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ORIGINAL PAPER

Synthesis and thermal characterization of novel poly(tetramethyl-1,3-silphenylenesiloxane) derivative bearing adamantyl moiety

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Abstract A novel poly(tetramethyl-1,3-silphenylenesiloxane) derivative having adamantyl moiety, i.e., poly(tetramethyl-5-adamantyl-1,3-silphenylenesiloxane) (**P1**) was synthesized by solution polycondensation of a novel disilanol monomer, i.e., 1-[3,5-(dimethylhydroxysilyl)phenyl]adamantane (**M1**). **M1** was prepared by the Grignard reaction using chlorodimethylsilane and 1-(3,5-dibromophenyl)adamantane, followed by the hydrolysis catalyzed by 5% palladium on charcoal. **P1** exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, benzene, and toluene at ambient temperature. **P1** was also soluble in hot hexane, diethyl ether, and ethyl acetate. The glass transition temperature (T_g) and temperature at 5% weight loss (T_{d5}) of **P1** were 85 and 517 °C, respectively, and much higher than those of poly(tetramethyl-1,3-silphenylenesiloxane), indicating that **P1** is a new polysiloxane derivative with good solubility as well as good thermostability.

Keywords Polysiloxane · Polycondensation · Adamantane · Heat-resistant polymer

Introduction

Adamantane (tricycle[3.3.1.1^{3,7}]decane) is a highly symmetrical and rigid tricyclic hydrocarbon consisting of fused chair-form cyclohexane rings [1] and has been incorporated into a polymer as a part of backbone [2–10] and as a pendant group [11–17]. Adamantyl-incorporated polymers generally exhibit high glass transition temperature (T_g) as well as chain stiffness with reduced crystallinity and enhanced

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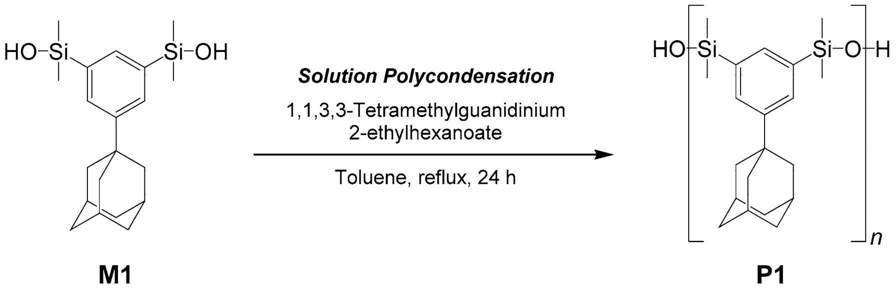
solubility, because the diamond-like cage structure of adamantane tends to inhibit packing of polymer chains [2–17]. Additionally, the UV–vis transparency of adamantane attracts much attention for incorporating into polymeric materials for short wavelength microlithography [18–20].

On the other hand, linear polysiloxanes have been well-known to show the particular characteristics, such as flexibility of the main chain, low T_g, hydrophobicity based on alkyl side chain, thermostability, stability against atomic oxygen, and physiological inertness [21, 22]. Polysiloxane derivatives have been one of candidates for negative photo-resist materials via cross-linking [23]; however, rarely used as positive photo-resist materials owing to the low T_g of polysiloxane derivatives. If polysiloxane derivatives exhibiting the high T_g and good thermostability can be prepared, they would be applied as the positive-type photo-resist materials; because polysiloxane backbones can be cleaved by some photo-acid or photo-base generator owing to the ionic property of siloxane bonding [21, 22].

One of the methods for raising T_g is incorporation of bulky and rigid moieties such as adamantyl moiety into the main chain or side-chain functional groups [24]. As an example of the introduction of adamantyl moiety into the main chain of a polysiloxane derivative, Weber et al. [25] reported the syntheses of the polysiloxane derivatives having 1,3-adamantyl moiety in the main chain and the thermostability of the obtained polysiloxane derivatives higher than that of poly(dimethylsiloxane). We also reported the synthesis of poly(tetramethylsilarylenesiloxane) derivative having adamantyl moiety in the main chain and revealed the high T_g of 115 °C as well as the high temperature at 5% weight loss (T_{d5}) of 523 °C of the resulting polymer [10].

