

# Synthesis and Characterization of 2-Oxazoline-benzoxazine Compound and its Polymer

Hongwei Cao, Riwei Xu, Dingsheng Yu\*

*The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*

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**ABSTRACT:** A novel 2-oxazoline-benzoxazine (POB) was synthesized with 2-(hydroxylphenyl)-2-oxazoline, 1,3,5-triphenylhexahydro-1,3,5-triazine and paraformaldehyde. The chemical structure of the monomer was confirmed by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and MS. The curing behavior of the monomer was studied by DSC and FTIR, and the ring opening reaction of the monomer was found to occur from 187.5°C. The results of DMA and TGA demonstrated that the thermal properties of polymer for POB monomer (P-m) are better than polymer for POB precursor (P-p), because

that the oligomer in benzoxazine precursor decreased the perfection of the polymer's network structure; it was also found that the thermal properties of P-m and P-p are much better than the common polybenzoxazine and the composite material of benzoxazine and 2-oxazoline. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1502–1508, 2008

**Key words:** benzoxazine; 2-oxazoline; polybenzoxazine; thermal properties; heteroatom-containing polymers; thermosets

## INTRODUCTION

Polybenzoxazine (PBZ), as a new kind of thermosetting resin, can be synthesized from inexpensive raw materials and has received more and more attention because of its good performance. It was reported previously that PBZ can provide heat resistance, flame retardance, low water absorption, relatively low dielectric constant, and other unique performances such as dimensional stability and near-zero shrinkage upon curing.<sup>1–8</sup> Although there is a problem that the precursor of PBZ, synthesized by Mannich reaction, usually contains benzoxazine monomer and oligomer, it is very difficult to separate benzoxazine monomer from its precursor because the monomer and oligomer have similar physical and chemical properties.

The synthesis and polymerization of oxazolines have been described in several review articles.<sup>9–17</sup> Among the oxazolines, 2-oxazolines are important monomers. 2-Oxazolines can react with carboxylic acids, anhydrides, aldehydes, epoxides, amines, hydroxy groups, and so on.<sup>18,19</sup> Based on the

chemical activity, 2-oxazolines are widely used in polymer matrix. There are literatures reported that bisoxazolines can be used as the chain extender or crosslinking agent of some polymers.<sup>20–23</sup> Kimura et al.<sup>24,25</sup> reported that the incorporation of bisoxazoline into bisphenol A-based benzoxazine (BBZ) decreased the melt viscosity of the system, and the oxazoline ring could react with the phenolic hydroxyl group generated by the ring opening of benzoxazine. Yu and coworkers<sup>26</sup> found that bisoxazoline is an excellent compatibilizer in the PBZ/POSS (polyhedral oligomeric silsesquioxane) nanocomposites.

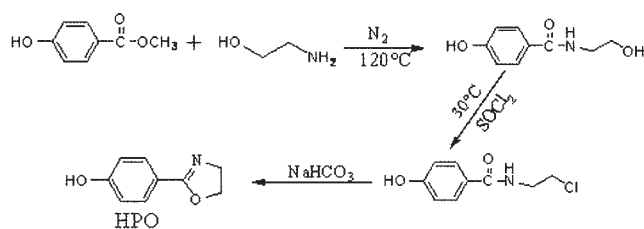
Though many researches indicated that 2-oxazolines are easily incorporated in benzoxazine and composite effect is well, it is speculated 2-oxazoline-benzoxazine compound may exhibit more excellent properties compared with composites of benzoxazine and 2-oxazoline, and the application of benzoxazine may be further extended due to the chemical activity of 2-oxazoline moiety.

In the article, benzoxazine ring and 2-oxazoline ring are combined in *p*-(2-oxazoline)-3-phenyl-3, 4-2H-1, 3-benzoxazine (POB). It is found that the POB monomer could be separated from precursor by simple separating process, and pure benzoxazine monomer is obtained. DMA and TGA results demonstrate that the thermal properties of POB polymers [especially for polymer for POB monomer (P-m)] are better than the polymer of benzoxazine and the composite material of 2-oxazoline and benzoxazine.

\*Present address: The College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China.

Correspondence to: D. Yu (yuds@mail.buct.edu.cn).

