Synthesis and Characterization of 4,4′-Diaminodiphenyl Methane-Based Benzoxazines and Their Polymers

Weiwei Men, Zaijun Lu

School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China

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ABSTRACT: A series of diamine-based benzoxazine precursors have been prepared using 4,4′-diaminodiphenyl methane, formaldehyde, and different phenol derivatives including phenol, *p*-cresol, and 2-naphthol. Their chemical structures were identified by FTIR, ^{1}H NMR, and elemental analysis. The curing reactions of those precursors were monitored by FTIR and DSC. The obtained materials exhibited higher glass transition temperature and char yields than the corresponding bisphenol-A based polybenzoxazines. The polybenzoxazine prepared from phenol showed the highest char yields of 65% and thermal stability with 5 and 10% weight-loss temperatures at 346 and 432°C, respectively. The polybenzoxazine prepared from 2-naphthol exhibited the highest glass transition temperature at 244°C. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2769–2774, 2007

Key words: benzoxazine; diamine; synthesis; ring-opening polymerization; thermal properties

INTRODUCTION

Phenolic resins have been widely used in the construction, electronics, and aerospace fields because of their low cost and excellent properties such as heat resistance, electrical insulation, and flame retardance. However, conventional phenolic resins often release the volatiles during the curing process. This often leads to the formation of microvoids so as to harm the performance of the final materials.

In recent year, a new type of phenolic resin, called polybenzoxazine, has attracted considerable attention because of its capability to overcome the above-mentioned shortcomings. Benzoxazine precursors were first discovered as Mannich reaction products by Holly and Cope.[1] Ishida and coworkers[2–18] subsequently reported the synthesis of bisphenol A-based polybenzoxazines (Scheme 1). Kimura et al.[19–21] prepared the terpenediphenol-based benzoxazine and modified with epoxy resin or bisoxazoline. Agag et al.[22,23] prepared bisphenol A-based polybenzoxazine/inorganic hybrid nanocomposites. Liu et al.[24,25] prepared bisphenol A-based polybenzoxazines containing maleimide and furan groups.

However, all these investigations only related to the preparation of bisphenol-based polybenzoxazines. The synthesis of diamine-based polybenzoxazines has been reported only in few articles so far.[26]

In our previous works, we have synthesized diamine-based benzoxazine precursor using the phenol and prepared the glass cloth laminate. Its flexural strength is 267 MPa at 180°C, which can be comparable to bismaleimide-based glass cloth-reinforced laminate.[27]

Herein, we reported the systematical synthesis of diamine-based polybenzoxazines via varying the phenol derivatives. Specifically, 4,4′-diaminodiphenyl methane (DDM) was chosen to react with formaldehyde and a series of phenol derivatives to synthesize the diamine-based benzoxazine precursors. Subsequently, these precursors were cured into phenolic materials via ring-opening reaction initiated by heat (Scheme 2). The performance of diamine-based polybenzoxazines was also compared to bisphenol A-based polybenzoxazines.

EXPERIMENTAL

Materials

4,4′-Diaminodiphenyl methane was purified by recrystalization from ethanol. Other regents such as formaldehyde (37 wt % in water), phenol, *p*-cresol, 2-naphthol, 1,4-dioxane, and triethylamine were purchased from Shanghai Chemistry Reagent Company (Shanghai, China) and used as received.

Synthesis of 3,4-dihydro-2*H*-1,3-benzoxazine precursors

3,3′-Phenylmethanebis(3,4-dihydro-2*H*-1, 3-benzoxazine) (**1**)

To a 250-mL three-necked flask, 23.1 mL (0.3 mol) of formaldehyde aqueous solution, 14.9 g (0.075mol)

