



Preparation of a soluble polysilsesquioxane containing a macrocyclic structure and capture of palladium ions

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Abstract

In this study, a soluble polysilsesquioxane containing a macrocyclic structure (PSQ-MC) was successfully prepared by the hydrolytic condensation of a dual site-type silane coupling agent, i.e., bis{3-[3-(trimethoxysilyl)propylthio]propyl}phthalate (BTTP), using hydrochloric acid as the catalyst in an acetone/ethyl acetate mixed solvent. Based on the results of ²⁹Si NMR and gel permeation chromatography and the fact that the dimer of the cyclized BTTP was present in the intermediate after the reaction of BTTP in a dilute solution at room temperature, PSQ-MC was assumed to be a polymer in which an 8-membered cyclic siloxane with two 23-membered rings was linked by a single siloxane bond. In addition, PSQ-MC was able to capture palladium ions.

Introduction

Polymers containing macrocyclic structures that can capture ions or molecules depending on the ring size and functional groups have promise as metal scavengers and stationary phases for chromatographic separation [1–4]. Cyclopolymerization is used to prepare such polymers with representative examples being crown ether-containing polymers [1–8]. To facilitate the formation of a macrocyclic structure, polymerization is typically performed in the presence of appropriate templates [9–12]. In addition to this method, another preparation strategy involves cyclopolymerization utilizing the defined conformation of a cyclohexane ring and a hydrogen bond of a urethane bond [13, 14]. As described above, a number of polymers containing macrocyclic structures have been developed thus far. However, in all cases, the main chains comprise organic bonds. To our knowledge, the preparation of polymers containing

macrocyclic structures with inorganic main chains has not been reported thus far

The sol–gel method has been employed for the facile formation of inorganic framework materials, such as silica gels and various metal oxides [15]. Furthermore, silsesquioxanes (SQs) can also be obtained by this reaction, which have recently attracted the field of organic–inorganic hybrid materials from the perspectives of both academic and research applications [16–23]. SQs constituting the (RSiO_{1.5})_n structure are typically prepared by the sol–gel reaction (hydrolytic condensation) of trifunctional silanes (so-called silane coupling agents), such as organotrialkoxysilanes and organotrichlorosilanes. This interest stems from their various functional groups as side chains (R) because of their remarkable compatibility with organic materials like polymers [24–27], in addition to their superior thermal and chemical stabilities due to the siloxane (Si–O–Si) bond frameworks with a high bond energy. The hydrolytic condensation of such trifunctional silanes is often facile and forms randomly structured (three-dimensional) insoluble polySQs (PSQs) [17] or polyhedral oligomeric SQs (POSSs) [28–38]. Because of the insolubility of randomly structured PSQs, composite manufacturing is difficult after PSQ preparation. In addition, because POSSs are typically crystalline oligomers, they do not exhibit film-forming properties. Meanwhile, PSQs with one-dimensional structures, such as ladder-like PSQs [39–43] and polymers containing POSS units in their main chains [44–46], exhibit excellent solubilities and film-forming properties, in

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addition to the typical characteristics of SQs. Thus far, our group has reported the facile preparation of soluble ladder-like PSQs containing ionic side chains by the hydrolytic condensation of organotrialkoxysilanes containing functional side-chain groups, which can be converted into ionic groups during reactions [23, 47–53]. Furthermore, our group has also reported a convenient one-step method for preparing soluble POSS-linking polymers via hydrolytic condensation [54]. However, the preparation of these structurally controlled soluble PSQs is not typical, and types of side-chain structures are limited. Therefore, the preparation of PSQs as inorganic polymers containing macrocyclic structures has not been reported, as described above.

In this study, a new PSQ was prepared, which combines the properties of polymers containing macrocyclic structures and structurally controlled soluble PSQs. To achieve this goal, a dual site-type silane coupling agent, bis{3-[3-(trimethoxysilyl)propylthio]propyl}phthalate (BTPP), was evaluated, which was used to prepare highly dispersible zirconia nanoparticles [55]. Because the structure of this silane coupling agent is flanked by two alkoxysilyl-containing substituents bonded to the ortho position of the benzene ring, it was assumed that intramolecular cyclization preferentially occurs during the reaction in a dilute solution, and intermolecular condensation occurs via an increase in the concentration and temperature of the reaction solution. In this paper, the preparation and characterization of a soluble PSQ containing macrocyclic structure (PSQ-MC) and its formation mechanism and the capture of palladium (Pd) ions using PSQ-MC are described.

Experimental

Materials

BTPP was prepared according to previously-reported procedures [55]. Other reagents and solvents were commercially purchased and used without further purification.

