
31. Ishii T, Mizumo T, Kaneko Y (2014) Facile preparation of ionic liquid containing silsesquioxane framework. Bull Chem Soc Jpn 87:155–159
32. Ishii T, Enoki T, Mizumo T, Ohshita J, Kaneko Y (2015) Preparation of imidazolium-type ionic liquids containing silsesquioxane frameworks and their thermal and ion-conductive properties. RSC Adv 5:15226–15232
33. Harada A, Koge S, Ohshita J, Kaneko Y (2016) Preparation of a thermally stable room temperature ionic liquid containing cage-like oligosilsesquioxane with two types of side-chain groups. Bull Chem Soc Jpn 89:1129–1135
34. Hasebe R, Kaneko Y (2019) Control of crystalline-amorphous structures of polyhedral oligomeric silsesquioxanes containing two types of ammonium side-chain groups and their properties as protic ionic liquids. Molecules 24:4553
35. Maeda D, Ishii T, Kaneko Y (2018) Effect of lengths of substituents in imidazolium groups on the preparation of imidazolium-salt-type ionic liquids containing polyhedral oligomeric silsesquioxane structures. Bull Chem Soc Jpn 91:1112–1119
36. Liu J, Kaneko Y (2018) Preparation of polyhedral oligomeric silsesquioxanes containing carboxyl side-chain groups and isolation of a cage-like octamer using clay mineral. Bull Chem Soc Jpn 91:1120–1127
37. Toyodome H, Kaneko Y, Shikinaka K, Iyi N (2012) Preparation of carboxylate group-containing rod-like polysilsesquioxane with hexagonally stacked structure by sol–gel reaction of 2-cyanoethyltriethoxysilane. Polymer 53:6021–6026
38. Kozuma T, Kaneko Y (2019) Preparation of carboxyl-functionalized polyhedral oligomeric silsesquioxane by a structural transformation reaction from soluble rod-like polysilsesquioxane. J Polym Sci Part A Polym Chem 57:2511–2518
39. Yagihashi F, Igarashi M, Nakajima Y, Sato K, Yumoto Y, Matsui C, Shimada S (2016) Unexpected selectivity in cyclotetrasiloxane formation by the hydrolytic condensation reaction of trichloro(phenyl)silane. Eur J Inorg Chem 2882–2886
40. Kinoshita S, Watase S, Matsukawa K, Kaneko Y (2015) Selective synthesis of *cis-trans-cis* cyclic tetrasiloxanes and the formation of their two-dimensional layered aggregates. J Am Chem Soc 137:5061–5065
41. Gao X, Yan X, Yao X, Xu L, Zhang K, Zhang J, Yang B, Jiang L (2007) The dry-style antifogging properties of mosquito compound eyes and artificial analogues prepared by soft lithography. Adv Mater 19:2213–2217
42. Liu K, Yao X, Jiang L (2010) Recent developments in bio-inspired special wettability. Chem Soc Rev 39:3240–3255
43. Sun Z, Liao T, Liu K, Jiang L, Kim JH, Dou SX (2014) Fly-eye inspired superhydrophobic anti-fogging inorganic nanostructures. Small 10:3001–3006
44. Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, Kitamura A, Shimohigoshi M, Watanabe T (1997) Light-induced amphiphilic surfaces. Nature 388:431–432
45. Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, Kitamura A, Shimohigoshi M, Watanabe T (1998) Photogeneration of highly amphiphilic TiO_2 surfaces. Adv Mater 10:135–138
46. Sun RD, Nakajima A, Fujishima A, Watanabe T, Hashimoto K (2001) Photoinduced surface wettability conversion of ZnO and TiO_2 thin films. J Phys Chem B 105:1984–1990
47. Tricoli A, Righettoni M, Pratsinis SE (2009) Anti-fogging nanofibrous SiO_2 and nanostructured SiO_2-TiO_2 films made by rapid flame deposition and in situ annealing. Langmuir 25:12578–12584
48. Chemin JB, Bulou S, Baba K, Fontaine C, Sindzingre T, Boscher ND, Choquet P (2018) Transparent anti-fogging and self- cleaning TiO_2/SiO_2 thin films on polymer substrates using atmospheric plasma. Sci Rep. 8:1–8
49. Maeda T, Hamada T, Tsukada S, Katsura D, Okada K, Ohshita J (2021) Antifogging hybrid materials based on amino-functionalized polysilsesquioxanes. ACS Appl Polym Mater 3:2568–2575
50. Howarter JA, Youngblood JP (2008) Self-cleaning and next generation anti-fog surfaces and coatings. Macromol Rapid Commun 29:455–466
51. Zhao J, Meyer A, Ma L, Ming W (2013) Acrylic coatings with surprising antifogging and frost-resisting properties. Chem Commun 49:11764–11766
52. Lee H, Alcaraz ML, Rubner MF, Cohen RE (2013) Zwitter-wettability and antifogging coatings with frost-resisting capabilities. ACS Nano 7:2172–2185
53. Zhang T, Fang L, Lin N, Wang J, Wang Y, Wu T, Song P (2019) Highly transparent, healable, and durable anti-fogging coating by combining hydrophilic pectin and tannic acid with poly(ethylene terephthalate). Green Chem 21:5405–5413
54. Kozuma T, Mihata A, Kaneko Y (2021) Preparation of soluble POSS-linking polyamide and its application in antifogging films. Materials 14:3178
55. Okumura Y, Ito K (2001) The polyrotaxane gel: a topological gel by figure-of-eight cross-link. Adv Mater 13:485–487
56. Haraguchi K, Takehisa T (2002) Nanocomposite hydrogels: a unique organic–inorganic network structure with extraordinary mechanical, optical, and swelling/de-swelling properties. Adv Mater 14:1120–1124
57. Gong JP, Katsuyama Y, Kurokawa T, Osada Y (2003) Double-network hydrogels with extremely high mechanical strength. Adv Mater 15:1155–1158
58. Sakai T, Matsunaga T, Yamamoto Y, Ito C, Yoshida R, Suzuki S, Sasaki N, Shibayama M, Chung U (2008) Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. Macromolecules 41:5379–5384
59. Yanagie M, Kaneko Y (2018) Preparation of irrefrangible polyacrylamide hybrid hydrogels using water-dispersible cyclotetrasiloxane or polyhedral oligomeric silsesquioxane containing polymerizable groups as cross-linkers. Polym Chem 9:2302–2312