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Synthesis and Thermal Characterization of Novel Fluorene-Based Polysiloxane Derivatives

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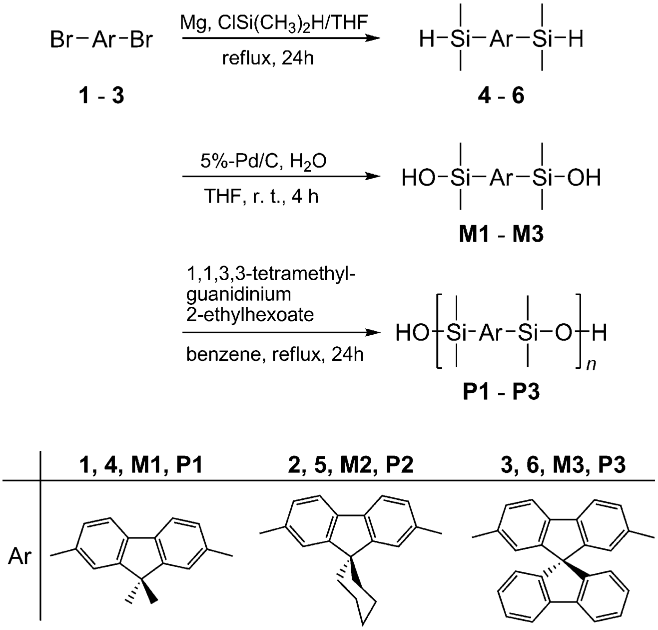
Summary

Three novel poly(tetramethylsilfluorenylenesiloxane) derivatives having different substituent at 9-position of fluorenylene moiety, i.e. dimethyl (**P1**), spirocyclohexyl (**P2**), and spirofluorenyl (**P3**) substituents, were obtained by polycondensation of novel three disilanol monomers, i.e. 2,7-bis(dimethylhydroxysilyl)-9,9-dimethylfluorene (**M1**), 2',7'-bis(dimethylhydroxysilyl)-spiro(cyclohexane-1,9'-fluorene) (**M2**), 2,7-bis(dimethylhydroxysilyl)-9,9'-spirobifluorene (**M3**), respectively. **P1**–**P3** exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. It was suggested from the differential scanning calorimetry (DSC) and the X-ray diffraction analysis that **P1** exhibited the crystallinity whereas **P2** and **P3** were amorphous polymers. The glass transition temperature (T_g) determined by DSC and the temperature at 5% weight loss (T_{d5}) determined by thermogravimetry (TG) were dependent on the substituent at 9-position on fluorene; both orders of T_g and T_{d5} were **P3** > **P2** > **P1**, indicating the bulkiness of substituent at 9-position of fluorene resulted in the good thermal stability. It is noteworthy that amorphous **P3** exhibiting very high T_g of 156°C and T_{d5} of 535°C is a new heat-resistant polysiloxane derivative as well as a promising candidate for blue-light-emitting materials.

Introduction

Fluorene is one of most attractive molecules suitable for applications in electronics and optoelectronics, such as organic light emitting diodes (OLEDs). Especially, OLEDs based on polymeric materials have been expected as next generation devices for large flexible panel displays, and many fluorene-based conjugating polymers have been reported to be promising candidates for blue-light-emitting polymers [1-3]. High thermal and oxidative stabilities are required for blue-light-emitting polymers because blue-light emissions are associated with high energy gaps and high electrical field intensities. Another major problem in obtaining blue-light emission from polymeric materials is the decline of the color stability of the light emission resulting from the changes of the emission spectra, which becomes more serious upon exposure to heat, [4-7] because of the formation of aggregates and/or interchain excimers. Thus, the inhibition of thermal oxidation as well as the reduction of excimer formation should be required for the enhancement of color stability [4-7]. The incorporation of functional groups, such as alkyl chain [5-7], perfluoroalkyl chain [8], or bulky moieties [3,4,9-12], into 9-position of fluorene has been reported to be effective for the inhibition of thermal oxidation as well as the reduction of excimer formation. The improvement of glass transition temperature (T_g) and the decrease in the tendency toward crystallization of the polymer chain are also effective in suppressing the formation of aggregates and/or interchain excimers [4-7,9-12].