Preparation of PSQ-MC

PSQ-MC was prepared by the following procedure. Concentrated hydrochloric acid (HCl) (36%, 1.519 g, 15.0 mmol) was diluted with acetone to prepare a 1.0 mol L⁻¹ solution (15 mL), and this solution was added to an ethyl acetate solution of BTPP (ca. 0.1 mol L⁻¹), which was prepared by mixing BTPP (3.195 g, 5.0 mmol) with ethyl acetate (50 mL) while stirring at room temperature. The resulting solution was further stirred for 24 h at room temperature. Next, this solution was heated ca. 50 °C in an open system until the solvent was completely evaporated to accelerate the condensation. The resulting solid

product was maintained at 100 °C for 2 h. Subsequently, after dissolving the product in ethyl acetate (ca. 20 mL) and concentrating (ca. 5.0 mL) using a rotary evaporator, the solution was added to toluene (ca. 250 mL) for precipitation. Then, the toluene-insoluble part was recovered by decantation and washed with toluene (ca. 20 mL × 3) to remove the low-molecular-weight compounds. The resulting product was dried under reduced pressure at room temperature to yield PSQ-MC as a yellow solid in 0.775 g (yield = ca. 31% based on the ideal average chemical formula of one unit of this product, i.e., C₂₀H₂₈O₇Si₂S₂, FW = 500.7). ¹H NMR (400 MHz, CDCl₃): δ 7.76–7.63 and 7.58–7.45 (br, 4H, Ph), δ 4.50–4.23 (br, 4H, –SCH₂CH₂CH₂OC(=O)–), δ 2.74–2.41 (br, 8H, –SiCH₂CH₂CH₂SCH₂–), δ 2.09–1.87 (br, 4H, –SCH₂CH₂CH₂OC(=O)–), δ 1.85–1.54 (br, 4H, –SiCH₂CH₂CH₂S–), δ 0.94–0.61 (br, 4H, –SiCH₂CH₂CH₂S–). IR (KBr): 1126 and 1045 cm⁻¹ (siloxane bond). Solid-state ²⁹Si NMR: δ –50 to –62 (T²), δ –62 to –73 (T³).

Isolation of the intermediate derivative

The intermediate derivative was isolated via the following procedure. Concentrated HCl (36%, 0.304 g, 3.0 mmol) was diluted in acetone to prepare a 1.0 mol L⁻¹ solution (3.0 mL), and this solution was added to an ethyl acetate solution of BTPP (ca. 0.1 mol L⁻¹), which was prepared by mixing BTPP (0.639 g, 1.0 mmol) with ethyl acetate (10 mL) while stirring at room temperature. The resulting solution was further stirred for 24 h. Subsequently, triethylamine (purity: 99%, 1.022 g, 10.0 mmol) and chlorotrimethylsilane (purity: 98%, 1.109 g, 10.0 mmol) were added to the resulting solution, which was further stirred ca. 50 °C for 24 h. After removing the insoluble part via filtration, the soluble part was concentrated (ca. 5.0 mL) using a rotary evaporator. Then, the resulting solution was added to water (ca. 250 mL). The water-insoluble part was isolated via decantation, washed with water (ca. 20 mL × 3), and dried under reduced pressure at room temperature. The resulting crude product was dissolved in ethyl acetate (ca. 20 mL), and the solution was concentrated (ca. 5.0 mL) using a rotary evaporator. After the resulting solution was added to methanol (ca. 250 mL), the methanol-soluble part was isolated by decantation, and methanol was removed using a rotary evaporator. The resulting product was dried under reduced pressure at room temperature to yield the trimethylsilylated intermediate as a light yellow sticky solid in 0.125 g (yield = ca. 21% based on the chemical formula of the dimer of cyclized BTPP containing two trimethylsilyl groups, i.e., C₄₆H₇₆O₁₆Si₆S₄, FW = 1181.9, because the introduction ratio of the silylating agent was equimolar to BTPP, which was confirmed by the ¹H NMR spectrum of the trimethylsilylated intermediate). ¹H NMR (400 MHz,

CDCl_3): δ 7.77–7.67 and 7.59–7.49 (br, 4H, Ph), δ 4.47–4.32 (br, 4H, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})-$), δ 2.68–2.47 (br, 8H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2-$), δ 2.06–1.93 (br, 4H, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})-$), δ 1.79–1.54 (br, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}-$), δ 0.85–0.60 (br, 4H, $-\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}-$), δ 0.17–0.06 (br, 9H, $-\text{SiOSiCH}_3$).

Capture of Pd ions using PSQ-MC

The typical experimental procedure for capturing Pd ions using PSQ-MC was as follows. Palladium(II) chloride (PdCl_2) (purity: 98%, 0.011 g, 0.06 mmol) was dissolved in aqueous HCl (1.0 mol L^{-1} , 30 mL), and this solution was added to PSQ-MC (0.090 g, 0.18 mmol unit) in chloroform (30 mL). After this solution with two phases was vigorously stirred for 30 min at room temperature, the solvent in the colored chloroform phase was evaporated to obtain the solid product.

