Study of thermal properties of difunctional benzoxazines

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Abstract: Three difunctional benzoxazine monomers bis (3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl) methane, (abbreviated as BF-a), bis (3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl) isopropane, (abbreviated as BA-a), bis (3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl) biphenyl, (abbreviated as BP-a) were successfully synthesized via phenol (bisphenol A, 4,4'-Biphenol, bisphenol F), aniline and paraformaldehyde. Their structures were identified by $^1$H NMR and FT-IR. The monomers were thermally treated at 200 °C for 2 h in nitrogen to give corresponding prepolymers. The thermal properties of the monomers were investigated by TGA under nitrogen atmosphere. The thermal properties of the prepolymers were investigated by TGA under nitrogen and air atmosphere. It was found that the monomers of BF-a and BA-a showed lower melting points and exhibited wider processing windows than BP-a. The prepolymers from BP-a showed good thermal stabilities, compared with the prepolymers from BF-a and BA-a.

Keywords: benzoxazines; benzoxazine monomers; prepolymers; thermal property

Introduction

Phenolic resins have been used for many years in various applications mainly because of their low flammability, high temperature resistance, inherent hardness and dielectric insulation properties. Nonetheless, a number of disadvantages also exist, such as their brittleness, use of strong catalyst for polymerization, and volatiles generated as a result of the condensation reaction [1]. Polybenzoxazines as a novel type of phenolic resin not only possess the advantages of traditional phenolic resins, but also display lots of unique characteristics, including could do without harsh catalysts, nearly zero shrinkage and no release of volatiles upon curing, low water absorption, good dielectric properties and molecular design flexibility [2, 3]. Consequently, they have received considerable attention and have been developed for many fields such as the electronics and aerospace industries.

Conventionally, benzoxazines are synthesized via Mannich condensation of phenol, formaldehyde and primary amine and polymerized by ring-opening polymerization with no reaction byproducts released and no catalyst required [4-8]. Various types of phenols and amines have been utilized for synthesis of benzoxazine. However, it has been reported that monofunctional benzoxazine molecules do not form large molecular weight polymers despite the possibility of forming a linear polymer [9]. To overcome this problem, variety of difunctional phenolic compounds or difunctional amines were used to synthesize difunctional benzoxazines [10-12] to obtain crosslinked polymers with useful properties. Recently, bisphenol A type benzoxazine has been studied in detail as precursor of polybenzoxazine. However, because of the...
spacer \(-\text{C(CH}_3)_2\)\-, the thermal and mechanical properties of its cured polymer are restricted. Although benzoazaines with biphenyl linkages can lead to excellent mechanical and thermal properties, the higher crystallinity may lead to difficult processing. So far, appropriate benzoazaines containing these advantages have received significant attention.

In this study, similar type of difunctional benzoazine was prepared using bisphenol F instead of bisphenol A and the pure monomer was referred as BF-a. Until now, the investigation of BF-a was with regard to it as the copolymer \([13, 14]\) and modifier \([15]\). But the thermal property of pure BF-a have not been reported. In this paper, three difunctional benzoazaines (Scheme 1) were presented to study their thermal behaviours, which will contribute to the further investigation of these benzoazaines. The structures of all benzoazaines were characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), and their properties were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The monomers were cured and their properties were evaluated by TGA.

![Scheme 1. Chemical structures of benzoazine monomers.](image)

**Results and discussion**

**Characterization of benzoazine monomers**

The proton NMR spectra of the monomers are shown in Fig. 1. The shifts and splitting patterns of \(^1\text{H} \text{NMR (DMSO-}_d_6\) spectra of the three monomers are given as follows: BF-a: \(\delta 3.71\) (2H, -CH\(_2\)), \(\delta 4.60\) (4H, -N-CH\(_2\)-Ph), \(\delta 5.39\) (4H, -N-CH\(_2\)-O), \(\delta 6.60–7.22\) (16H, Ph-H). BA-a: \(\delta 1.25\) (6H, -CH\(_3\)), \(\delta 4.58\) (4H, -N-CH\(_2\)-Ph), \(\delta 5.33\) (4H, -N-CH\(_2\)-O), \(\delta 6.69–7.25\) (16H, Ph-H). And BP-a: \(\delta 4.70\) (4H, -N-CH\(_2\)-Ph), \(\delta 5.47\) (4H, -N-CH\(_2\)-O), \(\delta 6.75–7.36\) (16H, Ph-H). No signals appear at around 3.10 and 3.60 ppm, attributed to the case when the oxazine ring opens.
The benzoxazine monomers were also characterized by FT-IR in order to confirm their structures further (Fig. 2). The characteristic absorptions of benzoxazine structures are at 1230 cm\(^{-1}\) assigned to the asymmetric stretching of Ar-O-C group, 951 and 1494 cm\(^{-1}\) due to the trisubstituted benzene ring and 1323 cm\(^{-1}\) assigned to CH\(_2\) wagging of oxazine ring. Additionally, the antisymmetric and symmetric C-N-C stretching modes at 1240 and 830 cm\(^{-1}\) are observed, respectively. The C-H out-of-plane bending vibration of benzene ring is observed at 698 cm\(^{-1}\). These results indicate that all of the monomers contain hexagonal heterocyclic rings. Besides, a characteristic absorption of BA-a is at 2969 cm\(^{-1}\) assigned to CH\(_3\) stretching,
compared to that of BF-a at 2904 cm\(^{-1}\) due to CH\(_2\) stretching. Along with \(^1\)H NMR, FT-IR confirms the structures of the monomers.

