

DEVELOPMENT OF CERAMICS FROM ORGANOSILICON POLYMERS BY HEAT TREATMENT

M. YAZDI, D. DOLLIMORE and D. AGER

Department of Chemistry, University of Toledo, Toledo, OH 43606 (U.S.A.)

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ABSTRACT

Special heat resistant materials are obtained by heat treatment of organosilicon polymers at atmospheric pressure in a stream of N_2 . Organosilicon polymers are made of polycarbosilanes which are referred to as types I and II. Type I is stable up to $450^\circ C$ and begins to decompose when it reaches this temperature. The first decomposition is completed around $650^\circ C$ with almost 90% residue up to $1000^\circ C$. Type II is stable up to almost $1000^\circ C$ in an inert atmosphere; however, it begins to decompose in dry air at $550^\circ C$ with a 90% residue. These polymers may gradually be converted to β -silicon carbide (β -SiC) by further pyrolysis above $1000^\circ C$. X-Ray diffraction powder, diffuse reflectance IR Fourier transform (DRIFT), thermogravimetry (TG) analysis, and differential thermal analysis (DTA) have been used for analyses of these polymers. The X-ray diffraction powder of types I and II below $1000^\circ C$ has shown an amorphous pattern with no existence of free carbon in the polymers.

INTRODUCTION

The technique of making carbon by pyrolysis of organic material has existed from primitive ages. It is now possible to obtain fibers of high strength and elasticity from polyorganic materials by use of synthetic fibers and by applying tension during part of the pyrolysis process. In order to obtain a ceramic composed of a metallic element and a non-metallic element, the pyrolysis of an organometallic polymer comes to mind. Recent advances in high temperature electronics, turbine engine technology, power systems for satellites, nuclear reactor instrumentation, and rocket propulsion have stimulated interest in silicon carbide (SiC) as a refractory material because of its high resistance to oxidation, corrosion, and thermal shock. Since SiC is not readily sintered, it is difficult to obtain high strength products of complicated shape with this material [1].

The technological potential of polysilanes as ceramic precursors is, however, limited by the troublesome pyrolytic conversion to polycarbosilanes. The further heat treatment of polycarbosilanes under a nonoxidizing atmosphere causes the formation of SiC material. These polymers can also be used as a

binder for sintered SiC powder [2]. In converting an organometallic polymer to a ceramic, the product is composed of ultrafine particles or amorphous material. Since a ceramic is composed of fine particles, a material such as SiC, which normally does not sinter, is liable to cohesion and, hence, sintering. The mechanism will probably be evaporation, followed by condensation, since the vapor pressure during pyrolysis will be relatively high [3]. This paper deals with the synthesis, analysis, and formation of organosilicon polymers as precursors of SiC.

EXPERIMENTAL

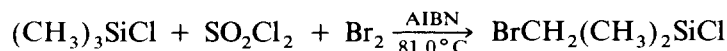
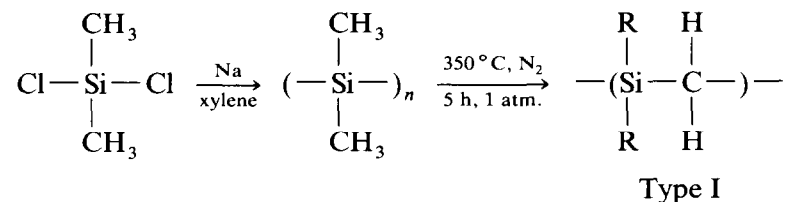
Preparation of compounds

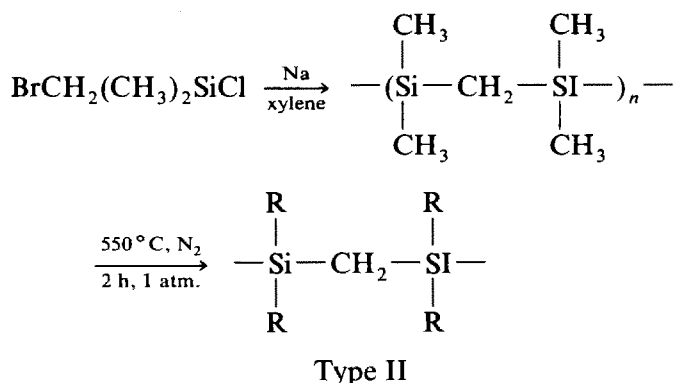
Organosilicon polymer precursors developed in our laboratory are of the polycarbosilane type, which has a main chain of alternating silicon and carbon atoms. The preparation of polyborodiphenylsiloxane has been reported previously [4].

