



# Preparation and thermal properties of soluble polysilsesquioxanes containing hydrophobic side-chain groups and their hybridization with organic polymers



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## ABSTRACT

In this study, a series of soluble polysilsesquioxanes (PSQs) containing hydrophobic side-chain groups (**PSQ-Ph**, **PSQ-CyC<sub>6</sub>**, **PSQ-C<sub>6</sub>**, and **PSQ-C<sub>11</sub>**) were prepared by the facile reaction of a ladder-like PSQ containing ammonium groups with the corresponding hydrophobic carboxylic acid chlorides (i.e., benzoyl, cyclohexanecarbonyl, heptanoyl, and dodecanoyl chlorides, respectively) in the presence of triethylamine in a mixed solvent of water and *N,N*-dimethylformamide. The resulting hydrophobic PSQs were soluble in chloroform. The weight-average molecular weights of the hydrophobic PSQs estimated by gel permeation chromatography with chloroform as the eluent and polystyrene standards ranged from  $1.92 \times 10^4$  to  $6.49 \times 10^4$ . The pyrolysis temperatures of **PSQ-Ph** estimated by thermogravimetric analyses were relatively high ( $T_{d5} = 391$  °C and  $T_{d10} = 425$  °C) due to the presence of the thermally stable phenyl side-chain groups and Si–O–Si main-chain. Moreover, hybrid films of the hydrophobic PSQs and two organic polymers, poly(methyl methacrylate) (**PMMA**) and polystyrene (**PS**), were prepared by drying the chloroform solutions of the mixtures of these polymers. The **PMMA/PSQ-C<sub>6</sub>**, **PMMA/PSQ-C<sub>11</sub>**, and **PS/PSQ-Ph** hybrids were highly transparent. For **PS/PSQ-Ph** hybrid films, the thermal stability increased with increasing amount of **PSQ-Ph**.

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## 1. Introduction

Silsesquioxanes (SQs), which have the general formula  $[\text{RSiO}_{1.5}]_n$ , are a class of siloxane-based materials that exhibit superior thermal, mechanical, and chemical stabilities derived from the siloxane (Si–O–Si) bond framework [1,2]. In addition, they have attracted considerable attention in organic–inorganic hybrid material research in both academic and industrial settings because they are inorganic materials with remarkable compatibilities with organic materials such as polymers [3–9].

Although polyhedral oligomeric silsesquioxane (POSS) compounds containing various types of side-chain groups are well known as soluble SQs [10–18], polymeric SQs (PSQs), such as ladder-like PSQs, have only been obtained in the limited cases [19–26] because PSQs are prepared by the hydrolytic polycondensation of trifunctional silane monomers. The

polycondensation of these monomers generally results in the formation of insoluble PSQs with irregular three-dimensional network (random) structures. Therefore, polymeric materials containing POSS components in their side [27–33] or main chains [34–43] have developed as soluble PSQs.

The side-chain groups of the soluble ladder-like PSQs prepared by the hydrolytic condensation of trifunctional silane compounds are often restricted to aryl groups, such as phenyl [19,20], disc-like triphenylene [22], carbazole [24], and dibenzothiophene [25] groups. On the other hand, it is difficult to prepare soluble ladder-like PSQs containing aliphatic side-chain groups by the hydrolytic polycondensation of trifunctional silane compounds. To prepare ladder-like PSQs containing methyl groups, it is necessary to first synthesize cyclic tetrasiloxane derivatives with controlled stereostructures as precursors [21,23,26]. Complicated synthetic reaction, separation, and purification are required to form these cyclic tetrasiloxane derivatives. Therefore, 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 was not reported until the

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previous our following reports [44–53]. The development of such functional ladder-like PSQs would likely allow the preparation of many kinds of soluble ladder-like PSQs via simple polymer reactions (introduction reactions) with various compounds.

To date, we have successfully prepared soluble ladder-like (rod-like) PSQs by the hydrolytic polycondensation of organotrialkoxysilanes containing substituent groups that can be converted into ionic groups during the reaction; for example, amino groups can be converted to ammonium cations [44–51], cyano groups can be converted to carboxylate anions [52], and mercapto groups can be converted to sulfonate anions [53]. These PSQs form hexagonally stacked structures in the solid state. The ionic side-chain groups prepared from the monomers and catalysts during hydrolytic polycondensation were found to be essential for the formation of these soluble PSQs with regular structures. In particular, ladder-like PSQs containing ammonium groups can be easily converted into soluble PSQs with various side-chain groups such as phthalimido [54], chiral [55,56], and (meth)acrylamido [57,58] groups.

