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Formaldehyde-Free Polybenzoxazines for High Performance Thermosets

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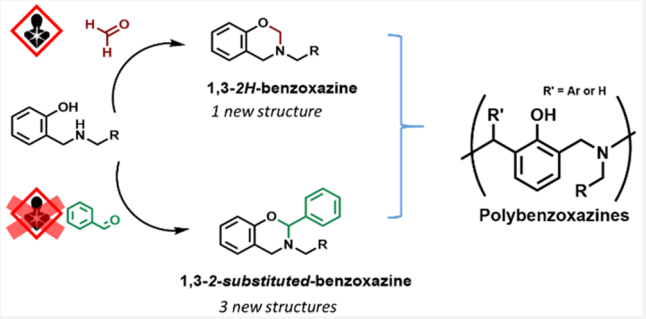
ABSTRACT: We report the synthesis and ring-opening polymerization of new formaldehyde-free benzoxazines. The polybenzoxazines obtained displayed high thermal stability and high char yields. Data from the literature combined with our analyses by differential scanning calorimetry and thermogravimetric 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. In particular, 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 CO_2 capture,[7] anticorrosion coatings,[8] 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-benzoxazine architectures,[11] two of them appearing to be predominant in the articles published at this time.[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 three-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 consists in the formation of the oxazine ring by reacting formaldehyde with the phenol moiety and the secondary amine.

These synthetic methods were used to obtain a wide range of benzoxazine monomers, which allowed researchers to find the parameters having an influence on thermal properties of polybenzoxazine networks. For instance, electron-withdrawing groups on the phenol moiety have a strong effect on the ring-opening temperature. High aromatic content and high cross-link densities are required to get high degradation temperatures and improved char yields. For instance, Endo and Nalakathu Kolanadiyil investigated the influence of the oxazine ring number in benzoxazine monomers on their thermal stabilities, evidencing that a higher content of oxazine rings improves thermal stability of cured thermosets.[18] However, an increase of the monomers functionality leads to a decrease of

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the reactivity, thus requiring higher curing temperatures. The design of benzoxazine monomers is therefore crucial to reach the desired thermal properties.

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

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

EXPERIMENTAL SECTION

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

Synthesis of Salicylamines. *Synthesis of 2-((Benzylamino)-methyl)phenol (Scheme 1, Compounds **A** and **B**, R_1 = Bz).* Here, 11.40 g of salicylaldehyde was dissolved in 50 mL of methanol. Then, 10.0 g of benzylamine was added to the mixture, which was then refluxed for 2 h. After the reaction was cooled to room temperature, solvent was removed under reduced pressure. The corresponding imine was isolated for characterization purposes. Reduction was then performed by dissolving 10.52 g of the imine in 50 mL of methanol, and 3.68 g of sodium borohydride was added in small portions, at 0 °C, in order to limit foaming. After complete addition of the sodium borohydride, the reaction mixture was heated to reflux for another 2 h. After cooling to room temperature, the reaction mixture was quenched by precipitation in distilled water. The resulting viscous amine was then recovered by liquid−liquid extraction with ethyl acetate, the organic phase was dried over magnesium sulfate, and solvent was removed under reduced pressure to afford the desired product. A total of 15.30 g of yellow oil was recovered. Yield = 77%.

HRMS (*m*/*z*, positive mode, $[M + H]^+$): $C_{14}H_{16}NO$; calculated 214.1226; found 214.1236

