

Review Article

Preparation of Ionic Silsesquioxanes with Regular Structures and Their Hybridization

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This paper deals with our recent studies on the preparation of ionic silsesquioxanes (SQs) with regular structures. Cationic ladder-like polySQs (PSQs) with hexagonally stacked structures were successfully prepared by the sol-gel reactions of amino group-containing organotrialkoxysilanes in strong acid aqueous solutions. Self-organization of an ion pair (a salt) prepared from the amino group in the organotrialkoxysilane and an acid is the key factor for the formation of such regular structures of the PSQs. It is also reported that the control of the conformational structure of the PSQs was performed by the introduction of the chiral moieties. In addition, we investigated the correlation between the pK_a s of acid-catalysts and the structures of SQs prepared by the hydrolytic condensation of amino group-containing organotrialkoxysilane, that is, the use of the superacid aqueous solution resulted in the formation of cage-like octaSQ, while the ladder-like PSQs with hexagonally stacked structures were formed from the strong acid aqueous solutions under the same reaction conditions. Furthermore, anion-exchange behaviors of the cationic ladder-like PSQ were investigated with various organic and inorganic compounds, such as anionic surfactants, a polymer, and layered clay minerals, to obtain the functional hybrid materials.

1. Introduction

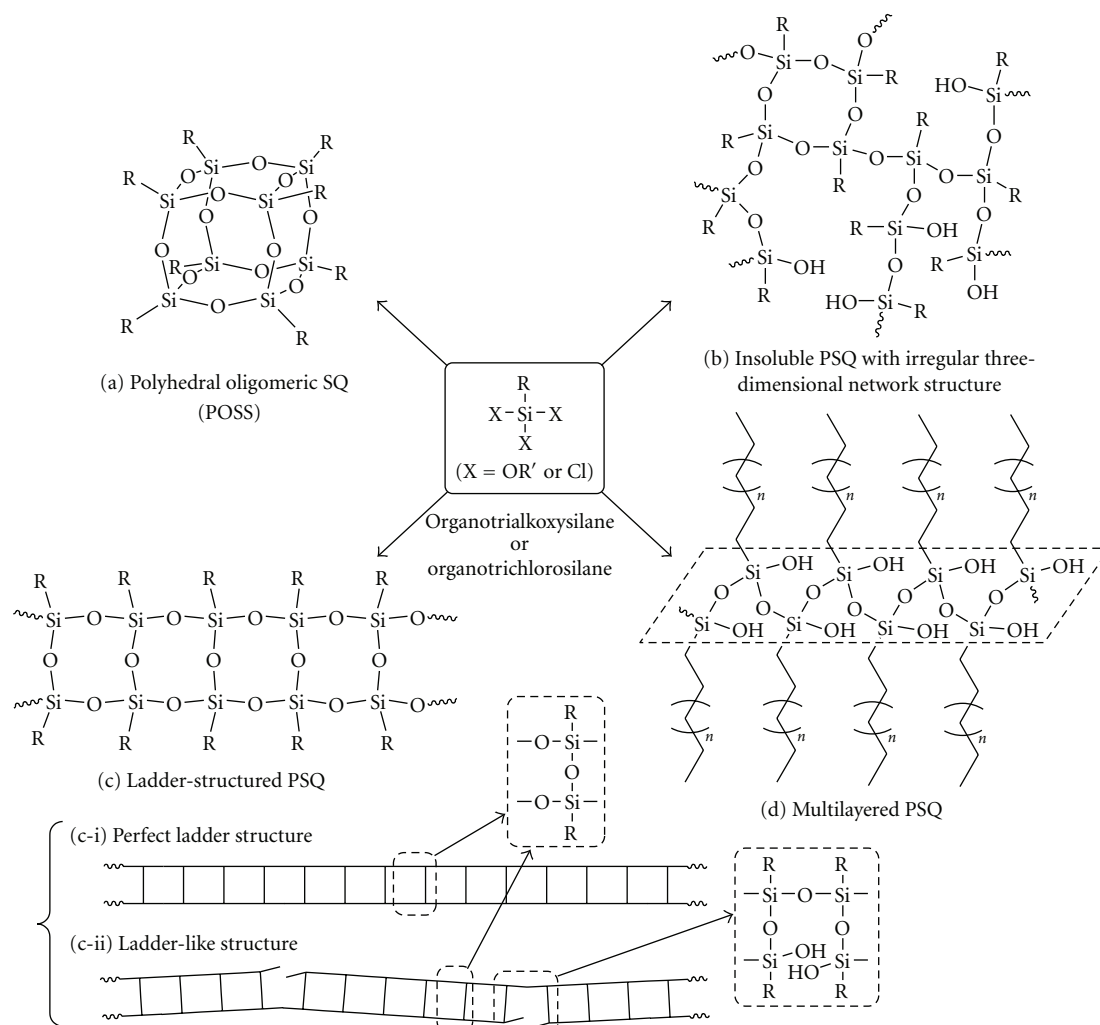
Silsesquioxanes (SQs), the materials containing the structure of $\text{RSiO}_{1.5}$, have attracted much attention in the research fields of organic-inorganic hybrid materials for academic and application reasons [1, 2] because they can contain the various functional groups as side-chains (R) and are inorganic materials indicating the remarkable compatibility with organic materials such as polymers [3–6], in addition to exhibiting superior thermal, mechanical, and chemical stabilities derived from siloxane (Si–O–Si) bond frameworks 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 1(a)) [7–12], 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 1(b)) [2]. If the 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 1(c)) [13–17]. These structures are classified into two types: “perfect ladder structure” (Scheme 1(c-i)) and “ladder-like structure” (Scheme 1(c-ii)) [18]. 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 [19], 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 1(c-ii).

The ladder-like PSQs exhibit rigidity and anisotropy in addition to the aforementioned superior physical properties



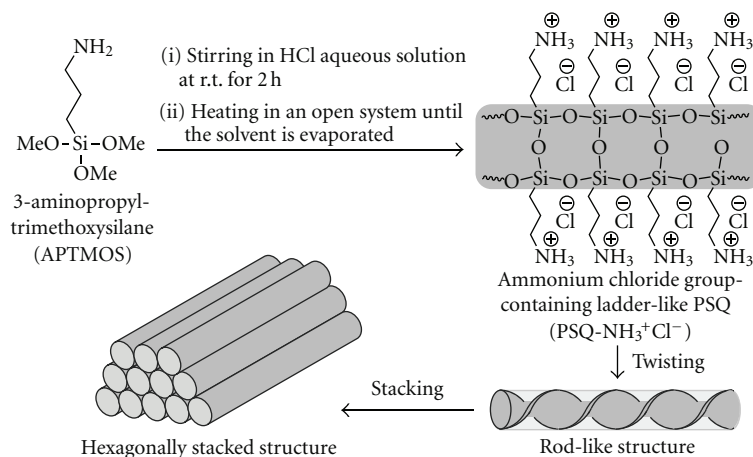
SCHEME 1: Preparation of silsesquioxanes (SQs) with various structures.

