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A study of the oxidation curing mechanism of polycarbosilane fibre by solid-state high-resolution nuclear magnetic resonance

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The chemical structure of oxidation-cured polycarbosilane fibres has been studied by IR and chemical analysis, but its structure has not been identified in detail. In this work, the molecular structure was examined by chemical analysis, and solid state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. Si–O–Si, Si–O–C(I) and Si–O–C(II) bonds were formed by the oxidation curing process. The six chemical bonds (Si–C, Si–H, Si–Si, Si–O–Si, Si–O–C(I) and Si–O–C(II)) in oxidation-cured polycarbosilane were determined quantitatively, and the chemical structural model was shown. Solid state ^{29}Si resolution NMR spectroscopy has proved to be a powerful tool for investigating the curing mechanism of oxidation-cured polycarbosilane fibres.

1. Introduction

Polycarbosilane (PC) which consists of the skeleton of alternate carbon and silicon atoms has been used as a precursor for ceramic materials, like silicon carbide fibre [1]. The PC fibre is obtained first by melt-spinning of PC, and then cured by heating in air at 110 to 200° C. The curing process which makes the PC infusible [2] is cross-linking of the PC molecules by oxygen introduced in the heating. The influence of oxygen introduced during the production of the SiC fibre on the properties of the fibre was previously reported [3]. However, these problems are related to the chemical structure of PC. In order to produce PC with a high yield and to improve the properties of the ceramics obtained by the pyrolysis process, the chemical structure of PC must be studied in detail. It is important to determine the chemical structure of the oxidation-cured PC fibres, but the structure of PC fibre has not been clarified.

The combination of cross-polarization (CP), high-power resonant proton decoupling, and magic angle sample spinning (MAS) makes high-resolution nuclear magnetic resonance (CP/MAS NMR) spectra possible in solids [4]. Such spectra are particularly useful in the characterization of the chemical structure of infusible materials. Solid-state NMR experiments can be used to determine the structure of molecules.

In the present work, the chemical structure of PC and oxidation curing mechanism of PC fibre were determined more quantitatively by solid state NMR spectroscopy.

2. Experimental details

The PC was synthesized by the thermal decomposition of polydimethylsilane (PDMS) in nitrogen gas flow and by condensation which removes the components with low boiling points [3]. The PC fibres were obtained first by melt-spinning of PC at 310° C in nitrogen gas flow, and cured by heating in oxygen gas flow in the temperature range between 145 and 195° C. Two kinds of fibre samples were used in this research; one was that heated in oxygen gas flow at 145, 160, 175, 180, 185, 190 and 195° C (P145, P160, P175, P180, P190 and P195, respectively), and the other was not heated in oxygen gas flow (P151-F).

Since all the oxidation-cured PC fibres are insoluble in all solvents, all the cured PC fibres are investigated by ^{13}C and ^{29}Si NMR in solids. All the samples were also investigated by chemical analysis for major constituents: silicon, carbon, hydrogen and oxygen. The NMR spectra in solids were measured with JEOL FX-60Q Fourier transformed NMR spectrometer combined with Doty's magic angle sample spinning system [5] at 59.9 MHz for proton (^1H), 15.04 MHz for ^{13}C and 11.9 MHz for ^{29}Si. The spinning frequency is about 2.0 kHz. The radio-frequency field strength was 51.1 kHz.

^{13}C chemical shifts are reported in parts per million (p.p.m.) relative to tetramethylsilane (TMS) taking a shift to low field as positive. The spectra were originally referenced to the carbon resonance of solid adamantane, a thin compressed disc which was sandwiched between two lumps of the powder samples. The methylene carbon resonance of solid adamantane was observed at 89.8 p.p.m. up field from the position of liquid benzene. With the literature chemical shift value of 128.5 p.p.m. [6] relative to TMS for benzene, the chemical shift of the methylene carbon resonance of