Measurements

^1H NMR spectra were recorded on an ECX-400 spectrometer (JEOL RESONANCE, Inc., Tokyo, Japan). Solid-state ^{29}Si NMR spectra were recorded on an ECX-400 NMR spectrometer (JEOL RESONANCE, Inc., Tokyo, Japan) operating at a ^{29}Si frequency of 79.43 MHz (under a static magnetic field of 9.4 T). A double-resonance probe with an 8 mm MAS probe head was used. The sample was packed into a zirconia magic-angle spinning rotor. The MAS spinning speed was set to 2.5 kHz (± 2 Hz), and experiments were performed at room temperature. A single-pulse excitation method with high-power proton decoupling was employed to obtain the ^{29}Si NMR spectra. The 90° pulse lengths were 7.2 μs for ^1H and 6.5 μs for ^{29}Si . Two-pulse phase modulation ^1H dipolar decoupling with a ^1H field strength of 83.3 kHz was applied during the detection of free-induction decay. The dwell time and acquisition time were 62.94 μs and 16.11 ms, respectively, and a pulse delay of 140 s was used. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer (JASCO Corporation, Tokyo, Japan). The weight-average molecular weights (M_w) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) using polystyrene standards. GPC analyses were performed using a HITACHI pump L-2130 and a HITACHI RI detector L-2490 (Hitachi High-Tech Science Corporation, Tokyo, Japan) on Shodex GPC KF-805L (bead size: 10 μm , measurable molecular weight range: from 10^2 to 4×10^6) and KF-803L columns (bead size: 6 μm , measurable molecular weight range: from 10^2 to 7×10^4). As the eluent, chloroform was pumped through the system at a flow rate of 1.0 mL min^{-1} at 40 $^\circ\text{C}$. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements of

the products were performed using a Voyager Biospectrometry Workstation Ver. 5.1 (SHIMADZU Co., Kyoto, Japan) with 2,5-dihydroxybenzoic acid (DHB) as the matrix in the positive ion mode. The atom ratios of Pd/S in the products were confirmed by energy-dispersive X-ray (EDX) analyses using an XL30 scanning electron microscope (FEI Co. Japan Ltd, Tokyo, Japan).