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 compounds due to hybridization with organic functional materials.

Furthermore, the 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 1(d)) [20, 21]. 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 [22]. 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. Therefore, the present paper reviews our recent researches on the preparation of ionic PSQs with regular structures. In the second part, we describe the preparation of cationic ladder-like PSQs with hexagonally stacked structures by sol-gel reaction of amino group-containing organotrialkoxysilane monomers and their detailed characterizations. In the third part, the introduction of the chiral moieties into the ladder-like PSQ is described to investigate the conformational structures of the resulting PSQs. In the fourth part, we report the correlation between the pK_a of acid-catalysts and the structures of cationic SQs prepared by hydrolytic condensation of an amino group-containing organotrialkoxysilane monomer. The fifth part deals with anion-exchange reactions of the



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

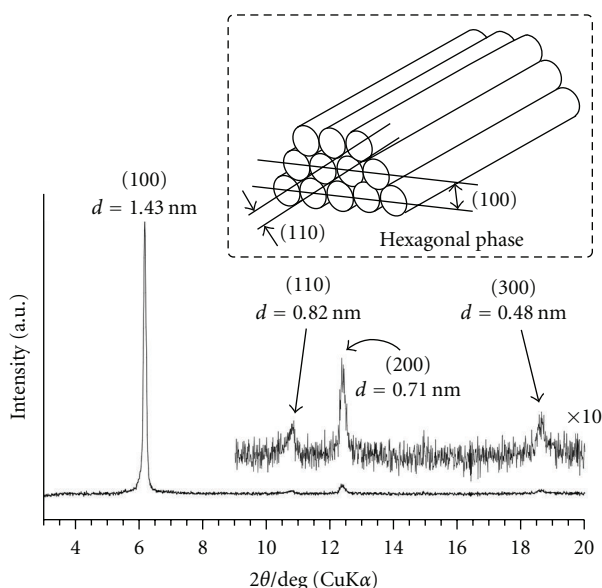


FIGURE 1: XRD pattern of PSQ-NH₃⁺Cl⁻. Relative humidity (RH) during XRD measurements was 50%.

cationic ladder-like PSQ with various organic and inorganic compounds, such as anionic surfactants, a polymer, and layered clay minerals, to obtain the functional hybrid materials.

2. Preparation of Ammonium Group-Containing Ladder-Like PSQs with Hexagonally Stacked Structures

We have developed the preparation method for ammonium group-containing PSQs with controlled molecular and higher-ordered structures by sol-gel reaction of organotrialkoxysilane monomers containing amino groups in aqueous inorganic acids [23–26].

2.1. Sol-Gel Reaction of 3-Aminopropyltrimethoxysilane. The first example of monomer to prepare the aforementioned PSQs was 3-aminopropyltrimethoxysilane (APTAMOS) [23]. The sol-gel reaction of APTAMOS was performed by stirring in an acid, for example, a hydrochloric acid (HCl), 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 a water-soluble ammonium chloride group-containing PSQ (PSQ-NH₃⁺Cl⁻). Here, a feed molar ratio of HCl to APTAMOS is a very important factor for the formation of the regular structures of the PSQ, that is, HCl/APTAMOS ratio needs more than one. The higher-ordered structure of the product was mainly characterized by the X-ray diffraction (XRD) measurements, while the molecular structure was discussed using the results of ²⁹Si NMR, XRD, and static light-scattering (SLS) measurements.

The XRD pattern of the cast film prepared by drying PSQ-NH₃⁺Cl⁻ aqueous solution 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 (Figure 1). These 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 rod-like polymers. Therefore, the influence of relative humidity (RH) was investigated on the *d*-value in the XRD measurements of PSQ-NH₃⁺Cl⁻. As shown in Figure 2, the diffraction peaks shifted by varying RH that is, 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, we assumed that this hexagonal phase originated from the stacking of rod-like polymers.

We next discuss the molecular structure of PSQ-NH₃⁺Cl⁻. The analysis method to prove ladder structure of oligoSQs has already been established [19]. Because

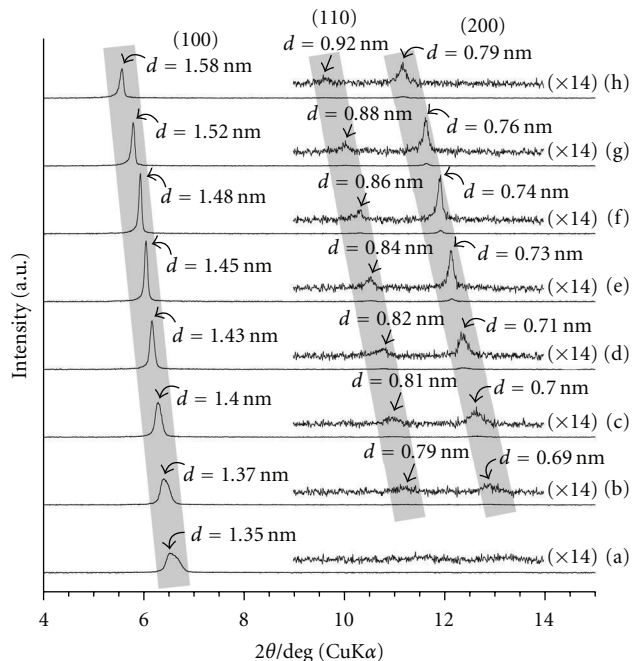


FIGURE 2: XRD patterns of PSQ-NH₃⁺Cl⁻ under various RH conditions: (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70, (g) 80, and (h) 90% RH. Amount of each product on glass was *ca.* 2.0 mg/cm².

this material forms a single crystal, its ladder structure can be confirmed by single crystal XRD measurements. In addition, the formation of ladder structure of oligoSQs can be discussed by IR spectra because the theoretical absorption peaks have been calculated [27]. On the other hand, decisive analysis methods for the ladder-like structure of PSQ have not yet been established. This is because it is difficult to obtain the single crystal of PSQ and to calculate the theoretical absorption peaks in IR spectra due to high molecular weight. Therefore, the evidence necessary to confirm the molecular structure was collected by performing multiple analyses. The ladder-like PSQ simultaneously satisfies the following conditions: (i) to be soluble in solvents, (ii) relatively high molecular weight, (iii) relatively small width of the molecule, and (iv) observation of large T³ peak and small T² peak in ²⁹Si NMR spectrum.

