



HAL
open science

Formaldehyde-Free Polybenzoxazines for High Performance Thermosets

Romain Tavernier, Lérays Granado, Gabriel Foyer, Ghislain David, Sylvain Caillol

► **To cite this version:**

Romain Tavernier, Lérays Granado, Gabriel Foyer, Ghislain David, Sylvain Caillol. Formaldehyde-Free Polybenzoxazines for High Performance Thermosets. *Macromolecules*, 2020, 53 (7), pp.2557-2567. 10.1021/acs.macromol.0c00192 . hal-02546388

HAL Id: hal-02546388

<https://hal.science/hal-02546388>

Submitted on 7 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

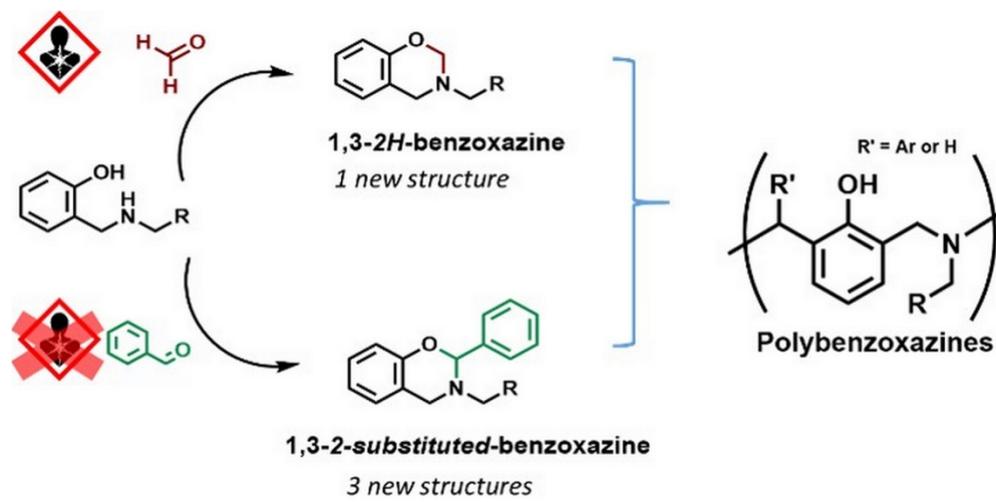
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Formaldehyde-free polybenzoxazines for high performance thermosets

Journal:	<i>Macromolecules</i>
Manuscript ID	ma-2020-00192c.R1
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Tavernier, Romain; Ecole Nationale Supérieure de Chimie de Montpellier, Granado, Lerys; ICGM, Foyer, Gabriel; ArianeGroup David, Ghislain; Ecole Nationale Supérieure de Chimie de Montpellier, Caillol, Sylvain; Institut Charles Gerhardt de Montpellier

SCHOLARONE™
Manuscripts



148x76mm (600 x 600 DPI)

Formaldehyde-free polybenzoxazines for high performance thermosets

Romain Tavernier^a, Lérys Granado^a, Gabriel Foyer^b, Ghislain David^a, Sylvain Caillol^{a,*}

^aICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

^bArianeGroup, Rue de Touban, 33185 Le Haillan, France

*corresponding author : Sylvain Caillol, Institut Charles Gerhardt, 240 Av Prof Emile Jeanbrau, 34296

Montpellier Cedex 5, sylvain.caillol@enscm.fr

Abstract

We report the synthesis and ring-opening polymerization of new formaldehyde-free benzoxazines. The polybenzoxazines obtained displayed high thermal stability and high char yields. Data from literature combined with our analyses by differential scanning calorimetry and thermogravimetric analyses gave deeper understanding about the use of aromatic aldehydes instead of formaldehyde for the generation of polybenzoxazines. Using pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS) at different temperatures, we provided qualitative data to propose some polymerization and degradation mechanisms associated with these new structures. A dialdehyde was also used for the first time in order to obtain difunctional monomers, instead of using diamines or bisphenols. Interestingly, we demonstrated that formaldehyde, which is a CMR (Carcinogenic, Mutagenic and/or Reprotoxic) substance, could be avoided for the synthesis of polybenzoxazines without any loss of thermal performance. Finally, some interesting structure-properties relationships are herein discussed. Particularly, the use of benzyl amines, rather than aromatic amines, was found to significantly increase the char yields.

Introduction

During the last 30 years, research on polybenzoxazine has been growing fast, at the forefront of the innovations in phenolic thermosets. Compared to the century old phenol-formaldehyde, benzoxazine chemistry presents several advantages among them we find condensation-free cross-linking, a near zero volumetric shrinkage, high glass transition temperature, high degradation temperatures and high char yields.¹⁻³ In contrast, their industrialization suffers from the inconvenient crystallinity of the monomers/prepolymers and the requirement of elevated temperatures to achieve the cross-linking of the thermoset during curing. It is believed that these issues being solved, polybenzoxazines can find many applications in cutting-edge technologies, such as chelation agents for metal recovery in aqueous media,⁴ high performance composites,⁵ spatial radiation insulating shields,⁶ porous materials for CO₂ capture,⁷ anti-corrosion coatings⁸ or even self-healing and shape-memory polymers.⁹

Since the first benzoxazine synthesis, performed by Holly and Cope,¹⁰ benzoxazine chemistry has shown high versatility. Traditionally, obtained from the condensation of formaldehyde between a phenolic moiety and a primary amine, benzoxazine synthesis is therefore compatible with a wide range of chemical functionalities. Andreu *et al.* have identified three main pathways to obtain 1,3-benzoxazines architectures,¹¹ two of them appearing to be predominant in the articles published nowadays.¹²⁻¹⁵ The one-pot method is the most practical one, used either in bulk or in solution, and developed for the most reactive amines. The 3-step method is used with less reactive amines, or to prevent the formation of oligomers by using salicylaldehyde to form an imine.^{16,17} A secondary amine is then obtained by imine reduction, forming the first part of the heterocycle. The last step

1
2 consists in the formation of the oxazine ring by reacting formaldehyde with the phenol moiety and the secondary
3 amine.
4

5 These synthetic methods were used to obtain a wide range of benzoxazine monomers, which allowed
6 researchers to find the parameters having an influence on thermal properties of polybenzoxazine networks. For
7 instance, electron-withdrawing groups on the phenol moiety have a strong effect on the ring-opening
8 temperature. High aromatic content and high crosslink densities are required to get high degradation
9 temperatures and improved char yields. For instance, Endo and Nalakathu Kolanadiyil investigated the influence
10 of the oxazine ring number in benzoxazine monomers on their thermal stabilities, evidencing that a higher
11 content of oxazine rings improves thermal stability of cured thermosets.¹⁸ However, an increase of the
12 monomers functionality leads to a decrease of the reactivity, thus requiring higher curing temperatures. The
13 design of benzoxazine monomers is therefore crucial to reach the desired thermal properties.
14
15
16

17 One of the biggest drawback of benzoxazine is the use of the harmful formaldehyde in the synthesis of
18 monomers. Formaldehyde substitution is challenging since the use of aliphatic aldehydes is detrimental to the
19 final thermal stability. So far, only two examples of formaldehyde-free 1,3-benzoxazines have been published,
20 for thermoset applications. Ohashi *et al.* were the first team to report the synthesis of two 2-substituted
21 benzoxazines using salicylaldehyde route¹⁹ namely, a monobenzoxazine based on benzaldehyde and aniline and
22 a bisbenzoxazine (one monomer with two oxazine rings) with the *p*-phenylenediamine. The authors reported
23 good thermal performances after curing, with rather high char yields (25% and 48%, respectively). More recently,
24 Pereira *et al.* reported the polymerization of two hydrogenated cardanol-based benzoxazines using
25 benzaldehyde and valeraldehyde, but the preparation of the starting phenolic compounds still required the use
26 of formaldehyde and their thermal performances were rather limited.²⁰ Overall, we found a lack in the literature
27 of alternatives to formaldehyde for synthesizing more sustainable benzoxazines with high thermal performances.
28
29
30
31

32 In response, we aim in this work at providing new formaldehyde-free benzoxazines structures using the
33 aforementioned salicylaldehyde reaction pathway. Monofunctional benzaldehyde and benzylamine are reacted
34 to produce monobenzoxazines. Moreover, difunctional terephthalaldehyde (TPA) and meta-xylylenediamine (m-
35 XDA) are employed to synthesize bisbenzoxazines. We propose herein a systematic study on the effect of the
36 aromatic aldehyde and amine, and their functionality, on the syntheses and properties, in close comparison with
37 previous literature data. We provide a qualitative analysis for the determination of polymerization mechanisms,
38 especially by analyzing the released compounds during polymerization with a gas chromatography technique.
39 Finally, we show that these new benzoxazines display very high thermal performances, showcasing one
40 important benefit of the formaldehyde substitution.
41
42
43
44

45 **Experimental Section**

46 **Materials.** Salicylaldehyde and terephthalaldehyde were purchased from TCI. Benzylamine, paraformaldehyde,
47 meta-xylylenediamine (m-XDA), sodium borohydride, and benzaldehyde were purchased from Sigma-Aldrich.
48 Anhydrous magnesium sulphate, toluene, ethyl acetate, dichloromethane, cyclohexane and methanol were
49 purchased from VWR. Deuterated chloroform was purchased from Eurisotop. All solvents and reagents were
50 used without further purification.
51
52

53 **Synthesis of salicylamines**

54
55 Synthesis of 2-((benzylamino)methyl)phenol (Scheme 1, **A** and **B**, R₁=Bz)
56
57
58
59
60

1
2 11.40 g of salicylaldehyde were dissolved in 50 mL of methanol. 10.0 g of benzylamine were added to the mixture
3 and then refluxed for 2 h. After cooling to room temperature, solvent was removed under reduced pressure.
4 Corresponding imine was isolated for characterization purpose. Reduction was then performed by dissolving
5 10.52 g of the imine in 50 mL of methanol, and 3.68 g of sodium borohydride were added in small portions, at
6 0 °C, in order to limit foaming. After complete addition of the sodium borohydride, reaction mixture was heated
7 to reflux for another 2 h. After cooling to room temperature, the reaction mixture was quenched by precipitation
8 in distilled water. The resulting viscous amine was then recovered by liquid-liquid extraction with ethyl acetate,
9 organic phase was dried over magnesium sulfate and solvent was removed under reduced pressure to afford the
10 desired product. 15.30 g of yellow oil was recovered. Yield = 77%.

