Chapter 4

Design and Synthesis of Bio-Based Benzoxazines

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.76104

Abstract

Polybenzoxazine (PBz) resins are a new type of high-performance synthetic resins that are attractive alternatives to traditional resins. Their properties include near-zero shrinkage upon polymerization, fast evolution of mechanical properties with the conversion, glass transition temperatures much higher than curing temperatures, low water absorption, and excellent dielectrical and mechanical properties. The development of polybenzoxazines has always been linked to petro-based feedstocks, but for the last 5 years, the number of studies related to bio-based benzoxazines is exploding as a consequence of the versatility of the design of the chemical structure of their monomers. Benzoxazine (Bz) monomers are subjected to cationic ring-opening polymerization (ROP), activated by a thermal treatment in the range of 160–250°C. In addition, Bz synthesis promotes the use of naturally occurring phenolic compounds instead of petroleum-based ones to develop high-performance materials from renewable resources and to fit to REACH restrictions. For this purpose, vanillin, eugenol, and cardanol are examples of bio-phenols bridged with several kinds of aromatic and aliphatic diamines. In this chapter, the synthesis and the properties of di-functional benzoxazine monomers prepared from naturally occurring phenolic compounds are reviewed. Symmetric and asymmetric monomers will be detailed. The last part of the chapter is dedicated to the use of bio-phenols to functionalize polymers and to provide benzoxazine functional groups.

Keywords: benzoxazine, bio-based, cardanol, vanillin, phloretic acid

1. Introduction

Traditional thermosets resins are well known for their high-performance properties [1]. However, these multicomponent thermosets can exhibit shortcomings such as high brittleness, as well as the formation of by-products during curing. They are bi-component materials

and their short shelf life prevents any long-time storage [2, 3]. Besides, the raw materials used for the production of the resins are today largely petroleum derived and are increasingly subject to European regulation on registration, evaluation, authorisation and restriction of chemicals (REACH) restrictions. The current concern about the use of petroleum-based materials along with new European restrictions has encouraged researchers to develop sustainable alternatives. Among them, benzoxazine are mono-component resins that have recently emerged as a new class of thermosets and are under continuous development [4].

Polybenzoxazines (PBz) have a wide range of properties to be tailored to a wide range of applications [5]. It makes them attractive alternatives to current applications. In addition to properties similar to phenolic or epoxy resins, PBz have unique features compared to other commodity polymers. They include near-zero shrinkage upon polymerization [6], fast evolution of mechanical properties with the conversion [7], one of the highest char yield among processable resins [8], glass transition temperatures much higher than curing temperatures [8], low water absorption [9], and excellent dielectrical and mechanical properties. Strong acid catalysts are not required for their curing [10]. PBz have similar and even lower costs than epoxy and bismaleimides resins [4]. Due to these outstanding properties and their intrinsically rich molecular design flexibility allowing good compatibility with other active structures, PBz have been promoted, over epoxy and traditional phenolic resins, as better candidates for the application of corrosion protection [11–15]. Indeed, their chemical structure can be easily tailored to meet the requirements of various conditions. Nevertheless, the development of polybenzoxazines has always been linked to petro-based feedstocks while the materials synthesized from petroleum derivatives are becoming more and more a concern for the environment and their use in the industry is thus strongly impeded. In consequence, for the last 5 years, the number of studies related to bio-based benzoxazines is exploding as a consequence of the versatility of the design of the chemical structure of their monomers [16]. Some applications of bio-based polybenzoxazine anticorrosive coatings have already been reported, confirming the great interest in the development of new bio-based PBz with promising physical and mechanical properties for industrial applications [17].

In the following paragraphs, we have chosen to only discuss difunctional benzoxazine monomers as they are more suitable for the elaboration of high-performance materials than monofunctional ones. However, more details can be obtained from the reading of the two following books dedicated to benzoxazine science: Handbook of Benzoxazine Resins [18] and Advanced and Emerging Polybenzoxazine Science and Technology [19].

2. Synthesis and polymerization of benzoxazine

2.1. Synthesis of benzoxazine monomers

Benzoxazine (Bz) resins, typically 1,3-benzoxazines, can be synthesized through a Mannich-like condensation of phenolic derivatives, formaldehyde, and primary amines, followed by a ring-closure process on the phenolic derivative (**Figure 1**) [4].

The general chemical structure of the different kind of benzoxazine monomers is depicted on **Figure 2**. This scheme highlights the great versatility in the design of benzoxazine monomers, gathered in different classes depending on their functionality.

First, there are mono-benzoxazine monomers (m-Bz) which are monomers composed of a single benzoxazine group (**Figure 2a**), in opposition to di-benzoxazine monomers (di-Bz), composed of at least two benzoxazine groups. Symmetric di-Bz monomers can be prepared either from a diphenol (class A, **Figure 2b**) or a diamine (class B, **Figure 2b**). Asymmetric di-Bz can also be obtained (**Figure 2d**) [10]. Finally, multifunctional amines or phenolic derivatives can be used to synthesize polymers bearing multiple benzoxazine groups. Di-phenolic compounds and diamines can also be combined to yield a linear polymer having benzoxazine rings in the main chain. These two last categories are gathered in class C (**Figure 2e**) [4].