On the other hand, the incorporation of silyl substituent onto aromatic species has been reported to result in extremely high fluorescence quantum yield [13-16]. If the silyl substituent is incorporated onto fluorene, the development of the highly efficient fluorophore is presumably promised. Actually, polysiloxanes and polysilanes having fluorenyl moiety in the main chain have been reported; however, the polysiloxane derivatives were reported to be obtained as oil products, indicating the T_g of the polysiloxane derivative was extremely low [17]. Thus, the use of polysiloxane derivatives as polymeric OLED materials seems to be inadequate because of their extremely low T_g [18,19] inducing the formation of aggregates and/or interchain excimers, even though the other properties of polysiloxanes such as good thermostability and stability against atomic oxygen [18] seem to be appropriate for the polymeric OLED materials. One of methods for raising T_g is incorporation of bulky and rigid moieties into the main chain. For example, the T_g of poly(dimethylsiloxane) has been reported to be –123°C [18]; however, that of poly(tetramethyl-1,4-



Scheme 1. Synthesis of poly(tetramethylfluorenylenesiloxane) having dimethyl (**P1**), spirocyclohexyl (**P2**), and spirofluorenyl moiety (**P3**) at 9-position of fluorenylene moiety

silphenylenesiloxane) (1,4-PTMPS), which is a representative polymer of poly(tetramethylsilarylenesiloxane) derivatives, to be –20°C owing to the incorporation of bulky phenylene moieties into the backbone [20-23].

Generally, the properties of poly(tetramethylsilarylenesiloxane) derivatives depend on the kind of arylene moiety [22-28] as well as the substituent on the silyl moieties [28]. It has been reported that the improvement of T_g of poly(tetramethylsilarylenesiloxane) derivatives is realized by the incorporation of bulky naphthylene [26], anthrylene [27], or phenanthrylene [27] moieties into the backbone or by the introduction of phenyl substituents onto the silyl moieties [28].

From these points of view, we report here the preparation of novel poly(tetramethylfluorenylenesiloxane) having dimethyl (**P1**), spirocyclohexyl (**P2**), and spirofluorenyl (**P3**) moiety at 9-position of fluorenylene moiety, as shown in Scheme 1. The present article will reveal that the T_g and the crystallinity of the obtained polymers are controlled by the substituents at 9-position of fluorenylene moiety and that the bulky substituent result in the improvement of T_g up to 156°C as well as the decrease in the tendency toward crystallization.

Experimental Part

Materials

2,7-Dibromo-9,9-dimethylfluorene (**1**) [29], 2',7'-dibromo-spiro(cyclohexane-1,9'-fluorene) (**2**) [12], and 2,7-dibromo-9,9'-spirobifluorene (**3**) [4,9] were prepared by the methods described in the literature. Magnesium (KANTO KAGAKU), chlorodimethylsilane (Acros organics), and 5% palladium on charcoal (Escat 103, from Aldrich) were commercially available and used as received. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate, which has been reported to be one of most effective catalysts for polycondensation of disilanol derivatives [30], was prepared from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.). The purity of all prepared compounds with low-molecular weight was confirmed to be over 99 % by GC analysis. Benzene 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 ($CDCl_3$) 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. X-ray diffraction patterns were recorded on a Philips PW1830 X-ray diffractometer, equipped with a Philips HTK-2-HC thermal controller.

*Preparation of Bis(dimethylsilyl)-Substituted Fluorene Derivatives (**4**-**6**)*