Correspondence to: Z. Lu (z.lu@sdu.edu.cn).
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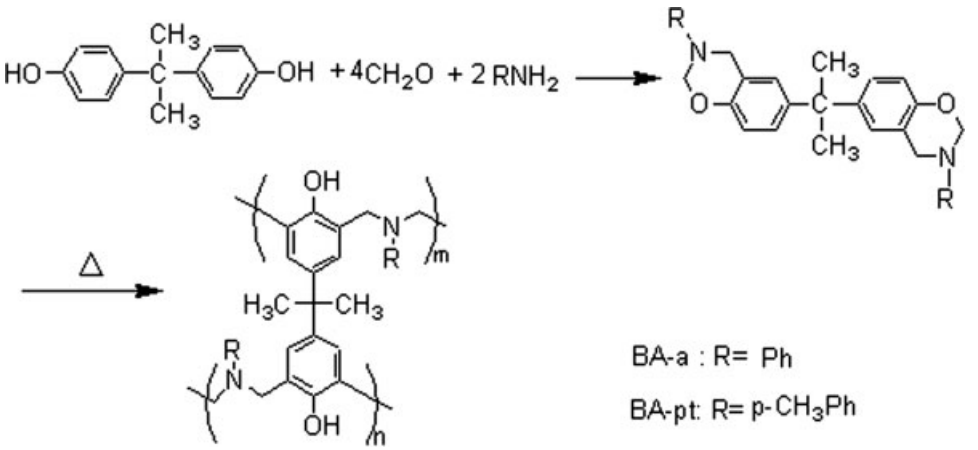


Scheme 1 Synthetic route to bisphenol A-based polybenzoxazines.

DDM, 0.7 g triethylamine, and 75 mL dioxane were added at 30°C. After 16.2 g (0.15 mol) phenol was added, the temperature was raised to reflux for 5 h. The solvent was removed with a rotary evaporator. The residual was dissolved in 50 mL dichloromethane and washed several times with distilled water. Evaporating the dichloromethane resulted in a yellowish viscous liquid.

^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.79 ppm (Ar—CH_2—Ar), 4.54 ppm (Ar—CH_2—N), 5.33 ppm (—O—CH_2—NR—), 6.64–7.13 ppm (Ar—H). FTIR (KBr) ν: 1513 and 813 cm^{-1} (para-substituted benzene); 1033 cm^{-1} (C—O—C symmetric stretching); 1226 cm^{-1} (C—O—C asymmetric stretching); 941 cm^{-1} (oxazine ring).

3,3′-Phenylmethanebis(3,4-dihydro-6-methane-2*H*-1,3-benzoxazine) (**2**)

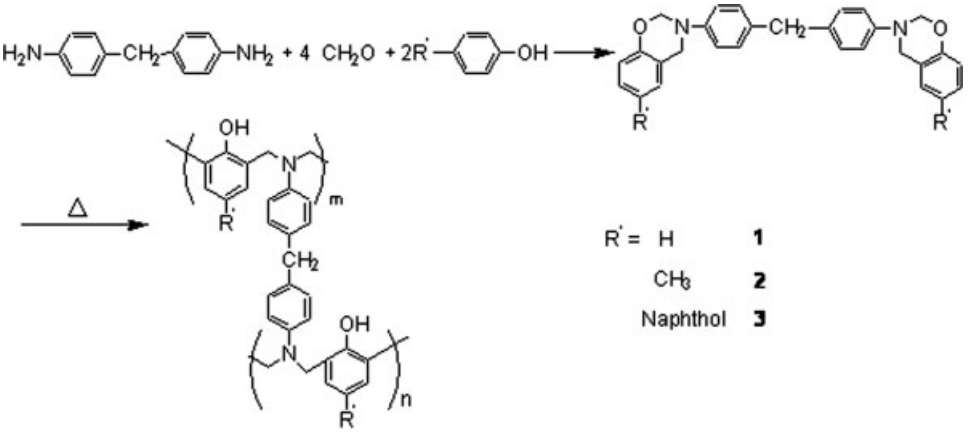
Replacing the phenol with *p*-cresol, a similar procedure was used to synthesize the precursor **2**. The purification of **2** was accomplished by washing its dichloromethane solution with 3*N* NaOH solution repeatedly. After recrystallizing from the mixture of ethanol and toluene, the white crystals were obtained in 84% yield. The melting point was 152°C.

