# Sol–gel synthesis of ladder polysilsesquioxanes forming chiral conformations and hexagonal stacking structures

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Ladder polysilsesquioxanes containing ammonium chloride and chiral groups as side-chains were prepared by sol–gel copolycondensation of 3-aminopropyltriethoxysilane and chiral organotriethoxysilane under acidic conditions, forming chiral conformations and hexagonal stacking structures.

## Introduction

The important functions of biological macromolecules such as proteins, nucleic acids, and polysaccharides are known to be reflected by not only their primary structures but also secondary and higher-ordered structures.[1] Therefore, precise control of such hierarchical structures of the synthetic materials is one of the important subjects in the research field of materials chemistry, for academic and application reasons.

The preparation of siloxane (SiO)-based materials, *e.g.*, silsesquioxanes ($RSiO_{1.5}$) and silicas ($SiO_2$), is an extensively investigated area in materials chemistry due to their superior thermal, mechanical, and chemical properties. Hydrolysis and (poly)condensation, *i.e.*, sol–gel reaction, of alkoxysilanes is well-known as one of the important methods for the preparation of SiO-based materials.[2] However, it is generally difficult to control the structures of SiO-based materials by using the sol–gel method. The (organo)alkoxysilane starting materials for synthesizing silsesquioxanes and silicas are tri- and tetrafunctional monomers, which result in the formation of irregular network structures composed of siloxane bonds.

So far, some attempts for control of these materials have been reported. Polyhedral oligomeric silsesquioxanes (POSS) and ladder polysilsesquioxanes, synthesized from organotrialkoxysilanes, are known to be SiO-based materials with controlled primary structures.[3] Another is the sol–gel polycondensation of alkoxysilanes in the presence of surfactants.[4] This is one of the methods for controlling higher-ordered structures of SiO-based materials. The surfactants forming micelles of various hypermorphs, such as hexagonal and lamellar phases, act as templates and allow the sol–gel polycondensation of alkoxysilanes to form silica–surfactant hybrid materials with regular higher-ordered structures. In addition, the sol–gel polycondensation of trichlorosilane,[5] trialkoxysilane,[6] and oligosiloxane[7] covalently bonding to long alkyl chains has been performed to obtain polysilsesquioxanes and silicas with regular higher-ordered structures. Self-organization of the surfactants and long alkyl chains by hydrophobic interactions has been proposed as a driving force for the formation of regular higher-ordered structures.

Recently, we have developed a new preparation method of SiO-based materials with regularly controlled higher-ordered structure, *i.e.*, the sol–gel polycondensation of aminoalkyltrialkoxysilanes in aqueous solutions of inorganic strong acids, such as hydrochloric and nitric acids, without using the surfactants and long alkyl chain moieties.[8] The resulting polysiloxanes (polysilsesquioxanes) had rodlike structures forming hexagonal phases in the solid state, and were soluble in water to obtain transparent solutions due to the presence of hydrophilic ammonium groups on the surface of each rod. Self-organization of an ion complex prepared from the amino group of the organotrialkoxysilane and an inorganic acid used as a catalyst is a key factor for the formation of a regular higher-ordered structure. In addition, the primary structure of this polysilsesquioxane was assigned to a ladder structure,[8c] and the ladder was assumed to be twisted to form the rodlike molecule.

Thus, we have investigated the control of primary and higher-ordered structures of SiO-based materials, but still there remains the problem of controlling the secondary structure in the nanometre scale, *e.g.*, formation of a chiral conformation that is a motif for biological macromolecules such as DNA, protein, and amylose. We suppose that control of the secondary structure would be one of the important subjects in the next stage of sol–gel chemistry. Such a secondary structure of the biological macromolecules is generally caused by chiral moieties of the monomer units.[1]

In this study, to control not only the primary and higher-ordered structures of SiO-based materials, but also their nanoscale secondary structures, we investigated the introduction of chiral organotrialkoxysilane as a monomer into the sol–gel polycondensation of aminoalkyltrialkoxysilane under acidic conditions. Consequently, we found that ladder polysilsesquioxanes containing ammonium chloride and chiral groups as side-chains could be prepared, which formed chiral conformations as well as hexagonal stacking structures (Scheme 1).

