Synthesis and Heat Resistance of Arylenedioxy-organosilanylene Polymers with Adamantane Units

Takayuki Maehara[a, b], Hiroshi Hashimoto[a], and Joji Ohshita[a]

[a] Department of Applied Chemistry, Graduate School of Engineering, Higashi-Hiroshima 739-8527, Japan
[b] Tsukuba Research Lab., Tokuyama Corporation, Tsukuba 300-4247, Japan

Reprint requests to Prof. J. Ohshita. Fax: +81-82-424-7743. E-mail: jo@hiroshima-u.ac.jp

Z. Naturforsch. **2009**, *64b,* 1567 – 1570; received June 27, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

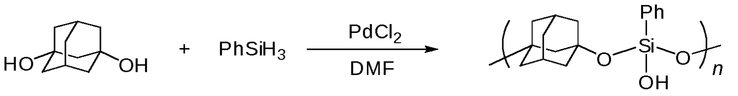
Arylenedioxy-organosilanylene polymers with adamantane units in the backbone were prepared by Rh-catalyzed dehydrocoupling of bis(4-hydroxyphenyl)adamantanes with organohydrosilanes, and their heat resistance was evaluated by thermogravimetric analysis in nitrogen. Among these polymers, the highest Td_{10} (10 % weight loss temperature) of 547 °C was achieved for polymer **2a** prepared from 1,3-bis(4-hydroxyphenyl)adamantane and phenylsilane. Polymer **2a** exhibited good heat resistance even in air with Td_{10} = 387 °C, and standing of the polymer at 150 °C for 8 h resulted in no evident weight loss.

Key words: Adamantane, Organosilicon Polymer, Heat Resistance

Introduction

Heat-resistant polymers are of high importance because of their utility as, for example, insulating films and encapsulation materials for electronic devices. In this context, polymers with adamantane units in the backbone have been synthesized, expecting that the cage structure provides high thermal stability to the polymers [1 – 7]. Recent examples include poly(adamantane-1,3-diyl)s prepared by ring-opening polymerization of dehydroadamantane, whose thermogravimetric analysis (TGA) in nitrogen showed high heat resistance with a Td_{10} (10 % weight loss temperature) ranging from 421 to 486 °C [1]. However, the presence of rigid adamantane units in the polymer backbone causes solubitity problems. One possible solution is the introduction of long alkyl side chains, but this may decrease the thermal stability of the polymers.

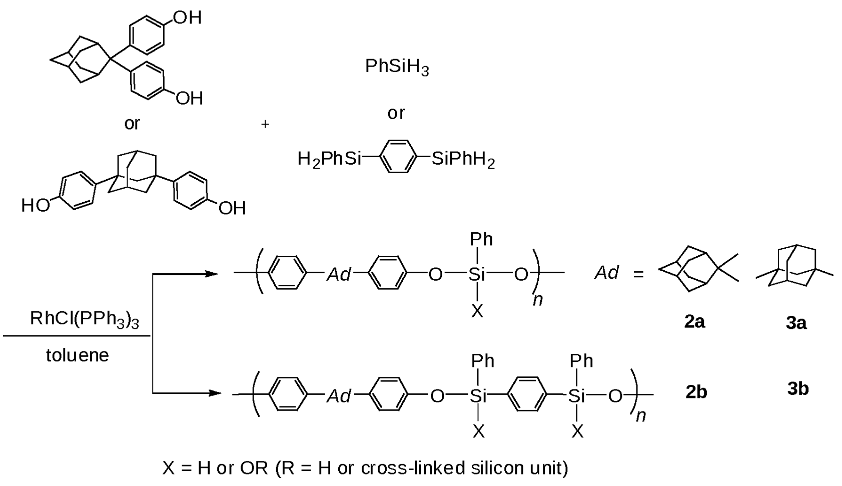
To obtain novel adamantane-based heat-resistant polymers, we prepared a polymer composed of repeating units of adamantanediyl-siloxane by Pd-catalyzed dehydrocoupling of 1,3-adamantanediol and $PhSiH_3$, as shown in Eq. 1 [8], in which thermally stable and flexible Si–O bonds are anticipated to improve the polymer solubility without suppressing the thermal stability. As expected, the polymer showed high solubility in organic solvents and high heat resistance with Td_{10} = 512 °C in nitrogen, which was higher than those of poly(adamantane-1,3-diyl)s [1]. However, the reaction gave only a low yield of the polymer (16 %), together with a large amonut of oligomers (33 %). This is probably due to the low reactivity of adamantanediol. Consequently, we studied bis(hydroxyphenyl)adamantanes as new monomers. The introduction of phenylene units would reduce the steric hindrance of the diol reactive center and was also expected to lead to an even higher heat resistance of the resulting polymers.



