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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.

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 catalyst 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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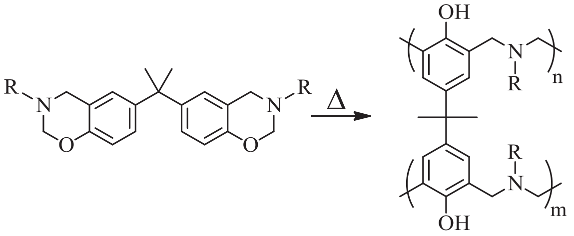
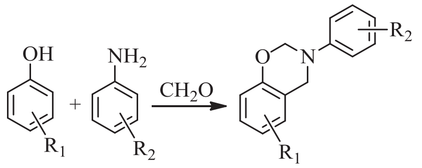


Scheme 1. Thermally induced ring opening polymerization of bisbenzoxazine monomers.



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

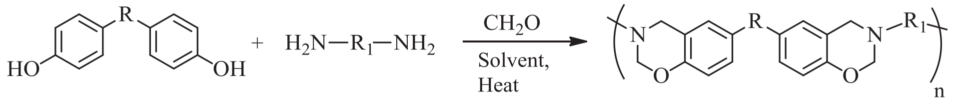
Liu and Ishida had shown the concept of oligomeric benzoxazine resins first where oxazine rings are in the main chain by using difunctional amine and phenols in Liu's Ph.D. thesis in 1995 [40]. Later, this concept was independently reported by Takeichi [33] and Ishida [35] as a simple route for obtaining 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^{-1} were obtained using $CHCl_3$ 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^{-1}, 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.

mechanical stability, the char yield of the cross-linked oligomer was 55% at 800 °C which is a 10% higher than that of the polymer equivalency [43].

A study on the preparation of main chain benzoxazine polymer was performed by using fluorinated diamines and diphenols and their properties were compared with hydrogenated analogous. The chemical structures of the polymeric benzoxazines were confirmed by spectral analysis and some methylol and phenolic groups were detected. The molecular weight of the polymers were around 6400–7300 Da with a broad distribution caused by incomplete conversion of the reaction. Two distinct exothermic peaks on the DSC thermograms of the aliphatic diamine based prepolymers were observed. The detected low temperature cross-linking was favored by the traces of methylol groups on the polymer which reacted with the oxazine ring during thermal treatment. On the other hand such hydroxyl by-products were not observed on the analysis of aromatic diamine based polymers [44].

There was a variation also in the form or type of hydrogen bonding of each polymer network. While aliphatic diamine based prepolymers generates OH···N intramolecular hydrogen bonding as evidenced by the strongest hydroxyl absorbance, the corresponding aromatic diamine based systems exhibit OH···O intermolecular hydrogen bonding. This bonding difference expressed itself in the dynamic mechanical properties of benzoxazines. In the transition zone, the storage modulus for the densely aromatic polymers was higher than that of the corresponding aliphatic counterpart. The glass transition temperature (T_g) and the storage modulus of the polymers at room temperature observed was close to the values of the most commonly studied polybenzoxazine, BA-a (bisphenol-A and aniline) and P-ad6 (phenol and hexanediamine). T_g was 20 °C higher in the aliphatic amine based polybenzoxazine than the aromatic based ones. Contrarily, as calculated from dynamic mechanical studies, the number of cross-links per chemical repeat unit was found to be higher for aromatic based polybenzoxazine due to the further attaching of the open oxazine rings to additional site by increasing the cross-linking of the material [44].

The important role of fluorine in the polymer chain was discerned during degradation process. The weight loss of the hydrogenated amine based polymers is faster than the fluoro substituted ones. Expectedly, the polymerization condition affects the fluorinated polybenzoxazines more than hydrogenated equivalencies. The thermal curing of prepolymers under nitrogen increased the T_g of the fluorinated materials around 40 °C compare to under air curing, whereas this difference was around 20 °C for hydrogenated diamine based polymers. Additionally, the high hydrophobicity, which is an important factor for the low dielectric constant materials, is another outstanding property of the highly fluorinated benzoxazine main chain prepolymers. The reduced dielectric constant is due to the strong electron-withdrawing inductive effect of the fluorine atom [44].

