

Hydrosilylation Polymerization for the Synthesis of Organosilicon Polymers Containing Adamantane Units

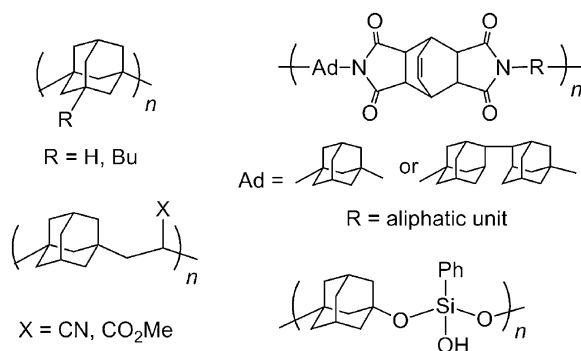
By Takayuki MAEHARA, Joji OHSHITA,* Ryo TAKETSUGU, Koichi HINO, and Atsutaka KUNAI

Hydrosilylation of diethynylbenzene with bis(dihexylsilylpropoxy)-, bis(diphenylsilylpropoxy)-, and bis(methylphenylsiloxy)-adamantane (**1a**, **1b**, and **1c**) afforded the corresponding hydrosilylated polymers. A similar reaction of bis(allyloxy)-adamantane with **1b** also gave a polymer with repeating units of Ad-propylene-silanylene-propylene (Ad = adamantanediyl). Heat-resistance of the resulting polymers was examined by the thermogravimetric analysis and the highest T_{d_5} and $T_{d_{10}}$ (temperatures of 5 and 10% weight loss) among the present polymers were noted to be 370 °C and 393 °C, respectively, for the polymer prepared from the reaction of diethynylbenzene with **1c**. Cross-linking hydrosilylation of a vinylsiloxane polymer with **1c** was also studied.

KEY WORDS: Adamantane / Organosilicon Polymer / Siloxane / Hydrosilylation / Heat-Resistance /

There has been interest in the synthesis of adamantane unit-containing polymers. The cage structure of adamantane allows their application as heat-resistance materials and polymers containing adamantane units as the side,¹ backbone,^{2–4} and end-capping groups⁵ have been reported so far. Adamantane-based epoxy resins were also reported regarding their use as encapsulants for light-emitting diode (LED).⁶ For the polymers with adamantane units in the backbone, poly(adamantanediyl)s were recently prepared by ring-opening polymerization of dehydroadamantane, whose thermogravimetric analysis (TGA) showed high heat-resistance properties with $T_{d_{10}}$ (10% weight loss temperatures) of 421 °C and 486 °C in nitrogen for R = H and Bu, respectively (Scheme 1).² Copolymers of dehydroadamantane and vinyl compounds (AN and MA),³ and adamantane unit-containing polyimides⁴ shown in Scheme 1 were also synthesized and their heat-resistance was reported.

To obtain novel adamantane-based polymers, we prepared polymers composed of repeating units of -Ad-O-Si-O- by dehydrocoupling of adamantanediol and PhSiH_3 (Scheme 1) and found that these polymers showed higher $T_{d_{10}}$ of 512 °C in nitrogen than poly(adamantanediyl)s.⁷ However, the polymers contained Si-OH bonds, arising from hydrolysis of the Si-H groups, which may cause disadvantages when applied to insulating films and encapsulation materials for electronic devices. For example, the Si-OH units may decrease the electric resistance of the polymer film and their condensation liberating water may cause the aging deterioration. In the hope of obtaining heat-resistant adamantane unit-containing organosilicon polymers without SiOH units, we studied hydrosilylation polymerization of diethynylbenzene and bis(allyloxy)-adamantane with bis(hydrosilyl)-substituted adamantane derivatives. An application of bis(methylphenylsiloxy)adamantane prepared by dehydrocoupling of adamantanediol and PhMeSiH_2 , as a cross-linking reagent was also examined.



Scheme 1. Heat-resistant polymers with adamantane units in the backbone.

