

## Synthesis and Characterization of Carborane-containing Poly(hydroxy ethers) with Excellent Thermal Stability\*

Zhen Yang<sup>a†</sup>, Ning Li<sup>b†</sup>, Xiao-xue Yang<sup>a</sup>, Xiao-a Zhang<sup>a\*\*</sup>, Sheng-ling Jiang<sup>a</sup> and Ya-fei Lyu<sup>a</sup>

<sup>a</sup> 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

<sup>b</sup> School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China

**Abstract** *o*-Carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were synthesized via “advancement reaction” of *o*-carborane-containing bisphenol (**4**) and diglycidyl ether of bisphenols (DGEBA and **1**). FTIR and <sup>1</sup>H-, <sup>13</sup>C-, and <sup>11</sup>B-NMR were utilized to characterize the obtained polymers. TGA test was conducted under nitrogen and air. It is found that the shielding effect of carborane moiety on its adjacent aromatic structures contributes to high initial decomposition temperatures, while oxygen in air has an adverse effect on the initial decomposition temperature. The oxygen can combine with polymer chain to form peroxide and hydroperoxide groups, which are more reactive during the degradation process. Besides, *o*-carborane-containing poly(hydroxy ethers) have high char yield at elevated temperatures. The boron atom combines with oxygen from the polymer structure or/and from air, thus to form a three-dimensional network linked with B—O—B and B—C bonds, and retain the polymer weight to a large extent.

**Keywords** Carborane; Poly(hydroxy ethers); Thermal stability

### INTRODUCTION

Poly(hydroxy ethers) are also called epoxy thermoplastics because they are derived from epoxy-containing building blocks. These polymers can be utilized to manufacture a host of advanced materials, such as protective coatings, fibers, adhesives, and membranes in various industrial fields<sup>[1–3]</sup>. The functional polar hydroxyl groups endow the polymers with robust adhesion to a variety of surfaces, satisfactory mechanical behavior, and high reactivity<sup>[4]</sup>. Poly(hydroxy ethers) have good compatibility with epoxy thermosets owing to their similar structures, and thus can also be selected as toughener for the latter. In order to improve their thermal behavior, many heat-resistant structural units have been introduced into poly(hydroxy ether) systems, such as fluorene<sup>[5]</sup>, sulfonamide<sup>[6]</sup>, biphenyl<sup>[7]</sup>, polyhedral oligomeric silsesquioxane (POSS)<sup>[8]</sup>, and multi-walled nanotubes (MWNT)<sup>[9]</sup>. Researchers have been putting a great deal of efforts to explore epoxy systems with both excellent adhesive and thermal properties.

Polymers with *closo*-carboranes (C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) in their structures show excellent thermal stability<sup>[10–13]</sup>. Bulky carborane moiety displays strong shielding effect on adjacent structures in polymers, and the “superaromatic” carborane cage can also absorb energy during its isomerization process<sup>[14]</sup>. Furthermore, B—H bonds on the cage can combine with oxygen from the polymer or atmosphere to form three-dimensional network linked by B—O—B and B—C bonds, contributing to the thermal and thermo-oxidative stabilities of the polymer at elevated

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

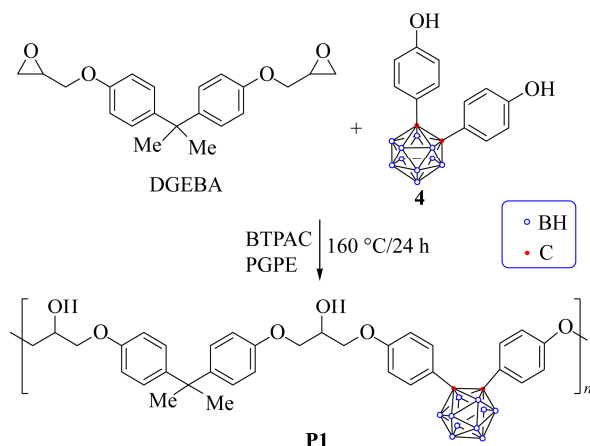
† These authors contributed to this work equally.

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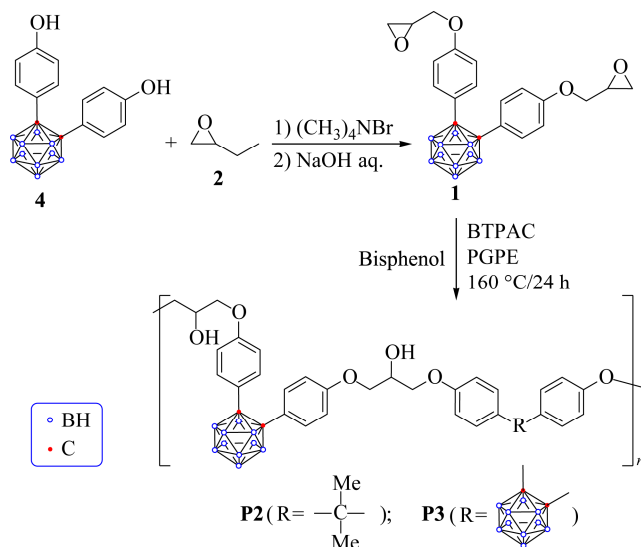
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temperatures<sup>[11, 12]</sup>. In our previous works, carborane bisphenols were utilized to synthesize phenolic resins and epoxy thermosets, which showed good adhesive strength and ultrahigh char yield under nitrogen and air<sup>[15–19]</sup>.

In this work, three *o*-carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were synthesized from *o*-carborane bisphenol (**4**) via the polymerization of diepoxides with dinucleophilic bisphenols in the presence of ammonium salt as a catalyst (Schemes 1 and 2). The obtained high molecular weight polymers were carefully characterized, and could be recognized as hydroxyl-functionalized polymers with carborane moiety. The thermal stability was also studied, and the application of poly(hydroxy ethers) as reinforcer and heat-resistant additive for epoxy thermosets was explored.



