

Synthesis of a Novel Benzoxazine-Containing Benzoxazole Structure and Its High Performance Thermoset

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ABSTRACT: A novel benzoxazine containing benzoxazole structures (Boz-BOA) was synthesized and its thermoset [P(Boz-BOA)] was prepared. For comparison, another benzoxazine-based 4,4'-diamine diphenyl methane (Boz-MDA) was also synthesized using a simplified procedure. The structure of Boz-BOA and Boz-MDA was confirmed by Fourier transform infrared (FTIR) and $^1\text{H-NMR}$. Using FTIR and differential scanning calorimetric scans method, the curing behavior of Boz-BOA was probed, and the structure of P(Boz-BOA) was addressed, which was similar to that of P(Boz-MDA). Data of dynamic mechanical analysis showed

that P(Boz-BOA) exhibited a better modulus retention at high temperature than P(Boz-MDA), which was attributed to benzoxazole structure restricting the mobility of chains, even at high temperature. P(Boz-BOA) also exhibited high glass transition temperature (T_g), excellent thermal stability, and low coefficient of thermal expansion value at wide temperature range. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2415–2422, 2012

Key words: synthesis; benzoxazine; benzoxazole structure; thermal properties

INTRODUCTION

Recently, a novel class of thermosetting resins called polybenzoxazines has received much attention in the materials science as a hopeful candidate of next materials due to the highly desirable properties at low cost. They have been used in the areas of microelectronics, aeronautical technology, and astronautical technology. The major advantages of polybenzoxazines are good thermal stability, good flame retardance, excellent resistance to chemicals and UV light, low dielectric properties, low surface energy, low water absorption, near-zero volumetric shrinkage, and no volatile release during polymerization.^{1–10}

A lot of works were in pursuit of improving the T_g and thermal stability of polybenzoxazines, because their thermal properties were not good enough to be used in harsh conditions. Increasing crosslink density can effectively enhance thermal stability by incorporating polymerizable groups, such as propargyl ether, allyl, nitrile, and maleimide, into benzoxazines structure.^{11–14} The reason was that higher crosslink density reduced chain mobility. However, the polymerizable groups made the benzoxazines need higher curing temperature.

As literature reported, hydrogen bonding played an important role in fostering the excellent properties of polybenzoxazines, such as modulus.^{15–17} Upon increasing temperature, hydrogen bond would be broken as well known.¹⁸ Hence, the modulus retention at high temperature, which was very important at practical applications, would drop rapidly because intensity of hydrogen bond lowered.

Here, we reported another approach to improve thermal stability, which was introduction of rigid structures into benzoxazine. Rigid structure could restrict chain mobility, resulting in higher T_g , and furthermore, weaken the influence of hydrogen bond on modulus retention at high temperature. The rigid structure in this work was benzoxazole structure.

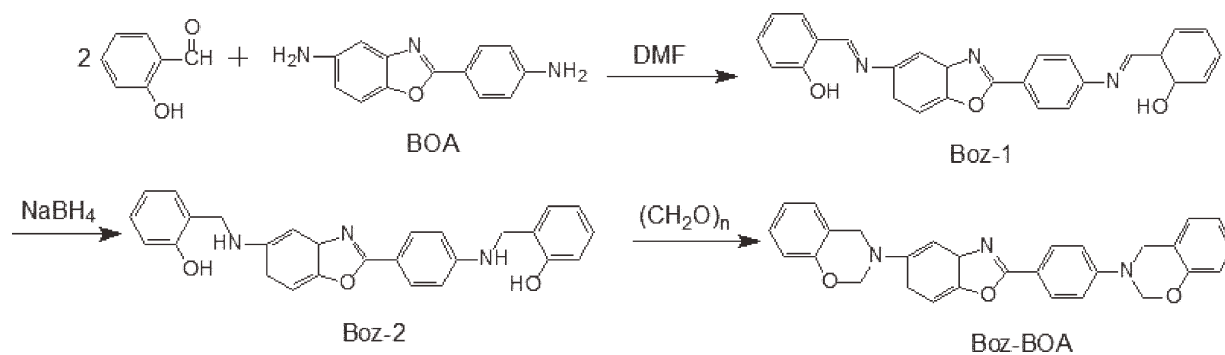
EXPERIMENTAL

Materials

4,4'-Diamine diphenyl methane (MDA, CP grade) was purchased from YanTai WanHua Chemical Raw Material Co. (China), purified by recrystallization in ethanol. 2-(4-aminophenyl)-1H-benzoxazole-5-amine (BOA, AR grade) was obtained from ChangZhou Sunlight Medical Raw Material Co. (China). Paraformaldehyde (95%) was supplied by Fydsa (Spain). *Orth*-hydroxybenzaldehyde (CP grade), sodium borohydride (AR grade), sodium hydroxide (AR grade), *N,N*-dimethylformamide (AR grade), 1,4-dioxine (AR grade), toluene (AR grade), and ethanol (AR grade) were purchased from ChengDu Kelong

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Scheme 1 Synthesis of Boz-BOA.

Chemical Reagents Corp. (China) and used without further purification.

Synthesis and characterization of the novel benzoxazine-containing benzoxazole structure (Boz-BOA)

Boz-BOA was synthesized as shown in Scheme 1.

Synthesis and characterization of Boz-1

Orth-hydroxybenzaldehyde (24.4 g, 0.2 mol), BOA (24.4 g, 0.1 mol), and *N,N*-dimethylformamide (DMF; 120 mL) were introduced into a 250-mL three-necked flask under nitrogen atmosphere. The mixture was stirred at 50°C for 4 h. After the mixture cooling to room temperature, the precipitate was filtered and dried in a vacuum oven at 150°C for 2 h to give yellow powder (42.4 g, 98% yield) with a melting point of 267°C (DSC) and a melting enthalpy of 108 J/g. Fourier transform infrared (FTIR; KBr, cm^{-1}): 1056 and 1174 (vibration of benzoxazole), 1616 (CH=N stretch), and 3404 (OH stretch).