Anal. Calcd. for $C_{31}H_{30}N_2O_2$: C, 80.52%; H, 6.49%; N, 6.06%. Found: C, 80.63%; H, 6.57%; N, 6.14%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 2.23 ppm (Ar—CH_3), 3.78 ppm (Ar—CH_2—Ar), 4.53 ppm (Ar—CH_2—N), 5.28 ppm (—O—CH_2—NR—), 6.67–7.04 ppm (Ar—H). FTIR (KBr) ν: 1516 and 815 cm^{-1} (para-substituted benzene); 1037 cm^{-1} (C—O—C symmetric stretching); 1227 cm^{-1} (C—O—C asymmetric stretching); 939 cm^{-1} (oxazine ring).

3,3′-Phenylmethanebis(3,4-dihydro-2*H*-1,3-naphthoxazine) (**3**)

Replacing the phenol with 2-naphthol, precursor **3** was obtained in 87% yield using the similar synthetic procedure of **2**. The final product was white crystals, and the melting point was 194°C.

Anal. Calcd. for $C_{37}H_{30}N_2O_2$: C, 88.10%; H, 5.95%; N, 5.56%. Found: C, 88.32%; H, 6.10%; N, 5.67%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.77 ppm



Scheme 2 Synthetic route to diamine-based polybenzoxazines.

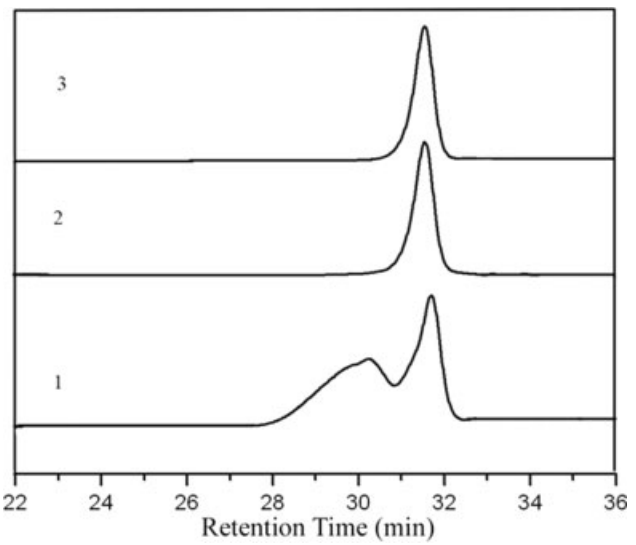


Figure 1 SEC chromatograms of benzoxazine precursor **1**, **2**, and **3**.

(Ar—CH_2—Ar), 4.88 ppm (Ar—CH_2—N), 5.35 ppm (—O—CH_2—NR—), 6.99–7.75 ppm (Ar—H). FTIR (KBr) ν: 1511 and 805 cm^{-1} (para-substituted benzene); 1057 cm^{-1} (C—O—C symmetric stretching); 1227 cm^{-1} (C—O—C asymmetric stretching); 936 cm^{-1} (oxazine ring).

Thermal curing of benzoxazine precursors

The benzoxazine precursors were heated in a rectangle stainless mold with a stepwise cure in an air-circulating oven. The step profile was as follows: 100°C for 2 h, 140°C for 2 h, 180°C for 2 h, and 200°C for 2 h.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a 20SX spectrometer using KBr pellets. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance 300 instrument. Deuterated chloroform was used as solvent and tetramethylsilane was used as an internal standard. Elemental analysis was performed with an elemental analyzer Vario EI III. Size exclusion chromatography (SEC) measurements were carried out in THF (1 mL/min) at 40°C using a Waters 515 liquid chromatography equipped with three styragel columns (HR-3, HR-4, and HR-6) and a refractive index detector. Differential scanning calorimetry (DSC) thermograms were recorded with a DSC822e instrument at a heating rate of 10°C/min under N_2 atmosphere. Thermogravimetric analysis (TGA) was performed on a TA instrument SDT Q600 at a heating rate of 10°C/min under N_2 atmosphere. The gas flow rate was 100 mL/min. Dynamic mechanical analysis (DMA) was taken on a Netzsch DMA 242 instrument, a specimen with dimensions of approximately 16 × 6 × 3 mm^3 was tested in single cantilever mode with a frequency of 1 Hz, and the sample was heated at a rate of 3°C/min from room temperature to 250°C.