11
12
13
14 HRMS (*m/z*, positive mode, [M + H]⁺): C₁₄H₁₆NO; calculated 214.1226, found 214.1236.

15
16 Synthesis of 2,2'-(((1,3-phenylenebis(methylene))bis(azanediyl))bis(methylene))diphenol (Scheme 1, **A** and **B**, R₁
17 = m-xylylene)

18
19 17.91 g of salicylaldehyde were dissolved in 50 mL of methanol. 10.03 g of m-XDA were added to the mixture
20 and then refluxed for 2 h. After cooling to room temperature, solvent was removed under reduced pressure.
21 Corresponding imine was isolated for characterization purpose. Reduction was then performed by dissolving the
22 imine in 50 mL of methanol, and 5.61 g of sodium borohydride were added in small portions, at 0 °C, in order to
23 control the foaming. After complete addition of the sodium borohydride, reaction mixture was heated to reflux
24 for another 2 h. After cooling to room temperature, the reaction mixture was quenched by precipitation in
25 distilled water. The resulting viscous amine was then recovered by liquid-liquid extraction with ethyl acetate,
26 organic phase was dried over magnesium sulfate and solvent was removed under reduced pressure to afford the
27 desired product. 24.81 g of a viscous pale-yellow oil were recovered that further crystallized as a white solid.
28 Yield = 97%.

29
30
31
32 HRMS (*m/z*, positive mode, [M + H]⁺): C₂₂H₂₅N₂O₂; calculated 349.1911, found 349.1927.

33 34 35 **Synthesis of benzoxazine monomers.**

36
37 Synthesis of 1,3-bis((2H-benzo[e][1,3]oxazin-3(4H)-yl)methyl)benzene (**Ph-mxda**) (Scheme 1, **C**, R₁= m-xylylene
38 and R₂= H)

39
40 1.03 g of 2,2'-(((1,3-phenylenebis(methylene))bis(azanediyl))bis(methylene))diphenol were dissolved in 20 mL of
41 toluene. 0.17 g of paraformaldehyde were added to the mixture, and then refluxed for 2 h with a Dean-Stark
42 apparatus. After cooling to room temperature, solvent was removed under reduced pressure. Product was
43 recovered as a transparent viscous oil. Yield > 99%.

44
45 HRMS (*m/z*, positive mode, [M + H]⁺): C₂₄H₂₅N₂O₂; calculated 373.1911, found 373.1918. NMR ¹H (CDCl₃, 7.26
46 ppm) δ = 7.38 (1H), 7.27-7.35 (m, 3H), 7.16 (t, 2H), 6.82-6.95 (m, 6H), 4.89 (s, 2H), 3.98 (s, 2H), 3.94 (s, 2H). NMR
47 ¹³C (CDCl₃, 77.16) δ = 154.26, 138.56, 129.55, 128.67, 128.16, 127.87, 127.79, 120.78, 120.11, 116.58, 82.39,
48 55.60, 49.81.

49
50
51 Synthesis of 1,3-bis((2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)methyl)benzene (**Ph-mxda[2]ba**) (Scheme 1, **C**,
52 R₁= m-xylylene and R₂= Ph)

53
54
55 10.99 g of 2,2'-(((1,3-phenylenebis(methylene))bis(azanediyl))bis(methylene))diphenol were dissolved in 100 mL
56 of toluene. 3.36 g of benzaldehyde were added to the mixture, and then refluxed for 19 h with a Dean-Stark
57

1
2 apparatus. After cooling to room temperature, solvent was removed under reduced pressure. Product was
3 precipitated in cyclohexane and centrifugated to afford 14.28 g of the product as a yellow vitreous solid. Yield =
4 86%.
5

6 HRMS (m/z , positive mode, $[M + H]^+$): $C_{36}H_{33}N_2O_2$; calculated 525.2537, found 525.2557. NMR 1H ($CDCl_3$, 7.26
7 ppm) δ = 7.65-7.68 (m, 4H), 7.37-7.41 (m, 5H), 7.30-7.34 (m, 5H), 7.21-7.24 (m, 2H), 7.05 (d, 2H), 6.90 (d, 4H),
8 6.01 (d, 2H), 3.86 (m, 8H). NMR ^{13}C ($CDCl_3$, 77.16) δ = 153.72, 153.70, 139.57, 139.24, 139.22, 139.13, 139.12,
9 139.09, 129.87, 129.12, 129.10, 18.97, 128.96, 128.91, 128.81, 128.77, 128.56, 128.53, 128.25, 128.13, 128.11,
10 128.08, 128.07, 127.97, 127.93, 127.83, 127.63, 127.60, 127.42, 126.75, 90.49, 90.46, 53.55, 53.45, 46.97, 46.91.
11
12

13 Synthesis of 3-benzyl-2-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (**Ph-ba[2]ba**) (Scheme 1, **C**, R_1 = Bz and R_2 =
14 Ph)
15

16 1.02 g of 2-((benzylamino)methyl)phenol were dissolved in 20 mL of toluene. 0.50 g of benzaldehyde were added
17 to the mixture, and then refluxed for 24 h with a Dean-Stark apparatus. After cooling to room temperature,
18 solvent was removed under reduced pressure. Product was then recrystallized from toluene, leading to 0.89 g of
19 a colorless powder. Yield = 54%.
20
21

22 HRMS (m/z , positive mode, $[M + H]^+$): $C_{21}H_{19}NO$; calculated 302.1539, found 302.1548. NMR 1H ($CDCl_3$, 7.26 ppm)
23 δ = 7.65 (d, 2H), 7.27-7.40 (m, 8H), 7.20 (m, 1H), 7.01 (d, 1H), 6.88 (d, 2H), 6.00 (s, 1H), 3.85 (m, 4H). NMR ^{13}C
24 ($CDCl_3$, 77.16) δ = 153.72, 139.21, 138.96, 128.89, 128.77, 128.53, 128.50, 128.09, 127.92, 127.85, 127.28,
25 126.75, 120.73, 119.92, 116.64, 90.53, 53.48, 46.91.
26
27

28 Synthesis of 1,4-bis(3-benzyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-2-yl)benzene (**Ph-ba[2,2']tpa**) (Scheme 1, **C**,
29 R_1 = Bz and R_2 = p-phenylene)
30

31 1.01 g of 2-((benzylamino)methyl)phenol were dissolved in 20 mL of Toluene. 315 mg of terephthalaldehyde
32 were added to the mixture, and then refluxed for 24 h with a Dean-Stark apparatus. After cooling to room
33 temperature, the product spontaneously recrystallizes as a colorless solid, and was rinsed with toluene. It was
34 then dried under reduced pressure, leading to 576 mg of a colorless powder. Yield = 46%.
35
36

37 HRMS (m/z , positive mode, $[M + H]^+$): $C_{36}H_{33}N_2O_2$; calculated 525.2537, found 525.2546. NMR 1H ($CDCl_3$, 7.26
38 ppm) δ = 7.65 (s, 1H), 7.24-7.37 (m, 10H), 7.20 (m, 2H), 7.01 (d, 2H), 6.88 (d, 2H), 5.98 (d, 2H), 3.84 (m, 8H). NMR
39 ^{13}C ($CDCl_3$, 77.16) δ = 153.66, 153.63, 139.04, 139.01, 138.89, 138.89, 128.78, 128.76, 128.74, 128.61, 128.50,
40 127.94, 127.85, 127.54, 127.29, 127.28, 126.87, 126.86, 120.75, 119.87, 119.86, 116.62, 90.42, 90.35, 53.64,
41 53.57, 46.87, 46.83.
42
43

44 Curing of benzoxazine samples

45 Between 80 and 120 mg of benzoxazine monomer is weighed in small aluminum pans, which are then inserted
46 in an oven preheated at 200 °C, for 6 hours at atmospheric pressure.
47
48

49 Measurements

50 1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 400 NMR spectrometer, in
51 $CDCl_3$ using non-deuterated residual solvent as reference.
52
53

54 High Resolution Mass Spectrometry measurements (HRMS) were performed on a Waters Synapt G2-S High
55 Resolution Mass Spectrometer equipped with an ESI (electrospray) ionization source.
56
57

1
2 Attenuated total reflectance Fourier transform infrared absorption spectroscopy (ATR-FTIR) measurements were
3 carried out with a Nicolet 6700 spectrometer from Thermo-Scientific, equipped with a
4 mercury–cadmium–tellurium detector, in the middle infrared range with a resolution of 4 cm⁻¹ and 32 scans
5 were coadded to each spectrum.
6

7
8 Differential Scanning Calorimetry (DSC) on a DSC-3 F200 Maia (Netzsch GmbH) equipped with an intracooler
9 module. The atmosphere was dry nitrogen at a flow rate of 70 mL·min⁻¹. The temperature sensor was calibrated
10 with biphenyl, indium, bismuth, and CsCl standards at 10 °C·min⁻¹. High-pressure stainless-steel pans and lids
11 (100 MPa, sealed at 3 N·cm) were used to prevent signal from volatile evaporation. Pans were weighed before
12 and after the analysis to verify that there were no leaks during the analysis. Between 8 and 12 mg of samples
13 were weighed into the pans.
14
15

16 Thermogravimetric analysis (TGA) was performed with a TGA-3 libra (Netzsch GmbH). Between 10 and 12 mg of
17 monolithic sample was weighed in platinum pans. The atmosphere was 40 mL·min⁻¹ nitrogen. The heating rate
18 was 10 °C·min⁻¹ to monitor the thermal performances of cured resins from room temperature (RT) to 900 °C.
19