**Thermal properties of benzoxazines**

The DSC curves of all the synthesized benzoxazine monomers are shown in Fig. 3. The thermogram shows the sole thermal transition peaks for BF-a and BA-a at about 110 °C and 117 °C, respectively. These are endothermic type assigned to the melting process of the solid state. In contrast, BP-a shows no obvious melting peak within this temperature range. This can be due to the alkyl groups (CH\(_2\), C(CH\(_3\))\(_2\)) in the structures of BF-a and BA-a, which result in lower melting points than BP-a with rigid structure.

![DSC curves](image)

**Fig. 3.** DSC curves of benzoxazine monomers.

To further study the thermal properties of the three monomers, heat treatments of these samples were precured at 200 °C for 2 h under nitrogen atmosphere [16]. The prepolymer derived from BF-a, BA-a and BP-a were hence referred to as PBF-a, PBA-a and PBP-a respectively.

The thermal stability of the monomers and the prepolymer were analyzed by TGA. The values of 5% and 10% weight loss temperatures and the char yields at 800 °C are summarized in Table 1. As shown in Fig. 4, the initial weight loss temperature of the monomers appears at around 150 °C. This phenomenon possibly affects the processability of benzoxazines resulting from volatilization of monomers. It is also observed that the temperature for 5% weight loss (\(T_{5\%}\)) for BA-a is obviously higher than that of the other monomers. Then the weight loss is aggravated. At the temperature of 245 °C, the weight percentage of BF-a is 81.64%, while of BA-a and BP-a are among 86-89%. The results can attribute to the volatilization of monomers and the cleavage of the oxazine rings (the cleavage of the C-N bond). The second stage of degradation begins at 250 °C, and it is observed that the rate of weight loss for BA-a is aggravated markedly until 500 °C. Compared to BF-a, BP-a undergoes less weight losses at every temperature after 250 °C. These results show that BP-a exhibit better thermal stability than BF-a and BA-a because of the thermally labile aliphatic groups in the latter. Combined with the DSC results, BF-a and BA-a monomers exhibit wide processing windows between the melting points of monomers
and the temperatures of polymerization, while BP-a exhibits a narrow processing window in that BP-a has been polymerized during melting.

Furthermore, it is obvious that the decomposition pattern of prepolymers is different from that of their monomers. The latter show a well-separated two-stage weight loss process. Instead, the prepolymers show an overlapped two-stage weight loss process. For prepolymers, weight loss starts at about 250 °C. This result indicates that most monomers were involved in the ring-opening polymerization during curing. It also proves that the curing of monomers is an auto-catalyzed reaction [17]. Moreover, the higher temperatures of 5% and 10% weight loss indicate that prepolymers have formed cross-linked networks which are the characteristics of polymeric difunctional benzoxazines [18]. However, the rate of thermal degradation for PBA-a is severe than that of the others observed in Fig. 4. This can be attributed to the weak bond (-C(CH3)2-) which affects its thermal stability. It is observed that PBP-a exhibits a higher T5% degradation temperature (366 °C) and a higher char yield (55.65%) at 800 °C than the other prepolymers. The result may also be attributed to the rigid structure of PBP-a.

Fig. 4. TGA curves of benzoxazine monomers and the prepolymers after thermal treatments in nitrogen.

Tab. 1. TGA analysis results of benzoxazine monomers and prepolymers in nitrogen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T5% (°C)</th>
<th>T10% (°C)</th>
<th>Char yield (%) at 800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF-a</td>
<td>208</td>
<td>227</td>
<td>41.55</td>
</tr>
<tr>
<td>BA-a</td>
<td>224</td>
<td>237</td>
<td>30.83</td>
</tr>
<tr>
<td>BP-a</td>
<td>217</td>
<td>229</td>
<td>52.70</td>
</tr>
<tr>
<td>PBF-a</td>
<td>336</td>
<td>381</td>
<td>48.13</td>
</tr>
<tr>
<td>PBA-a</td>
<td>301</td>
<td>333</td>
<td>34.14</td>
</tr>
<tr>
<td>PBP-a</td>
<td>336</td>
<td>374</td>
<td>55.65</td>
</tr>
</tbody>
</table>

