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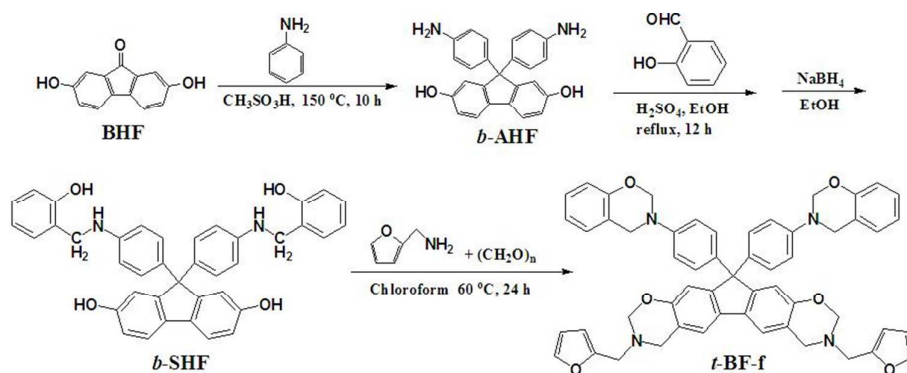
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## Graphical Abstract

**Manuscript Title: Synthesis of novel furan-containing tetrafunctional asymmetric fluorene-based benzoxazine monomer and its high performance thermoset**

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## COMMUNICATION

# Synthesis of novel furan-containing tetrafunctional fluorene-based benzoxazine monomer and its high performance thermoset

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**A novel furan-containing tetrafunctional fluorene-based benzoxazine monomer with bisphenol- and diamine-type oxazine rings was successfully prepared. The resulting polybenzoxazine exhibits extremely higher glass transition temperature (440 °C) and better thermal stability than those of difunctional furan-containing fluorene-based and traditional multifunctional benzoxazine resins.**

Polybenzoxazines, as recently developed phenolic resins, are prepared by the cationic ring-opening polymerization of the corresponding benzoxazine monomers without the addition of any extra catalysts and without generating by-products or volatiles. This new material seeks to combine the thermal properties of phenolics with the mechanical performance and design flexibility of advanced epoxy resins. The physical and mechanical characterization has revealed that this family of resins possessed excellent high thermal stability, high char yields, high glass transition temperature ( $T_g$ ), low flammability, good dielectric properties and near-zero shrinkage upon curing, and so forth.<sup>1-4</sup> These unique characteristics make the polybenzoxazine become a better candidate over traditional phenolic resins and epoxies. Benzoxazine monomers as the polybenzoxazine precursors are characterized by their cost effectiveness since they can be prepared from inexpensive raw materials as well as renewable sources, including phenols, primary amines and formaldehyde. The large varieties of phenols and amines allow considerable molecule-design flexibility for benzoxazines.<sup>5-9</sup> Recently, multifunctional benzoxazines with three or more oxazine rings have entered our field of vision gradually. The polyfunctionality required forming an infinite network structure that may be achieved through the synthesis of monomer utilizing either a multi-functional phenolic molecule with a monoamine or a multi-functional amine paired with a mono-phenol. Subrayan<sup>10</sup> and Lu<sup>11</sup> reported a novel class of triazine-containing benzoxazine monomers with three oxazine rings. Kuo et al. prepared a series of novel benzoxazine-containing polyhedral oligomeric silsesquioxane (POSS) with eight oxazine rings.<sup>12-14</sup> Multifunctional star-shaped benzoxazines with inorganic constituent were also synthesized by Kiskan<sup>15</sup> and Liu<sup>16</sup>. Recently, a difunctional asymmetric benzoxazine monomer has been synthesized by Yagci<sup>7</sup>. In addition, Tzou et al opened an issue about the varnish

composition for glass fiber laminate, in which the tetra-phenol-functional benzoxazine monomer was used as one of the component.<sup>17</sup> However, there has not hitherto been a report on the synthesis, curing behaviour and rheological property of tetra-functional benzoxazine monomer simultaneously containing bisphenol- and diamine-type oxazine rings in one molecule, as well as the thermal properties of its polymer.

