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Highly branched benzoxazine monomer based on cyclotriphosphazene: Synthesis and properties of the monomer and polybenzoxazines

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ABSTRACT

A hyperbranched organic–inorganic hybrid benzoxazine monomer based on cyclotriphosphazene (CP) has been synthesized, which possesses six organic benzoxazine moieties distributed on the inorganic ring of CP. The high molecular weight (1491 g/mol) monomer showed excellent solubility in common organic solvents. Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) were used to study the thermal ring-opening polymerization reaction of the novel benzoxazine monomer. FT-IR spectrum implied that the characteristic absorption peaks of the benzoxazine ring disappeared completely after curing at 240 °C for 1 h, which illustrated that the completion of polymerization reaction. DSC plots indicated that the melting point of the new monomer was 77 °C and an exothermic peak was 225 °C owing to the ring-opening polymerization of the monomer. Due to its highly steric crosslinking structure with rigid and thermal stable inorganic CP as the core, the polybenzoxazine based on the new monomer showed excellent thermal stability and mechanic properties. The char yield of the polymer at 850 °C was 66.9% in nitrogen, and the T_g of the polybenzoxazine was 152 °C.

1. Introduction

Recently, there has been an increasing interest in design and preparation of polybenzoxazine because the materials are developed class of high-performance thermosetting resins instead of common phenolic–formaldehyde resin in high-tech field. These thermosetting resins not only possess all the advantages of traditional phenolic resins such as excellent mechanical and thermal properties, but also have unique advantages of near-zero shrinkage upon curing, thermal and flame retardant, low water absorption and remarkable molecular design flexibility [1]. Furthermore, the polybenzoxazine resins can be easily gained from corresponding monomers under heat polymerization with or without catalyst, and the corresponding monomers can be conveniently generated by the Mannich condensation reaction of phenol, formaldehyde, and primary amine [2].

However, there are also several shortcomings that limit the application of common polybenzoxazine resins, such as high polymerization temperature, difficulty in processing and poor mechanic strength (low toughness) [3] and low-level flame retardant. To properly solve these problems and overcome the encountering disadvantages, lots of researchers have attempted many methods. Generally, the methodologies can be summarized in three approaches:

(i) Blending with other high-performance polymers or filling with inorganic materials. Rubber [4], polycarbonate [5], poly (ε-caprolactone) [6], polyurethane [7], epoxy [8] and other polymers were blended with the benzoxazine resins to improve the mechanic and thermal properties. Phosphorus-containing resin [9,10], clay [11] and magnetic Fe_3O_4 [12] were added to polybenzoxazine to modify flame retardant and thermal stability, or to prepare functional materials.

(ii) Synthesis of new polymeric precursors. There were three modes: (a) Main-chain precursors: Liu [13] and Ishida reported the concept of oligomeric benzoxazine resins where oxazine rings were in the main chain. Pedro and his copartners [14] synthesized a series of highly fluorinated main chain polybenzoxazines. Commonly, high molecular weight polybenzoxazine precursors were mostly synthesized from aromatic or aliphatic diamine and bisphenol with paraformaldehyde; (b) Side-chain precursors: Side-chain polymer strategy was a way to incorporate benzoxazine moieties into a polymer backbone to achieve a highly dense network, "click reaction" was the most popular routine to achieve this aim [15–17]. Using this method, benzoxazine groups were grafted to PVC, polystyrene, polybutadiene; (c) Cross-linkable telechelic polymers with benzoxazine moieties at the chain

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end [18,19]. These three kinds of polymeric precursors with benzoxazine moieties were allowed later crosslinking for dimensional stability, chemical resistance, and high-temperature stability.

(iii) Design and synthesis of new benzoxazine monomers with additional functionality. One strategy was introducing additional polymerizable groups into benzoxazine, such as nitrile [20], acetylene [21], propargyl [22], allyl [23], maleimide [24] or epoxy [25] functionalities. This approach allowed increasing crosslinking density and minimizing dangling side groups, thus leading to improving toughness and thermal properties. Another strategy was introducing self-catalyst groups into benzoxazine. Carboxylic acid [26], oxyalcohol [27] and primary amine [28] functional groups were connected to benzoxazine to lower the polymerization temperature. Furthermore, the effect of different substituted groups on polymerization temperature and thermal stability of polybenzoxazine were also investigated in-depth [29].

Among the mentioned above the three methods to improve the performance of polybenzoxazine, designing new benzoxazine monomer is a more attractive approach to overcome the shortcomings of traditional polybenzoxazine. By now, although most of benzoxazine monomers consisted of organic element only, more and more attention has been paid to design and synthesis of inorganic heteroatom-containing benzoxazine monomer [30–35]. Cyclotriphosphazene (CP) derivatives are typical classes of organic–inorganic compounds with a planar non-delocalized cyclic ring consisting of alternating N and P atoms. Six functional groups can be attached onto a CP ring and the groups are normally projected above and below the CP plane due to steric hindrance [36–38]. Because of the versatility of cyclotriphosphazene chemistry, the CP ring of high stability and biocompatibility allows a wide range of functional groups to be attached onto CP. Highly branched conductive polyaniline with high electrochromic contrast based on CP [39], star-branched polymers with CP cores [40], catalysts of transition metal ionic compounds based on CP [41], CP conjugates with varied properties in vitro [42] and flame-retardant CP-containing polyurethanes [43] were prepared through different methods. By introducing the CP units into the polymers or compounds, the corresponding hybrid materials were endowed with thermal stability and environment-friendly flame-retardant properties or other functionalities.

In current study, a star-like benzoxazine monomer based on CP has been synthesized, and the new benzoxazine monomer possesses six benzoxazine moieties substituted onto CP ring. The new hyperbranched benzoxazine monomer underwent ring-opening polymerization with or without catalysts to produce highly dimensional crosslinking structure with rigidly inorganic CP as the core. The structure of the new monomer was confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and elemental analysis. Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) were used to study the thermal ring-opening polymerization reaction of the monomer; the thermal property and mechanic performance of the thermoset polymer were also evaluated by thermal gravimetric analyzer and dynamic mechanical thermal analysis (DMA), respectively.

2. Experimental

2.1. Materials

4-acetamidophenol (98%) was purchased from Alfa Aesar Reagent Co., Ltd., USA. Salicylaldehyde (≥98%), sodium borohydride (96%), paraformaldehyde (95%), phenol, p-hydroxylbenzoic acid (≥99%), p-aminobenzoic acid (≥99%), sodium hydroxide (≥96%), and potassium carbonate were all gained from Sinopharm Chemical Reagent Co., Ltd., China. Hexachlorocyclotriphosphazene (synthesized as described in the literature [44]) was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp 112.5–113.0 °C). Hexaphenoxycyclotriphosphazene (HPP) was prepared according to the report [45]. All solvents were purified by standard procedures.

