

Crosslinked Polycarbosilanes. Synthesis and Properties

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ABSTRACT: New crosslinked polycarbosilanes (PCSs) having biphenyl, biphenyl ether and naphthalene linkages, were synthesized by hydrosilylation reaction between multi-functional vinylsilanes and hydrosilanes. The PCSs were transparent rigid material without cracks or bubbles. The mechanical properties and glass transition temperatures (T_g s) of the PCSs were evaluated by flexural tests and differential scanning calorimeter (DSC) or dynamic mechanical analysis (DMA). Crosslinked PCSs **VIII–X** with high network chain density and rigid-rod spacers had T_g s at around 250°C and high flexural strength in the range of 75–96 MPa. 5% weight loss temperatures of PCSs under nitrogen ranged from 490°C to 544°C.

KEYWORDS Polycarbosilane / Crosslinked Polymer / Hydrosilylation Reaction / Mechanical Behavior / Thermal Property / Network Chain Density / Rigid-Rod Spacer /

Much attention has been focused on the structures and properties of polycarbosilanes (PCSs), containing Si–C bonds in polymer backbones.^{1–3}

Recently, the authors reported the synthesis and properties of linear PCSs produced by hydrosilylation polymerization.^{4,5} The synthesis and applications of crosslinked PCSs have been reported by Friedmann by hydrosilylation reaction and various carbon-based compounds as monomers which have vinyl groups.⁶

We demonstrated that the high network chain density and rigid-rod unit, [Si(Me)₂-*p*-C₆H₄-Si(Me)₂], was necessary to give high mechanical strength to crosslinked PCSs (Table I, PCS **II**).⁷ The present investigation obtained crosslinked PCS having a high T_g and good mechanical properties by introducing of rigid-rod spacer units, biphenyl and naphthalene linkages to PCS monomers. At first, spacer structures were optimized to increase T_g s and flexural properties, and network chain density was optimized. This article reports the synthesis of novel vinylsilanes and hydrosilanes. The mechanical properties and thermal stability are described.

EXPERIMENTAL

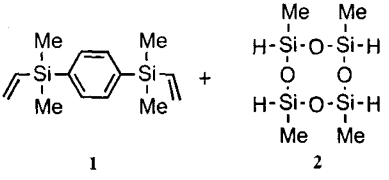
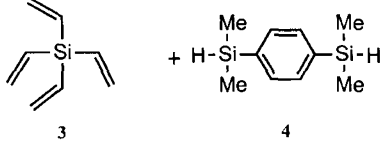
Molecular Characterization

¹H NMR spectra were recorded in CDCl₃ on a Bruker AMX-400. The high-resolution solid-state ²⁹Si NMR spectra were obtained by the combined use of dipolar-decoupling (DD) and magic-angle spinning (MAS).^{8,9} Spinning frequency was 5.0 kHz. Mass spectra were obtained on a Shimadzu GCMS QP-2000 A.

Thermal Characterization

Glass-transition temperatures were determined using a Shimadzu differential scanning calorimeter (DSC-50). Samples (5 mg) were used, and data from the second heating run were reported for a heating rate of 20°C min⁻¹ and a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 thermal analyzer at heating rate of 20°C min⁻¹ under a nitrogen atmosphere. Temperatures at 5% weight loss, T_{d5} , were noted.

Table I. Flexural properties and T_g s of crosslinked PCSs at 23°C

	Combinations of monomers	T_g / °C ^a	Modulus of elasticity / GPa	Maximum strength / MPa	Maximum strain / %
PCS I		85	1.55	47.4	5.0
PCS II		97	2.02	73.2	5.4

^a By DSC.

Mechanical Characterization

A three-point bending test was performed with a Shimadzu AUTO-GRAPH at maximum load cell of 100 kg, and a cross-head speed of 0.9 mm min^{-1} (JIS K 7203). The test at 200 or 250°C was performed 10 min later at setting specimen. Specimens, bars ($4.0 \times 0.6 \times \sim 0.14 \text{ cm}$), were cut from the cured sample by a cutter with a diamond-blade. DMA (dynamic mechanical analysis) was performed with a ITK DVA-200 in tensile mode at oscillation frequency of 10 Hz. The heating rate was $4^\circ \text{C min}^{-1}$.

