Synthesis of fully aromatic polysilarylenesiloxanes and their thermal properties

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The fully aromatic polysilarylenesiloxanes were synthesized via the solution polymerization and the melt-condensation polymerization from the corresponding disilanol monomers with diphenylsilyl group. And the thermal properties of these polymers were investigated by using DSC and TGA. The polymers synthesized via the solution polymerization were insoluble powders, and showed no glass transition and no weight loss in air below 500 °C. On the other hand, the products obtained by the melt-condensation polymerization partially dissolved in solvent, and showed a glass transition approximately at 80 °C and weight loss at about 300 °C. This low thermal stability compared with the polymers synthesized via the solution polymerization is promising method to provide the new type of high temperature coatings consisted of the fully aromatic polysilarylenesiloxanes.

Key words: polysilarylenesiloxane, thermal stability, solution polymerization, melt-condensation polymerization, glass transition

1. INTRODUCTION

An organosiloxane polymer is practically important material as an elastomer because of having useful characteristics of high thermal stability and good insulation property. Especially, polysilarylenesiloxanes [1, 2] and silarylenesiloxane/dimethylsiloxane copolymers [2-10] have been known as high temperature elastomers whose thermal degradation temperatures are greatly higher than that of polydimethylsiloxanes (PDMS). Poly(tetramethyl-p-silphenylene)siloxane (TMPS) of a typical polysilarylenesiloxane shows a glass transition temperature of -20 °C and a melting point of 135 °C, as reported by Okui et al. [2]. And the thermal degradation temperature (T_d) is 370-390 °C, according to Ikeda et al. [3] and Funt et al. [4]. On the other hand, we had reported the thermal properties of TMPS/PDMS copolymers [5]. These have two major transitions at around -120 °C corresponding to the $T_{\rm g}$ of PDMS moiety and at -10 °C related to the amorphous TMPS moiety. And their T_d was estimated at 300 °C, lower than that of TMPS homopolymer [3]. For these TMPS-containing polymers, the common characteristics of the high T_d and the low T_g , which result from their flexible dimethylsiloxane units in main chain, are desirable properties as a elastomer, so that these polymers are waxy or gum like materials at high temperature. Therefore, polysilarylenesiloxanes and their copolymers have been used as nothing but elastomers, although their interesting and unique properties have been expected from these kinds of organosiloxane materials. If obtaining new polysilarylenesiloxane with a high $T_{\rm g}$, it is possible that the polysilarylenesiloxane is applied to various fields, such as a high-temperature coating and a functionalized self-standing membrane. But such polysilarylenesiloxane showing a high T_g has never been reported.

We tried to introduce a diphenylsiloxane unit instead of a dimethylsiloxane unit in order to obtain a polysilarylenesiloxane showing a high T_g . Polydimethylsiloxane and polydiphenylsiloxane show -123 °C of a T_g and 265 °C of a melting point, respectively, according to the literatures [2, 11]. Therefore, the superior thermal mechanical properties will be expected of the poly(tetraphenyl-p-silarylene)siloxane compared with the corresponding poly(tetramethyl-p-silarylene)siloxane.

In this paper, two kinds of poly(tetraphenyl-p-silarylene)siloxanes introducing p-phenylene and p,p'-biphenylene moieties as the p-arylene group were synthesized via the solution polymerization (Method I) and the melt-condensation polymerization (Method II) from the arylenedisilanol monomers. The corresponding poly(tetramethyl-p-silarylene)siloxanes were also prepared. Then, the thermal properties of these polymers will be discussed by using differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA).

2. EXPERIMENTAL

2.1. Preparations of monomers

The three monomers 2a, 2b and 2c were synthesized according to the literature [1] (Scheme 1). 1,4-Bis(di-



methylhydroxysilyl)benzene (2d) was purchased from Chisso Corp., and purified by recrystallization from a mixture of tetrahydrofuran (THF) and *n*-hexane before use (see scheme 2).

