



# Poly(phenylene-carborane) for boron-carbide/carbon ceramic precursor synthesized via nickel catalysis



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## ARTICLE INFO

### Article history:

Received 23 December 2016

Received in revised form

20 February 2017

Accepted 16 March 2017

Available online 27 March 2017

### Keywords:

Ni(0)-catalyzed polymerization

Poly(phenylene-carborane)

Boron-carbide

## ABSTRACT

High thermally and thermo-oxidatively stable poly(phenylene-carborane) (PPB) was synthesized via Ni(0)-catalyzed polymerization of bis(aryl chloride) monomer containing carborane. This polymer was soluble in THF and NMP at room temperature, thus allowing molecular weight and spectroscopic analysis. Number-average molecular weight determined by <sup>1</sup>H-NMR spectroscopy was  $5.4 \times 10^3$  g/mol. The crystalline character of PPB was verified by XRD analysis. This polymer exhibited excellent thermal and thermo-oxidative stability with 5% weight loss temperature to be 707 °C and >1000 °C in nitrogen and air, respectively. High char yields of 93.2% and 97.9% were obtained at 1000 °C in nitrogen and air, respectively. Additionally, PPB has proven to be excellent sing-source precursor to boron-carbide/carbon ceramic materials with high ceramic yields in the range of 91.1%–92.6%. According to XRD analysis, boron carbide crystallization for PPB occurred between 1000 and 1200 °C.

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## 1. Introduction

Since first reported at the end of 1963 in both the United States and the USSR, carborane has received considerable attention for its unique properties, such as high thermal and chemical stability, three-dimensional structure, aromaticity and ease of functionalization [1]. Among of them, the high thermal stability of carborane has attracted the interest of polymer chemists seeking for high-temperature applications such as ceramic precursors and oxidation-resistant coatings [2–6]. Numerous polymers containing carborane cage structures have been reported [7–17], and polymers containing the carborane within the backbone exhibited high ceramic yields [6,18,19]. Our current research is focused on the synthesis and characterization of polymer materials containing carborane for high-temperature polymers and polymeric precursors for ceramics. The polymer-derived ceramics method offers many important advantages compared with the conventional powder-based ceramic fabricating process. For example, the structures, compositions, and properties of ceramics can be tailored at atomic, molecular, and nanoscales by changing the chemistries of precursors [20–25]. Additionally, this method of polymer-derived

ceramics also leads to more flexible shaping/forming processes for manufacturing ceramics compared with conventional ceramics fabricating processes. Fabrication of porous ceramics, ceramic fibers, composites, and ceramic films has been reported [23,26–30].

Ni(0)-catalyzed polycondensation of difunctional monomers is a very attractive approach toward high-performance polymers, because this process leads to formation of aromatic carbon-carbon bonds under mild conditions and tolerates a large variety of functional groups [31]. A number of functionalized polyphenylenes have been synthesized via nickel catalysis, such as poly(-benzophenone)s (PBPs) [32–35]. In this work, a novel poly(phenylene-carborane) (PPB) with excellent thermal and thermo-oxidative stability was synthesized via Ni(0)-catalyzed polycondensation of 1,2-bis(4-chloro-phenyl)-carborane. PPB proved to be excellent precursor to boron-carbide/carbon ceramic materials with high ceramic yield. Malenfant et al. have presented a powerful route for the preparation decaborane-containing polymers, which have proven to be excellent ceramic precursors [29,36,37]. Polymers reported by Malenfant's group were prepared via ruthenium-catalyzed ring-opening metathesis polymerization (ROMP). These polymers with high molecular weights and narrow molecular weight distributions are capable of forming ordered nanoscale structures via self-assembly, and self-assembly is a promising approach for achieving controlled nanoscale architectures in ceramics. However, monomers and polymers developed by

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Malenfant's group contain decaborane groups rather than carborane groups, so the monomers and polymers reported by Malenfant's group are not stable in air [37]. In this work, PPB with excellent thermal and thermo-oxidative stability has proven to be excellent precursor for boron-carbide/carbon ceramics with ceramic yields in the range of 91.1–92.6%, and these ceramics were well characterized by XRD, SEM, TEM, Raman and elemental analysis.

