

Production mechanism of polytitanocarbosilane and its conversion of the polymer into inorganic materials

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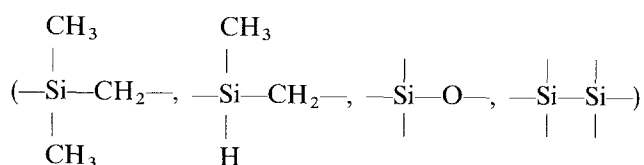
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The reaction of polycarbosilane with tetra-alkyltitanate proceeded at 300°C in nitrogen atmosphere by the condensation of Si-H bonds in polycarbosilane and the substituent groups of the tetra-alkyltitanate accompanied by evolution of alkan gas, and then the formation of Si-O-Ti bonds occurred. In this condensation reaction using tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate, activation energies of the initial rate of the increase in molecular weight were 17.04, 20.07 and 31.07 kcal mol⁻¹, respectively, and thus the more bulky the substituent group of tetra-alkyltitanate, the lower the reactivity became. Of these alkyltitanates, tetra-2-ethylhexyl titanate was found to be the most advantageous reactant for obtaining polytitanocarbosilane with a narrow molecular weight distribution, low gel fraction and high titanium concentration. Polytitanocarbosilane with high titanium concentration was converted into the densified amorphous inorganic material with high Si-C bonding energy in high yield. Titanium contained in the pyrolysed polytitanocarbosilane was furthermore found to have the effect of inhibiting crystalline grain growth of β-type SiC up to high temperature.

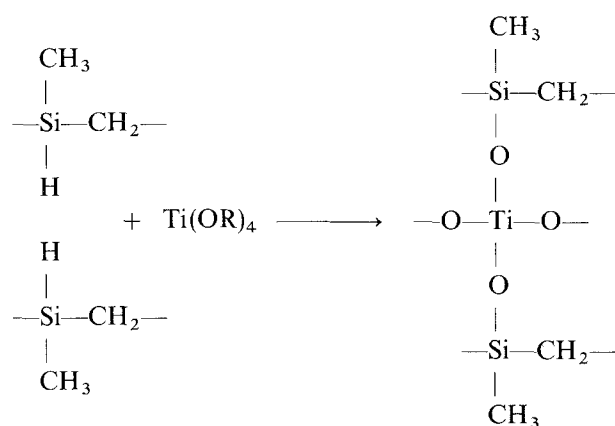
1. Introduction

Polytitanocarbosilane is a precursor of a continuous Si-Ti-C-O fibre with high mechanical strength, excellent heat resistance and good compatibility for composites [1-4]. Polytitanocarbosilane is synthesized by a reaction of polycarbosilane and tetra-alkyltitanate. During production of polytitanocarbosilane, the formation of a cross-linked structure in the following equation by a condensation between Si-H bonds included in the structural units



of polycarbosilane and tetra-alkyltitanate has been reported [5].

The number of cross-linking points has been found to be influenced by the reaction condition, and the existence of a pendant structure in several kinds of cross-linked structure has also been estimated from changes in the number of Si-H bonds [5].



The weight residue of polytitanocarbosilane has shown a higher value with increasing temperature than that of polycarbosilane, because polytitanocarbosilane has a cross-linked structure with the titanium compound [4, 5]. It is also known that the Si-Ti-C-O fibre, which is synthesized from polytitanocarbosilane, retains the amorphous state composed of silicon, titanium, carbon and oxygen up to high temperature in inert gas, in comparison with the Si-C-O fibre obtained from polycarbosilane, because of the presence of titanium atoms in the fibre [2, 4]. The

Si-Ti-C-O fibre with a high concentration of titanium also exhibited a higher oxidation resistance and lower reactivity to molten aluminium during the fabrication of aluminium matrix composite, than that of the fibre with a low concentration of titanium [2, 3].

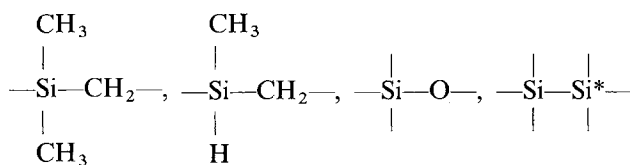
In this work, a more detailed production mechanism of polytitanocarbosilane by the reaction of polycarbosilane with tetra-alkyltitanate was clarified, and the effect of the substituent group of tetra-alkyltitanate on the reactivity of the above reaction was also revealed. In order to elucidate the reason why the inorganic material obtained from polytitanocarbosilane retains the amorphous state at higher temperature and exhibits more excellent oxidation resistance than that obtained from polycarbosilane, the structural changes from polytitanocarbosilane with different concentrations of titanium to the inorganic material were also investigated in detail. These results are reported here.

2. Experimental procedure

2.1. Synthesis of polycarbosilane and polytitanocarbosilane

Polytitanocarbosilane (PTC) was prepared by the reaction of polycarbosilane (PCB) with tetra-alkyltitanate (3.45×10^{-4} mol/PCB 1 g \sim 1.25×10^{-3} mol/PCB 1 g) at 300°C in a stream of nitrogen gas. Three kinds of tetra-alkyltitanate (tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate) were used in order to clarify the effect of substituent groups on the reactivity of the tetra-alkyltitanate with PCB. The PCB was synthesized by the reaction of polydimethylsilane (100 g) [6] with polyborodiphenylsiloxane (3 g) [7] at 340°C under nitrogen gas for 12 h. The weight average molecular weight, \bar{M}_w , of PCB was 1500.