20 The Py-GC/MS analytical setup consisted of an oven pyrolyzer connected to a GC/MS system. A Pyroprobe 5000
21 pyrolyzer (CDS Analytical) was used to pyrolyze the samples in a helium environment. This pyrolyzer is supplied
22 with an electrically heating platinum filament. One coil probe enables the pyrolysis of samples (less than 1 mg)
23 placed in quartz tube between two pieces of quartz wool. The sample was successively heated at 200, 300, 400,
24 500, 600 and 900 °C. Each temperature was held for 15 s before gases were drawn to the gas chromatograph for
25 5 min. The pyrolysis interface was coupled to a 450-GC gas chromatograph (Varian) by means of a transfer line
26 heated at 270 °C. In this oven the initial temperature of 70°C was held for 0.2 min, and then raised to 310 °C at
27 10 °C·min⁻¹. The column is a Varian Vf-5 ms capillary column (30 m×0.25 mm) and helium (1 mL·min⁻¹) was used
28 as the carrier gas; a split ratio was set to 1:50. The gases were introduced from the GC transfer line to the ion
29 trap analyzer of the 240-MS mass spectrometer (Varian) through the direct-coupled capillary column.
30 Identification of the products was achieved comparing the observed mass spectra to the American National
31 Institute of Standards and Technology mass spectral library.
32
33
34
35

36 Solid content was evaluated for all monomers after curing at 200 °C. For each monomer, 6 samples were weighed
37 before and after curing program, in order to determine the residual solid content. Results are displayed as a
38 mean for 6 samples with 1σ standard-deviation.
39
40

41 Insoluble fraction was determined by plunging cured samples in 10 mL of dichloromethane in sealed vials, for 48
42 h at room temperature. Samples were then dried 24 hours under vacuum and weighed in order to determine
43 the insoluble content. Results are displayed as a mean of at least 3 samples with 1σ standard deviation.
44
45

46 Nomenclature

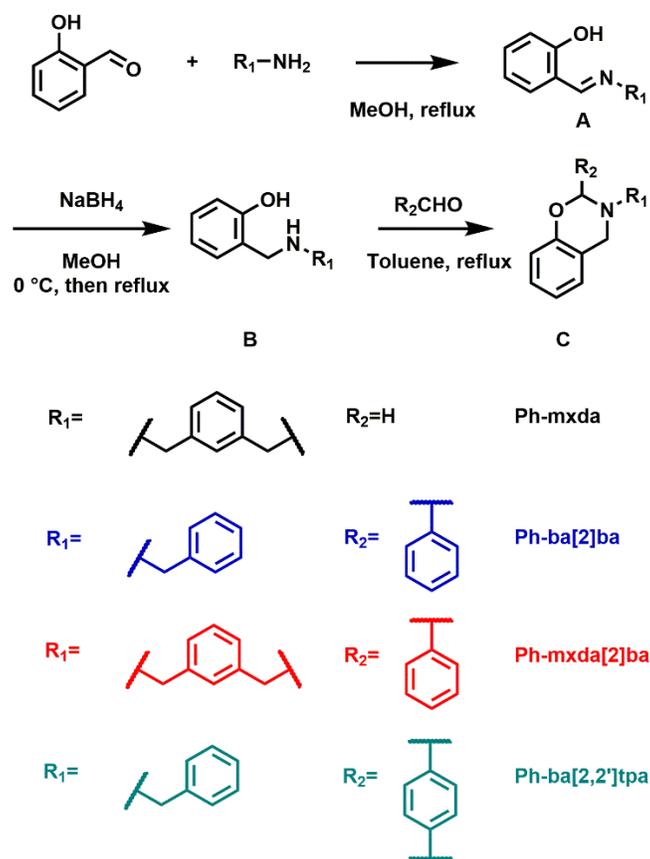
47 According to the benzoxazine abbreviation proposed by Ohashi *et al.*,¹⁹ the first letters represent the phenolic
48 moiety, “Ph” being the phenol, after the hyphen is represented the amine moiety, “ba” symbolizing the
49 benzylamine, and mxda the meta-xylylenediamine. The square brackets are used to precise the position where
50 the oxazine ring is substituted, and finally, after those brackets is displayed the abbreviation of the aldehyde, *i.e.*
51 “ba” stands for benzaldehyde and tpa for terephthalaldehyde. Thus, benzylamine and benzaldehyde based
52 monobenzoxazine is described as **Ph-ba[2]ba**, meta-xylylenediamine and benzaldehyde based bisbenzoxazine is
53 **Ph-mxda[2]ba**, and benzylamine and terephthalaldehyde-based benzoxazine is **Ph-ba[2,2']tpa**. For comparison
54 purpose, one formaldehyde-based benzoxazine was synthesized with the same method from meta-
55
56
57
58
59
60

xylylenediamine, abbreviated **Ph-mxda**, this structure having been described first by F. Setiabudi from Huntsmann in a patent.²¹

Results and discussion

Monomers synthesis and characterization

All formaldehyde-free benzoxazines have been synthesized according to the 3-step method developed by Ronda *et al.*, as illustrated in Scheme 1. First, salicylaldehyde was reacted with a stoichiometric amount of selected amine (1:1), in order to form the corresponding imine **A** (which was isolated for characterization purpose). Then, subsequent imine was reduced by sodium borohydride in order to get the aminomethylphenol **B**. Aza-acetalisation, *i.e.* aromatic aldehyde condensation with aminomethylphenol, resulted in the desired 2-substituted 1,3-benzoxazine **C**. Three formaldehyde-free benzoxazines have been successfully synthesized with good yields: a monobenzoxazine based on benzylamine and benzaldehyde ($R_1 = -CH_2Ph$ and $R_2 = Ph$), a bisbenzoxazine synthesized from meta-xylylenediamine and benzaldehyde ($R_1 = -CH_2PhCH_2-$, *meta* position and $R_2 = Ph$) and another bisbenzoxazine, based on benzylamine and a dialdehyde, terephthalaldehyde ($R_1 = CH_2Ph$ and $R_2 = -Ph-$, *para* position). Previous authors used Lewis or Brønsted acids to catalyze the condensation reaction between aldehyde and imine. For instance, Tang *et al.* studied the aza-acetalization of aromatic aldehydes with catalysts such as boron trifluoride²², stannic tetrachloride,^{23,24} trimethylsilyl chloride,^{25,26} and other Lewis or Brønsted acids. They showed in overall that the nucleophilicity of the amine moiety is a key-parameter of this reaction.²⁷ Ohashi *et al.* used a Brønsted acid catalyst for the synthesis of bisbenzoxazine from *p*-phenylenediamine.¹⁹ It shall be noted however that steric parameters have a strong influence on the amine reactivity, especially for secondary amines.²⁸ In our case, we did not use any catalyst since we obtained the desired bisbenzoxazine structures in reasonable time scales (≤ 26 h) with good yields.



Scheme 1 – General reaction pathway for the synthesis of 1,3-benzoxazines

¹H NMR spectra are displayed in Figure 1-a and in Figure S1-S4, of the supporting information. In formaldehyde-based benzoxazine, characteristic peak of the O-CH₂-N benzoxazine ring is observed as a singlet at 4.89 ppm whereas methylene groups of the oxazine ring or from the benzylic amine residue appear at 3.98 and 3.94 ppm. For formaldehyde-free benzoxazine, the characteristic peak resulting from the formation of the heterocycle *i.e.* O-CH-N proton, gives a singlet at 6.00 ppm for **Ph-ba[2]ba**, whereas methylene groups display more complex multiplicities. Since they are constrained in the heterocycle, methylene protons from the ring are not equivalent, and should appear as a doublet.²⁹ Moreover, the formation of the oxazine ring generates a stereocenter on the 2-position, thus the signal from the methylene is observed as an overlapped quadruplet with the signal of the other methylene of the benzylic amine residue, between 3.80 and 3.91 ppm. For 2-substituted bisbenzoxazine **Ph-mxda[2]ba**, we observe the O-CH-N signal as two singlets at 6.01 and 6.02 ppm, illustrating the presence of diastereomers (each benzoxazine ring generates asymmetry). The methylene protons signals show a complex multiplicity ranging from 3.80 to 3.90 ppm. The same multiplicity is observed in **Ph-ba[2,2']tpa** as protons from O-CH-N on the ring with two singlets at 5.97 and 5.98 ppm, and methylenes with a broad multiplet from 3.79 to 3.89 ppm. In ¹³C NMR spectra (Figure S5-S8) methylene carbon O-CH₂-N for **Ph-mxda** is observed at 82.39 ppm. We can observe the signal of O-ArCH-N carbon on the closed ring at 90.51 ppm for **Ph-ba[2]ba**. For **Ph-mxda[2]ba**, O-ArCH-N carbons appear at 90.46 and 90.49 ppm, and for **Ph-ba[2,2']tpa**, respectively at 90.42 ppm and 90.36 ppm. The presence of two peaks confirms the existence of diastereomers in formaldehyde-free bisbenzoxazines.

FTIR spectroscopy was performed for all the monomers and acquired spectra are displayed in Figure 1-b. Symmetric and asymmetric C_{Ar}-O-C stretching bands can be respectively found at 1022 and 1218 cm⁻¹.³⁰ For the

formaldehyde-based benzoxazine, **Ph-mxda**, we observe the characteristic band of oxazine ring skeletal vibration at 921 cm^{-1} .^{31,32} The actual vibration assignment of this complex band is challenging and has been recently reported elsewhere.³³ All these characteristic bands are also observed for formaldehyde-free benzoxazines. C_{Ar}-O-C bands are located at 1031 and 1219 cm^{-1} for **Ph-mxda[2]ba**, 1028 and 1231 cm^{-1} for **Ph-ba[2]ba** and 1033 and 1224 cm^{-1} for **Ph-ba[2,2']tpa**. Also, the specific benzoxazine ring band related to the O-C-N bonds is located respectively at 929 cm^{-1} for **Ph-mxda[2]ba**, 932 cm^{-1} for **Ph-ba[2]ba** and 930 cm^{-1} for **Ph-ba[2,2']tpa**. It is interesting to note that this characteristic band is split into two sharp signals, compared to the formaldehyde-based benzoxazine, which displays a broader unique band at 921 cm^{-1} . This is consistent with the work of Han *et al.* showing that the characteristic benzoxazine related mode is affected by substitution in position 2 of the oxazine ring.³³ Finally, the very similar signals between 1610 and 1450 cm^{-1} are attributed to the aromatic skeleton vibrations for all monomers. In addition, Mass Spectrometry was also used to complete the full characterization of the synthesized structures (Fig. S9-S14). Overall, the structural characterizations confirmed obtaining of the desired structures.