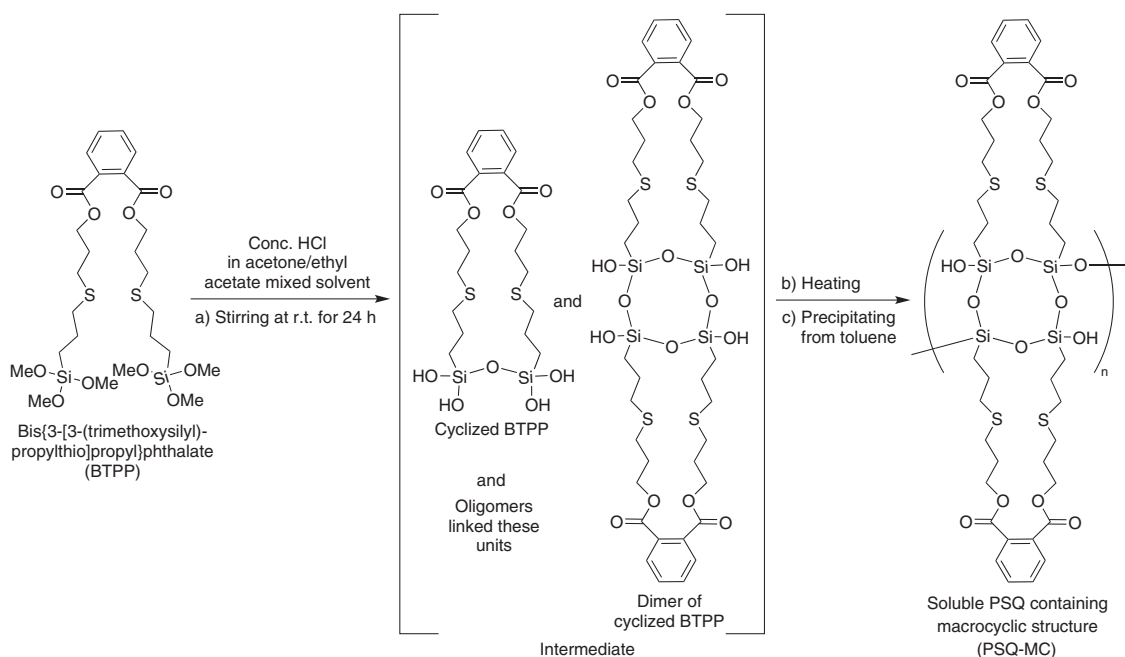
Results and discussion

Preparation and characterization of PSQ-MC

PSQ-MC was prepared via the following two-step reaction. In the first step, concentrated HCl was diluted with acetone to prepare a 1.0 mol L^{-1} solution, followed by the addition of this solution to an ethyl acetate solution of BTTP (ca. 0.1 mol L^{-1}) while stirring at room temperature. Next, the resulting solution was further stirred for 24 h (Scheme 1a). At this stage, the feed molar ratio of HCl to BTTP was 3:1. In the second step, this solution was heated ca. 50 $^\circ\text{C}$ in an open system until the solvent was completely evaporated (Scheme 1b). To remove low-molecular-weight compounds, after dissolving the product in ethyl acetate, the solution was added to toluene for precipitation (Scheme 1c). The toluene insoluble part was recovered by decantation, washed with toluene, and dried under reduced pressure to yield PSQ-MC (yield = 31%). PSQ-MC was soluble in dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetone, ethyl acetate, and chloroform, but it was insoluble in water, methanol, toluene, and *n*-hexane. The ^1H NMR spectrum of PSQ-MC in CDCl_3 exhibited peaks corresponding to the polymer side chain structure (Fig. 1).

To confirm the formation of the Si–O–Si bonds in PSQ-MC, IR and solid-state ^{29}Si NMR analyses were performed. The IR spectrum of PSQ-MC exhibited large absorption peaks at 1126 and 1045 cm^{-1} , which corresponded to the Si–O–Si bonds (Fig. 2). The solid-state ^{29}Si NMR spectrum of PSQ-MC exhibited peaks in the T^2 and T^3 regions at -50 to -62 ppm and -62 to -73 ppm, respectively (Fig. 3). Their integral ratio was ca. 1:1, which revealed the presence of large amount of Si–OH groups in the product. In addition, the M_w (M_w/M_n) of ca. 3.81×10^4 (2.16) for PSQ-MC was estimated by GPC in chloroform (Fig. 4a). Based on these results, the hydrolytic condensation of BTTP was confirmed to progress, and a soluble polymer formed.

As described above, because PSQ-MC is a soluble high molecular weight polymer, it was assumed that this PSQ is not a polymer with a random structure. Conversely, ladder-like PSQs are typically known to be soluble PSQs. However, because PSQ-MC contained a large amount of Si–OH groups, the present PSQ is apparently not ladder-like PSQ,



Scheme 1 Preparation of the soluble polysilsesquioxane containing macrocyclic structure (PSQ-MC)

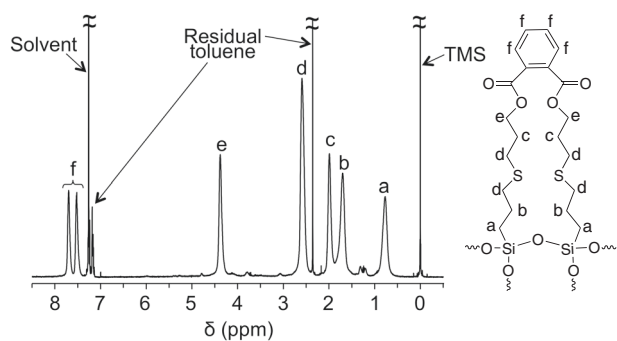


Fig. 1 ^1H NMR spectrum of PSQ-MC in CDCl_3 . Chemical shifts were referenced to tetramethylsilane (TMS, δ 0.0)

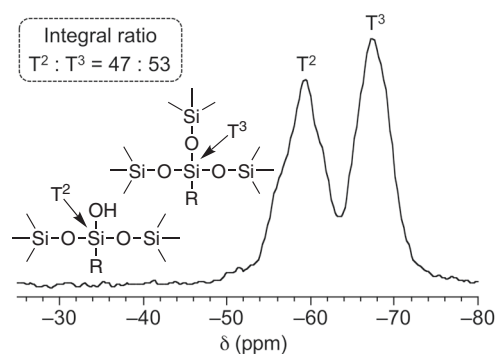


Fig. 3 Solid-state ^{29}Si NMR spectrum of PSQ-MC

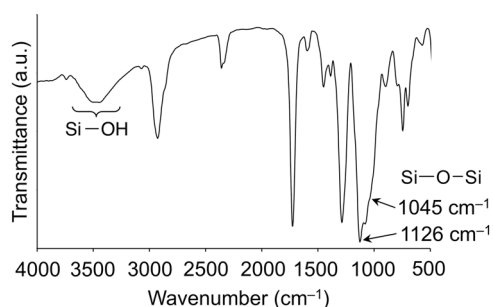


Fig. 2 IR spectrum of PSQ-MC

which contained a small amount of Si-OH groups. According to these results, the PSQ-MC structure is expected to include linking dimers of cyclized BTTP. Therefore, a dimer of cyclized BTTP as shown in Scheme 1 is likely formed as an intermediate during the first reaction step in a dilute solution at room temperature.