Typical procedure: Under a dry argon atmosphere, 1.067 g (2.25 mmol) of **3** and 0.64 g (6.76 mmol) of chlorodimethylsilane in 20 mL of dry THF were added dropwise to 0.120 g (5.02 mmol) of magnesium in 5 mL of dry THF at 60°C. The reaction mixture was refluxed for 24 h and poured into a mixture of 50 ml of ethyl acetate and 50 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 chromatography eluted with a mixed solvent of hexane/ethyl acetate (20/1 v/v). The collected fraction of R_f value of 0.65 was concentrated under reduced pressure and the residue was recrystallized from methanol to afford 2,7-bis(dimethylsilyl)-9,9'-spirobifluorene (**6**) as colorless crystals with the yield of 0.549 g (56 %). M.p.: 152°C. ^{1}H NMR ($CDCl_3$): $\delta = 7.87$ (dt, $J = 0.8, 7.5$ Hz, 2H, fluorenyl protons), 7.84 (dd, $J = 0.6, 7.5$ Hz, 2H, fluorenyl protons), 7.53 (dd, $J = 1.0, 7.5$ Hz, 2H, fluorenyl protons), 7.38 (dt, $J = 1.0, 7.5$ Hz, 2H, fluorenyl protons), 7.11 (dt, $J = 1.0, 7.5$ Hz, 2H, fluorenyl protons), 6.85 (s, 2H, fluorenyl protons), 6.72 (dt, $J = 0.8, 7.5$ Hz, 2H, fluorenyl protons), 4.25 (sept, $J = 3.7$ Hz, 2H, $\text{-Si-(CH}_3)_2H$), 0.19 (d, $J = 3.7$ Hz, 12H, $\text{-Si-(C}H_3)_2\text{H}$). ^{13}C NMR ($CDCl_3$): $\delta = 148.7$ (fluorenyl carbons), 148.4 (fluorenyl carbons), 142.7 (fluorenyl carbons), 141.8 (fluorenyl carbons), 137.5 (fluorenyl carbons), 133.4 (fluorenyl carbons), 129.5 (fluorenyl carbons), 127.8 (fluorenyl carbons), 127.6 (fluorenyl carbons), 124.2 (fluorenyl carbons), 120.0 (fluorenyl carbons), 119.6 (fluorenyl carbons), 66.0 (fluorenyl quaternary carbon), –3.7 ($\text{–Si(}C\text{H}_3)_2\text{–H}$). IR (KBr): 2117 (Si–H).

2,7-Bis(dimethylsilyl)-9,9-dimethylfluorene (**4**) and 2',7'-bis(dimethylsilyl)-spiro-(cyclohexane-1,9'-fluorene) (**5**) were prepared by the similar method as the preparation of **6** using **1** and **2** as the raw material, respectively. The spectral data for **4** and **5** are as shown below.

4: Yield: 48 % as colorless crystals recrystallized from methanol. M.p.: 83°C. ^{1}H NMR ($CDCl_3$): $\delta = 7.75$ (dd, $J = 0.7, 7.4$ Hz, 2H, fluorenyl protons), 7.61 (t, $J = 0.7$ Hz, 2H, fluorenyl protons), 7.52 (dd, $J = 1.0, 7.4$ Hz, 2H, fluorenyl protons), 4.50 (sept, $J = 3.7$ Hz, 2H, $\text{-Si-(CH}_3)_2H$), 1.52 (s ,6H, CH_3 on fluorene), 0.41 (d , $J = 3.7$ Hz, 12H, $\text{-Si-(C}H_3)_2\text{H}$). ^{13}C NMR ($CDCl_3$): $\delta = 153.0$ (fluorenyl carbons), 140.1 (fluorenyl carbons), 136.6 (fluorenyl carbons), 132.7 (fluorenyl carbons), 128.1 (fluorenyl carbon), 119.6 (fluorenyl carbon), 46.8 (fluorenyl quaternary carbon), 27.2 ($-CH_3$ on fluorene), –3.5 ($\text{–Si(}C\text{H}_3)_2\text{–H}$). IR (KBr): 2113 (Si–H).

5: Yield: 67 % as colorless crystals recrystallized from methanol. M.p.: 79°C. ^{1}H NMR ($CDCl_3$): $\delta = 7.75$ (s, 2H, fluorenyl protons), 7.68 (dd, $J = 0.6, 7.4$ Hz, 2H, fluorenyl protons), 7.46 (dd, $J = 0.9, 7.4$ Hz, 2H, fluorenyl protons), 4.43 (sept, $J = 3.7$ Hz, 2H, $\text{-Si-(CH}_3)_2H$), 1.92-1.82 (m, 4H, cyclohexyl protons), 1.79-1.73 (m, 2H, cyclohexyl protons), 1.72-1.66 (m, 4H, cyclohexyl protons), 0.33 (d, $J = 3.7$ Hz, 12H, $\text{-Si-(C}H_3)_2\text{H}$). ^{13}C NMR ($CDCl_3$): $\delta = 152.7$ (fluorenyl carbon), 140.6 (fluorenyl carbons), 136.1 (fluorenyl carbons), 132.6 (fluorenyl carbons), 129.9 (fluorenyl carbons), 119.5 (fluorenyl carbons), 50.3 (fluorenyl quaternary carbon), 35.6 (cyclohexyl carbons), 25.6 (cyclohexyl carbons), 22.8 (cyclohexyl carbons), –3.5 ($\text{–Si(}C\text{H}_3)_2\text{–H}$). IR (KBr): 2111 (Si–H).