**Scheme 1** Synthesis of *o*-carborane-containing poly(hydroxy ether) (**P1**)



**Scheme 2** Synthesis of *o*-carborane-containing poly(hydroxy ethers) (**P2** and **P3**)

## EXPERIMENTAL

### Materials

*o*-Carboranebisphenol (**4**) was obtained from Beihang University. Epichlorohydrin (ECH), sodium hydroxide (NaOH), and tetrabutylammonium bromide (TBAB) were obtained from Sinopharm and used as received. Diglycidyl ether of bisphenol A (DGEBA, 97%) and bisphenol A (BPA) were obtained from J&K Scientific,

which were purified by silica-gel column chromatography before use. Bis(triphenylphosphoranylidene) ammonium chloride (BTPAC) was purchased from ADAMS, and 4-*tert*-butyl phenol was obtained from TCI. Propylene glycol phenyl ether (PGPE) was obtained from Aladdin; toluene, methanol, *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were obtained from Sinopharm.

### 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 tested with a Waters 515 gel permeation chromatography (GPC) system, where THF was used as an eluent at 30 °C at a flow rate of 1.0 mL/min.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{11}\text{B}$ -NMR spectra were acquired in deuterated chloroform and acetone on a Bruker AV400 at a proton frequency of 400 MHz and the corresponding carbon and boron frequencies. Tetramethylsilane (TMS) 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, respectively. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 FOCUS (Bruker AXS, Germany) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm, 40 kV and 40 mA) to analyze the thermally treated polymer samples.

### Synthesis of Diglycidyl Ether of *o*-Carboranebisphenol (**1**)

Diglycidyl ether of *o*-carboranebisphenol (**1**) was synthesized and purified according to the synthetic method described in our previously published papers<sup>[16, 17]</sup>. Into a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added ECH (5.63 g, 60.9 mmol), *o*-carboranebisphenol (**4**, 2.0 g, 6.06 mmol), and TBAB (56 mg, 0.174 mmol). The mixture was stirred at 100 °C for 2 h under nitrogen. Then the system was cooled to 85 °C, and the aqueous sodium hydroxide solution (48 wt%, 1.0 g, 12 mmol) was added dropwise to the flask. After the addition of aqueous basic solution, the system was kept at 85 °C for additional 1.5 h, and then ECH was removed from the system under reduced pressure. Toluene (10 mL) was added to dissolve the resultant, and then aqueous sodium hydroxide solution (5 wt%, 1.0 g, 1.25 mmol) was added. The system was stirred at 85 °C for another 2 h, after which the epoxy value of the obtained resin was improved. 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 clear viscous liquid in a yield of 88.0%.  $M_w$ : 561;  $M_w/M_n$ : 1.08 (GPC, polystyrene calibration). Epoxy value (hydrochloric acid-acetone method): 0.368. FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3498, 3057, 3003, 2929, 2878, 2600, 1605, 1578, 1511, 1456, 1419, 1350, 1297, 1258, 1188, 1133, 1076, 1029, 971, 915, 893, 840, 765, 734, 698, 644, 580, 516.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 7.35, 6.67, 4.17, 3.81, 3.69, 3.29, 2.88, 2.71, 2.35, 2.16, 1.59.

### Synthesis of Carborane-containing Poly(hydroxy ethers) (**P1**, **P2** and **P3**)

*o*-Carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were synthesized according to the synthetic routes described in Schemes 1 and 2. The detailed procedure for the synthesis of **P1** was given below as an example.

In a 25 mL reaction tube DGEBA (0.537 g, 1.40 mmol) was dissolved in 1.08 mL of PGPE. Then *o*-carborane bisphenol (**4**, 0.449 g, 1.37 mmol) and BTPAC (7.89 mg, 13.7  $\mu\text{mol}$ ) were added to the tube. The solution was stirred at 160 °C for 24 h under nitrogen, and then cooled to 150 °C; 4-*tert*-butyl phenol (28.2 mg, 0.187 mmol) was added as a terminator. The solution was further stirred for 1 h, diluted with 1 mL of DMF, and added to a 400 mL cold mixed solvent of methanol/deionized water (1:1 by volume) through a cotton filter under stirring. The precipitate was dried at 120 °C for 2 h under reduced pressure. The crude product was purified by reprecipitation. White solid was obtained in a yield of 85.6%.  $M_w$ : 11900;  $M_w/M_n$ : 2.23 (GPC, polystyrene calibration). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3386, 3059, 2967, 2931, 2873, 2588, 1661, 1605, 1510, 1458, 1383, 1298, 1244, 1183, 1121, 1039, 936, 893, 753, 691, 577, 556, 512.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 7.47 (d, H), 7.09 (d, H), 6.77 (m, H), 6.09 (s, 2H), 4.19 (m, H), 4.02 (s, H), 3.60 (m, H), 3.12–1.22 (m, 10H), 3.05 (m, H), 2.16 (s, 2H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 159.8, 156.3, 143.6, 132.2, 129.5, 127.7, 121.2, 116.0, 114.1, 85.5, 73.5, 68.5, 66.0, 41.7, 30.8.  $^{11}\text{B}$ -NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -2.85, -9.31, -10.82.

**P2** was synthesized from **1** and bisphenol A by a similar method and the white solid was obtained in a yield

of 88.2%.  $M_w$ : 8190;  $M_w/M_n$ : 4.34 (GPC, polystyrene calibration). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3386, 3055, 2962, 2931, 2873, 2588, 1662, 1606, 1510, 1458, 1384, 1298, 1250, 1183, 1121, 1074, 1048, 941, 893, 832, 728, 478, 514.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 7.17 (d, H), 7.03 (d, H), 6.78 (s, H), 6.77 (m, H), 6.65 (m, H), 4.26 (s, 2H), 4.03 (m, 2H), 3.67 (m, H), 3.26 (m, H), 3.12–1.22 (m, 10H), 1.43 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 159.7, 143.4, 132.1, 130.1, 127.9, 126.0, 114.9, 114.0, 86.0, 73.7, 73.5, 68.4, 39.8, 30.1.  $^{11}\text{B-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): –2.85, –9.31, –10.82.

