

Synthesis, Characterization and Thermal Stability of Novel Carborane-Containing Epoxy Novolacs*

Guo Han, Zhen Yang, Xiao-xue Yang, Xiao-a Zhang**, Sheng-ling Jiang and Ya-fei Lu
Key Laboratory of Carbon Fiber and Functional Polymers of Ministry of Education, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Abstract Carborane bisphenol novolacs (**3** and **4**) were synthesized in the presence of acid catalyst from carborane bisphenols (**5** and **6**) and formaldehyde. Further epoxidization of carborane bisphenol novolacs with epichlorohydrin gave carborane bisphenol epoxy novolacs (**1** and **2**). The molecular weight and epoxy value of obtained resins were determined using the molecular weight of their precursors. The epoxy values of **1** and **2** were 0.48 and 0.52 respectively, higher than the maximum theoretical epoxy value (0.45) of difunctional carborane bisphenol epoxy resins. FTIR and NMR were utilized to characterize **1** and **2**. The curing behaviors were also studied by DSC and the optimized curing conditions were obtained. TGA analysis indicated that carborane moiety could shield its adjacent organic structures against initial decomposition. On the other hand, B–H on carborane cage could react with oxygen to form a three-dimensional network linked by B–O–B and B–C bonds, which further blocked the movement of formed radicals and thus the degradation process was inhibited.

Keywords: Carborane; Epoxy novolacs; Thermal stability.

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-016-1832-2>.

INTRODUCTION

As one of the most important thermosetting polymers, epoxy resin has been widely utilized as base polymer for adhesives, protective coatings, and advanced composites in various industrial fields due to their outstanding properties, such as high mechanical strength, good adhesion to numerous substrates, superior electrical insulation, and excellent chemical and thermal resistance^[1–3]. Epoxy novolacs possess much higher functionality than common bisphenol A-based epoxies, thus providing higher crosslinking degree, which facilitates the improvement of thermal stability of the cured products^[4]. Multifunctional cycloaliphatic and novel polyphenol-based epoxy resins further proved the positive effect of crosslinking degree on thermal stability^[5–8]. On the other hand, many studies have been reported for improving the thermal stability of epoxy resins by introducing bulky high-temperature moieties such as naphthyl^[4, 9, 10], siloxane^[11–15], imide^[16–18], phosphazene^[19–21], and triazole^[22]. These bulky moieties could impart strong shielding effect to their adjacent thermally unstable structures so as to enhance the thermal stability of the whole resin systems. To date the search for new high-temperature moieties is still attracting a great deal of attention.

Closo-carboranes ($C_2B_{10}H_{12}$) own an icosahedral geometry and thus are often described as three-dimensional inorganic benzene analogues. Aromatic hydrocarbons possess delocalized carbon-carbon π -bonding,

* This work was financially supported by the Fundamental Research Funds for the Central Universities (No. JD-1512).

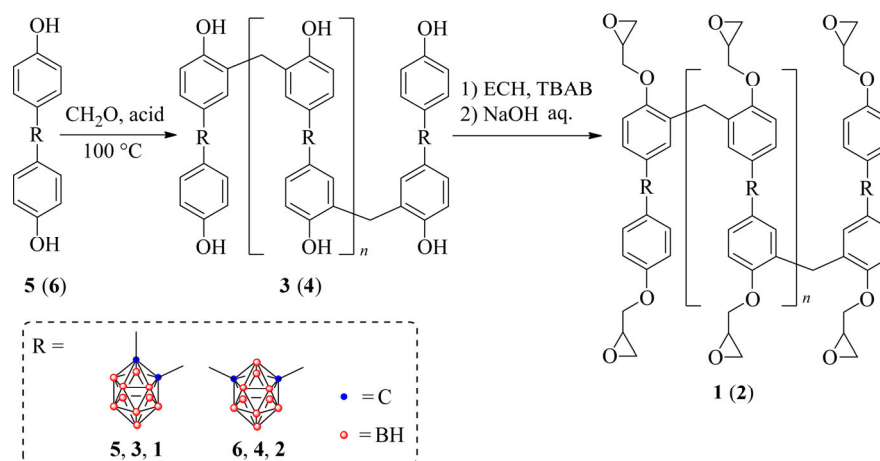
** Corresponding author: Xiao-a Zhang (张孝阿), E-mail: zhangxiaoa1982@163.com

Received March 23, 2016; Revised April 16, 2016; Accepted April 24, 2016

doi: 10.1007/s10118-016-1832-2

while the electron-delocalization of carboranes is related to σ -bonded interactions involving a set of orbitals tangential to the polyhedral surface and another set directed toward the center, sometimes labeled “superaromatic”. Due to their “superaromatic” electronic structures, carboranes could absorb energy like a kind of “power gauge” at high temperature^[23]. Besides, the three-dimensional bulky cage could confer strong shielding effect on adjacent segments. In consideration of both electronic and steric effects, carboranes are ideal building blocks for thermally stable polymers and have been incorporated into many synthetic polymers to improve their heat resistance and thermal stability including polysiloxanes^[24–32], aromatic polymers^[33–39], and thermosets^[40–42]. Carborane bisphenol-based resols and bifunctional epoxy resins were synthesized in our previous works^[43–45], and the cured resins show ultrahigh char yield at elevated temperatures under nitrogen and air.

In this work, carborane bisphenols (**5** and **6**) were further utilized as starting materials to synthesize carborane-containing novolacs (**3** and **4**) in the presence of acid catalyst, which were then epoxidized by epichlorohydrin (ECH) to give epoxy novolacs (**1** and **2**), shown in Scheme 1. The obtained epoxy novolacs were fully characterized, and their curing behaviors were carefully studied. The thermal stability was also studied and the structure transformation of the cured resins after treatment at elevated temperature was elucidated.



Scheme 1 Synthetic routes to carborane bisphenol epoxy novolacs (**1** and **2**)

EXPERIMENTAL

Materials

o-Carborane bisphenol and *m*-carborane bisphenol were synthesized and purified according to our previously published synthetic routes^[43–45]. *n*-Propanol, *i*-propanol, sodium hydroxide (NaOH), formaldehyde aqueous solution (37 wt%), concentrated hydrochloric acid (HCl, 37 wt%), *p*-toluene sulfonic acid (PTSA), oxalic acid, tetrabutylammonium bromide (TBAB), epichlorohydrin (ECH), and toluene were obtained from Beijing Chemical Reagent Company. Hexamethylenetetramine (HMTA), 4,4-diaminodiphenyl sulfone (DDS), and 4,4-diaminodiphenyl methane (DDM) were purchased from Aladdin. All materials were used without further purification.

Instrumentation

FTIR spectra were recorded on a Nexus 670 infrared spectrometer. Molecular weight (M_w) and polydispersity indices (M_w/M_n) of the precursors were determined using a Waters 515 gel permeation chromatography system. Tetrahydrofuran (THF) was used as an eluent at 30 °C at a flow rate of 1.0 mL/min. ¹H-, ¹³C-, and ¹¹B-NMR spectra were acquired in deuterated chloroform and acetone on a Bruker AV400 instrument at a proton frequency of 400 MHz and the corresponding carbon and boron frequencies. Tetramethylsilane was used as an

internal standard. Thermogravimetric analysis (TGA) was performed by a TA Instrument SDT-Q600 at a heating rate of 20 K/min from 50 °C to 900 °C under nitrogen and air atmosphere respectively. DSC measurements were carried on a TA Q1000 differential scanning calorimeter under a constant flow of a nitrogen atmosphere of 50 mL/min. The instrument was calibrated with a high-purity indium standard, and α -Al₂O₃ was used as the reference material. About 5 mg of sample was weighed into a hermetic aluminum sample pan at 25 °C, which was then sealed, and the samples were scanned by the nonisothermal method from 50 °C to 350 °C using 5, 10, 15 and 20 K/min heating rates under nitrogen atmosphere.