## Experimental

### Materials

All reagents and solvents were commercially purchased and used without further purification.

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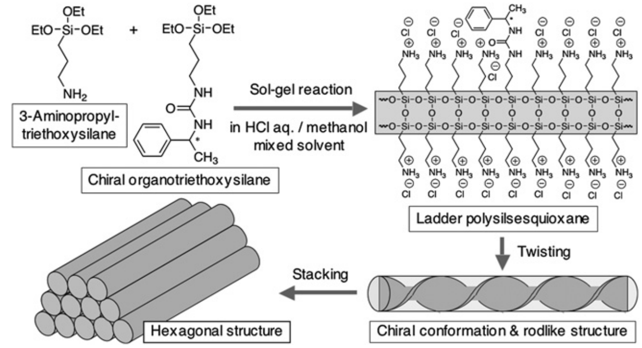


**Scheme 1** Synthetic strategy for a ladder polysilsesquioxane forming a chiral conformation and hexagonal stacking structure by the sol–gel method.

### Preparation of the polysilsesquioxanes

A typical experimental procedure for the polysilsesquioxane (*R*- or *S*-polymer) was as follows. A solution of (*R*)-(+)- or (*S*)-(−)-1-phenylethylamine (*R*- or *S*-PEA: 2.5 mmol = 0.303 g) in dichloromethane (10 mL) was added to 3-(triethoxysilyl)propyl isocyanate (TEOSPI: 2.5 mmol = 0.618 g) with stirring at room temperature. After the solution was stirred further for 15 min, dichloromethane was evaporated by heating. To the resulting product, methanol (60 mL) and a solution of 3-aminopropyltriethoxysilane (APTEOS: 22.5 mmol = 4.981 g) in 1.0 mol/L aqueous hydrochloric acid (37.5 mL) were successively added with stirring at room temperature. The reaction solution was stirred for 1 h at 50 °C, followed by heating to 60–70 °C in the open system until the solvent was completely evaporated. After the product was left for 2 h at 100 °C, it was dissolved in water (30 mL) and the product solution was poured into acetone (300 mL) to precipitate the powdered product. The precipitated product was isolated by filtration, washed with acetone and chloroform, and then dried under reduced pressure at room temperature to yield 3.968 g of white-powdered *R*- or *S*-polymer. $^1$H NMR (400 MHz, $D_2O$): δ 7.48–7.20 (5H, br, Ph), δ 4.81–4.61 (1H, br, $PhC\mathit{H}(CH_3)NHC(=O)NH$–), δ 3.31–2.76 (2H, br, $-NHC(=O)NHC\mathit{H_2}$– and $NH_3C\mathit{H_2}$–), δ 2.04–1.49 (2H, br, $-NHC(=O)NHCH_2C\mathit{H_2}CH_2Si$– and $NH_3CH_2C\mathit{H_2}CH_2Si$–), δ 1.47–1.25 (3H, br, $-C\mathit{H_3}$), δ 1.05–0.45 (2H, br, $-C\mathit{H_2}Si$–). IR: 1620 cm$^{-1}$ (C═O of the urea group), 1135 and 1040 cm$^{-1}$ (Si–O).

