Polymer 49 (2008) 2825–2831

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and thermal characterization of novel adamantane-based polysiloxane

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ARTICLE INFO

Article history:
Received 19 March 2008
Received in revised form 25 April 2008
Accepted 29 April 2008
Available online 2 May 2008

Keywords:
Polysiloxane
Polycondensation
Adamantane

ABSTRACT

Novel polysiloxane derivative having adamantyl moiety in the main chain (**P1**) was synthesized and characterized by differential scanning calorimetry (DSC), thermogravimetry (TG), and X-ray diffraction analysis. **P1** was obtained by bulk polycondensation without catalysts as well as solution polycondensation of novel disilanol monomer, i.e., 1,3-bis[4-(dimethylhydroxysilyl)phenyl]adamantane (**M1**), which was prepared by the Grignard reaction using chlorodimethylsilane and 1,3-bis(4-bromophenyl)adamantane, followed by the hydrolysis catalyzed by 5% palladium on charcoal. The molecular weight of **P1** was dependent on the concentration of **M1** in solution polycondensation, and the high concentration of **M1** would result in the high average molecular weight of **P1**. **P1** exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. The glass transition temperature (T_g) of **P1** determined from DSC would be dependent on the average molecular weight of **P1**. The highest T_g was 115 °C and much higher than that of poly(tetramethyl-1,4-silphenylenesiloxane) (−20 °C). The melting temperature (T_m) of **P1** seemed to be independent of the average molecular weight of **P1** and was in the range of 153–157 °C, which was comparable to the T_m of poly(tetramethyl-1,4-silphenylenesiloxane). The temperature at 5% weight loss (T_{d5}) of **P1** determined by TG was also comparable to that of poly(tetramethyl-1,4-silphenylenesiloxane), indicating that **P1** is a new polysiloxane derivative with the high T_g as well as good thermostability.

1. Introduction

Adamantane (tricyclo[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] and as a pendant group [3]. Adamantyl-incorporated polymers generally exhibit high glass transition temperature and chain stiffness with reduced crystallinity and enhanced solubility, because the diamond-like cage structure of adamantane tends to inhibit packing of polymer chains [2,3]. Additionally, the UV–vis transparency of adamantane attracts much attention for incorporating into polymeric materials for short wavelength microlithography [4].

On the other hand, linear polysiloxanes have been well-known to show 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 [5,6]. Polysiloxane derivatives have been one of the candidates for negative photo-resist materials via cross-linking [7]; however, rarely used as positive photo-resist materials owing to the low T_g of polysiloxane derivatives. One of the 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 [5]; however, that of poly(tetramethyl-1,4-silphenylenesiloxane) (1,4-PTMPS) to be −20 °C owing to the incorporation of the bulky phenylene moiety into the polysiloxane backbone [8–10]. 1,4-PTMPS is a representative polymer of poly(tetramethylsilarylenesiloxane) derivatives where aromatic moieties are incorporated into the polysiloxane backbone. The properties of poly(tetramethylsilarylenesiloxane) derivatives have been reported to depend on the kind of arylene moiety [11–15], the substituted position of dimethylsilyl groups [13,14,16] as well as the substituent [17–19] on the arylene moiety, and so on. It has been reported that the improvement of T_g of poly(tetramethylsilarylenesiloxane) derivatives is realized by the incorporation of naphthylene [13], anthrylene [14], or phenanthrylene [14] moieties into the main chain or by the introduction of phenyl groups as substituents into the silyl moieties [15].

In addition, polysiloxane backbones can be cleaved by acidic or basic reagents because of the ionic property of siloxane bonding [5,6]. If an adamantyl moiety is introduced into polysiloxane backbone, the resulting polysiloxane, which is expected to exhibit the high T_g and good thermostability, can be degraded by some photo-acid or photo-base generator to be applied as the positive-

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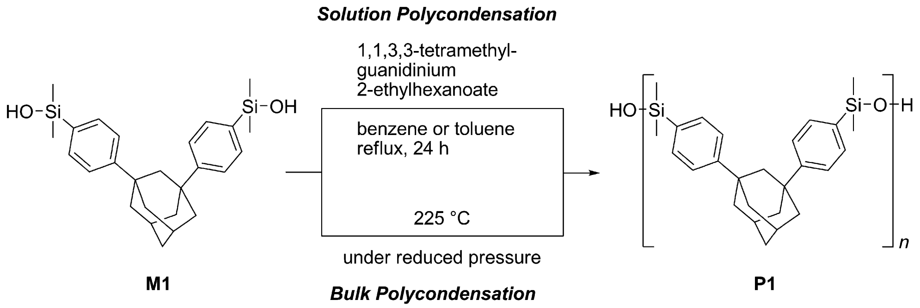
doi:10.1016/j.polymer.2008.04.053



Scheme 1. Synthesis of a novel adamantane-based polysiloxane (**P1**).

type photo-resist materials. Actually, an attempt to introduce an adamantyl moiety into polysiloxane backbone has been made by Weber and Pai [20], where 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) were reported; however, the thermal characterization of the obtained polysiloxane derivatives seemed to be insufficient.

