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Synthesis, curing behavior and thermal properties of fluorene containing benzoxazines

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ABSTRACT

A series of difunctional fluorene-based benzoxazine monomers were synthesized from the reaction of 9,9-bis-(4-hydroxyphenyl)-fluorene with formaldehyde and primary amines including aniline, *o*-toluidine, *n*-butylamine, and *n*-octylamine. Their chemical structures were confirmed by FT-IR, ^{1}H and ^{13}C NMR analyses. The curing behaviors of the precursors were monitored by differential scanning calorimetry (DSC) and FT-IR. The thermal properties of cured polymers were evaluated with DSC and thermogravimetric analysis (TGA). The fluorene-based polybenzoxazines show the typical curing characteristic of oxazine ring-opening for difunctional benzoxazines centred at 231–250 °C, and remarkably higher glass transition temperature and better thermal stability ascribed to the high rigidity, high aromatic content, and intermolecular and intramolecular hydrogen bonding. The thermal decomposition temperature and char yield of aromatic amine-fluorene-based polybenzoxazines are much higher than those of aliphatic amine-based polybenzoxazines.

1. Introduction

Polybenzoxazines, as a class of thermosetting phenolic resins formed by the thermal ring-opening of the corresponding benzoxazines monomers without any catalyst, have demonstrated various attractive properties such as high thermal stability, high char yields, high glass transition temperature (T_g), near-zero volumetric change upon curing, good mechanical and dielectric properties, low water absorption, and low flammability [1–6]. These unique characteristics make the polybenzoxazines a better candidate over epoxies and traditional phenolic resins in the electronics, aerospace, and other industries. Benzoxazine monomers as the polybenzoxazine precursors can be easily prepared from phenols or amines, formaldehyde, and primary amines or phenols. The polybenzoxazines that dominate the literature are bisphenolbased and diamine-based such as bisphenol A, dihydroxynaphthalene, dopotriol, benzophenone, biphenol, and aliphatic and aromatic diamine-based benzoxazines etc. [1,3,7–13]. The large varieties of aromatic bisphenols and monoamines allow considerable molecule-design flexibility for benzoxazines, and thus achieve the polyfunctionality required to form an infinite network structure through synthesis utilizing a bifunctional phenolic molecule with a monofunctional amine [14]. Moreover, some special functional groups or rigid aromatic groups, such as acetylene, phenylpropargyl, allyl, norbornene, nitrile, phthalonitrile, maleimide, adamantane, aromatic triamine, organic phosphorus compounds, etc., can be introduced via biphenols or monoamines to provide some desired properties [15–29].

9,9-Bis(4-hydroxyphenyl) fluorene (BHPF) has a structure of four phenyl rings connected to a quaternary carbon leads to severe rotational hindrance of the phenyl groups (Scheme 1). The stiff, bulky cardo moiety must arise from the higher rigidity of fluorene skeleton in the chain backbone [30]. Therefore, polymers containing fluorenyl

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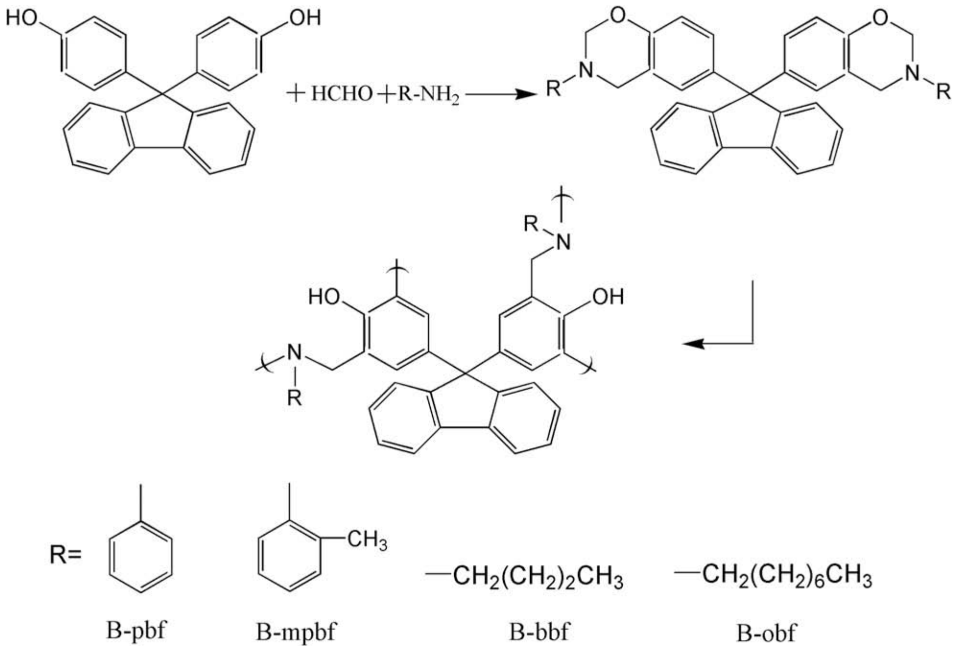


