

Control of Structure Formation of Polycarbosilane Synthesized from Polydimethylsilane by Kumada Rearrangement

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ABSTRACT: The control of structure formation of polycarbosilane (PCS) synthesized from polydimethylsilane (PDMS) was studied. It was found that the molecular structure of PCS was strongly dependent on the reaction time and reaction temperature. Shorter reaction time or lower reaction temperature is preferred to produce higher concentration of HSiC_3 group and less SiC_4 group in PCS skeleton, which was confirmed by ^{29}Si NMR analysis. Higher reaction temperature or longer reaction time tended to dissociate more Si-Si chains to give PCS with higher molecular weight and broader distribution, as veri-

fied by GPC characterization. By interrupting the structure evolution of PCS from PDMS at low reaction temperature with short reaction time, solid PCS with controllable molecular structure can be obtained after the removal of the low molecular fraction by precipitation with ethanol. A scissor-couple rearrangement model was proposed for the formation of the PCS skeleton. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3114–3121, 2008

Key words: heteroatom-containing polymers; polysilanes; structure; synthesis

INTRODUCTION

Silicon carbide fiber is one of the most promising candidates as the reinforcing fiber of ceramic matrix composites (CMCs) for high temperature applications,¹ because of its high tensile strength, thermal, and oxidation resistance. The first commercial fine diameter continuous SiC fiber² was produced by Nippon Carbon under the trade name "Nicalon," which was based on Yajima and his coworkers' pioneering work in the 1970s.^{3–5} Recently, two advanced fibers named "Hi-Nicalon"^{6,7} and "Hi-Nicalon Type S"^{8–10} were also developed by Nippon Carbon to improve the performances of Nicalon fiber. Hi-Nicalon uses electron radiation curing in a helium atmosphere instead of the oxidation curing for Nicalon fiber. Hi-Nicalon Type S is a near stoichiometric SiC fiber. Instead of pyrolysis in an inert atmosphere for Hi-Nicalon, Hi-Nicalon Type S is pyrolyzed in a hydrogen rich atmosphere to remove the excess carbon.⁹ All the Nicalon serial fibers are produced using polycarbosilane (PCS) as the polymer precursor, which is synthesized from polydime-

thylsilane (PDMS, $[(\text{Me})_2\text{Si}]_n$) by the Kumada rearrangement.¹¹

Until now, many organosilicon polymers have been developed to produce SiC-based ceramics and fibers.^{12–23} For example, polymetallopolycarbosilane (PMCS, $\text{M} = \text{Ti, Zr, Al}$) is used to manufacture TyrannoTM fibers by UBE Industries^{24,25} and polytitanocarbosilane is also used to produce SylramicTM fiber by Dow Corning²⁶ (now by ATK COI Ceramics); *N*-methylpolyborosilazane is developed to produce SiboramicTM fiber by Bayer;^{19,27} high molecular weight PCS is synthesized to produce UF and UF-HM fibers in University of Florida;²⁸ polycarbosilane is synthesized to prepare Si-C-N fibers in France;^{29,30} polymethylsilane^{31,32} and copolymerized polysilanes^{33–35} are investigated as SiC-based fiber precursors; linear polysilylenemethylenes derived by ring opening polymerization³⁶ and hyperbranched PCS³⁷ by Grignard reaction are used as the precursors for near-stoichiometric SiC ceramics; various kinds of boron-modified polysilazanes or polysilylcarbodiimides are developed to prepare Si-B-C-N ceramics.^{22,38–40}

Although many precursors are available, the most successful ones for commercial polycrystalline SiC-based fibers⁴¹ are PCS and PMCS ($\text{M} = \text{Ti, Zr, Al}$). Most ongoing research on SiC-based fibers in Japan,⁴² France,^{43,44} Russia,⁴⁵ Korea,^{46–48} and China⁴⁹ utilizes PCS as the precursor, because of its low cost and high ceramic yield.

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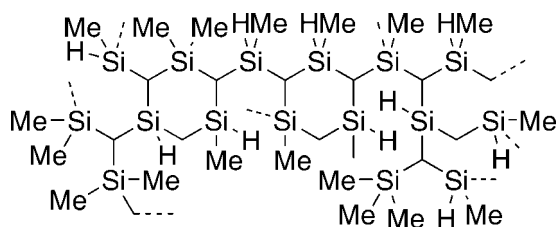


Figure 1 Molecular structure of PCS.

For application as CMC reinforcement, SiC fiber with small diameter is desired, so that it can be made into intricate two- or three-dimensional fabric preforms by weaving. The diameter of SiC fiber is largely determined by the spinnability of PCS. But unfortunately, PCS is very brittle and difficult to be melt-spun continuously into small diameter fiber.⁵⁰ To improve its spinnability, blending with polybutadiene,⁵¹ polyvinylsilane⁵² or polymethylsilane⁵³ have been studied. But they bring new problems at the same time, such as increased excess carbon, excessively high cost or complex synthetic procedures.