Materials

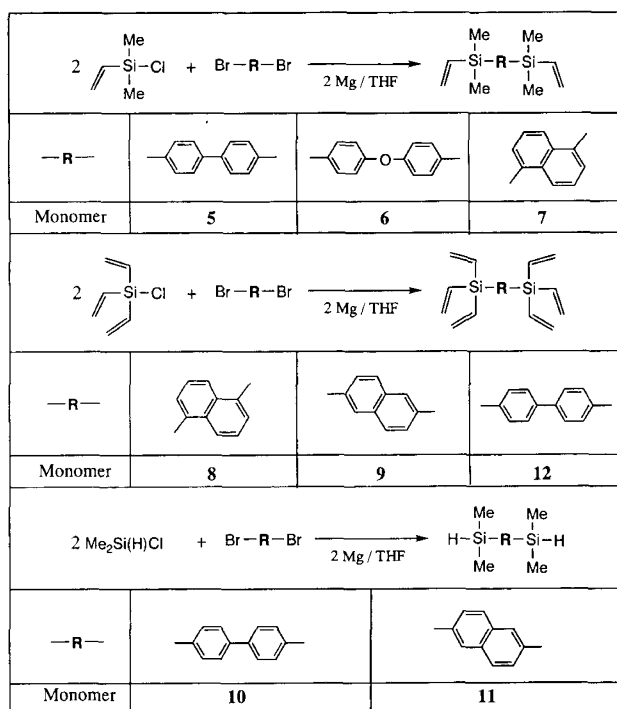
Dimethylvinylchlorosilane, dimethylchlorosilane and 1,3,5,7-tetramethylcyclotetrasiloxane (2) were purchased from Shin-Etsu Chemical Co., Ltd. Trivinylchlorosilane was purchased from Gelest Inc. 4,4'-dibromobiphenyl, 4-bromobiphenylether, dimethyl maleate and Mg were purchased from TOKYO KASEI Co., Ltd. 1,5-dibromonaphthalene and 2,6-dibromonaphthalene were from HODOGAYA CONTRACT LABORATORY Co., Ltd. Tetrahydrofuran (THF, Nacalai Tesque Co., Ltd.) was dried over Na/benzophenone and distilled before use during synthesis of monomer. The platinum catalyst $[\text{Pt} \{(\text{CH}_2=\text{CHSiMe}_2\text{O})_2\}]$ (3.0 wt% Pt) was purchased from Degussa Co., Ltd.

Synthesis of Monomer

The monomers (5)–(12) were synthesized following the same experimental procedure⁵ shown in Scheme 1.

4,4'-Bis(dimethylvinylsilyl)biphenyl (5)

In a 200-mL three-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar, a



Scheme 1. Synthesis of PCS monomers.

dropping funnel and a reflux condenser were placed magnesium turnings (1.0 g, 41 mmol), dimethylvinylchlorosilane (5.0 g, 41 mmol), and THF (20 mL). A solution of 4,4'-dibromobiphenyl (6.4 g, 21 mmol) in 50 mL of THF was slowly added for 1 h at room temperature. The mixture was stirred for 4 h under reflux and 12 h at room temperature. Hexane and water were added to the reaction mixture. The organic layer was separated and washed with brine. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvents were removed by evaporation under reduced pressure. Distillation of the residue under reduced pressure ($135-140^\circ \text{C}/0.3 \text{ mmHg}$) gave 2.6 g (39%) of (5).

GC/MS (*m/e*, %) 322 (M^+ , 34), 307 ($M^+ - 15$, 94), 59 (100). $^1\text{H NMR}$ (CDCl_3) δ 0.37 (s, SiCH_3 , 12H), 5.78 (dd, $\text{CH}_2=\text{CH}-$, *trans*, $J = 20$, 4 Hz, 2H), 6.07 (dd, $\text{CH}_2=\text{CH}-$, *cis*, $J = 15$, 4 Hz, 2H), 6.31 (dd, $\text{CH}_2=\text{CH}-$, $J = 20$, 15 Hz, 2H), 7.58 (d, aromatic, 8H).

Bis(4-dimethylvinylsilylphenyl)ether (6)

Monomer (6) was synthesized in a similar manner for (5). Magnesium turnings (2.5 g, 105 mmol), dimethylvinylchlorosilane (12.4 g, 103 mmol), and 4-bromobiphenylether (16.9 g, 52 mmol) were used. Distillation of the residue under reduced pressure ($150-160^\circ \text{C}/2.7 \text{ mmHg}$) gave a colorless oil 7.4 g (42%) of (6).

GC/MS (*m/e*, %) 338 (M^+ , 23), 323 ($M^+ - 15$, 100), 85 (10).

1,5-Bis(dimethylvinylsilyl)naphthalene (7)

Monomer (7) was synthesized in a similar manner for (5). Magnesium turnings (2.5 g, 105 mmol), dimethylvinylchlorosilane (12.4 g, 103 mmol), and 1,5-dibromonaphthalene (14.7 g, 52 mmol) were used. Distillation of the residue under reduced pressure ($144-160^\circ \text{C}/3.7 \text{ mmHg}$) gave 5.8 g (38%) of (7).

GC/MS (*m/e*, %) 338 (M^+ , 23), 323 ($M^+ - 15$, 100), 85 (10).

