

SYNTHESIS AND CHARACTERIZATION OF POLYBENZOXAZINE CONTAINING PHOSPHORUS*

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Abstract The novel benzoxazine monomer containing phosphorus has been synthesized based on multifunctional amine route from bis(4-aminophenyl)phenylphosphate, *p*-cresol and formaldehyde. Subsequently, the benzoxazine monomer was thermo-cured into polybenzoxazine containing phosphorus. The chemical structures were identified by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR). The curing reaction was monitored by differential scanning calorimetry (DSC) and FT-IR. The thermal and flame-retardant properties of obtained polybenzoxazine were evaluated by dynamic mechanical thermal analysis (DMA), thermal gravimetric analysis (TGA) and oxygen index meter, respectively. The results show that the novel polybenzoxazine has high limiting oxygen index (38.1) and glass transition temperature (232°C).

Keywords: Polybenzoxazine; Phosphorus-containing resin; Flame-retardant; Limiting oxygen index.

INTRODUCTION

With the rapid development of electronics, aerospace and construction industries^[1], the matrix resins having high heat-resistant and flame-retardant properties are urgently required. Polybenzoxazine is regarded as one of the best candidates to meet these requirements. This is because it has better heat-resistant, flame-retardant and processing properties than the traditional phenolic resin^[2–4]. However, the flame-retardant property of polybenzoxazine still needs to be improved further.

The commonly method used to enhance polymer flame retardancy is the physical blending of polymer system and flame retardants, such as halogen compound^[5], phosphorus compound *etc.*^[6–8]. Among them, the phosphorus compound has low toxicity and is the major flame-retardant additive at present^[9, 10]. The disadvantage of this method is the large dosage of phosphorus compound, which easily causes the damage of mechanical properties, moisture absorption and additive stability^[11, 12].

To overcome these problems, the chemical modification method has been developed. Chen *et al.*^[13] synthesized phosphorus-containing thermotropic liquid crystalline copolyesters with high molecular weight and thermal stability. Espinosa *et al.*^[14] reported the chemical blending of benzoxazine-phenolic resin with phosphorus-containing epoxide resin.

Recently, the incorporation of phosphorus into benzoxazine monomers was also explored. Based on multifunctional phenol route, benzoxazine monomers with phosphorus were synthesized using bis(4-hydroxyphenyl)phenylphosphine oxide (BHPPPO)^[15], bis(4-hydroxyphenoxy-4'-phenyl)phenylphosphine oxide

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(BPPPO), bis(4-hydroxyphenoxy)phenylphosphine oxide (BPHPO) and dopotriol^[16] as starting materials, respectively. Based on 2-hydroxybenzaldehyde route, benzoxazine monomers with phosphorus were synthesized using bis(*m*-aminophenyl)methylphosphine oxide (BAMPO)^[17], 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)^[18–20] and dopotriamine^[21], respectively.

In our previous studies, we have developed a multifunctional amine-based synthetic route^[22, 23]. The synthesis of benzoxazine monomer with phosphorus using this method has not been reported so far. Therefore, we herein aim to synthesize the inherent phosphorus-containing polybenzoxazine *via* the multifunctional amine-based route. Specifically, bis(4-aminophenyl)phenylphosphate (BAPP) was synthesized from *p*-nitrophenol and phenyldichlorophosphate, and then BAPP was reacted with formaldehyde and *p*-cresol to produce benzoxazine monomer containing phosphorus (BBZ). Subsequently, the polybenzoxazine containing phosphorus (PBBZ) was obtained *via* ring-opening reaction activated by heat.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was dried with sodium and distilled prior to use. Triethylamine (TEA) was dried with KOH and distilled prior to use. Other reagents including phenyldichlorophosphate (PDCP), *p*-nitrophenol, copper (I) chloride, tin (II) chloride dehydrated, formaldehyde (37 wt% in water), *p*-cresol and 1,4-dioxane were all purchased from Shanghai Chemistry Reagent Company and used as received.

