

Synthesis of Poly(tetramethylsilapyrenylenesiloxane) Derivatives

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A novel disilanol monomer, i.e. 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**), was synthesized and underwent polycondensation to afford the corresponding poly(tetramethyl-1,6-silapyrenylenesiloxane). The soluble parts in common organic solvents obtained by the polycondensation of **M1** were expected to be the cyclic oligomers as deduced from the measurements of gel permeation chromatography as well as the NMR and IR spectroscopy. The insoluble parts in common organic solvents were expected to be the linear polymer with high molecular weight. Thus, the copolymer (**CP1**) was synthesized by the copolymerization of **M1** and 1,4-bis(dimethylhydroxysilyl)benzene was carried out to afford the corresponding copolymer (**CP1**), which was soluble in common organic solvents, such as tetrahydrofuran, dichloromethane, chloroform, toluene, and so on. The results of the differential scanning calorimetry (DSC) and thermogravimetry (TG) indicated that **CP1** exhibited the crystallinity with relatively high thermal stability.

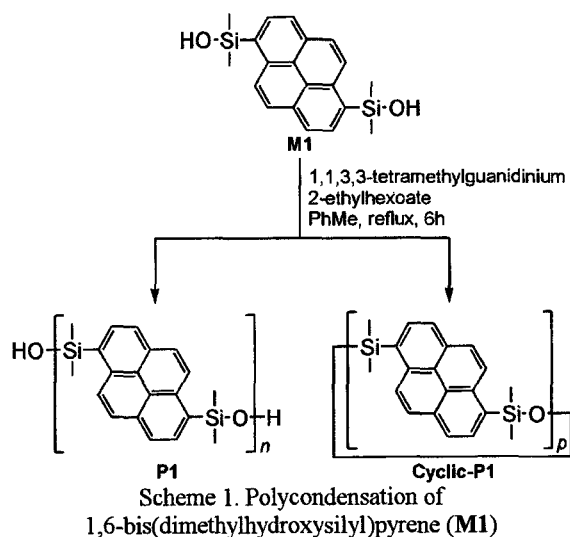
Key words: pyrene, polysiloxane, poly(tetramethylsilylenesiloxane), heat-resistant polymer

1. INTRODUCTION

Polysiloxanes have been well-known to exhibit the excellent properties, such as high bond energy between Si and O, flexibility of the main chain, low glass transition temperature (T_g), hydrophobicity based on alkyl side chain, thermostability, high gas-permeability, physiological and chemical inertness [1, 2]. Poly(tetramethyl-1,4-silphenylenesiloxane) (1,4-PTMPS) is a representative polymer where an aromatic moiety is incorporated into the polysiloxane backbone [3, 4], which would improve the excellent properties of poly(dimethylsiloxane) (PDMS) as mentioned above, especially the thermostability. There have been many reports for the synthesis of poly(tetramethylsilylenesiloxane) derivatives with various aromatics [5-13] via polycondensation of bis(dimethylhydroxysilyl) substituted aromatic compounds [5, 6, 9-13] or dehydrocoupling polymerization [7, 8]. The thermal properties of poly(tetramethylsilylenesiloxane) derivatives presumably depend on the kind of arylene moiety [9, 13].

On the other hand, poly(dimethylsiloxane-co-tetramethyl-1,4-silphenylenesiloxane) has been used as stationary phases for gas chromatography capillary columns [4] due to their excellent thermostability and good partitioning properties. The thermostability and partitioning properties of stationary phases would depend on the chemical structures of polymers used as stationary phases [4]. Therefore, poly(dimethylsiloxane-co-tetramethylsilylenesiloxane) derivatives having various aromatic moieties in the backbone would exhibit the different thermostability and partitioning properties from poly(dimethylsiloxane-co-tetramethyl-1,4-silphenylenesiloxane).

From these points of view, we report here the first attempt for synthesis of poly(tetramethylsilypyrenylenesiloxane) derivative via polycondensation of the corresponding disilanol derivative, i.e. 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**), as shown in Scheme 1.



