

Triazine-Containing Benzoxazine and Its High-Performance Polymer

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ABSTRACT: A new synthetic route was designed to significantly increase the content of triazine structure in benzoxazine resin. 2,4,6-Tri(4-hydroxyphenyl)-1,3,5-*s*-triazine (TP) was synthesized by cyclotrimerization of 4-cyanolphenol and then benzoxazine monomer-containing triazine [2,4,6-tri(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazin-6-yl)-1,3,5-*s*-triazine (BZ-ta)] was synthesized via Mannich reaction from TP. Finally, the cross-linked polymer P(BZ-ta) was produced by thermal polymerization of BZ-ta. BZ-ta was characterized by nuclear magnetic resonance spectroscopy (NMR), fourier transform infrared spectroscopy (FTIR), mass spectrum, elemental analysis, and viscosity measurement. Curing behavior of BZ-ta was studied by differential scanning calorimetry, FTIR, and gel permeation chromatography. The structure and properties of P(BZ-ta) were investigated by powder X-ray diffraction, dynamic mechanical analysis, and thermogravimetric analysis. The results showed that the P(BZ-ta) had high glass temperature ($T_g = 322^\circ\text{C}$), excellent thermal oxidation stability (5 and 10% weight loss temperatures in air up to 403 and 453°C, respectively), high char yield (64%, 800°C in nitrogen), and high flame-retardance (limiting oxygen index, 39.7). © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polybenzoxazine; triazine; heat-resistant property; thermal stability; flame-retardant property

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INTRODUCTION

In the past two decades, polybenzoxazine has attracted much attention, because it exhibited excellent thermal mechanical property and low cost.^{1–3} With the rapid development of the aerospace, microelectronics, and energy industries, there is an urgent requirement to further improve the properties of polybenzoxazine, such as heat resistance, flame retardance, toughness, low dielectric constant, and so forth.

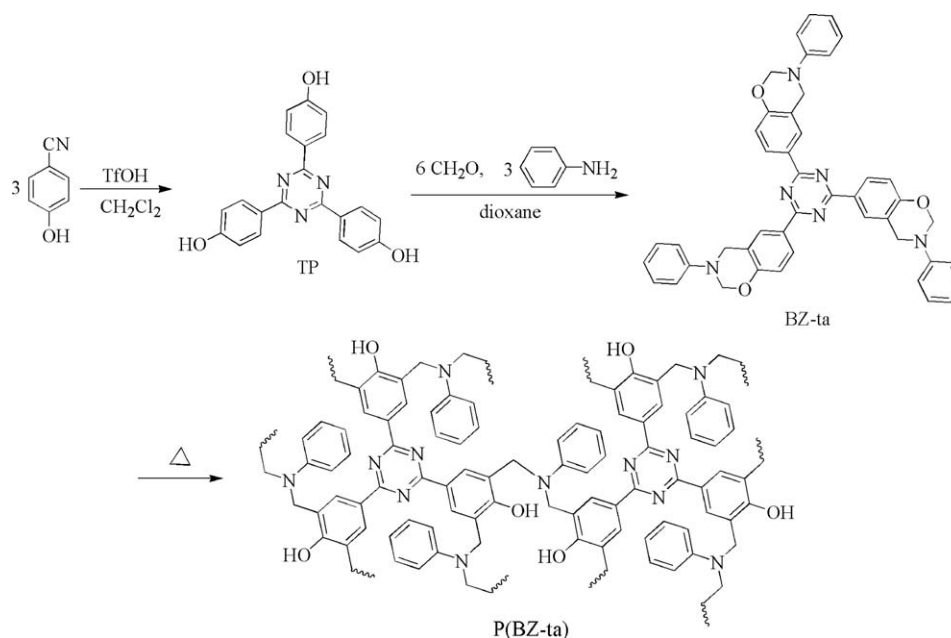
It is well-known that the activation energy of thermal degradation of triazine ring is much higher than that of benzene ring,⁴ and the triazine resin has excellent properties such as thermal stability, flame retardance, low dielectric content, and optoelectronic property.^{5–10} Therefore, the incorporation of a triazine structure into polybenzoxazine will enhance its heat-resistant and flame-retardant properties.

