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Synthesis and properties of novel poly(tetramethylsilnaphthylenesiloxane) derivatives

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Abstract

Novel poly(tetramethylsilnaphthylenesiloxane) derivatives were synthesized and characterized by differential scanning calorimetry (DSC), thermogravimetry (TG), and X-ray diffraction analyses. Poly(tetramethylsilnaphthylenesiloxane) derivatives were obtained by condensation polymerization of the corresponding disilanol derivatives, i.e. 1,4-, 1,5-, 2,6-, and 2,7-bis(dimethylhydroxysilyl)naphthalenes, which were prepared by the Grignard reaction using chlorodimethylsilane and the corresponding dibromonaphthalene derivatives followed by the hydrolyses, catalyzed by palladium on charcoal. The obtained poly(tetramethyl-1,5-silnaphthylenesiloxane) was insoluble in common organic solvents; however, the other polymers exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. The introduction of tetramethyl-1,5-silnaphthylenesiloxane units into the resulting polymer was confirmed by ^{1}H NMR spectrum of the copolymer obtained by condensation copolymerization of 1,5-bis(dimethylhydroxysilyl)naphthalene with 1,4-bis(dimethylhydroxysilyl)naphthalene. It was revealed from the DSC and X-ray diffraction measurements that poly(tetramethyl-1,5-silnaphthylenesiloxane) and poly(tetramethyl-2,6-silnaphthylenesiloxane) exhibited the crystallinity; however, poly(tetramethyl-1,4-silnaphthylenesiloxane) and poly(tetramethyl-2,7-silnaphthylenesiloxane) were amorphous. The glass transition temperature (T_g) and the temperature at 5% weight loss (T_{d5}) of poly(tetramethylsilnaphthylenesiloxane) derivatives with dimethylsilyl group at 1-position of the naphthylene moiety were higher than those at 2-position of the naphthylene moiety. The T_g and melting point (T_m) of the present polymers were higher than those of poly(tetramethyl-1,4-silphenylenesiloxane).

Keywords: Polysiloxane; Poly(tetramethylsilnaphthylenesiloxane); Polycondensation

1. Introduction

Linear polysiloxanes have been well-known to show 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].

Poly(tetramethyl-1,4-silphenylenesiloxane) is the representative polymer where a thermally stable aromatic moiety is incorporated into the polysiloxane backbone. On the other hand, poly(dimethylsiloxane-tetramethyl-1,4-silphenylenesiloxane) derivatives have been used for stationary phases for gas chromatography capillary columns [4] for their excellent thermal stabilities and good partitioning properties. The thermal stabilities and partitioning properties of stationary phases are known to depend on the chemical structures of polymers used for stationary phases. Therefore, poly(dimethylsiloxane-tetramethylsilarylenesiloxane) derivatives having various aromatic moieties in the backbone would exhibit the different thermal stabilities and partitioning properties from poly(dimethylsiloxane-tetramethyl-1,4-silphenylenesiloxane).

Generally, poly(silarylenesiloxane) derivatives can be obtained by condensation polymerization of disilanol monomers with various aromatics [3], as represented by the method of Merker and Scott [5]. Since the preparation of the disilanol monomers with various aromatics such as

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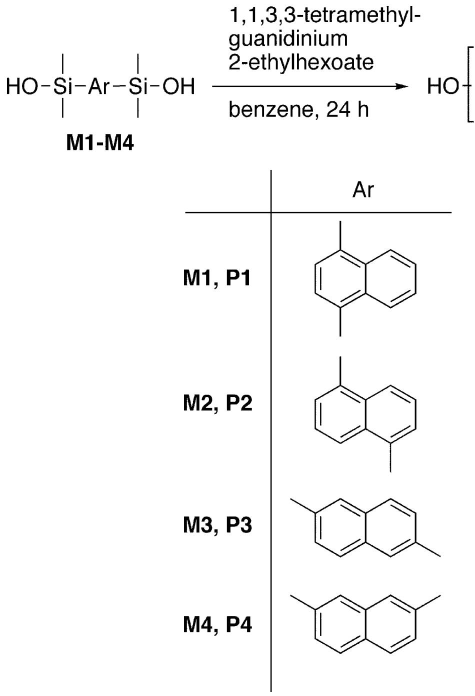
1,4-phenylene, 1,3-phenylene, 4,4′-biphenylene, 1,4-naphthylene, etc. was reported by Beck et al. [6], there have been many reports on the synthesis of poly(tetramethyl-1,4-silphenylenesiloxane) derivatives [3], including block-copolymers with poly(dimethylsiloxane) units [7], graft copolymers having side-chain poly(dimethylsiloxane) units [8], and alternating copolymers with dimethylsiloxane units [9]. Unfortunately, there have been a limited number of reports on poly(tetramethylsilarylenesiloxane) derivatives incorporating the aromatic moieties except phenylene moiety, though new polymerization methods to afford poly(tetramethylsilarylenesiloxane) derivatives have been reported even in recent years [10,11]. The variety of aromatics incorporated into poly(tetramethylsilarylenesiloxane) derivatives would affect various properties of these polymers. Patterson et al. [12] reported that poly(tetramethylsilarylenesiloxane) derivatives with perfluoroalkyl moiety in the main chain prepared from 1,3-bis[1,4-(hydroxydimethylsilyl)phenyl]hexafluoropropane exhibited the improved thermal stability and oxidative stability over poly(dimethylsiloxane). In addition, Kawakami et al. [13] reported catalytic dehydrocoupling copolymerization of 1,4-bis(dimethylsilyl)benzene with bis(dimethylsilyl) substituted aromatics to afford the copolymer of poly(tetramethyl-1,4-silphenylenesiloxane) with poly(tetramethylsilarylenesiloxane) units incorporating 4,4′-biphenylene or 9*H*-fluoren-9-ylidene bis(4,1-phenylene) moiety which exhibited the relatively good thermal stabilities. As an example of poly(silnaphthylenesiloxane) derivative, Andrianov et al. [14] reported the copolymer of poly(methylphenyl-1,4-silnaphthylenesiloxane) with poly(dimethylsiloxane); however, the detailed properties of the polymer were not clear in this report. Moreover, the substituted position of dimethylsilyl groups on arylene moiety would also exert influences on the properties of the resulting polymers as Mark et al. [15] reported that poly(tetramethyl-1,3-silphenylenesiloxane) has the lower glass transition temperature than poly(tetramethyl-1,4-silphenylenesiloxane), no crystallinity, and the good thermal stability.



Scheme 1. Synthesis of poly(tetramethylsilnaphthylenesiloxane) derivatives **P1**–**P4**.