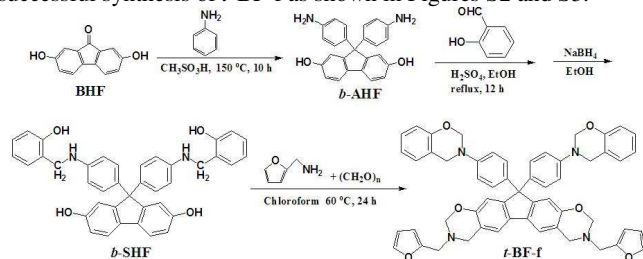
The preparation of specially designed novel benzoxazine monomer has shown considerable achievements in the developments of high performance polybenzoxazines. Fluorene contains two benzene rings linked with a five-membered ring and the incorporation of bulky fluorene group into thermosets has a significant increase in their thermal properties.<sup>18, 19</sup> In our previous studies, side chain type fluorene-based benzoxazines from bisphenolic or diamino fluorene have been successfully synthesized.<sup>20-22</sup> But the bulky pendant fluorene groups restrict the segment mobility, degrade the processing property of the benzoxazine precursors, and then lower the toughness of the obtained polybenzoxazine. In contrast, the main chain type fluorene-based benzoxazines could efficiently overcome these shortcomings. Hence they provide much better properties than those of side chain type fluorene-based benzoxazines. Additionally, 2-furfurylamine is often used as a modifier in high performance thermosets due to its crosslinkable furan ring. The introduction of furan groups into benzoxazine can increase the crosslinking densities of the resulting polymer, and further enhance its  $T_g$  value and thermal stability due to the formation of furfurylamine Mannich bridges during polymerization.<sup>23, 24</sup>

This work describes the successful preparation of a novel high performance furan-containing tetrafunctional fluorene-based benzoxazine monomer (*t*-BF-f) with bisphenol- and diamine-type oxazine rings in a single-molecule structure. The synthesis, curing behaviour and rheological property of *t*-BF-f, as well as the thermal properties of the obtained polybenzoxazine (poly(*t*-BF-f)) are investigated.

In terms of molecular design, the prepared benzoxazine monomer, namely *t*-BF-f, contains two different types of oxazine rings. Thus, the synthesis method of *t*-BF-f becomes difficult due to the selectivity problem during the monomer preparation. And two approaches are applied in current study. In the first approach, the bisphenol-type oxazines were synthesized preferentially. Firstly, the

protection of amine groups was achieved using trifluoroacetic anhydride as the protecting agent. And then bisphenol-based benzoxazine monomer containing trifluoroacetamide was prepared through traditional one-pot solvent method. After that, the protecting agent was removed by sodium boron hydride or potassium carbonate, respectively (Scheme S1). However, as shown in Figure S1 ( $^1\text{H}$  NMR spectra of the deprotecting reaction), the protecting groups was successfully removed during this process, however, the peaks attributed to the ring-opening products could be observed, indicating the damage of the existing benzoxazine groups. Studies have reported that the strong basicity of the amine could lower the stability of the oxazine ring in alkaline environment.<sup>25, 26</sup> Thus, the basic furfurylamine leads to the ring-opening of oxazine ring in the presence of these basic deprotecting agents.

The second approach is to prepare the diamine-type oxazine rings firstly, in which the combination of three-step synthesis and classical one-step synthesis strategy is applied. The synthesis route is shown in Scheme 1. The experimental methods are also described (see ESI† for experimental details). Firstly, 9,9-bis(4-aminophenyl)-2,7-dihydroxy-fluorene (*b*-AHF) was prepared via direct condensation reaction of 2,7-dihydroxy-9-fluorenone and aniline using methylsulfonic acid as the catalyst. Next, *b*-AHF reacted with 2-hydroxybenzaldehyde in the presence of  $\text{H}_2\text{SO}_4$  to yield an *o*-hydroxyl phenylimine, and subsequently the reduction was carried out using sodium borohydride as the reductant to produce *b*-SHF. Finally, *b*-SHF was reacted with 2-furfurylamine and paraformaldehyde to obtain the furan-containing tetrafunctional fluorene-based benzoxazine monomer. The  $^1\text{H}$  NMR spectra of *t*-BF-f along with its intermediates and the  $^{13}\text{C}$  NMR spectrum of *t*-BF-f confirm the successful synthesis of *t*-BF-f as shown in Figures S2 and S3.