PSQ-NH₃⁺Cl⁻ had a rod-like structure with relatively small diameter, that is, short molecular width (*ca.* 1.6–1.7 nm, estimated from *d*-value of (100) peak in XRD pattern of Figure 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 Figure 3. In addition, PSQ-NH₃⁺Cl⁻ was soluble in water, despite its *M_w* was relatively high (*ca.* 12000, estimated by Zimm plot method using the SLS in water), 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 1(c-ii).

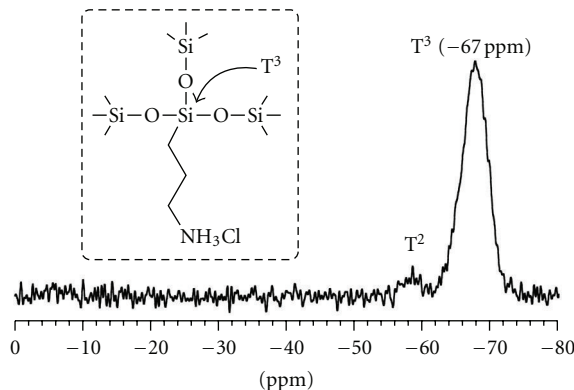


FIGURE 3: Solid-state ²⁹Si NMR spectrum of PSQ-NH₃⁺Cl⁻.

We 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 (Figures 2(b)–2(h)), meanwhile those with RH lower than 20% did not show such the diffraction peaks (Figure 2(a)). 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⁻.

When the sol-gel reaction of APTMOS was performed under alkaline conditions using ammonia (NH₃) aqueous solution, insoluble PSQ with three-dimensional network structure was prepared. On the basis of all results as described above, we considered that self-organization of the ion pair prepared from the amino group of APTMOS and the acid was the driving force for the formation of regular molecular and higher-ordered structures of the PSQ.

2.2. Sol-Gel Reaction of (3-(2-Aminoethylamino)propyl)trimethoxysilane. As another monomer, organotrialkoxysilane containing two amino groups, that is, (3-(2-aminoethylamino)propyl)trimethoxysilane (AEAPTMO), was employed for the preparation of regular-structured PSQ [24]. The procedure for sol-gel reaction of AEAPTMO was similar to that of APTMOS.

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 changed by varying the RH, although the *d*-value ratios of (110)/(100) and (200)/(100) did not change (Table 1). The same behavior was observed

TABLE 1: d -Values of diffraction peaks in the XRD patterns of the PSQ obtained from AEAPTMOS under various RH conditions.

RH (%)	d -value (nm)		
	(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	—	—

with the aforementioned PSQ-NH₃⁺Cl⁻ (Figure 2). 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.

3. Preparation of Ladder-Like PSQs Containing Chiral and Ammonium Chloride Side-Chain Groups

In the previous part, we described the assumption that the ladder-like PSQ was twisted to form the rod-like structure, resulting in the formation of the hexagonally stacked structure. However, the twisting direction would not be controlled, that is, the twisted ladder-like PSQ was probably obtained in racemic form. We suppose that controlling the conformational structure of the PSQ, for example, formation of the chiral conformation that is motif for biological macromolecules such as DNA, protein, and amylose, is one of the important subjects. Such a conformational structure of the biological macromolecules is generally caused by chiral moieties of monomer units. In this part, therefore, the introduction of the chiral moieties into the ladder-like PSQs is described to control not only the molecular and higher-ordered structures of PSQs but also their conformational structures.

3.1. Preparation by Copolymerization Method. To prepare chiral ladder-like PSQs, the introduction of the chiral moieties into the PSQs was first investigated by acid-catalyzed copolycondensation of two organotrialkoxysilanes containing chiral and amino groups, respectively [28]. 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

= 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 3(a)).

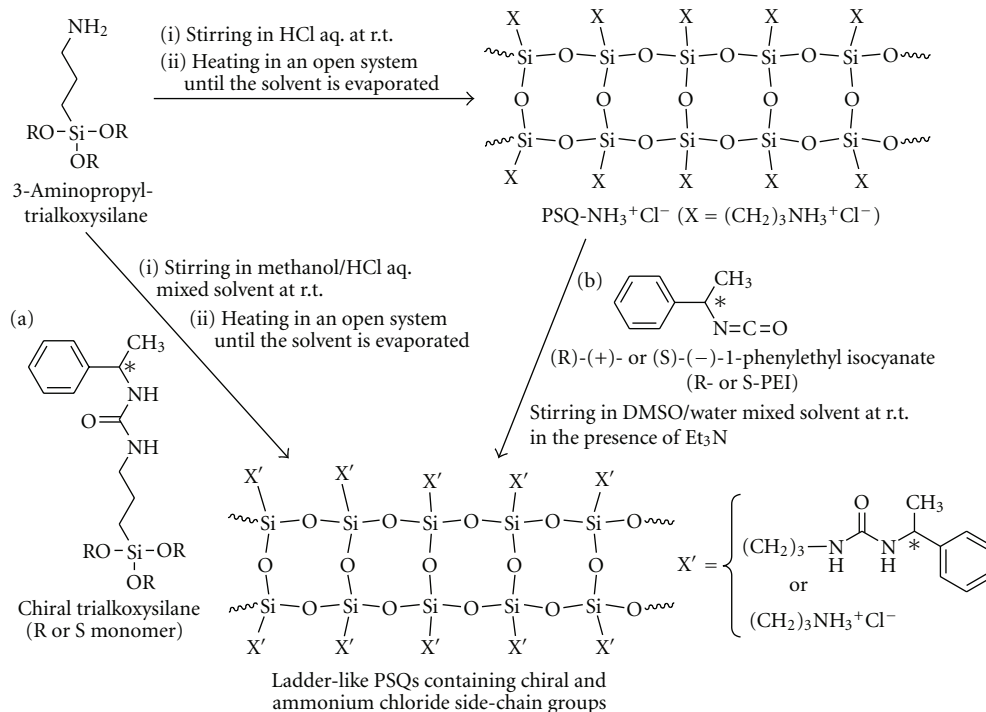
The compositional ratio of the chiral groups to the ammonium chloride groups in the products was calculated to be 6:94 from the ¹H NMR spectra. Therefore, the resulting PSQs are denoted as R₆- and S₆-PSQs, according to the stereostructure and functionality of the chiral groups. In the IR spectra of R₆- and S₆-PSQs, large absorption bands at 1135 and 1040 cm⁻¹ assigned to the Si–O–Si bonds were observed. In addition, the ²⁹Si NMR spectra in DMSO-*d*₆ at 40°C of these PSQs exhibited the large peaks in the regions of T³. These results indicate the complete progress of sol-gel copolycondensation of the chiral trialkoxysilanes and APTEOS, and the formation of Si–O–Si bonds. The M_w s of R₆- and S₆-PSQs estimated by the Zimm plot method using SLS in water 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/√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 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 ²⁹Si NMR spectrum. In addition, these PSQs were soluble in water and DMSO, despite the M_w s 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 as shown in Scheme 1(c-ii).