So far, there are few reports on incorporation of triazine structure into polybenzoxazine. The synthetic method is that nitrile group is first introduced into benzoxazine monomer and subsequently converted into triazine ring. For example, Ishida and coworkers^{11–13} reported the synthesis of phenylnitrile- and phthalonitrile-functional benzoxazine monomers based on ami-

nobenzonitrile homologues and their thermal or/and catalytic curing. Liu and coworkers^{14,15} reported the synthesis of cyano-functional benzoxazine monomer from 2,6-bis(4-diaminobenzoyl)benzonitrile and formation of triazine ring. Qi et al.¹⁶ synthesized phenylnitrile benzoxazine monomer through the reaction of 4-cyanophenol with 4'-diamino diphenylether and demonstrated that nitrile groups did not change significantly when curing temperature was below 250°C.

In spite of the success, it is difficult to obtain high triazine contents in polybenzoxazine. The reason is that cyclotrimerization reaction of nitrile group needs relatively harsh conditions. In addition, the formation of cross-linked network significantly reduced the mobility of nitrile group. Herein, we describe a new synthetic method for the preparation of polybenzoxazine with high content of triazine structure. The key is to preferentially incorporate triazine structure into benzoxazine monomer rather than nitrile group. Specifically, the 2,4,6-tri(4-hydroxyphenyl)-1,3,5-*s*-triazine (TP) was first synthesized by trimerization of 4-cyanophenol, and then TP was converted into benzoxazine monomer-containing triazine via Mannich reaction. Finally, the benzoxazine monomer was thermally cured into cross-linked polybenzoxazine, and thus high content of triazine structure was obtained in polybenzoxazine.

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Scheme 1. Synthetic route to BZ-ta and its polymer.

EXPERIMENTAL

Materials

4-Cyanophenol (99%) and trifluoromethanesulfonic acid (99%) were purchased from Sinopharm Chemical Reagent. Paraformaldehyde, aniline, dioxane, and triethylamine (Et₃N) were purchased from Tianjin Kermel Chemical Reagent. All reagents were used as received.

Synthesis of 2,4,6-Tri(3-phenyl-3,4-dihydro-2H-1,3-benzoxazin-6-yl)-1,3,5-s-triazine

TP was synthesized from 4-cyanophenol according to the literature.^{17,18} ¹H-NMR (300 MHz, CDCl₃, ppm): 6.97 (d, 6 H, Ph-H), 8.55 (d, 6 H, Ph-H), and 10.29 (s, 3 H, Ph-O-H).

To a 250-mL flask with a magnetic stirring device, aniline (2.7 mL, 0.03 mol), paraformaldehyde (1.8 g, 0.06 mol), diox-

ane (50 mL), and Et₃N (1 mL) were added. After the mixture was stirred for 0.5 h at room temperature, TP (3.57 g, 0.01 mol) was added into the reaction system. The resulting mixture was maintained at 90°C for 2 h. The crude product was washed with Na₂CO₃ solution and pure water until the mixture was neutral. After crystallization from ethanol, white powder (5.4 g) was obtained. Yield: 76%. ¹H-NMR (300 MHz, CDCl₃, δ, ppm): 4.80 (s, 6 H, N-CH₂-Ph), 5.47 (s, 6 H, N-CH₂-O), 6.93–8.53 (m, 24 H, Ar-H). ¹³C-NMR (75 MHz, CDCl₃, δ, ppm): 170.6 (Triazine ring-C), 158.2, 148.1, 129.5, 129.1, 128.9, 127.8, 121.9, 120.8, 118.6, 117.3 (Ar-C), 80.3 (N-CH₂-O, oxazine ring), and 50.6 (N-CH₂-Ph, oxazine ring). FTIR (KBr, cm⁻¹): 3037, 2916 (Ph-H), 1521, 1364 (triazine), 1601, 1583, 1496 (Ph), 941 (benzene ring attached with oxazine ring), 1250, 1232 (stretch, C-O-C), 820 (C-H vibration of benzene), and 753 (C-H,