### Measurements

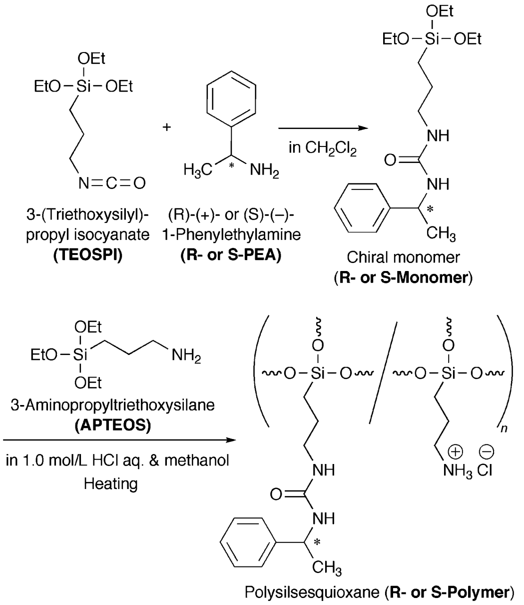
The $^1$H and $^{29}$Si NMR spectra were recorded using a JEOL ECX-400 spectrometer. The IR spectra were recorded using a Shimadzu FTIR-8400 spectrometer. The molecular weights ($M_w$) of the products were estimated by the Zimm plot method using static light scattering (SLS) equipment; an Otsuka Electronics DLS-8000. The X-ray diffraction (XRD) measurements were performed at a scanning speed of $2\theta = 0.2$ °/min using a Rigaku Geigerflex RAD-IIB diffractometer with Ni-filtered Cu K$\alpha$ radiation (= 0.15418 nm). The vibrational circular dichroism (VCD) spectra were measured in a $CaF_2$ cell (cell length = 0.1 mm) at room temperature using a Jasco FVS-4000 spectrometer. The UV-Vis and electronic circular dichroism (ECD) spectra were measured in a quartz cell (cell length = 10 mm) at room temperature using a Jasco V-650Q1 spectrophotometer and a Jasco J-820 spectropolarimeter, respectively.

## Results and discussion

### Preparation and characterization of the polysilsesquioxanes (*R*- and *S*-polymers)

The chiral monomers (*R*- and *S*-monomers) were synthesized by reaction of TEOSPI with *R*- and *S*-PEAs in dichloromethane at room temperature for 15 min, respectively, followed by evaporation of the dichloromethane (Scheme 2). The sol–gel copolycondensations of APTEOS with the resulting chiral monomers (feed molar ratio is 9 : 1) were performed in a mixed solvent of aqueous hydrochloric acid (1.0 mol/L) and methanol by heating (*ca.* 60–70 °C) in an open system until the solvent was completely evaporated (Scheme 2). The products were isolated as fractions insoluble in acetone, washed with acetone and chloroform, and then dried under reduced pressure at room temperature to yield the white powdered polysilsesquioxanes (*R*- and *S*-polymers). The products were soluble in water and dimethyl sulfoxide (DMSO), but insoluble in typical organic solvents such as methanol, acetone, chloroform, and *n*-hexane.

The $^1$H NMR spectra, in $D_2O$ at 60 °C, of the products show the signals indicating the presence of both the components of APTEOS and the chiral monomers (Fig. 1); this indicates that the products were copolymers composed of APTEOS and chiral monomers. The unit ratios of the ammonium chloride groups to the chiral groups in the products were calculated to be 94 : 6 by the integrated ratios of the signal **a** due to –$C\mathit{H_2}Si$ to the signal **g** due to the phenyl group. The IR spectra of the products show absorptions at 1620 cm$^{-1}$ attributed to the C═O bond of the urea groups (Fig. 2), indicating the existence of the units of chiral groups in the products.



