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The conversion process from polydimethylsilane to polycarbosilane in the presence of polyborodiphenylsiloxane

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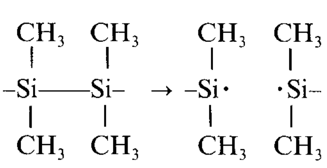
The pyrolytic reaction of polydimethylsilane to polycarbosilane in the presence of polyborodiphenylsiloxane have been studied by the use of organosilicon intermediates obtained during the initial pyrolytic stage of polydimethylsilane. In this reaction, the cleavage of the framework of Si–Si bonds occurred. Si–CH_2–Si and Si–H bonds were subsequently formed by the rearrangement reaction between radicals formed and Si–CH_3 bonds. The formation of Si–Si bonds by dehydrogenation between Si–H bonds then proceeded simultaneously or stepwise. It is assumed that polyborodiphenylsilane plays a role in accelerating the polycondensation reaction, that is, the propagation reaction occurred by dehydrogenation between the Si–H bonds, but takes no part in the radical rearrangement reaction from Si–Si bonds to Si–CH_2–Si bonds.

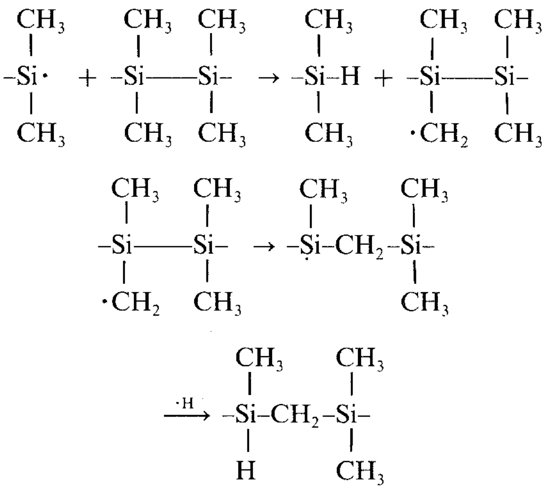
1. Introduction

Several methods for synthesis of a polycarbosilane for producing SiC materials have been reported [1–5]. The well-known methods for obtaining polycarbosilanes are heat-treatment of a tetramethylsilane at temperatures above 650° C in the recycling system [1, 2], pyrolysis of a polydimethylsilane [$\leftarrow\!Si(CH_3)_2\!\rightarrow_n$, $n \simeq 30$] under atmospheric pressure at a temperature above 450° C [3, 4], and the direct reaction of vinylsilanes or chloromethylsilanes using metallic sodium or potassium to form silicon–carbon bonds [5]. Of these, the pyrolytic method of producing polycarbosilane from polydimethylsilane is the most advantageous for obtaining continuous SiC fibres with high mechanical strengths [1, 2]. Through further investigations on the pyrolysis of polydimethylsilane, a more convenient method, i.e. the reaction of polydimethylsilane with a small amount of polyborodiphenylsiloxane at a temperature below 350° C, has been found to produce polycarbosilane with a high yield [6].

In the conversion process of polydimethylsilane to polycarbosilane, the cleavage of the framework of Si–Si bonds in polydimethylsilane, the rearrangement of the silicon radicals formed and the recombination of various radical species, seem to occur simultaneously or stepwise. The mechanism of this conversion at temperatures above 450° C in an inert gas has been reported to be [7]



$$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}}}\!-\!\!-\!\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}-}} \rightarrow \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}\cdot}}\quad \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\cdot\mathrm{Si}-}}$$



$$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}\cdot}} + \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}}}\!-\!\!-\!\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}-}} \rightarrow \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{H}}} + \underset{\cdot\mathrm{CH_2}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}}}\!-\!\!-\!\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}-}}$$

$$\underset{\cdot\mathrm{CH_2}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}}}\!-\!\!-\!\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}-}} \rightarrow \overset{\mathrm{CH_3}}{\underset{\cdot}{-\mathrm{Si}}}\!-\mathrm{CH_2}-\!\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}-}}$$

$$\xrightarrow{\cdot\mathrm{H}} \underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{-\mathrm{Si}}}\!-\mathrm{CH_2}-\!\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}-}} \qquad (1)$$