Synthesis and characterization of Boz-2

Boz-1 (21.7 g, 0.05 mol) and ethanol (120 mL) were introduced into a 250-mL three-necked flask with a nitrogen inlet and a magnetic stirrer. About 5.7 g (0.15 mol) of sodium borohydride (NaBH_4) was added portions while the mixture was stirred. After 12 h, the mixture was poured into deionized water (500 mL), and the precipitate was filtered and dried in a vacuum oven at 105°C for 2 h. About 21.6 g (99% yield) of pale yellow powder with a melting point of 208°C (DSC) was obtained.

$^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 4.22 and 4.27 (4H, $-\text{NH}-\text{CH}_2-\text{Ar}-$), 5.89 and 6.03 (2H, $\text{Ar}-\text{NH}-\text{CH}_2-$), 9.57 (2H, $-\text{Ar}-\text{OH}$), 6.61–7.81 (15H, Aromatic *H*). FTIR (KBr, cm^{-1}): 1072 and 1184 (vibration of benzoxazole), 1272 (C–N stretch), 1522 (N–H bending), 3409 (N–H stretch), and 3200–3500 (OH stretch).

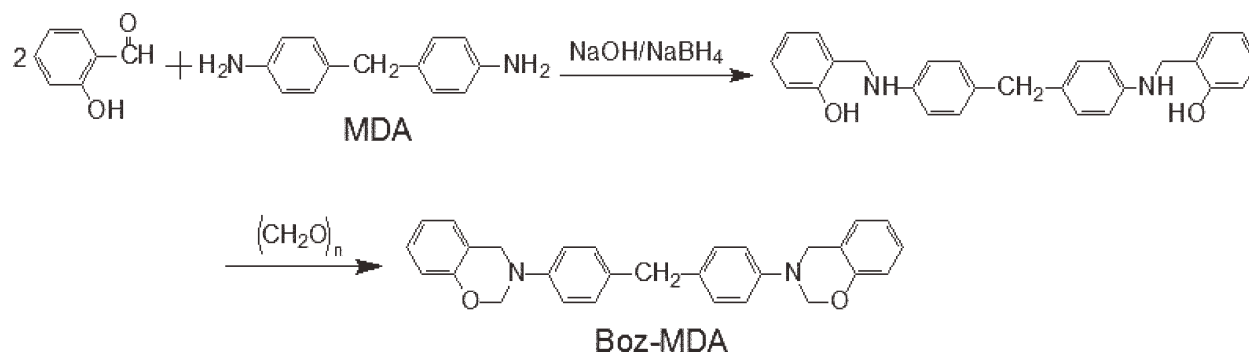
Synthesis and characterization of Boz-BOA

Boz-2 (16.4 g, 0.04 mol), paraformaldehyde (2.64 g, 0.088 mol), 1,4-dioxane (100 mL), and DMF (10 mL) were introduced into a 250-mL three-necked flask. The mixture was stirred at 85°C for 8 h. After the mixture was cooled to room temperature, the precipitate was filtered and recrystallized in DMF. After drying in a vacuum oven at 140°C for 2 h, 15.3 g (83% yield) of light yellow powder with a melting peak of 208°C (DSC) and a curing peak temperature of 267°C were obtained. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 4.69 and 4.78 (4H, $-\text{N}-\text{CH}_2-\text{Ar}-$), 5.48 and 5.55 (4H, $-\text{N}-\text{CH}_2-\text{O}-$), 6.71–8.01 (15H, Aromatic *H*). FTIR (KBr, cm^{-1}): 927 and 943 (oxazine), 1034 ($\text{Ar}-\text{O}-\text{C}$ symmetric stretch), 1225 ($\text{Ar}-\text{O}-\text{C}$ asymmetric stretch), 1373 (C–N stretch), 1062, and 1188 (vibration of benzoxazole).

Synthesis and characterization of the benzoxazine-based 4,4'-diamine diphenyl methane (Boz-MDA)

Boz-MDA was synthesized as shown in Scheme 2: *ortho*-hydroxybenzaldehyde (24.4 g, 0.2 mol), MDA (19.8 g, 0.1 mol), and ethanol (120 mL) were introduced into a 250-mL three-necked flask under nitrogen atmosphere. After stirring at room temperature for 4 h, 2 g of sodium hydroxide and 11.4 g (0.3 mol) of sodium borohydride (NaBH_4) were added portions while the mixture was stirred at room temperature for another 8 h. Then the mixture was poured into water, and the precipitate was filtered and washed with ethanol. After that, the precipitate was introduced into a 250-mL three-necked flask with paraformaldehyde (6 g, 0.2 mol) and toluene (100 mL), and the mixture was reacted at 85°C for 5 h. Finally, toluene was removed using a rotary evaporator. After recrystallization in toluene, white powder (36.5 g, 84% yield) with a melting peak of 128°C (DSC) and a curing peak temperature of 269°C was obtained.

$^1\text{H-NMR}$ ($\text{DMSO-}d_6$, ppm): 3.34 (2H, $\text{Ar}-\text{CH}_2-\text{Ar}$), 4.58 (4H, $-\text{N}-\text{CH}_2-\text{Ar}-$), 5.37 (4H,



Scheme 2 Synthesis of Boz-MDA.

—N—CH₂—O—, 6.71–8.01 (16 H, Aromatic *H*). FTIR (KBr, cm⁻¹): 933 (oxazine), 1034 (Ar—O—C symmetric stretch), 1227 (Ar—O—C asymmetric stretch), and 1375 (C—N stretch).