Depending on the reagents, temperature, time, solvent, and synthetic procedure, the synthesis of the Bz monomer yields from 70 to 90%. The synthesis can be carried out with or without solvent [20]. This approach is feasible when the mixture of the reactants is liquid or in the molten state at working temperature [21].

2.2. Benzoxazine polymerization

Benzoxazine monomers are subjected to cationic ring-opening polymerization (ROP), activated by a thermal treatment in the range of 160–250°C (**Figure 3**) [20]. The ROP takes place upon heating due to the small amount of impurities generally found in the monomers, such as phenolic raw materials or benzoxazine oligomers. The polymerization is then auto-catalyzed by the formation of phenolic compounds [20].

Mono-functional Bz commonly leads upon polymerization to a linear and low-molecular-weight polymer from few hundreds to some thousands g/mol [22]. Nonetheless, if the aromatic ring is reactive enough, *that is* with available *para* positions for instance, a mono-functional Bz can lead to a cross-linked polymer.

Systematically difunctional or polyfunctional benzoxazine monomers lead to cross-linked structures due to their higher functionality [20]. Thus, difunctional Bz monomers are preferred for the elaboration of high-performance PBz materials.

Although the polymerization of benzoxazine monomers is thermally activated and auto-catalyzed, it requires high temperatures and relatively long reaction time for the complete polymerization. As a result, the use of some initiators or catalysts to accelerate the polymerization

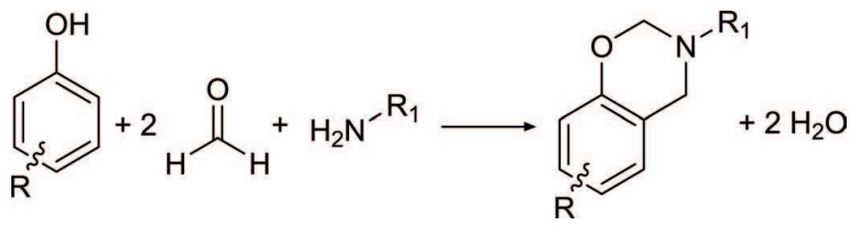


Figure 1. Synthesis of benzoxazine monomer.

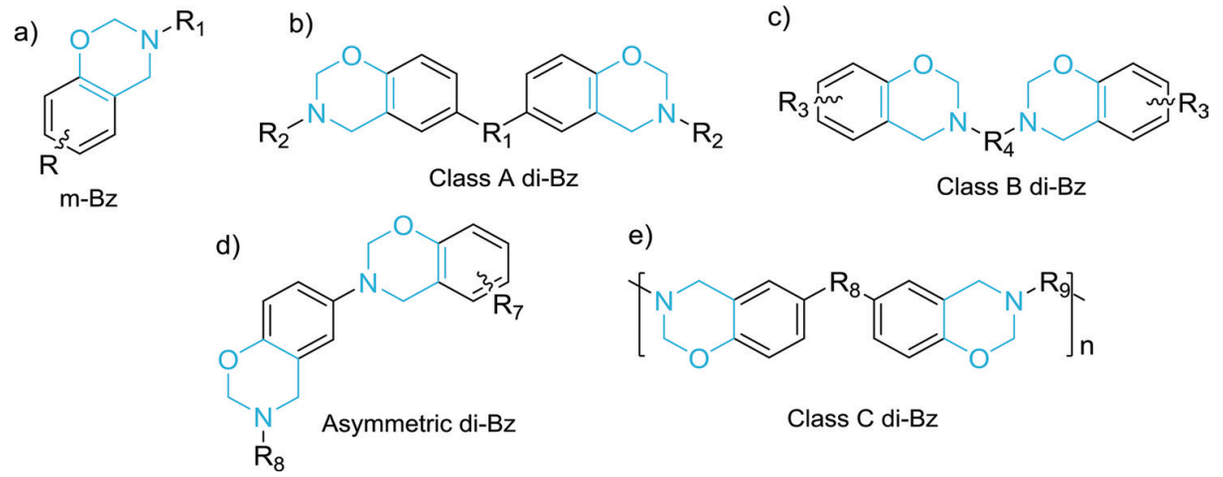


Figure 2. Schematic representation of benzoxazine monomers. Blue labelled rings in the structures correspond to the benzoxazine ring.

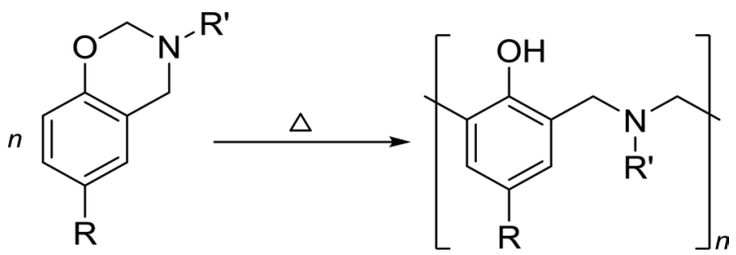


Figure 3. Ring-opening polymerization of benzoxazines.

or to trigger it to lower temperatures is investigated [23]. Most of effective catalysts reported are acidic catalysts, as ROP is a cationic process. Wang et al. [24] studied the use of acidic catalyst for reducing the curing temperature of bisphenol A-aniline–based Bz monomers (BA-a). The polymerization of (BA-a) monomers with 5 mol % of several catalysts was carried out at room temperature during 20 h. The thermal properties of the Bz monomers cured in the presence of Lewis acids such as PCl_5, PCl_3, $POCl_3$, and $TiCl_4$ showed glass transition temperature (Tg) higher than 200°C.