From these points of view, we report here the preparation of a novel polysiloxane derivative having adamantyl moiety in the main chain (**P1**) obtained by bulk polycondensation without catalysts as well as solution polycondensation of 1,3-bis[4-(dimethylhydroxysilyl)phenyl]adamantane (**M1**) as shown in Scheme 1. The present paper also describes the results of thermal and X-ray diffractometric analyses of the obtained polymer.

2. Experimental

2.1. Materials

1,3-Dibromoadamantane (**1**) was prepared by the bromination of adamantane (Tokyo Kasei Kogyo Co., Inc.) according to the literature [21] and partly supplied from Mitsubishi Gas Chemical Co., Inc. Bromobenzene was used after distillation over calcium hydride. Anhydrous iron(III) chloride (Merck), 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 [13]. 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 ($CDCl_3$) 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. 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 5 °C min^{-1} or 10 °C min^{-1} under a nitrogen flow rate of 10 mL min^{-1}. Thermogravimetry (TG) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C min^{-1} under 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 Shimadzu GCMS-QP2020A instrument. The purity of all prepared compounds with low-molecular weight was confirmed to be over 99% by GC analysis. X-ray diffraction patterns were recorded on a Philips PW1830 X-ray diffractometer, equipped with a Philips HTK-2-HC thermal controller.

2.3. Synthesis of 1,3-bis(4-bromophenyl)adamantane (**2**)

After the mixture of 2.94 g (10.0 mmol) of 1,3-dibromoadamantane (**1**), 0.0648 g (0.40 mmol) of anhydrous iron(III) chloride, and 25.12 g (160 mmol) of bromobenzene was refluxed for 16 h under a dry argon atmosphere, the reaction mixture was poured into a mixture of 50 mL of 0.1 mol L^{-1} HCl aqueous solution and 50 mL of ethyl acetate. 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 0.45 was concentrated and recrystallized from hexane to afford **2** as colorless crystals with the yield of 2.44 g (54.7%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (dt, $J = 8.8$, 2.4 Hz, 4H, phenyl protons), 7.25 (dt, $J = 8.8$, 2.4 Hz, 4H, phenyl protons), 2.35–2.28 (m, 2H, adamantyl protons (–CH_2–C*H*(CH_2–)–CH_2–)), 1.95 (s, 2H, adamantyl protons (quaternary C–CH_2– quaternary C)), 1.91 (d, $J = 2.6$ Hz, 8H, adamantyl protons (quaternary C–CH_2–CH–)), 1.77 (t, $J = 2.6$ Hz, 2H, adamantyl protons (–CH–CH_2–CH–)). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.4 (quaternary phenyl carbon), 131.2 (quaternary phenyl carbons), 126.8 (phenyl carbons (=CH–)), 119.6 (phenyl carbon (=CH–)), 48.7 (adamantyl carbon (quaternary C–*C*H_2– quaternary C)), 42.0 (adamantyl carbons (quaternary C–*C*H_2–CH–)), 37.1 (quaternary adamantyl carbons), 35.6 (adamantyl carbons (–CH–*C*H_2–CH–)), 29.3 (adamantyl carbons (–CH_2–*C*H(CH_2–)–CH_2–)). Mass (EI, *m*/*z*): 448 ($M^+ + 4$), 446 ($M^+ + 2$), 444 (M^+), 310, 308, 288, 286, 277 ($M^+ + 2 -$ [Br–Ph–CH_2^+]), 275 ($M^+ -$ [Br–Ph–CH_2^+]), 171 (Br–Ph–CH_2^+), 169 (Br–Ph–CH_2^+). Mp: 123 °C.

2.4. Synthesis of 1,3-bis[4-(dimethylsilyl)phenyl]adamantane (**3**)

Under a dry argon atmosphere, 2.78 g (6.23 mmol) of **2** and 1.62 g (17.1 mmol) of chlorodimethylsilane in 70 mL of THF were added dropwise to 0.416 g (17.1 mmol) of magnesium in 70 mL of THF at 60 °C. The reaction mixture was refluxed for 24 h and poured into a mixture of 50 mL of diethyl ether and 50 mL of 0.1 mol L^{-1} 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 fraction with an R_f value of 0.51 was concentrated and recrystallized from methanol to afford **3** as colorless crystals with the yield of 1.50 g (59.5%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (dt, $J = 8.4$, 1.6 Hz, 4H, phenyl protons), 7.40 (dt, $J = 8.4$, 1.6 Hz, 4H, phenyl protons), 4.41 (sept, $J = 4.0$ Hz, 2H, –Si(CH_3)$_2$–*H*), 2.36–2.29 (m, 2H, adamantyl protons (–CH_2–CH(CH_2–)–CH_2–)), 2.05 (s, 2H, adamantyl protons (quaternary C–CH_2– quaternary C)), 1.96 (d, $J = 2.4$ Hz, 8H, adamantyl protons (quaternary C–CH_2–CH–)), 1.80 (t, $J = 2.4$ Hz, 2H, adamantyl protons (–CH–CH_2–CH–)), 0.33 (d, $J = 4.0$ Hz, 12H, –Si(CH_3)$_2$–H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.6 (quaternary phenyl carbon), 134.3 (quaternary phenyl carbon), 134.0 (phenyl carbons (=CH–)), 124.5 (phenyl carbons (=CH–)), 48.6 (adamantyl carbon (quaternary C–CH_2– quaternary C)), 42.2 (adamantyl carbons (quaternary C–CH_2–CH–)), 37.3 (quaternary adamantyl carbons), 35.9 (adamantyl carbons (–CH–CH_2–CH–)), 29.5 (adamantyl carbons (–CH_2–CH(CH_2–)–CH_2–)), −3.7 (–Si(CH_3)$_2$–H). IR (KBr, cm^{-1}): 2111 (Si–H). Mass (EI, m/z, intensity): 404 (M^+), 403 ($M^+ - H$), 345 ($M^+ - [Si(CH_3)_2]$). Mp: 120 °C. Anal. calcd for $C_{26}H_{36}Si_2$: C, 77.16; H, 8.97; found: C, 77.09; H, 9.05.