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Scheme 1

## EXPERIMENTAL

### Materials

2,2'-(1,3-Phenylene)-bis(4,5-dihydro-oxazoles) (PBO) was purchased from Takeda Chemical Industries. Methyl *p*-hydroxybenzoate, ethanolamine, thionyl chloride, sodium hydrogen carbonate, paraformaldehyde, and aniline were all commercially available from Beijing Chemical Reagents and used without further purification. All reagents were of AR grade. The bisphenol A-based benzoxazine (BBZ) was prepared from aniline, paraformaldehyde, and bisphenol A by using a solvent method described in previous literatures.<sup>1,2</sup>

### Characterization

FTIR spectra were obtained with Nicolet-60SXB spectrophotometer using KBr discs at room temperature. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were collected on a 600 MHz Bruker Avance-600MHz NMR spectrometer, tetramethylsilane was used as an internal standard. Gel-permeation chromatographer (GPC) was performed on Waters Styragel-HY3-ST5-ST6E; polystyrene standards were used for calibrating and tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. DSC was performed on DSC-Pyris with a heating rate of 10°C/min using a nitrogen purge and an empty aluminum pan as a reference, the gas flow rate was 20 mL/min. Dynamic mechanical analyses (DMA) were conducted on a Rheometrics Scientific<sup>TM</sup> DMTA-V at 1 Hz at a heating rate of 5°C/min; the dimensions of the samples were 25 × 5 × 1 mm<sup>3</sup>. Thermogravimetric analysis (TGA) was performed with a Toshiba Netzsch 209C thermogravimetric analyzer under nitrogen from ambient temperature up to 800°C (or 900°C) at a heating rate of 10°C/min; the gas flow rate was 100 mL/min. Electron Impact (EI) Mass spectrometry analysis was performed on a QuattroII ion trap mass spectrometer (Micromass, UK), the injector temperature was held at 200°C, mass range was 40–500 m/z, emission current was 10 μA (at 70-eV electron energy).

### Preparation of 2-(hydroxyphenyl)-2-oxazoline

2-(Hydroxyphenyl)-2-oxazoline (HPO) was synthesized and purified according to analogous procedures reported<sup>27,28</sup> as shown in Scheme 1, and finally white powdery 2-(hydroxyphenyl)-2-oxazoline (HPO) was obtained in the yield of 87%.

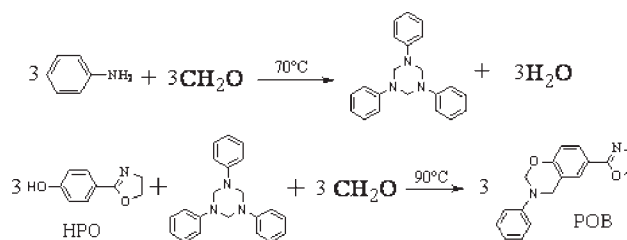
FTIR:  $\nu_{\text{O-H}} = 3423 \text{ cm}^{-1}$ ,  $\nu_{\text{C=N}} = 1634 \text{ cm}^{-1}$ ; <sup>1</sup>H-NMR (acetone-d<sub>6</sub>, ppm):  $\delta = 7.81, 6.90$  (H, benzene ring),  $\delta = 4.37, 3.98$  (H, —O—CH<sub>2</sub>—, —N—CH<sub>2</sub>— of 2-oxazoline ring),  $\delta = 9.02$  (H, —OH); mp = 209°C (determined by DSC).

### Preparation of POB

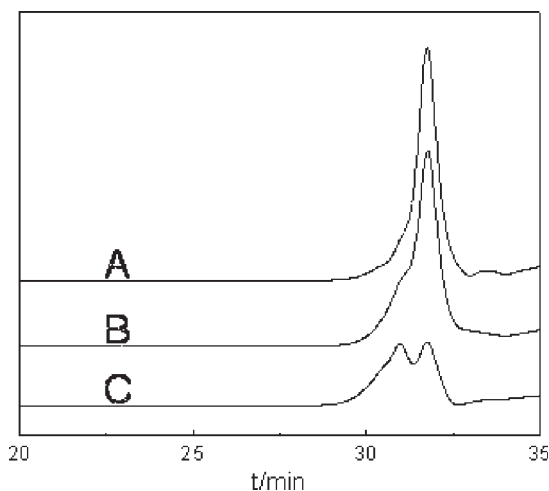
1,3,5-triphenylhexahydro-1,3,5-triazine was first prepared from aniline and paraformaldehyde according to the literature,<sup>29</sup> and then HPO, paraformaldehyde and 1,3,5-triphenylhexahydro-1,3,5-triazine were used to synthesize POB (Scheme 2). A detailed synthesis procedure is as follows: to a mixture of 4.89 g (0.03 mol) HPO and 3.15 g (0.01 mol) 1,3,5-triphenylhexahydro-1,3,5-triazine/DMF solution in a 100-mL three-necked flask equipped with condenser and Teflon stirrer, 0.9 g (0.03 mol) paraformaldehyde was added slowly at 0°C. The temperature was then raised and the mixture was kept at 90°C for 2 h. Finally, the reaction solution was poured in 80 mL ethyl ether and washed with 1N NaOH aqueous solution and de-ionized water for three times, respectively. The product solution was dried by magnesium sulfate and distilled by reducing pressure, a light yellow viscous POB precursor was obtained in the yield of 75%.