*Synthesis of 2,2′-(((1,3-Phenylenebis(methylene))bis(azanediyl))-bis(methylene))diphenol (Scheme 1, Compounds **A** and **B**, R_1 = m-Xylylene).* First 17.91 g of salicylaldehyde was dissolved in 50 mL of methanol. Then 10.03 g of *m*-XDA was added to the mixture, which was then refluxed for 2 h. After the reaction was cooled to room temperature, solvent was removed under reduced pressure. The corresponding imine was isolated for characterization purpose. Reduction was then performed by dissolving the imine in 50 mL of methanol, and 5.61 g of sodium borohydride was added in small portions, at 0 °C, in order to control the foaming. After complete addition of the sodium borohydride, the reaction mixture was heated to reflux for another 2 h. After cooling to room temperature, the reaction mixture was quenched by precipitation in distilled water. The resulting viscous amine was then recovered by liquid−liquid extraction with ethyl acetate, organic phase was dried over magnesium sulfate and solvent was removed under reduced pressure to afford the desired product. 24.81 g of a viscous pale-yellow oil were recovered that further crystallized as a white solid. Yield = 97%.

HRMS (*m*/*z*, positive mode, $[M + H]^+$): $C_{22}H_{25}N_2O_2$; calculated 349.1911; found 349.1927.

Synthesis of Benzoxazine Monomers. *Synthesis of 1,3-Bis((2H-benzo[e][1,3]oxazin-3(4H)-yl)methyl)benzene **(Ph-mxda)** (Scheme 1, Compound **C**, R_1 = m-Xylylene and R_2 = H).* First, 1.03 g of 2,2′-(((1,3-phenylenebis(methylene))bis(azanediyl))bis-(methylene))diphenol was dissolved in 20 mL of toluene. Then, 0.17 g of paraformaldehyde was added to the mixture, which was then refluxed for 2 h with a Dean−Stark apparatus. After the mixture cooled to room temperature, solvent was removed under reduced pressure. Product was recovered as a transparent viscous oil. Yield >99%.

HRMS (*m*/*z*, positive mode, $[M + H]^+$): $C_{24}H_{25}N_2O_2$; calculated 373.1911; found 373.1918. NMR ^{1}H ($CDCl_3$, 7.26 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 ^{13}C ($CDCl_3$, 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, 55.60, 49.81.

*Synthesis of 1,3-Bis((2-phenyl-2H-benzo[e][1,3]oxazin-3(4H)-yl)-methyl)benzene **(Ph-mxda[2]ba)** (Scheme 1, Compound **C**, R_1 = m-Xylylene and R_2 = Ph).* First, 10.99 g of 2,2′-(((1,3-phenylenebis-(methylene))bis(azanediyl))bis(methylene))diphenol was dissolved in 100 mL of toluene. Then, 3.36 g of benzaldehyde was added to the mixture, which was then refluxed for 19 h with a Dean−Stark apparatus. After the mixture cooled to room temperature, solvent was removed under reduced pressure. Product was precipitated in cyclohexane and centrifugated to afford 14.28 g of the product as a yellow vitreous solid. Yield = 86%.

HRMS (*m*/*z*, positive mode, $[M + H]^+$): $C_{36}H_{33}N_2O_2$; calculated 525.2537; found 525.2557. NMR ^{1}H ($CDCl_3$, 7.26 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), 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, 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, 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.

*Synthesis of 3-Benzyl-2-phenyl-3,4-dihydro-2H-benzo[e][1,3]-oxazine **(Ph-ba[2]ba)** (Scheme 1, Compound **C**, R_1 = Bz and R_2 = Ph).* First, 1.02 g of 2-((benzylamino)methyl)phenol was dissolved in 20 mL of toluene. Then 0.50 g of benzaldehyde was added to the mixture, which was then refluxed for 24 h with a Dean−Stark apparatus. After the mixture cooled to room temperature, solvent was removed under reduced pressure. Product was then recrystallized from toluene, leading to 0.89 g of a colorless powder. Yield = 54%.

HRMS (*m*/*z*, positive mode, $[M + H]^+$): $C_{21}H_{19}NO$; calculated 302.1539; found 302.1548. NMR ^{1}H ($CDCl_3$, 7.26 ppm): 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 ($CDCl_3$, 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, 126.75, 120.73, 119.92, 116.64, 90.53, 53.48, 46.91.

