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Perspectives on the Curing of Benzoxazine Resins

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Abstract:

Benzoxazines are a class of heterocyclic compounds that can be polymerized to form polybenzoxazines, which have excellent properties such as thermal stability, flame retardance, low shrinkage, and chemical resistance. The curing of benzoxazines involves a thermal cationic ring-opening polymerization, which can be influenced by various factors such as catalysts, co-monomers, temperature, and time. In general, the curing temperatures of benzoxazines are considered as high and lie between 180 ºC and 260 ºC depending on the monomer structure. This nature of benzoxazine resins could limit their wider applications in different areas. Therefore, lowering the curing temperatures could play a critical role in the benzoxazine resin chemistry. This review summarizes the recent advances in the understanding of the curing mechanisms of benzoxazine resins, with a focus on the factors influencing the curing kinetics and the resulting material properties.

Keywords: Benzoxazines, polybenzoxazine, ring-opening polymerization, catalysis

Benzoksazin Reçinlerinin Kürlenmesi Üzerine Perspektif

Özet:

Benzokazinler, bir heterosiklik bileşik sınıfıdır ve polimerleştirilerek polibenzoksazinlere dönüştürülebilirler. Polibenzokazinlerin genel özellikleri sırasıyla termal kararlılık, alev geciktirme, oluşumları sırasında boyutsal kararlılık ve kimyasallara, asit ve bazlara karşı yüksek gösterirler. Benzokazinlerin kürlenmeleri, çeşitli faktörler tarafından etkilenebilen termal olarak tetiklene ve sürdürülen katyonik halka açılım polimerizasyonunu şeklindedir. Bu faktörler arasında katalizörler, ko-monomerler, sıcaklık ve kürlenme zamanı bulunmaktadır. Genel olarak, benzokazinlerin kürlenme sıcaklıkları yüksek olarak kabul edilir ve monomerin yapısına bağlı olarak 180 ºC ile 260 ºC arasında değişir. Benzokazin reçinelerin bu doğası, farklı alanlarda daha geniş uygulamalarını sınırlayabilir. Bu nedenle, kürleme sıcaklıklarını düşürmek, benzokazin reçine kimyasında kritik bir rol oynayabilir. Bu derleme, benzokazin reçinelerinin kürlenme mekanizmalarının anlaşılmasında son zamanlardaki ilerlemeleri, kürlenme kinetiğini etkileyen faktörleri ve ortaya çıkan malzeme özelliklerini özetlemektedir.

Anahtar Kelimeler: Benzoksazin, polibenzoksazin, halka açılma polimerizasyonu, kataliz

REVIEW

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1. Introduction

Classical phenolic resins, namely phenol-formaldehyde resins, have maintained a continuous interest in the industry since their first production at the beginning of the 1900s. Especially, phenolic resins are still widely preferred for commodity production, construction, and even for high-tech materials, due to their noteworthy features. These properties can be given shortly as good mechanical and thermal performance, resistance to various chemicals, acids, and bases. Additionally, they exhibit good performance under fire, and emit relatively low amounts of smoke, when exposed to flames. Therefore, phenolic resins can compete with systems based on epoxy in thermo-structural applications within the aerospace industry. Phenolic resins such as Novolac and Resol are the second dominant polymer class, after epoxy resins when fundamental properties of high-performance materials are considered for applications (Kiskan & Yagci, 2020; Pilato, 2010).

Moreover, phenolic resins can be modified to enhance their properties. For example, boron-modified phenolic resins (BPF) have excellent heat resistance and ablative properties, good mechanical and wear resistance, and flame retardancy. Alternatively, lignin is a promising substitute for phenol in phenolic resin production and can be obtained from biomass. These

modified resins can be used as adhesives for wood-based products(Zakzeski et al., 2010).

On the other hand, another noteworthy phenolic system is polybenzoxazines. Particularly, these polymers are strong contenders to Novolac. Because the structure of polybenzoxazines resembles the Novolac molecular structure to a high extent. Therefore, polybenzoxazines were commercialized successfully among the hundreds of other polymers introduced in scientific literature (Ghosh et al., 2007; Nair, 2004).

