Synthesis and Characterization of Carborane Bisphenol Resol Phenolic Resins with Ultrahigh Char Yield[*]

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Abstract Two carborane-containing resol phenolic resins (**P1** and **P2**) with high boron content were synthesized *via* the reaction of carborane bisphenols (**1** and **2**) with formaldehyde in the presence of alkaline. HRMS results indicate that **P1** is mainly composed of hydroxymethylated *o*-carborane bisphenols, the M_w of which was restrained around 500 due to the strong steric hindrance of *o*-carborane bisphenol. In contrast, the molecular weight of **P2** was well regulated under various reaction conditions. The obtained resins were characterized with spectroscopic techniques including FTIR, ^{1}H-NMR, ^{13}C-NMR, and ^{11}B-NMR, which gave satisfactory results. TGA studies show that **P2** shows char yield of 88.9% and 92.9% at 900 °C under nitrogen and air respectively. The imported carborane cage endows phenolic resin with ultrahigh char yield. Particularly, the char yield of the obtained carborane-containing phenolic resin under air is higher than that under nitrogen. FTIR and XRD confirm that the carborane cage could react with oxygen to form B_2O_3 at elevated temperatures, which postpones the thermal decomposition of phenolic resin and accounts for the high char yield.

Keywords: Carborane-containing resol phenolic resin; High boron content; Char yield.

INTRODUCTION

Phenolic resins have been widely used as raw materials to prepare various industrial products such as fire-proofing materials, plastics, fibers, adhesives, and composites due to their excellent mechanical strength, bonding property, and high-temperature and ablation resistance[1]. Although phenolic resins have been invented for over 100 years, they still attracted considerable research effort[2, 3].

Generally, there are two ways of attaining phenolic resins with novel structure and high performance. On one hand, various chemical reactions are considered to import new curing mechanism of phenolic resins. Reactive groups such as allyl, triple bond, and benzoxazine ring have been introduced into phenolic resins, which follow an addition curing mechanism[4–9]. Addition-curable phenolic resins could be cured at normal pressure without releasing volatiles and thus own low curing shrinkage and good dimensional stability.

On the other hand, new atoms and moieties are incorporated into the cured resins to improve their high temperature stability without changing their cure mechanism. As an example, boron-containing phenolic resins have been prepared by adding boron compound to the synthetic systems and the obtained resins show higher char yield than boron-free resins[10–14]. The introduced boron atoms partially replace chemical bonds of low bonding energy such as hydroxyl and ether linkages so that the decomposition temperature of the cured resin is also elevated. Furthermore, boron-containing segment could be oxidized to form inorganic boron oxide at

elevated temperatures under air, which in turn postpone further decomposition of the resin. Therefore, boron-containing phenolic resins are irreplaceable materials for high temperature structures and equipments in high-tech areas. However, the boron content of the above resins is usually below 10 wt%, which limits further improvement of high-temperature and ablation resistance of phenolic resins[15, 16].

Closo-carboranes ($C_2B_{10}H_{12}$) present an icosahedral geometry, whose three isomers are shown in Chart 1[17]. Carboranes could be served as a kind of "power gauge" at high temperatures owing to their "superaromatic" electronic structure. Besides, the large three-dimensional structure endows carboranes with strong shielding effect over adjacent segments. Therefore, carboranes are excellent building blocks for constructing curable oligomers and polymers with high thermal stability. *m*-Carborane was introduced into the main chain of polysiloxanes by several groups and the obtained poly(*m*-carborane-siloxane)s exhibit excellent high temperature performance[18–21]. Aromatic polyesters containing carborane moiety were mainly prepared by Russian chemists and the anticipated products show extraordinarily high char yield (up to 85 wt%) under air at 900 °C and new type of mesophase[22, 23]. Other carborane-containing polymers such as bisphenol-type epoxy resins and aliphatic polyesters were also studied[24, 25].
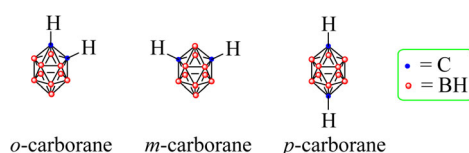

o-carborane   *m*-carborane   *p*-carborane
Chart 1 Structures of three carborane isomers

We succeeded in incorporating *m*-carborane to phenolic resin and the resultant resins show ultrahigh char yield at elevated temperature[26]. However, the effect of carborane isomers on synthesis should be fully studied and the structure variation of the obtained resins should be further elucidated. In this work, on the basis of our previous work, we report our studies on the synthesis of *o*-carborane and *m*-carborane containing phenolic resins. The effect of carborane isomers on the resin synthesis has been carefully studied and the obtained resins have been fully characterized. The thermal stability of the resins has been checked and the structure-property relationship of the cured resin after aging at elevated temperature is shown.