Fig. 5 displays TGA curves of the same prepolymers, but the tests were performed in air in order to investigate their thermo-oxidative stability. TGA results are summarized in Tab. 2. For most of the thermosetting resins, thermo-oxidation processes start at
about 500 °C and char yields at 600 °C are equal to zero [19]. It is observed that the thermo-oxidative process of prepolymer PBF-a appears at about 300 °C, and at 600 °C they exhibit char yields of 33.62% and 21.02% by weight, respectively. Moreover, they exhibit \( T_{5\%} \), in the temperature range of 355-366 °C. However, the poorest performance among all the prepolymer is PBA-a. It exhibits \( T_{5\%} \) at 317 °C and char yield at 600 °C only 2.92%. It is possibly because PBA-a relatively contains lowly cross-linked Mannich-based networks, and the thermally labile isopropyl group is easily oxidatively decomposed. These results reveal that a further modification needs to be done on difunctional benzoxazines.

![TGA curves of prepolymer after thermal treatments in air.](image)

**Fig. 5.** TGA curves of prepolymer after thermal treatments in air.

**Tab. 2.** TGA analysis results of prepolymer in air.

<table>
<thead>
<tr>
<th>Prepolymer</th>
<th>( T_{5%} (°C) )</th>
<th>( T_{10%} (°C) )</th>
<th>Char yield (%) at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBF-a</td>
<td>366</td>
<td>425</td>
<td>21.02</td>
</tr>
<tr>
<td>PBA-a</td>
<td>317</td>
<td>360</td>
<td>2.92</td>
</tr>
<tr>
<td>PBP-a</td>
<td>355</td>
<td>393</td>
<td>33.62</td>
</tr>
</tbody>
</table>

**Conclusions**

Three benzoxazine monomers, namely, BF-a, BA-a and BP-a, were successfully synthesized, and their structures were confirmed by \(^1\)H NMR and FT-IR. The processing windows of BF-a and BA-a are wider than that of BP-a. Prepolymer PBP-a exhibits the best thermal stability in nitrogen and thermo-oxidative stability in air compared to other two prepolymer. Compared to BA-a, BF-a will receive more attention and used widely in industries. A further study on the reaction mechanism of benzoxazine ring-opening reaction is underway in our laboratory.

**Experimental part**

**Materials**

Bisphenol A (Tianjin Guangfujingxi Chemical Research Institute, China), 4,4''- Biphenol (Henan Yanhua Chemical Co., Ltd, China), paraformaldehyde (Tianjin
Kemiou Chemical Co., Ltd, China) and aniline (99.5%, Chengdu Kelong Chemical Reagent Factory, China) were used as received. Bisphenol F was prepared following the literature method [20]. The other solvents were used as received.

**Synthesis of benzoxazine monomers**

Benzoxazine monomers are typically synthesized either by employing solution or solventless methods. There are many disadvantages for the former method [21]. To overcome these shortcomings, Ishida et al. developed a solventless synthesis in the melted state [22]. The main advantages of the solventless method are improvement of reaction times and formation of fewer unwanted intermediates and by-products. Consequently, in this study benzoxazine monomers were synthesized by the solventless method.

The benzoxazine monomers were prepared according to the literature [22-24]. A typical synthesis of BA-a monomer was performed as follows. To a flask equipped with a mechanical stirrer, 0.2 mole aniline and 0.4 mole paraformaldehyde were added. The mixture was stirred at 40 °C until the solid dissolved completely. Then 0.1 mole bisphenol A was added. The temperature was increased up to 100 °C and stirred for 30 min. The resulting transparent and yellow viscous liquid solution was obtained. To purify the monomer, the reaction product was redissolved in ethyl ether. The solids were filtered out, and the solution was washed three times with a 3N NaOH aqueous solution in a separatory funnel, and water was used for the final wash. The ether phase was dried over sodium sulfate and the solvent evaporated in a rotary evaporator. A very fine white powder was obtained. Synthesis of BP-a and BF-a monomers was performed in the same way. The overall synthetic procedure is shown in Scheme 2.

**Scheme 2.** Synthesis of benzoxazine monomers.

**Measurements**

Proton nuclear magnetic resonance (¹H NMR) spectra were performed by Bruker Advance-400 MHz spectrometer, using DMSO-δ6 as a solvent and tetramethylsilane as the internal standard.

Fourier transform infrared spectra (FT-IR) were recorded with a Nicolet FTIR-380 by the KBr salt slice method.

Differential scanning calorimetry (DSC) was conducted using U.S TA Q200. Samples were heated from 30 to 200 °C at a heating rate of 10 °C/min under nitrogen (50 mL/min).
Thermogravimetric analysis (TGA) were performed by US TA Q500. Samples were heated from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen and air (60 mL/min).

Acknowledgements
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References
[23] Ishida, H; Rodriguez, Y. Polymer. 1995, 36, 3151.