As stated, polybenzoxazines share some structural units with Novolacs, thus they inherit many similar properties. However, they differ in repeat units compared to Novolacs. They contain phenolic –OH and –CH_2–NR–CH_2– bridges in close proximity (see Scheme 1). This unique structure creates inter- and intra-molecular hydrogen bonds between these groups and significantly influences the orientation of polymer chains (Ishida & Agag, 2011).

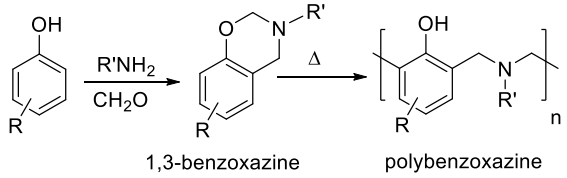
Typically, polybenzoxazines exhibit key characteristics, including minimal shrinkage during curing, high mechanical strength, a high glass transition temperature (T_g) and can reach as much as 350 °C, and a good amount of char yields above 600 ºC. Additionally, these polymers exhibit chemical resistance against acids and bases similar to Novolac resins. And interestingly, polybenzoxazines differ from Novolacs extensively when compared to water absorption because polybenzoxazines display low water adsorption, as a consequence of intramolecular hydrogen bonding. The appealing properties of polybenzoxazines captured much interest from the industry and led to diverse applications of polybenzoxazines, particularly in composites, electronic circuit boards, and high-performance material production (Ishida & Agag, 2011)

The benzoxazine structure has different isomers (1,2–, 1,4–, and 3,1–), but it is known that only the 1,3-isomers could be polymerized to produce polybenzoxazines until this date. Although benzoxazines could act as monomers for polybenzoxazine production this property was unknown at the initial introduction of these molecules.(Ishida & Agag, 2011) The initial synthesis of 1,3-benzoxazines was documented in 1944. The standard method for synthesizing benzoxazines requires using one equivalent of phenol (or diphenol or multifunctional phenols), one equivalent of primary amine, and two equivalents of formaldehyde. This synthesis involves both Mannich and simultaneous ring-closure reactions. To achieve ring-closure reaction, it is essential to choose a phenol with an unoccupied ortho position. (Scheme 1) (Burke, 1949; Burke et al., 1952; Burke et al., 1954; Burke & Weatherbee, 1950; Holly & Cope, 1944).

While benzoxazines have been in the scientific spotlight since the 1940s, their early applications in the 1950s and 60s were primarily centered around exploring potential medicinal effects against tumors. Unfortunately, the 1,3-benzoxazine isomer showed limited efficacy, prompting a shift in research focus toward other oxazine isomers and oxazinones. After having more insights into the limited medicinal capacity of 1,3-benzoxazines. The research on 1,3-benzoxazine chemistry continued sluggishly until 1973 (Burke et al., 1965; Gaines & Swanson, 1971; Schreiber H, 1973).

The potential of these compounds as monomers in polymer science gained recognition in 1973 with a patent of Schreiber on the formation of oligobenzoxazines from 1,3-benzoxazines. Thereafter, the breakthrough continued in 1985 with the patenting of a thermoset based on polybenzoxazine obtained from multifunctional benzoxazines. The detailed properties of polybenzoxazines were finally revealed in 1994 by Ning and Ishida, as a significant milestone in the exploration of these compounds in polymer and material science (Higginbottom, 1985; Ning & Ishida, 1994; Schreiber H, 1973).

Subsequently, numerous reports were published about various aspects of benzoxazine polymerization, their distinctive features, curing behaviors, and more.(Ghosh et al., 2007) Notably, these studies highlighted that the polymerization of benzoxazines could be achieved by directly heating monomers to temperatures ranging from 180 to 250 °C, which is the common method without the use of catalysts, as depicted in Scheme 1. The curing temperature is a critical parameter that affects the properties of benzoxazines. Higher curing temperatures generally lead to higher crosslinking density, which results in improved mechanical and thermal properties of the cured polymers. However, excessively high curing temperatures can cause thermal degradation and adversely affect the properties of the cured polymers (Pei et al., 2021).