EXPERIMENTAL

General Procedure

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 until use. Bis(allyloxy)adamantane^{6b} and bis(methylphenylsiloxy)-adamantane (**1c**)⁷ was prepared as reported in the literature.

Preparation of Bis(hydrosilylpropoxy)adamantanes

A solution of 0.82 g (3.3 mmol) of bis(allyloxy)adamantane, 1.38 g (6.91 mmol) of dihexylsilane, and 4.6 mg (0.0049 mmol) of $\text{RhCl}(\text{PPh}_3)_3$ in 10 mL of toluene was stirred at room temperature for 3 h. The resulting mixture was directly subjected to silica gel column chromatography eluting with toluene to give 1.77 g (82% yield) of bis(dihexylsilylpropoxy)-adamantane (**1a**) as colorless oil: IR 2097 cm^{-1} (Si-H); ^1H NMR (δ in CDCl_3) 0.51–0.59 (m, SiCH_2), 0.86 (t, $J = 7.0$ Hz, CH_3), 1.23–1.29 (m, $\text{SiCH}_2(\text{CH}_2)_4\text{CH}_3$), 1.47–1.74 (m, Ad and OCH_2CH_2), 2.28 (s, Ad OCCH_2CO), 3.34 (t, $J = 7.0$ Hz, OCH_2), 3.66 (quint, $J = 3.1$ Hz, SiH); ^{13}C NMR (δ

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

*To whom correspondence should be addressed (Tel: +81-82-424-7743, Fax: +81-82-424-5494, E-mail: jo@hiroshima-u.ac.jp).

in CDCl₃) 7.44 (O(CH₂)₂CH₂), 11.24, 14.12, 22.59, 24.59 (Hex), 25.84 (OCH₂CH₂), 31.56, 33.03 (Hex), 30.80, 35.49, 40.73, 45.52 (Ad CH and CH₂), 63.06 (OCH₂), 74.09 (Ad q-C); Anal. Calcd for C₄₀H₈₀O₂Si₂: C, 74.00; H, 12.42. Found: C, 73.70; H, 12.43.

Bis(diphenylsilylpropoxy)adamantane (**1b**) was obtained in 87% yield in a manner similar to that above, using diphenylsilane instead of dihexylsilane as the reactant: colorless oil; IR 2116 cm⁻¹ (Si-H); ¹H NMR (δ in CDCl₃) 1.09–1.15 (m, CH₂Si), 1.44–1.71 (m, Ad and OCH₂CH₂), 2.24 (s, Ad OCCH₂CO), 3.35 (t, *J* = 6.7 Hz, OCH₂CH₂), 4.84 (t, *J* = 3.6 Hz, SiH), 7.30–7.38 (m, Ph), 7.53 (d, *J* = 7.5 Hz, Ph); ¹³C NMR (δ in CDCl₃) 8.49 (CH₂Si), 25.48 (OCH₂CH₂), 30.72, 35.40, 40.61, 45.38 (Ad CH and CH₂), 62.55 (OCH₂CH₂), 74.10 (Ad q-C), 127.94, 129.51 (Ph CH), 134.35 (Ph ipso C), 135.13 (Ph CH); Anal. Calcd for C₄₀H₄₈O₂Si₂: C, 77.87; H, 7.84. Found: C, 77.60; H, 8.00.

