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Synthesis of continuous silicon carbide fibre with high tensile strength and high Young's modulus

Part 1 *Synthesis of polycarbosilane as precursor*

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Polycarbosilane as the precursor of continuous SiC fibre was synthesized by thermal decomposition of polydimethylsilane. The structure of the polycarbosilane is concluded to be similar to that of polysilapropylene by the measurements of i.r. spectra, NMR spectra and chemical analyses. Its formation mechanisms are initially the formation of carbosilane by thermal decomposition of polydimethylsilane and then the increase in molecular weight by dehydrogenation-condensation of the carbosilane. Molecular structure and molecular weight distribution of the polycarbosilane depend on the reaction temperature.

1. Introduction

Continuous silicon carbide fibre developed in the authors' laboratory [1–3] is obtained as follows. Resinous polycarbosilane synthesized by thermal decomposition of polysilane is first melt-spun at about 350° C. The fibre is then heat-treated at a high temperature above 1000° C in vacuum or inert gas. The resulting continuous SiC fibre, which is a cohesion of β-SiC crystallites, has high tensile strength and high Young's modulus.

Polycarbosilane as the precursor of continuous SiC fibre is obtained by thermal decomposition of dodecamethylcyclohexasilane [1, 2, 5] or polydimethylsilane. Polydimethylsilane is easily synthesized from dimethyldichlorosilane at low cost, so it is advantageous over the other polysilanes in industrial production of the polycarbosilane.

Required properties of the precursor for continuous SiC fibre are the following; high spinnability, large strength and easy handling of the resultant fibre, low oxygen content in the molecule, little weight loss in conversion into the inorganic, and little free carbon produced at surface and interior of the fibre, all resulting in high SiC purity. These are, of course, intimately related to the properties of the polycarbosilane itself. It is thus necessary to clarify these properties in order to study in detail the conversion mechanisms of polycarbosilane into SiC.

In the present study, to examine the variety of factors influencing properties of the continuous SiC fibre, attention is given to polycarbosilane as the precursor produced by thermal decomposition of polydimethylsilane. From the information acquired by measurements of the properties, therefore, molecular structure of the polycarbosilane is determined and its formation mechanism is inferred. A second objective is to seek better synthesis of polycarbosilane as the precursor of continuous SiC fibre.

2. Experimental

2.1. Synthesis of polydimethylsilane

In a 5 litre three-necked flask with dropping funnel and reflux condensor were put 2500 ml of xylene (distillation-refined with sodium metal as a dessicant) and 410 g of metallic sodium. The mixture was then heated under a nitrogen atmosphere.

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After melting of the sodium, it was stirred. Then, 1000 ml of dimethyldichlorosilane (distillation-refined) was introduced with the dropping funnel, taking about 45 min. About 10 h after the introduction of the dimethyldichlorosilane, the temperature of the content of the flask rose to that of boiling xylene; this was taken as the termination of the reaction.

Xylene was removed by suction filtration from the resulting bluish-purple precipitate. Residual sodium was then removed by treatment with 3 litre methanol. By addition of 9 litre water, a white powder was obtained [6]. After standing overnight, the powder was washed with water and then with acetone. It was dried naturally and subsequently in vacuum by heating at 150° C for 6 h. The resultant white powder, polydimethylsilane, was insoluble in ordinary solvents; the amount obtained was 425 g (yield 88.7%).

2.2. Synthesis of polycarbosilane

In a 1 litre autoclave was put 250 g of the polydimethylsilane, with filling by argon at 1 atm. It was then stirred while heating at a rate of about 400° C h^{-1}. The polymerization temperatures were at 450, 460 and 470° C, respectively for 14 h. At these polymerization temperatures, the final pressures were 82, 92 and 105 kg cm^{-2}, respectively. These did not stay constant, always tending to rise.

Each product was a yellowish-brown viscous substance. It was dissolved in *n*-hexane and the solution filtered. The solvent was removed with a rotary evaporator. By vacuum distillation, the fraction up to 280° C under 1 mm Hg was removed, resulting in the final product of a yellowish-brown glassy polycarbosilane. After concentration the amounts of polymer obtained at the polymerization temperatures of 450, 460 and 470° C were 127 g (yield 50.8%), 140 g (yield 56.0%) and 147 g (yield 58.8%), respectively. These products, hereafter, are referred to as PC-450, PC-460 and PC-470. The distillate fraction obtained by vacuum distillation of PC-470 is referred to as PC(280).