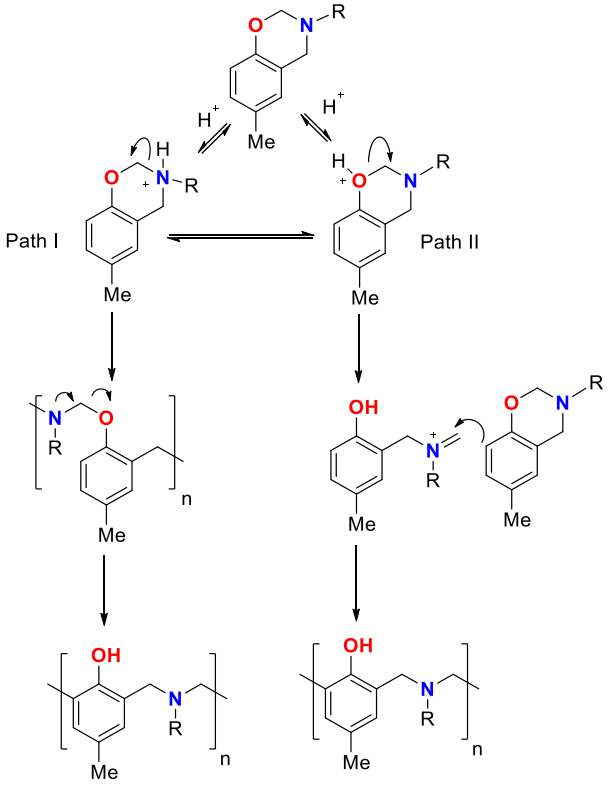


Scheme 1. Synthesis and ring-opening polymerization of 1,3-benzoxazines.

The curing behavior of benzoxazines is affected by several factors, such as the structure and reactivity of the monomers, the presence and type of catalysts, the ratio and compatibility of co-monomers, the curing temperature and time, and the degree of conversion. These factors can influence the kinetics, thermodynamics, gelation, network formation, and properties of the cured polybenzoxazines. Therefore, it is important to understand the curing process of benzoxazines to optimize their performance and applications (Jubsilp et al., 2006; Kim et al., 1999).

According to mechanistic studies, a general consensus developed on the major pathways of curing reactions of benzoxazines. Accordingly, the polymerization of benzoxazines occurs via a cationic pathway initiated by the reaction of the residual phenolic –OH groups of the monomers. This process can be summarized as follows; Protonation: There are two protonation possibilities, either on the N or O atom, leading to two different routes for the initiation of polymerization. Initiation: The protonated N and O atoms present on the oxazine ring form relatively stabilized cations, and then ring-opening takes place. Propagation: After the formation of cationic intermediates an electrophilic aromatic substitution or etherification over phenolic oxygen takes place to form benzoxazine dimer. Then, the repetitions of the abovementioned reactions create polybenzoxazine. Although the initiation site affects the intermediates and creates different pathways for ring-opening polymerization the final polymer structure is considered to be the same for all pathways because the aryl ether structure undergoes a rearrangement reaction to form polybenzoxazine (Scheme 2). However, there are some restrictions to consider such as high curing temperatures. The polymerization of benzoxazines does not require additional catalysts or curative, but high curing temperatures are a limitation. Because high temperatures result in high amount of energy consumption and degrade the thermally susceptible functional groups on polybenzoxazines (Chutayothin & Ishida, 2010; Furuncuoğlu Özaltın et al., 2018; Hamerton et al., 2013; Kasapoglu et al., 2003; Urbaniak et al., 2017; Wang et al., 2020).

Therefore, lower ring-opening polymerization (ROP) temperatures would be significant. This perspective article summarizes the major strategies that are used to overcome the high ring opening polymerization temperatures of benzoxazines. And provides insights into the polymerization part of the benzoxazine chemistry.



Scheme 2. The summarized mechanism for ring-opening polymerization of a typical benzoxazine

2. Major Strategies to Reduce the Cure Temperature of Benzoxazines

The polymerization of benzoxazines is a complex process involving cationic initiation, protonation, and ring-opening. Lower ROP temperatures would be beneficial for energy economy and to prevent thermally susceptible functional groups on polybenzoxazines from degradation. Further research is needed to develop methods for reducing the curing temperature and optimizing the polymerization process.