With these in mind, we present here an example of the introduction of adamantyl moiety into the side-chain of a polysiloxane derivative, i.e., the synthesis of a novel poly(tetramethyl-1,3-silphenylenesiloxane) (1,3-PTMS) derivative bearing side-chain adamantyl moiety (**P1**), as shown in Scheme 1. The present article will reveal the effects of side-chain adamantyl moiety on the thermal property of polysiloxane derivative.



Scheme 1 Synthesis of poly(tetramethyl-5-adamantyl-1,3-silphenylenesiloxane) (**P1**) via polycondensation of 1-[3,5-(dimethylhydroxysilyl)phenyl]adamantane (**M1**)

Experimental

Materials

1-Bromoadamantane (**1**, Tokyo Kasei Kogyo Co., Inc.), 1,3-dibromobenzene (NACALAI TESQUE, INC.), anhydrous aluminum bromide (Aldrich), 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 was prepared according to the literature [26]. Toluene 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. Assignment of ^{13}C NMR signals was carried out using the DEPT (distortionless enhancement by polarization transfer) spectra together. IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer. Gas chromatography-mass spectroscopy (GC/MS) was carried out using a Shimadzu GCMS-QP2020A instrument. 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 or cooling 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.

1-(3,5-Dibromophenyl)adamantane (**2**)

Under a dry argon atmosphere, 5.01 g (23.3 mmol) of 1-bromoadamantane (**1**) and 24.3 g (103 mmol) of 1,3-dibromobenzene were added dropwise to 24.3 g (103 mmol) of 1,3-dibromobenzene with 0.994 g (3.72 mmol) of anhydrous aluminum bromide at 0 °C. The reaction mixture was stirred at 0 °C for 69 h and poured into a mixture of dichloromethane (50 ml) and 0.03 mol/l HCl aqueous solution (50 ml). 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 fraction with an R_f value of 0.74 was concentrated under reduced pressure, and the resulting residue was recrystallized from the mixed solvent of ethyl acetate/methanol to afford **2** as colorless crystals with the yield of 3.37 g (39.1%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (t, $J = 1.7$ Hz, 1H, phenyl proton), 7.40 (d, $J = 1.7$ Hz, 2H, phenyl protons), 2.12–2.08 [m, 3H, adamantyl protons

[–CH_2–C*H*(CH_2–)–CH_2–)], 1.85 [d, *J* = 2.6 Hz, 6H, adamantyl protons (quaternary C–CH_2–CH–)], 1.82–1.68 [m, 6H, adamantyl protons (–CH–CH_2–CH–)]. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.4 (quaternary phenyl carbon), 131.1 [phenyl carbon (=*C*H–)], 127.2 [phenyl carbon (=*C*H–)], 122.8 (quaternary phenyl carbon), 42.8 [adamantyl carbons (quaternary C–*C*H_2–CH–)], 36.6 [adamantyl carbons (–CH–*C*H_2–CH–)], 36.5 (quaternary adamantyl carbon), 28.7 [adamantyl carbons (–CH_2–*C*H–CH_2–)]. T_m: 116 °C.

1-[3,5-(Dimethylsilyl)phenyl]adamantane (**3**)