*Preparation of Monomers (**M1** – **M3**)*

Typical procedure: Under a dry argon atmosphere, **6** (1.45 g, 3.35 mmol) in dry THF (2.0 mL) was added dropwise to 5%-Pd on C (6.15 mg) with H_2O (0.17 g, 9.44 mmol) in THF (0.8 mL) in an ice bath. The reaction mixture was stirred at ambient temperature for 4 h and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from a mixed solvent of toluene/hexane to afford 2,7-bis(dimethylhydroxysilyl)-9,9'-spirobifluorene (**M3**) as colorless crystals with the yield of 1.32 g (85 %). M.p.: 191°C. ^{1}H NMR ($CDCl_3$): δ = 7.89-7.83 (m, 4H, fluorenyl protons), 7.58 (dd, J = 1.0, 7.5 Hz, 2H, fluorenyl protons), 7.36 (dt, J = 1.0, 7.5 Hz, 2H, fluorenyl protons), 7.08 (dt, J = 1.0, 7.5 Hz, 2H, fluorenyl protons), 6.91 (s, 2H, fluorenyl protons), 6.69 (d, J = 7.5 Hz, 2H, fluorenyl protons), 1.72 (s, 2H, Si–OH), 0.25 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($CDCl_3$): δ = 148.5 (fluorenyl carbons), 142.9 (fluorenyl carbons), 141.8 (fluorenyl carbons), 139.2 (fluorenyl carbons), 132.6 (fluorenyl carbons), 128.4 (fluorenyl carbons), 127.8 (fluorenyl carbons), 127.6 (fluorenyl carbons), 124.1 (fluorenyl carbons), 120.0 (fluorenyl carbons), 119.7 (fluorenyl carbons), 66.0 (fluorenyl quaternary carbon), 0.10 ($–Si(CH_3)_2–$). IR (KBr): 3340 (-OH).

2,7-bis(dimethylhydroxysilyl)-9,9-dimethylfluorene (**M1**) and 2',7'-bis(dimethylhydroxysilyl)-spiro(cyclohexane-1,9'-fluorene) (**M2**) were prepared by the similar method as the preparation of **M3** using **4** and **5** as the raw material, respectively. The spectral data for **M1** and **M2** are as shown below.

M1: Yield: 70 % as colorless crystals recrystallized from chloroform. M.p.: 190°C. ^{1}H NMR ($CDCl_3$): δ= 7.80 (dd, J = 0.6, 7.4 Hz, 2H, fluorenyl protons), 7.71 (m, 2H, fluorenyl protons), 7.51 (dd, J = 0.9, 7.4 Hz, 2H, fluorenyl protons), 5.89 (s, 2H, Si-OH), 1.44 (s, 6H, $–CH_3$ on fluorene), 0.28 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($CDCl_3$): δ= 152.7 (fluorenyl carbon), 140.1 (fluorenyl carbon), 139.6 (fluorenyl carbon), 132.0 (fluorenyl carbon), 127.2 (fluorenyl carbon), 119.7 (fluorenyl carbon), 46.5 (fluorenyl quaternary carbon), 27.3 ($-CH_3$ on fluorene), 1.0 ($–Si(CH_3)_2–$). IR (KBr): 3247 (-OH).