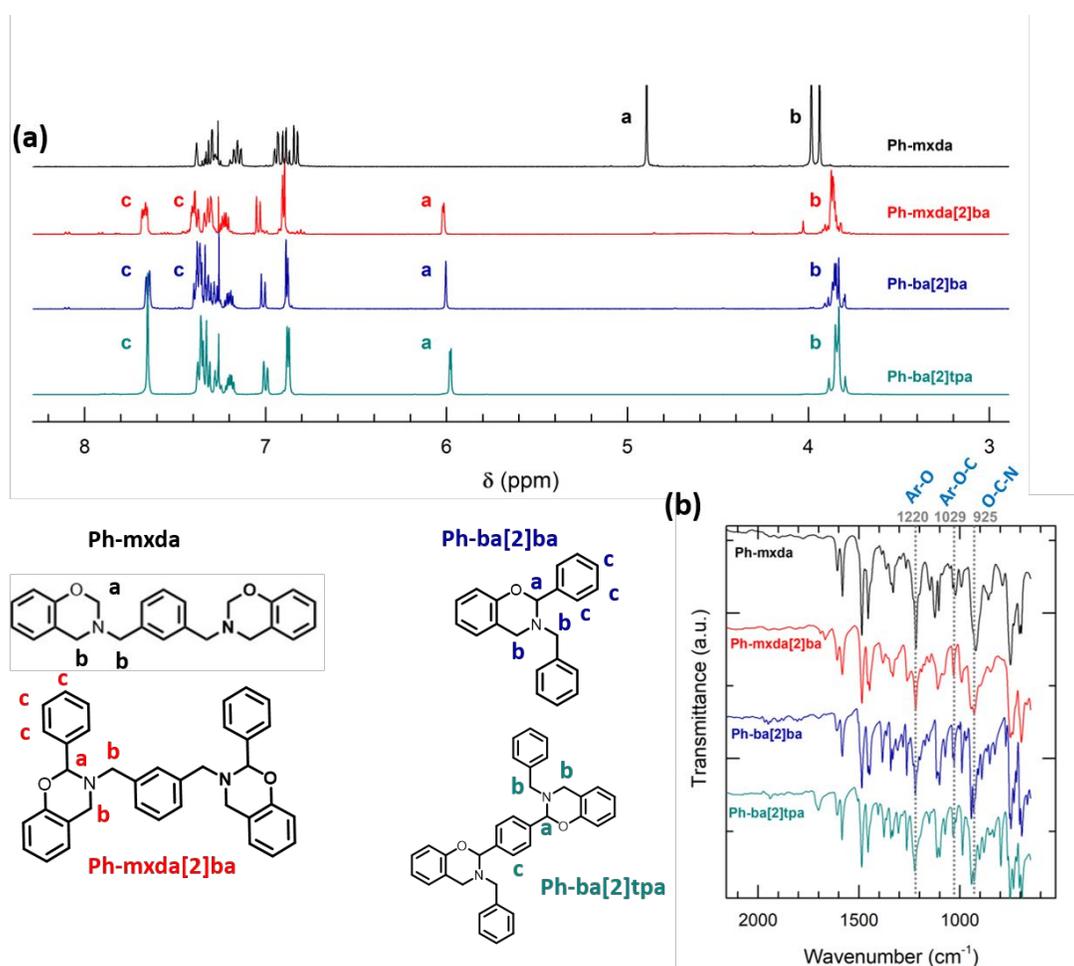


Figure 1 – (a) ¹H NMR spectra of Ph-mxda (1), Ph-mxda[2]ba (2), Ph-ba[2]ba (3) and Ph-ba[2,2']tpa (4) (full spectra available in SI) in chloroform-d with according structures and proton assignments. (b) FTIR spectra of benzoxazine monomers in the fingerprint region (shifted vertically).

Polymerization behavior and mechanisms

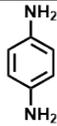
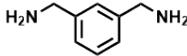
Ring-opening polymerization (ROP) has been investigated by DSC (Figure 2-a). Table 1 compares our data with the literature. First, most of the thermograms show an endothermic transition due to monomer melting.

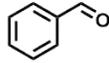
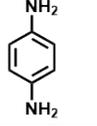
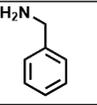
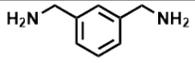
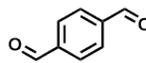
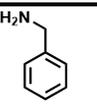
Interestingly, **Ph-mxda** and **Ph-mxda[2]ba** were confirmed to remain amorphous liquids, whereas the other solid benzoxazine monomers displayed a neat melting transition. Similar observation were reported for meta-phenylenediamine-based benzoxazine.¹³ We noticed that the use of meta-substituted monomers tends to be favorable to produce desirable liquid monomers at room temperature. We also noticed that monomers having more aromatic moiety lead to higher melting temperature, e.g. 56°C for **Ph-a** and 70-75°C for **Ph-ba**, (2 rings), and 200 °C **Ph-ba[2,2']tpa** and **Ph-pda[2]ba** (5 rings).

Following the melting transition, the exothermic peak is characteristic of polybenzoxazine ROP. One notes that m-XDA benzoxazines exhibit two overlapped exotherms suggesting two reaction pathways (one single peak is observed for others). Most of our benzoxazines polymerize in the range of 200-300 °C. However, **Ph-mxda[2]ba** polymerizes at a lower temperature (peak maximum at 194 °C). Ren *et al.* showed that meta-oriented bisbenzoxazines have lower polymerization temperatures.¹³ It could be attributed to the electronic configuration of meta-oriented amine which could favor the ring opening.²⁰ This phenomenon is increased by the electronic effect of the aromatic cycle attached to the oxazine ring, which enhances the ring-opening kinetics.

Generally, bisbenzoxazines exhibit higher molar enthalpy than their monobenzoxazines counterpart, having more reactive moieties per monomer (higher functionality). In the case of monofunctional monomers, polymerization enthalpies values are higher for formaldehyde-free benzoxazine bearing a phenyl ring on the 2-position. However, the trend is reversed for bisbenzoxazines and 2-substituted bisbenzoxazines, the latter have lower polymerization molar enthalpies (ca. 50%). For instance, **Ph-mxda** has a polymerization enthalpy of 82 kJ·mol⁻¹ and **Ph-mxda[2]ba** 47 kJ·mol⁻¹. This is confirmed when comparing **Ph-pda** and **Ph-pda[2]ba**, with respectively 51 kJ·mol⁻¹ and 21 kJ·mol⁻¹ of total enthalpies. Those lower polymerization enthalpies may be explained by the steric hindrance that may reduce the reactive species diffusion in 2-substituted benzoxazines compared to formaldehyde-based ones. Those results are in accordance with the work of Pereira *et al.*, which also reported lower polymerization molar enthalpies for formaldehyde-free benzoxazines (with lower activation energies).²⁰

Table 1 - DSC data for all benzoxazines studied. All data were generated from DSC at 10 °C·min⁻¹. Polymerization temperature (T_{polym}) is the temperature at peak maximum)

Entry	Aldehyde	Amine	T_m (°C)	T_{polym} (°C)	ΔH_{polym} (J·g ⁻¹) [kJ·mol ⁻¹]	Ref
Ph-a			56	262	85 [18]	11
Ph-pda			180	255	415 [51]	34
Ph-ba			70-75	261	35 [8]	35
Ph-mxda			n.d.	246	220 [82]	This work
Ph-a[2]ba			100	238	73 [22]	19

Ph-pda[2]ba			170-175	238	42 [21]	19
Ph-ba[2]ba			110	262	46 [13]	This work
Ph-mxda[2]ba			n.d.	194	90 [47]	This work
Ph-ba[2,2']tpa			199	259	89 [47]	This work

