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Short communication

# Syntheses and polymerization of epoxy monomers consisting of carbosilane segments and properties of the networked polymers

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ABSTRACT

Two diglycidyl ethers which consist of a flexible carbosilane segments and of rigid phenylene moieties (**1** and **2**) were synthesized and investigated in order to evaluate their heat-curing behavior (epoxy homopolymerization) as well as thermal and mechanical properties of the networked polymers. Differential scanning calorimetry (DSC) analysis revealed that melting points of both diepoxides were −73.9 and −50.7 °C, respectively. Networked polymers of **1** and **2** showed glass transition temperature ($T_g$)s below ambient temperature of 2.2 and 18.7 °C, respectively. High thermal stability of cured **1** and **2** were confirmed by thermogravimetric analysis (TGA) (5% weight loss temperature ($T_{d5}$) = 369 °C for **1** and 351 °C for **2**). Tensile tests of cured **1** and **2** clarified that their Young's moduli were $(9.76 \pm 0.135)^{-2}$ and $(1.29 \pm 0.114)^{-1}$ MPa, respectively.

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## 1. Introduction

Epoxy resins are one of the most important thermoset materials in the industrial applications such as coatings, adhesives, electrical insulations, and composites [1–5]. Epoxy resins require high chemical and thermal stabilities, high durability, good adhesion and mechanical properties as well as good reactivities. In addition, fine-tuning of these properties are of the necessary for particular applications. To control the characteristics of epoxy resins, introducing a heteroatom component is considered great effective. Thus, we focused on introducing carbosilane as a component for epoxy resins. Polycarbosilanes, consisting of whole backbone C–Si–C, generally show high thermal stabilities with low glass transition temperature ($T_g$) [6–11]. Although polysiloxanes exhibit low $T_g$, the chemical stability of carbosilanes are higher than those of siloxanes in general. Because Si–C bond is less polarized than Si–O bond, Si–C bonds are less prone to be hydrolysed or attacked by nucleophiles [17]. A great number of researches on development of siloxane-based epoxy resins have been reported [12], while studies about carbosilane-based epoxy resins have been limited so far. Poly[1,1-diethylsilabutane-*co*-1-(3,4-epoxybutyl)-1-methylsilabutane] has been reported from our laboratory. It can be cationically cured to provide networked polymers with good thermal stability ($T_{d5}$ of >380 °C) [13], which suggested a large potential of carbosilane-based network polymers.

In this study, we synthesized carbosilane-based epoxy monomers **1** and **2**, which consist of not only flexible C–Si–C bonds and alkyl chains but also rigid phenylene units, and compared their reactivity for cationic polymerization and the properties of their cured resins with the representative epoxy monomer bisphenol A diglycidyl ether (**BADGE**). We expected that the epoxy resins bearing a carbosilane segment would show lower $T_g$ and Young's moduli as well as high thermal properties, which will be a useful information in the development of new epoxy resins for the elastomer applications.

## 2. Experimental

### 2.1. Analyses and measurements

$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on JEOL JME-ECS 400 NMR spectrometer in $CDCl_3$. Chemical shifts were determined relative to internal TMS ($^1$H, $\delta$ 0.00) or internal $CDCl_3$ ($^{13}$C, $\delta$ 77.16). Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) analyses were recorded by using a Thermo Scientific Nicolet iS10 spectrometer equipped with a Smart iTR diamond ATR sampling accessory. Differential scanning calorimetry (DSC) analyses were carried out using Seiko Instrument

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DSC-6200R in an aluminum pan under a nitrogen flow of 50 mL $\text{min}^{-1}$. Thermogravimetric analysis (TGA) were performed on a Seiko Instrument TG-DTA 6200 using an aluminum pan under nitrogen atmosphere (flow rate 100 mL $\text{min}^{-1}$) at a heating rate of 10 °C $\text{min}^{-1}$. Tensile testing was conducted and recorded on tensile testing machine (EZ-LX, SHIMADZU) using dumbbell-shaped films (ca. 0.3 mm (T) × 2 mm (W) × 12 mm (L)) with speed of 500 mm/min. Reported values of Ultimate strength, Strain at break and Young's modulus ($E$) are average and standard deviations of three samples.

