



## Thermally curable main-chain benzoxazine prepolymers via polycondensation route

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### ABSTRACT

Polybenzoxazines are addition-cure thermosetting polymers exhibiting versatility in a wide range of applications due to their good mechanical properties, dimensional stability, chemical resistivity, flame resistance property phenolic or epoxy resins have myriad applications in diverse fields starting from commodity materials to high technology aerospace industries. In this paper, we present synthetic strategies to incorporate thermally curable benzoxazine functionality into polymers as main-chain fashion in order to further improve various properties. The strategies successfully employed including monomer synthesis and polycondensation routes like Mannich reaction, click chemistry, hydrosilylations, and coupling reactions. The structure–property relationships of the cured materials have also been presented and discussed.

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### 1. Introduction

Polybenzoxazines are addition-cure phenolic systems, having a wide range of fascinating features, which overcome several shortcomings of conventional novolac and resole type phenolic resins. Accordingly, they have a good combination of attractive properties, can be useful for a wide range of applications from composite materials [1] to printed circuit boards, etc., such as (i) no strong acid catalysts required for curing, (ii) high char yield, (iii) high glass transition temperatures, in some cases higher than cure temperature, (iv) low water absorption, (v) near zero volumetric change upon curing, and (vi) release of no or limited by-product during curing, which can be important for environmental issues. The cured materials also possess thermal and flame retarding properties of phenolics along with improved mechanical performance [2,3]. The dimensional stability during polymerization is a noteworthy feature stemming from the ring opening polymerization of their monomers [4]. And this polymerization is a thermally induced self-polymerization taking place without any initiator or curative (Scheme 1) [5,6]. Moreover, it was shown that benzoxazines can also be polymerized by photochemical means. The structures of the polymers prepared by photoinitiated cationic polymerization were complex and related to the ring-opening

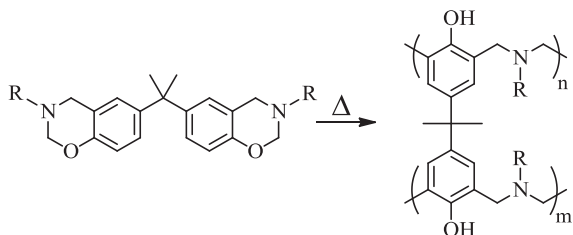
process of the protonated monomer either at the oxygen or nitrogen atoms [7].

Even though benzoxazines were first synthesized by Cope and Holly in 1940s [8], the potency of polybenzoxazines has been recognized much later and the interest in this area has gained attention and increasing number of researches are being involved in polybenzoxazine chemistry [9–12]. Accordingly, there has been a massive work on new monomers to improve thermal and mechanical performance of polybenzoxazines and also develop new application fields by taking advantage of design flexibility of benzoxazine monomers coming from simple preparation by using inexpensive and commercially available phenols, primary amines, and formaldehyde [13–22] (see Scheme 2).

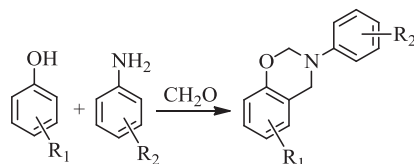
Typically, various new benzoxazine monomers with additional polymerizable groups were developed to increase the crosslinking density and glass transition temperature [23–27]. However, in practical applications some limitations emerged from the use of monomer precursors, since fabrication of films from monomers is rather difficult and most of the monomers are in powder form. Apparently, there are only few examples for liquid monomers [17,24]. Additionally, the formed polymers from especially monofunctional benzoxazines are brittle as a consequence of the low molecular weight of the network structure. To overcome these problems, new strategies involving synthesis of linear benzoxazine polymers as curable precursors have been developed. This way, some properties of polymeric structures such as processibility, flexibility, high crosslink density after cure, reductions in the vapor pressure during process and fragility for cured end-structures were imparted to polybenzoxazines. In a way, polymeric benzoxazines

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**Scheme 1.** Thermally induced ring opening polymerization of bisbenzoxazine monomers.



**Scheme 2.** Synthesis of mono-functional 1,3-benzoxazines.

behave like a processable and crosslinkable thermoplastic polymer, and able to yield thermosets after thermally activated ring opening polymerization just simply by heating up to around 200 °C [28,29]. Thus, the resultant resin may present properties that are the combination of thermoplastic and thermosetting polymers. A wide range of chemistries such as polyesterification [30,31], Mannich type condensation using difunctional phenols or amines [32–35], coupling reactions [36,37], Huisgen type click reaction [38,39] can be utilized for the synthesis of new curable precursors. Obviously, each route would reflect the characteristics of the polymer formed and modify the properties of the resulting polybenzoxazines for specific applications. The above mentioned chemistries can be classified as polycondensation route, which are commonly used in polymer chemistry from research laboratories to industrial mass productions of polymers.

