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



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#### 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 hightemperature 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<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub>), bis(triphenylphosphine)nickel(II) dichloride  $(NiCl_2(Ph_3)_2),$ 1ethynylbenzene, 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<sub>2</sub> 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 µm MIXED-D columns and one 5 µm 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 °C min<sup>-1</sup> from 30 to 1000 °C. The differential scanning calorimetry (DSC) was measured on Mettler DSC822 DSC under a nitrogen flow (50 mL min<sup>-1</sup>) at a heating rate of 10  $^{\circ}$ C  $min^{-1}$  from 25 °C to 500 °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  $1.26 \text{ g} (1.80 \text{ mmol}) \text{ of } PdCl_2(PPh_3)_2, 1.14 \text{ g} (5.85 \text{ mmol}) \text{ of } Cul, 21.5 \text{ g} (90.0 \text{ mmol}) \text{ of } 1\text{-chloro-4-iodobenzene}.$ 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 °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<sub>14</sub>H<sub>9</sub>Cl: C, 79.07%; H, 4.26%. FT-IR (KBr, cm<sup>-1</sup>): 3047.9 (Ar-H), 1495.2 (C=C), 1090.9, 755.7, 686.7. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.54–7.49 (m, 2H), 7.47–7.42 (m, 2H), 7.36–7.32 (m, 3H), 7.33–7.29 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>10</sub>H<sub>12</sub>(CH<sub>3</sub>CN)<sub>2</sub>, and 400 mL of toluene. The reaction mixture was magnetically stirred under nitrogen for 2 h at 100 °C and then stirred for 12 h at 115 °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<sub>10</sub>H<sub>12</sub>(CH<sub>3</sub>CN)<sub>2</sub>. 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<sub>14</sub>H<sub>19</sub>B<sub>10</sub>Cl: C, 50.82%; H, 5.79%. FT-IR (KBr, cm<sup>-1</sup>): 3059.7 (Ar-H), 2577.7 (B-H), 1590.1 (C=C), 1492.2 (C=C), 1450.1, 1075.4, 836.2. <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta$  7.42 (d, I = 8.2 Hz, 1H), 7.35 (d, I = 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). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 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<sub>14</sub>H<sub>19</sub>B<sub>10</sub>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<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 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), thrimethylsilvethynylene (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 °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<sub>14</sub>H<sub>8</sub>Cl<sub>2</sub>: C, 68.04%; H, 3.26%. FT-IR (KBr, cm<sup>-1</sup>): 1908.5, 1492.5 (C=C), 1396.3, 1088.9, 1011.2, 825.6, 656.9. <sup>1</sup>H NMR  $(500 \text{ MHz}, \text{CDCl}_3)$ :  $\delta$  7.44 (d, J = 8.6 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 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<sub>14</sub>H<sub>18</sub>B<sub>10</sub>Cl<sub>2</sub>: C, 46.03%; H, 4.96%. FT-IR (KBr, cm<sup>-1</sup>): 3080.6 (Ar-H), 2569.7 (B-H), 1597.3 (C=C), 1493.2 (C=C), 1402.6, 829.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 (d, *J* = 8.8 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 4H).

 $^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  136.97 (s), 131.85 (s), 129.06 (s), 128.75 (s), 84.16 (s). MS (MALDI-TOF) m/z: M+ calculated for C14H18B10Cl<sub>2</sub> 365.17; found 365.17.