Synthesis of Carborane Bisphenol Novolacs (3 and 4)

Carborane bisphenol novolacs (**3** and **4**) were synthesized according to Scheme 1. The detailed procedures for the synthesis of **3** were given below as an example. Into a 50 mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added 1,2-bis(4-hydroxyphenyl)-*o*-carborane (**5**, 1.0 g, 3.03 mmol) and 5 mL of *n*-propanol. The mixture was heated at 60 °C and stirred until clear solution was obtained. Then aqueous formaldehyde solution (37 wt%, 0.9 mL, 12 mmol) and concentrated hydrochloric acid (37 wt%, 9 μ L, 0.1 mmol) were added dropwise to the flask sequentially. The system was stirred at 100 °C for 14 h. The solvent was removed under reduced pressure, and thus a yellow solid was obtained in a yield of 74.6%. $M_w = 565$; $M_w/M_n = 1.07$ (GPC, polystyrene calibration; Table 2, No. 3). FTIR, ν (cm⁻¹, in KBr pellet): 3323 (—OH), 2972 (—CH₂—), 2603 (B—H), 1608, 1594, 1511 (Ph). ¹H-NMR (400 MHz, acetone-d₆, TMS, δ): 8.84 (s, 1H), 7.28 (d, 4H), 6.70 (d, 4H), 3.90 (m, 2H), 3.57–1.13 (m, 10H). ¹³C-NMR (400 MHz, acetone-d₆, TMS, δ): 160.15, 133.46, 122.58, 115.91, 88.48.

4 was synthesized from 1,7-bis(4-hydroxyphenyl)-*m*-carborane (**6**) in *i*-propanol and a yellow solid was obtained in a yield of 78.5%. $M_w = 789$; $M_w/M_n = 1.34$ (GPC, polystyrene calibration; Table 1, No. 5). FTIR, ν (cm⁻¹, in KBr pellet): 3320 (—OH), 2975 (—CH₂—), 2605 (B—H), 1614, 1594, 1511 (Ph). ¹H-NMR (400 MHz, acetone-d₆, TMS, δ): 8.84 (s, 1H), 7.28 (d, 4H), 6.70 (d, 4H), 3.95 (m, 2H), 3.57–1.13 (m, 10H). ¹³C-NMR (400 MHz, acetone-d₆, TMS, δ): 159.06, 129.94, 128.52, 127.09, 116.10, 79.53, 31.24.

Synthesis of Carborane Bisphenol Epoxy Novolacs (1 and 2)

Carborane bisphenol epoxy novolacs (**1** and **2**) were synthesized according to the synthetic routes in Scheme 1. The detailed procedures for the synthesis of **1** were given below as an example. **3** (0.39 g, 2.36 mmol of phenolic hydroxyl), epichlorohydrin (ECH, 3.05 g, 33 mmol), and tetrabutylammonium bromide (TBAB, 12.9 mg, 0.04 mmol) were added to a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The mixture was first reacted at 100 °C for 2 h until the solution changed to colorless from yellow. Then the system was cooled to 85 °C and aqueous sodium hydroxide solution (48 wt%, 0.4 g, 4.8 mmol) was added dropwise to the flask. After the addition of aqueous basic solution, the system was kept at 85 °C for additional 3 h, and then epichlorohydrin was removed from the system under reduced pressure. 5 mL of toluene was added to solve the resultant and aqueous sodium hydroxide solution (5 wt%, 20 mg, 0.025 mmol) was added to further close the ring at 85 °C for 2 h to increase the epoxy value of the obtained resin. After cooling down, the reaction solution was filtered to remove the salt, and the organic phase was washed three times with deionized water. Then toluene was removed by rotary evaporator to give a light-yellow transparent viscous liquid in a yield of 84.8%. $M_w = 735$; $M_w/M_n = 1.28$ (GPC, polystyrene calibration). FTIR, ν (cm⁻¹, in KBr pellet): 2918 (—CH₂—), 2591 (B—H), 1601, 1511, 1513, 1460 (Ph), 917 (epoxy ring). ¹H-NMR (400 MHz, CDCl₃, TMS, δ): 7.37 (d, 2H), 6.67 (d, 2H), 4.19 (m, 2H), 3.89 (m, 2H), 3.32 (m, 1H), 2.75 (m, 2H), 0.86–2.91 (m, 10H). ¹³C-NMR (400 MHz, CDCl₃, TMS, δ): 159.76, 132.26, 123.49, 114.01, 68.74, 49.78.

2 was synthesized from **4** by a two-step method similar to the synthesis of **1** and a yellow transparent viscous liquid was obtained in a yield of 85.1%. $M_w = 706$; $M_w/M_n = 1.29$ (GPC, polystyrene calibration). FTIR, ν (cm⁻¹, in KBr pellet): 3435 (—OH), 3052, 2918, 2872 (—CH₂—), 2598 (B—H), 1608, 1576, 1518, 1447 (Ph), 917 (epoxy ring). ¹H-NMR (400 MHz, CDCl₃, TMS, δ): 7.39 (d, 2H), 6.84 (d, 2H), 4.54 (s, 2H), 4.25 (m, 2H), 3.95 (m, 2H), 3.78 (m, 1H), 3.36 (m, 1H), 2.76 (m, 2H), 1.22–2.94 (m, 10H). ¹³C-NMR (400 MHz, CDCl₃, TMS, δ): 158.85, 129.16, 128.20, 114.31, 68.88, 64.75, 50.06, 44.66.

Curing of Carborane Bisphenol Epoxy Novolacs (1 and 2)

Carborane bisphenol epoxy novolacs (**1** and **2**) were cured by 4,4-diaminodiphenyl sulfone (DDS) and 4,4-diaminodiphenyl methane (DDM). The curing process of **1** by DDS was given below as an example. *o*-Carborane bisphenol epoxy novolac (**1**) and stoichiometric 4,4-diaminodiphenyl sulfone (DDS) were dissolved in THF at room temperature. Then THF was evaporated under vacuum and the resultant mixture was heated according to a temperature-programmed process (150 °C/1 h + 180 °C/1 h + 220 °C/1 h).

Characterization data for cured **1** by DDS: yellow solid; FTIR, ν (cm⁻¹): 3448 (OH); 2929, 2859 (CH₂); 2590 (B—H); 1598, 1509 (Ph); 1045 (C—O). Characterization data for cured **1** after TGA test under nitrogen: FTIR, ν (cm⁻¹): 3429 (OH); 2925, 2929, 2854 (CH₂); 1615 (Ph); 1087 (C—O—C). Characterization data for cured **1** after TGA test under air: FTIR, ν (cm⁻¹): 3335 (OH); 2929 (CH₂); 1615 (Ph); 1428 (B—O), 1193 (B—C), 1089 (C—O—C), 641 (B—C).

Characterization data for cured **2** by DDS: yellow solid; FTIR, ν (cm⁻¹): 3368 (OH); 2932, 2871 (CH₂); 2591 (B—H); 1613, 1593, 1512, 1464 (Ph); 1140, 1100 (C—O—C). Characterization data for cured **2** after TGA test under nitrogen atmosphere: FTIR, ν (cm⁻¹): 3429 (OH); 2920, 2849 (CH₂); 1615 (Ph). Characterization data for cured **2** after TGA test under air atmosphere: FTIR, ν (cm⁻¹): 3428 (OH); 2819 (CH₂); 1625 (Ph); 1427 (B—O), 1187 (B—C), 1087 (C—O—C), 649 (B—C).

RESULTS AND DISCUSSION

Synthesis of Carborane Bisphenol Novolacs (3 and 4)

Carborane bisphenol novolacs (**3** and **4**) were synthesized from carborane bisphenols (**5** and **6**) and formaldehyde aqueous solution with acid catalyst in propanol according to Scheme 1. The reactions proceeded smoothly, and desired novolacs were obtained in satisfactory yields (about 75%–82%). Both of the novolacs were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained (see Experimental section for details).