For Reaction 1 to proceed smoothly and effectively to give a polycarbosilane with a high yield, either an autoclave system or a recycling system is usually applied. On the other hand, if a small amount of polyborodiphenylsiloxane is used as a catalyst the reaction can be performed at lower temperature below 350° C, rather than ~450° C found with no-catalyst system, and a high yield of polycarbosilane is attained even in nitrogen gas at atmospheric pressure. The catalytic effect of polyborodiphenylsiloxane, which accelerates the formation of the carbosilane structure and the increase in molecular weight, has been studied [6], but its effect is still ambiguous because this reaction is complicated and indistinct.

During conversion from polydimethylsilane to polycarbosilane, the first step of the reaction has been considered to be the cleavage of the framework of Si–Si bonds in polydimethylsilane. The intermediates with structural units of Si–Si, Si–CH_2–Si, Si–CH_3

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and/or Si–H bonds, are then thought to be formed and presumably to react with each other.

To clarify the detailed catalytic effect of polyborodiphenylsiloxane, which can be assumed to play an important role in the reaction of the above intermediates in the production of polycarbosilane, the reaction process of the organosilicon intermediates obtained during the initial stages of pyrolysis of polydimethylsilane in the presence of polyborodiphenylsiloxane have been studied. These results are reported here.

2. Experimental procedure

2.1. Synthesis of organosilicon intermediates

Polydimethylsilane (PS), was synthesized by dechlorination of dimethyldichlorosilane (1000 ml) with sodium metal (410 g) in xylene (2500 ml) under nitrogen gas [8]. After PS was heat-treated at 340° C in an autoclave for 1 h in nitrogen atmosphere, reaction products were obtained. Two types of organosilicon intermediates, A and B, were separated from the reaction products by distillation. A and B have boiling points in the range 80 to 230° C and 230 to 340° C, respectively. Another two organosilicon intermediates, C and D, which were distilled residues, were separated by the fractional precipitation method in a xylene/ethanol system, and thus intermediate D was precipitated in ethanol. The weight ratio of A, B, C and D thus obtained was about 4 : 2 : 3 : 1.

The polyborodiphenylsiloxane (PBDS, 240 g) used as a catalyst was obtained by mixing and refluxing boric acid (50 g) and diphenyl dichlorosilane (307 g) in 485 ml anhydrous *n*-butyl ether for 18 h, and then heat treating for 1 h at 300° C under reduced pressure.

Each organosilicon intermediate (30 g), A, B, C and D, was reacted with 0.1 to 0.9 g PBDS at 340° C for 3 to 12 h in a nitrogen atmosphere under atmospheric pressure. In order to investigate the above heat treatment of A, B, C and D during synthesis of polycarbosilane (PC), the intermediates were also heat treated without PBDS under the same conditions.

2.2. Measurements

Infrared spectra were measured in a $2\,\mathrm{g\,l^{-1}}$ *n*-hexane solution with a Hitachi IR-430 grating infrared spectrometer with a 0.1 cm light-path length of the solution cell. The absorptivities of Si–Si, $\mathrm{Si{-}CH_2{-}Si}$, $\mathrm{Si{-}CH_3}$ and Si–H bonds in A, B, C, D and the polymerized products were calculated from the following equation [9].

$$K = \frac{1}{CL}\log\left(I_0/I\right) \qquad (2)$$

where K is the absorptivity ($\mathrm{l\,g^{-1}\,cm^{-1}}$), C the concentration ($\mathrm{g\,l^{-1}}$), L the light-path (cm), $\log(I_0/I)$ the absorbance. Ultraviolet spectra were measured in a $0.02\,\mathrm{g\,l^{-1}}$ *n*-hexane solution using a 1 cm light-path length of the solution cell. The absorptivities of the specimens were also calculated from Equation 2. Gel permeation chromatograms (GPC) were taken with a Toyo Soda HCL-801 A with G-4000 HXL, G-3000 HXL, G-2000 HXL(× 2) and G-2000 H8(× 2) packings and tetrahydrofran eluent at a flowrate of $1\,\mathrm{ml\,min^{-1}}$ at 40° C using polystyrene as a standard specimen.