2. Experimental

2.1 Materials

1,6-Dibromopyrene (**1**) was prepared from pyrene according to the literature of Grimshaw *et al* [14]. *n*-Butyllithium in hexane solution (2.6 mol/L, KANTO KAGAKU), chlorodimethylsilane (Acros Organics), 5% palladium on charcoal (Wako Pure Chemical Industries, Ltd.) were commercially available and used as received. 1,1,3,3-Tetramethylguanidinium 2-ethylhexoate was obtained from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.). *N,N,N',N'*-tetramethylethylenediamine (Tokyo Kasei Kogyo Co., Inc.) was used after distillation over calcium hydride. Toluene and tetrahydrofuran (THF, Wako Pure Chemical Industries, Ltd.) were used after distillation over sodium. The purity of all synthesized low molecular weight compounds was confirmed to be over 99% from GC analysis.

2.2 Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform (CDCl_3) or dimethylsulfoxide [$(\text{CD}_3)_2\text{SO}$] at ambient temperature. IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer. Melting point (T_m) and glass transition temperature (T_g) were determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under a nitrogen flow rate of $10\text{ mL}/\text{min}$. Thermogravimetry (TG) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Number-average (M_n) and weight-average (M_w) molecular weights were estimated by size-exclusion chromatography (SEC) on a SHOWA DENKO Shodex GPC-101 system with polystyrene gel columns (a pair of Shodex GPC LF-804), eluted with THF using a calibration curve of polystyrene standards. Gas chromatography-mass spectroscopy (GC/MS) was carried out using a Hitachi M-9000 GC/3DQMS instrument.

2.3 Synthesis of 1,6-bis(dimethylsilyl)pyrene (2)

Under a dry argon atmosphere, 2.6 mol/L *n*-butyllithium in hexane (9.62 mL , 25 mmol) was added dropwise to the mixture of 1,6-dibromopyrene (**1**, 1.80 g , 5 mmol), dry THF (50 mL) and *N,N,N',N'*-tetramethylethylenediamine (2.92 g , 25 mmol) for 15 min at $-78\text{ }^\circ\text{C}$. After the resulting orange-colored solution was stirred for 2 h , chlorodimethylsilane (1.19 g , 12.5 mmol) was added to this solution at room temperature. The reaction mixture was stirred for 12 h and poured into 100 mL of 0.2 mol/L HCl aqueous solution with stirring. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography eluted with hexane (R_f value: 0.50) and chloroform/hexane (Vol. ratio $1:1$, R_f value: 0.90). The collected fraction was concentrated under reduced pressure. The residue was recrystallized from methanol to afford 1,6-bis(dimethylsilyl)pyrene (**2**) as colorless crystal with the yield of 64.4% (1.03 g , 3.22 mmol).

M.p.: $134\text{ }^\circ\text{C}$. ^1H NMR (400 MHz , CDCl_3 , ppm): δ 8.41 (d, $J = 9.13\text{ Hz}$, 2H , pyrenyl protons), 8.22 (d, $J = 7.57\text{ Hz}$, 2H , pyrenyl protons), 8.19 (d, $J = 7.62\text{ Hz}$, 2H , pyrenyl protons), 8.12 (d, $J = 9.13\text{ Hz}$, 2H , pyrenyl protons), 5.09 (sept, $J = 3.75\text{ Hz}$, 2H , $-\text{Si}(\text{CH}_3)_2-\text{H}$), 0.60 (d, $J = 3.79\text{ Hz}$, 12H , $-\text{Si}(\text{CH}_3)_2-$). ^{13}C NMR (100 MHz , CDCl_3 , ppm): δ 135.8 (pyrenyl carbon), 133.1 (pyrenyl carbon), 132.2 (pyrenyl carbon), 131.8 (pyrenyl carbon), 127.6 (pyrenyl carbon), 127.5 (pyrenyl carbon), 124.6 (pyrenyl carbon), 124.1 (pyrenyl carbon), -2.90 ($-\text{Si}(\text{CH}_3)_2-$). IR (KBr, cm^{-1}): 2100 (Si—H). Mass (EI, m/z , intensity): 318 (M^+ , 53%), 259 ($M^+ - [\text{Si}(\text{CH}_3)_2-\text{H}]$, 100%).