The infrared spectrum of PCB as the starting material is shown in Fig. 1. The absorption at 2950 cm^{-1} (C-H stretching), 2100 cm^{-1} (Si-H stretching), 1400 cm^{-1} (C-H deformation), 1350 cm^{-1} (CH_2 deformation of Si- CH_2 -Si bond), 1250 cm^{-1} (Si- CH_3 deformation), 1080 cm^{-1} (Si-O stretching), 1020 cm^{-1} (CH_2 wagging of Si- CH_2 -Si bond) and 820 cm^{-1} (Si-C stretching), are observed. The unit structures of PCB are considered to be as follows [5].



2.2. Measurements

Infrared spectra of PTC and PCB were measured in a 2 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-H, Si- CH_2 -Si and Si- CH_3 bonds in the starting material

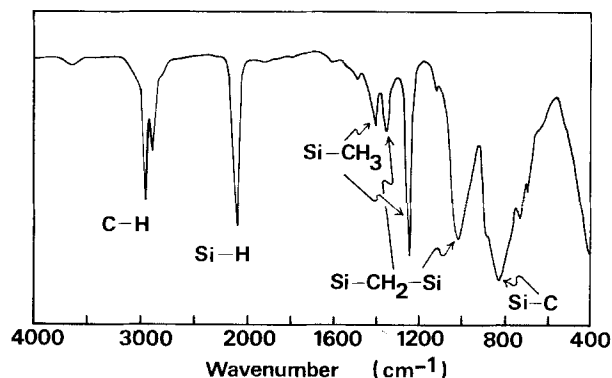


Figure 1 Infrared spectrum of PCB.

and the polymerized products were calculated from

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

where K is the absorptivity ($\text{l g}^{-1}\text{ cm}^{-1}$), C the concentration (g l^{-1}), L the light-path length (cm), $\log(I_0/I)$ the absorbance.

Infrared spectra of heat-treated PTC were measured by the KBr tablet method with the Hitachi IR-430 grating infrared spectrometer.

Gel-permeation chromatograms (GPC) were taken with a Toyo Soda HCL-801 A, with G-4000 HXL, G-3000 HXL, G-2000 HXL ($\times 2$) and G-2000 H8 ($\times 2$) packing and tetrahydrofuran eluent at a flow rate of 1 ml min^{-1} at 40°C using polystyrene as a standard specimen.

Gaseous by-products during the reaction of PCB with tetra-alkyltitanates were separated from nitrogen gas at -73°C using dry ice/methyl alcohol and identified by means of gas chromatography and mass spectrometry. These by-products were determined by the gravimetric technique.

Thermo-gravimetric analysis (TGA) was carried out using a Rigaku Micro TG-DTA (high-temperature type) machine by raising the temperature at 5°C min^{-1} up to 1400°C in a nitrogen flow of $50\text{ cm}^3\text{ min}^{-1}$.

Chemical analysis of pyrolysed PTC was made for four elements: silicon (by a gravimetric method), titanium (by a colorimetric method), carbon (by a combustion volumetric method), and oxygen (by gas analysis).

The pyrolysed PTC was pulverized, and the X-ray diffraction pattern of this powder was recorded with a Rigaku X-ray diffractometer using CuK_α radiation with a nickel filter.

3. Results and discussion

3.1. The reaction process of polycarbosilane with different kinds of tetra-alkyltitanate

The reaction process of PCB with three kinds of tetra-alkyltitanate was investigated in detail, in order to

*The existence of the Si-Si bonds was detected by ultraviolet spectroscopy.

clarify the effect of substituent groups on the reactivity of the tetra-alkyltitanate with PCB. The changes in the weight average molecular weight, \bar{M}_w , of the products during the reactions of PCB with three kinds of tetra-alkyltitanate are shown in Fig. 2. The reactivities of tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate with PCB become slow in that order, as seen from comparison with the initial rate of increase in the \bar{M}_w of the reaction products. In all cases, the reaction rates become small as the reactions proceed.

Fig. 3 shows the changes in infrared absorptivities at 2100, 1350 and 1400 cm^{-1} corresponding to Si-H bond, Si-CH₂-Si bond and Si-CH₃ bond in PCB, respectively, during the reaction of PCB with each tetra-alkyltitanate. An enormous decrease in the number of Si-H bonds is observed at the beginning of all reactions, whereas no changes in the numbers of Si-CH₂-Si and Si-CH₃ bonds are recognized. The rate of the decrease in the number of Si-H bonds is almost the same as the rate of the increase, given in Fig. 2, in the \bar{M}_w of the reaction products.

The evolution of the alkane gas based on the substituent group of tetra-alkyl titanate was observed in this reaction. As shown in Fig. 4, the evolutions of propane, butane and 3-methylheptane increase as the reaction of PCB with tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate proceeds, respectively.