To synthesize *m*-carborane bisphenol novolac (**4**), concentrated hydrochloric acid was first chosen as catalyst, which has been widely utilized as acid catalyst for the synthesis of novolacs^[46]. *i*-Propanol was used as solvent for its good dissolving ability to *m*-carborane bisphenol (**6**). The reaction was conducted at 80 and 90 °C for 14 h, and the obtained novolac showed rather low molecular weight (M_w about 500, Table 1, Nos. 1 and 2). To further increase M_w value, the reaction temperature was increased to 100 °C. The effect of both reaction time (*t*) and the molar ratio of phenolic hydroxyl to formaldehyde (P/F) was carefully studied and the highest molecular weight ($M_w = 789$) was obtained when the reaction time was extended to 14 h and the molar ratio was set to be 1:2 (Table 1, No. 5). Considering that many novolacs are generally synthesized with a molar ratio of 1:(0.5–0.8)^[46, 47], the dosage of formaldehyde in this study was extraordinarily high. The possible reason lies in the fact that carborane-containing bisphenols own poorer reactivity with formaldehyde than unsubstituted phenol due to the steric hindrance and the electron-withdrawing nature of the carborane cage^[48]. Other catalysts were also tried to synthesize *m*-carborane bisphenol-based novolac (**4**) such as *p*-toluene sulfonic acid (PTSA) and oxalic acid. When the reaction was catalyzed by PTSA, the obtained **4** was partially insoluble in common solvents such as tetrahydrofuran (THF) and chloroform, although the soluble part showed very high molecular weight (M_w about 936, Table 1, No. 8). Besides, oxalic acid failed to obtain product with high molecular weight.

To transform *o*-carborane bisphenol (**5**) into the corresponding novolac **3**, the reaction was conducted at 100 °C in the presence of concentrated hydrochloric acid. *n*-Propanol could dissolve **5** completely and thus was chosen as the reaction solvent. The effect of molar ratio (P/F) and reaction time was fully considered and the results are shown in Table 2. It is clear that the obtained **3** exhibits relatively high molecular weight ($M_w = 579$) when the reaction lasted for 5 h. However, the molecular weight failed to increase with the reaction time, even though the latter was prolonged to 20 h. Furthermore, the molecular weight reduced to about 500 with the decrease of formaldehyde dosage in the reaction, which again confirms that more formaldehyde contributes to high molecular weight of carborane bisphenol novolac.

Table 1. The synthesis of *m*-carborane bisphenol novolac (**4**)^a

No.	Catalyst ^b	P/F ^c	<i>T</i> (°C)	<i>t</i> (h)	yield (%)	<i>M_w</i> ^d	<i>M_w</i> / <i>M_n</i> ^d	Char ^e (%)
1	HCl	1:2	80	14	76.2	492	1.13	87.0
2	HCl	1:2	90	14	75.4	493	1.12	83.4
3	HCl	1:2	100	5	81.8	499	1.12	86.3
4	HCl	1:2	100	10	80.2	497	1.12	85.1
5	HCl	1:2	100	14	78.5	789	1.34	86.5
6	HCl	1:1.5	100	14	79.3	506	1.13	86.3
7	HCl	1:1	100	14	78.2	578	1.18	87.8
8 ^f	PTSA	1:2	100	14	82.0	936	1.43	83.3
9	Oxalic acid	1:2	100	14	72.8	526	1.13	85.8

^a Carried out in *i*-propanol; ^b Catalyst dosage is 3.28 mol% of bisphenol; ^c P/F is the molar ratio of phenolic hydroxyl to formaldehyde; ^d Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration; ^e *m*-Carborane bisphenol novolac (**4**) was cured with 10 wt% hexamethylenetetramine (HMTA) under curing condition of 170 °C/4 h + 200 °C/6 h; Char is the residual weight percentage of cured **4** at 900 °C under nitrogen; ^f The product is partly insoluble in THF, and the soluble part was chosen to conduct GPC test.

Table 2. The synthesis of *o*-carborane bisphenol novolac (**3**)^a

No.	Catalyst ^b	P/F ^c	<i>t</i> (h)	yield (%)	<i>M_w</i> ^d	<i>M_w</i> / <i>M_n</i> ^d	Char ^e (%)
1	HCl	1:2	5	70.2	579	1.07	89.5
2	HCl	1:2	10	76.3	577	1.07	88.7
3	HCl	1:2	14	74.6	565	1.07	91.1
4	HCl	1:2	20	74.1	575	1.07	89.8
5	HCl	1:1.5	14	68.3	504	1.14	86.8
6	HCl	1:1	14	70.6	499	1.13	86.7

^a Carried out at 100 °C in *n*-propanol; ^b Catalyst dosage is 3.28 mol% of bisphenol; ^c P/F is the molar ratio of phenolic hydroxyl to formaldehyde; ^d Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration; ^e *o*-Carborane bisphenol novolac (**3**) was cured with 10 wt% hexamethylenetetramine (HMTA) under curing condition of 170 °C / 4 h + 200 °C / 6 h; Char is the residual weight percentage of cured **3** at 900 °C under nitrogen atmosphere.

Synthesis of Carborane Bisphenol Epoxy Novolacs (**1** and **2**)

Carborane bisphenol epoxy novolacs (**1** and **2**) were synthesized from the above obtained carborane-containing novolacs (**3** and **4**) and epichlorohydrin (ECH) by a two-step method according to Scheme 1. At the first etherification step, tetrabutylammonium bromide (TBAB) was chosen as phase-transfer catalyst^[44] and the coupling reactions of novolacs and ECH proceeded at 100 °C for 2 h. Then stoichiometric amount of sodium hydroxide was added to carry out the dehydrochlorination step at moderate temperature. The synthetic results of carborane bisphenol epoxy novolacs are shown in Table 3. It is obvious that the obtained epoxy novolacs have similar molecular weight as their precursory novolacs. Meanwhile, the epoxy values of epoxy novolacs (**1** and **2**) are 0.48 and 0.52 respectively, which are much higher than those of carborane bisphenol epoxy resins with two epoxy groups in each molecule^[44]. Actually the above epoxy values are even higher than the maximum theoretical epoxy value (0.45) of difunctional carborane bisphenol epoxy resins, which in turn indicates successful synthesis of carborane-containing novolacs (**3** and **4**).

Table 3. The synthesis of carborane bisphenol epoxy novolacs (**1** and **2**)

No.	Epoxy resin	Yield (%)	<i>M_w</i> ^a	<i>M_w</i> / <i>M_n</i> ^a	Epoxy value ^b	Char at 700 °C ^c (%)	Char at 900 °C ^c (%)
1	1	84.8	735	1.28	0.48	70.1	69.2
2	2	85.1	706	1.29	0.52	70.5	68.7

^a Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration; ^b Epoxy value is defined as the mole number of epoxy group per 100 grams of epoxy resin and was measured by acid-base titration; ^c Carborane bisphenol epoxy novolacs (**1** and **2**) were cured with 4,4-diaminodiphenyl sulfone (DDS) under curing condition of 150 °C/1 h + 180 °C/1 h + 220 °C/1 h; Char is the residual weight percentage of cured resins under nitrogen atmosphere.

Structural Characterization

The structures of the obtained carborane bisphenol novolacs (**3** and **4**) and epoxy novolacs (**1** and **2**) were 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 FTIR spectra of *m*-carborane bisphenol novolac (**4**) and epoxy novolac (**2**) are shown in Fig. 1; the spectrum of its corresponding bisphenol monomer (**6**) is also given in the same figure for comparison. It is clear that, similar to monomer **6**, both **4** and **2** show strong absorption band at 2600 cm^{-1} ascribed to the stretching vibrations of B—H bonds, indicating that the carborane cage still exists after the synthesis and epoxidation of carborane-containing novolacs. Compared to bisphenol **6**, new absorption peaks appear in the spectrum of novolac **4** at 940 and 2970 cm^{-1} associated with three-substituted aromatics and methylene groups which bridge the aromatic rings respectively, confirming the formation of novolac. After the epoxidation, strong absorption bands around 3320 cm^{-1} disappear completely and new characteristic peak at 916 cm^{-1} appears in the spectrum, demonstrating full consumption of phenolic hydroxyls and formation of epoxy groups. The absorption peak at 3435 cm^{-1} may be assigned to the stretching vibration of newly formed hydroxyl during the synthesis of epoxy novolac. Besides, the strong absorption peaks around 2930 cm^{-1} are attributed to the stretching vibrations of methylene groups next to the epoxy ring. These peaks overlap with the absorption peak of methylene groups between aromatic rings.