Preparation of P(Boz-BOA) and P(Boz-MDA)

Boz-BOA and Boz-MDA were melted and transferred to an aluminum mold and cured stepwise at 140°C (3 h), 150°C (3 h), 160°C (3 h), 170°C (3 h), 180°C (3 h), 190°C (3 h), 200°C (3 h), and 220°C (1 h) to obtain polybenzoxazines named as P(Boz-BOA) and P(Boz-MDA), respectively. Then, the samples were cooled to room temperature slowly to prevent cracking. After cure, the samples obtained were reddish brown and optically transparent.

Characterization

FTIR studies were performed in KBr pellets using a Nicolet Magna 650 spectroscope at a resolution

of 4 cm⁻¹. The scanned wavenumbers range from 4000 to 400 cm⁻¹. ¹H-NMR measurements were conducted on a Bruker TD-65536 NMR (400 MHz) in DMSO-*d*₆ as solvent with tetramethylsilane as the internal reference. Differential scanning calorimetric scans (DSC) were obtained with a TA Instruments Q20 under nitrogen atmosphere at a heating rate of 10°C/min. Dynamic mechanical analyzer (DMA) was performed with a TA Instruments DMA Q800 at 1 Hz at a heating rate of 5°C/min in three-point bending model under nitrogen. Thermal mechanical analysis (TMA) was measured with a TA TMA/Q400 at a heating rate of 10°C/min under nitrogen atmosphere. Coefficient of thermal expansion (CTE) was measured in the range of 30–150°C. Thermogravimetric analysis (TGA) was performed with a TA Instruments' High Resolution Q600 thermogravimetric analyzer under nitrogen atmosphere from 40 to 800°C at a heating rate of 10°C/min.

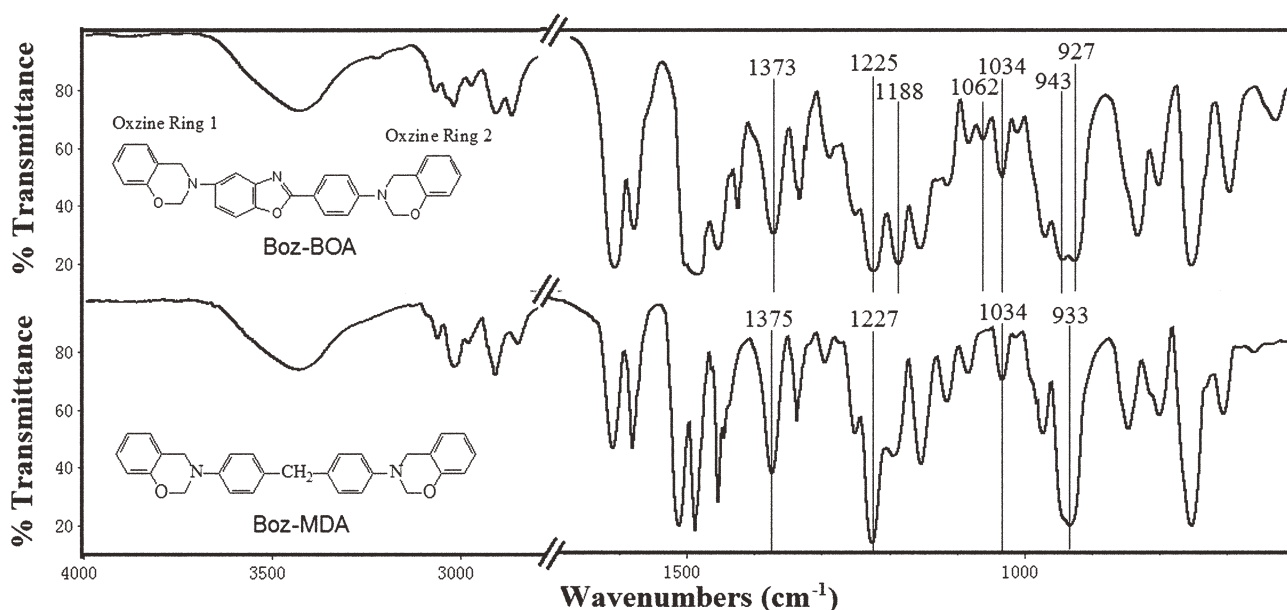


Figure 1 FTIR spectra of Boz-BOA and Boz-MDA.