Synthesis of Bis(4-nitrophenyl)phenylphosphate (BNPP)

To a 250 mL round-bottom flask, 14.1 g (0.1 mol) of *p*-nitrophenol, 72 mL THF and 12.9 mL (0.1 mol) triethylamine were added and then the solution was stirred under an ice bath. After adding 0.18 g Cu₂Cl₂, a solution of 7.35 mL (0.046 mol) phenyldichlorophosphate in 36 mL THF was added dropwise over 30 min. The solution was stirred at 0°C for 2 h and then stirred at room temperature for 48 h. The precipitation was removed by filtering, while the filtrate was washed with THF and finally extracted with ethyl acetate (EA) three times. After recrystallization from ethanol, the yellowish crystals were obtained in 86% yield.

¹H-NMR (CDCl₃/TMS, δ): 7.16–7.36 (aromatic protons near NO₂ groups), 6.68–7.02 (–P–O–C₆H₅), 6.58–6.61 (aromatic protons near O–P=O bonding); ³¹P-NMR (CDCl₃/H₃PO₄, δ): –14.92. IR: 856 cm^{–1} (–C–NO₂–), 960 cm^{–1} (P–O–Ph symmetric stretching), 1186 cm^{–1} (P–O–Ph asymmetric stretching), 1236 cm^{–1} (–P=O), 1348 and 1524 cm^{–1} (Ph–NO₂).

Synthesis of Bis(4-aminophenyl)phenylphosphate (BAPP)

To a 500 mL round-bottom flask, 10 g of BNPP and 72 g power tin (II) chloride dihydrate were added. Next, a solution of 80 mL fuming hydrochloric acid in 160 mL ethanol was introduced into the flask and then the reaction mixture was stirred at room temperature for 5 h. The solution was neutralized by 25% NaOH aqueous solution and then was extracted with chloroform. The organic layer was concentrated and then the obtained solid was recrystallized from dichloromethane to give the final product with 80% yield.

¹H-NMR (CDCl₃/TMS, δ): 7.16–7.36 (–P–O–C₆H₅), 6.94 (4H, d); 6.58 (4H, d); 3.61 (2H, s, –NH₂); ³¹P-NMR (CDCl₃/H₃PO₄, δ): –15.6. IR: 963 cm^{–1} (P–O–Ph symmetric stretching), 1194 cm^{–1} (P–O–Ph asymmetric stretching), 1278 cm^{–1} (–P=O), 3452 and 3363 cm^{–1} (Ph–NH₂).

Synthesis of Phosphorus-containing Benzoxazine Monomer (BBZ)

To a 250 mL three-necked flask, 24 mL (0.3 mol) of formaldehyde aqueous solution, 25.6 g (0.075 mol) BAPP, 0.7 g triethylamine and 75 mL dioxane were added at 30°C. After 15.5 g (0.15 mol) *p*-cresol was added, the temperature was raised to reflux for 5 h. The product was vacuum-distilled to eliminate the solvent. The residual was dissolved in 50 mL dichloromethane and washed several times with 3 mol/L NaOH aqueous solution and distilled water. The obtained product was purified by column chromatography (using ethyl acetate as eluent). The final product was obtained with 75% yield.

¹H-NMR (CDCl₃/TMS, δ): 6.68–7.30 (19H, Ar–H); 5.27 (4H, s, –O–CH₂–N); 4.54 (4H, s, Ar–CH₂–

N); 2.24 (6H, s, Ar—CH₃); ³¹P-NMR (CDCl₃/H₃PO₄, δ): -16.19. IR: 955 cm⁻¹ (benzene ring to which an oxazine ring is attached), 966 cm⁻¹ (P—O—Ph symmetric stretching), 1026 cm⁻¹ (C—O—C symmetric stretching), 1192 cm⁻¹ (P—O—Ph asymmetric stretching), 1227 cm⁻¹ (C—O—C asymmetric stretching), 1297 cm⁻¹ (—P=O), 1383 cm⁻¹ (C—N stretching), 1505 and 815 cm⁻¹ (*para*-substituted benzene).

