

# Synthesis and Characterization of Bisphenol A Diphthalimide Bisbenzoxazine Monomers and the Properties of Their Polybenzoxazines

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**ABSTRACT:** Three bisphenol A diphthalimide bisbenzoxazine monomers were successfully synthesized through a two-step procedure. First, a new bihydric phenol, bishydroxyphenyl bisphenol A diphthalimide, was prepared from bisphenol A dianhydride and 4-aminophenol. Then, different bisphenol A diphthalimide bisbenzoxazine monomers were synthesized from bishydroxyphenyl bisphenol A diphthalimide, paraformaldehyde, and various amines, such as aniline, allylamine, and 3-aminophenylacetylene. The chemical structures and compositions of the novel monomers were identified by proton nuclear magnetic resonance, Fourier transform infrared spectroscopy, and elemental analysis. The curing behavior of the three monomers after various thermal treat-

ments was investigated by differential scanning calorimetry and Fourier transform infrared analysis. The polybenzoxazines from the three monomers had excellent high-temperature properties demonstrated by dynamic mechanical analysis. The thermal stabilities of the three polybenzoxazines were also studied by thermogravimetric analysis. The results revealed that the 5 and 10% weight loss temperatures were as high as over 360 and 405°C, respectively, and the char yields at 800°C were 41 to 61%, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2778–2787, 2011

**Key words:** benzoxazine; bisphenol A diphthalimide; crosslinking; thermal stability; thermosets

## INTRODUCTION

Polybenzoxazines, obtained by the ring-opening polymerization of benzoxazine monomers, have been investigated and developed recently as a new type of thermosetting phenolic resin.<sup>1,2</sup> They have not only the typical properties of traditional phenolic resins, such as the excellent thermal properties and flame retardance,<sup>3</sup> but also unique characteristics, such as nearly zero shrinkage or expansion upon polymerization<sup>4–6</sup> and low water absorption.<sup>7</sup> Therefore, they overcome the flaws of traditional phenolic resins. Benzoxazine monomers can be easily synthesized with phenols, formaldehyde, and primary amines by either solution or solventless methods.<sup>8,9</sup> Polybenzoxazines can be formed by the thermally activated ring opening of benzoxazines without any

catalysts, and no byproducts or volatiles are released.<sup>2,10–12</sup> The variation of raw materials allows flexible design at the molecular level to synthesize benzoxazine monomers; this is important for meeting the specific requirements of various applications. However, there are still some disadvantages for polybenzoxazines derived from the typical monofunctional and bifunctional benzoxazines 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine and bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane. For example, these polybenzoxazines are quite brittle, and the polymerization temperature is relatively high. The glass transition temperatures of poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) and poly-[bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane] (PBa) are 161 and 185°C,<sup>13,14</sup> respectively, which is still too low for high-temperature applications. Further enhancement of the properties of typical polybenzoxazines is, therefore, desirable.

Some approaches enable one to improve the performance of polybenzoxazine for (1) enhancing the toughness of polybenzoxazines through blending with elastomers,<sup>15–17</sup> (2) reinforcing polybenzoxazines with inorganic materials<sup>18–21</sup> or fibers,<sup>22–25</sup> and (3) improving the thermal stability of polybenzoxazines through blending with high-performance

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polymers<sup>26,27</sup> or introducing other polymerizable groups, such as ethynyl or phenyl ethynyl,<sup>28–30</sup> nitrile,<sup>31–34</sup> propargyl groups,<sup>35</sup> and allyl group,<sup>36–40</sup> into the benzoxazine structure. These functional groups form highly crosslinking network structures after curing. Thus, the glass-transition temperature ( $T_g$ ) and the thermal decomposition temperature of the polybenzoxazines would be improved significantly compared with typical polybenzoxazines.

Polyimides are considered to be high-performance polymers containing imide moieties in the molecular backbone. They have a unique temperature stability, high mechanical performance, and excellent chemical resistance. By taking advantage of the molecular design flexibility, researchers have synthesized benzoxazine monomers with imide moieties, named *imide benzoxazines*, and the properties of their polybenzoxazines were investigated in a previous study. The imide moieties were introduced into benzoxazines to improve their heat resistance.<sup>41</sup> A series of benzoxazine and benzylamine-type intermediates were synthesized from hexamethylenetetramine and *N*-(hydroxyphenyl)succinimides, and their structures were investigated.<sup>42</sup> Maleimidobenzoxazines were synthesized from hydroxyphenylmaleimide (HPMI), formalin, and various amines.<sup>13</sup> The effect of HPMI on the curing behavior and thermomechanical properties of rubber-modified polybenzoxazine were also studied.<sup>43</sup> The thermal and mechanical properties were enhanced through the polymerization of HPMI with a benzoxazine monomer or by the incorporation of HPMI into amine-terminated butadiene acrylonitrile rubber(ATBN)-modified PBa. A benzoxazine compound was prepared with a maleimide group, 3-phenyl-3,4-dihydro-2H-6-(*N*-maleimido)-1,3-benzoxazine, from *N*-(4-hydroxyphenyl) maleimide, formaldehyde, and aniline.<sup>44</sup> The completely cured polymer exhibited good thermal stability and flame retardancy. Maleimide and norbornene-functionalized benzoxazines were synthesized,<sup>45</sup> and the polybenzoxazines from these benzoxazine monomers had char yields above 55% and  $T_g$  values above 250°C. These polybenzoxazines had excellent thermomechanical properties and thermal stability, superior to those of traditional phenolics, epoxies, or most of high-performance thermoplastics.