Various phenolic compounds derived from the opening of the oxazine ring or benzoxazine oligomers catalyze benzoxazine ring-opening polymerization reactions, resulting in the autocatalyzed nature of benzoxazine polymerization. In addition, the presence of phenolic structures with free *ortho* positions has a catalytic effect on the curing reaction. Reaction induction time is then decreased, while the reaction rate is enhanced [25]. The benzoxazine polymerization can also be catalyzed by the use of strong acids and/or carboxylic acids. In summary, a broad variety of catalysts may be used for the ring-opening polymerization of Bz monomers at moderate temperature.

Small amount of monocarboxylic monomer induced a reduction of about 20–30°C of the polymerization temperature. When comparing the Tg of the PBz materials, it could be observed that materials obtained from carboxylic-containing Bz monomers tend to have higher Tgs. These results were most probably due to higher cross-linking due to hydrogen bonding with increasing content of carboxylic acid functions.

Specific functional groups have a strong impact on the thermal ROP activation as well as on the mechanical properties of the resultant PBz. In addition, class B Bz monomers promote the use of naturally occurring phenolic compounds instead of petroleum-based ones to develop high-performance materials from renewable resources and to fit to REACH restrictions. For this purpose, vanillin [26], eugenol [27, 28], and cardanol [29–31] have been bridged with several kinds of aromatic and aliphatic diamines. This is discussed in the following part.

3. Bio-based symmetric benzoxazines

3.1. From cardanol

Growing interest has arisen toward the synthesis of Bz monomers stemming from cardanol. Indeed, the particular chemical structure of cardanol appears as a clear asset for the synthesis of PBz materials. Cardanol displays a similar reactivity as phenol through the presence of the hydroxyl group. Furthermore, the long alkyl chain in *meta* position imparts hydrophobicity and flexibility, through internal plasticization of the alkyl chain, to the usually brittle PBz materials. Moreover, the *ortho* and *para* positions of cardanol are available for the synthesis of Bz monomers and their polymerization, respectively.

The chemical structures as well as the thermal properties of cardanol-based di-Bz monomers and their corresponding materials are resumed in **Table 1**.

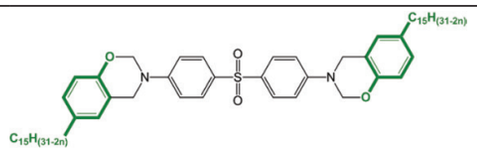
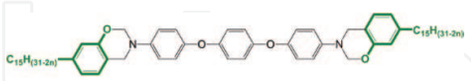
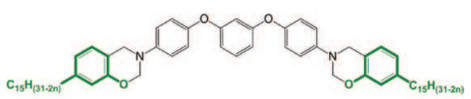
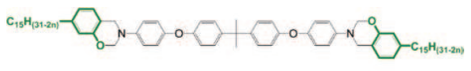
	Bz monomer	T_m (°C)	T_p (°C)	$T_{5\%}$ (°C)	Ref.
(1)	 **Cardanol**/4,4′-diamino diphenyl sulfone (dds)	—	251	299	[32] [33]
(2)	 **Cardanol**/ (4-(4-aminophenoxy)phenyl)ether (44 appe)	114	233	348	[32] [33]
(3)	 **Cardanol**/bis-(3-(4-aminophenoxy)phenyl)ether (34 appe)	70	267	354	[32] [33]
(4)	 **Cardanol**/2,2-bis(4-(4-aminophenoxy)phenyl)propane (appp)	—	263	323	[32] [33]

Table 1. Thermal properties of cardanol-based Bz monomers, synthetized from diamines, and $T_{5\%}$ of their corresponding PBz materials.

Almost all the reported cardanol-based Bz monomers synthesized with short amines did not display a melting endotherm. This phenomenon could be attributed to the steric hindrance generated by the C15 alkyl side chain of cardanol that prevents crystallization. However, it can be noticed that high melting temperatures were observed for cardanol-based di-Bz monomers with rigid aromatic diamine as bridging groups, such as bis-(3-(4-aminophenoxy)phenyl)ether or (4-(4-aminophenoxy)phenyl)ether (Tm = 70 and 114°C, respectively) (**Table 1**, lines 2 and 3).

It is noteworthy the thermo-mechanical properties of these PBz materials were almost never characterized by DMA analysis, as it is very difficult to obtain self-supported materials due to the steric hindrance of the alkyl side chain, yielding low-molecular-weight polymers. Consequently, cardanol-based Bz monomers displayed wide processing windows owing to their low melting temperatures due to the steric hindrance brought by the C15 alkyl chain. However, the low cross-linking density and Tg of the corresponding PBz materials, as well as the high polymerization temperatures, are drawbacks for the elaboration of high-performance thermosets and emphasize the use of cardanol-based di-Bz as processing aid (*i.e.,* reactive diluent) for other benzoxazines [34].

3.2. From vanillin

Vanillin is a phenolic compound with a *para* formyl group and *ortho* methoxy group, issued from vanilla seedpod. Vanillin can also be obtained industrially from the processing of lignin [35, 36]. Its use as a precursor for the synthesis of bio-based Bz monomers was recently studied [37].

