

Synthesis and Characterization of Poly(tetramethyl-1,4-silphenylenesiloxane) Derivatives with Oxyethylene Substituent on Phenylene Moiety

Nobukatsu Nemoto (✉), Yoshie Watanabe, Jun Umemiya, Yumiko Otomo

Department of Materials Chemistry and Engineering, College of Engineering, Nihon University, Tamura-machi, Koriyama, Fukushima 963-8642, Japan
E-mail: nemoto@chem.ce.nihon-u.ac.jp; Fax: +81-24-956-8812

Received: 10 April 2006 / Revised version: 16 June 2006 / Accepted: 29 June 2006
Published online: 21 July 2006 – © Springer-Verlag 2006

Summary

Novel poly(tetramethyl-1,4-silphenylenesiloxane) derivatives having 2-methoxyethoxy or 2-(2-methoxyethoxy)ethoxy substituents at both 2- and 5-positions on phenylene moieties were synthesized and characterized by differential scanning calorimetry and thermogravimetry analyses. Poly(tetramethyl-1,4-silphenylenesiloxane) derivatives were obtained by condensation polymerization of the corresponding disilanol derivatives, *i.e.*, 1,4-bis(dimethylhydroxysilyl)-2,5-bis(2-methoxyethoxy)benzene and 1,4-bis(dimethylhydroxysilyl)-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene, which were prepared by the Grignard reaction using chlorodimethylsilane and the corresponding dibromobenzene derivatives followed by the hydrolyses, catalyzed by palladium on charcoal. The introduction of 2-methoxyethoxy groups on the phenylene moiety made the melting point high, compared with poly(tetramethyl-1,4-silphenylenesiloxane); however, that of 2-(2-methoxyethoxy)ethoxy groups made it low, indicating the longer oxyethylene moiety induced the lowering of the melting point. There were no significant differences in the thermostabilities of both present polymers, suggesting the length of oxyethylene moiety would not affect the thermostability, though the introduction of polar oxyethylene group onto the phenylene moiety induced a decline of thermostability.

Introduction

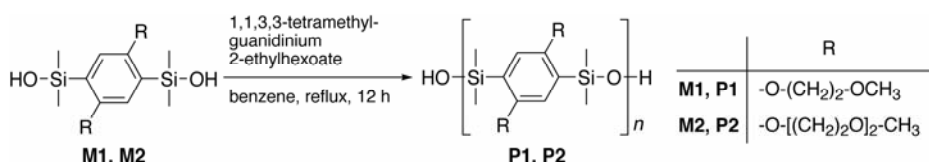
Poly(tetramethyl-1,4-silphenylenesiloxane) is a representative polymer where a thermally stable aromatic moiety is incorporated into the polysiloxane backbone. Polysiloxanes have been well-known to exhibit the particular characteristics, such as flexibility of the main chain, low glass transition temperature, hydrophobicity based on alkyl side chain, thermostability, stability against atomic oxygen, and physiological inertness [1, 2]. The incorporation of thermally stable aromatics into the polysiloxane backbone could presumably improve their good properties, especially the thermostability [3].

On the other hand, poly(dimethylsiloxane-tetramethyl-1,4-silphenylenesiloxane) derivatives have been used as stationary phases for gas chromatography capillary

columns [4] due to their excellent thermostabilities and good partitioning properties. The thermostabilities and partitioning properties of stationary phases have been known to depend on the chemical structures of polymers used as stationary phases [4]. Therefore, poly(dimethylsiloxane-tetramethyl-1,4-silphenylenesiloxane) derivatives having substituents on the phenylene moiety are expected to exhibit the different thermostabilities and partitioning properties from poly(dimethylsiloxane-tetramethyl-1,4-silphenylenesiloxane). Generally, poly(tetramethyl-1,4-silphenylenesiloxane) can be obtained by condensation polymerization of disilanol monomers, as represented by the method of Merker and Scott [5]. Since the preparation of the disilanol monomers with various aromatics was reported by Beck *et al* [6], there have been many reports on the synthesis of poly(tetramethyl-1,4-silphenylenesiloxane) derivatives [3], including block copolymers [7], graft copolymers [8], and alternating copolymers with dimethylsiloxane units [9]. Unfortunately, there have been limited number of reports on poly(tetramethylsilphenylenesiloxane) derivatives having substituents on the phenylene moieties such as tetramethyl-substituted [6], perfluoro-substituted [10], and trifluoromethyl-substituted [11] phenylene moieties.