2.2. Measurements

The structure of the compound was verified by proton (^{1}H), carbon (^{13}C) and phosphorus (^{31}P) nuclear magnetic resonance spectroscopy (NMR) using Bruker AV400 NMR spectrometer at proton frequency of 400 MHz as well as the corresponding carbon and phosphorus frequencies at room temperature using deuterated solvents as the solvent. Signals were averaged from 256 transients for ^{1}H NMR and ^{31}P NMR, and 1024 transients for ^{13}C NMR to yield spectra with sufficient signal-to-noise ratio. Thermal transitions were monitored with a differential scanning calorimeter (DSC), Model 204F1 from NETZSCH Instruments, and scan rate of 10 °C/min over a temperature range of 30–300 °C and nitrogen flow rate of 20 mL/min were used in DSC experiments. Thermogravimetric analysis (TGA) was performed with a NETZSCH Instruments' High Resolution STA 409PC thermogravimetric analyzer that was purged with nitrogen at a flow rate of 70 mL/min. A heating rate of 20 °C/min was used and scanning range was from 40 °C to 850 °C. Infrared spectra were recorded using a Bruker VERTEX 70 Fourier transform infrared spectrometer (FT-IR) with a heating device. Elemental analysis was carried out on a German Vario Micro cube microanalyzer. Mechanical properties were measured using a dynamic mechanical thermal analysis (DMA) apparatus (PerkinElmer, Diamond DMA). Specimens (50 × 10 × 1.0 mm) were tested in 3 point bending mode. The thermal transitions were studied in the scope of 20–200 °C at a heating rate of 4 °C/min and at a fixed frequency of 1 Hz.

2.3. Synthesis of [$N_3P_3(OC_6H_4\{NHC(O)CH_3\}$-4)$_6$] (***I***)

This compound was synthesized as reported [46]. White crystal, Yield: 91%, MP. 252–255 °C ^{1}H NMR (DMSO-d$_6$, TMS, ppm): 9.92 (1H, –NH), 6.79–7.45(4H, dd, Ar–H), 2.04(3H, –CH$_3$). ^{13}C NMR (DMSO-d$_6$, TMS, ppm): 168.0(C=O), 144.9(C–O), 136.4(C–N), 120.5 (CH), 119.9(CH), 23.8(CH$_3$). ^{31}P NMR (DMSO-d$_6$, ppm): 9.18.

2.4. Synthesis of [$N_3P_3(OC_6H_4\{NH_2\}$-4)$_6$] (***II***)

The compound was synthesized as reported [46]. White powder, yield: 80%, MP. 172–174 °C ^{1}H NMR (DMSO-d$_6$, TMS, ppm):

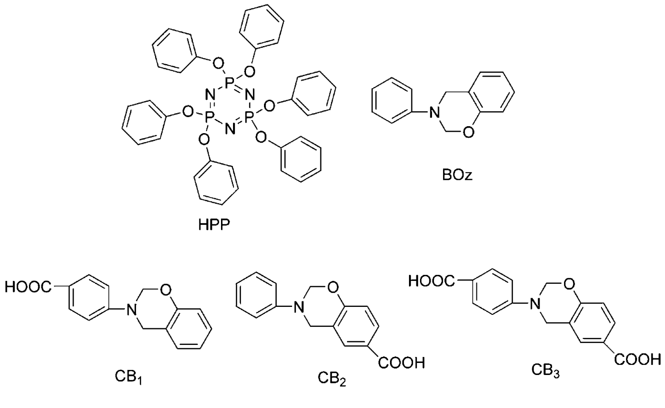
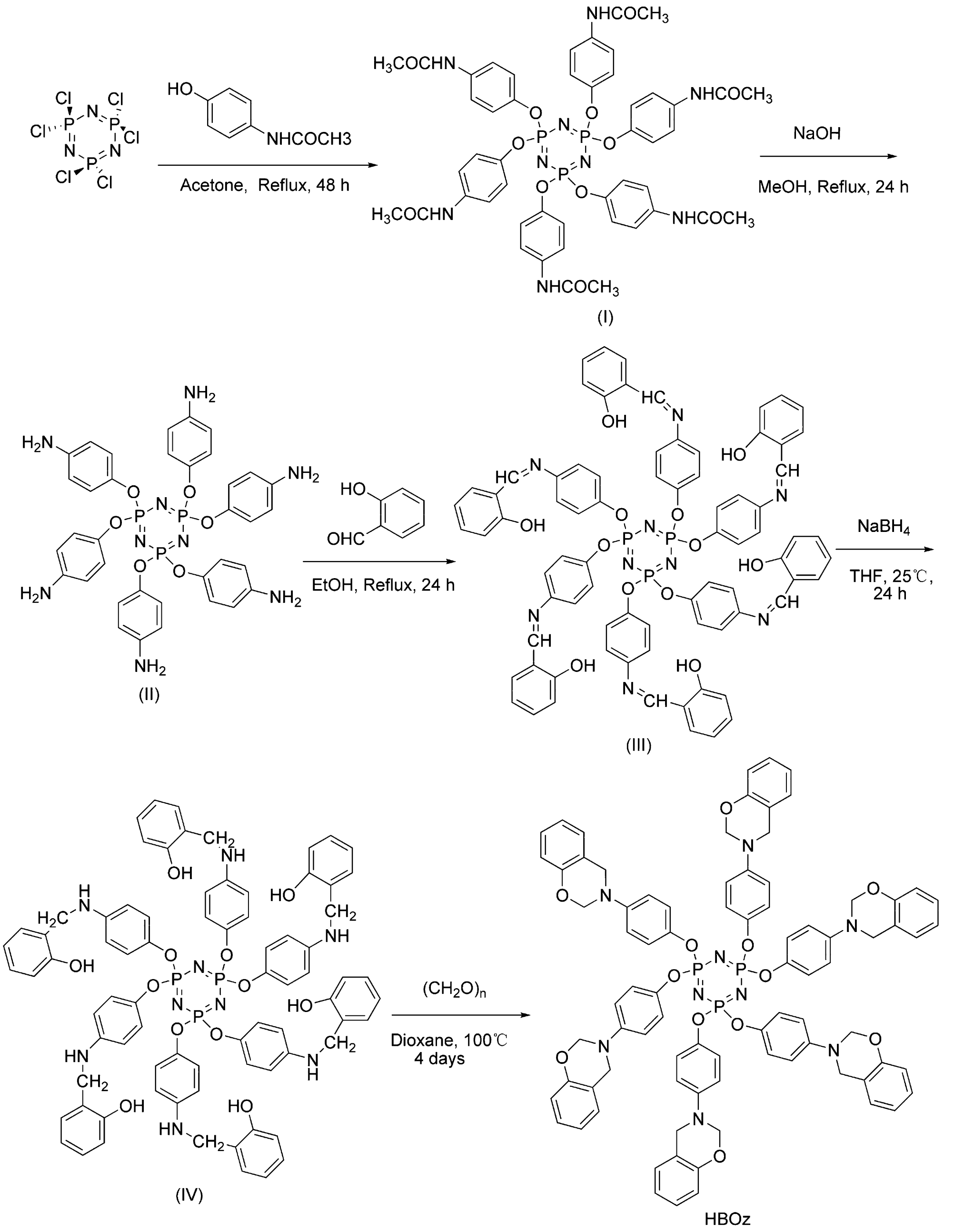


Fig. 1. The structures of HPP, BOz, CB$_1$, CB$_2$ and CB$_3$.



