

Precise Synthesis of Poly(silphenylenesiloxane)s with Epoxy Side Functional Groups by Tris(pentafluorophenyl)borane as a Catalyst

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ABSTRACT: 1, ω -Dimethylhydroxysilyl, -dimethylhydrosilyl, -dimethylmethoxysilyl -terminated tetramethylsilphenylenesiloxane prepolymers were prepared by sequential palladium-catalyzed dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with water, reduction with lithium aluminium hydride, and palladium-catalyzed methanolysis. 1,4-Bis[(glycidyl- or cyclohexene oxide-functionalized alkyl)methylhydrosilyl]benzene and methyl dimethoxysilanes with the same epoxy groups were synthesized by hydrosilylation of 1,4-bis(methyldihydrosilyl)benzene and methyl dimethoxysilane with (terminal olefin-functionalized alkyl) substituted epoxides in the presence of platinum catalyst. 1,4-Bis[(glycidyl- or cyclohexene oxide-functionalized alkyl)methyl(hydroxy or methoxy)silyl]benzenes were obtained by hydrolysis and methanolysis of the hydrosilyl derivatives. Poly(silphenylenesiloxane)s with epoxy side groups were synthesized by hetero-polycondensation of the hydrosilane, hydroxysilane and methoxysilane functional groups in the prepolymer and 1,4-bis[(epoxy-functionalized alkyl)methylsilyl]benzene, or 1,1-dimethoxy(epoxy-functionalized alkyl)methylsilane in the presence of a catalyst. Tris(pentafluorophenyl)borane was found to be an excellent catalyst for the polymerization. Cross-linking a polymer with 1,4-diaminobenzene gave stretchable polymer film by solution cast method. [doi:10.1295/polymj.PJ2006171]

KEY WORDS Palladium Catalyst / Tris(pentafluorophenyl)borane / Hydrosilylation / Dehydrocoupling Polymerization / Poly(silphenylenesiloxane) / Epoxy Side Groups / Cross-Linked Polymer Film /

Modern technologies have continuous demands on development of high-temperature elastomeric materials. Polysiloxanes are a kind of good candidates as high-temperature elastomer because of the property originated from flexible and heat-resistant Si-O-Si backbone, which is also the origin of good dielectric and surface properties, and so on.^{1–3}

However, some thermal degradation reaction of polysiloxanes was noticed at high temperature. Corriu⁴ elucidated that the main course of degradation of polysiloxane is the intermolecular exchanges of Si-O bonds, followed by intramolecular exchanges of Si-O bonds to depolymerize. Incorporation of rigid aromatic units into the siloxane backbone generally interrupts the siloxane redistribution reaction at high temperature, and improves both mechanical and thermal properties without simultaneous loss of other good features of polysiloxanes. Thus, polysilylarylenesiloxanes, derivatives of polysiloxanes by partially replacing -O- by arylene groups, show better thermal and mechanical property than polysiloxanes.^{2,3,5,6}

Polysilphenylenesiloxanes, a class of typical polysilylarylenesiloxane, were intensively reported as materials possessing thermal stability and satisfying low temperature elasticity, although their crystallinity is

usually higher than polysiloxanes, which is a possible obstacle in various applications, for instance, application in electronic device materials as a thin film. One of the attractive aspects of these polymers is the easiness of introducing variety of functional substituents, such as vinyl, phenyl, hydrido, fluoroalkyl, etc.^{7–11} These functional groups were found to significantly affect the thermal property and crystallinity of polymers.

Meanwhile, cross-linked materials have many superior properties as elastomers.¹² Epoxy resins have found use in a wide variety of applications due to their desirable properties, such as high strength and modulus properties, excellent adhesive property, good thermal-mechanical and electrical properties and adjustment of crystallinity. Although generally hard and relatively brittle nature of the epoxy resins has limited the application of the materials in many fields, they have been utilized as insulation materials.¹³

The properties of elastomers, such as silicone rubber and poly(tetramethylsilphenylenesiloxane) (PTMPS), thus precisely modified with epoxy group will find a good chance to be used as insulating materials because of the improved properties.^{14–16}

However, efficient synthetic methods of PTMPS's

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having epoxy side groups with precisely regulated sequence have not been established. In this research, we were dedicated to the development of new synthetic method to obtain **PTMPS** having epoxy side groups with regulated interval along the main chain. Special stress was given to the use of tris(pentafluorophenyl)borane as excellent catalyst to form siloxane bond from silane and methoxysilane or hydroxysilane, by suppressing homo-condensation of hydroxysilane.

Cross-linking of the epoxy groups by 1,4-diaminobenzene was also carried out, and change in thermal degradation behavior was briefly discussed.

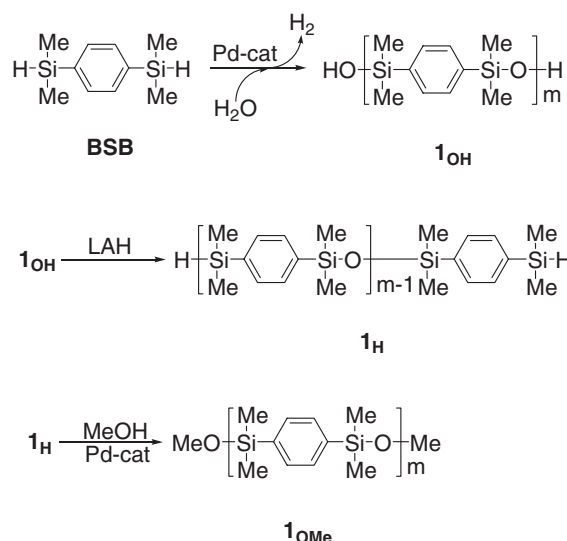
EXPERIMENTAL

Measurements

^1H NMR spectra were obtained in CDCl_3 on a Varian 500 MHz spectrometer model Unity INOVA. Chemical shifts are reported in ppm relative to CHCl_3 (δ 7.26). Gel permeation chromatography (GPC) analysis was performed on a JASCO HPLC Gulliver 900 equipped with a UV detector on the combination of Shodex KF-801 (exclusion limit: polystyrene, 1.5×10^3 dalton) and KF-802 (exclusion limit: polystyrene, 5.0×10^3 dalton), or KF-803L (exclusion limit: polystyrene, 7.0×10^4 dalton) and KF-804 (exclusion limit: polystyrene, 4.0×10^5 dalton) columns using tetrahydrofuran (THF) as an eluent (flow rate, 1 mL/min). The differential scanning calorimetric (DSC) analysis was performed on a Seiko DSC6200 instrument at a heating rate of $10.0^\circ\text{C}/\text{min}$ in air. The thermogravimetric analysis (TGA) was performed on a Seiko Instruments TGA/DTA 220 with a heating rate of $10.0^\circ\text{C}/\text{min}$ under nitrogen flow or in air. IR spectra were obtained on a JASCO VALOR-III spectrophotometer.