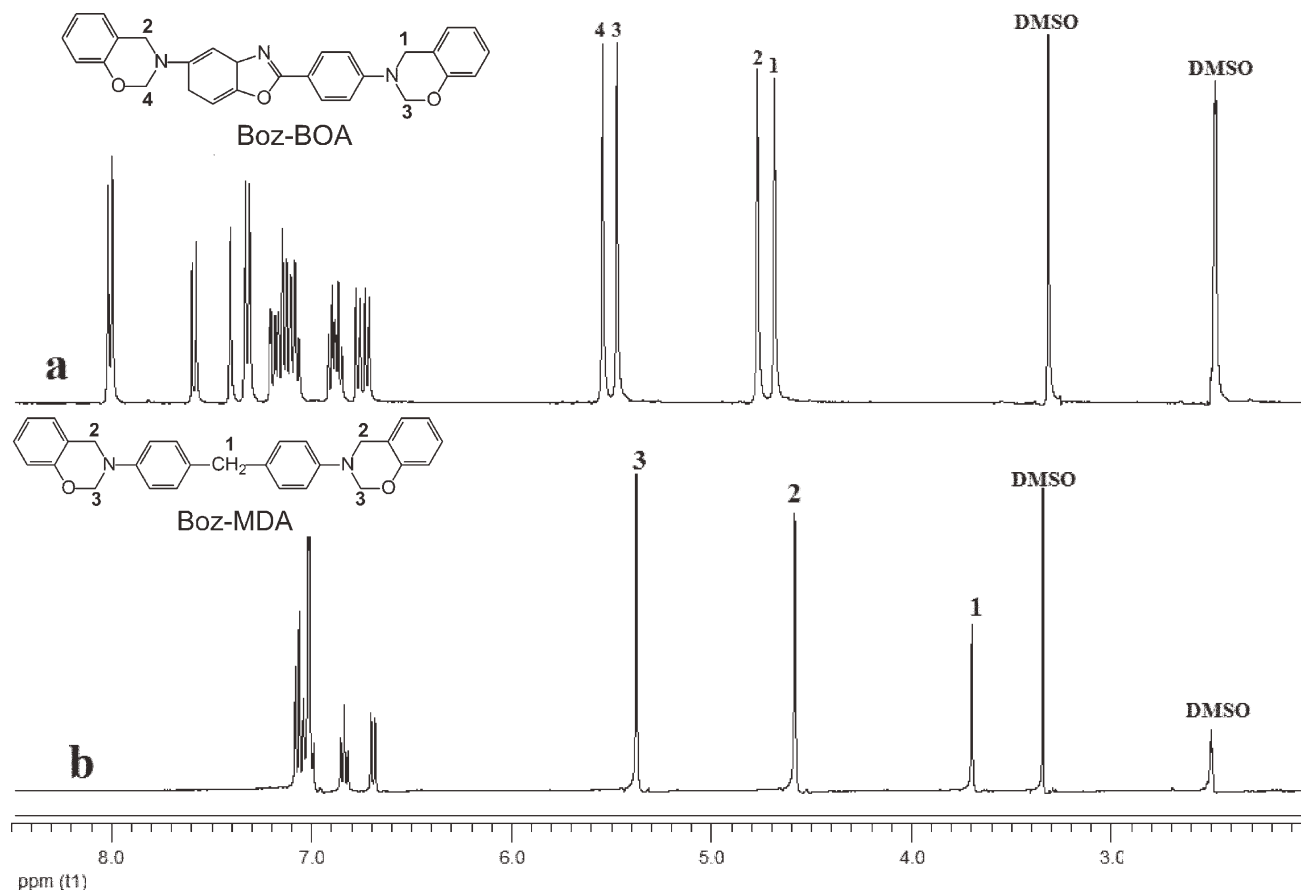


Figure 2 $^1\text{H-NMR}$ spectra ($\text{DMSO-}d_6$) of Boz-BOA (a) and Boz-MDA (b).

RESULTS AND DISCUSSION

Synthesis and characterization of Boz-BOA and Boz-MDA

Boz-BOA was synthesized in three steps as shown in Scheme 1. Nonpolar solvent, such as chloroform, toluene, and xylene, was regarded as appropriate solvent to synthesize benzoxazines in general.^{19,20} However, because of the poor solubility of Boz-2 in nonpolar solvent, DMF was added to 1,4-dioxane as a cosolvent in this case. The chemical structure of Boz-BOA was confirmed by FTIR (Fig. 1) and $^1\text{H-NMR}$ [Fig. 2(a)]. The bands assigned to benzoxazole can be seen at 1062 and 1188 cm^{-1} , indicating that the benzoxazole structure was preserved in Boz-BOA. Interestingly, two characteristics absorptions at 927 and 943 cm^{-1} corresponded, respectively, to oxazine ring 2 and oxazine ring 1 were observed due to its asymmetric structure. The absorption for Boz-BOA appeared at 1034 , 1225 , and 1373 cm^{-1} , which assigned to the symmetric and asymmetric stretching vibration of C-O-C , stretching of C-N , respectively. The $^1\text{H-NMR}$ was used to further confirm the structure of Boz-BOA. In accord with the FTIR, the resonances of the oxazine rings also appeared with two groups of singlets at 5.48 ppm and 4.69 ppm , 5.55 ppm , and

4.78 ppm , which assigned to $-\text{O-CH}_2-\text{N}-$ and $\text{Ar-CH}_2-\text{N}-$, respectively. The aromatic protons were noticed in the range of $6.71\text{--}8.01\text{ ppm}$.

Boz-MDA has been reported by Xiang and Lin^{21,22} using a complex method. Considering the good solubility of MDA in ethanol, Boz-MDA was synthesized

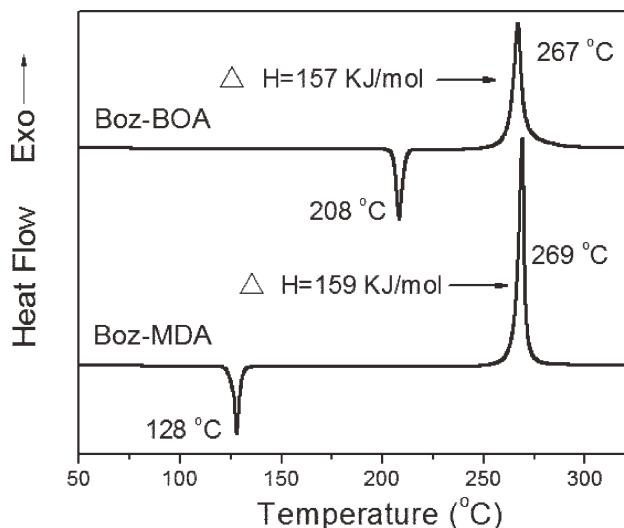


Figure 3 DSC thermograms of Boz-BOA and Boz-MDA.