The POB precursor, obtained from the above synthesis procedure, was a mixture of monomer and oligomer. To obtain pure product, POB precursor was recrystallized from acetone, and washed with methanol for several times. Finally, a white crystal POB monomer was obtained in the yield of 53%.

1,3,5-Triphenylhexahydro-1,3,5-triazine, FTIR:  $\nu = 1597, 1500, 755, 691 \text{ cm}^{-1}$  (benzene ring),  $\nu = 1166, 1199, 1340 \text{ cm}^{-1}$  (C—N—C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm):  $\delta = 4.89$  (H, —CH<sub>2</sub>—); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm):  $\delta = 147, 129, 125, 117$  (benzene ring), 65(—CH<sub>2</sub>—); mp = 145°C (determined by DSC). The characterization of POB will be discussed subsequently.



Scheme 2



**Figure 1** GPC chromatograms of A (POB monomer), B (POB precursor), and C (residues of POB precursor).

### Preparation of polymers

#### Polymers of P-p and P-m

POB precursor and monomer were processed into molds at room temperature, and then, the molds were put in a vacuum oven at 70°C for 2 h. P-p and P-m were obtained in an air-circulating oven by heating the molds at 120°C for 1 h, 180°C for 1 h, 220°C for 1 h and 240°C for 30 min.

#### Polymer for BBZ

Polymer for BBZ (PBBZ) was prepared according to the same procedure of P-p and P-m.

#### Composite of PBBZ and polymer for PBO

PBO and BBZ were blended together with molar ratio 1 : 1, then the temperature was gradually increased to 140°C and the system was stirred until both the PBO and BBZ had melted completely. Upon cooling, the mixture gave a transparent light yellow solid, which was used to prepare the composite of PBBZ and polymer for PBO (PPBO), the procedure was similar.

## RESULTS AND DISCUSSION

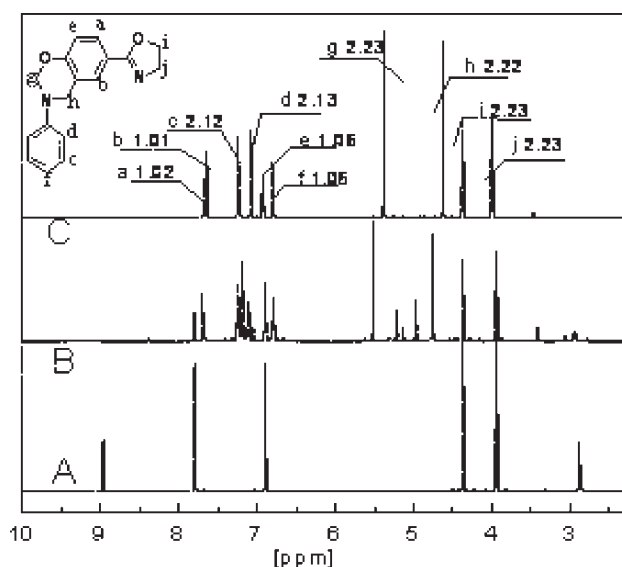
### POB monomer and POB precursor

As reported by other researchers,<sup>1-8,29</sup> it is difficult to separate benzoxazine monomer from its precursor, because the monomer and oligomer have similar physical and chemical properties, although product is washed with NaOH solution and de-ionized water during synthesis procedure. At the same time, it will be very convenient for us to investigate the chemical

properties of benzoxazine monomer and the thermal properties of the polymer if benzoxazine monomer could be separated abundantly. As to POB, it is feasible to obtain POB monomer.

By being recrystallized from acetone, POB precursor is divided into two portions, one is the POB monomer, the other is the residues of POB precursor. Figure 1 shows the GPC chromatograms of POB products. B curve presents POB precursor, A curve presents POB monomer obtained from POB precursor, C curve shows the residues of POB precursor. It can be seen that the peak at 31.8 min retention time is assigned to POB monomer; A shows a single strong peak, B shows a strong peak and a little broad peak in the left-hand side, which indicates POB precursor contains POB monomer (mostly) and oligomer; the oligomer and a little monomer are dissolved in acetone after recrystallizing of POB precursor, just as shown in C curve. The results demonstrate that pure POB monomer could be obtained from POB precursor by recrystallizing from acetone.