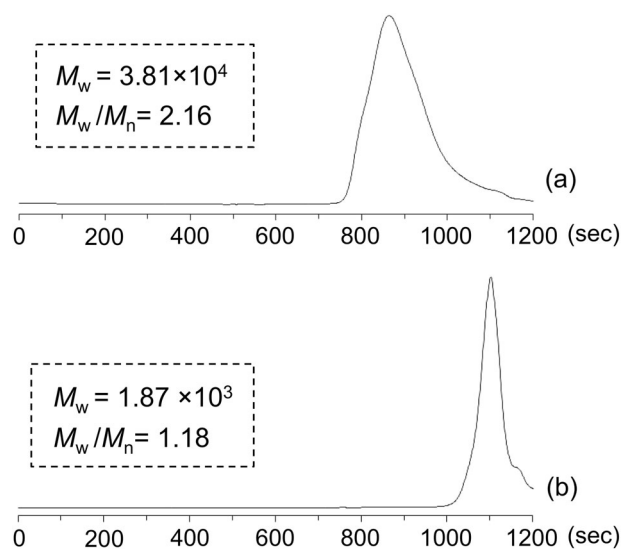
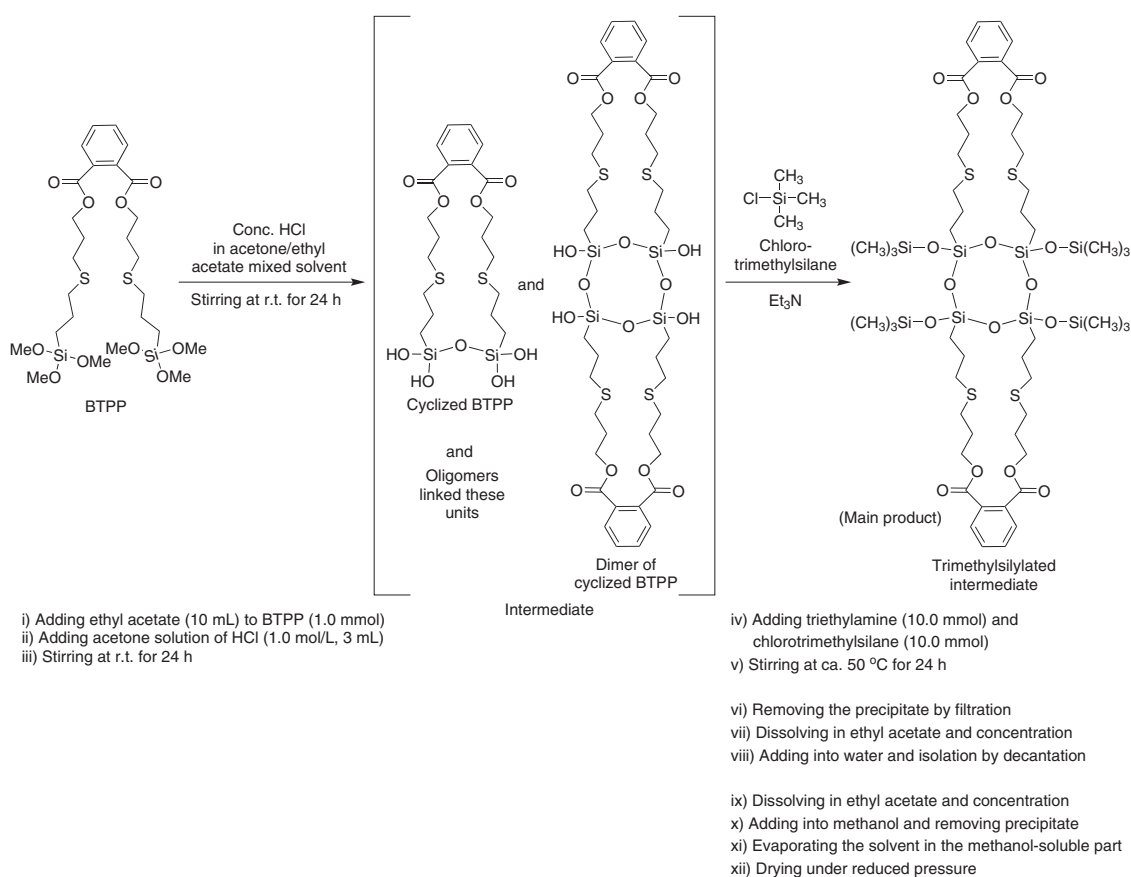


Fig. 4 GPC curves of (a) PSQ-MC and (b) the trimethylsilylated intermediate (eluent: chloroform, standard: polystyrenes)