**P3** was synthesized from **1** and **4** by a similar method and the white solid was obtained in a yield of 88.2%.  $M_w$ : 13000;  $M_w/M_n$ : 3.59 (GPC, polystyrene calibration). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3398, 3070, 2932, 2876, 2588, 1662, 1605, 1510, 1456, 1418, 1298, 1254, 1184, 1125, 1073, 1037, 935, 892, 835, 753, 728, 690, 660, 580, 513.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 7.34 (d, H), 6.66 (d, H), 3.99 (s, H), 3.82 (m, H), 3.74 (m, H), 3.12–0.90 (m, 10H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 159.5, 132.2, 130.0, 114.2, 86.2, 68.8, 68.5.  $^{11}\text{B-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): –2.85, –9.31, –10.82.

Carborane-free poly(hydroxy ether), **P0**, was also synthesized from BPA and DGEBA by the similar method, and the white solid was obtained in a yield of 83.2%.  $M_w$ : 31000;  $M_w/M_n$ : 2.49 (GPC, polystyrene calibration). FTIR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3386, 3059, 2967, 2931, 2873, 1661, 1605, 1510, 1458, 1383, 1298, 1244, 1183, 1121, 1039, 936, 893, 753, 691, 577, 556.

#### **Curing and Lap Shear Strength of Epoxy Resins Modified by *o*-Carborane-containing Poly(hydroxy ethers)**

*o*-Carborane-containing poly(hydroxy ethers) were utilized to improve the adhesive strength of thermoset epoxy systems at high temperature. DGEBA and **1** were selected as thermoset epoxy resins, in which **P1** or **P3** was added as a modifier. The detailed bonding and curing process of DGEBA/**1** system was given below as an example. Into a 50 mL beaker were added DGEBA (5 g), diaminodiphenylsulfone (DDS, 1.6 g), and **1** (0.75 g). THF (2 mL) was then added to facilitate the preparation of epoxy mixture, which was brushed onto the lap sheets. The lap shear joints were prepared, and then the strength was tested according to GB/T 7124-2008. The joints were cured according to a temperature-programmed process (150 °C/2 h + 200 °C/2 h). High temperature lap shear strength was tested after the bonded joints were placed under constant temperature for 30 min.

## **RESULTS AND DISCUSSION**

### **Synthesis of *o*-Carborane-containing Poly(hydroxy ethers) (**P1**, **P2** and **P3**)**

*o*-Carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were synthesized via “advancement reaction” of *o*-carborane-containing bisphenol (**4**) and diglycidyl ether of bisphenols (DGEBA and **1**) according to Schemes 1 and 2. The advancement reaction is defined to be a kind of reaction, by which high molecular weight epoxy polymer can be prepared from low molecular weight epoxy oligomer. According to the polymerization mechanism, **P1** and **P2** had exactly the same molecular structures, although different reactants were utilized. The reactions proceeded smoothly, and desired poly(hydroxy ethers) were obtained in the satisfactory yields (~77%–90%). All of the poly(hydroxy ethers) were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained (see Experimental section for details).

**P1** was synthesized from *o*-carborane bisphenol (**4**) and DGEBA in PGPE according to Scheme 1, by using BTPAC as a catalyst and 4-*tert*-butyl phenol as a terminator<sup>[7]</sup>. The reaction was conducted at 180 °C, and the obtained poly(hydroxy ethers) showed rather low molecular weight ( $M_w \sim 6550$ , Table 1, Nos. 1–5). The temperature was adjusted from 140 °C to 190 °C to increase  $M_w$ , but the result was rather disappointing. When the reaction was conducted at 160 °C, relatively higher  $M_w$  of 6910 was obtained (Table 1, No. 8). It is seen that the reaction temperature has little effect on the molecular weight of **P1**. The concentration of **4** was further controlled, and the high molecular weight products were obtained ( $M_w \sim 11900$ , Table 1, Nos. 13 and 14). When the concentration of reactants increased further, the viscosity of the reaction solution became higher. In consideration of the adverse effect of high concentration on the polymerization, the ideal bisphenol concentration is 0.789 mol/L.

**Table 1** The synthesis of *o*-carborane-containing poly(hydroxy ether) (**P1**)<sup>a</sup>

| No. | [Bisphenol] (mol/L) | <i>T</i> <sup>b</sup> (°C) | <i>t</i> <sup>c</sup> (h) | Yield (%) | <i>M</i> <sub>w</sub> <sup>d</sup> | <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup> |
|-----|---------------------|----------------------------|---------------------------|-----------|------------------------------------|------------------------------------------------------------|
| 1   | 0.132               | 180                        | 2                         | 82.5      | 4470                               | 1.65                                                       |
| 2   | 0.132               | 180                        | 6                         | 85.5      | 5480                               | 1.79                                                       |
| 3   | 0.132               | 180                        | 12                        | 84.9      | 6420                               | 1.92                                                       |
| 4   | 0.132               | 180                        | 18                        | 89.2      | 6470                               | 1.93                                                       |
| 5   | 0.132               | 180                        | 24                        | 88.4      | 6550                               | 1.92                                                       |
| 6   | 0.132               | 140                        | 24                        | 85.4      | 5950                               | 1.98                                                       |
| 7   | 0.132               | 150                        | 24                        | 83.9      | 6630                               | 2.06                                                       |
| 8   | 0.132               | 160                        | 24                        | 88.2      | 6910                               | 2.41                                                       |
| 9   | 0.132               | 170                        | 24                        | 90.1      | 6610                               | 2.11                                                       |
| 10  | 0.132               | 190                        | 24                        | 84.3      | 5970                               | 2.09                                                       |
| 11  | 0.263               | 160                        | 24                        | 81.2      | 10400                              | 2.29                                                       |
| 12  | 0.526               | 160                        | 24                        | 77.5      | 10700                              | 2.18                                                       |
| 13  | 0.789               | 160                        | 24                        | 85.6      | 11900                              | 2.23                                                       |
| 14  | 1.052               | 160                        | 24                        | 82.1      | 11900                              | 2.43                                                       |

<sup>a</sup> Carried out in propylene glycol phenyl ether (PGPE) using bis(triphenylphosphoranylidene) ammonium chloride (BTPAC) as a catalyst and 4-*tert*-butyl phenol as a terminator, the dosage of catalyst and terminator is 1.00 mol% and 13.69 mol% of bisphenol respectively, the ratio of [DGEBA] to [bisphenol] is 1.02:1; <sup>b</sup> *T* is polymerization temperature; <sup>c</sup> *t* is polymerization time; <sup>d</sup> Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration.