1,5-Bis(trivinylsilyl)naphthalene (8)

Monomer (8) was synthesized in a similar manner for (5). Magnesium turnings (3.6 g, 147 mmol), trivinylchlorosilane (21.3 g, 147 mmol), and 1,5-dibromonaphthalene (20.0 g, 70 mmol) were used. Distillation of the residue under reduced pressure ($144-147^\circ \text{C}/0.4 \text{ mmHg}$) gave 11.0 g (46%) of (8); mp, 54°C .

GC/MS (*m/e*, %) 344 (M^+ , 15), 317 ($M^+ - 27$, 11), 235 ($M^+ - 109$, 22), 83 (100). $^1\text{H NMR}$ (CDCl_3) δ 5.86 (dd, $\text{CH}_2=\text{CH}-$, *trans*, $J = 20$, 4 Hz, 6H), 6.22 (dd, $\text{CH}_2=\text{CH}-$, *cis*, $J = 15$, 4 Hz, 6H), 6.47 (dd, $\text{CH}_2=\text{CH}-$, $J = 20$, 15 Hz, 6H), 7.43 (dd, aromatic, $J = 7$, 8 Hz, 2H), 7.77 (d, aromatic, $J = 7$ Hz, 2H), 8.19 (d, aromatic, $J = 8$ Hz, 2H).

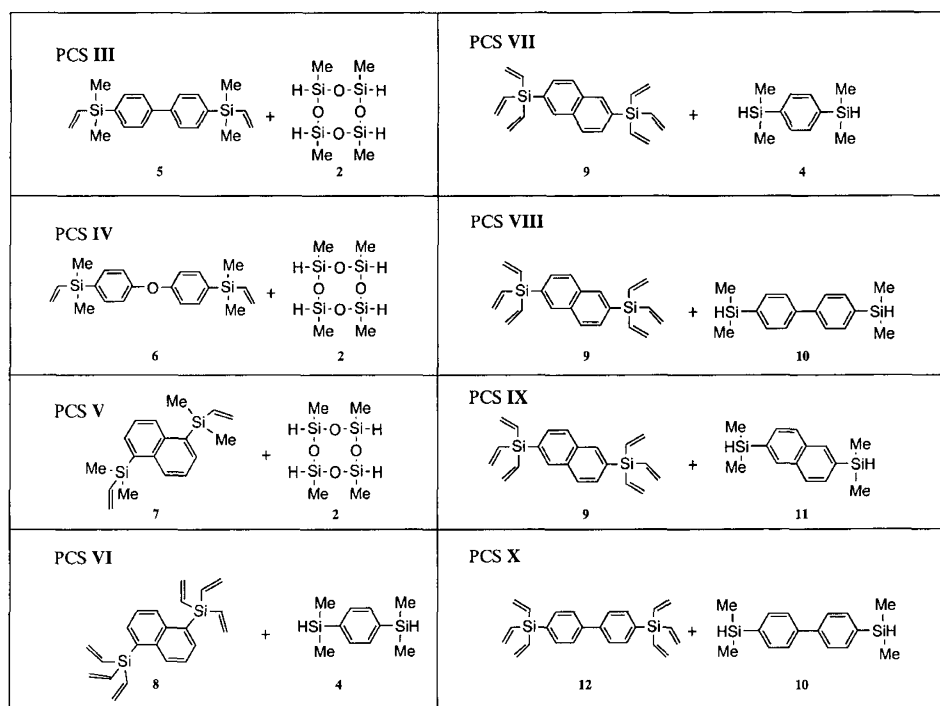
2,6-Bis(trivinylsilyl)naphthalene (9)

Monomer (9) was synthesized in a similar manner for (5). Magnesium turnings (3.6 g, 147 mmol), trivinylchlorosilane (21.3 g, 147 mmol), and 2,6-dibromonaphthalene (10.0 g, 35 mmol) were used. Distillation of the residue under reduced pressure ($140^\circ \text{C}/0.4 \text{ mmHg}$) gave

Table II. Preparation of crosslinked PCSs ^a

	PCS monomers		Pt cat. ^b ($\times 10^{-5}$)	DM ^c	THF / mL
	Si-vinyl, g / mmol	Si-H, g / mmol			
PCS III	5,3.64 (11.3)	2,1.36 (5.7)	10	100	5
PCS IV	6,3.69 (10.9)	2,1.31 (5.5)	1	100	5
PCS V	7,3.56 (12.0)	2,1.44 (6.0)	1	100	5
PCS VI	8,1.54 (4.5)	4,2.60 (13.4)	1	100	3
PCS VII	9,1.54 (4.5)	4,2.60 (13.4)	1	100	3
PCS VIII	9,1.04 (3.0)	10,2.39 (8.8)	1	100	3
PCS IX	9,1.11 (3.2)	11,2.33 (9.5)	1	100	3
PCS X	12,1.37 (3.7)	10,2.92 (10.8)	1	100	4

