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SYNTHESIS AND CHARACTERIZATION OF POLY(DIMETHYLSILYLENE-DIPHENYLSILYLENE) AS A PRECURSOR TO SILICON CARBIDE

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Abstract – Poly(dimethylsilylene-diphenylsilylene) copolymer, $[(SiMe_2)_x(SiPh_2)]_n$, where x=1.0 to 8.0, was synthesized by condensation polymerization of dimethyldichlorosilane and diphenyldichlorosilane in xylene. In the thermogravimetric analysis of the copolymer, weight loss started at 170 °C and the weight residue at 1,000 °C was 32 %. The copolymer was stabilized by thermal oxidation at 80 to 110 °C for 5 hr in air, and its thermal stability increased as the temperature increased. The copolymer heat treated above 700 °C showed no organic bonds of C-H and $Si-CH_3$, while Si-C and Si-O bonds were observed. Amorphous SiC was obtained by pyrolysis at 1,000 °C and β-SiC at 1,200 to 1,400 °C, in which better crystallinity of β-SiC was observed at a higher temperature.

Key words : Poly(dimethyl-diphenylsilane), Thermal Oxidation, Pyrolysis

INTRODUCTION

The use of chemical approaches to improve the processing, properties and performance of advanced ceramic materials is a rapidly growing area of research and development. One approach involves the preparation of organometallic polymer precursors and their controlled pyrolysis to ceramic materials [Chandra et al., 1988]. Silicon-containing preceramic polymers are useful precursors for ceramic powders and fibers and for ceramic binder applications [Chandra et al., 1988].

The earliest work on silicon carbide-related fibers was done by Verbeek and Winter. By using the principles developed earlier by Fritz et al., Verbeek and Winter reported that the high temperature pyrolysis of tetramethylsilane or methylchlorosilane gave branched polycarbosilane polymers containing a structure with alternating silicon and carbon atoms [Verbeek et al., 1974]. In 1975, Yajima and co-workers discovered that polysilane polymers were precursors for β-silicon carbide [Yajima et al., 1975, 1976]. Their process for making β-SiC began with permethylpolysilane [Yajima et al., 1976] first synthesized by Burkhard in 1949 from dimethyldichlorosilane and sodium [Burkhard, 1949]. The polysilane was pyrolyzed at above 400 °C to produce a polymeric carbosilane as a precursor to silicon carbide [Hasegawa et al., 1980]. West and co-workers [West et al., 1984] prepared polysilastyrene polymers by the sodium coupling of phenylmethyldichlorosilane and dimethyldichlorosilane. One aspect of these extensive studies dealt with the pyrolysis of these polymers to ceramic powders, fibers, and films. Shilling et al. [1983] used the known reaction of chlorosilanes to produce polycarbosilane polymers with controlled levels of cross-linking. In this study, poly(dimethyl-diphenylsilane) PDPS was prepared to investigate its chemical property and characteristics of pyrolysis, including the conversion characteristics of the copolymer into SiC-based ceramic material by a thermally stabilized experiment and heat treatment of the copolymer.

EXPERIMENTAL

1. Materials

Dimethyldichlorosilane (DDS) and diphenyldichlorosilane (DPS), extra pure GC analytical grade from Fluka Chemica were used without purification. Xylene (95 %), THF (95 %), and methanol (99 %) were provided by Oriental Chem. Ind., and drying metal sodium (99.8 %) was supplied by BDH Chem. Co. Ltd. All the other chemicals used for this study were purified by standard procedures.

2. Preparation of Poly(dimethyl-diphenylsilane) (PDPS)

Polymerization was conducted as follows: a 500 ml, three-necked round bottom flask was fitted with addition funnel, a motor stirrer (high-speed, for making dispersion), a thermometer, a reflux condenser, a heating mantle and nitrogen inlet and outlet. The synthesis conditions of PDPS are shown in Table 1.

