New Method for Synthesizing Polyorganozircosilazane as a Si/Zr/C/N-Based Ceramic Precursor

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ABSTRACT: A new kind of polyorganozircosilazane as a Si/Zr/C/N-based ceramic precursor was synthesized from the condensation reaction of hexamethylcyclotrisilazane lithium salts and zirconium tetrachloride. The pyrolysis of the precursor was carried out at 800°C under nitrogen. The results indicated that the precursor preparation temperature could affect the pyrolytic yields. The precursor, which was synthesized at 80°C, gave the highest pyrolytic yield. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2080–2082, 2003

INTRODUCTION

Zirconinium nitride (ZrN) exhibits excellent properties, including high hardness, a high melting point, corrosion resistance, and high electrical conductivity. Recently, attention has been focused on the alloying of ZrN with other covalent refractory materials such as Si_3N_4 and SiC. Seyferth and coworkers[1,2] mixed Zr powders with polymers (polysilazane, polycarbosilazane, and polysilane) and pyrolyzed the resultant polymer/metal composite powders to obtain ZrN or ZrC–SiC ceramics. Corriu et al.[3] found that the thermal conversion of poly[(silylene)diacetylene]–zirconium oxide composites under nitrogen resulted in the formation of SiC–ZrN ceramics of defined compositions. Now, attention can also be directed to the pyrolysis of ceramic precursors containing zirconium in their structures. In general, the dispersion of zirconium at the atomic level in the precursors may control the stoichiometry and microstructure of resultant ceramics. Chandra and Zank[4] used organohalogendisilane to react with zirconium tetrachloride ($ZrCl_4$) in the presence of a redistribution catalyst under argon and obtained a zirconium-containing polysilane, which contained a low amount of zirconium (<1%). A novel route, the condensation reaction of hexamethylcyclotrisilazane lithium salts (D_3^{NLi}) and $ZrCl_4$, for synthesizing polyorganozircosilazane as a Si/Zr/C/N-based ceramic precursor is presented in this article. The precursor was pyrolyzed under a nitrogen environment to obtain Si_3N_4/SiC–ZrN/ZrC ceramics. The pyrolytic yields depended on the precursor preparation temperature.

EXPERIMENTAL

Materials

The hexamethylcyclotrisilazane was made in our laboratory and purified by distillation. Tetrahydrofuran (THF), toluene, and *n*-hexane were commercially available. They were dried via refluxing over sodium and were distilled under a nitrogen atmosphere. *N,N,N′,N′*-Tetramethyl ethylene diamine (TMEDA) was dried via refluxing over calcium hydride (CaH_2) and was distilled under a nitrogen atmosphere before use. $ZrCl_4$ was obtained from Acros. The reactions were carried out in glass equipment, which was oven-dried and flushed with dry nitrogen just before being used.

Measurements

^{29}Si NMR spectra of samples were recorded with a Unity 200-MHz spectrometer with deuteriobenzene as a solvent and hexamethyldisiloxane (MM, $\delta = 6.90$) as an external reference in ^{29}Si-NMR. Thermogravimetric analysis (TGA) curves of samples were obtained with a PerkinElmer 7 thermal balance in a 40 cm^3/min nitrogen flow up to 800°C at a heating rate of 10°C/min. The amounts of carbon and hydrogen were measured with a Heraeus CHN rapid instrument. The amount of nitrogen was analyzed with the Coulomb titration method.[5] Silicon and zirconium were determined by inductively coupled plasma emission spectroscopy (IRIS/AP).
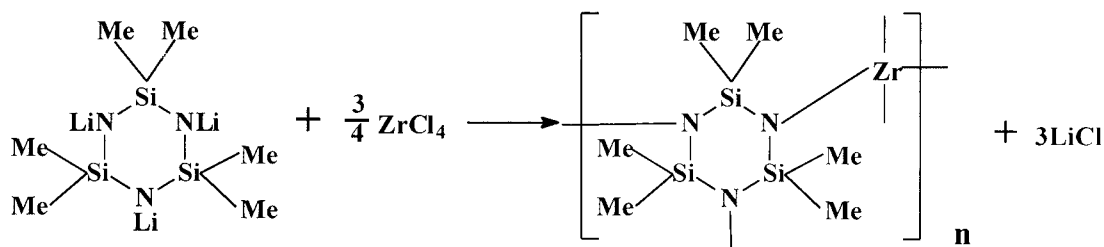
Scheme 1

Synthesis

D$_3^{NLi}$ synthesis

D$_3^{NLi}$ was prepared according to the method of Fink with some modifications.[6–9] For example, in a 100-mL, three-necked, round-bottomed flask equipped with a dropping funnel and a gas inlet tube, 50 mL of freshly distilled n-hexane and 36.88 mmol of n-butyllithium (solution in n-hexane) were charged by syringe after the air in the flask was replaced by dry nitrogen. To the solution, a mixture of 36.50 mmol of hexmethyl-cyclotrisilazane [(Me$_2$SiNH)$_3$ or D$_3^N$] and 10 mL of n-hexane was added dropwise with stirring. A white precipitate immediately formed. The reaction mixture was stirred for 1 h at room temperature. Then, the solvent was removed by filtration under nitrogen. The white precipitate was washed with n-hexane and dried in vacuo to give 8.47 g of D$_3^{NLi}$ (98%). D$_3^{NLi}$ was very sensitive to air and moisture, so it needed to be kept under an inert atmosphere.