2.4 Synthesis of 1,6-bis(dimethylhydroxysilyl)pyrene (M1)

Under a dry argon atmosphere, 1,6-bis(dimethylsilyl)pyrene (**2**, 3.84 g , 12.1 mmol) dissolved in dry THF (9 mL) was added dropwise to a mixture of dry THF (30 mL), H_2O (0.6 g , 33.6 mmol) and 5% Pd-C (0.03 g , 0.014 mmol) at room temperature. The mixture was stirred for 24 h and filtered. The solvent was removed under

reduced pressure. The residue was recrystallized from toluene to afford 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**) as colorless crystal with the yield of 51.1% (2.16 g , 6.16 mmol).

M.p.: $200\text{ }^\circ\text{C}$. ^1H NMR (400 MHz , CDCl_3 , ppm): δ 8.62 (d, $J = 9.20\text{ Hz}$, 2H , pyrenyl protons), 8.27 (s, 4H , pyrenyl protons), 8.20 (d, $J = 9.21\text{ Hz}$, 2H , pyrenyl protons), 6.37 (s, 2H , $-\text{OH}$), 0.55 (s, 12H , $-\text{Si}(\text{CH}_3)_2-$). ^{13}C NMR (100 MHz , CDCl_3 , ppm): δ 135.8 (pyrenyl carbon), 133.1 (pyrenyl carbon), 132.2 (pyrenyl carbon), 131.8 (pyrenyl carbon), 127.6 (pyrenyl carbon), 127.5 (pyrenyl carbon), 124.6 (pyrenyl carbon), 124.1 (pyrenyl carbon), -2.90 ($-\text{Si}(\text{CH}_3)_2-$). IR (KBr, cm^{-1}): 3300 ($-\text{OH}$). Mass (EI, m/z , intensity): 350 (M^+ , 100%), 335 ($M^+ - \text{CH}_3$, 96%).

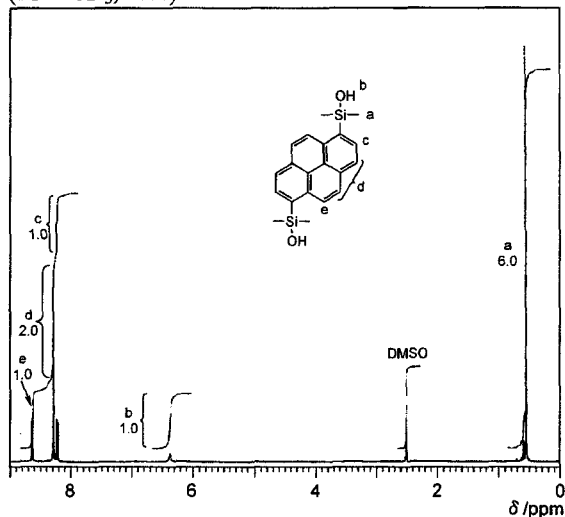


Figure 1. ^1H NMR spectrum of **M1**.

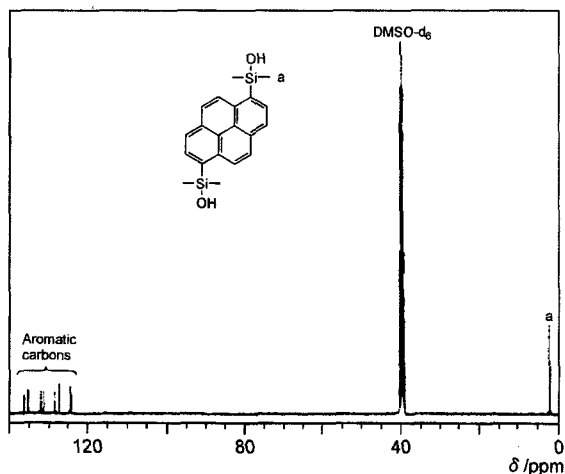


Figure 2. ^{13}C NMR spectrum of **M1**.