Under a dry argon atmosphere, 6.88 g (18.6 mmol) of **2** and 4.84 g (51.2 mmol) of chlorodimethylsilane in 140 ml of THF were added dropwise to 1.25 g (51.4 mmol) of magnesium in 140 ml of THF under reflux. The reaction mixture was refluxed for 8 h and poured into a mixture of diethyl ether (50 ml) and 0.1 mol/l HCl aqueous solution (50 ml). 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, and the crude product was purified by column chromatography packed with silica gel eluted with hexane. The fraction with an R_f value of 0.69 was concentrated under reduced pressure, and the resulting residue was recrystallized from the mixed solvent of ethyl acetate/methanol to afford **3** as colorless crystals with the yield of 3.55 g (58.1%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, *J* = 1.1 Hz, 2H, phenyl protons), 7.47 (t, *J* = 1.1 Hz, 1H, phenyl proton), 4.36 [sept, *J* = 3.7 Hz, 2H, –Si$(CH_3)_2$–*H*], 2.06–2.01 [m, 3H, adamantyl protons (–CH_2–C*H*(CH_2–)–CH_2–)], 1.87 [d, *J* = 2.8 Hz, 6H, adamantyl protons (quaternary C–CH_2–CH–)], 1.76–1.66 [m, 6H, adamantyl protons (–CH–CH_2–CH–)], 0.29 [d, *J* = 3.7 Hz, 12H, –Si(CH_3)$_2$–H]. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.5 (quaternary phenyl carbon), 136.9 (quaternary phenyl carbon), 136.2 [phenyl carbon (=*C*H–)], 131.5 [phenyl carbon (=*C*H–)], 43.1 [adamantyl carbons (quaternary C–*C*H_2–CH–)], 36.7 [adamantyl carbons (–CH–*C*H_2–CH–)], 36.2 (quaternary adamantyl carbon), 28.9 [adamantyl carbons (–CH_2–*C*H–CH_2–)], –3.6 [–Si(*C*H_3)$_2$–H]. IR (KBr): 2117 (Si–H). Mass (EI, *m/z*): 328 (M^+), 313 (M^+–CH_3), 269 (M^+–[Si$(CH_3)_2$H]). T_m: 81 °C.

1-[3,5-(Dimethylhydroxysilyl)phenyl]adamantane (**M1**)

Under an argon atmosphere, 0.999 g (3.04 mmol) of **3** in 1.7 ml of THF was added dropwise to 0.198 g of 5% Pd on C with 0.200 g (11.1 mmol) of H_2O in 1.7 ml of THF in an ice bath. The reaction mixture was stirred at ambient temperature for 40 min and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from a mixed solvent of toluene/hexane to afford **M1** as colorless crystals with the yield of 1.023 g (93.3%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (s, 3H, phenyl protons), 2.13–2.09 [m, 3H, adamantyl protons (–CH_2–C*H*(CH_2–)–CH_2–)], 1.94 [d, *J* = 2.7 Hz, 6H adamantyl protons (quaternary C–CH_2–CH–)], 1.92 [bs, 2H, –Si$(CH_3)_2$–O*H*], 1.84–1.72 [m, 6H, adamantyl protons (–CH–CH_2–CH–)], 0.42 [s, 12H, –Si(CH_3)$_2$–OH]. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.6 (quaternary phenyl carbon), 137.9 [phenyl carbon

(=*C*H–)], 135.0 (quaternary phenyl carbon), 130.9 [phenyl carbon (=*C*H–)], 43.1 [adamantyl carbons (quaternary C–*C*H$_2$–CH–)], 36.7 [adamantyl carbons (–CH–*C*H$_2$–CH–)], 36.2 (quaternary adamantyl carbon), 28.9 [adamantyl carbons (–CH$_2$–*C*H–CH$_2$–)], 0.0 [–Si(*C*H$_3$)$_2$–OH]. IR (KBr, cm^{-1}): 3310 (–OH). Mass (EI, *m*/*z*): 360 (M$^+$), 345 (M$^+$–CH$_3$). T_m: 176 °C.

Poly(tetramethyl-5-adamantyl-1,3-silphenylenesiloxane) (**P1**)

Under a dry atmosphere, 0.02 g of 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate was added to 0.195 g (0.541 mmol) of **M1** dissolved in 0.6 ml of toluene, and the reaction mixture was refluxed for 24 h. The reaction mixture was filtered and poured into 100 ml of acetone to isolate **P1** as white precipitates. Yield: 0.104 g (56.1%) as white powder solid. The number-average molecular weight (M_n) and polydipersity index (M_w/M_n) were estimated to be 5.96 × 10^4 and 1.69, respectively, from SEC eluted with THF using polystyrene standards.