2.3. Measurements

The polydimethylsilane and PC-450, PC-460, PC-470 and PC(280) were subjected to the measurements as follows:

I.r. spectra were measured with an Hitachi 285 grating infra-red spectrometer by the KBr pellet method, except for PC(280) which was sandwiched in between two KBr plates.

U.v. spectra were measured with a Shimadzu multipurpose recording spectrometer MPS-5000 by the Nujol mull method for polydimethylsilane, and in a 0.1 g l^{-1} *n*-hexane solution for polycarbosilane.

Number-average molecular weights $\bar{M}n$ were measured with an Hitachi 117 molecular weight apparatus by vapour pressure osmometry (VPO) in benzene solution, using benzil as the standard material.

Molecular weight distributions of PC-450, PC-460 and PC-470 were obtained with a TSK HLC-801A by Gel Permeation Chromatography (GPC) with G2000H6 and G4000H6 packing and tetrahydrofuran eluent at a flow rate 1 ml min^{-1} at room temperature, using a differential refractometer for the detector.

TG-DTA curves of polydimethylsilane were obtained by a Rigaku micro TG-DTA high-temperature type by raising the temperature at 5° C min^{-1} up to 800° C in a N_2 flow of 50 cm^3 min^{-1}.

NMR spectra were measured with a JEOL JNM-FX60 high-resolution FT NMR spectrometer at 60 MHz at room temperature with a C_6D_6 solvent.

Chemical analyses of PC-460, PC-470 and polydimethylsilane were made for four elements; Si (by a gravimetric method dissolving with sodium carbonate and sodium peroxide), C (by a combustion volumetric method), and O and H (by gas analysis).

3. Results and discussion

3.1. Polydimethylsilane

The i.r. spectrum of polydimethylsilane is shown in Fig. 1. Absorptions are at 2950, 2900 and 1400 cm^{-1} (C–H), 1250, 835, 750, 690 and 635 cm^{-1} (Si–Me) [8], 1000 to 1100 cm^{-1} (Si–O), and 3200 to 3600 cm^{-1} (O–H).

The u.v. spectrum of polydimethylsilane is shown in Fig. 2. In u.v. spectra of polysilane measurements are generally made for permethylated polysilane, $Me\text{-}(SiMe_2)_n\text{-}Me$ up to $n = 8$ [8], in organic solvents. With increasing *n*, however, it becomes more insoluble in organic solvents. For the synthesized polydimethylsilane, the spectrum could not be measured in solution. Thus, it was measured by dispersing it in liquid paraffin and then sandwiching it in between two quartz plates.

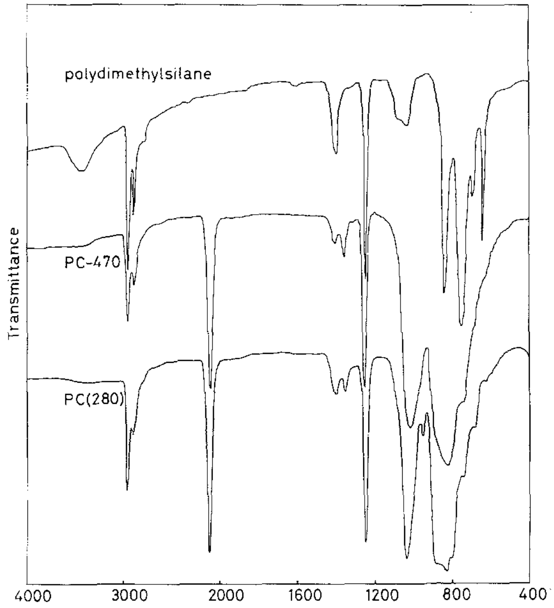


Figure 1 I.r. spectra of polydimethylsilane, PC-470 and PC(280).