The molecular weight of PTC may be assumed to increase by the formation of Si-Si bonds by the condensation of Si-H bonds, according to the similar mechanism of the increase in the molecular weight of PCB [8, 9]. However, at the production temperature of PTC, 300°C, no increase in the number of Si-Si bonds, as given in Fig. 5, is observed with increase in the molecular weight, because the used PCB, which

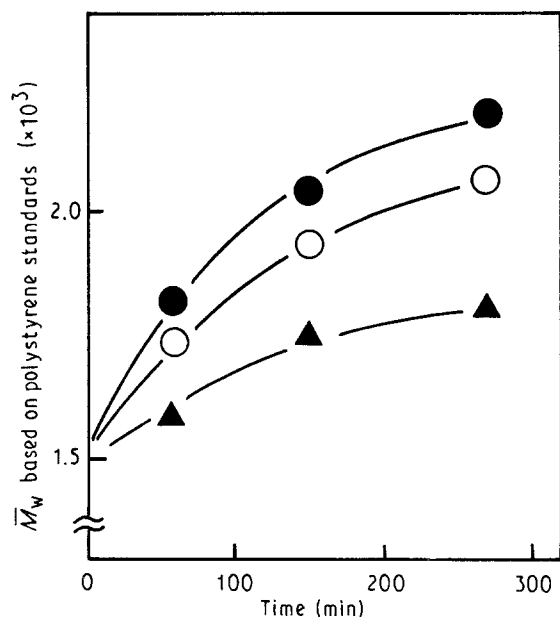


Figure 2 Changes in \bar{M}_w of the products as a function of time in the polymerization of PCB with 5.87×10^{-4} mol/PCB 1 g tetra-alkyltitanates at 300°C. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

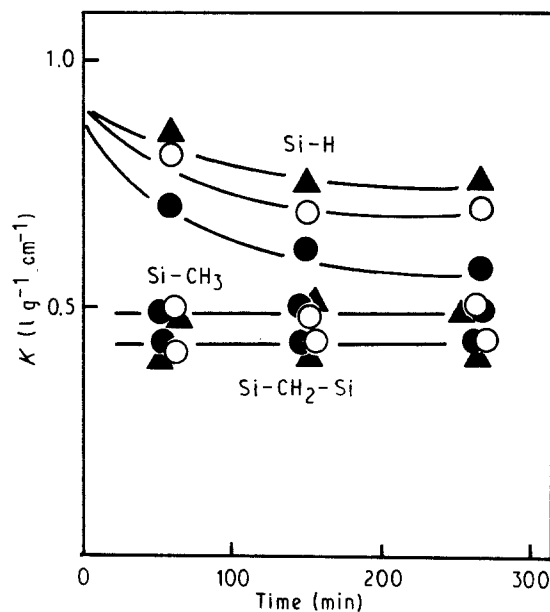


Figure 3 Changes in infrared absorptivity at 2100 cm^{-1} (Si-H bond), 1350 cm^{-1} (Si-CH₂-Si bond) and 1400 cm^{-1} (Si-CH₃ bond) during reaction of PCB with 5.87×10^{-4} mol/PCB 1 g tetra-alkyltitanates at 300°C. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

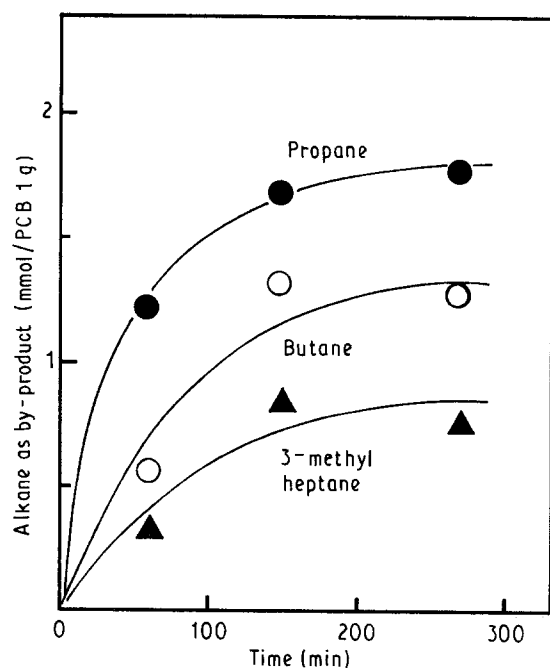


Figure 4 The quantities of the alkane gas evolved by the reaction of PCB and 5.87×10^{-4} mol/PCB 1 g tetra-alkyltitanates at 300°C. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

was synthesized at 340°C, is stable at 300°C, and then the condensation of the Si-H bonds themselves rarely occurs at that temperature. The infrared absorption at 1080 cm^{-1} corresponding to Si-O bond, also (stretching) increases during all reactions, as shown in Fig. 6, and the appearance of the shoulder peak, corresponding to Si-O-Ti bonds at 900-930 cm^{-1} of the infrared spectra, is also observed. From these results, the increase in molecular weight during the reaction of PCB with tetra-alkyltitanate is

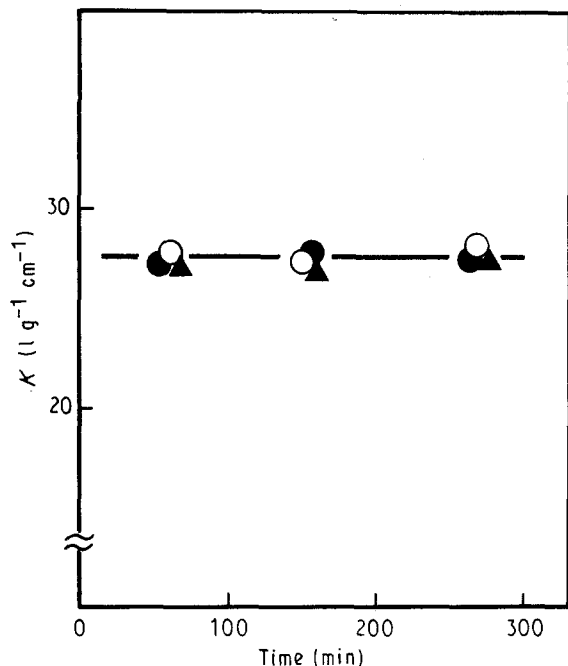


Figure 5 Changes in ultraviolet absorptivity at the wavelength of 212 nm (Si-Si bond) during reaction of PCB with 5.87×10^{-4} mol/PCB 1 g tetra-alkyltitanates at 300°C. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