RESULTS AND DISCUSSION

Synthesis and characterization of diamine-based benzoxazines

Figure 1 shows the SEC chromatograms of benzoxazine compositions of precursors **1**, **2**, and **3**. In the SEC trace of the precursor **1**, the strongest peak at 31.6 min retention time is assigned to the difunctional benzoxazine monomer. The other peaks at shorter retention times are assigned to the dimers and higher oligomers. Therefore, the precursor **1** is a mixture of benzoxazine monomers, dimmers, and higher oligomers. The quantitative amount of difunctional benzoxazine monomer in the composition can be calculated by dividing the area under the monomer peak with the whole area of the SEC chromatograph. The calculated monomer content in the precursor **1** was found to be 47%. It must be noted that the calculations yield weight percentage instead of molar percentage. **2** and **3** precursors show the narrow single peaks, suggesting that the compositions of these two precursors are only difunctional benzoxazine monomers.

Figure 2 shows the ^{1}H NMR spectra of **1**, **2**, and **3** precursors. In the ^{1}H NMR spectrum of precursor **1**, the resonances at 5.33 and 4.54 ppm correspond to the methylene protons of O—CH_2—N and

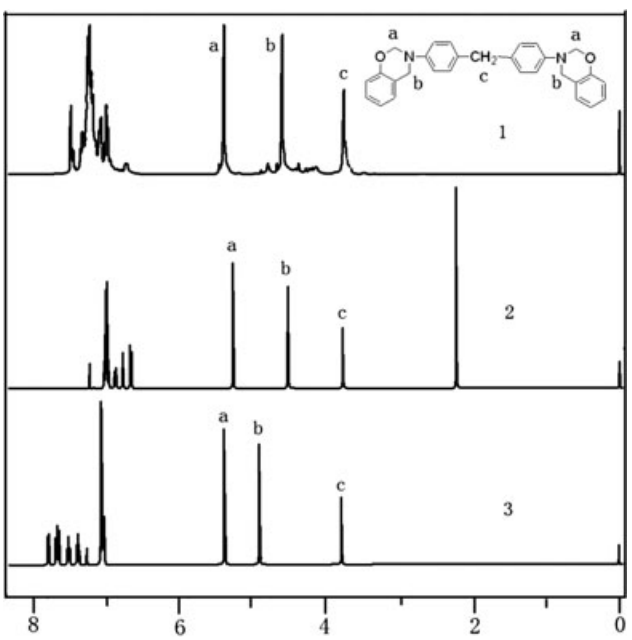


Figure 2 ^{1}H NMR spectra of **1**, **2**, and **3** precursors.

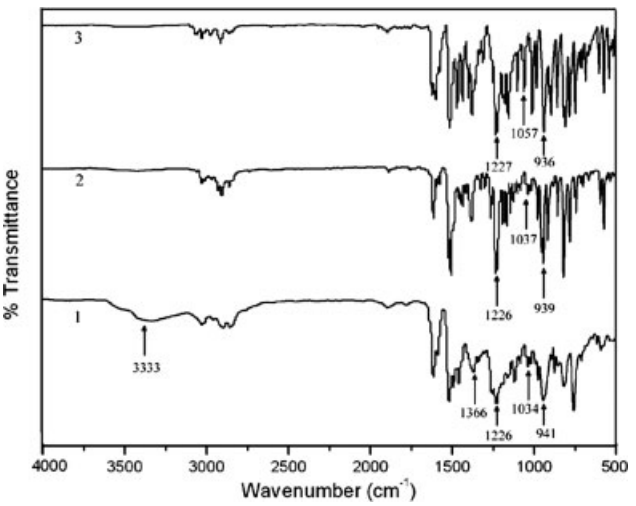


Figure 3 FTIR spectra of **1**, **2**, and **3** precursors.

Ar—CH_2—N in the oxazine ring, respectively. The resonance at 3.79 ppm corresponds to the methylene protons of Ar—CH_2—Ar. The resonances at 4.11–4.39 ppm correspond to the protons of open Mannich base, indicating the presence of dimers and higher oligomeric compounds.[14] It is known that the activating reaction site on the aromatic ring is the ortho- and para-position to the hydroxyl group.[15] When the Mannich reaction occurred at ortho-position, it formed the oxazine ring. When the reaction occurred at para-position, some byproducts containing phenolic hydroxyl groups were produced.