Synthesis of Benzoxazine Monomer DBZ

Benzoxazine monomer DBZ was synthesized from 4,4'-Diaminodiphenyl methane, phenol and formaldehyde following a reported method^[22].

¹H-NMR (CDCl₃/TMS, δ): 3.79 (Ar—CH₂—Ar), 4.54 (Ar—CH₂—N), 5.33 (—O—CH₂—NR—), 6.64–7.13 (Ar—H). IR: 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).

Polymerization of BBZ and DBZ

The benzoxazine monomer BBZ and DBZ 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.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer (Madison, Wisconsin, USA). Samples were prepared as KBr pellets. Nuclear magnetic resonance (¹H-NMR and ³¹P-NMR) spectra were recorded on a Bruker Avance 300 instrument (Newport, Virginia, USA). Deuterated chloroform was used as solvent and tetramethylsilane was used as an internal standard.

Differential scanning calorimetry (DSC) thermograms were recorded with a METTLER TOLEDO DSC822^o instrument (Zurich, Switzerland) at a heating rate of 10 K/min under N₂ atmosphere. Dynamic mechanical thermal analysis (DMA) thermograms were recorded with a METTLER TOLEDO DMA/SDTA 861^o instrument (Zurich, Switzerland). A specimen (2 mm × 2 mm × 1 mm) was tested in the shear mode at a heating rate of 3 K/min and a fixed frequency of 1 Hz. The thermal transitions were studied in the range of 50–300°C. Thermal gravimetric analysis (TGA) was performed on a TA instrument SDT Q600 (New Castle, Delaware, USA) at a heating rate of 10 K/min under nitrogen atmosphere. The gas flow rate was 100 mL/min.

Limiting oxygen index (LOI) values were measured on an FTT Oxygen Index/FTA (SC48) (East Grinstead, UK). The dimensions of specimens were 4 mm × 6 mm × 10 mm and the testing standard was GB/T2406-1993. The percentage O₂ in the O₂-N₂ mixture just sufficient to sustain the flame was taken as the LOI.