### 2.2. *Materials*

1,4-bis(dimethylsilyl)benzene and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex in xylene [2 wt%] were purchased form Aldrich. Bisphenol A diglycidyl ether (**BADGE**, 99% purity) was purchased from ADEKA corporation. Methanol and chloroform were purchased from Wako Pure Chemical Industry (Osaka, Japan). 2-methylbenzylmethyl-*p*-hydroxyphenylsulfonium hexafluoroantimonate (SAN-AID SI-80) was purchased from Sanshin Chemical Industry co., ltd. 4-vinylbenzyl glycidylehter was purchased from AGC Seimi Chemical (Kanagawa, Japan). All the reagents were used without further purification. Silica gel 60 (70–230 mesh ASTM) for column chromatography was purchased from Merck (Japan).

#### 2.2.1. *Synthesis of 1,4-bis(dimethyl(3-(oxiran-2-ylmethoxy)propyl)silyl)benzene (**1**)*

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex in xylene [2 wt%] (0.02 mL, 0.9 μmol) was added to a mixture of 1,4-bis(dimethylsilyl)benzene (975 mg, 5.01 mmol) and allyl glycidyl ehter (1.19 g, 10.4 mmol) at 0 °C under a $N_2$ atmosphere. After stirring for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was purified by silica column chropatography using hexane–ether (2:1) as an eluent to give a colorless oil (2.05 g, 97%). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 7.48 (s, 4H), 3.68 (dd, $J = 8.7$ and 2.4 Hz, 2 H), 3.42 (m, 4H), 3.36, (m, 2H), 3.13 (m, 2H), 2.79, (t, $J = 3.9$ Hz, 2H), 2.60 (m, 2H), 1.62 (m, 4H), 0.74 (m, 4H), 0.27 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 139.88, 133.00, 74.47, 71.59, 51.00, 4452, 24.23, 11.76, −3.07. $^{29}$Si NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 2.73. ATR-FTIR ($\upsilon$, $\text{cm}^{-1}$): 2930, 2866, 1380, 1337, 1248, 1133, 1105, 1057, 909, 833, 797, 764, 735. HRMS [FAB] *m*/*z* Calcd. for $C_{22}H_{38}O_4Si_2$: 422.2309, Found [M + $H^+$] 423.2384.

#### 2.2.2. *Synthesis of 1,4-bis(dimethyl(4-((oxiran-2-ylmethoxy)methyl)phenethyl)silyl)benzene (**2**)*

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex in xylene [2 wt%] (0.02 mL, 0.9 μmol) was added to a mixture of 1,4-bis(dimethylsilyl)benzene (978 mg, 5.03 mmol) and 4-vinylbenzyl glycidylehter (1.90 g, 9.99 mmol) at 0 °C under a $N_2$ atmosphere. After stirring for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was purified by silica column chropatography using hexane–ether (2:1) as an eluent to give a colorless oil (2.57 g, 90%). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 7.53 (s, 4H), 7.24 (d, $J = 6.3$ Hz, 4 H), 7.16 (d, $J = 6.3$ Hz, 4 H), 4.54 (quart., $J = 8.4$ Hz, 4 H), 3.73 (dd, $J = 8.7$ and 2.4 Hz, 2 H), 3.41 (m, 2H), 3.18 (m, 2H), 2.79 (t, $J = 3.9$ Hz, 2H), 2.66–2.61 (m, 6H) 1.11, (m, 4H), 0.29 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$, ppm): 144.80, 139.84, 133.05, 128.08, 127.96, 73.33, 70.75, 51.02, 44.47, 29.79, 17.76, −3.02. $^{29}$Si NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 3.02. ATR-FTIR ($\upsilon$, $\text{cm}^{-1}$): 2951, 1513, 1417, 1380, 1248, 1133, 1090, 1019, 902, 834, 811, 767, 691. HRMS [FAB] *m*/*z* Calcd. for $C_{34}H_{46}O_4Si_2$: 574.2935, Found: [$M^+$]574.2925.

### 2.3. *Preparation of cured resins of 1 and 2*

Monomer **1** or **2** (4 mmol) and 2-methylbenzylmethyl-*p*-hydroxyphenylsulfonium hexafluoroantimonate (SAN-AID SI-80) (0.2 mmol) were dissolved in a solution of chloroform–methanol (8:1/v:v). The solution was casted into Petri dish made from polytetrafluoroethylene and the solvents were evaporated at room temperature for 15 h. The sample was further dried under vacuum at room temperature for 24 h. The sample was heated at 100 °C for 2 h, then 130 °C for 1 h under a $N_2$ atmosphere.