The oxazine ring content in the whole composition can be calculated by the following equation:

$$\text{Ring content } (\%) = I/2I' \times 100$$

where I is the integrated intensity of the methylene protons of Ar—CH_2—N in the benzoxazine ring, I' is the integrated intensity of the methylene protons of Ar—CH_2—Ar. The ring content thus determined for precursor **1** is 65%.

In the ^{1}H NMR spectra of **2** and **3** precursors, the characteristic resonances of the methylene protons in the oxazine ring are observed at 5.28, 4.53 ppm, and 5.35, 4.88 ppm, respectively. The ring contents thus determined are both quantitative. This is because the para-positions of the *p*-cresol and 2-naphthol are substituted. The Mannich reaction can only occur at ortho-positions, which is prone to form the oxazine ring.

Figure 3 shows the FTIR spectra of **1**, **2**, and **3** precursors. In the FTIR spectrum of precursor **1,** the characteristic absorption band at 941 cm^{-1} corresponding to the oxazine ring was observed. The absorption bands at 1226 and 1034 cm^{-1} correspond to the asymmetric and symmetric stretching of C—O—C. The absorption band at 1366 cm^{-1} was assigned to the C—N.[28] In addition, an absorption band at 3333 cm^{-1} due to phenolic hydroxyl groups was also observed, suggesting the presence of the dimers and higher oligomeric compounds in precursor **1**.

The FTIR spectra of **2** and **3** precursors also exhibited the similar characteristic absorption bands to the precursor **1**. The absorption bands of oxazine ring appeared at 936 and 939 cm^{-1}, and the absorption bands of asymmetric and symmetric stretching of C—O—C appeared at 1226, 1037 cm^{-1} and 1227, 1057 cm^{-1}, respectively.

Polymerization of the benzoxazine precursors

The thermal curing reactions of precursors **1**, **2**, and **3** were studied by DSC (Fig. 4). The precursors **2** and **3** showed endothermic melting peaks at 155 and 193°C, respectively. The exothermic peaks of the ring-opening polymerization for precursors **2** and **3** centered at 265 and 256°C were observed, respectively. Comparing with **2** and **3**, the precursor **1** showed a much lower and broader exothermic peak. The onset exothermic temperature was at about 115°C, and the maximum exothermic temperature was at 226°C. Therefore, the thermal polymerization temperature of the precursor **1** was much lower than the polymerization temperatures of precursors **2** and **3**.

The reason for this phenomenon is that the ring-opening polymerization of precursors **2** and **3** are thermally self-dissociation, which needs high temperature. However, the precursor **1** is a mixture containing phenolic structures with free ortho-positions. Riess et al.[29] have already proved that the phenols with free ortho-position functioned as initiators in the oligomerization of benzoxazine compounds, thus the curing induction time of benzoxazine precursor

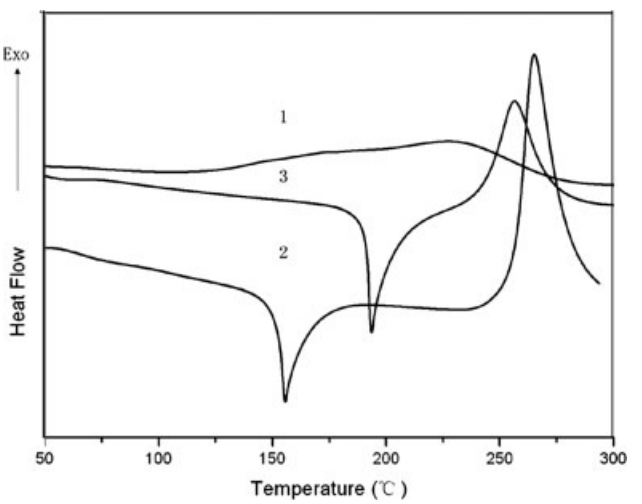


Figure 4 DSC thermograms of precursor **1**, **2**, and **3** cures.

