

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Preparation of Ionic Polysilsesquioxanes with Regular Structures and Their Ion-Exchange Behaviors

Yoshiro Kaneko

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/45732>

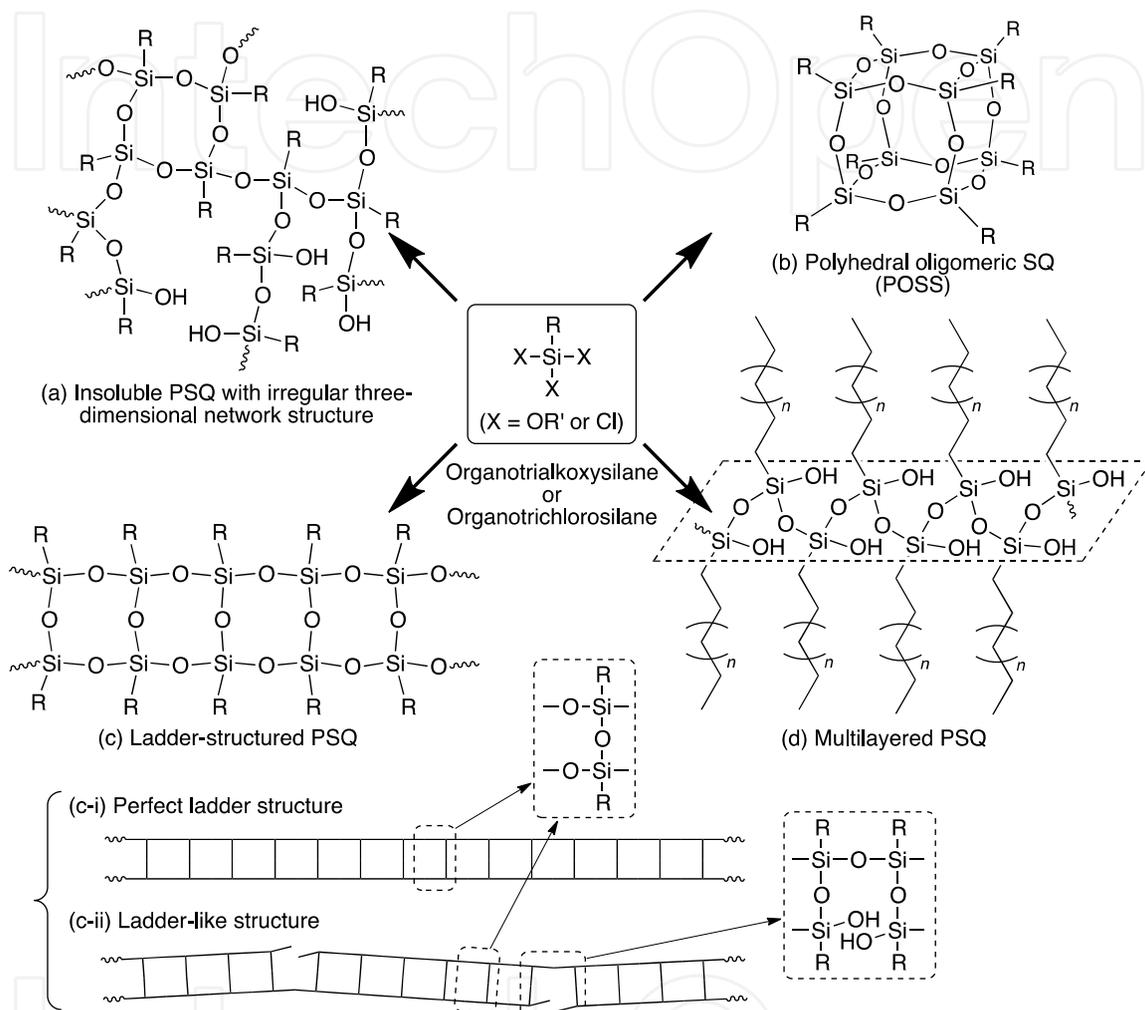
1. Introduction

Silsesquioxanes (SQs: $\text{RSiO}_{1.5}$), one class of the materials containing Si–O framework, have attracted much attention in the research fields of materials chemistry for academic and application reasons (Baney et al., 1995; Loy et al., 2000) because they can contain the various functional groups as side chains (R) and are inorganic materials indicating the remarkable compatibility with organic materials such as polymers (Choi et al., 2001; Kim & Chujo, 2003; Yu et al., 2010; Wang et al., 2011), in addition to having superior thermal, mechanical, and chemical properties derived from Si–O framework with high bond energy compared with C–C bonds.

However, even though various kinds of polyhedral oligomeric SQs (POSS) are known as SQs with controlled molecular structures (Scheme 1b) (Feher & Wyndham, 1998; Laine et al., 1998; Zhang et al., 2007; Cordes et al., 2010; Tanaka et al., 2010; Tanaka & Chujo, 2012), the regularly structured polySQs (PSQs) have only been obtained in the limited cases. This is because PSQs are prepared by polycondensation of the trifunctional silane monomers such as organotrialkoxysilanes and organotrichlorosilanes. These multifunctional monomers generally result in the formation of insoluble polymers with irregular three-dimensional network structures of Si–O–Si bonds (Scheme 1a) (Loy et al., 2000). If the molecular, conformational, and higher-ordered structures of PSQs can be controlled, they are expected to be applicable for a wide range of materials research fields.

Ladder-structured PSQs are one of a few PSQs with controlled molecular structures (Scheme 1c) (Brown et al., 1960; Brown et al., 1964; Unno et al., 2005; Zhang et al., 2006; Seki et al., 2010). These structures are classified into two types: “perfect ladder structure” (Scheme 1c-i) and “ladder-like structure” (Scheme 1c-ii) (Abe & Gunji, 2004). The latter has slight defects

in Si–O–Si bond main-chain. Even though oligomeric SQ with “perfect ladder structure” could be synthesized by a step-by-step method and its characterization methods were established (Unno et al., 2002), it is difficult to prepare PSQs with such structures and to characterize them. In most cases, the ladder-structured PSQs probably do not have “perfect ladder structure” but have “ladder-like structure” as shown in Scheme 1c-ii.



Scheme 1. Preparation of silsesquioxanes (SQs) with various structures.

The ladder-like PSQs exhibit rigidity and anisotropy in addition to the aforementioned superior physical properties of SQs because they have one-dimensional network structures of Si–O–Si bonds. Furthermore, ladder-like PSQs are colorless materials due to no absorptions of Si–O–Si bonds in the visible light region and can be used as transparent solutions owing to good solubility in any solvents. These properties of ladder-like PSQs would be useful for versatile applications, in particular, as inorganic fillers due to hybridization with organic functional materials.

Furthermore, control of the higher-ordered structures (nanostructures) of PSQs would also be significant to apply to various supramolecular organic–inorganic hybrid materials. For example, it has been reported that trifunctional silane monomers containing long alkyl

chains were hydrolyzed to form amphiphilic molecules having silanol groups, resulting in the formation of multilayered PSQs by polycondensation (Scheme 1d) (Parikh et al., 1997; Shimojima et al., 1997). Another method for controlling higher-ordered structures of PSQs is sol-gel reaction (hydrolytic polycondensation) of 1,4-bis(trialkoxysilyl)benzene as a monomer in the presence of surfactants (Inagaki et al., 2002). The resulting material has a hexagonal array of mesopores and crystal-like frameworks. Self-organization of long alkyl chains by hydrophobic interactions is a driving force to form such regular higher-ordered structures.

From the aforementioned background, it is evident that the development of PSQs with regularly controlled molecular and higher-ordered structures is one of the important issues for research fields of SQs. In this chapter, therefore, the author first describes the preparation of cationic PSQs with controlled molecular and higher-ordered structures by simple sol-gel method and their detailed characterizations in section 2. The resulting PSQs indicated the anion-exchange properties due to existence of cationic functional groups as side-chains. Then, the author also describes the anion-exchange behaviors with various organic and inorganic compounds such as anionic surfactants (section 3), a polymer (section 4), layered clay minerals (section 5), and a dye molecule (section 6) to obtain the functional hybrid materials.