## 3. Results and discussion

### 3.1. *Syntheses of epoxy monomers 1 and 2*

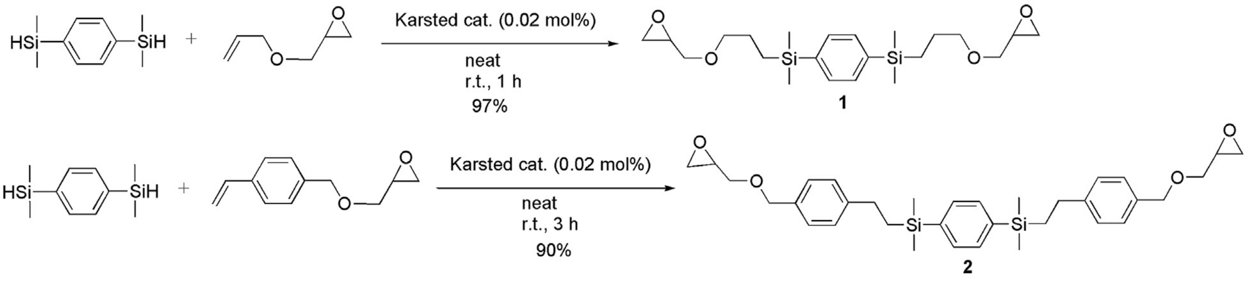
Syntheses of carbosilane-containing diepoxy monomers **1** and **2** were outlined in Scheme 1. Hydrosylilation of allylglycidylether or 4-vinylbenzylglycidylether with 1,4-bis(dimethylsilyl)benzene were carried out using Karsted's catalyst to obtain diepoxy monomers **1** and **2** in 97 and 90% yields, respectively. Compound **1** has been already reported [14], but curing properties of monomer **1** has not been studied. Nuclear magnetic resonance (NMR) spectroscopy confirmed the chemical structures of **1** and **2**. $^1$H NMR spectra of **1** and **2** in $CDCl_3$ are shown in Fig. 1. A 12H singlet signal corresponding to Si–$CH_3$ protons (b) was observed in upfield region (0.265 ppm for **1** and 0.290 ppm for **2**). Ten protons on diglycidyl ether moieties (f, g, h, i, j for **1** and h, i, j, k, l for **2**) around 2.5–4 ppm and 4H singlet signals on bis(dimethylsilyl)phenylene at 7.48 ppm for **1** and 7.53 ppm for **2** were also observed, which confirmed the corresponding chemical structures of **1** and **2**.

### 3.2. *Curing behavior of 1 and 2*

Differential scanning calorimetry (DSC) scans of monomers **1** and **2** are shown in Fig. 2a. The melting points of **1** and **2** are determined to be −73.9 and −50.3 °C from the peak top of heating cycle of DSC scans. These low melting points might be due to the C–Si–C bonds and flexible alkyl chains.

To gain insight into the thermal cationic polymerization, DSC analyses of **1** and **2** were performed with mixing 5 mol% of the thermally-latent cationic initiator: 2-methylbenzylmethyl-*p*-hydroxyphenylsulfonium hexafluoroantimonate (The chemical structure is shown in supporting information). DSC analysis of **BADGE** was also performed under the same condition as reference experiment. With the addition of the thermally-latent initiator, DSC curve (heating scan) of **1** showed exothermic peak around 70–160 °C, which can be attributed to the exotherm by ring-opening polymerization of the epoxy moieties (Fig. 2b). Similar tendencies were also observed for **2** and **BADGE** (see supporting information). Further experimental information about the cationic ring-opening reactions of these glycidyl ethers **1** and **2** were obtained by DSC analyses conducted at different heating rate. The samples containing 5 mol% of 2-methylbenzylmethyl-*p*-hydroxyphenylsulfonium hexafluoroantimonate were scanned at heating rates of 5, 10, 15, and 20 °C/min. The DSC curves of **1** and **2** are shown in Fig. 3a and b along with the peak top temperature ($T_p$). As increasing the heating rate, the $T_p$s were shifted to higher temperature. From these results, activation energies ($E_\alpha$)s of **1**, **2** and **BADGE** were estimated using both Ozawa's method (eq (1)) and Kissinger's method (eq (2)) [15,16], as follows:

$$\ln q = -1.052 \ \times E_a/RT_p + \ln(AE_a/R) \ - \ln F_{(x)} - 5.331 \qquad (1)$$