The <sup>1</sup>H-NMR spectra of HPO, POB precursor, and POB monomer are shown in Figure 2. The obvious resonances (in A, B, and C spectra) at 4.37 and 3.98 ppm are assigned to the methylene of 2-oxazoline ring. The resonances (in B and C spectra) at 4.65 and 5.39 ppm are assigned to the methylene bridges of benzoxazine ring. Comparing with C spectrum, B spectrum has several unwanted resonances: 4.90 ppm indicated the existence of few unreacted 1,3,5-triphenylhexahydro-1,3,5-triazine; 5.22 and 5.13 ppm are assigned to the oligomer of PBO. C spectrum demonstrates the chemical structure of pure POB monomer. Figure 3 shows the <sup>13</sup>C-NMR spectrum of POB monomer, the resonance at 77.10 ppm is



**Figure 2** <sup>1</sup>H-NMR spectra of HPO (A), POB precursor (B), and POB monomer (C).

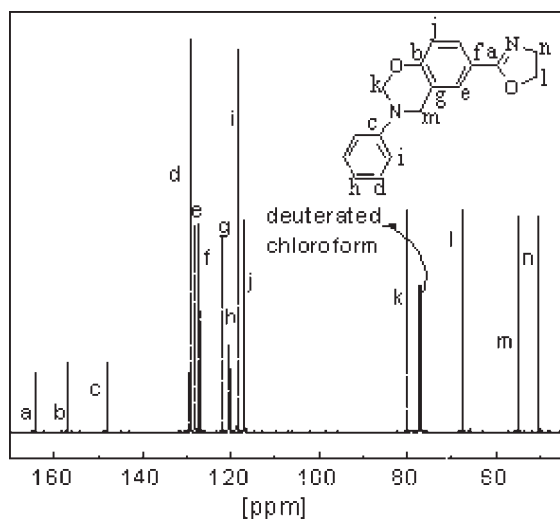


Figure 3  $^{13}\text{C}$ -NMR spectrum of POB monomer.

assigned to the deuterated chloroform (as the solvent), other resonances in Figure 3 accord greatly with the chemical structure of POB monomer.

Figure 4 shows the EI mass spectrum of POB monomer. It can be seen that the largest ion  $m/z$  280 corresponds to POB monomer and the strongest ion  $m/z$  77 is assigned to benzene ring.

### Curing behavior of POB monomer

It is known that there are two reactive groups (2-oxazoline ring and benzoxazine ring) in the POB structure. The curing behaviors of the two groups have been reported respectively.<sup>3,5,24–26</sup> In this communication, the DSC thermograms of POB monomer are shown in Figure 5. A profile has a melt point (204.9°C) and a reaction peak (208.3°C), which indicates 2-oxazoline in HPO reacts quickly after its melt. B profile has a melt point (106.3°C) and a single

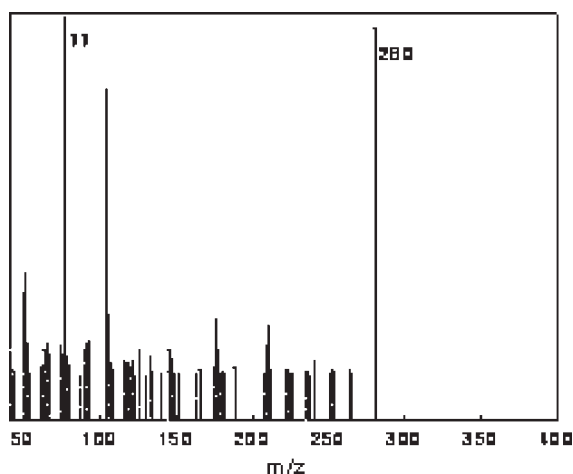


Figure 4 EI-mass spectrum of POB monomer.

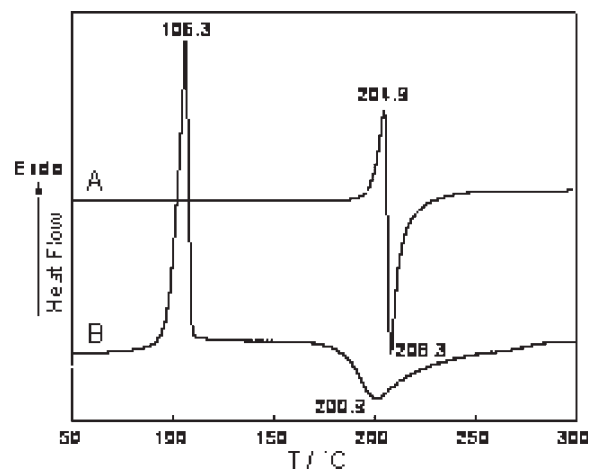


Figure 5 DSC thermograms of HPO (A) and POB monomer (B).

little broad exotherm peak (200.9°C), the onset temperature of the exotherm peak is at 187.5°C. It is known that 2-oxazoline and benzoxazine ring open by heating via a cationic mechanism, although Kimura et al.<sup>24,25</sup> reported that phenol hydroxyl of the ring-opened benzoxazine can react with 2-oxazoline. So we speculated that the ring-opening reaction of 2-oxazoline and benzoxazine are simultaneous at around 200.9°C, ring-opened 2-oxazoline can also participate in the reaction of benzoxazine, synergistic effect occurs during the reaction of POB monomer. So the curing temperature of POB is lower than that of HPO.