PCS actually contains branches and rings^{11,54} (Fig. 1). Generally speaking, PCS with less branches or rings and more linear structure is expected to have better spinnability.⁵⁰ Interestingly, the backbone of PDMS, a pre-polymer for the synthesis of PCS, is essentially linear. However, PDMS is infusible and insoluble.⁵⁵ It must be converted into PCS to be spinnable. The spinnability of PCS is strongly dependent on its molecular structure. In this work, the structure formation of PCS from PDMS by the Kumada rearrangement was investigated for different reaction temperature and heating rate. A rearrangement model was proposed to illustrate how to preserve the linearity of PDMS during its conversion to PCS.

EXPERIMENTAL

Materials

PDMS (Xinhua Chemical Plant, China) and ethanol (99.8% Sinoparm China) were used as purchased. Spectrum pure hexane (Acros) was used as received for UV measurement. Dry hexane was obtained by distilling under nitrogen from sodium benzophenone. Polysilapropylene was synthesized according to literature procedures.⁵⁶

Characterization

Evolved gas analysis (EGA) mode of pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was used to investigate the thermal property of PDMS. The pyrolyzer (Double-Shot Pyrolyzer PY-2020iD, Frontier Laboratories, Japan) was hyphenated to GC-MS (Agilent GC6890N-MSD5975, Agilent Technolo-

gies, USA). Pyrolyzed fragments were delivered to mass detector with an empty capillary column (Ultra Alloy-DTM-2.5N, 2.5 m, Frontier Laboratories, Japan) maintained at 300°C using GC oven temperature controller. For pyrolysis, 0.1 mg PDMS was loaded. The pyrolyzer was heated from 150 to 800°C (20°C/min) using helium as a carrier gas with a constant pressure of 0.1 MPa. The GC-MS operation parameters were set as: split ratio 30 : 1, GC injector 300°C, ion source 280°C, quadrupole 150°C, mass scan range 2–1050 (m/z), energy for electron impact (EI) source 70 eV, respectively.

Inverse gated ²⁹Si NMR spectra were recorded on a NMR spectrometer (Bruker Advance II-300, 300 MHz) at room temperature with a pulse delay time of 28 s. CDCl₃ or C₆D₆ was used as the solvent, and Me₄Si (TMS) as the external standard.

The number-average molecular weight (M_n) was estimated by gel permeation chromatograph (GPC, Agilent 1100 Series). It was equipped with a refractive-index detector and gel columns (Waters Styragel HR 3 and HR 1). Tetrahydrofuran was used as the eluent at a flow rate 0.8 mL/min. The gel columns were calibrated with narrow-molecular-weight polystyrene standards (PDI ≤ 1.05, Shoko, Japan). The UV spectra were obtained with a UV spectrophotometer (Varian Cary 50 Bio) in a 0.5 mg/mL hexane solution.

Preparation of PCS at 470°C

PCS was synthesized with modified procedures described in literature¹¹ as following: 50 g PDMS was charged into 300 mL autoclave (Autoclave Engineers EZE-Seal, USA). The autoclave was then degassed and refilled with argon (0.1 MPa) three times at room temperature and at 300°C (10°C/min). The temperature was then increased to 470°C (25°C/min) and maintained for 3 h. During the reaction, the pressure inside the container rose very quickly up to about 9.0 MPa. After reaction, 100 mL dry hexane was introduced into the container to dissolve the product. The resultant solution was filtered to remove the insoluble black byproduct (0.2 g). Then, the solvent of the filtrate was evaporated to give 34 g (yield 68%) pale yellow solid PCS (PCS-U). Finally, 30 g PCS-U was crashed into fine powder and put into 800 mL ethanol while stirring for 12 h, the remaining insoluble product was collected by filtration and dried under vacuum to give 23 g pale yellow solid PCS (PCS-UP).