**Scheme 1.** Syntheses of **1** and **2**.

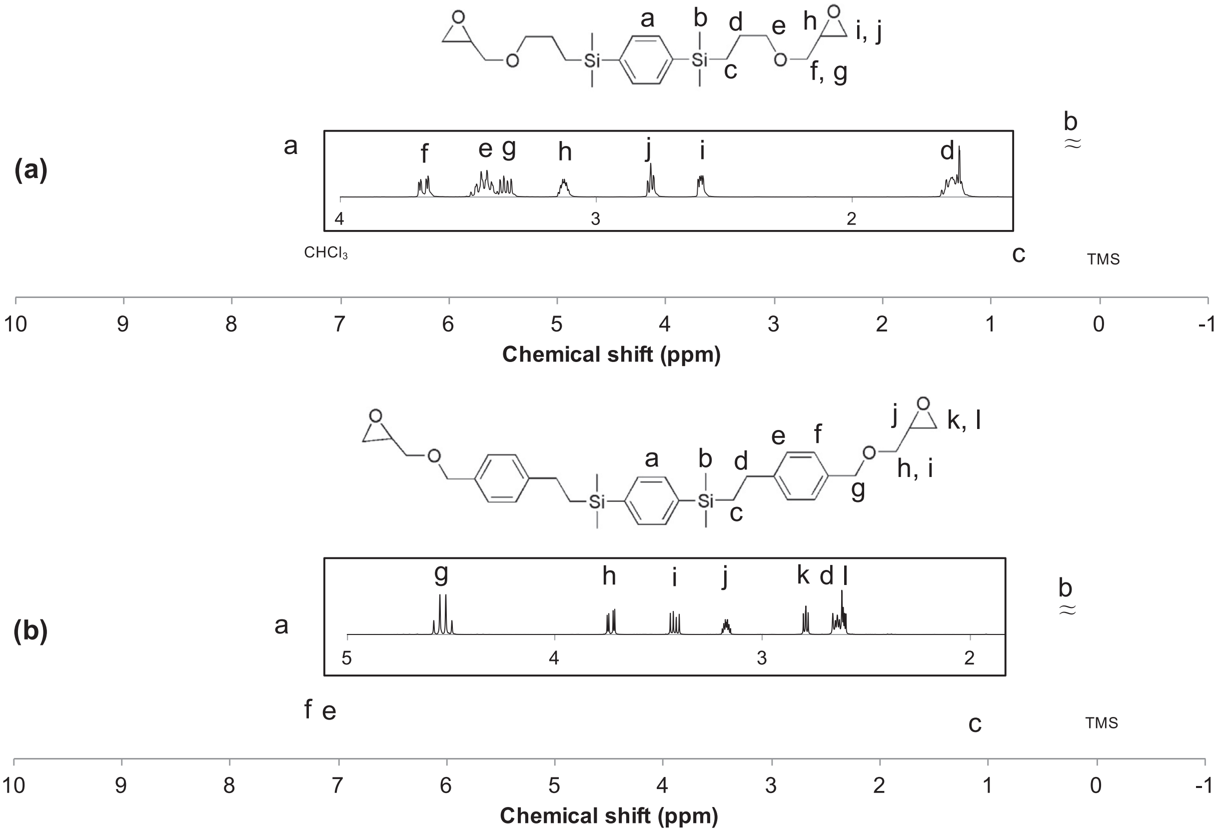


**Fig. 1.** $^1$H NMR spectra of **1** (a) and **2** (b) in $CDCl_3$.

$$-\ln\left(q/T_p^2\right) = E_a/RT_p - \ln\left(AR/E_a\right) \qquad (2)$$

where $q$ is heating rate, $T_p$ is the absolute temperature of exothermic peak, A is the frequency factor, R is the gas constant, $F(x)$ is conversion dependent term. $E_\alpha$ can be provided from the slope of the plot of ln ($q$) against $1/T_p$ using Ozawa's method (Fig. 3c). As for the Kissinger's method, the plot of −ln ($q/T_p$ [2]) versus $1/T_p$ gave the straight line, whose slope can be used to give $E_\alpha$ (Fig. 3d). The $E_\alpha$ obtained from both Ozawa's and Kissinger's methods are summarized in Table 1. In comparison of $E\alpha$ estimated by Ozawa's method, **1**, **2** and **BADGE** showed $E_\alpha$ of 230, 100 and 128 kJ/mol, respectively. In the case of $E_\alpha$ of Kissinger's method, similar results were obtained. The lower $E_\alpha$ of **2** might be due to the electron withdrawing effect of benzyl alcoxy groups that activate epoxy rings on **2**. It is noteworthy that the $E_\alpha$ of **2** is comparable for that of **BADGE**.