M2: Yield: 67 % as colorless crystals recrystallized from chloroform. M.p.: 151°C. ^{1}H NMR ($CDCl_3$): δ= 7.83 (s, 2H, fluorenyl protons), 7.71 (dd, J = 0.6, 7.4 Hz, 2H, fluorenyl protons), 7.52 (dd, J = 0.9, 7.4 Hz, 2H, fluorenyl protons), 1.92-1.82 (m, 4H, cyclohexyl protons), 1.79-1.73 (m, 2H, cyclohexyl protons), 1.73-1.67 (m, 4H, cyclohexyl protons), 1.53 (s, 2H, -OH), 0.41 (s, 12H, $-Si-(CH_3)_2-$). ^{13}C NMR ($CDCl_3$): δ = 152.6 (fluorenyl carbon), 140.6 (fluorenyl carbon), 137.7 (fluorenyl carbon), 132.4 (fluorenyl carbon), 128.7 (fluorenyl carbon), 119.4 (fluorenyl carbon), 50.1 (fluorenyl quaternary carbon), 35.4 (cyclohexyl carbons), 25.4 (cyclohexyl carbons), 22.7 (cyclohexyl carbons), 0.0 ($–Si(CH_3)_2–$). IR (KBr): 3260 (-OH).

*Polycondensation of **M1 – M3***

Typical Procedure: Under a dry atmosphere, 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate (0.02 g) was added to **M3** (0.306 g, 0.66 mmol) dissolved in dry benzene (12.5 mL), and the reaction mixture was refluxed for 24 h. The reaction mixture was poured into methanol (100 mL) to isolate **P3** as white precipitates with the yield of 0.160 g (54 %). ^{1}H NMR ($CDCl_3$): δ= 7.79 (d, J = 7.5 Hz, 2H, fluorenyl protons), 7.71 (d, J = 7.5 Hz, 2H, fluorenyl protons), 7.34 (dd, J = 0.9, 7.5 Hz, 2H, fluorenyl protons), 7.28 (dt, J = 0.9, 7.5 Hz, 2H, fluorenyl protons), 6.98 (dt, J = 0.9, 7.5 Hz, 2H, fluorenyl protons), 6.75 (s, 2H, fluorenyl protons), 6.57 (d, J = 7.5 Hz, 2H, fluorenyl protons), –0.09 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($CDCl_3$): δ = 148.2 (fluorenyl carbons), 147.7 (fluorenyl carbons), 142.1 (fluorenyl carbons), 141.2 (fluorenyl carbons), 139.3 (fluorenyl carbons), 131.8 (fluorenyl carbons), 127.9

(fluorenyl carbons), 127.2 (fluorenyl carbons), 126.9 (fluorenyl carbons), 123.6 (fluorenyl carbons), 119.3 (fluorenyl carbons), 118.9 (fluorenyl carbons), 65.4 (fluorenyl quaternary carbon), 0.0 (–Si(CH_3)$_2$–). IR (KBr): 1000-1100 (Si-O).

P1 and **P2** were prepared by the similar method as the preparation of **P3** using **M1** and **M2** as a monomer, respectively. The spectral data for **P1** and **P2** are as shown below.

P1: Yield: 37 % as colorless powder solid. ^{1}H NMR ($CDCl_3$): δ= 7.71 (d, J = 7.5 Hz, 2H, fluorenyl protons), 7.63 (m, 2H, fluorenyl protons), 7.53 (dd, J = 0.8, 7.5 Hz, 2H, fluorenyl protons), 1.46 (s, 6H, -CH_3 on fluorene), 0.38 (s, 12H, –Si(CH_3)$_2$–). ^{13}C NMR ($CDCl_3$): δ = 152.9 (fluorenyl carbon), 140.2 (fluorenyl carbon), 139.1 (fluorenyl carbon), 131.8 (fluorenyl carbon), 127.1 (fluorenyl carbon), 119.5 (fluorenyl carbon), 46.7 (fluorenyl quaternary carbon), 27.2 (-CH_3 on fluorene), 1.1 (–Si(CH_3)$_2$–). IR (KBr): 1000-1100 (Si-O).