From these points of view, we report here the preparation of novel poly(tetramethylsilnaphthylenesiloxane) derivatives obtained by condensation polymerization of bis(dimethylhydroxysilyl)naphthalene derivatives, where the different positions on the naphthylene moiety are substituted by dimethylhydroxysilyl groups, as shown in Scheme 1. The present paper also describes the results of thermal and X-ray diffractometric characterization of the obtained polymers.

2. Experimental

2.1. Materials

1,4-Dibromonaphthalene (**1**) was prepared by the bromination of 1-bromonaphthalene (Tokyo Kasei Kogyo Co., Inc.) according to the literature [16]. The Sandmeyer reaction using 1,5-diaminonaphthalene (Tokyo Kasei Kogyo Co., Inc.) afforded 1,5-dibromonaphthalene (**2**) [17]. The bromination of 6-bromo-2-naphthol and naphthalen-2,7-diol (Tokyo Kasei Kogyo Co., Inc.) using triphenylphosphine dibromide gave 2,6- and 2,7-dibromonaphthalene (**3** and **4**), respectively [18]. Triphenylphosphine (KANTO KAGAKU) was recrystallized from ethyl acetate before use. Bromine, magnesium, sodium (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, toluene, and tetrahydrofuran (THF) were used after distillation over sodium.

2.2. 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 points and glass transition temperatures were measured on a RIGAKU ThermoPlus DSC 8230 at a heating rate of 10 °C/min under a nitrogen flow rate of 10 ml/min. Thermogravimetry was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C/min under 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. Gas chromatography-mass spectroscopy (GC/MS) was carried out using a Shimadzu GCMS-QP2020A instrument. X-ray diffraction patterns were recorded on a Philips PW1830 X-ray diffractometer, equipped with a Philips HTK-2-HC thermal controller.

*2.3. Typical procedure for synthesis of bis(dimethylsilyl) naphthalene derivative (1,5-bis(dimethylsilyl)naphthalene (**6**))*

Syntheses of bis(dimethylsilyl)naphthalene derivatives were carried out by the modified method of Beck et al. [6]. Under a dry nitrogen atmosphere, 11.4 g (40 mmol) of 1,5-dibromonaphthalene (**2**) and 11.4 g (120 mmol) of chlorodimethylsilane in 140 ml of dry THF were added dropwise to 2.3 g (95 mmol) of magnesium in 140 ml of dry THF at 60 °C. The reaction mixture was stirred at 60 °C for 24 h and poured into the mixture of 200 ml of diethyl ether and 100 ml of 0.5 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 dissolved in hexane and purified by silica gel chromatography eluted with hexane (R_f value: 0.71). The collected hexane solution of the purified material was evaporated and recrystallized from hexane to afford 1,5-bis(dimethylsilyl)naphthalene (**6**) as colorless crystals with the yield of 6.6 g (68%). The purity was confirmed to be over 99% from GC analysis. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.16 (d, $J=8.4$ Hz, 2H, naphthylene protons), 7.74 (dd, $J=1.6$, 6.8 Hz, 2H, naphthylene protons), 7.50 (dd, $J=6.8$, 8.4 Hz, 2H, naphthylene protons), 4.86 (sept, $J=3.6$ Hz, 2H, $-\mathrm{Si(CH_3)_2}-H$), 0.49 (d, $J=3.6$ Hz, 12H, $-\mathrm{Si(C}H_3)_2-\mathrm{H}$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 136.7 (naphthylene carbon), 136.6 (naphthylene carbon), 133.3 (naphthylene carbon), 129.6 (naphthylene carbon), 125.2 (naphthylene carbon), -3.2 ($-\mathrm{Si(CH_3)_2}-$). IR (KBr, cm^{-1}): 2119 (Si–H). Mass (EI, *m/z*, intensity): 244 (M^+, 38%), 185 ($M^+-[\mathrm{Si(CH_3)_2H}]$, 100%), 169 ($M^+-[\mathrm{Si(CH_3)_2H}+\mathrm{CH_4}]$, 45%). Mp 53 °C.

2.4. Spectroscopic data for bis(dimethylsilyl)naphthalene derivatives

The other bis(dimethylsilyl)naphthalene derivatives **5**, **7**, and **8** were prepared by the similar method as the preparation of **6** using **1**, **3**, and **4** as the raw materials, respectively. The purity of products was confirmed to be over 99% from GC analysis.

*2.4.1. 1,4-Bis(dimethylsilyl)naphthalene (**5**)*

Yield: 4.7 g (48%) obtained as colorless liquid using 11.4 g (40 mmol) of **1** as the raw material. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.14 (dd, $J=3.2$, 6.4 Hz, 2H, naphthylene protons), 7.70 (s, 2H, naphthylene protons), 7.54 (dd, $J=3.2$, 6.4 Hz, 2H, naphthylene protons), 4.86 (sept, $J=3.6$ Hz, 2H, $-\mathrm{Si(CH_3)_2}-H$), 0.49 (d, $J=3.6$ Hz, 12H, $-\mathrm{Si(C}H_3)_2-\mathrm{H}$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.8 (naphthylene carbon), 136.5 (naphthylene carbon), 132.9 (naphthylene carbon), 128.6 (naphthylene carbon), 125.6 (naphthylene carbon), -3.3 ($-\mathrm{Si(CH_3)_2}-$). IR (KBr, cm^{-1}): 2121 (Si–H). Mass (EI, *m/z*, intensity): 244 (M^+, 21%), 185 ($M^+-[\mathrm{Si(CH_3)_2H}]$, 100%), 169 ($M^+-[\mathrm{Si(CH_3)_2H}+\mathrm{CH_4}]$, 29%).

*2.4.2. 2,6-Bis(dimethylsilyl)naphthalene (**7**)*

Yield: 0.44 g (17%) obtained as colorless liquid using 3.0 g (10.5 mmol) of **3** as the raw material. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.10 (s, 2H, naphthylene protons), 7.89 (d, $J=8.4$ Hz, 2H, naphthylene protons), 7.68 (d, $J=8.4$ Hz, 2H, naphthylene protons), 4.65 (sept, $J=3.6$ Hz, 2H, $-\mathrm{Si(CH_3)_2}-H$), 0.50 (d, $J=3.6$ Hz, 12H, $-\mathrm{Si(C}H_3)_2-\mathrm{H}$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 135.6 (naphthylene carbon), 134.5 (naphthylene carbon), 133.3 (naphthylene carbon), 130.3 (naphthylene carbon), 127.1 (naphthylene carbon), -3.7 ($-\mathrm{Si(CH_3)_2}-$). IR (KBr, cm^{-1}): 2119 (Si–H). Mass (EI, *m/z*, intensity): 244 (M^+, 35%), 229 ($M^+-\mathrm{CH_3}$, 38%), 185 ($M^+-[\mathrm{Si(CH_3)_2H}]$, 100%), 169 ($M^+-[\mathrm{Si(CH_3)_2H}+\mathrm{CH_4}]$, 27%).