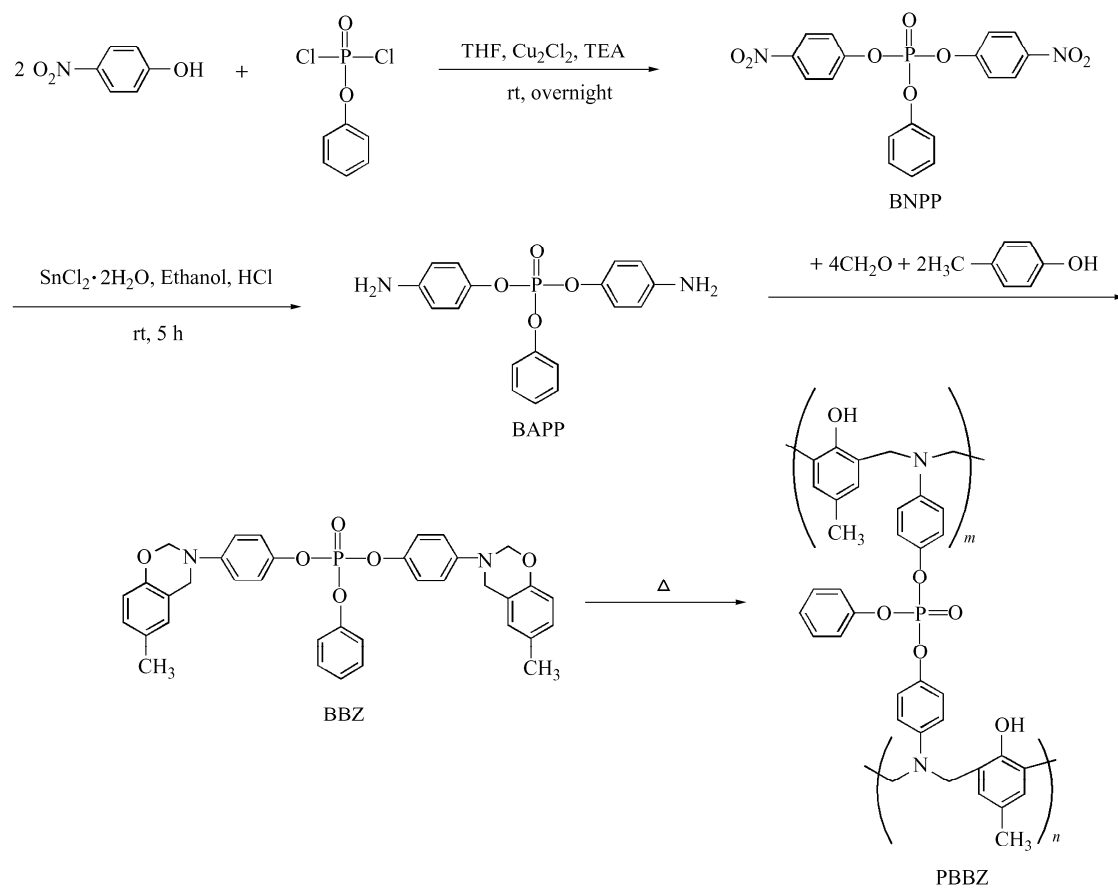
RESULTS AND DISCUSSION

Synthesis and Characterization of BBZ

Scheme 1 illustrates our strategy for the preparation of the phosphorus-containing benzoxazine monomer (BBZ). First, bis(4-nitrophenyl)phenylphosphate (BNPP) was synthesized by esterification of *p*-nitrophenol with phenyldichlorophosphate, and then was hydrogenated to result in the BAPP. Finally, the phosphorus-containing benzoxazine monomer (BBZ) was synthesized by Mannich reaction from BAPP, formaldehyde and *p*-cresol in a molar ratio of 1:4:2.

Figure 1 shows the ¹H-NMR spectrum of BBZ. The resonances at δ = 5.27 and 4.44 corresponded to the methylene protons of —O—CH₂—N= and Ar—CH₂—N= in the benzoxazine ring, respectively. The peaks at δ = 2.24 were assigned to the methyl protons of Ar—CH₃. The ¹H-NMR spectrum was the evidence of the existence of oxazine ring.

Figure 2 shows the ³¹P-NMR spectrum of BBZ. Only a single peak at δ = -16.19 was observed, indicating the phosphate structure had been introduced into the benzoxazine.



Scheme 1 Synthetic route to polybenzoxazine

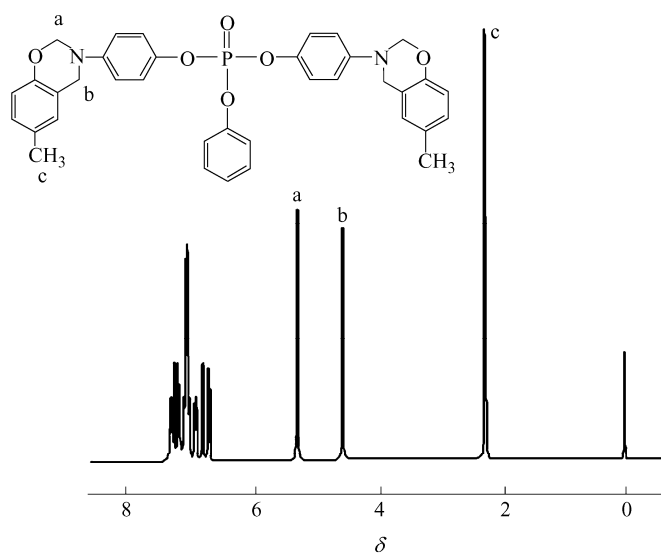
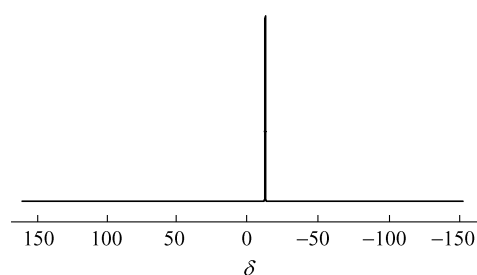
Fig. 1 ^1H -NMR spectrum of BBZ monomerFig. 2 ^{31}P -NMR spectrum of BBZ monomer