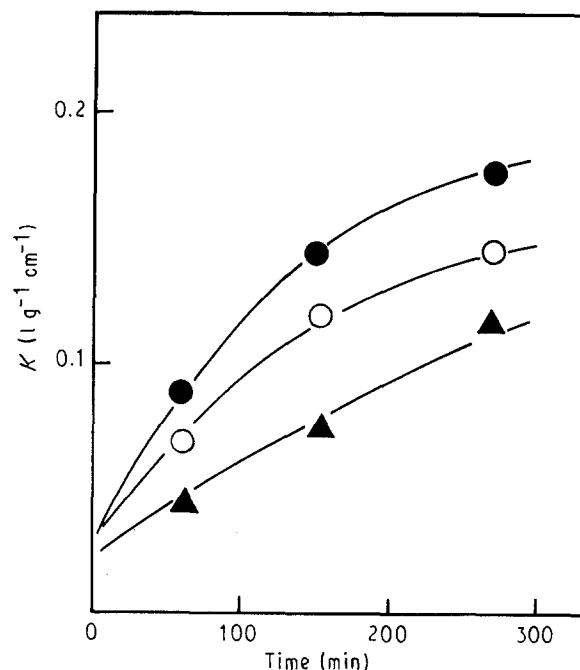
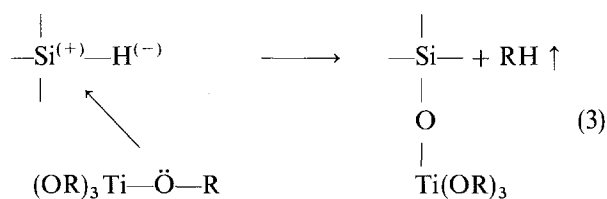


Figure 6 Changes in infrared absorptivity at 1080 cm^{-1} (Si-O bond) during the reaction of PCB with 5.87×10^{-4} mol/PCB 1 g tetra-alkyltitanates at 300°C. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

assumed to depend not upon the condensation of Si-H bonds themselves, but upon the condensation between Si-H bonds in PCB and the substituent group of tetra-alkyltitanate, accompanied by evolution of alkane gas and then the formation of Si-O-Ti bonds.

The difference in electronegativities of silicon, carbon and hydrogen (Si 1.8, H 2.1, C 2.5) gives rise to the polarity of the Si-C and Si-H bonds. The Si-C and Si-H bonds, therefore, have polarity $\text{Si}^{(+)}\text{-C}^{(-)}$ and $\text{Si}^{(+)}\text{-H}^{(-)}$, respectively. In this condensation between Si-H bonds in PCB and the substituent group of tetra-alkyltitanate, accordingly, the following reaction scheme, which contains the nucleophilic attack of a lone pair electrons of an oxygen atom to a silicon atom, is considered, because the silicon atoms existing in the backbone of PCB are subject to nucleophilic attack.



From the results given in Figs 2-6, the order of the reactivities of tetra-alkyltitanate to PCB is expressed as $R_{\text{TPT}} > R_{\text{TBT}} > R_{\text{TOT}}$, where R_{TPT} is reactivity of tetra-isopropyl titanate to PCB, R_{TBT} the reactivity of tetra-*n*-butyl titanate to PCB, and R_{TOT} the reactivity of tetra-2-ethylhexyl titanate to PCB. The reactivity of tetra-alkyltitanate with the bulky alkyl group is low, and this behaviour is presumably caused by the steric hindrance of the bulky alkyl group.

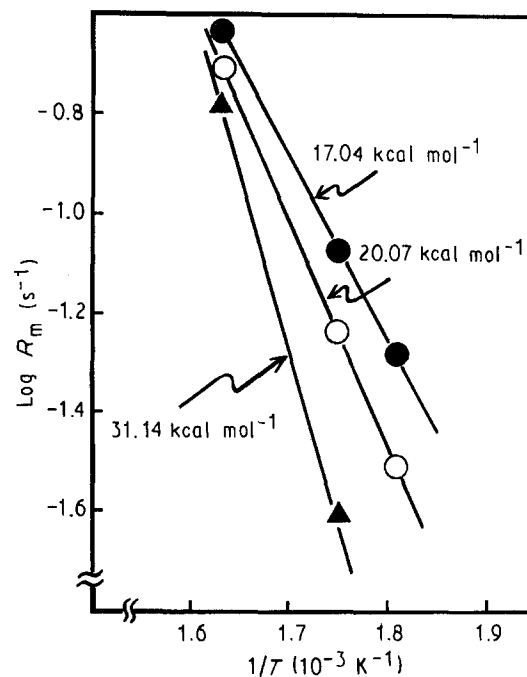


Figure 7 Arrhenius plot of the initial rate, R_m , of increase in the molecular weight, \bar{M}_w , in the reaction of PCB with 5.87×10^{-4} mol/PCB 1 g tetra-alkyltitanates. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