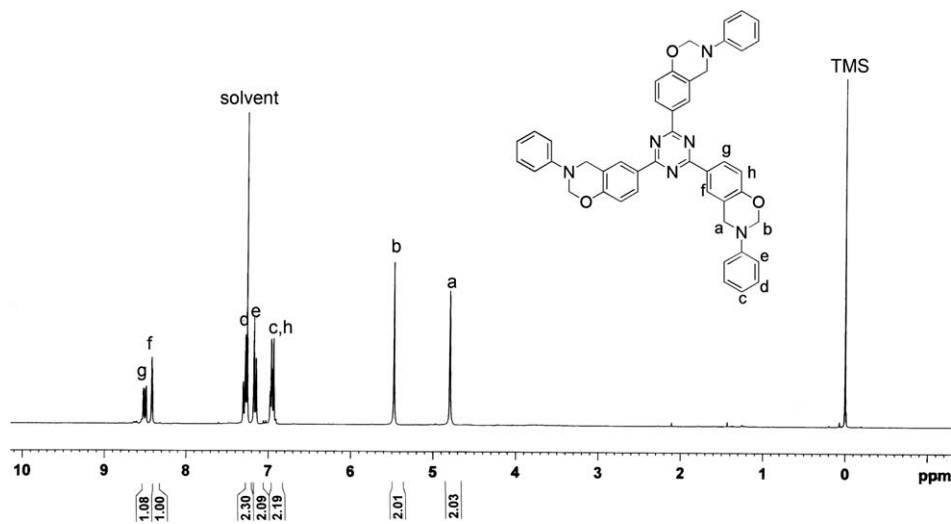


Figure 1. ¹H-NMR spectrum of BZ-ta.

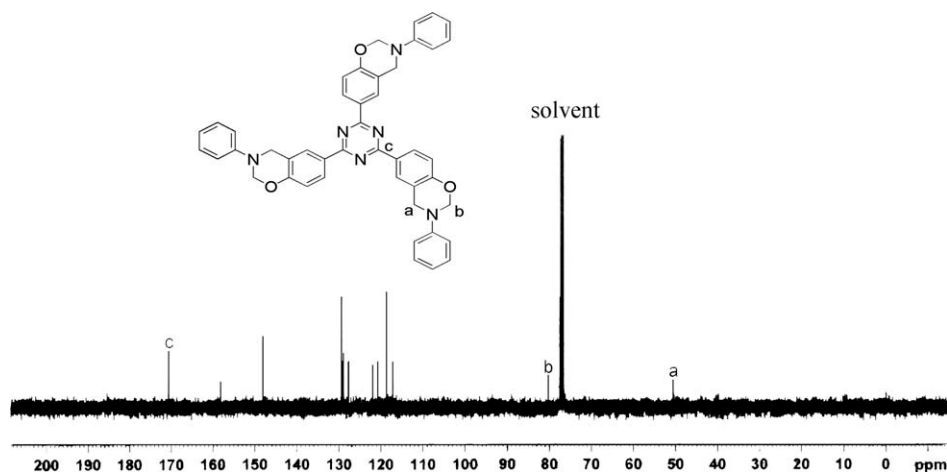


Figure 2. ^{13}C -NMR spectrum of BZ-ta.

bending of benzene). High-resolution mass spectrum (HRMS): Calcd. for $\text{C}_{45}\text{H}_{36}\text{N}_6\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 709.2882, found: 709.2907. Anal. Calcd. for $\text{C}_{45}\text{H}_{36}\text{N}_6\text{O}_3$: C, 76.25%; H, 5.12%; N, 11.86%. Found: C, 76.27%; H, 5.12%; N, 11.84%.

Thermal Curing of BZ-ta

The monomer was cured in a rectangular aluminum foil mold in an air-circulating oven. The step profiles of temperature and time were as follows: 140°C for 2 h, 160°C for 2 h, 180°C for 2 h, 200°C for 2 h, 220°C for 2 h, and 240°C for 2 h.

Measurements

FTIR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer (Bruker, GM). Samples were prepared as KBr pellets.

^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker Avance 300 instrument (Bruker). Deuterated chloroform was used as the solvent, and tetramethylsilane was used as the internal standard.

Elemental analysis (EA) was performed with a VarioEL III elemental analyzer (Elementar, GM).

HRMS was recorded on an Agilent Q-TOF6510 mass spectrometer (Agilent Technologies).

Viscosity measurement was performed in NDJ-8S rotational viscometer equipped with a 4[#] rotor (Jing Tian, CN). The rotation speed was 0.3–6.0 rad/min, and 60 g samples were added to a tube.

Powder X-ray diffraction (XRD) pattern was recorded with a D8 Advance X-ray power diffractometer (Bruker, GM). The work voltage and current were 40 kV and 40 mA, respectively. $\text{Cu K}\alpha$ radiation with a graphite filter was used. The sample powder was mounted and pressed on the glass holder and scanned from 10 to 80° at a scan rate of 5°/min.

Differential scanning calorimetry (DSC) thermogram was recorded with a Mettler-Toledo DSC822^c instrument (Mettler-Toledo, CH) at a heating rate of 10°C/min under nitrogen.

Gel permeation chromatography (GPC) measurement was performed on a Waters 515 HPLC Pump equipped with three Waters Styragel columns and Waters 2414 differential refractive index detector (Waters Corporation, Milford, MA). Tetrahydrofuran (THF) was used as the eluant. The flow rate was 1.0 mL/min, and the temperature was 40°C. Monodispersed polystyrene samples were used as standards.