**Scheme 2** Preparation of the polysilsesquioxanes by sol–gel copolycondensation.

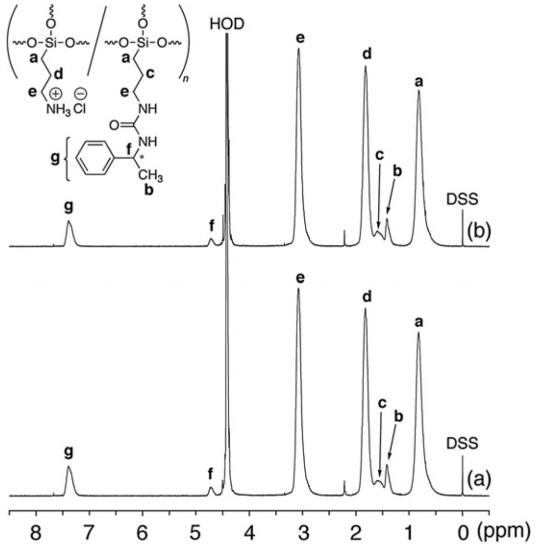


**Fig. 1** $^1$H NMR spectra in $D_2O$ at 60 °C of (a) *R*-polymer and (b) *S*-polymer. Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (δ 0.00).

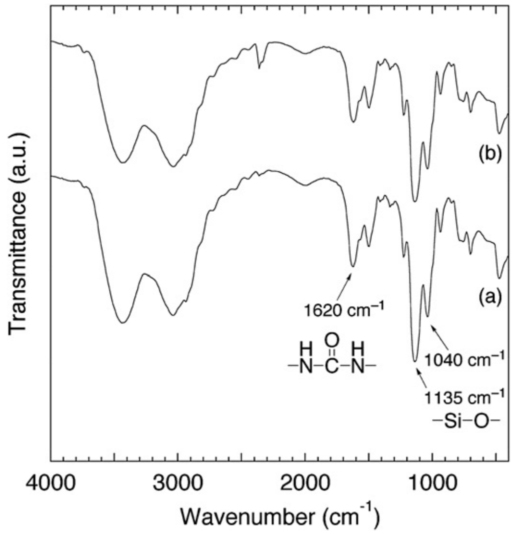


**Fig. 2** IR spectra of (a) *R*-polymer and (b) *S*-polymer.

The IR and $^{29}$Si NMR spectrometries are useful analytical methods to confirm the formation of Si–O bonds. In the IR spectra of the products, large absorption bands at 1135 and 1040 cm$^{-1}$ attributable to the Si–O–Si bonds were observed (Fig. 2), indicating the formation of polysilsesquioxanes. In addition, the $^{29}$Si NMR spectra in DMSO-$d_6$ at 40 °C of the products exhibit the signals in the regions of $T^3$, which means Si atoms with three siloxane bonds (Fig. 3). These results indicate that the progress of the sol–gel copolycondensation of APTEOS and the chiral monomers, and the formation of Si–O–Si bonds, is complete. The regularity of the primary structure of the products is discussed in detail hereinafter. The average molecular weights ($M_w$) of the products (*R*- and *S*-polymers) estimated by the Zimm plot method using a SLS apparatus were assessed to be 10 700 and 9800, respectively, indicating that the products were not oligomeric compounds but macromolecules.

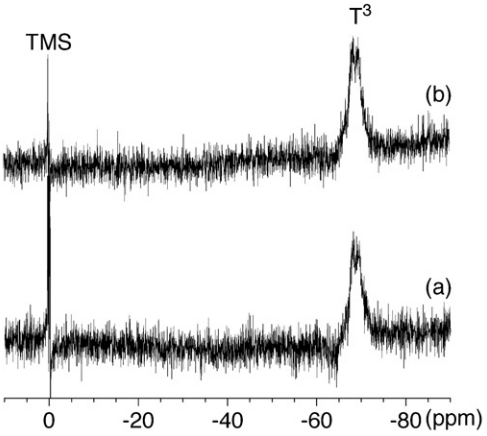


**Fig. 3** $^{29}$Si NMR spectra in DMSO-$d_6$ at 40 °C of (a) *R*-polymer and (b) *S*-polymer. Chemical shifts were referenced to tetramethylsilane (TMS) (δ 0.00).

### Higher-ordered structure of *R*- and *S*-polymers

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 profiles of the product films show three diffraction peaks with the *d*-value ratio of $1 : 1/\sqrt{3} : 1/2$, indicating that the products have regular higher-ordered structures such as hexagonal phases (Fig. 4). Because the products were soluble in water and DMSO, we supposed that these hexagonal phases originated not from porous-type structures but from the stacking of rodlike polymers. The diameters of the rodlike products calculated from *d*-values of (100) peaks (1.47–1.48 nm) were assessed to be *ca.* 1.7 nm.