The flask was charged with 150 ml of xylene (dried by refluxing for 24 hr over sodium metal) and 11.5 g of metallic sodium. The xylene was refluxed and a high speed stirrer was used to create a sodium dispersion. The heating mantle was removed and the dispersion in xylene was allowed to cool down to 70 °C, whereupon a mixture of Me_2SiCl_2 (DDS) and Me_2SiPh_2 (DPS) was added dropwise to the given conditions.

After reacting at 100 °C for 15 hr, the reaction was cooled down, and the mixture was quenched by adding 100 ml of methanol dropwise and then 200 ml of water. The organic layer was separated and the crude polymer was obtained. The crude polymer was dissolved in THF, and a small THF-insoluble fraction was separated by centrifugation. Then 150 ml of methanol was added to the THF solution to obtain PDPS.

3. Thermal Stability

Thermal stability of PDPS copolymer is important in the use of this material as a precursor to silicon carbide; if the

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Table 1. Synthesis conditions of PDPS

PDPS	Reactants					Reaction condition	
	DDS (mole)	DPS (mole)	DDS : DPS	Na (mole)	Xylene (ml)	Time (hr)	Temp. (°C)
1	0.250	0.250	1 : 1	0.5	150	15	100
2	0.333	0.167	2 : 1	0.5	150	15	100
3	0.375	0.125	3 : 1	0.5	150	15	100
4	0.400	0.100	4 : 1	0.5	150	15	100
5	0.417	0.083	5 : 1	0.5	150	15	100

copolymers are not stabilized, most of the silicon is volatilized during thermolysis rather than remaining as slicon carbide. To transform soluble, meltable copolymer into insoluble resins, PDPS copolymer was stabilized by heating at 80, 90, 100, and 110 °C for 5 hr in air.

To confirm stabilized copolymer structure, infrared spectroscopy was carried out by the KBr pellet method.

4. Heat Treatment

Heat treatment experiments were performed in the furnace under nitrogen atmosphere. The apparatus has a water-cooled stainless steel jacket and a sample holder equipped with a set of small alumina crucibles containing the stabilized PDPS copolymer. With the furnace, heat treatment experiments were performed at 500, 700, 1,000, 1,200, and 1,400 °C and maintained at this temperature for 1 hr.

After heat treatment, the structures of the residues resulting from heat treatment were confirmed by IR spectra and an X-ray diffractometer.

5. Measurements

Fourier transform infrared spectra were measured with a Perkin Elmer 1750 spectrometer by the KBr pellet method. The spectrometer was used at a resolution 2 cm^{-1} with coaddition of 100 scans. The Mw and Mn values were determined by GPC on a Waters Model 150 C-ALC/GPC instrument in tetrahydrofurane (THF). ^{1}H-NMR spectra were measured with a Bruker FT-80A NMR spectrometer at 60 MHZ at room temperature with $CDCl_3$ solvent using TMS as the internal standard. TGA curves of the copolymer were obtained by a Shimazu TG-50 high temperature type. The heating rate was 10 °C/min. All runs were performed in a nitrogen atmosphere up to 1,000 °C. Thermal transitions were measured by Dupont 9,900 differential scanning calorimeter (DSC) under nitrogen atmosphere at a heating rate 10 °C/min up to 400 °C. X-ray diffractogram patterns were recorded on a Rigaku Geiger Flex D-Max IIIa instrument using nickel filtered CuKα radiation (λ=1.52 Å).

RESULTS AND DISCUSSION

1. Synthesis of PDPS

The PDPS copolymer was synthesized by referring to the method of West [11]. The structure of PDPS can be discussed qualitatively by using IR and NMR spectra. Fig. 1 shows the infrared transmission spectra of a representative selection of the PDPS copolymers. Absorption was seen at 2,950 and 2,900 cm^{-1} (C-H streching in methyl), 1,400 cm^{-1} (C-H deformation in Si-CH_3), 1,260 cm^{-1} (Si-Me deformation) and in the vicinity of 800 cm^{-1} (Si-Me deformation and Si-C stretching), 3,066 and 3,047 cm^{-1} (C-H stretching in phenyl), 1,954, 1,820, and 1,770 cm^{-1} (overlapping phenyl), 1,482, 1,426 cm^{-1} (C-C stretching phenyl), 730, 697 cm^{-1} (C-H deformation phenyl). From these results, the presence of PDPS was confirmed.