2.5 Polycondensation of M1

Under a dry atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexoate (0.02 g) was added to **M1** (0.151 g , 0.43 mmol) dissolved in toluene (13 mL), and the reaction mixture was refluxed for 6 h with stirring. The soluble parts in THF were poured into acetone (150 mL) to generate the white precipitates. Yield: 50.3% (0.07 g , 0.22 mmol) as white powder. ^1H and ^{13}C NMR spectra could not be obtained for the poor solubility in common organic solvents. IR (KBr, cm^{-1}): 1071 (Si—O).

2.6 Synthesis of poly(tetramethyl-1,4-silphenylene-siloxane-co-tetramethyl-1,6-silpyrenylenesiloxane) (CP1)

CP1 was synthesized by the similar method of polycondensation of **M1** using **M1** and 1,4-bis(dimethylhydroxysilyl)benzene as the comonomers. Yield: 84.3 % (0.51 g, 1.92 mmol) as white powder solid. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.51 (d, $J = 9.04$ Hz, 2H, pyrenyl protons), 8.21 (s, 2H, pyrenyl protons), 8.02 (d, $J = 8.20$ Hz, 4H, pyrenyl protons), 7.54 (s, 4H, phenyl protons), 0.62 (s, 0.90H, $-\text{Si}(\text{CH}_3)_2-$), 0.32 (s, 1.10H, $-\text{Si}(\text{CH}_3)_2-$). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 40.8 (phenyl carbon), 135.5 (pyrenyl carbon), 132.3 (pyrenyl carbon), 132.2 (pyrenyl carbon), 131.8 (pyrenyl carbon), 131.5 (phenyl carbon), 128.5 (pyrenyl carbon), 127.2 (pyrenyl carbon), 124.8 (pyrenyl carbon), 124.2 (pyrenyl carbon), 2.51 (pyrenyl $-\text{Si}(\text{CH}_3)_2-$), 0.89 (phenyl $-\text{Si}(\text{CH}_3)_2-$).

3. RESULTS AND DISCUSSION

3.1 Preparation of 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**)

A synthetic route for a novel disilanol derivative, i.e. 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**), is described in Scheme 2. 1,6-Dibromopyrene (**1**) was prepared by the bromination [14] of pyrene in carbon tetrachloride. 1,6-Bis(dimethylsilyl)pyrene (**2**) was synthesized by the reaction between chlorodimethylsilane and lithiated [15] derivative of **1** generated by *n*-butyllithium in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). 1,6-Bis(dimethylhydroxysilyl)pyrene (**M1**) was obtained by the hydrolysis of **2** catalyzed by 5%-Pd on C. The structure of **M1** was confirmed by the spectroscopic data described in the Experimental parts and the NMR spectra as shown in Figures 1 and 2.

3.2 Polycondensation of **M1**

Polycondensation of **M1** was carried out in toluene with reflux using 1,1,3,3-tetramethylguanidinium 2-ethylhexoate as a catalyst. The precipitate was generated in polycondensation. After the polycondensation, the soluble parts in THF were poured into acetone to afford the precipitate. The soluble parts in THF are composed of ca. 10 monomer units, which were calculated from the ratio of the M_n determined by SEC as shown in Figure 3 to the molecular weight of **M1**.

Additionally, no absorption bands based on hydroxyl moieties and absorption bands based on siloxane bonding (1071 cm^{-1}) were observed in the IR spectrum of these soluble parts as described in Figure 4, suggesting that the soluble parts in THF obtained by the polycondensation of **M1** were composed of cyclic compounds. It would be expected that the insoluble parts in THF were composed of the linear polymer with high molecular weight.