Hydrosilylation Polymerization

A solution of 0.46 g (0.71 mmol) of **1a**, 0.090 g (0.71 mmol) of 1,4-diethynylbenzene, 1.7 mg (0.0018 mmol) of RhCl(PPh₃)₃ in 2 mL of toluene was stirred at 70 °C for 24 h. The resulting mixture was passed through a short silica gel column eluting with toluene to remove the catalyst. After evaporation of the solvent, the residue was reprecipitated from chloroform-methanol to give 0.26 g (47%) of the hydrosilylated polymer (**2a**) as light yellow oil: ¹H NMR (δ in CDCl₃) 0.44–0.65 (m, SiCH₂(CH₂)₄CH₃), 0.86 (t, *J* = 7.0 Hz, SiCH₂(CH₂)₄CH₃), 1.21–1.31 (m, SiCH₂(CH₂)₄CH₃ and O(CH₂)₂CH₂Si), 1.47–1.76 (m, Ad and OCH₂CH₂CH₂Si), 2.27 (s, OCCH₂CO), 3.19 (t, *J* = 7.0 Hz, gem OCH₂(CH₂)₂Si), 3.34 (t, *J* = 7.0 Hz, trans OCH₂(CH₂)₂Si), 5.76 (d, *J* = 2.6 Hz, C=CH₂), 6.11 (d, *J* = 2.6 Hz, C=CH₂), 6.70 (d, *J* = 19.1 Hz, CH=CH), 6.92 (d, *J* = 19.1 Hz, CH=CH), 7.43–7.32 (m, benzene ring H); ¹³C NMR (δ in CDCl₃) 7.68 (gem O(CH₂)₂CH₂Si), 7.74 (trans O(CH₂)₂CH₂Si), 11.02, 13.94, 22.39, 23.61 (Hex), 27.56 (gem OCH₂CH₂CH₂Si), 27.62 (trans OCH₂CH₂CH₂Si), 29.30 (Ad CH and CH₂), 31.37, 33.08 (Hex), 35.41, 40.35, 45.55 (Ad CH and CH₂), 67.18 (gem OCH₂(CH₂)₂Si), 67.21 (trans OCH₂(CH₂)₂Si), 74.46 (Ad q-C), 118.07, 123.00, 126.04 (benzene ring CH, CH=CH and C=CH₂), 131.95 (benzene ring ipso C), 137.97 (C=CH₂), 147.44 (CH=CH). In the NMR data, gem and trans indicate the signals of α- and β-silylated units, respectively. The ratio of β-silylation/α-silylation units was determined to be 88/12 by the integration of the ¹H NMR signals.

Other hydrosilylated polymers were obtained in a manner similar to that above. Data for polymer **2b** obtained from hydrosilylation of 1,4-diethynylbenzene with **1b**, followed by reprecipitation from chloroform-ethanol: yellow solid; ¹H NMR (δ in CDCl₃) 1.23–1.16 (m, CH₂Si), 1.84–1.44 (m, Ad and OCH₂CH₂), 2.24 (s, OCCH₂CO), 3.24 (t, *J* = 7.0 Hz, gem OCH₂CH₂), 3.36 (t, *J* = 6.7 Hz, trans OCH₂CH₂), 5.68 (d, *J* = 2.1 Hz, C=CH₂), 6.17 (d, *J* = 2.1 Hz, C=CH₂), 6.70 (d, *J* = 19.0 Hz, CH=CH), 6.91 (d, *J* = 19.0 Hz, CH=CH), 7.31–7.56 (m, benzene ring H); ¹³C NMR (δ in CDCl₃) 9.43 (trans

CH₂Si), 9.50 (trans CH₂Si), 25.01 (gem OCH₂CH₂), 25.06 (trans OCH₂CH₂), 30.73, 35.41, 40.66, 45.43 (Ad CH and CH₂), 62.98 (gem OCH₂CH₂), 63.05 (trans OCH₂CH₂), 74.09 (Ad q-C), 122.82, 123.87, 126.81, 127.85, 129.35, 134.16, 135.29, 135.55 (benzene ring C, CH=CH, and C=CH₂), 137.98 (C=CH₂), 147.47 (CH=CH). The ratio of β-silylation/α-silylation units was determined to be 77/23 by the integration of ¹H NMR signals. Polymer **2b'** prepared by Pt-catalyzed hydrosilylation gave essentially the same NMR spectra as those above, except for the slightly higher β-silylation/α-silylation ratio of 81/19.