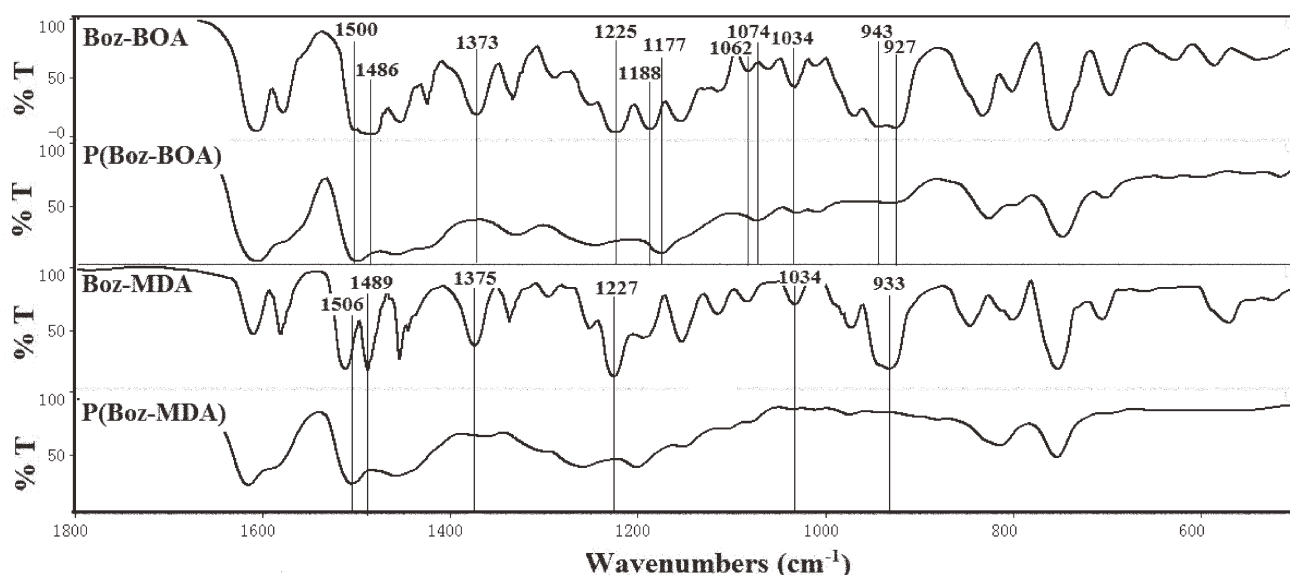
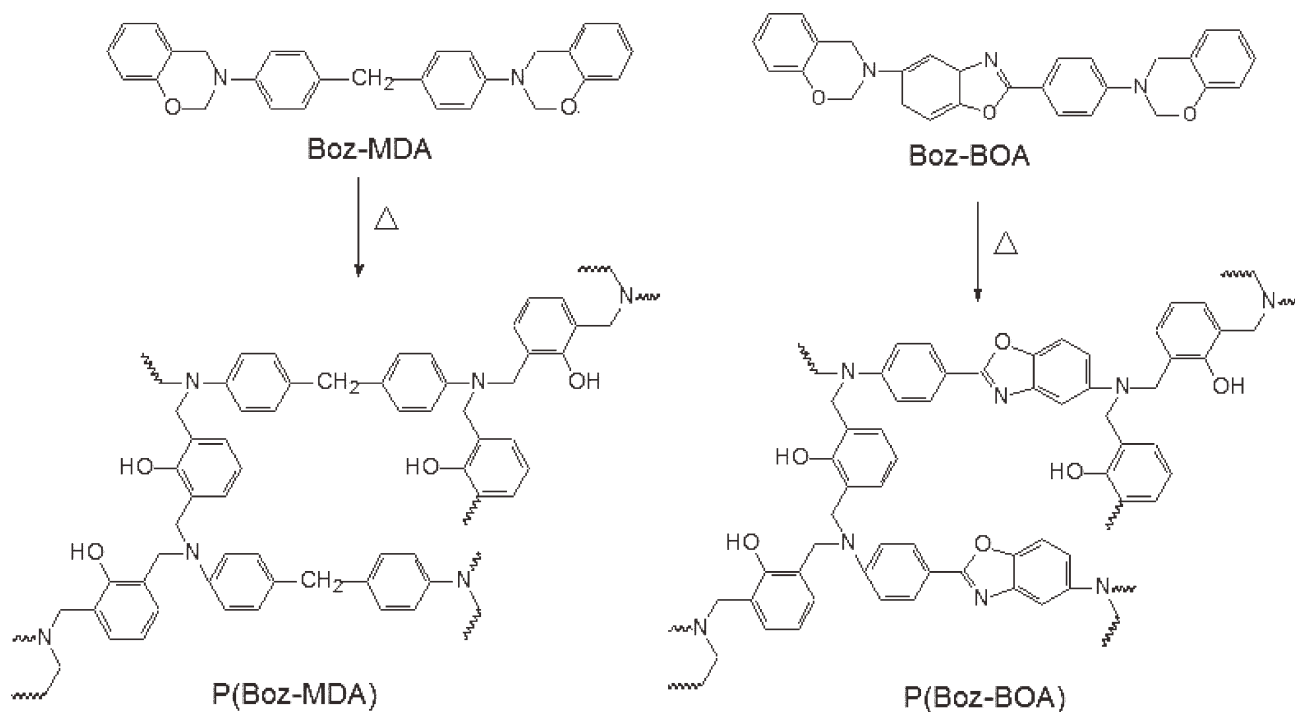


Figure 4 FTIR spectra of Boz-BOA, P(Boz-BOA), Boz-MDA, and P(Boz-MDA).

using a simplified procedure as Scheme 2 shown in this work. The chemical structure of Boz-MDA was confirmed by FTIR and $^1\text{H-NMR}$. The absorption appeared at 933 cm^{-1} proved the formation of the oxazine ring (Fig. 1). The $^1\text{H-NMR}$ was used to further confirm the structure of Boz-MDA [Fig. 2(b)]. The resonance of the oxazine ring was observed at 5.37 ppm and 4.58 ppm, which was assigned to $-\text{O}-\text{CH}_2-\text{N}-$ and $\text{Ar}-\text{CH}_2-\text{N}-$, respectively. The results suggested that Boz-MDA was synthesized successfully.

Thermal curing behavior of Boz-BOA and Boz-MDA

The curing behavior of Boz-BOA and Boz-MDA was investigated by DSC (Fig. 3). The melting point of Boz-BOA and Boz-MDA was 208°C and 128°C , respectively. And the sharp melting point also confirmed the high purity of Boz-BOA and Boz-MDA. As it also can be seen from Figure 3, Boz-BOA exhibited a single broader exothermic peak centered at 267°C , and a relatively narrower peak centered at



Scheme 3 The structure of P(Boz-MDA) and P(Boz-BOA).