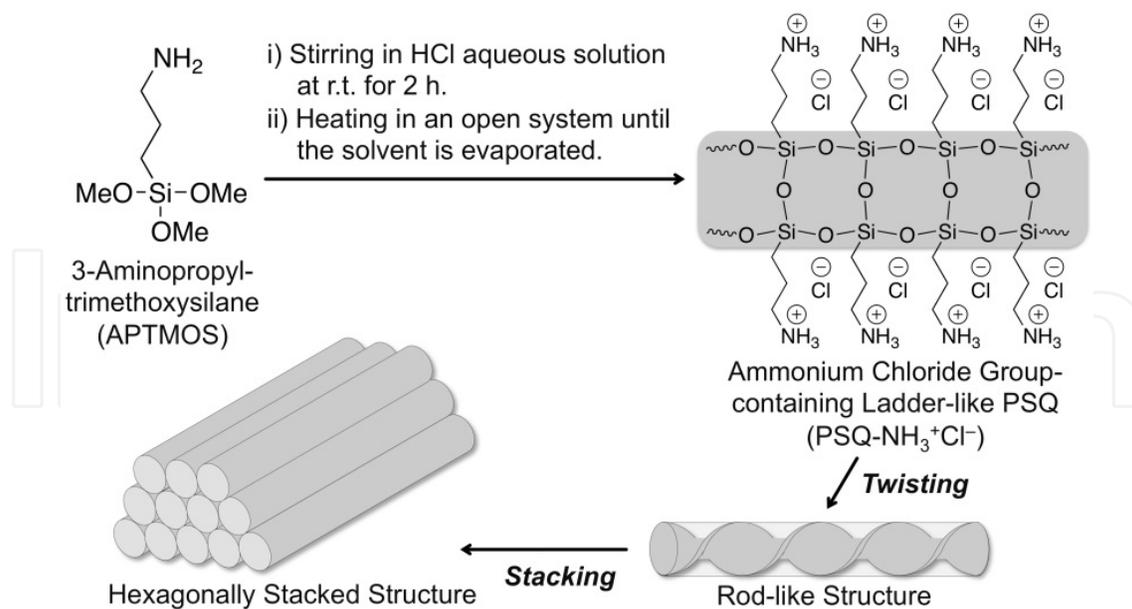
2. Preparation of ammonium group-containing ladder-like PSQs with hexagonally stacked structures

The author and co-workers have developed a preparation method for ammonium group-containing PSQs with controlled molecular and higher-ordered structures by hydrolytic polycondensation (sol-gel reaction) of organotrialkoxysilane monomers containing amino groups in aqueous inorganic acids (Kaneko et al., 2004a; Kaneko et al., 2005a; Kaneko & Iyi, 2007; Kaneko & Iyi, 2010).

2.1. Sol-gel reaction of 3-aminopropyltrimethoxysilane

Preparation of ladder-like PSQs with hexagonally stacked structures was achieved by sol-gel reaction of organotrimethoxysilanes containing amino groups. The first example of monomer to form these materials was 3-aminopropyltrimethoxysilane (APTMOs) (Kaneko et al., 2004a).

The sol-gel reaction of APTMOs was performed by stirring in an acid, *e.g.*, a hydrochloric acid, aqueous solution at room temperature for 2 h, followed by heating (*ca.* 50–60 °C) in an open system until the solvent was completely evaporated (Scheme 2). The resulting product was dissolved in water and this aqueous solution was lyophilized to obtain ammonium chloride group-containing PSQ (PSQ-NH₃⁺Cl⁻). Here, a feed molar ratio of the acid to APTMOs is very important factor for the formation of the regular structures of PSQ. The higher-ordered structure of the product was characterized by the X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and nitrogen adsorption-desorption isotherm measurements, and the molecular structure was characterized by ²⁹Si NMR, XRD, and static light scattering (SLS) measurements.



Scheme 2. Preparation of an ammonium chloride group-containing ladder-like PSQ (PSQ-NH₃⁺Cl⁻) with a hexagonally stacked structure by sol-gel method.

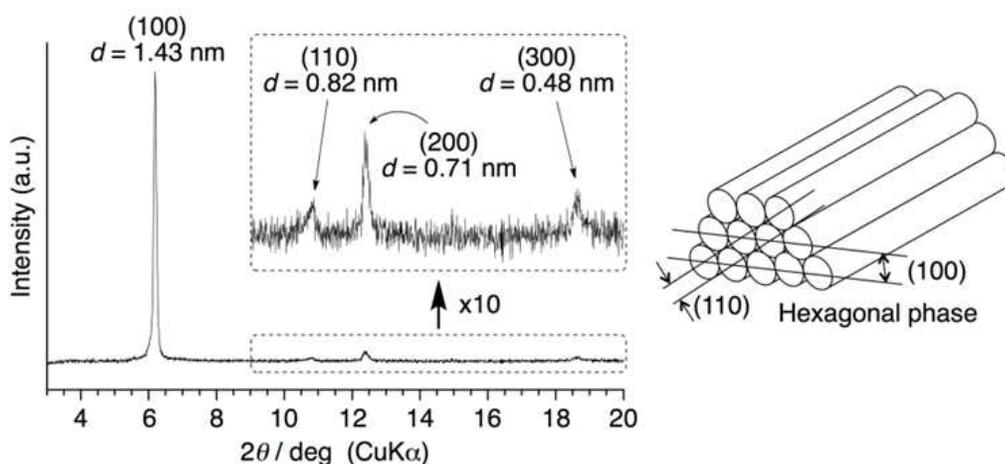


Figure 1. XRD pattern of PSQ-NH₃⁺Cl⁻. Relative humidity (RH) during XRD measurements was 50%.

RH (%)	<i>d</i> -Value		
	(100)	(110)	(200)
20	1.35	–	–
30	1.37	0.79	0.69
40	1.40	0.81	0.70
50	1.43	0.82	0.71
60	1.45	0.84	0.73
70	1.48	0.86	0.74
80	1.52	0.88	0.76
90	1.58	0.92	0.79

Table 1. *d*-Values of diffraction peaks in the XRD patterns of PSQ-NH₃⁺Cl⁻ under various RH conditions.

For the XRD measurements, the films of the products on the glasses were obtained by drying the aqueous product solutions spread on flat glass substrates. The XRD pattern of PSQ-NH₃⁺Cl⁻ film showed diffraction peaks with the d -value ratio of 1 : 1/√3 : 1/2 : 1/3, strongly indicating that PSQ-NH₃⁺Cl⁻ had a hexagonal phase (Fig. 1). These three peaks were assigned to the (100), (110), (200), and (300) peaks, respectively. However, based on only these data, it could not be determined whether this hexagonal phase originated from a porous-type structure or a stacking of a rod-like polymer. Therefore, the influence of relative humidity (RH) was investigated on the d -value in the XRD measurements of PSQ-NH₃⁺Cl⁻. As shown in Table 1, the d -values of the diffraction peaks changed by varying RH, *i.e.*, the d -value increased for a high RH and decreased for a low RH, although the d -value ratios of (110)/(100) and (200)/(100) did not change. Such a behavior cannot be expected for hexagonal-structured porous materials. Therefore, it was assumed that this hexagonal phase originated from the stacking of rod-like polymers.

The TEM image of the product showed a stripe pattern, indicating that the rod-like PSQs were stacked parallel. In addition, the SEM image showed the aggregate, which lined up in a regular direction. This indicates that nano-ordered regular structure of PSQ affected the structures in the micro-ordered aggregate. Furthermore, the real image of PSQ-NH₃⁺Cl⁻ obtained by lyophilization seemed to be reflected by the regular nano- and micro-structures. The Brunauer–Emmett–Teller (BET) surface area of the product evaluated by the nitrogen adsorption–desorption isotherm measurement at 77K was much too small (*ca.* 6 m²/g), indicating that the rod-like PSQ stacked densely. These results supported the regular higher-ordered structure of PSQ-NH₃⁺Cl⁻ characterized by the aforementioned XRD measurements, *i.e.*, rod-like structure forming hexagonal phase.