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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, Compound* ***C****, R_1 = Bz and R_2 = p-phenylene).* First, 1.01 g of 2-((benzylamino)-methyl)phenol was dissolved in 20 mL of toluene. Then, 315 mg of terephthalaldehyde was added to the mixture, which was then refluxed for 24 h with a Dean−Stark apparatus. After the mixture cooled to room temperature, the product spontaneously recrystallized as a colorless solid and was rinsed with toluene. It was then dried under reduced pressure, leading to 576 mg of a colorless powder. Yield = 46%.

HRMS (m/z, positive mode, $[M + H]^+$): $C_{36}H_{33}N_2O_2$; calculated 525.2537; found 525.2546. NMR ^{1}H ($CDCl_3$, 7.26 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 ^{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, 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, 53.57, 46.87, 46.83.

Curing of Benzoxazine Samples. Between 80 and 120 mg of benzoxazine monomer was weighed in small aluminum pans, which were then inserted in an oven preheated at 200 °C, for 6 h at atmospheric pressure.

Measurements. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 400 NMR spectrometer, in $CDCl_3$ using nondeuterated residual solvent as reference.

High resolution mass spectrometry measurements (HRMS) were performed on a Waters Synapt G2-S high resolution mass spectrometer equipped with an ESI (electrospray) ionization source.

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

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

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

The Py-GC/MS analytical setup consisted of an oven pyrolyzer connected to a GC/MS system. A Pyroprobe 5000 pyrolyzer (CDS Analytical) was used to pyrolyze the samples in a helium environment. This pyrolyzer is supplied with an electrically heating platinum filament. One coil probe enables the pyrolysis of samples (less than 1 mg) placed in quartz tube between two pieces of quartz wool. The sample was successively heated at 200, 300, 400, 500, 600, and 900 °C. Each temperature was held for 15 s before gases were drawn to the gas chromatograph for 5 min. The pyrolysis interface was coupled to a 450-GC gas chromatograph (Varian) by means of a transfer line 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 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 as the carrier gas; a split ratio was set to 1:50. The gases were introduced from the GC transfer line to the ion trap analyzer of the 240-MS mass spectrometer (Varian) through the direct-coupled capillary column. Identification of the products was achieved comparing the observed mass spectra to the U.S. National Institute of Standards and Technology mass spectral library.

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

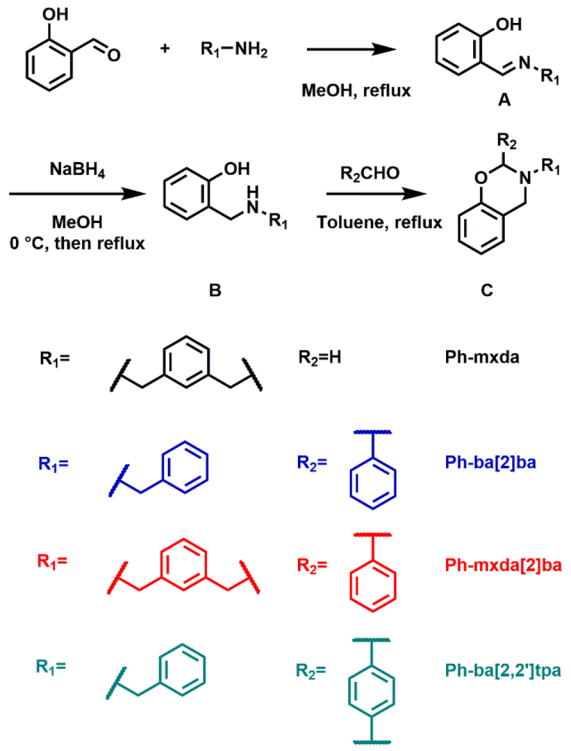
Insoluble fraction was determined by plunging cured samples in 10 mL of dichloromethane in sealed vials, for 48 h at room temperature. Samples were then dried 24 h under vacuum and weighed in order to determine the insoluble content. Results are displayed as a mean of at least three samples with 1σ standard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