Preparation of PCS at 390°C

The procedures are the same as described earlier, except that PDMS (50 g) was heated at a lower heating rate (1°C/min) to 390°C and maintained for 3 h to give 35 g (yield 70%) pale yellow liquid PCS (PCS-I). During the reaction, the pressure inside the

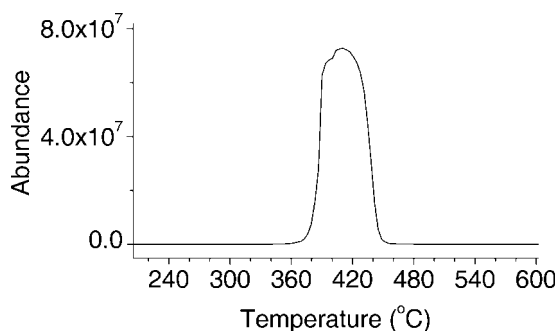


Figure 2 Total ion current of fragments generated from pyrolyzed PDMS.

container rose slowly up to about 2.0 MPa. PCS-I of 30 g was heated at 280°C under vacuum (1 mmHg) to remove the volatile compounds, giving 7.8 g pale yellow liquid PCS (PCS-IV).

When the reaction time was prolonged to 15 h, it produced 36 g (yield 72%) pale yellow liquid PCS (PCS-IA). During the reaction, the pressure inside the container rose slowly up to about 4.0 MPa. PCS-IA of 30 g was added into 800 mL ethanol while stirring for 12 h to give a white precipitate, which was collected by filtration and dried under vacuum to produce 16 g white powder PCS (PCS-IP).

Preparation of PCS by step-by-step heating to 410°C and 430°C

The procedures are the same as earlier, except that PDMS (50 g) was heated to 390°C slowly (1°C/min) and maintained for 3 h. The temperature was then raised to 410°C very slowly (0.2°C/min) and maintained for 2 h to give 36 g (yield 72%) pale yellow liquid PCS (PCS-SA). During the reaction, the pressure inside the container rose slowly up to about 4.5 MPa. PCS-SA of 30 g was put into 800 mL ethanol while stirring for 12 h to give a white precipitate, which was collected by filtration and dried under vacuum to produce 18 g white powder PCS (PCS-SP).

When the final reaction temperature rose to 430°C instead of 410°C and maintained for 2 h, it gave 33 g (yield 66%) pale yellow liquid PCS (PCS-SB). During the reaction, the pressure inside the container rose slowly up to about 4.8 MPa. PCS-SB of 30 g was added into 800 mL ethanol while stirring for 12 h to give a white precipitate, which was collected by filtration and dried under vacuum to produce 19 g white powder PCS (PCS-SC).

RESULTS AND DISCUSSION

Thermal property of PDMS

The thermal property of PDMS has been studied by TG and Pyrolysis-GC analysis.⁵⁷ It was found that

the decomposition of PDMS began at 250°C and was completed at 460°C. In one of our attempts, when PDMS was pyrolyzed at 300°C for several hours, the unreactive PDMS suggests that it is very stable at 300°C in argon atmosphere. Therefore, Py-GC-MS was used to study the starting pyrolysis temperature of PDMS with EGA mode. Mass detector can obtain the abundance of pyrolyzed fragments of PDMS. As shown in Figure 2, when pyrolyzed temperature is below 360°C, no fragments generated from PDMS are detected by mass detector, which suggests that PDMS is stable below 360°C. Appreciable PDMS decomposition signal can be obtained within 360°C to 460°C, which is quite similar to the previous TG analysis with exception of more precious starting pyrolysis temperature.⁵⁷

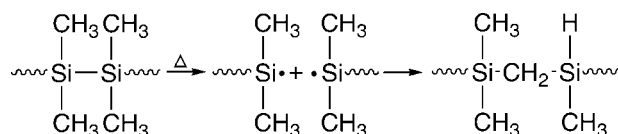
NMR characterization of PCS

PCS prepared at 470°C

The reaction mechanism of PCS synthesized from PDMS by thermal decomposition is referred to as the well-known Kumada rearrangement.^{11,48,58} According to this mechanism, silicon free radical is formed first when Si-Si bond is cleaved by heating, followed by rearrangement involving insertion of methylene group in Si-Si chain to give Si-CH₂-Si and Si-H groups (Scheme 1).^{11,59} Therefore, it is very important to control the dissociation of Si-Si chain in the first step. The dissociation is mainly determined by the energy supplied, in other words, its reaction temperature.

To study the structure formation of PCS after quick PDMS dissociation, the PDMS is heated from 300 to 470°C quickly (25°C/min) and maintained for 3 h to give PCS-U. Fast heating rate (25°C/min) is used to minimize the residence at lower temperature during heating.

The inverse gated ²⁹Si NMR spectrum of the PCS-U is shown in Figure 3(A). The peaks are mainly distributed in three regions. They are assigned to the following groups respectively based on the earlier work:^{60,61} SiC₄ (-5 ~ 5 ppm), HSiC₃ (-20 ~ -10 ppm) and Si-Si (-38 ~ -36 ppm). The broad peak between -135 and -75 ppm is due to SiO₂ in the glass NMR tube. Compared with PDMS (δ_{Si} = -34.5 ppm),⁶² the result shows that most of Si-Si bonds in the linear PDMS chain are cleaved and converted into HSiC₃ and SiC₄ groups in the skeleton of PCS-U



Scheme 1 Reaction mechanism of PCS.