Materials

Methyldichlorosilane and dimethoxymethylsilane were obtained from Shin-Etsu Chemical. 1,4-Dibromobenzene, allyl glycidyl ether (AGE), 1,2-epoxy-5-hexene (EH), 4-vinyl-1-cyclohexene-1,2-epoxide (VCHE), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene ($\text{Pt}(0)(\text{DVTMDS})_2$), di-*n*-butyltin dilaurate, tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$), and tris(pentafluorophenyl)borane were purchased from Sigma-Aldrich. Lithium aluminum hydride (LAH) was purchased from Kanto Chemical Co. Inc. 1,4-diaminobenzene was obtained from Nacalai Co. Inc. 1,4-Bis(dimethylsilyl)benzene (BSB) and **PTMPS** were prepared according to the literatures.^{17–19} Hexane, tetrahydrofuran (THF), methanol and diethyl ether were dried before use.



Scheme 1.

Synthesis of Prepolymer and Monomers

The synthetic pathways of prepolymers with bis-(hydroxysilyl, hydrosilyl and methoxysilyl) terminal groups, needed for the synthesis of polymers in Scheme 3, are shown in Scheme 1.

Poly(silphenylenedisiloxane) Prepolymer (**1OH**)

To a 200 mL Schlenk flask were added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.15 g, 0.15 mmol), BSB (26.8 g, 0.15 mol) and THF (60 mL) in argon atmosphere. Distilled water (2.97 g, 0.17 mol) was added slowly with a syringe at room temperature. Hydrogen gas evolution occurred and ceased. After stirring for 5 h, the reaction system was exposed to air and stirred for 3 h to destroy the catalyst. The decomposed catalyst was removed by filtration through a short Florisil column using chloroform as an eluent. Fractional precipitation was carried out by adding saturated toluene solution of the polymeric products into methanol as a poor solvent to obtain the prepolymer **1OH**.

Yield: 28.5 g. $M_n = 2,800$, $M_w/M_n = 1.04$. δ : 0.32 (s, SiCH_3), 7.53 (s, C_6H_4). E_{LEM} . A_{NAL} . Calcd for $(\text{C}_{10}\text{H}_{16}\text{Si}_2\text{O})$: C, 57.63%, H, 7.74%. Found: C, 57.51%, H, 7.70%.

Poly(silphenylenedisiloxane) Prepolymer (**1H**)

A solution of prepolymer **1OH** (22.0 g, 15.7 mmol -OH) in THF (50 mL) was slowly added to LAH (0.60 g, 15.7 mmol) in THF (10 mL) solution at an ice-water bath temperature. After the addition, the reaction mixture was warmed to room temperature, and stirred for 18 h. The product mixture was diluted with ether (50 mL), and 1 N HCl was slowly added at ice-water bath temperature. The organic layer was washed with distilled water (30 mL each) for three times in a separatory funnel, and dried over anhydrous sodium

sulfate. Evaporation of the solvent and precipitation in methanol gave the product.

Yield: 68%. $M_n = 2,700$ (2,720 by $^1\text{H NMR}$), $M_w/M_n = 1.04$. δ : 0.33 (s, $\text{Si}(\text{CH}_3)_2$), 0.40 (d, $J = 3.7$ Hz, 12H, $\text{HSi}(\text{CH}_3)_2$), 4.42 (h, $J = 3.7$ Hz, 2H, SiH), 7.54 (s, C_6H_4). E_{LEM} . A_{NAL} . Calcd for $(\text{C}_{10}\text{H}_{16}\text{Si}_2\text{O})$: C, 57.63%, H, 7.74%. Found: C, 57.40%, H, 7.80%.

Poly(silphenylenedisiloxane) Prepolymer (IOMe)

Methanol (0.40 g, 12.5 mmol) was added to the solution of prepolymer **1H** (6.75 g, 5.00 mmol -H) in THF (30 mL) and $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.005 g, 5.00 μmol). After stirring for 10 h, the catalyst was separated by a short Florisil column using chloroform as an eluent. After evaporation of the solvent, the product was re-dissolved in a small amount of toluene, and precipitated into methanol.

Yield: 56%. $M_n = 2,900$, $M_w/M_n = 1.03$. δ : 0.33 (s, $\text{Si}(\text{CH}_3)_2$), 3.44 (s, 6H, SiOCH_3), 7.54 (s, C_6H_4).

Synthesis of comonomers for polycondensation is shown in Scheme 2.

1,4-Bis(methylchlorosilyl)benzene (2)

To the mixture of methylchlorosilane (103.7 g, 0.90 mol) and magnesium turning (10.9 g, 0.45 mol) in THF (60 mL), 1,4-dibromobenzene (35.4 g, 0.15 mol) in THF (50 mL) was slowly added, and stirred for 8 h at room temperature. The yellowish crude product, obtained as the hexane extract after evaporation of THF, was purified by fractional distillation to obtain the pure product as colorless liquid.

Yield: 42% (63 °C/65 Pa). δ : 0.78 (d, $J = 3.1$ Hz, 6H, SiCH_3), 5.32 (q, $J = 3.1$ Hz, 2H, SiH), 7.71 (s, 4H, C_6H_4).