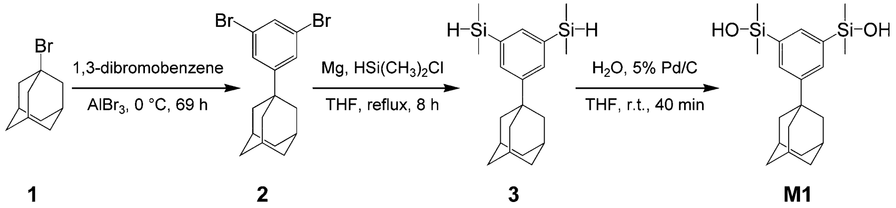
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.59 (s, 2H, phenyl protons), 7.57 (s, 1H, phenyl proton), 2.06–2.01 [m, 3H, adamantyl protons (–CH$_2$–C*H*(CH$_2$–)–CH$_2$–)], 1.87 (d, $J = 2.3$ Hz, 6H, adamantyl protons (quaternary C–C*H*$_2$–CH–)], 1.76–1.66 (m, 6H, adamantyl protons (–CH–C*H*$_2$–CH–)], 0.33 [s, 12H, (–Si(C*H*$_3$)$_2$–)]. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 148.9 (quaternary phenyl carbon), 138.3 [phenyl carbon (=*C*H–)], 134.8 (quaternary phenyl carbons), 130.5 [phenyl carbon (=*C*H–)], 43.1 [adamantyl carbons (quaternary C–*C*H$_2$–CH–)], 36.7 [adamantyl carbons (–CH–*C*H$_2$–CH–)], 36.2 (quaternary adamantyl carbon), 28.9 [adamantyl carbons (–CH$_2$–*C*H–CH$_2$–)], 1.28 [–Si(*C*H$_3$)$_2$–]. IR (KBr, cm^{-1}): 1000–1100 (Si–O). T_g: 85 °C, T_m: 127 °C (determined by differential scanning calorimetry). T_{d5}: 517 °C (determined by thermogravimetry).

Results and discussion

Monomer synthesis

Scheme 2 shows the pathways for the synthesis of a novel disilanol monomer, i.e., 1-[3,5-(dimethylhydroxysilyl)phenyl]adamantane (**M1**).

M1 was obtained by the hydrolysis of 1-[3,5-(dimethylsilyl)phenyl]adamantane (**3**), which had been prepared from 1-(3,5-dibromophenyl)adamantane (**2**) via the Grignard reaction with chlorodimethylsilane.



Scheme 2 Synthetic pathways for 1-[3,5-(dimethylhydroxysilyl)phenyl]adamantane (**M1**)

The structure of **M1** was confirmed by the ^{1}H and ^{13}C NMR as well as IR spectroscopy as noted in the Experimental section. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of **M1**. Assignment of each NMR signal is also described in Fig. 1. The integrated ratio of each ^{1}H NMR signal was consistent with the structure of **M1** as described in Fig. 1a. ^{13}C NMR signals were assigned using the DEPT spectrum of **M1** together.

On the other hand, Fig. 2 shows the IR spectra of **3** and **M1**. The strong absorption band based on Si–H moiety was observed at 2,117 cm^{-1} in the IR spectrum of **3** as shown in Fig. 2a; this absorption band disappeared, and instead, the strong absorption band based on OH moiety was observed at 3,000–3,500 cm^{-1} in the IR spectrum of **M1** as shown in Fig. 2b.