Scheme 1. Synthesis of highly branched benzoxazine HBOz.

6.41–6.52(4H, dd, Ar–H), 4.91(2H, Ar–NH_2). ^{13}C NMR (DMSO-d_6, TMS, ppm): 145.3(C–N), 140.5(C–O), 120.6(CH), 113.9(CH). ^{31}P NMR (DMSO-d_6, ppm): 10.67.

2.5. *Synthesis of [$N_3P_3(OC_6H_4\{NCHC_6H_4(2\text{-}OH)\}\text{-}4)_6$] (**III**)*

A solution of salicylaldehyde (18.3 g, 149.9 mmol) in ethanol (50 mL) was added to a solution of **II** (16.3 g, 20.8 mmol) in ethanol (200 mL) under argon atmosphere, and the mixture was refluxed under vigorous stirring for 24 h. The resulting yellow solid (compound **III**) was filtered off and washed with a large excess of water, ethanol (3 × 5 mL), and hexane (3 × 5 mL) and dried in vacuum at 40 °C for 48 h. Yield: 27.5 g (96%), MP. 152–154 °C ^1H NMR (DMSO-d_6, TMS, ppm): 12.88(1H, CH=N), 8.84(1H, HO–Ar), 6.86–7.49(8H, Ar–H). ^{13}C NMR (DMSO-d_6, TMS, ppm): 164.5(C–OH), 161.3(C=N), 149.6(C–O), 146.5(C–N), 134.4(CH), 133.7(CH), 123.8(CH), 122.6(CH), 120.3(C), 120.2(CH), 117.7(CH). ^{31}P NMR (DMSO-d_6, ppm): 9.12. Elemental analysis Calcd. (%) for $C_{78}H_{60}N_9O_{12}P_3$: C, 66.52; H, 4.29; N, 8.95. Found: C, 65.46; H, 4.33; N, 9.00.

2.6. *Synthesis of [$N_3P_3(OC_6H_4\{NHCH_2C_6H_4(2\text{-}OH)\}\text{-}4)_6$] (**IV**)*

Sodium borohydride (1.8 g, 46.1 mmol) was added to a solution of **III** (18 g, 12.8 mmol) in 150 mL tetrahydrofuran (THF) in small portion while stirring. After reaction at 25 °C for 12 h, 100 mL water was added to the solution, and the mixture was stirred at 25 °C for another 12 h. Then the solution was evaporated under reduced pressure to remove the organic solvent, the resulting solid was extracted with CH_2Cl_2, washed with water, dried over anhydrous Na_2SO_4, concentrated and precipitated in petroleum ether. Pale

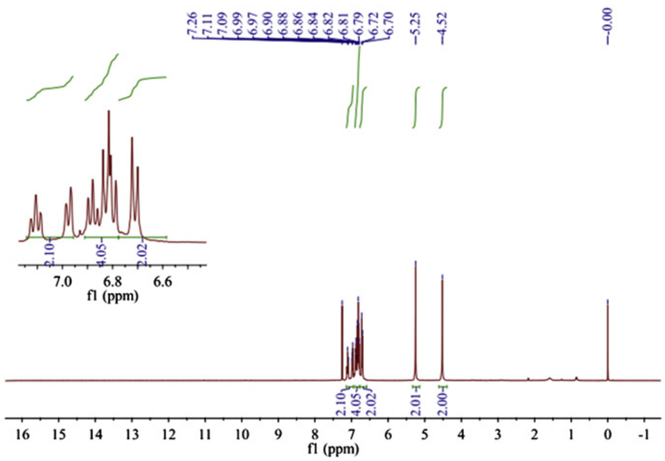


Fig. 2. ^1H NMR spectrum of HBOz (solvent: $CDCl_3$).

powder was gained, and dried in vacuum at 40 °C for 48 h. Yield: 16.3 g (90%), MP. 154–156 °C ^1H NMR (Acetone-d_6, TMS, ppm): 9.50 (1H, HO–Ar), 6.41–7.17(8H, Ar–H), 5.78(1H, NH), 4.14–4.16(2H, CH_2). ^{13}C NMR (Acetone-d_6, TMS, ppm): 155.9(C–OH), 146.8(C–N), 134.9(C–O), 129.2(C–CH_2), 128.3(CH), 126.4(CH), 121.8(CH), 119.6 (CH), 115.7(CH), 113.2(CH), 42.8(CH_2). ^{31}P NMR (Acetone-d_6, ppm): 10.62. Elemental analysis Calcd. (%) for $C_{78}H_{72}N_9O_{12}P_3$: C, 65.96; H, 5.11; N, 8.88. Found: C, 65.78; H, 5.06; N, 8.88.

2.7. *Synthesis of [$N_3P_3(OC_6H_4\{NCH_2CH_2C_6H_4(2\text{-}O)\}\text{-}4)_6$] (HBOz)*

A solution of **IV** (10.0 g, 7.0 mmol) and paraformaldehyde (1.9 g, 63.4 mmol) in 150 mL 1,4-dioxane was stirred at 100 °C for 4 days under an argon atmosphere. Then the solution was evaporated under reduced pressure to remove the organic solvent, the resulting solid was dissolved in CH_2Cl_2, and washed with diluted solution of sodium hydroxide. The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated and then precipitated in petroleum ether. A light yellow powder was collected, dried in vacuum at 40 °C for 48 h. Yield: 9.9 g (95%), MP. 75–77 °C.

2.8. *Synthesis of $C_6H_4NCH_2CH_2C_6H_4(2\text{-}O)$ (BOz), (4-COOH) $C_6H_4NCH_2CH_2C_6H_4(2\text{-}O)$ (CB_1), $C_6H_4NCH_2CH_2C_6H_3(2\text{-}O)(4\text{-}COOH)$ (CB_2), and (4-COOH)$C_6H_4NCH_2CH_2C_6H_3(2\text{-}O)(4\text{-}COOH)$ (CB_3)*

The structures of BOz, CB_1, CB_2 and CB_3 were showed in Fig. 1 and synthesized as reported methods [26].