Taking into account the above described background, herein we present synthetic strategies to prepare main-chain benzoxazine functional polymers by taking advantage of various polymerization methods particularly polycondensation routes.

## 2. Main chain precursors via Mannich route

Liu and Ishida had shown the concept of oligomeric benzoxazine resins first where oxazine rings are in the main chain by using difunctional amine and phenols in Liu's Ph.D. thesis in 1995 [40]. Later, this concept was independently reported by Takeichi [33] and Ishida [35] as a simple route for obtaining polymers containing benzoxazine moieties in the main chain (Scheme 3). In recent studies, this strategy has been further expanded by differentiating diphenols and diamines for various application purposes [41,42]. The choice of the right conditions for the Mannich route is critical for attaining polymers with high yields and high number-average molecular weights ( $M_n$ ) with a minimum by-product formation. For example, polybenzoxazine precursors with  $M_n$  in the range of 2200–2600 g mol<sup>-1</sup> were obtained using CHCl<sub>3</sub> as solvent medium. However, in the case of toluene and 1,4-dioxane instead of soluble polybenzoxazine precursors only gels were

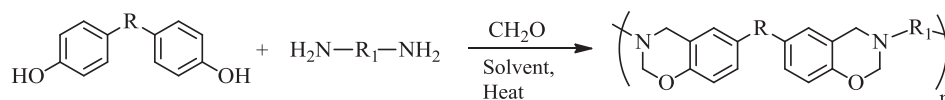
formed. Moreover, using toluene/ethanol mixtures as solvent resulted in soluble polymers in high yields with molecular weights as high as 24,000 Da [34]. Notably, the cross-linked polybenzoxazine films from the high molecular weight precursors obtained by using this method exhibited much higher toughness compared to the cured film from typical low molecular weight monomeric benzoxazines. Additionally, the viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were significantly high, i.e., 238–260 °C. And besides, these novel polybenzoxazine thermosets showed excellent thermal stability [41,42].

### 2.1. Aromatic and aliphatic main chain polycondensates

The first linear prepolymer with oxazine ring in the main chain was synthesized from an 4,4'-methylene-bis-(2,6-dimethylaniline), bisphenol-A and formaldehyde by Mannich condensation. But usage of aromatic diamine gave rigid polymers with low molecular weights and broad polydispersity. In order to increase solubility by using more flexible segments, a novel benzoxazine precursor with molecular weight of approximately 10,000 Da was prepared. The detailed spectroscopic analysis showed that linear polymeric chain ends contained phenol and methylol hydroxyl groups. Notably, the molecular distribution of the synthesized prepolymer was unexpectedly high. The determined polydispersity index (PDI = 3.0) was higher than the theoretical value of 2 for condensation polymers. This broadening on distribution was attributed to side reactions or Mannich bridge opening caused by the reaction of aminomethylol species with benzene ring in polymer chain. A low temperature exotherm (161 °C) recorded on thermal curing of this thermoplastic polymer is ascribed to the crosslinking of the methylol end groups [35].

In an independent study, aromatic or aliphatic diamines were used in conjunction with bisphenol-A giving linear polymeric precursors with cyclic benzoxazines in the main chain which are converted into flexible polymeric films under curing. The Mannich reaction produced a white powder polymer with 87% yield and relatively low molecular weight. In these polymer chains, ring-closed and ring-opened structures coexist randomly. After curing, the flexible, colorless and transparent polymeric benzoxazine precursor films showed improved toughness compared with the PB-a film and even 150 μm thick films could be easily bent. The preformed long precursor backbone provided high tensile strength and  $T_g$  values and as expected more aromatic group in the chain increased the modulus and thermal stability [33].

The main chain benzoxazine precursors were used to develop a new resin, namely transfer molding (RTM) resin offering desirable dimensional, physical and mechanical properties. The shortcomings of prepolymeric benzoxazines was attempted to overcome by using a flexible and thus more soluble segment like Bisphenol-F in the synthesis. Thus, an oligomer resin was prepared from isomeric mixture of more soluble segment Bisphenol-F, aniline and aromatic diamine by Mannich condensation ( $M_n = 1527$  g mol<sup>-1</sup>, PDI = 1.70). The viscosity of the resin which is a key factor for developing a new RTM material was measured by blending of oligomer with monomer to control the viscosity of the mixture. The viscosity was obtained as low as 1 Pa s at 120 °C for 50% monomer-oligomer mixture. On the other hand,  $T_g$  of the thermoset polymerized from oligobenzoxazine was as high as 213 °C. Besides



**Scheme 3.** Synthesis of main chain precursors via Mannich route.

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