TABLE I Chemical analyses of polydimethylsilane, PC-460 and PC-470

Material	Si (wt%)	C (wt%)	O (wt%)	H (wt%)
polydimethylsilane	47.40	39.50	0.52	9.24
PC-460	47.13	36.99	0.84	7.00
PC-470	49.988	37.88	0.99	6.60

As seen in the figure, there is broad absorption with a maximum absorbance at 345 nm (29 000 cm^{-1}). The ultra-violet absorption peak of polysilane not containing the π-electron system [7–9], in the linear system, is shifted to longer wavelengths with increasing length of the silicon chain. In the cyclic system, $\mathrm{{\left(Me_2Si\right)}_n}$, the absorption peak is shifted to longer wavelengths with decreasing n. At $n = 5$, however, it is only 272 nm [8, 9]. On the other hand, the absorption peak of branching polysilane is shifted to shorter wavelengths from that of the linear system having the same number of silicon atoms. It is therefore inferred that the polydimethylsilane synthesized has a chain structure and that its degree of polymerization is about 30 as deduced from the n–$\nu_{\max}$ relation of permethylated polysilane.

The results of chemical analysis of the polydimethylsilane are shown in Table I. Its empirical formula was found to be $SiC_{1.94}O_{0.02}H_{5.46}$.

On the basis of the i.r. spectrum, u.v. spectrum and chemical analysis results, the polydimethylsilane synthesized was found to be of $\mathrm{HO{\left(SiMe_2\right)}_nOH}$ with polymerization degree n about 30.

3.2. Polycarbosilane

The i.r. spectrum of PC-470 is shown in Fig. 1. Spectra of PC-450 and PC-460 are the same as for PC-470. Absorptions are at 600 to 920 cm^{-1} (Si–Me), 1020 and 1355 cm^{-1} (Si–CH$_2$–Si), 2100 cm^{-1} (Si–H) [10–12], and 1250, 1400, 2900 and 2950 cm^{-1}, which were observed also in polydimethylsilane. Fig. 1 also shows the spectrum of PC(280). The absorption at 955 cm^{-1} possibly is due to Si–H deformation in SiH$_2$. It is seen that the absorption intensities at 1400 and 1355 cm^{-1} are the reverse of those in PC-470.

The u.v. spectrum of PC-470 is shown in Fig. 2. No absorption due to $\mathrm{{\left(Si\right)}_n}$ ($n \geq 3$) could be observed. Results for PC-450 and PC-460 are also the same. There was no ultra-violet absorption at all in PC(280).

NMR spectra of PC-450, PC-460, PC-470 and PC(280) are shown in Fig. 3. Chemical shifts δ are based on 0.00 p.p.m. of tetramethylsilane for the internal standard. Peaks exist at 4.4 (Si–H), 0.2 (Si–Me) and −0.3 p.p.m. (CH$_2$) in PC(280), and at 4.5 (Si–H) and 0.3 p.p.m. (Si–Me) in PC-450, PC-460 and PC-470. Though the signal due

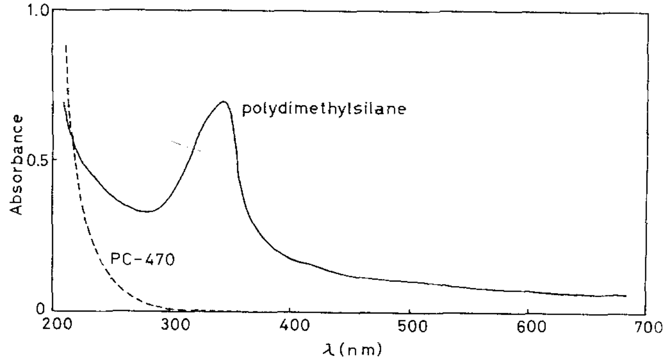


Figure 2 U.v. absorption spectra of polydimethylsilane and PC-470.

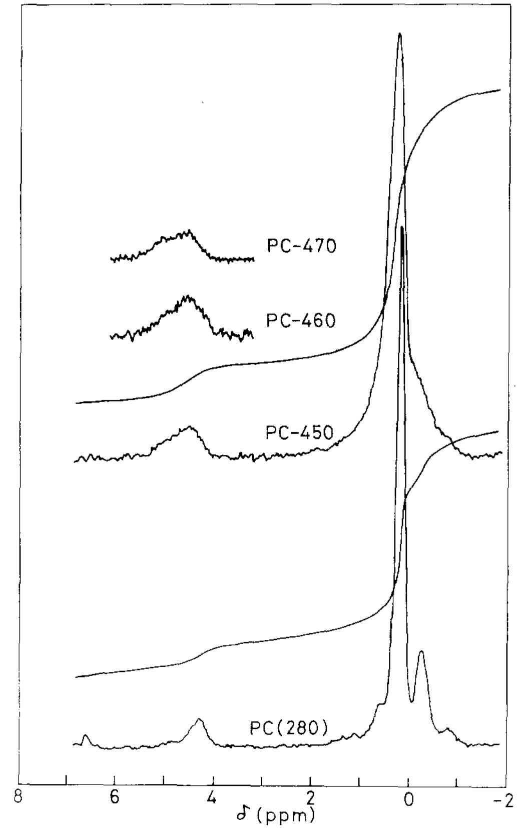


Figure 3 NMR spectra of polycarbosilane (solvent C_6D_6, at 60 MHz).

to CH_2 is not distinct, the NMR spectra are all characteristic of carbosilane [7, 12, 13].