*2.4.3. 2,7-Bis(dimethylsilyl)naphthalene (**8**)*

Yield: 1.15 g (45%) obtained as colorless liquid using 3.0 g (10.5 mmol) of **4** as the raw material. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.05 (s, 2H, naphthylene protons), 7.81 (d, $J=8.4$ Hz, 2H, naphthylene protons), 7.61 (d, $J=8.4$ Hz, 2H, naphthylene protons), 4.55 (sept, $J=3.6$ Hz, 2H, $-\mathrm{Si(CH_3)_2}-H$), 0.42 (d, $J=3.6$ Hz, 12H, $-\mathrm{Si(C}H_3)_2-\mathrm{H}$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 135.1 (naphthylene carbon), 134.8 (naphthylene carbon), 134.1 (naphthylene carbon), 132.4 (naphthylene carbon), 130.7 (naphthylene carbon), 126.9 (naphthylene carbon), -3.7 ($-\mathrm{Si(CH_3)_2}-$). IR (KBr, cm^{-1}): 2123 (Si–H). Mass (EI, *m/z*, intensity): 244 (M^+, 32%), 229 ($M^+-\mathrm{CH_3}$, 29%), 185 ($M^+-[\mathrm{Si(CH_3)_2H}]$, 100%), 169 ($M^+-[\mathrm{Si(CH_3)_2H}+\mathrm{CH_4}]$, 13%). Mp 49 °C.

*2.5. Typical procedure for synthesis of bis(dimethylhydroxysilyl)naphthalene derivatives (1,5-bis(dimethylhydroxysilyl)naphthalene (**M2**))*

Bis(dimethylhydroxysilyl)naphthalene derivatives were prepared by the hydrolyses of the corresponding bis(dimethylsilyl)naphthalene ones [19]. Under a dry nitrogen atmosphere, 1.0 g (4.1 mmol) of 1,5-bis(dimethylsilyl)-naphthalene (**6**) in 0.8 ml of dry THF was added dropwise to 0.0038 g of 5%-Pd on C with 0.18 g (10 mmol) of H$_2$O in

2.3 ml of THF in an ice bath. The reaction mixture was stirred at ambient temperature for 2 h and filtered. The filtrate was evaporated and the residue was recrystallized from the mixed solvent of benzene and hexane to afford 1,5-bis(dimethylhydroxysilyl)naphthalene (**M2**) as colorless crystals with the yield of 0.70 g (62%). The purity was confirmed to be over 99% from GC analysis. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.29 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 7.73 (dd, $J = 1.2$, 6.6 Hz, 2H, naphthylene protons), 7.50 (dd, $J = 6.6$, 8.4 Hz, 2H, naphthylene protons), 6.17 (s, 2H, –OH), 0.40 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 139.4 (naphthylene carbon), 136.4 (naphthylene carbon), 132.6 (naphthylene carbon), 130.2 (naphthylene carbon), 125.0 (naphthylene carbon), 2.0 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 3180 (–OH), 1030–1100 (Si–O). Mass (EI, *m/z*, intensity): 276 (M^+, 50%), 261 ($M^+ - CH_3$, 81%), 243 ($M^+ - [CH_3 + H_2O]$, 100%). Mp 189 °C.

2.6. Spectroscopic data for bis(dimethylhydorxysilyl) naphthalene derivatives

The other bis(dimethylhydorxysilyl)naphthalene derivatives **M1**, **M3**, and **M4** were prepared by the similar method as the preparation of **M2** using **5**, **7**, and **8** as the raw materials, respectively. The purity of products was confirmed to be over 99% from GC analysis.

2.6.1. 1,4-Bis(dimethylhydroxysilyl)naphthalene (*M1*)

Yield: 3.0 g (68%) obtained as colorless crystals using 5.0 g (20 mmol) of **5** as the raw material. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (dd, $J = 3.2$, 6.4 Hz, 2H, naphthylene protons), 7.71 (s, 2H, naphthylene protons), 7.51 (dd, $J = 3.2$, 6.4 Hz, 2H, naphthylene protons), 6.17 (s, 2H, –OH), 0.40 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 140.3 (naphthylene carbon), 136.3 (naphthylene carbon), 132.2 (naphthylene carbon), 129.2 (naphthylene carbon), 125.4 (naphthylene carbon), 1.9 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 3291 (–OH), 1004, 1030–1100 (Si–O). Mass (EI, *m/z*, intensity): 276 (M^+, 47%), 261 ($M^+ - CH_3$, 100%), 243 ($M^+ - [CH_3 + H_2O]$, 87%). Mp 186 °C.

2.6.2. 2,6-Bis(dimethylhydroxysilyl)naphthalene (*M3*)

Yield: 0.54 g (48%) obtained as colorless crystals using 1.0 g (4.1 mmol) of **7** as the raw material. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.10 (s, 2H, naphthylene protons), 7.89 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 7.64 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 6.01 (s, 2H, –OH), 0.32 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 138.9 (naphthylene carbon), 133.3 (naphthylene carbon), 132.9 (naphthylene carbon), 129.7 (naphthylene carbon), 128.5 (naphthylene carbon), 127.1 (naphthylene carbon), 0.85 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 3179 (–OH), 1085 (Si–O). Mass (EI, *m/z*, intensity): 276 (M^+, 28%), 261 ($M^+ - CH_3$, 100%), 243 ($M^+ - [CH_3 + H_2O]$, 4%). Mp 133 °C.

2.6.3. 2,7-Bis(dimethylhydroxysilyl)naphthalene (*M4*)

Yield: 1.05 g (93%) obtained as colorless crystals using 1.0 g (4.1 mmol) of **8** as the raw material. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.10 (s, 2H, naphthylene protons), 7.85 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 7.67 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 6.01 (s, 2H, –OH), 0.32 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 138.4 (naphthylene carbon), 133.9 (naphthylene carbon), 132.0 (naphthylene carbon), 130.2 (naphthylene carbon), 128.5 (naphthylene carbon), 126.7 (naphthylene carbon), 0.88 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 3255 (–OH), 1100 (Si–O). Mass (EI, *m/z*, intensity): 276 (M^+, 32%), 261 ($M^+ - CH_3$, 100%), 243 ($M^+ - [CH_3 + H_2O]$, 4%). Mp 106 °C.