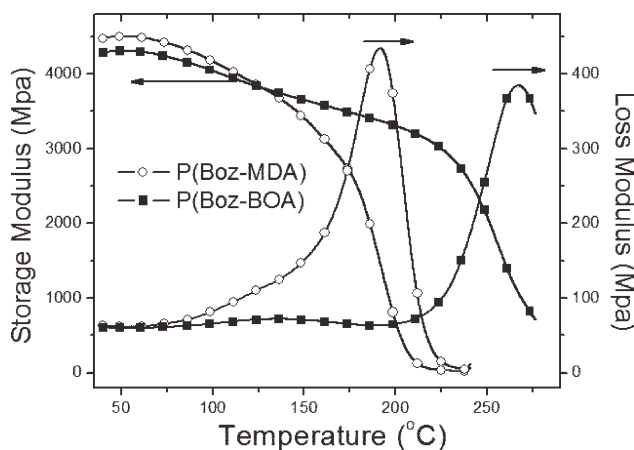


Figure 5 DMA curves of P(Boz-MDA) and P(Boz-BOA).

269°C was observed for Boz-MDA. This broader exothermic peak of Boz-BOA was possibly caused by the asymmetry structure.²³

To better understand the curing behavior, the spectra of Boz-BOA and P(Boz-BOA) were recorded by FTIR (Fig. 4). The oxazine absorptions at 927 and 943 cm^{-1} , the Ar—O—C absorptions at 1034 and 1225 cm^{-1} , the C—N—C absorptions at 1373 cm^{-1} , and the 1,2-disubstituted benzene absorptions at 1486 cm^{-1} disappeared after curing, but the absorption band at 1500 cm^{-1} revealed the generate of 1,2,3-trisubstituted benzene. Moreover, the benzoxazole absorption at 1062 and 1188 cm^{-1} shifted to 1074 and 1177 cm^{-1} , respectively, after curing, illustrating that the benzoxazole structure was retained in the network. In comparison with Boz-MDA curing behavior [Fig. 4 [Boz-MDA and P(Boz-MDA)]], the oxazine absorptions at 933 cm^{-1} , the Ar—O—C absorptions at 1034 and 1227 cm^{-1} , the C—N—C absorptions at 1375 cm^{-1} and the 1,2-disubstituted benzene absorp-

tions at 1489 cm^{-1} disappeared after curing, indicating that the curing behavior of P(Boz-BOA) was similar to that of P(Boz-MDA). According to the FTIR study, the structures of P(Boz-BOA) and P(Boz-MDA) were suggested and shown in Scheme 3.

Thermal properties of P(Boz-MDA) and P(Boz-BOA)

The glass transition temperature was an important property of thermosetting resins. DMA and TMA were applied to probe the glass transition temperature of P(Boz-BOA) and P(Boz-MDA) (see Figs. 5 and 6, respectively). The T_g s of P(Boz-BOA) and P(Boz-MDA) were summarized in Table I.

The T_g s of P(Boz-BOA) and P(Boz-MDA) were 269°C and 192°C, respectively, which were obtained from the maximum of the loss modulus (E''). For P(Boz-MDA), the storage modulus started to decrease sharply at around 60°C, whereas the storage modulus of P(Boz-BOA) exhibited a slight decrease at around 60°C and a sharp decrease at about 220°C. The T_g s of P(Boz-BOA) and P(Boz-MDA) were also measured by TMA with 231°C and 155°C, respectively. The T_g of P(Boz-BOA) was much higher than P(Boz-MDA). The CTE of P(Boz-BOA) and P(Boz-MDA) was obtained from TMA measurement. The measured value of P(Boz-BOA) was 46 ppm/°C, and for P(Boz-MDA), it was 52 ppm/°C, in the range of 30–150°C. The CTE value of P(Boz-BOA) was 48 ppm/°C even in the range of 30–220°C, indicating the excellent dimension stability of P(Boz-BOA) in wide range.

If polybenzoxazines were expected for applications in harsh conditions, the modulus retention at high temperature should be concerned. According to ISO 6721-1, the storage modulus (E') of DMA was

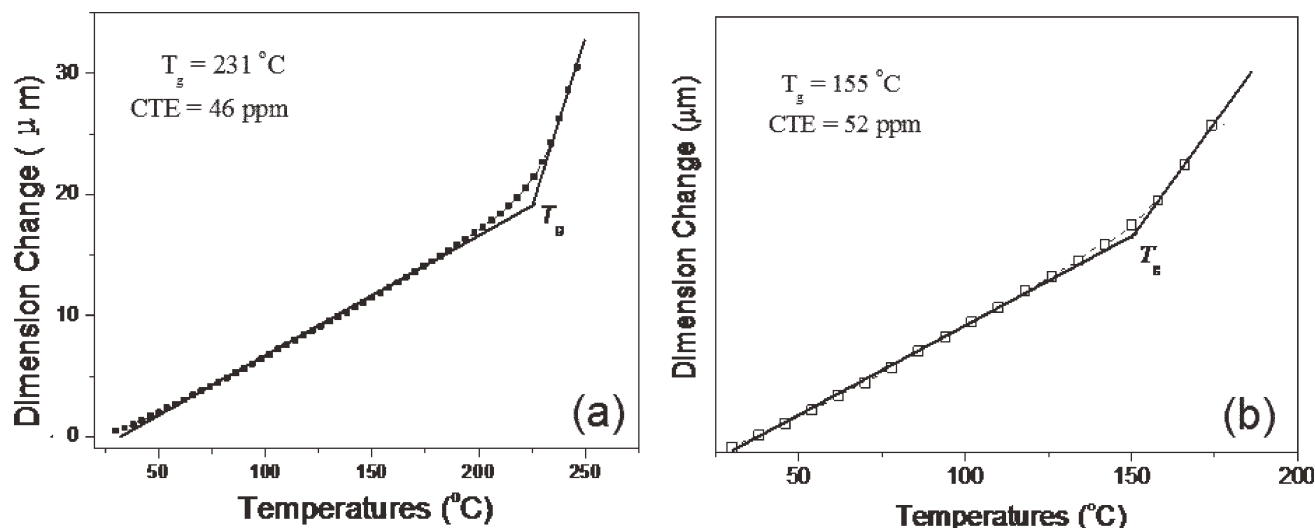


Figure 6 TMA curves of P(Boz-BOA) (a) and P(Boz-MDA) (b).

