



# Preparation of a one-dimensional soluble polysilsesquioxane containing phosphonic acid side-chain groups and its thermal and proton-conduction properties



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## ABSTRACT

A soluble polysilsesquioxane (PSQ) containing phosphonic acid side-chain groups (**PSQ-PO<sub>3</sub>H<sub>2</sub>**) was successfully prepared by hydrolytic polycondensation of 2-(diethoxyphosphoryl)ethyltriethoxysilane using concentrated hydrochloric acid as a catalyst. The <sup>29</sup>Si NMR spectrum of **PSQ-PO<sub>3</sub>H<sub>2</sub>** indicated two broad T<sup>3</sup> and T<sup>2</sup> signals with an integrated ratio of ca. 0.88:0.12. The weight-average molecular weight of **PSQ-PO<sub>3</sub>H<sub>2</sub>**, as determined via the Debye-plot method using the static light scattering in dimethyl sulfoxide, was ca. 1.8 × 10<sup>4</sup>. Furthermore, a soluble PSQ containing phosphonate side-chain groups (**PSQ-PO<sub>3</sub>HK**) was obtained by treatment of **PSQ-PO<sub>3</sub>H<sub>2</sub>** with aqueous potassium hydroxide. The X-ray diffraction pattern of the **PSQ-PO<sub>3</sub>HK** cast film showed diffraction peaks derived from a hexagonal phase formed by regular stacking of one-dimensional rod-like PSQs. According to these results, the resulting PSQs would have ladder-like structures. In addition, **PSQ-PO<sub>3</sub>H<sub>2</sub>** exhibited superior thermal stability (*T*<sub>d10</sub> > 460 °C) and relatively high proton conductivity (6.3 × 10<sup>-2</sup> S cm<sup>-1</sup> at 80 °C and 90% relative humidity).

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## 1. Introduction

Silsesquioxanes (SQs) are compounds that contain the (RSiO<sub>1.5</sub>)<sub>n</sub> structure; they can generally be prepared by hydrolytic condensation of trifunctional silane compounds (so-called silane coupling agents) such as organotrialkoxysilanes and organotrichlorosilanes. SQs have attracted much attention in the research field of organic–inorganic hybrid materials for both academic and application reasons [1,2]. This interest stems from their ability to accommodate various functional groups as side-chains (R) from their remarkable compatibility with organic materials such as polymers [3–6], which is a consequence of their organic nature, and from their superior thermal, mechanical, and chemical stabilities, which are derived from SQs' siloxane (Si–O–Si) bond frameworks with high bond energy.

Several soluble oligomeric SQs with regular structures have been reported, including SQs with cage [7], open cage [8,9], double-

decker [10,11], and ladder structures [12,13]. Meanwhile, soluble polySQs (PSQs) with controlled structures, such as ladder-like PSQs, have only been obtained in limited cases [14–18] because hydrolytic polycondensation of trifunctional silane compounds usually affords randomly structured insoluble PSQs [2]. Although the literature contains a few reports regarding ladder-like PSQs, side-chain groups of the ladder-like PSQs directly prepared from the trifunctional silane compounds are often restricted to aromatic groups such as phenyl [14,15], disc-like triphenylene [16], carbazole [17], and dibenzothiophene groups [18]. Preparing ladder-like PSQs containing aliphatic side-chain groups such as methyl groups requires the synthesis of cyclotetrasiloxanetetrols with controlled stereostructures as precursors [19–21]. Because complicated synthesis, separation, and purification methods are required to prepare and isolate these cyclosiloxane derivatives, this preparation method for ladder-like PSQs may lack general versatility. In addition, the preparation of soluble ladder-like PSQs containing functional or reactive aliphatic side-chain groups had not been reported prior to our previous work [22–28]. These functional PSQs would likely find numerous applications depending on the properties of their side-chain groups. Another reason for the limited reports on

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the preparation of ladder-like PSQs is that analysis methods to unambiguously demonstrate the ladder-like structure have not yet been established. Given the aforementioned research background of SQs, we are convinced that the development of new preparation and characterization methods for ladder-like PSQs is an important and challenging theme in this research field.