EXPERIMENTAL

Materials

o-Carborane bisphenol was obtained from Beihang University. *m*-Carborane bisphenol was synthesized and purified according to our previously published synthetic route[26]. Isopropanol, sodium hydroxide, barium hydroxide octahydrate, formaldehyde aqueous solution (37 wt%), and ammonia water (25 wt%) were obtained from Beijing Chemical Reagent Company. Hexamethylenetetramine was purchased from Aladdin and used as received. Boron-containing phenolic resin (M_n = 800, boron content = 5 wt%) was purchased from Bengbu Tianyu High Temperature Resin Materials Ltd.

Instrumentation

FTIR spectra were measured on a Nicolet Nexus 670 FTIR spectrophotometer with a scanning range from 4000 cm^{-1} to 400 cm^{-1}. ^1H- and ^{13}C-NMR spectra were measured on a Bruker AV 400 NMR spectrometer using tetramethylsilane (TMS; δ = 0) as internal standard. Molecular weights (M_w and M_n) and polydispersity indexes (PDI, M_w/M_n) of the polymers were estimated in THF by a Waters gel permeation chromatography (GPC) system. A set of monodisperse polystyrene standards covering molecular weight range of 10^3–10^7 was used for molecular weight calibration. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2-S Q operating in a negative ESI-TOF mode. The thermogravimetric analysis (TGA) was conducted on a TA SDT-Q600 thermogravimetric analyzer, in which a sample of ~5 mg was heated to 900 °C at a rate of 20 K/min and under a flow of nitrogen or air stream. X-ray diffraction (XRD) patterns were recorded using a Bruker D8

FOCUS (Bruker AXS, Germany) with Cu Kα radiation (λ = 0.154 nm, 40 kV and 40 mA) to analyze the structural variation of the thermally treated products.

Synthesis of o-Carborane Bisphenol Resol Phenolic Resin (P1)

P1 was synthesized according to the synthetic route shown in Scheme 1. *o*-Carborane bisphenol (**1**, 0.200 g, 0.61 mmol) and isopropanol (5 mL) were added into a 50 mL flask. The mixture was stirred at 45 °C till complete dissolution of **1**. Then sodium hydroxide (2.928 mg, 0.073 mmol) and formaldehyde aqueous solution (37%, 0.119 g, 1.464 mmol) were added into the flask. The reaction system was stirred at 100 °C for 8 h. After evaporation of the solvent and water by a rotary evaporator, an orangey-red viscous liquid was obtained as crude product. The crude product was dissolved in 5 mL of methanol and then added dropwise to a 300 mL mixed solvents of deionized water and methanol (8/2 by volume) through a cotton filter under vigorous stirring. The precipitate was allowed to stand for 24 h and then filtered with a Gooch crucible. The obtained polymer was washed with deionized water for three times and dried in oven over night. A yellow solid (86.9%) was obtained as target product. FTIR, v (cm^{-1}): 3446 (OH); 3053, 2940, 2851 (CH$_2$); 2547 (B$-$H); 1608, 1577, 1505, 1453 (Ph); 1405, 1288 (Ph$-$OH); 1247, 1175, 1144 (C$-$O$-$C); 1010 (C$-$O). ^{1}H-NMR (400 MHz, acetone-d_6), δ (TMS): 7.41 (m, 4H), 6.68 (m, 4H), 4.71 (m, 2H), 3.50 (m, 1H), 3.10–0.90 (m, 10H). ^{13}C-NMR (100 MHz, acetone-d_6), δ (TMS): 160.3, 157.8, 133.6, 131.5, 122.5, 116.0, 89.0, 64.4. ^{11}B-NMR (128 MHz, acetone-d_6), δ (TMS): −3.42, −9.34, −11.28. HRMS (ESI-TOF): *m/z* 327.2421, 357.2529, 387.2634, 417.2738, 655.4909, 686.4990, 728.5102, 758.5335, 1098.7690, 1128.7796.

Synthesis of m-Carborane Bisphenol Resol Phenolic Resin (P2)

P2 was synthesized according to the synthetic route shown in Scheme 2. P2 was synthesized from *m*-carborane bisphenol (**2**) by a procedure similar to that used for preparation of P1. A yellow solid (88.9%) was obtained as target product. FTIR, v (cm^{-1}): 3334 (OH); 2973, 2929, 2813 (CH$_2$); 2605 (B$-$H); 1613, 1596, 1514, 1443 (Ph); 1379, 1271 (Ph$-$OH); 1180, 1124, 1080 (C$-$O$-$C); 1021 (C$-$O). ^{1}H-NMR (400 MHz, acetone-d_6), δ (TMS): 7.28 (m, 4H), 6.71 (m, 4H), 4.41 (m, 2H), 3.53 (m, 1H), 3.7–1.04 (m, 10H). ^{13}C-NMR (100 MHz, DMSO-d_6), δ (TMS): 155.1, 129.8, 124.8, 114.9, 78.7, 62.2, 25.3. ^{11}B-NMR (128 MHz, acetone-d_6), δ (TMS): −6.51, −10.65, −12.63. HRMS (ESI-TOF): *m/z* 327.2405, 357.2504, 387.2612, 418.2663, 447.5462, 654.4883, 684.4974, 715.5029, 746.5115, 777.5164, 983.7344, 1074.7557, 1103.7665, 1135.7771.