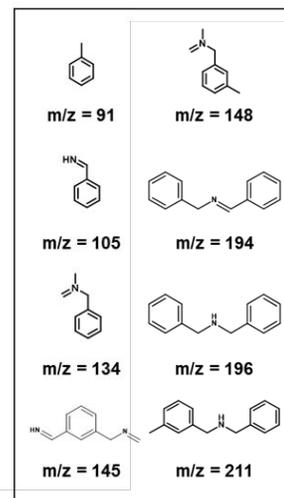
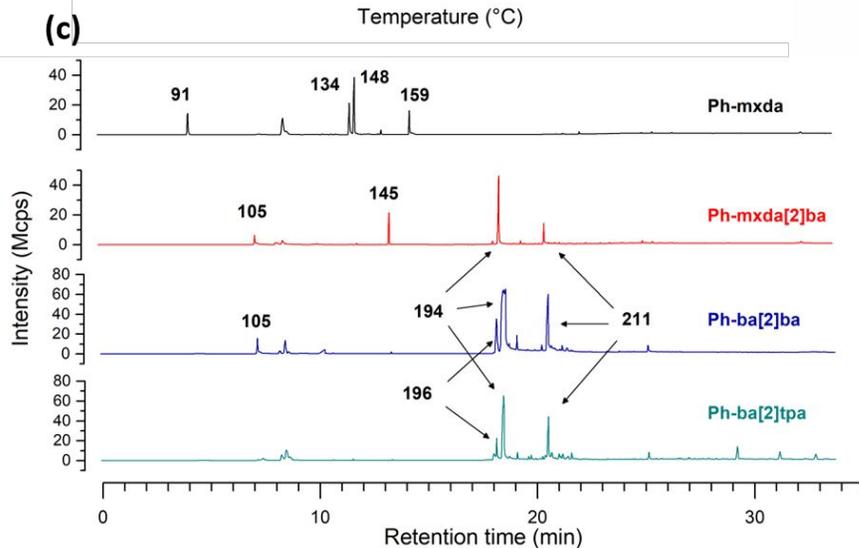
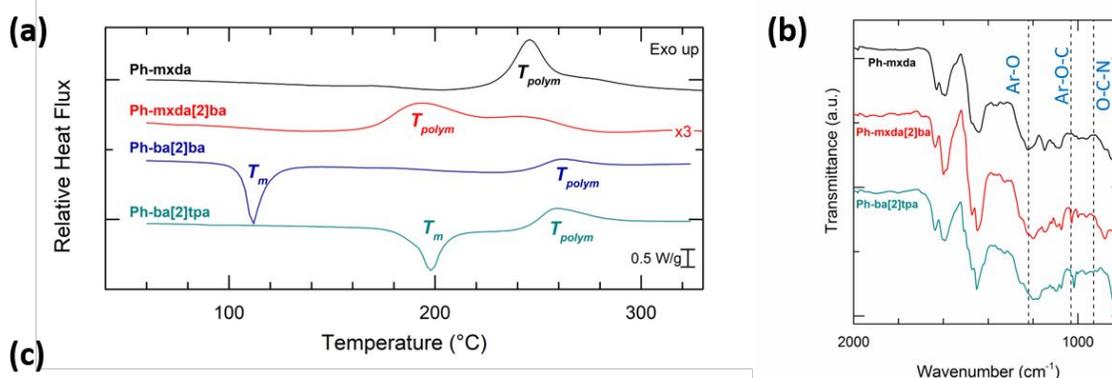


Figure 2 – (a) DSC thermograms of Ph-mxda, Ph-mxda[2]ba, Ph-ba[2] and Ph-ba[2,2']tpa at 10 °C/min. (b) IR of cured polybenzoxazine between 800-2000 cm^{-1} . (c) Py-GC/MS Chromatograms of all benzoxazines, at 200°C, with the corresponding m/z (Da).

After full curing at 200 °C, all polybenzoxazine were verified to be fully cross-linked, (no residual enthalpy in DSC, Figure S15). Furthermore, they were confirmed to be perfectly insoluble in a good solvent (Table S1).

FTIR spectroscopy has been used to compare the monomer and polymer structures. For all the synthesized monomers, we can observe the disappearance of the specific benzoxazine band around 920-950 cm^{-1} after curing, confirming the ring opening of the structures (Figure 2-b). For the formaldehyde-based benzoxazine **poly(Ph-mxda)**, we can observe a residual band around 1220 cm^{-1} while the 1022 cm^{-1} band have disappeared, and a free OH band is observed as a shoulder around 3200 cm^{-1} (Figure S16). This observation is in line with a

Mannich-type conformation of the cured network (Scheme 2), as demonstrated by Wang *et al.*³⁶ For 2-substituted benzoxazines, Mannich-type structure is also present for **poly(Ph-mxda[2]ba)**, as confirmed by the presence of the free OH band at 3200 cm⁻¹ and the 1200 cm⁻¹ band, while the 1028 cm⁻¹ band decreased but did not completely disappeared, meaning that there is a mixed structure of N,O-acetal and Mannich-type. **Poly(Ph-ba[2,2']tpa)** also displayed mixed structure, since there is in one hand a broad band of free OH, showing the Mannich-type structure, and two bands at 1178 and 1017 cm⁻¹ that are characteristics of the N,O-acetal structures. However in that case, those bands were slightly shifted compared to the monomer (1224 and 1033 cm⁻¹). Bands attributed to the aromatic skeletons are still observed for all materials, in the range 1610-1450 cm⁻¹. The enlargement of those signals indicates additional substitution that occurred during crosslinking. Due to the low residual mass after thermal treatment, **poly(Ph-ba[2]ba)** could not be analyzed by FT-IR.

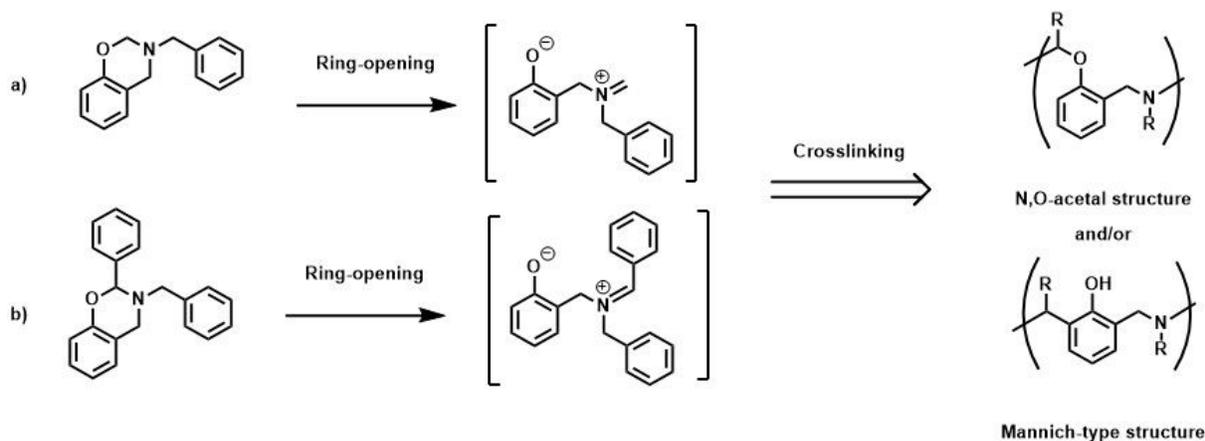
Sometimes described as polyaddition resin and volatile-free thermosets, it is known that ring-opening polymerization produce volatile organic compounds, such as amines or imines, which identification are clues for the comprehension in the polymerization mechanism.^{18,37,38} In our case, dry content was calculated by comparing the weight of a sample before and after curing at 200 °C, in order to determine the volatiles formation during polymerization. For **poly(Ph-mxda)**, dry content is 81.0 ± 0.7 wt %, and for the benzaldehyde-based one, **poly(Ph-mxda[2]ba)**, 81.7 ± 0.3 wt % remains in the network, showing that replacing formaldehyde by benzaldehyde does not seem to impact degassing during polymerization. More volatiles are produced during the curing of **Ph-ba[2]tpa**, since only 68.0 ± 0.5 wt % remains in the cured samples. For the monobenzoxazine however, dry content is only 14.7 ± 0.8 wt %, which is consistent with the fact that this is the lightest monomer, and that monobenzoxazines are known to only produce small oligomers, that can be volatilized or degraded during the polymerization.

The structure of those volatiles can be of precious help in order to understand the curing mechanism. Direct Pyrolysis-MS has been used in the literature in order to characterize the volatile during polymerization.³⁸ This technique has the advantage to prevent chemical recombination that could occur by trapping the volatiles in a solvent or by condensation.³⁷ We thus performed a Pyrolysis coupled to GC/MS at 200 °C, separation performed by gas chromatography allowed better MS resolutions. We observed that formaldehyde-free benzoxazines and **Ph-mxda** had a slightly different behavior in terms of volatile releasing. Figure 2-c represents the chromatograms of benzoxazine monomers after pyrolysis at 200 °C for 15 s, with associated *m/z* for main peaks. Retention times, *m/z* and proposed chemical structures of detected compounds are reported in Table S2 with some of the associated MS spectra (Figure S20-S22). For **Ph-mxda**, toluene was observed (91 Da) that could result from solvent trapped into the viscous monomer or fragmentation. Methylphenol was also observed (108 Da) and the two main peaks can be attributed to the reactive imines (134 and 148 Da) formed from the scission of the monomer on the oxazine ring, as reported by several publications.^{18,37-40} Another imine can also be found with a lower quantity, at 159 Da, corresponding to the scission on the two nitrogen atoms of the *m*-XDA residue. All MS spectra of imines or amines proposed are shown in Supporting Information file.

For all formaldehyde-free monomers, volatiles were different, except for methylphenol that was released by all samples. Retention times, *m/z*, proposed structures and corresponding monomers are reported in Figure 2-c and in Table S3. MS spectra are reported Figure S23-S33. Some ions were detected in the three monomers, such as imine with one or two phenyl groups (105 and 194 Da), or an amine with two phenyl groups that could be part of the network with crosslinking on the phenyl ring of the amine residue (211 Da). Other heavier ions were detected corresponding either to the monomer for **Ph-ba[2]ba** (300 Da) or opened fragments (286 or 311 Da) for **Ph-ba[2,2']tpa**. In the recent work of Pereira *et al.*, TGA of monomers showed early weight loss, around

200 °C.²⁰ They associated those losses to the degradation of pending alkyl chain. However, when comparing both their TGA with DSC data, we can notice that those first weight losses correspond to the ring-opening polymerization temperatures. Since the second weight loss of monomers corresponds to the one occurring for crosslinked monomers, the first weight loss corresponds to volatilization of reactive species during polymerization and not early degradation.

The polymerization mechanism that is currently the most accepted by the community implies the formation of a very reactive imine, by the ring-opening of the heterocycle on the oxygen atom (Scheme 2-a).³⁹⁻⁴¹ The observation of imine compounds that are volatilized during the polymerization are in accordance with this mechanism. As they are observed both in formaldehyde-based and formaldehyde-free benzoxazine, we can conclude that the polymerization of 2-substituted benzoxazines follow the same mechanism, *i.e.* the ring-opening occurs via the formation of a reactive imine, which is reactive towards nucleophilic ortho positions of the phenolic moiety (Scheme 2-b). The cured networked structures as analyzed by IR and the volatile structures are in accordance with the accepted polybenzoxazines mechanisms.