2.5. Synthesis of 1,3-bis[4-(dimethylhydroxysilyl)phenyl]adamantane (**M1**)

Under an argon atmosphere, 0.994 g (2.46 mmol) of **3** in 0.7 mL of THF was added dropwise to 0.145 g of 5% Pd on C with 0.133 g (7.37 mmol) of H_2O in 2.1 mL of THF in an ice bath. The reaction mixture was stirred at ambient temperature for 2 h and filtered. The filtrate was evaporated; then, the residue was recrystallized from a mixed solvent of toluene/hexane to afford **M1** as colorless crystals with the yield of 0.551 g (51.4%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (dt, $J = 8.4$, 1.6 Hz, 4H, phenyl protons), 7.43 (dt, $J = 8.4$, 1.6 Hz, 4H, phenyl protons), 2.35–2.30 (m, 2H, adamantyl protons (–CH_2–CH(CH_2–)–CH_2–)), 2.05 (s, 2H, adamantyl protons (quaternary C–CH_2– quaternary C)), 1.97 (d, $J = 2.4$ Hz, 8H, adamantyl protons (quaternary C–CH_2–CH–)), 1.83 (s, 2H, –Si(CH_3)$_2$–OH), 1.82–1.78 (m, 2H, adamantyl protons (–CH–CH_2–CH–)), 0.40 (s, 12H, –Si(CH_3)$_2$–OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.1 (quaternary phenyl carbon), 136.0 (quaternary phenyl carbon), 133.1 (phenyl carbons (=CH–)), 124.5 (phenyl carbons (=CH–)), 48.6 (adamantyl carbon (quaternary C–CH_2– quaternary C)), 42.3 (adamantyl carbons (quaternary C–CH_2–CH–)), 37.3 (quaternary adamantyl carbons), 35.8 (adamantyl carbons (–CH–CH_2–CH–)), 29.5 (adamantyl carbons (–CH_2–CH(CH_2–)–CH_2–)), 0.0 (–Si(CH_3)$_2$–OH). IR (KBr, cm^{-1}): 3200–3500 (Si–OH). Mass (EI, m/z): 436 (M^+), 421 ($M^+ - CH_3$), 403, 347, 327, 271, 203. Mp: 166 °C. Anal. calcd for $C_{26}H_{36}O_2Si_2$: C, 71.50; H, 8.31; found: C, 71.45; H, 8.46.

2.6. Solution polycondensation of **M1** to afford **P1**

Typical procedure (Run 1 in Table 1): Under a dry atmosphere, 0.02 g of 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate was added to 0.200 g (0.458 mmol) of **M1** dissolved in 0.92 mL of toluene, and the reaction mixture was refluxed for 24 h. The reaction mixture dissolved in THF was filtered and poured into 100 mL of acetone to isolate the corresponding polymer as white precipitates. Yield: 0.085 g (44%) as white powder solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, $J = 8.4$ Hz, 4H, phenyl protons), 7.38 (d, $J = 8.4$ Hz, 4H, phenyl protons), 2.35–2.28 (m, 2H, adamantyl protons (–CH_2–CH(CH_2–)–CH_2–)), 2.06 (s, 2H, adamantyl protons (quaternary C–CH_2– quaternary C)), 1.98–1.92 (m, 8H, adamantyl protons (quaternary C–CH_2–CH–)), 1.82–1.76 (m, 2H, adamantyl protons (–CH–CH_2–CH–)), 0.32 (s, 12H, –Si(CH_3)$_2$–). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.6 (quaternary phenyl carbon), 136.8 (quaternary phenyl carbon), 133.0 (phenyl carbons (=CH–)), 124.3 (phenyl carbons (=CH–)), 48.7 (adamantyl carbon (quaternary C–CH_2– quaternary C)), 42.2 (adamantyl carbons (quaternary C–CH_2–CH–)), 37.3 (quaternary adamantyl carbons), 35.9 (adamantyl carbons (–CH–CH_2–CH–)), 29.5 (adamantyl carbons (–CH_2–CH(CH_2–)–CH_2–)), 1.0 (–Si(CH_3)$_2$–). IR (KBr, cm^{-1}): 1000–1100 (Si–O). Anal. calcd for $(C_{26}H_{34}OSi_2)_n$ C, 74.58; H, 8.18; found: C, 74.36; H, 8.28.