Synthesis and characterization of polymer

The obtained **M1** underwent solution polycondensation by use of 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst to afford poly(tetramethyl-5-adamantyl-1,3-silphenylenesiloxane) (**P1**). Toluene was used as a solvent for polycondensation of **M1**; however, any solvent forming azeotropic mixtures with water and dissolving both monomer and the resulting polymer, such as toluene and benzene, can be used for the present polycondensation as reported previously [26–29]. The low monomer concentration resulted in the formation of not polymer but the corresponding cyclic compounds. Thus, we used the minimum amount of solvent, which dissolved both monomer and the resulting polymer. The most important factor for polymer formation seems to be the monomer concentration during polycondensation.

The structure of **P1** was confirmed by ^{1}H and ^{13}C NMR as well as IR spectroscopy. Figure 3 shows the ^{1}H and ^{13}C NMR spectra of **P1**. The ^{1}H and ^{13}C

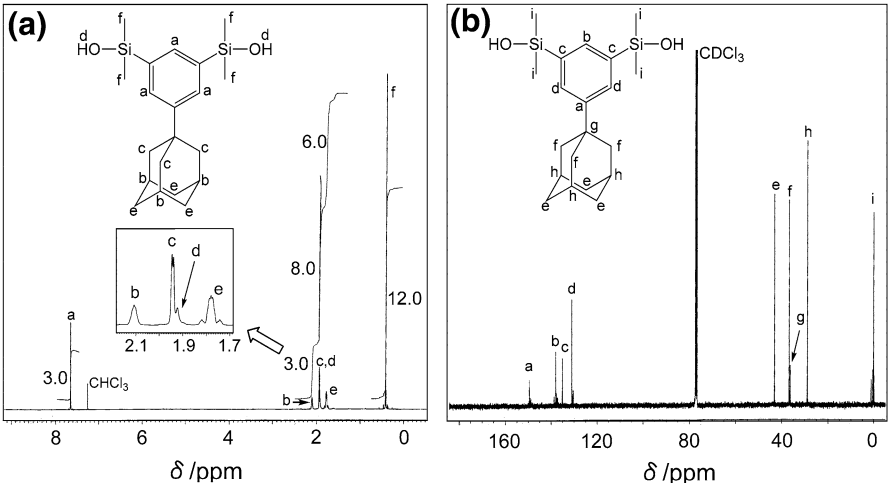


Fig. 1 (**a**) ^{1}H NMR (solvent: CDCl$_3$, 400 MHz, numerals at signal's side are the integral values of each signal) and (**b**) ^{13}C NMR spectra (solvent: CDCl$_3$, 100 MHz) of **M1**

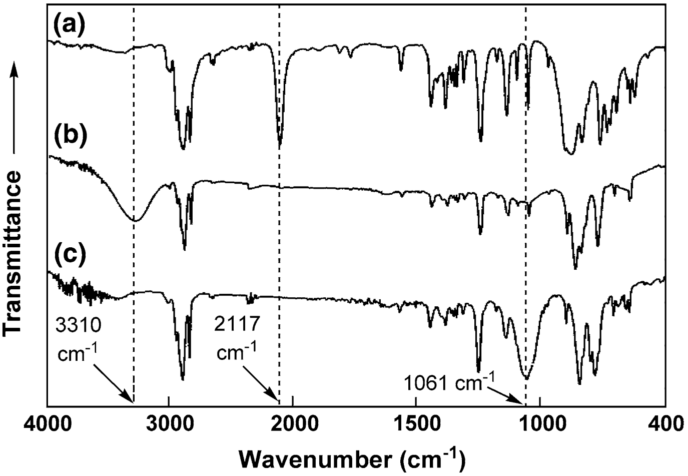


Fig. 2 IR spectra of (**a**) **3**, (**b**) **M1**, and (**c**) **P1**

NMR spectra of **P1** were almost similar to those of **M1**, except the disappearance of a signal at 1.92 ppm based on OH groups as observed in the ^{1}H NMR spectrum of **M1**.