Scheme 2 Procedure for trimethylsilylation of the intermediate

Isolation and characterization of the intermediate derivative

To confirm the structure of this intermediate, a stable compound was prepared via the protection of the Si–OH group in the intermediate using chlorotrimethylsilane as the silylating agent. This intermediate was protected via the continuous addition of triethylamine and chlorotrimethylsilane to the reaction solution, which was prepared in the first reaction step of BTTP using HCl in acetone/ethyl acetate at room temperature for 24 h, followed by stirring ca. 50 °C for 24 h (Scheme 2, i–v). After removing the precipitate via filtration, the filtrate was poured into water. Then, the water-insoluble part was recovered by decantation, washed with water, and dried under reduced pressure (Scheme 2, vi–viii). Subsequently, this product was dissolved in ethyl acetate, concentrated, and added into an excess amount of methanol. After removing the precipitate by decantation, the solvent in the methanol-soluble part was evaporated, and the resulting solid was dried under reduced pressure to obtain the product (Scheme 2, ix–xii).

The ^1H NMR spectrum of the product exhibited a signal corresponding to the trimethylsilyl group at

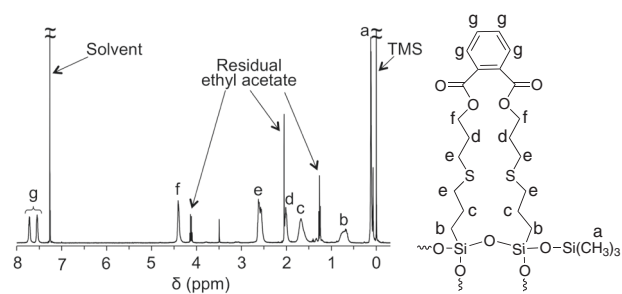


Fig. 5 ^1H NMR spectrum of the trimethylsilylated intermediate in CDCl_3 . Chemical shifts were referenced to TMS (δ 0.0)

0.17–0.06 ppm in addition to the signals corresponding to the side chain originating from BTTP, indicating that the protecting group was introduced into the intermediate (Fig. 5). However, the integral ratios also revealed that all silanol groups were not protected. In the GPC chart of the resulting product, a sharp peak corresponding to the oligomer with a M_w of 1.87×10^3 ($M_w/M_n = 1.18$) was observed (Fig. 4b).

In the MALDI-TOF mass spectrum of this product, the peaks corresponding to the masses of compound **i** in Fig. 6, where four Si–OH groups in the cyclized BTTP dimer were protected by the trimethylsilyl group,