Number-average molecular weights $\bar{M}n$ of PC-450, PC-460, PC-470 and PC(280) are 1250, 1450, 1750 and 320, respectively.

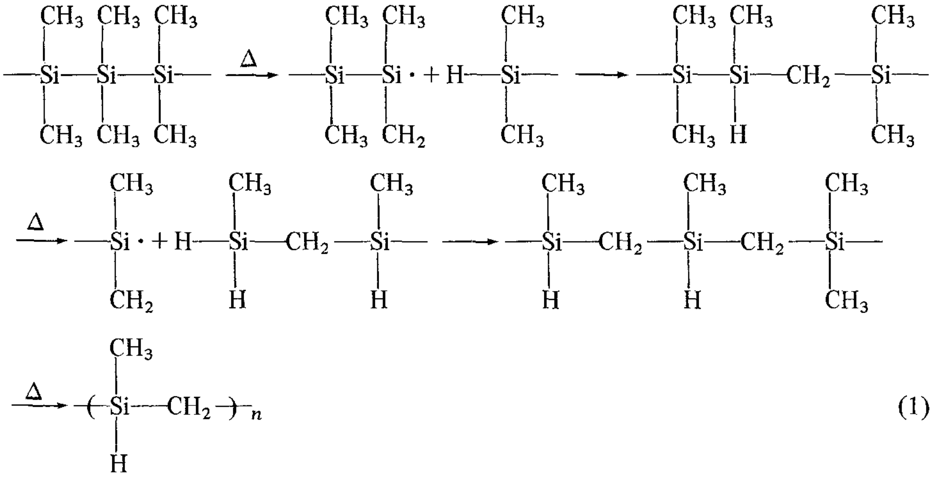
From the above results, synthesized PC-450, PC-460 and PC-470 were all found to be polycarbosilane with $\bar{M}n > 1000$. Even in PC(280), the structure $\leftarrow\!\mathrm{Si}\!\rightarrow_n$ $(n \geqq 3)$ is not contained so it also has the skeleton of carbosilane.

3.3. Formation mechanisms and structure of polycarbosilane

TG-DTA curves of polydimethylsilane are shown in Fig. 4. In the TG curve, weight loss starts at 180° C and the weight residue at 400° C is 5%. In the DTA curve the exothermic reaction also starts at about 180° C. This is possibly due to severance of the main chain in thermal decomposition of polydimethylsilane. The bond energy of Si–Si is 222 kJ mol^{-1}, so the bond is unstable as compared with Si–C (318 kJ mol^{-1}), Si–H (314 kJ mol^{-1}) and C–H (414 kJ mol^{-1}) [13]. It is indicated that at above 320° C there occur simultaneously exothermic and endothermic reactions. It is inferred that low molecular weight substances resulting from thermal decomposition of polydimethylsilane undergo thermal polymerization in such condensation.

Formation mechanisms for polycarbosilane by the thermal decomposition of polydimethylsilane may be based on the thermal decomposition of hexamethyldisilane [14–16] and of methoxydisilane [17]. That is, the formation mechanism of polysilapropylene may be as in Reactions 1, 2 or 3.

The formation of silapropylene and the addition reaction with the SiH bond are supported also by the existence of SiH_2 in the PC(280) i.r. spectrum.