^a Curing conditions: PCS III–V: 50°C / 17 h → 80°C / 5 h → 100°C / 21 h → 150°C / 24 h (in air), PCS VI, VII: 50°C / 20 h → 80°C / 8 h → 100°C / 16 h → 150°C / 24 h (in air) → 100°C / 1 h → 250°C / 1 h (in N₂), PCS VIII, IX: 50°C / 19 h → 80°C / 11 h → 100°C / 13 h → 150°C / 24 h (in air) → 100°C / 1 h → 250°C / 1 h (in N₂), PCS X: 50°C / 22 h → 80°C / 10 h → 100°C / 14 h → 150°C / 24 h (in air) → 100°C / 1 h → 280°C / 1 h (in N₂). ^b Pt[(CH₂=CHMe₂Si)₂O]₂, the mole equivalent rel. to the vinyl substituents of the Si-vinyl monomers. ^c Relative amount of dimethylmaleate (DM) to platinum catalyst.

**Scheme 2.** Preparation of crosslinked PCSs III–X.

3.4 g (28%) of (9); mp, 28°C.

GC/MS (m/e, %) 344 (M⁺, 42), 317 (M⁺–27, 11), 235 (M⁺–109, 54), 83 (100). ¹H NMR (CDCl₃) δ 5.88 (dd, CH₂=CH–, *trans*, J = 20, 4 Hz, 6H), 6.26 (dd, CH₂=CH–, *cis*, J = 15, 4 Hz, 6H), 6.42 (dd, CH₂=CH–, J = 20, 15 Hz, 6H), 7.63 (d, aromatic, J = 8 Hz, 2H), 7.85 (d, aromatic, J = 8 Hz, 2H), 8.06 (s, aromatic, 2H).

4,4'-Bis(trivinylsilyl)biphenyl (12)

Monomer (12) was synthesized in a similar manner for (5). Magnesium turnings (3.4 g, 141 mmol), trivinylchlorosilane (27.8 g, 192 mmol), and 4,4'-dibromobiphenyl (20.0 g, 64 mmol) were used. Distillation of the residue under reduced pressure (160°C/1.1 mmHg) gave a colorless oil 7.9 g (30%) of (12).

GC/MS (m/e, %) 370 (M⁺, 60), 343 (M⁺–27, 49), 261 (100). ¹H NMR (CDCl₃) δ 5.88 (dd, CH₂=CH–, *trans*, J

= 19, 4 Hz, 6H), 6.26 (dd, CH₂=CH–, *cis*, J = 15, 4 Hz, 6H), 6.39 (dd, CH₂=CH–, J = 19, 15 Hz, 6H), 7.64–7.65 (aromatic, 8 H).

4,4'-Bis(dimethylsilyl)biphenyl (10)

In a 500-mL three-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar, a dropping funnel and a reflux condenser were placed magnesium turnings (3.4 g, 141 mmol), dimethylchlorosilane (18.2 g, 192 mmol), and THF (50 mL). A solution of 4,4'-dibromobiphenyl (20.0 g, 64 mmol) in 140 mL of THF was slowly added for 3 h at room temperature. The mixture was stirred for 8 h under reflux. To this was added dry hexane, and the salt formed was filtered off. The solvents were evaporated under reduced pressure. Distillation of the residue under reduced pressure (140–150°C/2.0 mmHg) gave a colorless oil 10.6 g (58%) of (10).

GC/MS (m/e, %) 270 (M⁺, 42), 269 (M⁺–1, 16), 255

($M^+ - 15$, 61), 211 (100). $^1\text{H NMR}$ (CDCl_3) δ 0.43 (d, SiCH_3 , $J=4$ Hz, 12H), 4.35 (sept., Si-H , $J=4$ Hz, 2H), 7.63–7.70 (aromatic, 8H).

2,6-Bis(dimethylsilyl)naphthalene (11)

Monomer (11) was synthesized in a similar manner for (10). Magnesium turnings (3.4 g, 141 mmol), dimethylchlorosilane (18.2 g, 192 mmol), and 2,6-dibromonaphthalene (18.3 g, 64 mmol) were used. Distillation of the residue under reduced pressure (90°C/0.3 mmHg) gave a colorless oil 8.6 g (55%) of (11).

GC/MS (m/e, %) 244 (M^+ , 17), 229 ($M^+ - 1$, 17), 185 (100). $^1\text{H NMR}$ (CDCl_3) δ 0.44 (d, SiCH_3 , $J=4$ Hz, 12H), 4.57 (sept., Si-H , $J=4$ Hz, 2H), 7.62 (d, aromatic, $J=8$ Hz, 2H), 7.84 (d, aromatic, $J=8$ Hz, 2H), 8.04 (s, aromatic, 2H).

Preparation of Crosslinked PCS (Table II)

PCS III–PCS X was prepared in a similar manner as follows (Scheme 2).