Scheme 1. Synthesis of the fluorene-based benzoxazine monomers.

structure in the backbone (so called 'Cardo-type polymers') have many excellent improved properties such as good heat resistance, high char yield, high limited oxygen index, and good flame proofing. The development of these polymers has attracted extensive research interests during past few years [31–36]. The introduction of cardo fluorene moieties into the benzoxazine chains is expected to greatly improve the thermal stability and moisture resistance of the polymers. Ghetiya et al. reported the preparation of cardo bisbenzoxazines containing bisphenol-C (BCO) and phenolphthalein (PHO) [37]. Both BCO and PHO undergo selective ring-opening polymerization over the temperature range 100–150 °C, however, initial thermal decomposition temperature is about 250 °C. The char yield for PPHO and PBCO at 550 °C is 56–67% and 20–25%, respectively. The descriptions of the synthesis and thermal properties about difunctional fluorene-based cardo benzoxazine monomers and polymers are seldom reported up to now.

In this study, 9,9′-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl) fluorene (B-pbf), 9,9′-bis(3-*ortho*-methylphenyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl) fluorene (B-mpbf), 9,9′-bis(3-butyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl) fluorene (B-bbf), 9,9′-bis(3-octyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl) fluorene (B-obf) were synthesized and characterized by FT-IR, ^{1}H NMR and ^{13}C NMR. The curing behavior and thermal properties of the monomers and cured polymers were investigated by DSC, FT-IR, and TGA.

2. Experimental

2.1. Materials

9,9-Bis-(4-hydroxyphenyl)-fluorene (BHPF, 99.2%) was synthesized according to the literature [38]. Formaldehyde (37 wt% in water) was purchased from Tianjin fengchuan Chemical Reagent Co., Ltd. (China). Aniline, *o*-toluidine, *n*-butylamine and *n*-octylamine were obtained from Tianjin Bodi Chemical Co., Ltd. (China) and National Pharmaceutical Chemical Co., Ltd. (China), respectively, and used without further purification.

2.2. Monomer synthesis

Benzoxazine monomers were prepared using BHPF, formaldehyde, and primary amine as shown in Scheme 1.

2.2.1. Synthesis of B-pbf

Formaldehyde (6.4 g, 0.08 mol) and 1,4-dioxane (8 mL) were added to a 150 mL three neck round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and thermometer, stirred 30 min at room temperature. The mixture was cooled to below 5 °C in an ice bath, then aniline (3.74 g, 0.04 mol) was added drop-wise and reacted for 2 h. The temperature was raised gradually to 90 °C. Then, a solution of BHPF (7.0 g, 0.02 mol) in 16 mL mixed solvents including dioxane (8 mL) and ethanol (8 mL) as a cosolvent to improve the solubility of BHPF was added, and the mixture was kept stirring at 90 °C for 6 h. The solvent was removed by rotary evaporator. The yellowish powder was dissolved in diethyl ether, washed five times with 3 N NaOH aqueous solution and finally two times with distilled water. The ether solution was dried with anhydrous sodium sulphate, filtered, followed by evaporation of ether to afford a yellow crystals (56.3% yield). FT-IR (KBr, cm^{-1}): 1495 (C–H in-plane bending), 1327 (CH$_2$ wagging), 1234 (C–O–C asymmetric stretching), 1120 (C–N–C asymmetric stretching), 1068 (C–O–C symmetric stretching), 949 (C–H out-of-plane bending), 865 (C–N–C symmetric stretching), 820, 746, 693 (C–H out-of-plane bending). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): 6.71–7.79 (m, 24H, Ar–*H*), 5.32 (s, 4H, O–CH_2–N), 4.50 (s, 4H, Ar–CH_2–N). ^{13}C NMR (500 MHz, $CDCl_3$, ppm): 116.38–152.69 (36C, the carbons of benzene rings), 78.56 (2C, O–CH_2–N), 63.84 (1C, quaternary carbon in the fluorene ring), 50.24 (2C, N–CH_2–Ar).

