

Synthesis, Amphiphilic Property and Thermal Stability of Novel Main-chain Poly(*o*-carborane-benzoxazines)

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Abstract. Five poly(*o*-carborane-benzoxazines) were synthesized via Mannich reaction of *o*-carborane bisphenol, paraformaldehyde, and diamine, and their structures were well characterized. Light transmission and ¹H NMR in D₂O confirmed that poly(*o*-carborane-benzoxazines) with PEG segments showed excellent water solubility and amphiphilic property. TGA analyses were conducted under nitrogen and air, and the results showed that the polymers own high initial decomposition temperatures owing to the shielding effect of carborane moiety on its adjacent aromatic structures. Besides, poly(*o*-carborane-benzoxazines) own high char yield at elevated temperatures, for the boron atom could combine with oxygen from the polymer structure or/and the air and be oxidized to form boron oxide, and thus the polymer weight is retained to a large extent. PEG segments had an adverse effect on the initial decomposition and char yield, and thus their concentration should be adjusted to control the polymer's thermal stability.

1. Introduction

As a new type of addition-curable phenolic polymer, polybenzoxazines have exhibited many superior performances such as high thermal stability, no evolution of volatiles and near-zero shrinkage during curing, flexibility of molecular design, and tailored mechanical properties [1]. However, polybenzoxazines possess low density and are rather brittle, which limits their application [2]. Furthermore, benzoxazine resins are increasingly required to own higher properties such as thermal stability in high-tech fields. On one hand, to obtain higher thermal stability, benzoxazine resins were incorporated with addition reaction groups such as acetylenyl, allyl, cyano, maleimide, and furan which could participate in the curing reaction and thus improved the degree of curing [3-6]. On the other hand, bulky moieties such as fluorenyl, adamantane, and naphthalene were also introduced to the molecular structure of benzoxazine resins so as to enhance their heat resistance [7,8]. To date the search for new high-temperature units is still attracting much attention.

Closo-carboranes (C₂B₁₀H₁₂), with an icosahedral geometry, are excellent building blocks for thermally stable polymers [9]. Carboranes could absorb energy like a kind of "power gauge" at high temperature owing to its "superaromatic" electronic structure. Besides, the large volume of three-dimensional cage endows carboranes with strong shielding effect on adjacent segments. Therefore, carboranes were incorporated into many traditional polymers to improve their thermal stability including epoxy resins, phenolic resins, and aromatic polymers [10-12].

We have successfully synthesized carborane bisphenols and corresponding carborane-based epoxy resins, phenolic, and benzoxazine resins [10, 11, 13]. In this work, we report our studies on polybenzoxazines with *o*-carborane and PEG segments from *o*-carborane bisphenol and various functional diamines (Chart 1). Five Poly(*o*-carborane-benzoxazines) were synthesized by Mannich



reaction of *o*-carborane bisphenol, paraformaldehyde, and diamine according to Scheme 1 and Chart 2. Their chemical structures have been well characterized, and their amphiphilic property and thermal stability were studied.