2.7. Typical procedure for condensation polymerization (poly(tetramethyl-1,4-silnaphthylenesiloxane) (*P1*))

Under a dry atmosphere, 0.02 g of 1,1,3,3-tetramethylguanidinium 2-ethylhexoate [5] was added to 0.50 g (1.8 mmol) of **M1** dissolved in 12.5 ml of dry benzene, and the reaction mixture was refluxed for 24 h. The reaction mixture was poured into 100 ml of methanol to isolate the corresponding polymer as white precipitates. Yield: 0.37 g (79%) as white powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (dd, $J = 3.2$, 6.4 Hz, 2H, naphthylene protons), 7.71 (s, 2H, naphthylene protons), 7.30 (dd, $J = 3.2$, 6.4 Hz, 2H, naphthylene protons), 0.50 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.6 (naphthylene carbon), 136.3 (naphthylene carbon), 132.1 (naphthylene carbon), 129.3 (naphthylene carbon), 125.1 (naphthylene carbon), 2.1 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 1000–1100 (Si–O).

2.8. Spectroscopic data for polymers

The other poly(tetramethylsilnaphthylenesiloxane) derivatives **P2–P4** were prepared by the similar method as the preparation of **P1** using **M2–M4**, respectively.

2.8.1. Poly(tetramethyl-1,5-silnaphthylenesiloxane) (*P2*)

Yield: 89% as white powder solid. ^{1}H and ^{13}C NMR spectra could not be obtained for the poor solubility of **P2** in common organic solvents. IR (KBr, cm^{-1}): 1000–1100 (Si–O).

2.8.2. Poly(tetramethyl-2,6-silnaphthylenesiloxane) (*P3*)

Yield: 89% as white powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (s, 2H, naphthylene protons), 7.75 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 7.61 (d, $J = 8.4$ Hz, 2H, naphthylene protons), 0.40 (s, 12H, $–Si(CH_3)_2–$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9 (naphthylene carbon), 133.5 (naphthylene carbon), 133.2 (naphthylene carbon), 129.4 (naphthylene carbon), 127.2 (naphthylene carbon), 2.1 ($–Si(CH_3)_2–$). IR (KBr, cm^{-1}): 1000–1100 (Si–O).

2.8.3. *Poly(tetramethyl-2,7-silnaphthylenesiloxane) (**P4**)*

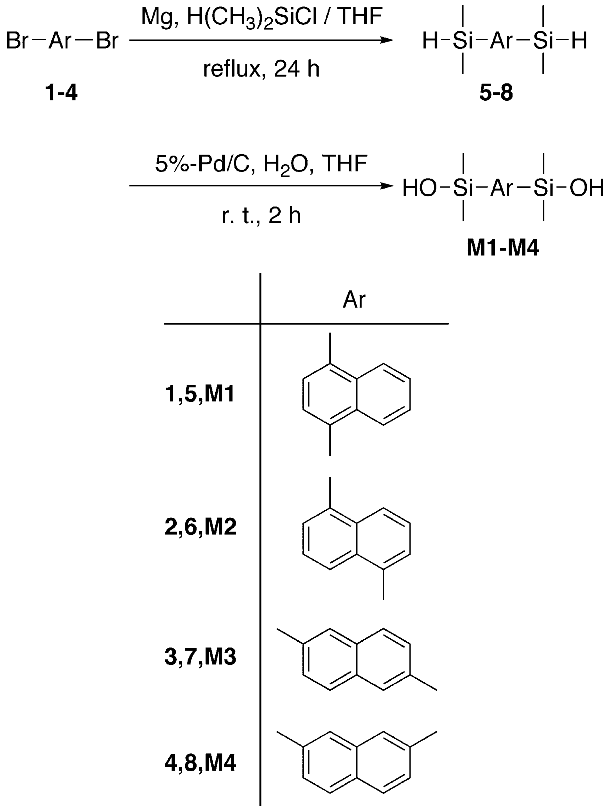
Yield: 50% as white powder solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.99 (d, $J=0.8$ Hz, 2H, naphthylene protons), 7.76 (d, $J=8.0$ Hz, 2H, naphthylene protons), 7.62 (dd, $J=0.8$, 8.0 Hz, 2H, naphthylene protons), 0.40 (s, 12H, –Si(CH_3)$_2$–). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 137.3 (naphthylene carbon), 134.3 (naphthylene carbon), 134.0 (naphthylene carbon), 132.2 (naphthylene carbon), 130.0 (naphthylene carbon), 126.8 (naphthylene carbon), 0.95 (–Si(CH$_3$)$_2$–). IR (KBr, cm^{-1}): 1000–1100 (Si–O).

2.8.4. *Poly(tetramethyl-1,4-silnaphthylenesiloxane-co-tetramethyl-1,5-silnaphthylenesiloxane) (**P5**)*

Yield: 67% as white powder solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.25 (d, $J=8.4$ Hz, 0.98H, 1,5-naphthylene protons), 8.22 (dd, $J=3.2$, 6.4 Hz, 1.02H, 1,4-naphthylene protons), 7.67–7.73 (m, 2H, naphthylene protons), 7.27–7.33 (m, 2H, naphthylene protons), 0.43 (s, 12H, –Si(CH_3)$_2$–).

2.8.5. *Poly(tetramethyl-1,4-silnaphthylenesiloxane-co-tetramethyl-1,5-silnaphthylenesiloxane) (**P6**)*

Yield: 94% as white powder solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.25 (d, $J=8.4$ Hz, 1.26H, 1,5-naphthylene protons), 8.22 (dd, $J=3.2$, 6.4 Hz, 0.74H, 1,4-naphthylene protons), 7.67–7.73 (m, 2H, naphthylene protons), 7.27–7.33 (m, 2H, naphthylene protons), 0.43 (s, 12H, –Si(CH_3)$_2$–).



Scheme 2. Synthesis of monomers **M1**–**M4**.

2.9. *Molecular orbital calculation*

All calculations were done using the Spartan'04 for Windows (Wavefunction, Inc. Irvine, CA) [20] ab initio program. Geometries of molecules were optimized by the 6-31G* basis set.

3. Results and discussion

3.1. *Monomer syntheses*

Scheme 2 shows the pathways for the syntheses of naphthalene-based disilanol derivatives **M1**–**M4**.

Four naphthalene-based disilanol derivatives **M1**–**M4** were synthesized by the hydrolyses of the corresponding bis(dimethylsilyl)naphthalene derivatives **5**–**8**, which had been obtained from the corresponding dibromonaphthalene derivatives via the Grignard reactions with chlorodimethylsilane. Beck et al. reported [6] that **M1** was obtained by the hydrolysis of **5** with the yield of 29% 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 of 30%. On the other hand, it has been reported [19] that hydrolysis of 1,4-bis(dimethylsilyl)benzene using the metal catalysts such as 5%-Pd on charcoal, Pd on alumina, Pt on charcoal, Pt on alumina, and Ru on charcoal afforded 1,4-bis(dimethylhydroxysilyl)benzene with good yields. In the present study, it was also revealed that **M1** could be obtained by the hydrolysis of **5** using 5% Pd on charcoal as a catalyst with the yield of 68%. Thus, we carried out the hydrolysis of bis(dimethylsilyl)naphthalene derivatives using 5% Pd on charcoal as a catalyst. We could obtain three novel monomers **M2**–**M4** by the similar method as the preparation of **M1** with good yields. The spectroscopic data described in Section 2 indicated the syntheses of novel monomers were achieved. As a typical example, ^{1}H and ^{13}C NMR spectra of **M2** are described in Fig. 1. The structures of the other monomers were also confirmed by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy.