2.2.2. Synthesis of B-mpbf

B-*mpbf* monomer was synthesized by the same procedureas as B-*pbf*. The molar ratio of BHPF, formaldehyde, and *o*-toluidine was 1 to 4 to 2. The yield of B-*mpbf* with yellowish crystals was 54.8%. FT-IR (KBr, cm^{-1}): 1493 (C–H in-plane bending), 1325 (CH_2 wagging), 1235 (C–O–C asymmetric stretching), 1123 (C–N–C asymmetric stretching), 1068 (C–O–C symmetric stretching), 949 (C–H out-of-plane bending), 864 (C–N–C symmetric stretching), 820, 742 (C–H out-of-plane bending). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 6.71–7.78 (m, 22H, Ar–*H*), 5.16 (s, 4H, O–CH_2–N), 4.27 (s, 4H, Ar–CH_2–N), 2.34 (s, 6H, Ar–CH_3). ^{13}C NMR (500 MHz, $CDCl_3$, ppm): 116.74–153.05 (36C, the carbons of benzene rings), 80.85 (2C, O–CH_2–N), 64.34 (1C, quaternary carbon in the fluorene ring), 50.94 (2C, N–CH_2–Ar), 18.39 (2C, –CH_3).

2.2.3. Synthesis of B-bbf

Synthesis of B-bbf was performed in the same way, giving monomer as white crystals in 53.9% yield. FT-IR (KBr, cm^{-1}): 1495 (C–H in-plane bending), 1320 (CH_2 wagging), 1232 (C–O–C asymmetric stretching), 1121 (C–N–C asymmetric stretching), 1070 (C–O–C symmetric stretching), 955 (C–H out-of-plane bending), 865 (C–N–C symmetric stretching), 820, 739 (C–H out-of-plane bending). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 6.66–7.79 (m, 14H, Ar–*H*), 4.82 (s, 4H, O–CH_2–N), 3.85 (s, 4H, Ar–CH_2–N), 2.71 (t, 4H, N–CH_2–), 1.53 (m, 4H, CH_2–CH_2–CH_2), 1.30 (m, 4H, CH_2–CH_2–CH_2), 0.91 (t, 6H, –CH_3). ^{13}C NMR (500 MHz, $CDCl_3$, ppm): 116.09–152.92 (24C, the carbons of benzene rings), 82.34 (2C, O–CH_2–N), 64.32 (1C, quaternary carbon in the fluorene ring), 51.19 (2C, N–CH_2–Ar), 50.50 (2C, N–CH_2–CH_2), 30.24 (2C, CH_2–CH_2–CH_2), 20.37 (2C, CH_2–CH_2–CH_3), 13.99 (2C, –CH_3).

2.2.4. Synthesis of B-obf

Synthesis of B-obf was performed in the same way, giving monomer as white crystals in 50.1% yield. FT-IR (KBr, cm^{-1}): 1494 (C–H in-plane bending), 1319 (CH_2 wagging), 1231 (C–O–C asymmetric stretching), 1121 (C–N–C asymmetric stretching), 1070 (C–O–C symmetric stretching), 954 (C–H out-of-plane bending), 864 (C–N–C symmetric stretching), 819, 739 (C–H out-of-plane bending). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 6.66–7.79 (m, 14H, Ar–*H*), 4.82 (s, 4H, O–CH_2–N), 3.84 (s, 4H, Ar–CH_2–N), 2.72 (t, 4H, N–CH_2–), 1.34–2.21 (m, 24H, CH_2–CH_2–CH_2), 0.92 (t, 6H, –CH_3). ^{13}C NMR (500 MHz, $CDCl_3$, ppm): 116.10–152.93 (24C, the carbons of benzene rings), 82.33 (2C, O–CH_2–N), 64.33 (1C, quaternary carbon in the fluorene ring), 51.51 (2C, N–CH_2–Ar), 50.51 (2C, N–CH_2–CH_2), 22.68–31.85 (12C, CH_2–CH_2–CH_2), 14.13 (2C, –CH_3).

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer in the range of 4000–500 cm^{-1}, which was equipped with a deuterated triglycine sulphate (DTGS) detector and KBr optics. Transmission spectra were obtained at a resolution of 4 cm^{-1} resolution after averaging two scans by casting a thin film on a KBr plate for monomers and cured samples. ^{1}H and ^{13}C NMR characterizations were performed on a Bruker AVANCE-500 NMR spectrometer using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as an internal standard. The average number of transients for ^{1}H and ^{13}C NMR is 16 and 2048, respectively. A relaxation delay time of 1s was used for the integrated intensity determination of ^{1}H NMR spectra. DSC measurements were evaluated on a TA Q200 differential scanning calorimeter under a constant flow of a nitrogen atmosphere of 20 mL/min. The instrument was calibrated with a high-purity indium standard, and α-Al_2O_3 was used as the reference material. About 10 mg of sample was weighed into a hermetic aluminum sample pan at 25 °C, which was then sealed, and the sample was tested immediately. The dynamic scanning experiments ranged from 30 to 350 °C at heating rates of 20 °C/min. Thermogravimetric analysis (TGA) was done with TA Instruments Q 50 at a heating rate of 20 °C/min from 30 to 800 °C under nitrogen atmosphere at a flow rate of 60 mL/min.