On the other hand, poly(ethyleneoxide) has been used as polar stationary phases for gas chromatography capillary columns. Thus, we intend to introduce the 2-methoxyethoxy or 2-(2-methoxyethoxy)ethoxy moiety, which is considered to be the analogous moiety of poly(ethyleneoxide), onto the phenylene moiety of poly(tetramethyl-1,4-silphenylenesiloxane).

From these points of view, we report here the preparation of novel poly(tetramethyl-1,4-silphenylenesiloxane) derivatives having 2-methoxyethoxy (**P1**) or 2-(2-methoxyethoxy)ethoxy (**P2**) substituents at both 2- and 5-positions on the phenylene moieties obtained by condensation polymerization of 1,4-bis(dimethylhydroxysilyl)-2,5-bis(2-methoxyethoxy)benzene (**M1**) or 1,4-bis(dimethylhydroxysilyl)-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene (**M2**), as shown in Scheme 1. The present paper also describes the results of thermal characterization of the obtained polymers using differential scanning calorimetry (DSC) and thermogravimetry (TG) analyses.



Scheme 1. Synthesis of poly[2,5-bis(2-methoxyethoxy)-1,4-silphenylenesiloxane] (**P1**) and poly[2,5-bis[2-(2-methoxyethoxy)ethoxy]-1,4-silphenylenesiloxane] (**P2**)

Experimental Part

Materials

2,5-Dibromohydroquinone (**1**) was prepared by the bromination of hydroquinone (KANTO KAGAKU) using bromine (KANTO KAGAKU) in acetic acid [12]. 2-Methoxyethyl 4-toluenesulfonate and 2-(2-methoxyethoxy)ethyl 4-toluenesulfonate were prepared by the reaction of 4-toluenesulfonyl chloride (Tokyo Kasei Kogyo Co., Inc.) with 2-methoxyethanol and 2-(2-methoxyethoxy)ethanol (KANTO KAGAKU), respectively [13]. Magnesium, potassium hydroxide, ethanol (KANTO KAGAKU),

chlorodimethylsilane (Acros organics), and 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.). Benzene 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.

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 points were measured on a RIGAKU ThermoPlus DSC 8230 at a heating or cooling rate of $10^\circ\text{C}/\text{min}$ under a nitrogen flow rate of 10 mL/min. Thermogravimetry (TG) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size-exclusion chromatography (SEC) using a SHOWA DENKO Shodex GPC-101 system and polystyrene gel columns (a pair of Shodex GPC LF-804) eluted with THF using a calibration curve of polystyrene standards.

Preparation of **2a** and **2b**

Under a dry argon atmosphere, 2,5-dibromohydroquinone (**1**, 12.86 g, 48.0 mmol) and potassium hydroxide (8.14 g, 145 mmol) were dissolved in ethanol (100 mL). To this solution, 2-methoxyethyl 4-toluenesulfonate (33.27 g, 144 mmol) was added dropwise and the reaction mixture was refluxed for 10 h. Then, the reaction mixture was poured into the mixture of chloroform (200 mL) and NH_4Cl aqueous solution (100 mL). The organic layer was washed with NH_4Cl aqueous solution, dried over anhydrous MgSO_4 , and filtered. The filtrate was concentrated under reduced pressure. The residue was recrystallized from the mixed solvent of ethyl acetate/hexane to afford 1,4-dibromo-2,5-bis(2-methoxyethoxy)benzene (**2a**) as colorless crystals with the yield of 75.4 % (13.91 g, 36.2 mmol). M.p.: 101°C . ^1H NMR (400 MHz, CDCl_3 , ppm): δ 3.47 (s, 6H, $-\text{OCH}_3$), 3.77 (t, $J=4.4$ Hz, 4H, $-\text{CH}_2-\text{O}-\text{CH}_3$), 4.11 (t, $J=4.4$ Hz, 4H, $\text{Ph}-\text{O}-\text{CH}_2-$), 7.15 (s, 2H, phenylene protons). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 59.4 ($-\text{OCH}_3$), 70.1 ($-\text{OCH}_2-$), 70.9 ($-\text{OCH}_2-$), 111.5 (phenylene carbons), 119.2 (phenylene carbons), 150.4 (phenylene carbons). IR (KBr, cm^{-1}): 1216 (aromatic ether), 1124 (aliphatic ether).