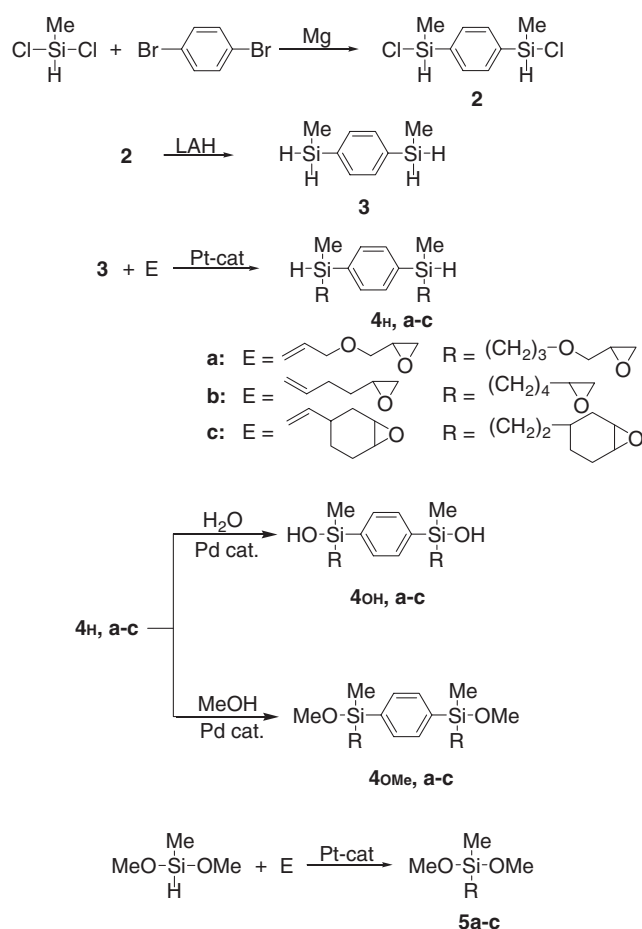
1,4-Bis(methylsilyl)benzene (3)

Compound **2** (13.5 g, 57.4 mmol) was diluted with diethyl ether (30 mL), and added slowly to a flask containing LAH (2.18 g, 57.4 mmol) in diethyl ether (20 mL) solution. After stirring for 20 h at room temperature, a small amount of concentrated HCl was slowly added to the mixture that was diluted with ether (30 mL) at an ice-bath temperature. The organic layer was washed three times with distilled water (20 mL each) in a separatory funnel, dried over sodium sulfate, and evaporated to remove the solvents. Distillation under reduced pressure gave a colorless liquid.

Yield: 52% (26 °C/66 Pa). δ : 0.45 (t, $J = 4.2$ Hz, 6H, SiCH_3), 4.36 (q, $J = 4.2$ Hz, 4H, SiH), 7.60 (s, 4H, C_6H_4).

1,4-Bis[(epoxy-functionalizedalkyl)methylsilyl]benzenes (4H,a-c)

A solution of $\text{Pt}(0)(\text{DVTMDS})_2$ in xylene (0.01 g,



Scheme 2.

27.0 μmol) was added to a mixture of **3** (4.50 g, 27.0 mmol) and AGE or EH or VCHE (27.0 mmol) in THF. After stirring at 60 °C, the catalyst was separated by a short Florisil column. The products were isolated by silica gel column chromatography using toluene/hexane (2/1, v/v) as the eluent.

4H,a: Yield: 46% (Rf = 0.2). δ : 0.36 (d, $J = 6.7$ Hz, 6H, SiCH_3), 0.77 (m, 4H, SiCH_2), 1.59 (m, 4H, SiCH_2CH_2), [2.58 (q, $J = 2.7$ Hz), 2.77 (q, $J = 4.6$ Hz), 4H, CH_2 in epoxy ring], 3.17 (m, 2H, CH in epoxy ring), [3.33 (q, $J = 5.7$ Hz), 3.66 (q, $J = 3.0$ Hz), 4H, $\text{Si}(\text{CH}_2)_3\text{OCH}_2$], 3.41 (m, 4H, $\text{Si}(\text{CH}_2)_2\text{CH}_2\text{O}$), 4.82 (q, $J = 6.7$ Hz, 2H, SiH), 7.47 (s, 4H, C_6H_4). Calculated molecular weight: 394.6572. EI-MS (m/z): 394.6571 ($[\text{M}]^+$), 393.6493 ($[\text{M}-\text{H}]^+$).

4H,b: Yield: 61% (Rf = 0.4). δ : 0.35 (d, $J = 6.1$ Hz, 6H, SiCH_3), 0.72 (m, 4H, SiCH_2), 1.49–1.70 (m, 12H, $\text{SiCH}_2(\text{CH}_2)_3$), [2.43 (q, $J = 2.7$ Hz), 2.72 (q, $J_2 = 3.9$ Hz), 4H, CH_2 in epoxy ring], 2.89 (m, 2H, CH in epoxy ring), 4.35 (q, $J = 6.1$ Hz, 2H, SiH), 7.53 (s, 4H, C_6H_4).

4H,c: Yield: 33% (Rf = 0.3). δ : 0.37 (d, $J = 6.2$ Hz, 6H, SiCH_3), 0.73, (m, 4H, SiCH_2), 1.10–2.20 (m, 18H, SiCH_2CH_2 and CH_2CH in cyclohexane ring),

3.12 (m, 4H, CH in epoxy ring), 4.53 (q, $J = 6.2$ Hz, 2H, SiH), 7.49 (s, 4H, C₆H₄).

1,4-Bis[(epoxy-functionalized alkyl)methylsilyl]benzenes with Hydroxyl and Methoxyl Terminal Groups (4H,a-c and 4OMe,a-c)

Hydrolysis or methanolysis, similarly to the case of prepolymer, changed the terminal groups of the compounds 4H,a-c to OH (4OH,a-c) or OMe (4OMe,a-c) groups. The products were also purified by column chromatography.

4OH,a: Yield: 51% (R_f = 0.4). δ : 0.42 (s, 6H, SiCH₃), 0.73 (t, $J = 8.6$ Hz, 4H, SiCH₂), 1.56 (m, 4H, SiCH₂-CH₂), 2.11 (s, 2H, SiOH), [2.60 (q, $J = 2.6$ Hz), 2.72 (q, $J = 4.1$ Hz), 4H, CH₂ in epoxy ring], 3.18 (m, 2H, CH in epoxy ring), [3.33 (q, $J = 5.9$ Hz), 3.67 (q, $J = 3.0$ Hz), 4H, Si(CH₂)₃OCH₂], 3.39 (m, 4H, Si(CH₂)₂-CH₂O), 7.51 (s, 4H, C₆H₄). Calculated molecular weight: 426.6560. EI-MS (m/z): 426.6465 ([M]⁺), 409.6389 ([M-OH]⁺).