2.4. Curing of benzoxazine monomers

All the fluorene-based benzoxazines were polymerized without initiator or catalyst according to the followings schedule: 180 °C/2 h, 200 °C/2 h, 230 °C/2 h, and 260 °C/2 h with the pressure of 0.1 MPa. The following abbreviations will be used for this series of polybenzoxazines: poly(B-pbf), poly(B-mpbf), poly(B-bbf), and poly(B-obf) for aniline, *o*-toluidine, *n*-butylamine and *n*-octylamine, respectively.

3. Results and discussion

3.1. Synthesis and structure of the benzoxazine monomers

The synthesis of biphenol fluorene baesd benzoxazine monomers is presented in Scheme 1 according to the traditional solvent method. Since solubility of BHPF in nonpolar solvents such as 1,4-dioxane or chloroform is very limited, the mixed solvents of 1,4-dioxane and ethanol were used in the reaction process. Ishida and Low verified that nonpolar solvents, for example, chloroform, carbon tetrachloride, dioxane, or *n*-hexane, help ring closure of the open Mannich base, and reduce the chances of ring opening [39]. In this work, the yields of all fluorene-based benzoxazine monomers are lower than 60% while the volume ratio of ethanol and 1,4-dioxane is 1:1. The reasons may be attributed to the disadvantageous effect of polar solvent and great steric hindrance of bulky fluorenyl group on the formation of oxazine ring. The peaks located at approximately 3.7 ppm corresponding to the ring opening of benzoxazine are observed in ^{1}H NMR spectra, revealing the presence of dimers and oligomeric compounds.

The structure of the monomers was confirmed by FT-IR, ^{1}H and ^{13}C NMR. Fig. 1 shows the FT-IR spectra of all monomers. The absorption bands assigned to the out-of-plane

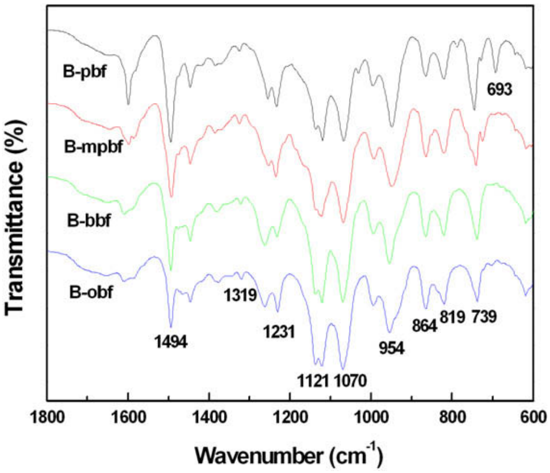


Fig. 1. FT-IR spectra of the fluorene-based benzoxazine monomers.

bending vibrations of C–H located at 949–955 cm^{-1} are due to the characteristic mode of benzene with an attached oxazine ring [12,22]. Also the asymmetric and symmetric stretching vibrations of C–O–C located at 1231–1235 cm^{-1} and 1068–1070 cm^{-1} and the asymmetric and symmetric stretching vibrations of C–N–C located at 1120–1123 cm^{-1} and around 865 cm^{-1} are observed, indicating that monomers containing benzoxazine structure are obtained [40]. The very strong and sharp bands at 1493–1495 cm^{-1} and the medium intensity bands at around 820 cm^{-1} are corresponded to the C–H in-plane and out-of-plane bending mode of the tri-substituted benzene ring. The absorption bands at 739–746 cm^{-1} are attributed to the C–H out-of-plane bending mode of the *ortho*-disubstituted benzene of fluorene ring and *ortho*-methylphenyl group [11–13,17]. For B-pbf, the absorption bands at 746 and 693 cm^{-1} are assigned to the mode of mono-substituted benzene [18].

The ^{1}H and ^{13}C NMR spectra were also measured to confirm the structure (Figs. 2 and 3). The aromatic protons are observed at 6.66–7.79 ppm. The characteristic peaks assigned to methylene (O–CH_2–N) and methylene (Ar–CH_2–C) of oxazine ring for the aromatic amine-based benzoxazines appear at 5.16–5.32 and at 4.27–4.50 ppm, respectively, and for aliphatic amine-based benzoxazines appear at about 4.82 and 3.85 ppm, respectively. The methyl proton of B-mpbf shows peaks at 2.34 ppm. Also, the methyl and methylene protons of B-bbf and B-obf appear at 0.91–2.72 ppm, confirming the formation of precursor [41].

