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Synthesis of continuous silicon carbide fibre

Part 4 *The structure of polycarbosilane as the precursor*

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The structure of polycarbosilane is represented by three structural elements, but their quantification is difficult. Polycarbosilanes were synthesized by three methods and the respective molecular structures were examined by measurements of the molecular weight and the intrinsic viscosity, infrared, ultraviolet, ^{1}H-, ^{13}C- and ^{29}Si-NMR spectral measurements, and chemical analysis. The three structural elements (SiC_4, SiC_3H, SiC_xSi_{4-x}) in the polycarbosilane molecule were determined quantitatively. By the comparison between ^{1}H-NMR spectral data and calculation assuming a linear chain structure, the number of linkages in the unit consisting of ten silicon atoms was estimated to be 3 to 4. This result is in agreement with the result from the intrinsic viscosity; it was found that the shape of the polycarbosilane molecule is planar.

1. Introduction

We reported previously the methods of synthesis of polycarbosilanes (PC) and continuous SiC fibres from PCs and the pyrolysis process of PCs [1–3]. Consequently, structures and properties of PC and SiC fibre were shown. There are some problems in the industrial production of SiC fibres. The high cost of the raw materials, for example, was solved by the synthesis of PC from polydimethylsilane at normal pressure with a yield of about 65% [3], instead of using an autoclave under pressure. The influence of oxygen introduced during the production of the SiC fibre on the properties of the fibre were studied [4–6]. However, these problems are related to the structure of PC. In order to produce PC with a high yield and to improve the properties of the ceramic obtained by pyrolysis from the PC, the structure of PC and its pyrolysis process must be studied in detail. In studies of the oxidation of PC and the pyrolysis process of the oxidized (cured) PC, exact quantification of the three structural elements in the PC molecule is necessary: silicon bonded with four carbon atoms (SiC_4), silicon bonded with three carbon atoms and one hydrogen atom (SiC_3H), and silicon bonded with x carbon atoms and $(4 - x)$ silicon atoms (SiC_xSi_{4-x}, $x = 1$, 2 or 3).

In the present work, the structures of PCs synthesized by three methods were determined more quantitatively by characterization of PC [3] and infrared spectrum and intrinsic viscosity.

2. Experimental techniques

2.1. Synthesis of polycarbosilanes

PCs were synthesized by three methods [1–3]: PC by thermal decomposition and condensation of tetramethylsilane (TMS) for 14 to 29 h, recycling the vapour in a quartz tube heated at 760 to 775° C, as in the method described by Fritz *et al.* [7] (PC-TMS); PC by thermal decomposition and condensation of polydimethylsilane (PDMS) in an autoclave at 450, 460 and 470° C for 14 h (PC-450, PC-460 and PC-470); and PC by thermal decomposition and condensation of PDMS added with 3.2 and 5.5 wt % borodiphenylsiloxane at 350° C for 10 h under nitrogen gas flow (PC-B3.2 and PC-B5.5).

These PCs were condensed by removal of the components with low boiling points, after removal of those insoluble in hexane or xylene by filtration. The synthetic conditions and the yields of PCs are shown in Table I.

2.2. Measurements

The following measurements were made for the respective PCs.

The number average molecular weight ($\bar{M}_n$) was measured, using an Hitachi 117 molecular weight apparatus, by the vapour pressure osmometry method in benzene solution, and using benzil as the standard material.

The molecular weight distribution was measured using an Hitachi HLC-655, Shodex A-804 as a GPC* column, in THF† solution, at a flow rate of 1 ml min^{-1} and a pressure of 8 kg cm^{-2}, the detection with a wave length of 254 nm of a variable wavelength UV monitor.

The intrinsic viscosity (η) was measured with Ubbelohde's viscometer at 25.0° C in benzene solution.

An Hitachi 295 infrared spectrophotometer, was

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*Gel permeation chromatography.
†Tetrahydrofuran.

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TABLE I Synthesis of polycarbosilanes

PC	Reaction time (h)	Reaction temperature (°C)	Distillation temperature / Pressure (°C/torr)	Yield (%)	$\bar{M}_n$	η (cm^3 g^{-1})	Elemental analysis (%)				
							Si	C	H	O*	B
PC-450	14	450	150/1	66.3	730	1.71	–	–	–	–	–
	14	450	280/1	50.8	1250	–	–	–	–	–	–
PC-460	14	460	280/1	56.0	1450	–	47.13	36.99	7.00	0.84(< 0.93)	–
PC-470	14	470	105/1	66.4	860	1.94	–	–	–	–	–
	14	470	200/1	59.7	1210	2.14	–	–	–	–	–
	14	470	280/1	58.8	1680	2.46	48.18	39.92	6.85	0.81(< 0.88)	–
PC-B3.2	10	350	280/1	50.0	1740	–	44.50	35.80	8.00	4.83(< 1.72	0.02
PC-B5.5	10	350	320/760	64.8	1310	–	44.90	39.20	7.44	3.56(< 1.73)	0.06
PC-TMS	27	760	200/1	6.5	620	1.55	44.80	39.90	6.79	1.21(0)	–
	29	760	200/1	5.1	820	1.73					
	14	770	200/1	10.0	740	–					
	16	770	200/1	6.5	930	1.76					
	21	775	200/1	9.3	830	–					