2.2. Polyetherdiamine based main chain polycondensates

The brittleness of polybenzoxazines was intended to be overcome by the incorporation of toughening agents like a long polyether backbone in the structure of the prepolymer. For this purpose, a series of highly viscous polyether-based main-chain benzoxazine polymers have been prepared from bisphenol-A and primary amine terminated Jeffamines, ED-600, ED-900, ED-2003. All synthesized polymers were soluble in common organic solvents such as toluene and chloroform. Moreover, a slight water and alcohol solubility was also achieved with increasing molecular weight of the poly(ethylene glycol) backbone. These prepolymers were viscous liquids at room temperature with increasing viscosity proportional to polyetheramine molecular weight [45].

The tough and flexible thermosetting materials could be produced from these polymeric benzoxazine precursors by thermal crosslinking. The length of the etheric chain in the polymeric benzoxazine affected the thermal ring opening polymerization characteristics. While the onset and maxima of the crosslinking increased by increasing poly(ether diamine) length in the polymer, the total enthalpies decreased due to the dilution effect of the oxazine ring in the polymeric precursor. Besides, the longer polyether diamine based benzoxazine main chain prepolymers showed lower T_g than that of the short chain precursors with a complex transition behavior because of the repressing of the extra-long polyether character on the benzoxazine structure. As the length of the polyether chain increased in these main chain benzoxazine prepolymers, the onset temperature of the degradation increased unexpectedly. It was explained in terms of thermally weak link arising from the higher concentration of C—N bond at the shorter polyether chain/benzoxazine linkage. However conversely, the char yield at 800 °C increased as the chain length decreased as a result of the high benzoxazine crosslinking density in the main chain. Additionally, the char yields of these polyether diamine based polybenzoxazines were found to be around 7–18% which is a rather low value compared to simple polybenzoxazines. Nevertheless, it is still remarkably high for elastomeric materials as the majority of the elastomers show near 0% char yield [45].

Multifunctional thermoplastic main-chain benzoxazine prepolymers were utilized as high performance toughener additives to obtain covalently bonded chemically induced phase separation (CIPS) morphologies in an adjustable manner. Thermally curable polymeric precursors were prepared by polycondensation of bisphenol-A with poly(propylene oxide) (PPO, Jeffamine D-2000) as aliphatic diamine and poly(tetramethylene oxide) (PTMO, Versalink P-1000) as aromatic diamine in the presence of paraformaldehyde. In this study, Taden et al. named these precursor series as TBox0 – Tbox100 (**T**hermoplastic main-chain **B**enz**ox**azine prepolymers) with a systematic variation in the PTMO/PPO ratio that allows the control of the micro-phase separation and morphology of polybenzoxazines. In the set of TBox, the polyethers were considered as soft segments whereas the benzoxazine units were hard segments since they covalently bonded to the network [46].

The viscosity of TBox prepolymers, with a molecular weight of around 15,000 Da and PDIs of around 3, was apparently influenced by the chain length of the polyetheric segment because of changing on the H-bonding and π–π interactions between the benzoxazine units. The open oxazine ring structures were detected on NMR analysis of these high molecular weight polymeric benzoxazines. The increase on the PTMO/PPO ratio increases also the hard/soft segment ratio due to the benzene rings coming from PTMO end functionalities, yielding a higher T_g value for the prepolymers. The same trend was also observed for thermally cured TBox homopolymers. The cured films of 2.5 mm in thickness were transparent and remarkably flexible. For morphological and mechanical investigations, the films composed of 3,3′-(methylene-di-4,1-phenylene)bis[3,4-dihydro-2H-1,3-benzoxazine](P-mda)/N-phenyl-3,4-dihydro-2H-1,3-benzoxazine(P-a) mixture as benzoxazine resin and TBox as a thermoplastic toughener in 20% weight ratio were prepared and cured. The transparencies of polybenzoxazine mixture thermosets were decreased by increasing PPO content on the used TBox due to the incompatibility of the toughener in the cured matrix forming a gross micro-phase separation. In parallel, it was inferred from TEM and AFM images that densely PPO presence on the toughening samples resulted an increment on number and size of the domains in matrixes. Therefore, a clear morphological situation during the curing process was observed as the toughener TBox separates out in a controlled manner and covalently bonds from benzoxazines in the main chain to the surrounding matrix. Inversely to the TBox thermoplastics and their cured polybenzoxazines, toughened thermoset composites presented a higher T_g value with increasing PPO content.