4OH,b: Yield: 71% (R_f = 0.6). δ : 0.34 (s, 6H, SiCH₃), 0.75 (t, $J = 8.1$ Hz, 4H, SiCH₂), 1.47–1.70 (m, 12H, SiCH₂(CH₂)₃), 2.09 (s, 2H, SiOH), [2.44 (q, $J = 2.7$ Hz), 2.76 (q, $J = 3.7$ Hz, 4H, CH₂ in epoxy ring], 2.88 (m, 2H, CH in epoxy ring), 7.53 (s, 4H, C₆H₄).

4OH,c: Yield: 47% (R_f = 0.5). δ : 0.35 (s, 6H, SiCH₃), 0.77, (t, $J = 8.3$ Hz, 4H, SiCH₂), 1.09–2.16 (m, 18H, SiCH₂CH₂ and CH₂CH in cyclohexane ring), 2.18 (s, 2H, SiOH), 3.09 (m, 4H, CH in epoxy ring), 7.49 (s, 4H, C₆H₄).

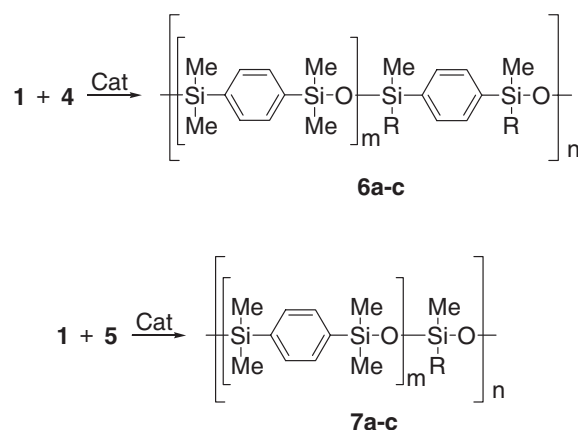
4OMe,a: Yield: 44% (R_f = 0.2). δ : 0.39 (s, 6H, SiCH₃), 0.83 (t, $J = 8.3$ Hz, 4H, SiCH₂), 1.59 (m, 4H, SiCH₂CH₂), [2.55 (q, $J = 2.7$ Hz), 2.71 (q, $J = 4.5$ Hz), 4H, CH₂ in epoxy ring], 3.17 (m, 2H, CH in epoxy ring), [3.34 (q, $J = 6.1$ Hz), 3.66 (q, $J = 3.2$ Hz), 4H, Si(CH₂)₃OCH₂], 3.42 (m, 4H, Si(CH₂)₂CH₂O), 3.55 (s, 6H, SiOCH₃), 7.43 (s, 4H, C₆H₄). Calculated molecular weight: 454.7096. EI-MS (m/z): 454.6972 ([M]⁺), 423.6535 ([M-OMe]⁺).

4OMe,b: Yield: 53% (R_f = 0.4). δ : 0.36 (s, 6H, SiCH₃), 0.72 (t, $J = 8.5$ Hz, 4H, SiCH₂), 1.58–1.75 (m, 12H, SiCH₂(CH₂)₃), [2.39 (q, $J = 2.6$ Hz), 2.67 (q, $J = 3.7$ Hz), 4H, CH₂ in epoxy ring], 3.20 (m, 2H, CH in epoxy ring), 3.58 (s, 6H, SiOCH₃), 7.43 (s, 4H, C₆H₄).

4OMe,c: Yield: 39% (R_f = 0.4). δ : 0.37 (s, 6H, SiCH₃), 0.77, (t, $J = 8.1$ Hz, 4H, SiCH₂), 1.08–2.16 (m, 18H, SiCH₂CH₂ and CH₂CH in cyclohexane ring), 3.10 (m, 4H, CH in epoxy ring), 3.53 (s, 6H, SiOCH₃), 7.46 (s, 4H, C₆H₄).

(Epoxy-functionalized alkyl)methyldimethoxysilanes (5,a-c)

A solution of Pt(0)(DVTMDS)₂ in xylene (0.01 g, 36.0 μ mol) was added to a mixture of dimethoxy-



Scheme 3.

methylsilane (3.82 g, 36.0 mmol) and AGE or EH or VCHE (54.0 mmol) in THF. After stirring at 60 °C, the reaction mixture was filtered by a short florisil column. The products were purified by column chromatography.

5a: Yield: 53% (R_f = 0.5). δ : 0.07 (s, 3H, SiCH₃), 0.95 (t, $J = 7.0$ Hz, 2H, SiCH₂), 1.60 (m, 2H, SiCH₂-CH₂), [2.58 (q, $J = 2.7$ Hz), 2.77 (q, $J = 4.6$ Hz), 2H, CH₂ in epoxy ring], 3.11 (m, 1H, CH in epoxy ring), [3.36 (q, $J = 3.1$ Hz), 3.68 (q, $J = 3.2$ Hz), 2H, Si(CH₂)₃OCH₂], 3.43 (m, 2H, Si(CH₂)₂CH₂O), 3.57 (s, 6H, SiOCH₃).

5b: Yield: 44% (R_f = 0.7). δ : 0.08 (s, 3H, SiCH₃), 0.63 (t, $J = 7.7$ Hz, 2H, SiCH₂), 1.63–1.81 (m, 6H, SiCH₂(CH₂)₃), [2.44 (q, $J = 2.7$ Hz), 2.67 (q, $J = 3.4$ Hz), 2H, CH₂ in epoxy ring], 3.28 (m, 1H, CH in epoxy ring), 3.57 (s, 6H, SiOCH₃).

5c: Yield: 58% (R_f = 0.6). δ : 0.07 (s, 3H, SiCH₃), 0.69, (t, $J = 7.3$ Hz, 2H, SiCH₂), 1.04–2.08 (m, 9H, SiCH₂CH₂ and CH₂CH in cyclohexane ring), 3.11 (m, 2H, CH in epoxy ring), 3.48 (d, 6H, SiOCH₃).

Polymerization

Hetero-condensation routes with the combination of different functional groups with different catalyst were carried out as shown in Scheme 3.

Tin catalyst was selected as a classical catalyst, and tris(pentafluorophenyl)borane was used as a newly developed active catalyst. Typical examples were given.

By Tris(pentafluorophenyl)borane²⁰

To the mixture of **1OH** (0.42 g, 0.30 mmol) or **1OMe** (0.44 g, 0.30 mmol) and **4H** (0.30 mmol) in dry toluene (5 mL), B(C₆F₅)₃ (0.002 g, 3.00 μ mol) was added as the catalyst. After reacting at room temperature for 5 h, the polymer was precipitated into methanol.

