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Synthesis and Thermal Characterization of Novel Poly(tetramethylsilanthrylenesiloxane) and Poly(tetramethylsilphenanthrylenesiloxane) Derivatives

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Summary

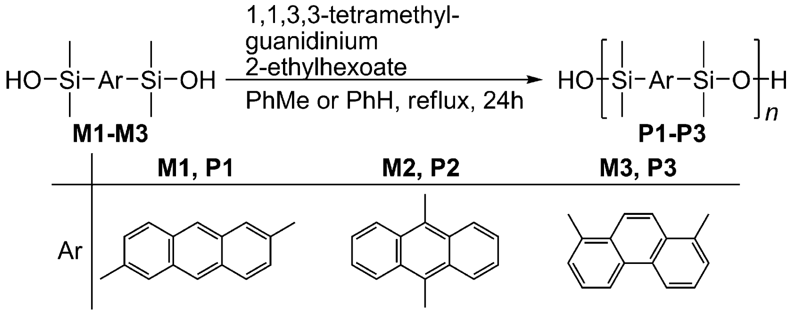
Novel poly(tetramethylsilarylenesiloxane) derivatives, i.e. poly(tetramethyl-2,6-silanthrylenesiloxane) (**P1**), poly(tetramethyl-9,10-silanthrylenesiloxane) (**P2**), and poly(tetramethyl-1,8-silphenanthrylenesiloxane) (**P3**), were synthesized by polycondensation of novel disilanol monomers, i.e. 2,6-bis(dimethylhydroxysilyl)-anthracene (**M1**), 9,10-bis(dimethylhydroxysilyl)anthracene (**M2**), and 1,8-bis(dimethylhydroxysilyl)phenanthrene (**M3**), respectively. **P1** and **P3** were soluble in common organic solvents, such as benzene, toluene, chloroform, dichloromethane, tetrahydrofuran, *etc.* whereas **P2** was almost insoluble in common organic solvents. It was revealed that **P1** and **P3** were amorphous and that **P2** exhibited the crystallinity, as deduced from differential scanning calorimetry (DSC) and X-ray diffraction measurements. The glass transition temperatures (T_g's) of **P1** (118°C) and **P3** (100°C) were much higher than that of poly(tetramethyl-1,4-silphenylenesiloxane). The temperature at 5% weight loss (T_{d5}) of **P3** was 500°C, which was higher than those of **P1** and **P2**, and comparable to that of poly(tetramethyl-1,4-silphenylenesiloxane). It would be speculated that the thermostability of the series of poly(tetramethylsilarylenesiloxane) derivatives is dependent on the stability of arylene moieties incorporated.

Introduction

It has been well-known that linear polysiloxanes exhibit the particular characteristics, such as flexibility of the main chain, low glass transition temperature (T_g), hydrophobicity based on alkyl side chain, thermostability, stability against atomic oxygen, and physiological 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 presumably improve the good properties of polysiloxane, especially the thermostability. There have been many reports on the syntheses of poly(tetramethylsilarylenesiloxane) derivatives with various aromatics [5-12] via polycondensation of bis(dimethylhydroxysilyl)-substituted aromatic compounds [6]. The properties of poly(tetramethylsilarylenesiloxane) derivatives depend on the kind of arylene moiety [7-10], the substituted position of dimethylsilyl groups [9,11] as well as the substituent [6,12] on the arylene moiety, and so on. We reported that poly(tetramethylsilnaphthylenesiloxane) derivatives, where the different positions on the naphthylene moiety were substituted by dimethylsilyl groups, exhibited the high T_g compared with 1,4-PTMPS and that their thermal properties were dependent on the substituted position of dimethylsilyl groups on the naphthylene moiety [9].

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

With these in mind, we report here the preparation of novel poly(tetramethyl-2,6-silanthrylenesiloxane) (**P1**), poly(tetramethyl-9,10-silanthrylenesiloxane) (**P2**), and poly(tetramethyl-1,8-silphenanthrylenesiloxane) (**P3**) via polycondensation of the corresponding novel disilanol derivatives, i.e. 2,6-bis(dimethylhydroxysilyl)-anthracene (**M1**), 9,10-bis(dimethylhydroxysilyl)anthracene (**M2**), and 1,8-bis-(dimethylhydroxysilyl)phenanthrene (**M3**), respectively, 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).