1,4-Dibromo-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene (**2b**) was prepared by the similar method as the preparation of **2a** using 2-(2-methoxyethoxy)ethyl 4-toluenesulfonate as the raw material. Yield: 62.2 % as colorless crystals. M.p.: 63°C . ^1H NMR (400 MHz, CDCl_3 , ppm): δ 3.40 (s, 6H, $-\text{OCH}_3$), 3.56-3.60 (m, 4H, $-\text{O}-(\text{CH}_2)_2-\text{OCH}_3$), 3.74-3.79 (m, 4H, $-\text{O}-(\text{CH}_2)_2-\text{OCH}_3$), 3.88 (t, $J=4.4$ Hz, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 4.13 (t, $J=4.4$ Hz, 4H, $\text{Ph}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 7.16 (s, 2H, phenylene protons). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 59.1 ($-\text{OCH}_3$), 69.6 ($-\text{OCH}_2-$), 70.2 ($-\text{OCH}_2-$), 71.0 ($-\text{OCH}_2-$), 72.0 ($-\text{OCH}_2-$), 111.4 (phenylene carbons), 119.1 (phenylene carbons), 150.3 (phenylene carbons). IR (KBr, cm^{-1}): 1216 (aromatic ether), 1146, 1131, 1102 (aliphatic ether).

Preparation of **3a** and **3b**

Under a dry argon atmosphere, **2a** (6.00 g, 15.6 mmol) and chlorodimethylsilane (4.43 g, 46.8 mmol) in dry THF (80 mL) were added dropwise to magnesium (0.868 g, 35.7 mmol) in dry THF (80 mL) at 60°C. The reaction mixture was stirred at 60°C for 24 h and poured into the mixture of diethyl ether (100 mL) and 0.5 mol/L HCl aqueous solution (100 mL). The organic layer was washed with saturated NaHCO₃ aqueous solution, dried over anhydrous MgSO₄, and filtered. The filtrate was concentrated under reduced pressure. The residue was dissolved in the mixed solvent of hexane/ethyl acetate and purified by silica gel chromatography eluted with the mixed solvent of hexane/ethyl acetate (vol. ratio 2:1, R_f value: 0.78). The collected fraction of the purified material was concentrated under reduced pressure. The residue was recrystallized from the mixed solvent of hexane/ethyl acetate to afford 1,4-bis(dimethylsilyl)-2,5-bis(2-methoxyethoxy)benzene (**3a**) as colorless crystals with the yield of 60.1 % (3.21 g, 9.37 mmol). M.p.: 68°C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.34 (d, *J*=3.6 Hz, 12H, Si-(CH₃)₂), 3.43 (s, 6H, -OCH₃), 3.73 (t, *J*=4.4 Hz, 4H, -CH₂-O-CH₃), 4.09 (t, *J*=4.4 Hz, 4H, Ph-O-CH₂-), 4.37 (sept, *J*=3.6 Hz, 2H, Si-H), 6.91 (s, 2H, phenylene protons). ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.84 (Si-(CH₃)₂), 58.0 (-OCH₃), 66.8 (-OCH₂-), 70.2 (-OCH₂-), 116.8 (phenylene carbons), 127.5 (phenylene carbons), 156.5 (phenylene carbons). IR (KBr, cm⁻¹): 2114 (Si-H), 1205 (aromatic ether), 1110 (aliphatic ether).

1,4-Bis(dimethylsilyl)-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene (**3b**) was prepared by the similar method as the preparation of **3a** using **2b** as the raw material. Yield: 64.3 % as colorless liquid. ¹H NMR (400 MHz, CDCl₃, ppm): δ 0.33 (d, *J*=3.6 Hz, 12H, Si-(CH₃)₂), 3.39 (s, 6H, -OCH₃), 3.54-3.59 (m, 4H, -O-(CH₂)₂-OCH₃), 3.68-3.72 (m, 4H, -O-(CH₂)₂-OCH₃), 3.83 (t, *J*=4.4 Hz, 4H, Ph-O-CH₂-CH₂-O-), 4.12 (t, *J*=4.4 Hz, 4H, Ph-O-CH₂-CH₂-O-), 4.36 (sept, *J*=3.6 Hz, 2H, Si-H), 6.90 (s, 2H, phenylene protons). ¹³C NMR (100 MHz, CDCl₃, ppm): δ -4.86 (Si-(CH₃)₂), 57.9 (-OCH₃), 66.7 (-OCH₂-), 68.8 (-OCH₂-), 69.5 (-OCH₂-), 70.8 (-OCH₂-), 116.6 (phenylene carbons), 127.3 (phenylene carbons), 156.3 (phenylene carbons). IR (KBr, cm⁻¹): 2114 (Si-H), 1203 (aromatic ether), 1109 (aliphatic ether).