3. Results and discussion

3.1. Characterization of organosilicon intermediates

The infrared spectra of PS and four kinds of organosilicon intermediates (A, B, C and D) are shown in Fig. 1. The absorptions at $2950\,\mathrm{cm^{-1}}$ (C–H stretching), $1400\,\mathrm{cm^{-1}}$ (C–H deformation), $1250\,\mathrm{cm^{-1}}$ (Si-Me deformation), $1040\,\mathrm{cm^{-1}}$ (Si–O stretching), $820\,\mathrm{cm^{-1}}$ (Si–C stretching), $2100\,\mathrm{cm^{-1}}$ (Si–H stretching), $1355\,\mathrm{cm^{-1}}$ ($\mathrm{CH_2}$ deformation of $\mathrm{Si{-}CH_2{-}Si}$ bond) and $1020\,\mathrm{cm^{-1}}$ ($\mathrm{CH_2}$ wagging of $\mathrm{Si{-}CH_2{-}Si}$ bond) are observed.

Figure 2 shows the ultraviolet spectra of four kinds of intermediates (A, B, C and D). A very broad absorption at 210 to 300 nm corresponding to the Si–Si bond is recognized for every intermediate.

The absorptivities of these four intermediates corresponding to Si–H, $\mathrm{Si{-}CH_2{-}Si}$, $\mathrm{Si{-}CH_3}$ and Si–Si bonds, which are calculated from the results of Figs 1 and 2, are shown in Table I with weight average molecular weights ($\bar{M}_w$). The number of Si–H and $\mathrm{Si{-}CH_2{-}Si}$ bonds in A, B, C and D, is found to decrease in that order, whereas the number of $\mathrm{Si{-}CH_3}$ and Si–Si bonds in A, B, C and D, are found to increase in that order, with increase in $\bar{M}_w$.