The formyl group contained in the vanillin compound is of great interest for the synthesis of bio-based Bz monomers. Indeed, with the appropriate stoichiometric amount of reagents and through a convenient order of their introduction and reaction, the aldehyde function is not consumed during the synthesis. This function is thus considered as an additional reactive group on the Bz monomer, able to further react with other chemical compounds or to increase the material cross-linking density.

The chemical structures as well as the thermal properties of vanillin-based di-Bz monomers and their corresponding materials, reported in the literature, are summarized in **Table 2**.

It has been shown that the presence of the aldehyde group on vanillin has an immediate effect on the thermal properties of the Bz monomer. Indeed, the presence of this group induces the formation of inter and intramolecular H bonds. The effect of inter and intramolecular H bonding is further highlighted by the high melting temperatures of vanillin-based di-Bz monomers. Indeed, the melting temperatures of the monomers reported in **Table 2** were not found to be lower than 145°C (**Table 2**, line 4), reaching even 229°C for the di-Bz with 4, 4'-diamino diphenyl sulfone (dds) as diamine (**Table 2**, line 2). These high melting temperatures, really close to the polymerization temperatures are impeding the processing of these monomers (melting and shaping). Nevertheless, vanillin-based Bz monomers led remarkably to cross-linked materials in spite of substituted phenolic *ortho* and *para* positions, impeding the polymerization. However, it was shown that the additional cross-linking reactions, due to the presence of an aldehyde group within a Bz monomer, occur mainly at the *ortho* position of the phenolic compound [39].

As the vanillin *ortho* position is blocked by a methoxy group, it can be assumed that the additional cross-linking of vanillin-based Bz monomers is mainly caused by the decarboxylation

of the formyl group (**Figure 4**). Furthermore, some residual formyl groups, which did not undergo decarboxylation, are forming intermolecular H bonding, further increasing the PBz cross-linking density. Finally, the presence of the residual formyl groups is catalyzing the Bz monomers ROP [38, 39].

In consequence, due to the presence of the aldehyde functions and thus to the formation of inter- and intramolecular H bonds, vanillin-based materials were shown to display very high Tgs. Indeed, vanillin-based di-Bz monomers resulted in PBz networks with Tg values reaching 255°C (dds, **Table 2**, line 2). Nevertheless, di-vanillin Bz monomers are suffering from an evident drawback: their short processing windows. Indeed, melting temperatures of di-vanillin Bz monomers are too close to their polymerization temperatures, hindering their processing (molding and shaping) [38].

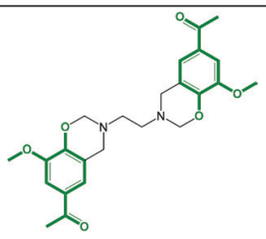
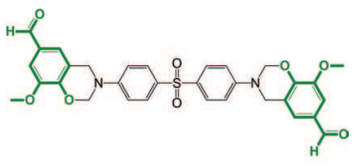
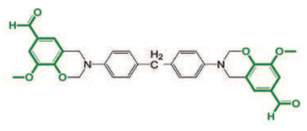
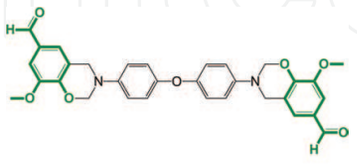
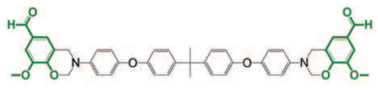
	Bz monomer	T_m (°C)	T_p (°C)	T_g (°C)	$T_{5\%}$ (°C)	Ref.
(1)	 Vanillin/Ethylene diamine	205	213	—	283	[38]
(2)	 Vanillin/4,4′-diamino diphenyl sulfone (dds)	229	277	255	339	[38]
(3)	 Vanillin/N,N diaminodiphenylmethane (ddm)	177	234	231	352	[38]
(4)	 Vanillin/ (4-aminophenyl)ether (dde)	145	234	227	322	[38]
(5)	 Vanillin/2,2-bis(4-(4-aminophenoxy)naphthalene (ndpa)	—	228	202	488	[38]

Table 2. Thermal properties of vanillin-based Bz monomers, synthetized from diamines, and T_g and $T_{5\%}$ of their corresponding PBz materials.