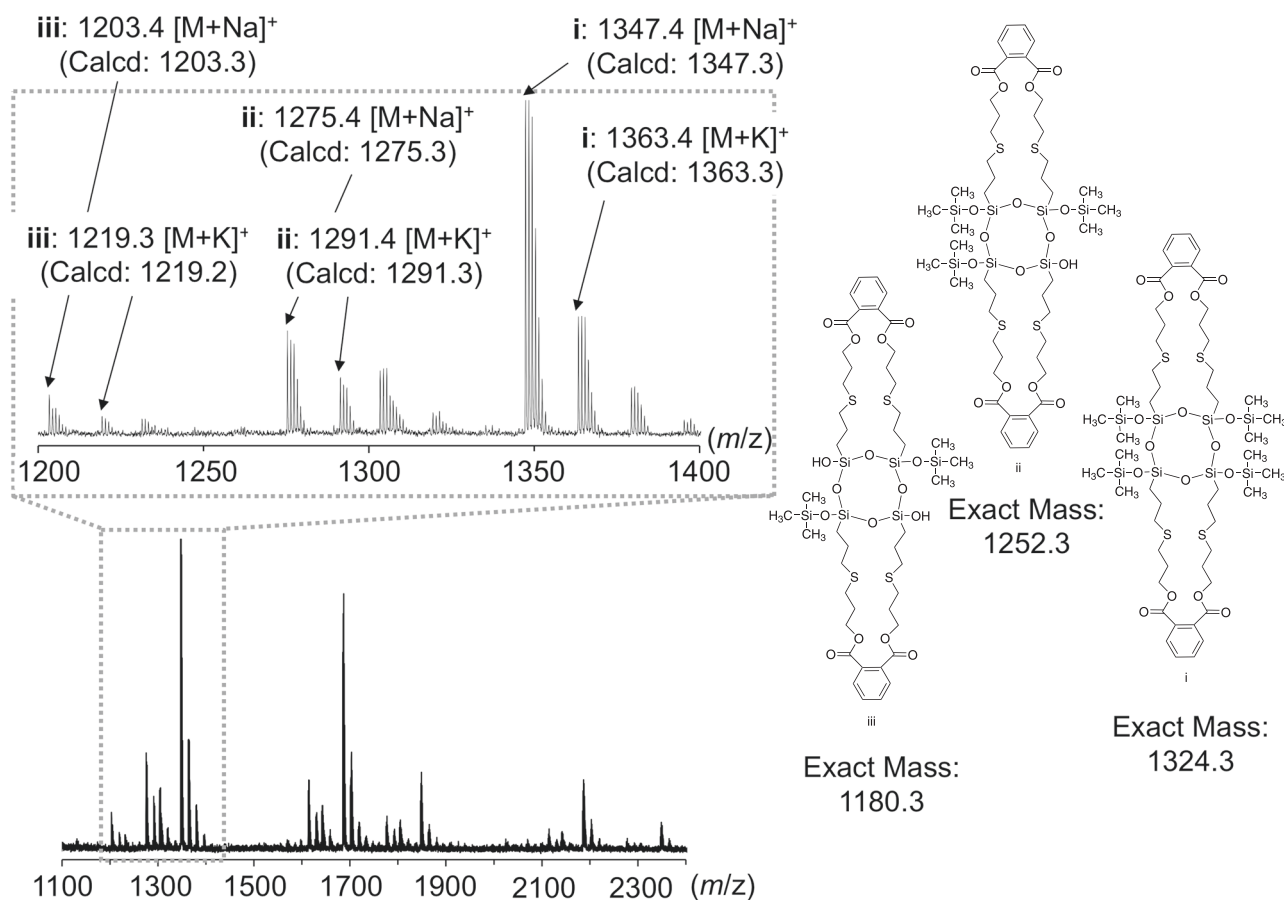


Fig. 6 MALDI-TOF mass spectrum of the trimethylsilylated intermediate

were mainly observed (found m/z 1347.4 $[M+Na]^+$; calcd 1347.3 and found m/z 1363.4 $[M+K]^+$; calcd 1363.3). In addition, several peaks corresponding to the dimers of cyclized BTTP containing three trimethylsilyl groups (compound ii: found m/z 1275.4 $[M+Na]^+$; calcd 1275.3 and found m/z 1291.4 $[M+K]^+$; calcd 1291.3) and two trimethylsilyl groups (compound iii: found m/z 1203.4 $[M+Na]^+$; calcd 1203.3 and found m/z 1219.3 $[M+K]^+$; calcd 1219.2) were observed (Fig. 6). However, several minor peaks were also observed.

Because these results suggested the formation of a cyclized BTTP dimer as shown in Scheme 1 after the first reaction step in the dilute solution at room temperature, this dimer was probably linked during the heating and concentration steps (second reaction step), leading to the formation of PSQ-MC. Perhaps all Si-OH groups in the dimers do not undergo condensation because of the steric hindrance of the bulky macrocyclic structure. Hence, the polymer containing the Si-OH groups was likely obtained. Based on the aforementioned results, PSQ-MC was concluded to be a polymer in which an 8-membered cyclic siloxane with two 23-membered rings is linked by a single siloxane bond (Scheme 1).

Necessity of the reaction in dilute solution at room temperature for the preparation of PSQ-MC

For comparison, to confirm that the reaction must be in a dilute solution at room temperature to prepare soluble PSQ-MC, a reaction of BTTP via heating and concentration was performed from the first step, i.e., without the reaction at room temperature for 24 h. The feed amounts of the starting material, catalyst, and solvents were the same as those utilized for the reaction as shown in Scheme 1. Consequently, most of the product was insoluble in common organic solvents and water. From the above results, a two-step reaction process (the dimer of cyclized BTTP was formed in dilute solution at room temperature in the first step and the condensation of the dimer via heating and concentration in the second step) was verified to be crucial to obtain soluble PSQ-MC.

Capture of Pd ions using PSQ-MC

As an application for PSQ-MC, the capture of Pd ions as a rare metal was investigated. Rare metals are globally scarce, and it is often difficult to find suitable alternatives

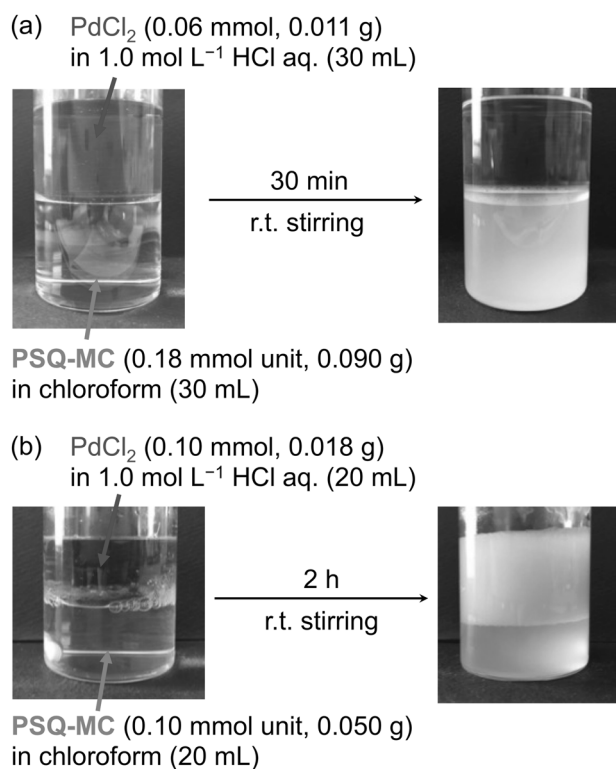


Fig. 7 Capture of Pd ions using PSQ-MC: Feed molar ratios of PdCl_2 to repeating units of PSQ-MC = (a) 1:3 and (b) 1:1