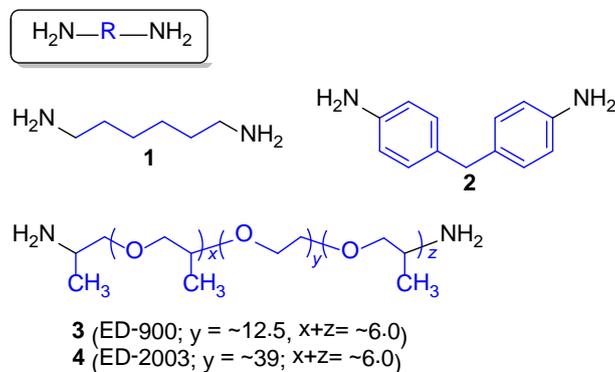


Figure 1. Functional diamines used in this work

2. Experimental

2.1 Materials

1,2-bis(4-hydroxyphenyl)-*o*-carborane (*o*-BC) was kindly supplied by Beihang University. Hexamethylenediamine (**1**) and 4,4'-diaminodiphenyl methane (DDM, **2**) were purchased from Aladdin. Polyetherdiamines (**3** and **4**) were obtained from Huntsman, whose structures are shown in Chart 1. The molecular weight of **3** is 900 g/mol, lower than that of **4** (2000 g/mol). Paraformaldehyde, toluene, ethanol, methanol, and *n*-hexane were obtained from Sinopharm Chemical Reagent Beijing Co. Ltd. All materials were used without further purification.

2.2 Instrumentation

Molecular weight (M_w) and polydispersity indices (M_w/M_n) of the polymers were tested in THF with a Waters 515 gel permeation chromatography system. Tetrahydrofuran (THF) was used as eluent at 30 °C at a flow rate of 1.0 ml/min. FTIR spectra were recorded on a Nexus 670 infrared spectrometer. ^1H , ^{13}C , and ^{11}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 was used as an internal standard. Ultraviolet spectrum(UV) were tested by UV-3600 Under the Ultraviolet light at 250 cm^{-1} . Thermogravimetric analysis (TGA) was performed by a TA Instrument SDT-Q600 at a heating rate of 20 °C/min from 50 to 900 °C under nitrogen and air respectively.

2.3 Synthesis of Poly(*O*-Carborane-Benzoxazines) (Poly(BC-1)-Poly(BC-4))

Poly(*o*-carborane-benzoxazine)s (poly(BC-1)-poly(BC-4)) were synthesized according to Scheme 1. The detailed procedures for the synthesis of poly(BC-1) were given below as an example. Into a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added 1,2-bis(4-hydroxyphenyl)-*o*-carborane (*o*-BC, 1.0 g, 3.03 mmol), **1** (0.352 g, 3.03 mmol), paraformaldehyde (0.39 g, 12.12 mmol), and 45 mL of toluene-ethanol mixed solvent (2:1 volume ratio). The system was stirred under reflux for 10 hours. The reaction mixture was allowed to cool to room temperature, followed by evaporation of toluene by stream of air. The resultant product was dissolved in 40 mL of chloroform, and then washed three times with 1 mol/L of sodium bicarbonate aqueous solution. The chloroform was removed by rotary evaporator, and the obtained product was placed under vacuum at 40 °C till constant weight was obtained. Besides, in order to increase the ring content, the chloroform solution could also be further reprecipitated in 80 mL of methanol, and the purified product was collected by suction filtration.

2.3.1 Characterization Data for Poly(BC-1). A yellow solid was obtained in a yield of 59.9 %. M_w : 8500; M_w/M_n : 6.55 (GPC, polystyrene calibration; Table 1, No. 9). FTIR, ν (cm^{-1} , in KBr pellet): 2933 (unsaturated C-H), 2856 (saturated C-H), 2587 (B-H), 1612, 1580, 1500, 1462 (Ph), 1329, 1125 (C-N-C), 1238, 1024 (C-O-C), 936. ^1H NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 7.20-6.48 (m, 6H), 4.78 (s, 2H), 3.83 (s, 2H), 2.56-0.9 (m, 10H), 2.61, 1.59, 1.31 (t, 2H). ^{13}C NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 155.95, 130.49, 123.08, 119.85, 116.16, 86.25, 83.04, 50.17.

2.3.2 Characterization Data for Poly(BC-2). A yellow solid was obtained in a yield of 47.6 %. M_w : 9500; M_w/M_n : 2.75 (GPC, polystyrene calibration). FTIR, ν (cm^{-1} , in KBr pellet): 3026 (unsaturated C-H), 2898 (saturated C-H), 2588 (B-H), 1612, 1582, 1505, 1422 (Ph), 1371, 1183 (C-N-C), 1247, 1074 (C-O-C), 936. ^1H NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 7.12-6.52 (m, 6H), 5.16 (s, 2H), 4.34 (s, 2H), 3.78, 3.74, 3.25-1.28 (m, 10H), 3.74 (m, 2H). ^{13}C NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 155.95, 146.06, 134.94, 129.75, 123.32, 120.61, 118.88, 116.90, 114.93, 85.51, 80.32, 50.17.