1,4-Bis(diphenylsilyl)benzene (1a)

A solution of 1,4-dibromobenzene (2.1 g, 9.0 mmol) in 10 ml of THF was added dropwise to the Grignard's reagent solution prepared from magnesium shavings (0.88 g, 37 mmol) and diphenvlchlorosilane (5.3 ml, 27 mmol) in 10 ml of THF under an argon atmosphere. After refluxed for 17 h, 1 ml of water was added to the mixture. The crude products were extracted with diethyl ether and washed with water. The organic layer was dried over anhydrous Na2SO4. After the solvents were evaporated, the residue was purified by column chromatography on silica gel with *n*-hexane as an eluent to afford 1.9 g of 1a as a colorless powder. Yield: 48 %. IR, v (cm⁻¹, KBr disk): 3041 (w), 3004 (w), 2110 (m, Si-H st), 1587 (w), 1483 (w), 1424 (s), 1133 (w), 1115 (m), 827 (m), 798 (s), 742 (s), 728 (s), 536 (s), 503 (s). ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 5.46 (2H, s), 7.38 (8H, m), 7.39 (4H, m), 7.57 (8H, m), 7.58 (4H, s). 1.4-Bis(diphenylhydroxysilyl)benzene (2a)

1a (1.5 g, 3.4 mmol) in THF/ethanol (30 ml/50ml) was added dropwise to 0.7 g of metal sodium soaked in 42 ml of anhydrous ethanol. After ceasing to generate hydrogen gas, NaOH (0.70 g) solution in methanol /water (7.0 ml/0.70 ml) was poured into the mixture, stirring for 30 min. 7.0 ml of NaOH (0.70 g) agua were added to the mixture, stirring for 30 min. KH₂PO₄ (11 g) aqua with excess ice was added to the mixture. Then, the precipitate was filtered, and washed with water. The mixture was recrystallized from a chloroform solution to afford 1.3 g of 2a as a colorless powder. Yield: 80%. Melting point (T_m): 227 °C. IR, v (cm⁻¹, KBr disk): 3208 (s, SiO-H st), 3044 (m), 3007 (m), 1585 (m), 1481 (m), 1425 (s), 1373 (m), 1138 (s), 1119, (s) 862 (s), 836 (s), 758 (m), 739 (m), 713 (s), 698 (s), 545 (s). ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 7.39 (4H, m), 7.41 (8H, m), 7.63 (8H, m), 7.65 (4H, s).

4,4'-Bis(diphenylsilyl)biphenyl (1b) was prepared from 4,4'-dibromobiphenyl in the same manners as 1a. Yield: 52%. IR, v (cm⁻¹, KBr disk): 3070 (m), 3003 (m), 2125 (s, Si-H), 1594 (w), 1428 (s), 1115 (s), 812 (s), 787 (s), 735 (m), 694 (s). ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 5.55 (2H, s), 7.43 (8H, m), 7.44 (4H, m), 7.64 (4H, m), 7.65 (8H, m), 7.70 (4H, m).



4,4'-Bis(diphenylhydroxysilyl)biphenyl (2h)was prepared in the same manners as 2a. Yield: 36%. $T_{\rm m}$: 198 °C. IR, v (cm⁻¹, KBr disk): 3292 (s, SiO-H st), 3062 (w), 3018 (w), 1694 (w), 1594 (w), 1424 (m), 1119 (s), 1001 (s), 857 (m), 831 (m), 805 (m), 706 (s), 507 (s). ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 7.41 (8H, m), 7.42 (4H, m), 7.62 (4H, m), 7.66 (8H, m), 7.71 (4H, m). 4,4'-Bis(dimethylsilyl)biphenyl (1c) was prepared from 4.4'-dibromobiphenyl and dimethylchlorosilane in the same manners as 1a. Yield: 61%. IR, v (cm⁻¹, KBr disk): 2962 (w), 2119 (m, Si-H), 1595 (w), 1249 (m), 1117 (m), 876 (s), 836 (m), 808 (m), 764 (m), 699 (m). ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 0.38 (12H, d, J=4.0Hz), 4.46 (2H, m), 7.60 (4H, d, J=8.4Hz), 7.63 (4H, d, J=8.4Hz). 4,4'-Bis(dimethylhydroxysilyl)biphenyl (2c)was prepared in the same manners as 2a. Yield: 27%. Tm: 178 °C. IR, v (cm⁻¹, KBr disk): 3262 (s, SiO-H st), 3062 (m), 3016 (m), 2961 (m), 1593 (w), 1383 (w), 1254 (s), 1120 (s), 1056 (w, br), 1003 (m), 875 (s), 826 (s), 783 (s), 699 (s), 645 (m), 512 (m). ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 0.45 (12H, d, J=4.0Hz), 7.61 (4H, d, J=8.0Hz), 7.67 (4H, d, J=8.0Hz).