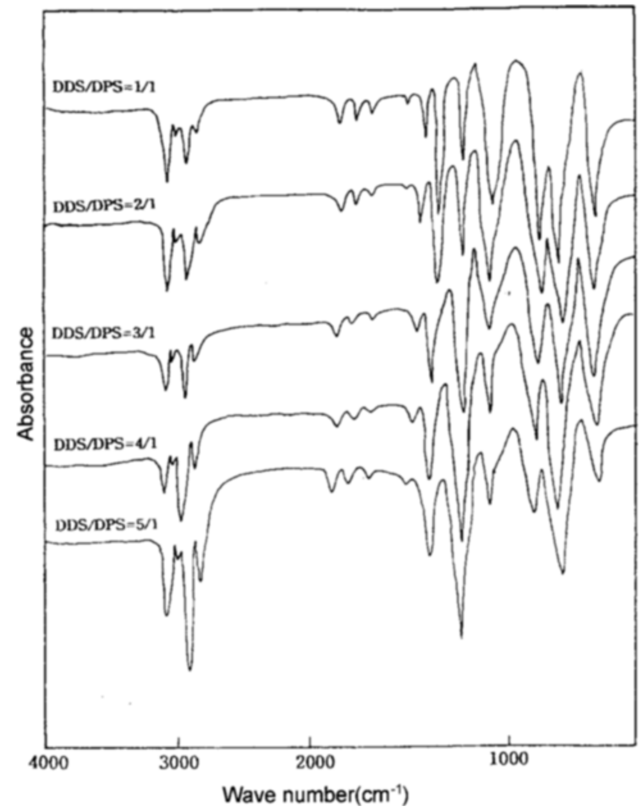

Fig. 1. IR spectra of PDPS according to the mole ratio.

Fig. 2 shows proton nuclear magnetic resonance (^{1}H-NMR) spectra. In all PDPS copolymers, a peak at 0.1 ppm and a peak at 7.0 ppm are observed; the former is due to C-H in methyl and the latter to phenyl. From the integral of the peak, the ratio of the methyl H to the phenyl H can be calculated as in Table 2. From the results in Table 2, it was found that PDPS copolymer, $[(\mathrm{SiMe_2})_x(\mathrm{SiPh_2})]_n$, where x=1.0 to 8.0, was synthesized. Molecular weight distributions of the copolymer are shown in Table 3, where the Mn and Mw are between 21,900-80,000 and 33,700-172,100, respectively. The molecular weight dispersity (Mw/Mn) increased as the mole of DDS monomer increased.

2. Thermal Properties of PDPS

The TGA curve of each PDPS copolymer is shown in Fig. 3. Weight loss of the copolymer started at 170 °C. In the temperature range from 350 to 650 °C, weight loss is about 60 % and the weight residue at 1,000 °C is 32 %. Fig. 4 shows DSC curves of the PDPS copolymer. It is seen that the melting temperature range of the copolymer increased as the mole of DDS monomer increased.

3. Thermal Stabilization of PDPS

As already mentioned, to use PDPS as the precursor for SiC material, it is necessary to stabilize the copolymer by oxidation in air at low temperatures. Thermal oxidation conditions are shown in Table 4. When the copolymers are heated in air to given temperature, oxygenation takes place to give insoluble co-