The increase in the molecular weight of PCB in this reaction was observed as described above. PTC, which is produced by the reaction of PCB with tetra-alkyltitanate, is regarded as having many cross-linking points composed of Si-O-Ti-O-Si bonds. If all substituent groups of tetra-alkyltitanate (5.87×10^{-4} mol/PCB 1 g) existing in this reaction system react with the Si-H bonds of PCB, 2.35 mmol alkane gas would evolve as by-product to 1 g PCB. As shown in Fig. 4,

the quantities of evolving alkanes were 1.75 mmol/PCB 1 g propane, 1.28 mmol/PCB 1 g butane and 0.83 mmol/PCB 1 g 3-methylheptane by the use of tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate, respectively, in the reaction at 300°C for 270 min. The percentages of these reacted substituents of tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate are then 75%, 54% and 35%, respectively. In other words, the numbers of reacted functional groups in one mol-

ecule of each tetra-alkyltitanate (the numbers of effective functional groups) result in 3.0 tetra-isopropyl titanate, 2.2 tetra-*n*-butyl titanate and 1.4 tetra-2-ethylhexyl titanate. The activation energies of the initial rate, R_m , of increase in molecular weight in the reaction, which were 17.04 kcal mol⁻¹ tetra-isopropyl titanate, 20.07 kcal mol⁻¹ tetra-*n*-butyl titanate and 31.07 kcal mol⁻¹ tetra-2-ethylhexyl titanate, were also calculated from the plot of log R_m versus $1/T$ given in Fig. 7. These values denote the same result as that of the above reactivity of tetra-alkyltitanates to PCB.

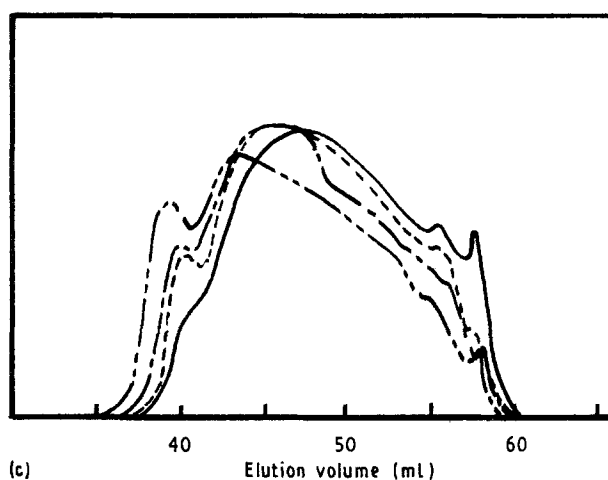
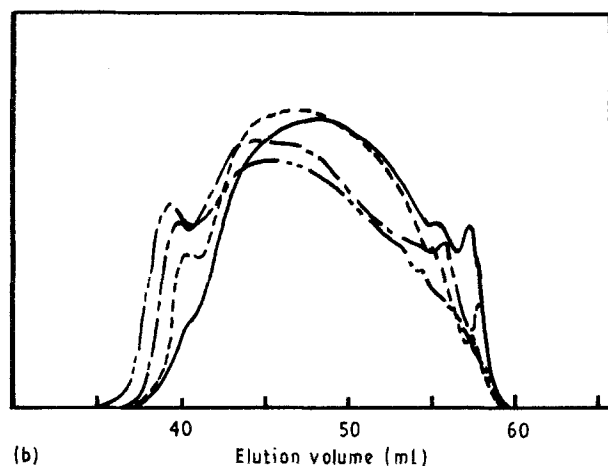
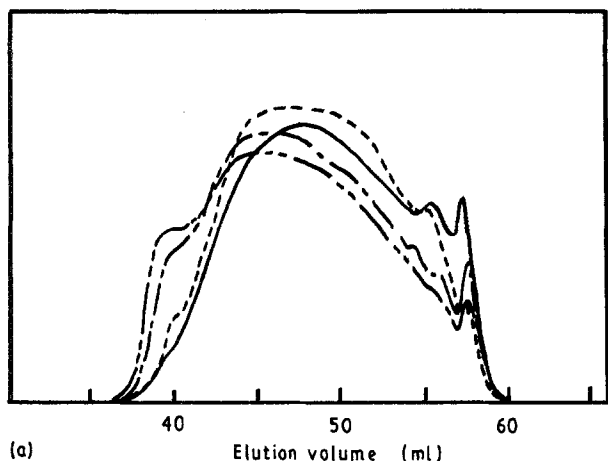


Figure 8 GPC of the reaction products using different concentrations of (a) tetra-2-ethylhexyl titanate, (b) tetra-*n*-butyl titanate and (c) tetra-isopropyl titanate. (—) 3.45×10^{-4} mol/PCB 1 g, (---) 5.87×10^{-4} mol/PCB 1 g, (— · —) 1.04×10^{-3} mol/PCB 1 g, (· · ·) 1.25×10^{-3} mol/PCB 1 g.