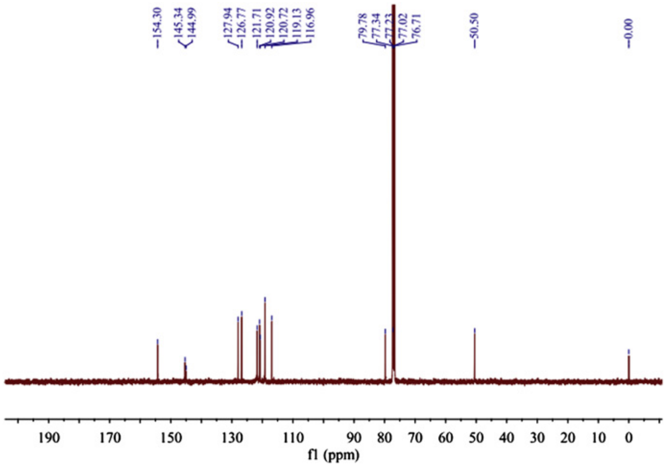


Fig. 3. ^{13}C NMR spectrum of HBOz (solvent: $CDCl_3$).

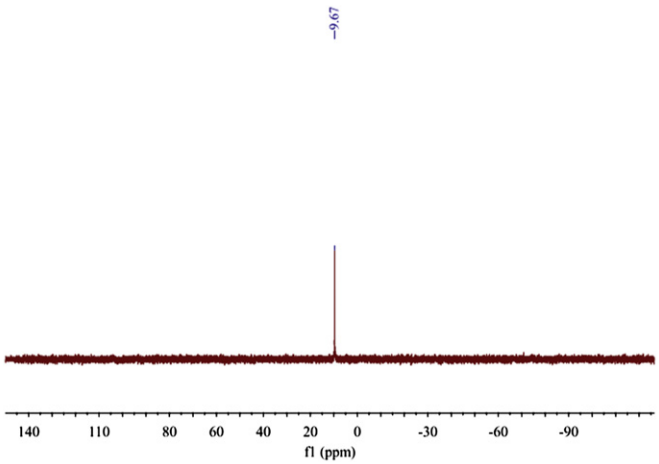


Fig. 4. ^{31}P NMR spectrum of HBOz (solvent: $CDCl_3$).

3. Results and discussion

3.1. *Synthesis and characterization*

The HBOz monomer was synthesized according to Scheme 1. The overall yield after five steps was about 60%. The purified sample was satisfactory for further analysis. Herein, the structure of the novel HBOz monomer was confirmed with ^1H, ^{13}C, ^{31}P NMR and element analysis.

Fig. 2 shows the ^1H NMR spectrum of HBOz. Resonances appearing at 4.52 ppm and 5.25 ppm are assigned to the methylene protons of Ar–CH_2–N and O–CH_2–N of the oxazine ring, respectively. The multiplets at 6.70–6.72, 6.79–6.88, and 6.90–7.11 ppm are assigned to the aromatic protons.

In the corresponding ^{13}C NMR spectrum in Fig. 3, resonances appearing at 50.5 ppm and 79.7 ppm are assigned to the methylene carbons of Ar–CH_2–N and O–CH_2–N of the oxazine ring, respectively. Other chemical shifts (ppm) are assigned to the aromatic carbon resonances: 154.3(C–O), 145.3(C–N), 144.9(C–O), 127.9 (CH), 126.8(CH), 121.7(C), 120.9(CH), 120.7(CH), 119.1(CH), 116.9 (CH).

The ^{31}P NMR is shown in Fig. 4, and there is a single peak at 9.67 ppm, which indicates that the substituted reaction onto CP ring was complete.

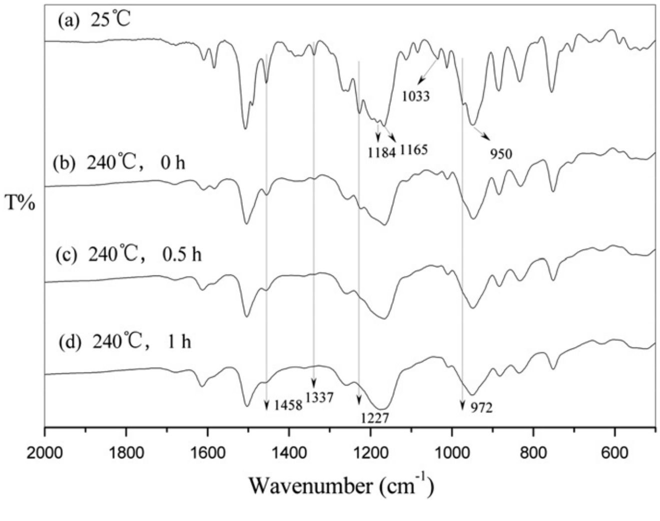


Fig. 5. The FT-IR spectra of HBOz and HBOz curing at 240 °C for different time in the region between 2000 and 500 cm^{-1}.

Elemental analysis for HBOz is following: Calcd. (%): C, 67.60; H, 4.86; N, 8.45. Found: C, 66.86; H, 4.91; N, 8.57. All analysis results indicate that the desired hyperbranched benzoxazine monomer has been prepared successfully.

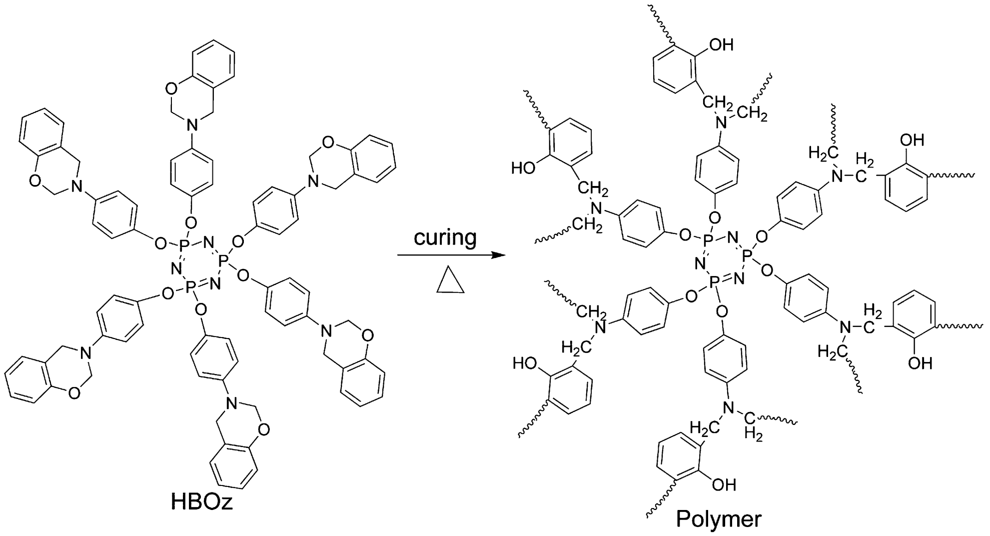
3.2. Curing behavior of HBOz monomer monitored by FT-IR

