1. Introduction

1.1 Motivation

From the first synthetic polymer, the Bakelite, in 1907 until now, tailoring basic polymers with additives, functional monomers or other modifications, keeps chemists and physicists occupied for a century to reach unchartered possible applications. [1] A large variety of different modifications and interesting new applications have been created. From artificial joints [2] over the use of liquid polymers in batteries [3] to 4D-printable polymers with shape memory effects. [4] This large variety of applications is achieved by tuning polymers' structure and morphology. Additional focus is drawn to tuning polymers properties to enable the substitution of other materials, e.g., metals. [5] However, to achieve such a substitution they are used in combination with fibers to obtain the necessary high mechanical strength. The combination of fibers and polymers as fiber reinforced plastics (FRP) are used since the middle of the 19th century for Linoleum. [6] Present attempts exchange metals with lighter materials like composites to reduce the total weight of transportation vehicles. Lighter transportation vehicles need less fuel, which is of high interest in consideration of the climate change. [7], [8] To reach such a substitution, polymers require high thermo-mechanical properties to exhibit stability over a larger temperature range for structural applications. While thinking about sustainable aspects, it is additionally beneficial if the materials can be manufactured from sustainable reactants, which is according to the EU's sustainable development goals.

Nevertheless, todays neat FRPs are not fulfilling all the necessary parameters regarding, e.g., flame retardancy (FR) for structural applications in the transport sector. [9] The FR is necessary to upkeep the safety of the passengers and varies in requirements for each transportation vehicle. [10], [11] However, current polymer systems either need a high amount of FR additives, e.g., polyesters or some epoxies, or, in case of phenols, are difficult and toxic in their preparation. [12], [13] In recent years benzoxazines as new type of phenolic polymer receive an increased attention. [14] Benzoxazines exhibit intrinsically promising thermo-mechanical and FR properties similar to phenolic based ones, which are known for their beneficial properties in those fields. [15] Additionally, they are usually polymerized *via* thermally induced ring-opening polymerization (ROP). Therefore, they release no volatile compounds and have a low volume shrinkage. [16] Due to their innate good FR properties only a low amount of FR additives are needed to achieve sufficient results. [17]

1.2 Scientific question

Even though patents and publications related to benzoxazines are increasing throughout the years, they are still on the verge of being used in different industrial applications. The most important reason is given by their challenging high polymerization temperatures up to 200 °C. In addition, although benzoxazines have an inherent flame-retardancy they often do not fulfil the specifications for structural applications without additional modifications, which are needed in transportation applications, e.g., in railway or shipping. Therefore, this work focuses on an increased thermal stability and an improved flame retardancy for polybenzoxazines, which will be investigated in two different concepts. On the one hand, new benzoxazine monomers with increased thermal stability (Publication 1) or with an incorporated flame-retardant group (Publication 2) are synthesized and their polymerization and polymeric properties are investigated. [18], [19] On the other hand, different flame-retardant additives (Publication 3 and 4) are investigated regarding their influence on the ring-opening polymerization as well as their incorporation into the polybenzoxazine network and thereof resulting properties. [20], [21]

For bio-based monomers (Publication 1) a sesamol and furfurylamine-based reference system is used as it shows promising thermal stability while only requiring a one-step synthesis. For FR concepts (Publication 2, 3 and 4) a bisphenol F, aniline and formaldehyde based benzoxazine (BF-a) is used as reference system as it exhibits a broad application spectrum and enables in-depth analysis for additive studies and the flame-retardant monomer approach.

In this work, new synthesis concepts are developed to obtain new benzoxazine monomers. For an improved thermal stability bifunctional benzoxazines based on sesamol and different diamines are investigated. The second synthesis concept focuses on bifunctional benzoxazine with a flame-retardant spacer group, which bases on a synthesis pathway with a spacer as presented by A. Trejo-Machin *et al.* [22] The structure of all developed benzoxazines is verified *via* FT-IR, NMR and HR-MS analysis.