So far, decisive analysis methods to prove the regular molecular structure such as ladder-like structure of PSQ have not been established. Therefore, necessary evidences for confirmation of the structures were collected by performing multiple analyses. The ladder-like PSQ simultaneously satisfies the following conditions: i) to be soluble in any solvents, ii) relatively high molecular weight, iii) relatively narrow molecular width, and iv) observation of large T³ peak and small T² peak in ²⁹Si NMR spectrum.

The PSQ-NH₃⁺Cl⁻ had a rod-like structure with relatively small diameter (*ca.* 1.6–1.7 nm, estimated from d -value of (100) peak in XRD pattern of Fig. 1) in spite of forming highly dense Si–O–Si bond network structure, which was confirmed by the observation of large T³ peak in the ²⁹Si NMR spectrum of Fig. 2. In addition, the PSQ-NH₃⁺Cl⁻ was soluble in water, despite its M_w was relatively high (*ca.* 12000, estimated by Zimm plot method using the SLS), which indicated no formation of three-dimensional network structure. These results satisfy the aforementioned conditions. All these things considered, it is reasonable to assume that the present PSQ has one-dimensional ladder-like molecular structure as shown in Scheme 1c-ii.

It was supposed that ladder-like PSQ-NH₃⁺Cl⁻ was twisted to form rigid rod-like structure in the solid state, resulting in the formation of the hexagonally stacked structure. The driving force for the formation of the twisted conformation is probably intramolecular

charge repulsion between the ammonium cations in side-chain groups of PSQ-NH₃⁺Cl⁻. Therefore, to investigate correlation between intramolecular charge repulsion and regular structure of PSQ-NH₃⁺Cl⁻, the XRD measurements were performed with changing RH. Stability of the ammonium cations is affected with RH because of hydration with water molecules. The XRD patterns of PSQ-NH₃⁺Cl⁻ with RH higher than 30% indicated three diffraction peaks derived from hexagonal phase, meanwhile those with RH lower than 20% did not show such the diffraction peaks. Because these results indicate the presence of correlation between the formation of the hexagonally stacked structure and higher RH, it is assumed that the twisted structure caused by intramolecular charge repulsion between the ammonium cations is plausible conformation of PSQ-NH₃⁺Cl⁻.

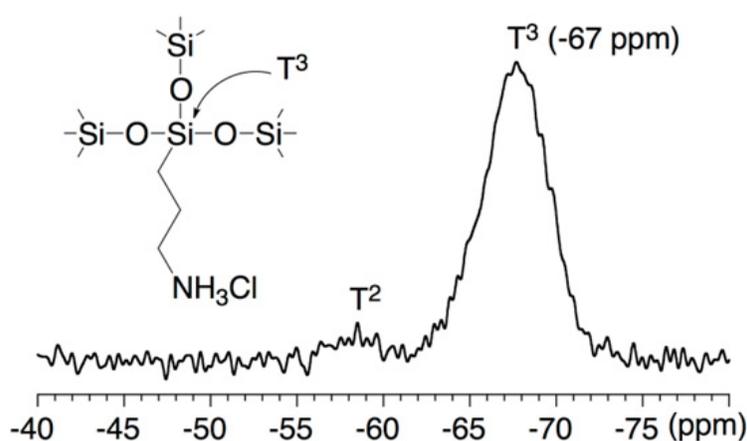


Figure 2. Solid-state ²⁹Si NMR spectrum of PSQ-NH₃⁺Cl⁻.

On the basis of the aforementioned results, it was considered that self-organization of the ion pair composed of ammonium cations in the side-chains of the PSQ and chloride anions was the driving force for the formation of regular molecular, conformational, and higher-ordered structures.

2.2. Sol-gel reaction of (3-(2-aminoethylamino)propyl)trimethoxysilane

As another monomer, organotrialkoxysilane containing two amino groups, *i.e.*, (3-(2-aminoethylamino)propyl)trimethoxysilane (AEAPTMO), was employed for the preparation of rod-like PSQ with hexagonally stacked structure (Kaneko et al., 2005a). The procedure for sol-gel reaction of AEAPTMO was similar to that of APTMO.

The XRD pattern of the resulting product film showed three diffraction peaks with the *d*-value ratio of 1 : 1/√3 : 1/2, indicating that the product had a hexagonal phase. The *d*-values of the diffraction peaks were shifted by varying the RH, although the *d*-value ratios of (110)/(100) and (200)/(100) did not change (Table 2). The same behavior was observed with the aforementioned PSQ-NH₃⁺Cl⁻ (Table 1). Therefore, the PSQ containing double-

ammonium groups in one repeating unit also had a hexagonal phase, which originated from the stacking of rod-like polymers. The d -value of (100) peak of this PSQ (1.85 nm for RH of *ca.* 50%) was larger than that of PSQ-NH₃⁺Cl⁻ (1.43 nm for RH of *ca.* 50%). This is because of difference in side-chain lengths between these PSQs.

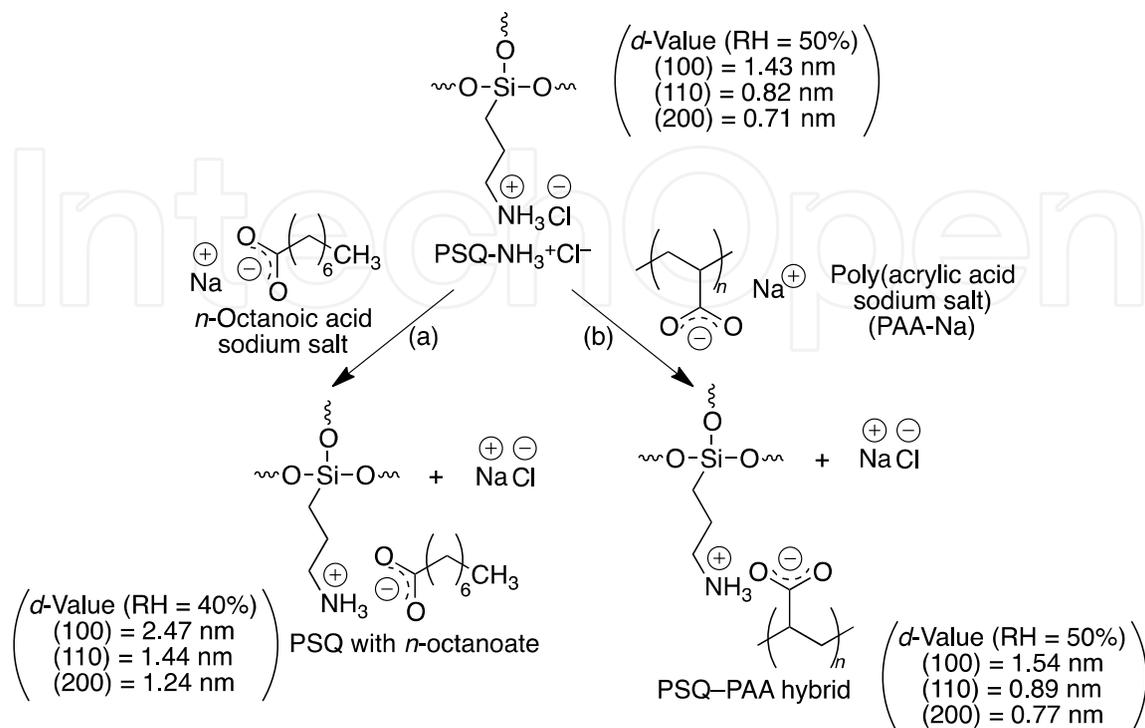
RH (%)	d -Value		
	(100)	(110)	(200)
20	1.68	0.97	0.84
30	1.74	1.01	0.87
40	1.80	1.04	0.89
50	1.85	1.07	0.93
60	1.93	1.12	0.97
70	2.00	1.16	0.99
80	2.06	1.20	1.03
90	2.15	–	–

Table 2. d -Values of diffraction peaks in the XRD patterns of the PSQ obtained from AEAPTMOS under various RH conditions.