## 2. Experimental

### 2.1. Materials

$B_{10}H_{12}(CH_3CN)_2$  was synthesized according to literature procedures [38]. Decaborane was purchased from Zhengzhou Sigma Chemical Co., Ltd. (China). Trimethylsilylacetylene, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), copper(I) iodide (CuI), bis(triphenylphosphine)palladium(II) dichloride ( $PdCl_2(Ph_3P)_2$ ), bis(triphenylphosphine)nickel(II) dichloride ( $NiCl_2(Ph_3P)_2$ ), 1-ethynylbenzene, 1-chloro-4-iodobenzene, and powdered zinc (99.99%) were purchased from J&K Chemical Co and used without further purification. Triphenylphosphine and bipyridine were purchased from aladdin and used as received. Acetonitrile, toluene, and triethylamine were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (China). Acetonitrile was distilled from phosphorus pentoxide prior to use. Triethylamine was distilled from  $CaH_2$  prior to use. Toluene was distilled from sodium and benzophenone prior to use. Standard narrow polystyrene for GPC calibration was purchased from Agilent Technologies (Part No.: PL2010-0501).

### 2.2. Measurements

All NMR spectra were measured on a Bruker AVANCE III 500 spectrometer. High performance liquid chromatography (HPLC) analysis was performed on an Alliance2695-2696 instrument. Elemental analysis was performed on an elemental analysis Vario EL series. Inductively coupled plasma-atomic emission spectrometry (ICP) was performed on an Optima2000DV instrument. The FT-IR spectra were obtained using a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. MALDI-TOF-MS measurement was performed on a Waters MALDI micro MX. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a D/Max 2400. The gel permeation chromatography (GPC) analysis was carried on the Agilent PL-GPC 50 with two PL 7.5  $\mu m$  MIXED-D columns and one 5  $\mu m$  guard column. The system was calibrated against standard narrow polystyrene and conducted by using THF as eluent. Scanning electron microscopy (SEM) images were obtained with a QUANTA 450. The samples were gold coated. A working distance of approximately 5–5.5 mm and an accelerating voltage of 30 kV were used. Transmission electron microscopic (TEM) image was obtained with a Tecnai F30. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in nitrogen or air atmosphere at a heating rate of 20  $^{\circ}C \text{ min}^{-1}$  from 30 to 1000  $^{\circ}C$ . The differential scanning calorimetry (DSC) was measured on Mettler DSC822 DSC under a nitrogen flow (50  $\text{mL min}^{-1}$ ) at a heating rate of 10  $^{\circ}C \text{ min}^{-1}$  from 25  $^{\circ}C$  to 500  $^{\circ}C$ .

### 2.3. Synthesis of 1-chloro-4-(2-phenylethynyl)benzene

A 500 mL flask, equipped with a magnetic stirrer and a rubber septum, was charged with 1.26 g (1.80 mmol) of  $PdCl_2(PPh_3)_2$ , 1.14 g (5.85 mmol) of CuI, 21.5 g (90.0 mmol) of 1-chloro-4-iodobenzene. The flask was purged with dry nitrogen. DBU (72.0 mL), 1-ethynylbenzene (10.0 mL), distilled water (1.30 mL), and

acetonitrile (250 mL) were then added by syringe. The reaction flask was covered in aluminum foil and was stirred at 60  $^{\circ}C$  for 48 h. The reaction mixture was poured into 500 mL of distilled water. The precipitate was filtered and washed with distilled water. The pure product was obtained by recrystallization from *n*-hexane in 79% yield (15.1 g). Purity: 99.93% (HPLC). Found: C, 79.06%; H, 4.04%. Anal. Calcd for  $C_{14}H_9Cl$ : C, 79.07%; H, 4.26%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3047.9 (Ar-H), 1495.2 (C=C), 1090.9, 755.7, 686.7.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.54–7.49 (m, 2H), 7.47–7.42 (m, 2H), 7.36–7.32 (m, 3H), 7.33–7.29 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ ):  $\delta$  134.29 (s), 132.84 (s), 131.63 (s), 128.72 (s), 128.51 (s), 128.43 (s), 122.97 (s), 121.82 (s), 90.36 (s), 88.28 (s).