In the second concept, the polymerization and network properties of benzoxazines will be tuned using additives. This attempt is investigated as additives often show a reduced synthesis effort in comparison to the functionalization of monomers. For this purpose, five additives namely resorcinol bis(diphenyl phosphate) (RDP); Poly(1,3-phenylene methylphosphonate) (PMP); 4-((4′-Hydroxyphenylimino)(6-oxido-6H-dibenz(c,e) (1,2) oxaphosphorin-6-yl)methyl)phenol (DOPO-AP); 6,6′-(((Methylenebis(1,4-phenylene))-bis(azanediyl))bis((4-hydroxy-3-methoxyphenyl)methylene))bis(6H-dibenzo(c,e)(1,2) oxaphosphine 6-oxide (DOPO-Van); and 2-(6-Oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-

6-yl)-1,4-hydroxy phenylene (DOPO-HQ) are used. These additives showed for different systems, e.g., epoxies, improving effects on their flame retardancy and are mixed with BF-a. PMP and the DOPO based additives are used due to their reactive hydroxyl and/or amine groups, which can lower the polymerization temperature of benzoxazines.

It is investigated how the new monomers, and the formulated mixtures affect the ROP process. For the monomer concept, it is of interest to obtain insights on both the impact of increasing aliphatic chain units (Publication 1) and the incorporation of a FR group (Publication 2) on the melting points and temperature of the ROP begin (T_{onset}). For the additive based concept, additives are mixed in different amounts based on either their phosphorous content or their molar equivalent to the reference system. By this, the influence is determined from their reactive groups and their overall impact on the polymerization process. Differential scanning calorimetry (DSC) and rheological analysis *via* rheometer are used to obtain information on T_{onset} and the melt viscosities to handle the polymerization of DMA samples. Furthermore, monomers and formulated mixtures are tested *via* thermogravimetric analysis (TGA) on their initial degradation temperature to avoid degradation processes during the polymerization.

The influence from the structural differences of new monomers and additives on the polymeric network are investigated *via* dynamic-mechanical analysis (DMA) to obtain insights on their thermo-mechanical properties.

The thermal stability of new benzoxazines and polybenzoxazines is determined *via* TGA. For the sesamol based approach, the focus of the investigation is set on the effect of sesamol and different chain lengths and their influence on the network stability. For the FR-based concepts, it is of interest how the flame-retardant functions affect the polybenzoxazines network stability with increasing temperature.

The effects of different flame-retardant groups are analyzed in different small scale burning tests to screen their performances. For this purpose, small scale samples are tested on their initial response against small flames *via* limiting oxygen index (LOI) and UL-94. Furthermore, neat pBF-a and either RDP or PMP containing samples are examined *via* cone calorimetry and smoke chamber analysis to evaluate their impact on their heat release and a charring effect on a macroscopic scale. Sesamol and diamine based polybenzoxazines are investigated on their heat release *via* micro cone calorimetry (MCC) as this method needs only sample amounts in the mg range.

Based on the results for monomers and additives a hypothesis will be concluded which type of additive and FR functional group may be most effective for different applications.

Furthermore, the influence of FR groups on the polymeric network should be more explainable. Lastly, it will be exploited if the additional synthesis effort of monomers is delivering beneficial properties in comparison to an additive-based approach.

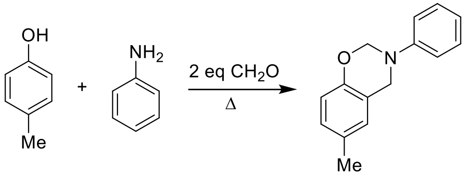
2. Theoretical Background

2.1 Benzoxazine

2.1.1 Properties of Benzoxazines

Benzoxazines contain a benzene ring with a covalently attached heterocyclic oxazine ring, which is a cyclic 6-membered ring with oxygen and nitrogen atom. As the position of the nitrogen and oxygen atoms can differ, different structural isomers with different names are possible, including 1,3-, 1,4- and 3,1-benzoxazines. Hereby the numbering is made with the oxygen position proceeding those of the nitrogen. [23] Mainly, the 1,3-benzoxazine is the subject of interest for the ring-opening polymerization and therefore, all benzoxazines mentioned in this work will refer to the 1,3-benzoxazine isomer.