In ^{13}C NMR spectra of benzoxazines, the resonances below 40, 40–90, and 110–160 ppm are assigned to the methyl carbons, the methylene carbons, and the aromatic carbons, respectively [42]. The chemical shifts located at 78.6–82.3 ppm are attributed to the carbon atom resonances of O–CH$_2$–N of oxazine rings. The characteristic peaks of Ar–CH$_2$–N for the aromatic and aliphatic amine-based benzoxazines locate at 50.2–50.9 and 51.2–51.5 ppm, respectively. The peaks at 63.8–64.3 ppm are assigned to the quaternary carbon atom of fluorene ring, and other peaks of fluorene ring are consistent with references [38,43], further confirming the successful synthesis of the fluorene-based benzoxazine monomers.

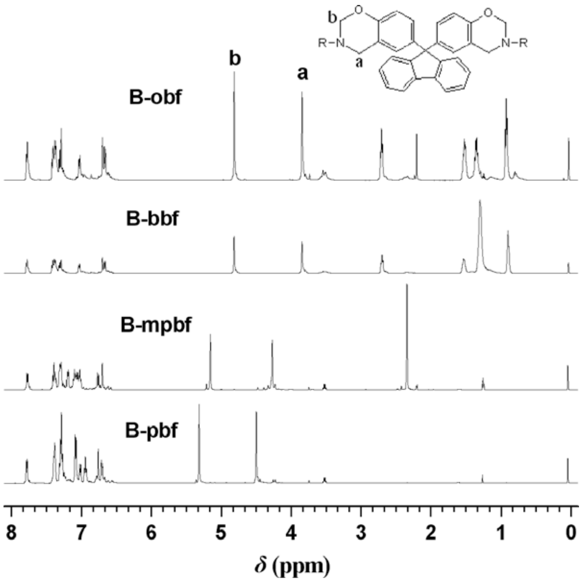


Fig. 2. ^{1}H NMR spectra of the fluorene-based benzoxazine monomers.

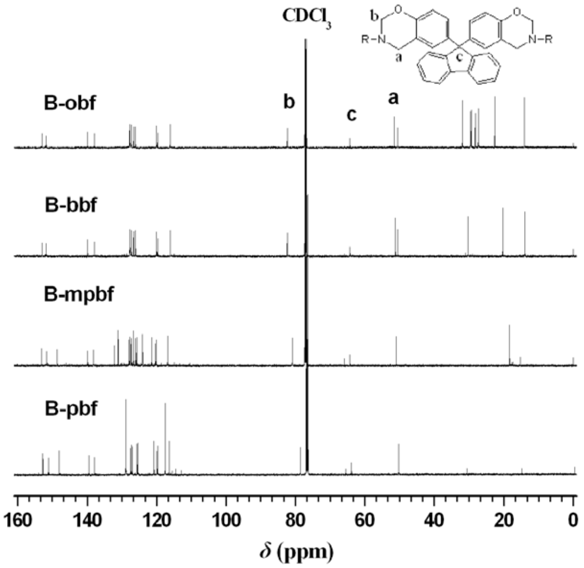


Fig. 3. ^{13}C NMR spectra of the fluorene-based benzoxazine monomers.

3.2. Curing behavior of the benzoxazine monomers

The curing behavior of the novel fluorene-based benzoxazine monomers was studied by DSC and FT-IR. The non-isothermal DSC thermograms and FT-IR spectra of these monomers are shown in Figs. 4 and 5. According to the previous work, 1,3-benzoxazines exhibited exothermic ring-opening reaction around 200–250 °C. For typical bisphenol A–aniline based polybenzoxazine (BA-a), it

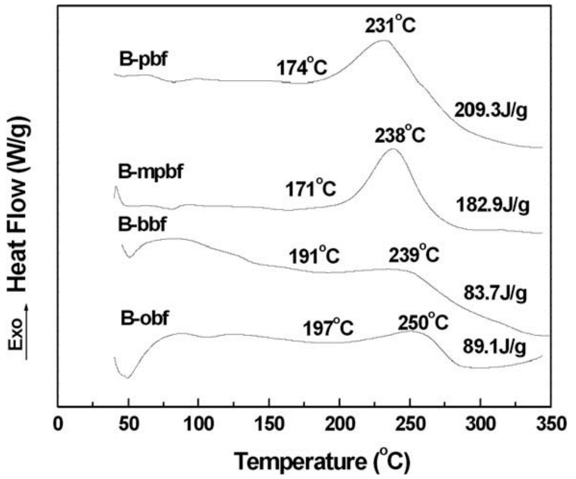


Fig. 4. DSC thermograms of the fluorene-based benzoxazine monomers.