In this study, a series of soluble PSQs containing hydrophobic side-chain groups were prepared by the facile reaction of an ammonium-group-containing ladder-like PSQ with the corresponding hydrophobic carboxylic acid chlorides (benzoyl, cyclohexanecarbonyl, heptanoyl, and dodecanoyl chlorides). The thermal properties of the resulting hydrophobic PSQs were then investigated. In addition, the hybrids of two organic polymers, poly(methyl methacrylate) (PMMA) and polystyrene (PS), with the resulting hydrophobic PSQs were prepared by drying the chloroform solutions of the mixtures of these polymers, and their optical and thermal properties were investigated.

## 2. Experimental section

### 2.1. Materials

An ammonium-group-containing ladder-like PSQ (PSQ-NH<sub>3</sub>Cl; weight-average molecular weight ( $M_w$ ) = ca.  $1.20 \times 10^4$ , estimated by static light scattering (SLS)) was prepared according to a literature procedure by the hydrolytic polycondensation of 3-aminopropyltrimethoxysilane monomers in aqueous hydrochloric acid [44,49]. PMMA ( $M_w$  = ca.  $4.43 \times 10^4$  and molecular weight distribution ( $M_w/M_n$ ) = 1.78, estimated by gel permeation chromatography (GPC)) and PS ( $M_w$  = ca.  $9.56 \times 10^3$  and  $M_w/M_n$  = 2.39, estimated by GPC) were prepared via the free-radical polymerization of the corresponding monomers (50 mmol), methyl methacrylate (purity = ca. 98%, 5.108 g) and styrene (purity = ca. 99%, 5.260 g), initiated with 2,2'-azobis(isobutyronitrile) (AIBN; purity = ca. 98%, 0.168 g, 1.0 mmol) under an argon atmosphere in degassed toluene (10 mL) at 80 °C for 5 h followed by reprecipitation from methanol (600 mL). Other reagents and solvents were commercially purchased and used without further purification.

### 2.2. Preparation of soluble PSQs containing hydrophobic side-chain groups

#### 2.2.1. Preparation of PSQ containing phenyl side-chain groups (PSQ-Ph)

*N,N*-Dimethylformamide (DMF, 2.0 mL) was added to an aqueous solution (3.0 mL) of PSQ-NH<sub>3</sub>Cl (0.147 g, 1.0 mmol unit), and the resulting mixture was stirred at room temperature for 30 min to obtain a homogeneous solution. Subsequently, triethylamine (purity = ca. 99%, 0.511 g, 5.0 mmol) and a solution of benzoyl chloride (purity = ca. 99%, 0.568 g, 4.0 mmol) in DMF (1.0 mL) were successively added under vigorous stirring at room temperature, and the solution was stirred for an additional 5 min.

After the addition of 1.0 mol/L aqueous hydrochloric acid (6.0 mL, 6.0 mmol) to this mixture, the precipitated product was isolated by filtration, washed with diethyl ether (ca. 50 mL) and water (ca. 100 mL), and then dried under reduced pressure at room temperature to yield 0.160 g of PSQ containing phenyl side-chain groups. This PSQ is hereafter denoted as PSQ-Ph (yield = ca. 75% based on the ideal chemical formula of one unit of this product [SiO<sub>1.5</sub>(CH<sub>2</sub>)<sub>3</sub>NHC(=O)C<sub>6</sub>H<sub>5</sub>, FW = 214.3]). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.05–6.90 (br, aromatic, overlapping with solvent), δ 3.65–2.95 (br, –CH<sub>2</sub>NHC(=O)–), δ 2.10–1.46 (br, –SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHC(=O)–, overlapping with residual water), δ 0.95–0.30 (br, –SiCH<sub>2</sub>–). IR (KBr): 1639 and 1543 cm<sup>–1</sup> (amido group), 1130 and 1041 cm<sup>–1</sup> (siloxane bond).