Scheme 2 – Illustration of ring-opening of the oxazine ring in a) formaldehyde-based benzoxazines³⁹⁻⁴¹ and in b) 2-phenyl substituted benzoxazine²⁰

Thermal stability and degradation

The thermal stability has been evaluated by TGA up to 900 °C. The thermograms are shown in Figure 3-b and the results compared with literature data in Figure 3-c.^{19,35,42} Char yield at 800 °C and temperature at 5% weight loss ($T_{d5\%}$) are usual parameters to compare the thermal stability of thermosets. All the synthesized polybenzoxazines displayed superior thermal resistance, with char yields in the range of 48-65% and $T_{d5\%}$ = 310-350 °C. Derivative TGA (DTG) showed the main steps of materials degradation. Degradation patterns displayed up to three steps for **poly(Ph-ba[2]ba)** and two main steps for all of the other samples. Early degradations around 300 °C occurred in **poly(Ph-mxda)** and **poly(Ph-ba[2]ba)**, that account respectively for 3% and 4% of weight. This early degradation step is attributed to the cleavage of amine fragments^{38,43} and this is confirmed by the Py-GC/MS discussed below. Around 400 °C, we observed DTG peaks for **poly(Ph-ba[2]ba)**, **poly(Ph-mxda[2]ba)** (Figure 3-a) and **poly(Ph-ba[2,2']tpa)** (Figure S19), that correspond to the starting of the network degradation. Finally, for all the samples, the major weight loss happened over 500 °C according to the DTG, and corresponding to the char formation.

The degradation behavior has also been investigated using Py-GC/MS, as shown in Figure 3-c for **Ph-mxda[2]ba** and in Figure S17-S19 for all monomers. It shall be noted that the coherence between the TGA and Py-GC/MS results was affected by the fact that TGA uses continuous heating ramp, whereas a stepwise program was used

for the pyrolysis. After the initial pyrolysis at 200 °C, several pyrolysis steps have been performed, by heating each sample to 300, 400, 500, 600 and 900 °C, with a cooling to room temperature between each step. We observed that for the same sample, the volatile releasing was very low compared to the curing step at 200°C, for all benzoxazines. However as the temperature raised, the quantity of volatiles increased, which is correlated to high degradation temperature of the cured networks. In early stages of decomposition we can observe the same volatiles than during the polymerization. Those compounds could have been trapped in the network and are released over the T_g of the material.⁴⁴ They can also originate from the early degradation of the network, as it has been shown before.³⁸ All the monomers displayed nearly the same degradation pathway, releasing at high temperature aromatic fragments such as benzene (78 Da), toluene (91 Da), xylene (106 Da), phenol (94 Da), benzonitrile (103 Da), methylphenol (108 Da), methylbenzonitrile (117 Da), phenantrenol (194 Da, Figure S34), pyrene (208 Da) which is characteristic of charring materials, especially polybenzoxazines.^{45,46} The higher is the pyrolysis temperature, the lower is the molecular weight of the released compounds.

As a conclusion, even if the formaldehyde-based **poly(Ph-mxda)** still demonstrates maximum performances, these results prove that benzaldehyde and terephthalaldehyde are effective and promising alternatives to formaldehyde.

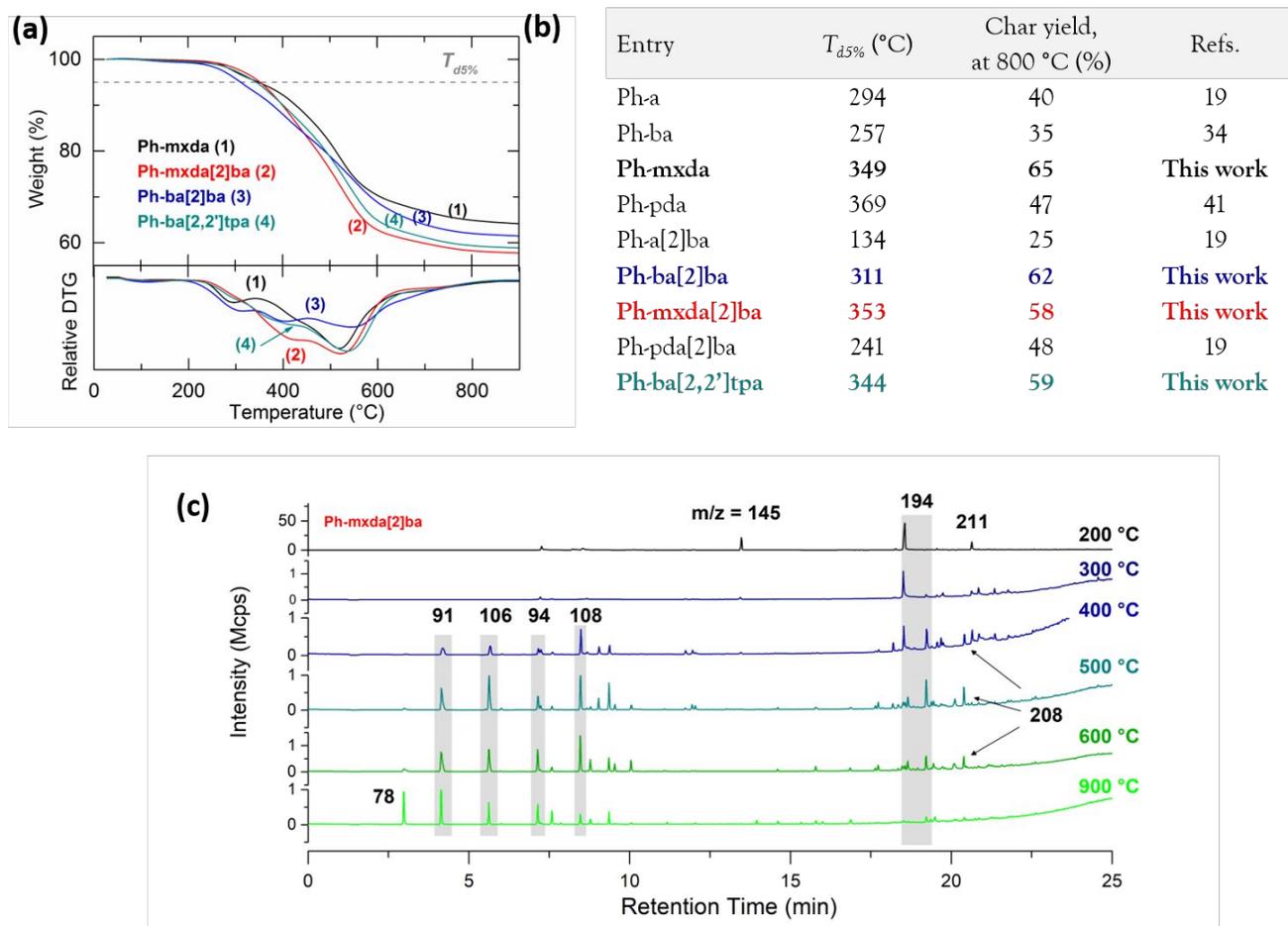


Figure 3 - (a) TGA and DTG thermograms of all synthesized benzoxazines, under nitrogen, at 10°C/min. (b) Comparison of temperature at 5% degradation and char yield of the synthesized polybenzoxazines with literature. (c) Py-GC/MS chromatograms of Ph-mxda[2]ba under the isothermal treatments (T reported next to the curves) with associated m/z (Da).

1
2 Some interesting trends can also be envisioned about the structure-thermal property relationships of
3 salicylaldehyde benzoxazines. Fig. 4 proposes a short meta-analysis comparing our results and literature data
4 (detailed in Figure 3-c). Owing the fact that we compare a relatively small amount of data, we hereafter outline
5 tendencies rather than definitive conclusions. Three input categories of structures are compared (amine and
6 aldehyde types and functionality of monomers) with a focus on char yield and $T_{d5\%}$ as outputs.
7
8

9 The amine type seems to be the key factor to increase char yields with a relatively good significance (p -value <
10 0.1). We observe that benzylic amines (benzylamine and m-XDA) gave rise to higher char yields than the aromatic
11 aniline and p-PDA (+12% char yield in average). The same trends are suggested for the degradation temperatures
12 but with a lower level of significance (+70 °C). These higher thermal performances, that suggest higher
13 crosslinking density, could be readily explained with the crosslinking mechanisms. As shown in Scheme 2, the
14 imine intermediates would be more reactive in the case of aromatic amine, but it would also be more hindered,
15 *i.e.* less available for nucleophilic attacks. On the other hand, because the benzylic amines are less hindered, they
16 are supposedly more prone to react with nucleophilic moieties, *i.e.* the phenolates, which would finally lead to
17 higher crosslink density and upgraded thermal performances.
18
19
20

21 The functionality of the benzoxazine monomers does not seem to be an important factor. Both mono- and bis-
22 benzoxazine lead to similar thermal performances. In fact, increasing the functionality of the amine could lead
23 to lower gelation time and lower volatile contents (observed in this work between benzylamine and m-XDA). Yet,
24 comparing mono- and bis-benzoxazines, the reaction mechanisms are expected to remain the same. Both cured
25 materials would have similar cross-linking density explaining the observed equivalent thermal performances.
26
27

28 From a perspective of sustainable development, it is interesting to compare formaldehyde-based to
29 benzaldehyde-based benzoxazines. The herein compared benzaldehyde benzoxazines display lower degradation
30 temperatures than formaldehyde ones (-80 °C). However, this trend is not significant, considering the dispersity
31 of the data. In contrast, very similar average char yields are recorded for the two groups. Therefore, we consider
32 that benzaldehyde (or terephthalaldehyde) can effectively replace the toxic formaldehyde without a significant
33 loss of thermal resistances.
34
35

36 Finally, among all synthesized and discussed benzoxazines, the network **Ph-mxda(2)ba** is particularly attractive.
37 With benzaldehyde rather than formaldehyde, the synthesis does not involve any CMR (Carcinogenic, Mutagenic
38 and/or Reprotoxic) precursor (yet, to be nuanced because of the known sensitizing effects of m-XDA). One very
39 interesting feature is that the monomer is liquid with no melting transition at ambient conditions, which
40 considerably facilitates the processing conditions (along with other benzylic amine-based benzoxazine).
41 Furthermore, **Ph-mxda(2)ba** possesses the lowest polymerization temperature of all systems herein studied and
42 discussed. We envision that such monomer could be used with existing industrial processes. The advantage of
43 using bisbenzoxazine (*i.e.* m-XDA rather than benzylamine) is its relatively high solid content after full curing (low
44 VOC). **Ph-mxda(2)ba** displayed very good thermal performances, among the highest of the systems discussed.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