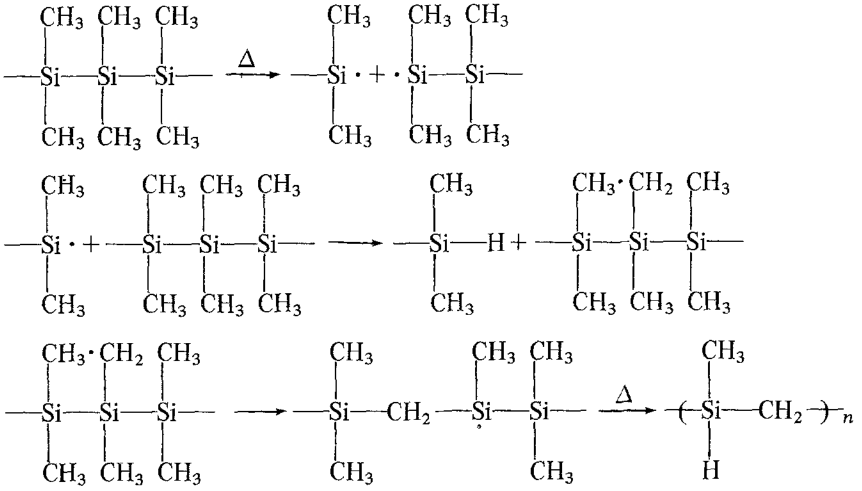


$$-Si(CH_3)_2-Si(CH_3)_2-Si(CH_3)_2- \xrightarrow{\Delta} -Si(CH_3)_2-Si(CH_3)(CH_2)\cdot + H-Si(CH_3)_2- \longrightarrow -Si(CH_3)_2-SiH(CH_3)-CH_2-Si(CH_3)_2-$$

$$\xrightarrow{\Delta} -Si(CH_3)(CH_2)\cdot + H-SiH(CH_3)-CH_2-SiH(CH_3)- \longrightarrow -SiH(CH_3)-CH_2-SiH(CH_3)-CH_2-Si(CH_3)_2-$$

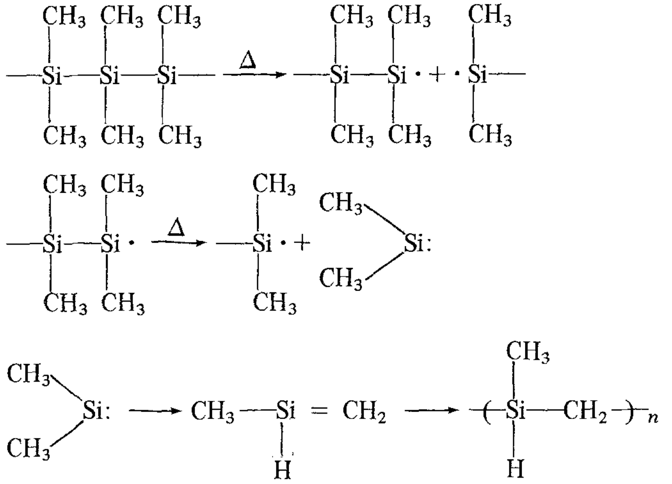
$$\xrightarrow{\Delta} \leftarrow\!SiH(CH_3)-CH_2\!\rightarrow_n \qquad (1)$$

Carbosilanes are also formed by a radical transition reaction.



(2)

Further formation of dimethylsilene is possible.



(3)

Of course in the autoclave there form a variety of radicals, so in addition to Reaction 1, 2, or 3, side reactions should also take place such as branching due to chain transfer and ring formation.

The results of chemical analyses of PC-460 and PC-470 are shown in Table I. The empirical formulae of PC-460 and PC-470 were $SiC_{1.83}O_{0.03}H_{4.16}$ and $SiC_{1.77}O_{0.03}H_{3.70}$, respectively. Comparing this with polysilapropylene (SiC_2H_6) it seems that H atoms are present in low concentration.

Molecular weight distributions in GPC chromatograms of PC-450, PC-460 and PC-470 are shown in Fig. 5. It is obvious that, as the polymerization temperature is higher, $\bar{M}n$ increases and the molecular weight distribution is also shifted to higher molecular weights. In the u.v. spectrum, the structure $(\mathrm{Si})_n$ in PC-450 is not contained, and therefore thermal decomposition of the polydimethylsilane is complete at the polymerization temperature 450° C. With increasing polymerization temperature there appears another peak at a higher molecular weight. For example, the distribution in PC-470 is a two-peak, or even a three-peak one. Formation mechanisms for polycarbosilane therefore are initially the formation of carbosilane by Reactions 1, 2, or 3, and then the increase in molecular weight of the carbosilane.