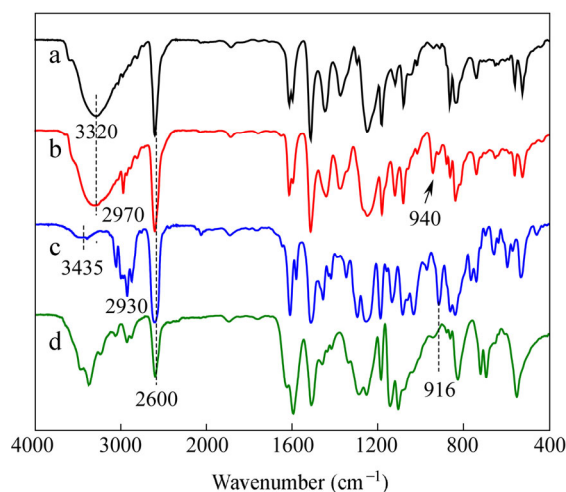


Fig. 1 FTIR spectra of (a) *m*-carborane bisphenol (**6**), (b) *m*-carborane bisphenol novolac (**4**, Table 1, No. 4), (c) *m*-carborane bisphenol epoxy novolac (**2**), and (d) **2** cured by DDS

Figure 2 shows the ^1H -NMR spectra of *m*-carborane bisphenol novolac (**4**), epoxy novolac (**2**), and their starting material (**6**). Compared with **6**, new peak appears at $\delta = 3.95$ in the spectrum of **4** which is ascribed to protons on the methylene between aromatic rings, indicating the formation of the anticipated novolac. The obtained epoxy novolac (**2**) also shows resonance peaks well associated with its expected structures. Same to its precursor **4**, **2** shows resonance peaks of aromatic protons at $\delta = 7.39$ and 6.84 , while the peak at $\delta = 3.95$ is attributed to protons on the methylene between aromatic rings. Noteworthy, protons on the methylene of epoxy group show their resonance peaks at $\delta = 2.92$ and 2.76 , while protons on the methine of epoxy group resonate at 3.36 and protons of methylene next to epoxy group show resonance peaks at $\delta = 4.25$ and 3.97 . Furthermore, resonance peaks at $\delta = 3.78$ and 4.54 could be assigned to the protons on the formed hydroxyl and methine next to it. Baseline prominence and unrecognized peaks at $\delta = 3.10\text{--}0.90$ are ascribed to protons on the carborane cage. In conclusion, *m*-carborane-containing epoxy novolac (**2**) was successfully obtained with a certain amount of hydroxyl in its chemical structure.

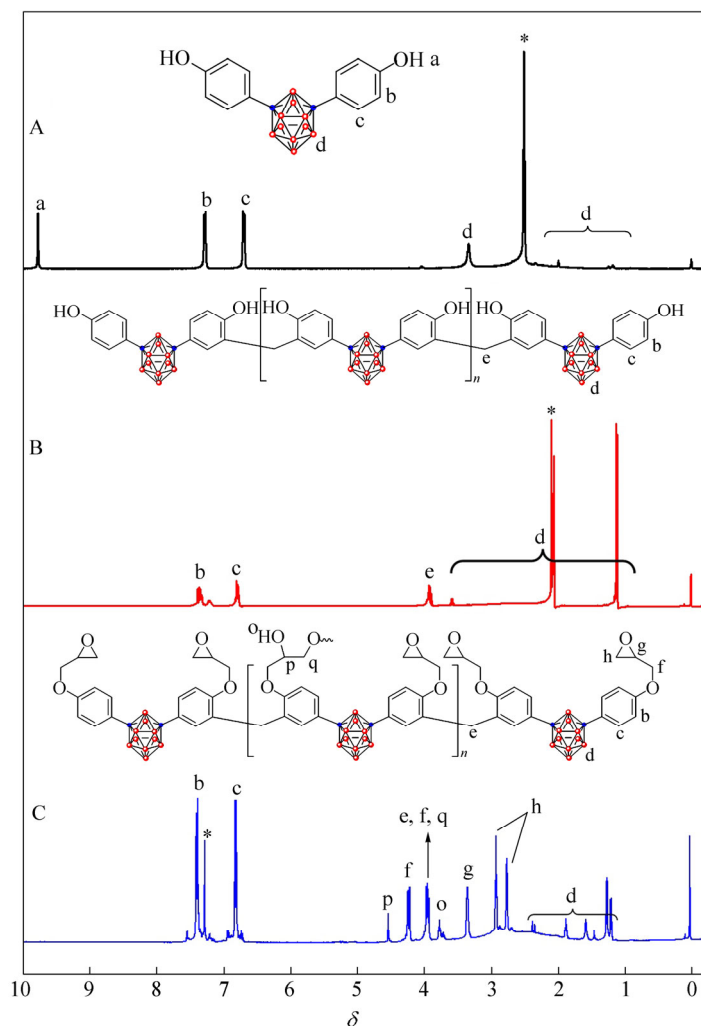


Fig. 2 ¹H-NMR spectra of (A) *m*-carborane bisphenol (**6**) in DMSO-*d*₆, (B) *m*-carborane bisphenol novolac (**4**, Table 1, No. 4) in acetone-*d*₆, and (C) *m*-carborane bisphenol epoxy novolac (**2**) in CDCl₃ (The solvent peaks are marked with asterisks.)

The structure of *m*-carborane bisphenol novolac (**4**) and epoxy novolac (**2**) was further analyzed by ¹³C-NMR shown in Fig. 3. Aromatic carbons of both **4** and **2** resonate in the low field range of $\delta = 160.0\text{--}110.0$, while carbons on carborane cage show weak resonance peaks around $\delta = 79.5$, similar to their starting bisphenol **6**. It is noted that new resonance peak appears at $\delta = 22.4$ in the spectrum of **4** assigned to carbon on methylene between aromatic rings, which again indicates the formation of the novolac. As for epoxy novolac **2**, new resonance peaks at $\delta = 44.7$ and 50.1 are ascribed to carbons on the methylene and methine of epoxy group, while new peak at $\delta = 68.9$ is related with carbon on the methylene next to epoxy group. Besides, hydroxyl formation was also confirmed by new peaks appearing at $\delta = 64.8$ and 71.8 that were attributed to carbons on methine linked to the hydroxyl and methylene next to the methine. The ¹¹B-NMR spectra of **4** and **2** are shown in Fig. 4. It is clear that boron atoms on carborane-containing novolacs and epoxy novolacs show three resonance peaks at around $\delta = -6, -10$, and -13 , similar to the resonance of borons on carborane bisphenol-based resols^[45], indicating the formation of resins with intact carborane structures.