In this study, three bisphenol A diphthalimide bisbenzoxazine monomers were designed and expected to produce polymers with superior properties to the traditional polybenzoxazine. The designed monomers, containing other types of polymerizable groups, such as allyl and ethynyl groups, were expected to improve the thermal stability of the polymers. The three bisphenol A diphthalimide bisbenzoxazine monomers were synthesized through a two-step procedure. First, a new bihydric phenol, bishydroxyphenyl bisphenol A diphthalimide

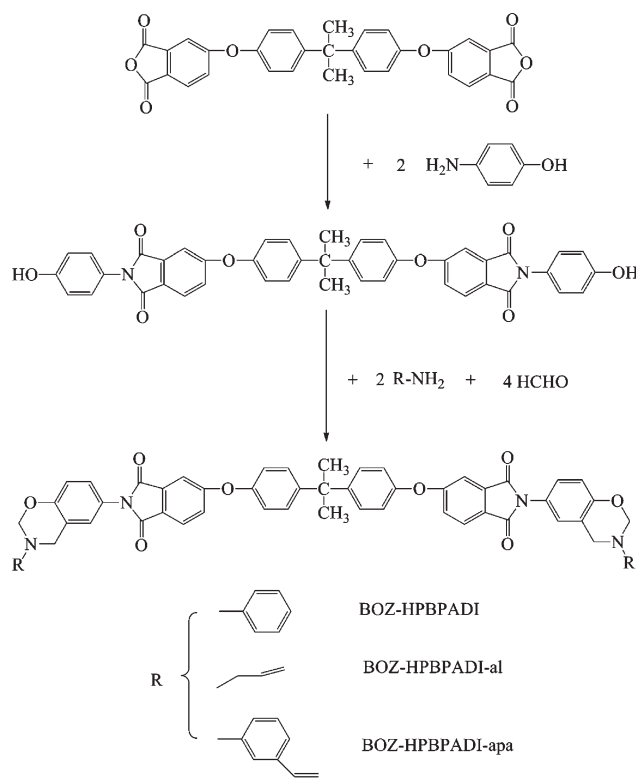
(HPBPADI), was prepared from bisphenol A dianhydride (BPADA) and 4-aminophenol. Then, different bisphenol A diphthalimide bisbenzoxazine monomers were synthesized from HPBPADI, paraformaldehyde, and one of three amines, aniline, allylamine, and 3-aminophenylacetylene. The structures of the novel monomers were identified by proton nuclear magnetic resonance (<sup>1</sup>H-NMR), Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. The curing behavior of the new monomers after various thermal treatments was investigated by differential scanning calorimetry (DSC) and FTIR analysis. The thermal mechanical properties and thermal stability of the novel polybenzoxazines were also investigated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

## EXPERIMENTAL

### Materials and characterization

BPADA was obtained from Shanghai Research Institute of Synthetic Resins (Shanghai, China). 4-Aminophenol (98%), 3-aminophenylacetylene, and allylamine were from Aladdin Reagent (Shanghai, China). Aniline (99%), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), chloroform, toluene, *N*-methyl-2-pyrrolidone, and paraformaldehyde (95%) from Sinopharm Chemical Reagent (Shanghai, China). All chemicals were used as received.

The <sup>1</sup>H-NMR spectra, used to identify the structures of the monomers, were recorded on a Bruker Avance III (400-MHz) instrument (Fällanden, Switzerland). All resonances were referenced with respect to the proton signal of tetramethylsilane. FTIR spectra were recorded at a resolution of 4 cm<sup>-1</sup> with the co-addition of 32 scans on a Thermo-Fisher Nicolet 6700 FTIR (Massachusetts, USA). All samples were prepared as KBr pellets. The quantitative element analysis of C, H, and N was carried out on a Horiba EMGA-620W oxygen/nitrogen analyzer (Massachusetts, USA). DSC was conducted on a Mettler Toledo DSC1 (Zurich, Switzerland) at a heating rate of 10°C/min over the temperature range 50–350°C under a nitrogen flowing atmosphere. DMA of the polybenzoxazine films was performed on a Mettler Toledo Star<sup>e</sup> System DMA/SDTA861<sup>e</sup> instrument (Zurich, Switzerland). The film specimens, which were about 10.5 × 4 × 0.4 mm<sup>3</sup>, were tested in tension mode over the temperatures range 30–350°C. The heating rate and dynamic frequency were 5°C/min and 1.0 Hz, respectively. TGA was carried out on a Mettler Toledo TGA/DSC1 (Zurich, Switzerland) with a heating rate of 10°C/min over the temperature range 50–1000°C under a nitrogen flow at a rate of 30 mL/min.



**Figure 1** Synthesis of the bisphenol A diphthalimide bisbenzoxazine monomers.

### Synthesis of three benzoxazine monomers

Three bisphenol A diphthalimide bisbenzoxazine monomers were synthesized through a two-step procedure. First, an intermediate bihydric phenol (HPBPADI) was prepared from BPADA and 4-aminophenol. Second, the three bisphenol A diphthalimide bisbenzoxazine monomers were obtained through the reaction of HPBPADI, paraformaldehyde, and three amines, aniline, allylamine, and 3-aminophenylacetylene. The three monomers, bis[3-phenyl-2,4-dihydro-2H-1,3-benzoxazinyl] bisphenol A diphthalimide (BOZ-HPBPADI), bis[3-allyl-2,4-dihydro-2H-1,3-benzoxazinyl] bisphenol A diphthalimide (BOZ-HPBPADI-al), and bis[3-(3-phenylacetylene)-2,4-dihydro-2H-1,3-benzoxazinyl] bisphenol A

diphthalimide (BOZ-HPBPADI-apa), were produced, as shown in Figure 1.

### Synthesis of the intermediate bihydric phenol HPBPADI

BPADA (5.2 g, 10 mmol) and *p*-aminophenol (2.18 g, 20 mmol) were dissolved in 50 mL of glacial acetic acid in a 100-mL, three-necked, round-bottom flask at ambient temperature. The mixture was then stirred at 140°C for 24 h in an oil bath, and a white precipitate was obtained. The precipitate was washed by glacial acetic acid and then dried in a vacuum chamber at 120°C for 24 h. The final product was white crystals of 6.17 g (88%), with a melting point of 272°C. The HPBPADI product could be dissolved in DMF, DMAc, and DMSO but not in chloroform or toluene.

<sup>1</sup>H-NMR for HPBPADI (400 MHz, DMSO-*d*<sub>6</sub>, 298 K,  $\delta$ , ppm): 1.71 (s, 6H, 2CH<sub>3</sub>), 6.85–7.94 (20H, Ar), 9.73 (s, 2H, 2OH).