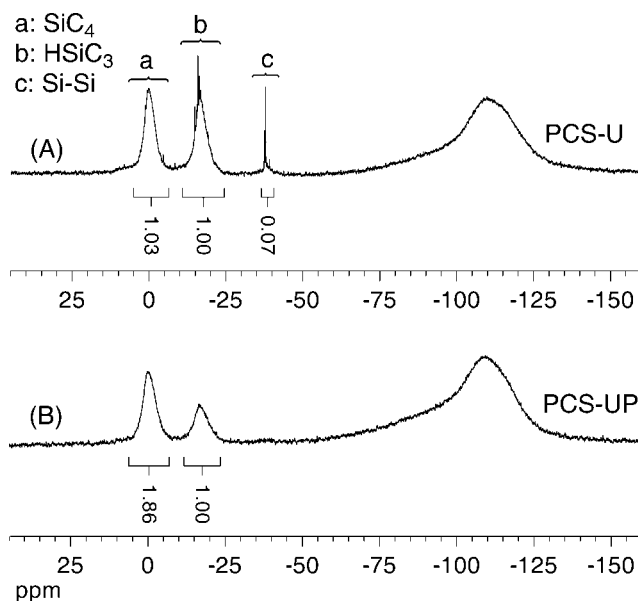


Figure 3 Inverse gated ^{29}Si NMR spectra of (A) PCS-U, (B) PCS-UP in CDCl_3 .

through Kumada rearrangement under this reaction condition.

For producing SiC fiber, the low molecular weight fragments in the as-synthesized PCS should be removed.⁶³ In this work, the low molecular weight fragments of the PCS-U were extracted by ethanol to give white powder PCS-UP. The inverse gated ^{29}Si NMR spectrum of the PCS-UP is shown in Figure 3(B), the disappearance of the signal at $-38 \sim -36$ ppm indicates that the undecomposed Si-Si bonds in PCS-U mainly locates in the skeleton of low molecular weight fragments which can be removed by ethanol. Moreover, the ratio of $\text{SiC}_4/\text{HSiC}_3$ in the PCS-UP increases to 1.86/1 (Fig. 3) from 1.03/1 in PCS-U (Table I), suggesting that most of SiC_4 sites mainly locate in the skeleton of high molecular weight fragments of PCS-U.

According to the previous research,⁵⁴ the SiC_4 fragments in PCS represent the “cross-linked” frac-

tion and HSiC_3 fragments represent the “linear” fraction. Therefore, PCS with more HSiC_3 fragments and less SiC_4 fragments should have better spinnability. The high concentration of SiC_4 fragments in the PCS-UP indicates that it has lots of branched and ring substructures in its skeleton. The PCS-UP was found to be incapable of spinning into continuous fiber.

PCS prepared at 390°C

To study the structure formation of PCS after slow PDMS dissociation, it was heated from 300 to 390°C slowly ($1^\circ\text{C}/\text{min}$) and maintained for 3 h to produce PCS-I. The inverse gated ^{29}Si NMR spectrum of the PCS-I is shown in Figure 4(A). The peaks between