3.2. *Syntheses and characterization of polymers*

Four naphthalene-based disilanol derivatives **M1**–**M4** underwent the condensation polymerization by use of 1,1,3,3-tetramethylguanidinium 2-ethylhexoate as a catalyst [5] to afford the corresponding poly(tetramethylsilnaphthylenesiloxane) derivatives **P1**–**P4**, 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 concentration of monomer 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

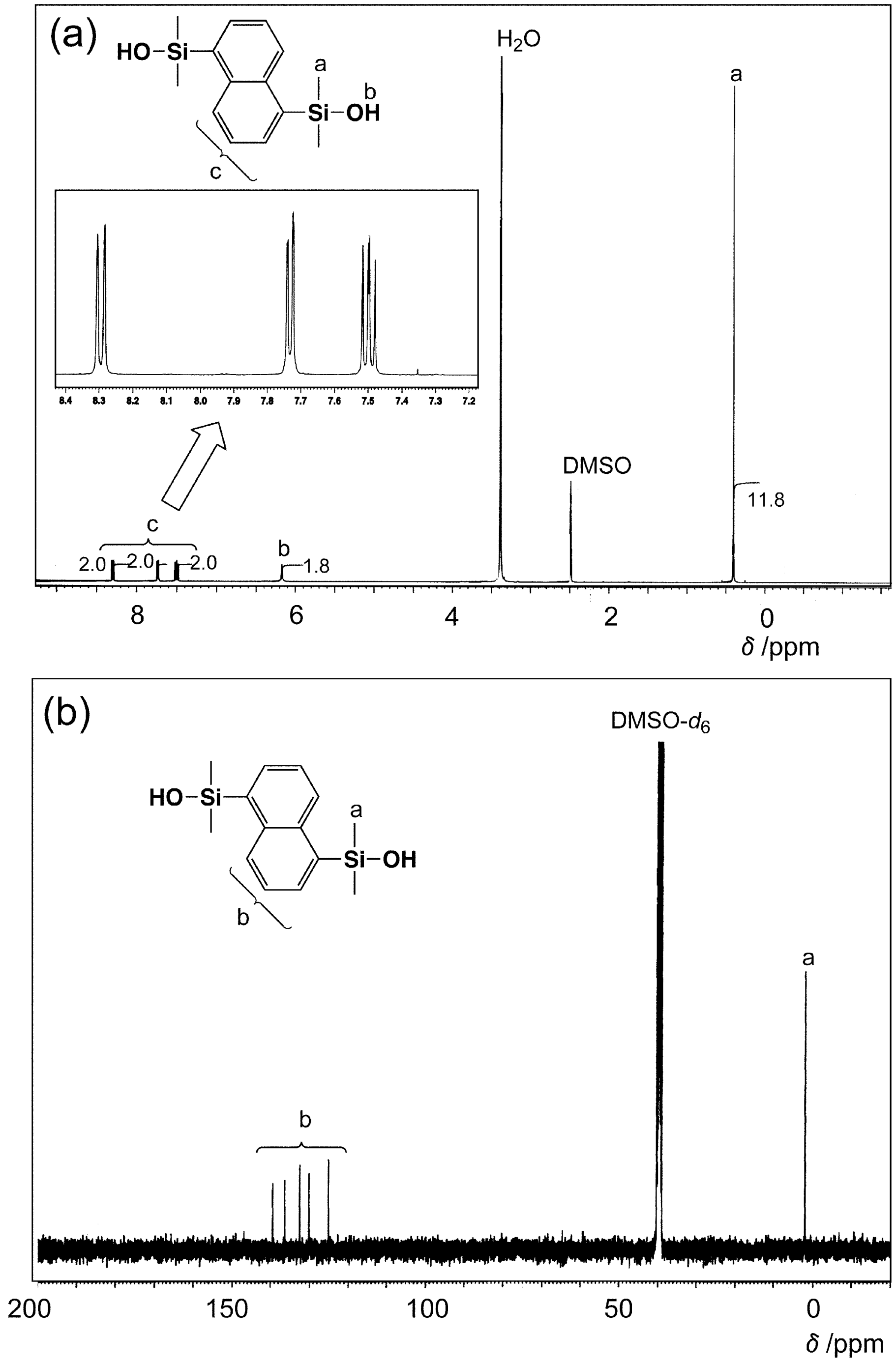


Fig. 1. (a) ^{1}H NMR (solvent: $(CD_3)_2SO$, 400 MHz) and (b) ^{13}C NMR spectra (solvent: $(CD_3)_2SO$, 100 MHz) of **M2** at ambient temperature.

important factor influencing the formation of the polymers seems to be the concentration of the monomers. The GPC traces of **P1**, **P3**, and **P4** indicated the obtained polymers were unimodal. The structures of **P1**, **P3**, and **P4** were confirmed by ^{1}H and ^{13}C NMR and IR spectroscopy; however, the solubility of poly(tetramethyl-1,5-silnaphthylenesiloxane) (**P2**) in common organic solvents at ambient temperature was so poor that the NMR spectra of **P2** could not be obtained. The difference in the solubility between **P1** and **P2** would be mainly due to the difference in the mobility of the naphthylene moieties. As for the 1,4-substituted naphthalene, naphthylene moiety could be rotated freely between two silicon atoms; however, it would be difficult for 1,5-substituted naphthylene moiety between two silicon atoms to be rotated freely. Thus, the intermolecular stacking between 1,5-substituted naphthylene moieties would be very stable to make the solubility of **P2** poor. As a typical example, ^{1}H and ^{13}C NMR spectra of **P1** are described in Fig. 2. The characterization of **P1**–**P4** is summarized in Table 1.