### Synthesis of the bisphenol A diphthalimide bisbenzoxazine monomers

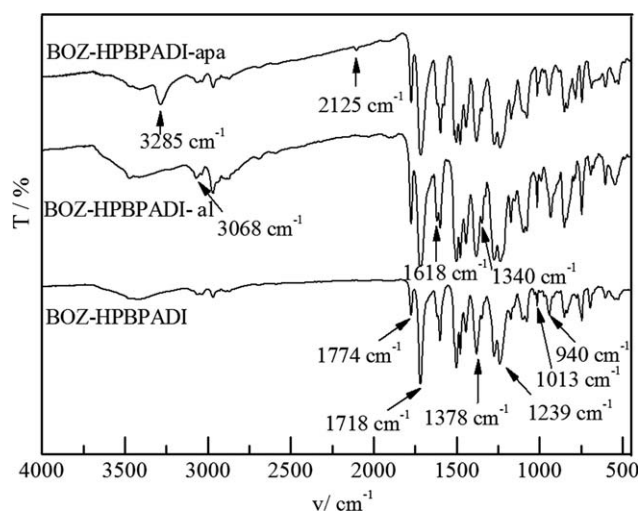
Three bisphenol A diphthalimide bisbenzoxazine monomers were synthesized by the same method: HPBPADI (10 mmol), paraformaldehyde (40 mmol), and one each amine of the three (20 mmol) were mixed in DMF (50 mL) and stirred at 105°C for 48 h. The products were precipitated into distilled water, and the precipitates were washed with ethanol at least three times and then vacuum-dried. The melting points of the three synthesized monomers tested by DSC and the results of their elemental analyses are listed in Table I.

### Preparation of the polybenzoxazines

The monomers were polymerized into polybenzoxazine films with thicknesses of 0.3–0.5 mm in the following procedure: (1) the monomers were dissolved in *N*-methyl-2-pyrrolidone (10 wt %), (2) the solutions were cast onto glass plates and kept at 70°C

**TABLE I**  
Yields, Melting Points, and Elemental Analyses of the Three Benzoxazine Monomers

Monomer	BOZ-HPBPADI	BOZ-HPBPADI-al	BOZ-HPBPADI-apa	
Molecular formula	C <sub>59</sub> H <sub>44</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>53</sub> H <sub>44</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>63</sub> H <sub>44</sub> N <sub>4</sub> O <sub>8</sub>	
Appearance	Yellow powder	Yellow powder	Brown powder	
Yield (%)	80	75	78	
Melting point (°C)	130	126	134	
Theoretical value				
	C (%)	75.63	73.60	76.82
	H (%)	4.73	5.13	4.50
	N (%)	5.98	6.48	5.69
Experimental value				
	C (%)	74.99	73.88	76.18
	H (%)	5.62	5.49	5.20
	N (%)	6.57	6.42	6.23



**Figure 2** FTIR spectra of the monomers ( $T$  = transmittance,  $\nu$  = wave number).

for 10 h for solvent evaporations, and (3) the resulting films were cured at 150°C for 5 h, 180°C for 4 h, 200°C for 3 h, 220°C for 2 h, and 250°C for 2 h subsequently. The films were then released from the glass plates in a water bath at ambient temperature and vacuum-dried at 100°C for 24 h.

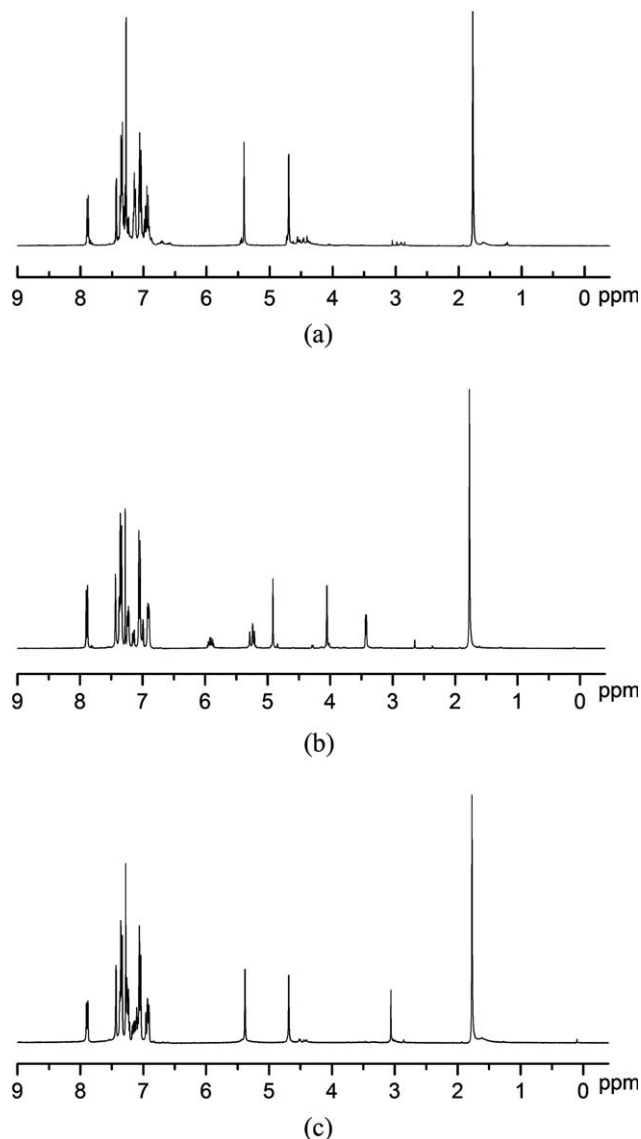
## RESULTS AND DISCUSSION

### Characterization of the monomers

Three benzoxazine monomers were found to be dissolvable in many common organic solvents, including acetone, chloroform, tetrahydrofuran, dioxane, and DMF. The chemical structures of the monomers were verified by FTIR,  $^1\text{H-NMR}$ , and elemental analysis. Figure 2 depicts the FTIR spectra of the three monomers. The imide  $\text{C}=\text{O}$  stretching absorptions appeared at 1718 and 1774  $\text{cm}^{-1}$  (symmetric and asymmetric), and the  $\text{C}-\text{N}$  stretching absorption appeared at 1378  $\text{cm}^{-1}$ .<sup>46</sup> The characteristic absorptions of the benzoxazine ring appeared at 1239  $\text{cm}^{-1}$  (asymmetric stretching of  $\text{C}-\text{O}-\text{C}$ ), 1013  $\text{cm}^{-1}$  (symmetric stretching of  $\text{C}-\text{O}-\text{C}$ ), 1340  $\text{cm}^{-1}$  (wagging vibrations of  $\text{CH}_2$ ), and 940  $\text{cm}^{-1}$  (trisubstituted benzene ring),<sup>11</sup> whereas the characteristic absorptions of BOZ-HPBPADI-al, assigned to the allyl group, appeared at 3068  $\text{cm}^{-1}$  (stretching of  $=\text{C}-\text{H}$ ) and 1618  $\text{cm}^{-1}$  (stretching of  $\text{C}=\text{C}$ ),<sup>36</sup> and those of BOZ-HPBPADI-apa, assigned to the propargyl structure, appeared at 3285  $\text{cm}^{-1}$  (stretching of  $\text{H}-\text{C}\equiv$ ) and 2125  $\text{cm}^{-1}$  (stretching of  $\text{C}\equiv\text{C}$ ).<sup>35</sup>

