

## Structure and properties of polytitanocarbosilane as the precursor of SiC-TiC fibre

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Polytitanocarbosilane (PTC) as the precursor of SiC-TiC fibre is synthesized by the reaction of titanium alkoxide ( $Ti(OR)_4$ ) with polycarbosilane (PC) which is prepared by the thermal decomposition of polydimethylsilane [1], or by co-pyrolysis of a mixture of titanium alkoxide, polydimethylsilane and a small amount of polyborodiphenylsiloxane [2]. This pre-ceramic polymer can be converted by pyrolysis into a mixture of silicon carbide and titanium carbide with a high yield. The latter method has been used in the production of Tyranno fibre [3], a new continuous SiC-TiC fibre. However, polytitanocarbosilane with higher atom ratio of Ti/Si can be synthesized by the former method as its reaction temperature is lower than that in the latter method [4]. In this letter, we report the synthesis of PTC with different atom ratio of Ti/Si from titanium tetrabutoxide ( $Ti(OBu)_4$ ) and polycarbosilane (PC) according to different molar ratios of  $Ti(OBu)_4/PC$  and the effect of this molar ratio on the structure and properties of PTC.

PC, as the starting material, was synthesized by thermal decomposition and condensation of polydimethylsilane which was produced by the dechlorination of dimethyldichlorosilane with sodium. The synthesis conditions, number average molecular weight  $\bar{M}_n$  and melting point  $T_m$  of PC are shown in Table I. PTC was synthesized from polycarbosilane (PC) shown in Table I and  $Ti(OBu)_4$ . PC and  $Ti(OBu)_4$  were mixed in 0.25, 0.5, 1, 2, 3 molar ratios, respectively, with xylene in a three-necked flask with a reflux condenser and a thermometer. The solution was heated in a nitrogen gas flow to 140°C and refluxed for 1 h. Then xylene was distilled off and the temperature was raised to 240°C. The reaction was further carried out at 240°C for 1 h. Thus, PTC as black viscous liquid or black solid was obtained.

The infrared spectra of PC and PTCs were measured using a Hitachi 270-30 infrared spectrophotometer with a fixed-thickness (0.2 mm) cell of KBr in  $CCl_4$  solution. Number average molecular weights ( $\bar{M}_n$ ) of PC and PTCs were measured with a corona 114 molecular weight apparatus by the VPO method

TABLE I Synthesis conditions, melting point and number average molecular weight of polycarbosilane

Polycarbosilane (PC)	reaction temp (°C)	reaction time (h)	$T_m$ (°C)	$\bar{M}_n$
PC-1	440	10	115	1120
PC-2	400	10	55	870
PC-3	360	10	8	700

in toluene solution, and their molecular weight distribution were measured using Waters-244 with ULTRASTYRAGEL as a GPC column in toluene solution. The melting point ( $T_m$ ) was obtained with a melting apparatus. TG curves of PC and PTCs were obtained by a thermogravimetric analyser (Model WRT-1, made in China) in  $40\text{ cm}^3\text{ min}^{-1}$  nitrogen flow up to 900°C at a heating rate of  $10^\circ\text{C min}^{-1}$ .

The synthesis conditions and properties of PTCs synthesized from PC-2 and  $Ti(OBu)_4$  in different  $Ti(OBu)_4/PC$  molar ratios are shown in Table II. The relationship between  $Ti(OBu)_4/PC$  molar ratio and melting point and spinnability of the PTC produced can be represented by a curve as shown in Fig. 1. Curves for PTCs prepared from PC-1 and PC-3 are also shown in the figure (for simplicity, the experimental data are not listed in Table II).