2.3.3 Characterization Data for Poly(BC-3). The resultant product was precipitated in *n*-hexane, and a yellow liquid was obtained in a yield of 59.9 %. M_w : 8500; M_w/M_n : 6.55 (GPC, polystyrene calibration). FTIR, ν (cm^{-1} , in KBr pellet): 3475 (-OH), 2872 (-CH₂-), 2589 (B-H), 1611, 1582, 1501, 1454 (Ph), 1351 (C-N-C), 1248, 1108 (C-O-C), 936. ^1H NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 7.62-6.48 (m, 6H), 4.89 (s, 2H), 3.94 (s, 2H), 3.65 (d, 2H), 3.51-3.04 (s, 2H), 2.60-1.25 (m, 10H), 1.20-1.00 (m, 3H). ^{13}C NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 158.85, 132.26, 129.57, 125.52, 121.85, 115.18, 86.18, 81.50, 62.61, 55.58. ^{11}B NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 30.67, -3.99, -12.36.

2.3.4 Characterization Data for Poly(BC-4). The resultant product was precipitated in *n*-hexane, and a yellow liquid was obtained in a yield of 59.9 %. M_w : 8500; M_w/M_n : 6.55 (GPC, polystyrene calibration). FTIR, ν (cm^{-1} , in KBr pellet): 3509 (-OH), 2871 (-CH₂-), 2589 (B-H), 1610, 1582, 1501, 1455 (Ph), 1106, 1285 (C-O-C), 1350 (C-N-C), 936. ^1H NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 7.40-6.45 (m, 6H), 4.90 (s, 2H), 3.96 (s, 2H), 3.65 (d, 2H), 2.60-1.35 (m, 10H), 1.33-0.93 (m, 3H). ^{13}C NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 156.47, 132.22, 129.56, 125.49, 122.63, 115.18, 86.15, 81.41, 62.61, 55.56. ^{11}B NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 31.05, -4.43, -12.20.

2.4 Synthesis of Poly(*O*-Carborane-Benzoxazines) (Poly(BC-2-3))

Poly(BC-2-3) was synthesized by the reaction of 1,2-bis(4-hydroxyphenyl)-*o*-carborane (*o*-BC) with the mixed amines of **2** and **3**, and the polymer structure is shown in Chart 2. The resultant product was precipitated in *n*-hexane, and a yellow liquid was obtained in a yield of 62.1%. M_w : 8500; M_w/M_n : 2.67 (GPC, polystyrene calibration). FTIR, ν (cm^{-1} , in KBr pellet): 3157 (-OH), 2874 (-CH₂-), 2590 (B-H), 1610, 1590, 1515, 1452 (Ph), 1108, 1289 (C-O-C), 1351 (C-N-C), 936. ^1H NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 7.36-6.47 (m, 6H), 4.89 (s, 2H), 3.85 (s, 2H), 3.59 (d, 2H), 2.60-1.42 (m, 10H), 1.32-0.90 (m, 3H). ^{13}C NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 156.48, 131.32, 128.57, 122.41, 115.19, 88.15, 82.41, 62.69, 55.58. ^{11}B NMR (400 MHz, Chloroform-*d*), δ (TMS, ppm): 30.25, -4.30, -12.45.

3. Results and Discussion

3.1 Synthesis of Poly(*O*-Carborane-Benzoxazines) (Poly(Bc-1)-Poly(Bc-4))

Poly(*o*-carborane-benzoxazines) (poly(BC-1)-poly(BC-4)) were synthesized from 1,2-bis(4-hydroxyphenyl)-*o*-carborane (*o*-BC), diamines (**1-4**), and paraformaldehyde in toluene-ethanol solvent according to Scheme 1. The polymerization reactions proceeded smoothly, and desired polybenzoxazines were obtained in satisfactory yields (~ 67.1 %). The obtained polymers were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained (see "Experimental" for details).