For the case of prepolymer **1H** (0.41 g, 0.30 mmol), monomer **4OH** (0.30 mmol) and **4OMe** (0.30 mmol) were used.

6a: Yield: 75%. δ : [0.32 (s, Si(CH₃)₂), 0.38 (s, Si-CH₃), integral area ratio, 26/1], 0.84 (t, $J = 8.1$ Hz, SiCH₂), 1.66 (m, SiCH₂CH₂), [2.64 (q, $J = 2.7$ Hz), 2.84 (q, $J = 4.6$ Hz), CH₂ in epoxy ring], 3.14 (m, CH in epoxy ring), 3.34 (q, $J = 5.9$ Hz), 3.68 (q, $J = 3.1$ Hz), Si(CH₂)₃OCH₂], 3.47 (m, Si(CH₂)₂CH₂O), [7.53 (s, C₆H₄ in TMPS unit), 7.55 (s, C₆H₄ in functionalized unit), integral area ratio, 13/1]. E_{LEM.} A_{NAL.} Calcd for ((C₁₀H₁₆Si₂O)_{13.0}C₂₀H₃₂Si₂O₅): C, 57.78%, H, 7.76%. Found: C, 57.57%, H, 7.68% (from **1OH** and **4H**); C, 58.01, H, 7.84 (from **1H** and **4OH**); C, 58.16, H, 7.81 (from **1H** and **4OMe**).

6b: Yield: 80%. δ : 0.52 (t, $J = 8.2$ Hz, SiCH₂), 1.61–1.86 (m, SiCH₂(CH₂)₃), [2.40 (q, $J = 2.6$ Hz), 2.67 (q, $J_2 = 3.6$ Hz), CH₂ in epoxy ring], 3.20 (m, CH in epoxy ring). Other signals appeared at correspondent reasonable positions.

6c: Yield: 69%. δ : 0.73, (t, $J = 8.5$ Hz, SiCH₂), 1.08–2.23 (m, SiCH₂CH₂ and in cyclohexane ring), 3.12 (m, CH in epoxy ring). Other signals appeared at correspondent positions.

In the synthesis of polymer **7**, since the monomers **5** with –H and –OH functional groups were difficult to get, we used hetero-polycondensation polymerization of **1H** with **5** having –OMe terminal group in the presence of tin catalyst.

7a: Yield: 85%. δ : [0.07 (s, SiCH₃), 0.32 (s, Si(CH₃)₂), integral area ratio, 1/26], 0.88 (t, $J = 7.1$ Hz, SiCH₂), 1.64 (m, SiCH₂CH₂), [2.61 (q, $J = 2.7$ Hz), 2.79 (q, $J = 4.6$ Hz), CH₂ in epoxy ring], 3.15 (m, CH in epoxy ring), [3.30 (q, $J = 3.0$ Hz), 3.75 (q, $J = 3.1$ Hz), Si(CH₂)₃OCH₂], 3.44 (m, Si(CH₂)₂CH₂O), 7.53 (s, C₆H₄). E_{LEM.} A_{NAL.} Calcd for ((C₁₀H₁₆Si₂O)_{13.0}C₇H₁₄SiO₃): C, 57.07%, H, 7.76%. Found: C, 57.35%, H, 7.80%.

7b: Yield: 89%. δ : 0.52 (t, $J = 7.2$ Hz, SiCH₂), 1.47–1.74 (m, SiCH₂(CH₂)₃), 2.33 (q, $J = 2.6$ Hz), 2.56 (q, $J = 3.4$ Hz), CH₂ in epoxy ring], 3.05 (m, CH in epoxy ring). Other signals appeared at correspondent reasonable positions.

7c: Yield: 64%. δ : 0.74, (t, $J = 7.4$ Hz, SiCH₂), 1.09–2.22 (m, SiCH₂CH₂ and CH₂CH in cyclohexane ring), 3.18 (m, CH in epoxy ring). Other signals appeared at correspondent positions.

By Di-*n*-butyltin Dilaurate

Di-*n*-butyltin dilaurate (0.002 g, 3.00 μ mol) was added to a mixture of prepolymer **1OH** (0.42 g, 0.30 mmol) or **1OMe** (0.44 g, 0.30 mmol) and monomer **4OMe** or **4OH** (0.30 mmol) in THF. After stirring at 40 °C, the reaction mixture was filtered by a short Florisil column to separate the catalysts. Removal of the solvent gave the products. The products were purified by reprecipitation from toluene into methanol. The yield of polymers were 34–60%.

Formation of Film and Cross-Linking

Polymer **6a** ($M_n = 6,400$, 0.50 g, 0.32 mmol for epoxy group) obtained by tris(pentafluorophenyl)borane-catalyzed polymerization and 1,4-diaminobenzene (0.017 g, 0.16 mmol–0.0086 g, 0.080 mmol) were dissolved in toluene (5 mL), and cast to obtain a film. When it was difficult to obtain a film directly, the solution was heated at 80 °C for 5 h, then cast, this is the general case. The film was heat-treated further at 80 °C for 24 h under nitrogen.

FT-IR (neat, cm⁻¹): 669, 697, 736, 796, 1080, 1138, 1199, 1260, 1357, 1380, 2956, 3629, 3723.

RESULTS AND DISCUSSION

Synthesis and Characterization

Prepolymers

Poly(silphenylenesiloxane)s have been generally synthesized by homo-condensation reaction of phenylenedisilanol, or hetero-condensation of disilanol with suitable difunctional compound, having chloro-, acetoxy-, amino-, ureido-,^{21,22} or alkoxy- groups. When two different silanols are used, obstacle is often encountered by the contamination of homo-condensed product in the hetero-condensed product, which significantly damages the control of the regular structure of the formed polymers.

To improve the selectivity of hetero-condensation by averting side reactions, **PTMPS** prepolymers with three different terminals, hydroxy, methoxy and hydro groups, were prepared starting from BSB for hetero-polycondensation reaction. By using slightly excess amount of water in the palladium-catalyzed dehydrocoupling polymerization of BSB,^{21,23,24} followed by careful fractional precipitation, prepolymer **1OH** with narrow polydispersity was obtained. In the case of prepolymers **1H**, it was difficult to obtain a prepolymer with controlled high molecular weight from BSB directly (see Table I), and the prepolymer with hydro terminal was obtained by LAH reduction. Prepolymer **1OMe** was obtained by Pd-catalyzed methanolysis of **1H**. Molecular characteristics of prepolymers are summarized in Table I.