# 2.7. Synthesis of model compound MCPB

A 25 mL Schlenk flask equipped with a magnetic stirrer was charged with 0.065 g (0.10 mmol. 0.1 equiv) of NiCl<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub>, 0.052 g (0.20 mmol, 0.2 equiv) of triphenylphosphine, 0.016 g (0.10 mmol, 0.1 equiv) of bipyridine, 0.20 g (3.1 mmol, 3.1 equiv) of zinc, and 0.030 g (0.20 mmol, 0.2 equiv) of sodium iodide. The flask was sealed with a septum, evacuated and refilled with nitrogen three times, and charged with 1 mL of THF via syringe. The catalyst mixture was stirred and heated in an oil bath at 60 °C for several minutes. Once the color of the catalyst mixture changed from deep green to dark red, 0.33 g (1.0 mmol) of 1-(4-chlorophenyl)-2phenyl-carborane was added under nitrogen flow. The reaction continued at 60  $\,^\circ\text{C}$  for 12 h. The reaction mixture was then precipitated into 10% hydrochloric acid to remove excess zinc and extracted with chloroform. Then the organic layer was washed with brine and dried over anhydrous sodium sulfate overnight, followed by vacuum evaporation. The crude product was finally passed through silica gel column chromatography using petroleum ether as an eluent. Petroleum ether was removed under reduced pressure to give needle-crystal (92% yield). Found: C, 56.97%; H, 6.49%. Anal. Calcd for C<sub>28</sub>H<sub>38</sub>B<sub>20</sub>: C, 56.92%; H, 6.48%. FT-IR (KBr, cm<sup>-1</sup>): 3062.6 (Ar-H), 2571.9 (B-H), 1605.3 (C=C), 1495.2 (C=C), 1444.6, 688.6. <sup>1</sup>H NMR (500 MHz, THF):  $\delta$  7.53 (dd, I = 13.4, 5.0 Hz, 4H), 7.39 (d, I = 8.6 Hz, 2H), 7.23 (t, I = 7.3 Hz, 1H), 7.16 (t, I = 7.7 Hz, 2H). <sup>13</sup>C NMR (126 MHz, THF): § 140.77 (s), 131.11 (s), 130.72-130.39 (m), 130.26 (s), 128.37 (s), 126.66 (s), 85.32 (s), 84.65 (s). MS (MALDI-TOF) m/z: M+ calculated for C<sub>28</sub>H<sub>38</sub>B<sub>20</sub> 590.49; found 590.49.

## 2.8. Synthesis of PPB

A 25 mL Schlenk flask equipped with a magnetic stirrer was charged with 0.26 g (0.40 mmol, 0.1 equiv) of NiCl<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub>, 0.21 g (0.80 mmol, 0.2 equiv) of triphenylphosphine, 0.062 g (0.40 mmol, 0.1 equiv) of bipyridine, 0.81 g (12 mmol, 3.1 equiv) of zinc, and 0.12 g (0.80 mmol, 0.2 equiv) of sodium iodide. The flask was sealed with a septum, evacuated and refilled with nitrogen three times, and charged with 4 mL of THF via syringe. The catalyst mixture was stirred and heated in an oil bath at 60 °C for several minutes. Once the color of the catalyst mixture changed from deep green to dark red, 1.5 g (4.0 mmol) of 1,2-bis(4-chlorophenyl)-carborane was added under nitrogen flow. The reaction continued at 60 °C for 12 h. The reaction mixture was then precipitated into 200 mL of 40% HCl/ methanol to remove excess zinc and stirred overnight. The precipitate was collected by suction filtration, washed with saturated sodium bicarbonate and methanol, redissolved in THF, and reprecipitated into methanol. The polymer was extracted with methanol for 24 h and dried in a vacuum oven to give 1.0 g of white powder (85% yield). Found: C, 57.12%; H, 5.85%. Anal. Calcd for (C<sub>14</sub>H<sub>18</sub>B<sub>10</sub>)<sub>n</sub>: C, 57.12%; H, 6.16%. FT-IR (KBr, cm<sup>-1</sup>): 3043.6 (Ar-H), 2593.9 (B-H), 1607.9 (C=C), 1496.2 (C=C), 1396.6, 1005.9, 831.6. <sup>1</sup>H NMR (500 MHz, THF): δ 5.90-5.74 (d, 37H), 5.73-5.57 (d, 37H), 5.47 (t, J = 9.3 Hz, 1H), 5.41 (t, J = 7.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, THF):  $\delta$  138.80 (s), 129.32 (s), 128.64 (d, J = 42.1 Hz), 126.42 (s), 124.72 (s), 83.34 (s). Ni content by ICP analysis:  $2.32 \times 10^{-2}$ %.