Data for polymer **2c** obtained by hydrosilylation of 1,4-diethynylbenzene with **1c**, followed by reprecipitation from THF-hexane: yellow solid; ¹H NMR (δ in CDCl₃) 0.29 (br, MeSiO), 0.48 (MeSiCH=CH), 0.54 (br, MeSiC=CH₂), 1.26–2.17 (m, Ad), 5.68–6.09 (m, H₂C=) 6.53 (br d, *J* = 19.0 Hz, CH=CH), 6.93 (br d, *J* = 19.0 Hz, CH=CH), 7.16–7.44, 7.50–7.66 (br m, benzene ring H); ¹³C NMR (δ in CDCl₃) 0.12, (SiMe), 25.60, 31.29, 34.62, 43.70, 43.90, 44.23, 44.45, 44.71, 54.18, 54.38, 67.97, 68.04 (Ad CH and CH₂), 74.27 (Ad q-C), 126.46, 126.88, 127.49, 127.68, 127.80, 127.95, 129.59, 133.68, 133.91 (benzene ring C). The ratio of CH=CHSiPhMeO/CH₂=CSiPhMeO/OSiPhMeO units in the backbone was determined to be 14/72/14 by the integration of the ¹H NMR signals.

Data for polymer **3b** obtained from hydrosilylation of bis(allyloxy)adamantane with **1b**, followed by reprecipitation from chloroform-ethanol: yellow solid; ¹H NMR (δ in CDCl₃) 1.04–1.254 (m, O(CH₂)₂CH₂Si), 1.44–1.66 (m, Ad and OCH₂CH₂CH₂Si), 2.24 (s, Ad OCCH₂CO), 3.31 (t, *J* = 6.7 Hz, OCH₂), 7.58–7.32 (m, benzene ring H); ¹³C NMR (δ in CDCl₃) 8.55 (CH₂Si), 24.78 (OCH₂CH₂), 30.70, 35.37, 40.61, 45.37 (Ad CH and CH₂), 63.18 (OCH₂CH₂), 74.08 (Ad q-C), 127.75, 129.12, 134.89 (benzene ring C), 135.90 (benzene ring ipso C).

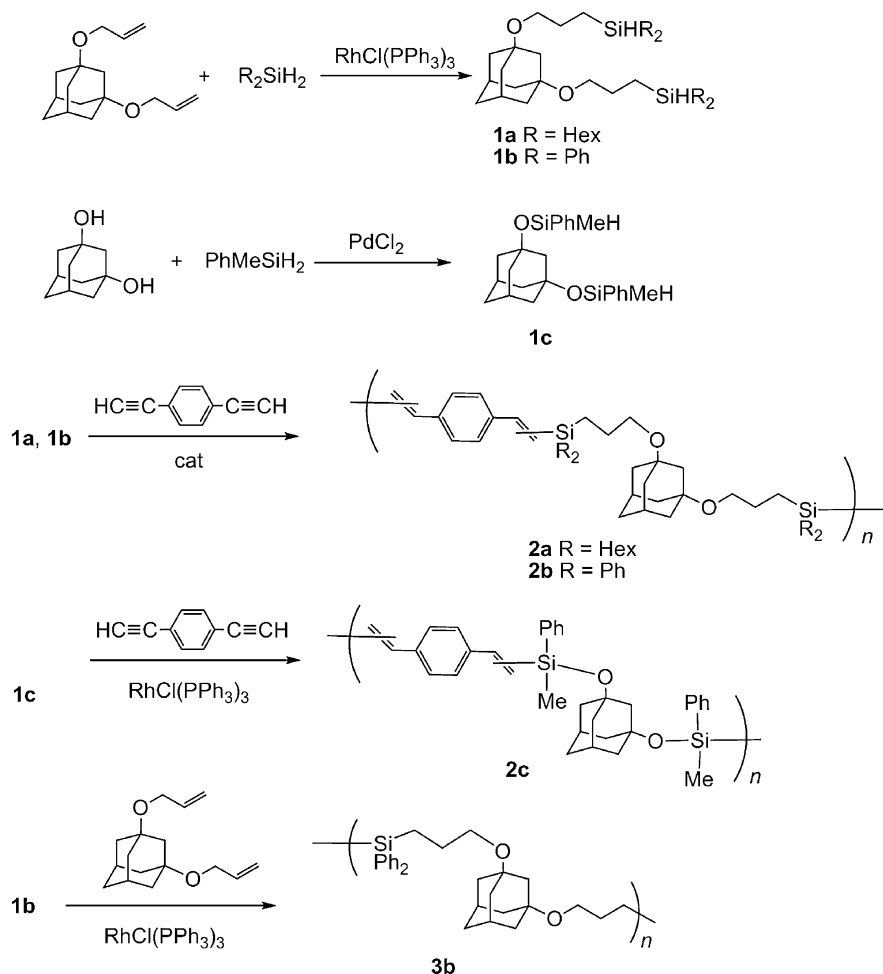
Cross-linking Reactions of Poly[(dimethylsiloxane)-co-(methylvinylsiloxane)] (**4**) with **1c**