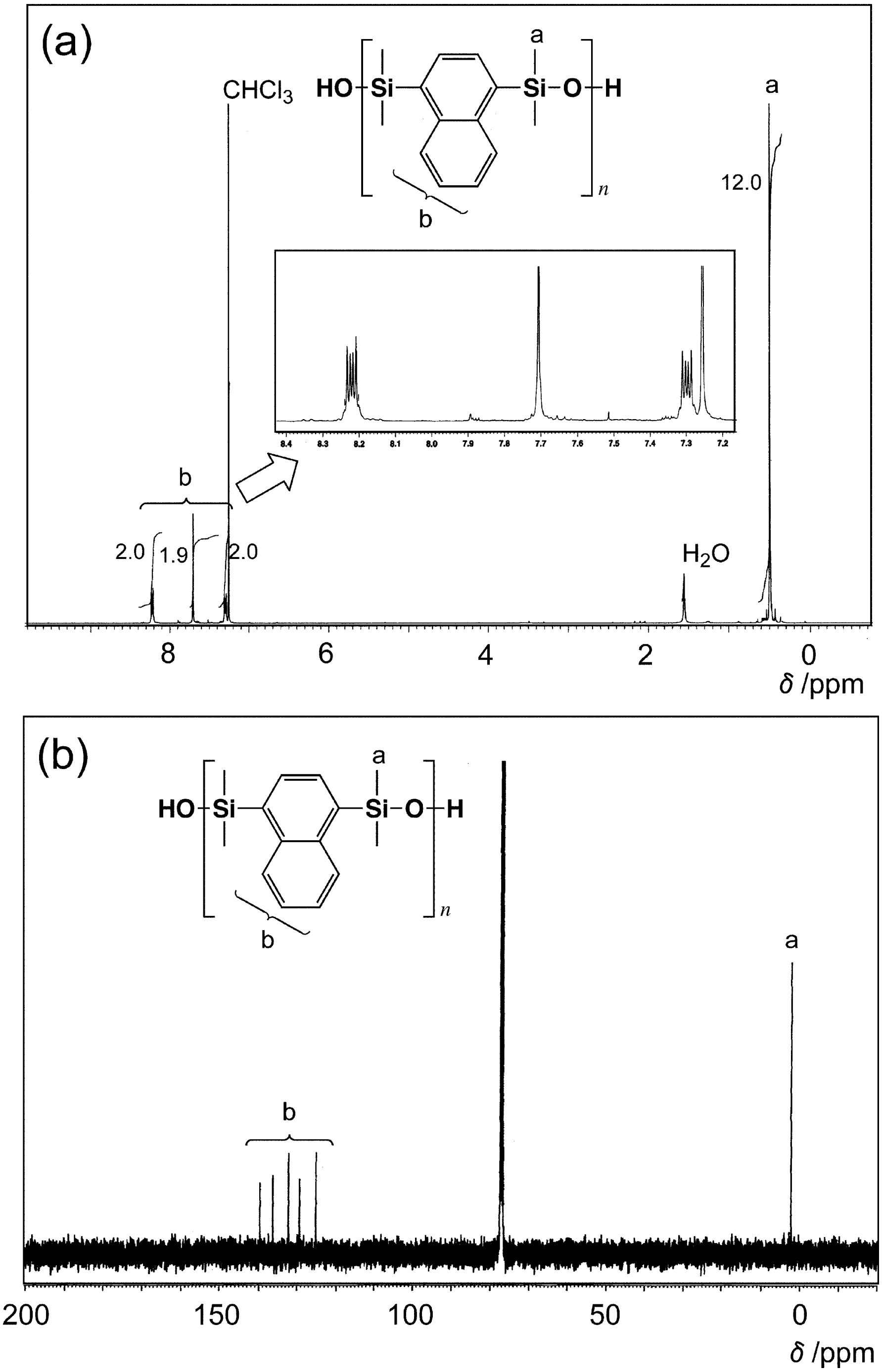


Fig. 2. (a) ^{1}H NMR (solvent: $CDCl_3$, 400 MHz) and (b) ^{13}C NMR spectra (solvent: $CDCl_3$, 100 MHz) of **P1** at ambient temperature.

P1, **P3**, and **P4** were soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. Glass transition temperatures (T_gs) and melting points (T_ms) of **P1–P4** were determined by DSC as summarized in Table 1. The glass transition was observed in all present polymers **P1–P4** in each DSC thermogram. Fig. 3 shows the DSC traces of **P1–P4** on a second heating scan. The glass transition of **P2** was not clear in Fig. 3(a), thus, the T_g of **P2** was determined using a first heating scan.

The T_gs of **P1–P4** were much higher than that of poly(tetramethyl-1,4-silphenylenesiloxane) (−20 °C) [21]. The introduction of bulky naphthylene moiety into the main chain would make T_g high. The order of T_g was **P1–P2**> **P3–P4** as shown in Table 1. This order would involve the degree of inhibition of the backbone mobility, indicating that the backbone mobility of poly(tetramethylsilnaphthylenesiloxane) derivatives with dimethylsilyl group at 1-position of the naphthylene moiety was restricted

Table 1
Characterization of **P1**–**P4**

Polymer	M_n [a]	M_w/M_n [b]	T_g (°C) [c]	T_m (°C) [c]	T_{d5} (°C) [d]	Temperature at maximum rate of weight loss (°C) [e]
P1	66,700	2.33	60	–[f]	488	522
P2	–[g]	–[g]	62	225	480	526
P3	49,600	1.93	29	156	442	528
P4	21,100	2.26	26	–[f]	396	518

Reaction conditions: monomer, 1.8 mmol; solvent, benzene 12.5 ml.

[a] Number-average molecular weight estimated from GPC eluted with THF based on polystyrene standards.

[b] Polydispersity index.

[c] Determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min under nitrogen atmosphere.

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

[e] Determined by thermogravimetry (TG) under nitrogen atmosphere.

[f] Not observed in DSC measurement between −50 and 400 °C.

[g] Not determined due to the insolubility in common organic solvents.

comparing with that at 2-position of the naphthylene moiety. These findings could relate the thermal stability of the obtained polymers. The T_{d5}s of **P3** and **P4** were low compared with those of **P1** and **P2** where the mobility of the main chain was more restricted than **P3** and **P4**. On the other hand, there were no significant differences in the temperatures at the maximum rate of weight loss of the present polymers as summarized in Table 1, suggesting the restriction of the backbone mobility presumably contributes to raising the temperature to initiate the decomposition of the present polymers. The T_{d5}s of **P1** and **P2** were comparable to that of poly(tetramethyl-1,4-silphenylenesiloxane) [3]. On the other hand, **P2** and **P3** clearly exhibited the endothermal peak based on melting; however, **P1** and **P4** did not, as shown in Fig. 3. The T_m of poly(tetramethyl-1,4-silphenylenesiloxane) (M_n: 186,000, 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. [21]. The present T_ms of **P2** and **P3** are found to be higher than that of poly(tetramethyl-1,4-silphenylenesiloxane).

Fig. 4 shows the X-ray diffraction patterns of **P1**–**P4** at ambient temperature.