To reduce the high curing temperatures required for the ring-opening polymerization (ROP) of benzoxazines, various catalysts have been employed, including organic or Lewis acids and compounds with nucleophilic character. For example, PCl_5, $POCl_3$, $AlCl_3$, $TiCl_4$, and $FeCl_3$ with suitable solvents have been shown to have good catalytic activities. The use of a mixture of a Lewis acid and a nucleophilic catalyst has also been found to be effective in promoting the polymerization, with acetylacetonato complexes of transition metals of the 4th period acting as highly efficient catalysts. However, these active catalysts often initiate ROP of benzoxazines at room temperature and can increase the viscosity of benzoxazine based formulations significantly prior to usage and during storage. Therefore, these catalyst administrations can reduce the shelf life of benzoxazine formulations in practical use. To overcome this problem, latent catalysts that are dormant at room temperature or certain temperatures but generate active initiators by heating have been developed. For example, diamines, thiols, elemental sulfur and toluene sulfonates have been successfully used to reduce ROP temperatures for classical mono- and di-functional benzoxazines.

Specially designed benzoxazine monomers with free phenolic -OH groups or naphthoxazines have also been found to reduce the ROP temperature to certain values. In conclusion, various catalysts have been employed to reduce the high curing temperatures required for the ROP of benzoxazines. While admixed catalysts can initiate ROP at room temperature, latent catalysts that generate active initiators by heating have been developed to overcome this problem. Further research is needed to optimize the polymerization process and reduce the curing temperature of benzoxazines. Accordingly, this manuscript discusses the major strategies to reduce the cure temperature of benzoxazines (Akkus et al., 2019, 2020; Coban et al., 2021; Deliballi et al., 2021; Espinosa et al., 2003; Kaya et al., 2018; Kocaarslan et al., 2017; Kudoh et al., 2010; Liu et al., 2013; Liu, Shen, Sebastián, et al., 2011; Lochab et al., 2021; Oie et al., 2010; Sudo et al., 2010)

2.1 Acid Catalyzed Systems

Acidic initiators are commonly preferred for their commercial availability and different acidic strengths, which makes them good candidate to mediate cationic ring-opening polymerization (ROP) of benzoxazines. These acid initiators can protonate oxygen or the nitrogen atom of the oxazine ring, facilitating the formation of intermediate iminium ions (see Scheme 2). The protonation of nitrogen atom resulting an iminium ion intermediate, which is relatively a stable cationic species. Consecutive electrophilic reactions result in O-attack, N-attack, and aryl-attack on the benzoxazine monomer which then led to the growth of the polymer. Due to the N and O attacks the polymer may contain phenoxy and phenolic linkages. When ortho-positions are obstructed either by a steric hindrance or a functional group the polymerization is anticipated to take place at an accessible para-position to the benzoxazine ring. In summary, acidic initiators play a crucial role in mediating the cationic ROP of benzoxazines by protonating the oxygen or nitrogen atom of the oxazine ring, leading to the formation of stable iminium ion intermediates and subsequent polymer growth. This mechanism is essential for understanding the polymerization process and optimizing the synthesis of benzoxazine-based polymers (Andreu et al., 2008; Dunkers & Ishida, 1999; Kim & Ishida, 2001; Yagci et al., 2009; Zúñiga et al., 2011).

Ishida *et al.* (Ishida & Rodriguez, 1995) examined the utilization of phenols possessing an unoccupied ortho-position, such as butylated hydroxyanisole (BA), poly(p-hydroxystyrene), 2,2'-dihydroxybenzophenone, and 2,6-di-tert-butyl-p-cresol. They also investigated both mild and strong organic and mineral acids, including acetic, adipic, benzoic, sebacic, sulfuric, *p*-toluenesulfonic, and phosphoric acids, as catalysts for the ring-opening polymerization of the benzoxazine monomer. Among these, adipic acid at 6 mol% was found to be the most effective catalyst, demonstrating a significant 17% decrease in the curing temperature.