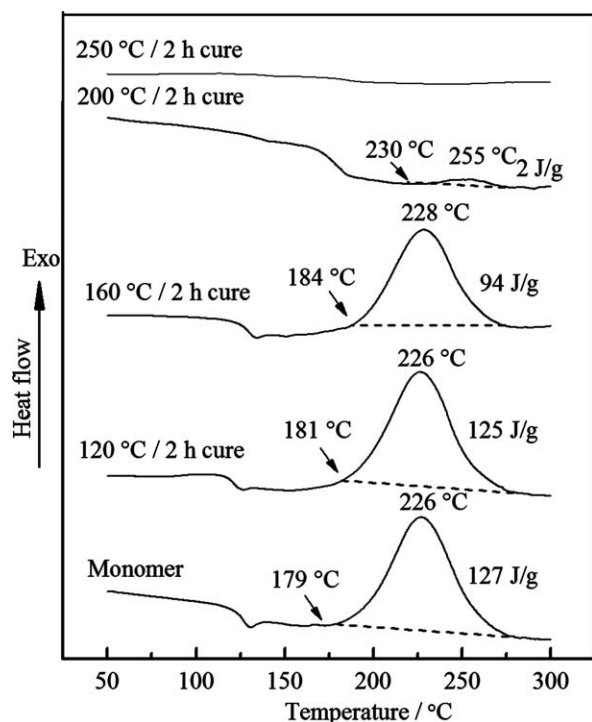
Figure 3 shows the  $^1\text{H-NMR}$  spectra of the three monomers in  $\text{CDCl}_3$ . For the BOZ-HPBPADI [Fig. 3(a)], the characteristic protons of the oxazine ring appeared at 4.66 ( $-\text{Ar}-\text{CH}_2-\text{N}-$ ) and 5.37 ppm ( $-\text{O}-\text{CH}_2-\text{N}-$ ), respectively.<sup>2</sup> The singlet at 1.76 ppm was assigned to the protons of  $-\text{CH}_3$ . The mul-

tiplet at 6.84–7.47 ppm was attributed to protons of the aromatic ring. For BOZ-HPBPADI-al [Fig. 3(b)], the characteristic protons of the oxazine ring appeared as two singlets at 4.05 and 4.91 ppm, whereas the methyl protons appeared as a singlet at 1.77 ppm, and the aromatic protons appeared as a multiplet at 6.90–7.90 ppm. Two multiples at 5.21–5.28 and 5.87–5.94 ppm belonged to the protons of  $=\text{CH}_2$  and  $=\text{CH}-$  in the allyl group, and a doublet at 3.41–3.43 ppm belonged to the protons of  $-\text{CH}_2-$  of the allyl group.<sup>36</sup> For the BOZ-HPBPADI-apa [Fig. 3(c)], the characteristic protons of the oxazine ring appeared as two singlets at 4.69 and 5.38 ppm, whereas the methyl protons and the aromatic protons appeared the same, as a singlet at 1.77 ppm and a multiplet at 6.92–7.90 ppm, respectively. A singlet at 3.06 ppm belonged to the protons of  $\equiv\text{C}-\text{H}$ .<sup>35</sup> In summary, all of the peak assignments



**Figure 3**  $^1\text{H-NMR}$  spectra of (a) BOZ-HPBPADI, (b) BOZ-HPBPADI-al, and (c) BOZ-HPBPADI-apa.



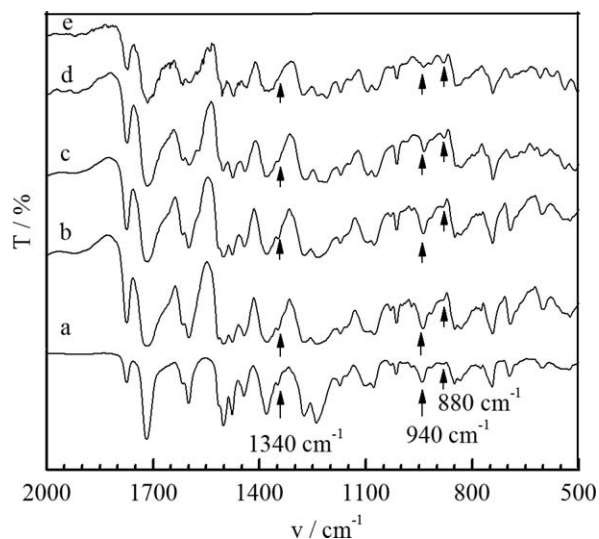


**Figure 4** DSC curves of BOZ-HPBPADI after each cure stage.

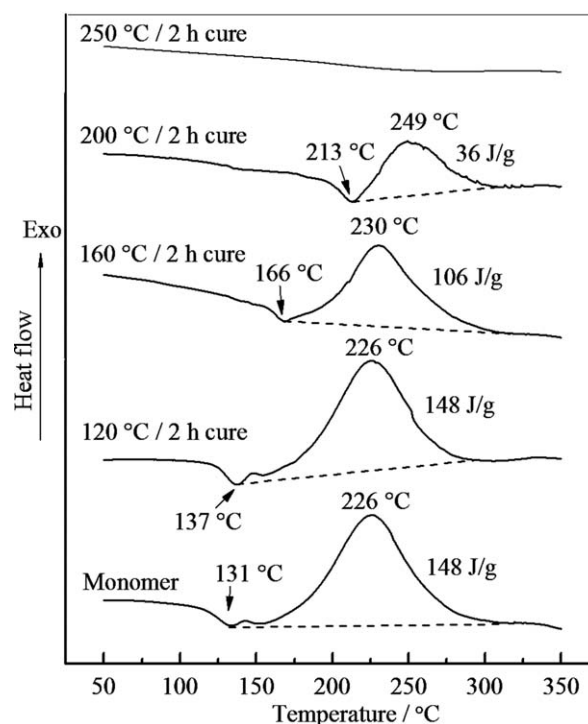
in the  $^1\text{H-NMR}$  spectra confirmed that the structures of the designed monomers occurred in the synthesized monomers.