Taking full advantage of the reaction diversity of diepoxides with dinucleophilic bisphenols, carborane moiety could also be imported into poly(hydroxy ethers) by utilizing diglycidyl ether of *o*-carboranebisphenol (**1**) as the monomer. Diglycidyl ether of *o*-carboranebisphenol (**1**) was synthesized and purified according to our previously described synthetic methods<sup>[16, 17]</sup>. The epoxy value was determined to be 0.368, which indicated that **1** had DGEBA-like structure as expected.

The monomer **1** was further reacted with bisphenols to synthesize *o*-carborane-containing poly(hydroxy ethers) (**P2** and **P3**). The ideal synthetic conditions of **P1** were applied to the reactions. The synthetic results are given in Table 2. It can be seen that the obtained **P2** exhibits lower molecular weight compared with **P1**, although both of them have the same molecular structures. **P3** shows the highest carborane concentration since both of the reactants contain carborane moieties. **P0** was also synthesized as a control from carborane-free reactants, BPA and DGEBA, in order to study the effect of carborane concentration on the thermal stability of poly(hydroxy ethers).

**Table 2** The synthesis of *o*-carborane-containing poly(hydroxy ethers) (**P1–P4**)<sup>a</sup>

| No. | Bisphenol | Epoxy    | Poly(hydroxy ethers) | Yield (%) | <i>M</i> <sub>w</sub> <sup>b</sup> | <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>b</sup> |
|-----|-----------|----------|----------------------|-----------|------------------------------------|------------------------------------------------------------|
| 1   | <b>4</b>  | DGEBA    | <b>P1</b>            | 85.6      | 11900                              | 2.23                                                       |
| 2   | BPA       | <b>1</b> | <b>P2</b>            | 88.2      | 8190                               | 4.34                                                       |
| 3   | <b>4</b>  | <b>1</b> | <b>P3</b>            | 84.8      | 13000                              | 3.59                                                       |
| 4   | BPA       | DGEBA    | <b>P0</b>            | 83.2      | 31000                              | 2.49                                                       |

<sup>a</sup> Carried out at 160 °C for 24 h in propylene glycol phenyl ether (PGPE) using bis(triphenylphosphoranylidene) ammonium chloride (BTPAC) as a catalyst and 4-*tert*-butyl phenol as a terminator, the dosage of catalyst and terminator is 1.00 mol% and 13.69 mol% of bisphenol respectively, the ratio of [bisepoxy] to [bisphenol] is 1.02:1, [bisphenol] = 0.789 mol/L; <sup>b</sup> Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration.

### Structure Characterization

The structures of the obtained *o*-carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were characterized by FTIR and NMR. The analysis data are quite satisfactory corresponding to the expected molecular structures (see Experimental section for details).

The FTIR spectrum of poly(hydroxy ether) (**P1**) as an example is shown in Fig. 1. The spectra of its corresponding monomers (DGEBA and **4**) are also given in the same figure for comparison. It is clear that, similar to *o*-carborane bisphenol (**4**), the obtained **P1** shows a strong absorption band at 2588 cm<sup>-1</sup>, ascribed to

the stretching vibration of B—H bonds, indicating that the carborane cage is incorporated into **P1** structure after the polymerization. The broad absorption peak at  $3386\text{ cm}^{-1}$  may be assigned to the stretching vibration of newly formed hydroxyl groups during the polymerization, while the peaks around  $2967\text{ cm}^{-1}$  are attributed to the stretching vibrations of methylene and methane groups adjacent to the hydroxyl group. Besides, the obtained **P1** shows no characteristic peak at  $915\text{ cm}^{-1}$  ascribed to epoxy group. Poly(hydroxy ether) is derived from epoxy building blocks, and thus also called as thermoplastic epoxy polymer. However, the polymer shows high molecular weight and has no epoxy groups in the molecular structure.

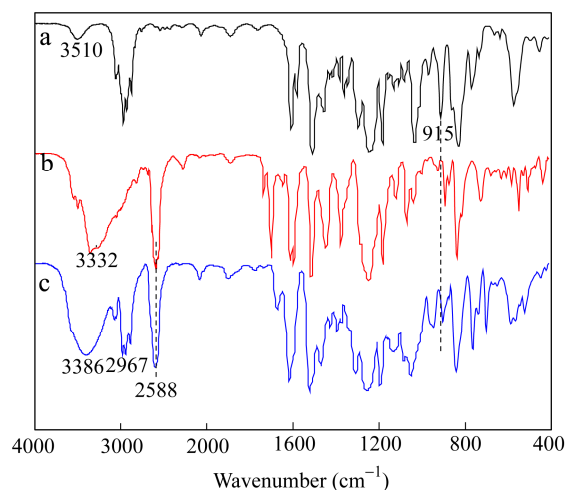


**Fig. 1** FTIR spectra of (a) diglycidyl ether of bisphenol A (DGEBA), (b) *o*-carboranebisphenol (**4**) and (c) *o*-carborane-containing poly(hydroxy ether) (**P1**) (**P1** sample is from Table 1 No. 13 or Table 2 No. 1.)

Figure 2 shows the  $^1\text{H}$ -NMR spectra of **P1**, DGEBA and **4**. It is seen that both DGEBA and **4** contain similar aromatic structures in the molecular structure. DGEBA shows the resonance signals of aromatic protons at  $\delta = 7.19$  and  $6.88$  ppm, while the counterpart peaks of **4** appear at  $\delta = 7.39$  and  $6.69$  ppm. After polymerization, **P1** shows four resonance peaks around  $\delta = 7.00$  ppm, ascribed to four aromatic protons of different electron density, which is well consistent with the expected structures. Furthermore, a new peak appears at  $\delta = 3.60$  ppm, ascribed to the proton of the newly formed hydroxyl group. Protons of methylene and methine next to hydroxyl show the resonance peaks around  $\delta = 4.00$  ppm, and the protons of methyl resonate at  $\delta = 1.59$  ppm. It is noted that methine and methylene of epoxy group show the proton resonance at  $\delta = 3.37$ ,  $2.93$ , and  $2.77$  ppm, which disappears in the spectrum of **P1**. In conclusion,  $^1\text{H}$ -NMR spectroscopy indicates that **P1** contains a certain amount of hydroxyl groups and two kinds of bisphenol units in its molecular structure, *i.e.*, *o*-carborane bisphenol and bisphenol A.