All the prepolymers gave reasonable elemental analysis data, when the low molecular weight of the prepolymer is considered. Number-average molecular weight was determined by ¹H NMR for **1H**. The values by SEC and ¹H NMR are quite close. Both prepolymers, **1H** and **1OMe** had almost the same degree of polymerization and narrow polydispersities with the starting **1OH**, determined by SEC, which indicated almost no degradation reaction had occurred during the functional transformation from SiOH to Si-methoxy group through SiH.

Table I. Molecular characteristics of prepolymers and polymers with epoxy side groups

Prepolymers and polymers	Molecular weight ^a		PDI	m/n
	$M_w \times 10^3$	$M_n \times 10^3$		
1H	2.8	2.7 (2.72) ^c	1.04	13/— (13.0/—) ^c
1H* ^b	1.6	1.6	1.01	8/—
1OH	2.9	2.8	1.04	13/—
1OMe	3.0	2.9	1.03	13/—
6a	11.6	6.4	1.81	13/2
6b	17.8	9.8	1.80	13/3
6b* ^d	9.9	6.2	1.59	8/3
6c	12.5	6.8	1.83	13/2
7a	18.6	13.2	1.40	13/5
7b	19.8	17.8	1.11	13/6
7c	14.1	9.9	1.41	13/3
PTMPS	15.3	12.4	1.23	—

^aDetermined by SEC in relation with polystyrene standard.

^bLow molecular weight oligomer was prepared by changing the ratio of SiH and water. ^cCalculated by ¹H NMR spectrum.

^d Starting from low molecular weight oligomer.

Monomers

Monomers containing hydro, hydroxy, and methoxy groups were synthesized starting from 1,4-dibromobenzene. Since only one Si-Cl group of the starting dichlorosilanes is required to be consumed in the Grignard reaction, excess dichlorosilanes were used in the synthesis of **2**. The reaction was controlled to proceed at room temperature within a relatively short reaction time in order to minimize the unexpected disproportionation reaction of the silane derivatives, which is often observed in such reactions involving silanes containing at least one hydro-substituent.^{23–25}

Compound **3** with silane terminal was synthesized by the reduction with LAH. This compound was stable enough in air, and can be used to introduce various functional groups.

Compounds **4** and **5** were prepared by hydrosilylation reaction. Compounds **4**'s with hydroxy and methoxy functional groups were obtained by hydrolysis and methanolysis reaction, respectively. EI-MS analysis of the compounds **4a** indicated the complete conversion of silane group to epoxy-containing side groups.

Polymerization

Hetero-polycondensation reactions were carried out in the presence of tin and borane catalysts. Tin catalyst gave lower yield of the products (39–58%). The process to remove catalyst might be one reason to reduce the yield. ¹H NMR spectra of the polymers prepared under different conditions are compared in Table II and Figure 1.

Table II. Influence of catalyst in the synthesis of poly(silphenylenesiloxane) **6a**

No.	Catalysts	Reaction temperature (°C)	Time (h)	Yield (%)
1)	B(C ₆ F ₅) ₃	r.t.	5	87
2)	di- <i>n</i> -butyltin dilaurate	40	8	58
3)	di- <i>n</i> -butyltin dilaurate	40	8	45
4)	B(C ₆ F ₅) ₃	r.t.	5	89
5)	B(C ₆ F ₅) ₃	r.t.	5	73
6)	B(C ₆ F ₅) ₃	r.t.	5	61
7)	di- <i>n</i> -butyltin dilaurate	40	8	39

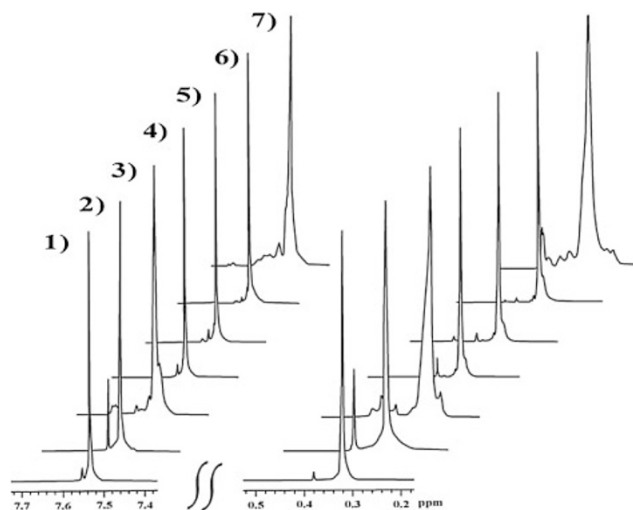


Figure 1. ¹H NMR spectra of polymer **6a** in the methyl and phenyl regions obtained in the hetero-condensation polymerization systems by the combination of:

1) 1OH, **4H**, **a**; **2)** 1OH, **4OH**, **a**; **3)** 1OH, **4OMe**, **a**; **4)** 1H, **4OH**, **a**; **5)** 1H, **4OMe**, **a**; **6)** 1OMe, **4H**, **a**; **7)** 1OMe, **4OH**, **a**.

Combination of functional groups of hydroxy and methoxy in either monomer or prepolymer, catalyzed by tin gave polymers with broad methyl and phenyl signals at 0.33 and 7.55 ppm [**3**] and **7**] in Figure 1] with extra peaks. Especially in **7**), strong peak was seen at 0.42 and 7.57 ppm assignable to **4OH** unit, which was considerably stronger than the calculated value as an ideal copolymer. Homo-condensation of functionalized monomer **4** seemed to have been caused by tin catalyst, resulting in various non-controlled chemical structure of the formed polymer. Combination of silanol and silanol catalyzed by tin [**2**] in Figure 1] gave sharper methyl signal, but considerably strong signal was again seen at 0.42 ppm, indicating the occurrence of homo-condensation of **4**.