# 2.9. Preparation of ceramic

In a typical pyrolysis of PPB, a sample specimen disks (0.6–0.8 g) of PPB with a diameter of 2.54 cm was prepared by press-molding PPB powder at room temperature. The compacted polymer disk

was subsequently placed into a boron nitride crucible and transferred into a tube furnace. The sample was then heated under argon to 1000 °C at a heating rate of 5 °C/min and held at 1000 °C for 2 h. The obtained sample was named as PPB-1000. PPB-1200, PPB-1400, and PPB-1500 were prepared using similar procedure and pyrolyzed at 1200, 1400, and 1500 °C for 2 h, respectively. The element composition and ceramic yields of the resulting ceramics are summarized in Table 5. Ni content by ICP analysis: PPB-1000, 1.93 × 10<sup>-2</sup>%; PPB-1200, 1.87 × 10<sup>-2</sup>%; PPB-1400, 1.90 × 10<sup>-2</sup>%; PPB-1500, 1.78 × 10<sup>-2</sup>%.

# 3. Results and discussion

# 3.1. Preparation and characterization of monomers and polymers

The synthetic route of model monomer and bischloride monomer is illustrated in Scheme 1. 1-Chloro-4-(2-phenylethynyl)benzene and 1,2-bis(4-chlorophenyl)ethyne were synthesized via Sonogashira coupling reaction. The reaction proceeded smoothly and gave the target monomers in high yields. 1-(4-Chlorophenyl)-2-phenyl-carborane and 1,2-bis(4-chlorophenyl)-carborane were synthesized using a similar procedure according to a previous literature [6]. The chemical structures of 1-chloro-4-(2phenylethynyl)benzene, 1-(4-chlorophenyl)-2-phenyl-carborane, 1,2-bis(4-chlorophenyl)ethyne, and 1,2-bis(4-chlorophenyl)-carborane were confirmed by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and elemental analysis (The FT-IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectra of 1-(4chlorophenyl)-2-phenyl-carborane were listed in the supporting information). The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of 1,2-bis(4chlorophenyl)-carborane were showed in Fig. 1. The broad peak at  $\delta$  1.5–3.5 ppm was assigned to the protons of *o*-carborane cage [39]. All of the protons and carbons in 1-(4-chlorophenyl)-2-phenylcarborane and 1,2-bis(4-chlorophenyl)-carborane were detected as expected, confirming that 1-(4-chlorophenyl)-2-phenyl-carborane and 1,2-bis(4-chlorophenyl)-carborane were successfully synthesized. In the FT-IR spectra of 1-(4-chlorophenyl)-2-phenyl-carborane and 1,2-bis(4-chlorophenyl)-carborane (see supporting information), the absorption peak at 2596 cm<sup>-1</sup> was attributed to the stretching vibration of B-H in carborane cage.

Ni(0)-catalyzed coupling reaction of aryl chlorides is an effective approach for the formation of aromatic carbon-carbon bonds. Many studies on the mechanism of this reaction have resulted in a better understanding of the role of reactant structure, ligands, temperature, and reducing metal on the reaction. The presence of electronwithdrawing groups ortho or para to the reactive site accelerates the reaction rate by activating that site to oxidative addition by the



Scheme 1. Synthetic route of model monomer and bischloride monomer.

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Fig. 1. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of 1,2-bis(4-chlorophenyl)-carborane in CDCl<sub>3</sub>.

Ni(0) complex, and thus aryl chlorides with electron-withdrawing substituents show higher reactivity and give higher yields of coupling products [33,40]. The electron-withdrawing property of *o*-carborane cage [41,42] should increase the Ni(0)-catalyzed reactivity of 1,2-bis(4-chlorophenyl)-carborane, and the polymerization of 1,2-bis(4-chlorophenyl)-carborane via Ni(0)-catalyzed coupling reaction may lead to high molecular weight polymers. In order to verify the reactivity of 1,2-bis(4-chlorophenyl)-carborane was conducted (Scheme 2), and the reaction condition was listed in Table 1. The model reactions were performed in THF using NiCl<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub> as a catalyst, Zn as a reducing agent, and triphenylphosphine and



Scheme 2. Synthesis of MCPB and polymerization of 1,2-bis(4-chlorophenyl)-carborane.