*Calculated values in parentheses.

used to obtain IR spectra using a fixed-thickness (0.2 mm) cell of KBr, in CCl_4 solution. The UV spectrum was measured with an Hitachi 228 spectrophotometer in 0.1 g l^{-1} hexane solution, using a quartz cell of thickness 1 cm. ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were measured with a Jeol JNM-FX60 high-resolution FT NMR spectrometer at 60 MHz for ^{1}H, 15 MHz for ^{13}C and 11.9 MHz for ^{29}Si in $CDCl_3$ solution, using TMS as the internal standard. Measurements of ^{1}H- and ^{29}Si-NMR spectra, in particular, were made accurately compared with those in the previous work [3].

Silicon, carbon, hydrogen, oxygen and boron [3], and especially oxygen were determined by chemical analysis, with the accuracy of the results checked by remeasurement.

Values of $\bar{M}_n$ and η and the results of the chemical analysis are given in Table I. Chemical analysis of PC-TMS was performed as for the mixed PC-TMS.

3. Results

3.1. Molecular shape

In Table I, $\bar{M}_n$ of the respective PCs is shown. $\bar{M}_n$ increases with increase of reaction temperature as seen in PC-450, PC-460 and PC-470, and changes largely with the degree of removal of the low molecular weight components. $\bar{M}_n$ is thus influenced by the synthesis of conditions. Fig. 1 shows the elution curves obtained from gel permeation chromatography (GPC) of PC-450, PC-460, PC-470 and PC-TMS; Fig. 2 shows the curves for PC-B3.2 and PC-B5.5. The molecular weight distributions are characteristic of the methods of synthesis, that is, the molecular weight distributions of PC-450, PC-460 and PC-470 are narrower than those of PC-B3.2, PC-B5.5 and PC-TMS; the values of $\bar{M}_w/\bar{M}_n$ of PC-450, PC-470, PC-B3.2, PC-B5.5 and PC-TMS are 1.6, 2.0, 3.5, 4.8 and 2.8, respectively. Of these PCs, PC-470, PC-B3.2, PC-B5.5 and PC-TMS are usable as the precursors of SiC fibre [2, 3]. Whether or not PC can be used as a precursor is related not only to $\bar{M}_w/\bar{M}_m$ and $\bar{M}_n$. For example, the difference between PC-450 or PC-460 and PC-470 is eliminated by removal of the low molecular weight components from PC-450 or PC-460, and chemical properties of PC-470 and PC-TMS are different [3]. In any case, the size distribution of the respective PC molecules differ according to the methods of synthesis.

The molecular shape of the PC molecules was then examined. In Fig. 3, the relationship between η and

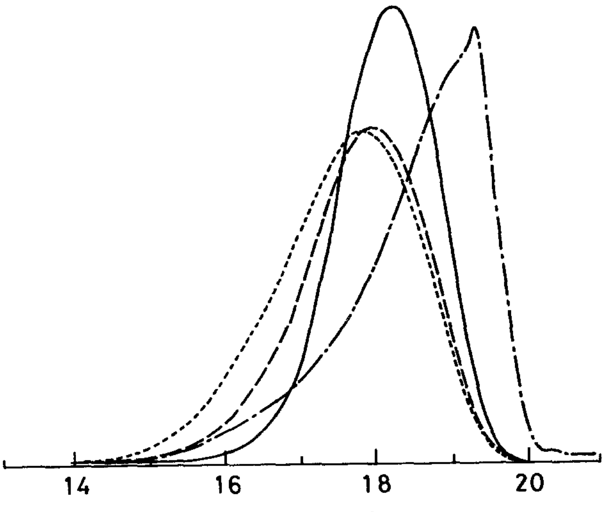


Figure 1 Elution curves of polycarbosilanes: ——— PC-450; – – – PC-460; · · · · PC-470; – · – PC-TMS.

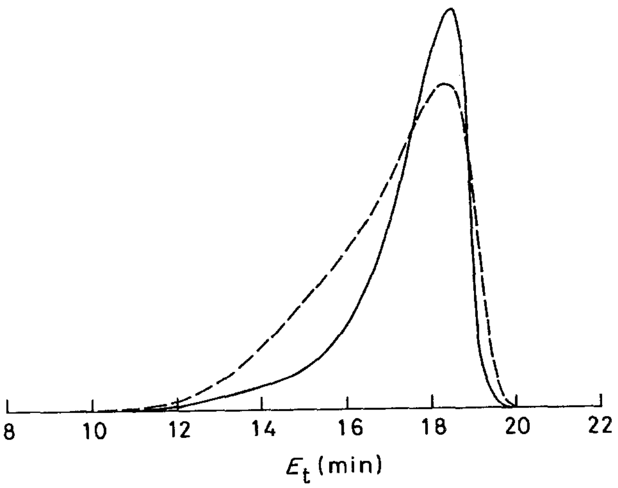


Figure 2 Elution curves of polycarbosilanes: ——— PC-B3.2; – – – PC-B5.5.