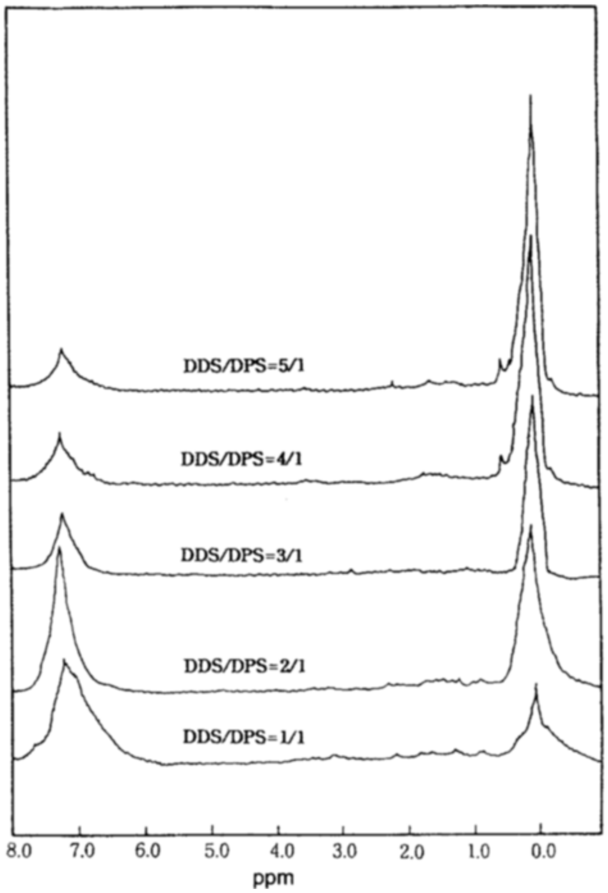

Fig. 2. ^{1}**H-NMR spectra of PDPS according to the mole ratio.**

Table 2. Composition of SiPh$_2$ in PDPS determined by ^{1}H-NMR

PDPS	Mole ratio SiMe$_2$: SiPh$_2$	SiPh$_2$ (mole%)	(Methyl H)/ (Phenyl H)
1	1 : 1	50.0	0.6
2	2 : 1	29.9	1.4
3	3 : 1	20.8	2.3
4	4 : 1	13.6	3.8
5	5 : 1	11.1	4.8

Table 3. Molecular weight of PDPS determined by GPC

Mole ratio DDS : DPS	Mn ($\times 10^{-4}$)	Mw($\times 10^{-4}$)	Mw/Mn
1	2.19	3.37	1.54
2	3.18	5.08	1.60
3	3.43	6.80	1.74
4	4.78	9.44	1.85
5	8.00	17.21	1.91

polymers. The infrared spectra of the oxidized copolymers indicate that they contain Si-O-Si and Si-O-C bonds. Fig. 5 shows the infrared absorption spectra before and after the oxidation of the copolymer at 80, 90, 100, and 110 °C. A strong absorption is observed at 1,000 to 1,100 cm^{-1} (Si-O stretching in Si-O-Si), showing clearly the oxidation phenomenon. In addition, the intensity of the absorption peak at 1,000 to 1,100 cm^{-1} increased as the oxidation temperature increased.

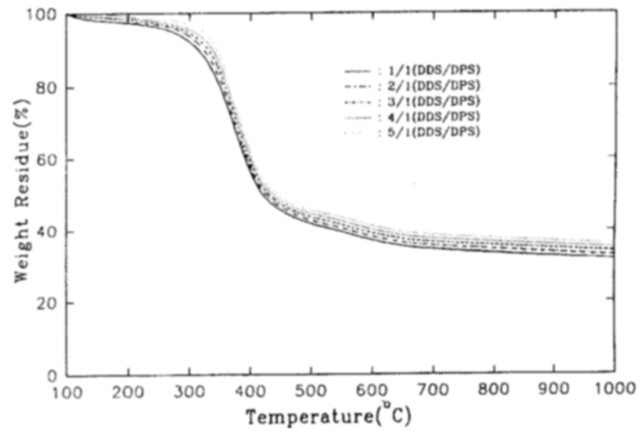

Fig. 3. TGA thermograms of PDPS.