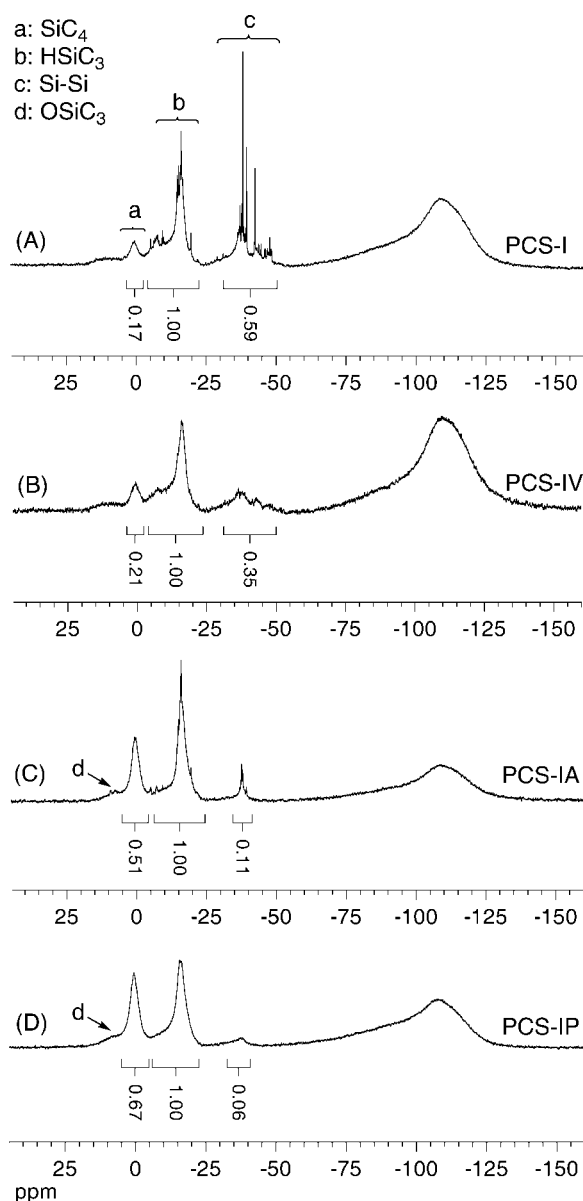


Figure 4 Inverse gated ^{29}Si NMR spectra of (A) PCS-I, (B) PCS-IV, (C) PCS-IA in C_6D_6 , and (D) PCS-IP in CDCl_3 .

TABLE I
The Ratios of $\text{SiC}_4/\text{HSiC}_3$ and $\text{HSiC}_3/\text{Si-Si}$ in PCS^a

Polymer	$\text{SiC}_4/\text{HSiC}_3$	$\text{HSiC}_3/\text{Si-Si}$	Property (25°C)
PCS-U	1.03/1	1/0.07	Pale yellow solid
PCS-UP	1.86/1	–	White powder
PCS-I	0.17/1	1/0.59	Pale yellow liquid
PCS-IV	0.21/1	1/0.35	Pale yellow liquid
PCS-IA	0.51/1	1/0.11	Pale yellow liquid
PCS-IP	0.67/1	1/0.06	White powder
PCS-SA	0.41/1	1/0.18	Pale yellow liquid
PCS-SP	0.66/1	1/0.07	White powder
PCS-SC	0.75/1	1/0.04	White powder

^a The ratio of $\text{SiC}_4/\text{HSiC}_3$ in commercial PCS is 1.50/1 detected by ^{29}Si CP MAS NMR.⁶¹

-50 and -30 ppm are attributed to Si-Si units of linear polysilane backbone ($-\text{SiMe}_2-\text{SiMe}_2-$, $-\text{SiMe}_2-\text{HSiMe}-$, etc.) according to the literature.^{48,60,64} The broad peaks at $-5 \sim 5$ ppm and $-20 \sim -5$ ppm are assigned to SiC_4 and HSiC_3 groups, respectively. The ratios of $\text{SiC}_4/\text{HSiC}_3$ and $\text{HSiC}_3/\text{Si-Si}$ in the PCS-I are 0.17/1 and 1/0.59, respectively, suggesting that the dissociated Si-Si bonds in PDMS mainly convert into HSiC_3 groups in PCS-I through Kumada rearrangement under this reaction condition. Only a few of SiC_4 groups were formed and there were lots of Si-Si bonds in PDMS remained undecomposed.

Interestingly, the resultant PCS-I is found to be a liquid at room temperature. Attempt to obtain solid product by precipitation with ethanol has failed. When PCS-I is heating to 280°C under vacuum (1 mmHg) to remove the low molecular weight fragments, the product (PCS-IV) is still a liquid at room temperature. This is believed to be due to its low fraction of cross-linked SiC_4 fragments and large fraction of linear Si-Si fragments in its main skeleton, which is confirmed by ^{29}Si NMR characterization [Fig. 4(B)]. Consequently, the PCS-IV can not be used to spin into fiber at or above room temperature.

To obtain solid PCS and investigate the effect of reaction time on the structure formation of PCS, the reaction time was prolonged to 15 h. The resultant (PCS-IA) is still a liquid, because it contains lots of small liquid compounds, which can dissolve the higher molecular weight fragments. PCS-IA can be precipitated from ethanol to give white powder PCS (PCS-IP).

The inverse gated ^{29}Si NMR spectrum of the PCS-IA [Fig. 4 (C)] shows it contains more SiC_4 fragments ($-5 \sim 5$ ppm) and less Si-Si fragments ($-40 \sim -35$ ppm) compared with PCS-I (Table I). It indicates that the conversion of Si-Si group into HSiC_3 group is step-by-step at this reaction time, and it is accompanied by the formation of SiC_4 group. The result shows that longer reaction time tends to give HSiC_3 group with much more SiC_4 group and less Si-Si group.