Table 1
Results of polycondensation of **M1** and the characterization of **P1**

Run	Solvent	Conc. of **M1** (mol L^{-1})	Yield[a] (%)	M_n[b] 10^{-4}	M_w/M_n[c]	T_g[d] (°C)	T_m[e] (°C)	T_{d5}[f] (°C)
1	Toluene	0.5	44	3.30	1.98	105	153	519
2	Toluene	1.0	56	6.49	1.79	114	155	523
3	Toluene	2.0	18	7.43	1.39	115	157	523
4	Benzene	0.5	41	3.37	1.65	109	154	520
5	Benzene	1.0	61	6.64	1.72	114	157	523
6	Benzene	2.0	24	7.33	1.35	115	154	523

[a] Isolated part by reprecipitation from acetone using THF-soluble part.
[b] Number-average molecular weight estimated from SEC eluted with THF based on polystyrene standards.
[c] Polydispersity index.
[d] Glass transition temperature determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.
[e] Melting temperature determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.
[f] Temperature at 5% weight loss determined by thermogravimetry (TG) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

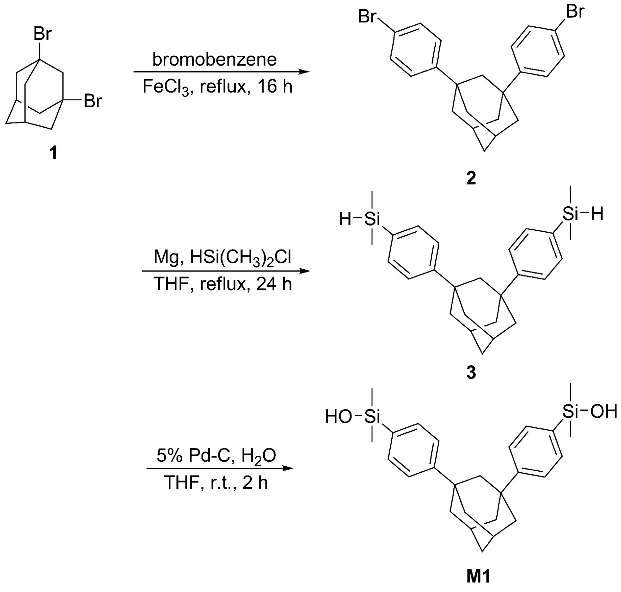
2.7. Bulk polycondensation of **M1** to afford **P1**

Bulk polycondensation of **M1** was carried out in a glass tube oven. **M1** (0.200 g, 0.46 mmol) was put into a glass tube; then, the temperature of the glass tube oven was set at 225 °C under reduced pressure. After the polycondensation was carried out for 1 h and cooled to ambient temperature, the reaction mixture was dissolved in 2 mL of chloroform; then, the solution was filtered and poured into 50 mL of acetone to isolate the corresponding polymer as white precipitates. Yield: 0.038 g (20%) as white powder solid. The NMR and IR spectra of the obtained product were consistent with those of the polymer obtained by solution polycondensation of **M1**. The M_n and polydispersity index (M_w/M_n) of the obtained polymer were estimated to be 1.75×10^4 and 1.29, respectively, from SEC measurement in THF eluent using polystyrene standards.

3. Results and discussion

3.1. Synthesis of monomer

Scheme 2 shows the pathways for the synthesis of novel disilanol monomer, i.e., 1,3-bis[4-(dimethylhydroxysilyl)phenyl]adamantane (**M1**).



Scheme 2. Synthetic pathways for 1,3-bis[4-(dimethylhydroxysilyl)phenyl]adamantane (**M1**).

M1 was obtained by the hydrolysis of 1,3-bis[4-(dimethylsilyl)phenyl]adamantane (**3**), which had been prepared from 1,3-bis(4-bromophenyl)adamantane (**2**) via the Grignard reaction with chlorodimethylsilane. As for the synthesis of **2**, Chalais et al. reported [22] that the Friedel–Crafts reaction between 1,3-dibromoadamantane and bromobenzene catalyzed by K10 clay-supported iron(III) chloride in carbon tetrachloride afforded a mixture of 1,3-bis(4-bromophenyl)adamantane (**2**), 1,3-bis(3-bromophenyl)adamantane and 1-(4-bromophenyl)-3-(3-bromophenyl)adamantane; however, the present Friedel–Crafts reaction using anhydrous iron(III) chloride as a catalyst as well as excess amount of bromobenzene afforded **2** selectively as deduced from NMR spectroscopy. The structure of a novel monomer **M1** was confirmed by the ^{1}H and ^{13}C NMR as well as IR spectroscopy as noted in Section 2. Fig. 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. 1(a). ^{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 2214 cm^{-1} in the IR spectrum of **3** as shown in Fig. 2(a); however, this absorption band disappeared, and instead, the strong absorption band based on OH moiety was observed at 3000–3500 cm^{-1} in the IR spectrum of **M1** as shown in Fig. 2(b).

3.2. *Synthesis of polymer*

The obtained **M1** underwent solution polycondensation by use of 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst to afford the corresponding poly(tetramethylsilarylenesiloxane) derivative **P1**. The results of the solution polycondensation of **M1** are summarized in Table 1.