Curing of Carborane Bisphenol Resol Phenolic Resins (P1 and P2)

Carborane bisphenol resol phenolic resin (P1 or P2, 0.200 g) and hexamethylenetetramine (0.020 g) were mixed by grinding to form a uniform powder which was then heated at normal pressure according to a temperature-programmed process (150 °C / 4 h + 180 °C / 2 h + 210 °C / 6 h).

Characterization data for cured P1: FTIR, v (cm^{-1}): 3334 (OH); 2973, 2929, 2813 (CH$_2$); 2605 (B$-$H); 1613, 1596, 1514, 1443 (Ph); 1379, 1271 (Ph$-$OH); 1180, 1124, 1080 (C$-$O$-$C); 1021 (C$-$O).

Characterization data for cured P2: FTIR, v (cm^{-1}): 3460 (OH); 2983, 2936, 2858 (CH$_2$); 2611 (B$-$H); 1613, 1596, 1514, 1443 (Ph); 1379, 1271 (Ph $-$ OH); 1180, 1119, 1080 (C $-$ O $-$ C); 1021 (C $-$ O). Characterization data for cured P2 after TGA test under air: FTIR, v (cm^{-1}): 3446 (OH); 2983, 2858 (CH$_2$); 1390 (B$-$O$-$B); 1080 (C$-$O$-$C).
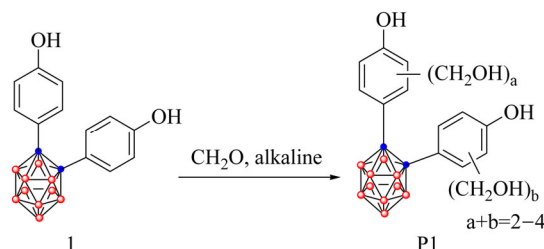
RESULTS AND DISCUSSION

Synthesis of o-Carborane Bisphenol Resol Phenolic Resin (P1)

o-Carborane bisphenol resol phenolic resin (P1) was synthesized *via* the reaction of *o*-carborane bisphenol (**1**) with formaldehyde in the presence of alkaline catalyst according to synthetic routes shown in Scheme 1.

At first sodium hydroxide was utilized as catalyst and the reaction of *o*-carborane bisphenol and formaldehyde was conducted at 80 °C for 4 h. The above reaction condition is widely used for the reaction of many phenols and formaldehyde and expected result will always be obtained[27, 28]. However, we failed to obtain *o*-carborane bisphenol resol phenolic resin (P1) with relatively high M_n (Table 1, No. 1). The temperature was

elevated, the reaction was prolonged, and the molar ratio of phenol to aldehyde was adjusted, but all the products show M_n around 500 (Table 1, Nos. 2−6). By using other catalysts such as barium hydroxide and ammonia water, the synthesis was conducted at 100 °C for 8 h and the result was still disappointing (Table 1, Nos. 7 and 8). Similar result was also obtained by Russian scientists and the low molecular weight was attributed to the strong steric hindrance of *o*-carborane bisphenol[29].

Scheme 1 Synthetic route to *o*-carborane bisphenol resol phenolic resin (**P1**)

Table 1. Synthesis of *o*-carborane bisphenol resol phenolic resin (**P1**)

No.	Catalyst [a]	C/F [b]	T (°C)	t (h)	M_n	M_w/M_n	char [c] (%)
1	NaOH	1/2.4	80	4	486	1.05	88.2
2	NaOH	1/2.4	90	4	491	1.05	89.5
3	NaOH	1/2.4	100	4	472	1.19	84.3
4	NaOH	1/2.4	100	8	436	1.10	86.9
5	NaOH	1/2.8	100	8	492	1.07	89.9
6	NaOH	1/3.2	100	8	519	1.06	89.8
7	Ba(OH)$_2$	1/2.4	100	8	450	1.08	86.2
8	Ammonia water	1/2.4	100	8	455	1.12	85.8
9 [d]	NaOH	1/2.4	100	8	440	1.20	90.2

[a] catalyst dosage is 12 mol% of bisphenol ([catalyst]/[bisphenol] = 0.12:1); [b] C/F is the molar ratio of phenol to aldehyde; [c] char yield of cured **P1** (or **P2**) at 900 °C under nitrogen (using hexamethylenetetramine as curing agent, curing condition: 150 °C / 4 h + 180 °C / 2 h + 210 °C / 6 h); [d] [catalyst]/[bisphenol] = 0.20:1.