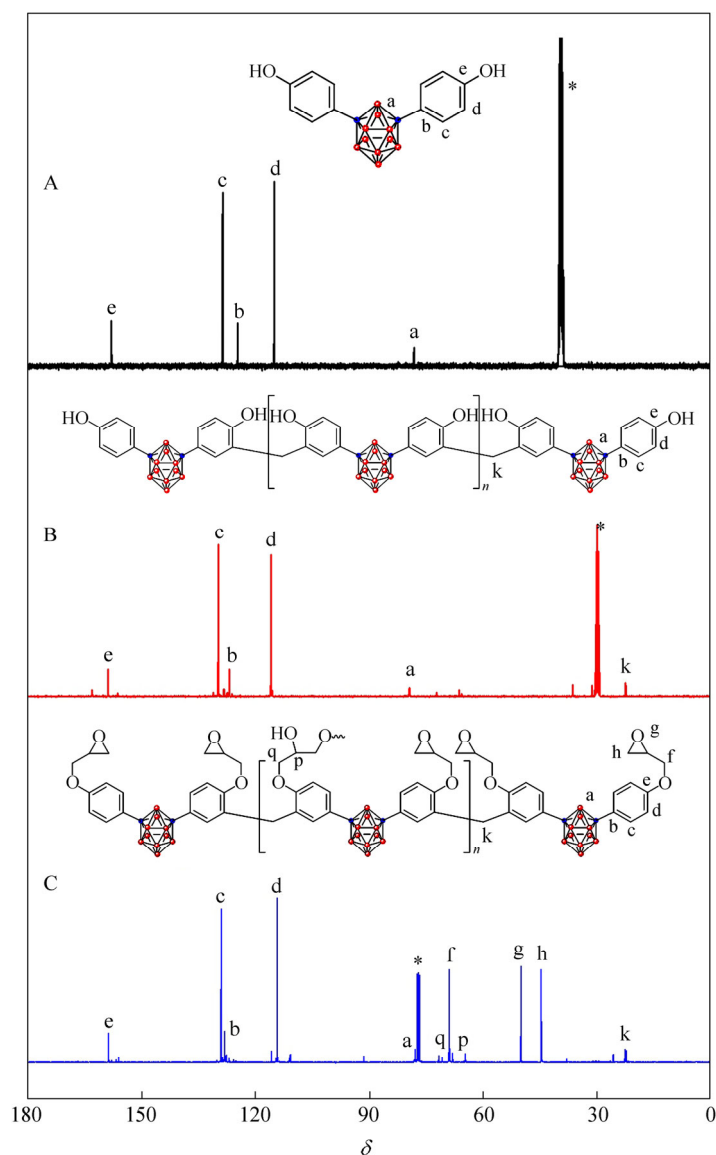


Fig. 3 ^{13}C -NMR spectra of (A) *m*-carborane bisphenol (**6**) in DMSO-d_6 , (B) *m*-carborane bisphenol novolac (**4**, Table 1, No. 4) in acetone-d_6 , and (C) *m*-carborane bisphenol epoxy novolac (**2**) in CDCl_3 (The solvent peaks are marked with asterisks.)

Curing Behavior of Carborane Bisphenol Epoxy Novolacs (**1** and **2**)

Both the obtained epoxy novolacs (**1** and **2**) are transparent viscous liquid and could be dissolved in common organic solvents such as acetone, tetrahydrofuran (THF), and chloroform to give clear solutions. Appropriate solvent could be selected to improve the compatibility of epoxy novolacs with solid curing agents. To obtain excellent high temperature performance, epoxy novolacs (**1** and **2**) were cured with aromatic amines such as 4,4'-diaminodiphenyl sulfone (DDS) and 4,4'-diaminodiphenyl methane (DDM). The curing behavior was studied by nonisothermal Differential Scanning Calorimetry (DSC). The nonisothermal DSC curves of DDS-cured *o*-carborane bisphenol epoxy novolac (**1**) at different heating rates are shown as an example in Fig. 5(a), and the DSC parameters of various curing systems are summarized in Table 4. It is clear that the exothermic peaks became sharper and the three characteristic temperatures (T_i , T_p , and T_f) shifted to higher temperatures with the increase of heating rate.

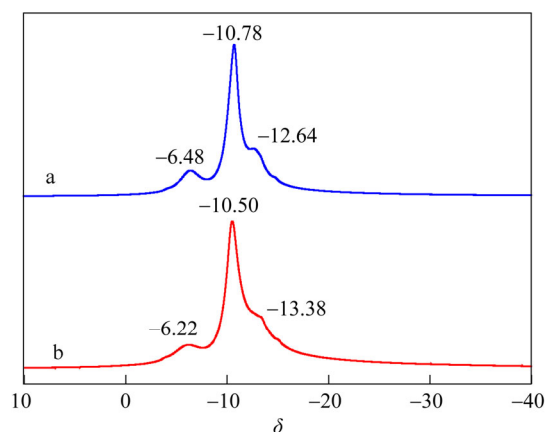


Fig. 4 ^{11}B -NMR spectra of (a) *m*-carborane bisphenol novolac (**4**, Table 1, No. 4) in acetone- d_6 , and (b) *m*-carborane bisphenol epoxy novolac (**2**) in CDCl_3

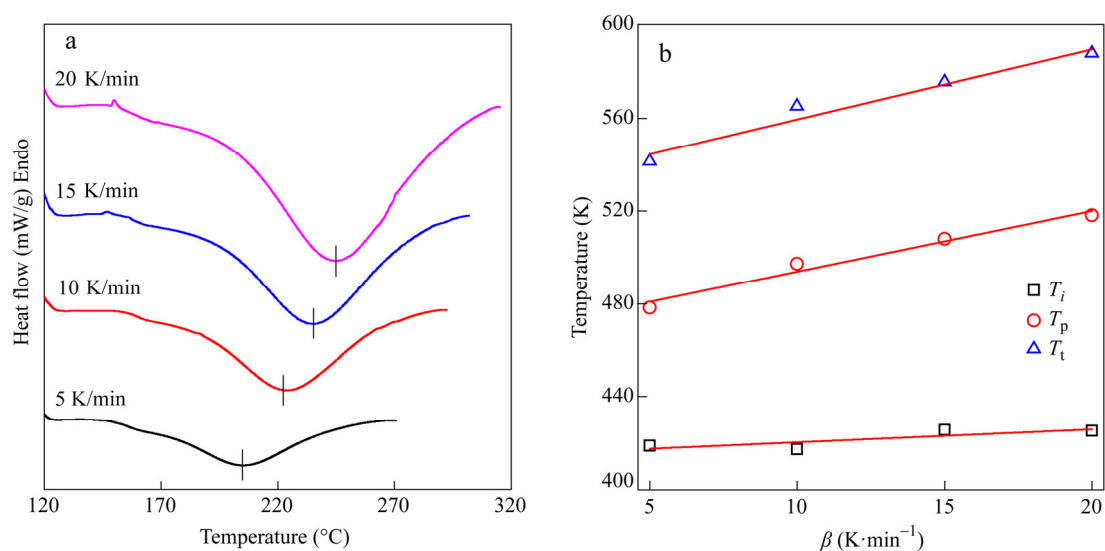


Fig. 5 (a) Nonisothermal DSC curves at different heating rates and (b) the linearity between characteristic temperatures (T_i , T_p , and T_t) and heating rates (β) for *o*-carborane bisphenol epoxy novolac (**1**) cured with DDS. T_i : initial curing temperature, T_p : peak temperature, T_t : terminal temperature.

Table 4. DSC data of curing reaction of various curing systems (**1**/DDS, **2**/DDS, and **2**/DDM) at different heating rates (β)

Curing system	β^a ($\text{K}\cdot\text{min}^{-1}$)	T_i^b ($^{\circ}\text{C}$)	T_p^c ($^{\circ}\text{C}$)	T_t^d ($^{\circ}\text{C}$)	ΔH^e ($\text{J}\cdot\text{mol}^{-1}$)
1 /DDS	5	145.6	205.1	267.7	317.1
	10	144.1	224.2	291.4	309.6
	15	152.5	234.8	301.9	291.5
	20	152.0	245.1	314.1	343.2
2 /DDS	5	165.9	184.4	233.1	137.3
	10	168.9	199.6	262.3	177.5
	15	170.8	208.6	309.0	252.5
	20	172.4	219.0	341.2	285.6
2 /DDM	5	50.5	120.6	180.7	141.5
	10	56.4	138.5	197.2	140.9
	15	61.6	149.7	210.3	139.9
	20	66.9	158.2	218.4	137.3

^a β : heating rate; ^b T_i : initial curing temperature; ^c T_p : peak temperature; ^d T_t : terminal temperature;

^e ΔH : exothermic enthalpy

Figure 5(b) shows the linearity between characteristic temperatures (T_i , T_p , and T_f) and heating rates (β) for DDS-cured **1**. By the extrapolation of the plots, the characteristic temperatures at a heating rate of 0 K/min (T_{i0} , T_{p0} , and T_{f0}) could be obtained (Table 5), on the basis of which the curing process could be optimized. FTIR analysis confirms that epoxy novolacs (**1** and **2**) could be fully cured by DDS under curing condition of 150 °C/1 h + 180 °C/1 h + 220 °C/1 h (Fig. 1d).