The first polycarbosilane, which is referred to as type I, is synthesized by the pyrolytic polymerization reaction of polydimethylsilane at 350°C at atmospheric pressure in a stream of nitrogen for 5 h with a yield of 58.8%. The polydimethylsilane is obtained by a dechlorination condensation reaction of dimethyldichlorosilane (Petrarch System, Inc., Bristol, PA) by the standard method [5]. Type I is much more heat resistant and much easier to obtain than the polymer that has been reported by Yajima et al. [2,6,7].

The second polycarbosilane, which is referred to as type II, is obtained by the pyrolytic polymerization reaction of polydisilylmethylene at 550°C in a N₂ atmosphere under normal pressure for a 2 h period with a yield of 54.0%. The polydisilylmethylene was obtained by a dehalogenation condensation reaction of bromomethyldimethylchlorosilane by the standard method [4]. The latest compound was synthesized from the mixture of 108.6 g Me₃SiCl, 79.9 g Br₂, 67.8 g SO₂Cl₂, and 1.0 g of azodiisobutyronitrile (AIBN) under reflux condition until the solution reached the temperature of 81.0°C [8].

The preparation processes of type I and type II are shown in the following reaction sequences.





where R is CH₃ or H.

Apparatus

TG and DTA experiments were carried out using a DuPont 1090 thermal analysis system at a heating rate of 10°C min⁻¹. Samples of less than 10.0 mg were used for TG. For DTA, samples of about 20.0 mg were used. Both studies were carried out in a dynamic atmosphere of air and nitrogen. The flow rate was 25.0 ml min⁻¹.

RESULTS AND DISCUSSION

From the reaction sequence given it appears that the formation of type I from polydimethylsilane occurs through α -hydrogen rearrangements of the methyl group. The DRIFT spectrum [9–12] of type I shows absorption bands, which may be assigned as follows: 1035 cm⁻¹ (Si—O); 1354 and 1150 cm⁻¹ [(Si—CH₂—Si)]; and 1260 cm⁻¹ (C—Si). The X-ray (Cu K α) diffraction powder of type I gave an amorphous pattern. Further heat treatment of this polymer at 1300°C under vacuum for 1 h yielded a grayish-yellow powder of β -SiC. This crystal gave a diffraction pattern with $2\theta = 35.60, 60.20,$ and 71.80 , which corresponds to the 111, 220, and 311 diffraction lines of SiC.

The TG of type I showed formation of a stable polymer up to 450°C in an inert or dry air atmosphere. The decomposition of this polymer is complete at 650°C with an overall weight loss of 10% and 12% at 1000°C in the stream of N₂ and dry air, respectively (Table 1 and Fig. 1). Since almost 90% of the material by weight remained up to 1000°C, there is evidence that organic bonds, such as C—H, decompose so that the polycarbosilane is gradually converted into a material containing mainly SiC bonds. The X-ray, DRIFT, and TG analyses of type I at 350°C and 1050°C show no formation of free carbon in this polymer.

TABLE 1

TG percent weight loss for type I and type III

Type I			Type III	
Temp. (C°)	Atmosphere		Temp. (°C)	Atmosphere N ₂
	N ₂	Air		
450-600	2.52	4.82	500-595	2.32
600-694	7.65	7.48	595-705	2.90
Total wt. loss	10.17	12.13		5.22

The heat treatment of polydimethylsilane at 350°C in the N₂ under normal pressure for 5 h in the presence of a few weight percent of polyborodiphenylsiloxane [2,4] produced a more stable polymer, referred to as type III (Table 1). This polymer began to decompose at 500°C in an inert atmosphere with decomposition complete at 700°C with an overall 5.0% weight loss up to 1000°C. The DRIFT spectrum of this polymer shows absorption bands at: 1260 and 804 cm⁻¹ (C—Si); 1354 and 1035 cm⁻¹ (Si—CH₂—Si); 2100 and 839 cm⁻¹ (Si—H); 1593 cm⁻¹ (Si—Ph); 1035 cm⁻¹ (Si—O); and 1452 cm⁻¹ (B—O).