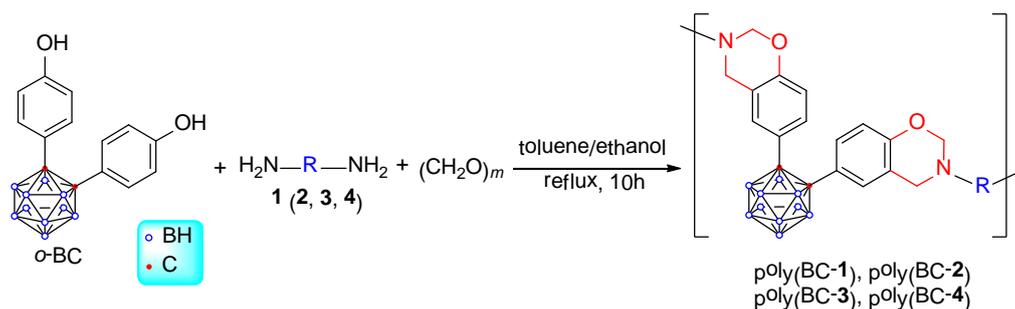


Figure 2. Synthetic routes to poly(*o*-carborane-benzoxazines) (poly(BC-1)- poly(BC-4))

To synthesize poly(BC-1) from *o*-carborane bisphenol (*o*-BC) and hexamethylenediamine (**1**), 1,4-dioxane was first selected as polymerization solvent, but the product was completely insoluble in most organic solvents such as THF, DMF, DMSO, and chloroform (Table 1, no 3). Then the polymerization was conducted in chloroform and xylene respectively, whereas the obtained products were partially soluble in organic solvents and the soluble fraction owned relatively low molecular weight (Table 1, nos 1 and 2). After trial and error, it was found that the polymerization solution became homogeneous in toluene-ethanol mixed solvent (2:1 volume ratio). The resultant product was well dissolved in the mixed solvent. High yield (87%) and acceptable ring content (64.5%) were obtained when the polymerization lasted for 10 h (Table 1, no 6). It is noted that the ring content could be greatly increased by further purifying the obtained polymers via precipitation in methanol, while the yield decreased accordingly (Table 1, nos 8-10). The obtained poly(BC-1) can be dissolved in common organic solvents such as chloroform, THF, and dichloromethane.

Table 1 The synthesis of Poly(*o*-carborane-benzoxazine) (poly(BC-1)) from hexamethylenediamine (**1**)

no.	$T, ^\circ\text{C}$	t, h	solvent	M_w^a	M_w/M_n^a	yield,%	ring content,% b
1	60	5	chloroform	1400 ^c	1.81	13.5	41.1
2	150	10	xylene	1500 ^c	1.96	8.30	34.5
3	100	10	1,4-dioxane	- ^d	-	50.6	-
4	80	2	toluene/EtOH	5800	7.97	7.90	67.8
5	80	5	toluene/EtOH	5900	6.28	14.5	53.6
6	80	10	toluene/EtOH	5900	4.52	87.0	64.5
7	80	15	toluene/EtOH	4400	5.90	68.0	66.5
8 ^e	80	5	toluene/EtOH	14000	7.36	47.3	86.4
9 ^e	80	10	toluene/EtOH	8500	6.55	59.9	89.9
10 ^e	80	15	toluene/EtOH	6100	5.79	57.7	89.6

^a Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration. ^b Calculated from NMR data, see "Structure Characterization" for detail. ^c Data for the soluble fraction; for the polymerization product was only partially soluble in THF. ^d The product was completely insoluble in common organic solvents such as THF, DMF, DMSO, and chloroform. ^e The product was further purified by precipitation in *n*-hexane.