Monomer (5) (3.64 g, 11.3 mmol), monomer (2) (1.36 g, 5.7 mmol), dimethyl maleate (33 mg), and Pt catalyst (23 mg, 9.71×10^{-5} mmol mg^{-1}) were dissolved in THF (2 mL). The solution was poured into a metal can (67 mm in diameter; 5 mm in depth), the inner surface of which was covered with polyimide film (APICAL 25 AH, Kaneka Corporation) so as to remove the cured specimen without difficulty. The can was covered with a lid and placed in an oven at 50°C for 17 h, and additionally heated stepwise (80°C/5 h → 100°C/21 h → 150°C/24 h). The cured sample (1.2 mm thickness) was transparent without cracks or bubbles. Gel content was 100% as measured as follows: A piece of cured specimen (*ca.* 200 mg) wrapped in a stainless steel net was immersed in THF (*ca.* 200 mL) for 12 h. Gel content here was defined as residual weight of the sample after dipping and drying (100°C/4 h). Other crosslinked PCS samples were

prepared in a similar manner.

RESULTS AND DISCUSSION

Synthesis of Monomer

Carbosilane monomers (5)–(12) were prepared Grignard reaction using chlorosilanes and dibrominated-aromatic compounds as starting materials (Scheme 1). Yields of the monomers were low, and isolated yield of (9) was only 28% (see EXPERIMENTAL Section). Mono-substituted compounds were obtained as by-products in all reactions, probably due to the low reactivity of Grignard reagents. The lithium reagents of the dibrominated species may thus lead to high yields of carbosilane monomers.

Preparation of Crosslinked PCSs

Crosslinked PCSs (Scheme 2) were prepared using hydrosilylation curing reaction between multi-functional vinylsilanes and hydrosilanes (Table II, see EXPERIMENTAL Section). Curing reaction was performed with, by casting, heating stepwise (50/80/100/150°C or 250°C). Hydrosilylation reactions were catalyzed by the 1,3-divinyltetramethyldisiloxane-platinum complex (Karsstedt's catalyst).¹⁰ Crosslinked PCSs were transparent

Table III. Physical properties of crosslinked PCSs^a

	Appearance	$T_g / ^\circ\text{C}$	Gel content / %
PCS III	Transparent, rigid	136 ^b	100
PCS IV	Transparent, rigid	32 ^b	94
PCS V	Transparent, rigid	65 ^b	96
PCS VI	Transparent, rigid	183 ^c	100
PCS VII	Transparent, rigid	218 ^c	100
PCS VIII	Transparent, rigid	250 ^c	100
PCS IX	Transparent, rigid	200 ^c	100
PCS X	Transparent, rigid	257 ^c	100

^a Structures are shown in Scheme 1. ^b By DSC. ^c By DMA.

Table IV. Flexural properties of crosslinked PCS III–V at 23°C

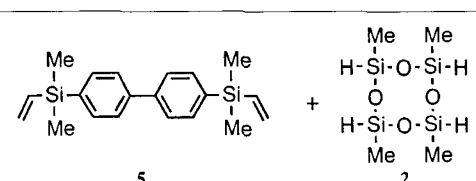
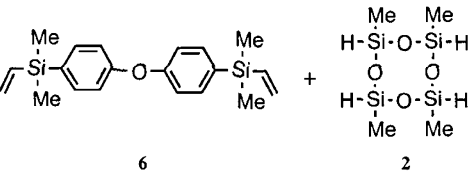
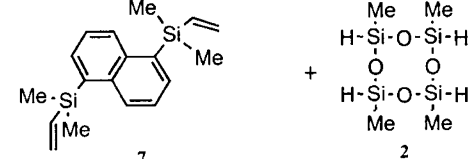
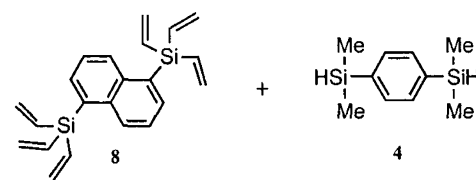
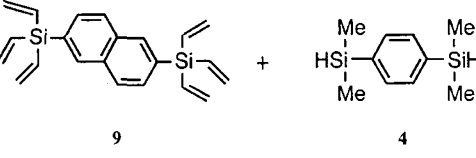
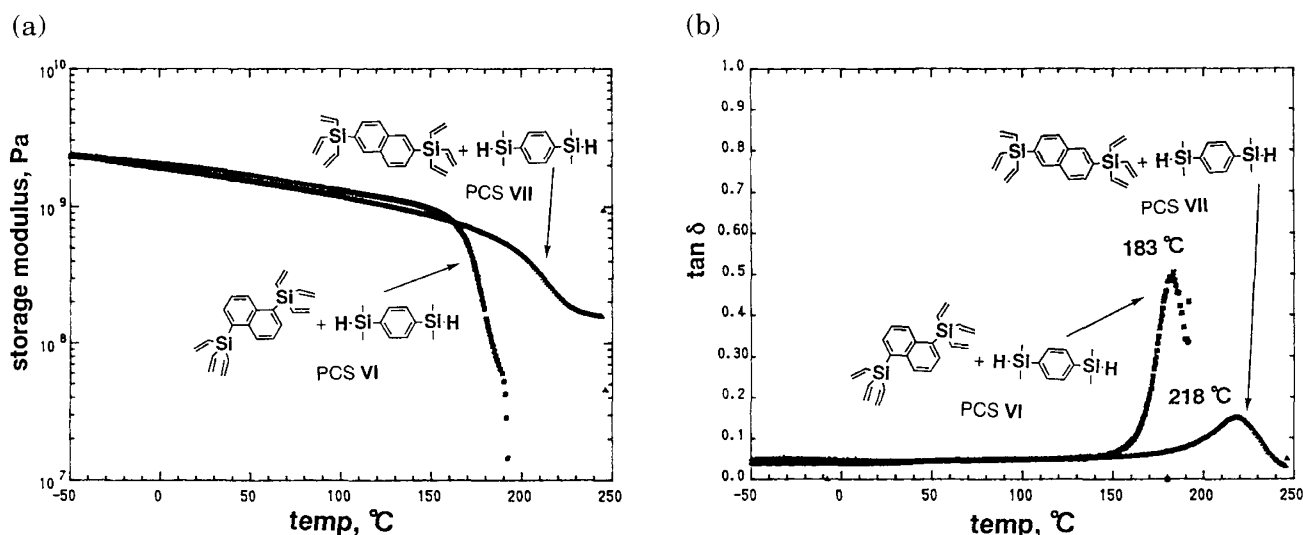
	Combinations of monomers	Modulus of elasticity / GPa	Maximum strength / MPa	Maximum strain / %
PCS III		1.47	58.7	7.5
PCS IV		0.33	8.0	6.0
PCS V		2.29	69.7	5.0