The versatility of multifunctional main chain benzoxazine prepolymers were showed by fusing them with water-based emulsion field. Their covalent incorporation into multifunctional surface active agents might minimize the negative side effects typically observed in dispersion systems. Benzoxazine protective colloids (PC) consist of thermally curable prepolymers with hydrophilic polymeric blocks (PEO, Jeffamine ED-2003) and benzoxazine moieties in the main chain. Two different types of benzoxazine prepolymers were synthesized with 10% of ring-opened structures, the poly(bisphenolbenzoxazine-jeffamines) (PC-A) was from hydrophilic diamine on the backbone with hydrophobic diamine (PTMO-based XTJ-542) end functionality and poly(bisphenolbenzoxazine-jeffamine) (PC-B) was from only one type of hydrophilic diamine. Expectedly, PC-B thermally polymerizes at slightly lower temperatures than PC-A due to better flexibility caused by longer aliphatic segment between the hard benzoxazine units. Their abilities used on the stabilization of benzoxazine miniemulsions. The incorporation of the dispersed colloids with resin (B-Hex) which is used on the preparation of o/w emulsions was proved by DSC thermograms of their mixtures. Moreover, the morphological behaviors of the cured films were investigated. The PC-B was compatible with the resin, whereas PC-A formed large domains within the network causing reduction on transparency. This behavior was also observed in the TEM images by domain sizes of up to 100 nm in PC-A & B-Hex (Bisbenzoxazine derived from bisphenol-A and hexylamine) mixture where the PC-B & B-Hex mixture with sizes of around 10 nm [47].

2.3. Polysiloxane based main chain benzoxazine polycondensates

The development of flexible thermosetting resins was achieved by including siloxane units in the main chain of the polymeric precursors. For this purpose, benzoxazine prepolymers containing polymethylsiloxane unit with high molecular weight have been synthesized by typical benzoxazine ring formation reaction. Mannich condensation of bisphenol-A with α,ω-bis(aminopropyl)polydimethylsiloxane (PDMS) with different molecular weights formed benzoxazine main chain prepolymers. Ring opened structures with 12–42% were detected on the spectral analysis and they lowered the curing temperatures which monitored by DSC analysis.

Effects of PDMS content and its molecular weight on thermal and mechanical properties of the resultant thermosets were investigated. Remarkably, improved tough and highly flexible transparent Polybenzoxazine-PDMS films presented increased elongation at break with proportional to molecular weight of PDMS used for prepolymer synthesis. In viscoelastic analysis of the polybenzoxazines, the lower storage modulus (E') by the introduction of longer siloxane unit was detected. The beneficial effect of the long backbone restricting the chain movement was also proved by higher T_g value of the poly(bisphenolbenzoxazine-dimethylsiloxane) in comparison with pristine PB-a [48].

The idea of thermoset preparation with improved properties by utilizing the diversity of multi-block copolymer morphological structures was carried out by two step Mannich polycondensation. The multi-block copolymer consists from main chain benzoxazine prepolymer and chemically incorporated polydimethylsiloxane (PDMS) unit which provides micro-phase separation acting as nano-phase by improving thermally and mechanically. These copolymers were prepared by two consecutive Mannich reaction: firstly, synthesis of hydroxyl terminated PBaDDM prepolymer from bisphenol-A and DDM (4,4′-diaminodiphenylmethane) and secondly, formation of PBaDDM-*b*-PDMS from the PBaDDM and variable amount of PDMS [49].

The molecular weights of these highly soluble copolymers were between 4560 and 7730 with a broad polydispersity. In contrast to the PBaDDM and PDMS blends [50] the homogeneity and transparency of these covalently bonded copolymers implies the absence of macro-phase separation. This comment was further proved by AFM images of cured polymers exhibiting nanostructured morphologies. Moreover, the scattering peak at 0.1–0.3 nm^{-1} indicated that the PBaDDM–PDMS multi-block copolymers were indeed micro-phase separated according to SAXS profiles. This morphology is a result of the immiscibility of PBaDDM and PDMS blocks resulting from their solubility difference. DSC profiles of the multi-block copolymer which was taken at different curing rates ensured an opportunity to calculate the curing activation energy (E_a) of the plain PBaDDM and PBaDDM–PDMS copolymer based on the Kissinger approaches [51]. E_a of the ring opening polymerization of copolymer was higher than that of the plain PBaDDM because it contains inert and flexible polysiloxane block micro-domains exerting a dilution effect during curing of prepolymer matrices [49].