The structures of poly(hydroxy ethers) (**P1**), DGEBA and **4** were further analyzed by  $^{13}\text{C}$ -NMR as shown in Fig. 3. It is clear that DGEBA contains four different aromatic carbons resonated at  $\delta = 156.2$ ,  $143.2$ ,  $127.8$ , and  $114.0$  ppm, respectively, while the resonance peaks of aromatic carbons of **4** appear at  $\delta = 160.0$ ,  $133.4$ ,  $122.6$ , and  $116.0$  ppm, respectively. Similar to the above  $^1\text{H}$ -NMR analysis, as the polymerization product, **P1** shows all the above aromatic carbon resonance peaks in the range of  $\delta = 160.0$ – $110.00$  ppm, further verifying that two kinds of bisphenol units are incorporated into the molecular structure of **P1**. Furthermore, the resonance peaks of carbons of methylene and methine next to newly-formed hydroxyl group appear at  $\delta = 73.5$ ,  $68.5$ , and  $66.0$  ppm. Two carbons on *o*-carborane cage of **P1** resonate at  $\delta = 85.5$  ppm, similar to the precursor **4**. Methyl carbon resonates at  $\delta = 30.8$  ppm, and quaternary carbon resonates at  $\delta = 41.7$  ppm.  $^{13}\text{C}$ -NMR analysis also confirms that **P1** with expected chemical structure is successfully synthesized.

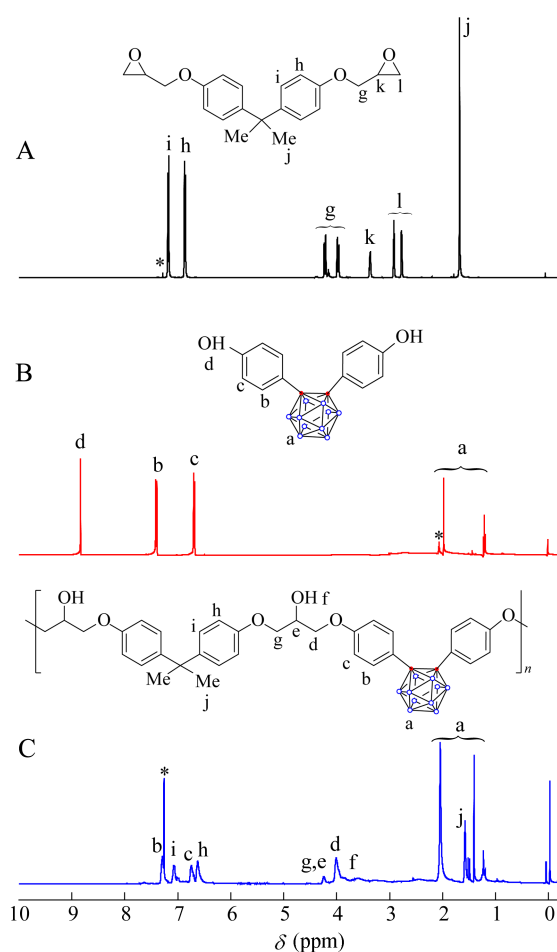


**Fig. 2** <sup>1</sup>H-NMR spectra of (A) diglycidyl ether of bisphenol A (DGEBA) in CDCl<sub>3</sub>, (B) *o*-carboranebisphenol (**4**) in (CD<sub>3</sub>)CO and (C) *o*-carborane-containing poly(hydroxy ether) (**P1**) in CDCl<sub>3</sub>

**P1** sample is from Table 1 No. 13 or Table 2 No. 1. The solvent peaks are marked with asterisks.

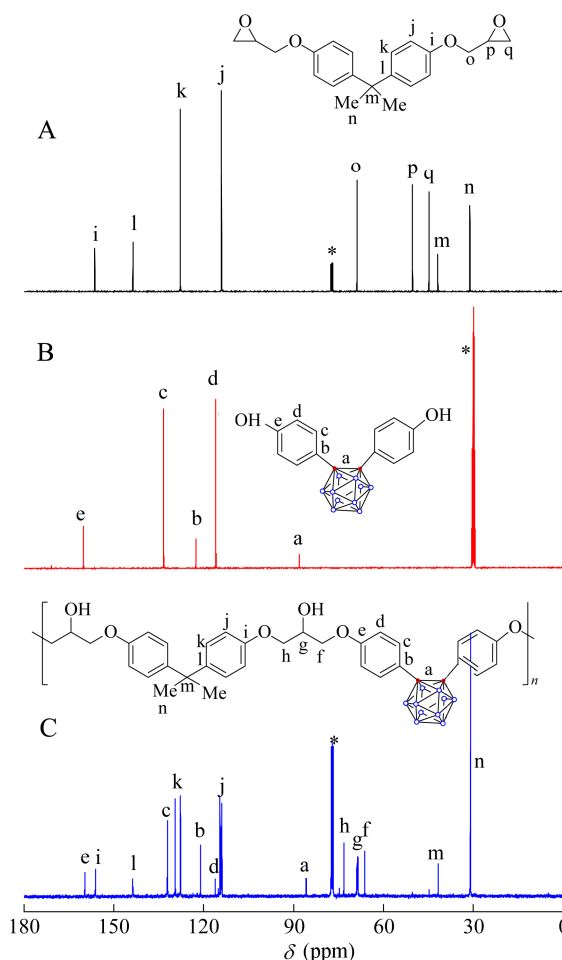


**Fig. 3** <sup>13</sup>C-NMR spectra of (A) diglycidyl ether of bisphenol A (DGEBA) in CDCl<sub>3</sub>, (B) *o*-carboranebisphenol (**4**) in (CD<sub>3</sub>)CO, and (C) *o*-carborane-containing poly(hydroxy ether) (**P1**) in CDCl<sub>3</sub>