As a yellow solid, the obtained **P1** could be solved in common organic solvents such as acetone, THF, and DMSO. **P1** could be stored and used as solid or in solution state. **P1** owned long working time at room temperature and could be transformed into cured resin by heating at program-controlled temperatures by using hexamethylenetetramine as curing agent. The cured **P1** was completely insoluble in common organic solvents such as acetone, THF, and chloroform, confirming that **P1** could be well crosslinked to form three-dimensional network under the above conditions. Thus, all the cured resins own very high char yield at 900 °C under nitrogen (Table 1), although the molecular weight of their prepolymers was restrained.

To accurately characterize the molecular weight of **P1**, high resolution mass spectrometry (HRMS) was adopted, and the result is shown in Fig. 1. According to the result of molar mass calculation, the peaks at 357, 387, 417, and 447 are ascribed to hydroxymethylated *o*-carborane bisphenols with 1, 2, 3, and 4 hydroxymethyl, respectively. Peak to peak mass is 30 g/mol and equivalent to the mass of hydroxymethyl minus one (M-1). Furthermore, there exist other two series of peaks in the range of 655−788 and 1000−1180, which are related with **P1** components containing two and three carborane cages respectively. These higher mass components could not be detected by GPC since their concentration is negligible compared to hydroxymethylated *o*-carborane bisphenol. Therefore, the structural diagram in Scheme 1 was utilized to demonstrate the synthesis of **P1**.

Fig. 1 High resolution mass spectrum of P**1** (Table 1, No. 5)

Synthesis of m-Carborane Bisphenol Resol Phenolic Resin (P2)

m-Carborane bisphenol resol phenolic resin (P**2**) was synthesized according to similar synthetic route to P**1**, shown in Scheme 2.

Scheme 2 Synthetic route to *m*-carborane bisphenol resol phenolic resin (P**2**)

To transform *m*-carborane bisphenol into the corresponding phenolic resin, we also utilized sodium hydroxide as catalyst and conducted the reaction at 80 °C. However, similar disappointing results were obtained: the number average molecular weight (M_n) of the resultant resin was below 500 and the char yields of cured resins were below 30.0 wt% (Table 2, Nos. 1 and 2). The electron-withdrawing ability of carbons on *m*-carborane is not as high as that of carbons on *o*-carborane so that *m*-carborane bisphenol exhibits lower reactivity than its ortho counterpart in the reaction of resol phenolic resin. As a result, the obtained P**2** owns less curable hydroxymethyl in its structure and leads to lower curing degree, which contributes to much lower char yield[30]. When the temperature was elevated to 90 °C, the reaction took place to such an extent that M_n increased from ~500 to ~700, and char yield at 900 °C was increased to ~70 wt% (Table 2, Nos. 3 and 4). Higher temperature resulted in higher M_n and char yield. Acceptable M_n (1040) and char yield at 900 °C (88.9 wt%) were obtained when the reaction was conducted at 100 °C for 8 h (Table 2, No. 6).

Product with the highest M_n (Table 2, No. 7) was obtained when the reaction time was prolonged to 12 h, which, however, gave rise to partial chemical gelation. Considering that gel is harmful to the homogeneity of the cured resin and prolonged reaction time is useless to get high char yield, the optimum reaction conditions is confirmed to be at 100 °C for 8 h. Molecular weight of P**2** could be further regulated by changing the molecular ratio of phenol to aldehyde (C/F). Higher M_n of 3180 was obtained when C/F is 1/3.2 (Table 2, No. 9). In this way, the M_n of P**2** is well controlled by adjusting the parameters of synthetic conditions.

Table 2. Synthesis of *m*-carborane bisphenol resol phenolic resin (P2)

No.	Catalyst [a]	C/F [b]	T (°C)	t (h)	M_n	M_w/M_n	char [c] (%)
1	NaOH	1/2.4	80	4	490	1.07	27.3
2	NaOH	1/2.4	80	8	450	1.14	29.8
3	NaOH	1/2.4	90	4	520	1.08	56.7
4	NaOH	1/2.4	90	8	730	2.37	70.1
5	NaOH	1/2.4	100	4	500	1.10	54.7
6	NaOH	1/2.4	100	8	1040	1.39	88.9
7	NaOH	1/2.4	100	12	3350	1.23	85.3
8	NaOH	1/2.8	100	8	1330	1.31	83.9
9	NaOH	1/3.2	100	8	3180	1.15	85.6
10	NaOH	1/3.6	100	8	2650	1.26	86.0

[a] [catalyst]/[bisphenol] is 0.12:1; [b] C/F is the molar ratio of phenol to aldehyde; [c] char of cured P2 at 900 °C under nitrogen (curing condition: 150 °C / 4 h + 180 °C /2 h + 210 °C / 6 h)