As seen in Fig. 1, the melting point of PTC increases with increase of  $Ti(OBu)_4/PC$  molar ratio, and tends to a maximum when this ratio is about 1, and then decreases again until the ratio is higher than 3. The spinnability of PTC changes with  $Ti(OBu)_4/PC$  molar ratio, too. When  $Ti(OBu)_4/PC$  molar ratio is lower

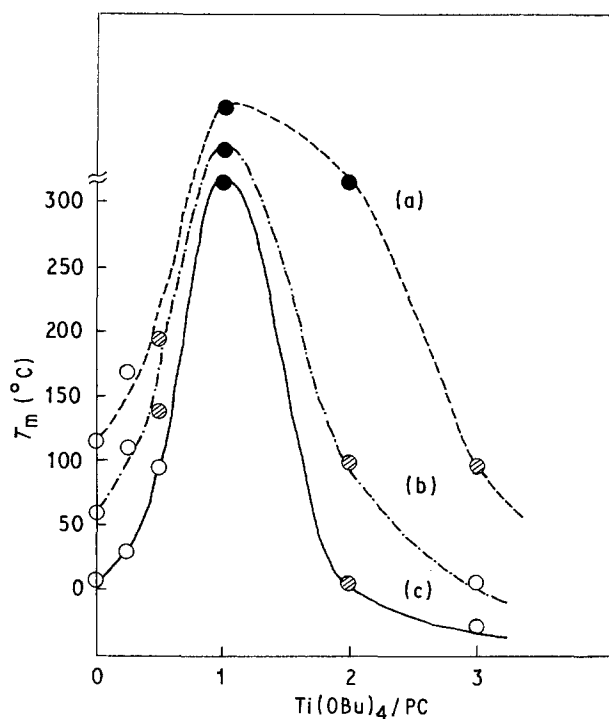


Figure 1 Relation between  $Ti(OBu)_4/PC$  molar ratio and  $T_m$  and spinnability\* of PTC\*\*.

\* Spinnability:  $\circ$  good,  $\otimes$  poor,  $\bullet$  unspinnable.

\*\* PC as starting material: (a) PC-1, (b) PC-2, (c) PC-3.

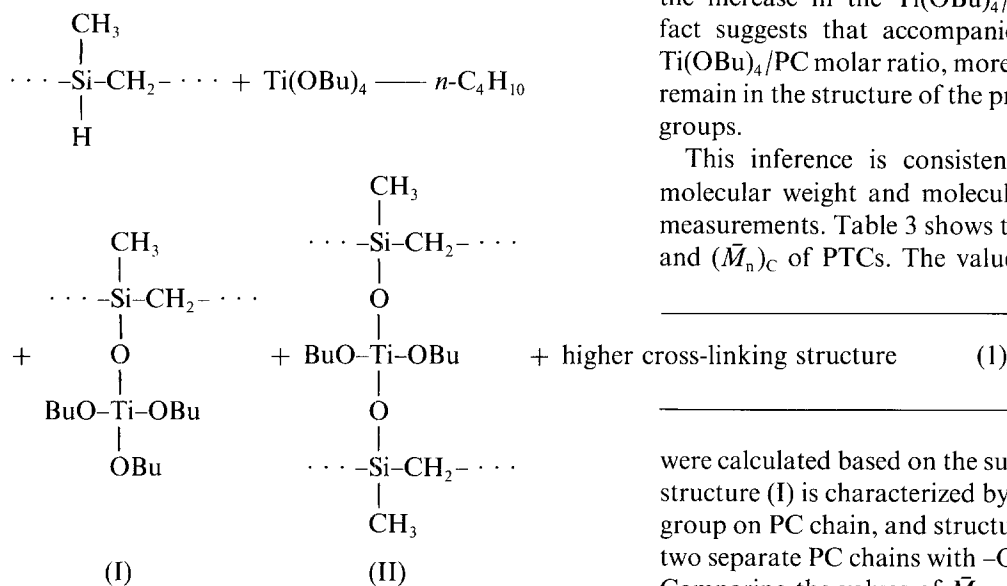
TABLE II Synthesis conditions, melting point, molecular weight and spinnability of polytitanocarbosilane

PTC	Ti(OBu) <sub>4</sub> /PC molar ratio	melting point <i>T<sub>m</sub></i> (°C)	molecular weight <i>M<sub>n</sub></i>	spinnability*
PTC-1	0.25	110	1373	good
PTC-2	0.5	138	1655	poor
PTC-3	1	> 300	> 4000	unspinnable
PTC-4	2	100	2166	poor
PTC-5	3	8	2470	good

\*Good: PTC melt could be spun evenly; poor: spinnable, but breakage of filament occurred frequently.

than 0.5, PTC melt can be spun evenly, as this ratio increases from 0.5 to 1, spinning characteristics of the PTC melt become worse and worse, eventually turn unspinnable. However, the PTC regains its spinnability when the molar ratio Ti(OBu)<sub>4</sub>/PC reaches 3. Furthermore, the molecular weight of starting material PC can affect the properties of the product PTC. The greater the *M<sub>n</sub>* of PC, the higher the *M<sub>n</sub>* and *T<sub>m</sub>* of PTC.