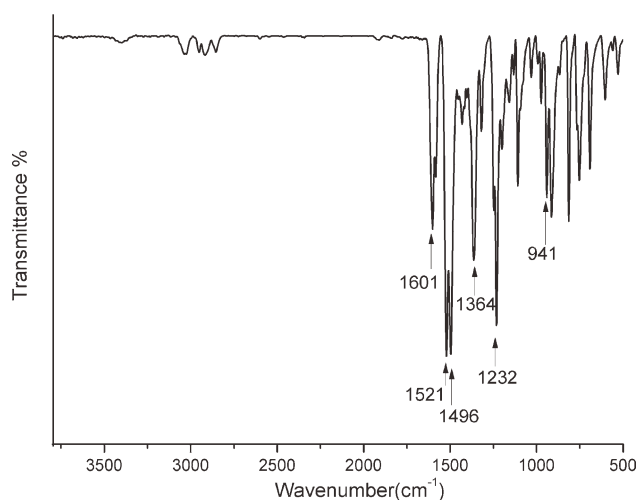


Figure 3. FTIR spectrum of BZ-ta.

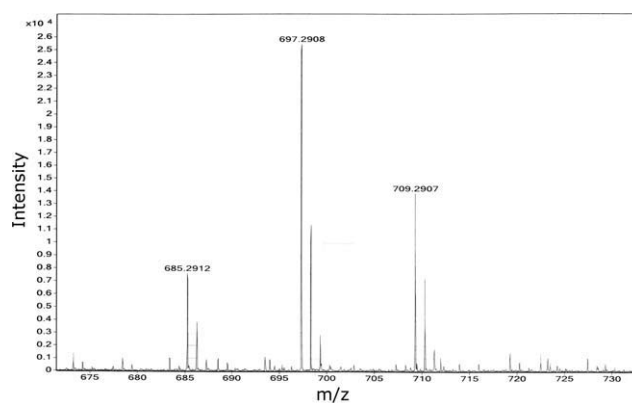


Figure 4. HRMS spectrum of BZ-ta.

Table I. Solubility of BZ-ta in Organic Solvents

Solvents ^a	Solubility (g/100 g) ^b
DMF	21.2
Dichloromethane	6.3
DMSO	5.68
THF	4.49
Chloroform	3.92
Acetone	1.82
Dioxane	1.0
Toluene	0.83
Ethyl acetate	0.55
Ethyl ether	0.37
Ethanol	0.34

^aAll solvents were analytical reagent, ^bThe measurement temperature was 20°C.

Dynamic mechanical analysis (DMA) was performed on a Mettler-Toledo DMA/SDTA861^e instrument (Mettler-Toledo). The specimen with dimensions of approximately 5.00 × 4.00 × 0.6 mm³ was tested by a shear mode with a frequency of 10 Hz, and the sample was heated at a rate of 3°C/min from 35 to 370°C.

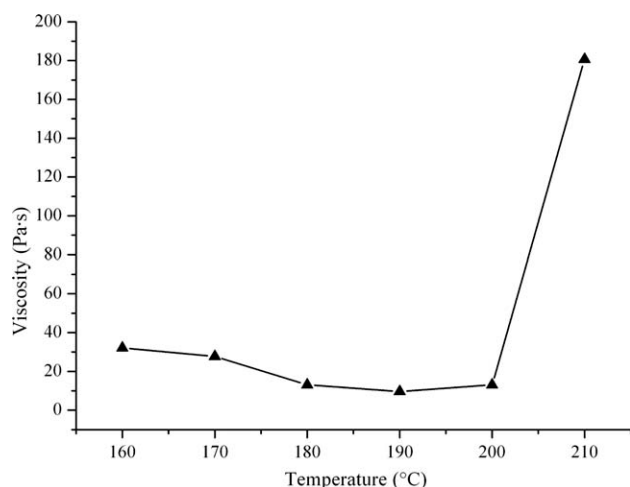
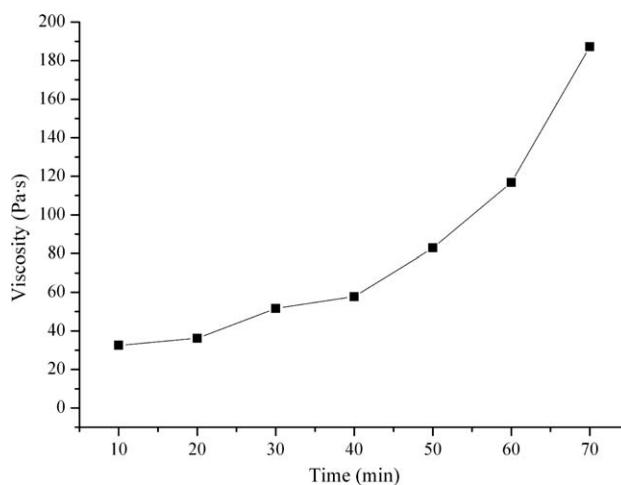
Thermogravimetric analysis (TGA) was performed on a TA SDTQ600 (TA) at a heating rate of 10°C/min under nitrogen or air atmosphere. The gas flow rate was 100 mL/min.