Table V. Flexural properties of crosslinked PCS **VI** and **VII** at 23°C

	Combinations of monomers	Modulus of elasticity / GPa	Maximum strength / MPa	Maximum strain / %
PCS VI	 8 + 4	2.00	67.6	6.3
PCS VII	 9 + 4	1.80	61.5	6.8

**Figure 1.** Dependence of (a) storage modulus and (b) $\tan \delta$ on temperature for PCS **VI** and PCS **VII** measured at 10 Hz.

and rigid materials without cracks. Gel content of obtained PCSs was almost 100%.

Properties and Structures of Crosslinked PCSs

The authors reported T_g s and flexural properties of PCS **I** and **II** (Table I).⁷ High network chain density and rigid-rod unit [Si(Me)₂-*p*-C₆H₄-Si(Me)₂] were found necessary to give high mechanical strength to crosslinked PCSs. Spacer structures were initially optimized to increase T_g s and flexural properties, and then network chain density. T_g s were evaluated by DSC or DMA and flexural properties by a three-point bending test (see EXPERIMENTAL Section).

Table III shows T_g s, and Table IV, the influence of structures of spacers on flexural properties. Using monomer (5), for PCS **III**, T_g increased largely and maximum strength increased slightly compared with the conventional system (PCS **I**). Using monomer (6), in the case of PCS **IV**, T_g and maximum strength decreased largely, this possibly related to the high flexibility of ether linkage unit of the monomer (6). Maximum strength of PCS **V** improved compared with PCS **I**, T_g decreased slightly.

To improve flexural properties, the introduction of biphenyl and naphthalene linkage was effective.

Table V shows the flexural properties of PCS **VI** and **VII**. The influence of the following on properties was evaluated: 1) introduction of trivinylsilyl groups to the naphthalene monomers, and 2) positions of trivinylsilyl groups, 1,5-substitution or 2,6-substitution. T_g s of PCSs were not observed by DSC. Therefore, DMA was used. Figure 1 provides plots of (a) storage modulus and (b) $\tan \delta$ against temperatures for PCS **VI** and PCS **VII**. The storage modulus indicates static mechanical strength and a peak of $\tan \delta$ corresponds to a T_g by DSC. The storage modulus of PCS **VII** obtained using 2,6-substituted monomer (9), descended slower compared with PCS **VI**. The peak of $\tan \delta$ of PCS **VII** shifted to higher temperature, because the 2,6-substituted monomer (9) had higher linearity compared with the 1,5-substituted monomer (8). The same was reported for carbon-based polymer, polyamide.¹¹ Maximum strength of PCS **VI** and **VII** was 68 MPa, 62 MPa, respectively (Table V).