### Curing behavior of the monomers

The curing behavior of the three monomers, BOZ-HPBPADI, BOZ-HPBPADI-al, and BOZ-HPBPADI-apa, was studied with DSC after a series of heat treatments at each temperature of 120, 160, 200, and 250°C



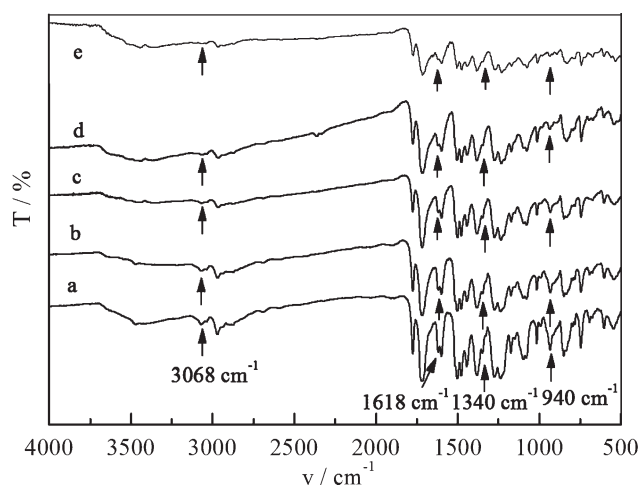
**Figure 5** FTIR spectra of BOZ-HPBPADI: (a) before curing, (b) after curing at 120°C for 2 h, (c) after curing at 160°C for 2 h, (d) after curing at 200°C for 2 h, and (e) after curing at 250°C for 2 h ( $T$  = transmittance,  $\nu$  = wave number).



**Figure 6** DSC curves of BOZ-HPBPADI-al after each cure stage.

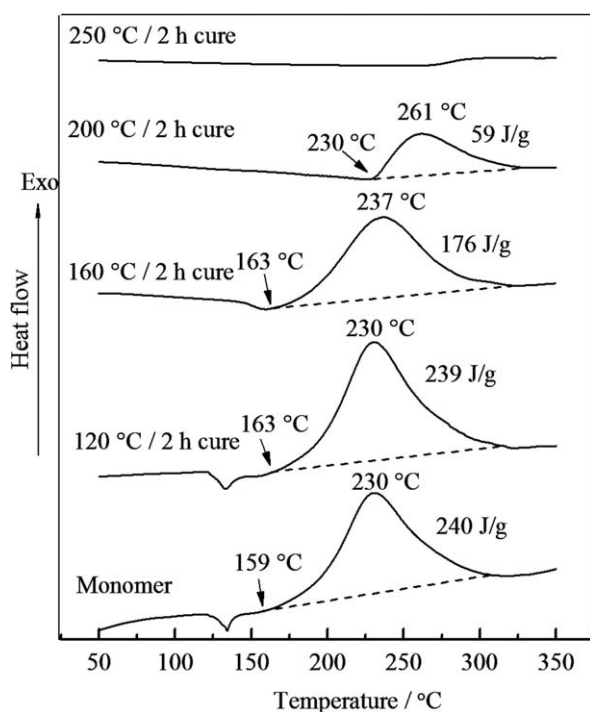
for 2 h. BOZ-HPBPADI showed an exotherm (Fig. 4) with onset at 179°C and a maximum at 226°C corresponding to the ring-opening polymerization of benzoxazine. The curing enthalpy of BOZ-HPBPADI was measured as 127 J/g (or 119 kJ/mol). The exothermic peaks gradually decreased after each cure cycle and disappeared completely after 250°C/2 h treatment. The cure behavior was also monitored with FTIR spectra for BOZ-HPBPADI after each curing treatment (Fig. 5). The FTIR spectra revealed that the characteristic absorption bands according to the benzoxazine structure at 940 and 1340  $\text{cm}^{-1}$  gradually decreased and disappeared after the 250°C curing. Instead, a new absorption appeared at 880  $\text{cm}^{-1}$  due to the tetra-substituted benzene ring mode.<sup>47</sup> This showed that the ring-opening reaction of benzoxazine was completed to form the crosslinked polybenzoxazine.

For the system of BOZ-HPBPADI-al, the DSC results in Figure 6 show that the exothermic peak was observed with the onset at 131°C and maximum point at 226°C. The measured enthalpy of exotherm was as high as 148 J/g (or 128 kJ/mol), which was much higher than that of BOZ-HPBPADI. The exotherm of BOZ-HPBPADI-al was attributed to both the crosslinking of the allyl group and the ring-opening polymerization of benzoxazine. However, the DSC curve of BOZ-HPBPADI-al had only the one exothermic peak, which was different from those of benzoxazines containing the oxazine ring and allyl groups, which showed two exothermic peaks corresponding to the crosslinking of carbon-

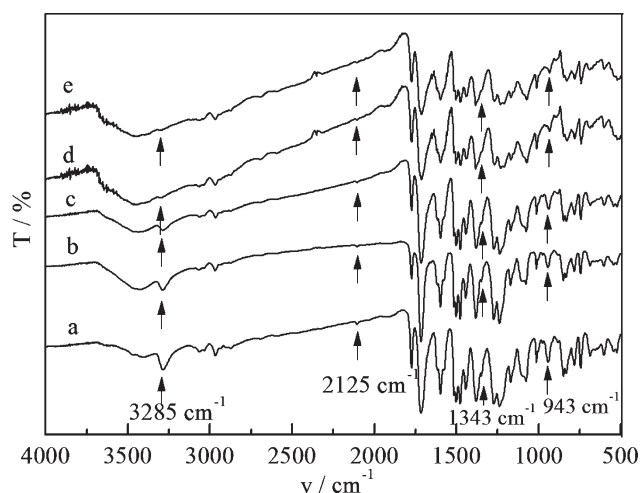


**Figure 7** FTIR spectra of BOZ-HPBPADI-al: (a) before curing, (b) after curing at 120°C for 2 h, (c) after curing at 160°C for 2 h, (d) after curing at 200°C for 2 h, and (e) after curing at 250°C for 2 h ( $T$  = transmittance,  $\nu$  = wave number).

carbon double bonds at about 210°C and the ring-opening polymerization of the oxazine ring at about 250°C.<sup>13,36</sup> It is believed that the single exotherm appearing in the DSC curve consisted of two parts occurring at a similar time. A possible explanation might be that a small number of phenolic hydroxyl groups of oligomers in the BOZ-HPBPADI-al monomer, on account of the difficulty of the purification, decreased the temperature of the oxazine ring opening; therefore, both the ring opening and allyl group crosslinking occurred almost simultaneously.<sup>36-40</sup>