Limiting oxygen index (LOI) was measured on a JF-3 oxygen index instrument equipped with an oxygen analyzer (Nanjing Jiangning, CN). The dimensions of specimens were 120 × 10 × 4 mm³ and the testing standard was GB/T2406-1993.

RESULTS AND DISCUSSION

Synthesis of BZ-ta and Its Polymer

Scheme 1 illustrates our strategy for the preparation of BZ-ta and its polymer. Using trifluoromethanesulfonic acid as catalyst, the cyclotrimeration of 4-cyanophenol afforded TP. Subsequently, TP reacted with paraformaldehyde and aniline at a

**Figure 5.** Viscosity-temperature curve of BZ-ta.**Figure 6.** Viscosity-time curve of BZ-ta at 160°C.

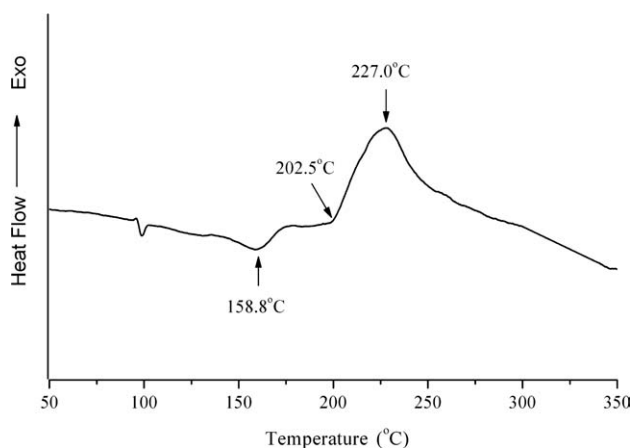
molar ratio of 1 : 6 : 3 to give 2,4,6-tri(3-phenyl-3,4-dihydro-2H-1,3-benzoxazin-6-yl)-1,3,5-s-triazine (BZ-ta) via Mannich reaction. Finally, BZ-ta formed the cross-linking network under thermal curing reaction.

Characterization of BZ-ta

Figure 1 shows ¹H-NMR spectrum of the BZ-ta. The resonances at 5.47 and 4.80 ppm were assigned to protons of —O—CH₂—N= and Ar—CH₂—N= in the benzoxazine ring, respectively. The integral ratio of those peaks was 2.01 : 2.03, which was close to the theoretical ratio of 2 : 2.

Figure 2 shows ¹³C-NMR spectrum of the BZ-ta. The resonances at 50.6 and 80.3 ppm corresponded to carbon atoms of Ar—CH₂—N= and —O—CH₂—N= in the oxazine ring, respectively. Moreover, the resonance at 170.6 ppm corresponded to carbon atoms in triazine ring.

Figure 3 shows FTIR spectrum of the BZ-ta. The characteristic bands at 1232 cm⁻¹ due to the stretching vibration of C—O—C in the oxazine ring and 941 cm⁻¹ due to the C—H out-of-plane vibration in the benzene ring to which an oxazine ring attached were clearly observed. The characteristic bands at 1521 and 1364 cm⁻¹ due to triazine ring and characteristic bands at 1601,

**Figure 7.** DSC thermogram of BZ-ta.

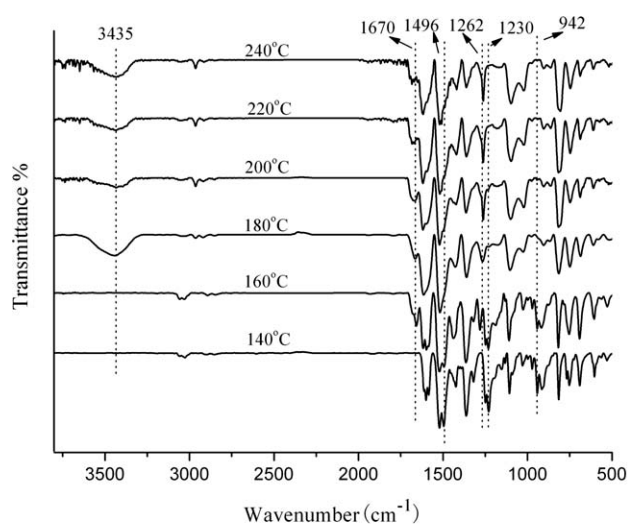


Figure 8. FTIR spectra of P(BZ-ta) after curing at different temperatures for 2 h.