Nomenclature. According to the benzoxazine abbreviation proposed by Ohashi et al.,[19] the first letters represent the phenolic moiety, "Ph" being the phenol, after the hyphen is represented the amine moiety, "ba" symbolizing the benzylamine, and mxda the *m*-xylylenediamine. The square brackets are used to precise the position where the oxazine ring is substituted, and finally, after those brackets are displayed, the abbreviation of the aldehyde, i.e., "ba" stands for benzaldehyde and tpa for terephthalaldehyde. Thus, benzylamine and benzaldehyde based monobenzoxazine is described as **Ph-ba[2]ba**, *m*-xylylenediamine and benzaldehyde-based bisbenzoxazine is **Ph-mxda[2]ba**, and benzylamine and terephthalaldehyde-based benzoxazine is **Ph-ba[2,2′]tpa**. For comparison purpose, one formaldehyde-based benzoxazine was synthesized with the same method from *m*-xylylenediamine, abbreviated **Ph-mxda**, this structure having been described first by Setiabudi from Huntsmann in a patent.[21]

RESULTS AND DISCUSSION

Monomers Synthesis and Characterization. All formaldehyde-free benzoxazines have been synthesized according to the three-step method developed by Ronda et al., as illustrated in Scheme 1. First, salicylaldehyde was reacted with a

Scheme 1. General Reaction Pathway for the Synthesis of 1,3-Benzoxazines



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-acetalization, i.e., aromatic aldehyde condensation with aminomethylphenol, resulted in the desired 2-substituted 1,3-benzoxazine **C**. Three formaldehyde-

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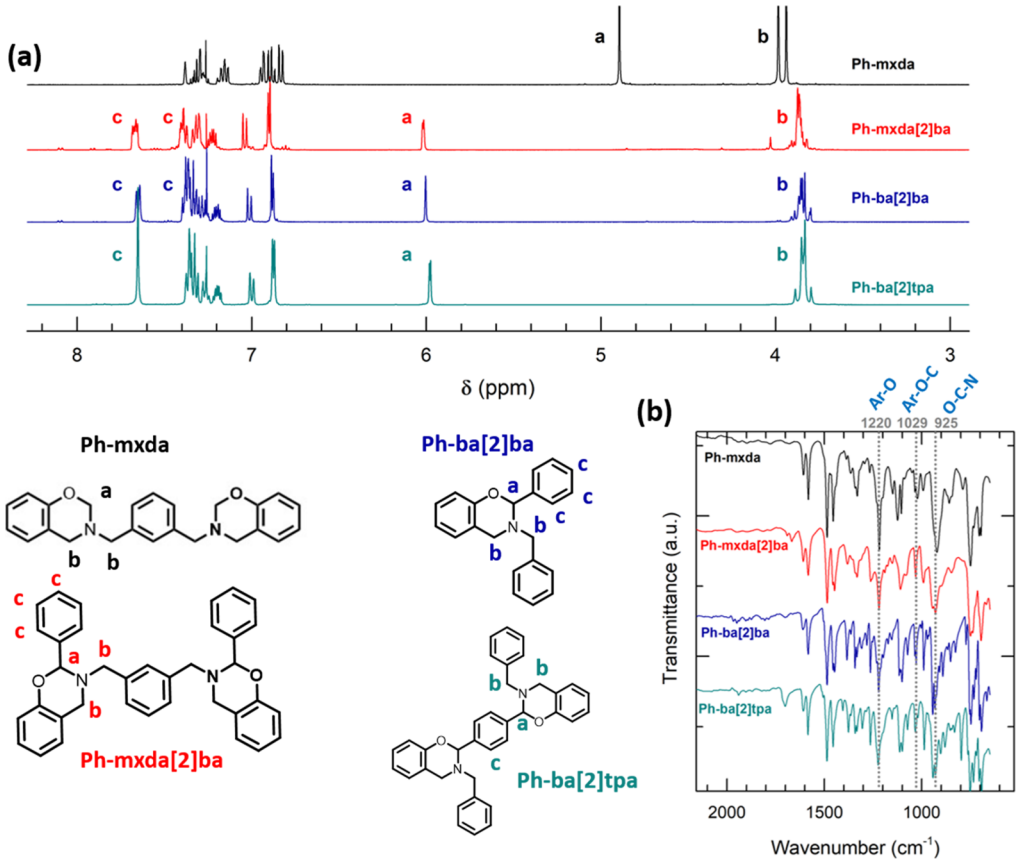