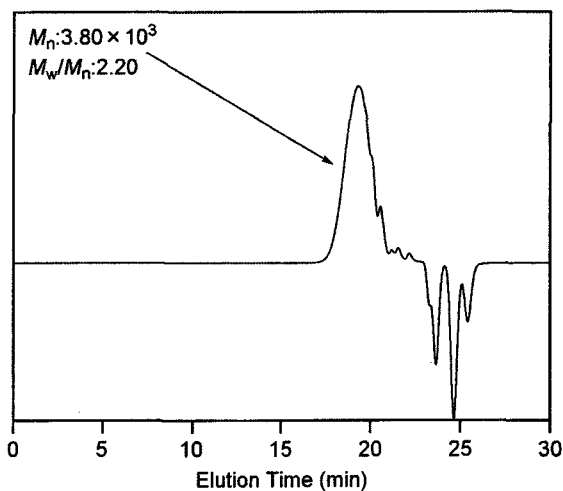


Figure 3. GPC profile of Cyclic-P1 eluted with THF.

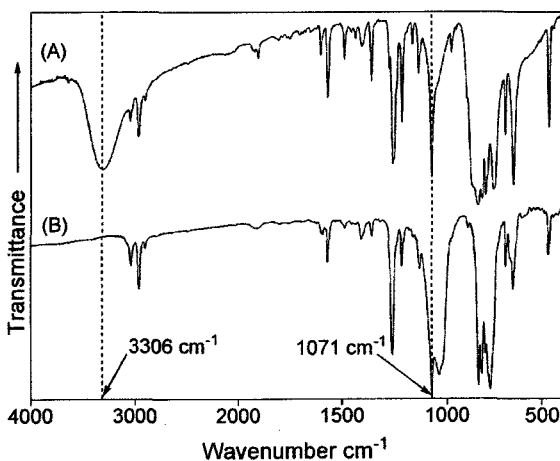
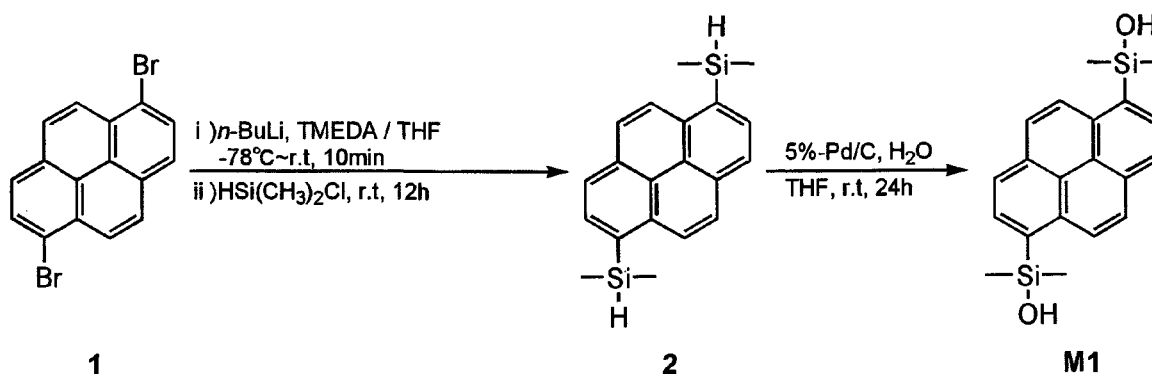
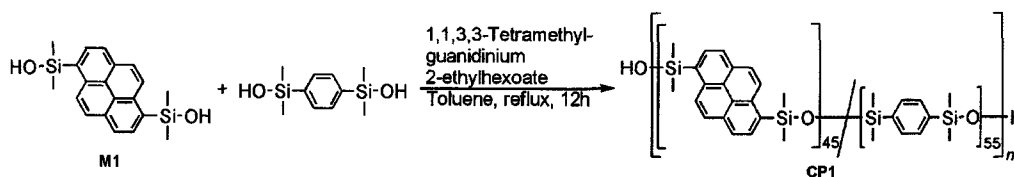


Figure 4. IR spectra of (A) **M1** and (B) Cyclic-P1.