Figure 3 shows the FT-IR spectrum of BBZ. The characteristic absorption band at 955 cm^{-1} is assigned to benzene ring to which an oxazine ring is attached. The bands at 1227 and 1026 cm^{-1} corresponded to the asymmetric and symmetric stretching of $\text{C}-\text{O}-\text{C}$, respectively^[24]. This was consistent with the ^1H -NMR spectrum, further indicating oxazine ring was formed. In addition, the absorption bands at 966 and 1192 cm^{-1} due to the asymmetric and symmetric stretching of $\text{P}-\text{O}-\text{Ph}$ were also observed, further indicating the existence of phosphate structure.

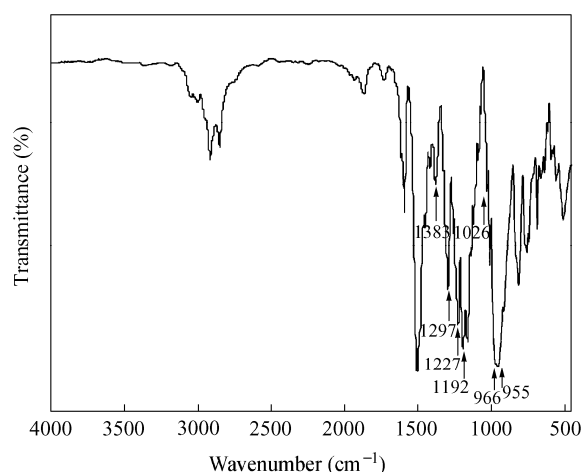


Fig. 3 FT-IR spectrum of BBZ monomer

The FT-IR, ^1H -NMR and ^{31}P -NMR data supported that benzoxazine ring with phosphonate structure has been synthesized successfully.

Polymerization of BBZ

Figure 4 shows the DSC thermogram of BBZ. The endothermic peak at 160°C was due to melting while the exothermic peak starting at 224°C with a maximum at 249°C was corresponding to polymerization of BBZ.