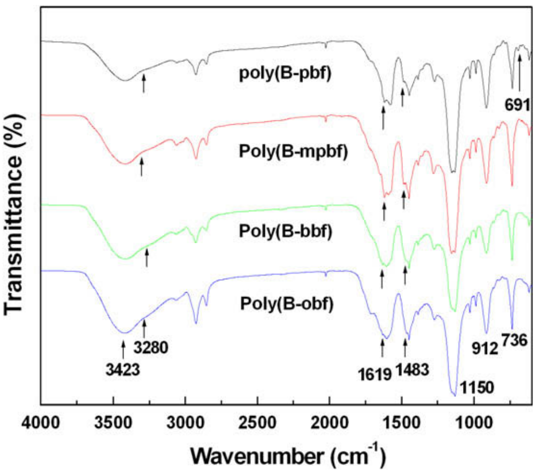


Fig. 5. FT-IR spectra of the fluorene-based polybenzoxazine after curing at 260 °C.

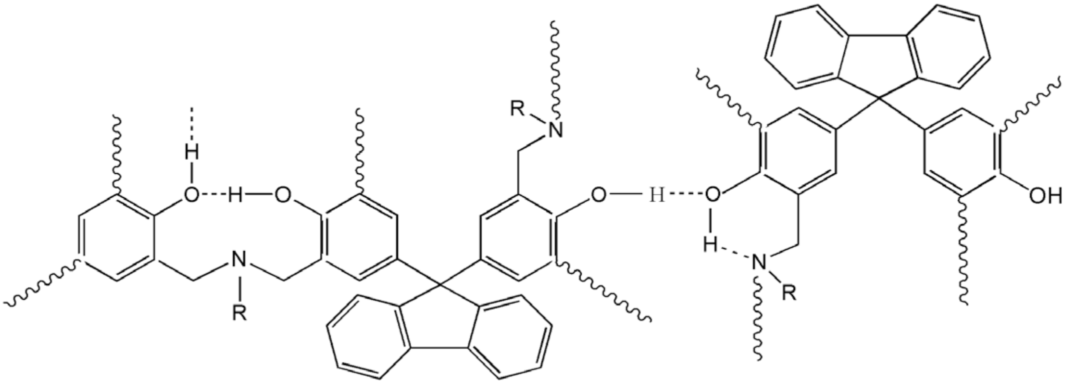
showed a sharp exotherm starting at about 220 °C with a maximum at 243 °C due to the ring-opening polymerization of the cyclic benzoxazine structure. As can be seen from Fig. 4, the DSC thermograms of the fluorene-based benzoxazine monomers show a curing exotherm with a peak located at 231–250 °C, which are the typical thermal curing characteristic of oxazine ring opening. The broad exotherms with an onset at a lower temperature than that of BA-a are observed. This shift of the cure exotherm to a lower temperature may be attributed to the presence of small amount of phenolic hydroxyl group derived from the ring opening of benzoxazine. Furthermore, the amount of exotherm of B-pbf and B-mpbf is 209 and 183 J/g, respectively, and is much greater than that of B-bbf and B-obf. The difference observed for the amount of exotherm is probably due to the difference of the molecular weights, and aliphatic and aromatic nature [44].

The IR spectra of the fluorene-based polybenzoxazines after the cure at 260 °C are depicted in Fig. 5. The characteristic absorption bands due to the benzoxazine structure at 949–955 cm^{-1} (vibrational mode of cyclic C–O–C), the asymmetric and symmetric stretching mode of C–O–C, CH_2 wagging at 1319–1327 cm^{-1}, and tri-substituted benzene ring around 1495 and 820 cm^{-1} completely disappear, indicating the completion of ring-opening at this stage. Meanwhile, the very strong bands assigned to the asymmetric stretching mode of C–N–C shift around 1150 cm^{-1}. The new absorptions appear around 1485 and 1620 cm^{-1}, which are ascribed to tetra-substituted benzene ring and intramolecular hydrogen bonded phenolic OH [45,46]. These indicate that the Mannich bridge linkage and phenolic hydroxyl groups were produced by the ring-opening polymerization of the fluorene-based benzoxazine monomers at elevated temperature. According to the reports by Ishida and coworkers, the network structure of the polybenzoxazine mainly consists of $O^-\cdots H^+N$ (around 2830 cm^{-1}), –OH···N (around 3170 cm^{-1}), –OH···O (around 3460 cm^{-1}), and –OH···π (around 3550 cm^{-1}) intramolecular hydrogen bonding and –OH···O (3330–3380 cm^{-1}) intermolecular hydrogen bonding [47,48]. From FT-IR spectra in Fig. 5, the broad bands appear around 3420 cm^{-1} with a shoulder near 3280 cm^{-1}, it implies the possibility of overlapped intramolecular (–OH···N and –OH···O) and intermolecular (–OH···O) hydrogen bonding exists in the network structure of fluorene-based polybenzoxazines, and the large portion of hydroxyl groups forms either –OH···O and weak –OH···N intramolecular hydrogen bonding or –OH···O intermolecular hydrogen bonding. The network structure of the fluorene-based polybenzoxazines is proposed in Scheme 2.