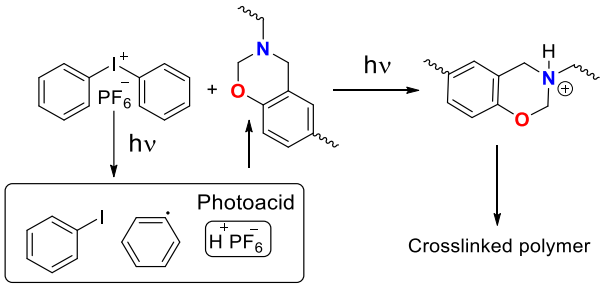
Interestingly, polybenzoxazines (PBZs) produced with strong carboxylic acids exhibited inferior properties compared to those formed with weak carboxylic acids. The acidity level, as indicated by the pKa of the acid, was identified as a crucial factor controlling the conversion of the intermediates, thereby influencing crosslinking of the system. The characteristic IR vibrations of oxazine ring at 1050 and 813 cm^{-1} exhibited a more rapid decrease in the presence of *p*-cresol (pKa = 10.2) compared to sebacic acid (pKa = 4.7, 5.4), supporting the notion that *p*-cresol mediates a faster oxazine ring-opening reaction.

Ishida and colleagues (Ishida & Rodriguez, 1995) provided more insights into the impact of phenols on the polymerization reaction and its associated pathways by investigating the reaction between 2,4-xylenol and 3-aryl substituted benzoxazine. This investigation revealed the formation of various inter- and intra-molecular rearranged products as intermediate species. Notably, Bisphenol F was found to be a more effective catalyst than BA, possibly due to the distinct electron-donating capabilities of the methylene versus isopropylidene bridge in biphenols. Furthermore, a substantial loading (~40 wt%) of cashew nut shell liquid (CNSL, contains phenolic compounds) in bisphenol A-aniline benzoxazine led to a decrease in both peak temperature and ΔH from 216 °C

and 246 J.g^{-1} to 197 °C and 194 J.g^{-1}, respectively. The ring opening polymerization reaction demonstrated an autocatalytic nature due to the formation of ring-opened phenolic structures after each addition of benzoxazine. For instance, resorcinol-aniline (Rc-a) benzoxazine exhibited polymerization at a much lower temperature compared to phenol-aniline (Ph-a), attributed to the formation of two phenolic –OH groups in the structure of Rc-a versus one in Ph-a. The presence of a low amount of phenols serves as an initiator, impacting the rate and temperature that are required for the successful ring-opening polymerization reaction.

Hamerton *et al.* reported that 3,3-thiodipropionic acid (TDA), with a higher pKa value (4.11), acts as a superior initiator compared to 3,3-thiodiphenol, resulting in a reduction of cure T_{onset} and a simultaneous increase in crosslink density, reflected in a higher T_g value in the resulting polymer. Additionally, renewable phenolic acids such as cinnamic, coumaric, ferulic, and phloretic acids were employed as catalysts to lower the polymerization temperature of the reaction (Hamerton et al., 2013).

The use of diphenyliodonium ($Ph_2I^+PF_6^-$) and triphenylsulfonium ($Ph_3S^+PF_6^-$) salts in photoinitiated cationic polymerization has been shown to result in the light-induced formation of protons, leading to the formation of polybenzoxazine with a 72% conversion (Scheme 3). At high monomer concentrations (>0.5 mol L^{-1}), oligomer formation occurred, indicating chain transfer reactions that have negative impact on polymerization. Additionally, carbon-centered radicals generated by the photolysis of 2,2-Dimethoxy-2-phenylacetophenone (DMPA) undergo oxidation to form the corresponding carbocations, initiating the polymerization of the monomer. Despite being initially considered moderate initiators, diphenyliodonium salts (ArI^+ X^-) have proven highly effective as photoinitiators. In their presence, the polymerization profiles of BA-a exhibited a broader curing exotherm at 162 °C. The polymerization takes place such as the decomposition of iodon,um salt and formation of H^+X^-, and the second step is protonation of benzoxazines and the initiation ring-opening. These findings highlight the effectiveness of diphenyliodonium and triphenylsulfonium salts as photoinitiators for cationic polymerization, with implications for the polymerization profiles and initiation activity of the photoinitiator salt (Deliballi et al., 2021; Kasapoglu et al., 2003).