Figure 6 shows the FTIR spectra of POB monomer at different curing stages. It can be seen that the characteristic absorptions of benzoxazine structure,

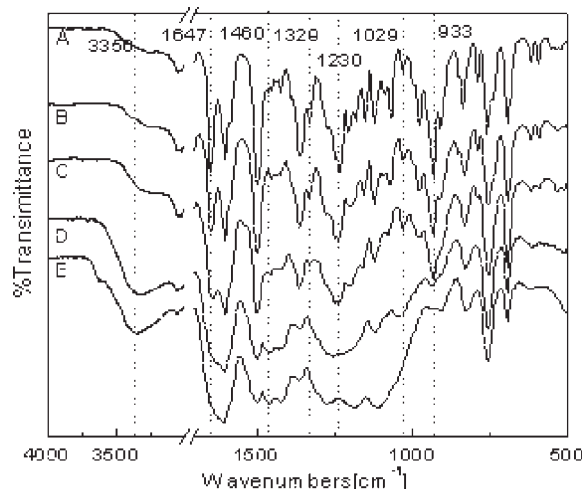
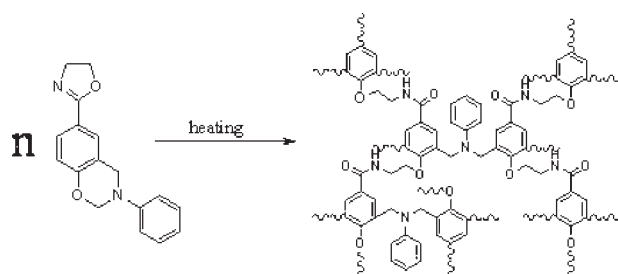


Figure 6 FTIR spectra of POB monomer at different curing temperatures: (A) at room temperature, (B) at 120°C for 30 min, (C) at 160°C for 30 min, (D) at 200°C for 30 min, and (E) at 230°C for 30 min.



Scheme 3

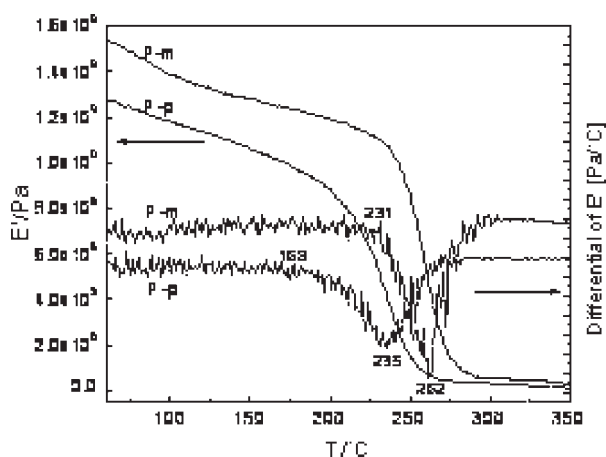
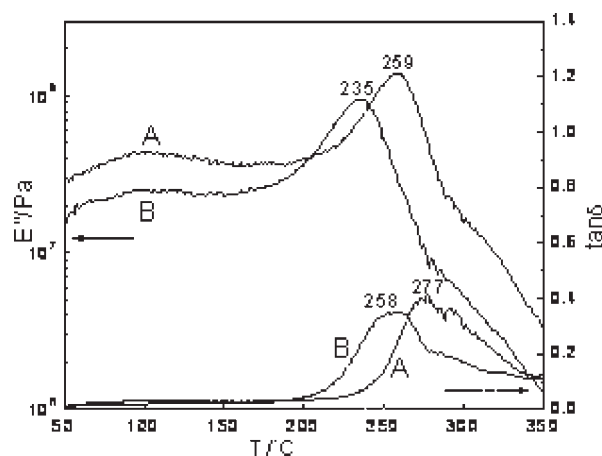
at 1329, 1230, 1029, and 933 $\text{cm}^{-1}$ , gradually decrease and then disappear after the 230 $^{\circ}\text{C}$  curing stage, which suggested the ring opening reaction of benzoxazine. At the same time, the absorption (at 1647  $\text{cm}^{-1}$ ), assigned to  $-\text{O}-\text{C}=\text{N}-$  of 2-oxazoline, gradually decreases during the curing stages, and shifts to the lower absorption (at 1620  $\text{cm}^{-1}$  overlapped with benzene ring), new absorptions at 3356 and 1460  $\text{cm}^{-1}$ , assigned to  $-\text{N}-\text{H}$  of amide, appear and increase during the curing stages. It is indicated that the cyclic imino ether structure of 2-oxazoline is isomerized to amide structure. The curing reaction is described in Scheme 3.