3.3. Glass transition temperature of the polybenzoxazines

The glass transition temperature (T_g) is affected both by the backbone rigidity of the polymers and by crosslink density. The T_g of the cured polymers can be elevated drastically by introducing some rigid groups into the backbone of polymers or by increasing crosslink density of cured polymer [32]. The T_gs of fluorene-based polybenzoxazines were obtained by DSC, and shown in Fig. 6.

As shown in Fig. 6, the T_g values of poly(B-pbf), poly(B-mpbf), poly(B-bbf), and poly(B-obf), which are 228.9, 225.6, 215.2, and 202.8 °C, respectively, are higher than that of the BA-a (around 171 °C by DMA) [41]. The results are mainly attributed to the higher rigidity of fluorene skeleton in the chain backbone, which restrains the internal rotations and thermal motion of polymer segments [32,43]. In addition, the tighter packing of the polymer chains due to the strong intermolecular and intramolecular hydrogen bonding has significant influence on the T_g of the fluorene containing polybenzoxazines, which confines segmental mobility and contributes to a rigidity of the polymer chains [47,49]. The aromatic amine-based polybenzoxazines are more chemically cross-linked and have tighter packing than the linear aliphatic amine-based polybenzoxazines [50]. As a result, the T_g values of poly(B-pbf) and poly(B-mpbf) are higher than that of poly(B-bbf) and poly(B-obf). The T_g values of aliphatic amine-based polybenzoxazines decrease as the increases of length of the



Scheme 2. Proposed structure of the fluorene-based polybenzoxazines.

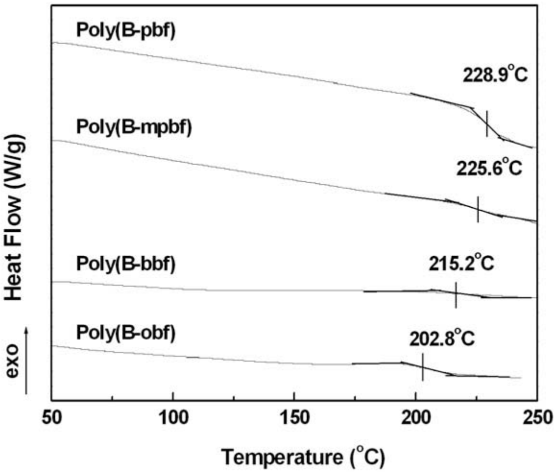


Fig. 6. DSC thermograms of the cured polybenzoxazine.

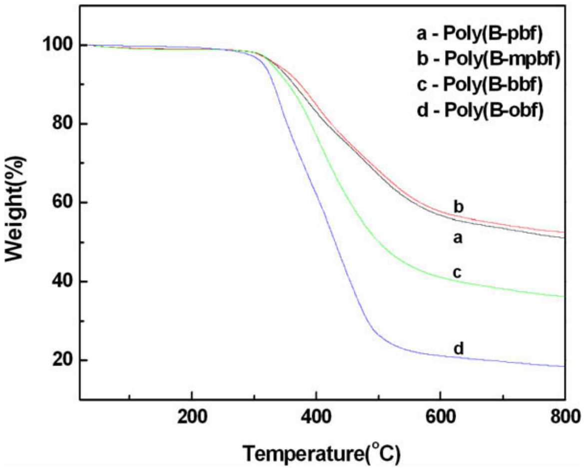


Fig. 7. TGA thermograms of the cured polybenzoxazines under nitrogen.

aliphatic chains due to the increase in mobility of the amine moiety, which agree well with the result made by Ishida and Low [51].