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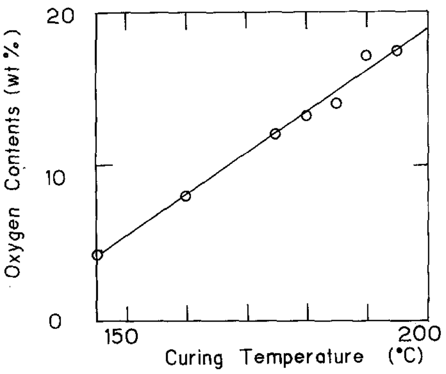


Figure 1 The relation between curing temperature and oxygen contents in cured polycarbosilane.

solid adamantane was determined to be +38.7 p.p.m. with respect to TMS. With this value as the reference, the ^{13}C chemical shift of all the PC fibres were converted to a value relative to TMS.

^{29}Si chemical shifts are also reported in p.p.m. relative to TMS by taking a shift to low field as positive. The spectra were originally referenced to solid PDMS, a thin compressed disc which was sandwiched between two lumps of the powder samples. The PDMS resonance was observed at 40.8 p.p.m. up field from the position of the resonance of liquid hexamethyldisiloxane (HMDSO). With the literature chemical shift value of +6.7 p.p.m. [7] relative to TMS for HMDSO, the chemical shift of PDMS was determined to be −34.1 p.p.m. with respect to TMS. With this value as the reference, ^{29}Si chemical shifts of all the PC fibres were converted to values relative to TMS.

When it is desired to assign the solid state NMR spectrum without recourse to a solution spectrum, a method comparable to that for solution spectra has been developed. A simple technique called "delayed decoupling" or "dipolar dephasing" yields a spectrum only from non-protonated carbon or silicons [4]. In this technique a small delay is inserted between the time when ^{13}C or ^{29}Si signal is created by cross-polarization and the acquisition period. The proton is not decoupled during this delay. The dipolar coupling is strong for protonated carbons or silicons. The delay is chosen so that signals from protonated carbons or silicons totally dephase during this period, where those from non-protonated carbons or silicons, for the most part, remain in phase.

3. Results and discussions

3.1. Chemical analysis

The results of chemical analysis are summarized in Table I. The oxygen contents increased linearly with increasing curing temperature as shown in Fig. 1.

TABLE I Empirical formulae of polycarbosilane fibres

Sample	Empirical formulae	Curing temperature (° C)
P151-F	$SiC_{1.94}H_{4.80}O_{0.01}$	not treated
P145	$SiC_{1.93}H_{4.55}O_{1.17}$	145
P160	$SiC_{1.80}H_{4.59}O_{0.39}$	160
P175	$SiC_{1.79}H_{4.52}O_{0.64}$	175
P180	$SiC_{1.80}H_{4.64}O_{0.65}$	180
P185	$SiC_{1.68}H_{4.24}O_{0.65}$	185
P190	$SiC_{1.69}H_{4.92}O_{0.82}$	190
P195	$SiC_{1.70}H_{4.35}O_{0.89}$	195

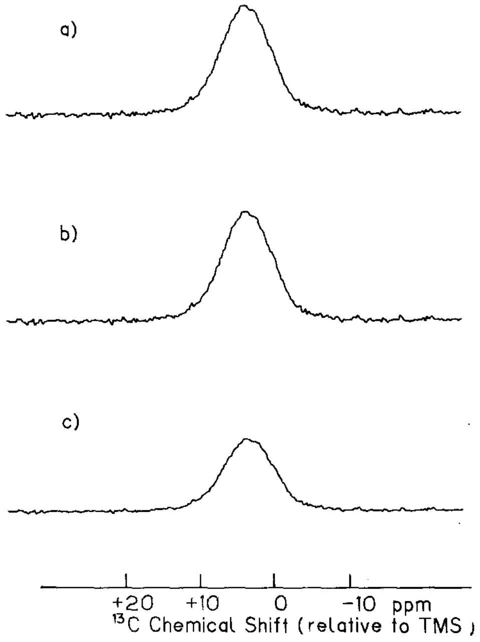


Figure 2 ^{13}C spectra of PC fibres (a) not treated in oxygen gas flow, (b) treated in oxygen gas flow at 175° C and (c) dipolar dephasing spectra of PC fibre treated in oxygen gas flow at 175° C.