We also attempted anionic polymerization of **1** and **2** using 2-ethyl-4-methylimidazole (see supporting information). However, significant exothermic curves were not observed.

### 3.3. *Preparation of cured epoxy resin of 1 and 2 by cationic polymerization*

A solution of **1** or **2** with 5 mol% of thermally-latent cationic polymerization initiator: 2-methylbenzylmethyl-*p*-hydroxyphenylsulfonium hexafluoroantimonate in chloroform−methanol (8:1) was casted on Petri dish that made of polytetrafluoroethylene. After removing solvents, the mixture was heated at 100 °C for 2 h, then 130 °C for 1 h. Photographs of the obtained resins of **1** and **2** are provided in supporting information.

Attenuated total reflection fourier transform infrared (ATR-FTIR) spectra of **1** and **2** were measured before and after curing procedure (Fig. 4). In the spectra of **1** and **2** after curing, absorption at

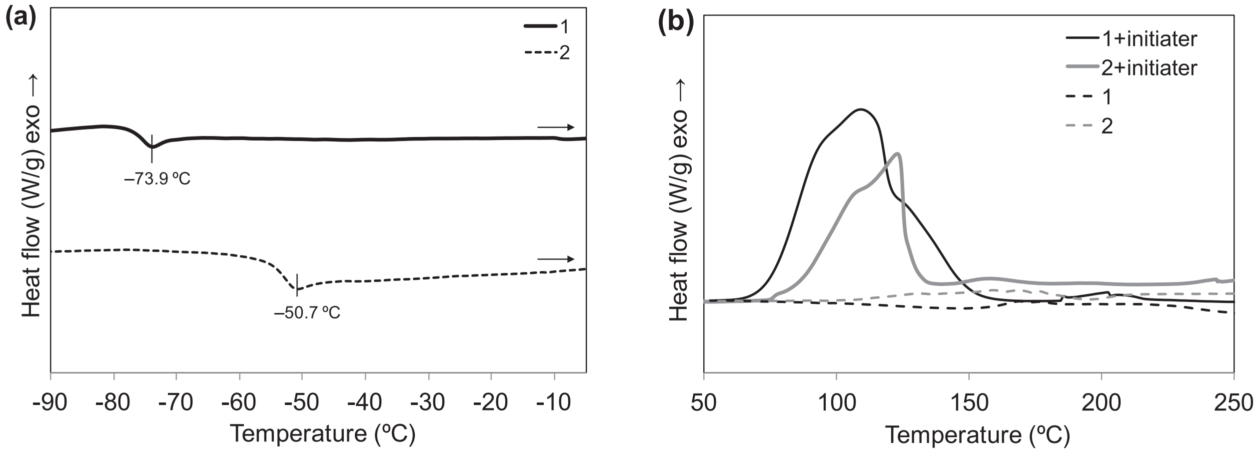


**Fig. 2.** (a) DSC scans of **1** (solid line) and **2** (dashed line). (b) DSC scans of **1** (black solid line) and **2** (gray solid line) including cationic initiator (5 mol%) and **1** (black dashed line) and **2** (gray dashed line) without cationic initiator.