Figure 1. (a) ^{1}H NMR spectra of **Ph-mxda** (1), **Ph-mxda[2]ba** (2), **Ph-ba[2]ba** (3) and **Ph-ba[2,2′]tpa** (4) (full spectra available in Supporting Information) in chloroform-*d* with according structures and proton assignments. (b) FTIR spectra of benzoxazine monomers in the fingerprint region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

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 *m*-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 trifluoride,[22] stain 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.

^{1}H NMR spectra are displayed in Figure 1a and in Figures S1−S4, of the Supporting Information. In formaldehyde-based benzoxazine, characteristic peak of the O−C**H**$_2$−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−C**H**−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−C**H**−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−C**H**−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 ^{13}C NMR spectra (Figures S5−S8) methylene carbon O−**C**H_2−N for **Ph-mxda** is observed at 82.39 ppm. We can observe the signal of O−Ar**C**H−N carbon on the closed ring at 90.51 ppm for **Ph-ba[2]ba**. For **Ph-mxda[2]ba**, O−Ar**C**H−N carbons appear at 90.46 and 90.49 ppm, and for **Ph-ba[2,2′]tpa**, respectively at 90.42 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 1b. 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

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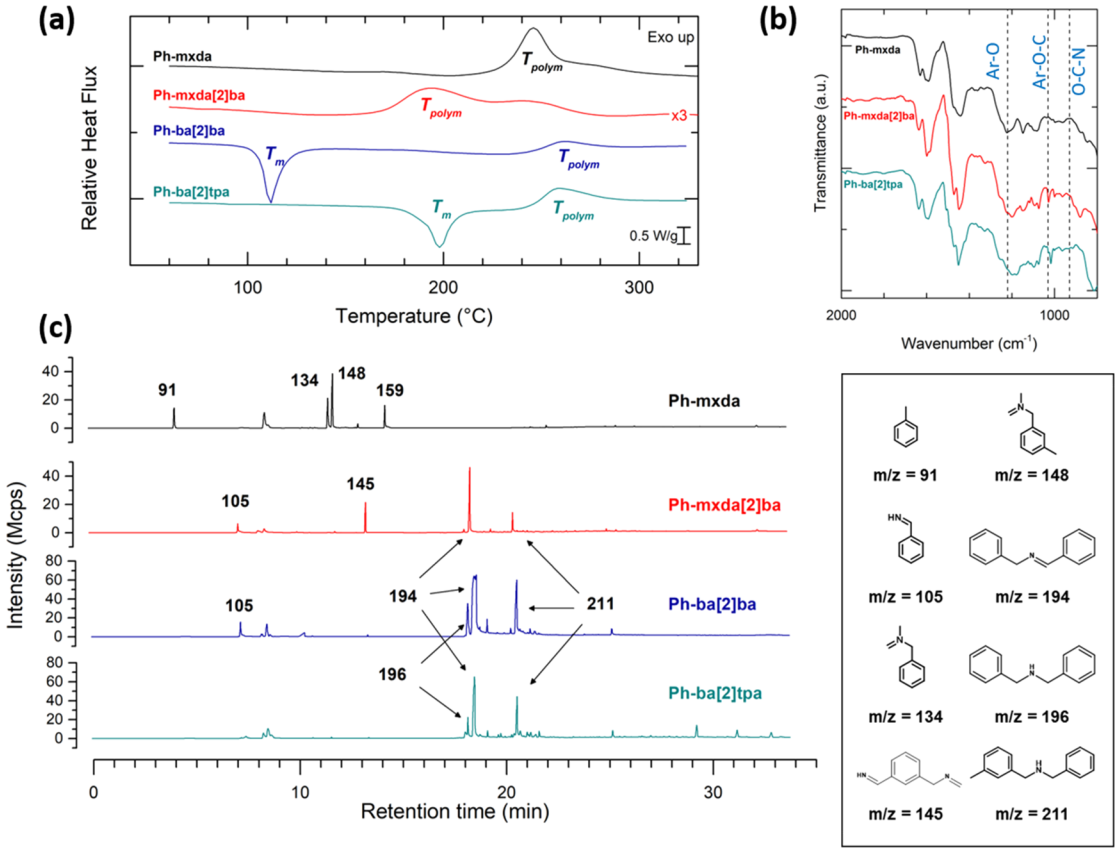