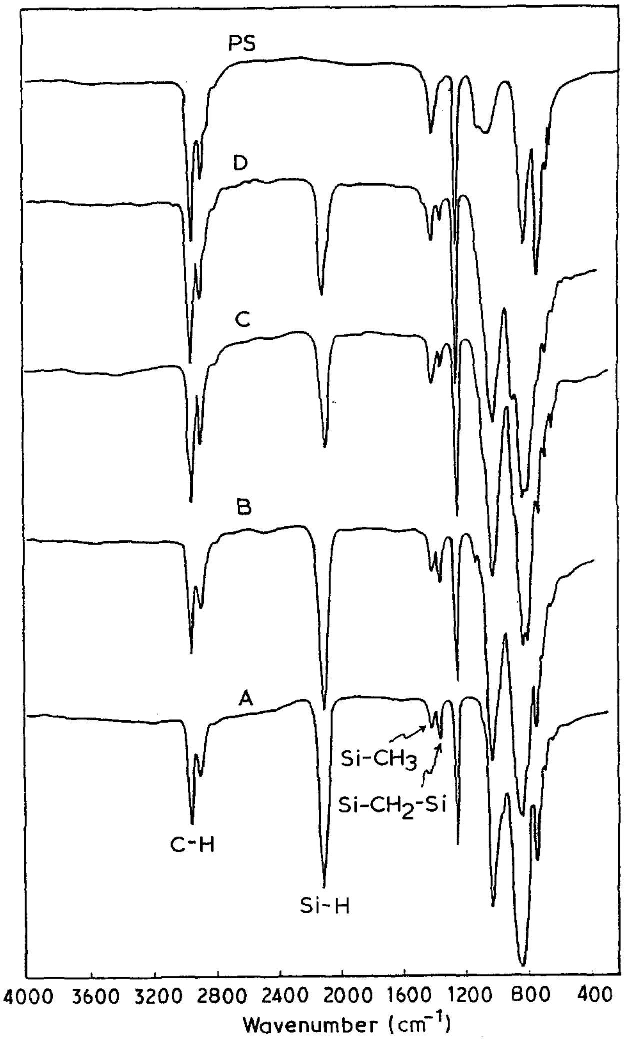


Figure 1 Infrared spectra of PS and organosilicon intermediates A, B, C and D.

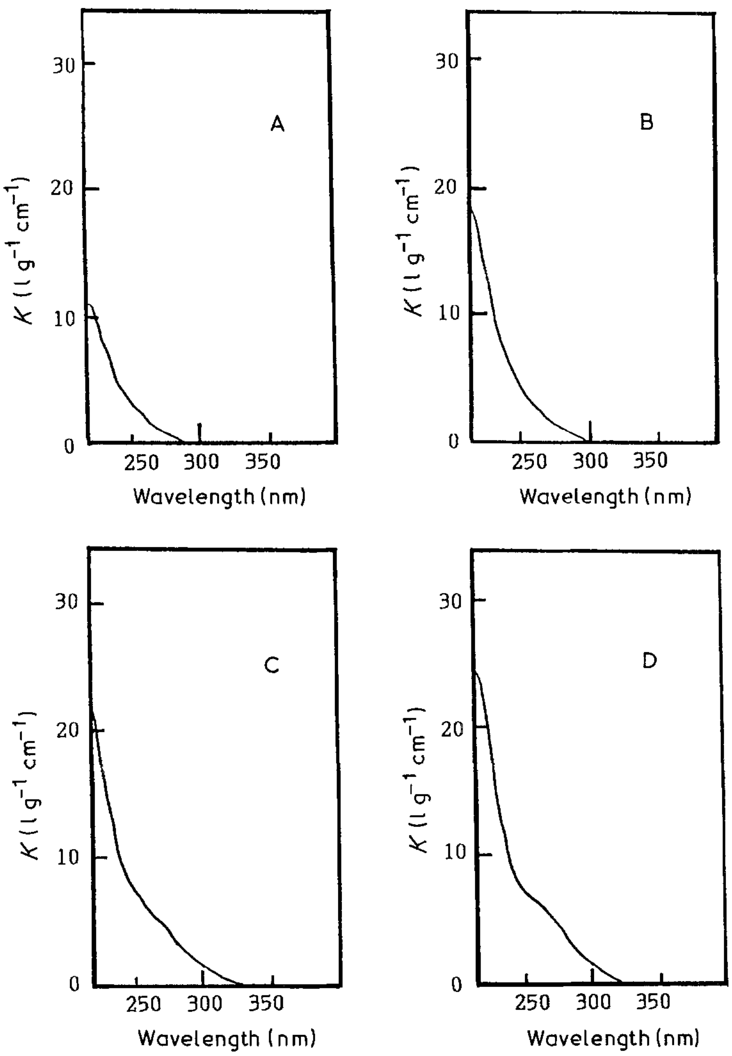


Figure 2 Ultraviolet spectra of organosilicon intermediates.

3.2. Reaction mechanism of polydimethylsilane to polycarbosilane with PBDS

In order to investigate the reaction mechanism of polydimethylsilane to polycarbosilane in the presence of PBDS, organosilicon intermediates (A, B, C, D) were heat treated in the presence of 3 wt % PBDS. As seen from Fig. 3, the $\bar{M}_w$ of A, B, C and D increase with reaction time and the extent of these increases in $\bar{M}_w$ become smaller as the reaction of each intermediate with PBDS proceeds. The initial rates of the reaction of the four intermediates, i.e. the ease of polymerization of A, B, C and D, were observed to decrease in that order. The faster the initial rate of polymerization, the larger the increase in $\bar{M}_w$ becomes.