Some peaks were observed in the X-ray diffraction patterns of **P2** and **P3**, indicating that **P2** and **P3** possess the

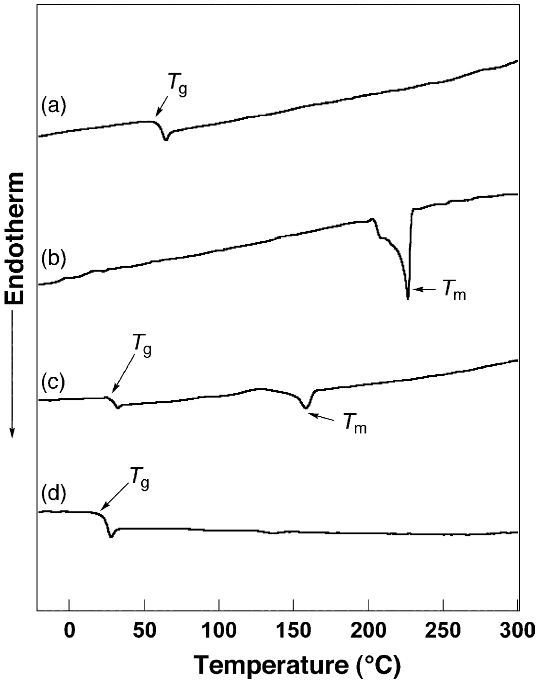


Fig. 3. DSC traces of (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P4** on a second heating scan at a heating rate of 10 °C/min under N_2 flow rate of 10 ml/min.

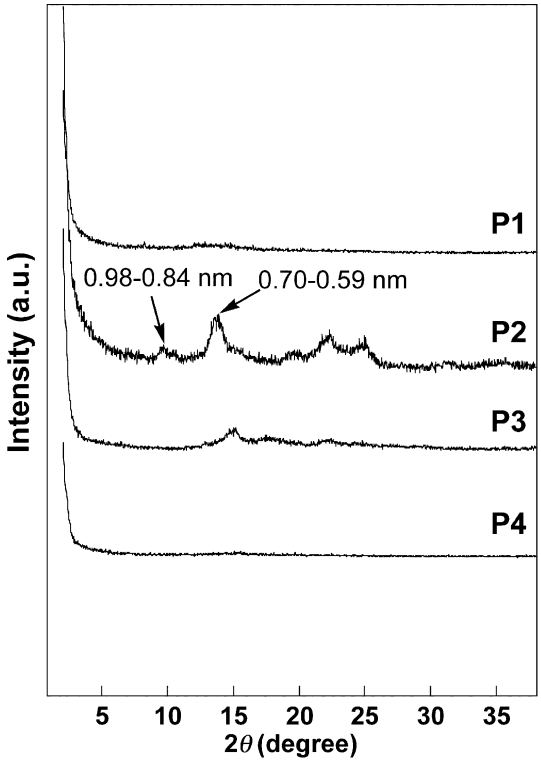


Fig. 4. X-ray diffraction patterns of **P1**–**P4** at ambient temperature.

Table 2
Results of copolymerization of **M1** and **M2**

Polymer	Yield (%)[a]	Molar ratio in feed (mol%)		Unit ratio in copolymer (mol%)[b]		M_n[c]	M_w/M_n[d]	T_g (°C)[e]	T_{d5} (°C)[f]	Temperature at maximum rate of weight loss (°C)[g]
		M1	**M2**	*x*	*y*					
P5	67	50	50	49	51	23,800	1.60	57	484	514
P6	94	33	67	37	63	33,100	1.97	61	492	520

Reaction conditions: monomer, 1.8 mmol; solvent, toluene 12.5 ml.

[a] Insoluble part in methanol.

[b] Estimated by ^{1}H NMR spectroscopy.

[c] Number-average molecular weight estimated from GPC eluted with THF based on polystyrene standards.

[d] Polydispersity index.

[e] Determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min under nitrogen atmosphere.

[f] Temperature at 5 wt% weight loss determined by thermogravimetry (TG) under nitrogen atmosphere.

[g] Determined by thermogravimetry (TG) under nitrogen atmosphere.

crystallinity. It was confirmed that these peaks disappeared beyond their T_ms. The diffraction peaks at around 9.0–10.5 and 12.7–15.0° in the X-ray diffraction pattern of **P2** correspond to the *d*-spacing of ca. 0.98–0.84 and 0.70–0.59 nm, respectively. Fig. 5 shows the spatial molecular configuration of the dimer of **M2** and that of 1,4-bis(dimethylhydroxysilyl)benzene optimized by the molecular orbital calculation (RHF/6-31G*).

It has been reported the spatial configuration of the unit cell of poly(tetramethyl-1,4-silphenylenesiloxane) with low molecular weight has a repeating distance of 1.55 nm [22]. In addition, the unit cell of poly(tetramethyl-1,4-silphenylenesiloxane) with high molecular weight has been reported to be with the values of $a=b=0.902$ nm and $c=1.54$ nm. The unit cell has been reported to involve two chains and two monomer per repeat unit in the chain as deduced from X-ray [23] and vibrational [24] studies. In Fig. 5(a), the distance between O3 and C14 is 1.46 nm, which presumably corresponds to the direction of the *c*-axis, suggesting the plausibility of the present optimization by the molecular orbital calculation. On the other hand, the distances between O2 and C12 as well as between O2 and C27 are 0.97 nm in the optimized molecular configuration of the dimer of **M2**, which are considered to correspond to the diffraction peak at around 9.0–10.5°; however, the detailed study using isothermally crystallized polymers will be the subject of future.

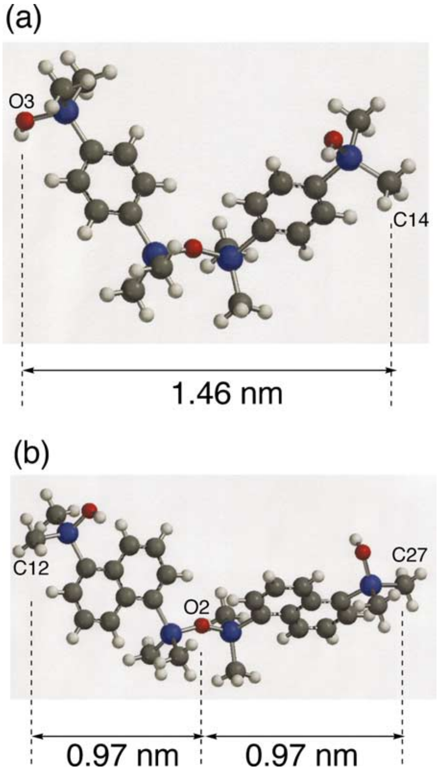
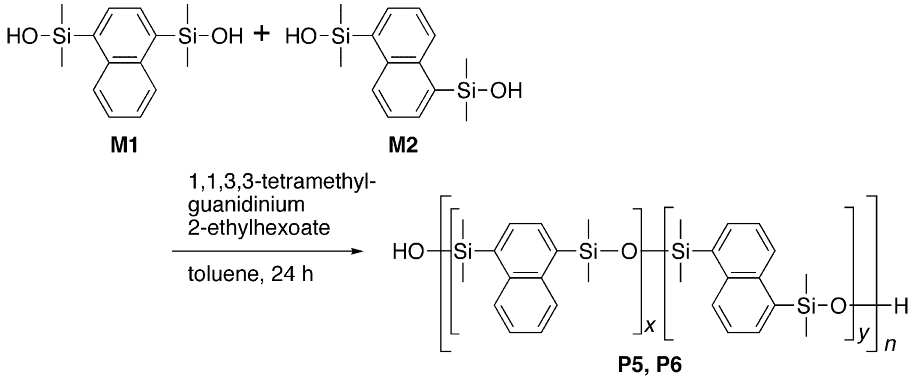