Scheme 1. Syntheses of poly(tetramethyl-2,6-silanthrylenesiloxane) (**P1**), poly(tetramethyl-9,10-silanthrylenesiloxane) (**P2**), and poly(tetramethyl-1,8-silphenanthrylenesiloxane) (**P3**).

Experimental Part

Materials

2,6-Dibromoanthracene (**1**) was prepared from 2,6-diamino-9,10-anthraquinone (Aldrich) according to the literature [13]. 1,8-Dibromophenanthrene (**3**) was prepared by the method reported by Mallory *et al* [14]. 9,10-Dibromoanthracene (**2**) was purchased from Tokyo Kasei Kogyo Co., Inc. and used after recrystallization from chloroform. *n*-Butyllithium in hexane solution (2.6 mol/L, KANTO KAGAKU), chlorodimethylsilane (Acros organics), magnesium (Merck), and 5% palladium on charcoal (Escat 103, from Aldrich) were commercially available and used as received. 1,1,3,3-Tetramethylguanidinium 2-ethylhexoate, which has been reported to be one of most effective catalysts for polycondensation of disilanol derivatives [15], was prepared from an equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.). *N,N,N',N'*-tetramethylethylene-diamine (TMEDA, Tokyo Kasei Kogyo Co., Inc.) was used after distillation over calcium hydride. Benzene, toluene, diethyl ether, and tetrahydrofuran (THF) were used after distillation over sodium.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide [$(CD_3)_2SO$] 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 10°C/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°C/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.

*Preparation of **4** and **5***

Synthesis of 2,6-bis(dimethylsilyl)anthracene (**4**) was carried out by the modified method of Alonso *et al* [16]. Under a dry argon atmosphere, 4.0 mL of 2.6 mol/L-*n*-butyllithium in hexane (10.4 mmol) was added to a slurry of 2,6-dibromoanthracene (**1**, 1.40 g, 4.17 mmol) and TMEDA (1.21 g, 10.4 mmol) in 35 mL of diethyl ether in an ice bath over a period of 5 min. The resulting deep red solution was stirred at room temperature for 10 min. Then, chlorodimethylsilane (1.20 g, 12.6 mmol) was added to the reaction mixture. After the reaction mixture was stirred for 3 h at room temperature, it was poured into 150 mL of water with stirring. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexane. The collected eluent containing the purified material was evaporated and the residue was recrystallized from methanol to afford **4** as pale yellow crystals with the yield of 0.40 g (33 %). M.p.: 82°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.40 (s, 2H, anthrylene protons), 8.22 (s, 2H, anthrylene protons), 7.99 (d, J = 8.4 Hz, 2H, anthrylene protons), 7.55 (dd, J = 8.4, 1.2 Hz, 2H, anthrylene protons), 4.58 (sept, J = 3.6 Hz, 2H, $-Si(CH_3)_2-H$), 0.46 (d, J = 3.6 Hz, 12H, $-Si(CH_3)_2-H$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 135.4 (anthrylene carbon), 134.7 (anthrylene carbon), 131.9 (anthrylene carbon), 131.6 (anthrylene carbon), 129.1 (anthrylene carbon), 127.4 (anthrylene carbon), 126.3 (anthrylene carbon), –3.8 ($-Si(CH_3)_2-$). IR (KBr, cm^{-1}): 2210 (Si-H). Mass (EI, *m/z*): 295 ($[M + H]^{+}$), 236 ($M^{+} - [Si(CH_3)_2]$), 220 ($M^{+} - [Si(CH_3)_2 + CH_4]$).

9,10-bis(dimethylsilyl)anthracene (**5**) was prepared by the similar method as the preparation of **4** using 9,10-dibromoanthracene (**2**) as the raw material. Yield: 35 % as pale yellow crystals. M.p.: 100°C (lit. 98-100°C [17]). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.57 (dd, J = 6.8, 3.4 Hz, 4H, anthrylene protons), 7.49 (dd, J = 6.8, 3.4 Hz, 4H, anthrylene protons), 5.46 (sept, J = 4.0 Hz, 2H, $–Si(CH_3)_2–H$), 0.70 (d, J = 4.0 Hz, 12H, $–Si(CH_3)_2–H$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.8 (anthrylene carbon), 136.2 (anthrylene carbon), 129.5 (anthrylene carbon), 124.5 (anthrylene carbon), –1.4 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 2151 (Si-H). Mass (EI, *m/z*): 294 (M^+), 235 ($M^+ – [Si(CH_3)_2H]$), 219 ($M^+ – [Si(CH_3)_2H + CH_4]$).