### 2.4. Synthesis of 1-(4-chlorophenyl)-2-phenyl-carborane

A 1000 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a reflux condensing tube was charged with 12.8 g (60.0 mmol) of 1-chloro-4-(2-phenylethynyl)benzene, 14.6 g (72.0 mmol) of  $B_{10}H_{12}(CH_3CN)_2$ , and 400 mL of toluene. The reaction mixture was magnetically stirred under nitrogen for 2 h at 100  $^{\circ}C$  and then stirred for 12 h at 115  $^{\circ}C$ . When the reaction was completed, the reaction solution was cooled to room temperature and 50 mL of methanol was added to resolve the unreacted  $B_{10}H_{12}(CH_3CN)_2$ . The toluene was evaporated under vacuum to afford crude product and the crude product was purified by silica gel column chromatography using petroleum ether as eluent. Petroleum ether was removed under reduced pressure to give white powder (11.8 g, 59.4% yield). Purity: 99.83% (HPLC). Found: C, 50.63%; H, 5.77%. Anal. Calcd for  $C_{14}H_{19}B_{10}Cl$ : C, 50.82%; H, 5.79%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3059.7 (Ar-H), 2577.7 (B-H), 1590.1 (C=C), 1492.2 (C=C), 1450.1, 1075.4, 836.2.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.42 (d,  $J = 8.2$  Hz, 1H), 7.35 (d,  $J = 8.8$  Hz, 1H), 7.26 (d,  $J = 5.4$  Hz, 1H), 7.18 (d,  $J = 7.7$  Hz, 1H), 7.11 (t,  $J = 5.6$  Hz, 1H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ ):  $\delta$  136.67 (s), 131.86 (s), 130.61 (s), 130.43 (s), 129.31 (s), 128.52 (s), 128.48 (s), 85.29 (s), 84.01 (s). MS (MALDI-TOF)  $m/z$ :  $M^+$  calculated for  $C_{14}H_{19}B_{10}Cl$  330.22; found 330.22.

### 2.5. Synthesis of 1,2-bis(4-chlorophenyl)ethyne

To 500 mL flask, equipped with a magnetic stirrer and a rubber septum, was charged with 1.26 g (1.80 mmol) of  $PdCl_2(PPh_3)_2$ , 1.14 g (5.85 mmol) of CuI, 42.9 g (180 mmol) of 1-chloro-4-iodobenzene. The flask was purged with dry nitrogen. DBU (72.0 mL), trimethylsilyl ethynylene (13.8 mL), distilled water (1.30 mL), and acetonitrile (250 mL) were then added by syringe. The reaction flask was covered in aluminum foil and was stirred at 60  $^{\circ}C$  for 48 h. The reaction mixture was poured into 500 mL of distilled water. The precipitate was filtered and washed with distilled water. The pure product was obtained by recrystallization from chloroform in 85% yield (18.9 g). Purity: 99.63% (HPLC). Found: C, 67.9%; H, 3.09%. Anal. Calcd for  $C_{14}H_8Cl_2$ : C, 68.04%; H, 3.26%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1908.5, 1492.5 (C=C), 1396.3, 1088.9, 1011.2, 825.6, 656.9.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.44 (d,  $J = 8.6$  Hz, 1H), 7.32 (d,  $J = 8.6$  Hz, 1H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ ):  $\delta$  134.54 (s), 132.80 (s), 128.77 (s), 121.45 (s), 89.18 (s).

### 2.6. Synthesis of 1,2-bis(4-chlorophenyl)-carborane

1,2-Bis(4-chlorophenyl)-carborane was prepared using the similar procedure for preparation of 1-(4-chlorophenyl)-2-phenyl-carborane except for using 1,2-bis(4-chlorophenyl)ethyne as reagent (55% yield). Found: C, 45.69%; H, 4.99%. Anal. Calcd for  $C_{14}H_{18}B_{10}Cl_2$ : C, 46.03%; H, 4.96%. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3080.6 (Ar-H), 2569.7 (B-H), 1597.3 (C=C), 1493.2 (C=C), 1402.6, 829.2.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.35 (d,  $J = 8.8$  Hz, 4H), 7.15 (d,  $J = 8.8$  Hz, 4H).

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