for applications in which they are utilized. Therefore, the efficient recovery of rare metals from nature, wastewater, and discarded high-tech products is crucial for the stable supply of rare metals and for general resource recycling and environmental sustainability. Because sulfur atoms can form specific interactions with rare metals, such as Pd, sulfur atom-containing polymers have been previously developed [56, 57]. Meanwhile, PSQ-MC also contains a sulfur atom in its macrocyclic side chains. Therefore, the capture of Pd ions using PSQ-MC was investigated. PdCl_2 was dissolved in aqueous HCl (1.0 mol L^{-1}), and this solution was added to a chloroform solution of PSQ-MC. First, it was investigated in a molar ratio of PdCl_2 to repeating units of PSQ-MC = 1:3 (Fig. 7a). Then, when this solution with two phases was vigorously stirred for 30 min at room temperature, the chloroform phase was visually confirmed to be colored. The EDX pattern of the solid product obtained by the evaporation of the solvent in the chloroform phase exhibited peaks corresponding to Pd (Pd/S atom ratio was 0.19) (Fig. 8a), which were not detected in that of PSQ-MC (Fig. 8b), indicating that PSQ-MC can capture Pd ions. Furthermore, when the capture of Pd ions using PSQ-MC was also investigated in a molar ratio of PdCl_2 to repeating units of PSQ-MC = 1:1 by stirring for 2 h at room temperature, an insoluble product precipitated in the aqueous phase (Fig. 7b). The insoluble

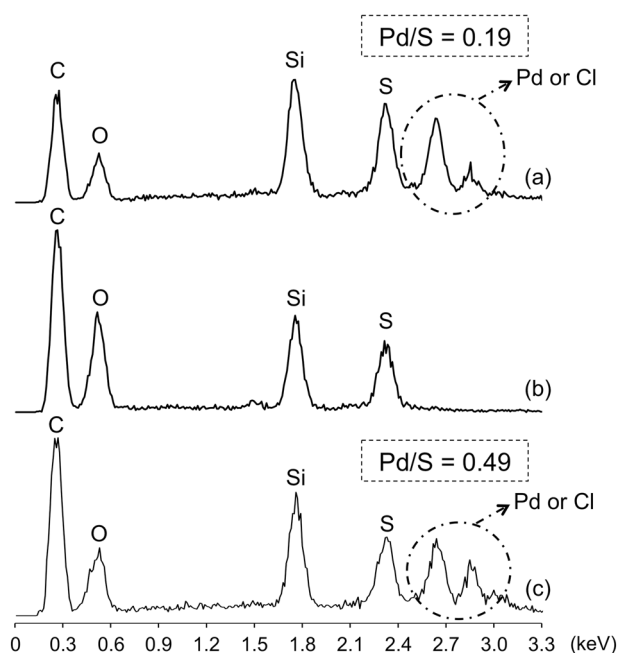


Fig. 8 EDX patterns of (a) the solid product recovered from the chloroform phase in the experiment shown in Fig. 7a, (b) PSQ-MC, and (c) the insoluble solid product in the experiment shown in Fig. 7b

product was recovered by filtration, and an EDX measurement of the product was performed. Consequently, the peaks derived from Pd were observed, and the Pd/S atom ratio (0.49) was higher than that of the product obtained in the aforementioned experiment (Fig. 8c). This value is likely the maximum capture amount of Pd for PSQ-MC. As a control experiment, when the same experiment as in Fig. 7a was performed using chloroform that does not contain PSQ-MC, the chloroform phase did not color at all. Furthermore, when the solvent of the chloroform phase was evaporated, no solid product was present. From these results, it is confirmed that PSQ-MC is involved in Pd ion capture.

Conclusions

In this study, a soluble PSQ containing macrocyclic structure, PSQ-MC, was successfully prepared by a two-step hydrolytic condensation of a dual site-type silane coupling agent, BTPP, using HCl as the catalyst in an acetone/ethyl acetate mixed solvent. Based on the ^{29}Si NMR and GPC results and the fact that the dimer of the cyclized BTPP was present in the intermediate after the first reaction step of BTPP in a dilute solution at room temperature, PSQ-MC was assumed to be a polymer in which an 8-membered cyclic siloxane with two 23-membered rings was linked by a single siloxane bond. In addition, PSQ-MC in chloroform could capture Pd ions in the aqueous phase.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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