From the ratio of Si–H and C–H absorption intensity areas in NMR spectra of PC-450, PC-460, PC-470 and PC(280), the values of C–H/Si–H ratio are as follows: 9.6 for PC-450, 10.3 for PC-460, 11.2 for PC-470 and 11.9 for PC(280). These

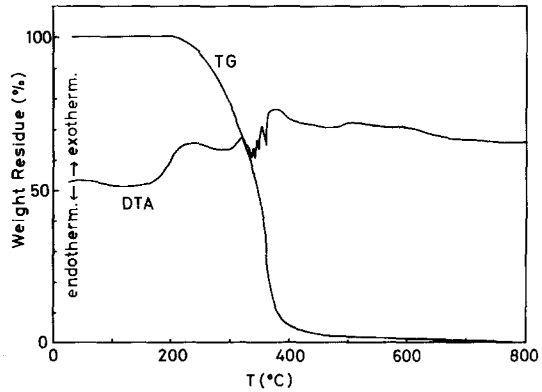


Figure 4 TG-DTA curves of polydimethylsilane.

values except PC(280) are dependent on $\bar{M}n$. With increasing $\bar{M}n$, C–H/Si–H ratio increases. Chemical analyses of PC-460 and PC-470 also show that the decrease of H/Si is related to the increase of $\bar{M}n$. It is therefore indicated that the Si–H bond plays an important role when the polysilapropylene, as produced in the thermal decomposition of polydimethylsilane, increases in molecular weight.

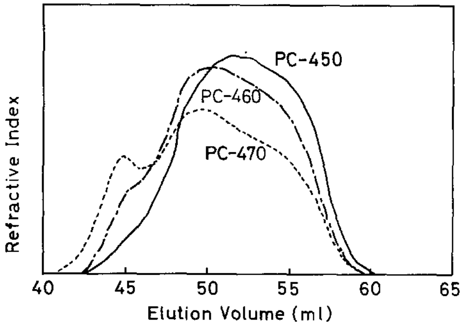
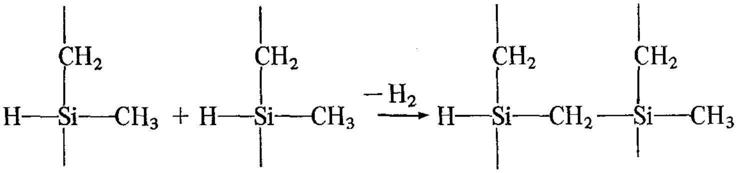


Figure 5 Elution curves of PC-450, PC-460 and PC-470.

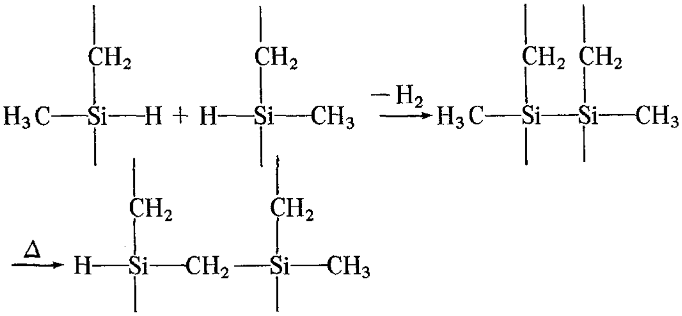
The Si–C bond is resistant to homolytic cleavage. In free radical reactions of organosilicon compounds, the cleavage of the C–H bond thus takes place earlier than that of Si–C bond. In the Si–H bond, on the other hand, the positive charge of the dipole exists on the silicon and the negative charge on the hydrogen; the reactivity is relatively high. The polarization direction in the Si–H bond is the reverse of that in the C–H bond.

Therefore, mechanisms for increasing the molecular weight are inferred to be:



$$\mathrm{H{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_3 + H{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_3 \xrightarrow{-H_2} H{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_2{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_3} \qquad (4)$$

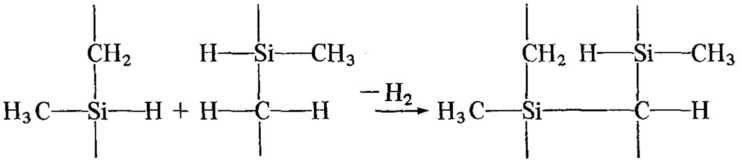
or



$$\mathrm{H_3C{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}H + H{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_3 \xrightarrow{-H_2} H_3C{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_3}$$