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The reaction condition of model study. <sup>a</sup>
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Entry	Temperature (°C)	Time (h)	Solvent	Halide (equiv)	HPLC yield (%)
1	60	12	THF	—	94.5
2	60	12	THF	NaBr (0.2)	97.1
3	60	12	THF	NaI (0.2)	100.0

<sup>a</sup> Reaction conditions: NiCl<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub> (0.1 equiv), triphenylphosphine (0.2 equiv), bipyridine (0.1 equiv), zinc (3.1 equiv). Equivalents were given with respect to the model monomer, 1-(4-chlorophenyl)-2-phenyl-carborane.

bipyridine as ligands. THF was chosen as the solvent because THF has been shown to minimize reduction and other side reactions [33]. Additionally, polar aprotic solvent such as dimethylacetamide (DMAC) and dimethylformamide (DMF) can lead to cage degradation reaction of o-carborane [43–45]. Without addition of sodium halide (Table 1 entry 1), the MCPB was obtained in a high yield of 94.5% according to high performance liquid chromatography analysis (HPLC), suggesting that 1,2-bis(4-chlorophenyl)-carborane could be used for Ni(0)-catalyzed polycondensation. The polymerization of 1,2-bis(4-chlorophenyl)-carborane was performed under this model reaction condition. However, only low molecular weight oligomer was obtained, and number-average molecular weight of the oligomer was determined to be  $1.0 \times 10^3$  according to gel permeation chromatography analysis (GPC). According to the previous reports, halide ions, especially iodide, enhance the reaction rate of Ni(0)-catalyzed homocoupling reactions [40,46]. In our model study, the addition of sodium halide indeed accelerated the reaction rate of Ni(0)-catalyzed homocoupling reaction, and the model reaction with addition of 0.2 equiv sodium iodide gave an excellent yield of 100%. High molecular weight polymer was prepared under the optimized reaction conditions, and the numberaverage molecular weight of the obtained polymer was determined to be  $12.4 \times 10^3$  by GPC (Table 2).

MCPB and PPB were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>11</sup>B-NMR, and FT-IR spectroscopies as well as elemental analysis. As shown in Fig. 2, FT-IR spectra of MCPB and PPB were very similar. Absorption band at 2596 cm<sup>-1</sup> in FT-IR spectra of MCPB and PPB was ascribed to the stretching vibration of B-H in carborane cage [47–49]. <sup>1</sup>H-NMR spectra of MCPB and PPB in THF-d and their assignments were shown in Fig. 3. As shown in Figure 3, <sup>1</sup>H-NMR spectrum of PPB showed two doublets and two smaller triplets. These two doublets at  $\delta$  7.54 and 7.36 ppm corresponded to the two hydrogen atoms in benzene ring of the polymer chain. While the two smaller triplets at  $\delta$  7.1 and 7.2 ppm were attributed to the hydrogen atoms in benzene of the polymer end groups and were used to calculate the degree of polymerization. It's worth mentioning that all the end groups of the polymer chain were phenyl groups rather than *p*-chlorophenyl groups based on <sup>1</sup>H-NMR study of PPB, which was attributed to the reduction reaction of arylnickel intermediates with protic sources during the reaction post-processing [40]. The degree of polymerization (DP) calculated from end group analysis by <sup>1</sup>H-NMR was 18.3, and thus the number-average molecular weight of PPB calculated from <sup>1</sup>H-NMR was 5.4  $\times$  10<sup>3</sup> g/mol. While number-average molecular weight determined by GPC was  $12.4 \times 10^3$ , this difference was attributed to the different hydrodynamic volumes of PPB and polystyrene. <sup>13</sup>C-NMR spectra of MCPB and PPB were shown in Fig. 4. All carbon atoms were well assigned as expected, confirming that polymerization of 1,2-bis(4-chlorophenyl)-carborane was successfully proceed. Aromatic carbon atoms of the polymer end groups were well detected in the <sup>13</sup>C-NMR spectrum, indicating that number-average molecular weight of PPB could not be too high, which was consistent with <sup>1</sup>H-NMR analysis. <sup>11</sup>B-NMR spectra of PPB and MCPB exhibited two absorption peaks, as shown in Fig S4. The <sup>11</sup>B signals of the carborane in PPB were significantly broadened as compared