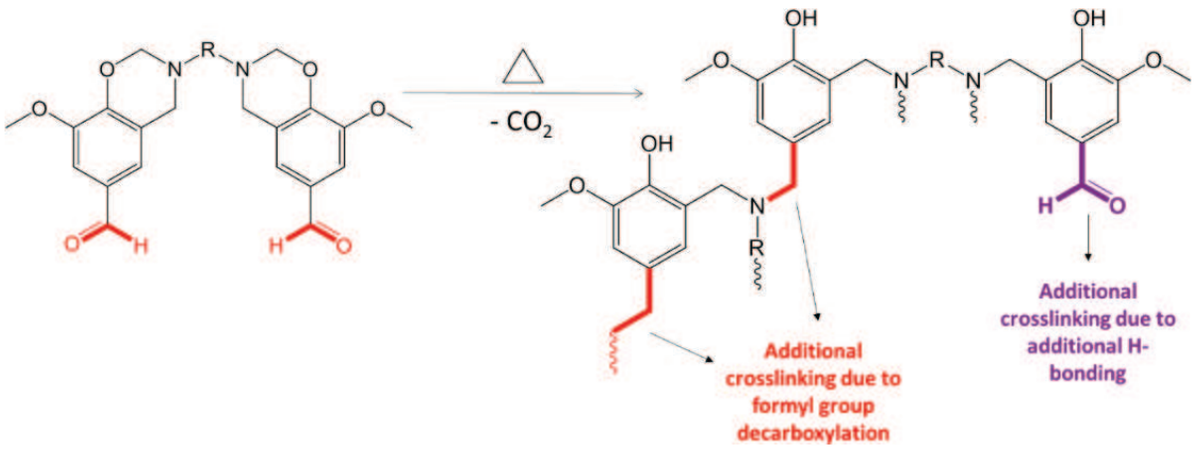


Figure 4. Cross-linking of vanillin-based di-Bz monomers [38].

3.3. From eugenol

Eugenol, through its availability and low cost, has also attracted attention for the synthesis of bio-based Bz monomers. Eugenol is the main component (72–90%wt) of the essential oil obtained from cloves. The chemical structure of eugenol is a disubstituted phenolic compound by a methoxy and allyl group at *ortho* and *para* positions, respectively. Consequently, due to blocked *ortho* and *para* positions, only the low reactive *meta* positions are available, impeding the formation of a cross-linked eugenol-based network (**Figure 5**).

Similar to di-Bz monomers from other naturally occurring phenolic compounds, di-Bz monomers from eugenol and various aromatic diamines were all displaying fairly high Tm > 90°C, hampering also the elaboration of eugenol-based PBz materials [40] (**Table 3**).

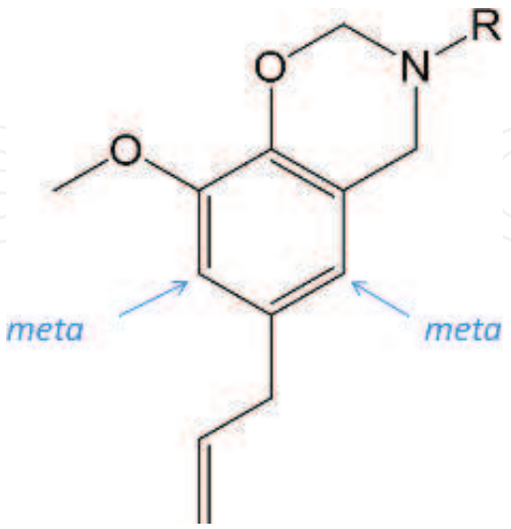


Figure 5. Available positions for ring opening polymerization of eugenol-based Bz monomer.

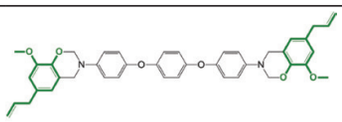
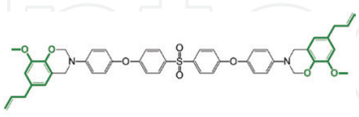
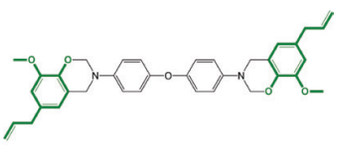
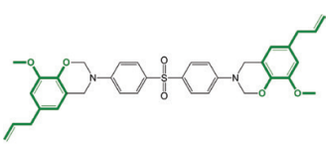
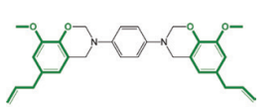
	Bz monomer	T_m (°C)	T_p (°C)	$T_{5\%}$ (°C)	Ref.
(1)	 **Eugenol**/ (4-(4-aminophenoxy)phenyl)ether (44appe)	90	250	260	[40]
(2)	 **Eugenol**/1,4(bis(4′-aminophenoxy)phenyl sulfone) (14apps)	100	250	275	[40]
(3)	 **Eugenol**/ (4-aminophenyl)ether (dde)	140	225	240	[40]
(4)	 **Eugenol**/4,4′-diamino diphenyl sulfone (dds)	130	255	295	[40]
(5)	 **Eugenol**/1,4-phenylene diamine	150	250	225	[41]

Table 3. Thermal properties of eugenol-based Bz monomers, synthetized from mono-functional amines or diamines, and $T_{5\%}$ of their corresponding PBz materials.

3.4. From other bio-phenols

Many other bio-phenols can be used for the design of benzoxazine monomers. Examples were reported with lignin-derivatives like coumaric acid, ferulic acid, phloretic acid [42], as well as coumarin [43], or urushiol [44, 45]. In most of the cases, only mono-benzoxazine has been prepared as the preparation of the monomers is hampered by substitution of the phenolic ring.

In conclusion, the use of naturally occurring phenolic compounds for the synthesis of Bz monomers allows the lowering of the carbon footprint and enables the introduction of some additional and/or functional groups within the Bz monomers. Nevertheless, most of the Bz monomers synthesized from bio-based phenolic compounds are suffering from several disadvantages, either for the synthesis of the Bz monomer, or the elaboration or the properties of the final materials.

An original and appropriate approach of adding different functionalities on Bz monomers consists of developing asymmetric di-Bz monomers from bio-phenols, using for example a diamine as bridging group between two phenolic derivatives exhibiting each a particular functionality. The different synthesis strategies developed to access asymmetric di-Bz monomers are presented in the following paragraphs.