A solution of 1.29 g of **4**, 65 mg of **1c**, and 23 mg of RhCl(PPh₃)₃ in 10 mL of toluene was stirred at 80 °C for 10 h. To this was added approximately 200 mg of triazinetrithiol (Sankyo Kasei Co. Ltd.) and the mixture was stirred for 30 min then was filtered to remove the catalyst. The solvent was evaporated to give 746 mg (58% yield) of the cross-linked polymer (**5**) as viscous oil: ¹H NMR (δ in CDCl₃) 0.09 (s, MeSi), 1.42–1.85 (m, Ad), 2.30 (s, OCCH₂CO), 5.73–6.20 (m, vinyl), 7.14–7.69 (m, Ph). Removal of the catalyst is essential to obtain soluble cross-linked products. Skipping this process resulted in the formation of only insoluble substances.

Other cross-linking reactions were carried out in a manner similar to that above. For Pt-catalyzed reactions, removal of the catalyst by using complexing reagent was not necessary.

RESULTS AND DISCUSSION

Hydrosilylation polymerization was performed as shown in



Scheme 2. Hydrosilylation polymerization leading to adamantane unit-containing linear polymers.

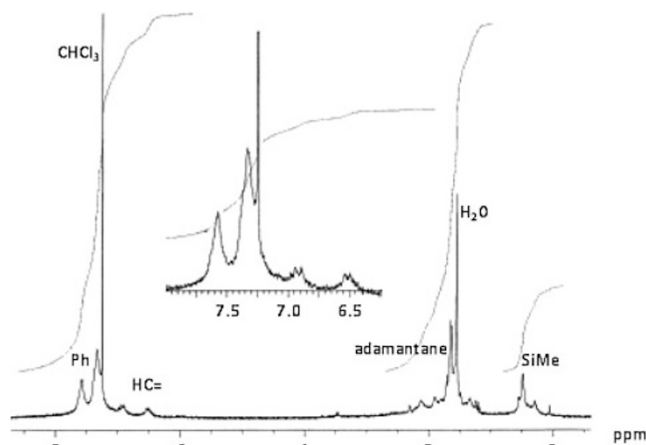
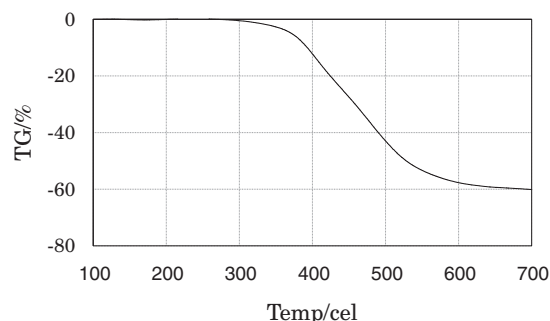
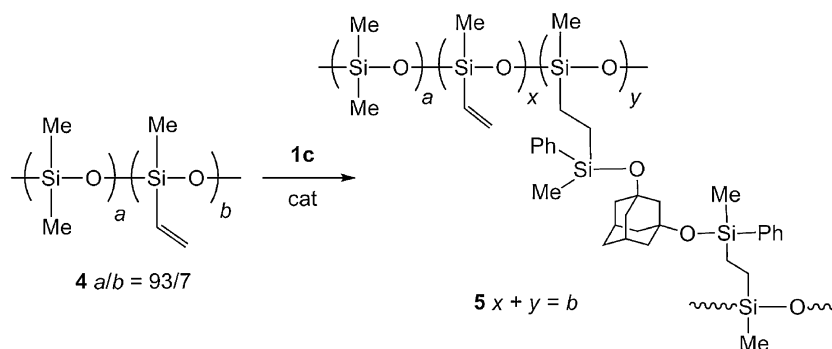
Table I. Hydrosilylation Polymerization