Figure 2. (a) DSC thermograms of **Ph-mxda**, **Ph-mxda**[2]**ba**, **Ph-ba**[2], and **Ph-ba**[2,2′]**tpa** at 10 °C/min. (b) IR of cured polybenzoxazine between 800 and 2000 cm^{-1}. (c) Py-GC/MS chromatograms of all benzoxazines, at 200 °C, with the corresponding *m*/*z* (Da).

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 (Figures S9−S14). Overall, the structural characterizations confirmed obtaining of the desired structures.

Polymerization Behavior and Mechanisms. Ring-opening polymerization (ROP) has been investigated by DSC (Figure 2a). 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 *m*-phenylenediamine-based benzoxazine.[13] We noticed that the use of *m*-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**, 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 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

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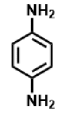
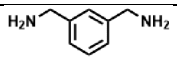
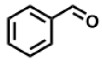
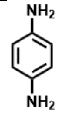
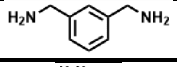
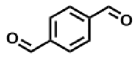
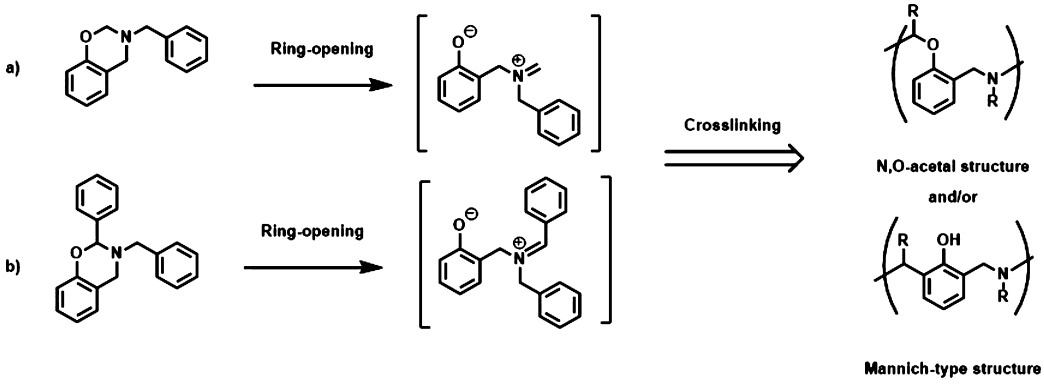
Table 1. DSC Data for All Benzoxazines Studied[a]

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**

[a]All data were generated from DSC at 10 °C·min^{-1}. Polymerization temperature (T_{polym}) is the temperature at peak maximum). References 11, 19, 34, and 35 are mentioned in the body of this table but linked here.