**Figure 8** DSC curves of BOZ-HPBPADI-apa after each cure stage.

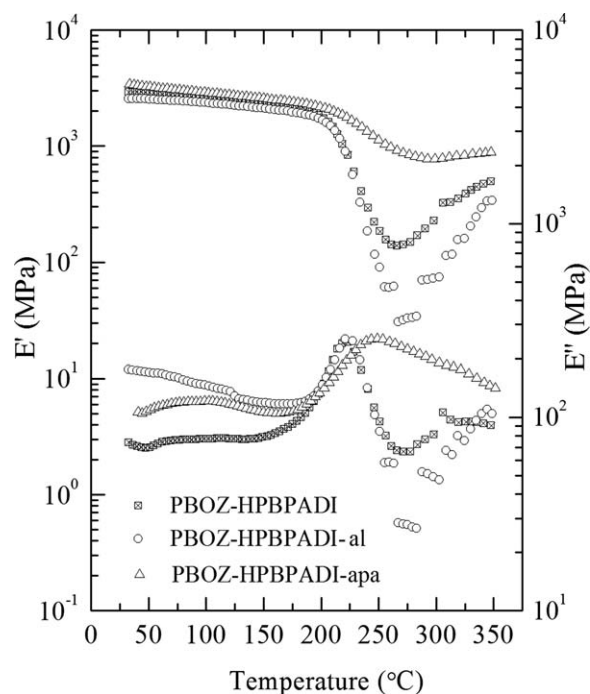


**Figure 9** IR spectra of BOZ-HPBPADI-apa: (a) before curing, (b) after curing at 120°C for 2 h, (c) after curing at 160°C for 2 h, (d) after curing at 200°C for 2 h, and (e) after curing at 250°C for 2 h ( $T$  = transmittance,  $\nu$  = wave number).

Similar to the results for BOZ-HPBPADI, the FTIR spectra for BOZ-HPBPADI-al showed that the absorptions peak of the benzoxazine ring (1340 and 940  $\text{cm}^{-1}$ ) decreased and disappeared after the completion of heat treatment at 250°C for 2 h. Moreover, the characteristic absorption band of BOZ-HPBPADI-al assigned to the unsaturated allyl group (3068 and 1618  $\text{cm}^{-1}$ ; Fig. 7) decreased gradually; this indicated the allyl groups were crosslinked after the heat treatments.

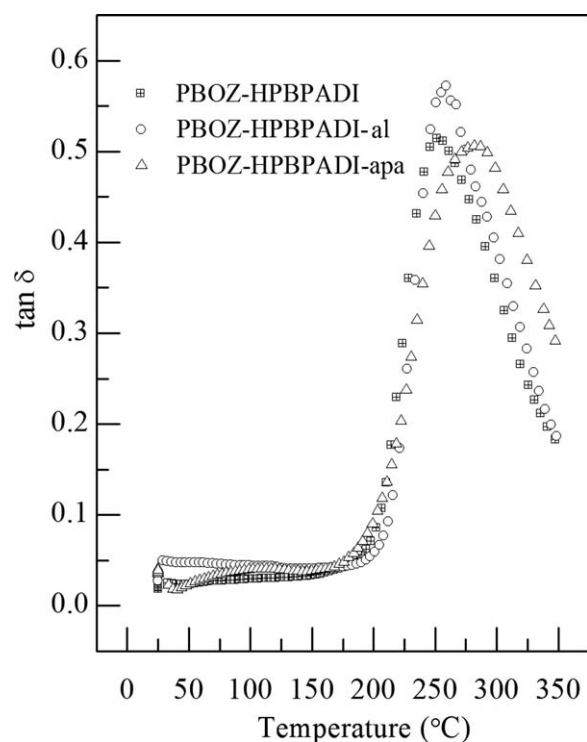
Figure 8 shows the cure behavior of BOZ-HPBPADI-apa after different curing treatment. BOZ-HPBPADI-apa showed an exotherm starting at 159°C with the maximum point at 230°C. The exothermic enthalpy of the monomer was measured as 240 J/g (or 236 KJ/mol) and was also much higher than those of BOZ-HPBPADI and BOZ-HPBPADI-al. The exotherm of BOZ-HPBPADI-apa was attributed to both the ring-opening polymerization of benzoxazine and the crosslinking of ethynyl group. The single exotherm also suggested that the curing regimes of the benzoxazine and ethynyl groups occurred simultaneously, as reported previously.<sup>36-40</sup> The exothermic enthalpy decreased after each curing cycle and disappeared after the 250°C/2 h curing; this indicated the completion of curing. The FTIR spectra of BOZ-HPBPADI-apa with different curing treatments are shown in Figure 9. The characteristic absorption bands at 3285 and 2125  $\text{cm}^{-1}$  were attributed to the diminishing ethynyl groups. In addition, similar to those for BOZ-HPBPADI and BOZ-HPBPADI-al, the FTIR spectra for BOZ-HPBPADI-apa showed the disappearance of the absorptions assigned to the benzoxazine ring.

In summary, the three monomers were cured completely after the designed heat treatment, and the BOZ-HPBPADI-apa monomer had the highest



**Figure 10** Viscoelastic analyses of PBOZ-HPBPADI, PBOZ-HPBPADI-al, and PBOZ-HPBPADI-apa.

enthalpy of 240 J/g. The FTIR results confirmed that the reactive groups in the three monomers, including oxazine ring and allyl and ethynyl groups cross-linked to form the polymer after the heat treatments.



**Figure 11** Temperature dependence of  $\tan \delta$  for PBOZ-HPBPADI, PBOZ-HPBPADI-al, and PBOZ-HPBPADI-apa.

**TABLE II**  
Summary of the DMA Results

Polymer	$E'$ at 50°C (GPa)	$T_g$ (°C)	
		$E''_{\max}$	$\tan \delta_{\max}$
PBa <sup>14</sup>	1.09	168	185
PB-ala <sup>36</sup>	—	—	298
PB-apa <sup>29</sup>	—	—	350
P(Mal-Bz) <sup>13</sup>	3.00–3.20	241	278
P(Mal-Bz-al) <sup>13</sup>	—	267	299
PBOZ-HPBPADI	2.91	223	252
PBOZ-HPBPADI-al	2.54	224	260
PBOZ-HPBPADI-apa	3.24	245	286