The ring-opening polymerization characteristic was monitored by FT-IR spectrometer, the results were shown in Fig. 5. The KBr pill containing HBOz powder was heated at 240 °C for different time and the FT-IR spectra were recorded. The characteristic absorption bands due to benzoxazine structure are situated at 972 cm^{-1} (out of plane-bending vibrations of C—H), 1227 cm^{-1} (asymmetric stretching of C—O—C), 1184 cm^{-1} (asymmetric stretching of C—N—C), 1033 cm^{-1} (symmetric stretching of C—O—C), and 1337 cm^{-1} (CH_2 wagging), respectively [47]. The wave-numbers from 700 cm^{-1} to 900 cm^{-1} and at 1458 cm^{-1} are assigned to disubstituted benzene ring; two very strong absorption peaks located at 950 cm^{-1} and 1165 cm^{-1} are corresponding to stretching of P—O—Ar and N=P, respectively. The spectrum of Fig. 5(b) was recorded immediately after the sample pill was quickly heated to 240 °C. It was found that the intensity of characteristic absorption of benzoxazine structure and disubstituted benzene ring obviously decreased, the characteristic peaks located at 972 cm^{-1} and 1337 cm^{-1} were nearly to disappear. When the curing time was prolonged to 0.5 h and 1 h at 240 °C, the intensity of benzoxazine characteristic peaks continued to decrease, then disappeared after 1 h. These results indicate that the HBOz monomer has been polymerized completely. At the same time, the intensity of disubstituted benzene ring's characteristic peaks located in the range of 700 cm^{-1}–900 cm^{-1} and 1458 cm^{-1} also began to decrease gradually, this indicated a high substitution pattern of the aromatic rings as a consequence of the crosslinking reactions, and the ring-opening reaction model of HBOz was displayed in Scheme 2. Besides, comparing the absorption peaks located at 950 cm^{-1} and 1165 cm^{-1} from Fig. 5(a–d), there were no significant changes even under high temperature for 1 h, which illustrated that the inorganic CP ring was thermally stable at such condition.

3.3. Curing behavior of HBOz monomer scanned by DSC

It is known that the high polymerization temperature is one important factor that limits the application of polybenzoxazine. The curing behavior of the new monomer HBOz was examined by DSC. Herein, several catalysts were used to estimate the possibility of decreasing the polymerization temperature of HBOz monomer by mixing the catalysts with HBOz powder. Three compounds whose boiling point temperatures are higher than 180 °C were utilized as the catalyst because of the high polymerization temperature of benzoxazines. These catalysts were imidazole (C_i), N, N-dimethylbenzylamine (C_{ii}) and a neutral salt [48] obtained from the reaction of diethanolamine and p-toluenesulfonic acid with the molar ratio 1:1 (C_{iii}). The results of the heat curing behaviors using the catalysts to reduce the polymerization temperatures of the monomer were shown in Fig. 6, a sharp exothermic peak corresponding to the ring-opening polymerization was observed for HBOz, the onset and maximum temperatures of the exotherm were 177 °C and 225 °C, respectively. The amount of exotherm for HBOz was 215.5 J/g. In addition, there was a small endothermic peak corresponding to melting point at 77 °C for HBOz. By adding curing catalysts with the content of 3 wt% to HBOz monomer, the exothermic peaks changed obviously from the DSC results. For HBOz/C_i-3 wt%, the onset and maximum temperatures of the exotherm were reduced to 132 °C and 215 °C, respectively. The corresponding amount of exotherm was lowered to 202.4 J/g; for HBOz/C_{ii}-3 wt% and HBOz/C_{iii}-3 wt%, the onset temperatures of the exotherm were both reduced to 135 °C, the maximum temperatures of the exotherm were separately lowered to 222 °C and 212 °C. And the corresponding amounts of exotherm were correspondingly diminished to 204.5 J/g and 70.8 J/g, respectively. Comparing to HBOz, the polymerization temperatures and enthalpies were obviously reduced. Besides, the HBOz/catalysts mixtures with catalysts' contents of 1 wt% and 5 wt% were also investigated and the results were summarized in Table 1. It was found that the onset exothermic temperatures, maximum exothermic temperatures and exothermic enthalpies were all decreased with the increase of the catalysts' content.

On the other hand, carboxylic acid-containing benzoxazines (Fig. 1) used as the functional catalysts were also studied. Andreu [26] reported that CB_1, CB_2 and CB_3 produced significant decrease in the polymerization temperature of BOz monomer. Herein, the carboxylic acid-containing benzoxazines were also added to HBOz monomer as curing catalysts. To carry out this study, several samples of HBOz/CB_1, HBOz/CB_2 and HBOz/CB_3 were prepared, and scanned by DSC. The results obtained from heating DSC plots were collected in Fig. 7. When small amount (3 wt%) of carboxylic acid-



Scheme 2. Polymerization of HBOz monomer under heating.

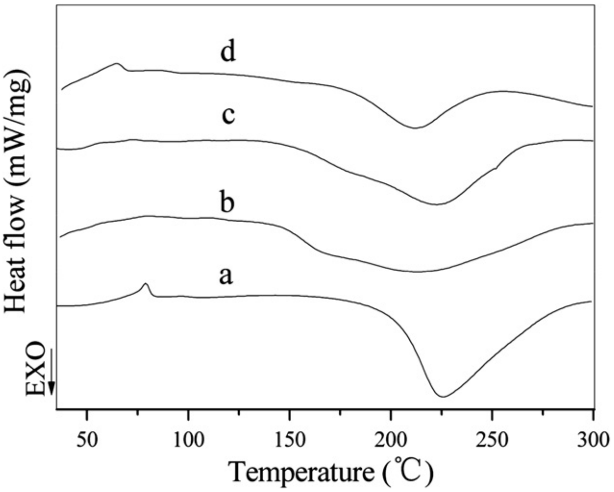


Fig. 6. DSC plots of HBOz monomer using common catalysts with the content of 3 wt%. a. HBOz, b. HBOz/C_i-3 wt%, c. HBOz/C_{ii}-3 wt%, d. HBOz/C_{iii}-3 wt%.