Table 5. E_a values and characteristic temperatures at a heating rate of 0 K/min obtained from nonisothermal data

Curing system	E_a (kJ·mol ⁻¹)		Characteristic temperatures		
	Kissinger's method	Ozawa's method	T_{i0} (°C)	T_{p0} (°C)	T_{f0} (°C)
1 /DDS	65.0	70.0	141.7	194.7	256.4
2 /DDS	65.8	70.0	164.2	174.7	193.7
2 /DDM	44.9	49.4	45.3	110.8	170.1

The apparent activation energies (E_a) were also calculated by using Kissinger's and Ozawa's methods^[49, 50]. According to Kissinger's equation:

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = \frac{E_a}{R} \quad (1)$$

where β is the heating rate, T_p is the exothermic peak temperature, A is the pre-exponential factor, E_a is the apparent activation energy, and R is the universal gas constant, plots of $\ln(\beta/T_p^2)$ against $1/T_p$ are prepared and shown as straight lines in Fig. 6(a). According to Ozawa's equation:

$$\ln\beta = -1.052 \frac{E_a}{RT_p} + C \quad (2)$$

where C is constant, plots of $\ln\beta$ against $1/T_p$ are prepared and shown as a straight line in Fig. 6(b). The apparent activation energies (E_a) of the curing reaction were calculated from the slope of lines in Fig. 6 and summarized in Table 5. It is seen that almost identical E_a values were obtained for DDS-cured **1** and **2** regardless of the calculation methods, implying that the isomeric carborane cages have little effect on the reactivity of epoxy novolacs.

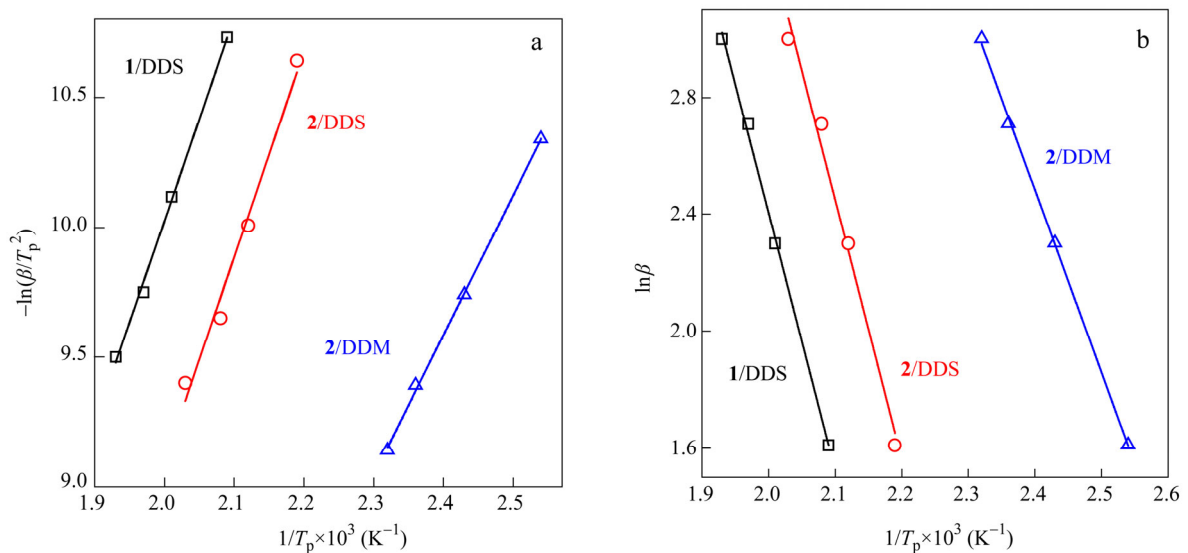


Fig. 6 (a) Plots of $\ln(\beta/T_p^2)$ as a function of $1/T_p$ and (b) plots of $\ln\beta$ as a function of $1/T_p$ for various curing systems (**1**/DDS, **2**/DDS, and **2**/DDM) to calculate E_a according to Kissinger's and Ozawa's methods

Thermal and Thermo-oxidative Stability

Carborane structure could endow polymers with high heat resistance, so it is of great importance to study the thermal stability of the cured resins. Carborane bisphenol novolacs (**3** and **4**) were first investigated by thermal gravimetric analysis (TGA) and the results are shown in Fig. 7. It is seen that cured **3** and **4** lose their 5% weight under nitrogen at 454 and 395 °C (T_5) respectively, much higher than that of commercial boric acid-modified phenolic resin (355 °C)^[45]. The great improvement of the initial decomposition temperature can be attributed to the shielding effect of the incorporated carborane cage on its adjacent phenolic structures. Besides, the cured **3** and **4** resulted high char yield under nitrogen at 900 °C (91.2% for **3** and 86.5% for **4**), almost identical to the values of carborane-containing resols^[45]. It is believed that B-H on carborane cage could combine with oxygen from phenolic structures to form a three-dimensional network linked by B—O—B and B—C bonds^[40]. The formed radicals during polymer degradation fail to move smoothly through this thermally stable network and undergo secondary recombination process, and thus the degradation process is largely blocked.

To further explore the effect of oxygen on the decomposition process, TGA test of cured **3** was also conducted under air. It is seen that the weight loss rate at 119 °C under air is 0.09%/°C, three times higher than that under nitrogen, indicating that the oxygen contributes greatly to the initial decomposition of the phenolic structure of cured **3**. The decomposition mechanism of carborane-containing phenolic resins below 200 °C is considered to be the same as carborane-free resins^[40]. It is worth mentioning that two weight gain peaks appear at 450 and 705 °C, which further illustrates that the carborane structure is oxidized more easily and adequately in the presence of oxygen.

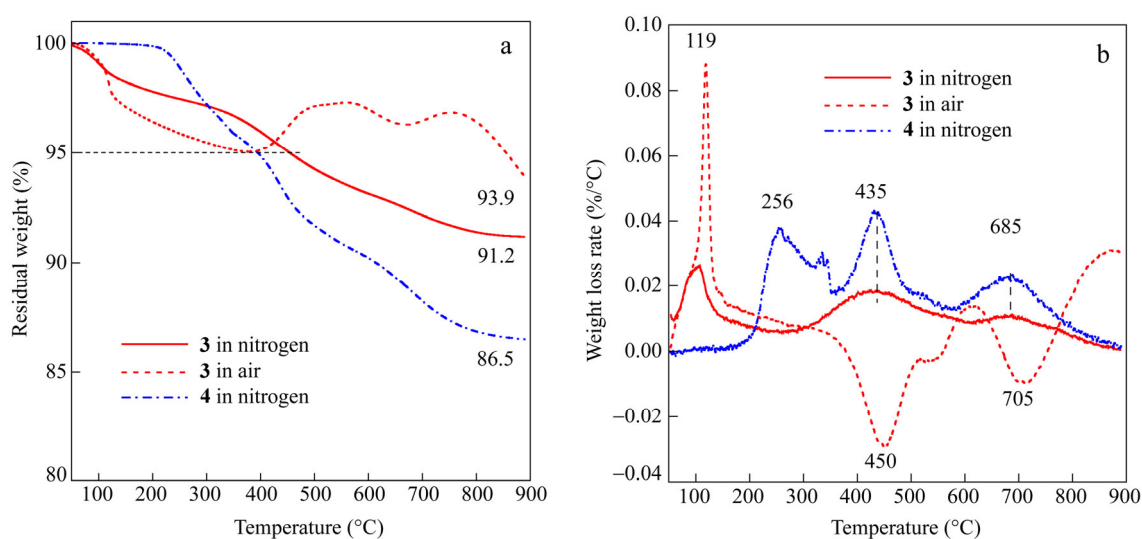


Fig. 7 TGA (a) and DTG (b) curves of carborane bisphenol novolacs (**3** and **4**) under nitrogen and air
3 and **4** were cured by heating under conditions of 170 °C / 4 h + 200 °C / 6 h.