Similarly, other diamines (**2-4**) were utilized to synthesize poly(*o*-carborane-benzoxazine)s and the results were shown in Table 2. Poly(BC-2) was synthesized from **2** by the same procedures, and the obtained polymer exhibits high molecular weight ($M_w = 9500$) and high ring content (92.3%). During the synthesis of poly(BC-3) and poly(BC-4), the crude products were reprecipitated in *n*-hexane rather than methanol, since the target products can be dissolved in methanol. Furthermore, poly(BC-2-3) (chart 2) was also designed and synthesized in order to carefully study the effect of hydrophilic chain on the water solubility of the obtained polymers.

Table 2 The synthesis of poly(*o*-carborane-benzoxazine)s from other diamines (**2-4**)^a

no.	diamine	poly(<i>o</i> -carborane-benzoxazine)	<i>t</i> , h	M_w^b	M_w/M_n	yield, %	ring content, % ^c
1	2	poly(BC-2)	10	9500	2.75	47.6	92.3
2	3	poly(BC-3)	10	7700	2.37	67.1	82.0
3	4	poly(BC-4)	10	15000	2.70	63.5	95.0
4	2 and 3	poly(BC-2-3)	10	8500	2.67	62.1%	85.7

^a Carried out at refluxing temperature in toluene/EtOH. ^b Estimated by gel permeation chromatograph (GPC) in THF on the basis of polystyrene calibration. ^c Calculated from NMR data, see "Structure Characterization" for detail.

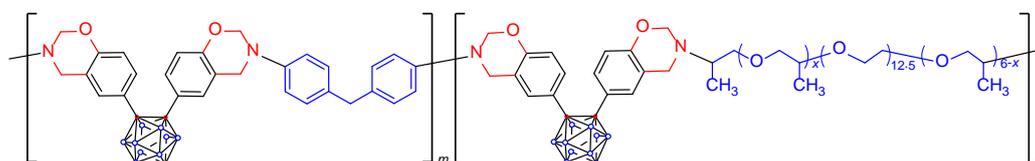


Figure 3. Poly(BC-2-3)

3.2 Structure Characterization

The structures of the obtained poly(*o*-carborane-benzoxazine)s 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 spectrum of poly(*o*-carborane-benzoxazine) (poly(BC-2)) is shown in Figure 1; the spectrum of starting bisphenol (*o*-BC) is also given in the same figure for comparison. It is seen that *o*-BC exhibits absorption peak at 2588 cm⁻¹, which is ascribed to the stretching vibration of B-H on carborane cage. This band is still present in the spectrum of poly(BC-2), indicating that the carborane cage remains intact during the polymerization. Besides, new peaks appear at 1074 and 1247 cm⁻¹ associated with the symmetric and asymmetric vibrations of C-O-C, while absorption peaks at 1183 and 1371 cm⁻¹ are related with the symmetric and asymmetric vibrations of C-N-C, which confirms the formation of cyclic ether of benzoxazine structure. Furthermore, wide absorption band around 3332 cm⁻¹ ascribe to phenolic hydroxyl group almost disappears, which is further evidence that carborane bisphenol has been transformed into polybenzoxazine.

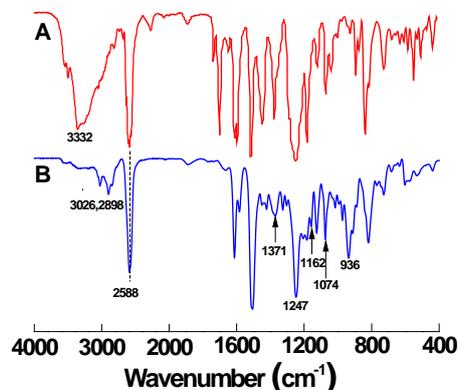


Figure 4. FTIR spectra of (A) *o*-carborane bisphenol (*o*-BC) and (B) poly(*o*-carborane-benzoxazine) (poly(BC-2), sample from Table 2 No. 1).