P2: Yield: 42 % as colorless powder solid. ^{1}H NMR ($CDCl_3$): δ= 7.84 (s, 2H, fluorenyl protons), 7.71 (d, J = 7.4 Hz, 2H, fluorenyl protons), 7.53 (d, J = 7.4 Hz, 2H, fluorenyl protons), 1.90-1.80 (m, 4H, cyclohexyl protons), 1.92-1.82 (m, 4H, cyclohexyl protons), 1.75-1.65 (m, 6H, cyclohexyl protons), 0.39 (s, 12H, -Si(CH_3)$_2$-). ^{13}C NMR ($CDCl_3$): δ = 152.6 (fluorenyl carbon), 140.7 (fluorenyl carbon), 138.6 (fluorenyl carbon), 131.6 (fluorenyl carbon), 128.9 (fluorenyl carbon), 119.3 (fluorenyl carbon), 50.2 (fluorenyl quaternary carbon), 35.6 (cyclohexyl carbons), 25.6 (cyclohexyl carbons), 22.8 (cyclohexyl carbons), 1.2 (–Si(CH_3)$_2$–).
IR (KBr): 1000-1100 (Si-O)

Results and Discussion

Monomer Synthesis

Novel three fluorene-based disilanol derivatives **M1**–**M3** were synthesized by hydrolyzing the corresponding bis(dimethylsilyl)fluorene derivatives **4**–**6**, which had been prepared from the corresponding dibromofluorene derivatives via the Grignard reactions using chlorodimethylsilane as shown in Scheme 1.

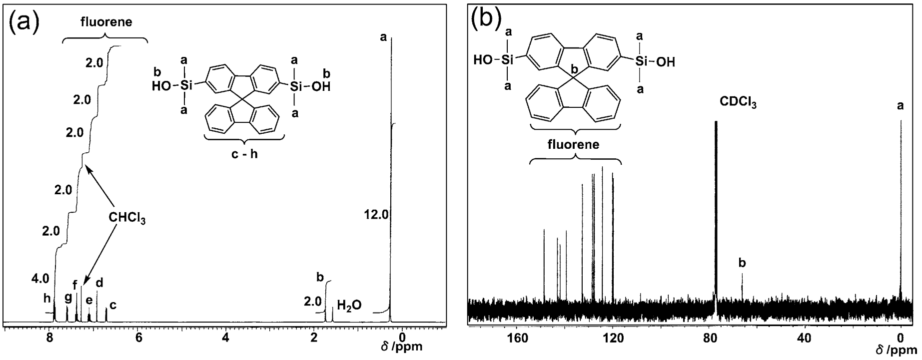


Figure 1. (a) ^{1}H NMR (solvent: $CDCl_3$, 400 MHz, numerals at signal's side are the integral values of each signal) and (b) ^{13}C NMR spectra (solvent: $CDCl_3$, 100 MHz) of **M3** at ambient temperature.

Beck *et al.* reported [23] that bis(dimethylhydroxysilyl)benzene derivatives were obtained by hydrolyzing the corresponding bis(dimethylsilyl)benzene derivatives with good yields using sodium ethoxide in ethanol followed by a treatment of buffer aqueous solution; however, the present **4**–**6** could not be hydrolyzed by this method, because of the poor solubility of **4**–**6** in alcoholic media. Therefore, we carried out the hydrolysis of **4**–**6** using a 5% Pd on charcoal catalyst [26,27,31-33] 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 **M3** are depicted in Figure 1. Each signal was consistently assigned.

Syntheses and Characterization of Polymers

Three fluorene-based disilanol monomers **M1**–**M3** underwent polycondensation by use of 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst to afford the corresponding poly(tetramethylsilfluorenylenesiloxane) derivatives **P1**–**P3**, respectively. As reported previously [26,27,32,33], 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 polycondensation. The structures of **P1**–**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 2.