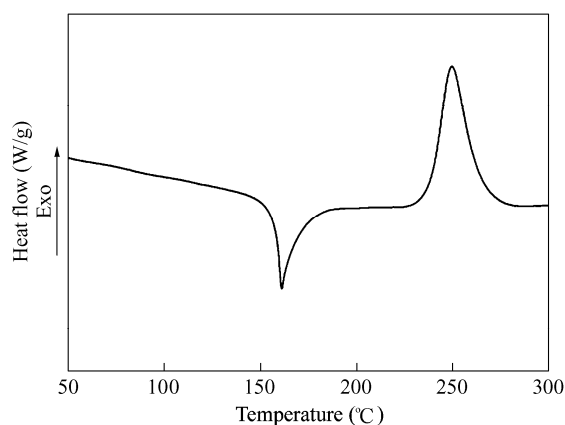


Fig. 4 DSC thermogram of BBZ polymerization

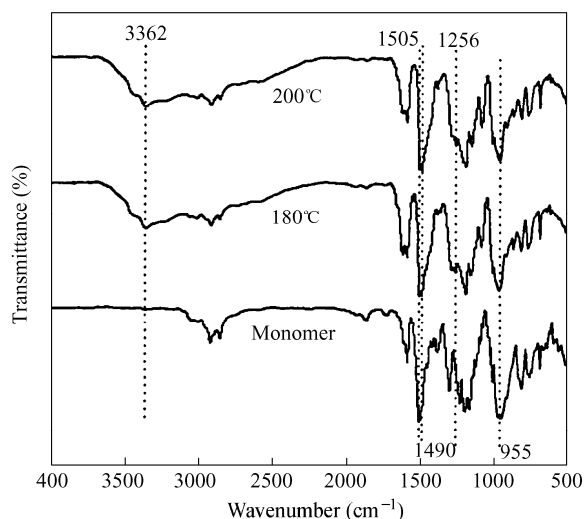


Fig. 5 FTIR spectra of PBBZ at each curing stage

Figure 5 shows the thermal curing reaction of BBZ monitored with FT-IR. As the temperature increased, the bands at 955 and 1227 cm^{-1} due to the benzene ring to which an oxazine ring attached decreased, indicating the occurrence of ring-opening reaction of BBZ. Meanwhile, the absorption band at 1505 cm^{-1} due to the trisubstituted benzene ring decreased, and the absorption band at 1490 cm^{-1} due to the tetrasubstituted benzene ring increased, suggesting the occurrence of polymerization of BBZ. The increase of band intensities at 3362 and 1256 cm^{-1} due to the —OH and C—O stretch of the phenolic group also supported the polymerization of BBZ.

Thermal and Flame-retardant Properties of Polybenzoxazine (PBBZ)

Figures 6 and 7 show the DSC and DMA thermograms of PBBZ respectively. Phosphorus-free polybenzoxazine PDBZ (shown as Scheme 2) was added as comparison. The thermal properties of polybenzoxazine (PBBZ) and PDBZ were summarized in Table 1. The glass transition temperature (T_g) of PBBZ was 226°C from the maximum of the loss modulus and 232°C from the maximum of the $\tan\delta$ peak, which was higher than that of PDBZ. Such phenomenon can be relevant with the chemical structure of PBBZ that owns a strong polar P=O group, which restricts the segmental mobility^[16, 18].

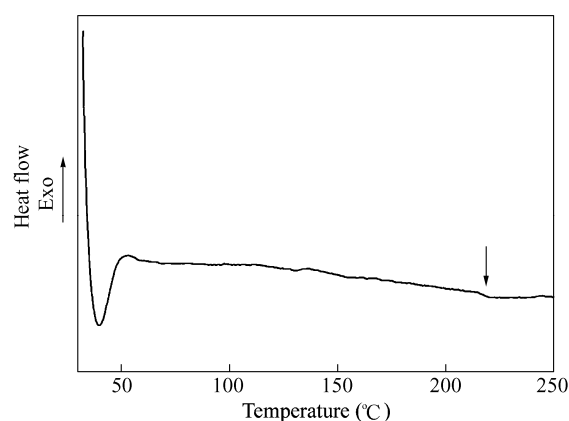


Fig. 6 DSC thermogram of PBBZ

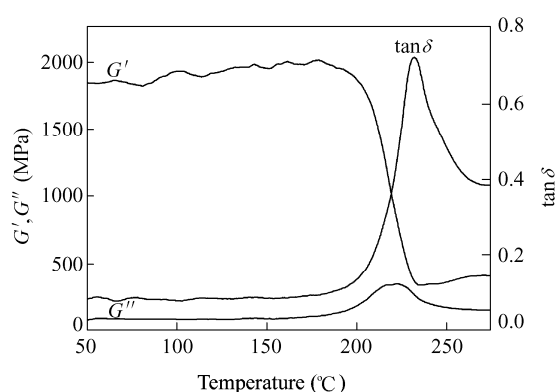
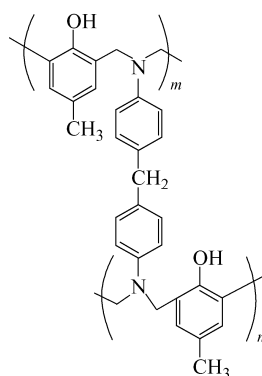