HRMS was also utilized to accurately characterize the obtained P**2**, and the result is shown in Fig. 2. Similar to the spectral designation of P**1**, the spectral lines at 357, 387, 417, and 447 are ascribed to hydroxymethylated *m*-carborane bisphenol (M**2**) with hydroxymethyl numbers of 1, 2, 3, and 4, while resultant products containing two carborane cages ("dimer", D**2**) exhibit lines at 654, 684, 715, 746, and 777. A small quantity of products containing three carborane cages show signals around 1000, which were also observed in the mass spectrum. Owing to the fact that P**2** is mainly composed of M**2** and D**2**, the synthetic route to P**2** is reasonably demonstrated in Scheme 2. Furthermore, it can be inferred from HRMS that P**2** contains much more "dimer" than P**1**, which means that the molecular weight of P**2** is easier to increase than that of P**1**. Weaker steric hindrance of two phenols in P**2** could account for this phenomenon.
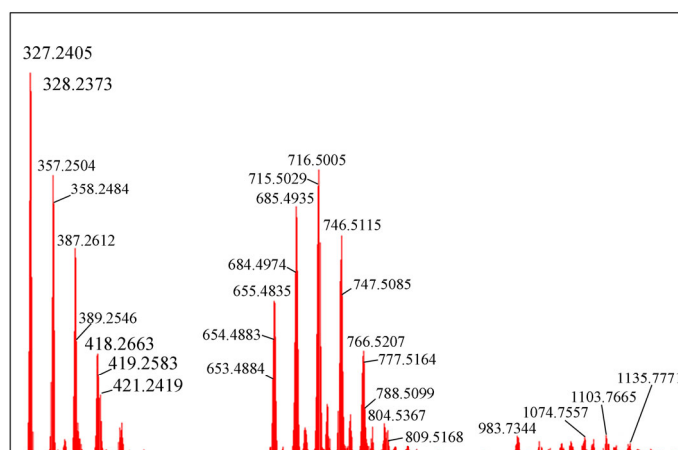
Fig. 2 High resolution mass spectrum of P**2** (Table 2, No. 6)

Characterization of P1 and P2

The structures of the obtained resol phenolic resins (P**1** and P**2**) were well characterized by standard spectroscopic methods such as FTIR and NMR. The analysis data were quite satisfactory corresponding to the expected molecular structures (see Experimental Section for details). An example of the IR spectrum of P**1** is shown in Fig. 3; the spectrum of its corresponding bisphenol monomer **1** is also given in the same figure for comparison. It is obvious that *o*-carborane bisphenol (**1**) shows strong absorption band at 2600 cm^{-1} which is ascribed to the stretching vibrations of B−H bonds on carborane cage. This band is still present in the IR spectrum of P**1**, indicating that the expected *o*-carborane-containing phenolic resin is successfully obtained. On the other hand, weak peaks around 2940 cm^{-1} are observed in the spectrum of P**1**, which are associated with C−H bonds of hydroxymethyl on benzene ring. The low extent of hydroxymethylation is believed to account for the corresponding weak peaks, which could be further confirmed by the fact that P**2** with high extent of hydroxymethylation shows strong absorption peaks around 2940 cm^{-1}.
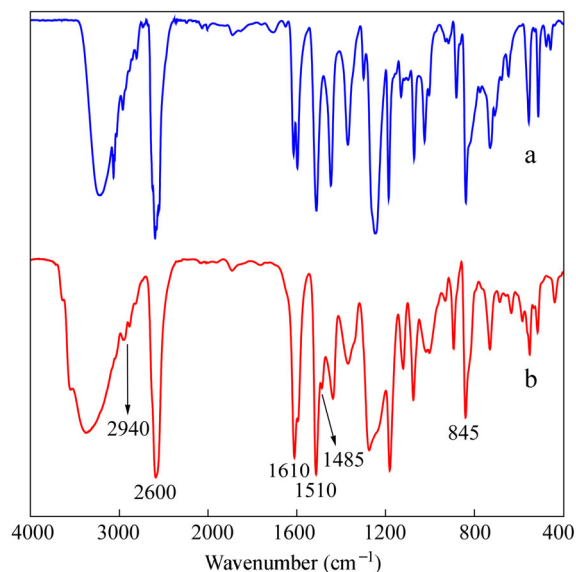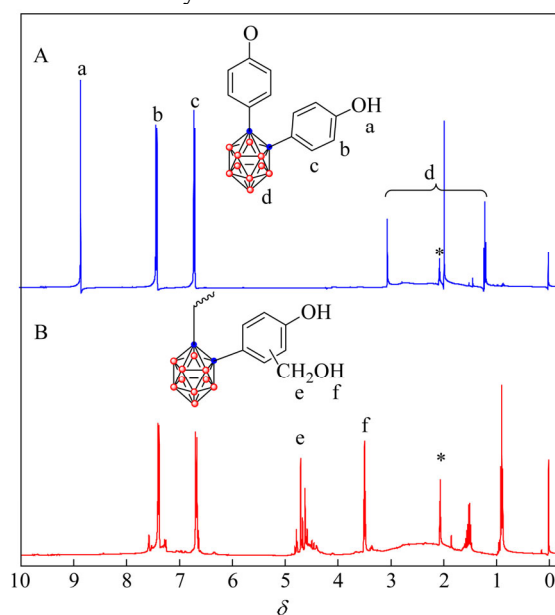
Fig. 3 IR spectra of (a) *o*-carborane bisphenol (**1**), and (b) *o*-carborane bisphenol resol phenolic resin (**P1**, Table 1, No. 5)