3.2. The effect of concentration of tetra-alkyl titanates on the production of PTC and the conversion of the PTC into inorganic material

Fig. 8a-c show the GPC curves of PTC obtained by the reaction using different concentrations of tetra-2-ethylhexyl titanate, tetra-*n*-butyl titanate and tetra-isopropyl titanate, respectively. The broad peak in the high molecular weight region grows with increase in concentration of the tetra-alkyltitanate in all cases. The height of this peak in the GPC curves for these PTC also corresponds closely to the reactivity of tetra-alkyltitanate used in the reaction with PCB. The changes in \bar{M}_w of these PTC are shown in Fig. 9. Of these, \bar{M}_w of the PTC obtained by the reaction using tetra-*n*-butyl titanate or tetra-isopropyl titanate, steeply increases with concentration of tetra-*n*-butyl titanate or tetra-isopropyl titanate. Addition of more than 10 mmol tetra-*n*-butyl titanate or tetra-isopropyl titanate to 1 g PCB results in the abrupt increase in \bar{M}_w of the PTC. The degree of increase in \bar{M}_w in the reaction of PCB with tetra-2-ethylhexyl titanate is

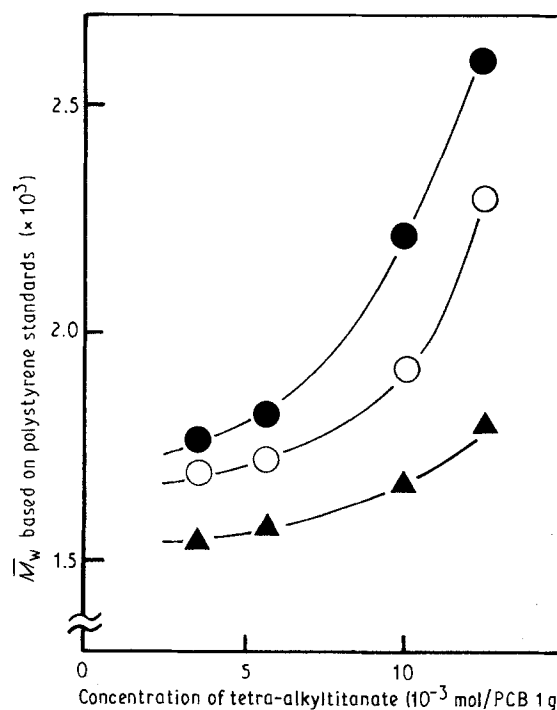


Figure 9 Changes in \bar{M}_w of the products as a function of concentration of tetra-alkyltitanate in the reaction of PCB with tetra-alkyl titanate at 300°C for 60 min. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

smaller than that in the reactions using tetra-*n*-butyl titanate or tetra-isopropyl titanate. These results correspond to the changes, given in Fig. 10, in Si-H bonds of PCB.

The formation of gel, which is insoluble in tetrahydrofuran at room temperature, with the increase in concentration of tetra-alkyltitanate is observed in these reactions, as shown in Fig. 11. In the each reaction using tetra-*n*-butyl titanate and tetra-isopropyl titanate particularly, the gel fraction abruptly increases at concentrations of more than 10 mmol tetra-*n*-butyl titanate or tetra-isopropyl titanate to 1 g PCB. The formation of gel in the reaction using tetra-2-ethylhexyl titanate was smallest in these reactions. Fibrous shaped PTC is prepared by melt-spinning to obtain continuous Si-Ti-C-O fibre. The melt-spinning closely depends upon the molecular weight distribution and the gel fraction of PTC. PTC with a narrow molecular weight distribution and low gel fraction is advantageous for the melt-spinning, whereas the heat resistance and compatibility for composite

materials of the Si-Ti-C-O fibre become better with increasing titanium concentration in the fibre [2]. The chemical analysis of the pyrolysed products of four kinds of PTC, which are synthesized by the use of different concentrations of tetra-2-ethylhexyl titanate, is shown in Table I. Titanium concentrations of the pyrolysed products are in proportion to the concentration of tetra-2-ethylhexyl titanate. In order to obtain the Si-Ti-C-O fibre with excellent properties, a high concentration of the tetra-alkyltitanate to PCB is thus desirable during the production of PTC. As described above, the increase in the \bar{M}_w and the gel fraction were observed with concentration of tetra-alkyltitanate. From these results, in the three tetra-alkyltitanates, tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate, tetra-2-ethylhexyl titanate is consequently found to be the most advantageous reactant for obtaining PTC with a narrow molecular weight distribution, low gel fraction and high titanium concentration, that is to say, the predominant precursor for obtaining the excellent Si-Ti-C-O fibre.

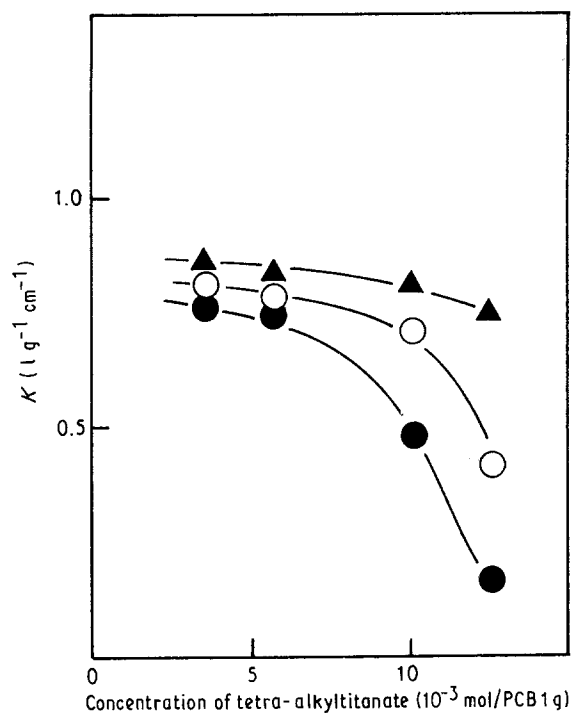


Figure 10 Changes in infrared absorptivity at 2100 cm^{-1} (Si-H bond) as a function of concentration of tetra-alkyltitanate in the reaction of PCB with tetra-alkyl titanate at 300°C for 60 min. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