Preparation of ***6***

Under a dry argon atmosphere, 1.50 g (4.46 mmol) of 1,8-dibromophenanthrene (**3**) and 2.55 g (27.0 mmol) of chlorodimethylsilane in 30 mL of THF were added dropwise to 1.00 g (41.1 mmol) of magnesium in 30 mL of THF at 60°C. The reaction mixture was refluxed for 24 h and then poured into a mixture of 100 mL of diethyl ether and 100 mL of 0.1 mol/L HCl aqueous solution. The organic layer was washed with saturated sodium hydrogen carbonate aqueous solution, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexane. The collected eluent containing the purified material was concentrated under reduced pressure and recrystallized from methanol to afford 1,8-(dimethylsilyl)phenanthrene (**6**) as colorless crystals with the yield of 1.06 g (81 %). M.p.: 75°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.79 (dd, J = 8.4, 1.2 Hz, 2H, phenanthrylene protons), 8.11 (s, 2H, phenanthrylene protons), 7.84 (dd, J = 6.9, 1.2 Hz, 2H, phenanthrylene protons), 7.65 (dd, J = 8.4, 6.9 Hz, 2H, phenanthrylene protons), 4.93 (sept, J = 3.8 Hz, 2H, $–Si(CH_3)_2–H$), 0.54 (d, J = 3.8 Hz, 12H, $–Si(CH_3)_2–H$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ136.1 (phenanthrylene carbon), 135.4 (phenanthrylene carbon), 133.9 (phenanthrylene carbon), 130.5 (phenanthrylene carbon), 126.9 (phenanthrylene carbon), 126.5 (phenanthrylene carbon), 124.4 (phenanthrylene carbon), –3.10 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 2120 (Si-H). Mass (EI, *m/z*): 294 (M^+), 236 ($M^+ – [Si(CH_3)_2]$), 220 ($M^+ – [Si(CH_3)_2 + CH_4]$).

Preparation of Monomers

Typical procedure: Under an argon atmosphere, **6** (0.40 g, 1.36 mmol) in THF (0.3 mL) was added dropwise to 5%-Pd on C (0.030 g) with H_2O (0.065 g, 3.61 mmol) in THF (0.8 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 toluene to afford 1,8-bis(dimethylhydroxysilyl)-phenanthrene (**M3**) as colorless crystals with the yield of 0.35 g (79 %). M.p.: 179°C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.70 (dd, J = 8.4, 1.2 Hz, 2H, phenanthrylene protons), 8.16 (s, 2H, phenanthrylene protons), 7.79 (dd, J = 6.9, 1.2 Hz, 2H, phenanthrylene protons), 7.55 (dd, J = 8.4, 6.9 Hz, 2H, phenanthrylene protons), 2.06 (s, 2H, –OH), 0.51 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.4 (phenanthrylene carbon), 135.1 (phenanthrylene carbon), 133.5 (phenanthrylene carbon), 130.7 (phenanthrylene carbon), 126.9 (phenanthrylene carbon), 125.7 (phenanthrylene carbon), 124.8 (phenanthrylene carbon), 1.54 (–Si$(CH_3)_2$–). IR (KBr, cm^{-1}): 3260 (-OH). Mass (EI, *m/z*): 326 (M^+), 311 ($M^+ - CH_3$), 293 ($M^+ - [CH_3 + H_2O]$).

2,6-Bis(dimethylhydroxysilyl)anthracene (**M1**) and 9,10-bis(dimethylhydroxysilyl)-anthracene (**M2**) were prepared by the similar method as the preparation of **M3** using **4** and **5** as the raw material, respectively.