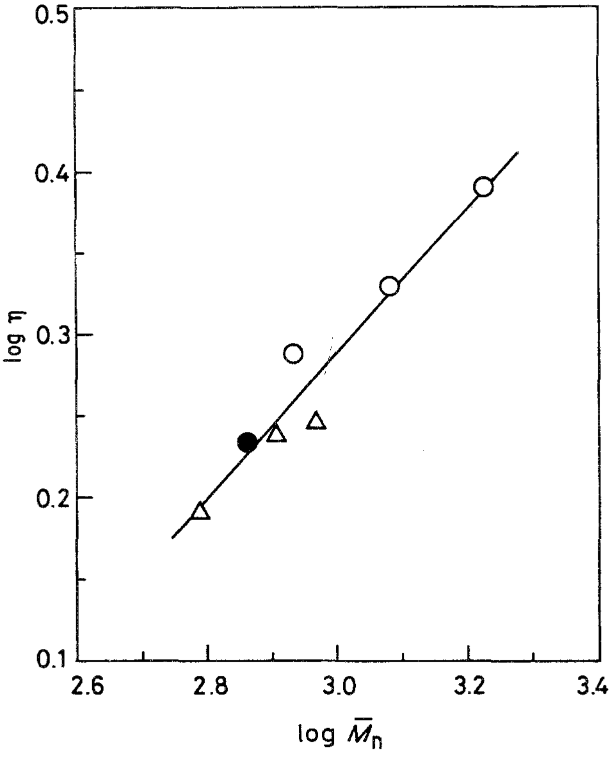


Figure 3 A logarithmic plot of the intrinsic viscosity in benzene solution at 25.0° C against the number average molecular weight: ● PC-450; ○ PC-470; △ PC-TMS.

$\bar{M}_n$ is shown. η was measured for PC-TMS, PC-450 and PC-470 having a relatively narrow molecular weight distribution as described above. A common empirical relation between molecular weight and η in polymers is the Sakurada–Houwink relation

$$\eta = KM^a \qquad (1)$$

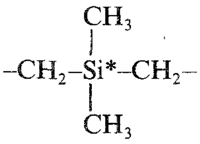
where K and a are constants determined by the polymer, solvent and temperature. Although it is difficult to treat η theoretically, there are the values for hydrolysed silicon tetraethoxide [8] and pitches [9, 10] in benzene solution; the molecular shapes are discussed in relation to the values of a determined from Equation 1. From Fig. 3, the value of a is found to be 0.47 by the least squares method. This value is comparable with values of 0.14 to 0.21 for pitches and 0.23 to 0.75 for hydrolysed silicon tetraethoxide. In rigid molecules, $a = 0$, 0.5 and 2 for spherical, planar and rod-like shapes, respectively. In polymers, the values are generally 0.5 to 1.0. For pitches, the molecular shape is thus considered to be three-dimensional, not planar, under oblate ellipsoid hypothesis [11]. In the hydrolysed silicon tetraethoxide, a varies with the degree of hydrolysis, and branches and crosslinkings form during the process of hydrolysis [8]. The values of a are also related to spinability; at $a > 0.5$, it is spinable, containing linear polymers and at $a > 0.5$, the molecular structure is three-dimensional.

By comparison with these results, the molecular shape of PCs is inferred to be planar, containing linear chains, because the value of $a = 0.47$ is larger than the values for pitches. This is supported by the fact that Fritz *et al.* [7] found many compounds with condensed six-membered rings when the products in pyrolysis and condensation of TMS were isolated and identified. Accordingly, it is considered that the shape of PC molecules is planar, containing a ring structure consisting of a carbosilane skeleton, e.g. a six-membered ring, or a condensed structure and a linear structure connecting the ring structures.

From measurements of the intrinsic viscosities, it is suggested that there are no differences in molecular shape according to the methods of synthesis. Of course, with the samples in the narrower molecular weight distribution, by examination of the dependence of η on temperature and solvent, some differences may be found between the PCs. This is a subject for future study. The chemical structures of the PCs will then be examined comparatively with the measurements of intrinsic viscosities.

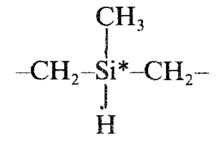
3.2. Molecular structure

As revealed by the measurement of intrinsic viscosities, the molecular shape of the PCs is not merely linear or ring. It is planar and complex, consisting of linear and ring structures, with branched chains and a crosslinked structure. Therefore, it is difficult to show precisely the molecular structure. It is important, however, to represent the chemical structure of the PC molecules in average structural elements. As reported in a previous paper [3], the silicon atoms in PC molecules fall into three groups with four atoms bonding to them: silicon bonded with four carbon atoms (SiC_4), silicon bonded with three carbon atoms and one hydrogen atom (SiC_3H), and silicon bonded with x carbon atoms and $(4 - x)$ silicon atoms (SiC_xSi_{4-x}, $x = 1$, 2 or 3). These are shown in the following structures; note the Si* atoms:



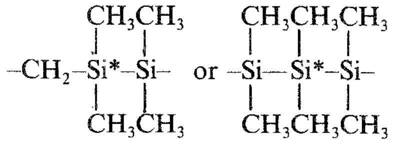
$-CH_2-\overset{CH_3}{\underset{CH_3}{Si^*}}-CH_2-$

SiC_4
(1)



$-CH_2-\overset{CH_3}{\underset{H}{Si^*}}-CH_2-$

SiC_3H
(2)



$-CH_2-\overset{CH_3}{\underset{CH_3}{Si^*}}-\overset{CH_3}{\underset{CH_3}{Si}}-$ or $-\overset{CH_3}{\underset{CH_3}{Si}}-\overset{CH_3}{\underset{CH_3}{Si^*}}-\overset{CH_3}{\underset{CH_3}{Si}}-$

SiC_xSi_{4-x}
(3)

It is assumed here that the PC molecules are in a linear chain. The problem must be re-examined, however, taking into consideration that the molecular sructure consists of linear and ring structures. In Table II, the fractions of the three elements calculated which have

TABLE II Fractions of SiC_4, SiC_3H and SiC_xSi_{4-x} in polycarbosilanes calculated from the NMR spectra assuming that the PCs are linear polymers [3]

PC	SiC_4	SiC_3H	SiC_xSi_{4-x}
PC-470	0.501	0.490	0
PC-B3.2	0.533	0.330	0.137
PC-B5.5	0.485	0.400	0.115
PC-TMS	0.864	0.136	0

TABLE III C–H/Si–H, SiC_4/SiC_3H and $SiC_xSi_{4-x}/(SiC_4 + SiC_3H)$ in polycarbosilanes calculated from the NMR spectra

PC	C–H/Si–H	SiC_4/SiC_3H	$SiC_xSi_{4-x}/(SiC_4 + SiC_3H)$
PC-450	8.9	0.66	very small
PC-460	10.5	1.06	very small
PC-470	11.4	1.13	0
PC-B3.2	31.1	–	0.159
PC-B5.5	28.4	–	0.130
PC-TMS	36.8	4.20	0

a linear chain are shown [3]. Analyses in the present work are similar to those in the previous work [3], but IR spectra were measured quantitatively in solution and NMR spectra were determined more accurately.

3.2.1. NMR spectra

The ^1H-NMR spectrum of the respective PCs [1, 3] shows a large peak centred at 0 p.p.m. and a small peak at 4 to 5 p.p.m.; the former is due to hydrogen atoms in $Si–CH_3$, $Si–CH_2–$ etc., (C–H), and the latter to a hydrogen atom in Si–H (Si–H). In each case, the spectrum was measured several times, more than in the previous work [3], and the ratio of C–H to Si–H was obtained from integration of the peaks. The values are shown in Table III. In PC-B3.2, PC-B5.5 and PC-TMS, however, the Si–H peak is very small, and the comparison with C–H/Si–H between present (Table III) and previous [3] work indicates that there is variation in this ratio. Therefore, it is not appropriate to determine the C–H/Si–H ratio from the ^1H-NMR spectrum for the PCs with a small Si–H peak.

Information relating to silicon atoms is obtained from the ^{29}Si-NMR spectra [3], which are shown in Fig. 4. The values of SiC_4/SiC_3H and $SiC_xSi_{4-x}/(SiC_4 + SiC_3H)$ are then obtained from integration of the peaks. These values, obtained by more measurements than in the previous work [3], are shown in Table III. The chemical shifts of SiC_4, SiC_3H and SiC_xSi_{4-x} (polysilane skeletons) and the spin–spin coupling constants of $^{29}Si–^1H$ (J_{Si-H}) are in good agreement with those in the literature [12–14] (Table IV). There are two problems in analysis of the ^{29}Si-NMR spectra. First, as indicated in Fig. 4, the peaks in PC-B are not separated sufficiently for determination of the SiC_4/SiC_3H ratio by integration. Second, the SiC_xSi_{4-x} peaks in PC-450 and PC-460 are too small for determination.

The spectra in PC-B will be considered first. The comparison between the ^1H decoupling and the non-decoupling spectra of PC-B3.2 in Fig. 4 indicates the following points. In the ^1H decoupling spectrum, the overall peak is opposite to that in the non-decoupling spectrum due to the negative nuclear Overhowser effect (NOE) [14]. It is characteristic of a compound whether the NOE is positive or negative, and whether the peak is upward or downward depends on this sign. For example, the NOEs in dodecamethylcyclohexasilane (DMCHS) and polydimethylsiloxane (PDMSO) are negative, and in hexamethyldisilane (HMDS) and hexamethyldisiloxane (HMDSO) positive [3]. In PC-B3.2, therefore, it appears that there are several peaks around 0 p.p.m. which cancel each other due to the different NOEs. The peaks overlapping the peak of SiC_4 around 0 p.p.m. are considered to be due to the oxidized silicon atoms. The peaks of HMDSO and PDMSO generally appear in this lower magnetic field [3], and the peaks of $-Si(CH_3)_2-O-$ and $-O-Si(CH_3)_2-O-$ lie in the magnetic field lower than -23 p.p.m. [14]. The peaks due to these siloxane units should thus appear in PC-B. This is in agreement with the fact that PC synthesized at low temperature, i.e. PC-B, is oxidized easily [15] and that the oxygen content in PC-B determined by elemental analysis is larger than the value calculated from the oxygen content in the raw material (Table I). From the measurement of