Changes of the properties of PTCs result from the changes in their structure, formed in reaction between PC and Ti(OBu)<sub>4</sub>. This reaction, according to [5, 6], can be represented by the following equation



That is, PTC is formed by the reaction between Si-H bonds in PC and OBU groups in Ti(OBu)<sub>4</sub> resulting in formation of Si-O-Ti bonds and liberation of *n*-butane. Depending on the reaction conditions, the reaction products PTC may consist of structural unit (I), that is PC on which -Ti(OBu)<sub>3</sub> is hung as the pendant group or structural unit (II), that is PC cross-linked by -O-Ti(OBu)<sub>*x*</sub>-O- (*x* = 0, 1, 2) as bridge or their mixture. IR-spectra of PC-1 and PTC-4 are shown in Fig. 2, absorptions are at 2100 cm<sup>-1</sup> (Si-H), 1250 and 600 to 920 cm<sup>-1</sup> (Si-CH<sub>3</sub>), 1400, 2900 and 2950 cm<sup>-1</sup> (C-H), 1020 and 1355 cm<sup>-1</sup> (-CH<sub>2</sub>-). From a comparison of the IR spectrum of PTC with that of PC, it can be seen that PTC is composed of about the same Si-C skeleton as PC. But a decrease in absorption peak at 2100 cm<sup>-1</sup> (Si-H) and appearance of absorption peak at 1090 cm<sup>-1</sup> (Ti-O-C) in the spectrum of PTC shows the difference in its structure with PC. Selecting the absorbance at 1250 cm<sup>-1</sup> (Si-CH<sub>3</sub>) as inner standard, we may estimate the degree of reaction

of Si-H bonds (*P<sub>Si-H</sub>*) by the equation:

$$P_{\text{Si-H}}(\%) = \frac{(A_{2100}/A_{1250})_{\text{PC}} - (A_{2100}/A_{1250})_{\text{PTC}}}{(A_{2100}/A_{1250})_{\text{PC}}} \quad (2)$$

where *A<sub>2100</sub>* and *A<sub>1250</sub>* are the absorbances of peaks at 2100 cm<sup>-1</sup> (Si-H) and 1250 cm<sup>-1</sup> (Si-CH<sub>3</sub>), respectively.

Plotting *P<sub>Si-H</sub>* and the absorbance at 1090 cm<sup>-1</sup>, *A<sub>Ti-O-C</sub>*, against the Ti(OBu)<sub>4</sub>/PC molar ratio, as shown in Fig. 3, we can see that *P<sub>Si-H</sub>* increases slowly with increasing Ti(OBu)<sub>4</sub>/PC (for example, when Ti(OBu)<sub>4</sub>/PC increases from 1 to 2, *P<sub>Si-H</sub>* increases only from 34% to 56%), while *A<sub>Ti-O-C</sub>* increases steadily with the increase in the Ti(OBu)<sub>4</sub>/PC molar ratio. This fact suggests that accompanied by the increase in Ti(OBu)<sub>4</sub>/PC molar ratio, more and more OBU groups remain in the structure of the product PTC as pendant groups.

This inference is consistent with the results of molecular weight and molecular weight distribution measurements. Table 3 shows the values of *M<sub>n</sub>*, (*M<sub>n</sub>*)<sub>P</sub> and (*M<sub>n</sub>*)<sub>C</sub> of PTCs. The values of (*M<sub>n</sub>*)<sub>P</sub> and (*M<sub>n</sub>*)<sub>C</sub>

were calculated based on the supposition that pendant structure (I) is characterized by hanging -O-Ti(OBu)<sub>3</sub> group on PC chain, and structure (II) by cross-linking two separate PC chains with -O-Ti(OBu)<sub>2</sub>-O- group. Comparing the values of *M<sub>n</sub>* with those of (*M<sub>n</sub>*)<sub>P</sub> and (*M<sub>n</sub>*)<sub>C</sub>, we are convinced that the structures of PTC-1,