3.2. ^{13}C NMR spectra

Information on polysilane, carbosilane and siloxane skeletons in PC molecules in solution was examined by ^{13}C NMR spectra [3]. As shown in Fig. 2, however,

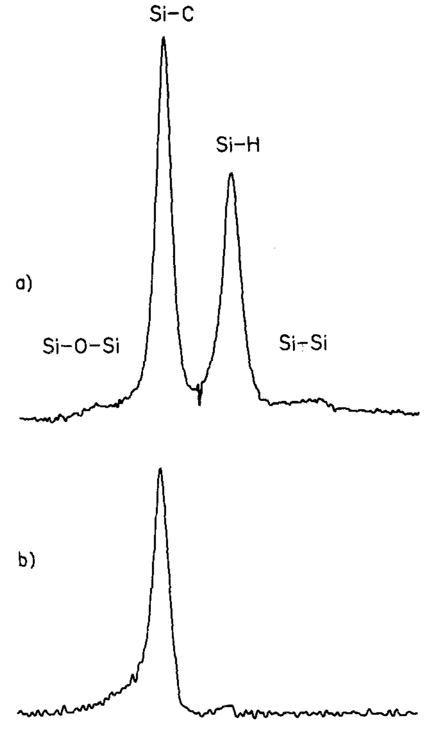


Figure 3 ^{29}Si NMR spectra of PC fibres (a) CP/MAS spectra of PC fibres not treated in oxygen gas flow, (b) dipolar-dephasing spectra of PC fibre not treated in oxygen gas flow.

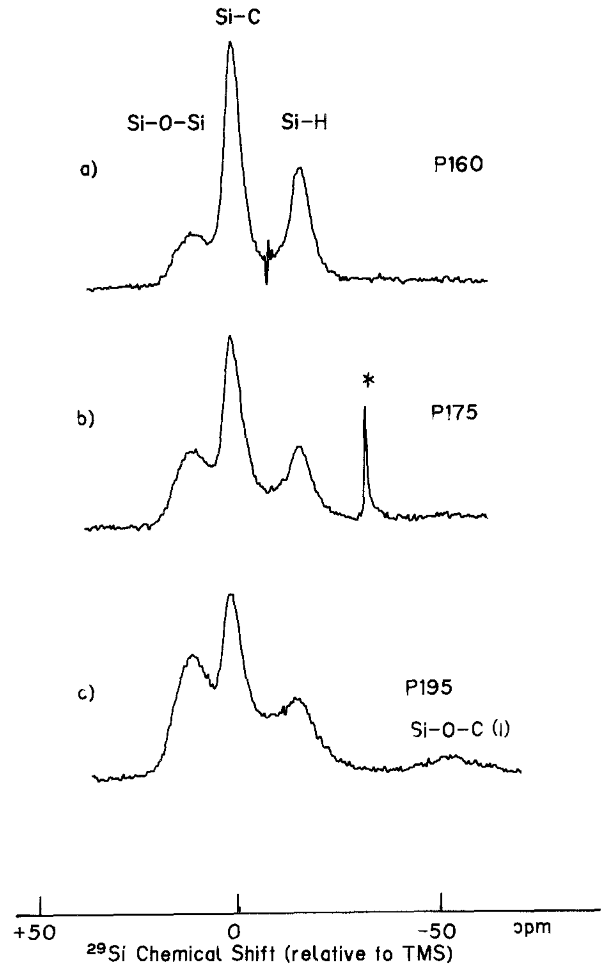


Figure 4 ^{29}Si CP/MAS NMR spectra of PC fibres (a) treated in oxygen gas flow at 160° C, (b) treated in oxygen gas flow at 175° C. A sharp signal denoted by an asterisk is a resonance line of PDMS which is used as an external reference. (c) PC fibre treated in oxygen gas flow at 195° C.

the ^{13}C NMR spectra of all PC fibres in solid show a very broad resonance line and the polysilane skeleton is not resolved in this spectrum. The signals coming from methyl, methylene and methyne carbon groups are not resolved, because the PC fibres are amorphous. Fig. 2c shows the "dipolar dephasing" spectra of P-175. No difference was observed between Figs 2b and c. From ^{13}C NMR spectra, valuable information about the chemical structure of PC fibres was not obtained.