Scheme 1. Synthesis route of *t*-BF-f

The curing behaviour of *t*-BF-f was studied by FTIR and DSC, respectively. Figure S4 shows the FTIR spectra of *t*-BF-f at each curing stage, the absorptions at 1225, 1148, and 925  $\text{cm}^{-1}$ , which are assigned to the characteristic modes of C–O–C, C–N–C, and bisphenol-type oxazine rings connected with fluorene, respectively, almost disappear. However, the very weak peak located at 946  $\text{cm}^{-1}$  can be observed, indicating that the diamine-type oxazine rings connected with benzene incompletely open at 260 °C. In the meantime, other cross-linking reaction such as substitution can be found. The new absorption at 1483  $\text{cm}^{-1}$  is ascribed to 1,2,3,5-tetra-substituted benzene ring, showing that the Mannich bridge linkage is produced by the oxazine ring-opening polymerization at elevated temperature.<sup>27</sup> Moreover, the absorption of furan ring at 1583–1608  $\text{cm}^{-1}$  becomes broad after polymerization, indicating the formation of disubstituted furan ring. This implies that the furan ring participates in the polymerization reactions and the furfurylamine Mannich bridges are formed.<sup>23</sup> The network structure of poly(*t*-BF-f) is proposed in Scheme S2.

The DSC thermograms of *t*-BF-f at each curing stage are shown in Figure 1. As demonstrated in Figure 1, the endothermal peak at 98 °C for *t*-BF-f is assigned to the melting point of the benzoxazine monomer and the exothermal behaviour observed at high temperature region is attributed to the ring-opening polymerization

of oxazine rings. Moreover, *t*-BF-f exhibits shoulders in its curing exotherms, which is expected since each monomer contains two different oxazine rings.<sup>7</sup> The data also shows that each type of oxazine ring has its own curing maximum over a broad temperature range. The bulky *t*-BF-f meets steric hindrance in polymerization, so a broad exothermic peak is resulted.<sup>23</sup> Also, it can be seen from Figure 1 that the amount of this exotherm is gradually reduced with the increase of heat-treatment temperature, while the degree of curing is gradually raised. When the sample is cured at 150, 180, 210, 240 and 260 °C, the degree of curing attains 2.0, 32.5, 58.4, 92.3 and 95.0 %, respectively. The total conversion cannot be achieved after cure, which is attributed to the ring-opening of the residual diamine-type oxazines.

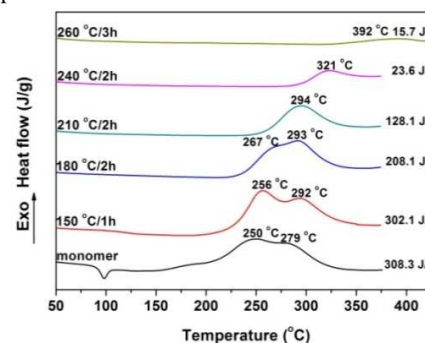


Figure 1. DSC thermograms of *t*-BF-f at each curing stage

The rheological property is able to provide the basic insights about the processability of *t*-BF-f, Figure 2 shows the plot of dynamic viscosity (Pa·s) as a function of temperature for *t*-BF-f. In Figure 2, the main thermal event at low temperature range, here called the liquefying point, is attributed to the transformation of solid to liquid. The thermal event at high temperature range is called the gel point, which is the transition of liquid to solid, in other words, the transition of benzoxazine monomers to polybenzoxazine. The temperature from liquefying point to gel point is regarded as the processing window.<sup>28</sup> For consistency in this study, the liquefying and gel temperatures of *t*-BF-f are defined at the viscosity values of 1000 Pa·s in the low and high temperature regions, respectively. The result indicates that the liquefying temperature and the gel temperature are about 112 and 184 °C, respectively. The processing window for *t*-BF-f attains 72 °C, which is wide enough for processing *t*-BF-f in molten methods. On the other hand, the processing window of *t*-BF-f is close to those of traditional bisphenol-A based benzoxazines, but apparently exceeds that of difunctional furan-containing fluorene-based benzoxazine.<sup>29, 30</sup> The fluorene groups in the main chain and the flexible methylene of furan groups are beneficial to increase the mobility of molecular chains, lower the viscosity of *t*-BF-f, and then improve its processing property.