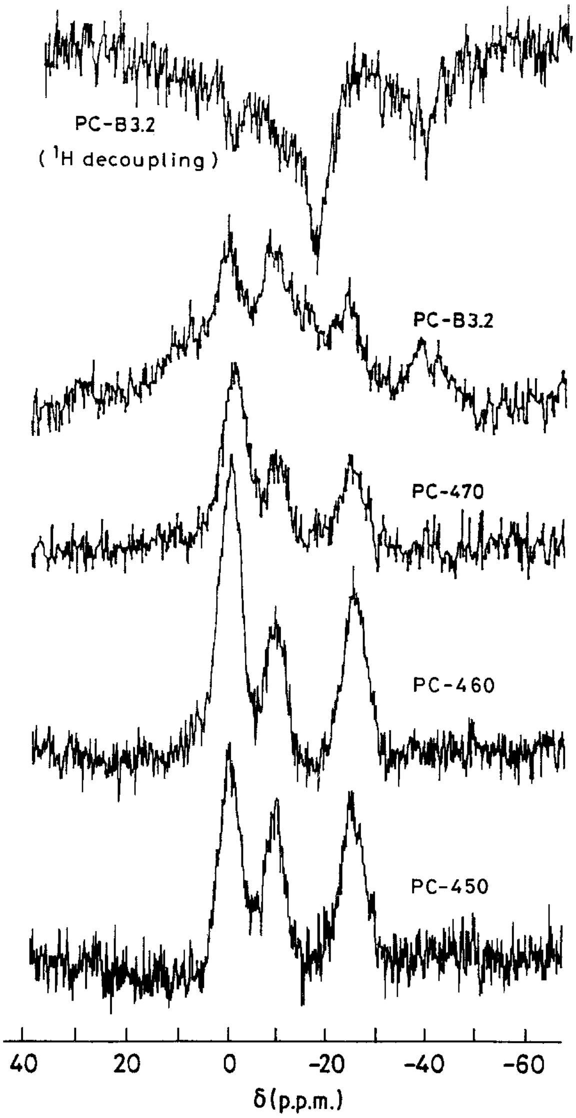


Figure 4 ^{29}Si–NMR spectra of PC-450, PC-460, PC-470 and PC-B3.2 and ^1H decoupling ^{29}Si-NMR spectrum of PC-B3.2.

TABLE IV ^{29}Si-NMR spectral data of polycarbosilanes in $CDCl_3$

PC	$\delta(SiC_4)$ (p.p.m.)	$\delta(SiC_3H)$ (p.p.m.)	J_{Si-H} (Hz)	$\delta(SiC_xSi_{4-x})$ (p.p.m.)
PC-450	-0.75	-17.50	182	–
PC-460	-0.75	-17.50	182	–
PC-470	-0.75	-17.50	182	–
PC-B3.2	0.50	-16.01	180	-38.48
PC-B5.5	0.50	-16.43	180	-38.48
PC-TMS	-0.75	-17.50	182	–

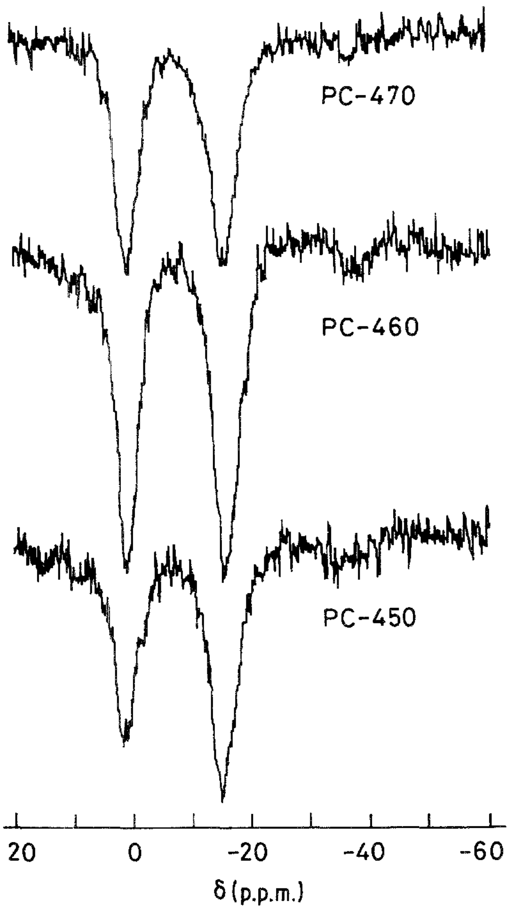


Figure 5 ^{1}H decoupling ^{29}Si-NMR spectra of PC-450, PC-460 and PC-470.