polymer	yield/% ^b	M_n (M_w/M_n) ^c	mp/°C	TGA ^a	
				T_{d5} /°C	T_{d10} /°C
2a	47	5400 (1.8)	oil		
2b	68	4000 (1.6)	60–69	341	384
2b'	79	4000 (1.5)	57–63	265	359
2c	67	3900 (3.5)	81–89	370	393
3b	59	3000 (1.3)	54–59	340	371

^aIn a nitrogen atmosphere, at the rate of 10°C/min. T_{d5} and T_{d10} are temperatures of 5% and 10% weight loss, respectively. ^bAfter reprecipitation. ^cDetermined by GPC, relative to polystyrene standards.

Scheme 2 and Table I. The reaction of diethynylbenzene with hydrosilane **1a** gave polymer **2a** as viscous light yellow oil, while with phenyl-substituted hydrosilanes **1b** and **1c**, the corresponding hydrosilylated polymers **2b** and **2c** were obtained as yellow solids. These polymers are soluble in common organic solvents, such as chloroform, diethyl ether, THF, and toluene, but insoluble in methanol. The solubility decreased in the order of **2a** > **2b** > **2c** and polymer **2c** could be purified by reprecipitation even from hexane. Molecular weights of the polymers were determined by GPC to be $M_n = 3000$ – 5400 , relative to polystyrene standards. The rather

low molecular weights seem to be ascribed to low reactivity of the hydrosilanes due to the steric hindrance. Regioselectivity of the hydrosilylation was estimated by the ¹H NMR spectra of the polymers to be β -silylation/ α -silylation = 88/12 and 77/23 for **2a** and **2b**, respectively. Using $H_2PtCl_6 \cdot 6H_2O/iPrOH$ (Spier's catalyst) instead of $RhCl(PPh_3)_3$ for the reaction with **1b** led to the formation of polymer **2b'** with a little higher degree of β -silylation ($\beta/\alpha = 81/19$). The ¹H NMR spectrum of polymer **2c** revealed three broad MeSi signals at 0.29, 0.48, and 0.54 ppm in a ratio of 14/72/14 (Figure 1). Two at 0.48 and 0.54 ppm were due to those of β - and α -silylated units, respectively, while one at 0.29 ppm was assigned to siloxane units that would be formed by hydrolysis of terminal Si-H units during the workup, by comparison with the literature data.⁸ The formation of the siloxane units is probably responsible for the higher polydispersity (M_w/M_n) of **2c** than those of **2a** and **2b**. Hydrosilane **1b** reacted also with bis(allyloxy)adamantane smoothly to give polymer **3b** as a yellow solid. This polymerization proceeded regioselectively, and no α -silylated units were found to be formed in the polymer backbone. These polymers are stable and standing them at room temperature in air under room light for several months led to no detectable changes in their spectra.


 Figure 1. ^1H NMR spectrum of polymer **2c** in CDCl_3 .

 Figure 2. TGA curve of polymer **2c** in nitrogen.


Scheme 3. Cross-linking hydrosilylation of a vinylsiloxane polymer.