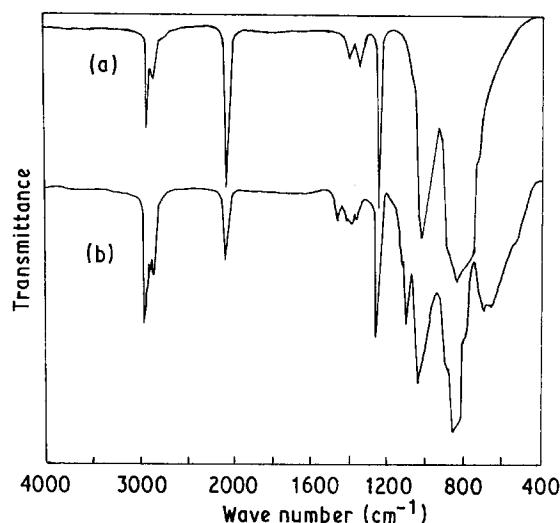


Figure 2 Infrared spectra of (a) PC-1 and (b) PTC-4.

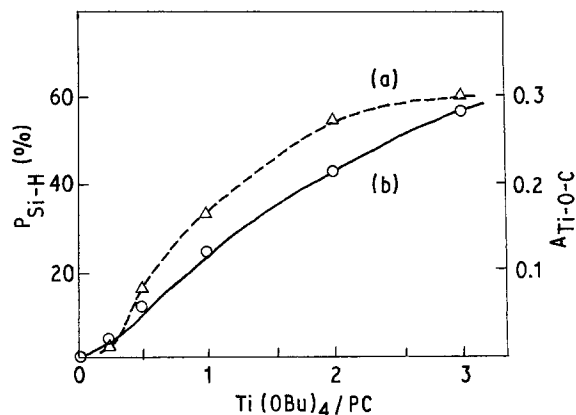


Figure 3 Effect of the  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio on (a)  $P_{\text{Si-H}}$  and (b)  $A_{\text{Ti-O-C}}$ .

PTC-2 and PTC-3 are cross-linked, while structures of PTC-4 and PTC-5 consist mainly of pendant structure (I). That is, the  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio has a profound influence on the structure of PTC. When the  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio is in the range of 0.25 to 1, PTC with cross-linked structure is obtained. As this ratio increases from 1 to 3, the PTC formed with more and more  $-\text{O}-\text{Ti}(\text{OBu})_3$  groups hung on the chain.

Fig. 4 shows the GPC patterns of PTC-1, PTC-2, PTC-4, PTC-5 and PC-1 used as starting material. As PTC-3 was sparingly soluble in toluene, its GPC could not be taken. Comparing the GPC patterns of PTCs, we notice the influence of  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio on the molecular weight distribution of the PTC. When  $\text{Ti}(\text{OBu})_4/\text{PC}$  is in the range of 0.25 to 1, the content of high molecular weight components in PTC increases with increasing  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio. In the GPC pattern for PTC-2 (corresponding to  $\text{Ti}(\text{OBu})_4/\text{PC} = 0.5$ ), a new peak between 32 and 34 min of elution time is seen which suggests that cross-linked structure with  $-\text{O}-\text{Ti}(\text{OBu})_2-\text{O}-$  as bridge is formed. PTC-3 (corresponding to  $\text{Ti}(\text{OBu})_4/\text{PC} = 1$ ) might contain more cross-linkages so that it could not be dissolved completely in toluene. As  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio increases from 1 to 3, the GPC pattern of the products (PTC-4 and PTC-5) does not show peak between 32 and 34 min of elution time any more. Obviously, pendant structure (I) becomes the main structure in these PTCs.