Scheme 2. Illustration of Ring-Opening of the Oxazine Ring in (a) Formaldehyde-Based Benzoxazines[39−41] and in (b) 2-Phenyl-Substituted Benzoxazine[20]



comparing **Ph-pda** and **Ph-pda**[**2**]**ba**, with respectively 51 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]

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 2b). For the formaldehyde-based benzoxazine **poly**(**Ph-mxda**), we can observe a residual

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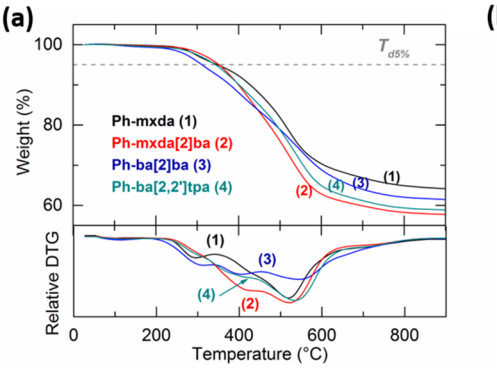

(b)

Entry	$T_{d5\%}$ (°C)	Char yield, at 800 °C (%)	Refs.
Ph-a	294	40	19
Ph-ba	257	35	34
Ph-mxda	**349**	**65**	**This work**
Ph-pda	369	47	41
Ph-a[2]ba	134	25	19
Ph-ba[2]ba	**311**	**62**	**This work**
Ph-mxda[2]ba	**353**	**58**	**This work**
Ph-pda[2]ba	241	48	19
Ph-ba[2,2']tpa	**344**	**59**	**This work**

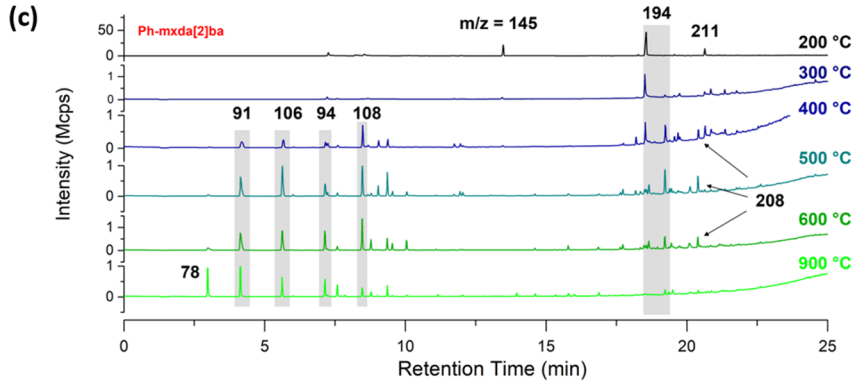

Figure 3. (a) TGA and DTG thermograms of all synthesized benzoxazines, under nitrogen, at 10 °C/min. (b) Comparison of temperature at 5% degradation and char yield of the synthesized polybenzoxazines with literature. (c) Py-GC/MS chromatograms of **Ph-mxda[2]ba** under the isothermal treatments (T reported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

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, a 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 disappear, meaning that there is a mixed structure of *N,O*-acetal and Mannich-type. **Poly(Ph-ba[2,2′]tpa)** also displayed a mixed structure, since there is on 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, on the other hand. 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 cross-linking. Due to the low residual mass after thermal treatment, **poly(Ph-ba[2]ba)** could not be analyzed by FT-IR.

Sometimes described for polyaddition resin and volatile-free thermosets, it is known that ring-opening polymerization produces volatile organic compounds, such as amines or imines, which identification is a clue for 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, which 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, where 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 2c 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 (Figures 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

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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 the Supporting Information.