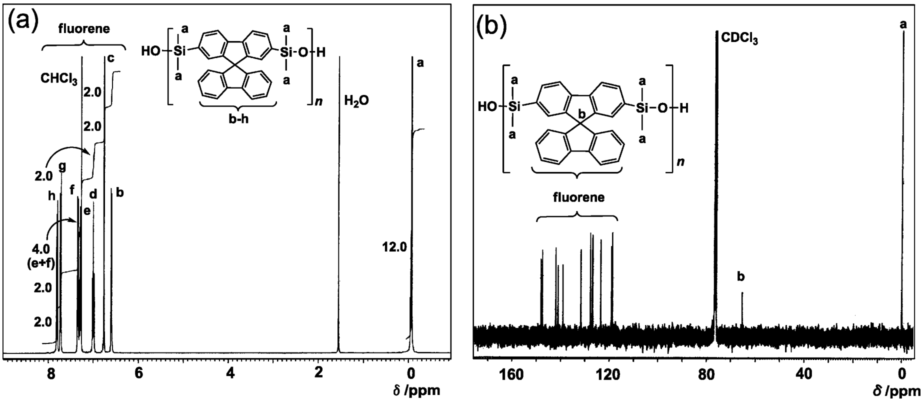


Figure 2. (a) ^{1}H NMR (solvent: $CDCl_3$, 400 MHz, numerals at signal's side are the integral values of each signal) and (b) ^{13}C NMR spectra (solvent: $CDCl_3$, 100 MHz) of **P3** at ambient temperature.

Each signal was consistently assigned. The ^{1}H and ^{13}C NMR spectra of **P3** were almost similar to those of **M3**, except the disappearance of a signal at 1.72 ppm based on –OH groups as observed in the ^{1}H NMR spectrum of **M3**. The integrated ratio of each ^{1}H NMR signal was consistent with the structure of **P3** as described in Figure 2(a). These results strongly support that no side-reactions occurred during the present polycondensation. The characterization of **P1**–**P3** is summarized in Table 1. **P1**–**P3** are soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. The SEC profiles of **P1**–**P3** indicated that the obtained polymers were unimodal and that the low-molecular-weight species as a cyclic dimer or trimer were almost completely removed by reprecipitation in methanol. Glass transition temperatures (T_g's) and melting points (T_m's) of **P1**–**P3** were determined by

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

Polymer[a]	10^{-4} M_n[a]	M_w/M_n[a]	T_g(°C)[b]	T_m(°C)[c]	T_{d5}(°C)[d]
P1	7.30	1.56	67	196	464
P2	2.65	1.67	84	------[e]	495
P3	10.1	2.26	156	------[e]	535

a) Estimated from SEC eluted with THF based on polystyrene standards.

b) Glass transition temperature determined by DSC at a heating rate of 10°C/min under a nitrogen atmosphere.

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

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

e) Not observed in DSC measurement between -50 and 400°C.

DSC as summarized in Table 1. Figure 3 shows the DSC traces of **P1**–**P3** on a second heating scans and that of **P1** on a first heating scan under a nitrogen atmosphere at a heating rate of 10°C/min.

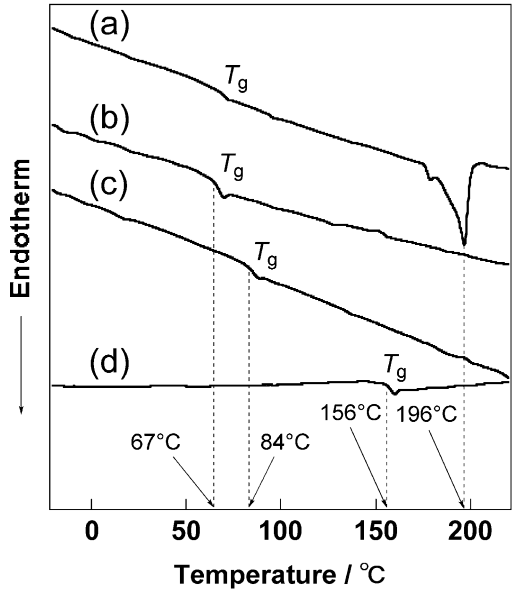


Figure 3. DSC thermograms of (a) **P1** on a first heating scan as well as (b) **P1**, (c) **P2**, and (d) **P3** on a second heating scans under a nitrogen flow rate of 10 mL/min and a cooling or heating rate of 10°C/min.

An endothermic peak was observed only in the first heating scan of **P1**; however, no endothermic peaks were done in those of **P2** and **P3**. The second heating scan of **P1** exhibited only glass transition and no endothermic peaks. These findings presumably suggest that **P1** exhibits the low crystallinity and **P2** and **P3** are amorphous polymers. The incorporation of bulky substituent at 9-position of fluorene has been reported to reduce the tendency toward crystallization [9-12]. Therefore, **P2** and **P3** exhibited no melting behavior owing to the incorporation of the bulky spirocyclohexyl or spirofluorenyl moiety at 9-position of fluorene.

