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

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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 $T_{d10}$ (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 $T_{d10} = 387$ °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(adaman tanadiyl-siloxane) prepared by Pd-catalyzed dehydrocoupling of 1,3-adamantanediol and PhSiH3, 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 $T_{d10} = 512$ °C in nitrogen, which was higher than those of poly(adamantane-1,3-diyl) [1]. However, the reaction gave only a low yield of the polymer (16 %), together with a large amount of oligomers (33 %). This is probably due to the low reactivity of adamantane diol. 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.

To obtain novel adamantane-based heat-resistant polymers, we prepared a polymer composed of repeating units of adamantanediyil-siloxane by Pd-catalyzed dehydrocoupling of 1,3-adamantanediol and PhSiH3, 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 $T_{d10} = 512$ °C in nitrogen, which was higher than those of poly(adamantane-1,3-diyl) [1]. However, the reaction gave only a low yield of the polymer (16 %), together with a large amount 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.
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). Precipitation 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 $M_n = 3100 – 7800$, except for polymer 2a, which exhibited a bimodal molecular weight distribution with $M_n = 5200$ and $M_n > 1 \times 10^6$ 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 $M_n = 3100$ (Mw/Mn = 1.2). Using PdCl$_2$ as the catalyst also decreased the polymer molecular weight to $M_n = 2500$ (Mw/Mn = 1.2) for 2a (58 % yield).

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-

![Scheme 1](image)
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 $T_{d5} = 504 \degree C$ and $T_{d10} = 547 \degree C$, 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 $T_{d5}$ value of 2a was higher than that reported for a similar arylenedioxy-silanylene polymer without adamantane units shown in Fig. 3 ($T_{d5} = 456 \degree C$) by about 50 °C [10]. Polymer 2a showed high heat resistance even in air with $T_{d5} = 357 \degree C$ and $T_{d10} = 387 \degree C$. Heating of the polymer to 150 °C in air for 8 h resulted in no evident weight loss (ca. 0.7%).

The slightly inferior heat resistance of 2b to that of 2a is ascribed to the higher content of adamantane units in the polymer backbone for 2a. It is also interesting that polymers 2a and 2b with 2,2-adamantane-diyi units showed slightly higher heat resistance than the 1,3-adamanatenediyi 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.

**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(PPh₃)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. – ¹H NMR (395 MHz, CDCl₃): 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: ¹H NMR (395 MHz, CDCl₃): 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: ¹H NMR (395 MHz, CDCl₃): 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: ¹H NMR (395 MHz, CDCl₃): 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: ¹H NMR (395 MHz, CDCl₃): 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.

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