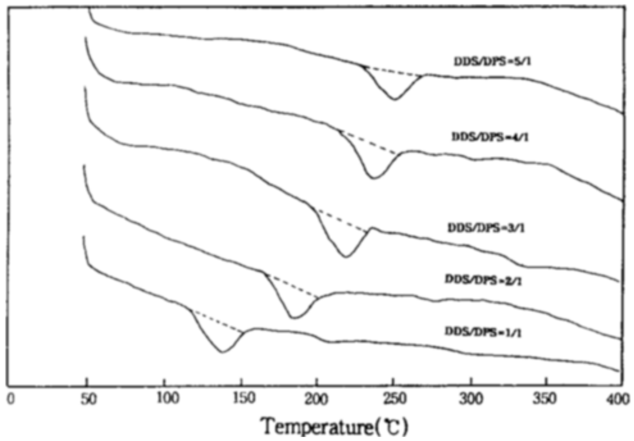

Fig. 4. DSC diagram of PDPS according to the mole ratio.

Table 4. Thermal oxidation conditions of PDPS

PDPS	Heating rate (°C/hr)	Oxidation temp. (°C)	Oxidation time (hr)
PDPS-1A	15	80	5
PDPS-1B	15	90	5
PDPS-1C	15	100	5
PDPS-1D	15	110	5

4. Characterization of Thermally Stabilized PDPS

The heat treatment of thermally stabilized PDPS was performed in the given conditions to investigate conversion characterization of PDPS copolymer into an SiC-based ceramic material. The changes in the infrared spectra of PDPS on heat treatment are shown in Fig. 6. Up to 500 °C all the expected absorption peaks corresponding to the theoretical formula of the PDPS are observed (i.e., C-H in methyl at 2,900 and 2,950 cm^{-1}, C-H in phenyl at 3,066 and 3,047 cm^{-1}, C-C stretching phenyl at 1,482 and 1,426 cm^{-1}; C-H deformation phenyl at 730 and 697 cm^{-1}). Above 700 °C there appeared no organic bonds of C-H and Si-CH$_3$, which are characteristic of the organic state while Si-C and Si-O large bonds (between 800 and 1,100 cm^{-1}) were observed. These results show that the conversion of PDPS into the inorganic SiC ceramic material is completed with increasing temperature.

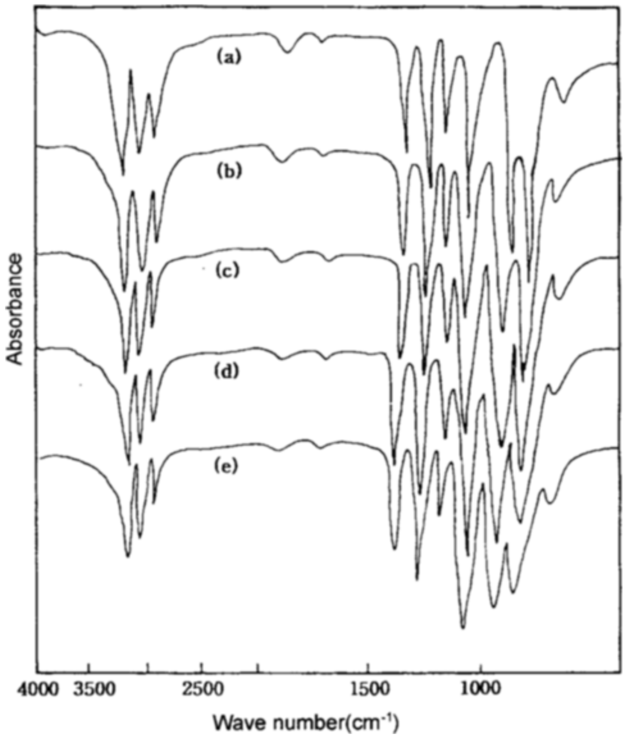

Fig. 5. IR spectra of PDPS-1 before and after thermal oxidation.
(a) before thermal oxidation, (b) 80 °C, (c) 90 °C, (d) 100 °C, (e) 110 °C