To further characterize the phenolic resins, NMR spectroscopy is an effective method. ^{1}H-NMR spectra of **P1** and **1** are shown in Fig. 4. It can be seen that the resonance peaks are well associated with the expected structure of **1**. The phenolic hydroxyl proton shows resonance peak at $\delta = 8.84$ and aromatic protons at $\delta = 7.41$ and 6.68 respectively; while baseline prominence and peaks at $\delta = 3.10$–0.90 are ascribed to protons connected with boron atoms on carborane cage. As for **P1**, new peaks appear around $\delta = 4.71$ and 3.50 which are associated with the resonance of methylene and hydroxyl protons, indicating that the obtained phenolic resin contains a certain amount of hydroxymethyl ortho to phenolic hydroxyl. Both IR and ^{1}H-NMR spectra confirm that the carborane cage remains intact during the synthesis of phenolic resins, which is consistent with the theoretical consideration that it is impossible to break C—H bonds on carborane cage under the synthetic conditions such as temperatures up to 100 °C and alkli metal catalysts[17].
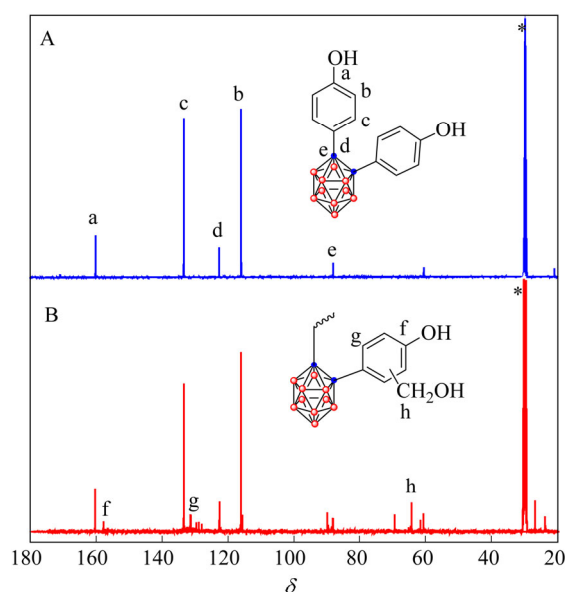

Fig. 4 ^{1}H-NMR spectra of (A) *o*-carborane bisphenol (**1**), and (B) *o*-carborane bisphenol resol phenolic resin (**P1**, Table 1, No. 5) in acetone-d_6 (The solvent peaks are marked with asterisks.)

The ^{13}C-NMR spectra of P**1** and **1** are shown in Fig. 5. The aromatic carbon atoms of **1** resonate at δ = 160.3, 133.6, 122.5, 116.0, and carbon atoms on carborane cage show resonance peak at δ = 89.0. As for P**1**, new resonance peaks appear at δ = 157.8 and 131.5 which are ascribed to aromatic carbon atoms after the hydroxylmethylation of bisphenol. On the other hand, new peaks around δ = 64.4 are observed which are associated with methylene of hydroxylmethyl. Like the IR spectra, the NMR spectra duly confirm that *o*-carborane bisphenol resol phenolic resin (P**1**) is successfully synthesized *via* the hydroxymethylation of *o*-carborane bisphenol (**1**). The ^{11}B-NMR spectra of P**1** and P**2** are shown in Fig. 6. The characteristic peaks of boron atoms of carborane bisphenol resol phenolic resins are well consistent with their precursory carborane bisphenol[31].