UV spectra, it was shown that the siloxane units in PC-B were formed by oxidation of the polysilane skeleton (SiC_xSi_{4-x}) [15]. Therefore, the peaks overlapping the SiC_4 peak in this low magnetic field should be assigned to SiC_xSi_{4-x}. The peaks cannot be separated, however, and so in analysis of the ^{29}Si-NMR spectra the peaks in this low magnetic field are all assigned to SiC_4 or SiC_3H. This is the cause for the inseparable peaks in PC-B and leads to errors in the determinations of SiC_xSi_{4-x} and SiC_4/SiC_3H.

The determination of SiC_xSi_{4-x} in PC-450 and PC-460 is now considered. Although it is not clear in Fig. 4, the existence of peaks at about −34 p.p.m. is indicated by the ^{1}H decoupling spectra of PC-450 and PC-460 in Fig. 5. If there is a structural element of SiC_xSi_{4-x} in the PC molecule, this should exhibit strong absorption in the UV spectrum [3]. In Fig. 6, the UV spectra of PC-470 and PC-450 are shown. The UV absorption is larger in PC-450 than in PC-470 in the region below 300 nm, so that the amount of polysilane skeleton should be larger in the former. It is difficult, however, to determine SiC_xSi_{4-x} in PC-450 and PC-460 from the ^{29}Si-NMR spectra.

Information on polysilane, carbosilane and siloxane skeletons in PC molecules should be obtained from the ^{13}C-NMR spectra [12, 16]. As shown in Fig. 7, however, the ^{13}C-NMR spectra of PC-470 and PC-B3.2 show only a broad peak, and the large difference between PC-470 and PC-B3.2, i.e. the polysilane skeleton is not detected in the spectra.

As seen above, the C–H/Si–H ratio in PC-B and PC-TMS, SiC_xSi_{4-x} in PC-B, PC-450 and PC-460, and SiC_4 and SiC_3H in PC-B, cannot be obtained accurately from the NMR spectra.

3.2.2. *IR spectra*

In the analysis of NMR spectra, a small or broad peak led to uncertain values of C–H/Si–H and SiC_4/SiC_3H in PC-B and PC-TMS, and the shift of peaks by oxidation and indistinct peaks in PC-B also led to uncertain values of $SiC_xSi_{4-x}/(SiC_4 + SiC_3H)$. However, on the basis of the exact values determined by NMR spectrum, the uncertainties can be corrected by analysis of the IR spectra, measured in solution, in Fig. 8. For this purpose, values of PC-470 not containing SiC_xSi_{4-x} are used as the reference values. From Table III, the fractions of SiC_4, SiC_3H and SiC_xSi_{4-x} are then determined easily, as follows.

The number of hydrogen atoms bonded to a silicon atom is not more than one and so SiC_3H can be determined by comparing the absorbance of the sharp

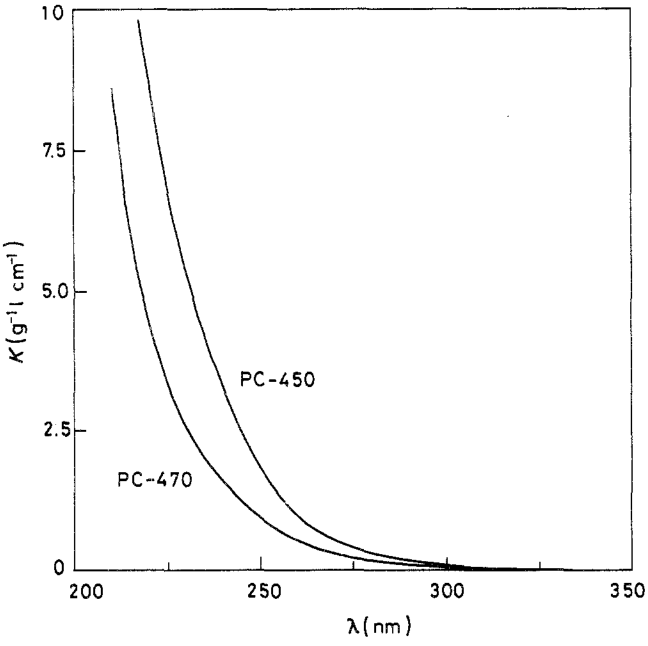


Figure 6 UV absorption spectra of PC-450 and PC-470.

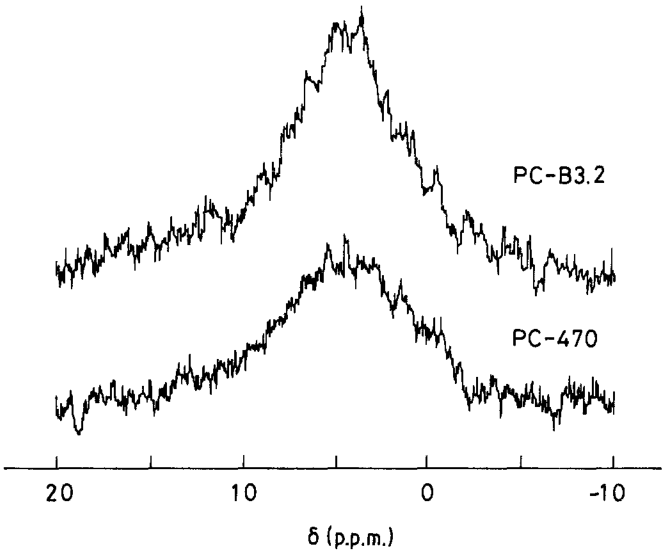


Figure 7 ^{13}C-NMR spectra of PC-470 and PC-B3.2.