In order to investigate the contribution of different structural units in the intermediates (A, B, C and D) to the formation of polycarbosilane in the presence of PBDS, changes in the numbers of various bonds, i.e. Si-H, Si-Si, Si-CH_2-Si and Si-CH_3 bonds, in the intermediates were examined. During the reaction, an enormous decrease in Si-H bonds in all intermediates is observed at the beginning of the reaction up to 5 h, as shown in Fig. 4. The Si-H bonds in the starting materials with large numbers of this bonds tend to decrease enormously, and furthermore, changes in the number of Si-H bonds in all reaction products are rarely observed after 6 h.

The changes in the ultraviolet absorptivity at a wavelength of 212 nm, which corresponds to the Si-Si

TABLE I The properties of organosilicon intermediates (OSI)

OSI	Absorptivity ($l g^{-1} cm^{-1}$)				M_w‡
	Infrared*			Ultraviolet†	
	Si-H (2100 cm^{-1})	Si-CH_2-Si (1350 cm^{-1})	Si-CH_3 (1400 cm^{-1})	Si-Si (212 nm)	
A	3.47	0.54	0.26	11	213
B	2.20	0.39	0.30	19	298
C	1.56	0.32	0.52	22	340
D	1.11	0.27	0.63	24	404

*Absorptivity in a 2 $g l^{-1}$ n-hexane solution.
†Absorptivity in a 0.02 $g l^{-1}$ n-hexane solution.
‡Weight average molecular weight converted by polystyrene.

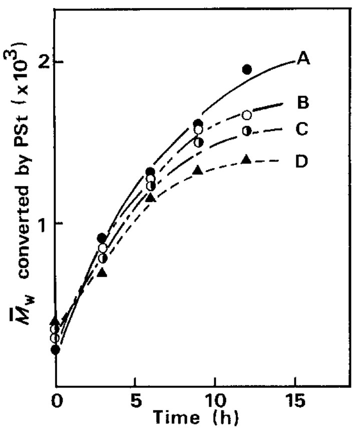


Figure 3 The changes in $\bar{M}_w$ during reaction of the four intermediates with 3 wt % PBDS at 340° C.

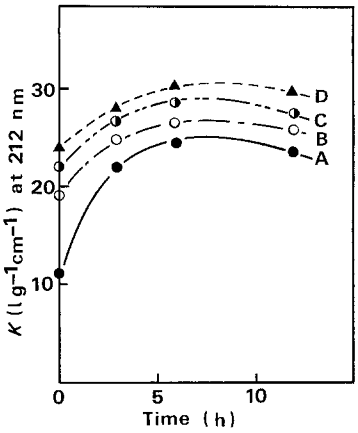


Figure 5 The changes in the ultraviolet absorptivity at the wavelength of 212 nm (Si–Si bond) during reaction of the four intermediates with 3 wt% PBDS at 340° C.

bond, are shown in Fig. 5. The number of Si–Si bonds increases up to 6 h, and the amount of A greatly increases. From comparison of the changes in $\bar{M}_w$, Si–H and SI–Si bonds, given in Figs 3, 4 and 5, respectively, it is assumed that the increase in Si–Si bonds correlates closely with the variation of both Si–H bonds and $\bar{M}_w$, i.e. that the increase in $\bar{M}_w$ in the initial stage of the reaction up to 6 h may be attributed to the condensation by dehydrogenation between Si–H bonds which is predominant when using an intermediate with a large number of Si–H bonds as the starting material, and can result in the formation of Si–Si bonds. This good interrelation between the changes in Si–H, Si–Si bonds and $\bar{M}_w$, however, is not observed in the reaction after 6 h, after which $\bar{M}_w$ continuously increases, whereas the number of Si–H bonds remains unchanged and the number of Si–Si bonds decreases slightly. This ambiguous behaviour will be explained later.