M1: Yield: 61 % as pale yellow crystals. M.p.: 139°C. ^1H NMR (400 MHz, $(CD_3)_2SO$, ppm): δ 8.55 (s, 2H, anthrylene protons), 8.27 (s, 2H, anthrylene protons), 8.05 (d, J = 8.5 Hz, 2H, anthrylene protons), 7.62 (dd, J = 8.5, 0.9 Hz, 2H, anthrylene protons), 6.05 (s, 2H, –OH), 0.35 (s, 12H, –Si$(CH_3)_2$–). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, ppm): δ 138.2 (anthrylene carbon), 134.2 (anthrylene carbon), 131.7 (anthrylene carbon), 131.2 (anthrylene carbon), 128.8 (anthrylene carbon), 127.3 (anthrylene carbon), 126.3 (anthrylene carbon), 0.8(–Si$(CH_3)_2$–). IR (KBr, cm^{-1}): 3275 (-OH). Mass (EI, *m/z*): 325 ($M^+ - H$), 178 ($M^+ - 2[Si(CH_3)_2O]$).

M2: Yield: 48 % as pale yellow crystals. M.p.: 216°C. ^1H NMR (400 MHz, $(CD_3)_2SO$, ppm): δ 8.69 (dd, J = 6.9, 3.3 Hz, 4H, anthrylene protons), 7.43 (dd, J = 6.9, 3.3 Hz, 4H, anthrylene protons), 6.6-6.3 (br, 2H, –OH), 0.62 (s, 12H, –Si$(CH_3)_2$–). ^{13}C NMR (100 MHz, $(CD_3)_2SO$, ppm): δ 138.9 (anthrylene carbon), 135.9 (anthrylene carbon), 129.3 (anthrylene carbon), 124.1 (anthrylene carbon), 5.0 (–Si$(CH_3)_2$–). IR (KBr, cm^{-1}): 3232 (-OH). Mass (EI, *m/z*): 326 (M^+), 293 ($M^+ - [CH_3 + H_2O]$), 178 ($M^+ - 2[Si(CH_3)_2O]$).

Polycondensation

Typical procedure: Under a dry atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexoate (0.02 g) was added to **M3** (0.25 g, 0.77 mmol) dissolved in benzene (12.5 mL), and the reaction mixture was refluxed for 24 h. The reaction mixture was poured into methanol (100 mL) to isolate poly(tetramethyl-1,8-silphenanthrylene-siloxane) (**P3**) as white precipitates with the yield of 0.14 g (59 %). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.67 (d, J = 8.2 Hz, 2H, phenanthrylene protons), 8.07 (s, 2H, phenanthrylene protons), 7.78 (d, J = 6.9 Hz, 2H, phenanthrylene protons), 7.50 (m, 2H, phenanthrylene protons), 0.51 (s, 12H, –Si$(CH_3)_2$–). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.9 (phenanthrylene carbon), 135.0 (phenanthrylene carbon), 133.3 (phenanthrylene carbon), 130.6 (phenanthrylene carbon), 126.8 (phenanthrylene carbon), 125.6 (phenanthrylene carbon), 124.6 (phenanthrylene carbon), 2.29 (–Si$(CH_3)_2$–). IR (KBr, cm^{-1}): 1000-1100 (Si-O).

Poly(tetramethyl-2,6-silanthrylenesiloxane) (**P1**) and poly(tetramethyl-9,10-silanthrylenesiloxane) (**P2**) were prepared by the similar method as the preparation of **P3** using **M1** and **M2** as a monomer, respectively, and polycondensation was carried out in toluene. No NMR spectral data of **P2** were obtained because of the very poor solubility of **P2** in common organic solvents.

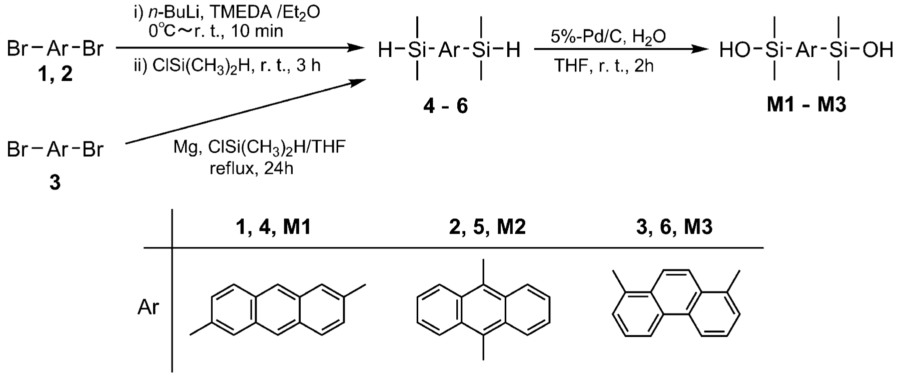
P1: Yield: 55 % as pale yellow powder solid. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22 (s, 2H, anthrylene protons), 8.15 (s, 2H, anthrylene protons), 7.82 (d, J = 8.6 Hz 2H, anthrylene protons), 7.55 (d, J = 8.6 Hz, 2H, anthrylene protons), 0.46 (s, 12H, –Si$(CH_3)_2$–). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 134.9 (anthrylene carbon), 134.6 (anthrylene carbon), 131.1 (anthrylene carbon), 130.4 (anthrylene carbon), 127.4 (anthrylene carbon), 126.5 (anthrylene carbon), 125.5 (anthrylene carbon), –0.46 (–Si$(CH_3)_2$–). IR (KBr, cm^{-1}): 1000-1100 (Si-O).