When silane functional group was used in either monomer or prepolymer, a clean and sharp methyl

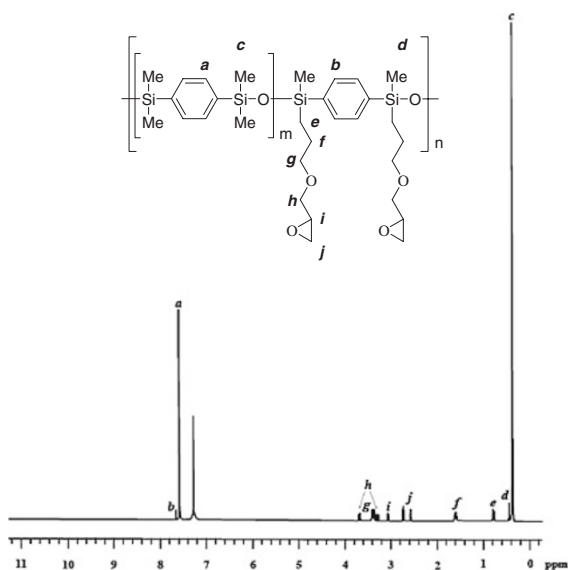


Figure 2. ^1H NMR spectrum of **6a**.

and phenyl signals with ideal area ratio was obtained in higher yield even at room temperature (No. 1: 87; No. 4: 89% in Table II) by the borane catalyst. The integral ratio of peaks at 0.42 and 7.57 ppm to those at 0.33 and 7.55 ppm is consistent with the feed ratio of the prepolymer and monomer by considering the degree of polymerization of the prepolymer. No homo-condensation of **1OH** was observed (No. 1). Elemental analysis of the polymer reasonably well coincided with the calculated value within experimental error. Elemental analysis of the polymer from **1H** and **4OH,a** deviated a little more from the calculated value. Homo-condensation of **4OH,a** might have occurred to a small extent (No. 4). Homocondensation of **4,a** were completely suppressed by using **4OMe,a** (No. 5), or **4H,a** (No. 6). However, the yield was rather lower in these combinations compared with No. 1 and No. 4, and the deviation of the elemental analysis was a little bigger. The ^1H NMR signal contained small impurity peaks. Some unknown side reaction might have occurred. So, we chose tris(pentafluorophenyl)borane as an excellent catalyst to synthesize polymers with regulated sequence using the combination of **1OH** and **4H**.

The hetero-condensation polymerization of prepolymer **1** with compounds **4** and **5** gave smoothly polymer **6** and **7**. The yield was rather poor for cyclohexene oxide substituted **4c** or **5c**. Some steric hindrance might be operating. Typical spectra were given for **6a** and **7a** (Figures 2 and 3).

Distinct difference in ^1H NMR between **6a** and **7a** can be observed at methyl signals as shown in Figure 3. Methyl protons in functionalized unit of polymer **6a** appeared at 0.41 ppm, and that of polymer **7a** appeared at 0.07 ppm. This fact also supports the

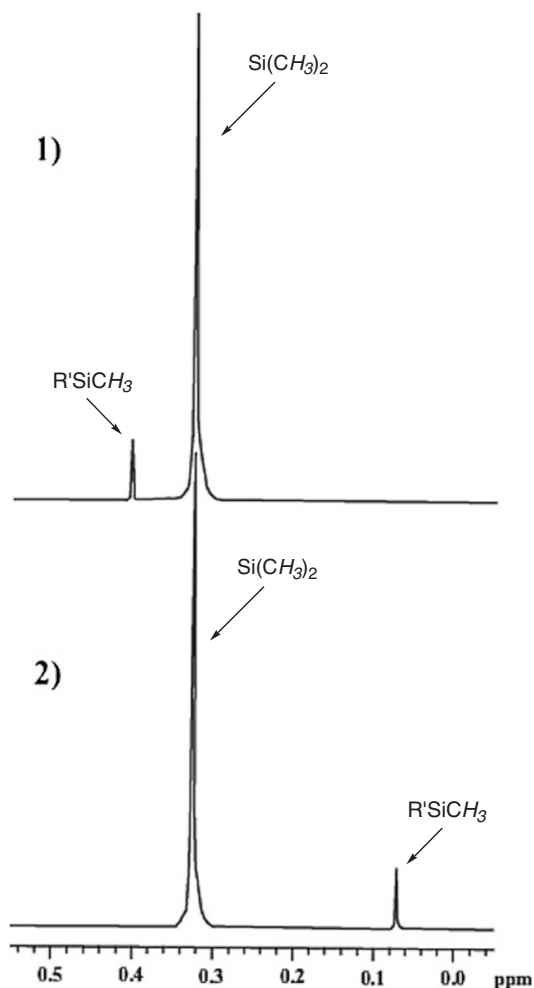


Figure 3. ^1H NMR spectra of the methyl region of **1** (polymer **6a**) and **2** (polymer **7a**).

complete alternative structure of the polymers **6a** and **7a**. Thus, NMR confirmed the exactly alternating structure of polymer **6a** and **7a**. The functional units are very well dispersed in the polymer chain.

Polymers with epoxy groups, **6** and **7**, are white powder after precipitation in methanol at room temperature. Characteristic data of the polymers are also summarized in Table I.

It was established that the tris(pentafluorophenyl)borane was an excellent catalyst to synthesize **PTMPS** with controlled amounts of epoxy groups in regular structure.

Cross-Linking

The epoxy functional groups can be used to form cross-linked structures, which can be coat on the surface of the materials to make the films. Cross-linked poly(silphenylenesiloxane) was obtained from **6a** and 1,4-diaminobenzene as a cross-linker. The slightly cross-linked film was further cross-linked by heating for 18 h at 80 °C to give film with improved mechanical strength (self standing stretchable).

In **6a**, cross-linked (1:1) system, obtained with the 1:1 molar ratio of monomer unit and 1,4-diaminobenzene (1:1 for epoxide and *p*-NH; 1 to 2 for epoxide and all NH), the NH stretching of primary amino group in the initially mixed polymer system at 3420 and 3580 cm⁻¹ became weaker by preheating, and became to a further weaker peak at 3345 cm⁻¹ in polymer film, and new broad peak appeared at around 3550–3700 cm⁻¹ assignable to OH stretching. This indicated the opening of epoxy ring, but the existence of remaining primary amino group, which was an evidence for the existence of free primary amino group on one terminal of 1,4-diaminobenzene, suggested incomplete cross-linking of the system.

In cross-linked **6a**, cross-linked (2:1) obtained with 2:1 molar ratio for epoxy and amino functional groups (1:1 for epoxide and NH), the NH stretching of primary amino group has almost completely disappeared. The cross-linking reaction seemed to have occurred, unfortunately, characteristic CH stretching vibration of epoxy ring to determine the extent of the reaction of epoxy group could not be clearly identified because of the overlapping with aromatic CH stretching.