4. Bio-based asymmetric benzoxazines

It is well known that additional functionalities on Bz monomers strongly influence the properties of the benzoxazine monomers and their corresponding thermoset materials [37, 40, 46]. The use of bio-based phenolic compounds naturally bearing various functionalities is thus considered as a clear asset to the synthesis of benzoxazine monomers with tailored properties. However, the presence of additional functional groups on Bz monomers may also impact their processability or polymerization. For instance, the position of the functional group on the phenolic compound, possible induced steric hindrance or short processing window due to high melting temperature of the monomer, may strongly hamper the processing and polymerization of the Bz monomers and thus affect the overall performance of the PBz materials. In consequence, drawbacks of some bio-based phenolic compounds could be offset by the assets of others to yield Bz monomers with large processing windows and corresponding high-performance PBz materials. To overcome such difficulties frequently encountered with Bz monomers synthetized with bio-based phenolics, some research groups reported the synthesis of asymmetric Bz monomers.

4.1. Eugenol/phenol asymmetric Bz

Among the available bio-based phenolic compounds, eugenol represents a high potential for the synthesis of Bz monomers. Nonetheless, the two main Bz polymerization sites of eugenol are hindered with methoxy and allyl groups in *ortho* and *para* positions, respectively. The elaboration of a highly cross-linked network is thus clearly hampered. Consequently, Dumas et al. proposed the preparation of a partially bio-based mixture of symmetric and asymmetric Bz monomers synthetized from phenol, eugenol, and 1,4-phenylenediamine, with (phenol: eugenol) ratio ranging from (1, 1) to (1.8, 0.2) [27, 28]. Three different chemical structures of Bz monomers, depicted in **Figure 6**, were found to constitute the mixture at the end of the reaction.

The synthesis yielded in two symmetric Bz monomers, a di-eugenol monomer and a di-phenol monomer, and one asymmetric Bz monomer showing both eugenol and phenolic moieties. The introduction of the synthesis of the asymmetric Bz monomer induced additional polymerization sites on the phenol moiety, increasing the cross-link density of the resulting material. Furthermore, the introduction of the eugenol part within the molecule allowed a solvent-free synthesis. Finally, the Tg increased from 120 to 220°C with the increasing (phenol: eugenol) ratio.

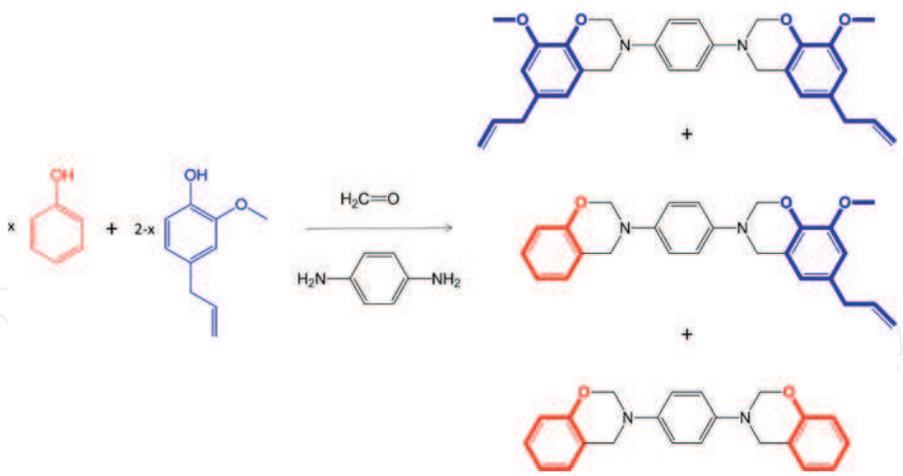


Figure 6. Synthesis of blends of di-eugenol, di-cardanol and asymmetric eugenol/cardanol di Bz monomers.

4.2. Vanillin/cardanol asymmetric Bz

Vanillin is another interesting and promising bio-based compound for the synthesis of Bz monomers. Due to the presence of the aldehyde function and thus due to the formation of inter- and intramolecular H bonds, vanillin-based Bz materials display high Tg. However, symmetric di-Bz monomer synthetized from vanillin and ethylenediamine (EDA) suffers from a major drawback: its melting temperature (Tm = 218°C) is too close to its polymerization temperature (Tp = 225°C) making its processing (molding and shaping) very challenging [47].

Cardanol, a bio-phenol bearing a C15 alkyl chain in *meta* position able to provide better processability and flexibility to the material through internal plasticization is relevant for the synthesis of usually brittle Bz materials. Cardanol di-Bz is of great interest due to low melting temperatures. The corresponding PBz material elaboration is nevertheless impeded by the steric hindrance of the alkyl side chain, resulting in long gelation time, low polymerization enthalpy value in DSC analysis, and a poorly cross-linked polymer material which creeps above Tg.

To tackle these highlighted issues, Puchot et al. proposed an efficient strategy to lower the melting temperature of vanillin-based Bz monomers in order to enable their processing [48]. Cardanol was shown to provide flexibility to the resulting materials through plasticizing effect of the C15 alkyl chain and to result in a Bz monomer with low melting temperature [33, 49]. More importantly, the low reactivity of cardanol offers the possibility to control the synthesis of a mono-cardanol Bz with a free primary amine moiety that can be further coupled with another bio-based phenol like vanillin. The authors aimed at synthetizing an asymmetric bio-phenol-based di-Bz monomer by combining cardanol and vanillin via a two-step synthesis pathway with ethylene diamine including a controlled mono-substitution of a cardanol-based Bz, followed by a coupling with vanillin (**Figure 7**).