The inverse gated ^{29}Si NMR spectrum of the PCS-IP is shown in Figure 4(D). The PCS-IP also contains more SiC_4 fragments ($-5 \sim 5$ ppm) and less Si-Si fragments ($-40 \sim -35$ ppm) than those in PCS-IV, but less SiC_4 fragments and more Si-Si fragments than those in PCS-UP (Table I). Moreover, low fraction of OSiC_3 fragment ($5 \sim 10$ ppm)⁶⁴ is also witnessed. The formation of OSiC_3 fragment is due to the hydrolysis of Si-H group and formation of Si-O-Si group in PCS during the precipitation treatment from ethanol. The PCS-IP can be spun into continuous fiber.

PCS prepared by step-by-step heating to 410°C and 430°C

As shown and discussed earlier, the structure formation of PCS can be controlled by its reaction time.

Shorter reaction time is preferred to produce higher concentration of HSiC_3 group and less SiC_4 group in PCS. Therefore, the effects of reaction temperature on the structure formation of PCS are carried out with short reaction time. It is conducted by heating from 300 to 390°C slowly ($1^\circ\text{C}/\text{min}$) and maintaining for 3 h, following by further heating to 410°C very slowly ($0.2^\circ\text{C}/\text{min}$) and maintaining for 2 h to give PCS-SA. The PCS-SA is precipitated using ethanol to give PCS-SP. When the final reaction temperature is increased to 430°C instead of 410°C , the precipitates from ethanol is PCS-SC.

As shown in the inverse gated ^{29}Si NMR spectrum [Fig. 5(A)], the ratios of $\text{SiC}_4/\text{HSiC}_3$ and $\text{HSiC}_3/\text{Si-Si}$ in the PCS-SA are 0.41/1 and 1/0.18, respectively. It suggests that the conversion of Si-Si group into HSiC_3 group is also step-by-step at this reaction condition.

The PCS-SA is also a liquid at room temperature and can be also precipitated from ethanol to give white powder PCS-SP. As the inverse gated ^{29}Si NMR spectrum shows [Fig. 5(B)], the ratio of $\text{SiC}_4/\text{HSiC}_3$ in the PCS-SP is 0.66/1, which is closed to that in the PCS-IP, indicating that the increase of reaction temperature but shorter reaction time can

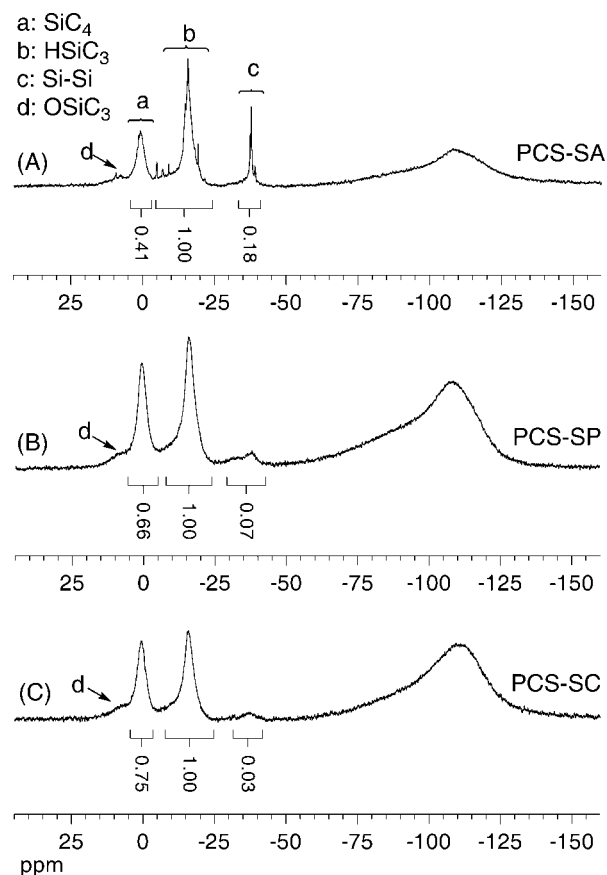


Figure 5 Inverse gated ^{29}Si NMR spectra of (A) PCS-SA in C_6D_6 and (B) PCS-SP, (C) PCS-SC in CDCl_3 .

also achieve the result provided by PCS-IP. The PCS-SP can be also spun into continuous fiber.

When the reaction temperature is increased to 430°C, the resultant is also a liquid at room temperature and solid product (PCS-SC) can be obtained by precipitation from ethanol. The ratios of SiC₄/HSiC₃ and HSiC₃/Si-Si in the PCS-SC are 0.75/1 and 1/0.03, respectively [Fig. 5(C)]. The PCS-SC contains more SiC₄ fragments (-5 ~ 5 ppm) and less HSiC₃ fragments (-25 ~ -5 ppm) compared with PCS-SP (Table I). It shows the formation of HSiC₃ group is deeply accompanied by the formation of SiC₄ group and the disappearance of Si-Si group. Therefore, in order to give more "linear" HSiC₃ group and less "cross-linked" SiC₄ group in the resultant PCS, lower reaction temperature is preferred.