FTIR analysis was utilized to further explore the oxidation of carborane cage at elevated temperature. Figure 8(A) shows the FTIR spectra of cured **4** after TGA test under nitrogen up to 300 (b), 500 (c), and 900 °C (d). It can be seen that, when the sample was thermally treated up to 500 °C, broad characteristic absorption band around 1440 cm^{-1} appears in the spectrum, corresponding to B—O—B antisymmetric stretch vibration. The oxidation of B—H bonds on carborane cage leads to the formation of a three-dimensional network linked by B—O—B and B—C bonds, although residual B—H bonds still exist (2600 cm^{-1})^[40]. B—H bonds were fully oxidated and consumed when cured **4** was heated up to 900 °C, indicating that a denser network was obtained. The characteristic absorption peak of phenyl at 1600 cm^{-1} disappears simultaneously in the oxidation of B—H bonds.

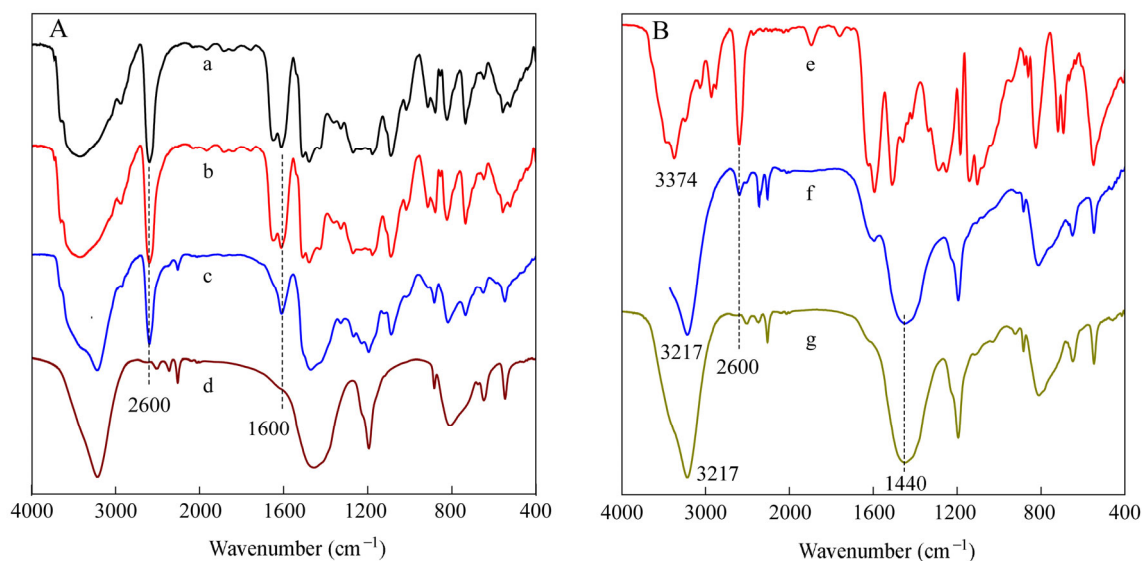


Fig. 8 FTIR spectra of (A) cured **4** (a), cured **4** after TGA test under nitrogen to 300 (b), 500 (c) and 900 °C (d), and (B) DDS-cured **2** after TGA test under nitrogen to 300 (e), 600 (f) and 900 °C (g)

TGA analysis was utilized to study the thermal stability of carborane bisphenol epoxy novolacs (**1** and **2**) under nitrogen, and the results are shown in Fig. 9. It is seen that, cured with DDS, carborane bisphenol epoxy novolacs show high initial decomposition temperatures, 392 °C for **1** and 376 °C for **2**. The introduction of carborane moiety into epoxy resins greatly improves their thermal stability, which has already been confirmed by our previously synthesized difunctional carborane bisphenol epoxy resins^[44]. DDS-cured **1** and **2** also have high char yield under nitrogen at 700 °C (70.1% for **1** and 70.5% for **2**), 5%–7% higher than that of difunctional carborane bisphenol epoxy resins. The existence of boron confers excellent ablation resistance on epoxy novolacs, just like it does on novolacs. When conducted under air, **1** shows a weight gain peak at 684 °C on its TGA curve, just like its precursor **3** does at 450 and 705 °C. This weight gain seems not obvious because large weight loss occurs at 415 °C.

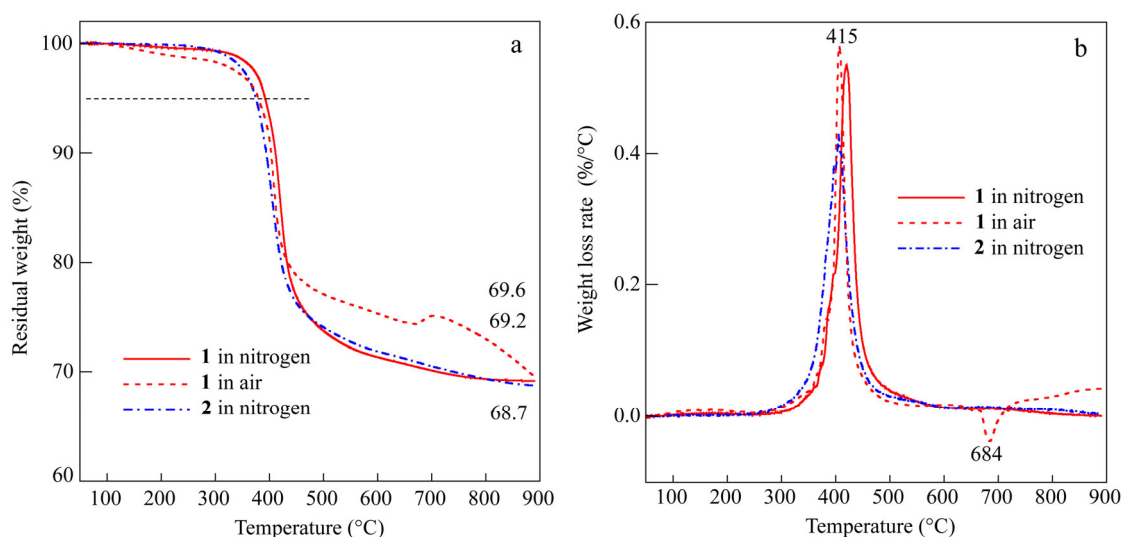


Fig. 9 TGA (a) and DTG (b) curves of carborane bisphenol epoxy novolacs (**1** and **2**) under nitrogen and air atmosphere

1 and **2** were cured with DDS by heating under conditions of 150 °C/1 h + 180 °C/1 h + 220 °C/1 h.