The intensities of the diffraction peaks of the present product (*R*-polymer: Fig. 5b) were weaker than those of the polysilsesquioxane without a chiral group, as shown in our previous study (Fig. 5c),[8a] although these peaks indicated the formation of hexagonal phases. On the other hand, the intensities of the diffraction peaks of the polysilsesquioxane containing a higher ratio of chiral group (*ca.* 10%) become very weak (Fig. 5a),

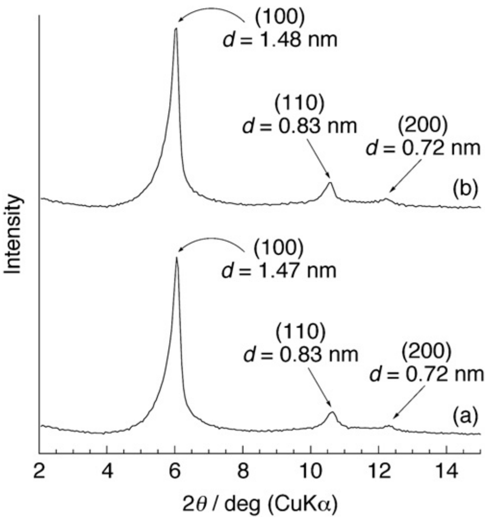


**Fig. 4** XRD patterns of (a) *R*-polymer and (b) *S*-polymer. Relative humidity on XRD measurements was *ca.* 60%.

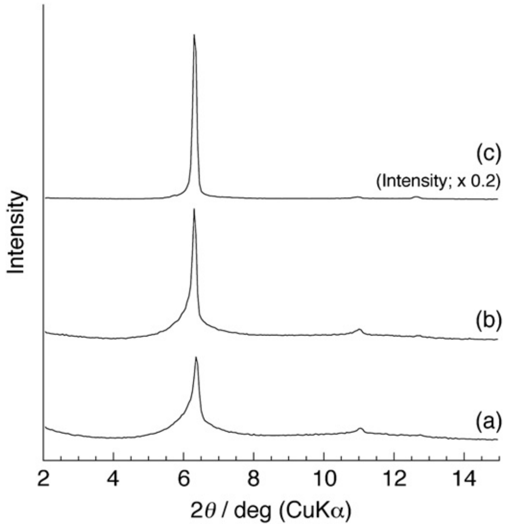


**Fig. 5** XRD patterns of *R*-polymers containing different ratios of chiral groups: (a) 10%, (b) 6%, and (c) 0%. The amount of each product on glass was *ca.* 10 mg/cm$^2$. Relative humidity on XRD measurements was *ca.* 50%.

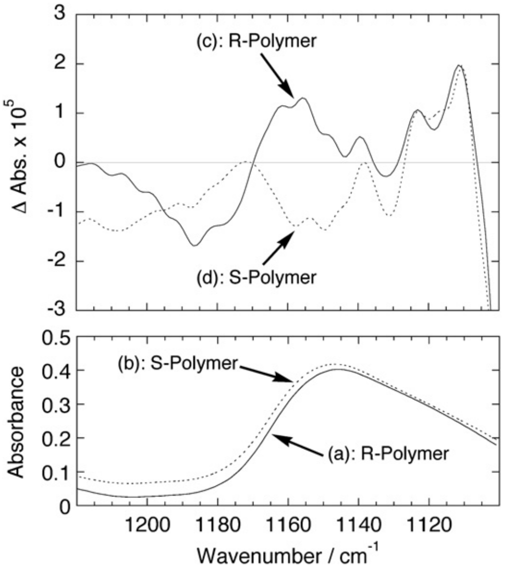


**Fig. 6** IR spectra in DMSO of (a) *R*-polymer and (b) *S*-polymer, and VCD spectra in DMSO of (c) *R*-polymer and (d) *S*-polymer. Concentrations of polymer solutions in DMSO were 0.1 mol unit/L.