P2: Yield: 63 % as pale yellow powder solid. IR (KBr, cm^{-1}): 1000-1100 (Si-O).

Results and Discussion

Monomer Synthesis

Scheme 2 shows the pathways for the syntheses of novel disilanol monomers **M1**, **M2**, and **M3**.



Scheme 2. Pathways for syntheses of disilanol monomers **M1**-**M3**.

M1–**M3** were obtained by hydrolyzing the corresponding bis(dimethylsilyl)-substituted aromatic compounds, **4**–**6**, respectively. 1,8-Bis(dimethylsilyl)-phenanthrene (**6**) was obtained from 1,8-dibromophenanthrene (**3**) via the Grignard reaction with chlorodimethylsilane. In contrast, bis(dimethylsilyl)anthracene derivatives (**4**,**5**) could not be obtained by the Grignard reaction using dibromoanthracene derivatives and chlorodimethylsilane. As for the synthesis of **5**, the similar results have been reported by Beck *et al.* [5], presumably owing to the formation of a relatively stable metal-complex of anthracene derivative with magnesium and THF as reported by Alonso *et al* [16].

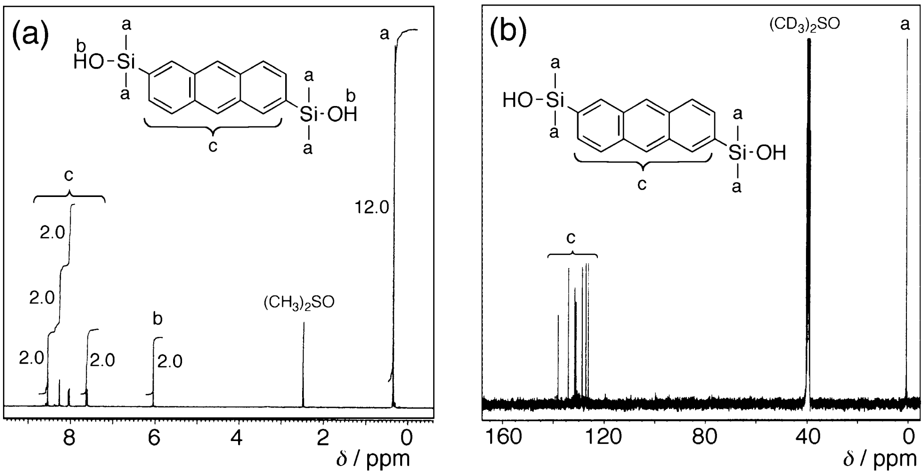


Figure 1. (a) ^{1}H NMR (solvent: $(CD_3)_2SO$, 400 MHz, numerals at signal's side are the integral values of each signal) and (b) ^{13}C NMR spectra (solvent: $(CD_3)_2SO$, 100 MHz) of **M1**.

Thus, the use of lithiation reagent [16] and chlorodimethylsilane successfully incorporated dimethylsilyl moieties onto anthracene derivatives. Beck *et al.* reported [5] to hydrolyze the bis(dimethylsilyl)-substituted aromatic compounds using sodium ethoxide in ethanol followed by a treatment of buffer aqueous solution to obtain the corresponding bis(dimethylhydroxysilyl)-substituted aromatic ones with good yields; however, this reaction was unable to be applied to hydrolyzing the present **4–6**, because of the poor solubility of **4–6** in alcoholic media. Therefore, we hydrolyzed **4–6** using a 5% Pd on charcoal catalyst [18] in THF and successfully obtained the corresponding novel disilanol monomers **M1–M3**. The spectroscopic data described in the experimental part indicated the syntheses of novel monomers were achieved. As a typical example, ^{1}H and ^{13}C NMR spectra of **M1** are depicted in Figure 1. Each signal was consistently assigned as described in Figure 1.