The use of benzene or toluene as a solvent afforded the similar results in solution polycondensation of **M1** as summarized in Table 1. Namely, any solvents forming azeotropic mixtures with water and dissolving monomer, such as benzene and toluene, can be used for the present polycondensation as reported previously [13,14,18,19]. On the other hand, the higher concentration of **M1** in the polycondensation resulted in the higher average molecular weight of **P1**, as shown in Table 1. We defined the "yield" of polymer as the isolated part by reprecipitation from acetone using THF-soluble part. It would be observed that the high concentration of **M1** resulted in the high yield of **P1** as shown in Runs 1 and 2 as well as Runs 4 and 5 in Table 1; however, too high concentration of **M1** in polycondensation resulted in the low yield of **P1** as shown in Runs 3

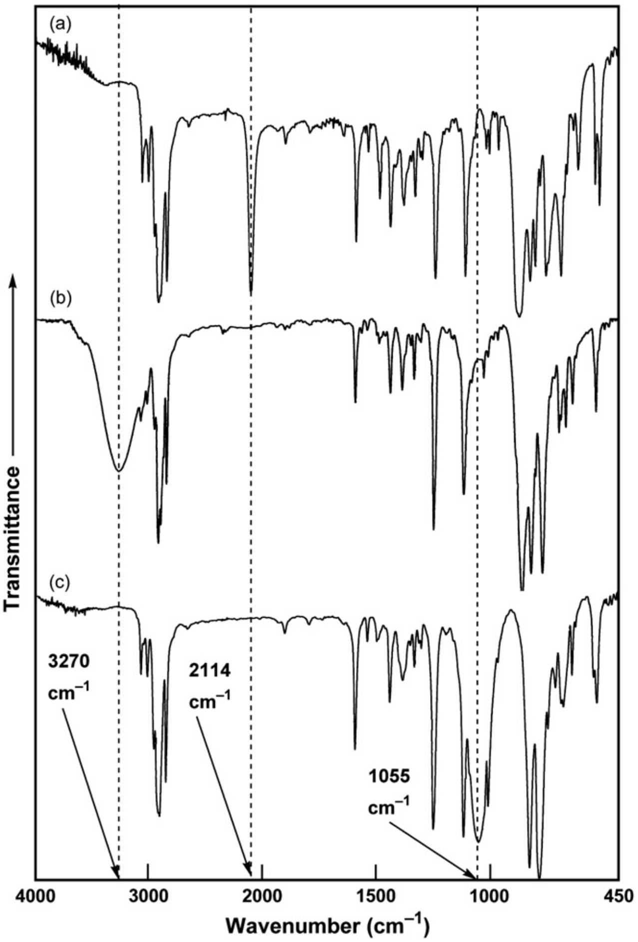


Fig. 2. IR spectra of (a) **3**, (b) **M1**, and (c) **P1**.

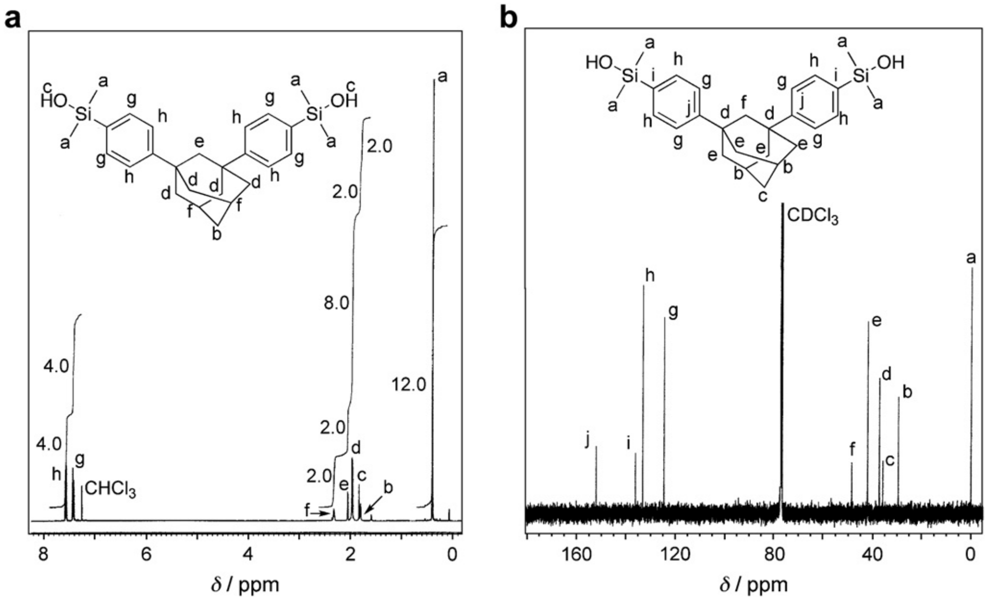


Fig. 1. (a) ^{1}H NMR (solvent: CDCl$_3$, 400 MHz) and (b) ^{13}C NMR spectra (solvent: CDCl$_3$, 100 MHz) of **M1**.

and 6 in Table 1, presumably because **P1** with the very high molecular weight would exhibit the relatively low solubility in the solvent used and resulted in the low yield of **P1**. Thus, the values of polydispersity index (M_w/M_n in Table 1) in the case of Runs 3 and 6 were smaller than those in the case of Runs 1 and 2 as well as Runs 4 and 5. On the contrary, too low concentration of **M1** in solution polycondensation afforded the cyclic oligomers as reported previously [13,14,18,19]. The SEC traces of **P1** indicated that the obtained polymers were unimodal. The structure of **P1** was confirmed by ^{1}H and ^{13}C NMR and IR spectroscopies. Fig. 3 shows the ^{1}H and ^{13}C NMR spectra of **P1** obtained by Run 3 in Table 1 as a typical example.