Chemical analysis of type II showed 39.44% Si, 38.90% C, and 7.60% H, which corresponds to an empirical formula of SiC_{2.37}H_{5.50}. The DRIFT spectrum of type II showed absorption bands at: 1250 and 741 cm⁻¹ (C—Si); 824 cm⁻¹ (Si—CH₃) or (C—Si); 1025 cm⁻¹ (Si—O); and

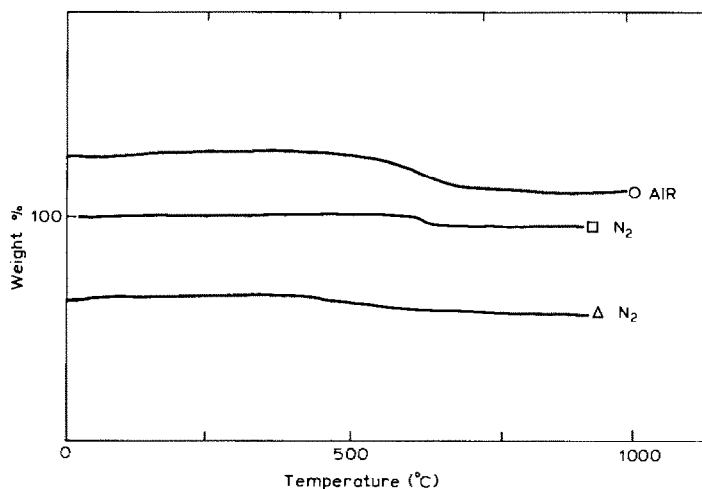


Fig. 1. TG of type I in (○) air and (Δ) stream of N₂; type III in (□) stream of N₂. Note results in air (○) and N₂ (Δ) are displaced.

TABLE 2
TG percent weight loss of type II and type IV

Type II			Type IV	
Temp. (°C)	Atmosphere		Temp. (°C)	Atmosphere N ₂
	N ₂	Air		
550–1000	2.67		550–1000	0.732
500– 620		9.56		
Total wt. loss	2.67	9.56		0.732

1354 and 1025 cm^{-1} (Si—CH₂—Si), which indicates the formation of a type II polymer. The X-ray (Cu $K\alpha$) powder diffraction of this compound shows an amorphous pattern up to 1000°C. Above this temperature a crystalline state pattern was observed. Further heat treatment of this polymer at 1300°C under vacuum for 1 h caused the formation of a greenish powder of β -SiC. This crystal has shown a diffraction pattern with $2\theta = 35.50, 60.20,$ and 71.80 , which corresponds to the 111, 220, and 311 diffraction lines of β -SiC.

TG of type II (Table 2) showed a stable compound up to 1000°C in the inert atmosphere with a 97.0% residue. This polymer began to decompose around 500°C in a dry air atmosphere, and decomposition was complete at 620°C. This resulted in a 90% residue at 1000°C. Upon addition of a few weight percent of polyborodiphenylsiloxane, into a polycarbosilane of type II with heat treatment for 2 h under 1 atm of nitrogen, the more stable type IV polymer was formed. The TG of this polymer (Table 2) shows a stable polymer up to 1000°C with a 99.3% residue in the inert atmosphere.

Type II polymer was left for a period of four months exposed to air at room temperature. The TG of this polymer in the dry air and N₂ atmosphere shows the same weight loss as before (Table 3).

The DRIFT spectrum of heat treatment of the type II polymer at 1050°C for 2 h in the N₂ atmosphere under normal pressure showed formation of β -SiC, with absorption bands at 1200 and 798 cm^{-1} (C—Si) and 1114

TABLE 3
TG percent weight loss of type II after being left for a period of 4 months exposed to air

Temp. (°C)	Atmosphere	
	N ₂	Air
550–1000	2.62	
500– 620		10.40
Total wt. loss	2.62	10.40

cm^{-1} (Si—O—Si). The X-ray, DRIFT, and TG analyses of this polymer showed no formation of free carbon.

The DTA of type I and type II polymers showed no obvious exothermic or endothermic peaks up to 850°C under experimental conditions. Although the TG of type I showed an overall 10% weight loss up to 1000°C in an inert atmosphere, the decomposition of type I can be seen in DTA as a very small wide range exothermic peak. The DTA of type II showed two very small wide range exothermic decomposition peaks, which can be clearly identified in the TG of type II in air.

CONCLUSIONS

β -SiC can be formed from type I and type II polymers. Type I showed more thermal stability, less weight loss, and less cost than the polymer in corresponding studies [2,5,6,10]. The thermal stability and pyrolytic polymerization of type II and type IV were studied for the first time in our laboratory. It appears that type II gradually converted to β -SiC at 1050°C , whereas type I showed no clear assignment at this temperature, as indicated by its DRIFT spectrum as well as its X-ray diffraction powder. The formation of the more stable type III and IV polymers as opposed to the type I and type II polymers may be due to the fact that polyborodiphenylsiloxane acts as a reaction accelerator. The reaction accelerator causes the formation of the strong structural polymer, which does not allow the oxidation (Si—O bond) and/or decomposition of the polymer, as indicated by the DRIFT spectrum. Since these polymers have been made at normal pressure and at a reasonable temperature with good heat resistance, the synthesis of these polymers may become more feasible industrially, i.e. without use of autoclave.

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