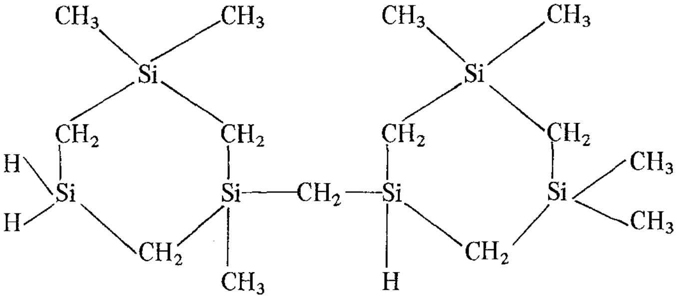
$$\mathrm{\xrightarrow{\Delta} H{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_2{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}CH_3} \qquad (5)$$

or

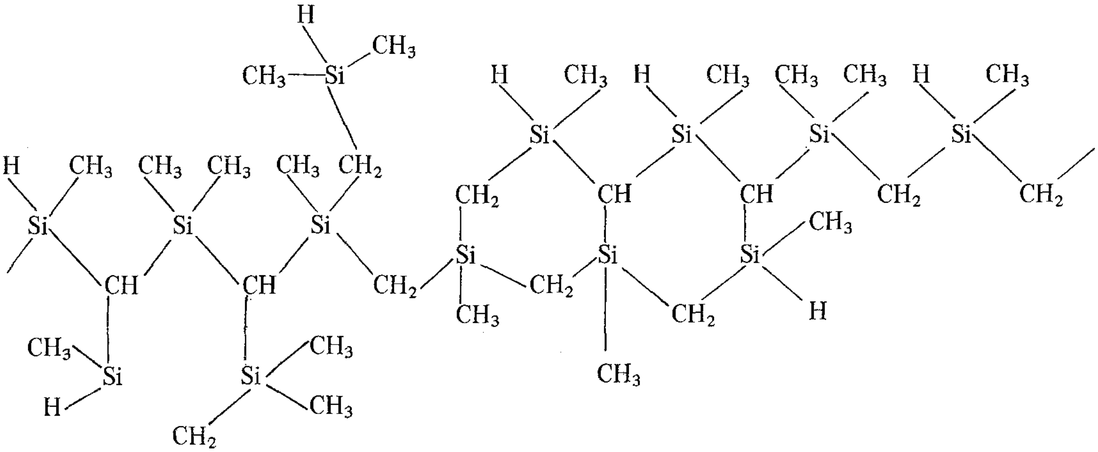


$$\mathrm{H_3C{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}H + H{-}\overset{H{-}\overset{|}{Si}{-}CH_3}{\underset{|}{C}}{-}H \xrightarrow{-H_2} H_3C{-}\overset{\overset{|}{CH_2}}{\underset{|}{Si}}{-}\overset{H{-}\overset{|}{Si}{-}CH_3}{\underset{|}{C}}{-}H} \qquad (6)$$

Concerning the structure of the synthesized polycarbosilane, the following are possible. In PC(280), during the formation of the polysilapropylene as represented by Reactions 1, 2 or 3, at a low molecular weight the reaction ceases due to ring formation. That is, though the molecular weight is small, the C–H/Si–H ratio is similar to that in PC-470. So the increase in molecular weight by dehydrogenation-condensation in Reactions 4, 5 or 6 does not proceed very far. In the autoclave, the existence of the vapour phase corresponds to this component of low molecular weight. The structure of the PC(280) is thus inferred as:



In PC-450, PC-460 and PC-470, on the other hand, which correspond to the liquid phase in the autoclave, the dehydrogenation-condensation reaction does proceed to raise the molecular weight. Their structure is inferred as:



4. Conclusions

Polycarbosilane as the precursor of continuous SiC fibre is very similar to polysilapropylene in structure. With increase in the polymerization temperature, however, as indicated by the reduction of Si–H bonds, the molecule contains large amounts of ladder-bonded structures, so the cross-linking between molecules should increase. There then appears the rigidity of the molecular chain, the formation of the microgel and a rise in softening point. For the precursor of continuous SiC fibre, it is desirable that the similarity to the polysilapropylene should be as close to the chain structure as possible, i.e. it should contain as many Si–H bonds as possible, and its molecular weight should be high. Detailed study of the formation mechanism of polysilapropylene is necessary in the future to find the most suitable polymerization conditions.

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