The ^{1}H and ^{13}C NMR spectra of **P1** were almost similar to those of **M1**, except the disappearance of a signal at 1.83 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. 3(a). In addition, the IR spectrum of **P1** is also described in Fig. 2(c). The strong absorption band based on OH moiety was observed at 3000–3500 cm^{-1} in the IR spectrum of **M1** as shown in Fig. 2(b); however, this absorption band disappeared, and instead, the absorption band based on Si–O–Si moiety was observed at 1000–1100 cm^{-1} in the IR spectrum of **P1** as shown in Fig. 2(c). These results strongly support that no side reactions occurred during the present polycondensation.

3.3. Characterization of polymer

The characterization of **P1** is also summarized in Table 1. **P1** with appropriate molecular weight was soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. The glass transition temperature (T_g) and melting temperature (T_m) of **P1** determined from DSC are also summarized in Table 1. Fig. 4 depicts the DSC traces of **P1** obtained by Run 3 in Table 1 on a first and a second heating scan under nitrogen atmosphere as a typical example.

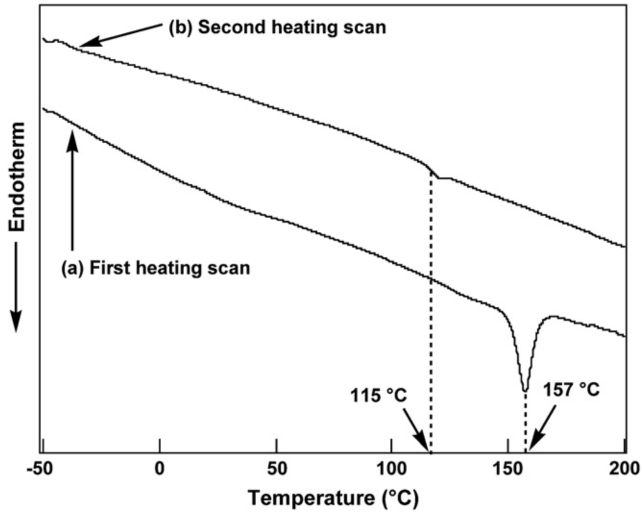


Fig. 4. DSC traces of **P1** obtained by Run 3 in Table 1 (a) on a first heating scan and (b) on a second heating scan at a heating rate of 10 °C min^{-1} under N_2 flow rate of 10 mL min^{-1}.

As seen in Fig. 4, the endothermic peak was observed at around 157 °C on a first heating scan, while the only glass transition was observed at 115 °C on a second heating scan. It is presumably owing to the relatively high degree of the crystallization of the sample used that the first heating scan did not show apparent T_g as observed in the case of the other 1,4-PTMS derivatives having oxyethylene moiety with high degree of crystallization [18]. 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 because of the formation of amorphous state. The similar tendency has been observed in the case of the other poly(tetramethylsilarylenesiloxane) derivatives [14]. It was confirmed that the similar thermograms were obtained for **P1** with different average molecular weights. There were no significant differences in the T_ms of **P1** with different average molecular weights; however, the low average molecular weight of **P1** seemed to lower the T_g as shown in Runs 1 and 4 in Table 1. The T_g of **P1** was much higher than that of 1,4-PTMPS (−20 °C) [8,9]. The incorporation of bulky adamantyl moieties into the backbone would restrict the mobility of backbone to result in the high T_g. On the other hand, the T_m of 1,4-PTMPS (M_n: 186 000, M_w/M_n: 1.82) prepared by polycondensation of 1,4-bis(dimethylhydroxysilyl)benzene in our laboratory was determined to be 130 °C by a DSC measurement. The thermodynamic T_m of 1,4-PTMPS has been reported to be 160 °C by Magill and Li [23]. The present T_m of **P1** is