Scheme 2. Synthetic pathways of 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**).

Scheme 3. Copolymerization of **M1** and 1,4-bis(dimethylhydroxysilyl)benzene.Table I. Characterization of **P1**, **Cyclic-P1** and **CP1**.

Polymer	Yield(%)	$10^{-4} M_n^a$	M_w/M_n^a	$T_g(^{\circ}\text{C})^b$	$T_m(^{\circ}\text{C})^b$	$T_{d5}(^{\circ}\text{C})^c$
P1	15	— ^{d)}	— ^{d)}	— ^{e)}	297	387
Cyclic-P1	50	0.38	2.20	65	132	453
CP1^{f)}	84	7.69	1.38	54	131	495

a) Determined by GPC in THF eluent using polystyrene standards.

b) Determined by DSC on a second heating scan at a heating rate of 5 °C/min under a nitrogen atmosphere.

c) Temperature at 5% weight loss determined by TG at a heating rate of 10 °C/min under a nitrogen atmosphere.

d) Not determined due to the insolubility in common organic solvents.

e) Not detected from -50 °C to 400 °C.

f) Equimolar amount of **M1** and 1,4-bis(dimethylhydroxysilyl)benzene was used in feed for copolymerization.

3.3 Copolymerization **M1** with 1,4-bis(dimethylhydroxysilyl)benzene.

The solubility of **P1** obtained from **M1** was too poor for the NMR spectroscopic data to be obtained. Thus, the copolymerization of **M1** and 1,4-(dimethylhydroxysilyl)benzene was carried out as shown in Scheme 3 for the confirmation of the introduction of **M1** units in the resulting polymer. The results of the copolymerization of **M1** and 1,4-(dimethylhydroxysilyl)benzene are summarized in Table I. The unit ratio of the resulting copolymer was estimated by a comparison of the integrated values of the ¹H NMR signal based on methyl protons derived from 1,4-(dimethylhydroxysilyl)benzene units at 0.32 ppm with those based on methyl protons derived from **M1** units at 0.62 ppm and approximately, which was almost equal to the molar ratio of **M1** and 1,4-bis(dimethylhydroxysilyl)benzene in feed. **CP1** was soluble in common organic solvents such as THF, chloroform, dichloromethane, and toluene. Glass transition and melting point were observed in DSC analysis of **CP1**, suggesting that **CP1** exhibited the crystallinity. **CP1** exhibited the relatively high thermal stability as deduced from the T_{d5} determined by the thermogravimetry.

Consequently, we achieved the synthesis of novel disilanol monomer, i.e. 1,6-bis(dimethylhydroxysilyl)pyrene (**M1**), which underwent polycondensation to afford the linear polymer as well as the cyclic oligomer. It was revealed that the copolymerization of **M1** with 1,4-bis(dimethylhydroxysilyl)benzene afforded the corresponding copolymer (**CP1**) with higher thermal stability than **Cyclic-P1** and **P1**. It was also revealed, unfortunately, that the T_{d5} 's of the present **Cyclic-P1**, **P1**, and **CP1** were lower than that of poly(tetramethyl-1,4-silphenylenesiloxane) [3].

Acknowledgment: This work was partly supported by the Japan Science and Technology Agency through Research for Promoting Technological Seeds (No. 03-066). The authors would like to appreciate Dr. Hiroyuki Tanaka, Professor in Nihon University, for the contribution in GC/MS measurements; and Ms. Satoko Tokiwa as well as Ms. Nami Sugashima, Nihon University College of Engineering Worldwide Research Center for Advanced Engineering & Technology (NEWCAT), for performing

NMR measurements.

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