



## New route to synthesize preceramic polymers for zirconium carbide

Xue Yu Tao<sup>a,c,\*</sup>, Wen Feng Qiu<sup>b</sup>, Hao Li<sup>b</sup>, Tong Zhao<sup>b</sup>, Xian Yong Wei<sup>c</sup>

<sup>a</sup> School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221116, China

<sup>b</sup> Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>c</sup> School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China

Received 1 April 2012

Available online 18 July 2012

### Abstract

A preceramic polymer, polyzirconosaa (PZSA), was synthesized by the ligand-exchange reaction between polyzirconoxane (PZO) and salicyl alcohol (SA). The precursor was air-stable and exhibited excellent solubility and rheology. These properties are useful for the processing of C/C–ZrC composites via precursor infiltration and pyrolysis (PIP) process. The polymer to ceramic conversion was investigated by TG, XRD and TEM. Nanosized ZrC was formed by pyrolysis of this precursor at 1300 °C in argon with ceramic yield of 57.8%.

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*Keywords:* Preceramic polymer; Zirconium carbide; Precursor infiltration and pyrolysis

Carbon fiber reinforced carbon matrix composites (C/C) have received much attention due to their excellent high-temperature strength, high thermal conductivity, low coefficient of thermal expansion (CTE) [1]. However, the poor oxidation resistance of the C/C restricts its high temperature applications. Introduction of ultra-high temperature ceramics (UHTCs) into C/C composites is an effective method to improve its ablation resistance at high temperature, such as carbides/borides [2]. Among the family of UHTCs, zirconium carbide (ZrC) has received much attention due to its good ablation resistance, high melting point (3693 K), high hardness (25.5 GPa) and excellent mechanical stability [3–6]. Especially, a molten ZrO<sub>2</sub> protective film formed in the ablation process can effectively reduce the diffusion rate of oxidizing atmosphere toward the composite.

The preceramic polymer method is an effective approach for preparing advanced ceramics by pyrolysis of the polymers [7]. The main advantages of such method of synthesizing polymer derived ceramics are the applicability of polymer-processing techniques, the homogeneity of the precursors on a molecular level, the low processing temperatures compared to conventional powder sintering methods. Despite the numerous studies based on the precursor synthesis routes for the different classes of preceramic polymers, such as polysilanes, polysiloxanes, polysilazanes, and so on, only a few papers have focused on the synthesis of preceramic polymer for ZrC by the chemical reactions and which is the key raw material for PIP process [8]. Up to now, the difficulty to prepare C/C–ZrC composites by PIP process comes mainly from the lack of proper ZrC precursors.

\* Corresponding author at: School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221116, China.  
E-mail address: [taoxueyu@iccas.ac.cn](mailto:taoxueyu@iccas.ac.cn) (X.Y. Tao).

Polyzirconoxane (PZO), as precursors for preparing zirconia ( $\text{ZrO}_2$ ) fibers, is an alkane- and arene-soluble, water-free polymer. Its ligands are quite labile in proton transfer reactions. A well-known reaction of this type is the ligand-exchange reaction between  $\text{Zr}(\text{acac})_4$  and phenols in organic solvents [9]. The reaction consists of proton transfer from phenols to acetylacetonate ligand and then ligand-exchange reaction with release of free acetylacetonate (Hacac) occurs. Salicyl alcohol (SA) also contains phenolichydroxyl and should be able to react with PZO. In addition, SA ligand acts as carbon source to the formation of ZrC during the process of carbothermal reduction reaction. Therefore, here, we use the ligand-exchange reaction between PZO and SA to synthesize the preceramic polymers for ZrC, and its characterization, properties and pyrolysis process were investigated.