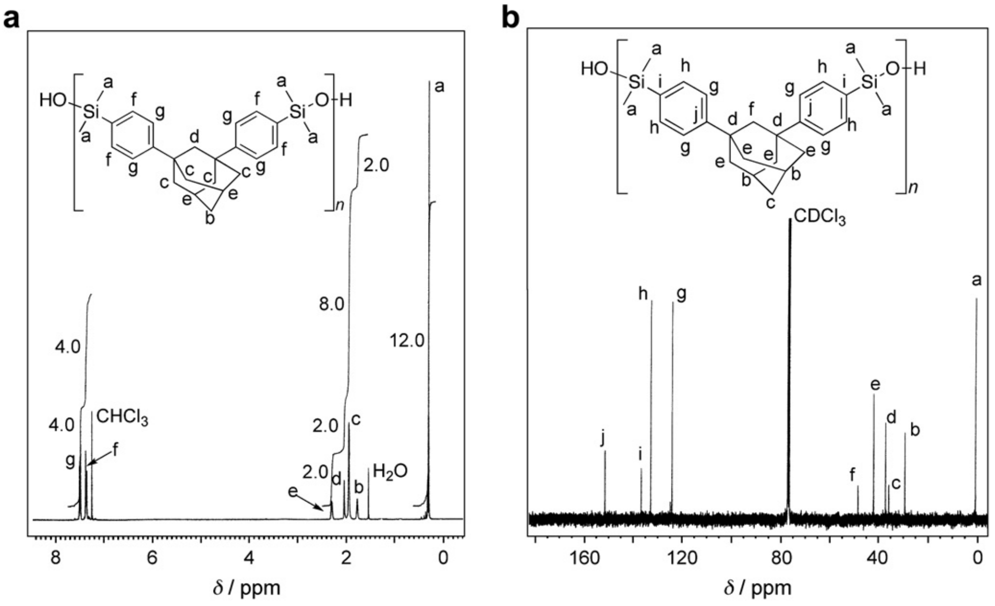


Fig. 3. (a) ^{1}H NMR (solvent: $CDCl_3$, 400 MHz) and (b) ^{13}C NMR spectra (solvent: $CDCl_3$, 100 MHz) of **P1**.

found to be almost equal to that of 1,4-PTMPS in spite of the incorporation of bulky adamantyl moieties into the main chain. These findings would presumably suggest that the crystallinity was mainly dependent on the phenylene moieties in the polysiloxane backbone.

Fig. 5 shows the X-ray diffraction patterns of **P1** obtained by Run 3 in Table 1 at various temperatures.

Some broad peaks were observed at around 4–8° in the X-ray diffraction patterns of **P1** at ambient temperature (Fig. 5(a)). The intensity of this peak became weak at 120 °C (Fig. 5(b)) and this peak was not observed at 180 °C, indicating that **P1** possesses the crystallinity at ambient temperature and at 120 °C. The diffraction peaks at around 4–8° in the X-ray diffraction pattern of **P1** correspond to the *d*-spacing of ca. 2.2–1.1 nm. Thus, the endothermic peak observed on a first heating scan in the DSC thermogram of **P1** was confirmed to be based on melting. In addition, broad peaks were also observed at around 15° and 21° in the X-ray diffraction patterns of **P1** at all temperatures. The *d*-spacing of the peaks observed at around 15° and 21° was calculated to be ca. 0.59 nm and 0.42 nm, respectively, which presumably means the distance of the main chains. It would be because the mobility of the main chain is inhibited by the bulkiness of the main chains that the peaks based on the distance of the main chains were observed. As for the peaks observed at around 15° and 21°, similar results for amorphous polysilarylenesiloxane derivatives were reported by Ito et al. [15]; therefore, the present **P1** is in an amorphous state above melting temperature.

Fig. 6 depicts the TG curve of **P1** obtained by Run 6 in Table 1 as a typical example.

The temperature at 5% weight loss (T_{d5}) of **P1** under nitrogen atmosphere was determined to be 523 °C from TG curve of **P1**, which was equal to that of 1,4-PTMPS. In other words, the thermostability of **P1** is comparable to that of 1,4-PTMPS. It can be seen from Table 1, there was little difference in the T_{d5}s of the present series of **P1** even though the somewhat low T_{d5}s were observed in the case of **P1** obtained by Runs 1 and 4 presumably owing to the relatively low average molecular weight.

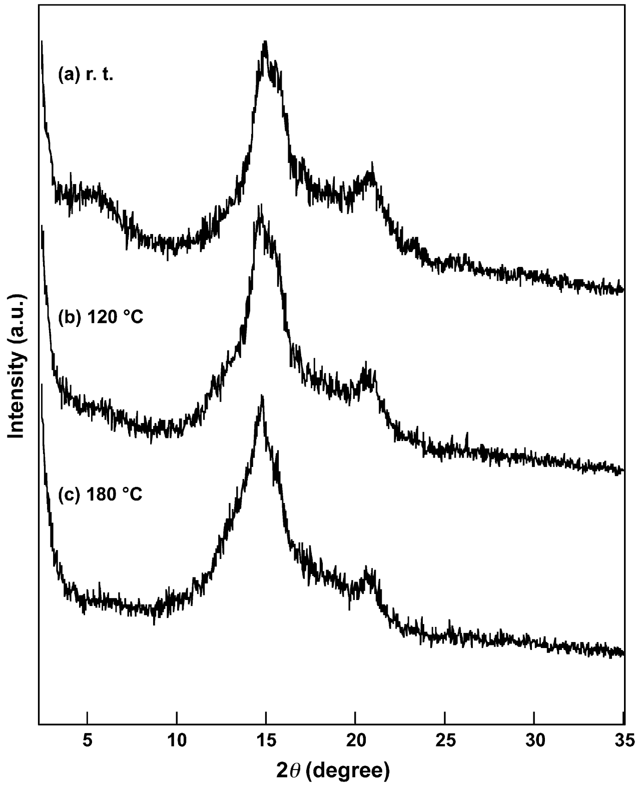


Fig. 5. X-ray diffraction patterns of **P1** obtained by Run 3 in Table 1 at various temperatures (a) ambient temperature, (b) 120 °C, and (c) 180 °C.