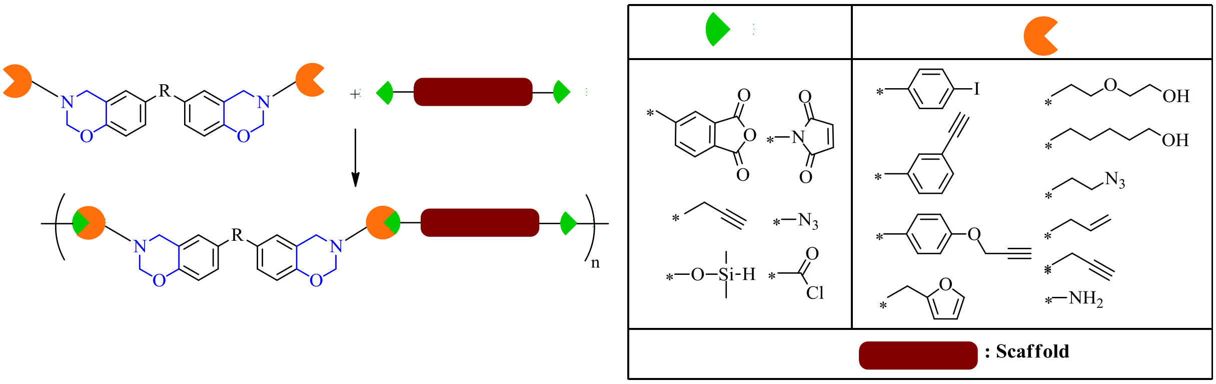
In the thermogravimetric analysis, it was observed that the initial temperature of the weight loss (5%) was significantly decreased by inclusion of the PDMS blocks as a result of the thermally labile aliphatic group increment. The PDMS content up to 50% or higher caused also lower residue of degradation than that of the plain PBaDDM. However, the micro-phase separation and insulation effect of the PDMS micro-domains induced higher char yield at 800 °C when the polysiloxane group is 46% or less. Expectedly, the surface hydrophobicity of these multi-block copolymers were improved by content of the highly non-polar group distributed PDMS increased in terms of the measurement of static contact angle.

2.4. Benzoxazine–sulfone copolymers

Polysulfones (PSU), another high-performance polymer family, are known to have good toughness and stability at high temperatures. They show high strength and stiffness, high continuous use and heat deflection temperatures, excellent resistance to hydrolysis by acids and bases, good dimensional stability, and the highest service temperature among all melt-processable thermoplastics [52]. Combination of benzoxazines with PSUs was reported earlier by using phenol terminated PSU to incorporate benzoxazine moieties to extent the properties of these thermosets for further applications. The free standing films of the reactive macromonomers was easily obtained and further cross-linked by thermal activation to produce tough films with good thermal stability [53,54]. In order to obtain highly cross-linked structures, additional benzoxazine monomers were required in the curing process since benzoxazine moieties were present only at the chain ends. Alternative approach to increase crosslink density comprises the preparation of oligomers containing benzoxazine moieties as repeat units. Thus, Mannich condensation of bisphenol-A with sulfonylbisoxydianiline in the presence of formaldehyde resulted in the formation of oligo(benzoxazine-*co*-sulfone) with a molecular weight of 2600 Da. The ring opening polymerization of the obtained precursor showed two maxima at 258 and 276 °C. Thermal stability analysis of the cured oligomers revealed that although the cleavage of Mannich base lowered the first degradation temperatures, the overall char yield was higher [55].

3. Polycondensates from difunctional benzoxazines

Mannich polycondensation is a versatile approach for the synthesis of main-chain benzoxazine containing polymers as mentioned above in detail. However, the molecular weights of resultant

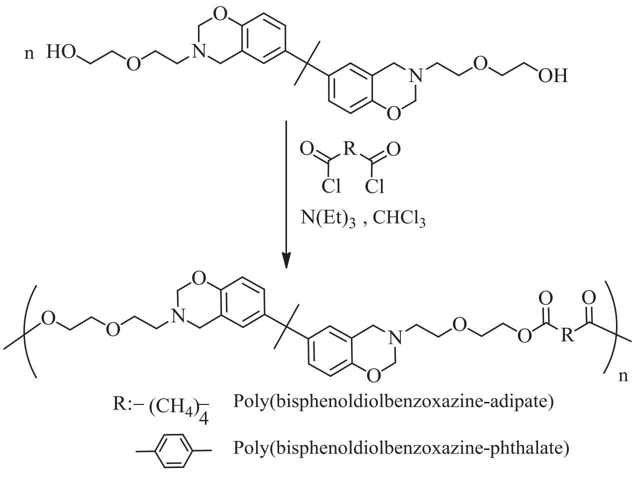


Scheme 4. Synthesis of polycondensates from difunctional benzoxazines.