Melting and Thermal Degradation Behavior

Heat of melting and thermal degradation behavior of prepolymers, polymers and cross-linked polymers are shown in Table III.

The prepolymers showed melting points at around 80–110 °C. The ΔH_{melt} was similar to that of **PTMPS** ($T_g = -22$ °C, $T_m = 110.8$ °C). They decomposed at around 330–340 °C in air and 370–395 °C in nitrogen.

Introduction of epoxide groups through tetramethylene spacer (1/14 and 1/9 per phenylenedisiloxane repeating unit in prepolymer **1H** and **1H***) to the polymer structure (**6b** and **6b***) increased the melting temperature a little, but reduced the melting enthalpy to around 20 J/g from 42.5 J/g of non-modified polymer (**PTMPS**). The polymers did not show T_g at around -40 ~ -20 °C. Introduction of epoxide through trimethyleneoxymethylene spacer, or cyclohexene oxide through ethylene spacer showed only small effects on the property of the polymers **6a** and **6c**. Introduction of siloxane linkage to the polymer structure (**7**) slightly influenced the property of the polymer.

TGA curves of polymers under nitrogen atmosphere and in air at a heating rate of 10 °C/min are shown in Figure 4.

It can be seen that a smooth single-step degradation process occurred in nitrogen, but a little complex multi-step processes in air. The results were also summarized in Tables III.

Poly(silphenylenedisiloxane)s having epoxy side groups generally exhibited lower degradation onset

Table III. Heat of melting and thermal degradation behaviors of prepolymers, polymers and cross-linked polymers

Compounds	T_m^a (°C)	ΔH_{melt} (J/g)	Onset of degradation		Residue at 800 °C (%)	
			$T_{\text{d,onset}}$ (°C) ^b		In air	In N ₂
			In air	In N ₂	In air	In N ₂
1H	89.0	46.8	337	394	32	30
1H* ^c	78.4	47.3	330	370	34	25
1OH	110.0	48.2	341	381	37	33
1OMe	95.6	46.9	334	374	31	30
6a	119.3	28.4	374	425	36	30
6b	118.1	21.2	375	452	43	37
6b* ^d	104.6	25.2	310	327	29	32
6c	108.5	18.8	353	364	34	30
7a	115.8	35.4	359	310	36	30
7b	122.6	35.0	364	350	44	35
7c	110.6	27.3	319	300	31	34
6a,cross-linked (1:1)	—	—	450	490	65	37
6a,cross-linked (2:1)	—	—	421	470	60	40
PTMPS	110.8	42.5	390	423	31	37

^aDetermined by DSC. ^bThe temperature at 5% weight loss.

^{c,d}See comments b, c in Table I.

temperature than **PTMPS**, probably by the enhanced degradation initiated by the ring-opening of epoxy functional groups. Glycidylpropyl and 3-(2,3-epoxycyclohexyl-1-yl) groups seemed to be the most easily degraded among the epoxy groups studied. Nevertheless, it is noticeable that the polymer **6b** with tetramethylene spacer groups showed the highest, or close to the highest onset temperature of degradation and residual yield both in air (375 °C, 43%) and nitrogen (452 °C, 37%).

The polymers seemed to have completely degraded during the heating process in both air and nitrogen and showed similar residual yield with **PTMPS** except for **6b** and **7b** in air. After undergoing thermal degradation process in air, the residue of every polymer is white hard solid, which looks quite different from the black residue under nitrogen.⁹ The white residue is considered to be silica formed from the thermo-oxidative degradation in air. Polymer **6b*** with higher concentration of epoxy group showed the lower onset temperature. Certain length of silphenylene siloxane units without perturbation of the structure seems to be necessary.

The cross-linked film **6a,cross-linked (1:1)** showed the onset temperature of degradation at 450 °C in air and 490 °C in nitrogen, which were much higher than those of **6a**. The residual yield in air (65%) became considerably higher than that of non-cross-linked polymer. Thermal properties of **6a, cross-linked (1:1)** and **6a,cross-linked (2:1)** were similar.

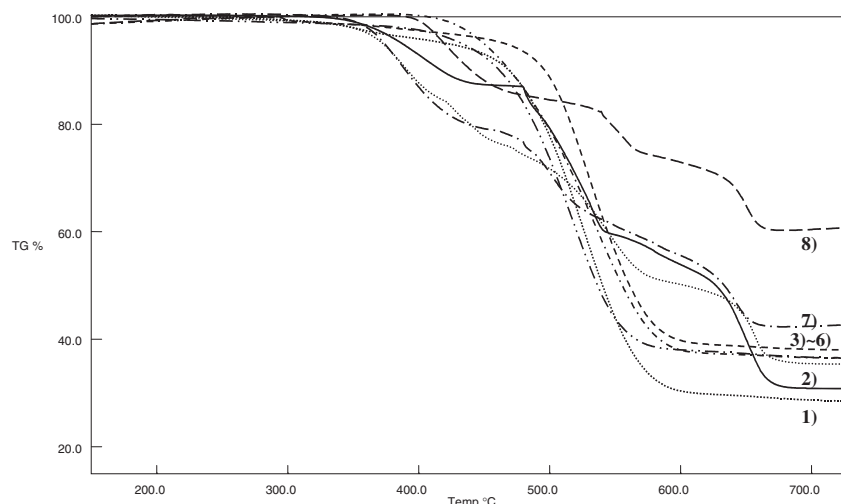


Figure 4. TGA* curves of poly(silphenylenesiloxane)s with epoxy side groups in air and in nitrogen.

*Measurements were carried out with a heating rate of 10 °C/min on about 5 mg sample.

- 1) --- 6a in nitrogen;
- 2) — PTMPS in air;
- 3) ... 6a in air;
- 4) -·- PTMPS in nitrogen;
- 5) --- 6b in nitrogen;
- 6) -- 6a,cross-linked (2:1) in nitrogen;
- 7) —·- 6b in air;
- 8) ——— 6a,cross-linked (2:1) in air.

CONCLUSIONS

Poly(silphenylenesiloxane)s containing epoxy functional side groups were successfully synthesized by polycondensation of silane, silanol, and methoxysilane functional groups of silphenylenesiloxane prepolymer and monomers with epoxy functional groups. Tris(pentafluorophenyl)borane was the most suitable catalyst in the hetero polycondensation reactions when silane functional group was used in monomer together with prepolymer having silanol terminal groups. Cross-linking of the film gave self-supporting film with higher thermal stability.

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