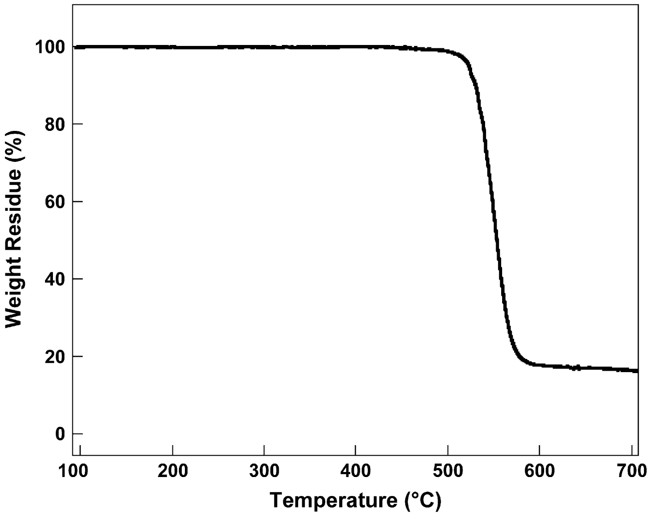


Fig. 6. TG curve of **P1** obtained by Run 6 in Table 1 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

On the other hand, Fig. 7 depicts a DSC trace of **M1** on a first heating scan under nitrogen atmosphere. The endothermic peak based on melting was observed at 166 °C, and the broad exothermic peak was also observed at around 200–240 °C.

The latter exothermic peak was expected to be based on the polycondensation of **M1**. Therefore, we carried out the bulk polycondensation of **M1** without catalysts using a glass tube oven at 225 °C under reduced pressure. Consequently, it was found that **M1** underwent polycondensation to afford **P1** as deduced from the ^{1}H and ^{13}C NMR spectroscopies and SEC measurement of the product, i.e., the ^{1}H and ^{13}C NMR spectra of the product obtained in bulk polycondensation of **M1** were consistent with those of the product obtained in solution polycondensation of **M1**. The M_n and M_w/M_n

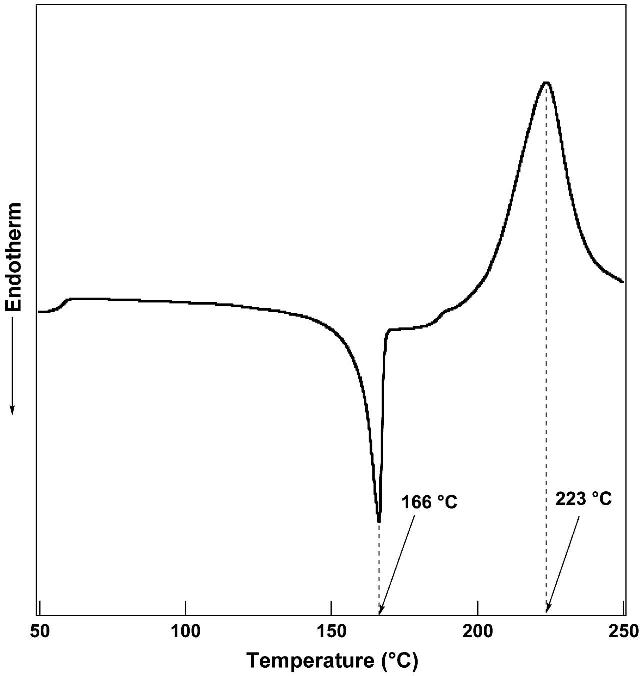


Fig. 7. DSC trace of **M1** on a first heating scan at a heating rate of 5 °C min^{-1} under N_2 flow rate of 10 mL min^{-1}.

were 17 500 and 1.29, respectively, determined by SEC. It was concluded that **P1** can be obtained via both bulk and solution polycondensation of **M1** as described in Scheme 1. The obtained **P1** is a new polysiloxane derivative with the high T_g and good thermostability.

4. Conclusions

Synthesis of a novel adamantane-based polysiloxane (**P1**) was achieved via bulk polycondensation without catalysts as well as solution polycondensation of novel disilanol monomer, i.e., 1,3-bis[4-(dimethylhydroxysilyl)phenyl]adamantane (**M1**). **P1** exhibited the good solubility in common organic solvents, such as tetrahydrofuran (THF), chloroform, dichloromethane, and toluene. The T_g of **P1** was much higher than that of 1,4-PTMPS (−20 °C), indicating that the introduction of the bulky and rigid adamantyl moiety in the main chain restricted the mobility of the main chain. The T_m and T_{d5} of **P1** were comparable to those of 1,4-PTMPS, indicating that the obtained **P1** is a new polysiloxane derivative with the high T_g as well as good thermostability.

Acknowledgments

This work was partly supported by the Japan Science and Technology Agency through Research for Promoting Technological Seeds (No. 03-066). The authors would like to appreciate Mitsubishi Gas Chemical Co., Inc. for gift of 1,3-dibromoadamantane. The authors would like to appreciate Dr. Chuichi Watanabe and Ms. Shihori Takeda, Frontier Laboratories Ltd., for the contribution in GC/MS analyses; and Ms. Satoko Tokiwa as well as Ms. Nami Sugashima, Nihon University College of Engineering Worldwide Research Center for Advanced Engineering and Technology (NEWCAT), for performing NMR measurements.

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