The vibrational circular dichroism (VCD) spectra of R₆- and S₆-PSQs showed the reversed absorptions at *ca.* 1145–1165 cm⁻¹, respectively (Figure 4), 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.

3.2. Preparation by Polymer Reaction Method. 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 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, that is, a lower ratio of ammonium chloride groups, the polymer reaction of chiral isocyanate compounds with the aforementioned PSQ-NH₃⁺Cl⁻ was investigated [29].



SCHEME 3: Preparation of ladder-like PSQs containing chiral and ammonium chloride side-chain groups by (a) copolycondensation method and (b) polymer reaction method.

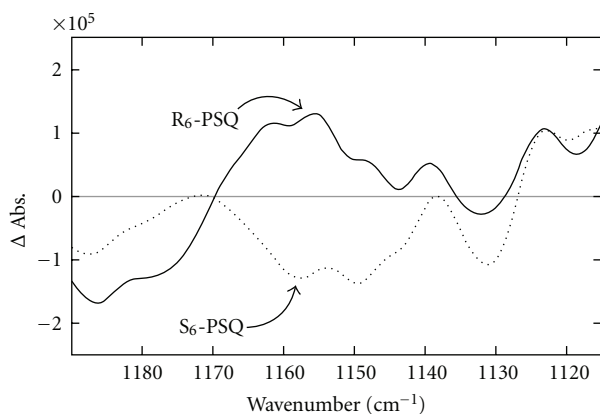


FIGURE 4: VCD spectra in DMSO of R₆- and S₆-PSQs.

The preparation 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 mixed solvent at room temperature for 10 min (Scheme 3(b)). 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 in methanol 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, that is, ammonium chloride groups. As described above, 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, for example, hydrogen bonding [30]. 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 [α]_D²² 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 [α]_D²² values were probably affected by solvent effects. Such a solvent effect on specific rotations indicates the presence of chiral conformations of these PSQs.

3.3. Chiral Induction Behavior from Chiral PSQ to Anionic Porphyrin Compound. 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

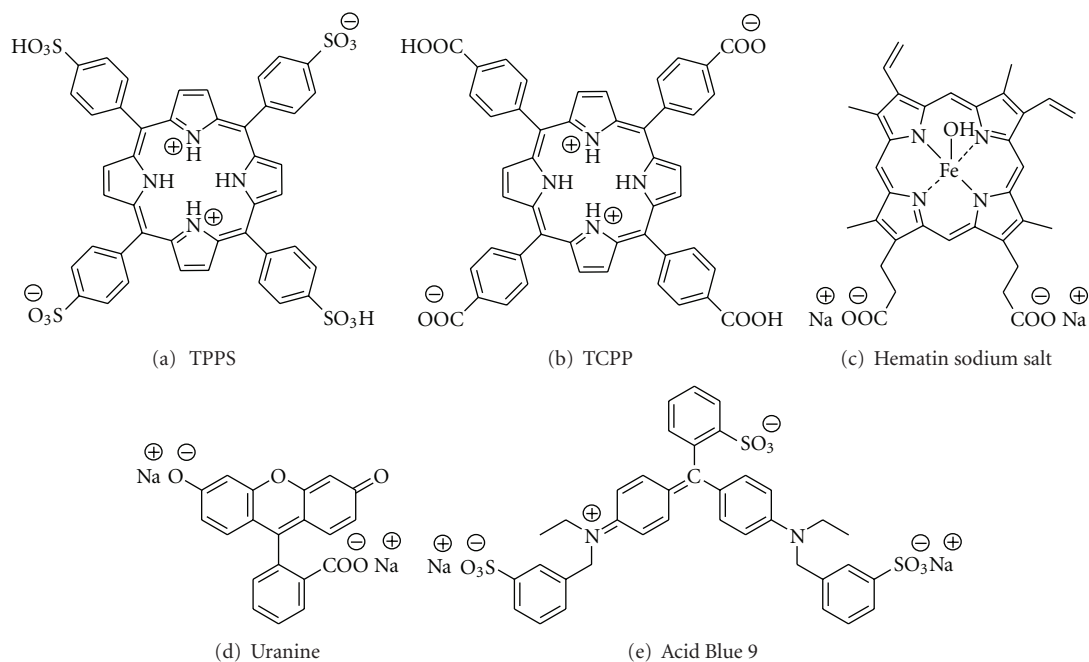


FIGURE 5: Structures of various dye compounds.

luminescent (CPL) materials. To achieve the preparation of these supramolecular hybrids by chiral induction from chiral molecules to photofunctional compounds, several combinations have been investigated, for example, anionic dye/cationic chiral surfactants [31], laser dye/cholesteric liquid crystal [32], pyrene derivatives/cyclodextrins [33], porphyrins/helical polyacetylene [34], and π -conjugated polymers/polysaccharides such as amylose [35], and schizophyllan [36]. 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. Therefore, the aforementioned ladder-like PSQs containing chiral and ammonium groups were applied to chiral inductors for hybridization with a dye compound such as an anionic achiral porphyrin, tetraphenylporphine tetrasulfonic acid (TPPS) (Figure 5(a)), by ionic interaction [28, 29].

In the UV-Vis spectra of TPPS/R₆- and S₆-PSQs aqueous mixtures (4 μ mol/L and 100 μ mol unit/L, resp.), absorptions due to the Soret band of TPPS in these mixtures were blue shifted (to 400 nm) compared with that of TPPS alone and indicated monomeric state with protonated (at 434 nm) and deprotonated (at 414 nm) species (Figure 6(a)). These results indicate that the negatively charged TPPS formed H aggregates along the positively charged ammonium groups as side-chains of the PSQs.

The electronic circular dichroism (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 (Figure 6(b)), 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 side-chains of PSQs, the same analyses were performed using R₈₀- and S₈₀-PSQs as chiral inductors.