The integrated ratio of each ^{1}H NMR signal was consistent with the structure of **P1** as described in Fig. 3a. In addition, the IR spectrum of **P1** is also described in Fig. 2c. The strong absorption band based on OH moiety was observed at 3,000–3,500 cm^{-1} in the IR spectrum of **M1** as shown in Fig. 2b; however, this absorption band disappeared, and instead, the absorption band based on Si–O–Si moiety was observed at 1,000–1,100 cm^{-1} in the IR spectrum of **P1** as shown in Fig. 2c. In addition, the SEC profile of **P1** indicated the formation of polymer and the absence

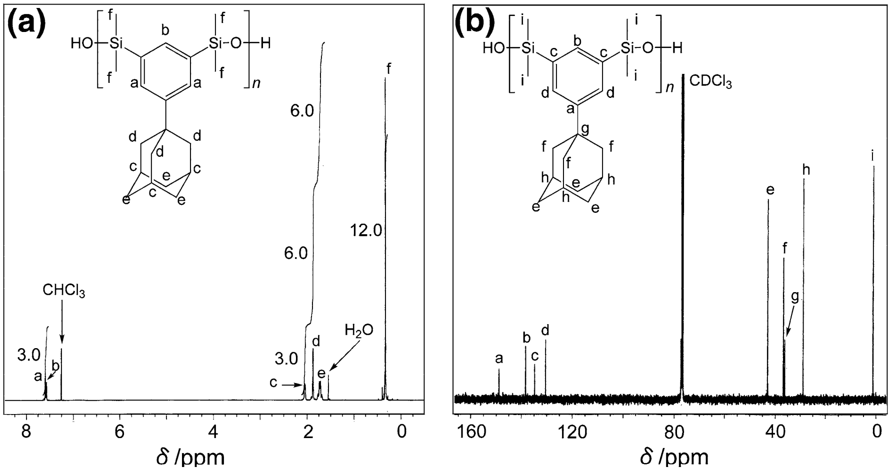


Fig. 3 (**a**) ^{1}H NMR (solvent: CDCl$_3$, 400 MHz, numerals at signal's side are the integral values of each signal) and (**b**) ^{13}C NMR spectra (solvent: CDCl$_3$, 100 MHz) of **P1**

of low molecular weight species such as cyclic dimer or trimer. The number-average molecular weight (M_n) and polydipersity index (M_w/M_n) were estimated to be 5.96×10^4 and 1.69 from SEC measurement. These results strongly support that no side-reactions occurred during the present polycondensation. **P1** exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, benzene, and toluene at ambient temperature, and was also soluble in hot hexane, diethyl ether, and ethyl acetate.

Figure 4 depicts the DSC traces of **P1** on a first and a second heating scan under nitrogen atmosphere. As seen in Fig. 4, the endothermic peak was observed at around 127 °C on a first heating scan while the only glass transition was observed at 85 °C on a second heating scan. It is presumably owing to the relatively high degree of crystallization of the sample used that the first heating scan did not show the apparent T_g as observed in the case of the other polysiloxane derivative having adamantyl moiety in the main chain [10]. On the contrary, once the present polymer melted, it would be difficult to be crystallized during the cooling scan; therefore, the second scan showed the apparent T_g, presumably because of the formation of amorphous state. The similar tendency has been observed in the case of the other polysiloxane derivative having adamantyl moiety in the main chain [10]. Thus, the T_g and T_m of **P1** were determined to be 85 and 127 °C, respectively. The T_g of **P1** (85 °C) was much higher than that of 1,3-PTMS (−52 °C) [30], indicating the incorporation of a bulky adamantyl moiety onto the phenylene moieties would restrict the mobility of backbone to result in the high T_g. On the other hand, it has been reported that the introduction of a phenolic hydroxy group onto the phenylene moieties of 1,3-PTMS is effective on raising T_g, because the intermolecular and/or intramolecular hydrogen bondings based on hydroxy groups would restrict the mobility of the main chain; however, the T_g of **P1** is higher than that of 1,3-PTMS