### Properties of cured polymers

#### P-m and P-p

The DMA and TGA results of P-m and P-p are shown in Figures 7–9.

It is well known that the storage modulus  $E'$  represents the polymer's rigidity, its differential curve indicates the decreasing rate of  $E'$  vs. temperature. Figure 7 shows  $E'$  and its differential curves of P-m and P-p. As we can see that P-m has higher storage modulus than P-p throughout the detecting temperature range (50–350 $^{\circ}\text{C}$ ). The differential curves shows the  $E'$  of P-m decreases sharply at about 231 $^{\circ}\text{C}$ ,

Figure 7  $E'$  and its differential curves of P-m and P-p.Figure 8 Loss modulus  $E''$  and loss factor  $\tan \delta$  curves of P-m (A) and P-p (B).

which is much higher than that of P-p (168 $^{\circ}\text{C}$ ), and the peak temperature (the maximum decreasing rate of  $E'$ ) of P-m and P-p are at 262 $^{\circ}\text{C}$  and 235 $^{\circ}\text{C}$ , respectively. All the results show that P-m has better rigidity and heat resistance than P-p.

Figure 8 shows the temperature dependence of loss modulus  $E''$  and loss factor  $\tan \delta$  for P-m and P-p. For P-m, the  $T_g$  is 259 $^{\circ}\text{C}$  from the maximum of  $E''$  and 277 $^{\circ}\text{C}$  from the maximum of  $\tan \delta$ , whereas the  $T_g$  of P-p is 235 $^{\circ}\text{C}$  and 258 $^{\circ}\text{C}$  from the maximum of  $E''$  and  $\tan \delta$ , respectively, which are much lower than P-m. Figure 9 shows the thermal stability of P-m and P-p, though the 5% and 10% weight loss temperature ( $T_5$  and  $T_{10}$ ) of P-m (339, 370 $^{\circ}\text{C}$ ) and P-p (338, 362 $^{\circ}\text{C}$ ) are closed, the difference becomes distinct with the temperature increasing, and the char yield of P-m is up to 53.36% at 900 $^{\circ}\text{C}$ , which is much higher than P-p (41.93%).

The results of DMA and TGA demonstrate that the thermal stability and heat resistance of P-m are much better than P-p. Comparing with POB precur-

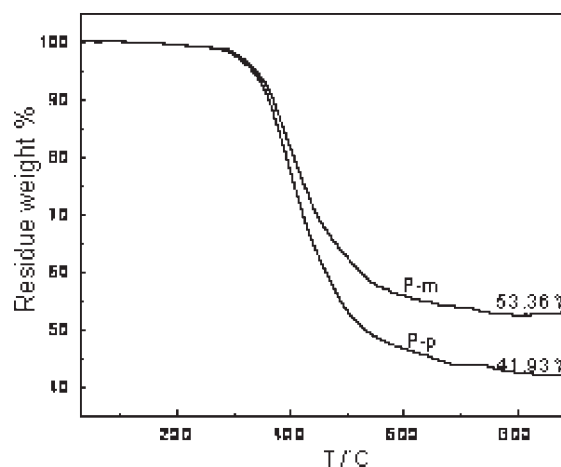
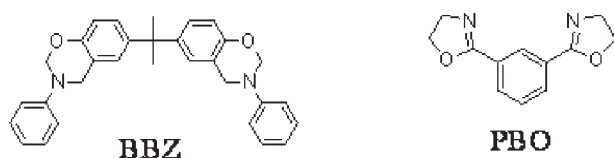


Figure 9 TGA thermograms of P-m and P-p.



Scheme 4

sor, POB monomer has more reactive groups at equal moles, and the cross-linking density of P-m is higher, so the network structure of P-m is more compact and perfect. Although POB precursor is the mixture of POB monomer and the oligomer, the reaction occurs between not only the monomer but also the oligomer and monomer, which result in the deficiency formation in the network structure of P-p.

#### P-m, PBBZ, and composite of PBBZ-PPBO

As shown in Scheme 4, BBZ is a common benzoxazine with two benzoxazine rings on its molecule, there are also two 2-oxazoline rings on PBO molecule, so the composite of PBBZ-PPBO (mol ratio 1 : 1) will have similar network moiety with P-m. In this section, the thermal properties of P-m, PBBZ, and composite of PBBZ-PPBO are investigated.