Figure 2 shows the ^1H NMR and ^{13}C NMR spectra of poly(BC-2) and its starting bisphenol (*o*-BC). It is seen that *o*-BC shows resonance peak at $\delta \sim 8.85$ associated with phenolic hydroxyl group (Figure 2A), which disappears in the spectrum of poly(BC-2) (Figure 2B), indicating the complete transformation of bisphenol to benzoxazine structure. New resonance peaks at $\delta \sim 5.16$ and 4.34 appear which are attributed to methylene protons on the oxazine ring, while a resonance peak at $\delta \sim 3.78$ is related with methylene protons of the opened structure (Figure 2B). Since the synthesized poly(*o*-carborane-benzoxazines) own both oxazine ring and opened structure, the integrated intensities of the above resonance peaks were utilized to calculate the percentage of benzoxazine ring, i.e. ring content, of the polymer and the results were shown in tables 1 and 2. It is seen from Figure 2D that new peaks appear at $\delta \sim 80.1$ and 50.1 which are attributed to methylene carbons on the oxazine ring, further verifying the formation of benzoxazine structures. Since the obtained polymers contain *o*-carborane in their structures, ^{11}B NMR data were also given in Experimental section, which are well consistent with their precursory carborane bisphenol[13].

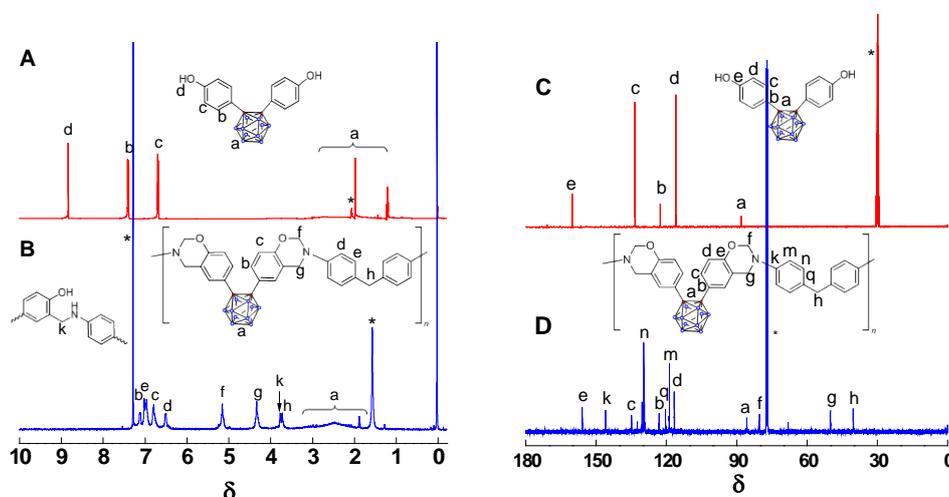


Figure 5. ^1H NMR and ^{13}C NMR spectra of *o*-carborane bisphenol (*o*-BC) in $(\text{CD}_3)\text{CO}$ (A, C) and poly(*o*-carborane-benzoxazine) (poly(BC-2), sample from Table 2 No. 1) in CDCl_3 (B and D). The solvent peaks are marked with asterisks.

3.3 Water Solubility and Amphiphilic Property

PEG chains have been widely incorporated into polymer molecules to prepare materials with functions such as water solubility, amphiphilicity, biocompatibility, and hydrogel formability. Therefore, PEG-containing poly(*o*-carborane-benzoxazines) (poly(BC-3) and poly(BC-4)) were designed and synthesized by using polyetherdiamines with different PEG chain length. To demonstrate their water solubility, different concentrations of polymer aqueous solutions were prepared and their light transmission spectra were recorded at room temperature.