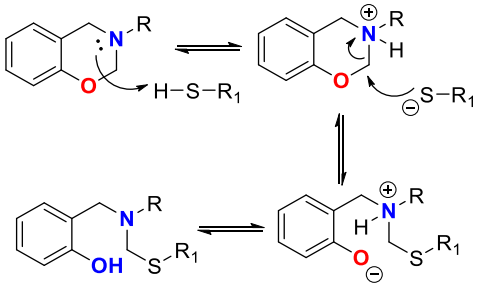


Scheme 3. Curing of benzoxazines via iodonium salt

Alternatively, cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) was also used in the curing of benzoxazines. The mechanism lies on the reaction of cyanuric chloride with humidity or other nucleophiles to produce acids (HCl and cyanuric acid) *in situ* for initiating ROP of Bz (Akkus et al., 2020).

Unlike phenols, thiophenols exhibit a reversible reaction with benzoxazine (Bz) monomers at room temperature, making them particularly promising for practical applications. Thiol compounds demonstrate greater efficiency at concentrations due to their hydrogen-donating capability. In 2011, Gorodisher et al. reported on the reaction of thiols with benzoxazines for adhesive purposes. This reaction was introduced as Catalytic Opening of the Lateral Benzoxazine Rings by Thiols (COLBERT) (Scheme 4). The initial step involves the protonation of the nitrogen atom by thiol, followed by the attack of thiolate ion to the methylene group on -N-CH_2-O- group, facilitating the oxazine ring-opening reaction. This overall process mirrors the acid-catalyzed nucleophilic addition that triggers ring-opening reaction of benzoxazines. Due to the reversible nature of the reaction, even low concentrations of thiols have a notable impact on reducing the polymerization temperature, as evident in the DSC studies. This reduction is attributed to the continuous regeneration of the thiol and iminium ion which, catalyze the polymerization reaction (Gorodisher et al., 2011; Gorodisher et al., 2013; Salnikov et al., 2014).

The rate-determining step of this reaction is found as the protonation of the N or O atom, which was supported by inhibitors. Moreover, mechanistic studies revealed that the reaction rate is significantly influenced by the acidity of the thiol and the nature of the solvent (protic vs. aprotic). Kawaguchi *et al.* investigated the interaction between *p*-cresol-anilin type benzoxazine (*p*C-a) and p-methoxythiophenol (pMOTPH), resulting in the formation of a ring-opened adduct. In these studies the reversible nature of the polymerization-depolymerization reaction was also shown. The yield of the adduct is observed to be higher in polar solvents unlike nonpolar solvents. This finding is attributed to the stabilization zwitterion/ammonium cation intermediates in polar solvents (Asei William Kawaguchi et al., 2012; Asei W. Kawaguchi et al., 2012; Kawaguchi et al., 2014).



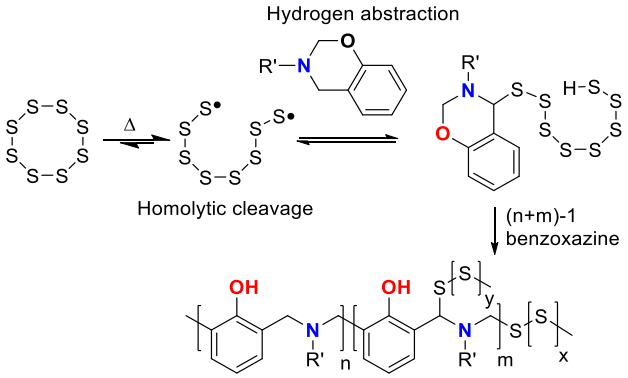
Scheme 4. Thiol initiated ROP of benzoxazines

Beyond monomers, the polymerization of main-chain type polybenzoxazine (PBz) was carried out at room temperature using different thiols, such as 1-butanthiol, 2-ethanethiol and thiophenol, in a $CH_3OH/CHCl_3$ solvent mixture over a 24-hour period. The successful integration of thiol compounds into PBz was validated through spectral and molecular weight characterizations (Bektas et al., 2015; Beyazkilic et al., 2012).