Thus far, we have reported the successful synthesis of one-dimensional (rod-like) soluble PSQs containing ammonium side-chain groups by hydrolytic polycondensation of amino-group-containing organotrialkoxysilanes using an aqueous strong acid such as hydrochloric acid (HCl) as a catalyst [22–26]. These rod-like PSQs could form hexagonally stacked structures in the solid state [22]. Their weight-average molecular weights ( $M_{w,s}$ ) were greater than  $ca. 1.2 \times 10^4$  and their  $^{29}\text{Si}$  NMR spectra showed strong signals in the  $T^3$  region [26]. Given the characterization results, we presumed that these PSQs have ladder-like structures. In addition, we also prepared soluble anionic rod-like PSQs containing carboxylate [27] and sulfo (sulfonate) [28] side-chain groups by hydrolytic polycondensation of organotrialkoxysilanes containing cyano and mercapto groups using an aqueous NaOH and an aqueous NaOH/ $\text{H}_2\text{O}_2$  mixture, respectively. On the basis of our aforementioned previous studies, ionic side-chain groups play an important role in the preparation of these regularly structured soluble PSQs.

In the present study, we investigated the preparation of PSQs containing phosphonic acid side-chain groups (**PSQ-PO<sub>3</sub>H<sub>2</sub>**). Poly(vinylphosphonic acid), which is a polymer material that contains phosphonic acid side-chain groups, exhibits high proton conductivity and is expected to function as a proton conductor for polymer electrolyte fuel cells (PEFCs) [29]. Therefore, we assumed that the aforementioned PSQs would exhibit high proton conductivity because of their phosphonic acid side-chain groups; we also expected these PSQs to exhibit outstanding thermal stability derived from their Si–O–Si bond main-chain framework.

Herein, we report the preparation of a soluble ladder-like PSQ containing phosphonic acid side-chain groups, **PSQ-PO<sub>3</sub>H<sub>2</sub>**, by the hydrolytic polycondensation of 2-(diethoxyphosphoryl)ethyltriethoxysilane (PETES) as a starting material using concentrated HCl (conc. HCl) as a catalyst. The ethoxyphosphoryl group in PETES can be converted into a phosphonic acid group by hydrolysis in the presence of conc. HCl. The phosphonic acid group is ionic, which is considered to be essential for the preparation of soluble PSQs with regular structures by our methods, as previously described. In addition, we found that a soluble ladder-like (rod-like) PSQ containing phosphonate side-chain groups (**PSQ-PO<sub>3</sub>HK**) obtained by treatment of **PSQ-PO<sub>3</sub>H<sub>2</sub>** with aqueous potassium hydroxide (KOH) could form a hexagonally stacked structure in the solid state. Moreover, we also report the thermal stabilities and proton conductivity of **PSQ-PO<sub>3</sub>H<sub>2</sub>**.

## 2. Experimental section

### 2.1. Materials

PETES and KOH were purchased from Gelest, Inc. (USA) and Nacalai Tesque, Inc. (Japan), respectively. Other reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. (Japan) and were used without further purification.

### 2.2. Preparation of PSQ-PO<sub>3</sub>H<sub>2</sub>

**PSQ-PO<sub>3</sub>H<sub>2</sub>** was prepared via the following procedure: Conc. HCl (concentration:  $ca. 36 \text{ wt}\%$ , density:  $ca. 1.18 \text{ g/mL}$ ,  $10 \text{ mL}$ ,  $116.5 \text{ mmol}$ ) was added to PETES (purity:  $95\%$ ,  $0.328 \text{ g}$ ,  $0.95 \text{ mmol}$ ) under stirring at room temperature, and the resulting solution was refluxed for 12 h using oil bath at  $110 \text{ }^\circ\text{C}$ . This solution was

subsequently heated at  $ca. 50\text{--}60 \text{ }^\circ\text{C}$  in an open system until the solvent was completely evaporated. After the resulting colorless solid was crushed in an agate mortar, it was washed with acetone ( $ca. 20 \text{ mL} \times 5$ ) to remove residual HCl. Finally, the product was dried under reduced pressure at room temperature to yield **PSQ-PO<sub>3</sub>H<sub>2</sub>** as a white solid ( $0.157 \text{ g}$ , quantitative yield ( $ca. 102\%$ )): the ideal chemical formula of one repeating unit of **PSQ-PO<sub>3</sub>H<sub>2</sub>** [ $\text{SiO}_{1.5}(\text{CH}_2)_2\text{PO}_3\text{H}_2$ , FW = 161.1] was used for the determination.  $^1\text{H}$  NMR (400 MHz, dimethyl sulfoxide (DMSO)- $d_6$ ):  $\delta$  8.16–6.61 (br,  $-\text{OH}$ ),  $\delta$  1.90–1.27 (br,  $-\text{CH}_2\text{P}-$ ),  $\delta$  1.15–0.39 (br,  $-\text{CH}_2\text{Si}-$ ).  $^{29}\text{Si}$  NMR (79.5 MHz, DMSO- $d_6$ ):  $\delta$   $-56.3$  to  $-61.1$  ( $T^2$ ),  $\delta$   $-64.2$  to  $-72.1$  ( $T^3$ ).  $^{31}\text{P}$  NMR (161.9 MHz, DMSO- $d_6$ ):  $\delta$  31.1–26.2. IR (KBr):  $1187 \text{ cm}^{-1}$  (P=O of phosphonic acid group),  $1009$  and  $938 \text{ cm}^{-1}$  (P–OH of phosphonic acid group),  $1135$  and  $1041 \text{ cm}^{-1}$  (Si–O–Si).