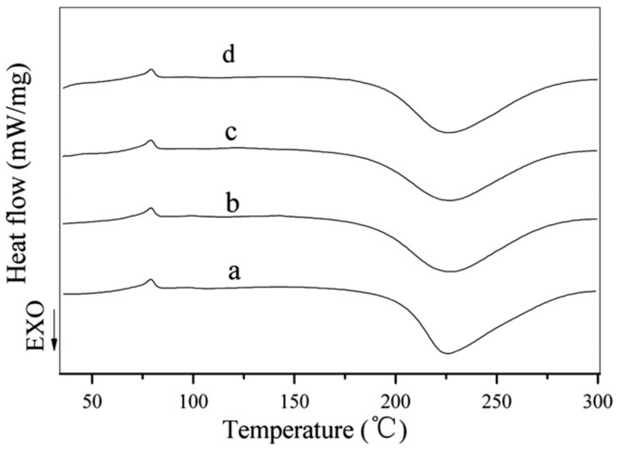


Fig. 7. DSC plots of HBOz monomer using functional catalysts with the content of 3 wt %. a. HBOz, b. HBOz/CB_1-3 wt%, c. HBOz/CB_2-3 wt%, d. HBOz/CB_3-3 wt%.

containing benzoxazines were added, the maximum exothermic peaks had little change, the onset temperatures of the exothermic peaks (T_o) just reduced a little comparing with that of pure HBOz: the T_o of HBOz/CB_1-3 wt%, HBOz/CB_2-3 wt% and HBOz/CB_3-3 wt% were lowered to 172 °C, 168 °C and 172 °C, respectively; and it was 177 °C for HBOz. However, the exothermic enthalpies had significant decrease: the enthalpies of HBOz/CB_1-3 wt%, HBOz/CB_2-3 wt% and HBOz/CB_3-3 wt% were reduced to 191.6 J/g, 197.7 J/g and 191.3 J/g, respectively; while it was 215.5 J/g for HBOz. Changing the amounts of carboxylic acid-containing benzoxazines at 1 wt% and 5 wt% level resulted in similar effect and the results were also summarized in Table 1. We can conclude that carboxylic acid-containing benzoxazines show little effect on decrease polymerization temperature, but the exothermic enthalpies are diminished obviously with increasing the catalysts' content and it will let the monomer mixture polymerize more mildly than that of pure monomer.

Comparing the two series of catalysts, it is clear to find that the common curing catalysts (C_i, C_{ii} and C_{iii}) are more suitable for the curing of HBOz than the carboxylic acid-containing benzoxazines, they effectively decrease the polymerization temperature. The carboxylic acid-containing benzoxazines reduced the polymerization temperature of BOz effectively in report [47], but not obviously in HBOz system. Possible reason is that the common curing catalysts can dilute the reaction mixture, low viscosity is a benefit to the polymerization rate; but functional carboxylic acid-containing catalysts can copolymerize with the monomer, the high viscosity system owing to the highly crosslinking polymerization reaction between HBOz and functional catalysts restrains the catalytic activity of the carboxylic acid groups located on the carboxylic acid-containing benzoxazines (Fig. 7).

Table 1
Thermal property of HBOz/Catalysts series samples.

Samples	T_m[a] (°C)	T_o[b] (°C)	T_{max}[c] (°C)	ΔH[d] (J/g)	$T_{5\%}$[e] (°C)	$T_{10\%}$[f] (°C)	T_{max}[g] (°C)	Y_c[h] (%)
HBOz	77	177	225	215.5	403	449	453	66.9
HBOz/C_i-1 wt%	80	140	224	213.6	374	431	445	60.4
HBOz/C_i-3 wt%	–	132	215	202.4	378	419	441	59.4
HBOz/C_i-5 wt%	88	115	208	193.5	373	405	459	57.8
HBOz/C_{ii}-1 wt%	70	167	228	207.2	341	401	440	56.7
HBOz/C_{ii}-3 wt%	–	135	222	204.5	379	422	435	57.2
HBOz/C_{ii}-5 wt%	78	130	225	202.7	301	402	471	30.3
HBOz/C_{iii}-1 wt%	78	138	220	135.2	363	401	420	60.5
HBOz/C_{iii}-3 wt%	68	135	212	70.88	329	374	434	51.2
HBOz/C_{iii}-5 wt%	–	130	203	60.1	331	384	423	43.5
HBOz/CB_1-1 wt%	78	176	225	199.6	395	435	492	61.4
HBOz/CB_1-3 wt%	79	172	225	191.6	409	450	478	62.4
HBOz/CB_1-5 wt%	76	168	222	153.1	415	457	461	59.0
HBOz/CB_2-1 wt%	78	170	225	203.7	398	436	450	58.7
HBOz/CB_2-3 wt%	78	168	225	197.7	400	441	474	60.3
HBOz/CB_2-5 wt%	78	160	225	189.0	393	436	470	60.1
HBOz/CB_3-1 wt%	77	175	225	202.1	390	429	445	57.7
HBOz/CB_3-3 wt%	79	172	225	191.3	395	437	468	59.3
HBOz/CB_3-5 wt%	75	168	221	187.5	387	429	462	58.5

[a] Melt point temperature determined by DSC (10 °C/min).
[b] Onset temperature of exothermic peak.
[c] Maximum of the polymerization exotherm.
[d] Polymerization enthalpy by DSC.
[e] $T_{5\%}$: The temperature for which the weight loss is 5% by TGA scan (20 °C/min) under nitrogen.
[f] $T_{10\%}$: The temperature for which the weight loss is 10%.
[g] T_{max}: Maximum weight loss temperature.
[h] Y_c: Char yields at 850 °C.

3.4. Thermal properties of the new polybenzoxazines

A series of samples forming by HBOz powder with different curing catalysts (see in Table 1) were added to test tubes, and the

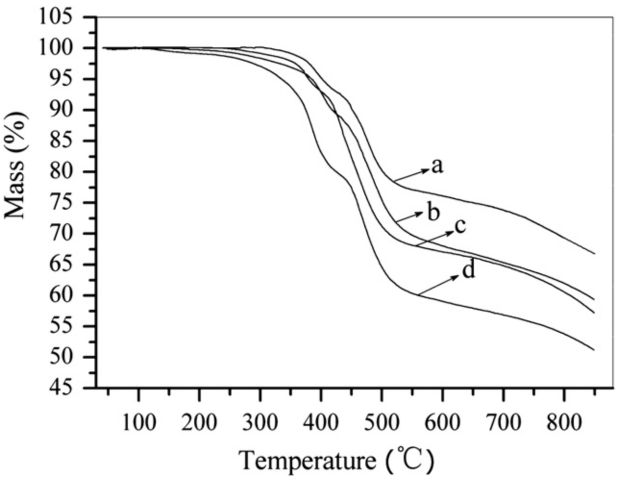


Fig. 8. TG curves of PHBOz by curing HBOz monomer using common curing catalysts with the content of 3 wt%. a. PHBOz, b. PHBOz/C_i-3 wt%, c. PHBOz/C_{ii}-3 wt%, d. PHBOz/C_{iii}-3 wt%.