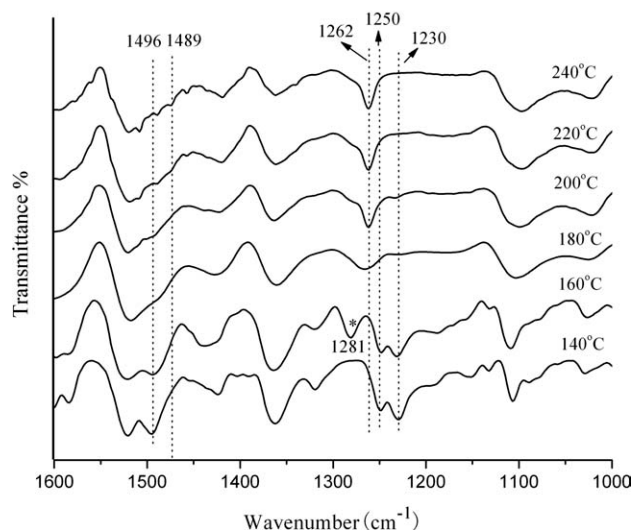


Figure 9. Conversion curves of BZ-ta at different curing temperature for 2 h (the band at 820 cm⁻¹ was used as internal standard).

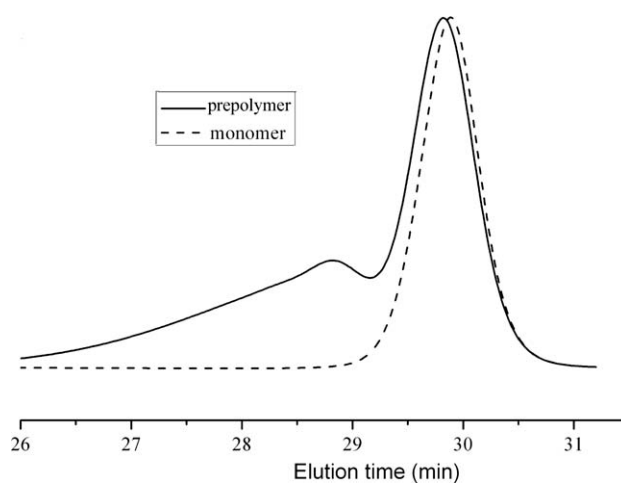


Figure 10. GPC curves of BZ-ta before and after curing at 170°C for 2 h.

1583, and 1496 cm⁻¹ due to the benzene ring were also clearly observed. FTIR spectrum is consistent with the NMR spectra.

Figure 4 shows HRMS spectrum of the BZ-ta. The molecular ion peak [M+H]⁺ was observed at 709.2907, which agreed well with the theoretical value of 709.2882. The other main peaks at 697.2908 and 685.2912 corresponded to the fragments with the loss of one or two carbons. The produce of fragments is ascribed to the cleavage of C—O and C—N bonds in the benzoxazine ring under acidic conditions.

The EA of BZ-ta provided the values of C, 76.27%; H, 5.12%; N, 11.84%, which were much close to the theoretical values of C, 76.25%; H, 5.12%; N, 11.86%.

The ¹H-NMR, ¹³C-NMR, FTIR, HRMS, and EA results confirmed that BZ-ta has been synthesized successfully.

Solubility of BZ-ta

Solubility data of BZ-ta were summarized in Table I. BZ-ta exhibits some degree of solubility in common solvents such as dichloromethane, chloroform, acetone, DMSO, THF, dioxane, especially good solubility in DMF. However, it has poor solubility in other solvents such as toluene, ethyl acetate, ethyl ether, and ethanol.