indicating a relatively irregular higher-ordered structure. This is probably because the contents of ion complexes, *i.e.*, ammonium chloride groups, decreased. The ion complex has an important role for the formation of a regular higher-ordered structure in this reaction system. In addition, the product obtained from a much higher feed molar ratio of the chiral monomer (20%) was insoluble in water. Therefore, the following characterizations were performed using the polysilsesquioxanes containing *ca.* 6% chiral groups, as described above.

### Primary structure of *R*- and *S*-polymers

The primary structures of the polysilsesquioxanes have often been characterized by IR spectrometry, and it has been suggested that ladder polysilsesquioxanes have exhibited two absorption bands due to the Si–O–Si bond at *ca.* 1140 and 1050 cm$^{-1}$.[3a,b,e] In fact, the IR spectra of the present products show two absorption bands at 1135 and 1040 cm$^{-1}$ (Fig. 2). In addition, to support the ladder structure of the products, we considered the results of the XRD and $^{29}$Si NMR measurements. The diameters of the rodlike polysilsesquioxanes were extremely small (*ca.* 1.7 nm), confirmed by the XRD measurements (Fig. 4), in spite of their highly dense Si–O–Si bond network structures (only T$^3$ signal), characterized by the $^{29}$Si NMR measurements in DMSO-$d_6$ at 40 °C (Fig. 3). Both the results of the XRD and $^{29}$Si NMR provide convincing evidence of the formation of regular ladder structures as shown in Scheme 1. On the basis of all results obtained by IR, XRD, and $^{29}$Si NMR, we proposed that the primary structures of the products were ladder structures.

### Secondary structure of *R*- and *S*-polymers

The VCD spectroscopy, which is an extension of the ECD into the IR region, is a powerful technique to obtain conformational information of chiral molecules.[9] The VCD spectra of *R*- and *S*-polymers show the reversed absorptions at *ca.* 1140–1165 cm$^{-1}$, respectively (Fig. 6c, d), corresponding to the absorptions assigned to the Si–O bond of the polymer's main-chains in the IR spectra (Fig. 6a, b). These results indicate that the present polysilsesquioxanes had chiral conformations of main-chains.

### Formation of chiral aggregates of achiral porphyrin induced from *R*- and *S*-polymers

The self-assembly of achiral chromophores such as porphyrins to form chiral aggregates has attracted much attention because of its potential application to optoelectronic materials.[10] To obtain chiral aggregates of porphyrins, chiral templates to support self-assembly of the porphyrins, such as biopolymers[11] and chiral synthetic polymers,[12] have often been employed. In this study, we investigated the formation of chiral aggregates of an anionic achiral porphyrin such as tetraphenylporphine tetrasulfonic acid (TPPS) using the present polysilsesquioxanes.

The UV-Vis spectra of aqueous mixtures of TPPS/polysilsesquioxanes (4 μmol/L and 100 μmol unit/L, respectively) are shown in Fig. 7a, b. Absorptions due to the Soret band of TPPS in these mixtures are blue-shifted (to 400 nm) compared with that of TPPS alone indicated a monomeric state with protonated (at 434 nm) and deprotonated (at 414 nm) species. These results indicate that the negatively charged TPPS formed H-aggregates along the positively charged ammonium groups as side-chains of the polysilsesquioxanes.

The ECD spectra of these TPPS/polysilsesquioxanes aqueous mixtures show the reversed absorptions due to the Soret bands of TPPS-aggregates, corresponding to *R*- and *S*-polymers as templates, respectively (Fig. 7c, d), indicating that TPPS-aggregates have chiralities induced from *R*- and *S*-polymers.