TABLE I
Results of DMA and TMA for P(Boz-MDA) and P(Boz-BOA)

Sample	T_g^a (°C)	E'_{40} (MPa)	E'_{180} (MPa)	R_{180}^b (%)	T_g^c (°C)	CET ^d
P(Boz-MDA)	192	4499	2434	54	155	52
P(Boz-BOA)	269	4307	3450	80	231	46

^a T_g (°C) value obtained from maximum of loss modulus (DMA).

^b The ratio (%) of thermal modulus retention at 180°C.

^c T_g (°C) measured by TMA.

^d Coefficient of thermal expansion (ppm/°C) in the range of 30–150°C.

roughly equal to the elastic modulus of materials. Therefore, the modulus of P(Boz-BOA) and P(Boz-MDA) at given temperature could be obtained from the storage modulus. In this work, an equation that was used to evaluate the thermal modulus retention of P(Boz-BOA) and P(Boz-MDA) was expressed as shown in Ref. 24:

$$R_T = \frac{E'_T}{E'_{40}} \times 100\% \quad (1)$$

where R_T represented the ratio of thermal modulus retention at given temperature, E'_{40} and E'_T were the storage modulus of samples at 40°C and T , respectively. The ratios of thermal modulus retention were calculated and shown in Figure 7 and Table I. The ratios of thermal modulus retention for P(Boz-BOA) and P(Boz-MDA) below 80°C were the same. However, P(Boz-BOA) exhibited higher ratios of thermal modulus retention than that of P(Boz-MDA) above 80°C. The ratios of thermal modulus retention for P(Boz-MDA) was 54% at 180°C and 80% for P(Boz-BOA). There was still 72% of the ratio of thermal

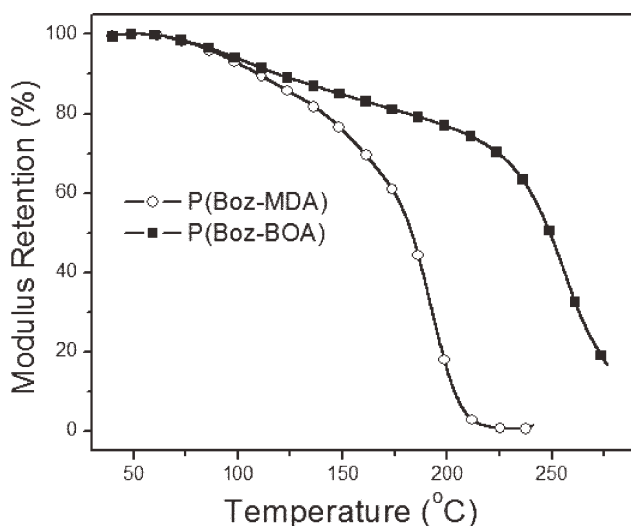


Figure 7 Modulus retention curves of P(Boz-MDA) and P(Boz-BOA).

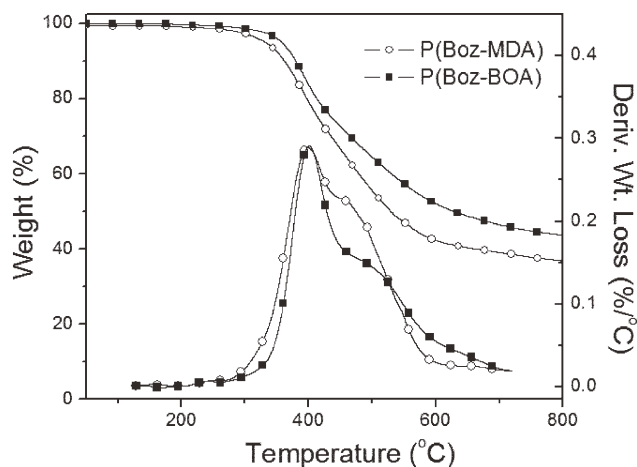


Figure 8 TGA and derivatives curves of P(Boz-MDA) and P(Boz-BOA).

modulus retention for P(Boz-BOA) at 220°C. The results suggested that the thermal modulus retention of P(Boz-BOA) was much better than that of P(Boz-MDA). Therefore, the thermal modulus retention of polybenzoxazines was enhanced by the incorporation of benzoxazole structures.

Despite the low crosslink densities of polybenzoxazines, hydrogen bonding could effectively enhance the stiffness of it and bring about its high T_g and high modulus.^{15–17} Nevertheless, hydrogen bonds were broken at high temperature, which would decrease the modulus of typical polybenzoxazines.¹⁸ In this work, benzoxazole structure, which was introduced into P(Boz-BOA) as a rigid structure, restricted the mobility of chains and weakened the influence of hydrogen bond on modulus retention at high temperature. Hence, P(Boz-BOA) exhibited not only high T_g and excellent dimensional stability but also good thermal modulus retention.