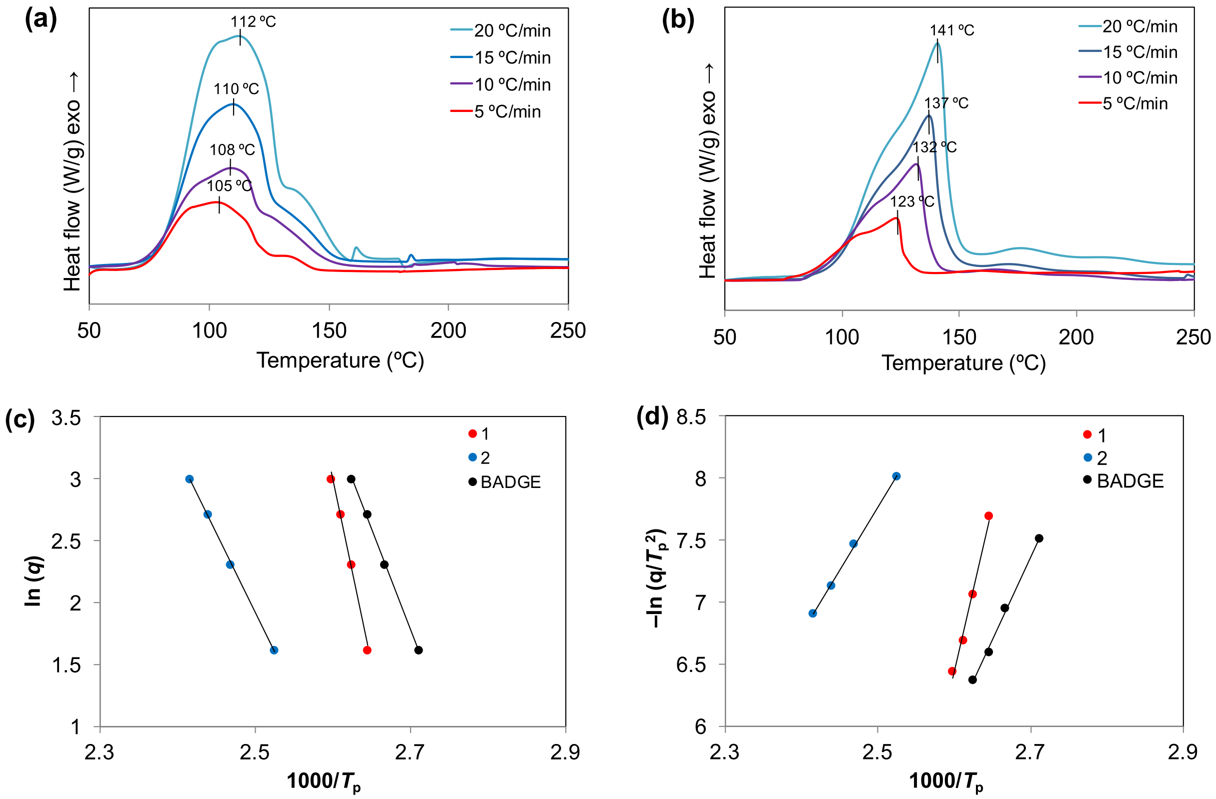


**Fig. 3.** DSC scans of **1** (a) and **2** (b) containing 5 mol% of thermal cationic initiator at different heating rate. (c) plot of ln($q$) versus 1000/$T_p$ using Ozawa's method (d) plot of ln($q$/$T_p$) versus 1000/$T_p$ using Kissinger's method.

**Table 1**
Curing behaviors of **1** and **2**.

| Compound | $E_\alpha$ (kJ/mol) Ozawa method | $E_\alpha$ (kJ/mol) Kissinger method |
|---|---|---|
| **1** | 230 | 220 |
| **2** | 100 | 84.7 |
| **BADGE** | 128 | 106 |

903 cm$^{-1}$ and 1248 cm$^{-1}$ that can be assigned to epoxy groups decreased, indicating that the epoxy moieties reacted. Remained epoxy groups in these networked polymers do not undergo further polymerization (discussed below), which might be due to the steric hinderance around the epoxy rings in the networked polymers.

### 3.4. Thermal properties of cured resins

DSC scans of cured **1**, **2** and **BADGE** are shown in Fig. 5a. In heating cycles of **1** and **2**, exothermic peaks that can be attributed to ring-opening polymerization were not observed, indicating that the epoxy groups in the cured resins of **1** and **2** do not undergo further reaction, due to the steric hinderance. $T_g$s of cured **1** and **2**