2.2. Polymerization

The polymers were obtained via the solution polymerization or the melt-condensation polymerization according to Scheme 2, except for **3b'** which was obtained by heating **3b** at 180 °C for 1h in air flow. *Solution Polymerization* [5] (Method I)

Each monomer (1.0 g) of 2d and three kinds of the synthesized monomers (2a-c) was refluxed for 24h-48h in benzene and toluene (5.0 ml), respectively, in the presence of a few drops tetramethylguanidine diethylhexanoate as a catalyst using an azeotropic trap to remove water. The mixture was poured into an excess amount of methanol to purify the obtained polymer. 3a and 3b were insoluble powders, IR spectra were shown in Figs. 1 and 2. 3c: ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 0.38 (12H, s), 7.59 (4H, d, J=8.4Hz), 7.63 (4H, d, J=8.4Hz). IR, v (cm⁻¹, KBr disk): 3067 (w), 3016 (w), 2956 (w), 1597 (w), 1256 (m), 1120 (s), 1056 (s), 1002 (m), 829 (s), 786 (s), 701 (m), 511 (w). 3d: ¹H-NMR, δ (ppm, CDCl₃, 400 MHz): 0.33 (12H, m), 7.56 (4H, s). IR, v (cm⁻¹, KBr disk): 3041 (m), 2952 (m), 1406 (m), 1252 (s), 1137 (s), 1067 (w), 1016 (m), 828 (s), 783 (s), 503 (m), 466 (m).

Melt-condensation Polymerization (Method II)

Each monomer of **2a** and **2b** (50 mg) mounted on a glass plate was heated at 290 °C for 10 min (**2a**) or 270 °C for 20 min (**2b**) above the each melting point on a heater with thermo-controller. The powder of the monomer changed to a transparent glassy solid (**4a**, **4b**). <u>2.3. Characterizations</u>

¹H-NMR spectra were measured on BurkerBiospin AVANCE DRX 400 spectrometer (400MHz). IR spectra were measured with PerkinElmer PARAGON FT-IR. Gel permeation chromatography (GPC) was carried out to determine the number-average (\overline{M} n) and weight-average (\overline{M} w) with Tosoh HLC-802A instrument by using THF as an eluent. Standard polystyrenes were used to calibrate the molecular weights. X-ray diffraction (XRD) patterns by the powder method were collected on a RIGAKU RINT 2000 diffractometer using CuK α radiation.

2.4. Thermal analysis

TGA was performed by using a Shimadzu DTG 60A

Table 1 Conditions and results of polymerizations

Polymer	Temp °C	Time h	Yield %	$\overline{Mn}/10^3$	$\overline{M}w/\overline{M}n$
3a	120	48	10	- c)	_c)
3b	120	24	55 ^{b)}	_ c)	_c)
3c	120	24	68	24	1.6
3d	80	24	80 ^{b)}	45	1.5
3b ' ^{a)}	180	1.0		-	
4a	290	0.17	-	2.4d)	10
4b	270	0.34	-	1.1 ^{d)}	1.2

a) This polymer was obtained by heating 3b at 180° C for 1h in air flow. b) Filtered precipitation after polymerization. c) Insoluble in common solvents. d) Soluble parts in THF.

at a heating rate of 10 °C/min with an air flow rate of 50 ml/min in order to investigate the thermal degradation behavior. DSC was conducted by using a Shimadzu DSC-60 at a heating rate of 10°C/min with nitrogen flow rate of 50 ml/min in order to determine a T_g .

3. Results and Discussion

3.1 Polymerization

The conditions and the results for the polymerizations of the arylenedisilanol monomers are listed in Table 1. **3a** and **3b** were precipitated in the polymerization solution, and obtained as insoluble powders against common solvents such as methanol, acetone, N,N-dimethylformamide, chloroform, dichloromethane, n-hexane, and THF. On the other hand, **4a** and **4b** were obtained as thin fragile films on the glass plates. And these films were partially dissolved in a solvent such as THF, chloroform and dichloromethane. In the both cases of the solution (Method I) and melt-condensation (Method II) polymerizations for **2a** and **2b**, the changes of IR spectra are shown in Figs. 1 and 2. The absorption



Fig. 2 IR spectra of 2b, 3b, 3b', and 4b.

peaks at 3200 cm⁻¹ of the O-H stretching vibration arising from silanol groups in the monomers (2a, 2b)disappeared for 3a, 3b, 4a and 4b, and anew the distinctive absorption of the Si-O-Si bond near at 1060 cm⁻¹ were observed for them. From these results, it was found that the condensation reactions occurred in the both cases.