Preparation of Monomers

Under a dry argon atmosphere, **3a** (3.07 g, 8.96 mmol) in dry THF (1.7 mL) was added dropwise to 5%-Pd on C (0.018 g) with H₂O (0.42 g, 23 mmol) in THF (5.0 mL) in an ice bath. The reaction mixture was stirred at ambient temperature for 2 h and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from benzene to afford 1,4-bis(dimethylhydroxysilyl)-2,5-bis(2-methoxyethoxy)benzene (**M1**) as colorless crystals with the yield of 40.2 % (1.35 g, 3.60 mmol). M.p.: 102°C. ¹H NMR (400 MHz, (CD₃)₂SO, ppm): δ 0.22 (s, 12H, Si-(CH₃)₂), 3.29 (s, 6H, -OCH₃), 3.63 (t, *J*=4.4 Hz, 4H, -CH₂-O-CH₃), 3.99 (t, *J*=4.4 Hz, 4H, Ph-O-CH₂-), 5.67 (s, 2H, Si-OH), 6.98 (s, 2H, phenylene protons). ¹³C NMR (100 MHz, (CD₃)₂SO, ppm): δ 1.31 (Si-(CH₃)₂), 58.3 (-OCH₃), 67.3 (-OCH₂-), 71.0 (-OCH₂-), 117.0 (phenylene carbons), 130.6 (phenylene carbons), 156.7 (phenylene carbons). IR (KBr, cm⁻¹): 3400 (-OH), 1207 (aromatic ether), 1127, 1102 (aliphatic ether).

1,4-Bis(dimethylhydroxysilyl)-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene (**M2**) was prepared by the similar method as the preparation of **M1** using **3b** as the raw material.

Yield: 39.8 % as colorless crystals recrystallized from the mixed solvent of toluene/hexane. M.p.: 61°C. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, ppm): δ 0.22 (s, 12H, Si-(CH₃)₂), 3.23 (s, 6H, -OCH₃), 3.42-3.48 (m, 4H, -O-(CH₂)₂-OCH₃), 3.54-3.59 (m, 4H, -O-(CH₂)₂-OCH₃), 3.70 (t, $J=4.4$ Hz, 4H, Ph-O-CH₂-CH₂-O-), 3.98 (t, $J=4.4$ Hz, 4H, Ph-O-CH₂-CH₂-O-), 5.65 (s, 2H, Si-OH), 6.98 (s, 2H, phenylene protons). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$, ppm): δ 1.31 (Si-(CH₃)₂), 58.3 (-OCH₃), 67.4 (-OCH₂-), 69.5 (-OCH₂-), 69.8 (-OCH₂-), 71.5 (-OCH₂-), 116.9 (phenylene carbons), 130.6 (phenylene carbons), 156.7 (phenylene carbons). IR (KBr, cm⁻¹): 3493 (-OH), 1205 (aromatic ether), 1139, 1128, 1103 (aliphatic ether).

Condensation Polymerization

Under a dry atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexoate (0.02 g) was added to **M1** (0.210 g, 0.56 mmol) dissolved in dry benzene (12.5 mL), and the reaction mixture was refluxed for 12 h. The reaction mixture was poured into methanol (100 mL) to isolate poly[tetramethyl-2,5-bis(2-methoxyethoxy)-1,4-silphenylenesiloxane] (**P1**) as white precipitates with the yield of 81.0 % (0.162 g). ^1H NMR (400 MHz, CDCl₃, ppm): δ 0.38 (s, 12H, Si-(CH₃)₂), 3.35 (s, 6H, -OCH₃), 3.63 (t, $J=4.4$ Hz, 4H, -CH₂-O-CH₃), 3.96 (t, $J=4.4$ Hz, 4H, Ph-O-CH₂-), 7.03 (s, 2H, phenylene protons). ^{13}C NMR (100 MHz, CDCl₃, ppm): δ 1.67 (Si-(CH₃)₂), 58.8 (-OCH₃), 67.1 (-OCH₂-), 71.2 (-OCH₂-), 116.8 (phenylene carbons), 130.0 (phenylene carbons), 156.9 (phenylene carbons). IR (KBr, cm⁻¹): 1205 (aromatic ether), 1000-1100 (Si-O).