To confirm that these induced circular dichroisms (ICD) of the TPPS-aggregates were not directly derived from chiral groups in the polysilsesquioxanes, the ECD measurements of the aqueous mixtures of TPPS and the chiral molecules existing in the polysilsesquioxanes, *i.e.*, *R*- and *S*-PEAs, (4 μmol/L and 6 μmol/L,

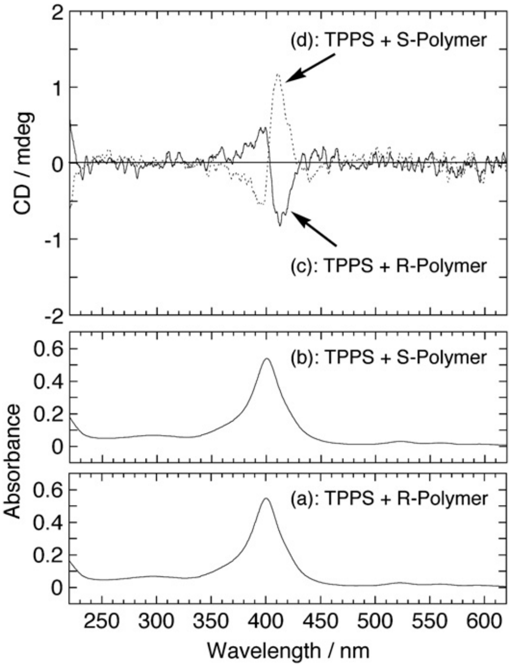


**Fig. 7** UV-Vis spectra of aqueous mixtures: (a) TPPS + *R*-polymer, (b) TPPS + *S*-polymer, and ECD spectra of aqueous mixtures: (c) TPPS + *R*-polymer, (d) TPPS + *S*-polymer. Concentrations of aqueous solutions of TPPS and polysilsesquioxanes were 4 μmol/L and 100 μmol unit/L, respectively.

respectively) were performed. As expected, these spectra do not show absorptions due to the chirality of TPPS (Fig. 8). In addition, when the polysilsesquioxane without the chiral group was added into the aforementioned aqueous mixture (TPPS = 4 μmol/L, PEA = 6 μmol/L, and achiral polysilsesquioxane = 100 μmol unit/L, respectively), the ECD spectra of this mixed solution do not also show the absorption band indicating the chirality of TPPS although H-aggregates of TPPS were formed (Fig. 9). These results indicate that the reversed absorptions due to chiral aggregates of TPPS as shown in Fig. 7 were induced not directly from chiral groups in the polysilsesquioxanes, but from their chiral conformations.

## Proposed formation mechanism

Based on all data described above, we regarded the present products as polysilsesquioxanes with hierarchically controlled primary (ladder), secondary (chiral conformation), and higher-ordered (hexagonal stacking) structures. Next, we propose the formation mechanism of the present polysilsesquioxanes. Hydrochloric acid acted not only as a catalyst for sol–gel polycondensation, but also as a reagent for the formation of the ion complex with the amino groups of APTEOS. First, the regular primary structure such as the ladder structure of polysilsesquioxanes would be formed by self-organization of the ion complex during the sol–gel polycondensation. Then, the rodlike molecules formed by twisting ladder polysilsesquioxanes stacked to form regular higher-ordered structures such as the hexagonal phase. The driving force for the formation of a rodlike structure by twisting ladder polysilsesquioxanes may be a mutual repulsion between the positively charged ammonium groups as the side-chains. During the formation of the rodlike structures, the twisting direction of the ladder polysilsesquioxanes would be