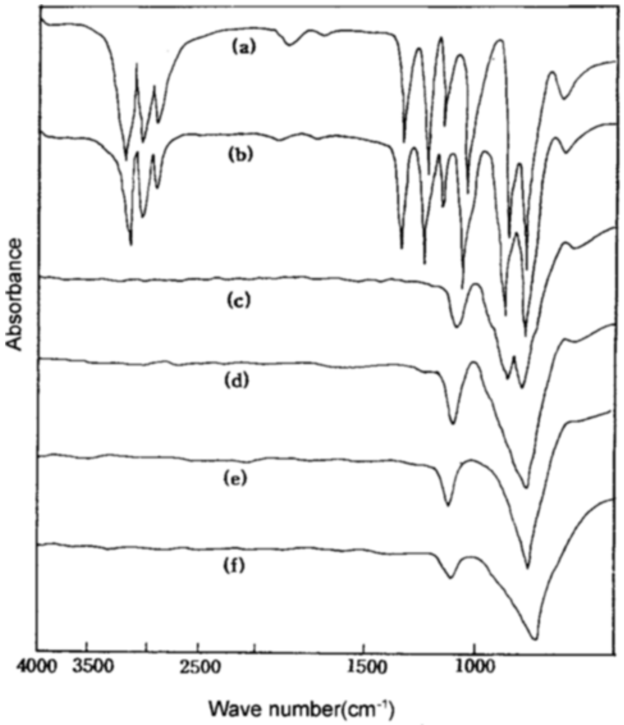

Fig. 6. IR spectra of organic-inorganic transition during the pyrolysis of PDPS-1.

The X-ray diffraction patterns of stabilized PDPS heat treated at 1,000 °C or above are shown in Fig. 7. As shown in Fig. 7 the separation of the diffraction peaks (111) and (220) of β-SiC is not distinct at 1,000 °C, so that the products should be in the amorphous state. Above 1,200 °C the diffraction peaks of β-SiC are observed. The diffraction peak becomes shaper and sharper as heat treatment temperature increases, suggesting a progressive crystallization process.

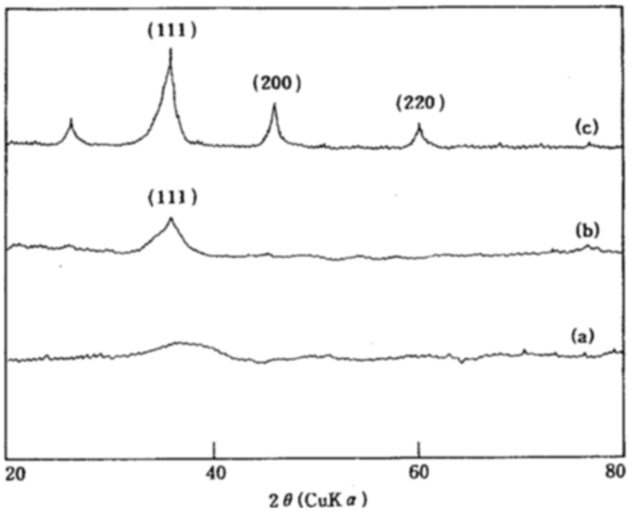

Fig. 7. X-ray diffraction patterns of the solids resulting from the pyrolysis of PDPS-1.
(a) 1,000 °C, (b) 1,200 °C, (c) 1,400 °C

CONCLUSION

Throuhout the present study, poly(dimethylsilylene-diphenylsilylene) as a precursor to SiC based ceramic material was synthesized, and its chemical properties and characteristics of pyrolysis were investigated. The following conclusions were obtained.

The composition of $SiPh_2$ in PDPS copolymer decreased 50 mol% to 11.1 mol% as the comonomer mole ratio increased. The weight loss of PDPS started at 170 °C, and the weight residue at 1,000 °C was 68 %. The thermal stability of heat-treated copolymer increased as the temperature of thermal oxidation increased. The copolymer heat treated above 700 °C showed no organic bonds of C-H and $Si\text{-}CH_3$, while Si-C and Si-O large bonds were observed. Amorphous SiC was obtained by pyrolysis at 1,000 °C and β-SiC at 1,200 to 1,400 °C, in which a better crystallinity of β-SiC observed at a higher temperature.

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