3. Ion-exchange behaviors of ladder-like PSQ with fatty acids

Because PSQ-NH₃⁺Cl⁻ has ammonium groups as side-chains and chloride anions (Cl⁻) as counterions, the anion-exchange property can be expected. Therefore, the ion-exchange reaction of the PSQs was performed with anionic organic compounds and the higher-ordered structures of the resulting products were characterized. First, a fatty acid salt such as *n*-octanoic acid sodium salt was employed as an anionic compound (Scheme 3a) (Kaneko et al., 2004a). By pouring PSQ-NH₃⁺Cl⁻ aqueous solution into aqueous solution of *n*-octanoic acid sodium salt, precipitation immediately occurred. The XRD pattern of the resulting water-insoluble product showed peaks for a typical hexagonal phase and the d -value of (100) peak increase more than those of the original PSQs (PSQ-NH₃⁺Cl⁻), indicating that the diameter of the rod-like PSQ increased when the Cl⁻ as the counterion was exchanged with the bulky *n*-octanoate. Thus, the hexagonal phase of the rod-like PSQ was maintained, in spite of the increase in the d -value by ion-exchange reaction with *n*-octanoic acid sodium salt.

On the other hand, when the ion-exchange reactions were performed using the fatty acid salts containing longer alkyl chains (*n*-decanoic acid sodium salt, *n*-dodecanoic acid sodium salt, and *n*-tetradecanoic acid sodium salt), the peaks due to the typical hexagonal phase were not obtained. This is because the hydrophobic interaction between the guest fatty acid salts containing longer alkyl chains was too strong to maintain the hexagonally stacked structure of rod-like PSQ.



Scheme 3. Ion-exchange reaction of PSQ-NH₃⁺Cl⁻ with (a) *n*-octanoic acid sodium salt and (b) poly(acrylic acid sodium salt).

4. Preparation of organic–inorganic polymer hybrids by ion-exchange reaction of ladder-like PSQ with organic polymer

Hybrids composed of organic and inorganic materials usually exhibit improved performance properties compared with conventional composites, mixtures on a micrometer scale (μm), due to their unique phase morphology and improved interfacial properties. For these reasons, nanostructured organic–inorganic hybrids have attracted considerable attention from both fundamental research and applications points of view (Usuki et al., 1993; Chujo, 1996). In particular, the organic–inorganic hybrids obtained from the synthetic polymers as organic species are important industrial materials.

In this section, the author describes the preparation of an organic–inorganic polymer hybrid (PSQ–PAA hybrid) with regular higher-ordered structure composed of the aforementioned PSQ-NH₃⁺Cl⁻ as the inorganic species and poly(acrylic acid sodium salt) (PAA-Na) as the organic species by the ion-exchange reaction (Kaneko et al., 2005b). To obtain PSQ–PAA hybrid, the ion-exchange reaction was performed by pouring PSQ-NH₃⁺Cl⁻ aqueous solution into PAA-Na aqueous solution (Scheme 3b).

The IR spectrum of PSQ–PAA hybrid displayed absorptions at 1044 and 1144 cm^{-1} assigned to the Si–O bond of the PSQ, and absorptions at 1407 and 1558 cm^{-1} due to the COO^- of the PAA, indicating that the product consisted of both organic and inorganic polymers. The CHN elemental analysis data showed that the C/N molar ratio for the product was 5.92. From this value, the ratio of the functional groups of the two polymers, *i.e.*, NH_3^+ and COO^- , was calculated to be *ca.* 1 : 1.

The XRD pattern of the resulting insoluble product showed formation of a hexagonal phase and the *d*-values of the diffraction peaks were different from those of PSQ– NH_3^+Cl^- (Scheme 3b), indicating formation of not a macroscopic mixture but the molecular-scale mixture of two polymers, *i.e.*, organic–inorganic hybrid.

5. Preparation of nanoporous materials composed of ladder-like PSQs and layered clay minerals by ion-exchange reaction

There have been intense research activities on layered silicates pillared with inorganic or organic clusters, which are called pillared interlayer clays (PILCs) (Otsuka, 1997; Kloprogge, 1998; Ding et al., 2001). PILCs have much higher surface areas and pore volumes than the original clays. Such properties make them useful catalysts, ion-exchangers, and adsorbents. These materials are normally prepared by the intercalative ion-exchange of layered clay minerals with a variety of nano-sized pillars, such as organic ions (Ogawa et al., 1994), inorganic ions (Pichowicz & Mokaya, 2004), and sol particles (Yamanaka et al., 1992).

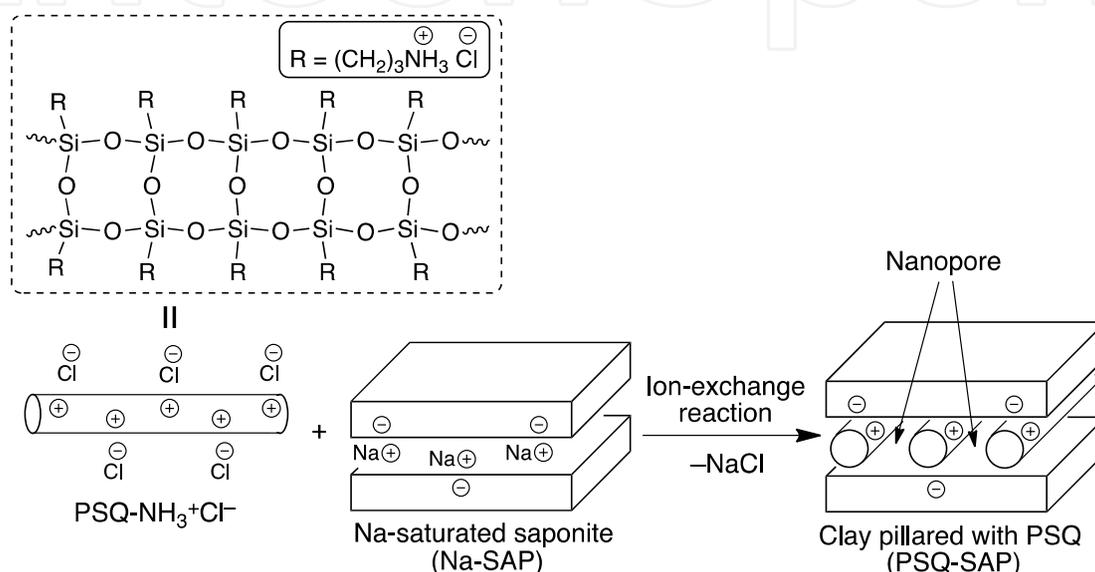
Even though the preparation of various polymers/clay hybrids (Pinnavaia & Beall, 2000) has already been reported, there have been a few studies on the preparation of PILCs using polymers. Because the polymers usually have a flexible structure, expansion of the interlayer space of clays by polymer incorporation is not enough for providing more free space.

The aforementioned PSQ– NH_3^+Cl^- has motivated the author and co-workers to develop new PILCs, because it has rigidity and bulkiness to expand the interlayer of clays and ability to intercalate molecules into the interlayer of anionic clays by ion-exchange reaction due to the presence of ammonium cations in side-chains of PSQ– NH_3^+Cl^- . In this section, therefore, the author describes the preparation of a clay pillared with rod-like cationic PSQ– NH_3^+Cl^- (Scheme 4) (Kaneko et al., 2004b).

The synthesis was performed by pouring the PSQ– NH_3^+Cl^- aqueous solution into an aqueous suspension of Na-saturated saponite (Na-SAP). After the mixture was vigorously stirred for 2 h at room temperature, the product was collected by filtration, washed with water, and then dried under reduced pressure at room temperature to obtain the clay pillared with PSQ– NH_3^+Cl^- (PSQ–SAP). The resulting product was characterized by IR, CHN elemental analysis, XRD, and nitrogen adsorption–desorption isotherm measurements.