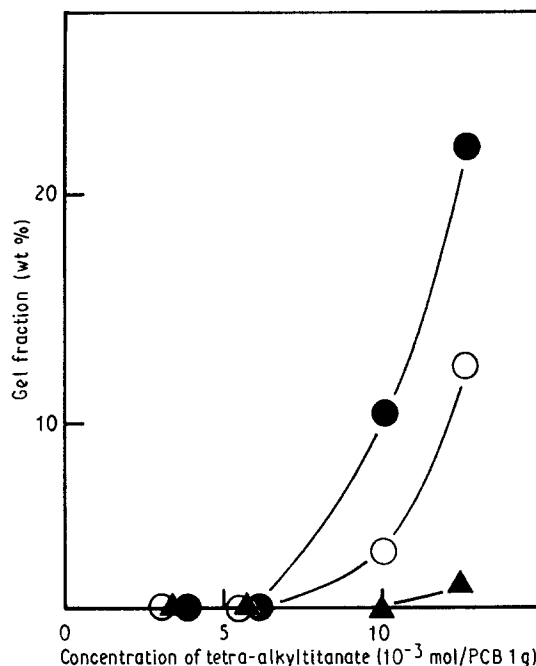


Figure 11 Changes in gel fraction as a function of concentration of tetra-alkyltitanate in the reaction of PCB with tetra-alkyl titanate at 300°C for 60 min. (●) Tetra-isopropyl titanate, (○) tetra-*n*-butyl titanate, (▲) tetra-2-ethylhexyl titanate.

TABLE I The chemical compositions of the pyrolysed PTC at 1300°C

Concentration of tetra-2-ethylhexyl titanate used for the polymerization	Chemical composition				Chemical formula
	Si (wt %)	Ti (wt %)	C (wt %)	O (wt %)	
3.45×10^{-4}	52.5	2.05	34.8	9.0	$\text{SiC}_{1.55}\text{O}_{0.30}\text{Ti}_{0.023}$
5.87×10^{-4}	51.9	3.46	33.6	9.4	$\text{SiC}_{1.52}\text{O}_{0.32}\text{Ti}_{0.039}$
1.04×10^{-3}	50.4	6.04	34.6	8.7	$\text{SiC}_{1.61}\text{O}_{0.30}\text{Ti}_{0.070}$
1.25×10^{-3}	49.2	7.13	34.1	9.5	$\text{SiC}_{1.62}\text{O}_{0.34}\text{Ti}_{0.085}$

The characteristics in the conversion of four kinds of PTC, which were synthesized by the use of different concentrations of tetra-2-ethylhexyl titanate, into the inorganic material were investigated. Fig. 12 shows TGA curves of the four kinds of PTC. The weight residue of PTC derived from PCB and a high concentration of tetra-2-ethylhexyl titanate, exhibits a much better value than that of another PTC obtained from PCB and a low concentration of tetra-2-ethylhexyl titanate. These TGA curves could be composed of three steps in all cases. The first step is the range from 250–450°C, the second step from 450–600°C and the third step from 600–800°C. The weight residues of each PTC are almost constant at more than 800°C, in all cases. Vaporization of low molecular weight organosilicon compounds occurs in the first step, as is also seen from the result of GC-mass analysis of evolved gas. The evolution of hydrogen and ethane from PTC takes place in the second step, and then the degradation of the main chain of PTC presumably proceeds in the third step. Of these steps, a clear difference in the third step of these TGA curves is observed, that is, the larger the concentration of tetra-2-ethylhexyl titanate to PCB, the smaller is the weight loss of the PTC in the third step.

Fig. 13 shows the relationship between the pyrolysing temperature and the wave number of the infrared absorption corresponding to Si–C bonds (stretching) in the pyrolysed PTC. All the absorptions abruptly shift to the lower wave number at temperatures from 600–800°C, than that of the original one. This temperature region corresponds to the temperature in the third step of the TGA curve given in Fig. 12. The shift to the lower wave number in the infrared absorption indicates a drop in the bonding energy of the Si–C bond, that is, an increase in the Si–C bonding length. The absorption shifts again to the high wave number above 800°C, and so the densification of all the pyrolysed PTC can be estimated to proceed abruptly above 800°C. During the pyrolysing process of PTC at temperatures from 600–800°C, the higher the titanium concentration in PTC, the smaller is the degree

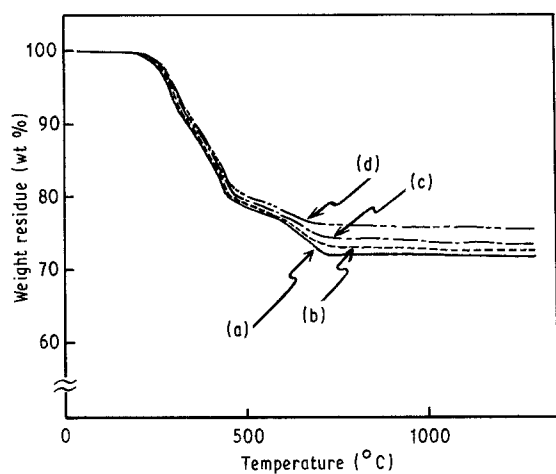


Figure 12 TGA curves of PTC prepared by the use of different concentrations of tetra-2-ethylhexyl titanate. (a) 3.45×10^{-4} mol/PCB 1 g, (b) 5.87×10^{-4} mol/PCB 1 g, (c) 1.04×10^{-3} mol/PCB 1 g, (d) 1.25×10^{-3} mol/PCB 1 g.

of shift to the low wave number in the infrared absorption corresponding to Si–C bonds. Furthermore, at a temperature greater than 800°C, the higher the titanium concentration in PTC, the larger is the degree of the shift to the high wave number in the infrared absorption. Titanium is, therefore, regarded as playing an important role in the enhancement of the Si–C bonding energy of the pyrolysed product, that is, the densification of the obtained inorganic material.