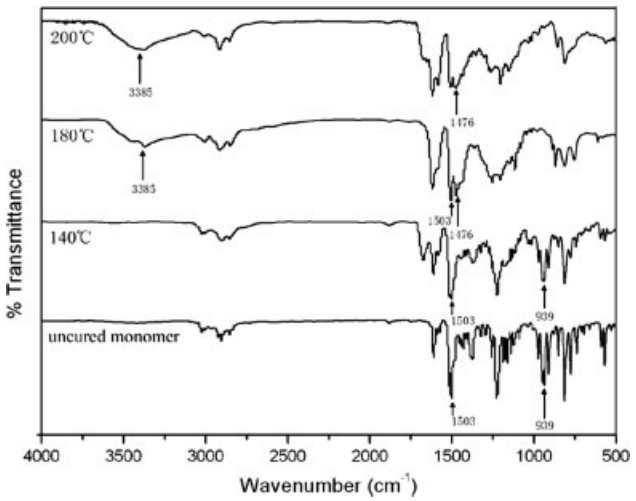


Figure 5 FTIR spectra of precursor **2** after each cure stage.

can be reduced and the reaction rate can be accelerated. As a result, the curing reaction of precursor **1** occurred at lower temperature.

To avoid the effects of byproducts on the polymerization, we chose the purified precursor **2** as the curing sample. The thermal curing reaction was monitored with FTIR (Fig. 5). After curing at 140°C for 2 h, the intensities of characteristic absorption bands at 939 cm^{-1} due to the benzoxazine ring and at

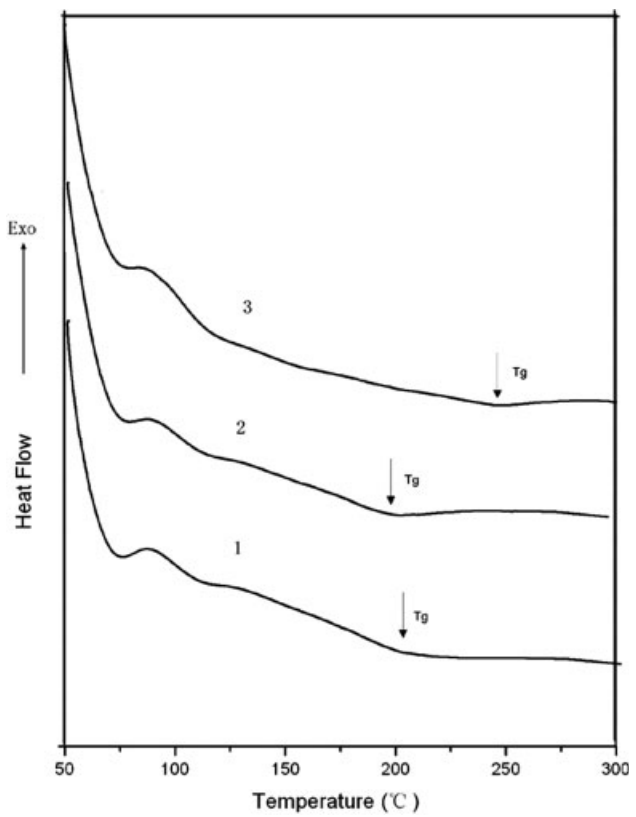


Figure 6 DSC thermograms of polybenzoxazines **1**, **2**, and **3**.

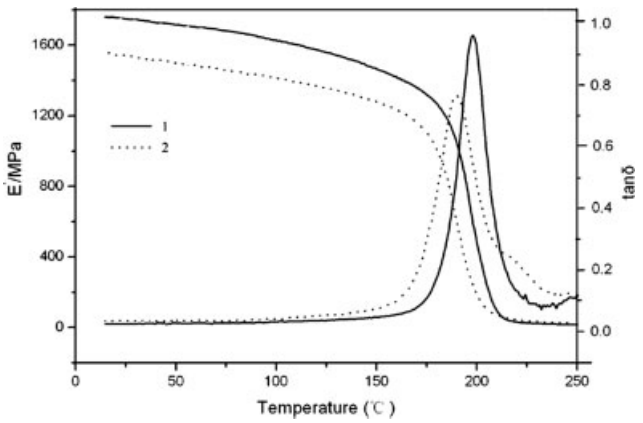


Figure 7 DMA spectra of polybenzoxazines **1** and **2**.