Such combination resulted in a Bz monomer with low melting temperature (Tm = 101°C), with a few impact on the activation temperature (Tp = 227°C) increasing the processing window of these bio-based thermosets (ΔTproc = 126°C, compared to ΔTproc = 7°C for di-vanillin Bz).

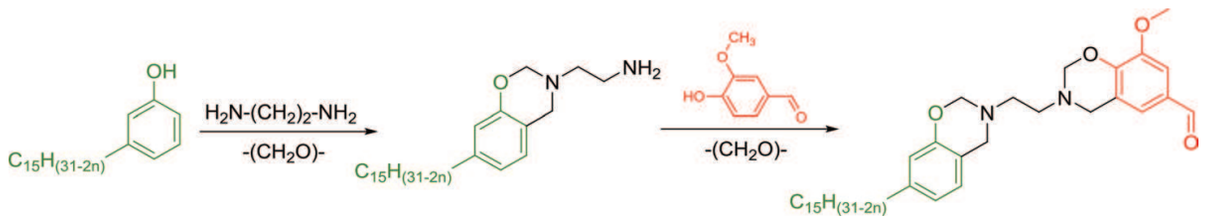


Figure 7. Representative scheme of the synthesis of vanillin/cardanol asymmetric Bz.

Furthermore, a second drawback of the di-vanillin Bz monomers was their thermal degradation occurring simultaneously to their melting and even before their polymerization ($T_{5\%}$ = 203°C). In the case of the asymmetric Vani-Card Bz monomer, no problem of thermal degradation of the monomer is further encounter due to the presence of the cardanol moiety. Indeed, the thermal degradation of the Vani-Card monomer occurred at higher temperature than melting and polymerization ($T_{5\%}$ = 280°C).

The asymmetric Bz monomer enabled thus, through a processing point of view, an easy elaboration of a cardanol- and vanillin-based PBz material. Furthermore, the synthesis of the asymmetric Vani-Card monomer was also shown to strongly influence the reactivity of the monomer. Indeed, the di-cardanol Bz monomer displayed a long gelation time (Tgel = [38, 40] min at 190°C) in comparison to a classical di-phenol Bz monomer (Tgel = [5, 6] min at 190°C). In the case of Vani-Card Bz, an interesting moderate gelation time of 8–9 min was reported.

Moreover, the characterizations of the asymmetric Vani-Card PBz material highlighted the obtaining of a thermoset material with good thermo-mechanical properties. Indeed, a Tg of 129°C and a storage modulus in the glassy state of 700 MPa were reported, indicating that Vani-Card PBz material displayed very comparable thermal and mechanical properties to other known polybenzoxazines particularly those partially or fully bio-based.

Finally, the presence of the cardanol moiety was shown to strongly influence the thermal stability of the PBz material. Indeed, a high thermal degradation onset temperature was recorded for Vani-Card PBz material ($T_{5\%}$ = 373°C) compared to classical di-phenol PBz material ($T_{5\%}$ = 273°C).

This versatile approach is a powerful tool to access a wide range of bio-based asymmetric benzoxazines given the wide number of bio-phenols available. It paves the way toward easily processable high performance bio-based benzoxazines. This strategy could, for example, be applied to further improve the processing of bio-based di-Bz monomers.

5. End-chain functionalization polymers

Beyond the elaboration of symmetric and asymmetric benzoxazine monomers, a recent challenge is to add benzoxazine functionalities to polymers, benefiting then from the versatile design of Bz monomers. The resultant materials possess properties specific both to benzoxazine, such as a high cross-linking density and high temperature stability, and to the backbone polymer, like processability and flexibility. End-chain, [50] main-chain [51–53], as well as side-chain [54] benzoxazine polymers have been reported. Therefore, Bz monomers have been anchored onto a wide range of

(bio)polymers like polybutadiene [55], polystyrene [56], polypropylene oxide [57], polyvinylchloride [58], cellulose [54], poly(*ε*-caprolactone) [59], and even onto macromonomers like lignin [60]. In almost all cases, harmful phenol has been used as a reactant to form the oxazine ring.

Naturally occurring phenolic compounds can also be used to functionalize the end-chain of existing polymers toward benzoxazine ring formation. Phloretic acid (PA) is an interesting bio-based compound for this purpose due to the presence of a propionic acid on the *para* position suitable for esterification [61]. Furthermore, *ortho* positions of PA are not substituted, an ideal asset for the design of benzoxazine monomers and for their polymerization. Trejo-Machin et al. proposed a sustainable strategy to functionalize hydroxyls (−OH)-bearing molecules. Ethylene glycol, and two polyethylene glycol with molar masses about 400 $g \cdot mol^{-1}$ (PEG400) and 2000 $g \cdot mol^{-1}$ (PEG2000), were reacted by esterification with PA. In the second step, these phenolic groups were reacted with furfurylamine to form benzoxazine end-capped molecules. The two-step synthesis of end-chain Bz monomers did not require neither solvent nor purification and led to a set of materials almost 100% bio-based (**Figure 8**) [62].