**P1** sample is from Table 1 No. 13 or Table 2 No. 1. The solvent peaks are marked with asterisks.

The <sup>11</sup>B-NMR analyses of poly(hydroxy ethers) (**P1**, **P2** and **P3**) were conducted in CDCl<sub>3</sub> and the obtained spectra are shown in Fig. 4. It is seen that boron atoms on *o*-carborane cage resonate at δ = −2.85, −9.31 and −11.31 ppm, indicating the formation of three polymers with intact carborane structures. These resonance peaks are located at similar positions as those of *o*-carborane-based novolac epoxy resin<sup>[18]</sup>.

### Thermal Stability

*o*-Carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were investigated by thermal gravimetric analysis (TGA) under nitrogen. The results are shown in Fig. 5. TGA measurement of carborane-free poly(hydroxy ether) (**P0**) is also conducted for the comparison. It is seen that **P1**, **P2**, and **P3** lose their 5% weight under nitrogen at 406, 365, and 439 °C (*T*<sub>5</sub>), respectively, much higher than that of poly(hydroxy ether) (**P0**) (310 °C). The initial decomposition temperatures of poly(hydroxy ethers) were significantly enhanced by the introduction of carborane cage into the molecular structure. The incorporated carborane moiety shows excellent shielding effect on the adjacent aromatic structures, and thus the thermal stability of poly(hydroxy ethers) is improved. It is noted that **P2** has lower *T*<sub>5</sub> than **P1** although they have exactly the same molecular structures, probably because **P2** has lower molecular weight.

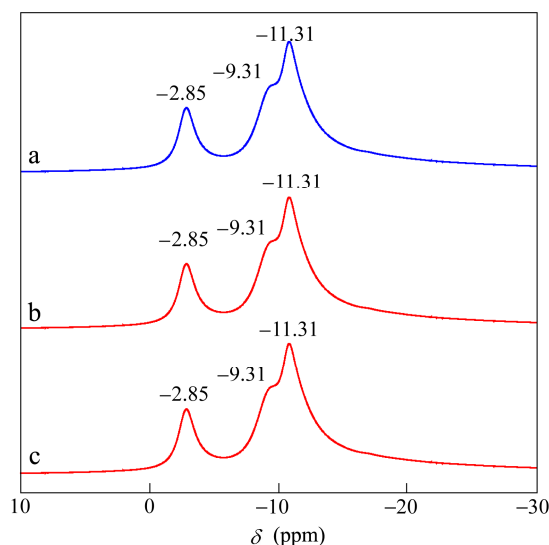


**Fig. 4**  $^{11}\text{B}$ -NMR spectra of (a) **P1**, (b) **P2** and (c) **P3** in  $\text{CDCl}_3$  (**P1** sample is from Table 1 No. 13 or Table 2 No. 1.)

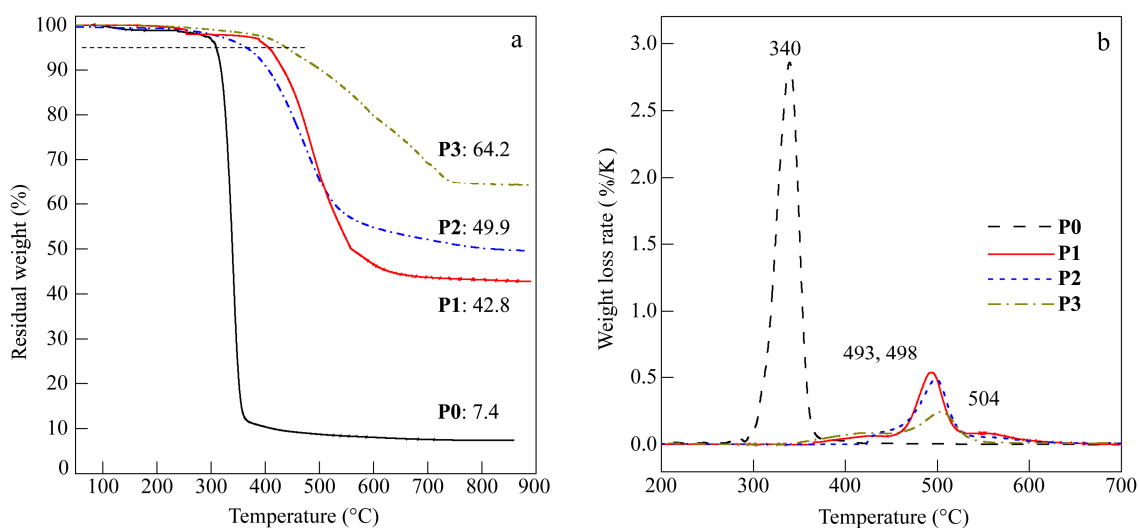


**Fig. 5** (a) TGA and (b) DTG curves of *o*-carborane-containing poly(hydroxy ethers) (**P1**, **P2**, and **P3**) under nitrogen **P1** sample is from Table 1 No. 13 or Table 2 No. 1. The curves of carborane-free poly(hydroxyl ether) (**P0**) are also given as a comparison.

Besides, *o*-carborane-containing poly(hydroxy ethers) exhibit high char yield under nitrogen at 850 °C (Fig. 5a), which is consistent with carborane bisphenol-based epoxy thermosets<sup>[16, 18]</sup>. This is a common phenomenon for boron-containing polymers. The boron atom can combine with oxygen at elevated temperature and be oxidized to form a three-dimensional network linked by B—O—B and B—C bonds<sup>[12, 19]</sup>. Therefore, the polymer weight is retained to a large extent. It is noted that the TGA measurements were conducted under nitrogen, hence the combined oxygen can be obtained only from the polymer. Owing to the formation of three-dimensional network, the formed radicals during polymer degradation fail to move freely and undergo secondary recombination process, and thus the degradation process is largely blocked<sup>[12]</sup>.