Thermal properties of the phenyl-substituted polymers were examined by TGA in nitrogen, and T_{d_5} and $T_{d_{10}}$ were noted as summarized in Table I. Of those, polymer **2c** showed the highest T_{d_5} and $T_{d_{10}}$ (Figure 2). They were lower than those reported for poly(adamantanediyl)s,² adamantane-AN and MA copolymers,³ biadamantane unit-containing polyimides,⁴ and adamantane-siloxane polymers,⁷ but higher than or comparable to those of adamantane unit-containing polyimides (Scheme 1).

The introduction of propylene chains into the backbone suppresses the heat-resistance of polymers **2b** and **3c**. However, it should be pointed out that polymer **2b** showed a little inferior but almost comparable heat-resistance to that of **2c** with respect to the $T_{d_{10}}$ values. Interestingly, polymer **2b'** prepared by platinum-catalyzed hydrosilylation showed inferior resistance to **2b**. This is probably ascribed to the higher content of α -silylated vinylene units ($\text{H}_2\text{C}=\text{C}<$) in polymer **2b**. It is likely that sterically less hindered vinylene units are more reactive than ethylene units ($-\text{CH}=\text{CH}-$) towards thermal cross linking that would be involved in the TGA process to enhance the resistance. In fact, when polymer **2c** was heated at 230°C for 10 min, the polymer became insoluble in organic solvents. Although no clear peaks were found in the differential thermal analysis (DTA), this is indicative of that some cross-linking reactions occurred to an extent. Attempted

 Table II. Cross-linking of Polysiloxane **4**^a with **1c**

4/1c	catalyst ^b	yield/%	x/y	M_n (M_w/M_n)
10/1	S	65	3.1/3.9	38000 (2.2)
22/1	S	73	5.5/1.5	24000 (2.0)
35/1	S	90	6.0/1.0	21000 (1.2)
20/1	W	55	4.5/2.5	41000 (2.6)

^a $M_n = 17000$, $M_w/M_n = 1.4$. ^bS: $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}/\text{iPrOH}$, W: $\text{RhCl}(\text{PPh}_3)_3$.

measurements of glass transition temperature failed. The differential scanning calorimetry of the polymers always showed no clear phase-transition, except for melting.

Next, we studied cross-linking hydrosilylation of vinylsiloxane polymer **4** with **1c** as shown in Scheme 3, and the results are summarized in Table II. The reactions proceeded smoothly to give cross-linked polymers **5** as viscous oil in good-high yields. No signals due to Si-H groups were detected in the IR and ^1H NMR spectra of **5**. Insoluble materials were always formed in these reactions, which were removed by filtration to decrease the yields. Heat-resistance of cross-linked polymers **5** was examined by TGA, to give $T_{d_5} = 330\text{--}440^\circ\text{C}$ and $T_{d_{10}} = 450\text{--}480^\circ\text{C}$ in nitrogen, which were lower than those of the parent polymer **4** ($T_{d_5} = 480^\circ\text{C}$ and $T_{d_{10}} = 533$

°C). This is probably due to the formation of small amounts of volatile by-products that were detected by GC analysis, under the reaction conditions.

In conclusion, we prepared adamantane unit-containing linear polymers by hydrosilylation of organic unsaturated compounds and bis(hydrosilyl)-substituted adamantanes. Unfortunately, their heat-resistance was not as high as we expected. Moreover, the UV spectra of the polymer films revealed tailing of the absorption band up to approximately 600 nm, indicating that the present polymers may not be suitable for LED encapsulants in the present form and tuning the chemical structure is required. However, the high solubility in organic solvents and moderately high heat-resistance may allow us to use this type of the polymers as the electronic device materials, such as sealing materials and insulating films. The adamantane-siloxane skeleton may be also useful as the backbone for adhesion materials. We also demonstrated that bis(methylphenylsilyloxy)adamantane is useful as a cross-linking reagent for unsaturated polymers by hydrosilylation reactions. Hydrosilylation polymerization would provide a new methodology to prepare adamantane unit-containing polymers and preparation of novel adamantane unit-containing polymers using it is now underway.

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