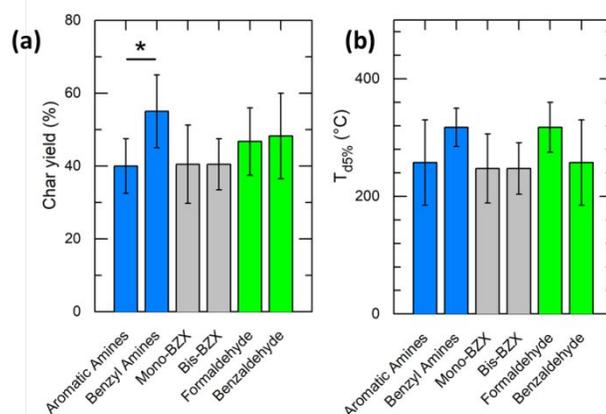


Figure 4 – Comparison of (a) char yield at 800 °C and (b) temperature at 5% degradation of amines (blue), monomer functionality (grey) and aldehydes (green) categories. The column bar values represent the average (of the data reported in Table 3-b) along with one standard deviation as error-bars. The star marks two significantly different average values (analysis of variance: p -value = 0.078).

Summary

We demonstrated that the synthesis of formaldehyde-free 1,3-benzoxazine is easily accessible in 3 steps with reasonable yields. We showed that in overall, polymerization enthalpies of such monomers are lower than formaldehyde-based ones, ($42\text{--}90\text{ J}\cdot\text{g}^{-1}$ versus $35\text{--}415\text{ J}\cdot\text{g}^{-1}$, respectively). Pyrolysis-GC/MS allowed identifying the volatile structures during thermal polymerization, which were in accordance to previously reported mechanisms for formaldehyde-based benzoxazines, leading to the hypothesis that ring-opening polymerization occurs *via* the same mechanisms. IR evidenced that the chemical structure of the network is similar for formaldehyde and aromatic aldehyde-based benzoxazines. Thermal stability for difunctional monomers are quite similar, leading to high char yields (58 % for m-XDA and benzaldehyde-based benzoxazine and 59% for benzylamine and terephthalaldehyde-based benzoxazine) and high degradation temperatures. In addition m-XDA and benzaldehyde-based structures showed lower polymerization temperature and enthalpy, with no melting point and high thermal stability. Structural characterization of cured materials revealed the same structural arrangement of the networks, leading to the conclusion that the addition of an aromatic ring on the 2-position does not affect polymerization mechanisms. Overall, we showed that we can avoid the use of formaldehyde without affecting neither the crosslinking mechanisms, the network structures nor the thermal stabilities of polybenzoxazines. With more in-depth studies on the crosslinking mechanisms of these benzoxazines and the selection of appropriate starting materials, it is expected to obtain seriously competitive and more sustainable polybenzoxazines for high performance applications.

Conflicts of interest

The authors declare no competing interest.

Acknowledgements

Authors wish to thank the French “Direction Générale de l’Armement” for the funding of the Ph.D. and the Laboratory of “Mesures Physiques” of University of Montpellier for the ESI-MS measurements.

Supporting Information

Full ^1H and ^{13}C NMR spectra, ESI-HRMS of monomers, dry contents and insoluble fractions of cured materials, DSC of cured samples and Py-GC/MS chromatograms and mass spectra.

References

- (1) Takeichi, T.; Kawauchi, T.; Agag, T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. *Polym. J.* **2008**, *40* (12), 1121–1131. <https://doi.org/10.1295/polymj.PJ2008072>.
- (2) Ghosh, N. N.; Kiskan, B.; Yagci, Y. Polybenzoxazines—New High Performance Thermosetting Resins: Synthesis and Properties. *Prog. Polym. Sci.* **2007**, *32* (11), 1344–1391. <https://doi.org/10.1016/j.progpolymsci.2007.07.002>.
- (3) Yagci, Y.; Kiskan, B.; Ghosh, N. N. Recent Advancement on Polybenzoxazine—A Newly Developed High Performance Thermoset. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47* (21), 5565–5576. <https://doi.org/10.1002/pola.23597>.
- (4) Iguchi, D.; Salum, M. L.; Froimowicz, P. Application of Benzoxazine-Based Dimers, Oligomers, and Polymers as Chelating Agents. *Macromol. Chem. Phys.* **2019**, *220* (1), 1800366. <https://doi.org/10.1002/macp.201800366>.
- (5) Kiskan, B.; Ghosh, N. N.; Yagci, Y. Polybenzoxazine-Based Composites as High-Performance Materials. *Polym. Int.* **2011**, *60* (2), 167–177. <https://doi.org/10.1002/pi.2961>.
- (6) Iguchi, D.; Ohashi, S.; Abarro, G. J. E.; Yin, X.; Winroth, S.; Scott, C.; Gleydura, M.; Jin, L.; Kanagasagar, N.; Lo, C.; et al. Development of Hydrogen-Rich Benzoxazine Resins with Low Polymerization Temperature for Space Radiation Shielding. *ACS Omega* **2018**, *3* (9), 11569–11581. <https://doi.org/10.1021/acsomega.8b01297>.
- (7) Xu, S.; He, J.; Jin, S.; Tan, B. Heteroatom-Rich Porous Organic Polymers Constructed by Benzoxazine Linkage with High Carbon Dioxide Adsorption Affinity. *J. Colloid Interface Sci.* **2018**, *509*, 457–462. <https://doi.org/10.1016/j.jcis.2017.09.009>.
- (8) Poorteman, M.; Renaud, A.; Escobar, J.; Dumas, L.; Bonnaud, L.; Dubois, P.; Olivier, M. G. Thermal Curing of Para-Phenylenediamine Benzoxazine for Barrier Coating Applications on 1050 Aluminum Alloys. *Prog. Org. Coatings* **2016**, *97*, 99–109. <https://doi.org/10.1016/j.porgcoat.2016.03.026>.
- (9) Kiskan, B. Adapting Benzoxazine Chemistry for Unconventional Applications. *React. Funct. Polym.* **2018**, *129* (January), 76–88. <https://doi.org/10.1016/j.reactfunctpolym.2017.06.009>.
- (10) Holly, F. W.; Cope, A. C. Condensation Products of Aldehydes and Ketones with O-Aminobenzyl Alcohol and o-Hydroxybenzylamine. *Journal of the American Chemical Society.* 1944, pp 1875–1879. <https://doi.org/10.1021/ja01239a022>.
- (11) Andreu, R.; Reina, J. A.; Ronda, J. C. Studies on the Thermal Polymerization of Substituted Benzoxazine Monomers: Electronic Effects. *Journal of Polymer Science Part A: Polymer Chemistry.* 2008, pp 3353–3366. <https://doi.org/10.1002/pola.22677>.
- (12) Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. Eugenol-Based Benzoxazine: From Straight Synthesis to Taming of the Network Properties. *J. Mater. Chem. A* **2015**, *3* (11), 6012–6018. <https://doi.org/10.1039/c4ta06636g>.
- (13) Ren, S.; Yang, X.; Zhao, X.; Zhang, Y.; Huang, W. An m-Phenylenediamine-Based Benzoxazine with Favorable Processability and Its High-Performance Thermoset. *J. Appl. Polym. Sci.* **2016**, *133* (18), 43368. <https://doi.org/10.1002/app.43368>.