3.3. ^{29}Si NMR spectra

The preliminary results of oxidation cured PC fibres have been published [8], and valuable information about the chemical structure of PC has been obtained. In this paper, oxidation curing temperatures were extended to 195° C. Fig. 3a shows the spectrum of PC fibre not heated in oxygen gas flow. The ^{29}Si NMR signals which belong to the PC fibre skeleton appear at -0.5, -17.5 and -38.5 p.p.m. The intensity of the -38.5 p.p.m. signal is very weak. Fig. 3b shows the "dipolar dephasing" spectrum of P151-F. Since the signal at -17.5 p.p.m. has almost completely disappeared, this signal is assigned to silicon which has the Si–H bond. The signals at -0.5 and -38.5 p.p.m. are assigned to Si–C and Si–Si bonds, respectively. These silicon compounds are represented by three simple bonds as shown in Scheme I:

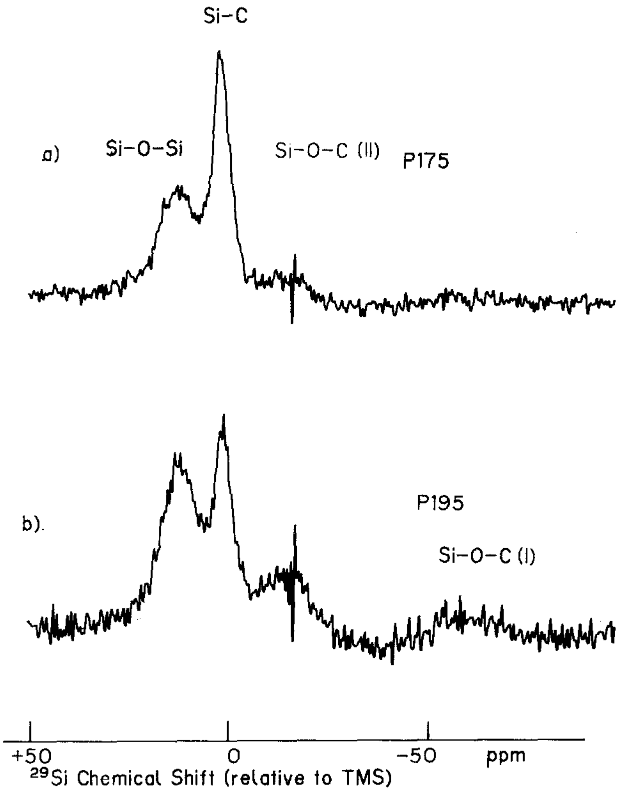
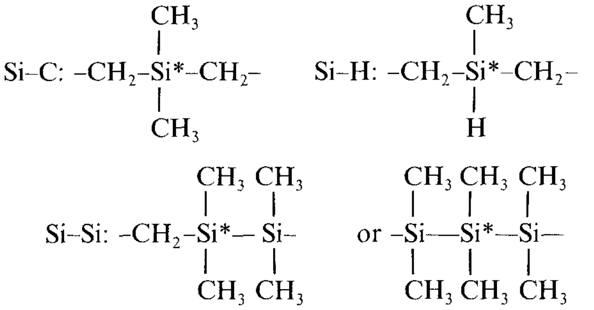


Figure 5 ^{29}Si NMR dipolar dephasing spectra of PC fibre (a) treated in oxygen gas flow at 175° C and (b) 195° C.



$$\text{Si–C: } -CH_2-\overset{CH_3}{\underset{CH_3}{Si^*}}-CH_2- \qquad \text{Si–H: } -CH_2-\overset{CH_3}{\underset{H}{Si^*}}-CH_2-$$