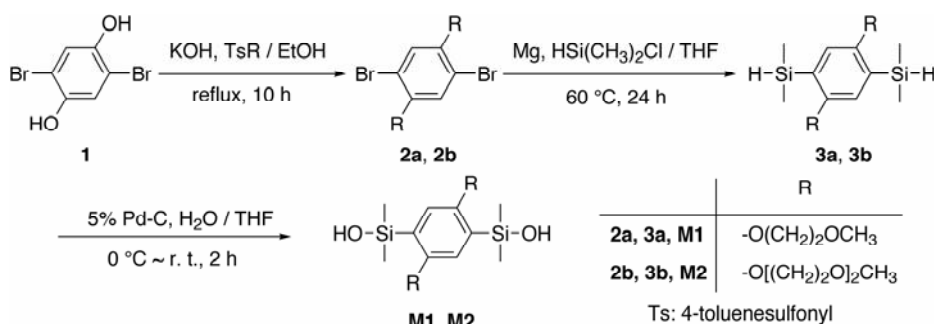
Poly{tetramethyl-2,5-bis[2-(2-methoxyethoxy)ethoxy]-1,4-silphenylenesiloxane} (**P2**) was prepared by the similar method as the preparation of **P1** using **M2** as a monomer. Yield: 77.5 % as colorless powders. ^1H NMR (400 MHz, CDCl₃, ppm): δ 0.40 (s, 12H, Si-(CH₃)₂), 3.35 (s, 6H, -OCH₃), 3.49-3.54 (m, 4H, -O-(CH₂)₂-OCH₃), 3.60-3.65 (m, 4H, -O-(CH₂)₂-OCH₃), 3.77 (t, $J=4.4$ Hz, 4H, Ph-O-CH₂-CH₂-O-), 4.01 (t, $J=4.4$ Hz, 4H, Ph-O-CH₂-CH₂-O-), 7.02 (s, 2H, phenylene protons). ^{13}C NMR (100 MHz, CDCl₃, ppm): δ 1.78 (Si-(CH₃)₂), 59.0 (-OCH₃), 67.1 (-OCH₂-), 70.0 (-OCH₂-), 70.4 (-OCH₂-), 71.9 (-OCH₂-), 116.6 (phenylene carbons), 130.1 (phenylene carbons), 156.8 (phenylene carbons). IR (KBr, cm⁻¹): 1203 (aromatic ether), 1000-1100 (Si-O).

Results and Discussion

Syntheses of Monomers

Scheme 2 shows the pathways for the syntheses of disilanol monomers **M1** and **M2**. **M1** and **M2** were synthesized by the hydrolyses of the corresponding bis(dimethylsilyl)benzene derivatives (**3a**, **3b**), which had been obtained from the corresponding dibromobenzene derivatives (**2a**, **2b**) via the Grignard reactions with chlorodimethylsilane. The spectroscopic data described in the experimental part indicated the syntheses of novel monomers were achieved. As an example, ^1H and ^{13}C NMR spectra of **M2** are described in Figure 1. Each signal was consistently assigned as described in Figure 1. The structure of **M1** was also confirmed by ^1H and ^{13}C NMR and IR spectroscopy. Beck *et al.* reported [6] that bis(dimethylhydroxysilyl)benzene derivatives were obtained by the hydrolysis of the corresponding bis(dimethylsilyl)benzene derivatives with good yields using sodium ethoxide followed by a

treatment of buffer aqueous solution. In this study, it was confirmed that **M1** could be obtained by the method of Beck *et al* [6] with the yield below 30 %. On the other hand, hydrolysis of 1,4-bis(dimethylsilyl)benzene using the metal catalyst such as 5%-Pd, Pt, or Ru on charcoal has been reported to afford 1,4-bis(dimethylhydroxy-silyl)benzene with high yields [14]. In the present study, it was also revealed that **M1** could be obtained by the hydrolysis of **3a** using 5 % Pd on charcoal as a catalyst with the yield of 40 %. Thus, we carried out the hydrolysis of bis(dimethylsilyl)benzene derivatives using 5 % Pd on charcoal as a catalyst.