- 1
2 (14) Lin, C. H.; Chang, S. L.; Hsieh, C. W.; Lee, H. H. Aromatic Diamine-Based Benzoxazines and Their High
3 Performance Thermosets. *Polymer (Guildf)*. **2008**, *49* (5), 1220–1229.
4 <https://doi.org/10.1016/j.polymer.2007.12.042>.
5
- 6 (15) Imran, M.; Kiskan, B.; Yagci, Y. Concise Synthesis and Characterization of Unsymmetric 1,3-Benzoxazines
7 by Tandem Reactions. *Tetrahedron Lett.* **2013**, *54* (36), 4966–4969.
8 <https://doi.org/10.1016/j.tetlet.2013.07.041>.
9
- 10 (16) Ohashi, S.; Kilbane, J.; Heyl, T.; Ishida, H. Synthesis and Characterization of Cyanate Ester Functional
11 Benzoxazine and Its Polymer. *Macromolecules* **2015**, *48* (23), 8412–8417.
12 <https://doi.org/10.1021/acs.macromol.5b02285>.
13
- 14 (17) Oie, H.; Sudo, A.; Endo, T. Synthesis of Polymers Bearing 1,3-Benzoxazine Moiety in the Side Chains from
15 Poly(Allylamine) and Their Crosslinking Behaviors. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49* (14),
16 3174–3183. <https://doi.org/10.1002/pola.24754>.
17
- 18 (18) Nalakathu Kolanadiyil, S.; Endo, T. Toward Elucidating the Role of Number of Oxazine Rings and
19 Intermediates in the Benzoxazine Backbone on Their Thermal Characteristics. *Macromolecules* **2016**, *49*
20 (22), 8466–8478. <https://doi.org/10.1021/acs.macromol.6b01965>.
21
- 22 (19) Ohashi, S.; Cassidy, F.; Huang, S.; Chiou, K.; Ishida, H. Synthesis and Ring-Opening Polymerization of 2-
23 Substituted 1,3-Benzoxazine: The First Observation of the Polymerization of Oxazine Ring-Substituted
24 Benzoxazines. *Polym. Chem.* **2016**, *7* (46), 7177–7184. <https://doi.org/10.1039/C6PY01686C>.
25
- 26 (20) Pereira, R. C. S.; Kotzebue, L. R. V.; Zampieri, D.; Mele, G.; Mazzetto, S. E.; Lomonaco, D. Influence of
27 Natural Substituents in the Polymerization Behavior of Novel Bio-Based Benzoxazines. *Mater. Today*
28 *Commun.* **2019**, *21* (August), 100629. <https://doi.org/10.1016/j.mtcomm.2019.100629>.
29
- 30 (21) Setiabudi, F. Thermosetting Composition. WO2010018008, 2010.
31
- 32 (22) Tang, Z.-L.; Wang, L.; Tan, J.-Z.; Wan, Y.-C.; Jiao, Y.-C. Synthesis and Fungicidal Activity of 1-
33 (Carbamoylmethyl)-2-Aryl-3,1-Benzoxazines. *Molecules* **2017**, *22* (7), 1103.
34 <https://doi.org/10.3390/molecules22071103>.
35
- 36 (23) Tang, Z.; Chen, W.; Zhu, Z.; Liu, H. Synthesis of 2,3-Diaryl-3,4-Dihydro-2H-1,3-Benzoxazines and Their
37 Fungicidal Activities. *J. Heterocycl. Chem.* **2011**, *48* (2), 255–260. <https://doi.org/10.1002/jhet.533>.
38
- 39 (24) Tang, Z.; Chen, W.; Zhu, Z.; Liu, H. SnCl₄-Catalyzed Aza-Acetalization of Aromatic Aldehydes: Synthesis
40 of Aryl Substituted 3,4-Dihydro-2H-1,3-Benzoxazines. *Synth. Commun.* **2012**, *42* (9), 1372–1383.
41 <https://doi.org/10.1080/00397911.2010.540691>.
42
- 43 (25) Tang, Z.; Zhu, Z.; Xia, Z.; Liu, H.; Chen, J.; Xiao, W.; Ou, X. Synthesis and Fungicidal Activity of Novel 2,3-
44 Disubstituted-1,3-Benzoxazines. *Molecules* **2012**, *17* (12), 8174–8185.
45 <https://doi.org/10.3390/molecules17078174>.
46
- 47 (26) Tang, Z.; Zhu, Z.; Yan, L.; Chang, S.; Liu, H. Efficient Synthesis of 2,3-Disubstituted-1,3-Benzoxazines by
48 Chlorotrimethylsilane-Mediated Aza-Acetalizations of Aromatic Aldehydes. *J. Heterocycl. Chem.* **2013**,
49 No. 1, 1116–1120. <https://doi.org/10.1002/jhet.1590>.
50
- 51 (27) Tang, Z.; Xia, Z.; Chang, S.; Wang, Z. Synthesis and Fungicidal Activity of Novel 2-Aryl-3-(1,3,4-
52 Thiadiazolyl)-6(8)-Methyl-1,3-Benzoxazines. *Bioorg. Med. Chem. Lett.* **2015**, *25* (16), 3378–3381.
53 <https://doi.org/10.1016/j.bmcl.2015.05.010>.
54
- 55 (28) Brotzel, F.; Chu, Y. C.; Mayr, H. Nucleophilicities of Primary and Secondary Amines in Water. *J. Org.*
56 *Chem.* **2007**, *72* (10), 3679–3688. <https://doi.org/10.1021/jo062586z>.
57
- 58 (29) Ejfler, J.; Krauzy-Dziedzic, K.; Szafert, S.; Lis, T.; Sobota, P. Novel Chiral and Achiral Benzoxazine
59
60

- 1
2 Monomers and Their Thermal Polymerization. *Macromolecules* **2009**, *42* (12), 4008–4015.
3 <https://doi.org/10.1021/ma900336m>.
- 4
5 (30) Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3rd Edition*; John
6 Wiley and Sons, 2004.
- 7
8 (31) Ran, Q.-C.; Zhang, D.-X.; Zhu, R.-Q.; Gu, Y. The Structural Transformation during Polymerization of
9 Benzoxazine/FeCl₃ and the Effect on the Thermal Stability. *Polymer (Guildf)*. **2012**, *53* (19), 4119–4127.
10 <https://doi.org/10.1016/j.polymer.2012.07.033>.
- 11
12 (32) Ishida, H.; Agag, T. Handbook of Benzoxazine Resins. In *Handbook of Benzoxazine Resins*; Elsevier, 2011.
13 <https://doi.org/10.1016/B978-0-444-53790-4.00089-8>.
- 14
15 (33) Han, L.; Iguchi, D.; Gil, P.; Heyl, T. R.; Sedwick, V. M.; Arza, C. R.; Ohashi, S.; Lacks, D. J.; Ishida, H. Oxazine
16 Ring-Related Vibrational Modes of Benzoxazine Monomers Using Fully Aromatically Substituted,
17 Deuterated, 15 N Isotope Exchanged, and Oxazine-Ring-Substituted Compounds and Theoretical
18 Calculations. *J. Phys. Chem. A* **2017**, *121* (33), 6269–6282. <https://doi.org/10.1021/acs.jpca.7b05249>.
- 19
20 (34) Rishwana, S. S.; Pitchaimari, G.; Vijayakumar, C. T. Studies on Structurally Different Diamines and
21 Bisphenol Benzoxazines. *High Perform. Polym.* **2016**, *28* (4), 466–478.
22 <https://doi.org/10.1177/0954008315587125>.
- 23
24 (35) Arslan, M.; Kiskan, B.; Yagci, Y. Ring-Opening Polymerization of 1,3-Benzoxazines via Borane Catalyst.
25 *Polymers (Basel)*. **2018**, *10* (3), 239. <https://doi.org/10.3390/polym10030239>.
- 26
27 (36) Wang, Y.; Ishida, H. Cationic Ring-Opening Polymerization of Benzoxazines. *Polymer (Guildf)*. **1999**, *40*
28 (16), 4563–4570. [https://doi.org/10.1016/S0032-3861\(99\)00074-9](https://doi.org/10.1016/S0032-3861(99)00074-9).
- 29
30 (37) Sudo, A.; Du, L.-C.; Hirayama, S.; Endo, T. Substituent Effects of N-Alkyl Groups on Thermally Induced
31 Polymerization Behavior of 1,3-Benzoxazines. *J. Polym. Sci. Part A Polym. Chem.* **2010**, *48* (13), 2777–
32 2782. <https://doi.org/10.1002/pola.24026>.
- 33
34 (38) Bagherifam, S.; Uyar, T.; Ishida, H.; Hacaloglu, J. The Use of Pyrolysis Mass Spectrometry to Investigate
35 Polymerization and Degradation Processes of Methyl Amine-Based Benzoxazine. *Polym. Test.* **2010**, *29*
36 (4), 520–526. <https://doi.org/10.1016/j.polymertesting.2010.03.003>.
- 37
38 (39) Liu, C.; Shen, D.; Sebastián, R. M.; Marquet, J.; Schönfeld, R. Mechanistic Studies on Ring-Opening
39 Polymerization of Benzoxazines: A Mechanistically Based Catalyst Design. *Macromolecules* **2011**, *44*
40 (12), 4616–4622. <https://doi.org/10.1021/ma2007893>.
- 41
42 (40) Furuncuoğlu Özeltin, T.; Catak, S.; Kiskan, B.; Yagci, Y.; Aviyente, V. Rationalizing the Regioselectivity of
43 Cationic Ring-Opening Polymerization of Benzoxazines. *Eur. Polym. J.* **2018**, *105*, 61–67.
44 <https://doi.org/10.1016/j.eurpolymj.2018.05.024>.
- 45
46 (41) Chutayothin, P.; Ishida, H. Cationic Ring-Opening Polymerization of 1,3-Benzoxazines: Mechanistic Study
47 Using Model Compounds. *Macromolecules* **2010**, *43* (10), 4562–4572.
48 <https://doi.org/10.1021/ma901743h>.
- 49
50 (42) Shamim Rishwana, S.; Mahendran, A.; Vijayakumar, C. T. Studies on Structurally Different Benzoxazines
51 Based on Diphenols and Diamines: Kinetics of Thermal Degradation and TG-FTIR Studies. *Thermochim.*
52 *Acta* **2015**, *618*, 74–87. <https://doi.org/10.1016/j.tca.2015.09.006>.
- 53
54 (43) Li, C.; Ran, Q.; Zhu, R.; Gu, Y. Study on Thermal Degradation Mechanism of a Cured Aldehyde-Functional
55 Benzoxazine. *RSC Adv.* **2015**, *5* (29), 22593–22600. <https://doi.org/10.1039/C5RA00350D>.
- 56
57 (44) Yee Low, H.; Ishida, H. Structural Effects of Phenols on the Thermal and Thermo-Oxidative Degradation
58 of Polybenzoxazines. *Polymer (Guildf)*. **1999**, *40* (15), 4365–4376. <https://doi.org/10.1016/S0032->

1
2 3861(98)00656-9.

- 3
4 (45) Low, H. Y.; Ishida, H. Mechanistic Study on the Thermal Decomposition of Polybenzoxazines: Effects of
5 Aliphatic Amines. *J. Polym. Sci. Part B Polym. Phys.* **1998**, *36* (11), 1935–1946.
6 [https://doi.org/10.1002/\(SICI\)1099-0488\(199808\)36:11<1935::AID-POLB15>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1099-0488(199808)36:11<1935::AID-POLB15>3.0.CO;2-8).
7
8 (46) Hemvichian, K.; Kim, H. D.; Ishida, H. Identification of Volatile Products and Determination of Thermal
9 Degradation Mechanisms of Polybenzoxazine Model Oligomers by GC–MS. *Polym. Degrad. Stab.* **2005**,
10 *87* (2), 213–224. <https://doi.org/10.1016/j.polymdegradstab.2003.11.005>.
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Formaldehyde-free polybenzoxazines for high performance thermosets

Romain Tavernier^a, Lérys Granado^a, Gabriel Foyer^b, Ghislain David^a, Sylvain Caillol^{a,*}

^aICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

^bArianeGroup, Rue de Touban, 33185 Le Haillan, France

For Table of Contents use only