### Table 2

Molecular weight and Thermal data for PPB.<sup>a</sup>

Polymer	$M_n$ ( $\times$ 10^{-3})	$M_w$ ( $ imes$ 10 <sup>-3</sup> )	PDI	T <sub>g</sub> (°C)	T <sub>5</sub> (°C) <sup>b</sup> N <sub>2</sub> /air	T <sub>10</sub> (°C) <sup>c</sup> N <sub>2</sub> /air
PPB	12.4	30.7	2.5	>450	706/>1000	>1000/>1000

<sup>a</sup> Polymerization conditions: NiCl<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub> (0.1 equiv), triphenylphosphine (0.2 equiv), bipyridine (0.1 equiv), zinc (3.1 equiv), Nal (0.2 equiv), 60 °C, 12 h. Equivalents were given with respect to the bischloride monomer, 1,2-bis(4-chlorophenyl)-carborane.

<sup>b</sup> 5% weight loss temperatures determined in nitrogen and air, respectively.

<sup>c</sup> 10% weight loss temperatures determined in nitrogen and air, respectively.





Fig. 3. <sup>1</sup>H-NMR spectra of MCPB and PPB in THF-d.

to the signals of the MCPB, suggesting that the mobility of the carborane groups in PPB was greatly restricted by polymer chain compared with MCPB.

During the polymerization of 1,2-bis(4-chlorophenyl)-carborane, PPB precipitated from the polymerization system, which prevented the further increase of molecular weight of PPB. The precipitated polymer could redissolve in NMP and excess THF, indicating that precipitation of the polymer was not caused by cross-linking reaction. This phenomenon was attributed to the crystalline character of PPB, which was verified by XRD analysis. As shown in Fig. 5, four sharp peaks were observed at  $2\theta = 14.8^{\circ}$ ,  $16.7^{\circ}$ ,  $21.6^{\circ}$ , and  $26.5^{\circ}$ , revealing its crystalline character. Solubility of PPB is summarized in Table 3 and PPB can be well dissolved in NMP at room temperature.



Fig. 4. <sup>13</sup>C-NMR spectra of MCPB and PPB in THF-d.



Fig. 5. Wide angle X-ray diffraction pattern for PPB.

Tabl	e 3
The	solubility of PPB. <sup>a</sup>

Solvent	CHCl <sub>3</sub>	THF	DMAC	DMSO	DMF	NMP
Solubility	-	+	-	-	-	+

 $^{\rm a}$  Key: +, soluble at room temperature (0.05 g of PPB in 1 mL of solvent), -, insoluble.

# 3.2. Thermal analysis of PPB

The differential scanning calorimetry (DSC) curve of PPB (Fig S5) was featureless line without any sign of glass transition in the temperature range of 25-450 °C, while the exothermic peak of

decomposition reaction of PPB began to appear when the temperature was above 450 °C. In consideration of the high rigidity of the polymer chain, it was reasonable that the glass transition temperature ( $T_g$ ) of PPB was above 450 °C. DSC curve of PPB showed no sign of endothermic melting peak up to 500 °C. Since the melting point of the MCPB was 281.8 °C (measured by DSC), a crystalline melting point for PPB of >500 °C seemed reasonable.