DMA results of the three polymers are shown in Figures 10 and 11. Figure 10 shows  $E'$  and its differential curves of P-m (A), PBBZ (C) and PBBZ-PPBO (B). It can be seen that P-m and PBBZ-PPBO have similar  $E'$  at room temperature, whereas the  $E'$  of PBBZ-PPBO decreases obviously at 88°C and the maximum decreasing rate occurs at 155°C, as shown in differential curves. The  $E'$  of PBBZ at room temperature is lower than P-m and PBBZ-PPBO, but its distinct decreasing temperature (122°C) and maximum decreasing rate temperature (167°C) are higher than PBBZ-PPBO. So it can be found that P-m has

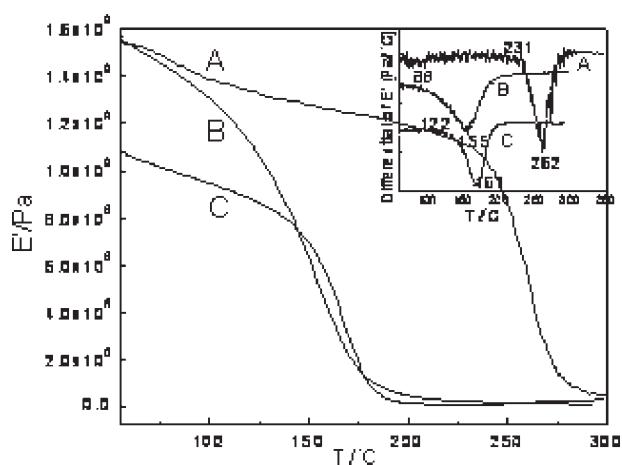


Figure 10  $E'$  and its differential curves of P-m (A), PBBZ (C), and composite of PBBZ-PPBO (B).

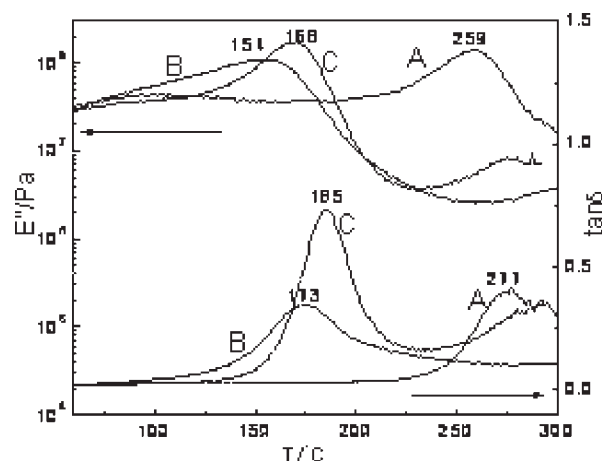


Figure 11 Loss modulus  $E''$  and loss factor  $\tan \delta$  curves of P-m (A), PBBZ (C) and composite of PBBZ-PPBO (B).

the best heat resistance among the three polymers, though the rigidity of PBBZ at room temperature is less than PBBZ-PPBO, the heat resistance of PBBZ at high temperature is much better than PBBZ-PPBO.

Figure 11 shows the temperature dependence of loss modulus  $E''$  and loss factor  $\tan \delta$  for the three polymers. It can be seen that P-m has the highest  $T_g$ , the  $T_g$  of PBBZ (168, 185°C from peak of  $E''$  and  $\tan \delta$ ) are respectively higher than PBBZ-PPBO (154, 173°C from peak of  $E''$  and  $\tan \delta$ ). Figure 12 shows the thermal stability of the three polymers, we found that the  $T_5$  and  $T_{10}$  of P-m (339, 370°C) are the highest compared with PBBZ-PPBO (334, 365°C) and PBBZ (322, 347°C). The char yield (at 800°C) of P-m, PBBZ, and PBBZ-PPBO are 53.76%, 35.42% and 40.83%, respectively. The results indicate that P-m has the most excellent thermal stability, and then PBBZ-PPBO, and PBBZ, respectively.

The results of DMA and TGA show that, compared with 2-oxazoline compound and benzoxazine

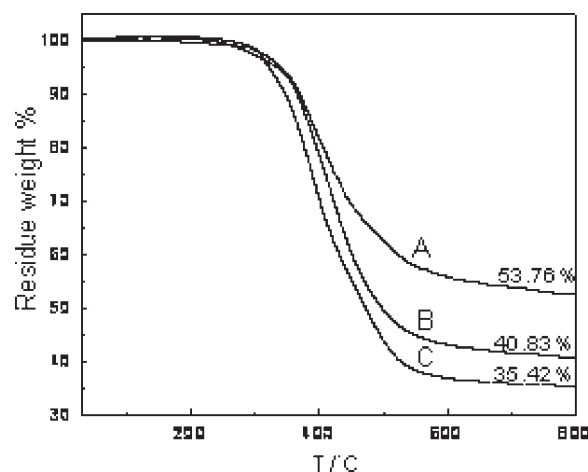


Figure 12 TGA thermograms of P-m (A), PBBZ (C) and PBBZ-PPBO (B).

compound, the P-m combined with 2-oxazoline and benzoxazine rings shows more excellent thermal properties. At the same time, the thermal properties of P-m, due to its impact and perfect network structure, are much better than the composite (equal moles) of 2-oxazoline and benzoxazine material.