3.4. Thermal stability of the polybenzoxazines

Thermal stability was evaluated by thermogravimetric analyses (TGA) under nitrogen atmosphere. The weight loss and derivative weight loss curves are shown in Figs. 7 and 8, and the values of 5% and 10% weight loss temperatures (T_5 and T_{10}), the temperature of the maximum weight loss rates (T_{max}), and the char yield (Y_c) at 800 °C are summarized in Table 1. As can be clearly seen in TGA thermograms and Table 1, the T_5, T_{10}, and Y_c values of the poly(B-pbf) and poly(B-mpbf) are almost the same, and are much higher than those of poly(B-bbf), poly(B-obf), typical BA-a (310 °C, 327 °C, and 32%, respectively), and cardo bisbenzoxazines containing phenolphthalein (initial thermal decomposition temperature at 250 °C, 56–67% char yield at 550 °C) due to the high aromatic contents [16,37]. This can be explained by the fact that electron delocalization between nitrogen and benzene ring makes it more difficult to break the C–N bond between the nitrogen and phenyl group. As a result, it is more difficult to lose the phenyl group in aromatic amine-fluorene-based polybenzoxazines at a higher temperature [52].

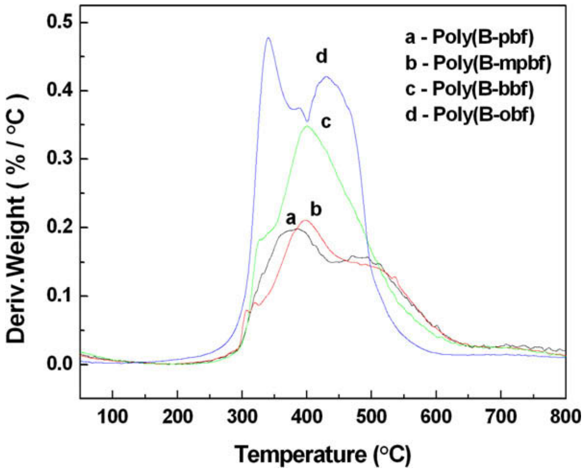


Fig. 8. Derivative weight loss for the cured polybenzoxazines under nitrogen.

Table 1
Thermal stability parameters of the polybenzoxazines.

Samples	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Y_c (%)
Poly(B-pbf)	334	364	385	51.1
Poly(B-mpbf)	337	374	399	52.1
Poly(B-bbf)	329	351	401	36.3
Poly(B-obf)	316	331	340	18.5

Poly(B-bbf) has the better thermal stability than poly(B-obf) ascribed to the shorter aliphatic chain. In spite of lower char yield, the T_5 and T_{10} values of poly(B-obf) are slightly higher than those of BA-a. This result shows that the introduction of rigid fluorene skeleton with bulky pendent cardo moieties into benzoxazine monomers can improve the inherent thermal stability of the thermosets dramatically. Furthermore, the intramolecular hydrogen bonding of the polymer chains, while intermolecular hydrogen bonds typically weaken significantly above T_g, has a tendency to stabilize the molecule [53]. These may contribute to the improvement of thermal stability of the fluorene-based polybenzoxazines. The increase in char yields suggests the reduction of evolved volatiles in the thermal degradation and depression of polymer flammability [18].

The derivative weight loss curves in Fig. 8 show that the polymers degrade in two or more stages weight loss process. From the comparison of four polymers, we observe that the amount of the weight loss of poly(B-obf) in the first step ascribed to the Mannich base cleavage at 310–340 °C is much higher than that of poly(B-pbf), poly(B-mpbf), and poly(B-bbf) due to the high content of thermally labile long aliphatic groups. The T_{max} for poly(B-obf), poly(B-pbf), poly(B-mpbf), and poly(B-bbf), which is assigned to the volatilization of phenols except poly(B-obf), is 341, 385, 399, and 401 °C, respectively. Also, the curves show the broadening of the derivative peaks, indicating a slower decomposition rate over a wider temperature range. This effect is beneficial from flammability point of view [54]. It reflects that the fluorene containing polybenzoxazines derived from aromatic amines and butylamine have the excellent thermal stability, which may be a good candidate for electronic encapsulation materials, laminate materials, high-performance composite matrices, and fire resistant materials.

4. Conclusion

Several different benzoxazine monomers have been prepared, and the thermal properties of these polymers are studied by DSC, IR and TGA. With the introduction of massive fluorenyl moieties, the cured polybenzoxazines exhibit higher glass transition temperature and thermal stability due to the high rigidity of the polymer chains and intermolecular and intramolecular hydrogen bonding. The polybenzoxazines derived from aromatic amines attributed to the high aromatic content have the better thermal stability than those derived from aliphatic amines. For aliphatic amine-based polybenzoxazines, the thermal decomposition temperature and char yield decrease as the increases of the length of aliphatic groups.

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