During the last 30 years the interest for benzoxazine kept rising as they show different beneficial properties like a high thermal stability, low water uptake, [24] high thermo-mechanical properties with a high glass transition temperature (T_g) [25] and, a good chemical resistance. [26], [27] Furthermore, benzoxazines do not release volatile substances during polymerization and have a low curing shrinkage, [28], [16] which is beneficial in comparison to other phenolic resins. The general synthesis pathway for benzoxazines bases on the use of a phenol, an amine and formaldehyde in a ratio of 1:1:2 (Scheme 1). Therefore, modifications can be easily incorporated by altering the reactants, which results in both different number of benzoxazine groups or the incorporation of a variety of different structural functionalities. To be precise, this flexible modularity enables to tune the properties of benzoxazines to fit for different specific applications and therefore, make them a promising starting point as alternative for phenolic resins.



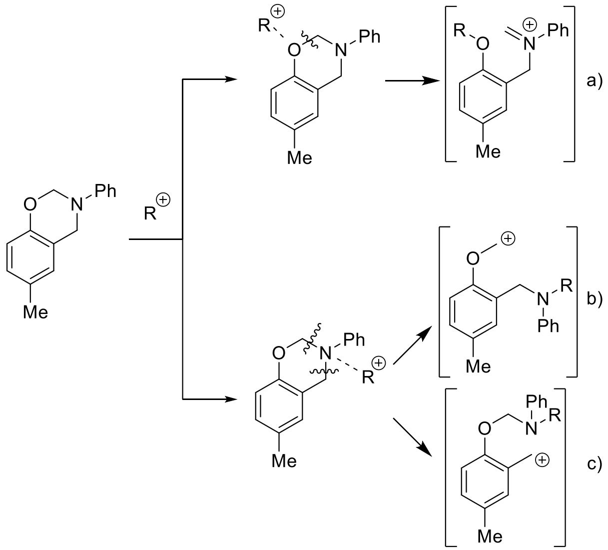
Scheme 1. Benzoxazine synthesis based on cresol, aniline and formaldehyde.

Benzoxazines were first mentioned almost 80 years ago by Holly and Cope. [29] In the 1950s and 1960s a large variety of benzoxazine molecules was synthesized by Burke *et al.* [30], [31], [32] Those Benzoxazines were synthesized in condensation reactions of different phenols, different primary amines, and formaldehyde. Benzoxazine based polymers and copolymers with epoxies and phenols were first mentioned by H. Schreiber in 1973. [33], [34] Higginbottom *et al*. used multifunctional phenols and amines to obtain cross-linked polybenzoxazine in 1985. [35], [36] Further research was done by Reiss *et al.* on reaction kinetics for the oligomer formation in 1985 as well as by Turpin and Thrane in 1988 for a coating formulation. [37], [38] However, the first description of polybenzoxazine properties was reported by Ishida and Ning as late as 1994. [39]

2.1.2 Polymerization conditions of Benzoxazines

Even though the benzoxazine polymerization is often called thermally induced ROP, its name is misleading as the main polymerization mechanism is that of a cationic ROP. To be accurate, a lower ROP temperature is often a result of small impurities like phenols that enable the cationic, exothermic polymerization. Pure benzoxazine monomers show a relatively poor reactivity for their ring-opening step. Therefore, it is better to call the polymerization thermally accelerated ROP. The ROP of benzoxazines can be catalyzed and initiated by a few different methods. One method is altering the molecular structure of the monomer itself, e.g., by modifying the substitution pattern on the aromatic ring and therefore the electron density. Another method includes the use of catalysts and initiators. Beside others, Lewis acids, [40] tosylated alcohols, [41] imidazoles, [42] carboxylic acids [43], [44] and amines [45], [46] showed to catalyze the ROP, whereas phenols reduced the temperature of the ROP and still were inbound to the polymeric network. [47], [48], [49], [50], [51], [52]

The detailed polymerization mechanisms of benzoxazines are complex and still part of current investigation. The proposed main polymerization process is that of a cationic ROP. Liu *et al.* [53] proposed a detailed polymerization pattern that includes three main steps: coordination and ring-opening by a catalyst on the oxazine ring, electrophilic attack from an intermediate towards another benzoxazine monomer and a rearrangement into the final phenolic structure. Depending on the coordination site of the catalyst in the first step, three cationic intermediates (a, b and c) can be formed (Scheme 2).