Syntheses and Characterization of Polymers

M1–**M3** underwent polycondensation catalyzed by 1,1,3,3-tetramethylguanidinium 2-ethylhexoate to afford the corresponding poly(tetramethylsilarylenesiloxane) derivatives **P1**–**P3**, respectively. Any solvents forming azeotropic mixtures with water as well as dissolving both monomer and the resulting polymer, such as benzene and toluene, can be used for the present polycondensation as reported previously [9,12]. Unfortunately, the resulting **P2** was almost insoluble in common organic solvents, presumably owing to the strong intermolecular stacking between anthrylene moieties. Poly(tetramethyl-1,5-silnaphthylenesiloxane) has been reported to exhibit the similar poor solubility in common organic solvents [9] in spite of the good solubility of poly(tetramethyl-1,4-silnaphthylenesiloxane) in common organic solvents. In contrast, **P1** and **P3** are soluble in common organic solvents such as THF, chloroform, dichloromethane, and toluene. The SEC profiles of **P1** and **P3** indicated the obtained polymers were unimodal. Figure 2 shows the SEC profile of **P3** eluted with THF as an example, indicating the formation of polymer, while very small amount of low molecular weight species such as a cyclic dimer or trimer existed.

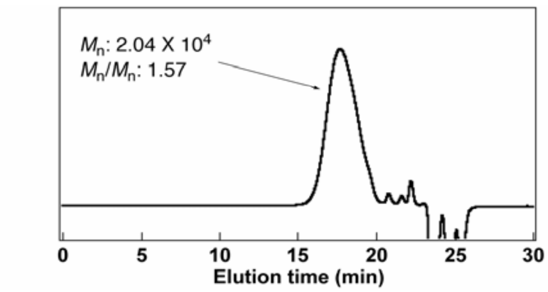


Figure 2. SEC profile of **P3** eluted with THF.

The structures of **P1** and **P3** were confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy. As a typical example, ^{1}H and ^{13}C NMR spectra of **P3** are described in Figure 3. Each signal was consistently assigned as described in Figure 3. On the other hand, the progress of polycondensation of **M2** was confirmed by IR spectroscopy. Figure 4 depicts the IR spectra of **M2** and **P2**. A broad absorption band around 3230 cm^{-1} based on the stretching vibration of –OH groups was clearly observed in the IR spectrum of **M2** as shown in Figure 4(a), whereas no absorption bands based on –OH groups were observed in the IR spectrum of **P2** as shown in Figure 4(b).

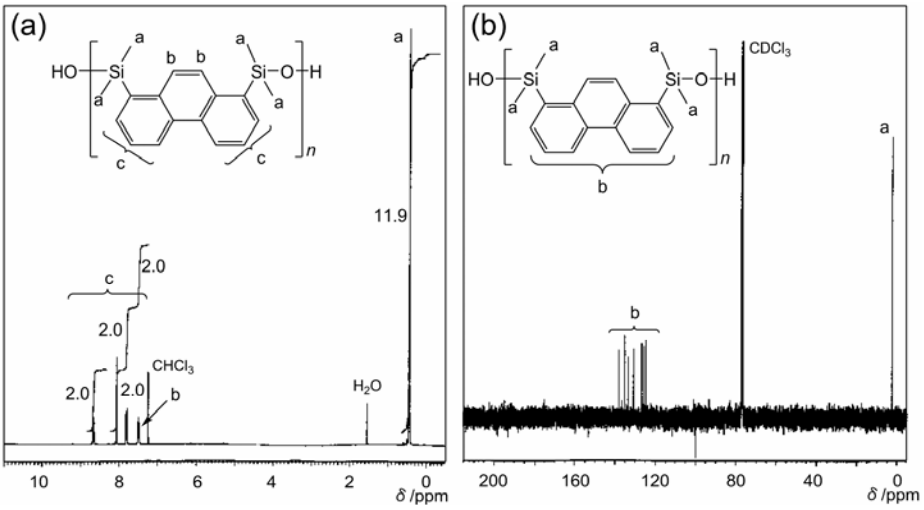


Figure 3. (a) ^{1}H NMR (solvent: $CDCl_3$, 400 MHz, numerals at signal's side are the integral values of each signal) and (b) ^{13}C NMR spectra (solvent: $CDCl_3$, 100 MHz) of **P3**.