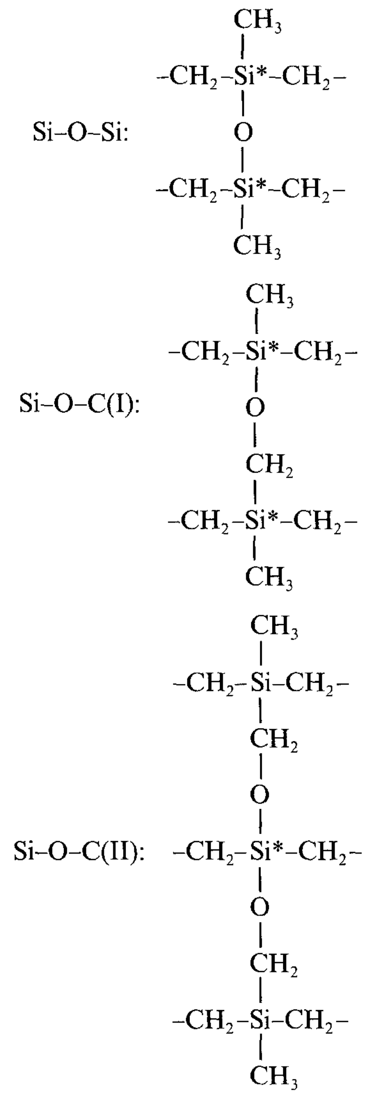
$$\text{Si–Si: } -CH_2-\overset{CH_3}{\underset{CH_3}{Si^*}}-\overset{CH_3}{\underset{CH_3}{Si}}- \quad \text{or } -\overset{CH_3}{\underset{CH_3}{Si}}-\overset{CH_3}{\underset{CH_3}{Si^*}}-\overset{CH_3}{\underset{CH_3}{Si}}-$$

Scheme I

Si–C represents silicon bonded with four carbon atoms, Si–H silicon bonded with three carbon atoms and one hydrogen atom and Si–Si silicon bonded with x carbon atom(s) and $(4 - x)$ silicon atom(s) $(SiC_xSi_{(4-x)}, x = 1, 2, \text{or } 3)$. Figs 4a, b and c show the spectra of PC fibres heated at 160, 175 and 195° C, respectively in oxygen gas flow. Two ^{29}Si NMR signals which are shown in Scheme II, appear at $+9.5$ and -53 p.p.m. in addition to three signals in the PC skeleton. The sharp signal with an asterisk (*) is the reference. The signal at $+9.5$ p.p.m. increases with an increase in curing temperature. The weak intensity signal at -53 p.p.m. is observed when the curing temperature is above 175° C and this signal slightly increases with a rise in the curing temperature. Fig. 5 shows the "dipolar-dephasing" of PC fibres heated in 175 and 195° C. The signal at -17.5 p.p.m., however, does not completely disappear with a rise of the curing temperature.

To assign the signals which belong to the chemical shifts of $+9.5$, -53 and -17 p.p.m. we assumed that the backbone bond (Si–C) of PC fibres does not change by oxidation curing. The signal at +9.5 p.p.m. increases linearly with increasing curing temperature (as shown in Fig. 6), thus, and from Fig. 1, this signal is due to the silicon which has a Si–O–Si bond. The signal at −53 p.p.m. slightly increased with increasing curing temperature and may be due to the silicon which has the Si–O–C(I) bond (as shown in Scheme II). From another viewpoint, it is possible to assign the signal at −53 p.p.m. as coming from the $SiCO_3$ bond [7]. However, in this case it is difficult to consider the $SiCO_3$ bond for the following reasons: (i) the signal at −53 p.p.m. which is due to Si–O–C(I) appearing before the signal at −17 p.p.m. (Si–O–C(II)) appeared and (ii) the backbone does not change by oxidation curing. The signal at −17.5 p.p.m. remained after the dipolar dephasing. As the Si–H bond is attacked by oxygen, the signal which comes from this bond almost disappears (see Fig. 6). The remaining signal at −17 p.p.m. is slightly shifted to down field and a broadening of the linewidth of this signal is observed. From this result, the signal −17 p.p.m. may be coming from Si–O–C(II) (as shown in Scheme II) [7].