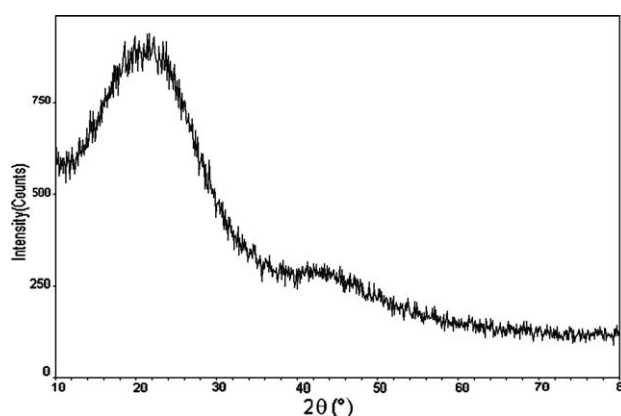


Figure 11. XRD pattern of P(BZ-ta).

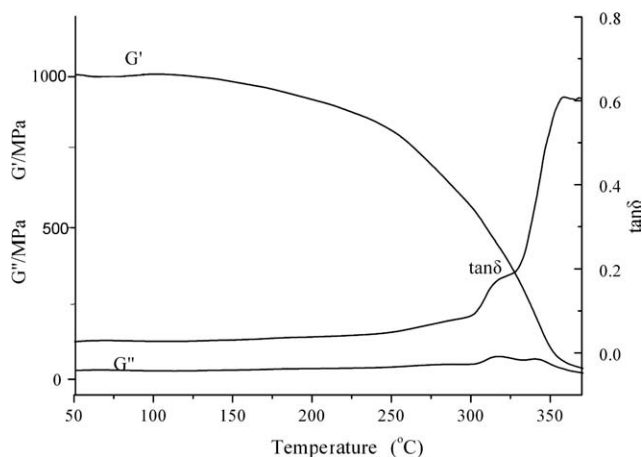


Figure 12. DMA spectrum of P(BZ-ta).

Viscosity of BZ-ta

Figure 5 shows viscosity–temperature curve of the BZ-ta. With increasing temperature, the viscosity slightly decreased. When the temperature was above 200°C, the viscosity sharply increased, indicating the occurrence of polymerization. BZ-ta exhibited quite low viscosity of 32 Pa s at 160°C in melt status.

Figure 6 shows viscosity–time curve of the BZ-ta at 160°C. With time extending, the viscosity showed an increasing tendency. However, it is still below 100 Pa s after 50 min at 160°C.

Polymerization of BZ-ta

Figure 7 shows DSC thermogram of the BZ-ta. The melting point is 158.8°C and the exothermic peak of the ring-opening polymerization is centered at 227°C. The starting and terminal exothermic temperatures are 202.5 and 245°C, respectively. Thermal polymerization of nitrile groups usually requires high temperature above 250°C. No clear peak is observed between temperatures of 250 and 350°C. Based on these data, we concluded that the curing temperature of BZ-ta is much lower than that of nitrile-functional benzoxazine.¹⁶

The polymerization was monitored by FTIR after each cure stage (Figure 8). After curing at 160°C for 2 h, a new band at 1670 cm⁻¹ appeared, which may be attributed to the C–N stretching of Schiff base byproduct formed in ring-opening

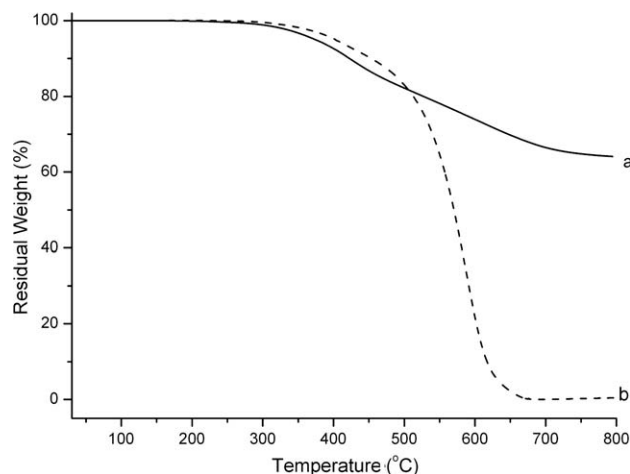


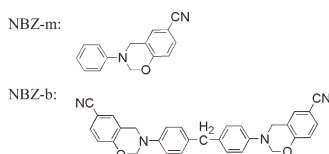
Figure 13. TGA spectra of P(BZ-ta) tested in nitrogen (a) and air (b).

reaction.^{19,20} Meanwhile, the band intensities at 1250, 1230, and 942 cm⁻¹ due to benzoxazine decreased compared with the monomer. After curing at 180°C for 2 h, a new band at 3435 cm⁻¹ due to phenol hydroxyl appeared, and the bands at 1250, 1230, and 942 cm⁻¹ due to benzoxazine disappeared, indicating that ring-opening reaction of oxazine was nearly completed. Conversely, the band at 1496 cm⁻¹ due to trisubstituted benzene ring reduced in intensity. A new band at 1262 cm⁻¹ appeared, which may correspond to the bridge model of (–CH₂–NR–CH₂–).²¹ These suggest that polymerization reaction has occurred. When the sample was continuously cured at 200 and 220°C, the band at 1496 cm⁻¹ further reduced and the band at 1262 cm⁻¹ increased, suggesting the further polymerization of BZ-ta. No significant change was observed after curing at 240°C for 2 h, indicating that the polymerization was completely performed at 220°C.