Scheme 2. Pathways for synthesis of disilanol monomers **M1** and **M2**

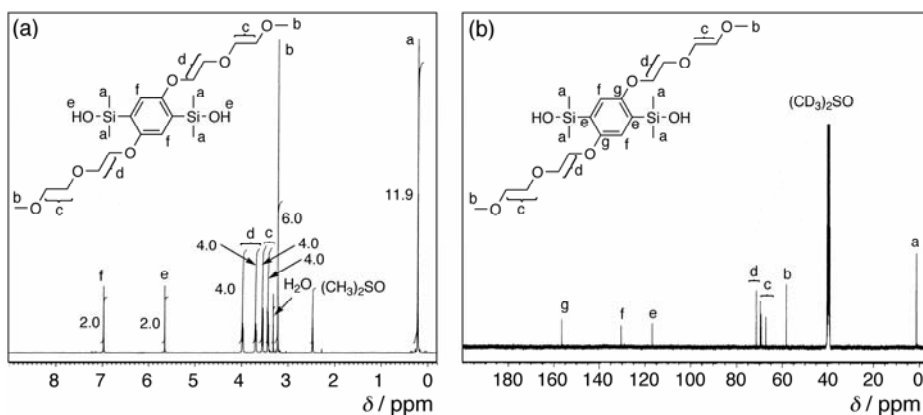


Figure 1. (a) ¹H NMR (solvent: (CD₃)₂SO, 400 MHz, numerals at signal's side are the integral values of each signal) and (b) ¹³C NMR spectra (solvent: (CD₃)₂SO, 100 MHz) of **M2** at ambient temperature.

Syntheses and Characterization of Polymers

M1 and **M2** underwent the condensation polymerization catalyzed by 1,1,3,3-tetramethylguanidinium 2-ethylhexoate [5] to afford the corresponding poly(tetramethyl-1,4-silphenylenesiloxane) derivatives **P1** and **P2**, respectively. Any solvents forming azeotropic mixtures with water and dissolving both monomer and the resulting polymer, such as benzene and toluene, can be used for the present polymerization. The low monomer concentration resulted in the formation of not

polymer but the corresponding cyclic compounds. Thus, we used the minimum amount of the solvent, which dissolved both monomers and the resulting polymers. The most important factor for polymer formation seems to be the monomer concentration during the condensation polymerization. The SEC profiles of **P1** and **P2** indicated the obtained polymers were unimodal. Figure 2 shows the SEC profile of **P2** eluted with THF, indicating the polymer formation and the absence of low molecular weight species such as cyclic dimer or trimer.

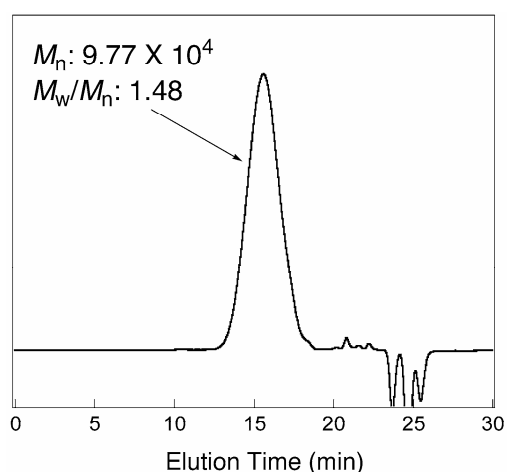


Figure 2. SEC profile of **P2** eluted with THF.

The structures of **P1** and **P2** were confirmed by ^1H and ^{13}C NMR and IR spectroscopy. As a typical example, ^1H and ^{13}C NMR spectra of **P2** are described in Figure 3. Each signal was consistently assigned as described in Figure 3.

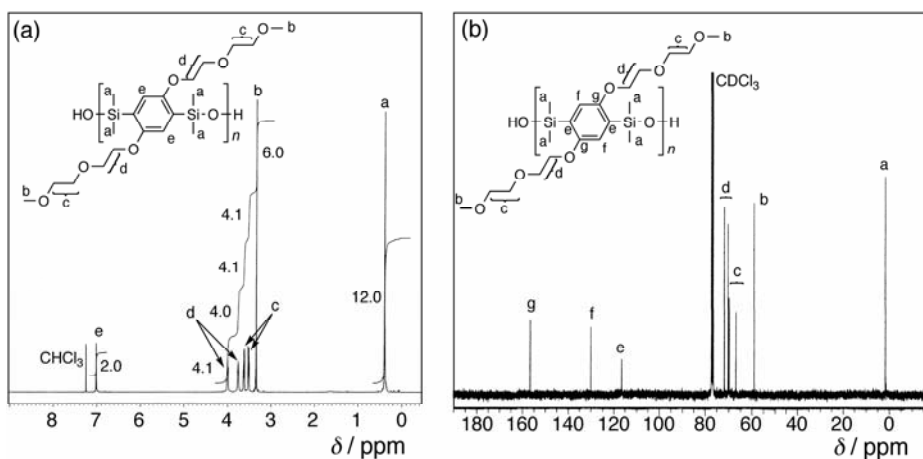


Figure 3. (a) ^1H NMR (solvent: CDCl_3 , 400 MHz, numerals at signal's side are the integral values of each signal) and (b) ^{13}C NMR spectra (solvent: CDCl_3 , 100 MHz) of **P2** at ambient temperature.