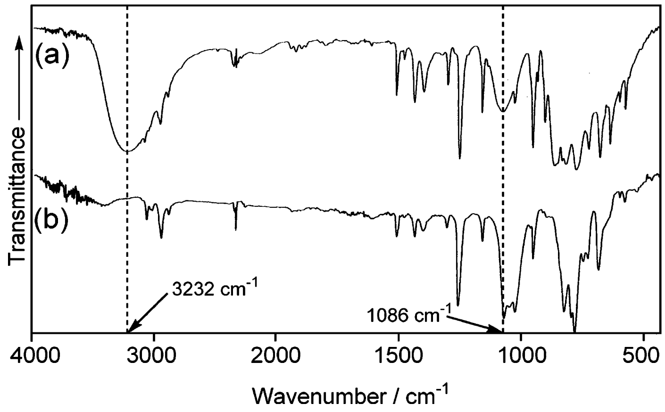


Figure 4. Infrared absorption spectra of (a) **M2** and (b) **P2**.

In addition, a broad absorption band around 1000-1100 cm^{-1} based on Si-O-Si moieties was clearly observed in the IR spectrum of **P2**. These findings may indicate the progress of polycondensation of **M2** to afford **P2**.

Figure 5 shows the DSC traces of **P1** and **P3** on a second heating scan and that of **P2** on a first heating scan under a nitrogen atmosphere at a heating rate of 10°C/min. As shown in Figures 5(a) and (c), the glass transition of **P1** and **P3** was clearly observed at 118°C and 100°C, respectively. On the other hand, some transition was observed in a DSC trace of **P2** around 240°C on a first heating scan. The second heating scan of **P2** exhibited no transition behavior such as glass transition or melting. We carried out the X-ray diffractometric analysis of **P2** to investigate the origin of the transition observed in a DSC trace of **P2** on a first heating scan.

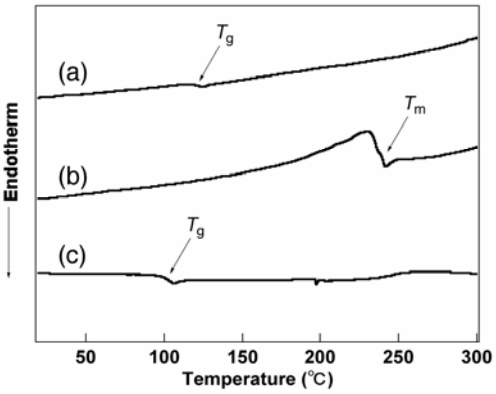


Figure 5. DSC thermograms of (a) **P1** and (c) **P3** on a second heating scan as well as (b) **P2** on a first heating scan under a nitrogen flow rate of 10 mL/min and a cooling or heating rate of 10°C/min.

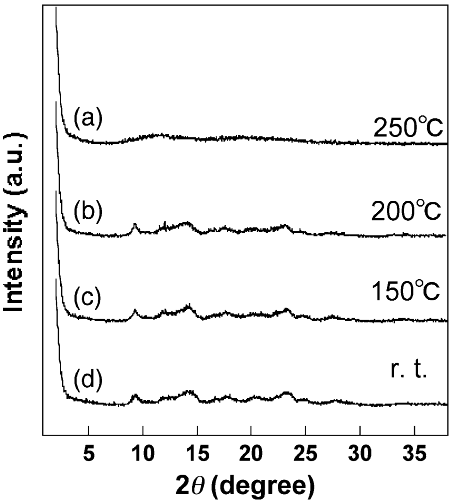


Figure 6. X-ray diffraction patterns of **P2** at various temperatures; measured at (a) 250°C, (b) 200°C, (c) 150°C, and (d) room temperature.

Figure 6 depicts the X-ray diffraction patterns of **P2** at various temperatures. Some weak diffraction peaks were observed below 200°C and no diffraction peaks were observed at 250°C as shown in Figure 6, indicating the crystallinity of **P2**. Therefore, the transition observed in a DSC trace of **P2** around 240°C as depicted in Figure 5(c) was presumably due to the melting. The change in the base line of a first heating scan of **P2** after melting was observed, presumably because the silyl moieties, which were incorporated to 9- and 10-positions of anthracene, perturbed the π-system of anthracene [17] to induce some reactions changing the polymer structure. It was also confirmed that no diffraction peaks were observed in the X-ray diffraction patterns for

P2 cooled from 250°C. Thus, the properties of **P1–P3** can be summarized as presented in Table 1.