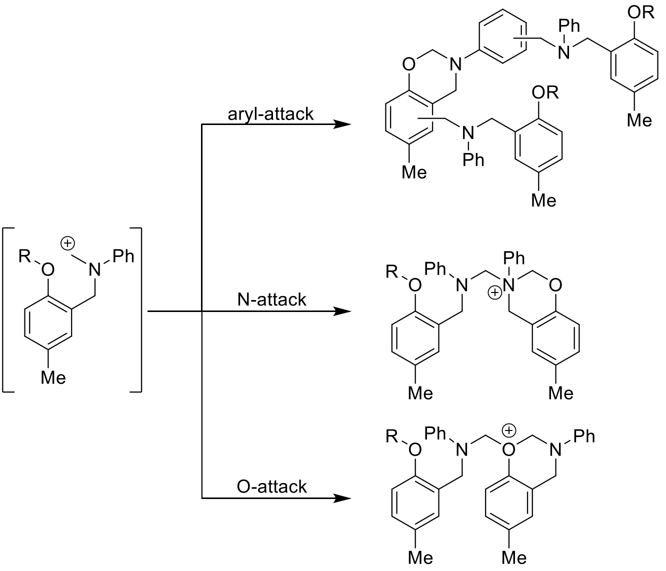


Scheme 2. Possible ring-opening intermediates based on a cresol and aniline based benzoxazine.

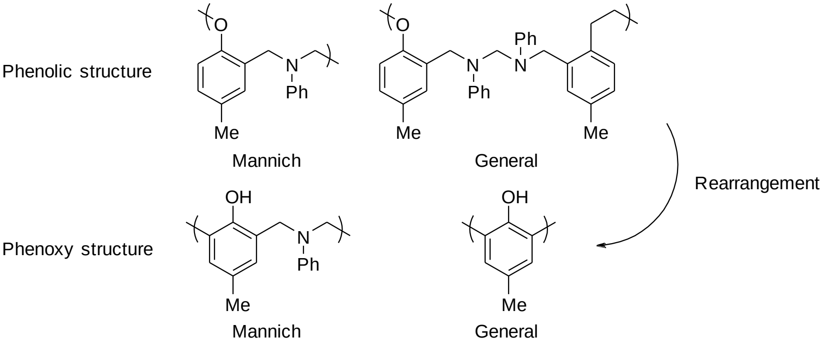
The three intermediates can then react *via O*-attack, *N*-attack or *aryl*-attack with another benzoxazine monomer resulting in the chain-propagation (Scheme 3). [54]

The *aryl*-attack of the intermediates can take place at various positions of a benzene ring, also including arylamines and arylaldehydes, whereas all reaction sites have a different reactivity. The electrophilic attacks ultimately lead to either a phenoxy-type or a phenolic-type structure, whereas longer reaction times or higher polymerization temperatures cause the rearrangement of phenoxy type structures into phenolic ones (Scheme 4). Additionally, a less common mechanism for benzoxazine polymerization is realized by the nucleophilic ROP. This will not be discussed as the compounds used in this work mainly react by cationic ROP. Overall, the various intermediates, potential reaction pathways and rearrangement reactions are the reason for the complexity of benzoxazine polymerizations. [53]

Besides the functionality, the network of the polybenzoxazines change drastically depending on the monomer’s substitution pattern as well.



Scheme 3. Reaction pathways for aryl-, O- and N-attacks for ring-opened intermediates, e.g., shown for the intermediate from Scheme 2.



Scheme 4. Rearrangement from phenoxy into phenolic structure.

In the phenol-based 1,3-benzoxazine the ortho, meta and para position are free to attack. In studies it was evaluated that mainly the ortho and para position are participating in the ROP of benzoxazines. By blocking these positions, the ability to polymerize decreases and this leads to a higher temperature for the polymerization's start (T_{onset}) and a lower T_g. As a result, highly substituted monofunctional benzoxazines exhibit lower cross-linking densities. [55]

Further analysis on the substitution effect on the ROP were performed by Martos *et al*. For this, they used different functional groups both electron donating and electron withdrawing groups, that in- or decreased the electro-negativity on the phenol. Both kinds of groups accelerate the polymerization process. Furthermore, it was indicated that electron-withdrawing groups induce a spontaneous or nucleophilically promoted ROP, whereas electron-donating substituents promote the polymerization *via* protonation. [56]