### 2.3. Preparation of PSQ-PO<sub>3</sub>HK

**PSQ-PO<sub>3</sub>H<sub>2</sub>** ( $0.0217 \text{ g}$ ,  $0.134 \text{ mmol}$  unit) was dissolved in water ( $0.67 \text{ mL}$ ) and  $0.2 \text{ mol/L}$  KOH aq. ( $0.67 \text{ mL}$ ,  $0.134 \text{ mmol}$ ) were added to this solution. After the resulting solution was stirred at room temperature for 1 h, it was dried on a glass substrate ( $2.8 \text{ cm} \times 4.8 \text{ cm} = 13.4 \text{ cm}^2$ ) at room temperature to obtain a cast film of **PSQ-PO<sub>3</sub>HK** ( $0.01 \text{ mmol cm}^{-2}$ ).

### 2.4. Measurements

The  $^1\text{H}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  NMR spectra were recorded using an ECX-400 spectrometer (JEOL Ltd.). The IR spectra were recorded using an FTIR-8400 spectrometer (SHIMADZU Co.). The  $M_{w,s}$  were estimated from a Debye plot constructed with data obtained by the static light scattering (SLS) analyses in DMSO using a ELSZ-2000ZS (Otsuka Electronics Co., Ltd.). The atomic ratios of the products were confirmed by the energy-dispersive X-ray (EDX) analyses using an XL30 scanning electron microscope (FEI Co.). The X-ray diffraction (XRD) patterns were recorded at a  $2\theta$  scanning speed of  $1.8^\circ \text{ min}^{-1}$  using an X'Pert Pro diffractometer (PANalytical) equipped with a Ni-filtered  $\text{Cu K}\alpha$  radiation source ( $0.15418 \text{ nm}$ ). The TEM observations were performed using a JEOL JEM-2100 electron microscope operated at  $200 \text{ kV}$  acceleration voltage. The sample was dissolved in pure water at  $1.0\%$  (w/v), and then  $10 \mu\text{L}$  of the resulting sample solution was dropped onto a carbon-coated grid (Oken Shouji Co.) with a surface made hydrophilic by glow discharge treatment under reduced pressure. After 3 min, the sample on the grid was blotted using filter paper and the grid was air-dried. The digital TEM data were obtained using a slow-scan charge-coupled device (CCD) camera (Gatan USC1000, Gatan Inc.) and converted into images with a frame size of  $1024 \times 1024$  pixels. The differential scanning calorimetry (DSC) analyses were performed on a DSC-60 Plus (SHIMADZU Co.). The sample was placed in an aluminium capsule and cooled to  $-120 \text{ }^\circ\text{C}$  at a rate of  $20 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen flow ( $50 \text{ mL min}^{-1}$ ) and subsequently heated from  $-120 \text{ }^\circ\text{C}$  to  $180 \text{ }^\circ\text{C}$  at the same rate. The curve in third set (from  $-120 \text{ }^\circ\text{C}$  to  $180 \text{ }^\circ\text{C}$  at a rate of  $20 \text{ }^\circ\text{C min}^{-1}$ ) was used as data to eliminate the heat histories in the samples. The thermogravimetric analyses (TGA) were performed on an Exstar TG/DTA6200 (Seiko Instruments Inc.) at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  to  $1000 \text{ }^\circ\text{C}$ ; samples were analyzed separately under atmospheres of flowing nitrogen and oxygen ( $250 \text{ mL min}^{-1}$ ). The pyrolysis temperatures were determined from the  $5\%$  ( $T_{d5}$ ) and  $10\%$  ( $T_{d10}$ ) weight losses. The proton conductivity was measured in the temperature range from  $20$  to  $80 \text{ }^\circ\text{C}$  and at  $90\%$  relative humidity (RH) by complex impedance spectroscopy using a chemical impedance meter (model 3532–80, HIOKI E. E. Corp.).

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