Molecular weight and its distribution

As shown in Table II, the molecular weight distribution (M_w/M_n) of PCS-I is narrower than that of PCS-U, while the molecular weight of PCS-I is lower than that of PCS-U. As indicated in ²⁹Si NMR analysis, most of Si-Si bonds in the linear PDMS chain were dramatically dissociated and converted into HSiC₃ and SiC₄ groups in the case of PCS-U. Since the more Si-Si bonds dissociates, the more Si-CH₂-Si groups forms through Kumada rearrangement. Therefore, the resultant polymer, PCS-U, will contain much larger substructure or longer chain in its main skeleton, leading to the higher molecular weight and the broader molecular weight distribution.

The molecular weight of PCS-IA is also higher than that of PCS-I but lower than PCS-U (Table II), indicating that the longer the reaction time (15 h) tends to produce PCS with higher molecular weight, but the higher the reaction temperature has a greater effect on the increase of the molecular weight.

Ultraviolet absorption spectra

Polysilanes, with linear Si-Si chain in its main skeleton, exhibit electronic transitions in the ultraviolet because of the existence of the σ conjugation in Si-Si chain.³³ It is interesting to note that the longer the

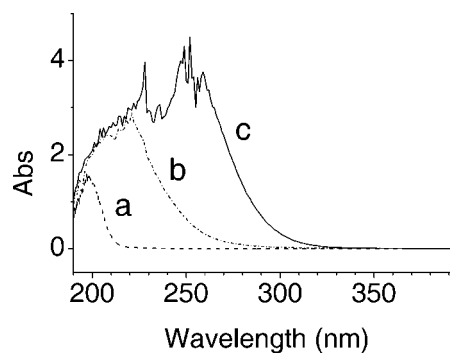


Figure 6 Ultraviolet absorption spectra of (a) Polysilpropylene, (b) PCS-U, (c) PCS-I at 25°C.

polysilanes chain length is, the larger its ultraviolet absorption λ_{max} is. For example, the wavelength of absorption band (λ_{max}) is 216, 235, 250, 260, 272 nm for Me[(Me)₂Si]_nMe, $n = 3, 4, 5, 6, 8$, respectively.⁶⁵ The λ_{max} levels off and becomes nearly constant as chain length $n \rightarrow \infty$.³³ The PDMS used as the starting materials for the commercial PCS was reported to have ultraviolet absorption of $\lambda_{max} \approx 340$ nm.^{11,62} Therefore, we can determine the length of Si-Si chain remained in the resultant PCS from its ultraviolet absorption spectrum.

For comparison, polysilpropylene with ideal linear formula [HSi(Me)CH₂]_n was synthesized according to literature procedures.⁵⁶ As shown in the ultraviolet absorption spectra (Fig. 6), polysilpropylene does not produce absorption at over 210 nm, supporting that Si-C and Si-H groups in PCS do not produce absorption over 210 nm. Meanwhile, PCS-U and PCS-I, which contain Si-Si, Si-C and Si-H groups in their skeletons, produce absorption over 210 nm. Therefore, the absorption over 210 nm is attributed to Si-Si group in PCS.⁶⁰ The PCS-I has a maximum absorption wavelength at $\lambda_{max} \approx 260$ nm, while the PCS-U has a maximum absorption wavelength at $\lambda_{max} \approx 225$ nm (Fig. 6), supporting that the PCS-I contains much longer Si-Si chains than those in the PCS-U. The PCS-U has a maximum absorption wavelength over 220 nm in ultraviolet absorption spectrum, indicating that there exists a small amount of short Si-Si chains in PCS-U, which is in agreement with the NMR analysis.

Proposed rearrangement model

As mentioned earlier, PCS can be produced in two extremes. One is above the complete decomposition temperature of PDMS to produce highly cross-linked skeleton SiC₄ with higher molecular weight, broader distribution (PCS-U), as confirmed by the ²⁹Si NMR, GPC, and UV analysis; the other is just above the starting temperature for the decomposition of PDMS to give much more linear polysilane backbone

TABLE II
Molecular Weight and Distribution of PCS

Polymer	M_n	M_w/M_n
PCS-U	1094	2.75
PCS-I	594	1.19
PCS-IA	721	1.38
PCS-IP	1122	1.35
PCS-SA	677	1.37
PCS-SP	1169	1.32
PCS-SC	1052	1.47
Commercial PCS ⁶¹	1200	2.97