peak of Si–H seen at 2120 cm^{-1} with the value in PC-470. There are no other peaks around this peak. It was confirmed that Beer's law holds here. In this way, the fractions of SiC_3H in the respective PCs were obtained, so that the fractions of SiC_4 in PC-450, PC-460 and PC-TMS were derived from the values of SiC_4/SiC_3H in Table III. The SiC_4 values for PC-450 and PC-460 are shown in Table V. For PC-TMS, a value of 0.76 was obtained, which is in agreement with 0.82 obtained from the ^{29}Si-NMR spectrum on the basis of $SiC_xSi_{4-x} = 0$; the usefulness of IR spectra for the determination of SiC_3H is thus shown. The SiC_3H values similarly obtained for PC-B are shown in Table V.

The fraction of the carbosilane skeleton in PCs can be estimated from the absorbance of the peak due to CH_2 deformation in the Si–CH_2–Si bond in the region of 1020 to 1040 cm^{-1}. By comparing the absorbance with that in PC-470, the fractions of carbosilane skeleton, i.e. SiC_4 + SiC_3H, in PC-450, PC-460, PC-B3.2, PC-B5.5 and PC-TMS were calculated from SiC_4 + SiC_3H in PC-470, assuming Beer's law holds. The values of SiC_xSi_{4-x} and SiC_4 were then obtained; the values for PC-B are shown in Table V. For PC-450, PC-460 and PC-TMS, the SiC_xSi_{4-x} values were found to be 0.07, 0.03 and -0.18, respectively, which are in agreement with those in Table V calculated from 1-(SiC_4 + SiC_3H). The usefulness of IR spectra for the determination of SiC_xSi_{4-x} is also shown.

On the other hand, the difference in SiC_xSi_{4-x} between NMR and IR spectra indicates the need for more exact values. The peak in the region of 1020 to 1040 cm^{-1} is due to CH_2 deformation in the carbosilane skeleton, easily influenced by its surroundings, and also to Si–O stretching. Consequently, in PCs with a large oxygen content, the method gives a large fraction of carbosilane skeleton and a small fraction of SiC_xSi_{4-x}. The value of SiC_xSi_{4-x} of PC-B in Table V is thus close to the actual value, as compared with the values obtained only from the NMR spectrum in Table II.

When the value of SiC_4 + SiC_3H is calculated from the area of the peak around 1020 to 1040 cm^{-1}, redrawn with absorbance instead of transmittance, by comparing it with that in PC-470, for PC-TMS it is found to be 0.98 so that SiC_xSi_{4-x} becomes 0.02. The value is superior to -0.18 obtained from the absorbance of the peak as described; the usefulness of peak areas in calculation of the SiC_4 + SiC_3H value is thus shown. In this method, however, caution is necessary

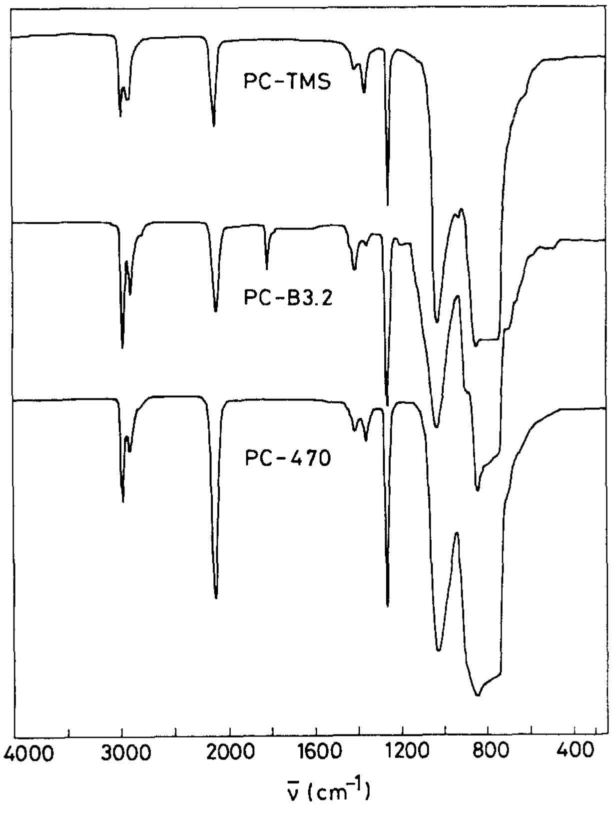


Figure 8 IR spectra of polycarbosilanes in CCl_4.