Fig. 6 shows the changes in infrared absorptivity at 1350 cm^{-1}, which corresponds to the Si–CH_2–Si bond, of the intermediates, during the reaction of the four intermediates with PBDS. The number of Si–CH_2–Si bonds in each intermediate increases gradually as this reaction proceeds, and the increment of this bond in the intermediates A, B, C and D, which increases in that order, is observed in the first stage of the reaction.

The number of Si–CH_3 bonds in the intermediates also decreases during the reaction as seen in Fig. 7. A reduction in the number of Si–CH_3 bonds in intermediates A, B, C and D which increases in that order, is found, and this tendency is in accord with that of the increase in Si–CH_2–Si bonds given in Fig. 6.

Because the initial rate of increase in Si–CH_2–Si bonds is found to be faster for the reaction of the intermediate with a large number of Si–Si and Si–CH_3 bonds, than that observed for the intermediate with a small number of these bonds, the formation of Si–CH_2–Si bonds is considered to be due to the cleavage of Si–Si bonds, and the rearrangement of the radicals so formed with Si–CH_3 bonds, as previously published [7]. For this formation of Si–CH_2–Si bonds, not only Si–Si bonds in the original intermediate, i.e. the starting materials, but also Si–Si bonds formed by the dehydrogenation of Si–H bonds during the reaction, are responsible. The fact that Si–Si bonds formed during the reaction contribute partly to the formation of Si–CH_2–Si bonds, is confirmed by the decrease in Si–Si bonds during this reaction after 6 h, as shown in Fig. 5. In the conversion from Si–Si bonds to Si–CH_2–Si bonds, the formation of Si–H bonds, which is accompanied by a decrease in Si–CH_3 bonds, i.e. the rearrangement reaction, should also occur without an increase in $\bar{M}_w$, as shown below.

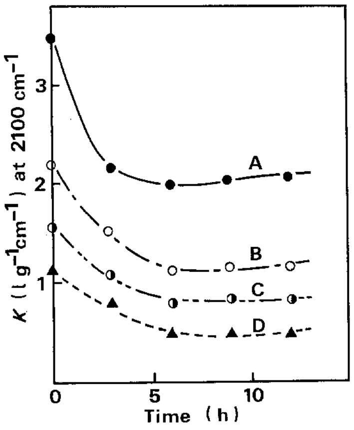


Figure 4 The changes in infrared absorptivity at 2100 cm^{-1} (Si–H bond) during reaction of the four intermediates with 3 wt % PBDS at 340° C.

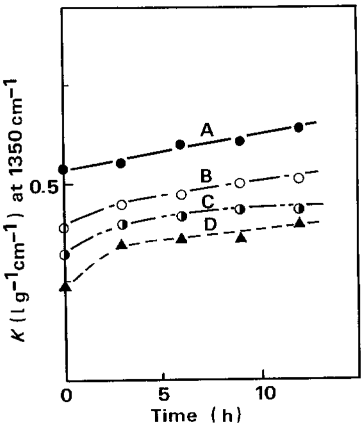


Figure 6 The changes in infrared absorptivity at 1350 cm^{-1} (Si–CH_2–Si bond) during reaction of the four intermediates with 3 wt % PBDS at 340° C.