The ECD spectra of TPPS/R₈₀- and S₈₀-PSQs mixtures in methanol (4 μ mol/L and 100 μ mol unit/L, resp.) exhibited the reverse absorptions (Figure 6(d)), corresponding to the absorptions assigned to the Soret bands of TPPS at 418 nm in the UV-Vis spectrum (Figure 6(c)). The absorption wavelength of this mixture was almost the same as that of dilute methanol solution of sole TPPS (concentration = 4 μ 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 the 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.

3.4. Influence of the Structures of Dye Compounds on Chiral Induction Behavior. To investigate the influence of the structures of dye compounds on the aforementioned chiral induction behavior, we performed the ECD and UV-Vis measurements of the mixtures in methanol of R₈₀- and S₈₀-PSQs with various dye compounds as shown in Figure 5. When tetrakis(4-carboxyphenyl)porphyrin (TCPP) (Figure 5(b)) was used as a dye compound, the reverse absorptions assigned to TCPP in these mixtures were observed in the ECD spectra (Figure 7(b)). These behaviors

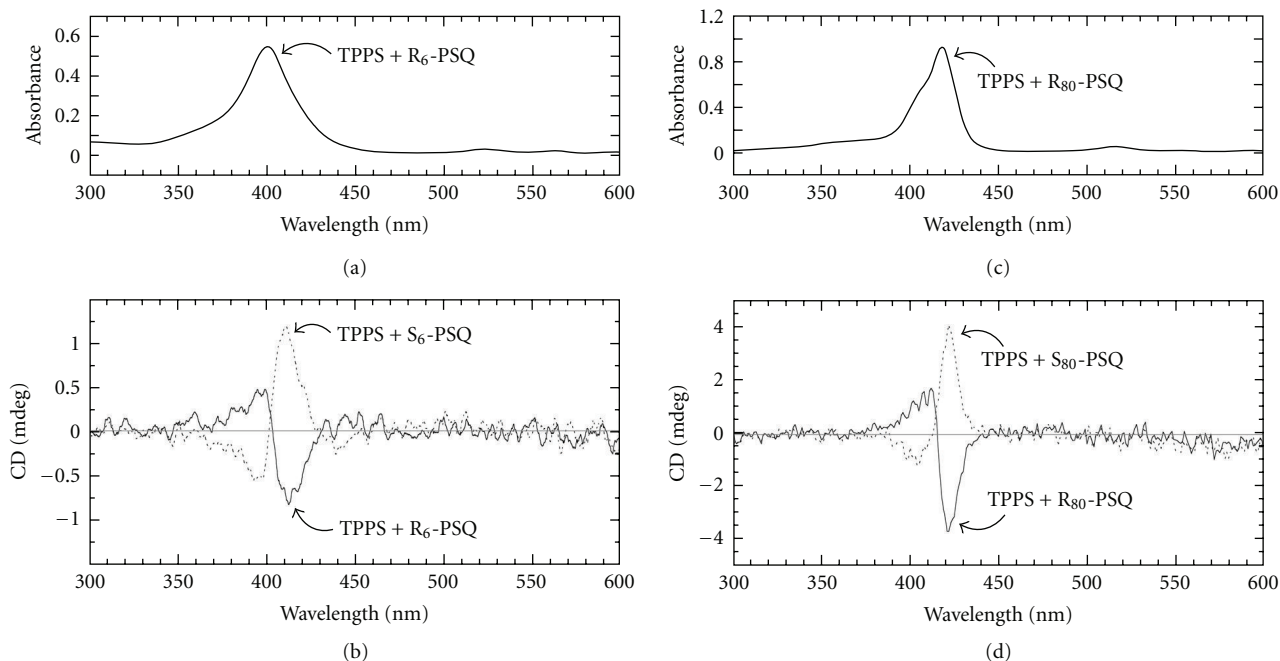


FIGURE 6: (a) UV-Vis spectrum of TPPS/R₆-PSQ aqueous mixture, (b) ECD spectra of TPPS/R₆- and S₆-PSQs aqueous mixtures, (c) UV-Vis spectrum of TPPS/R₈₀-PSQ mixture in methanol, and (d) ECD spectra of TPPS/R₈₀- and S₈₀-PSQs mixtures in methanol.

were similar to those using TPPS and indicated that the chiral induction from PSQs to TCPP was occurred. On the other hand, such the absorptions in the ECD spectra did not appear using Hematin sodium salt (Figure 5(c)), Uranine (Figure 5(d)), and Acid Blue 9 (Figure 5(e)) as dye compounds (Figures 7(d), 7(f), and 7(h)). Difference in the structures between the dye compounds indicated chiral induction (TPPS and TCPP) and the others (Hematin sodium salt, Uranine, and Acid Blue 9) are point symmetry, that is, the former had point-symmetric structure and the later did not have it. Therefore, we assumed that point symmetry of dye compounds was an important factor for the chiral induction behavior from R₈₀- and S₈₀-PSQs to these dye compounds.

4. Correlation between the pK_a of Acid-Catalysts and the Structures of SQs Prepared by Hydrolytic Condensation of APTMOS

As described above, the sol-gel reaction of APTMOS using HCl aqueous solution resulted in the formation of ladder-like PSQ with hexagonally stacked structure [23–26]. Furthermore, when another acid, for example, nitric acid (HNO₃) aqueous solution was used, we confirmed the formation of similarly structured PSQ [23]. On the other hand, when the hydrolytic condensation of APTMOS was performed using a superacid trifluoromethanesulfonic acid (CF₃SO₃H) aqueous solution under the same reaction conditions as those used for the preparation of the ladder-like PSQ as described

above, we found that cage-like octa(3-aminopropyl)SQ trifluoromethanesulfonate (OAP-POSS-CF₃SO₃) was prepared in *ca.* 93% yield with a total reaction time of *ca.* 5–6 h (Scheme 4) [37]. In the preparation of OAP-POSS, these values are considerably high yield and a short reaction time compared with those of the previous studies [7–9].