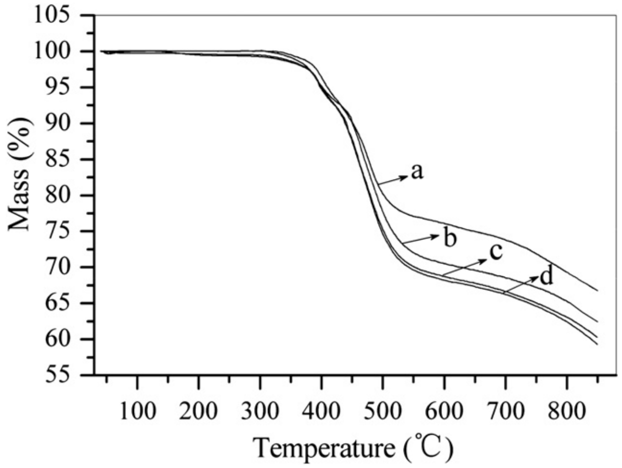


Fig. 9. TG curves of PHBOz by curing HBOz monomer using functional curing catalysts with the content of 3 wt%. a. PHBOz, b. PHBOz/CB_1-3 wt%, c. PHBOz/CB_2-3 wt%, d. PHBOz/CB_3-3 wt%.

sample tubes were cured stepwise at 120 °C for 1 h and 200 °C for 2 h, and then post-cured at 220 and 240 °C for 1 h each in salt-bath under an argon atmosphere. All the cured samples were dark red color. Thermal stability of the novel polybenzoxazines was investigated by TGA. The TGA profiles of polybenzoxazines from the polymerization of HBOz monomer, HBOz/C_i-3 wt%, HBOz/C_{ii}-3 wt%, and HBOz/C_{iii}-3 wt% were shown in Fig. 8. The 5% and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) for PHBOz were 403 and 449 °C, respectively. While with 3 wt% catalysts, the $T_{5\%}$ and $T_{10\%}$ were all lower than that of PHBOz: for PHBOz/C_i-3 wt%, they were 378 and 419 °C, respectively; for PHBOz/C_{ii}-3 wt%, they were 379 and 422 °C; meanwhile they were 329 and 374 °C for PHBOz/C_{iii}-3 wt%. Similarly, the maximum weight loss temperature (T_m) of PHBOz was also higher than those of the others with catalysts, and the details were shown in Table 1. The Char yields at 850 °C (Y_c) of polybenzoxazines were also recorded in Table 1. The Y_c of PHBOz was as high as 66.9%, and the others with 3 wt% these common catalysts were much lower than that of PHBOz, PHBOz/C_{iii}-3 wt% sample held the lowest yield, only 51.2%. It is well known that the common catalysts do not copolymerize with the monomer for lack of reactive groups; they remain in the polybenzoxazine systems after polymerization and act as unstable impurities. The remaining catalyst will accelerate the degradation of polybenzoxazine under high temperature and result in reducing the heat resistance (Fig. 9).

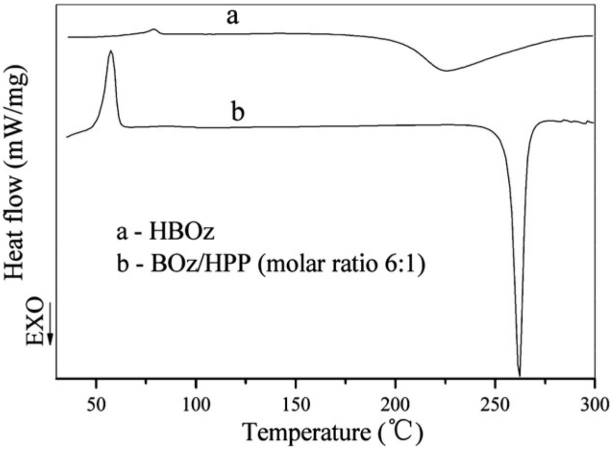


Fig. 10. DSC curves of HBOz and BOz/HPP (molar ratio 6:1).

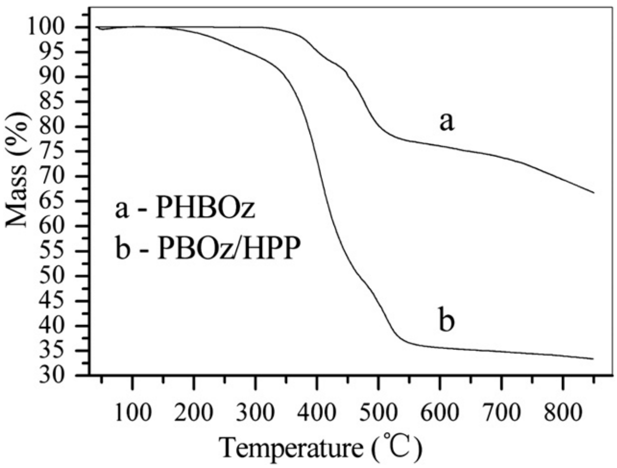


Fig. 11. TG curves of PHBOz and PBOz/HPP.

The thermal stability of the novel polybenzoxazines using functional curing catalysts (CB_1, CB_2 and CB_3) was also investigated by TGA, the results were shown in Fig. 9 and Table 1. It was excited to find that the thermal stability of the polybenzoxazines with acid-containing benzoxazines was as good as that of PHBOz, some of them were even higher than that of PHBOz. For example, the 5% and T_m for PHBOz/CB_1 were higher than that of PHBOz, they were 409 and 478 °C, respectively (PHBOz were separately 401 and 451 °C). The $T_{5\%}$ and $T_{10\%}$ of PHBOz with different contents of functional catalysts were separately located in the range of 390–410 °C and 430–460 °C. And the T_m and Y_c were mainly distributed in the range of 460–490 °C and 58%–62%, respectively. These factors reflecting to the thermal stability were better than that of PHBOz with common curing catalysts (C_i, C_{ii} and C_{iii}). The reasons maybe result from the reactive benzoxazines groups on the acid-containing benzoxazines, which can copolymerize with HBOz monomers and get into the skeleton of crosslinking system.