Urbaniak and colleagues proposed a mechanism wherein the reversible ring-opening of 1,3-benzoxazine with thiols occurs through an iminium ion intermediate. They suggested that the cyclic six-membered transition state had less effect on the reversible reaction. Their work clearly reveal the significance of the protonation step of benzoxazine with thiols under solvent/solvent-free conditions, wherein acidity dominates the nucleophilicity (Urbaniak et al., 2017).

In addition to thiol reagents, elemental sulfur (S) has been observed to lower the polymerization temperature of benzoxazine monomer. For instance, Shukla and colleagues demonstrated a reduction in peak temperature of pC-a monomer from 263°C to 185°C in the to a copolymerization (C-a and S_8) reaction temperature. Similarly, a significant ROP temperature reduction with sulfurs was reported by Arslan *et al.*(Akay et al., 2017; Arslan et al., 2016; Shukla et al., 2016)

The proposed mechanism suggests that generated (*in situ*) sulfur radicals react with the oxazine ring and abstract hydrogen atom from methylene linkages of oxazine. The abstracted hydrogen combines with sulfur radicals to form thiols and then thiols protonate the oxazine ring to open and then to form poly(C-a-*ran*-S) (Scheme 5). These copolymers containing sulfur have been utilized as cathodic materials in Li-S and Na-S batteries.

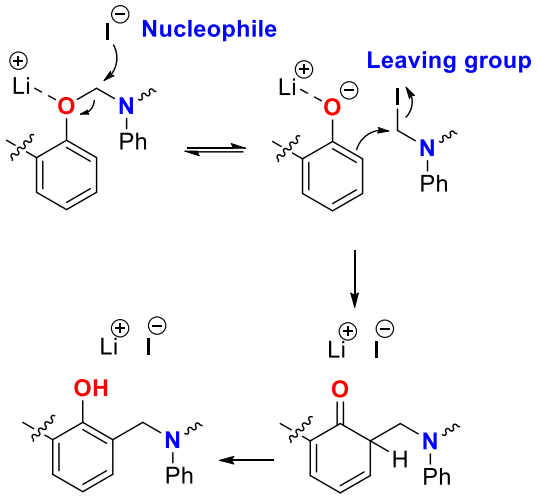


Scheme 5. Polymerization of benzoxazines via elemental sulfur

2.2. Salt and Nucleophile Catalyzed Systems

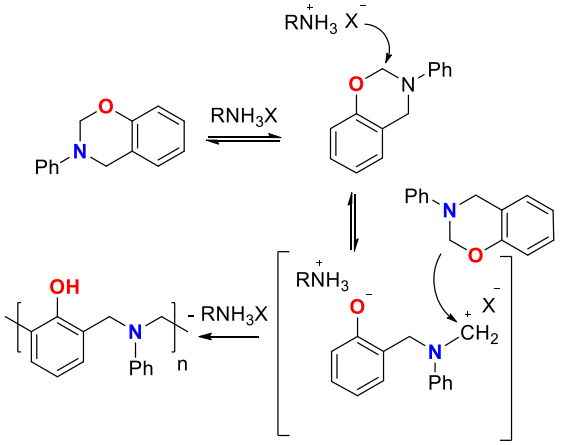
The processability and compatibility of many resins depend on the low polymerization temperature. This requirement is also valid for benzoxazine resins. One of the methods to achieve this goal is to mix Bz monomer with various salts. As well-known salts are consisted of anions and counter cations. While the cation part of the salt coordinates the oxygen atom in the oxazine ring during ring opening, the anion part acts as a nucleophile. The fact that the nucleophile is also a good leaving group accelerates the process. For this purpose, *Liu et al*. used LiI, LiBr, NaI, and LiBr/NaI salts and found that LiI was the most effective salt among these salts (Liu, Shen, Sebastián, et al., 2011). A mechanism for ring-opening of benzoxazines was proposed is shown in the Scheme 6.