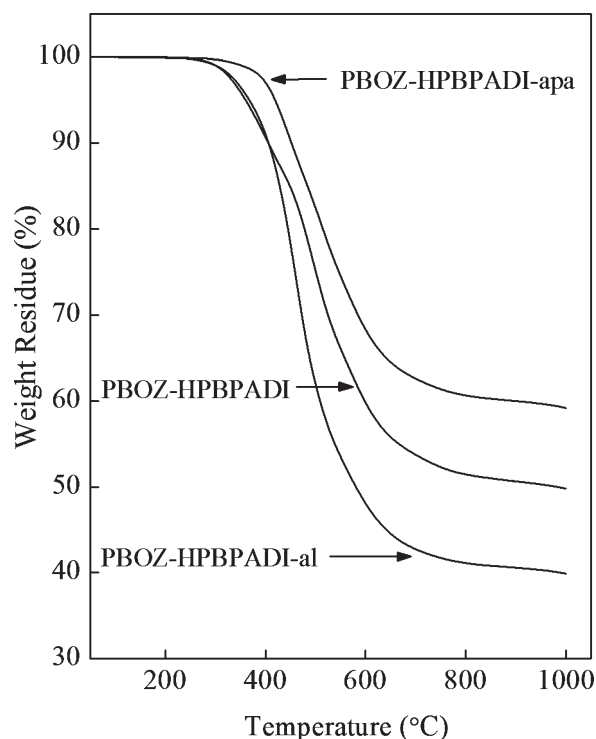
### Properties of the novel polybenzoxazines

#### DMA of the novel polybenzoxazines

The viscoelastic properties of the new polybenzoxazines from the three monomers, poly[bis(3-phenyl-2,4-dihydro-2H-1,3-benzoxazinyl) bisphenol A diphthalimide] (PBOZ-HPBPADI), poly[bis(3-allyl-2,4-dihydro-2H-1,3-benzoxazinyl) bisphenol A diphthalimide] (PBOZ-HPBPADI-al), and poly[bis[3-(3-phenylacetylene)-2,4-dihydro-2H-1,3-benzoxazinyl] bisphenol A diphthalimide] (PBOZ-HPBPADI-apa), were investigated with DMA. Figures 10 and 11 show the temperature dependence of the storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss factor ( $\tan \delta$ ) for the polybenzoxazines, respectively.  $E'$  at 50°C and  $T_g$  [defined from the peak values of  $E''$  ( $E''_{\max}$ ) or  $\tan \delta$  ( $\tan \delta_{\max}$ )] of the three polybenzoxazines are compared to those of relevant polybenzoxazines, such as polybenzoxazine from bisphenol A and aniline (PBa),<sup>14</sup> polybenzoxazine from bisphenol A and allylamine poly-[bis(3-allyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane] (PB-ala),<sup>36</sup> polybenzoxazine from bisphenol A and 3-aminophenylacetylene poly-[bis(3-(3-phenylacetylene)-2,4-dihydro-2H-1,3-benzoxazinyl) isopropane] (PB-apa),<sup>29</sup> polybenzoxazine from maleimide and aniline poly-[1-(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)maleimide] [P(Mal-Bz)],<sup>13</sup> and polybenzoxazine from maleimide and allylamine poly-[1-(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)maleimide] [P(Mal-Bz-al)],<sup>13</sup> in Table II.

$E'$  of PBOZ-HPBPADI was 2.91 GPa at 50°C and decreased dramatically at about 205°C, and its  $T_g$  values, defined from the peaks of  $E''$  and  $\tan \delta$ , were 223 and 252°C, respectively.  $E'$  of PBOZ-HPBPADI-al decreased more after 205°C than that of PBOZ-HPBPADI, but that of PBOZ-HPBPADI-apa retained a much greater value at a higher temperature. The  $E'$  decrease of PBOZ-HPBPADI-al may have been due to the extra-flexible aliphatic chain introduced in the additional polymerization of the allyl group. The high  $E'$  at the high temperature of the PBOZ-HPBPADI-apa may have been due to the bicyclic chromene rings formed during the polymerization of the ethynyl group. Although  $E'$  decreased,  $T_g$  of





**Figure 12** TGA of PBOZ-HPBPADI, PBOZ-HPBPADI-al, and PBOZ-HPBPADI-apa.

PBOZ-HPBPADI-al was similar or slightly higher than those of PBOZ-HPBPADI, whereas  $T_g$  of PBOZ-HPBPADI-apa appeared to be a lot higher than those of the other two polybenzoxazines. The increase in  $T_g$  might have been due to the increased crosslink density when additional crosslink sites were introduced.<sup>13</sup>

In Table II, PBOZ-HPBPADI, PBa, and P(Mal-Bz) were prepared from the same aniline with different phenolic compounds. PBOZ-HPBPADI had a higher  $E'$  and  $T_g$  than PBa. This may have been because of the stiffer imide ring in the main chain in the new polybenzoxazines. However, PBOZ-HPBPADI had lower  $E'$  and  $T_g$  values than P(Mal-Ba). This might have been because of the flexible aliphatic segments existing in the main chains of PBOZ-HPBPADI.

Although PBOZ-HPBPADI-al, PB-ala, and P(Mal-Bz-al) were all prepared from the same allylamine and different phenolic compounds, PBOZ-HPBPADI-al had a much lower  $T_g$  than PB-ala or P(Mal-Bz-al). The reason may have been because the BOZ-HPBPADI-al monomer had a greater molecular weight and longer molecular chains between the two oxazine rings or allylamine groups than the bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (B-ala) or 1-(3-allyl-3,4-dihydro-2*H*-benzo[e][1,3]oxazin-6-yl)maleimide (Mal-Bz-al) monomer. Thus, PBOZ-HPBPADI-al had a lower crosslink density than PB-ala and P(Mal-Bz-al), and the contribution of crosslink density to  $T_g$  may have been greater than

that of the imide groups in the main chains. A higher crosslink density led to a higher  $T_g$ . A similar trend to that of the polybenzoxazines from the same 3-aminophenylacetylene was found, in which PBOZ-HPBPADI-apa had a lower  $T_g$  than PB-apa.

In summary, a more rigid structure in the main chains led to a higher  $E'$  and a possibly increased crosslink density of the polybenzoxazines and contributed to a higher  $T_g$ . PBOZ-HPBPADI-apa had the highest  $E'$  and  $T_g$  values among the three novel polybenzoxazines.

