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A Novel Method to Synthesize Polyorganozircosilazane

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Abstract: A new kind of polyorganozircosilazane as Si/Zr/C/N-based ceramic precursor was synthesized from the condensation reaction of hexamethylcyclotrisilazane lithium salts (D_3^{NLi}) and zirconium tetrachloride ($ZrCl_4$). In the presence of N, N, N′, N′-tetramethyl ethylene diamine (TMEDA), polyorganozircosilazane was obtained in high yield.

Keywords: Polyorganozircosilazane, Si/Zr/C/N-based ceramic precursor, synthesis.

Zirconinium nitride(ZrN) exhibits excellent properties: high hardness, high melting point, corrosion resistance, high electrical conductivity and so on. Recent interests focus on the alloying of ZrN with other covalent refractory materials such as Si_3N_4 or SiC. According to the literatures[1-3], Si/Zr/C/N-based ceramics were prepared by mixing zirconium/zirconium oxide powder with polymers (polysilazane, polycarbosilazane and polysilane) and pyrolyzing the resultant polymer/metal composite. Now, attention also directes to the pyrolysis of ceramic precursors containing zirconium in their structures. Generally, the dispersion of zirconium at atomic level in the precursors may control the stoichiometry and microstructure of the resultant ceramics. Chandra[4] used organo-halogendisilane to react with $ZrCl_4$ in the presence of a redistribution catalyst under argon and obtained polysilane containing less than one percent zirconium. A novel route, the condensation reaction of hexamethylcyclotrisilazane lithium salts (D_3^{NLi}) and $ZrCl_4$, to synthesize the polyorganozircosilazane as Si/Zr/C/N-based ceramic precursor was presented in this paper. The precursor was obtained in high yield in the presence of N, N, N′, N′-tetramethyl ethylene diamine (TMEDA). To the best of our knowledge, this polyorganozircosilazane and its synthesis have not been reported in the literatures so far.

Experimental

^1H and ^{29}Si nuclear magnetic resonance (NMR) spectra of the samples were recorded with a Unity 200 MHz spectrometer, with deuterated benzene as a solvent and hexamethyldisiloxane (MM, δ ^{29}Si 6.90) as an external reference in ^{29}Si NMR. IR Spectra were measured on FT-IR spectrophotometer, PE-80. The amount of carbon and hydrogen

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were measured with HERAEUS CHN-Rapid instruments. The amount of nitrogen was analyzed by using Coulomb titration method[5]. Silicon and zirconium were determined by inductively coupled plasma emission spectroscope (ICP; IRIS/AP).

General procedure

Polyorganozircosilazane was synthesized from the reaction of D_3^{NLi} and $ZrCl_4$. D_3^{NLi} was prepared by the method of Fink with some modification[6-9]. D_3^{NLi} (0.1 mol) and 60 mL of toluene were added into a three-necked flask under nitrogen. TMEDA (0.3 mol) and $ZrCl_4$ powder (0.075 mol) were added into the solution 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 filtrate was distilled to give poly-organozircosilazane (90%) as an orange-red solid, ^{29}Si NMR: δ-4.26. FT-IR: 2960 (ν C-H),1258 (ν Si-C), 935 (ν Si-N-Si), 469 (ν Zr-N) cm^{-1}.

Scheme 1

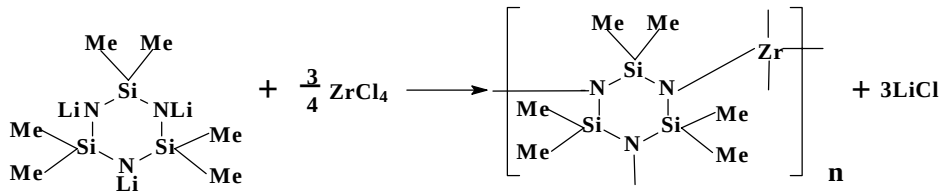

Table 1 Elemental analysis of polyorganozircosilazane

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

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