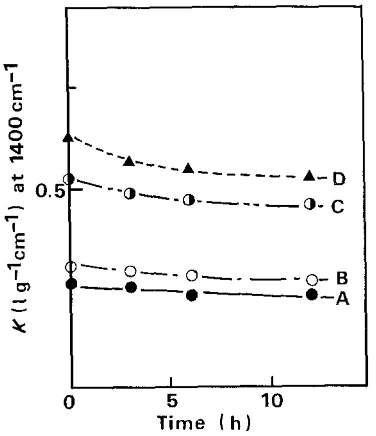
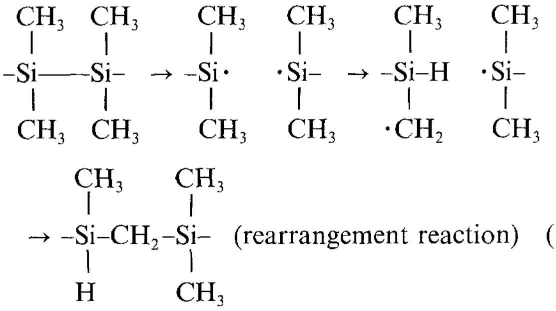


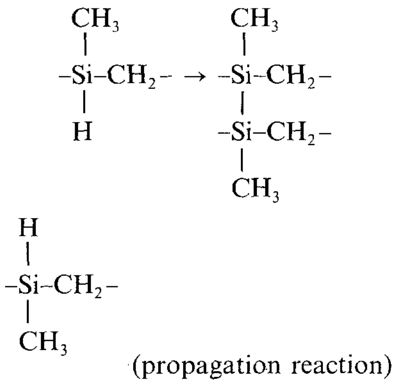
Figure 7 The changes in infrared absorptivity at 1400 cm^{-1} (Si–CH$_3$ bond) during reaction of the four intermediates with 3 wt % PBDS at 340° C.



$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}- \rightarrow -\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\cdot \quad \cdot\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}- \rightarrow -\underset{\cdot\mathrm{CH_2}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{H} \quad \cdot\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-$$

$$\rightarrow -\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}- \quad \text{(rearrangement reaction)} \quad (3)$$

On the other hand, the increase in molecular weight through the propagation reaction, can be assumed to be due to the dehydrogenation of Si–H bonds and then the formation of Si–Si bonds as given below.



$$-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_2}- \rightarrow \begin{array}{l} \quad\mathrm{CH_3} \\ \quad | \\ -\mathrm{Si}-\mathrm{CH_2}- \\ \quad | \\ -\mathrm{Si}-\mathrm{CH_2}- \\ \quad | \\ \quad\mathrm{CH_3} \end{array} \quad (4)$$

$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{Si}}}-\mathrm{CH_2}- \quad (4)$$

(propagation reaction)

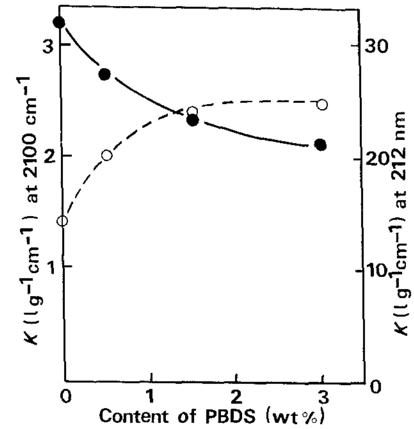


Figure 9 The changes in (●) infrared absorptivity at 2100 cm^{-1} (Si–H bond) and (○) ultraviolet absorptivity at 212 nm (Si–Si bond) during reaction of intermediate A with various contents of PBDS at 340° C.

The rearrangement reaction and the propagation reaction proceed simultaneously or stepwise during the reaction of the intermediates with PBDS to form PC. Although the rearrangement reaction accompanied by the increase in Si–H bonds and the decrease in Si–Si bonds should also occur, the predominant occurrence of the propagation reaction at the beginning of the reaction from 0 to 6 h can be considered from the results which show the abrupt decrease in Si–H bonds and the steep increase in Si–Si bonds and $\bar{M}_w$ as shown in Figs 4, 5 and 3. After 6 h reaction, the rearrangement reaction presumably becomes predominant because of both the decrease in the active functional groups (Si–H bonds) and the increase in the steric hindrance with progress of the propagation reaction. This phenomenon can be confirmed by the fact that few changes of Si–H and Si–Si bonds are apparently observed, in spite of the increase in $\bar{M}_w$ during the reaction after 6 h, as seen from Figs 3, 4 and 5.