Similarly, Kocaarslan *et al.* investigated the ROP of Bz using various amine HCl salts (NH_3OHCl, $PhNH_3Cl$, $PhNHNH_3Cl$, NH_4Cl, $EtNH_3Cl$) as a catalyst in 2017. As a result of the study, they found that amine HCl salts reduced the maximum ROP temperatures in *e.g.* from 224 ºC to 185 ºC (Kocaarslan et al., 2017).



Scheme 6. The probable mechanism of ROP of BZ in the presence of LiI.

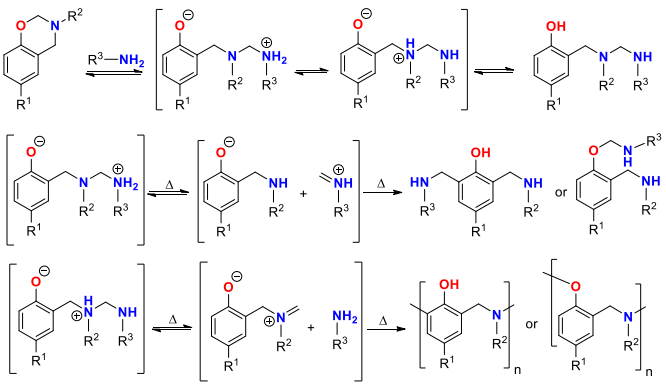
The effect of the nucleophilicity of counter ion of amine HX salts on the ROP of Bz was also studied (Scheme 7). The nucleophilicity of counter ions had shown significant effect on the ROP temperature. As nucleophilicity increases, a significant decrease in ROP temperature was observed. The general trend of reduction of ROP temperature was found to be in the order of $I^- > Br^- > Cl^-$. The study also revealed that the nucleophilic character of the counter ions, their solubility, and ionization ability of the salts in melt benzoxazine monomers had high impact on the catalytic ability (Akkus et al., 2019).



Scheme 7. Salt induced ROP of benzoxazines

In the study of Agag *et. al*. multiple exothermic peaks were observed at low temperatures in the ROP of the amine-functional benzoxazine (Agag et al., 2010). Accordingly, Sun *et. al.* reported a ring-opening addition reaction of benzoxazine with an amine (Sun et al., 2015). They suggested that polymerization occurred *via* a cationic mechanism (Scheme 8). In the beginning, a reversible reaction takes place between amine and benzoxazine resulting in the formation of zwitterionic intermediates with both phenolate and aminomethanaminium structures. When heated at high temperatures, aminomethanaminium generates iminium ion and these ions undergo electrophilic reactions with the aromatic ring, leading to the formation of a stable aminomethylphenols. The involvement of amines in polymerization allows the process to occur at lower temperatures (around 120 –150 ºC), leading to faster reaction rates. The activation energy (E_a) for polymerization reactions follows the basicity order of amines, with arylamine being greater than alicyclic amine, which is greater than alkylamine.

Amines, such as primary, secondary, and tertiary amines, play a crucial role in facilitating the ring-opening reaction of mono-oxazine in polar solvents. This allows for crosslinking reactions to occur when diamine reacts with bis-benzoxazine at room temperature (Zong & Ran, 2019).



Scheme 8. ROP of benzoxazines via amine catalyst

3. Conclusion

The focus of this review is to shed light on the significance of choosing the right benzoxazine polymerization conditions when designing polybenzoxazine based materials. The structure of Bz monomers greatly impacts the formation of polymers and their subsequent applications. On the other hand, efforts to lower the polymerization temperature continue to advance, either by molecular tailoring on the benzoxazine monomers or by adding external curatives/catalysts and/or copolymerization with other polymer structures. Accordingly, in this review the use of catalysis for benzoxazine resins was

emphasized, where catalysts play a vital role in controlling polymerization and tailoring polymer properties. Moreover, this review provides insights into catalyst selection and optimization that significantly impact efficiency and kinetics benzoxazine resin polymerization. Therefore, this manuscript could elevate research and broaden polybenzoxazine scopes, particularly for low polymerization temperatures of benzoxazines where needed.

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