The structures of spacer units were optimized to in-

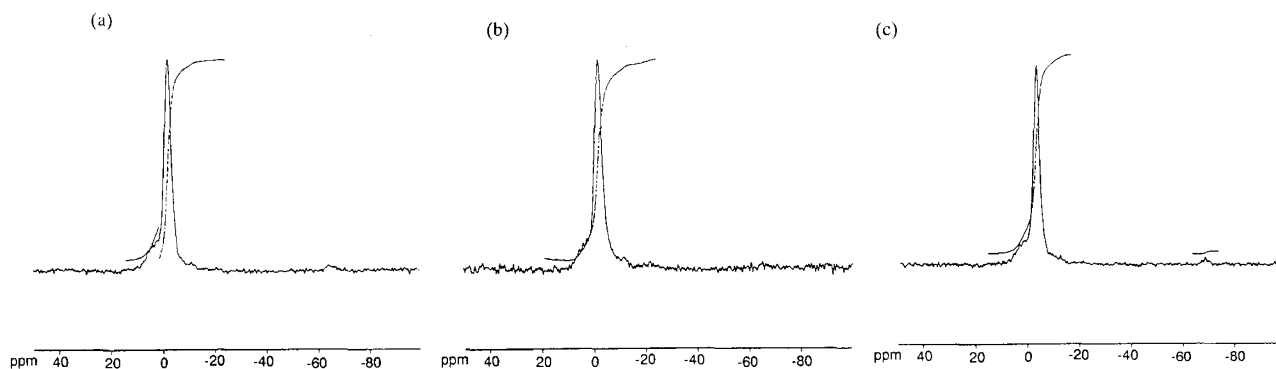


Figure 2. ^{29}Si DD/MAS spectra of (a) PCS VIII, (b) PCS IX, and (c) PCS X.

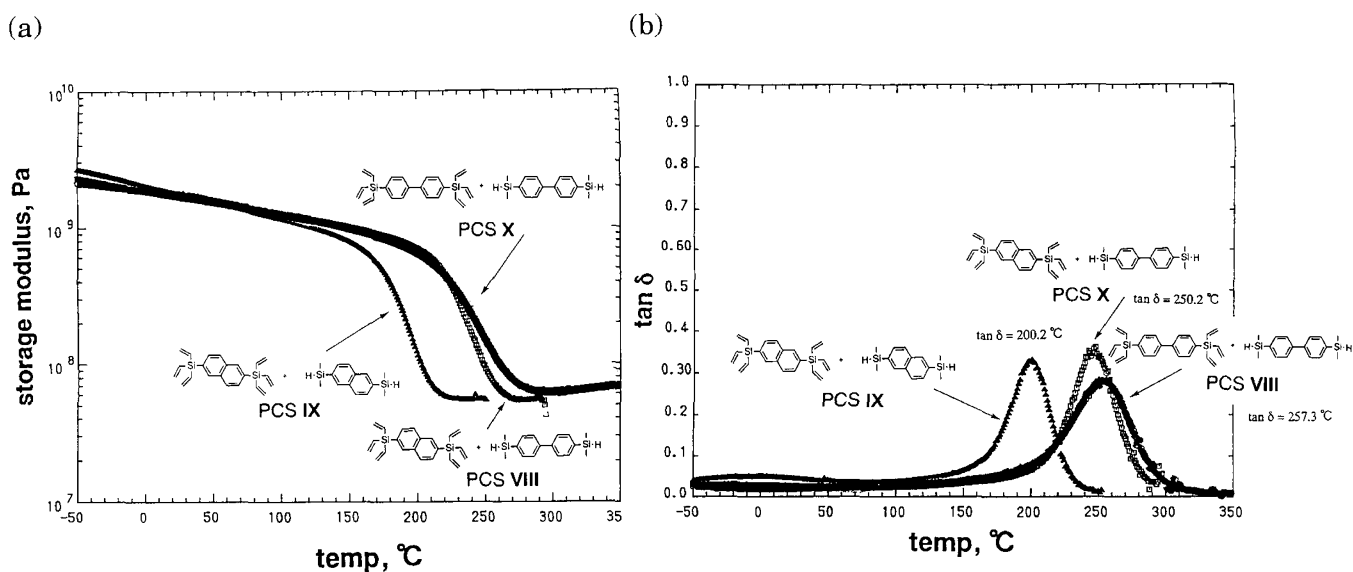
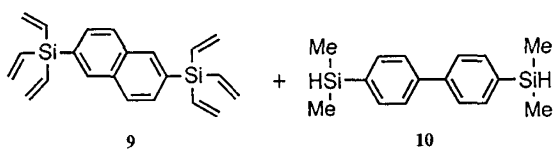
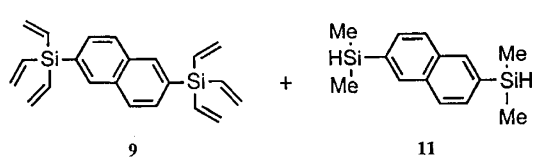
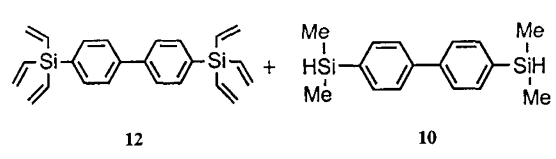


Figure 3. Dependence of (a) storage modulus and (b) $\tan \delta$ on temperature for PCS VIII–PCS X measured at 10 Hz.