Fig. 5 ^{13}C-NMR spectra of (A) *o*-carborane bisphenol (**1**), and (B) *o*-carborane bisphenol resol phenolic resin (P**1**, Table 1, No. 5) in acetone-d_6 (The solvent peaks are marked with asterisks.)
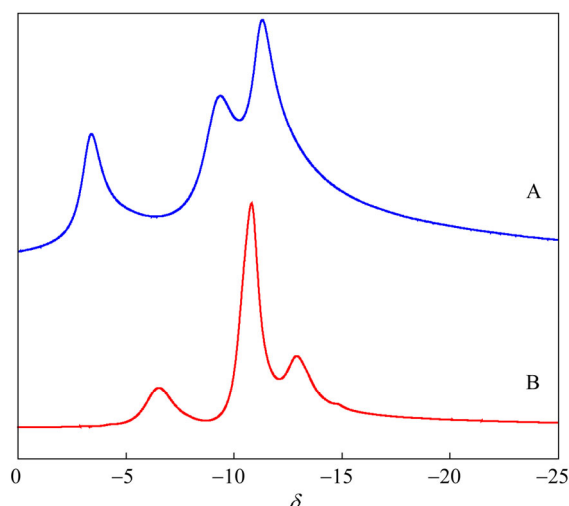
Fig. 6 ^{11}B-NMR spectra of (A) *o*-carborane bisphenol resol phenolic resin (P**1**, Table 1, No. 5) and (B) *m*-carborane bisphenol resol phenolic resin (P**2**, Table 1, No. 6) in acetone-d_6

Thermal Stability of P1 and P2

By far phenolic resin is the best heat-resistant synthetic polymer[1]. Besides, carborane-containing polymers are very famous for their high char yield at elevated temperatures, especially under air atmosphere[17]. Therefore, it is essential to carefully study the thermal stability of the obtained carborane bisphenol resol phenolic resins (**P1** and **P2**). Thermal gravimetric analysis (TGA) technique was utilized, and the recorded thermograms for the polymers are shown in Fig. 7. The TGA curve of a commercially available boron-containing phenolic resin (FB, MW = 800) is also given for comparison. In order to evaluate the initial decomposition behavior of polymers, T_d is defined as the temperature at which the polymer loses 5% of its original weight. It is seen from Fig. 7 that, heated under nitrogen at a heating speed of 20 K/min, FB owns a T_d of 355 °C which is much higher than that of general phenolic resins (~210 °C)[1], for boron atoms are incoporated into the polymer by utilizing boric acid as raw material. As for carborane-containing phenolic resins, **P1** and **P2** lose their 5% weight at 331 and 375 °C respectively, close to that of FB, which justifies the widely accepted argument that the initial decomposition of phenolic resins is related to the breakdown of hydroxylmethyl and methylene ether groups[4]. On the other hand, we are very excited to find that **P1** and **P2** maintain much higher char yield (86.9% and 88.9%) than FB (74.7%) at 900 °C, which is regarded as the "shining point" of carborane-containing resol phenolic resins. Maybe the ultrahigh char yield is transiently attributed to the high boron content of the resins.
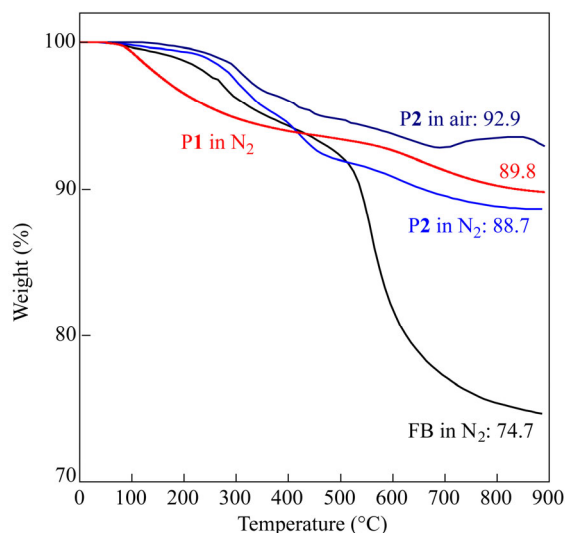

Fig. 7 TGA curves of **P1** (Table 1, No. 5) and **P2** (Table 1, No. 6) under nitrogen and air (TGA curve of commercially obtained boron-containing phenolic resin (FB) is given as comparison.)

Furthermore, **P2** loses its weight much slower under air than under nitrogen and the ultimate char yield at 900 °C is as high as 92.9%. Weight gain took place after 685 °C under air, which may be associated with the fact that carborane cage could absorb oxygen and be oxidized to form boron oxide (B_2O_3) at high temperatures under air[32]. On the other hand, protons generated from B-H bonds on carborane structure at high temperatures could be combined with free radicals delivered by the decomposition of phenolic resin so that the decomposition process could be postponed to a certain extent[26]. The ultrahigh char yield of the obtained carborane-containing resol phenolic resins is desirable because high heat and ablation resistance is required by many high-tech applications.