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 2c and in Table S3. MS spectra are reported in Figures 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 cross-linking 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 cross-linked 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 2a).[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 toward nucleophilic ortho positions of the phenolic moiety (Scheme 2b). The cured networked structures as analyzed by IR and the volatile structures are in accordance with the accepted polybenzoxazines mechanisms.

Thermal Stability and Degradation. The thermal stability has been evaluated by TGA up to 900 °C. The thermograms are shown in Figure 3b and the results compared with literature data in Figure 3c.[19,35,42] Char yield at 800 °C and temperature at 5% weight loss ($T_{d5\%}$) are the 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 3a) 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 3c for **Ph-mxda[2]ba** and in Figures 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 was 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.

Some interesting trends can also be envisioned about the structure-thermal property relationships of salicylaldehyde benzoxazines. Figure 4 proposes a short meta-analysis comparing our results and literature data (detailed in Figure 3c). Owing to the fact that we compare a relatively small amount of data, we hereafter outline tendencies rather than definitive conclusions. Three input categories of structures are

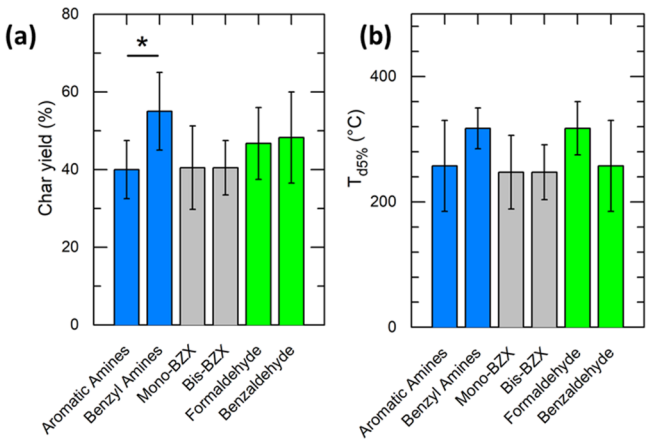

Figure 4. Comparison of (a) char yield at 800 °C and (b) temperature at 5% degradation of amines (blue), monomer functionality (gray), and aldehydes (green) categories. The column bar values represent the average (of the data reported in Figure 3b) along with one standard deviation as error bars. The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

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compared (amine and aldehyde types and functionality of monomers) with a focus on char yield and $T_{d5\%}$ as outputs.

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

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

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

Finally, among all synthesized and discussed benzoxazines, the network **Ph-mxda(2)ba** is particularly attractive. With benzaldehyde rather than formaldehyde, the synthesis does not involve any CMR (carcinogenic, mutagenic, and/or reprotoxic) precursor (yet, to be nuanced because of the known sensitizing effects of *m*-XDA). One very interesting feature is that the monomer is liquid with no melting transition at ambient conditions, which considerably facilitates the processing conditions (along with other benzylic amine-based benzoxazine). Furthermore, **Ph-mxda(2)ba** possesses the lowest polymerization temperature of all systems herein studied and discussed. We envision that such monomer could be used with existing industrial processes. The advantage of using bisbenzoxazine (i.e., *m*-XDA rather than benzylamine) is its relatively high solid content after full curing (low VOC). **Ph-mxda(2)ba** displayed very good thermal performances, among the highest of the systems discussed.

SUMMARY

We demonstrated that the synthesis of formaldehyde-free 1,3-benzoxazine is easily accessible in three steps with reasonable yields. We showed that, overall, polymerization enthalpies of such monomers are lower than formaldehyde-based ones, (42−90 $J{\cdot}g^{-1}$ versus 35−415 $J{\cdot}g^{-1}$, respectively). Pyrolysis-GC/MS allowed identifying the volatile structures during thermal polymerization, which were in accordance with 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 cross-linking mechanisms, the network structures nor the thermal stabilities of polybenzoxazines. With more in-depth studies on the cross-linking 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.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00192.

Full ^{1}H 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 (PDF)

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Notes

The authors declare no competing financial interest.

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