The IR spectrum of PSQ–SAP showed an absorption band at *ca.* 1515 cm^{-1} assigned to the ammonium ion of the PSQ component, indicating that the PSQ was inserted into the

interlayer of SAP. On the basis of the CHN analysis data, the exchange amount of a repeating unit of the PSQ component in PSQ–SAP was calculated to be 126 meq/100 g SAP. This value is higher than that of the cation exchange capacity (CEC) of Na-SAP (92 meq/100 g SAP) (Bujdák et al., 2002). The distance between the charges of PSQ would be shorter than that of SAP. Therefore, excess ammonium groups and counter anions (Cl^-) of $\text{PSQ-NH}_3^+\text{Cl}^-$ were inserted into the interlayer of SAP, which was confirmed by a Cl elemental analysis. The XRD pattern of PSQ–SAP was completely different from that of Na-SAP and $\text{PSQ-NH}_3^+\text{Cl}^-$. Accordingly, PSQ–SAP was not a mixture, but an intercalated nano-order material, *i.e.*, a hybrid.



Scheme 4. Preparation of a clay pillared with PSQ by ion-exchange reaction of $\text{PSQ-NH}_3^+\text{Cl}^-$ with Na-saturated saponite.

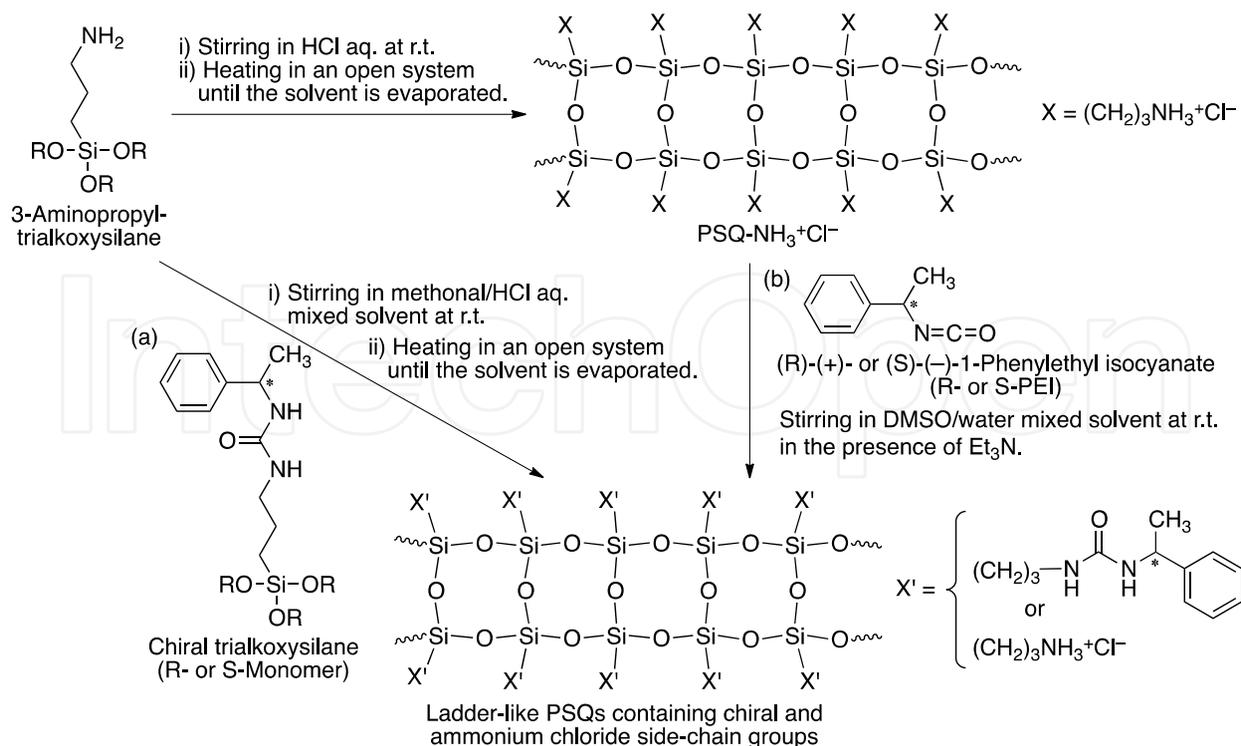
From the nitrogen adsorption–desorption isotherms at 77K, the surface area and pore volume of PSQ–SAP derived from the t -plot were estimated to be $370\text{m}^2/\text{g}$ and $0.15\text{ cm}^3/\text{g}$, respectively. This indicates that a porous material was prepared from the starting materials with dense structures (BET surface areas of Na-SAP and $\text{PSQ-NH}_3^+\text{Cl}^-$ were *ca.* 26 and $5\text{ m}^2/\text{g}$, respectively).

When a clay mineral with high CEC such as Li-saturated taeniolite was employed, such a porous material was not obtained by combination with $\text{PSQ-NH}_3^+\text{Cl}^-$ (BET surface area of the resulting product was *ca.* $53\text{ m}^2/\text{g}$), although a sufficient interlayer spacing existed as confirmed by the XRD measurement (d -value of the product was *ca.* 1.83 nm). Because the distance between the PSQs in the interlayer of taeniolite is short due to the higher CEC of the Li-saturated taeniolite (exchange amount of a repeating unit of PSQ was calculated to be $140\text{ meq}/100\text{ g}$ taeniolite), sufficient space was not provided. Furthermore, when polyallylamine hydrochloride (PAA-Cl) –a common cationic polymer– was used for pillaring in the SAP interlayer, a porous structure was not obtained (BET surface area of the product was *ca.* $52\text{ m}^2/\text{g}$). It was difficult for PAA-Cl to pillar the interlayer of SAP due to the lack of rigidity and bulkiness. From these results, it was considered that the rigidity and

bulkiness of the guest polymers and a sufficient distance between charges in the host layered clay minerals are necessary for preparing clays pillared with polymers.

6. Preparation of chiral ladder-like PSQs and hybridization with dye compounds by ion-exchange reaction

Self-assembled hybrids formed by noncovalent interactions between photofunctional compounds and chiral molecules have attracted much attention because of their potential applications in circularly polarized luminescent (CPL) materials. To achieve the preparation of these hybrids by chiral induction from chiral molecules to photofunctional compounds, several combinations have been investigated with respect to supramolecular organization, *e.g.*, anionic dye/cationic chiral surfactants (Franke et al., 2006), laser dye/cholesteric liquid crystal (Uchimura et al., 2010), pyrene derivatives/cyclodextrins (Kano et al., 1988), porphyrins/helical polyacetylene (Onouchi et al., 2006), and π -conjugated polymers/polysaccharides such as amylose (Ikeda et al., 2006), and schizophyllan (Li et al., 2005). On the other hand, there have been no reports regarding hybridization using inorganic compounds such as siloxane (SiO)-based materials as chiral inductors. The chiral inductors derived from SiO-based materials may enable the development of durable and thermostable hybrids with photofunctional compounds because the SiO-based materials exhibit superior thermal, mechanical, and chemical stabilities. In this section, therefore, the author describes the preparation of chiral ladder-like PSQs as the SiO-based chiral inductors and their chiral induction behaviors into dye compounds.



Scheme 5. Preparation of ladder-like PSQs containing chiral and ammonium chloride side-chain groups by (a) copolycondensation method and (b) polymer reaction method.

6.1. Copolycondensation of 3-aminopropyltrialkoxysilane with chiral group-containing trialkoxysilane

To prepare chiral ladder-like PSQs, the introduction of a chiral moiety into the PSQs was first investigated by acid-catalyzed copolycondensation of two organotrialkoxysilanes containing chiral and amino groups, respectively (Kaneko & Iyi, 2009).

The chiral trialkoxysilanes (R- and S-Monomers) were synthesized by reaction of 3-(triethoxysilyl)propyl isocyanate with (R)-(+)- or (S)-(-)-1-phenylethylamine in dichloromethane at room temperature for 15 min, respectively, followed by evaporation of the dichloromethane. The sol-gel copolycondensation of the resulting chiral trialkoxysilanes with 3-aminopropyltriethoxysilane (APTEOS) (feed molar ratio is 1 : 9) was performed in a mixed solvent of aqueous hydrochloric acid and methanol by heating in an open system until the solvent was completely evaporated (Scheme 5a). The products were isolated as the fractions insoluble in acetone, washed with acetone and chloroform, and then dried under reduced pressure at room temperature to yield the white powdered PSQs.