The thermal stability of PPB was evaluated by TGA under nitrogen and air atmosphere, and the thermograms were shown in Fig. 6. The weight loss temperatures of 5% and 10% ( $T_5$  and  $T_{10}$ ) and char yields at 1000 °C for PPB were summarized in Table 4. As shown in Fig. 6, PPB showed a two-step weight loss pattern beginning at about 400 °C and 600 °C, and char yield of PPB remained constant over the temperature range of 850–1000 °C. A high char yield of 93.2% at 1000 °C in nitrogen was finally obtained. DTG curve analysis was used to provide more information on the degradation process. As shown in Fig S6, the thermal degradation process of PPB in nitrogen atmosphere could be divided into two degradation stages. Assuming that hydrogen atoms in benzene were lost at first degradation stage and hydrogen atoms in carborane were lost at second degradation stage, the theoretical weight loss at first degradation stage and second degradation stage was 2.8% and 3.4%, respectively. In fact, weight loss of the two stages was 3.3% and 3.5% according to TGA analysis, which was agreed with the theoretical weight loss. So the peak of weight loss at 536 °C in the first thermal degradation stage could be attributed to the loss of hydrogen in benzene, while the peak of weight loss at 678 °C in the second thermal degradation stage could be attributed to the loss of hydrogen in carborane. Additionally, o-carborane undergoes an irreversible thermal reaction resulting in the formation of the *m*-carborane on heating at 470–600 °C in an inert atmosphere, and further heating to about 650-700 °C in inert atmosphere results in forming *p*-carborane [50–53]. So it is reasonable to attribute the second degradation stage to the loss of hydrogen in carborane. In contrast with TGA curve in nitrogen, TGA curve of PPB in air showed a slight weight gain from 500 °C, which was attributed to oxidation of boron atoms in the carborane upon exposure to oxidizing atmospheres at elevated temperatures [54–57]. The decomposition reaction was predominant at elevated temperature, so PPB began to lose weight when the temperature was above 610 °C under air atmosphere. PPB showed excellent thermal and thermo-oxidative stability with T<sub>5</sub> at 707 °C and >1000 °C in nitrogen and air, respectively.



Fig. 6. TGA curves of PPB in nitrogen and air.

#### 3.3. Ceramic conversion reactions of PPB

Pyrolysis was performed in a tube furnace under an argon atmosphere at 1000, 1200, 1400, and 1500 °C for 2 h to afford PPB-1000, PPB-1200, PPB-1400, and PPB-1500, respectively. The ceramics after pyrolysis were compact black disks, and the black color indicated that the ceramics contained excess carbon. SEM images (Fig S7) of the ceramic samples showed that the matrix of the ceramics was compact and with some microscale cracks. Elemental analysis data and ceramic yields were summarized in Table 5. Ceramic yields of PPB were in the range of 91.1–92.6%, which were higher than that reported in the previous studies [29,36,58]. The elemental analysis showed that all ceramics had B:C ratios lower than the 4:1 ration of B<sub>4</sub>C, suggesting the presence of excess carbon. Additionally, the presence of the free carbon was also confirmed by Raman analysis. As shown in Fig S8, the absorption bands at 1344 and 1594  $cm^{-1}$  were attributed to graphite in ceramics [19]. In consideration of the low content of hydrogen (<0.3%) in the ceramics, assuming that all of the hydrogen was lost and all the carbon was retained during the ceramic conversion, and then PPB would convert to boron-carbide ceramics according to the following equation to give a theoretical ceramic yield of 93.8%. Ceramic yield (Fig. 6) after TGA study up to 1000 °C in nitrogen was 93.2% and was very close to theoretical ceramic yield as shown in the following equation. In addition, the elemental composition of PPB-1000 was very close to the theoretical elemental composition, which were  $B_4C \cdot C_{4.73}$  and  $B_4C \cdot C_{4.6}$ , respectively.