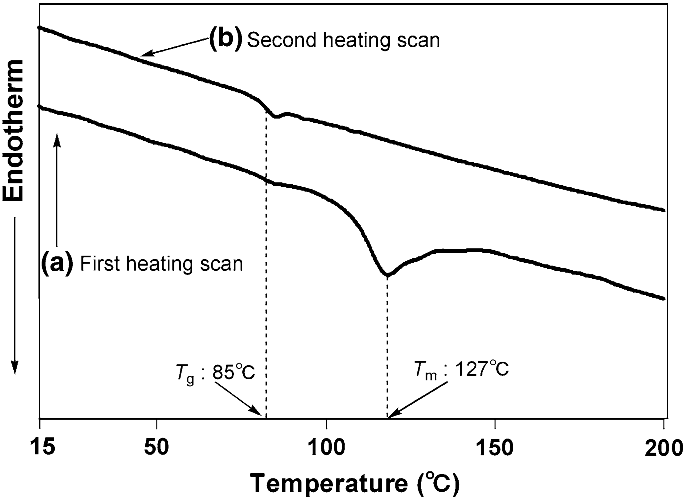


Fig. 4 DSC traces of **P1** (**a**) on a first heating scan and (**b**) on a second heating scan at a heating rate of 10 °C/min under N_2 flow rate of 10 ml/min

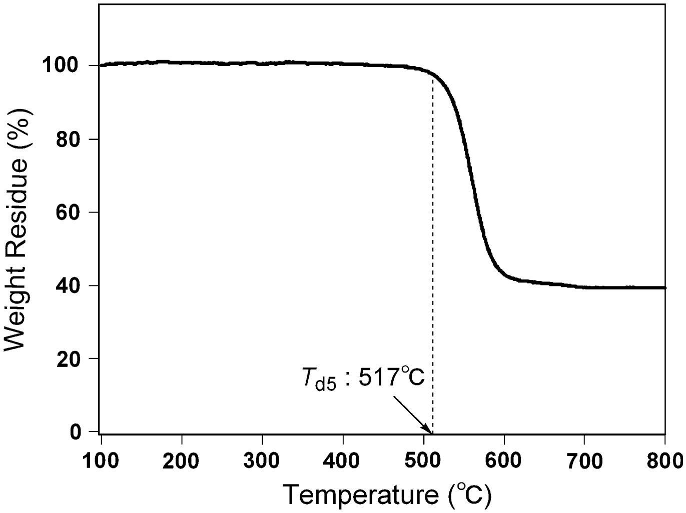


Fig. 5 TG curve of **P1** at a heating rate of 10 °C/min under nitrogen atmosphere

with phenolic hydroxy groups (40 °C) [29], indicating that the introduction of bulky adamantyl moieties would be more effective on raising T_g than that of phenolic hydroxy moieties.

For the investigation of the thermostability of **P1**, the thermogravimetry (TG) measurement of **P1** was carried out and the TG curve of **P1** is depicted in Fig. 5. The temperature at 5% weight loss (T_{d5}) of **P1** under nitrogen atmosphere was determined to be 517 °C from TG curve of **P1** as shown in Fig. 5, which was much higher than that of 1,3-PTMS [30]. As deduced from T_{d5}, the introduction of a bulky adamantyl group onto the phenylene moieties would improve the thermostability, presumably owing to the inhibition of interchain interactions by the bulkiness of adamantyl moiety.

Conclusions

We achieved the synthesis of a novel poly(tetramethyl-1,3-silphenylenesiloxane) derivative having adamantyl moiety, i.e., poly(tetramethyl-5-adamantyl-1,3-silphenylenesiloxane) (**P1**) via solution polycondensation of a novel disilanol monomer, i.e., 1-[3,5-(dimethylhydroxysilyl)phenyl]adamantane (**M1**). The obtained **P1** exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, benzene, and toluene at ambient temperature, and was also soluble in hot hexane, diethyl ether, and ethyl acetate. The T_g and T_{d5} of **P1** were much higher than those of poly(tetramethyl-1,3-silphenylenesiloxane), indicating that **P1** is a new polysiloxane derivative with good solubility as well as good thermostability.

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