1503 cm^{-1} due to trisubstituted benzene ring were unchanged, suggesting that the ring-opening polymerization did not occur at this stage. When the sample was further cured at 180°C for another 2 h, the absorption bands at 939 cm^{-1} nearly disappeared. The intensity of absorption bands at 1503 cm^{-1} due to the trisubstituted benzene ring decreased. On the other hand, some new absorption bands at 3385 cm^{-1} due to the phenolic hydroxy and at 1476 cm^{-1} due to the tetrasubstituted benzene ring appeared, suggesting that the ring-opening polymerization of benzoxazine precursors occurred and afforded polybenzoxazines. While the sample was postcured at 200°C for 2 h, the intensities of the absorption bands at 1476 and 3385 cm^{-1} increased, indicating the cross-linking reaction further performed and the crosslink density of polybenzoxazine increased.

Thermal properties of polybenzoxazines

The DSC, DMA, and TGA thermograms of polybenzoxazines prepared from **1**, **2**, and **3** are shown in Figures 6–8. The results are summarized in Table I.

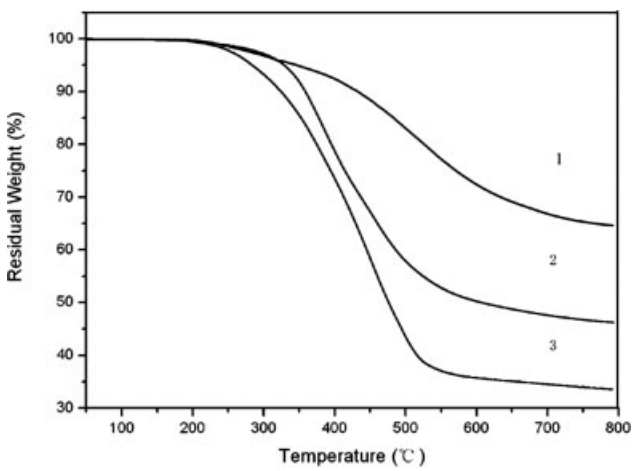


Figure 8 TGA curves of polybenzoxazines **1**, **2**, and **3**.

TABLE I
Thermal Property of the Polybenzoxazines

	1	2	3	PBA-a[14]	PBA-pt[14]
T_g[a] (°C)	205	195	244	168	158
T_g[b] (°C)	198	190	–[c]	–	–
5% Weight loss (°C)	346	329	284	315	305
10% Weight loss (°C)	432	359	324	348	330
Char yield (% at 800°C)	65	47	34	30	32

[a] Measured by DSC.
[b] Measured by DMA.
[c] The sample was too brittle to be measured by DMA.

The diamine-based polybenzoxazines exhibit the higher T_g than the corresponding bisphenol-A-based polybenzoxazines. The reason might be that the motion of segments in diamine-based polybenzoxazines was more difficult than in bisphenol-based polybenzoxazines, since the crosslinking structures between them are different.

The polybenzoxazine **1** is the highest thermally stable polymer, with the 5 and 10% weight-loss temperatures at 346 and 432°C, respectively. In addition, the polybenzoxazine **1** also exhibit the highest char yield of 65% at 800°C under N_2.

CONCLUSIONS

Three benzoxazine precursors **1**, **2**, and **3**, based on 4,4′-diaminodiphenyl methane were successfully prepared. The precursors were thermally cured through ring-opening reactions to form crosslinked phenolic structures. The composition of the precursor **1** consists of difunctional benzoxazine monomers, dimmers, and higher oligomers containing phenolic hydroxyl structures. The difunctional benzoxazine monomer content in precursor **1** calculated from SEC chromatogram is 47%. The oxazine ring content in precursor **1** calculated from ^{1}H NMR spectrum is 65%. The polymerization temperature of precursor **1** is much lower than polymerization temperatures of precursor **2** and **3** because of the presence of catalytic phenolic hydroxyl groups. The obtained polybenzoxazines exhibited the higher T_g and char yields than the corresponding bisphenol-A-based polybenzoxazines. Among these three polymers, the polybenzoxazine **3** showed the highest T_g at 244°C. The polybenzoxazine **1** showed the highest char yields of 65% and thermal stability with 5 and 10% weight-loss temperatures at 346 and 432°C, respectively.

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