The characterization of **P1** and **P2** is summarized in Table 1. **P1** and **P2** are soluble in common organic solvents such as THF, chloroform, dichloromethane, and toluene.

Table 1. Characterization of **P1** and **P2**

Polymer	$10^{-4} M_n^a)$	$M_w/M_n^b)$	$T_m(^{\circ}C)^c)$	$T_{d5}(^{\circ}C)^d)$
P1	3.77	1.75	178	393
P2	9.77	1.48	98	389

a) Number-average molecular weight estimated from SEC eluted with THF based on polystyrene standards.

b) Polydispersity index.

c) Melting point determined by DSC at a heating rate of 10°C/min under nitrogen atmosphere.

d) Temperature at 5 wt% weight loss determined by TG under nitrogen atmosphere.

Figure 4 shows the DSC traces of **P1** and **P2** on the first cooling and second heating scans under a nitrogen atmosphere at a cooling or heating rate of 10°C/min.

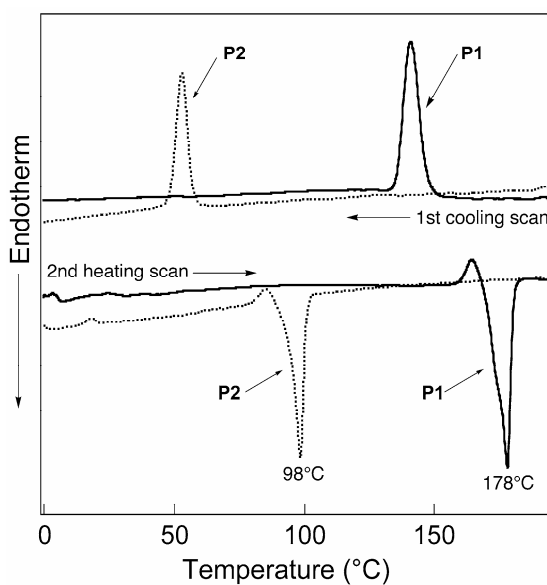


Figure 4. DSC thermograms of **P1** (line) and **P2** (dotted line) on a first cooling scan from 200°C and a second heating scan under a nitrogen flow rate of 10 mL/min and a cooling or heating rate of 10°C/min.

The exothermic peak based on crystallization was observed on the first cooling scans from 200°C of both polymers after a supercooling state. Small exothermic peaks in the DSC thermograms on the second heating scans around 30°C for **P1** and 20°C for **P2** were observed, presumably due to the partial crystallization of the polymer. The endothermic peak based on melting clearly appeared on the second heating scans of both polymers. These findings would indicate **P1** and **P2** exhibit the crystallinity.

The melting points (T_m 's) of **P1** and **P2** were determined to be 178 and 98°C, respectively, from each second heating scan; however, the glass transition temperatures (T_g 's) of **P1** and **P2** were not clearly observed between -50 and 400°C. The T_m of poly(tetramethyl-1,4-silphenylenesiloxane) (M_n : 186000, M_w/M_n : 1.82) prepared by condensation polymerization of 1,4-bis(dimethylhydroxysilyl)benzene in our laboratory was determined to be 130°C by a DSC measurement. The thermodynamic melting temperature of poly(tetramethyl-1,4-silphenylenesiloxane) has been reported to be 160°C by Magill *et al* [15]. The T_m of **P1** was found to be higher than that of poly(tetramethyl-1,4-silphenylenesiloxane), due to the interactions between methoxyethoxy groups as well as aromatic moieties. The T_m of **P2** is found to be lower than that of poly(tetramethyl-1,4-silphenylenesiloxane), presumably because the longer oxyethylene chains would inhibit the interactions between the bulky main-chain aromatic moieties. The length of oxyethylene moiety would induce the lowering of T_m .