3.5. Thermal properties of HBOz and PHBOz comparing to monofunctional benzoxazine and its polymers

To compare the thermal properties with common polybenzoxazines, another benzoxazine sample was introduced, which was prepared from the mixtures of BOz monomer and HPP at molar ratio of 6:1 (Its theoretical elemental composition is similar to HBOz). BOz/HPP was polymerized under the same curing condition of PHBOz to obtain PBOz/HPP polymer. The DSC curves of HBOz monomer and BOz/HPP are shown in Fig. 10. A sharp exothermic

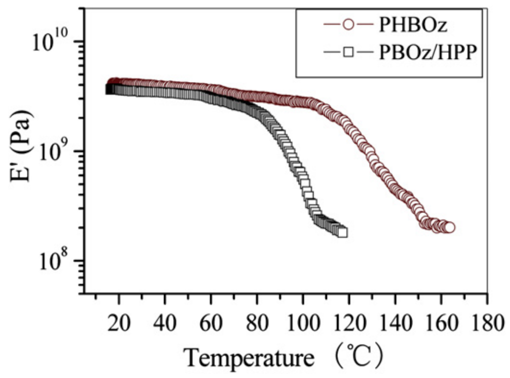


Fig. 12. Storage moduli of PHBOz and PBOz/HPP polybenzoxazines.

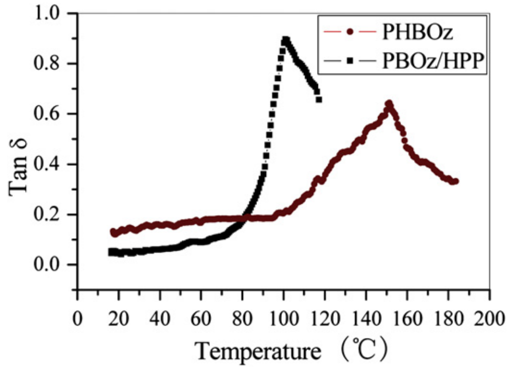


Fig. 13. Tanδ of PHBOz and PBOz/HPP polybenzoxazines.

peak is observed for BOz/HPP, and the maximum temperature of the exotherm is 262 °C, which is nearly 40 °C higher than that of HBOz monomer. An endothermic peak at 58 °C is assigned to the melting point of BOz/HPP mixture, which is a little lower than that of HBOz. The enthalpy of BOz/HPP is 211.2 J/g, which is near to 215.5 J/g of HBOz.

The thermal stability of PBOz/HPP and PHBOz was also carried out on TGA, the results were shown in Fig. 11. As expected, the thermal stability of PHBOz was much higher than that of PBOz/HPP, $T_{5\%}$ of them were 403 and 285 °C, respectively; and Y_c at 850 °C of them were 66.9% and 33.4%, respectively. The results illustrate that PHBOz polymer shows much higher thermal stability than that of common monofunctional polybenzoxazine composite. The reason is deemed that the inorganic cyclotriphosphazene ring possesses high thermal stability for its unique structure and can act as an ideal core to prepare high-performance organic–inorganic hybrid materials. At the same time the branched benzoxazine moieties are spatially distributed above and below the CP ring, and bring the new polybenzoxazine a highly spatial crosslinking structure which minimizes dangling side groups and improves dimensionally thermal stability.

3.6. *Mechanic property of the new polybenzoxazine*

The dynamic mechanical behavior of the cured benzoxazine resins was obtained as a function of the temperature beginning in the glassy state of each sample to the rubbery plateau of each material. As seen in Fig. 12, the storage modulus (E′) of PHBOz at room temperature is 4.14 GPa, which is a little higher than that of PBOz/HPP (3.64 GPa). The E′ value of PHBOz starts to decrease at about 120 °C, while the E′ value of PBOz/HPP begins to decrease at about 80 °C. Comparing the decreasing slope of the E′ value from glassy state to rubbery plateau for PHBOz and PBOz/HPP, it is found that the decreasing slope of PHBOz is obviously lower than that of PBOz/HPP. The glass transition temperatures (T_g) of the polybenzoxazines can be deduced in Fig. 13 from the corresponding temperature of peak of tanδ value. T_g of PHBOz and PBOz/HPP are 152 °C and 101 °C, respectively. The tanδ value of PHBOz is much lower than that of PBOz/HPP after 80 °C because of higher dimensional crosslinking structures of PHBOz. It is known to us that PBOz/HPP is low crosslinking structure, while it is highly steric crosslinking structure for PHBOz curing from the star-branched organic–inorganic hybrid benzoxazine. Besides, there are lots of rigid and stable CP in the PHBOz as crosslinking cores, which also contribute to improving the mechanic properties of PHBOz to some extent. For these reasons mentioned above, PHBOz shows higher mechanic performance than that of PBOz/HPP under heat.

4. Conclusions

We have synthesized a novel star-branched benzoxazine monomer based on CP ring, the new organic–inorganic hybrid benzoxazine monomer possesses low melting point (77 °C) and good solubility in common solvents though with high molecular weight. The new benzoxazine monomer could be ring-opening polymerized completely at 240 °C for 1 h, according to the disappearance of benzoxazine characteristic peaks located at 1227 cm^{-1} and 972 cm^{-1}. A sharp exothermic peak at 225 °C for ring-opening polymerization of the benzoxazine monomer was observed at DSC plots, and the onset polymerized temperature was about 180 °C. Two species of curing catalysts were used to reduce the polymerization temperature, the common catalysts (C_i, C_{ii} and C_{iii}) could effectively decrease the onset polymerization temperature and exothermic enthalpy with small amount of them ($\leq$5 wt%), but they led to reduction in corresponding polymers' thermal stability; while using the functional catalysts (carboxylic acid-containing benzoxazines: CB_1, CB_2 and CB_3), the onset polymerization temperatures had little decrease, but final polymers held excellent thermal stability from TGA results, some of them were even higher than that of the pure polybenzoxazine. Comparing to the blending resin of BOz/HPP, the polymerization temperature of the benzoxazine monomer was about 40 °C lower than that of BOz/HPP mixture. Besides, the hyperbranched polybenzoxazine also showed outstanding thermal stability and good mechanic performance resulting from the highly dimensional crosslinking structure with the core of rigid and stable inorganic CP ring. It had higher thermal stability ($T_{5\%}$ at 403 °C) and higher char yield (66.9% char yield at 850 °C) than that of PBOz/HPP blend. And the T_g of PHBOz was as high as 152 °C, which was about 50 °C higher than that of PBOz/HPP resin. The new polybenzoxazine may be an applicable material in the application of high technology for its excellent thermal stability and mechanic properties.

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Appendix. Supplementary material

Figures showing ^{1}H, ^{13}C, ^{31}P NMR, DSC plots and TGA curves can be found online at doi:10.1016/j.polymer.2011.01.003.

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