Table 1. Characterization of **P1–P3**

Polymer[a)]	10^{-4} M_n[b)]	M_w/M_n[b)]	T_g(°C)[c)]	T_m(°C)[c)]	T_{d5}(°C)[d)]
P1	1.96	2.81	118	------[f)]	436
P2	------[e)]	------[e)]	------[f)]	242	389
P3	2.04	1.57	100	------[f)]	500

a) Polycondensation was carried out in toluene for the preparation of **P1** and **P2**; in benzene for the preparation of **P3**.
b) Estimated from SEC eluted with THF based on polystyrene standards.
c) Determined by DSC at a heating rate of 10°C/min under a nitrogen atmosphere.
d) Determined by TG under a nitrogen atmosphere.
e) Not determined owing to the poor solubility in common organic solvents.
f) Not observed in DSC measurement between -50 and 400°C.

The T_g's of **P1** and **P3** were much higher than that of 1,4-PTMPS (-20°C) [19] as well as those of poly(tetramethylsilnaphthylenesiloxane) derivatives (in the range of 26-60°C) [9]. The increase in bulkiness of the arylene moiety incorporated into the main chain would restrict the mobility of the main chain to result in the improvement of T_g. The thermodynamic melting temperature of 1,4-PTMPS has been reported to be 160°C by Magill *et al* [19]. The T_m of **P2** was found to be higher than that of 1,4-PTMPS, presumably owing to the strong interactions between anthrylene moieties. On the other hand, the temperature at 5 % weight loss (T_{d5}) of **P3** (500°C) was found to be higher than those of **P1** and **P2**. Namely, the thermostability of poly(tetramethylsilarylenesiloxane) incorporating phenanthrylene moieties was better than that incorporating anthrylene ones. It may be because the silyl moieties at 9- and 10-positions of anthracene perturbed the π-system of anthracene [17] that **P2** exhibited the lowest T_{d5} among the present polymers. The T_{d5} of 1,4-PTMPS has been reported to be over 500°C [3]. The T_{d5}'s of **P1** and **P2** were low compared with that of 1,4-PTMPS; however, that of **P3** was comparable to that of 1,4-PTMPS. In addition, the T_{d5} of **P3** was higher than those of poly(tetramethylsilnaphthylenesiloxane) derivatives, whereas those of **P1** and **P2** were low compared with those of poly(tetramethylsilnaphthylenesiloxane) derivatives. These findings would be related to the stability of the arylene moieties incorporated. The constants obtained by dividing the resonance energy by the number of double bonds in the aromatic molecules have been reported [20]. According to this analysis, the order of stability based on this constant has been reported to be: phenanthrene > benzene > naphthalene > anthracene. This order seems to be similar to that of the thermostability of poly(tetramethylsiliarylenesiloxane) derivatives having the series of aromatic moieties. In summary, it would be suggested that the thermostability of the series of poly(tetramethylsilarylenesiloxane) derivatives is dependent on the stability of arylene moieties incorporated.

Conclusions

Novel poly(tetramethylsilarylenesiloxane) derivatives, i.e. poly(tetramethyl-2,6-silanthrylenesiloxane) (**P1**), poly(tetramethyl-9,10-silanthrylenesiloxane) (**P2**), and poly(tetramethyl-1,8-silphenanthrylenesiloxane) (**P3**), were obtained by polycondensation of the corresponding novel disilanol derivatives. **P1** and **P3** were soluble in common organic solvents, such as benzene, toluene, chloroform, dichloromethane, THF, *etc.,* while **P2** was almost insoluble in common organic solvents. It was revealed that **P1** and **P3** were amorphous and that **P2** exhibited the crystallinity as deduced from DSC and X-ray diffraction measurements. The T_g's of **P1** and **P3** were much higher than that of 1,4-PTMPS. The T_{d5} of **P3** was 500°C, which was higher than those of **P1** and **P2**, and comparable to that of 1,4-PTMPS. It was speculated that the thermostability of the series of poly(tetramethylsilarylene-siloxane) derivatives is dependent on the stability of arylene moieties incorporated.

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