Thermogravimetric Analysis of P(Boz-MDA) and P(Boz-BOA)

Thermal stability of P(Boz-BOA) and P(Boz-MDA) was investigated by TGA. The TGA thermogram was shown in Figure 8. The values of various decompositions and char yields were listed in Table II. The 5 and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) for P(Boz-MDA) were 332 and 362°C, respectively,

TABLE II
Temperature of Various Decomposition and Yields of P(Boz-MDA) and P(Boz-BOA)

Sample	$T_{5\% \text{ loss}}$ (°C)	$T_{10\% \text{ loss}}$ (°C)	Char yield at 800°C (%)
P(Boz-MDA)	332	362	37
P(Boz-BOA)	357	380	44

with char yield 37%. These values for P(Boz-BOA) were 357 and 380°C and 44%, respectively. The thermal stability of P(Boz-BOA) exceeded some polybenzoxazines containing functional groups such as allyl, phenylnitrile, furan, and phenylphosphine oxide.^{12-14,25-27}

Some earlier reports have demonstrated that the derivative curves of a TGA thermogram contained abundant information on revealing the network structure of polybenzoxazines.²⁸⁻³² For the typical polybenzoxazine-based bisphenol and aniline, the derivative of weight loss showed a three-stage degradation process. The three derivative peaks appeared approximately at 290, 390, and 460°C, which were assigned to the amine evaporation, the degradation of the Mannich bridge, and phenolic linkages, respectively.^{29,32} However, the process at around 290°C was not observed in P(Boz-MDA) and P(Boz-BOA), because the amine segment was introduced into network by their own spacer groups and retarded the evaporation of the amine cleavage.³⁰ For P(Boz-MDA), the first derivative peak appeared at 390°C with the rate of 0.29%/°C and the second with the rate of 0.23%/°C at around 464°C. For P(Boz-BOA), the first derivative peak was also found at 390°C with the rate of 0.29%/°C. In contrast, the second major derivative peak of P(Boz-BOA) was detected at ~ 538°C, demonstrating the effect of benzoxazole structures in the network. Thus, incorporation of benzoxazole structures could improve polybenzoxazines with thermal stability.

CONCLUSIONS

A novel benzoxazines containing benzoxazole (Boz-BOA) was synthesized and characterized. With the aid of FTIR and DSC, the structure of P(Boz-BOA) was proposed and shown. By introducing benzoxazole structures as a rigid structure in P(Boz-BOA), the polybenzoxazine exhibited high-glass transition temperature, good thermal modulus retention, excellent thermal stability, and low-CTE value.

References

- Macko, J. A.; Ishida, H. *Macromol Chem Phys* 2001, 202, 2351.
- Macko, J. A.; Ishida, H. *Polymer* 2001, 42, 227.
- Macko, J. A.; Ishida, H. *Polymer* 2001, 42, 6371.
- Su, Y. C.; Chang, F. C. *Polymer* 2003, 44, 7989.
- Wang, C. F.; Wang, Y. T.; Tung, P. H.; Kuo, S. W.; Lin, C. H.; Sheen, Y. C.; Chang, F. C. *Langmuir* 2006, 22, 8289.
- Liao, C. S.; Wang, C. F.; Lin, H. C.; Chou, H. Y.; Chang, F. C. *J Phys Chem C* 2008, 112, 16189.
- Ishida, H.; Allen, D. J. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
- Ishida, H.; Low, H. Y. *Macromolecules* 1997, 30, 1099.
- Liu, X.; Gu, Y. *J Appl Polym Sci* 2002, 84, 1107.
- Sudo, A.; Kudoh, R.; Nakayama, H.; Arima, K.; Endo, T. *Macromolecules* 2008, 41, 9030.
- Agag, T.; Takeichi, T. *Macromolecules* 2001, 34, 7257.
- Agag, T.; Takeichi, T. *Macromolecules* 2003, 36, 6010.
- Brunovska, Z.; Lyona, R.; Ishida, H. *Therm Acta* 2000, 357, 195.
- Liu, Y.; Chou, C. *J Polym Sci Part A: Polym Chem* 2005, 43, 5267.
- Dunker, J. P.; Zarate, E. A.; Ishida, H. *J Phys Chem* 1996, 100, 13514.
- Kim, H. D.; Ishida, H. *J Phys Chem A* 2002, 106, 3271.
- Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog Polym Sci* 2007, 32, 1344.
- Wirasate, S.; Dhumrongvaraporn, S.; Allen, D. J.; Ishida, H. *J Appl Polym Sci* 1998, 70, 1299.
- Liu, Y.; Lin, G.; Wu, C. *J Polym Sci Part A: Polym Chem* 2007, 45, 949.
- Agag, T.; Jin, L.; Ishida, H. *Polymer* 2009, 50, 5940.
- Xiang, H.; Ling, H.; Wang, J.; Song, L.; Gu, Y. *Polym Compos* 2005, 26, 563.
- Lin, C. H.; Chang, S. L.; Hsieh, C. W.; Lee, H. H. *Polymer* 2008, 49, 1220.
- Wang, X. Y.; Chen, F.; Gu, Y. *J Polym Sci Part A: Polym Chem* 2011, 49, 1443.
- Rana, A. K.; Mitra, B. C.; Banerjee, A. N. *J Appl Polym Sci* 1999, 71, 531.
- Kumar, K. S. S.; Nair, C. P. R.; Radhakrishnan, T. S.; Ninan, K. N. *Eur Polym J* 2007, 43, 2504.
- Qi, H.; Ren, H.; Pan, G.; Zhuang, Y.; Huang, F.; Du, L. *Polym Adv Technol* 2009, 20, 268.
- Choi, S. W.; Ohba, S.; Brunovska, Z.; Hemvichian, K.; Ishida, H. *Polym Degrad Stab* 2006, 91, 1166.
- Low, H. Y.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1998, 36, 1935.
- Low, H. Y.; Ishida, H. *Polymer* 1999, 40, 4365.
- Low, H. Y.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1999, 37, 647.
- Hemvichian, K.; Laobuthee, A.; Chirachanchai, S.; Ishida, H. *Polym Degrad Stab* 2002, 76, 1.
- Hemvichian, K.; Ishida, H. *Polymer* 2002, 43, 4391.