Thermal behavior and stability of Bz end-chain monomers were characterized by DSC and TGA, demonstrating the elaboration of thermoset materials. Moreover, DSC analyses showed on each thermogram an exothermic peak assigned to the thermal-activated ring-opening of the Bz monomers, with an onset ranging from 165 to 200°C. Rheological analyses were also carried out to evaluate the polymerization reactivity of the Bz monomers. The gelation time at 180°C was found to be 2, 3, and 28 min for benzoxazine prepared with ethylene glycol, PEG400, and PEG2000, respectively. The mechanical relaxation temperatures were decreasing from 112 to 27°C and −45°C, with increasing backbone chain length of the starting molecules, respectively. Finally, the thermal stability of the three PBz materials was studied by TGA analyses. Each of the synthetized PBz material exhibited much higher thermal stability as well as marked improvement in char yield over the origin polymers.

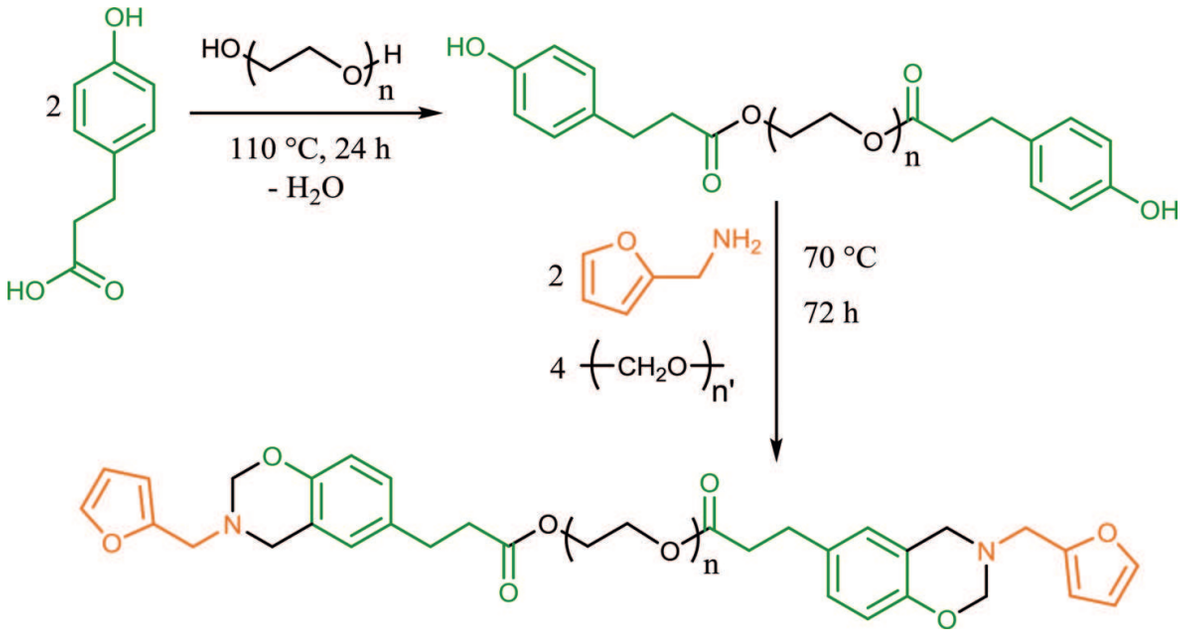


Figure 8. Two-step synthesis of end-chain benzoxazine monomers; n = 1, 9, and 45 and n′ = 8–100.

In conclusion, this innovative approach proved the suitability of phloretic acid to act as a renewable building block to functionalize hydroxyl-bearing molecules and polymers toward the synthesis of end-chain benzoxazine polymers.

6. Conclusions

The use of naturally occurring phenolic compounds for the synthesis of Bz monomers allows the lowering of the carbon footprint and enables the introduction of some additional and/or functional groups within the Bz monomers which can highly benefit the industrial applications of Bz where additional functional groups may be needed in order to enhance their properties. Alike petroleum-based Bz monomers, the nature of the diamine bridging group strongly affects the bio-based Bz monomers properties and their polymers. Short aliphatic diamine bridging groups, such as ethylene diamine, should as well be preferred for the synthesis of bio-based Bz monomers. Indeed, the use of short aliphatic diamines promotes moderate processing windows, while resulting in high cross-linked PBz materials with good thermal and mechanical properties.

Nevertheless, most of the Bz monomers synthetized from bio-based phenolic compounds are suffering from several disadvantages, either for the synthesis of the Bz monomer or for the elaboration and/or for the properties of the final materials. Naturally occurring phenolic compounds such as lignin-derivatives or coumarin compounds lead to highly cross-linked PBz materials with good thermo-mechanical properties, whereas their processing is hindered by narrow processing windows. On the contrary, bio-based Bz monomers synthetized from phenolic compounds like cardanol, urushiol, or eugenol display large processing windows but low cross-linking density and low Tg. As the overall performance of PBz is strongly affected by oxazine ring substitutions, drawbacks of some bio-based phenolic compounds could be offset by the assets of the others to yield Bz monomers with large processing windows and corresponding high-performance PBz materials.

Conflict of interest

There is no conflict of interest to declare.

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