On the other hand, there were no significant differences in the temperatures at 5 wt% weight loss (T_{d5} 's) of **P1** (393°C) and **P2** (389°C) determined by TG under a nitrogen atmosphere as summarized in Table 1, indicating the length of oxyethylene group would not affect the thermostability. The T_{d5} of poly(tetramethyl-1,4-silphenylenesiloxane) has been reported to be over 500°C [3]. The T_{d5} 's of **P1** and **P2** were low compared with that of poly(tetramethyl-1,4-silphenylenesiloxane). This finding would be attributed to the difference in the bond energies among Si-O, C-C and C-O bondings. The bond energies of C-C and C-O have been reported to be 346 and 358 kJ/mol, respectively, which are lower than that of Si-O (444 kJ/mol) [3]. Thus, the introduction of oxyethylene groups induces the lowering of T_{d5} ; however, the thermostabilities of **P1** and **P2** are acceptable as stationary phases for gas chromatography capillary columns [4]. It would be possible to prepare the new polar stationary phases for gas chromatography capillary columns by copolymerization using **M1** or **M2** with poly(dimethylsiloxane).

Conclusions

The syntheses of novel poly(tetramethyl-1,4-silphenylenesiloxane) derivatives having 2-methoxyethoxy (**P1**) or 2-(2-methoxyethoxy)ethoxy (**P2**) substituent at both 2- and 5-positions on phenylene moieties were achieved by condensation polymerization of novel disilanol derivatives, *i.e.*, 1,4-bis(dimethylhydroxysilyl)-2,5-bis(2-methoxyethoxy)benzene (**M1**) and 1,4-bis(dimethylhydroxysilyl)-2,5-bis[2-(2-methoxyethoxy)ethoxy]benzene (**M2**), respectively. The T_m of **P1** was higher than that of poly(tetramethyl-1,4-silphenylenesiloxane); however, that of **P2** was lower than that of poly(tetramethyl-1,4-silphenylenesiloxane), indicating the longer oxyethylene moiety would induce the lowering of T_m . There were no significant differences in the T_{d5} 's of **P1** and **P2**, which were low compared with that of poly(tetramethyl-1,4-silphenylenesiloxane). The introduction of oxyethylene groups induces the decline of thermostability; however, the length of oxyethylene moiety would not affect the thermostability.

Acknowledgements. The authors would like to appreciate Mr. Yoshikazu Sato, Associate Professor in Nihon University, for performing TG analyses; and Ms. Satoko Tokiwa as well as Ms. Nami Oyama, Nihon University College of Engineering Worldwide Research Center for Advanced Engineering & Technology (NEWCAT), for performing NMR measurements.

References

1. Mark J E (1990) Silicon-containing polymers. In: Ziegler JM, Gordon FW (eds) Silicon-based polymer science. American Chemical Society, Washington DC (Adv Chem Ser, vol 224, pp 47-90)
2. Brook MA (2000) Silicon in organic, organometallic, and polymer chemistry (chapter 9). John Wiley & Sons, Inc, New York
3. Dvornic PR, Lenz RW (1990) High temperature siloxane elastomers (chapter 2). Hüthig & Wepf Verlag, Basel, Heidelberg, New York
4. Day GM, Hibberd AI, Habsuda J, Sharp GJ (2003) Thermally stable siloxane polymers for gas chromatography. In: Clarson SJ, Fitzgerald JJ, Owen MJ, Smith SD, van Dyke ME (eds) Synthesis and properties of silicones and silicone-modified materials. American Chemical Society, Washington DC (ACS Symp Ser vol 838, pp 127-136)
5. Merker RL, Scott, MJ (1964) J Polym Sci: Part A 2: 15-29
6. Beck HN, Chaffee RG (1963) J Chem Eng Data 8: 602-3
7. Nagase Y, Nakamura T, Misawa A, Ikeda K, Sekine Y (1983) Polymer 24: 457-62
8. Nagase Y, Ochiai J, Matsui K, Uchikura M (1988) Polymer 29: 740-5
9. Dvornic PR, Lenz RW (1994) Macromolecules 27: 5833-8
10. Loree LA, Brown ED (1971) US Patent, 3, 576, 020
11. Grindhal GA (1971) US Patent, 3, 576, 021
12. Pelter A, Jenkins I, Jones DE (1997) Tetrahedron 30: 10357-400
13. (a) Ouchi M, Inoue Y, Wada K, Iketani S, Hakushi T, Weber E (1987) J Org Chem 52: 2420-7 (b) Ouchi M, Inoue Y, Kanzaki T, Hakushi T (1984) J Org Chem 49: 1408-12
14. Barnes Jr GH, Daughenbaugh NE (1966) J Org Chem 31: 885-7
15. Li HM, Magill JH (1978) J Polym Sci: Polym Phys Ed 16: 1059-70