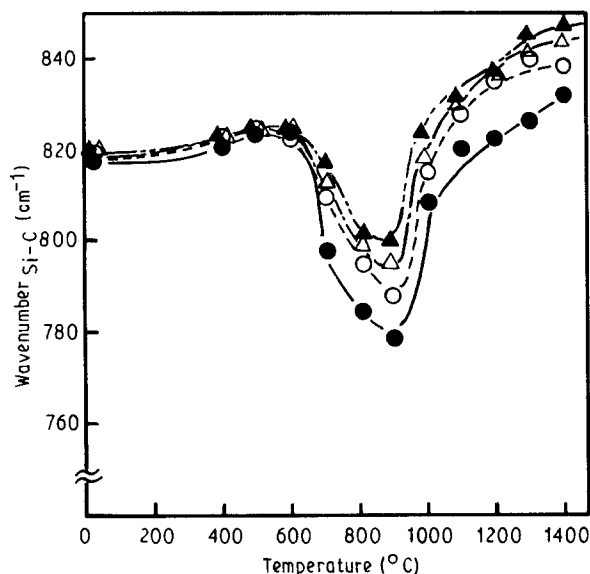


Figure 13 The relationship between the pyrolysing temperature and the wave number of infrared absorption corresponding to Si–C bond (stretching) in the pyrolysed PTC prepared by the use of different concentrations of tetra-2-ethylhexyl titanate. (●) 3.45×10^{-4} mol/PCB 1 g, (○) 5.87×10^{-4} mol/PCB 1 g, (△) 1.04×10^{-3} mol/PCB 1 g, (▲) 1.25×10^{-3} mol/PCB 1 g.

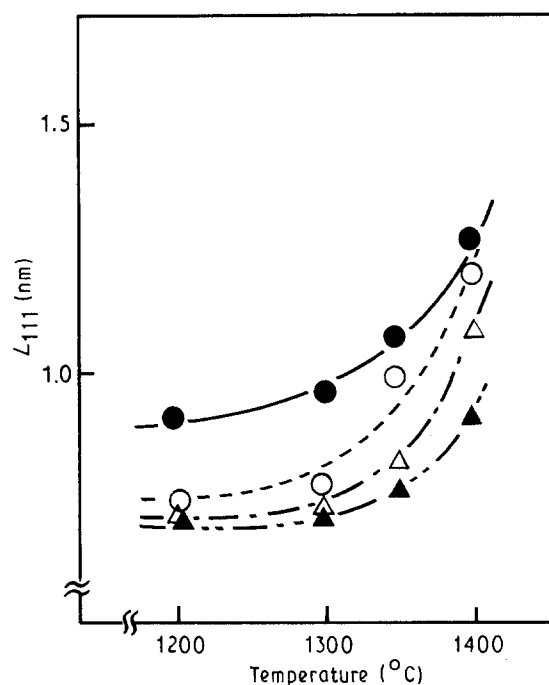


Figure 14 The apparent grain size of β -type SiC of the pyrolysed PTC prepared by the use of different concentrations of tetra-2-ethylhexyl titanate. (●) 3.45×10^{-4} mol/PCB 1 g, (○) 5.87×10^{-4} mol/PCB 1 g, (△) 1.04×10^{-3} mol/PCB 1 g, (▲) 1.25×10^{-3} mol/PCB 1 g.

The X-ray diffraction patterns (CuK_α) of all the pyrolysed PTC up to 1400°C showed only very broad bands, and then these pyrolysed products were found to be in the amorphous state. Fig. 14 shows the changes in the apparent grain size of β -type SiC derived from the diffraction line (1 1 1) at $2\theta = 35.6^\circ$ of the pyrolysed PTC. The crystalline grain size of the pyrolysed PTC with high titanium concentration is smaller than that with low titanium concentration. The titanium was, therefore, found to have the effect of inhibiting crystalline grain growth of β -type SiC up to high temperatures.

4. Conclusion

The reaction of PCB with tetra-alkyltitanate proceeds by the condensation of the Si-H bonds in PCB and the substituent group of the tetra-alkyltitanate accompanied by the evolution of alkane gas, to produce PTC. In this condensation reaction, the more bulky the substituent group of tetra-alkyltitanate, the lower the reactivity becomes. Tetra-2-ethylhexyl titanate was found to be the most advantageous reactant for obtaining PTC with a narrow molecular weight distribution and high titanium concentration, in three tetra-alkyltitanates (tetra-isopropyl titanate, tetra-*n*-butyl titanate and tetra-2-ethylhexyl titanate). The PTC with a high concentration of titanium exhibits a higher weight residue at high temperature than that with a low concentration of titanium. Titanium contained

in the pyrolysed PTC is considered to play an important role in the enhancement of the Si-C bonding energy of the pyrolysed PTC, and the inhibition of crystalline grain growth of β -type SiC up to high temperatures.

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