(1)

1a

Mn = 19000 (Mw/Mn = 1.7)
Td_5 = 420, Td_{10} = 512 °C



Scheme 1.

Results and Discussion

Polymer synthesis

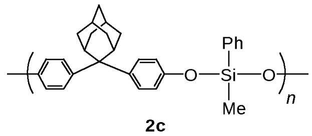
Dehydrocoupling reactions of 2,2- and 1,3-bis(4-hydroxyphenyl)adamantane with hydrosilanes were performed in the presence of a catalytic amount of $RhCl(PPh_3)_3$ in toluene at 150 °C (Scheme 1). Reprecipitation of the resulting organic products from toluene-hexane gave the corresponding polymers in good yield, as summarized in Table 1, except for **3a**. For **3a**, a large amount of hexane-soluble oligomers were formed, decreasing the polymer yield.

The GPC (gel permeation chromatography) analysis of the polymers revealed monomodal profiles with Mn = 3100–7800, except for polymer **2a**, which exhibited a bimodal molecular weight distribution with Mn = 5200 and Mn $> 1 \times 10^6$ in an area ratio of 86 : 14, indicating the existence of cross-linked units. Carrying out the reaction at lower temperature resulted in a decrease of the molecular weight. For example, polymer **2a** that was obtained at 100 °C in 62 % yield, showed a molecular weight Mn = 3100 (Mw/Mn = 1.2). Using $PdCl_2$ as the catalyst also decreased the polymer molecular weight to Mn = 2500 (Mw/Mn = 1.2) for **2a** (58 % yield).

Table 1. Polymer synthesis.

Polymer	Yield (%)	Mn (Mw/Mn)[a]	X = H/OR[b]	Td$_5$ (°C)[c]	Td$_{10}$ (°C)[c]
2a	56	5200 (1.8)[d]	6/4	504 357[e]	547 387[e]
2b	59	6300 (2.0)	9/1	476	514
2c	7	4800 (1.6)	–	347	445
3a	10	3100 (1.2)	8/2	256	310
3b	69	7800 (2.5)	9/1	414	516

[a] Determined by GPC, relative to polystyrene standards; [b] R = H or Si, based on integration ratios of HC(sp^2)/HSi in the ^{1}H NMR spectra; [c] determined by TGA at a rate of 10 °C min^{-1} in nitrogen; [d] GPC revealed a bimodal profile, together with a broad peak at high molecular weight (Mn $> 1 \times 10^6$); [e] measured in air.



2c

Fig. 1. Molecular formula of polymer **2c**.

These polymers were soluble in common organic solvents, such as toluene, chloroform, diethyl ether, and THF, but insoluble in hexane. They were obtained as pale-yellow solids and did not melt up to 300 °C. The ^{1}H NMR spectra of the polymers showed broad signals, ascribed to adamantane, Si–H, and benzene ring protons. However, the integration ratios disagreed with the ideal structures (X = H in Scheme 1). The integrals of the Si–H signals were lower than those calculated for the ideal structures, indicating that some of the Si–H bonds were hydrolyzed during the work-up process, producing Si–OH units. For polymer **2a**, it is likely that the Si–OH groups were further transformed into siloxane-cross-linked units to some extent. This is in contrast to polymer **1a** whose Si–H bonds were completely converted into Si–OH units during the work-up. Neither Si–H nor siloxane units were formed in polymer **1a**.

A similar polymerization of 2,2-bis(4-hydroxyphenyl)adamantane with methylphenylsilane gave polymer **2c** in 7 % yield (Fig. 1). GPC analysis of **2c** showed a monomodal profile, in contrast to other polymers **2a**, again indicating that the higher molecular weight fraction of **2a** was a result of hy-