CONCLUSIONS

In summary, carborane bisphenols (**5** and **6**) reacted with formaldehyde in the presence of acid catalyst to obtain carborane bisphenol novolacs (**3** and **4**), which were further epoxidized with epichlorohydrin to form carborane bisphenol epoxy novolacs (**1** and **2**). The synthetic conditions of **3** and **4** were well optimized to give acceptable molecular weight, which partially determines the molecular weight and epoxy value of **1** and **2**. The epoxy values of **1** and **2** were 0.48 and 0.52 respectively, which are higher than the maximum theoretical epoxy value (0.45) of difunctional carborane bisphenol epoxy resins. The obtained resins were characterized by spectroscopic techniques including FTIR, ^1H -NMR, ^{13}C -NMR, ^{11}B -NMR, which give satisfactory results. The nonisothermal DSC was utilized to study the curing behavior of carborane bisphenol epoxy novolacs (**1** and **2**), on the basis of which the optimized curing processes were obtained (150 °C/1 h + 180 °C/1 h + 220 °C/1 h). TGA analysis indicated that carborane moiety could shield its adjacent organic structures against initial decomposition, and thus high T_5 was obtained (392, 376, 454, and 395 °C for **1–4**). On the other hand, carborane-containing resins (**1–4**) own ultrahigh char yield at elevated temperatures due to the fact that B—H on carborane cage reacted with oxygen to form a three-dimensional network linked by B—O—B and B—C bonds, which further blocked the movement of formed radicals and the degradation process was inhibited.

REFERENCES

- 1 Paluvai, N.R., Mohanty, S. and Nayak, S.K., *Polym. Plast. Technol.*, 2014, 53: 1723
- 2 Auvergne, R., Caillol, S., David, G., Boutevin, B. and Pascault, J.P., *Chem. Rev.*, 2014, 114: 1082
- 3 Jin, F.L., Li, X. and Park, S.J., *J. Ind. Eng. Chem.*, 2015, 29: 1
- 4 Pan, G., Du, Z., Zhang, C., Li, C., Yang, X. and Li, H., *Polymer*, 2007, 48: 3686
- 5 Liu, W. and Wang, Z., *Macromol. Chem. Phys.*, 2011, 212: 926
- 6 Liu, W., Wang, Z., Chen, Z., Li, J. and Zhao, L., *Polym. Adv. Technol.*, 2012, 23: 367
- 7 Aouf, C., Nouailhas, H., Fache, M., Caillol, S., Boutevin, B. and Fulcrand, H., *Eur. Polym. J.*, 2013, 49: 1185
- 8 Szyndler, M.W., Timmons, J.C., Yang, Z.H., Lesser, A.J. and Emrick, T., *Polymer*, 2014, 55: 4441
- 9 Ren, H., Sun, J., Wu, B. and Zhou, Q., *Polymer*, 2006, 47: 8309
- 10 Ren, H., Sun, J., Zhao, Q., Zhou, Q. and Ling, Q., *Polymer*, 2008, 49: 5249
- 11 Mercado, L.A., Galia, M. and Reina, J.A., *Polym. Degrad. Stab.*, 2006, 91: 2588
- 12 Yang, X., Huang, W. and Yu, Y., *J. Appl. Polym. Sci.*, 2011, 120: 1216
- 13 Kang, N., Du, Z., Li, H. and Zhang, C., *J. Appl. Polym. Sci.*, 2012, 124: 4915
- 14 Wang, Z., Jiang, J., Zhang, D. and Cheng, R., *J. Appl. Polym. Sci.*, 2012, 123: 2485
- 15 Gao, N., Liu, W., Yan, Z. and Wang, Z., *Opt. Mater.*, 2013, 35: 567
- 16 Yang, S.J., Lee, C., Jang, W., Kwon, J., Sundar, S. and Han, H., *J. Polym. Sci., Part B: Polym. Phys.*, 2004, 42: 4293
- 17 Li, H.T., Chuang, H.R., Wang, M.W. and Lin, M.S., *Polym. Int.*, 2005, 54: 1416
- 18 Tao, Z., Yang, S., Chen, J. and Fan, L., *Eur. Polym. J.*, 2007, 43: 1470
- 19 Liu, R. and Wang, X., *Polym. Degrad. Stab.*, 2009, 94: 617
- 20 Xu, G.R., Xu, M.J. and Li, B., *Polym. Degrad. Stab.*, 2014, 109: 240
- 21 Liu, H., Wang, X. and Wu, D., *Polym. Degrad. Stab.*, 2014, 103: 96
- 22 Ryu, B.Y. and Emrick, T., *Macromolecules*, 2011, 44: 5693
- 23 Grimes, R.N., "Carboranes second edition", New York, Elsevier Inc, 2011, p. 16
- 24 Peters, E.N., *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, 23: 28
- 25 Henderson, L.J. and Keller, T.M., *Macromolecules*, 1994, 27: 1660
- 26 Sundar, R. and Keller, T.M., *J. Polym. Sci., Part A: Polym. Chem.*, 1997, 35: 2387
- 27 Izmailov, B.A., Nedelkin, V.I. and Gerr, I.S., *Russ. Chem. Bull.*, 1998, 47: 687
- 28 Patel, M., Swain, A.C., Skinner, A.R., Mallinson, L.G. and Hayes, G.F., *Macromol. Symp.*, 2003, 202: 47

- 29 Patel, M. and Swain, A.C., *Polym. Degrad. Stab.*, 2004, 83: 539
- 30 Patel, M., Swain, A.C., Cunningham, J.L., Maxwell, R.S. and Chinn, S.C., *Polym. Degrad. Stab.*, 2006, 91: 548
- 31 Zhang, X., Kong, L., Dai, L., Zhang, X., Wang, Q., Tan, Y. and Zhang, Z., *Polymer*, 2011, 52: 4777
- 32 Jiang, Y., Lv, Y., Li, Y. and Qi, S., *Polym. Mater. Sci. Eng.*, 2014, 30: 1
- 33 Vinogradova, S.V., Valetskii, P.M. and Kabachii, Y.A., *Russ. Chem. Rev.*, 1995, 64: 365
- 34 Peterson, J.J., Were, M., Simon, Y.C., Coughlin, E.B. and Carter, K.R., *Macromolecules*, 2009, 42: 8594
- 35 Kokado, K. and Chujo, Y., *Macromolecules*, 2009, 42: 1418
- 36 Kokado, K., Tominaga, M. and Chujo, Y., *Macromol. Rapid Commun.* 2010, 31: 1389
- 37 Kokado, K., Nagai, A. and Chujo, Y., *Macromolecules*, 2010, 43: 6463
- 38 Peterson, J.J., Davis, A.R., Were, M., Coughlin, E.B. and Carter, K.R., *ACS Appl. Mater. Interfaces*, 2011, 3: 1796
- 39 Davis, A.R., Peterson, J.J. and Carter, K.R., *ACS Macro Lett.*, 2012, 1: 469
- 40 Bekasova, N.I., *Russ. Chem. Rev.*, 1984, 53: 61
- 41 Men, X., Cheng, Y., Chen, G., Bao, J. and Yang, J., *High Perform. Polym.*, 2014, published on line, DOI: 10.1177/0954008314557049
- 42 Abramova, T.M., Alekseyeva, S.G., Valetskii, P.M., Golubenkova, L.I., Makarova, I.M., Slonim, I.Y., Urman, Y.G. and Shabadash, A.N., *Vysokomol soyed*, 1980, 22: 1637
- 43 Qi, S., Wang, Y., Wang, H., Zhang, X., Jiang, S. and Lu, Y., *J. Aeronautical Mater.*, 2014, 34: 46
- 44 Qi, S., Wang, Y., Han, G., Yang, Z., Zhang, X., Jiang, S. and Lu, Y., *Acta Polymerica Sinica (in Chinese)*, 2015, (8): 921
- 45 Qi, S., Han, G., Wang, H., Li, N., Zhang, X., Jiang, S. and Lu, Y., *Chinese J. Polym. Sci.*, 2015, 33(11): 1606
- 46 Mark, H.F., "Phenolic resins. *Encyclopedia of polymer science and technology*", London, Wiley, 2004, p. 322
- 47 Atta, A.M., Shaker, N.O. and Nasser, N.E., *J. Appl. Polym. Sci.*, 2008, 107: 347
- 48 Bekasova, N.I. and Komarova, N.G., *Russ. Chem. Rev.*, 1992, 61: 352
- 49 Kissinger, H.E., *Analy. Chem.*, 1957, 29: 1702
- 50 Ozawa, T.J., *J. Therm. Anal.*, 1970, 30: 301