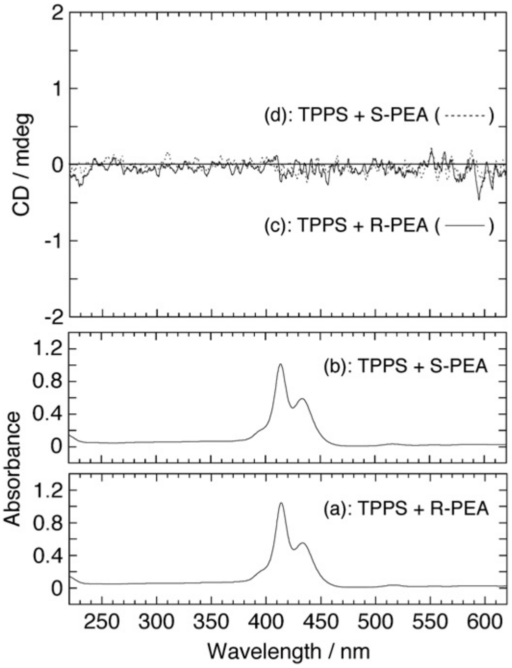


**Fig. 8** UV-Vis spectra of aqueous mixtures: (a) TPPS + *R*-PEA, (b) TPPS + *S*-PEA, and ECD spectra of aqueous mixtures: (c) TPPS + *R*-PEA, (d) TPPS + *S*-PEA. Concentrations of aqueous solutions of TPPS and PEA were 4 μmol/L and 6 μmol/L, respectively.

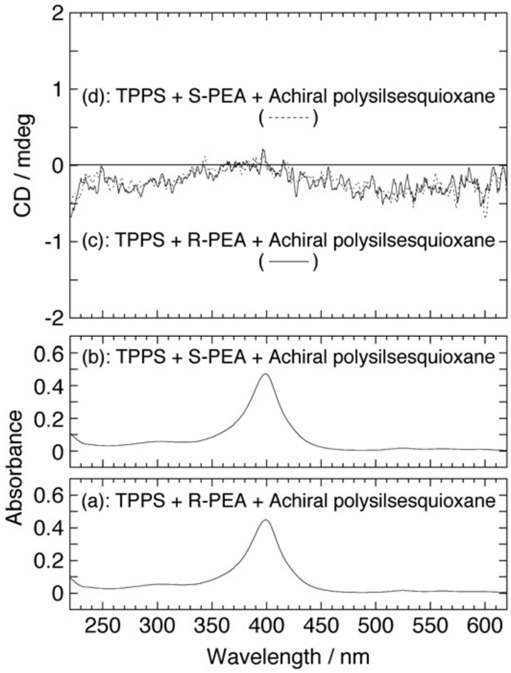


**Fig. 9** UV-Vis spectra of aqueous mixtures: (a) TPPS + *R*-PEA + achiral polysilsesquioxane, (b) TPPS + *S*-PEA + achiral polysilsesquioxane, and ECD spectra of aqueous mixtures: (c) TPPS + *R*-PEA + achiral polysilsesquioxane, (d) TPPS + *S*-PEA + achiral polysilsesquioxane. Concentrations of aqueous solutions of TPPS, PEA, and achiral polysilsesquioxane were 4 μmol/L, 6 μmol/L, and 100 μmol unit/L, respectively.

controlled by the function of the chiral groups, forming a chiral conformation. Thus, the primary, secondary, and higher-ordered structures of the polysilsesquioxanes were probably controlled by a combination of the functions of the ion complexes and the chiral groups.

## Conclusions

We have reported the preparation of ladder polysilsesquioxanes containing ammonium chloride and chiral groups, forming chiral conformations and hexagonal stacking structures. This was achieved by sol–gel copolycondensation of 3-aminopropyltriethoxysilane and chiral organotriethoxysilane in a mixed solvent of aqueous hydrochloric acid and methanol. The structures of the resulting products were characterized by $^{1}$H NMR, IR, $^{29}$Si NMR, SLS, XRD, VCD measurements. In addition, we investigated the formation of chiral aggregates of TPPS using the resulting polysilsesquioxanes. The ECD and UV-Vis spectra of aqueous mixtures of TPPS/polysilsesquioxanes indicated the formation of chiral H-aggregates of TPPS along the ammonium groups as side-chains of the polysilsesquioxanes.

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