The ^1H NMR spectra in D_2O at 60 °C of the products showed the signals indicating the presence of both the components of the chiral trialkoxysilanes and APTEOS; this indicates that the products were copolymers composed of both trialkoxysilanes. The unit ratio of the chiral groups to the ammonium chloride groups in the products was calculated to be 6 : 94. Therefore, the resulting PSQs are denoted as R₆- and S₆-PSQs, according to the stereostructure and functionality of the chiral groups. The IR spectra of R₆- and S₆-PSQs showed absorptions at 1620 cm^{-1} attributed to the C=O bond of the urea groups, indicating the existence of the units of chiral groups in the products.

In the IR spectra of R₆- and S₆-PSQs, large absorption bands at 1135 and 1040 cm^{-1} assigned to the Si–O–Si bonds were observed, indicating the formation of PSQs. In addition, the ^{29}Si NMR spectra in $\text{DMSO-}d_6$ at 40 °C of these PSQs exhibit the large peaks in the regions of T³. These results indicate that the complete progress of sol-gel copolycondensations of the chiral trialkoxysilanes and APTEOS, and the formation of Si–O–Si bonds. The M_{ws} of R₆- and S₆-PSQs estimated by the Zimm plot method using SLS apparatus were assessed to be 10700 and 9800, respectively, indicating that the products were not oligomeric compounds but polymers.

The XRD patterns of the films of R₆- and S₆-PSQs showed three diffraction peaks with the d -value ratio of 1 : $1/\sqrt{3}$: 1/2, indicating the formation of the hexagonal phases. Because these PSQs were soluble in water and DMSO, it was supposed that these hexagonal phases originated not from porous-type structures but from the stacking of rod-like polymers. The diameters of the rod-like PSQs calculated from d -values of (100) peaks (1.47–1.48 nm) were assessed to be *ca.* 1.7 nm.

As aforementioned, R₆- and S₆-PSQs had rod-like structures with relatively small diameter (*ca.* 1.7 nm) in spite of the presence of large T³ peak in the ^{29}Si NMR spectrum. In addition, these PSQs were soluble in water and DMSO, despite the M_{ws} of the PSQs were relatively high (*ca.* 9800–10700). These results satisfy the aforementioned conditions for ladder-like structure of PSQ. Therefore, the present chiral PSQs would also have one-dimensional ladder-like structure.

The vibrational circular dichroism (VCD) spectroscopy, which is the extension of the electronic circular dichroism (ECD) into the IR region, is a powerful technique to obtain conformational information of chiral molecules (Tang et al., 2007). The VCD spectra of R₆- and S₆-PSQs showed the reversed absorptions at *ca.* 1140–1165 cm⁻¹, respectively (Fig. 3), corresponding to the absorptions assigned to Si–O–Si bond of polymer main-chains. These results indicate that R₆- and S₆-PSQs had chiral conformations of main-chains.

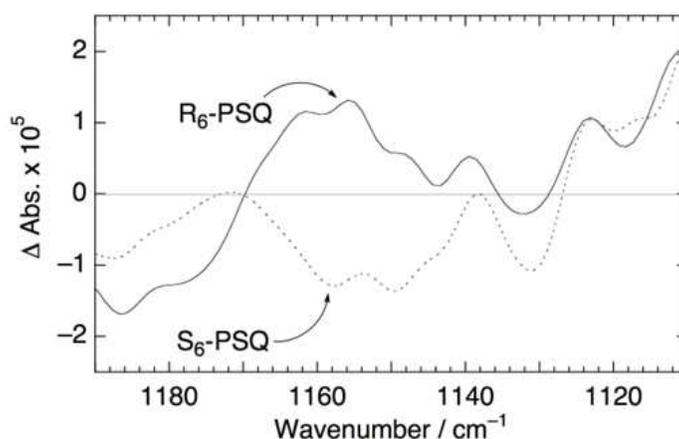


Figure 3. Vibrational circular dichroism (VCD) spectra in DMSO of R₆- and S₆-PSQs.

6.2. Polymer reaction of chiral group-containing compound with PSQ-NH₃⁺Cl⁻

To prepare ladder-like PSQs containing higher compositional ratios of chiral side-chain groups, the aforementioned acid-catalyzed copolycondensation was investigated with a higher feed molar ratio of chiral trialkoxysilanes (>20%). However, the resulting PSQs were insoluble in all solvents owing to the formation of irregular three-dimensional cross-linked network structures. This is because the number of ion pairs formed by the amino groups of APTEOS and the acid-catalysts decreased.

Therefore, to prepare soluble ladder-like PSQs containing higher ratio of chiral groups, *i.e.*, a lower ratio of ammonium chloride groups, the introduction reaction (polymer reaction) of chiral isocyanate compounds into the aforementioned PSQ-NH₃⁺Cl⁻ was investigated (Kaneko et al., 2011).

Synthesis was performed by reaction of (R)-(+)- or (S)-(-)-1-phenylethyl isocyanate (R- or S-PEI) with PSQ-NH₃⁺Cl⁻ in the presence of triethylamine in DMSO/water (9 : 1 (v : v)) mixed solvent at room temperature for 10 min (Scheme 5b). The products were isolated by precipitation in acetone. The compositional ratios of chiral groups to ammonium chloride groups in the resulting products were estimated from their ¹H NMR spectra and were found to depend on the feed molar ratio of PEI to ammonium chloride group of PSQ-NH₃⁺Cl⁻. Here, soluble PSQs with the compositional ratio of chiral groups to ammonium chloride groups = *ca.* 80 : 20 were prepared. These PSQs are denoted as R₈₀- and S₈₀-PSQs, respectively. The *M_ws* of R₈₀- and S₈₀-PSQs were estimated by the Zimm plot method using SLS apparatus and were assessed to be *ca.* 54000 and 46000, respectively.

The diffraction peaks in the XRD patterns of the PSQs were broadened compared with those of PSQ-NH₃⁺Cl⁻. This is due to the decrease in the number of ion pairs, *i.e.*, ammonium chloride groups. The ion pair has an important role in the construction of a regular higher-ordered structure. However, because the XRD pattern of the product film showed diffraction peaks with *d*-value of 1.80 nm, indicating a relatively regular stacking structure, the rigid structures of PSQs would be maintained.

The chiral conformations of many kinds of helical polymers are stabilized by intramolecular interaction, *e.g.*, hydrogen bonding (Zhao et al., 2004). Therefore, specific rotations of these polymers are generally changed by varying the solvents because their intramolecular interactions are affected by the nature of the solvent. The specific rotations $[\alpha]_{D^{22}}$ of R₈₀- and S₈₀-PSQs in methanol were +17.4° and -18.9°, respectively, while those in DMF were +8.6° and -8.5°, respectively. Because these PSQs have urea groups as side chains, which are involved in intramolecular hydrogen bonding, their $[\alpha]_{D^{22}}$ values were probably affected by solvent effects. Such a solvent effect on specific rotations indicates the presence of chiral conformations of these PSQs.

6.3. Chiral induction behavior of chiral PSQ to dye compound

These chiral ladder-like PSQs were applied to chiral inductors for hybridization with a dye compound such as an anionic achiral porphyrin by the ion-exchange reaction (Kaneko & Iyi, 2009; Kaneko et al., 2011). In this section, the author describes the chiral induction behavior from the aforementioned chiral ladder-like PSQs into an anionic achiral porphyrin such as tetraphenylporphine tetrasulfonic acid (TPPS).

In the UV-Vis spectra of TPPS/R₆- and S₆-PSQs aqueous mixtures (4 μmol/L and 100 μmol unit/L, respectively), absorptions due to the Soret band of TPPS in these mixtures were blue-shifted (to 400 nm) compared with that of TPPS alone indicated monomeric state with protonated (at 434 nm) and deprotonated (at 414 nm) species (Fig. 4a). These results indicate that the negatively charged TPPS formed H-aggregates along the positively charged ammonium groups as side-chains of the PSQs.

The ECD spectra of these TPPS/PSQs aqueous mixtures showed the reversed absorptions due to the Soret bands of TPPS-aggregates, corresponding to R₆- and S₆-PSQs as templates, respectively (Fig. 4b), indicating that TPPS-aggregates have chiralities induced from the chiral PSQs.