The temperature for the ROP of benzoxazines could be reduced to 120-180 °C by using nucleophilic and polar groups as substituents for the nitrogen-sided aryl moiety. More precisely, hydroxyl and carboxylate groups affect intramolecularly the ring-opened iminium moiety in the zwitterionic intermediate. Thus, the reverse cyclization of the intermediate into the benzoxazine moiety is prevented. As a result, it increases the intermolecular reaction rate of the phenoxide moiety and the chain propagation grows faster. [57] [58], [44]

2.1.3 Catalysts for the ROP

An auto-catalyzed process until vitrification is reached, from which onwards diffusion is the main controlling force, is the nature of benzoxazines ROP. [14], [59], [60] Therefore, potential catalysts should accelerate the ring-opening step of the polymerization. The catalysts need to coordinate effectively with either oxygen or nitrogen atoms to form the iminium cationic intermediate. Furthermore, favoring the formation of the more stable phenolic structure would be beneficial.

Acidic components, which accelerate the polymerization in a typical cationic pattern are most reported catalysts. Effective but less often described basic catalysts exist that accelerate the benzoxazine polymerization in a nucleophilic ring-opening manor.

Typical Lewis acids like $AlCl_3$, $TiCl_4$ or $POCl_3$ were used and verified as catalysts for benzoxazine’s cationic polymerization. [40] Beside Lewis acids, also carboxylic acids can be used whereby a differentiation between strong and weak carboxylic acids is observed. [52], [61] The use of trifluoroacetic acid shows the immediate ring-opening step followed by the electrophilic substitution step *via* a cationic iminium intermediate. [43] Furthermore, the use of weak carboxylic acids leads to the formation of ammino methyl esters. Those react into the active iminium ion and the electrophilic substitution takes place.

By comparing two different acidic catalysts like 3,3’-thiodipropionic acid (TDA) and 3,3’-thiodiphenol (TDP) it was observed that both catalysts influence the progress and termination of the polymerization differently, leading to distinct final properties. [52] The neat thermal polymerization and TDP catalyzed polymerization result both in a similar polybenzoxazine network with similar cross-linking densities and therefore, similar T_g values. However, by using the more acidic TDA the polymerization mechanism changed. Due to an increased number of ring-opened monomers the chain propagation became more branched which resulted in more reaction sites with a higher number of cross-links and subsequently, a higher T_g. However, in general weaker acids show an increased performance on the final properties in comparison to strong acids. [62] Furthermore, the formation of reactive phenolic intermediates during the ROP leads to an autocatalyzed polymerization process. [60] Therefore, the effect of various phenols like e.g. resorcinol, cresol or nitrophenol was investigated and shows a beneficial effect on the reduction of the temperature at which ROP takes place. *p*-Toluenesulfonic acid (PTS) as well as thiophenols are found as other cationic catalysts. [63], [64]

Some amines and imidazoles show promising results to accelerate the polymerization of benzoxazines. [42], [45], [46] However, they draw out less attention than the various acidic catalysts. This is mainly a result of their lower effectivity.

In a study of different basic catalysts it was shown that 1,8-diazabicyclo[5.4.0]undec-7-ene, 4-dimethylaminopyridine, and tributylphosphane have an increased effectivity while 2-ethyl-4-methylimidazole (EMI) show less impact and triphenylphosphate barely shift the polymerization onset temperature. [62] Overall, the influence of neat basic catalyst seems lower as for acidic catalysts.

In many cases, depending on the catalyst system, both anionic and cationic polymerization pathways may exist simultaneously. Therefore, an optimal catalyst system would contain a cationic part with an affinity toward oxygen and/or nitrogen as well as an anionic part with an aptitude for nucleophilic attacks and a good leaving group.

PTS and EMI were investigated as a dual catalyst system to obtain an insight on the influence of catalysts during different polymerization steps. [42] PTS acts advantageous for the C-O dissociation of benzoxazines, whereas the nucleophile EMI facilitates the C-O dissociation and prevents the recombination with the phenolic hydroxy groups. Therefore, the dual catalyst system helps to rearrange the main chain structure from phenoxy into the phenolic type of structure and therefore acts in a later stage as the ring-opening step.

Generally, the catalysts show their strongest impact on the ring-opening step. However, the impact on the later stages connected to the cross-linking is lower. [14], [59], [60] This might be related to a decreased freedom of motion as beside increased viscosity due to ongoing polymerization a hydrogen-bonding network is formed, which also increases the viscosity. Furthermore, the catalysts often have less influence on the rearrangement from