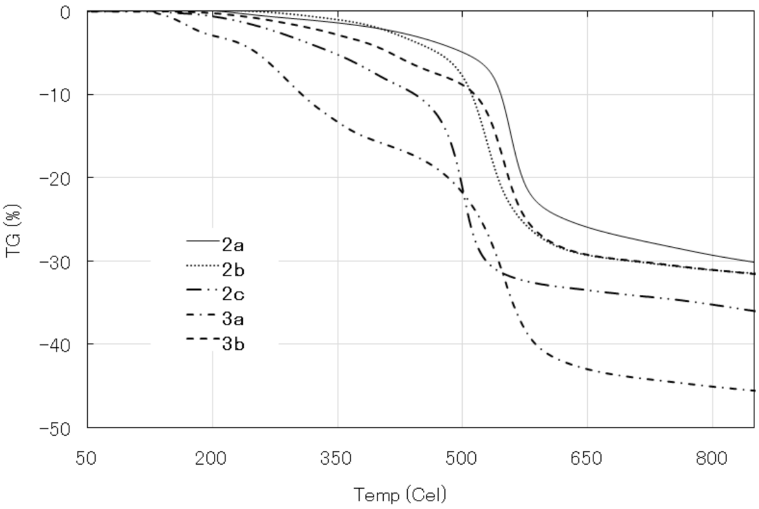


Fig. 2. TGA profiles for polymers **2a** – **c** and **3a**, **b** in nitrogen at a rate of 10 °C min^{-1}.

drolysis of Si–H bonds, as described above. We also examined 2,2- and 1,3-bis(hydroxymethyl)adamantane as the monomers under the same conditions. However, they always gave only insoluble products.

Heat resistance of the polymers

TGA profiles of the present polymers in nitrogen are presented in Fig. 2, and the 5 % and 10 % weight loss temperatures noted in the analysis are listed in Table 1. Of the present polymers, **2a** showed the highest heat resistance with Td_5 = 504 °C and Td_{10} = 547 °C, much higher than those reported for polymer **1a**. This seems to be due to the existence of the cross-linked siloxane units and also the lower content of Si–OH units in polymer **2a** relative to **1a**. The Si–OH units would be converted to siloxane units, thereby liberating water to increase the weight loss during the TGA. In addition, reactive Si–H units seem to be also responsible for the high heat-resistant properties of polymer **2a**. The silyl radical formation by homolytic cleavage of the Si–H bonds, followed by addition of the resulting silyl radicals to the benzene rings would produce cross-linked units in the polymeric substance to improve the heat resistance [9]. In fact, the IR spectrum of the polymer showed a decreased intensity of the Si–H stretching band after heating the polymer to 280 °C. The Td_5 value of **2a** was higher than that reported for a similar arylenedioxy-silanylene polymer without adamantane units shown in Fig. 3 (Td_5 = 456 °C) by about 50 °C [10]. Polymer **2a** showed high heat resistance even in air with Td_5 = 357 °C and Td_{10} = 387 °C. Heating of the polymer to 150 °C in air for 8 h resulted in no evident weight loss (*ca.* 0.7 %).

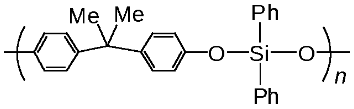


Fig. 3. Arylenedioxy-silanylene polymer without adamantane units.

The slightly inferior heat resistance of **2b** to that of **2a** is ascribed to the higher content of admantane units in the polymer backbone for **2a**. It is also interesting that polymers **2a** and **2b** with 2,2-adamantanediyl units showed slightly higher heat resistance than the 1,3-adamantanediyl analogs. Polymer **2a** probably has a more tightly screwed helical and folded structure than **3a**, which reduces the intramolecular distances between the reactive centers, thereby facilitating cross-linking reactions. A similar enhancement of the heat resistance for a helical polymer, compared with the linear analog, was reported for poly(phenylenesilylene)s [11]. The lower heat resistance of **2c** compared to **2a** is probably due to the absence of Si–H bonds and/or cross-linked siloxane units.

In conclusion, we prepared novel arylenedioxy-organosilanylene polymers bearing adamantane units in the backbone by dehydrocoupling of bis(hydroxyphenyl)adamantane with hydrosilanes in good yield. They showed high heat-resistant properties and good solubility in organic solvents. We also found that the existence of Si–H groups and siloxane cross-linking units are important to improve the heat resistance. Studies on the controlled introduction of siloxane cross-linked units in these polymers to tune the heat resistance and solubility are now in progress.

Experimental Section

All reactions were carried out in dry nitrogen. Toluene used as the reaction solvent was distilled from sodium and stored over activated molecular sieves at ambient temperature prior to use. NMR and IR spectra were recorded on a JEOL model LA-400 spectrometer and a Shimazu model FTIR-8700 instrument, respectively. TGA was carried out on a SIC model TG/DTA-6200 at a rate of 10 °C min^{-1}. Bis(4-hydroxyphenyl)adamantanes were prepraed as reported in the literature [6, 12].