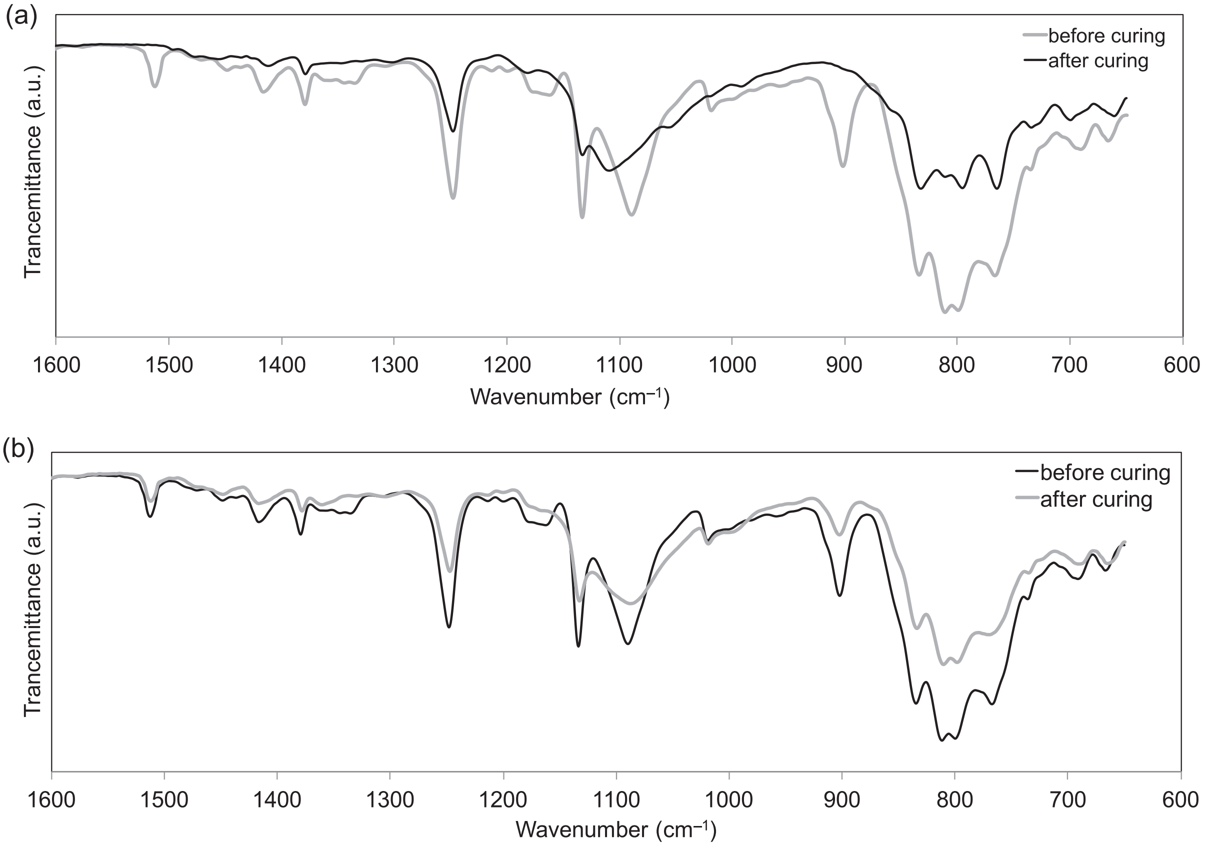


**Fig. 4.** IR spectra of **1** (a) and **2** (b) before and after curing.

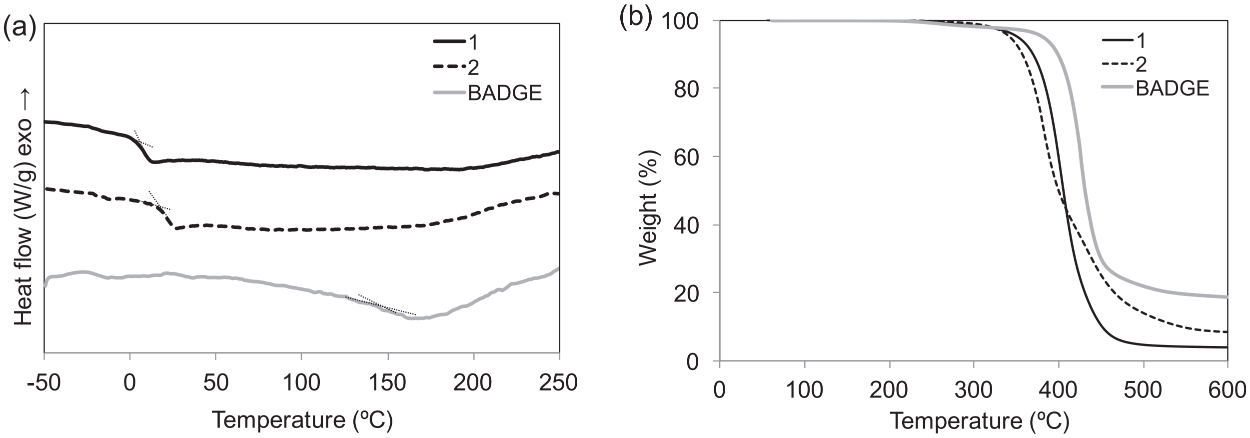


**Fig. 5.** (a) DSC scans of cured **1** (solid line) and cured **2** (dashed line). (b) TGA profiles of cured **1** (solid line), **2** (dashed line) and **BADGE** (gray line).

were determined to be 2.2 and 18.7 °C, respectively. As expected, $T_g$s of both cured **1** and **2** were below ambient temperature because of flexible Si—C bonds and alkyl chains, which lower than that of **BADGE** ($T_g = 147$ °C).