However, these mixtures did not show fluorescence emissions due to self-quenching of the excited state of the TPPS-aggregate. Therefore, to inhibit the formation of H-aggregates of TPPS by extension of the distance between the ammonium chloride side chains of PSQs, same analyses were performed using R₈₀- and S₈₀-PSQs as chiral inductors.

ECD spectra of TPPS/R₈₀- and S₈₀-PSQs mixtures in methanol (4 μmol/L and 100 μmol unit/L, respectively) exhibited the reverse absorptions at 418 nm (Fig. 4d), corresponding to the absorptions assigned to the Soret bands of TPPS in the UV-Vis spectrum (Fig. 4c). The

absorption wavelength of this mixture was almost same as that of dilute methanol solution of sole TPPS (concentration = 4 $\mu\text{mol/L}$), indicating that TPPS maintained the monomeric state in the mixture. These results indicate that the chiral induction from PSQs to TPPS was achieved without formation of H-aggregate of TPPS. In the present mixture, because of no formation of H-aggregate, the fluorescence spectrum excited at 420 nm showed an emission peak at 654 nm.

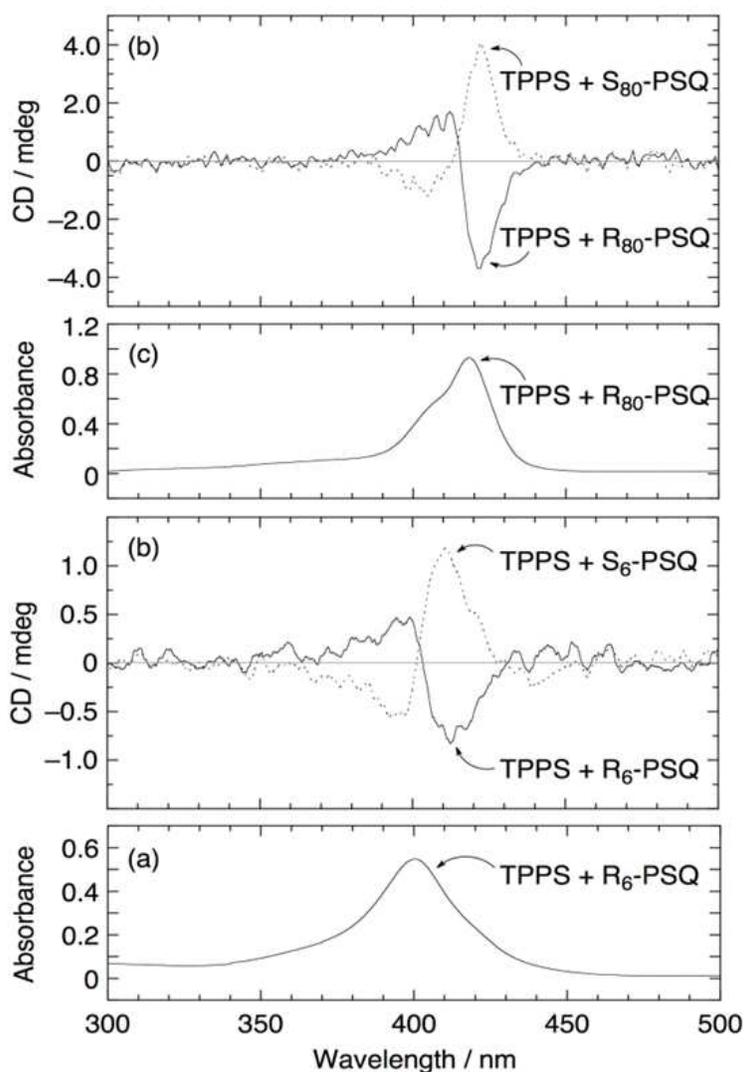


Figure 4. (a) UV-Vis spectrum of aqueous mixture of TPPS/R₆-PSQ, (b) ECD spectra of aqueous mixtures of TPPS/R₆- and S₆-PSQs, (c) UV-Vis spectrum of mixture in methanol of TPPS/R₈₀-PSQ, and (d) ECD spectra of mixtures in methanol of TPPS/R₈₀- and S₈₀-PSQs.

7. Conclusion

In this chapter, the author described the preparation of cationic ladder-like PSQs with hexagonally stacked structures by the sol-gel reaction of amino group-containing trialkoxysilane monomers using acid-catalysts. Then, their detailed characterizations were performed. The resulting PSQs indicated the anion-exchange properties due to existence of cationic functional groups as side-chains. Therefore, it is also described that the anion-exchange

behaviors with various organic and inorganic compounds such as anionic surfactants, a polymer, layered clay minerals, and a dye molecule to obtain the functional hybrid materials.

Author details

Yoshiro Kaneko

Graduate School of Science and Engineering, Kagoshima University, Japan

Acknowledgement

The author gratefully acknowledges Dr. Nobuo Iyi of National Institute for Materials Science (NIMS) for causing my research interests in the sol-gel chemistry, silsesquioxanes, and organic-inorganic hybrid materials. The author is indebted to the co-workers, whose names are found in references from this chapter, for their enthusiastic collaborations.

8. References

- Abe, Y. & Gunji, T. (2004). Oligo- and polysiloxanes, *Prog. Polym. Sci.* 29: 149-182.
- Baney, R. H., Itoh, M., Sakakibara, A., & Suzuki, T. (1995). Silsesquioxanes, *Chem. Rev.* 95: 1409-1430.
- Brown, J. F. Jr., Vogt, L. H. Jr., Katchman, A., Eustance, J. W., Kiser, K. M., & Krantz, K. W. (1960). Double chain polymers of phenylsilsesquioxane, *J. Am. Chem. Soc.* 82: 6194-6195.
- Brown, J. F. Jr., Vogt, L. H. Jr., & Prescott, P. I. (1964). Preparation and characterization of the lower equilibrated phenylsilsesquioxanes, *J. Am. Chem. Soc.* 86: 1120-1125.
- Bujdák, J., Iyi, N., Hrobáriková, J., & Fujita, T. (2002). Aggregation and decomposition of a pseudoisocyanine dye in dispersions of layered silicates, *J. Colloid Interface Sci.* 247: 494-503.
- Choi, J., Harcup, J., Yee, A. F., Zhu, Q., & Laine, R. M. (2001). Organic/inorganic hybrid composites from cubic silsesquioxanes, *J. Am. Chem. Soc.* 123: 11420-11430.
- Chujo, Y. (1996). Organic-inorganic hybrid materials, *Curr. Opin. Solid State Mater. Sci.* 1: 806-811.
- Cordes, D. B., Lickiss, P. D., & Rataboul, F. (2010). Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes, *Chem. Rev.* 110: 2081-2173.
- Ding, Z., Kloprogge, J. T., Frost, R. L., Lu, G. Q., & Zhu, H. Y. (2001). Porous clays and pillared clays-based catalysts. Part 2: A review of the catalytic and molecular sieve applications, *J. Porous Mater.* 8: 273-293.
- Feher, F. J. & Wyndham, K. D. (1998). Amine and ester-substituted silsesquioxanes: synthesis, characterization and use as a core for starburst dendrimers, *Chem. Commun.* 323-324.
- Franke, D., Vos, M., Antonietti, M., Sommerdijk, N. A. J. M., & Faul, C. F. J. (2006). Induced supramolecular chirality in nanostructured materials: Ionic self-assembly of perylene-chiral surfactant complexes, *Chem. Mater.* 18: 1839-1847.
- Ikeda, M., Furusho, Y., Okoshi, K., Tanahara, S., Maeda, K., Nishino, S., Mori T., & Yashima, E. (2006). A luminescent poly(phenylenevinylene)-amylose composite with supramolecular liquid crystallinity, *Angew. Chem. Int. Ed.* 45: 6491-6495.
- Inagaki, S., Guan, S., Ohsuna, T., & Terasaki, O. (2002). An ordered mesoporous organosilica hybrid material with a crystal-like wall structure, *Nature* 416: 304-307.