Table VI. Flexural properties of crosslinked PCS VIII–X at 23, 200, and 250°C, respectively.

	Combinations of monomers	Conditions	Modulus of elasticity / GPa	Maximum strength / MPa	Maximum strain / %
PCS VIII		23°C	1.86	96.0	8.3
		200°C	0.72	39.3	12.1
		250°C	0.37	15.1	6.4
PCS IX		23°C	2.36	93.6	5.8
		200°C	0.08	7.5	9.4
		250°C	0.08	6.1	6.5
PCS X		23°C	2.05	75.2	6.7
		200°C	0.76	23.4	6.9
		250°C	0.11	7.6	9.4

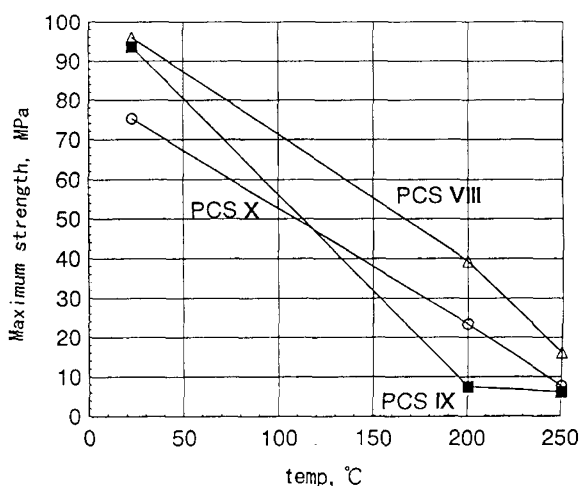


Figure 4. Dependence of maximum strength on temperature for PCS VIII, PCS IX, and PCS X.

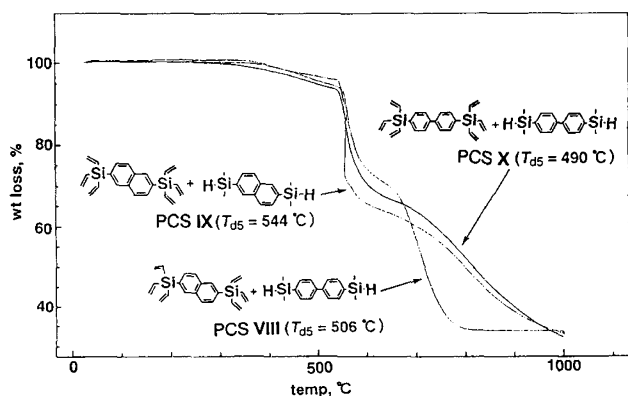


Figure 5. TGA thermograms of PCS VIII, PCS IX, and PCS X in nitrogen.

crease flexural properties. PCS VIII–X were synthesized (Scheme 2). Figure 2 shows the ^{29}Si NMR spectra of the PCSs. All spectra were almost same. This suggests that the hydrosilylation reactions proceed to same extent. Because signals were unresolved, the conversion of Si–vinyl groups was not able to be estimated.⁷ Figure 3 provides plots of (a) storage modulus and (b) $\tan \delta$ against temperatures. The peaks of $\tan \delta$ of PCS VIII and X improved drastically. Table VI shows the flexural properties of PCS VIII–X at 23, 200, and 250°C, respectively. Maximum strength of the PCSs was very high at 23°C possibly due to the high crosslinking density and rigid-rod spacer, biphenyl, naphthalene linkage. Maximum strength of the PCS VIII and IX was almost same,

and one PCS X was lower. This would be because the biphenyl linkage is more flexible than the naphthalene linkage. Because of high T_g s, the PCSs may have high thermally mechanical properties. Figure 4 shows the dependence of maximum strength on temperature. PCS VIII had the highest thermally mechanical stability. PCS IX, whose T_g was observed at 200°C, did not retain the flexural strength at higher temperature. Thermally mechanical stability thus increases with T_g .

Finally, chemically thermal stability of crosslinked PCSs is discussed. Thermogravimetric behavior of crosslinked PCSs was evaluated (Figure 5). Analysis was performed under a nitrogen stream. Temperatures at 5% weight loss, T_{d5} were observed around 500°C. Crosslinked PCSs thus have high chemically thermal stability.

CONCLUSIONS

Crosslinked polycarbosilanes (PCS III–X) were prepared using a hydrosilylation curing reaction between multi-functional vinylsilanes and hydrosilanes. Crosslinked PCSs VIII–X with high network chain density and rigid-rod spacers, had T_g s at around 250°C and high flexural strength in the range of 75–96 MPa. Crosslinked PCSs had high chemically thermal stability.

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