TABLE V Fractions of the structural elements in polycarbosilanes

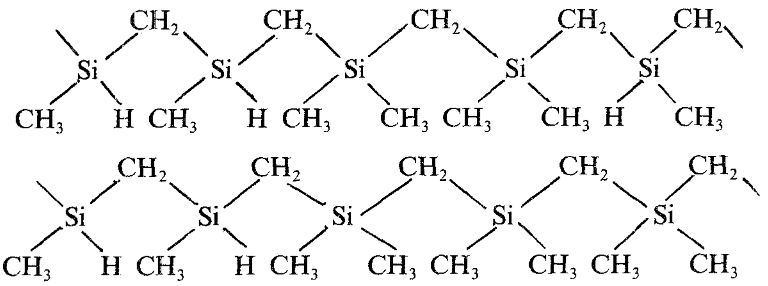
PC	SiC_4	SiC_3H	SiC_xSi_{4-x}	C–H/Si–H*
PC-450	0.38	0.57	0.05	10.86
PC-460	0.49	0.46	0.05	13.52
PC-470	0.53	0.47	0	14.02
PC-B3.2	0.40	0.16	0.44	41.50
PC-B5.5	0.44	0.15	0.41	44.86
PC-TMS	0.82	0.18	0	41.44

*Calculated, assuming a linear chain.

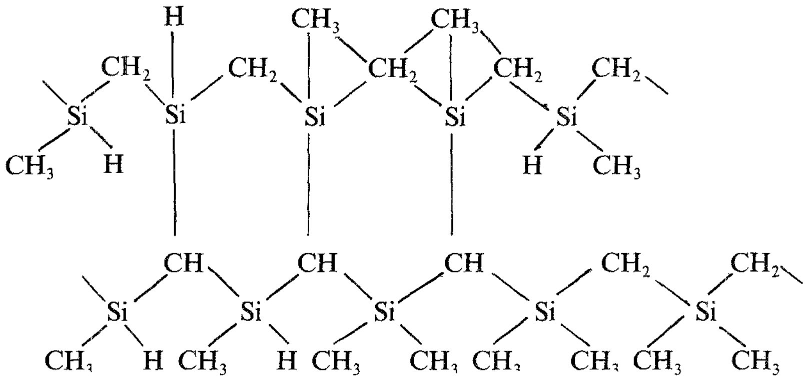
in such as PC-B, where in the absorption region peaks due to Si–O stretching and to phenyl groups with a strong absorption near 1100 cm^{-1} [17] introduced with the borosiloxane compound containing this phenyl group as the raw material, overlap.

3.2.3. Crosslinked structure

The value of C–H/Si–H in respective PCs was calculated from the structural elements 1, 2 and 3, assuming a linear chain structure for the PC molecule; the values are given in Table V. The values are larger than those in Table III obtained from the NMR spectra. The differences can be explained by the condensed structure between methyl groups or between methyl groups and methylene groups in the structural elements, with some C–Hs as CH_4, i.e. methane, being removed. Then, when the condensed portions are considered to be crosslinkings between the linear chain, the molecular shape should change from 4 to 5 (see below), as follows, one methane molecule being removed per crosslinking.



(4)



(5)

The number of methanes per silicon atoms was calculated for the respective PCs such that the value of C–H/Si–H would agree with that in Table III; the values are 0.28, 0.42, 0.31, 0.42, 0.62 and 0.21 for PC-450, PC-460, PC-470, PC-B3.2, PC-B5.5 and PC-TMS, respectively. While the values of C–H/Si–H in Table III have considerable error in PC-B and PC-TMS, the results indicate that the number of linkages between linear chains in the unit consisting of 10 silicon atoms in the PC molecules is 3 to 4. Structure 5 then corresponds to PC-470. The portion of crosslinkage is Si–$\overset{|}{C}$H– formed by the condensation between methyl and methylene groups, or Si–CH_2– formed by the condensation between methyl groups. A cyclic structure, other than a six-membered ring, may form and the linear chain structure may remain. In PC-450, PC-460 and PC-TMS, a structure similar to that in PC-470 may result by replacing some methyl groups with hydrogen atoms or vice versa in Structure 5, and in PC-B by replacing some $-CH_2-$ and $-\overset{|}{C}H-$ with $-Si(CH_3)_2-$ and $-\overset{|}{Si}CH_3-$.

As described, the molecular structures containing crosslinkage estimated from the NMR and IR spectra in Tables III and V are in agreement with the structure determined by measurement of the intrinsic viscosity, i.e. the molecular shape of PC is planar, with ring and chain structures.

4. Conclusions

Structure of the PCs synthesized by three methods is represented more exactly (Table V) than in the previous work [3] by three structural elements forming the PC skeleton. This was determined by measurements of the intrinsic viscosity, NMR and IR spectra. The molecular shape of PC was estimated to be planar, consisting of ring and chain structures.

Of the three, SiC_3H and SiC_xSi_{4-x} are the most important when PC is used as the precursor for the ceramic, because these two are related to the control of oxygen introduced during the curing process. The relationship between the structural elements and properties of the ceramic obtained from PC must be examined. It is also necessary to measure more exactly the intrinsic viscosity of the monodisperse polymer and the oxygen content, and to analyse likewise the NMR, IR and UV spectra.

In the next report, the mechanism of curing and the conversion of the cured PC fibre to SiC fibre will be described in detail, together with the three structural elements.

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