Furthermore, it is seen from Fig. 5(a) that the char yield of **P1** was lower than that of **P2** at the elevated temperature. This is seemingly inconsistent with the fact that they have the same molecular structures. The reasonable explanation is as follows. In order to obtain polymer with high molecular weight, the ratio of

[bisepoxy] to [bisphenol] is designated to be 1.02:1 in the polymerization. Besides, **P1** is synthesized from *o*-carborane bisphenol and DGEBA, while **P2** is derived from BPA and diglycidyl ether of *o*-carborane bisphenol (**1**). Considering the above monomer ratio, **P2** contains more carborane moieties than **P1**, and thus shows higher char yield at the elevated temperature.

To further explore the effect of oxygen on the degradation process, TGA measurements were conducted under air. The results are shown in Fig. 6. It is clearly seen that **P1**, **P2**, and **P3** lose their 5% weight under air at 308, 317, and 353 °C ( $T_5$ ), respectively. These temperatures are much lower than those under nitrogen, indicating that oxygen in air has an adverse effect on the initial decomposition temperature for *o*-carborane-containing poly(hydroxy ethers). It is known that the polymer chain of poly(hydroxy ether) is easier to break down under air, because the chain can combine with oxygen to form peroxide and hydroperoxide groups, which are more reactive during the degradation process<sup>[20]</sup>. Thus, the initial decomposition appears at a much lower temperature in air than that under nitrogen. On the other hand, oxygen in air promoted the formation of three-dimensional network linked by B—O—B and B—C bonds, thus the relatively higher char yield was obtained at elevated temperature under air (Fig. 6a) and the weight loss rate was also constrained to a lower degree (Fig. 6b).

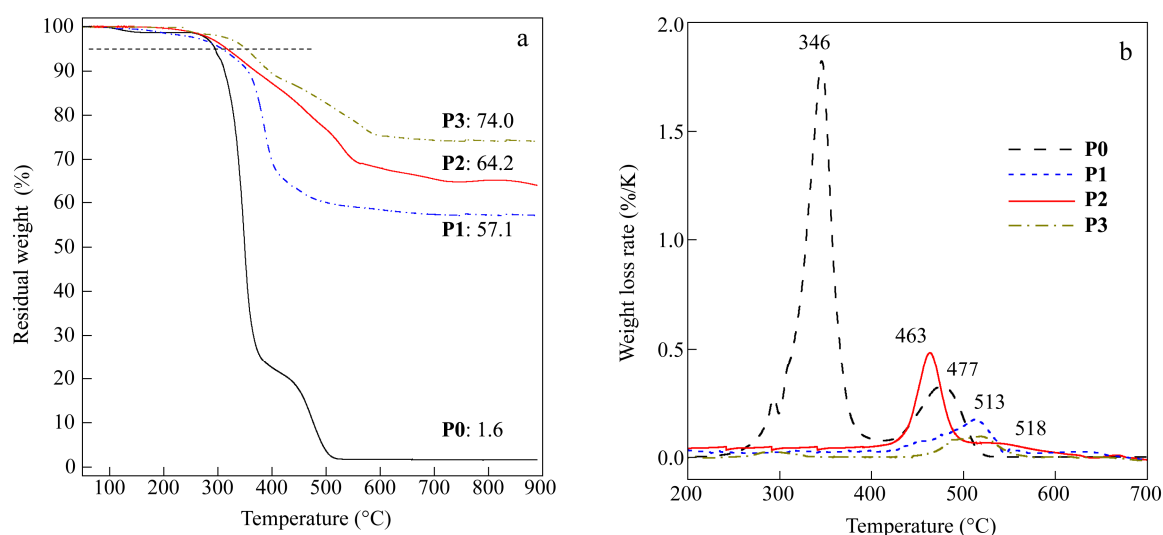


**Fig. 6** (a) TGA and (b) DTG curves of *o*-carborane-containing poly(hydroxy ethers) (**P1**, **P2**, and **P3**) under air. **P1** sample is from Table 1 No. 13 or Table 2 No. 1. The curves of carborane-free poly(hydroxy ether) (**P0**) are also given as a comparison.

FTIR was conducted to further explore the structural evolution of carborane cage at elevated temperature. Figure 7 shows the FTIR spectra of **P1** after TGA tests under nitrogen and air. It can be seen that both samples show new broad characteristic absorption band around 1440  $\text{cm}^{-1}$ , corresponding to B—O—B antisymmetric stretch vibration. At the same time, the strong absorption band at 2588  $\text{cm}^{-1}$  ascribed to the stretching vibrations of B—H bond disappears completely, indicating that B—H bonds were fully oxidized and consumed. Therefore, it is inferred that during TGA tests under nitrogen and air, the boron atoms on carborane cage combined with oxygen and were oxidized to form a three-dimensional network linked by B—O—B bonds. The oxygen was from polymer and/or the environment. Furthermore, the characteristic absorption peaks at 2967, 1600  $\text{cm}^{-1}$ , and other positions disappear simultaneously after TGA tests, which implies that the molecular segments such as methylene, methine, and phenyl groups were decomposed during the TGA measurement.

X-ray diffraction (XRD) technique was further utilized to confirm the formation of B—O—B three-dimensional network. **P3** was first thermally treated at 900 °C for 2 h, and then the obtained product was analyzed by XRD. The XRD patterns of **P3** before and after thermal treatment are shown in Fig. 8. It is seen that the initial polymer shows no diffraction peak. However, after thermal treatment, the polymer exhibits obvious

Bragg reflection at  $2\theta$  of  $28.1^\circ$ , which can be identified as crystalline diffraction peaks of boron oxide. Therefore, XRD analysis further confirms that a B—O—B network is formed after thermal treatment.