Polymer synthesis

In an autoclave were placed 0.321 g (1.00 mmol) of 2,2-bis(4-hydroxy phenyl)adamantane, 0.108 g (1.00 mmol) of phenylsilane, 27.8 mg (3.0 mol-%) of $RhCl(PPh_3)_3$, and 15 mL of toluene, and the mixture was heated at 150 °C for 12 h. Then 0.30 g of triazinetrithiol (Sankyo Kasei Co. Ltd.) was added, and the mixture was stirred for 30 min at r. t. Then it was filtered to remove the catalyst. After removal of the solvent, the residue was reprecipitated from toluene-hexane to give 0.24 g of **2a** as a pale-yellow solid. – ^{1}H NMR (395 MHz, $CDCl_3$): δ = 1.56 – 1.94 (br m, adamantane H), 5.31 (s, SiH), 6.75 – 7.66 (br m, benzene ring H). – IR (KBr): ν = 3340 (br OH), 2180 (SiH), 1128, 1074 (SiO) cm^{-1}.

The other polymers were obtained as pale-yellow solids in a fashion similar to that described above.

2b: ^{1}H NMR (395 MHz, $CDCl_3$): δ = 1.55 – 1.95 (br m, adamantane H), 5.65 (s, SiH), 6.76 – 7.63 (br m, benzene ring H). – IR (KBr): ν = 2133 (SiH), 1137, 1125 (SiO) cm^{-1}.

2c: ^{1}H NMR (395 MHz, $CDCl_3$): δ = 0.18 (br s, MeSi), 1.56 – 1.97 (br m, adamantane H), 6.73 – 7.67 (br m, benzene ring H). – IR (KBr): ν = 1122, 1070 (SiO) cm^{-1}.

3a: ^{1}H NMR (395 MHz, $CDCl_3$): δ = 1.20 – 2.35 (br m, adamantane H), 5.74 (s, SiH), 6.77 – 7.74 (br m, benzene ring H). – IR (KBr): ν = 3381 (OH), 2246 (SiH), 1261, 1093 (SiO) cm^{-1}.

3b: ^{1}H NMR (395 MHz, $CDCl_3$): δ = 1.25 – 2.23 (br m, adamantane H), 5.72 (s, SiH), 6.87 – 7.67 (br m, benzene ring H). – IR (KBr): ν = 2133 (SiH), 1138, 1120 (SiO) cm^{-1}.

Acknowledgement

We thank Sankyo Kasei Co. Ltd. for a gift of triazinetrithiol.

---

[1] T. Ishizone, S. Matsuoka, S. Sakai, W. Harada, H. Tajima, *Macromolecules* **2004**, *37*, 7069 – 7071.

[2] S. Matsuoka, N. Ogiwara, T. Ishizone, *J. Am. Chem. Soc.* **2006**, *128*, 8708 – 8709.

[3] S. Matsuoka, N. Ogiwara, Y. Uehara, T. Ishizone, *Macromol. Symp.* **2006**, *240*, 206 – 212.

[4] M. Mugisawa, K. Ohnishi, H. Sawada, *Colloid Polym. Sci.* **2007**, *285*, 737 – 744.

[5] A. S. Mathews, I. Kim, C.-S. Ha, *J. Appl. Polym. Sci.* **2006**, *102*, 3316 – 3326.

[6] X. Su, X. Jing, *J. Appl. Polym. Sci.* **2007**, *106*, 737 – 742.

[7] T. Maehara, J. Takenaka, K. Tanaka, M. Yamaguchi, H. Yamamoto, J. Ohshita, *J. Appl. Polym. Sci.* **2009**, *112*, 496 – 504.

[8] J. Ohshita, K. Hino, K. Inata, A. Kunai, T. Maehara, *Polymer* **2007**, *48*, 4301 – 4304.

[9] J. Ohshita, M. Ishii, Y. Ueno, A. Yamashita, M. Ishikawa, *Macromolecules* **1994**, *27*, 5583 – 5590.

[10] S. Tamai, C. Tanaka, T. Abe, T. Kuroki, J. Ishikawa, *High Performance Polymers* **2003**, *15*, 361–370.

[11] J. Ohshita, A. Shinpo, A. Kunai, *Macromolecules* **1999**, *38*, 5998 – 6002.

[12] B. M. Lerman, Z. Arefeva, F. Z. Galin, G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 720 – 722.