The effect of the concentration of PBDS on these reactions was then investigated to clarify further the reaction mechanism in the presence of PBDS. The changes in $\bar{M}_w$, Si–H, Si–Si, Si–CH$_2$–Si and Si–CH$_3$ bonds with the concentration of PBDS during the reaction using intermediate A as the starting material, are shown in Figs 8, 9 and 10. Increases in $\bar{M}_w$ and Si–Si bonds, and decreases in Si–H, are observed, whereas changes in Si–CH$_2$–Si and Si–CH$_3$ bonds

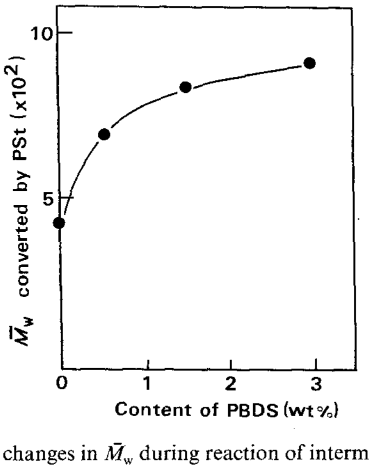


Figure 8 The changes in $\bar{M}_w$ during reaction of intermediate A with various contents of PBDS at 340° C for 3 h.

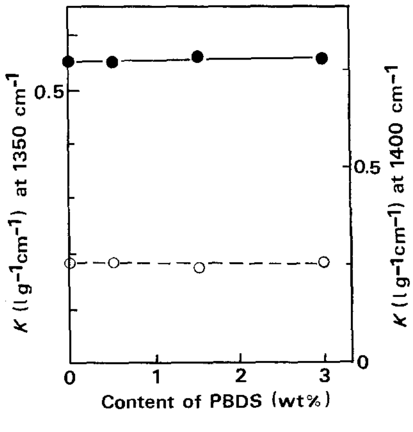


Figure 10 The changes in infrared absorptivities at (●) 1350 and (○) 1400 cm^{-1} (Si–CH$_2$–Si and Si–CH$_3$ bonds, respectively) during reaction of intermediate A with various contents of PBDS at 340° C for 3 h.

are virtually negligible as the concentration of PBDS increases. Therefore, it is assumed that PBDS plays a role in accelerating the polycondensation reaction, i.e. the propagation reaction occurred by dehydrogenation of Si–H bonds, but takes no part in the radical rearrangement reaction from Si–Si bonds to Si–CH_2–Si bonds. The absence of any subsequent rearrangement reaction from newly formed Si–Si bonds to Si–CH_2–Si bonds is due to the better stability of the Si–Si bonds than the PBDS, in comparison with that of Si–Si bonds contained in the starting materials.

4. Conclusions

In the conversion process from polydimethylsilane to polycarbosilane, which is available for producing SiC fibre in the presence of a small amount of PBDS, the cleavage of the framework of Si–Si bonds and the subsequent formation of Si–CH_2–Si and Si–H bonds due to rearrangement of the radicals formed and Si–CH_3 bonds, initially occur. Si–Si bonds are then formed by the dehydrogenation of Si–H bonds, i.e. the polycondensation reaction proceeds to form macromolecular polycarbosilane with cross-linking points. In the reaction, PBDS plays a role in accelerating the polycondensation reaction by dehydrogenation of Si–H bonds with the formation of Si–Si bonds.

Up to now it has been thought that PBDS may contribute to enhancement of the carbosilane skeleton [6]. In this investigation, however, it is assumed that PBDS plays no part in the radical rearrangement reaction from Si–Si bonds to Si–CH_2–Si bonds (carbosilane skeleton).

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