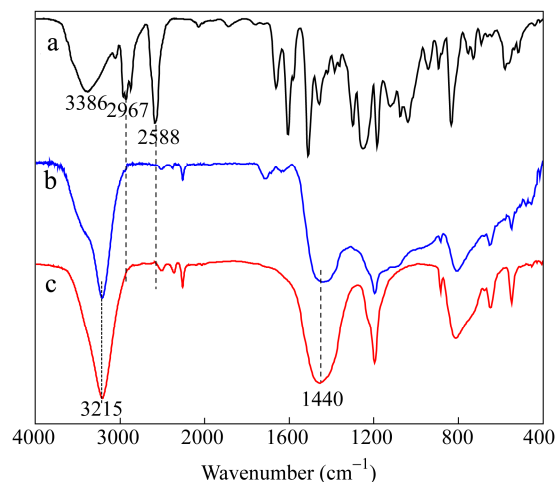


**Fig. 7** FTIR spectra of (a) **P1**, (b) **P1** after TGA test under nitrogen and (c) **P1** after TGA test under air  
**P1** sample is from Table 1 No. 13 or Table 2 No. 1.

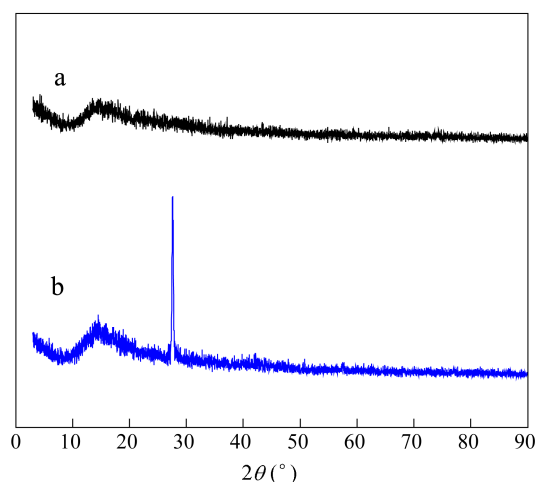


**Fig. 8** XRD patterns of **P3** (a) before and (b) after thermal treatment

#### Modification of Thermoset Epoxy by *o*-Carborane-containing Poly(hydroxy ethers)

The compatibility of *o*-carborane-containing poly(hydroxy ethers) (**P1**, **P2**, and **P3**) with epoxy thermosets was studied. The results show that these poly(hydroxy ethers) can be well dissolved in epoxy thermosets such as DGEBA and **1**. The excellent compatibility may be derived from their structural similarity. **P1** and **P3** were utilized to improve the high temperature adhesive strength of thermoset epoxy systems. The results are shown in Table 3. DGEBA and **1** were selected as thermoset epoxy resins, to which **P1** or **P3** was added as a modifier.

**Table 3** High temperature adhesive strength of epoxy systems modified with *o*-carborane-containing poly(hydroxy ethers)<sup>a</sup>

| No. | Epoxy system                  | Poly(hydroxyl ether) dosage, phr | Lap shear strength at RT (MPa) | Lap shear strength at 200 °C <sup>b</sup> (MPa) | Lap shear strength at 260 °C <sup>b</sup> (MPa) |
|-----|-------------------------------|----------------------------------|--------------------------------|-------------------------------------------------|-------------------------------------------------|
| 1   | DGEBA                         | 0                                | 17.3 ± 0.3                     | 7.2 ± 0.6                                       | 3.5 ± 0.6                                       |
| 2   | DGEBA/ <b>P1</b> <sup>c</sup> | 15                               | 18.6 ± 0.4                     | 10.2 ± 0.8                                      | 6.8 ± 1.1                                       |
| 3   | <b>1</b>                      | 0                                | 9.8 ± 0.3                      | 11.2 ± 0.6                                      | 7.0 ± 0.9                                       |
| 4   | <b>1/P1</b> <sup>c</sup>      | 15                               | 15.2 ± 0.4                     | 13.4 ± 0.8                                      | 7.8 ± 1.2                                       |
| 5   | <b>1/P3</b>                   | 15                               | 14.0 ± 0.4                     | 12.1 ± 0.4                                      | 7.4 ± 0.7                                       |

<sup>a</sup>Stoichiometric diaminodiphenyl sulfone (DDS) was utilized as a curing agent, and the epoxy systems were cured according to a temperature-programmed process (150 °C/2 h + 200 °C/2 h); <sup>b</sup>High temperature lap shear strength was tested after the bonded joints were placed under constant temperature for 30 min; <sup>c</sup>**P1** sample is taken from Table 1 No. 13 or Table 2 No. 1.

It can be seen from Table 3 that the lap shear strength of DGEBA has strong temperature dependence (No. 1). With test temperature increasing, the lap shear strength of pure DGEBA drops largely, from 17.3 MPa at room temperature to 3.5 MPa at 260 °C. The introduction of **P1** into DGEBA can improve the lap shear strength at elevated temperatures, although the effect of **P1** on the lap shear strength at room temperature is negligible (No. 2). Similarly, **P1** and **P3** can also improve the lap shear strength of **1** to some extent, even though pure **1** has carborane structure in the molecular structure.

#### CONCLUSIONS

In summary, *o*-carborane-containing poly(hydroxy ethers) (**P1**, **P2** and **P3**) were synthesized *via* “advancement reaction” of *o*-carborane-containing bisphenol (**4**) and diglycidyl ether of bisphenols (DGEBA and **1**). The

synthetic conditions were optimized to give acceptable molecular weights. The obtained polymers were characterized with spectroscopic techniques including FTIR,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR,  $^{11}\text{B}$ -NMR, which gave satisfactory results. TGA measurements were conducted under nitrogen and results showed that the polymers exhibited high initial decomposition temperatures ( $T_5$ , 406, 365, and 439 °C for **P1**, **P2**, and **P3**, respectively) due to the shielding effect of carborane moiety on its adjacent aromatic structures. Furthermore, TGA tests under air indicated that oxygen in air had an adverse effect on the initial decomposition temperature, because the polymer chain could combine with oxygen to form peroxide and hydroperoxide groups, which were more reactive during the degradation process. Besides, *o*-carborane-containing poly(hydroxy ethers) showed high char yield at the elevated temperatures, for the boron atom could combine with oxygen from the polymer structure or/and air to be oxidized to form a three-dimensional network linked by B—O—B and B—C bonds, thus the polymer weight was retained to a large extent.

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