## 1. Experimental

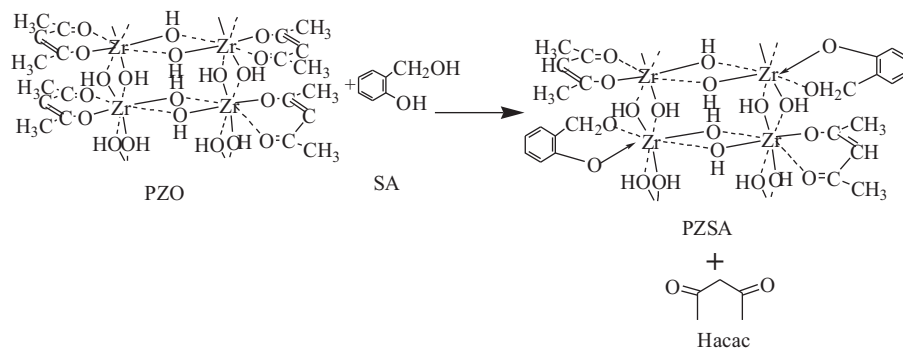
9.0 g (0.09 mol) acetylacetonate and then 12.2 g (0.12 mol) triethylamine was added dropwise into 260 mL methanol solution of 19.4 g (0.06 mol) zirconium oxychloride octahydrate (ZOC) below  $5^\circ\text{C}$  at molar ratio of  $\text{Et}_3\text{N}/\text{ZOC} = 2.0$ . The reaction mixture was stirred at room temperature for 2 h and then concentrated. Addition of 150 mL THF and filtration of the precipitate followed by concentration of the filtrate gave a highly viscous solution. PZO was isolated as a white powder by adding the viscous solution to 150 mL hexane. The molecular structure of PZO was polymers of a low degree of polymerization with  $\text{Zr}-\text{O}-\text{Zr}$  as main chain, the ligand acetylacetonate and hydroxyl group as pendants.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  3.6 (s, 1H,  $=\text{CH}-$  enol form), 3.1 (q, 2H,  $J = 8.0$  Hz), 2.1 (s, 3H,  $\text{CH}_3\text{CO}$  keto form), 1.4 (t, 3H,  $J = 8.0$  Hz); FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3415, 1592, 1529, 1483, 1368, 1280, 1027, 932, 652, 543 and 428.

PZSA was prepared by the reaction of PZO and SA. 1.14 g SA was added to a solution of 3.54 g PZO in 20 mL ethanol at room temperature with stirring. Then the reaction mixture was stirred at reflux temperature for 4 h and transparent orange solution was obtained. Removal of the ethanol on a rotary evaporator and drying in vacuo at  $50^\circ\text{C}$  for 8 h yielded a yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  6.70–7.30 (m, 4H,  $4 \times \text{ArH}$ ), 4.6 (s, 2H,  $-\text{CH}_2\text{O}-$  in phenyl ring), 3.1 (q, 2H,  $J = 8.0$  Hz), 2.1 (s, 3H,  $\text{CH}_3\text{CO}$  keto form), 1.25 (t, 3H,  $J = 8.0$  Hz). FT-IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3062, 2923, 2859, 1596, 1529, 1483, 1453, 1280, 1018, 752, 646 and 543.

## 2. Results and discussion

The synthetic route for the precursor was shown in Scheme 1. The PZSA precursor was prepared by the reaction of PZO and SA in a simple and cheap chemical route. When SA was added into the solution of PZO, the mixture changed into a homogeneous solution right after stirring and the product was isolated as an air-stable yellow solid. In the reaction between PZO and SA, SA deprotonation, proton transfer to acetylacetonate ligand, change of ligands and the release of free Hacac occurred. The obtained Zr-containing polymers on this route served as precursors for ZrC.

The advantages on the used process compared with the literature methods [2,5] were as follows. First, the polymer PZO was used as zirconium source, it was stable and less toxic than zirconium alkoxides. Second, the polymer PZSA was prepared by the chemical reaction between PZO and SA, in which Zr element dispersed at molecular level, not just by mixing of the materials. Last, when the precursor was exposed to air, it would not hydrolyze, so it was air-stable; and this precursor exhibited excellent solubility in common organic solvents, such as methanol, ethanol, THF and



Scheme 1. Synthetic route of the PZSA precursor.

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