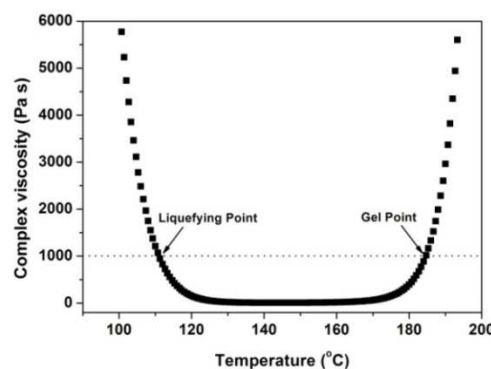


Figure 2. Relationship between dynamic viscosity and temperature of *t*-BF-f

Dynamic mechanical property of poly(*t*-BF-f) was examined by DMA as shown in Figure 3. A broad maximum of  $\tan \delta$  at 440 °C can be observed. This unusual broadness in the  $\tan \delta$  curve can then be explained by the broad distribution of molecular weights<sup>31</sup>. The  $T_g$  value of poly(*t*-BF-f) is 118, 125 and 211 °C higher than that of triazine-containing, difunctional furan-containing fluorene-based, and bisphenolic fluorene-based polybenzoxazine, respectively.<sup>11, 20, 23</sup> In comparison to these traditional difunctional fluorene-containing polybenzoxazines, the bulky fluorene groups located in the main chain avoid hanging in the network structure for poly(*t*-BF-f), lower the free volume of polybenzoxazine. In addition, the rigid fluorene group, the formation of these phenolic Mannich bridges and furfurylamine Mannich bridges during polymerization, all of which contribute to a higher degree of cross-linking and an increase of  $T_g$  value.

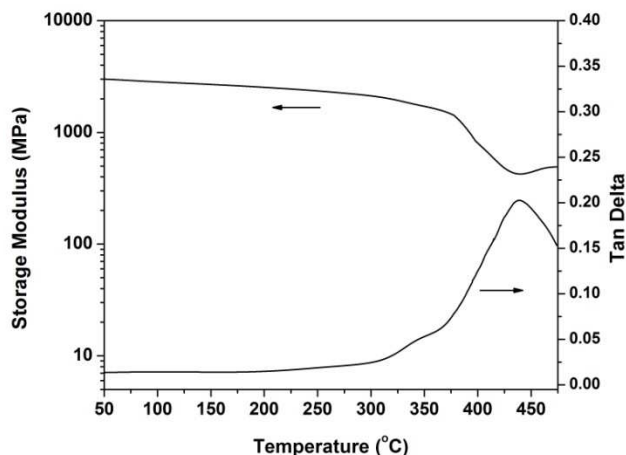


Figure 3. Temperature dependence curves of storage modulus and  $\tan \delta$  for poly(*t*-BF-f)

The thermal stability of poly(*t*-BF-f) was investigated by TGA under nitrogen atmosphere (Figure S5). The decomposition temperatures corresponding to 5% and 10% weight loss and char yield at 800 °C are 408, 466 °C and 64.3%, respectively, which are extremely higher than those of traditional side chain type fluorene-based polybenzoxazines, and slightly higher than those of difunctional furan containing fluorene-based and other multifunctional polybenzoxazines.<sup>14, 20</sup> This can be ascribed to its higher crosslinking density for poly(*t*-BF-f) as mentioned above.

## Conclusions

In this study, a novel furan-containing tetrafunctional fluorene-based benzoxazine with bisphenol- and diamine-type oxazine rings in a single-molecule structure was successfully prepared by the combination of three-step synthesis and classical one-step synthesis strategy. The chemical structure, polymerization behaviour and rheological property of *t*-BF-f are investigated. These results indicate that the processability of *t*-BF-f is better than that of difunctional furan-containing fluorene-based benzoxazine. Moreover, the thermal properties of its thermosets are also studied. Poly(*t*-BF-f) exhibits extremely higher  $T_g$  value (440 °C) and much better thermal stability than that of traditional difunctional and multifunctional polybenzoxazines due to much more cross-linked sites.

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## Notes and references

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