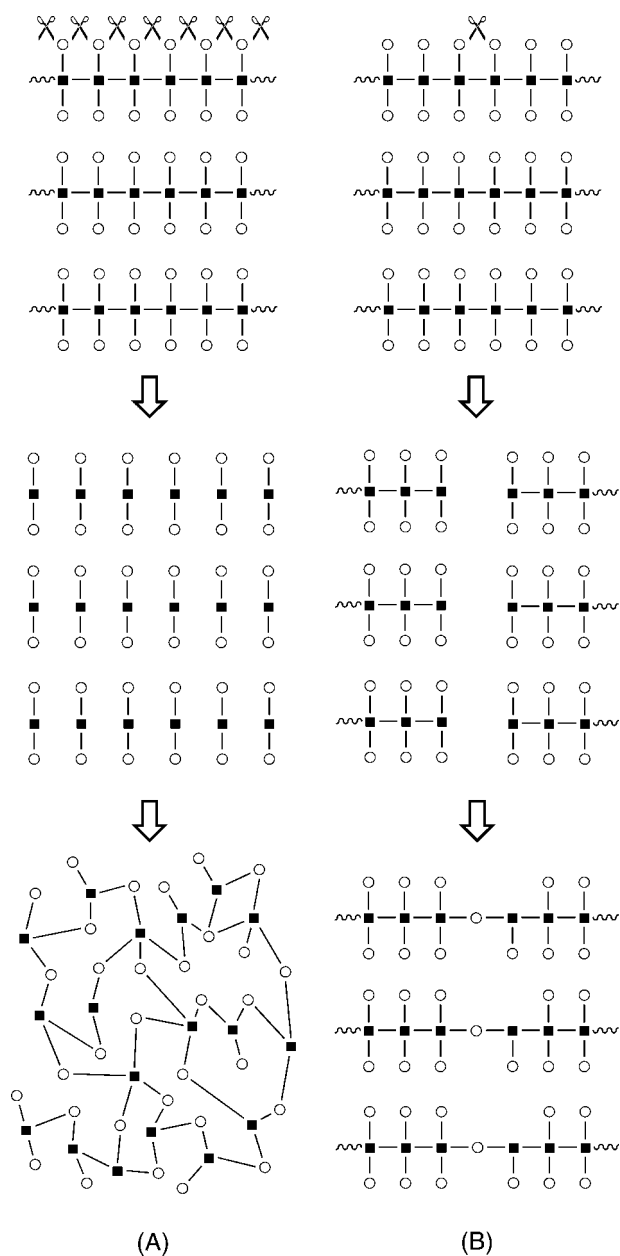


Figure 7 Scissor-couple rearrangement model for the conversion of linear PDMS into PCS (■ for "Si"; ○ for "C").

(PCS-I). A scissor-couple rearrangement model is proposed to demonstrate the structure formation of PCS in the two extremes as follows:

As shown in Figure 7(A), above the complete decomposition temperature of PDMS, all the Si-Si bonds in the linear main chains may scissor simultaneously. The silicon free radicals formed may couple at lots of different sites to form HSiC_3 and SiC_4 groups through Kumada rearrangement at the same time. Consequently, the skeleton of the resultant PCS may be highly unlinear, containing branches or rings.

In contrast, just above the starting temperature for the decomposition of PDM, only few of Si-Si chains

in PDMS break. The dissociated Si-Si groups mainly convert into HSiC_3 groups through Kumada rearrangement [Fig. 7(B)] and the formation SiC_4 groups will be rare. That is to say, the linear skeleton of the PDMS will be largely preserved in the resultant PCS.

According to this scissor-couple rearrangement model, the control of dissociation of Si-Si chain in PDMS is very important to control the structure of PCS. Therefore, in order to achieve higher concentration of HSiC_3 group and less SiC_4 group in PCS, lower reaction temperature and shorter reaction time is preferred.

CONCLUSIONS

The molecular structure of PCS can be tailored by carefully controlling its reaction temperature and reaction time. Higher reaction temperature and longer reaction time tend to scissor more Si-Si chains in PDMS and the conversion of Si-Si group into HSiC_3 group is accompanied by the formation of SiC_4 groups, while lower reaction temperature and shorter reaction time tend to result in PCS with better linearity, because the dissociation of Si-Si groups are mainly converted into HSiC_3 groups. Moreover, it was found that higher reaction temperature or longer reaction time tends to give PCS with higher molecular weight. By interrupting the structure evolution of PCS from PDMS at low reaction temperature with short reaction time, solid PCS with controllable molecular structure can be obtained after the removal of the low molecular fraction by precipitation with ethanol. The formation mechanisms of PCS from PDMS by Kumada rearrangement can be explained by the scissor-couple rearrangement model.

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