Fig. 5. Spatial molecular configuration of the dimer of (a) 1,4-bis(dimethylhydroxysilyl)benzene and (b) **M2** optimized by MO calculation (RHF/6-31G*).

3.3. Synthesis of copolymer

P2 obtained from **M2** was insoluble in any common organic solvent. The copolymerization of **M1** and **M2** was carried out as shown in Scheme 3 for the confirmation of the introduction of **M2** units in the resulting polymer.

The results of the copolymerization of **M1** and **M2** are summarized in Table 2. Toluene was used as a solvent for the copolymerization of **M1** and **M2** because the solubilities of both monomers and the resulting polymers in toluene were better than those in benzene. Fig. 6 shows the ^{1}H NMR spectrum of **P5**, which indicates that the introduction of the units based on **M2** was achieved. The unit ratio of the resulting copolymer was estimated by a comparison of the integrated values of the ^{1}H NMR signal derived from 1,4-naphthylene moiety at 8.22 ppm with those derived from 1,5-naphthylene moiety at 8.25 ppm and approximately equal to the molar ratio of **M1** and **M2** in feed. **P5** and **P6** were soluble in common organic solvents such as THF, chloroform, dichloromethane, and toluene. Glass transition was observed in DSC analyses of **P5** and **P6**;



Scheme 3. Condensation copolymerization of **M1** and **M2**.

however, no melting points were observed, suggesting that **P5** and **P6** are amorphous polymers. There were no significant differences in T_gs, T_{d5}s, and temperatures at the maximum rate of weight loss of **P1**, **P2**, **P5**, and **P6**.

4. Conclusions

The syntheses of four poly(tetramethylsilnaphthylenesiloxane) derivatives, i.e. poly(tetramethyl-1,4-silnaphthylenesiloxane) (**P1**), poly(tetramethyl-1,5-silnaphthylenesiloxane) (**P2**), poly(tetramethyl-2,6-silnaphthylenesiloxane) (**P3**), and poly(tetramethyl-2,7-silnaphthylenesiloxane) (**P4**), were achieved by condensation polymerization of the corresponding disilanol derivatives, i.e. 1,4-, 1,5-, 2,6-, and 2,7-bis(dimethylhydroxysilyl)naphthalenes (**M1**–**M4**). The structure of **P2** could not be confirmed by NMR spectroscopy due to the insolublity in common organic solvents; however, the introduction of **M2** units into the resulting polymer was confirmed by ^{1}H NMR spectrum of the copolymer obtained by condensation copolymerization of **M2** with **M1**. It was revealed from the DSC and X-ray diffraction measurements that **P2** and **P3** exhibited the crystallinity; however, **P1** and **P4** are amorphous polymers. The T_g and T_m of the present polymers were higher than those of poly(tetramethyl-1,4-silphenylenesiloxane). The order of T_{d5} was **P1**–**P2** > **P3** > **P4**, that of T_g was **P1**–**P2** > **P3**–**P4**, and that of T_m was **P2** > **P3**, indicating that T_{d5}, T_g, and T_m of poly(tetramethylsilnaphthylenesiloxane) derivatives with dimethylsilyl group at 1-position of the naphthylene moiety were higher than those at 2-position of the naphthylene moiety, presumably due to the

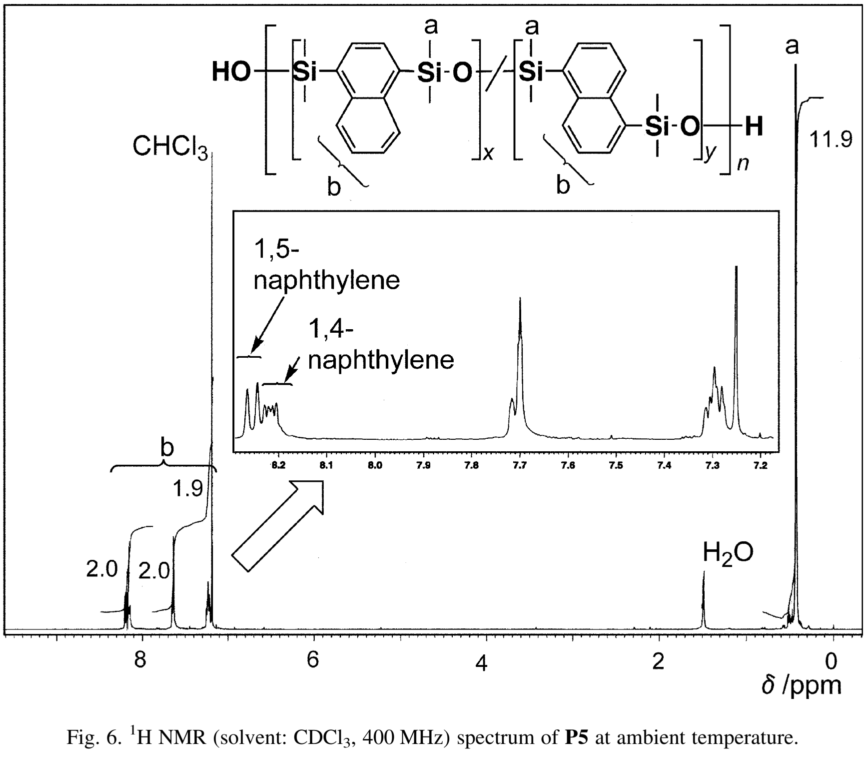


Fig. 6. ^{1}H NMR (solvent: $CDCl_3$, 400 MHz) spectrum of **P5** at ambient temperature.

backbone mobility of poly(tetramethylsilnaphthylenesiloxane) derivatives with dimethylsilyl group at 1-position of the naphthylene moiety was restricted comparing with that at 2-position of the naphthylene moiety.

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