- Kaneko, Y., Iyi, N., Kurashima, K., Matsumoto, T., Fujita, T., & Kitamura, K. (2004a). Hexagonal-structured polysiloxane material prepared by sol-gel reaction of aminoalkyltrialkoxysilane without using surfactants, *Chem. Mater.* 16: 3417-3423.
- Kaneko, Y., Iyi, N., Matsumoto, T., & Kitamura, K. (2004b). Preparation of a clay pillared with rodlike cationic polysiloxane, *Chem. Lett.* 33: 1486-1487.
- Kaneko, Y., Iyi, N., Matsumoto, T., & Kitamura, K. (2005a). Synthesis of rodlike polysiloxane with hexagonal phase by sol-gel reaction of organotrialkoxysilane monomer containing two amino groups, *Polymer* 46: 1828-1833.
- Kaneko, Y., Iyi, N., Matsumoto, T., & Kitamura, K. (2005b). Preparation of higher-ordered inorganic-organic nanocomposite composed of rodlike cationic polysiloxane and polyacrylate, *J. Mater. Chem.* 15: 1572-1575.
- Kaneko, Y. & Iyi, N. (2007). Sol-gel synthesis of rodlike polysilsesquioxanes forming regular higher-ordered nanostructure, *Z. Kristallogr.* 222: 656-662.
- Kaneko, Y. & Iyi, N. (2009). Sol-gel synthesis of ladder polysilsesquioxanes forming chiral conformations and hexagonal stacking structures, *J. Mater. Chem.* 19: 7106-7111.
- Kaneko, Y. & Iyi, N. (2010). Sol-gel synthesis of water-soluble polysilsesquioxanes with regular structures, *Kobunshi Ronbunshu* 67: 280-287.
- Kaneko, Y., Toyodome, H., & Sato, H. (2011). Preparation of chiral ladder-like polysilsesquioxanes and their chiral induction to anionic dye compound, *J. Mater. Chem.* 21: 16638-16641.
- Kano, K., Matsumoto, H., Yoshimura, Y., & Hashimoto, S. (1988). Binding sites of pyrene and related-compounds and chiral excimer formation in the cavities of cyclodextrins and branched cyclodextrins, *J. Am. Chem. Soc.* 110: 204-209.
- Kim, K. M. & Chujo, Y. (2003). Organic-inorganic hybrid gels having functionalized silsesquioxanes, *J. Mater. Chem.* 13: 1384-1391.
- Klopprogge, J. T. (1998). Synthesis of smectites and porous pillared clay catalysts: A review, *J. Porous Mater.* 5: 5-41.
- Laine, R. M., Zhang, C., Sellinger, A., & Viculis, L. (1998). Polyfunctional cubic silsesquioxanes as building blocks for organic/inorganic hybrids, *Appl. Organometal. Chem.* 12: 715-723.
- Li, C., Numata, M., Bae, A. H., Sakurai, K., & Shinkai, S. (2005). Self-assembly of supramolecular chiral insulated molecular wire, *J. Am. Chem. Soc.* 127: 4548-4549.
- Loy, D. A., Baugher, B. M., Baugher, C. R., Schneider, D. A., & Rahimian, K. (2000). Substituent effects on the sol-gel chemistry of organotrialkoxysilanes, *Chem. Mater.* 12: 3624-3632.
- Ogawa, M., Takahashi, M., Kato, C., & Kuroda, K. (1994). Oriented microporous film of tetramethylammonium pillared saponite, *J. Mater. Chem.* 4: 519-523.
- Ohtsuka, K. (1997). Preparation and properties of two-dimensional microporous pillared interlayered solids, *Chem. Mater.* 9: 2039-2050.
- Onouchi, H., Miyagawa, T., Morino, K., & Yashima, E. (2006). Assisted formation of chiral porphyrin homoaggregates by an induced helical poly(phenylacetylene) template and their chiral memory, *Angew. Chem. Int. Ed.* 45: 2381-2384.
- Parikh, A. N., Schivley, M. A., Koo, E., Seshadri, K., Aurentz, D., Mueller, K., & Allara, D. L. (1997). n-Alkylsiloxanes: From single monolayers to layered crystals. The formation of crystalline polymers from the hydrolysis of n-octadecyltrichlorosilane, *J. Am. Chem. Soc.* 119: 3135-3143.

- Pichowicz, M. & Mokaya, R. (2004). Stability of pillared clays: Effect of compaction on the physicochemical properties of Al-pillared clays, *Chem. Mater.* 16: 263-269.
- Pinnavaia, T. J. & Beall, G. W. (2000). *Polymer-Clay Nanocomposites*, John Wiley & Sons, Chichester, UK
- Seki, H., Kajiwara, T., Abe, Y., & Gunji, T. (2010). Synthesis and structure of ladder polymethylsilsesquioxanes from sila-functionalized cyclotetrasiloxanes, *J. Organomet. Chem.* 695: 1363-1369.
- Shimajima, A., Sugahara, Y., & Kuroda, K. (1997). Inorganic-organic layered materials derived via the hydrolysis and polycondensation of trialkoxy(alkyl)silanes, *Bull. Chem. Soc. Jpn.* 70: 2847-2853.
- Tanaka, K., Ishiguro, F., & Chujo, Y. (2010). POSS ionic liquid, *J. Am. Chem. Soc.* 132: 17649-17651.
- Tanaka, K. & Chujo, Y. (2012). Advanced functional materials based on polyhedral oligomeric silsesquioxane (POSS), *J. Mater. Chem.* 22: 1733-1746.
- Tang, H. Z., Garland, E. R., Novak, B. M., He, J. T., Polavarapu, P. L., Sun, F. C., & Sheiko, S. S. (2007). Helical polyguanidines prepared by helix-sense-selective polymerizations of achiral carbodiimides using enantiopure binaphthol-based titanium catalysts, *Macromolecules* 40: 3575-3580.
- Uchimura, M., Watanabe, Y., Araoka, F., Watanabe, J., Takezoe, H., & Konishi, G. (2010). Development of laser dyes to realize low threshold in dye-doped cholesteric liquid crystal lasers, *Adv. Mater.* 22: 4473-4478.
- Unno, M., Suto, A., & Matsumoto, H. (2002). Pentacyclic laddersiloxane, *J. Am. Chem. Soc.* 124: 1574-1575.
- Unno, M., Chang, S., & Matsumoto, H. (2005). *cis-trans-cis*-Tetrabromotetramethylcyclotetrasiloxane: A versatile precursor of ladder silsesquioxanes, *Bull. Chem. Soc. Jpn.* 78: 1105-1109.
- Usuki, A., Kojima, Y., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T., & Kamigaito, O. (1993). Synthesis of nylon 6-clay hybrid, *J. Mater. Res.* 8: 1179-1184
- Wang, F., Lu, X., & He, C. (2011). Some recent developments of polyhedral oligomeric silsesquioxane (POSS)-based polymeric materials, *J. Mater. Chem.* 21: 2775-2782.
- Yamanaka, S., Inoue, Y., Hattori, M., Okumura, F., & Yoshikawa, M. (1992). Preparation and properties of clays pillared with SiO₂-TiO₂ sol particles, *Bull. Chem. Soc. Jpn.* 65: 2494-2500.
- Yu, X. F., Zhong, S., Li, X. P., Tu, Y. F., Yang, S. G., Van Horn, R. M., Ni, C. Y., Pochan, D. J., Quirk, R. P., Wesdemiotis, C., Zhang, W. B., & Cheng, S. Z. D. (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.
- Zhang, X., Xie, P., Shen, Z., Jiang, J., Zhu, C., Li, H., Zhang, T., Han, C. C., Wan, L., Yan, S., & Zhang, R. (2006). Confined synthesis of a *cis*-isotactic ladder polysilsesquioxane by using a π -stacking and H-bonding superstructure, *Angew. Chem. Int. Ed.* 45: 3112-3116.
- Zhang, Z., Liang, G., & Lu, T. (2007). Synthesis and characterization of cage octa(aminopropylsilsesquioxane), *J. Appl. Polym. Sci.* 103: 2608-2614.
- Zhao, H., Sanda, F., & Masuda, T. (2004). Transformation of helical sense of poly(N-propargylamides) controlled by competition between structurally different enantiomeric amino acids, *Macromolecules* 37: 8888-8892.