#### 2.2.2. Preparation of PSQ containing cyclohexyl side-chain groups (PSQ-CyC<sub>6</sub>)

The reaction procedures were the same as those described above for the preparation of PSQ-Ph except that the hydrophobic carboxylic acid chloride was cyclohexanecarbonyl chloride (purity = ca. 97%, 0.605 g, 4.0 mmol), and the washing solvents were water (ca. 80 mL) and acetone (ca. 60 mL). Consequently, 0.144 g of the product was obtained. This PSQ is hereafter denoted as PSQ-CyC<sub>6</sub> (yield = ca. 66% based on the ideal average chemical formula of one unit of this product [SiO<sub>1.5</sub>(CH<sub>2</sub>)<sub>3</sub>NHC(=O)C<sub>6</sub>H<sub>11</sub>, FW = 220.3] × 0.972 + [SiO<sub>1.5</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>Cl, FW = 146.7] × 0.028 = 218.2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.80–2.70 (br, –CH<sub>2</sub>NHC(=O)– and –CH<sub>2</sub>NH<sub>3</sub>), δ 2.63–2.10 (br, –NHC(=O)CH<, δ 2.10–0.98 (br, –CH<sub>2</sub>– of cyclohexyl group, –SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHC(=O)–, and –SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>, overlapping with residual water), δ 0.95–0.18 (br, –SiCH<sub>2</sub>–). IR (KBr): 1647 and 1547 cm<sup>–1</sup> (amido group), 1142 and 1034 cm<sup>–1</sup> (siloxane bond).

#### 2.2.3. Preparation of PSQ containing hexyl side-chain groups (PSQ-C<sub>6</sub>)

The reaction procedures were the same as those described above for the preparation of PSQ-Ph and PSQ-CyC<sub>6</sub> except that the hydrophobic carboxylic acid chloride was heptanoyl chloride (purity = ca. 98%, 0.607 g, 4.0 mmol) and the washing solvents were water (ca. 100 mL) and methanol (ca. 100 mL). Consequently, 0.079 g of the product was obtained. This PSQ is hereafter denoted as PSQ-C<sub>6</sub> (yield = ca. 36% based on the ideal chemical formula of one unit of this product [SiO<sub>1.5</sub>(CH<sub>2</sub>)<sub>3</sub>NHC(=O)C<sub>6</sub>H<sub>13</sub>, FW = 222.4]). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.45–2.85 (br, –CH<sub>2</sub>NHC(=O)–), δ 2.42–2.08 (br, –NHC(=O)CH<sub>2</sub>–), δ 1.83–1.43 (br, –SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHC(=O)– and –NHC(=O)CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, overlapping with residual water), δ 1.43–1.18 (br, –NHC(=O)CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), δ 0.95–0.78 (br, –CH<sub>3</sub>), δ 0.75–0.35 (br, –SiCH<sub>2</sub>–). IR (KBr): 1643 and 1554 cm<sup>–1</sup> (amido group), 1138 and 1034 cm<sup>–1</sup> (siloxane bond).

#### 2.2.4. Preparation of PSQ containing undecyl side-chain groups (PSQ-C<sub>11</sub>)

The reaction procedures were the same as those described above for the preparation of PSQ-CyC<sub>6</sub> except that the hydrophobic carboxylic acid chloride was dodecanoyl chloride (purity = ca. 98%, 0.893 g, 4.0 mmol). Consequently, 0.245 g of the product was obtained. This PSQ is hereafter denoted as PSQ-C<sub>11</sub> (yield = ca. 84% based on the ideal chemical formula of one unit of this product [SiO<sub>1.5</sub>(CH<sub>2</sub>)<sub>3</sub>NHC(=O)C<sub>11</sub>H<sub>23</sub>, FW = 292.5]). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.45–2.85 (br, –CH<sub>2</sub>NHC(=O)–), δ 2.45–2.03 (br, –NHC(=O)CH<sub>2</sub>–, overlapping with residual acetone), δ 1.95–1.45 (br, –SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHC(=O)– and –NHC(=O)CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), δ 1.45–1.02 (br, –NHC(=O)CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), δ 0.99–0.80 (br, –CH<sub>3</sub>), δ 0.75–0.25 (br, –SiCH<sub>2</sub>–). IR (KBr): 1647 and 1551 cm<sup>–1</sup> (amido group), 1147 and 1034 cm<sup>–1</sup> (siloxane bond).

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