### CONCLUSION

A novel benzoxazine containing 2-oxazoline and benzoxazine moiety is synthesized; it is found that the benzoxazine monomer could be separated from its precursor by simple separated process, and the high purity is confirmed by measurements. The thermal properties of the P-m are much better than P-p, just as it is determined by DMA and TGA. The reason may be that benzoxazine monomer produces less deficiency during polymerization than benzoxazine precursor with oligomer. When compared with common benzoxazine and composite of benzoxazine and 2-oxazoline, P-m has excellent thermal properties, which are demonstrated by DMA and TGA.

### References

1. Ishida, H.; Allen, D. J. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
2. Shen, S. B.; Ishida, H. *J Appl Polym Sci* 1996, 61, 1595.
3. Ishida, H.; Krus, C. M. *Macromolecules* 1998, 31, 2409.
4. Wan, X. B.; He, J. B.; Xu, N. *Chem J Chin Univ* 2002, 22, 506.
5. Ishida, H.; Sanders, D. P. *Macromolecules* 2000, 33, 8149.
6. Agag, T.; Takeichi, T. *Macromolecules* 2001, 34, 7257.
7. Shen, S. B.; Ishida, H. *J Polym Sci Part B: Polym Phys* 1999, 37, 3257.
8. Agag, T.; Takeichi, T. *Macromolecules* 2003, 36, 6010.
9. Aoi, K.; Okada, M. *Prog Polym Sci* 1996, 21, 151.
10. Wiley, R. H.; Bennett, L. L. *Chem Rev* 1949, 44, 447.
11. Saegusa, T.; Kobayashi, S. *Macromolecular Science, International Review of Science, Physical Chemistry Series 2*; Butterworth: London; 1975, Vol. 8, Chapter 4.
12. Saegusa, T.; Kobayashi, S. *Encyclopedia of Polymer Science and Technology*; Wiley: New York; 1976, Vol. 1, p 220.
13. Kobayashi, S.; Saegusa, T. *Ring-Opening Polymerization*; Elsevier Applied Science: Essex, UK; 1984, Vol. 2, Chapter 11.
14. Kobayashi, S.; Saegusa, T. *Encyclopedia of Polymer Science and Engineering*; Wiley: New York; 1986, Vol. 4, p 525.
15. Kobayashi, S. *Prog Polym Sci* 1990, 15, 751.
16. Chujo, Y.; Saegusa, T. *Ring-Opening Polymerization*; Hanser: Munich; 1993, p 239.
17. Culbertson, B. M. *Prog Polym Sci* 2002, 27, 579.
18. Frump, J. A. *Chem Rev* 1971, 71, 483.
19. Stefano, C.; Dominique, S. *J Comb Chem* 2005, 7, 688.
20. George, P. K.; Eleni, A. P. *J Appl Polym Sci* 2000, 77, 2206.
21. Sano, Y. *J Polym Sci Part A: Polym Chem* 1989, 27, 2749.
22. Yuhua, T.; Feng, G.; Yong, Q. H.; Scott, R. S.; Bill, M. C. *Polym Adv Technol* 2002, 13, 311.
23. Loontjens, T.; Pauwels, K.; Derks, F.; Neilen, M.; Sham, C. K.; Serne, M. *J Appl Polym Sci* 1997, 65, 1813.
24. Kimura, H.; Matsumoto, A.; Hasegawa, K.; Fukuda, A. *J Appl Polym Sci* 1999, 72, 1551.
25. Kimura, H.; Taguchi, S.; Matsumoto, A. *J Appl Polym Sci* 2001, 79, 2331.
26. Chen, Q.; Xu, R. W.; Zhang, J.; Yu, D. S. *Macromol Rapid Commun* 2005, 26, 1878.
27. Percec, V.; Nava, H.; Rodriguezparada, J. M. *J Polym Sci: Polym Lett Ed* 1984, 22, 523.
28. Shiro, K.; Tsutomu, M.; Take, S. *Macromol Chem* 1984, 185, 441.
29. Zdenka, B.; Ping, L. J.; Ishida, H. *Macromol Chem Phys* 1999, 200, 1745.