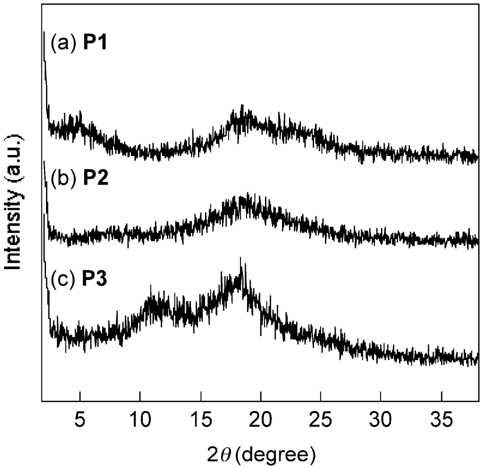


Figure 4. X-ray diffraction patterns of (a) **P1**, (b) **P2**, and (c) **P3** at ambient temperature.

Figure 4 depicts the X-ray diffraction patterns of **P1**-**P3** at ambient temperature. These patterns seemed to indicate that the present **P1**-**P3** are amorphous polymers; however, considering the exothermic peak on a first heating scan of **P1** for the DSC measurement, **P1** exhibits the rather low crystallinity. The very weak and broad diffraction peak observed for the X-ray diffraction pattern of **P1** at around 4-6 degree would be owing to some molecular orientation.

On the other hand, glass transition behavior was observed in all present polymers **P1**–**P3** in each DSC thermogram. The T_g's of **P1**, **P2**, and **P3** were 67, 84, and 156°C, respectively. The T_g of poly(tetramethyl-1,4-silphenylenesiloxane) (1,4-PTMPS), which is a representative derivative among poly(tetramethylsilarylenesiloxane)s, has been reported to be –20°C [20-23]. The T_g's of **P1**, **P2**, and **P3** were found to be much higher than not only that of 1,4-PTMPS but also those of a series of poly(tetramethylsilnaphthylenesiloxane) derivatives (in the range of 26-60°C) [26]. In addition, the increase in bulkiness of the substituent at 9-position of fluorene was found to elevate the T_g of a series of the present fluorene-based polysiloxanes because the bulky substituent inhibit the mobility of the backbone. It is noteworthy that **P3** having spirofluorenyl moiety at 9-position of fluorene exhibit the extremely high T_g. Further, the thermodynamic T_m of 1,4-PTMPS has been reported to be 160°C by Magill *et al.* [34] The present T_m of **P1** (196°C) without thermal aging to enhance crystallization was found to be higher than that of 1,4-PTMPS, indicating the strong interchain interaction in **P1**.

The temperatures at 5% weight loss (T_{d5}'s) of the present **P1**–**P3** were determined by TG as summarized in Table 1. As deduced from T_{d5}'s, the increase in bulkiness of the substituent at 9-position of fluorene seems to improve the thermostability of a series of the present fluorene-based polysiloxanes, presumably owing to the inhibition of interchain interactions by the bulkiness of substituent at 9-position of fluorene. The

T_{d5} of **P3** (535°C) was the highest among the present fluorene-based polysiloxanes and comparable to that of 1,4-PTMPS (ca. 530°C).

Conclusions

We achieved the synthesis of three novel poly(tetramethylsilfluorenylenesiloxane) derivatives having different substituent on 9-position of fluorenylene moiety, i.e. dimethyl (**P1**), spirocyclohexyl (**P2**), and spirofluorenyl (**P3**) substituents. It was revealed from the DSC measurements that **P1** exhibited the rather low crystallinity; however, **P2** and **P3** were amorphous polymers. The order of T_g and T_{d5} was **P3** > **P2** > **P1**, indicating that the order was dependent on the bulkiness of substituent at 9-position of fluorene. It is noteworthy that amorphous **P3** exhibiting very high T_g of 156°C and T_{d5} of 535°C is a new heat-resistant polysiloxane derivative and a promising candidate for blue-light-emitting materials. The optical properties of these fluorene-based polysiloxanes are now in progress.

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