For the confirmation of the OAP-POSS-CF₃SO₃ structure as shown in Scheme 4, the ²⁹Si NMR, matrix-assisted laser desorption ionization time of flight mass (MALDI-TOF MS), electrospray ionization mass (ESI MS), and IR measurements were carried out. The ²⁹Si NMR spectrum in DMSO-*d*₆ at 40°C of the product showed only a T³ signal at *ca.* –66 ppm. This indicates that the product has only one type of Si atoms, which are substituted with three siloxane bonds (i.e., the absence of a silanol group). Furthermore, in the MALDI-TOF MS spectrum of the product, only one significant peak was observed, which corresponded to the mass of OAP-POSS without CF₃SO₃[–] as counterions (*m/z* 881.9 [M+H]⁺). To support the mass result from the MALDI-TOF MS spectrum, we performed an ESI MS measurement of the product. Consequently, peaks corresponding to the mass of OAP-POSS were also observed. Additionally, the counterions of the product were exchanged (from CF₃SO₃[–] to Cl[–]) by treatment with the mixed solvent of 0.5 mol/L methanolic HCl and acetone to more easily evaluate the Si–O–Si stretching absorption band in the IR spectrum. The IR spectrum of the product with Cl[–] as the counterion showed only one absorption peak at 1125 cm^{–1} derived from Si–O–Si bonds. It has been reported that the IR spectra of cage-like octaSQs showed a single peak due to the Si–O–Si stretching absorption band because of their highly symmetrical structures [27]. From these results, it was

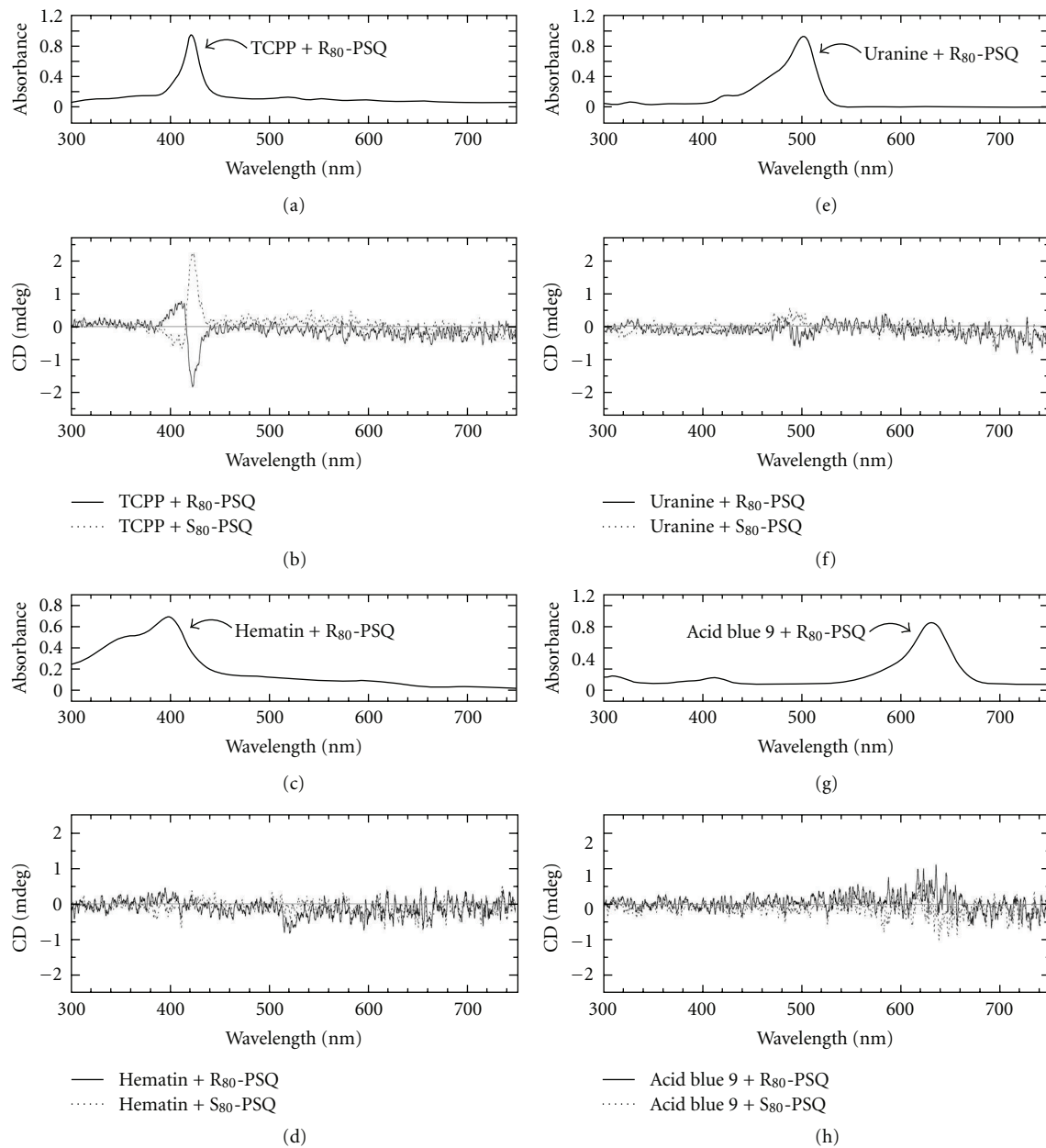
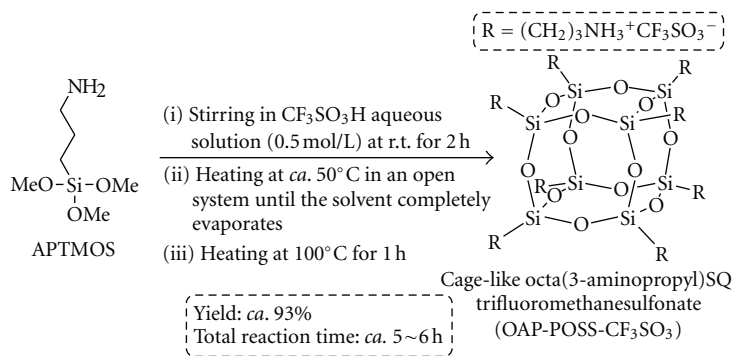


FIGURE 7: (a) UV-Vis spectrum of TCP/R₈₀-PSQ mixture, (b) ECD spectra of TCP/R₈₀- and S₈₀-PSQs mixtures, (c) UV-Vis spectrum of Hematin/R₈₀-PSQ mixture, (d) ECD spectra of Hematin/R₈₀- and S₈₀-PSQs mixtures, (e) UV-Vis spectrum of Uranine/R₈₀-PSQ mixture, (f) ECD spectra of Uranine/R₈₀- and S₈₀-PSQs mixtures, (g) UV-Vis spectrum of Acid Blue 9/R₈₀-PSQ mixture, and (h) ECD spectra of Acid Blue 9/R₈₀- and S₈₀-PSQs mixtures. In all cases, methanol was employed as a solvent, and the molar ratios of dye compound to one unit of PSQ were 1 : 25.