Structure Variation of P2 at Elevated Temperatures under Air

To check the structure variation of carborane bisphenol resol phenolic resins at elevated temperatures, the FTIR spectra of cured **P2** were tested before and after TGA test, and the result is shown in Fig. 8. It is seen that, just like **P2**, cured **P2** also shows characteristic absorption peak of B$-$H bond at 2600 cm^{-1}, indicating that the

carborane cage is intact after the curing of the resin. However, this absorption band disappears in the spectrum of cured P**2** after TGA test under air. At the mean time, fine absorption peaks below 1700 cm^{-1} disappear, while broad absorption band at 1400 cm^{-1} appears in the spectrum, which is ascribed to B－O－B antisymmetric stretch vibration. The above result indicates that the carborane cage is destroyed at high temperatures due to its oxidation reaction with oxygen in the air to form B_2O_3.
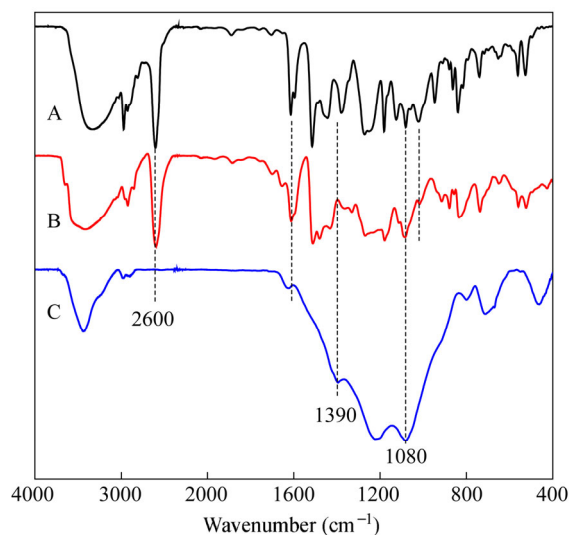

Fig. 8 FTIR spectra of (A) P**2** (Table 2, No. 6), (B) cured P**2**, and (C) cured P**2** after TGA test under air
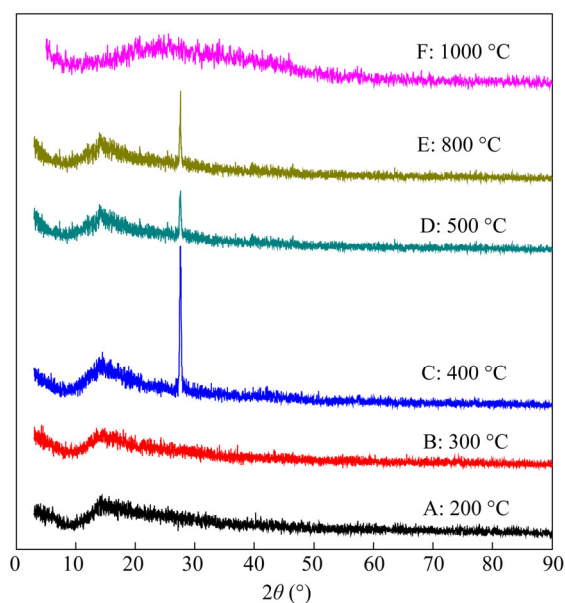

Fig. 9 XRD patterns of cured P**2** after thermal treatment at different temperatures
(A: 200 °C, B: 300 °C, C: 400 °C, D: 500 °C , E: 800 °C , F: 1000 °C) for 2 h

B_2O_3 formation is further confirmed by X-ray diffraction (XRD) technique. The cured P**2** was thermally treated under air at different temperatures for 2 h, and the XRD patterns are shown in Fig. 9. It is seen that, when the samples were thermally treated at 400, 500, and 800 °C, the Bragg reflections appear at 2θ of 28.1 (Fig. 9C, 9D, and 9E), which are identified as crystalline diffraction peaks from B_2O_3[32]. When the thermal treatment

temperature is below 300 °C, the crystalline diffraction peak of B_2O_3 does not appear, indicating that the carborane cage has not reacted with oxygen yet. On the other hand, after thermally treated at 1000 °C, the diffration peak could not be seen as well, which is due to the fact that the formed B_2O_3 could be nearly volatilized above 1000 °C[33].

CONCLUSIONS

In summary, two carborane-containing resol phenolic resins (P**1** and P**2**) were synthesized from *o*-carborane bisphenol (**1**) and *m*-carborane bisphenol (**2**) respectively. The molecular weight of P**2** was well regulated under various reaction conditions, while the M_w of P**1** was restrained around 500 due to the strong steric hindrance of *o*-carborane bisphenol. The obtained resins were characterized with spectroscopic techniques including FTIR, ^{1}H-NMR, ^{13}C-NMR, ^{11}B-NMR, which give satisfactory results. The introduction of carborane endows phenolic resin with ultrahigh char yield. Particularly, the char yield of the obtained carborane-containing phenolic resin under air is higher than that under nitrogen. For example, P**2** shows char yield of 88.9% and 92.9% at 900 °C under nitrogen and air respectively. This could be explained by the fact that the carborane cage could react with oxygen to form B_2O_3, which further postpones the thermal decomposition of phenolic resin and accounts for the high char yield.

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