As shown in Fig. 7, the TEM micrograph of PPB-1500 reveals lattice-plane structures of B<sub>4</sub>C and graphite nanocrystals in matrix of the ceramic sample. The measured *d*-spacings of about 0.24, 0.38, and 0.35 nm can be assigned to the (021) plane and (012) plane in B<sub>4</sub>C and (002) plane in graphite, respectively [59]. As shown in Fig. 8, XRD study of the bulk-ceramic residues indicated that boron carbide crystallization for PPB began between 1000 and 1200 °C, which was consistent with the previous study [58]. The boron carbide diffraction peaks began to appear in PPB-1200 and the diffraction intensity increased as increased pyrolysis temperature, indicating that high temperature promoted crystallization of boron carbide. The size of the boron carbide nanocrystallite was calculated to be 20.33 nm for PPB-1500 by the Scherrer equation using the full-width at half-maximum (fwhm) value of diffraction peak at  $2\theta = 37.5^{\circ}$ . The diffraction peaks located at  $2\theta = 26^{\circ}$  and  $42^{\circ}$  in XRD pattern of the ceramics were attributed to graphite [19,58].

In order to investigate the thermo-oxidative stability of the ceramics, TGA study of the ceramics was performed on pieces of ceramic sample in air. As shown in Fig. 9, the ceramics derived from PPB showed excellent thermo-oxidative stability with char yields range from 100.8% to 101.6% at 1000 °C in air, and the weight gain of the ceramic samples at 600 °C in the TGA curve was attributed to oxidation of boron in ceramics [54,56].

# 4. Conclusions

condition, Under the optimized polymerization а poly(phenylene-carborane) (PPB) with moderate number-average molecular weight was successfully synthesized via Ni(0)catalyzed polymerization of 1,2-bis(4-chloro-phenyl)-carborane and well characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>11</sup>B-NMR, FT-IR, and GPC. The number-average molecular weight of the obtained polymer was determined to be 5.4  $\times$  10<sup>3</sup> g/mol by <sup>1</sup>H-NMR spectroscopy analysis. The crystalline character of PPB was verified by XRD, which prevented the further increase of molecular weight of PPB during the polymerization. The glass transition temperature and melting point of PPB were all above its decomposition temperature (450 °C) due to the high rigidity of the polymer chain. Based on TGA Table 4

TGA data	of PPB in	air and	nitrogen. <sup>a</sup>

Polymer	$T_5/^{\circ}C(N_2)$	$T_{10}/^{\circ}C(N_2)$	Char yield/% (N <sub>2</sub> )	T <sub>5</sub> /°C (air)	T <sub>10</sub> /°C (air)	Char yield/% (air)
PPB	707	>1000	93.2	>1000	>1000	97.9

<sup>a</sup> T<sub>5</sub>: temperature for 5% weight loss; T<sub>10</sub>: temperature for 10% weight loss.

# Table 5

Ceramic data of PPB derived ceramics.<sup>a</sup>

Sample	Ceramic yield (%)	B (%)	C (%)	H (%)	composition
PPB-1000	92.6	40.97	58.74	0.29	$B_4C \cdot C_{4.73}$
PPB-1200	92.3	43.33	56.46	0.21	$B_4C \cdot C_{4,21}$
PPB-1400	92.2	43.15	56.68	0.17	$B_4C \cdot C_{4,25}$
PPB-1500	91.1	41.55	58.31	0.14	$B_4C \cdot C_{4.61}$

 $^{\rm a}\,$  Boron content of the ceramics was calculated from contents of C and H (100%-C %-H%).



Fig. 7. TEM image of PPB-1500.



Fig. 8. XRD patterns of ceramics derived from PPB.

analysis of PPB, PPB exhibited excellent thermal and thermooxidative stability with 5% weight loss temperature to be 707 °C and >1000 °C in nitrogen and air, and exhibited a high char yield of 93.2% and 97.9% at 1000 °C in nitrogen and air, respectively. PPB has



Fig. 9. TGA curves of the ceramics derived from PPB in air.

proven to be excellent sing-source precursors to boron-carbide/ carbon ceramic materials with high ceramic yield. Boron carbide crystallization for PPB began between 1000 and 1200 °C according to XRD analysis. Boron carbide as well as graphite crystallization in the ceramics was confirmed by TEM, XRD, and Raman analysis.

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# Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2017.03.036.

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