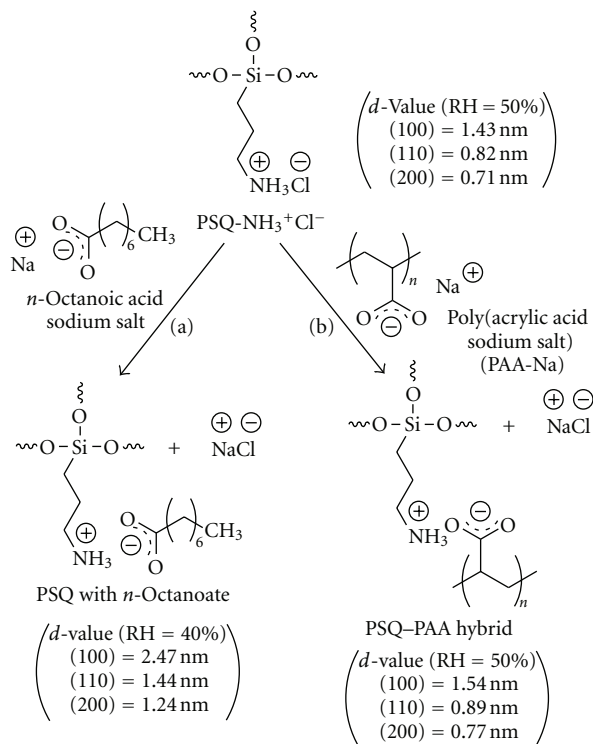
concluded that the product had cage-like structure as shown in Scheme 4.

As aforementioned, the ladder-like PSQs with hexagonally stacked structures can be prepared from APTMOS using the strong acids such as HCl and HNO₃ aqueous solutions under the same reaction conditions as those used for the preparation of OAP-POSS-CF₃SO₃. The differences between the CF₃SO₃H ($pK_a = -13$) and the acids used for the formation of the ladder-like PSQs (HCl and HNO₃, pK_a s = -3.7 and -1.8 , resp.) are associated with their acidity and

bulkiness. The pK_a of trifluoroacetic acid (CF₃COOH, $pK_a = 0.3$) is higher than that of CF₃SO₃H (i.e., the acidity of CF₃COOH is lower than that of CF₃SO₃H) although the bulkiness of both acids is similar. Therefore, to investigate the effect of these properties of the acids on the structures of the synthesized SQs, the hydrolytic condensation of APTMOS was performed using CF₃COOH aqueous solution. Consequently, we found that a hexagonally structured PSQ was obtained, as confirmed by XRD measurements. In addition, the ²⁹Si NMR spectrum showed a slight T² peak, indicating



SCHEME 4: Preparation of OAP-POSS- CF_3SO_3 using $\text{CF}_3\text{SO}_3\text{H}$ aqueous solution in higher yield with a shorter reaction time.



SCHEME 5: Ion-exchange reactions of $\text{PSQ-NH}_3^+\text{Cl}^-$ with (a) n -octanoic acid sodium salt and (b) poly(acrylic acid sodium salt).

that there was no formation of the OAP-POSS- CF_3SO_3 structure, which was confirmed by the presence of silanol groups. These results indicate that the lower $\text{p}K_a$ of the acid is an important factor for the preparation of OAP-POSS- CF_3SO_3 .

On the basis of these results, we concluded that the $\text{p}K_a$ of the acids was important to control the structures of SQs prepared by hydrolytic condensation of APTMOS, that is, the use of the superacid aqueous solution resulted in the formation of cage-like octaSQ, while the ladder-like PSQs with hexagonally stacked structures were formed from the strong acid aqueous solutions under the same reaction conditions (Figure 8). Detailed studies on the hydrolytic

condensations of APTMOS using other acid-catalysts with various $\text{p}K_a$ levels are now in progress.

5. Ion-Exchange Behaviors of Cationic Ladder-Like PSQs with Various Anionic Compounds

Because the aforementioned $\text{PSQ-NH}_3^+\text{Cl}^-$ has ammonium groups as side-chains and chloride anions (Cl^-) as counterions, the anion-exchange property can be expected. Therefore, ion-exchange reactions of the PSQs were performed with various anionic compounds.

5.1. Ion-Exchange with Fatty Acids. First, a fatty acid salt such as n -octanoic acid sodium salt was employed as an anionic compound (Scheme 5(a)) [23]. By pouring $\text{PSQ-NH}_3^+\text{Cl}^-$ 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 ($\text{PSQ-NH}_3^+\text{Cl}^-$), 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 the 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.

5.2. Ion-Exchange with Anionic 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

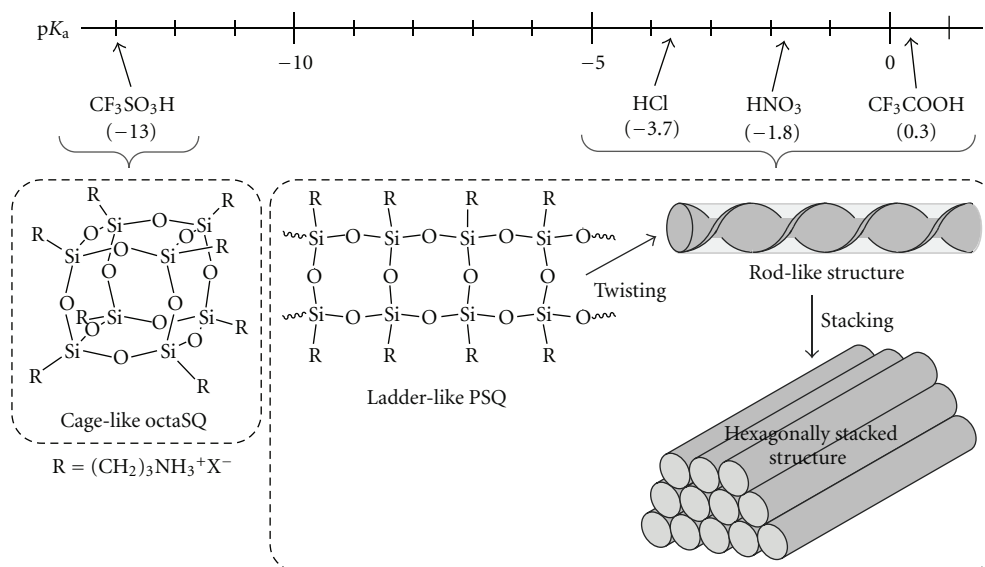


FIGURE 8: Correlation between the pK_a of acid-catalysts and the structures of SQs prepared by hydrolytic condensation of APTMOS.

organic-inorganic hybrids have attracted considerable attention from both fundamental research and applications points of view [38, 39]. In particular, the organic-inorganic hybrids obtained from the synthetic polymers as organic species are important industrial materials.