Fig. 7 DMA thermogram of PBBZ



Scheme 2 The structure of PDBZ

Figure 8 shows the TGA thermogram of PBBZ and PDBZ under nitrogen and air. The PDBZ showed one-stage weight loss behavior, with the 5% weight-loss temperatures under nitrogen and air at 329°C and 366°C, respectively. However, the phosphorus-containing PBBZ showed two-stage weight loss behavior no matter under nitrogen or air. The first stage of weight loss could be resulted from the decomposition of the phosphate groups, and the second stage of weight loss is due to the decomposition of polybenzoxazines. Similar phenomena were also observed on the thermal degradation of epoxy resin using BAPP as the curing agent^[25].

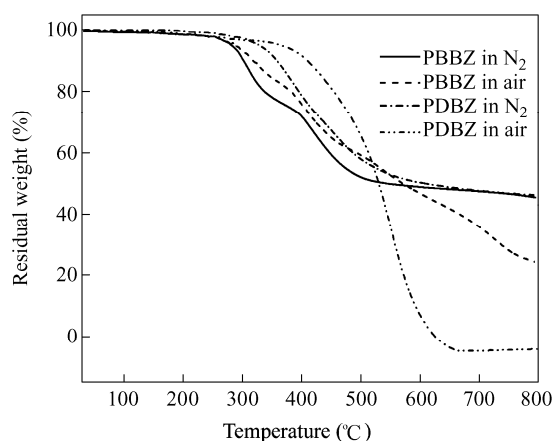


Fig. 8 TGA thermogram of PBBZ and PDBZ

Table 1. Thermal properties and limiting oxygen indexes of the polybenzoxazines

Sample	T_g^a (°C)	T_g^b (°C)		5% weight loss temperature (°C)		Char yield (% at 800°C)		LOI values
		G''	$\tan\delta$	N ₂	Air	N ₂	Air	
PBBZ	220	222	232	283	285	45	24	38.1
PDBZ	195	179	190	329	366	47	0 (at 626°C)	27.5

^a Measured by DSC; ^b Measured by DMA

The flame-retardant property of these polybenzoxazines was examined by measuring the values of the limiting oxygen index (LOI). PBBZ exhibited the LOI value of 38.1, which was much higher than that of PDBZ (LOI = 27.5). This indicates that the introduction of phosphorus into benzoxazine can improve the flame retardant property.

In addition, there is a close relationship between char yields and flame retardancy. The high char yields can limit the production of combustible gases and hinder the heat conduction, which benefits the flame retardancy^[26]. Therefore, the char yields of the phosphorus-containing PBBZ and phosphorus-free PDBZ were further examined at 800°C. Both PBBZ and PDBZ showed high char yields in nitrogen 45% and 47%, respectively. The char yields of PDBZ at 626°C were zero in air, while the phosphorus-containing PBBZ were found to be 24% at 800°C. This further suggested that the flame-retardant property of PBBZ has been greatly improved compared to PDBZ.

CONCLUSIONS

The benzoxazine monomer containing phosphorus was successfully synthesized based on multifunctional amine route from bis(4-aminophenyl)phenylphosphate, *p*-cresol and formaldehyde. The monomer was thermally cured through ring-opening reactions to form crosslinked structures. Comparing with phosphorus-free PDBZ, phosphorus-containing PBBZ showed higher LOI value, suggesting that the incorporation of phosphorus into benzoxazine can effectively enhance its flame-retardancy. In addition, owing to the existence of strong polar P=O groups, PBBZ showed higher glass transition temperature than PDBZ. Therefore, PBBZ can be used as a new type of flame-retardant material.

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