3.2. Thermal properties of the polymers obtained via the solution polymerization (Method I)

The DSC curves of **3a-d** are shown in Fig. 3. **3a** and **3b** did not have any transitions, and held solid states below 400 °C. Additionally these were amorphous polymers since broad hallows around at $2\theta = 22$ ° were only observed in the powder XRD patterns. **3c** and **3d** indicated a glass transition at 67 °C and a melting point at 136 °C, respectively. Then, it was revealed that the fully aromatic polysilarylenesiloxane, such as **3a** and **3b**, was one of the most thermally stable polymer-solids compared with the ever known polysilarylenesiloxanes.

Fig. 4 gives the thermogravimetry (TG) curves of 3a, 3b, and 3b'. 3a showed a good thermal chemical stability in air, but rapidly decomposed above 500 °C. 3b showed a slight weight loss at about 160 °C. 3b', which was obtained to treat 3b at 180 °C for 1 h, was thermally stable in the similar to 3a, so that the weight loss near at 160 °C for 3b would result from the dehydration between the chain-ends. The IR spectrum of 3b' in Fig. 2 also supported the dehydration because the absorption band arising from Si-O-Si vibration at 1060 cm⁻¹ increased compared with that of 3b.

Fig. 5 shows the TG curves of 3c and 3d. 3d exhibited obviously three steps of weight loss processes. Dvornic *et al.* [8] had described thus degradation



Fig. 3 DSC curves of **3a-3d** at a heating rate of 10 °C /min under a nitrogen flow (second heating).



Fig. 4 TG curves of **3a**, **3b**, and **3b'** at a heating rate of 10°C/min under an air flow.



Fig. 5 TG curves of **3c** and **3d** at a heating rate of 10°C /min under an air flow.

behavior as the followings; the first step of the thermal degradation at 400 °C was caused by the splitting off of the methyl groups with formation of crosslinks by oxygen bridges. The second step at 500~600 °C was done by formation of volatile organosilicone products due to the degradation. And the third step at 700 °C was done by thermo-oxidative degradation of the remaining organic content. In this work, it was found that the introduction of p, p'-biphenylene unit into the backbone suppressed this first step degradation, as shown in the TG curve of 3c in Fig. 5. Furthermore, because 3a and 3b in Fig. 4 exhibited no weight loss near at 400 °C, it was revealed that the transformation from dimethylsiloxane unit to diphenylsiloxane unit contributed to an increase of not only a T_g but also a thermal stability. 3.3. The thermal properties of polymers obtained via the

melt-condensation polymerization (Method II)

Fig. 6 gives the DSC curves of 4a and 4b. The glass transitions for the both samples were observed around at 80 °C although they were not clear. For each sample, the softening of the glassy polymer was observed on a hot plate over 80 °C. Considering the low T_g and the solubility of 4a and 4b, these samples obtained from Method II probably contained the low molar mass components such as monomer and oligomer. The thermal degradations of 4a and 4b began from 300 °C, and were much lower than that of 3a and 3b at 500 °C (Fig. 7). We will investigate whether the low thermal stability of polymers obtained from Method II result from chain-ends of silanol group or an another origin. However, 4a and 4b seem to be thermally stable in the similar to 3a and 3b, except for the initial weight loss.

4. Conclusions

Two kinds of the fully aromatic polysilarylenesiloxanes were synthesized via the solution polymerization (Method I) and the melt-condensation polymerization (Method II) from the arylenedisilanol monomers.

The fully aromatic polysilarylenesiloxanes obtained by Method I were insoluble powders, and did not have any transitions and held glassy states below 400 °C. Furthermore, these polymers showed good thermal chemical stability in air since no weight loss was observed under 500 °C. According to the literatures [8, 10], polysilarylenesiloxane copolymers had shown the high thermal stability (over 500 °C), but T_g or T_m of them was much lower than 500 °C. By contrast, our fully aromatic polysilarylenesiloxanes exhibited not only the high thermal stability but also high T_g in this work. Additionally we found that the fully aromatic



10°C/min under a nitrogen flow (second heating).



10°C/min under an air flow.

polysilarylenesiloxanes could be obtained as films via Method II. The low $T_{\rm g}$ and the low thermal stability of them would be related with chain-ends of silanol group resulted from the low molar mass contaminations. Finally, the improvement of Method II would bring an excellent thermal resistance film of the fully aromatic polysilarylenesiloxane from easyly handling monomer.

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