Here, we describe the preparation of an organic-inorganic polymer hybrid (PSQ-PAA) 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 an ion-exchange reaction [40]. To obtain PSQ-PAA, the ion-exchange reaction was performed by pouring PSQ-NH₃⁺Cl⁻ aqueous solution into PAA-Na aqueous solution (Scheme 5(b)).

The IR spectrum of PSQ-PAA indicated 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, that is, NH₃⁺ and COO⁻, was calculated to be *ca.* 1:1. The XRD pattern of PSQ-PAA showed the formation of a hexagonal phase, and the d -values of the diffraction peaks were different from those of PSQ-NH₃⁺Cl⁻ (Scheme 5(b)), indicating the formation of not a macroscopic mixture but the molecular-scale hybrid of two polymers.

5.3. Ion-Exchange with Layered Clay Minerals. There have been intense research activities on layered silicates pillared with inorganic or organic clusters, which are called pillared interlayer clays (PILCs) [41–43]. PILCs have much higher surface areas and pore volumes than those of the original clays. Such properties make them useful catalysts, ion-exchangers, and adsorbents. These materials are usually prepared by the intercalative ion-exchange of layered clay minerals with a variety of nanosized pillars, such as organic ions [44], inorganic ions [45], and sol particles [46].

Even though the preparation of various polymer/clay hybrids has already been reported [47], there have been a few studies on the preparation of PILCs using polymers. Because the polymers generally have a flexible structure, expansion of the interlayer space of clays by polymer incorporation is not enough for providing more free space.

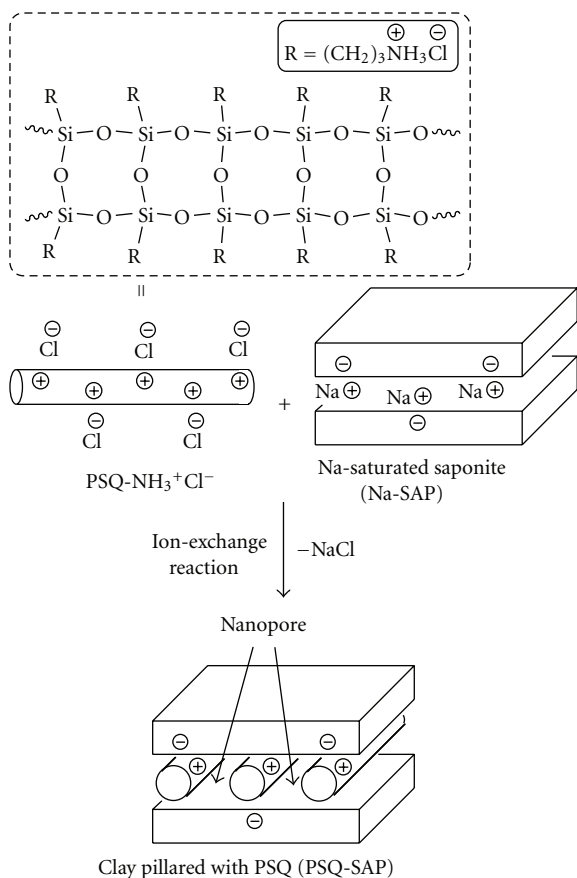
The aforementioned PSQ-NH₃⁺Cl⁻ has motivated us to develop new PILCs, because PSQ-NH₃⁺Cl⁻ has rigidity and bulkiness to expand the interlayer of clays and ability to intercalate molecules into the interlayer of anionic clays by the ion-exchange reaction due to the presence of ammonium cations in side-chains of PSQ-NH₃⁺Cl⁻. Therefore, we describe the preparation of a clay pillared with rod-like cationic PSQ-NH₃⁺Cl⁻ [48].

The preparation was performed by pouring PSQ-NH₃⁺Cl⁻ aqueous solution into an aqueous suspension of Na-saturated saponite (Na-SAP) as a clay mineral to obtain the clay pillared with PSQ-NH₃⁺Cl⁻ (PSQ-SAP) (Scheme 6). The resulting product was mainly characterized by IR, XRD, and nitrogen adsorption-desorption isotherm measurements.

The IR spectrum of PSQ-SAP showed the absorption assigned to the ammonium ion of the PSQ component, indicating that the PSQ was inserted into the interlayer of SAP. The XRD pattern of PSQ-SAP was completely different from that of Na-SAP and PSQ-NH₃⁺Cl⁻. Accordingly, PSQ-SAP was not a mixture, but an intercalated nanoorder material, that is, a hybrid.

From the nitrogen adsorption-desorption isotherms at 77 K, the surface area and pore volume of PSQ-SAP derived from the t -plot were estimated to be 370 m²/g and 0.15 cm³/g, respectively. This indicates that a porous material was prepared from the starting materials with dense structures (BET surface areas of Na-SAP and PSQ-NH₃⁺Cl⁻ were *ca.* 26 and 5 m²/g, resp.).

When a clay mineral with high cation-exchange capacity (CEC) such as Li-saturated taeniolite was employed, such a



SCHEME 6: Preparation of a clay pillared with PSQ by ion-exchange reaction of $\text{PSQ-NH}_3^+\text{Cl}^-$ with Na-saturated saponite.

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. Because the distance between the PSQs in the interlayer of taeniolite is short due to the higher CEC of the Li-saturated 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. Conclusion

In this review, we described the preparation of cationic ladder-like PSQs with hexagonally stacked structures by the sol-gel reaction of amino group-containing organotrialkoxysilane monomers in the acid solutions. It was considered that self-organization of the ion pairs prepared from the monomers and the acids was the driving

force for the formation of regular molecular and higher-ordered structures of the PSQs. In addition, to control the conformational structure of PSQ, the introduction of the chiral moieties into PSQ was performed. Furthermore, we found that the $\text{p}K_a$ of the acid-catalysts was important to control the structures of the ammonium group-containing SQs prepared by hydrolytic condensation of APTMOS, that is, the use of the superacid aqueous solution resulted in the formation of cage-like octaSQ, while the ladder-like PSQs with hexagonally stacked structures were formed from the strong acid aqueous solutions under the same reaction conditions. Finally, because the present ladder-like PSQs indicated the anion-exchange properties due to existence of cationic functional groups as side-chains, we described the anion-exchange behaviors with various organic and inorganic compounds, such as anionic surfactants, a polymer, and layered clay minerals, to obtain the functional hybrid materials.

Acknowledgments

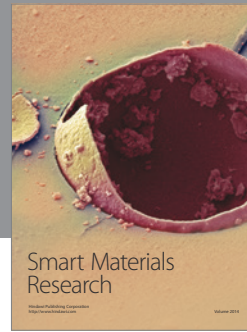
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