Precursor synthesis

Polyorganozircosilazane was prepared from the reaction of D$_3^{NLi}$ and ZrCl$_4$. The synthesis is described in Scheme 1. As an example, polyorganozircosilazane was synthesized as follows: 10.57 mmol of D$_3^{NLi}$ and 60 mL of toluene were added into a 100-mL, three-necked flask equipped with a gas inlet. To the solution, a powder of ZrCl$_4$ was added in a standard glove box at room temperature. The mixture was stirred for 48 h at 80°C. Then, the precipitated LiCl was removed by filtration, and the clear solution was distilled to give 1.53 g of polyorganozircosilazane as an orange-red solid.

Pyrolysis

Pyrolysis to 800°C (under N$_2$) was performed with an SK2-1-10 tube furnace equipped with a KSW-2-11 controller and a quartz tube. Fused silica boats were used to contain the precursor in the quartz tube. After the samples were introduced into the furnace, a purge flow of nitrogen at a rate of 200 cm^3/min was run for 15 min to remove oxygen before the heating. Then, the gas flow was decreased, and a flow of 80 cm^3/min was used during pyrolysis. The temperature program used was as follows: from ambient temperature to 300°C at 1°C/min, 300°C for 1 h, from 300 to 800°C at 2°C/min, and 800°C for 2 h.

RESULTS AND DISCUSSION

Synthesis and characterization of the polyorganozircosilazane precursors

The yields of the polyorganozircosilazanes prepared from the reaction of D$_3^{NLi}$ and ZrCl$_4$ in different solvents at 70°C are shown in Table I. According to Table I, no precursor was obtained when the solvent was nonpolar. The precursor yield increased with the increasing polarity of the solvent. After the addition of a nonpolar solvent to a mixture of the polar solvent, the highest yield was obtained. It was estimated that small quantities of a nonpolar solvent could decrease the solubility of LiCl in organic solvents.

It was assumed that the insufficient contact of the surface and the low reactivity of D$_3^{NLi}$ might be the reasons for the low yields. TMEDA was added as an accelerant, and it efficiently coordinated the lithium cation and promoted the reactivity of D$_3^{NLi}$. After the addition of TMEDA, the yield obviously progressed. The resultant yield data obtained at 80°C in toluene are shown in Table II.

TABLE I
Precursor Yields in Different Solvents

Solvent	Yield (%)
n-hexane	0
Toluene	14.0
Toluene/THF (5:1)	18.1
Toluene/n-hexane/THF (3:1:1)	32.1

TABLE II
Effect of TMEDA on Precursor Yield

	Precursor yield (%)
Absence of TMEDA	26
Presence of TMEDA	90

TABLE III
Elemental Analysis of Polyorganozircosilazane

	Element				
	Si	C	N	H	Zr
Composition (%)	24.14	23.05	12.88	7.06	19.10

The products were very complicated because of the 3–4 functional polycondensation between D_3^{NLi} and $ZrCl_4$. The complication was demonstrated by their NMR spectra and element analyses.

According to the elemental analysis data, the amounts of carbon, nitrogen, zirconium, and silicon were slightly low in comparison with the relatively large amount of hydrogen (Table III). It was assumed that some SiC, Si_3N_4, ZrN, and ZrC ceramics formed during the burning period of the elemental analysis. As a result, the amount of C, Zr, and Si decreased. Because of the incomplete break of Si—N bond in the samples, the amount of nitrogen decreased too. Simultaneously, the amount of H increased.

The ^{29}Si-NMR spectrum consists of one resonance peak, which is assigned to N–$SiMe_2$–N in the cyclic polysilazane (Fig. 1). In contrast to the chemical shift of D_3^N at -4.8 ppm, that of polyorganozircosilazane moved downfield to -4.26 ppm. It was assumed that adding zirconium to connect the nitrogen evenly distributed the electron cloud, decreased the primary electron density of the silicon atom next to the nitrogen, and resulted in the increased chemical shift in ^{29}Si-NMR. In a word, this was the reason for the $p\pi$–$d\pi$ conjugative effect.

We performed a series of similar pyrolysis and TGA experiments on precursors to investigate the relationship between the precursor preparation temperature
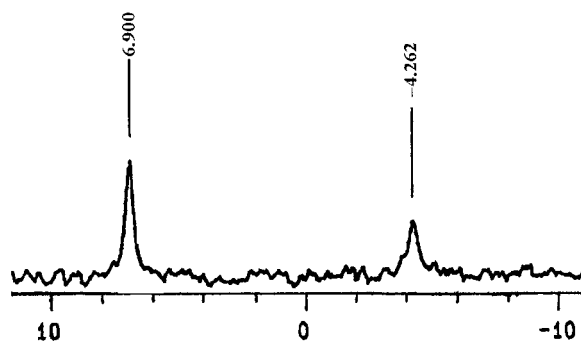

Figure 1 ^{29}Si-NMR spectrum of polyorganozircosilazane.

TABLE IV
Pyrolytic Yields at Different Temperatures of Precursor Preparation

Precursor preparation temperature (°C)	Pyrolytic yield (%)
50	29.32
80	39.71
110	28.73

and the pyrolytic yields. According to the data listed in Table IV, which were obtained in toluene in the presence of TMEDA, the precursor preparation temperature in toluene obviously could affect pyrolytic yields.

According to the data listed in Table IV, the highest pyrolytic yield was obtained when the precursor preparation temperature was 80°C. It was estimated that when the precursor preparation temperature was lower than 80°C, the degree of crosslinking of the precursor increased. However, when the temperature was greater than 80°C, some side reactions could induce the degradation of the preceramic polymer. This pyrolysis research is in its initial stage.

CONCLUSIONS

A new kind of polyorganozircosilazane as a Si/Zr/C/N-based ceramic precursor was synthesized. TMEDA as an accelerant obviously improved the precursor yields. An investigation into the pyrolysis of the precursors indicated that the appropriate precursor preparation temperature was helpful for increasing ceramic yields.

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