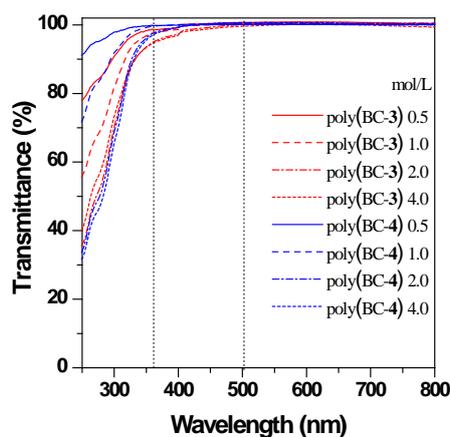


Figure 6. Light transmission spectra of the aqueous solution of poly(BC-3) and poly(BC-4) at polymer concentration of 0.5-4.0 mol/L.

As depicted in Figure 3, it is obvious that the transmittances of polymer aqueous solutions are 100% at wavelength longer than 510 nm, even when the polymer concentration is as high as 4.0 mol/L. In the region where the wavelength is shorter than 520 nm, the transmittances of polymer aqueous solutions decrease, and the declination is associated with the electronic absorption of the carborane bisphenol. The above phenomena suggest that PEG-containing poly(*o*-carborane-benzoxazines) can be dissolved in water to form clear aqueous solution.

The incorporation of PEG chains into polybenzoxazine backbone bestowed the resultant polymers with a segmented structure, which consists of hydrophobic segments and hydrophilic chains with different length. In aqueous solution, the hydrophobic part is encapsulated by the hydrophilic PEG segments. As a result, a single polymer chain takes a micelle-like configuration, and carborane bisphenol units of the polymers are insoluble in water, although clear aqueous solutions have been observed. This deduction was validated by the measurements of the ^1H NMR spectra of the polymers in D_2O at room temperature. The ^1H NMR spectra of poly(BC-3) in D_2O and CDCl_3 are shown in Figure 4 as an example. In CDCl_3 , the resonance peaks for the protons on phenyl groups and PPG chains can be found, and the resonance peaks for the protons on PEG segments are also clearly recognized (Figure 4A). This indicates the good solubilities of both the hydrophobic (carborane bisphenol unit and PPG chain) and hydrophilic (PEG segment) parts are soluble. While in D_2O , there exist only one peak at $\delta \sim 3.65$, which can be assigned to the resonance of protons of water soluble PEG chain (Figure 4B); but no other peaks are observed, indicating that hydrophobic carborane bisphenol units and PPG chains cannot be dissolved in water.

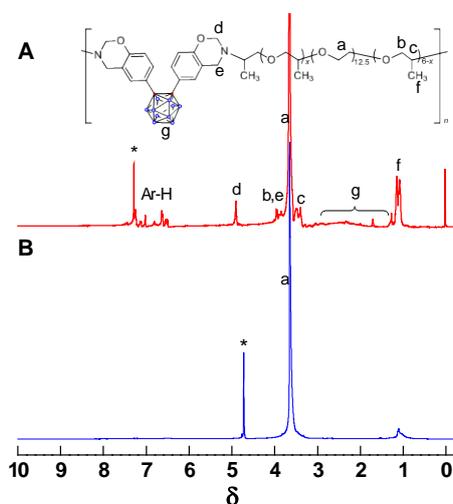


Figure 7. ^1H NMR spectra of poly(*o*-carborane-benzoxazine) (poly(BC-3), sample from Table 2 No. 2) in (A) CDCl_3 and (B) D_2O . The solvent peaks are marked with asterisks.