Based on intensity changes of the bands at 942 and 1262 cm⁻¹, we can quantitatively investigate the conversion of BZ-ta during curing process. Figure 9 shows the conversion curves of BZ-ta at different curing temperature for 2 h. It is found that the consumption of the benzoxazine ring is faster than the formation of polybenzoxazine. This phenomenon was also reported by Ishida and coworkers.²⁰ The reason may be the presence of arylether-based Mannich polymer²¹ that eventually was converted

Table II. Properties of Polybenzoxazines

Monomer	T_g^a (°C)	$T_{5\%}$ weight loss (°C) in nitrogen ^b	$T_{10\%}$ weight loss (°C) in nitrogen ^b	Char yield (wt % at 800°C) ^b	LOI values (%)
NBZ-m	230	352	389	64	
NBZ-b	258	367	403	68.5	36.2
BZ-ta	322	374	423	64	39.7



^aMeasured by DMA (by a shear mode), ^bMeasured by TGA.

into phenolic-based Mannich polymer ($-\text{CH}_2-\text{NR}-\text{CH}_2-$) upon heat treatment above 160°C .

To investigate reactive intermediates in curing processing, we carried on the GPC measurement after BZ-ta was cured at 170°C for 2 h. Figure 10 shows the GPC curves of BZ-ta before and after curing at 170°C for 2 h. The cured product shows the mixture of monomer and oligomer. Based on the integral area ratio, the oligomer has around 40% yields. In addition, the oligomer was soluble in THF, which indicated that the cross-linked network was not formed at this stage.

Phase Structure of P(BZ-ta)

Figure 11 shows XRD pattern of the P(BZ-ta). No sharp peaks were observed, indicating that crystal phase did not exist. Phase structure of P(BZ-ta) was amorphous.

Thermal Properties of P(BZ-ta)

Figure 12 shows DMA thermogram of P(BZ-ta). The T_g was observed at 322 and 320°C from the maximum of $\tan \delta$ and loss modulus, respectively.

Figure 13 shows TGA thermogram of P(BZ-ta). In nitrogen, 5 and 10% weight loss temperatures were 374 and 423°C , respectively. The char yield was 64% at 800°C . In air, 5 and 10% weight loss temperatures were 403 and 453°C , respectively, indicating that the P(BZ-ta) has excellent thermo-oxidation stability.

Flame-retardant Property of P(BZ-ta)

The flame retardance of P(BZ-ta) was evaluated by measuring LOI values (Table II). It is found that the LOI value of P(BZ-ta) was as high as 39.7. This means that P(BZ-ta) has excellent flame-retardant property.

These thermal property data were summarized in Table II, together with monofunctional polybenzoxazine P(NBZ-m) and bifunctional polybenzoxazine P(NBZ-b) as references. Compared to P(NBZ-m) and P(NBZ-b), the T_g of P(BZ-ta) increased 92 and 64°C , respectively. Similarly, the decomposition temperatures of 5 and 10% weight losses in nitrogen were also found with significant improvements. The LOI value of P(BZ-ta) was higher than that of P(NBZ-b).²² These modifications can be ascribed to the incorporation of rigid triazine structure into polybenzoxazine.

CONCLUSIONS

In conclusion, novel benzoxazine monomer-containing triazine structure (BZ-ta) was successfully synthesized by a new synthetic approach. It includes first synthesis of benzoxazine monomer-containing triazine (BZ-ta) via Mannich reaction from TP and sequential thermal polymerization of BZ-ta.

BZ-ta exhibited good solubility in most solvent and its melt viscosity is as low as 32 Pa s. P(BZ-ta) exhibited high glass transition temperature of 322°C . It had good thermal oxidation stability in air (5 and 10% weight loss temperatures up to 403 and 453°C , respectively) and high char yield in nitrogen (64% at 800°C). The flame-retardant property is also excellent and LOI value could reach 39.7. This new polybenzoxazine will have

great potential application in the field of advanced composite materials.

ACKNOWLEDGMENTS

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