These assignments of bonding elements in oxidation cured PC fibres by solid state ^{29}Si NMR are reasonable if compared to other analytical methods.



Scheme II

Further, fractions of silicon compounds in each PC fibre were determined and shown in Table II. The values are estimated on the assumption that the ^{29}Si NMR signal intensity due to Si–C does not change in all PC fibres. The values of the chemical shift of PC fibres are summarized in Table III. The signal intensities of Si–O–Si and Si–O–C(II) increase linearly, while that for Si–H decreases with increasing curing temperature (as shown in Fig. 6). The results indicate that in oxidation-cured PC fibres the oxygen atoms first attack the Si–H bond, and consequently the Si–H bond converts to a Si–O–Si bond, and also above 175° C converts to Si–O–C(II) and Si–O–C(I) bonds. This result is very clearly shown by solid-state ^{29}Si high-resolution NMR spectroscopy in contrast to infrared and ^{13}C NMR measurements.

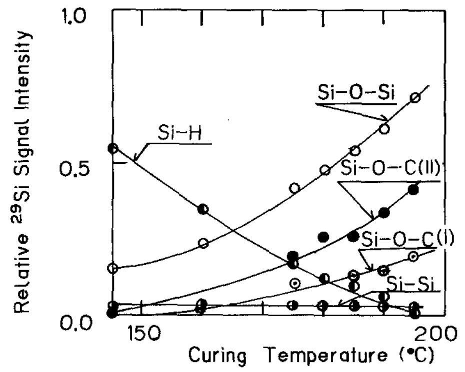


Figure 6 The relation between curing temperatures and relative ^{29}Si NMR signal intensities where the signal intensity of Si–C is taken to be unity.

3.4. Chemical structure

As revealed by measurements of intrinsic viscosities, the molecular shape of PC fibres is not merely linear or ring like. It is planar and complex, consisting of linear and ring structures, with branched chain and a cross-linking structure. As reported in a previous paper [8] and this research, the silicon atoms in the PC molecule fall into six groups with four atoms bonded to them (as shown in Schemes I and II). From this result, it is also clear that the Si–Si bond formed by oxidation curing could not be observed clearly by ^{29}Si NMR.

4. Conclusion

The change of chemical structure of the PC fibres cured by oxygen is represented here more exactly than in previous work [3, 8] by six structural elements (as shown in Schemes I and II) forming the PC skeleton.

TABLE II Relative ^{29}Si NMR signal intensities[a] of polycarbosilane fibres

Sample	Type of bonding				
	Si–H	Si–Si	Si–O–Si	Si–O–C(II)	Si–O–C(I)
P151-F	0.63	0.03	0.03	0.01	–
P145	0.55	0.03	0.15	0.01	–
P160	0.35	0.03	0.24	0.01	0.03
P175	0.17	0.03	0.42	0.20	0.11
P180	0.12	0.03	0.48	0.26	0.12
P185	0.10	0.03	0.54	0.26	0.13
P190	0.06	0.03	0.61	0.34	0.15
P195	0.01	0.03	0.72	0.41	0.20

[a]The intensity of ^{29}Si signal of Si–C is taken as unity.

TABLE III The values of chemical shifts of PC fibres

Bonds	^{29}Si chemical shifts in p.p.m. relative to TMS
Si–C	−0.5
Si–H	−17.5
Si–Si	−38.5
Si–O–C(II)	−17.0
Si–O–C(I)	−53.0
Si–O–Si	+9.5

This was determined by the measurements of solid-state ^{29}Si high-resolution NMR spectra.

Of the six elements, Si–C, Si–H, Si–O–Si and Si–O–C(II) are most important when PC is used as the precursor for ceramics. As these are closely related to the control of oxygen introduced during the curing process. The relationship between the structural elements and properties of the ceramics obtained from PC must be examined. It is also necessary to measure more exactly the solid-state proton high-resolution NMR spectra.

In future work, the convertion of the cured PC fibres will be described in detail combined with the solid-state proton high-resolution NMR.

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