3.4 Thermal Stability

Poly(*o*-carborane-benzoxazines) were investigated by thermal gravimetric analysis (TGA) under nitrogen and air, and the results are shown in Figure 5. It is seen that poly(BC-1) and poly(BC-2) lose their 5% weight under nitrogen at 420 and 543 °C (T_5), respectively, much higher than that of carborane-free polybenzoxazine. The initial decomposition temperatures of polybenzoxazine were highly improved by introduction of carborane cage into their backbones. The incorporated carborane moiety shows excellent shielding effect on its adjacent aromatic structures, and thus the thermal stability of polybenzoxazine is improved. It is interesting to note that poly(BC-1) and poly(BC-2) own much higher T_5 under air (553 and 708 °C) than under nitrogen. It is known that the carborane cage within polymer backbone can be oxidized to form boron oxide by absorbing oxygen from the polymer structure and/or the environment, so the weight loss is largely postponed. The oxygen in air can promote the oxidation reaction, and thus the polymer may absorb so much oxygen that the weight gain occurs over 500 °C for poly(BC-2). Besides, poly(BC-1) and poly(BC-2) own high char yield under nitrogen and air at elevated temperatures, which is consistent with other carborane-containing thermosets^[10, 11, 13, 14]. The oxidation-caused weight gain also contributes to higher char yield under air. Poly(BC-3) and poly(BC-4) are polybenzoxazines with PEG segments. It is seen that these two polymers exhibit much lower T_5 and char yield, indicating that the thermal degradation occurs easily. By selecting two kinds of diamines, poly(BC-2-3) was designed and synthesized with adjusted PEG concentration and controlled thermal stability.

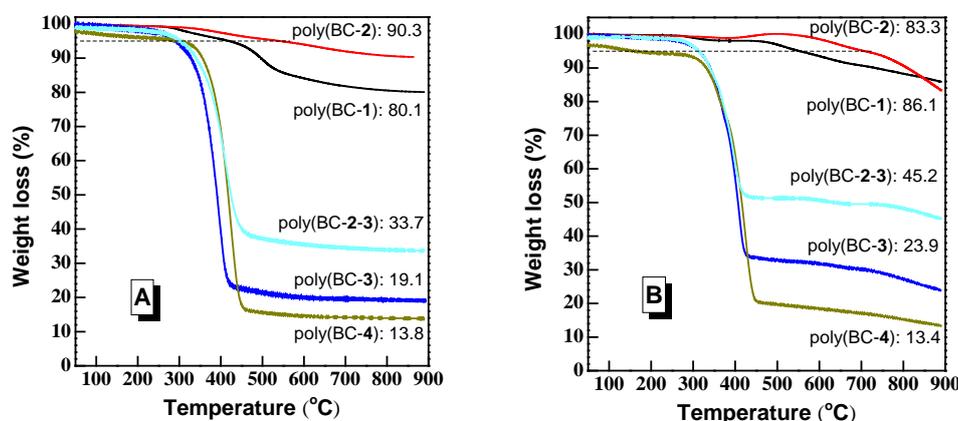


Figure 8. TGA curves of poly(*o*-carborane-benzoxazines) under nitrogen (A) and air (B). (P1 sample from Table 1 No. 9).

4. Conclusion

In summary, five poly(*o*-carborane-benzoxazines) were synthesized via Mannich reaction of *o*-carborane bisphenol, paraformaldehyde, and diamine. The synthetic conditions were well optimized to give acceptable molecular weights. The obtained polymers were characterized with spectroscopic techniques including FTIR, ^1H NMR, and ^{13}C NMR, which gave satisfactory results. Light transmission and ^1H NMR in D_2O confirmed that poly(*o*-carborane-benzoxazines) with PEG segments showed amphiphilic property. TGA analyses were conducted under nitrogen and air, and the results showed that the polymers own high initial decomposition temperatures owing to the shielding effect of carborane moiety on its adjacent aromatic structures. Besides, poly(*o*-carborane-benzoxazines) own high char yield at elevated temperatures, for the boron atom could combine with oxygen from the polymer structure or/and the air and be oxidized to form boron oxide, and thus the polymer weight is retained to a large extent. PEG segments had an adverse effect on the initial decomposition and char yield, and thus their concentration should be adjusted to control the polymer's thermal stability.

5. Acknowledgments

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