#### Thermal stabilities of the bisphenol A diphthalimide bisbenzoxazine thermosets

The thermal stabilities of the novel bisphenol A diphthalimide bisbenzoxazine thermosets were evaluated by TGA. The weight percentage versus temperature curves are shown in Figure 12. The 5 and 10% weight loss temperatures ( $T_5$  and  $T_{10}$ , respectively) and the char yields at 800°C in percentage are listed in Table III and compared to those of the PBa, PB-ala, PB-apa, P(Mal-Bz), and P(Mal-Bz-al) from the literature.

On the one hand,  $T_5$  and  $T_{10}$  of the three polybenzoxazines were as high as over 360 and 405°C, and their orders were PBOZ-HPBPADI  $\leq$  PBOZ-HPBPADI-al  $<$  PBOZ-HPBPADI-apa. The trend was similar to the data in refs. <sup>29</sup> and <sup>36</sup>: PB  $<$  PB-al  $<$  PB-apa. The initial thermal decomposition of polybenzoxazines was due to Mannich base cleavage (the cleavage of the C–N bond) and led to the volatilization of aniline derivative fragments.<sup>48–50</sup> Because PBOZ-HPBPADI-al or PBOZ-HPBPADI-apa processed more crosslinking points through the polymerization of allyl or ethynyl groups, the thermally labile Mannich bridge parts were anchored in the matrix and resulted in higher  $T_5$  and  $T_{10}$  values compared to that of PBOZ-HPBPADI, although the increase of PBOZ-HPBPADI-al is not significant. The ethynyl groups in PBOZ-HPBPADI-apa polymerized to form the cyclic chromene structure with a higher thermal stability and resulted in much higher  $T_5$  and  $T_{10}$  values than those of either PBOZ-HPBPADI or PBOZ-HPBPADI-al.

**TABLE III**  
Summary of the TGA Results

Polymer	$T_5$ (°C)	$T_{10}$ (°C)	Char yield at 800°C (%)
PBa <sup>36</sup>	310	327	32
PB-ala <sup>36</sup>	343	367	28
PB-apa <sup>29</sup>	458	524	74
P(Mal-Bz) <sup>13</sup>	349	376	62
P(Mal-Bz-al) <sup>13</sup>	394	412	59
PBOZ-HPBPADI	360	405	51
PBOZ-HPBPADI-al	368	406	41
PBOZ-HPBPADI-apa	419	452	61



The  $T_5$  and  $T_{10}$  values of the PBOZ-HPBPADI and PBOZ-HPBPADI-al were higher than those of the PBa and PB-ala, respectively. A reason may have been that the main chains of PBOZ-HPBPADI and PBOZ-HPBPADI-al had high-temperature-resistant imide groups. However, PBOZ-HPBPADI-apa with imide groups in the main chain had a lower  $T_5$  and  $T_{10}$  than PB-apa. The reason may have been that the bicyclic chromene rings from ethynyl groups had a much higher thermal stability than the imide groups, and PB-apa processed more ethynyl groups than PBOZ-HPBPADI-apa. So the bicyclic chromene ring contents of PB-apa were much greater than that of PBOZ-HPBPADI-apa; this resulted in a higher thermal stability of PB-apa.  $T_5$  and  $T_{10}$  of PBOZ-HPBPADI were higher than those of P(Mal-Bz) with the imide groups; this indicated that PBOZ-HPBPADI had a higher thermal stability than P(Mal-Bz). However,  $T_5$  and  $T_{10}$  for PBOZ-HPBPADI-al were lower than those of P(Mal-Bz-al). A possible reason may have been that P(Mal-Bz-al) had a higher crosslinking density than PBOZ-HPBPADI-al and this led to the higher thermal stability.

On the other hand, the char yields of the three polymers were found in following order: PBOZ-HPBPADI-al < PBOZ-HPBPADI < PBOZ-HPBPADI-apa. It is also similar to the order of the PB series in the literature: PB-al < PB < PB-apa. The char yield of PBOZ-HPBPADI-al (41%) was much lower than that of PBOZ-HPBPADI (51%). This was mainly because of the nature of the aliphatic segments formed from the allyl polymerization because the aliphatic segments caused a low thermal stability.<sup>51</sup> The char yield of PBOZ-HPBPADI-apa (61%) was the highest among the three polybenzoxazines; again, this may have been due to the higher thermal stability and the stiffening effect of the cyclic chromene structure. The char yields of PBOZ-HPBPADI and PBOZ-HPBPADI-al were higher than those of PBa and PB-ala because the imide groups had a higher char yield. However, the char yield of PBOZ-HPBPADI-apa was lower than that of PB-apa. This may have been because PB-apa had much greater cyclic chromene structure contents than PBOZ-HPBPADI-apa because of the higher crosslink density of PB-apa. The char yields of PBOZ-HPBPADI and PBOZ-HPBPADI-al were lower than those of P(Mal-Bz) and P(Mal-Bz-al) because P(Mal-Bz) and P(Mal-Bz-al) had higher contents of imide groups; this contributed to a higher char yield.

In summary, the three novel polybenzoxazines exhibited excellent thermal stabilities in terms of  $T_5$  and  $T_{10}$ , as high as over 360 and 405°C, and char yields at 800°C of 41–61%. PBOZ-HPBPADI-apa was proven to have the best thermal stability among the three polybenzoxazines.  $T_5$  and  $T_{10}$  of the PBOZ-

HPBPADI-apa were 419 and 452°C, respectively, and the char yield at 800°C was 61%.

## CONCLUSIONS

Three new benzoxazine monomers of bisphenol A diphthalimide bisbenzoxazine were synthesized from hydroxyphenyl bisphenol A diphthalimide, paraformaldehyde, and various amines through a two-step process. The benzoxazine monomers were crosslinked through a ring-opening polymerization. The exothermic enthalpies of BOZ-HPBPADI-al and BOZ-HPBPADI-apa were higher than that of BOZ-HPBPADI because of the additional exotherm of crosslinking of either allyl or ethynyl groups during curing. The three novel polybenzoxazines had high  $E'$  values (2.54–3.24 GPa) at 50°C, high  $T_g$  values (252–286°C), and high char yields (41–61%). PBOZ-HPBPADI-apa was proven to have the best dynamic mechanical properties and thermal stability among the three polybenzoxazines because it had a most rigid structure.  $E'$  of PBOZ-HPBPADI-apa at 50°C was 3.24 GPa, and the  $T_g$  was 286°C from  $\tan \delta_{\max}$ .  $T_5$  and  $T_{10}$  of the PBOZ-HPBPADI-apa were 419 and 452°C, respectively, and the char yield at 800°C was 61%. The novel polybenzoxazines, as resins, have potential application to process high-performance composites for the aerospace industry.

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