From the above-mentioned observations and discussions, it seems to us that the relation between the  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio and the properties of PTC produced is rather complicated. When  $\text{Ti}(\text{OBu})_4/\text{PC}$  molar ratio is in the range of 0.25 to 1, increase in  $T_m$  and  $\bar{M}_n$  and deterioration of spinning characteristics of PTC stem from the formation of cross-linked structure (II). As this ratio changes from 1 to 3, the pendant structure (I) becomes main structure, resulting in a

TABLE III The values of  $\bar{M}_n$ ,  $(\bar{M}_n)_p$  and  $(\bar{M}_n)_c$  of PTCs

PTC	PTC-1	PTC-2	PTC-3	PTC-4	PTC-5
$\bar{M}_n^*$	1373	1655	4000	2166	2470
$(\bar{M}_n)_p^\dagger$	941	1011	1152	1434	1716
$(\bar{M}_n)_c^\dagger$	1234	1964	$\infty$	$\infty$	$\infty$

\*The values of  $\bar{M}_n$  were measured by VPO method.

† Calculated values.

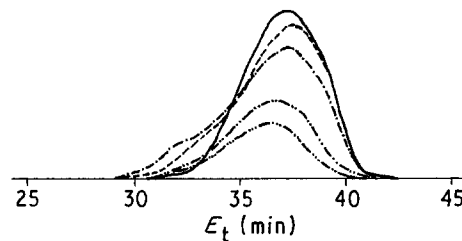


Figure 4 Molecular weight distribution of (—) PC-1, (---) PTC-1, (-·-·-) PTC-2, (-·-·-) PTC-4 and (-·-·-) PTC-5.

decrease in  $T_m$  and reappearance of spinnability of PTC.

The structure of PTC has also an influence on its pyrolysis yield which is important to polymer as the precursor of ceramics. TG curves of PC and PTCs are shown in Fig. 5 (curves of PTC-2 and PTC-3 are not shown in the figure, because they are almost identical with the curve of PTC-1). The conversion of PTCs and PC into inorganic compounds is completed at about  $700^\circ\text{C}$ , and the residue weight depends on the structure of PTC at a given temperature. PTC-1 is cross-linked in structure as stated above, and its weight residue at  $700^\circ\text{C}$  is 85% which is larger than the 79% found with PC-1. On the other hand, PTC-4 and PTC-5 which are mainly of pendant structure have 78% and 70% of weight residue, respectively. As shown in Fig. 3, there are more OBU groups in the structure of PTC-4 and PTC-5 than PTC-1 as a result of the formation of pendant structure with  $-\text{O}-\text{Ti}(\text{OBu})_3$  as side group. Consequently, it is reasonably considered that reduction in weight residue in PTC-4 and PTC-5 results from the thermal decomposition of OBU groups in their structure.

As suitable precursor of SiC-TiC fibre, polymer should have good spinnability, fixed melting point and high pyrolysis yield. Based on Fig. 1 and Fig. 5, we consider PTC-1 and PTC-2 as suitable precursors. In fact, these polymers were spun into fibres, cured and heat-treated under a nitrogen atmosphere up to  $1250^\circ\text{C}$ . The diameter, tensile strength and Young's modulus of SiC-TiC fibres obtained were  $10 \pm 2 \mu\text{m}$ ,

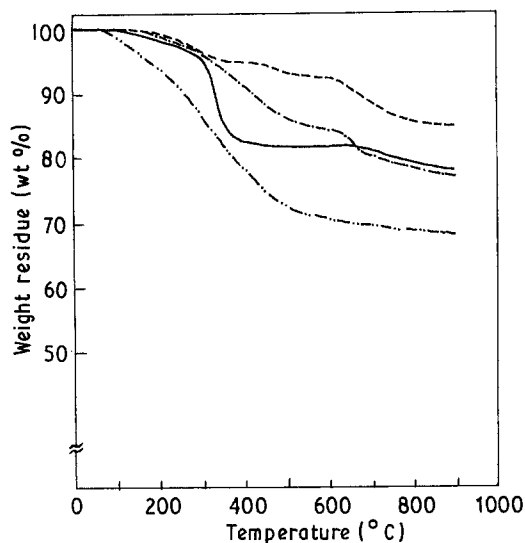


Figure 5 TG curves of (—) PC-1, (---) PTC-1, (-·-·-) PTC-4 and (-·-·-) PTC in  $\text{N}_2$  atmosphere.

$2.0 \pm 4$  GPa and  $170 \pm 10$  GPa, respectively. PTC-4 and PTC-5 with higher molar ratio of Ti/Si can also be used as precursors of ceramic materials, e.g. fibre, coating and binder.

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