Thermal stability of **1** and **2** were examined by thermogravimetric analysis (TGA) and compared with **BADGE**. The TGA profiles are shown in Fig. 5b. Thermal properties of cured resins of **1** and **2** including The 5% weight loss temperatures ($T_{d5}$) and the 10% weight loss temperature ($T_{d10}$) are provided in Table 2. $T_{d5}$ of **1** and **2** are estimated to be 369 and 351 °C. Although these values are lower than that of **BADGE** ($T_{d5} = 382$), a C—Si—C backbone in epoxy resin showed good thermal stability. We assume that the remained initiator and terminal hydroxyl groups could react with carbosilane at higher temperature because the Si—C bond is weaker than the C—C bond, which lead to lower thermal stability of cured **1** and **2** than cured **BADGE**.

**Table 2**
Thermal properties of cured **1** and **2**.

| Compound | $T_g$ (°C) | $T_{d5}$ (°C) | $T_{d10}$ (°C) |
|---|---|---|---|
| Cured-**1** | 2.2 | 369 | 356 |
| Cured-**2** | 18.7 | 351 | 342 |
| **BADGE** | 147 | 382 | 399 |

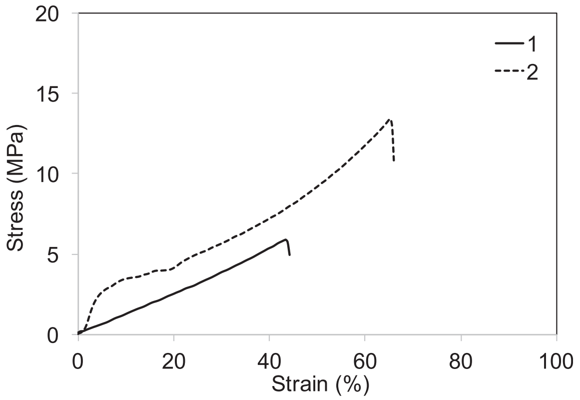


**Fig. 6.** Representative strain–stress curves of **1** (solid line) and **2** (dashed line).

**Table 3**
Mechanical properties of **1** and **2**.

| Sample | Ultimate strength (MPa) | Strain at break (%) | Young's modulus (GPa) |
|---|---|---|---|
| **1** | 5.42 ± 0.37 | 45.0 ± 1.52 | $(9.76 \pm 0.135)^{-3}$ |
| **2** | 12.2 ± 1.39 | 61.7 ± 3.42 | $(1.29 \pm 0.114)^{-2}$ |

### 3.5. *Mechanical properties of cured resins*

Tensile test of cured **1** and **2** were performed to examine their mechanical properties. The dumbbell shaped mold of **BADGE** for the tensile test could not be prepared in our methods because the cured **BADGE** provided too brittle film. Fig. 6 shows representative strain–stress curves of cured **1** and **2**. The curves of **1** and **2** were almost straight line and showed some stretchability. Mechanical properties including ultimate strength, strain at break, and Young's modulus are provided in Table 3. Cured **1** and **2** exhibited moderate ultimate strength of 5.42 ± 0.37 and 12.2 ± 1.39 MPa and elongation of 45.0 ± 1.52 and 61.7± 3.42%, respectively. These mechanical characters can be mainly attributed to these rubber state due to the lower $T_g$ below room temperature. Young's moduli of **1** and **2** were estimated to be $(9.76 \pm 0.135)^{-3}$ and $(1.29 \pm 0.114)^{-2}$ GPa, respectively. From these results, **1** and **2** are expected to be useful in the development of new elastic materials.

## 4. Conclusion

In this study, we synthesized diglycidyl ethers (**1** and **2**) which possess not only flexible carbosilane segments but also rigid phenylene moieties. We have also studied their potential curing behaviors and thermal and mechanical properties. Cured resins of **1** and **2** exhibited $T_g$ below room temperature ($T_g < 19$ °C) along with good thermal stability ($T_{d5} > 350$ °C). Moreover, films of cured **1** and **2** showed Young's moduli in the range of $9.76^{-2}$–$1.29^{-1}$ MPa. These results indicate that **1** and **2** can be promising monomers for the applications of epoxy resin-based network polymers.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.09.043.

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