polymers are rather low due to the branching and some side reactions arising from the nature of the reaction type. These limitations can be particularly important for the synthesis of polymeric products from monomers that are functionalized inadequately. Hence, a general need emerges to use other chemistries and convert benzoxazine monomers to suitable derivatives prior to polymerization in order to increase molecular weights and bring in various desired properties for corresponding polycondensates. Typical reported examples based on antagonist functionalities of benzoxazines and scaffolds are presented in Scheme 4 and discussed in detail below.

3.1. Esterification reaction

Polyesterification has recently become a popular strategy for designing versatile thermoset elastomers. Polyester based thermosets can be fabricated either in situ manner using monomers with an average functionality greater or post-reactions of the polymer chains. This strategy has recently received interest due to several factors including ease and flexibility of the synthesis and possibility to obtain cross-linked polyesters [56,57]. In our own laboratory, we have synthesized high molecular weight poly(etherester)s (PEE) containing benzoxazine units in the main chain by esterification reaction (see Scheme 5). Initially, diol functional benzoxazine monomer (B-etherdiol) was synthesized using bisphenol A, formaldehyde and 2-(2-aminoethoxy) ethanol. Polycondensation of the resulting B-etherdiol with adipoyl chloride and terephthaloyl dichloride in the presence of triethylamine resulted in corresponding PEE with molecular weight of 34,000 Da. The polymers were further cross-linked thermally leading to a network exhibiting properties of both polybenzoxazine and polyester. Transparent flexible thin films were prepared by the solvent casting method. The cured polymers exhibited remarkable thermal stability and toughness induced by the soft etherester structure [31].

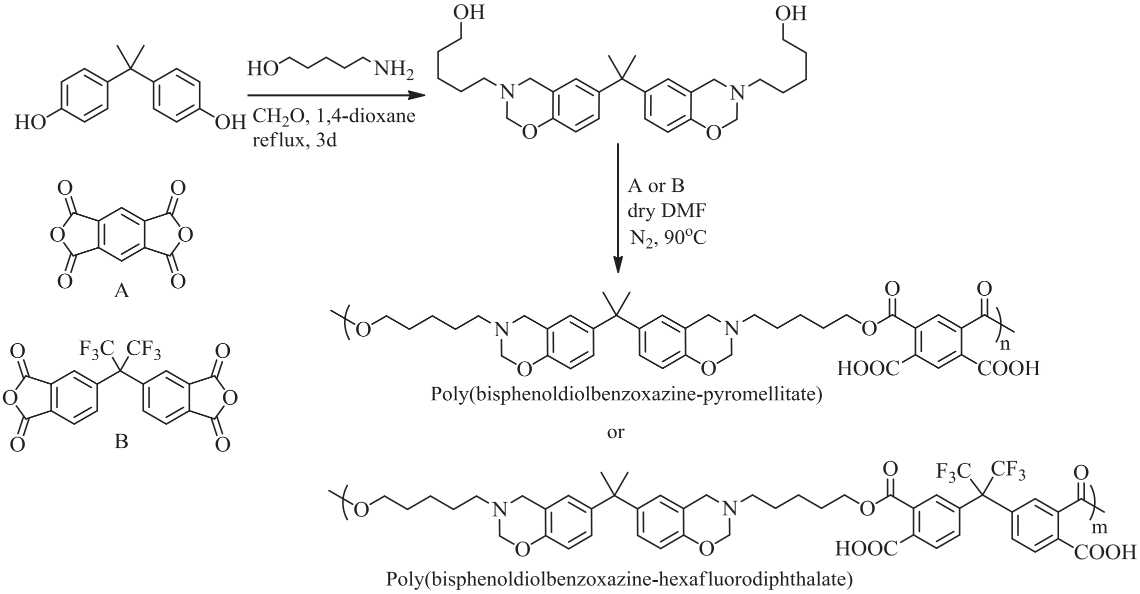


Scheme 5. Synthesis of poly(etherester-benzoxazines).

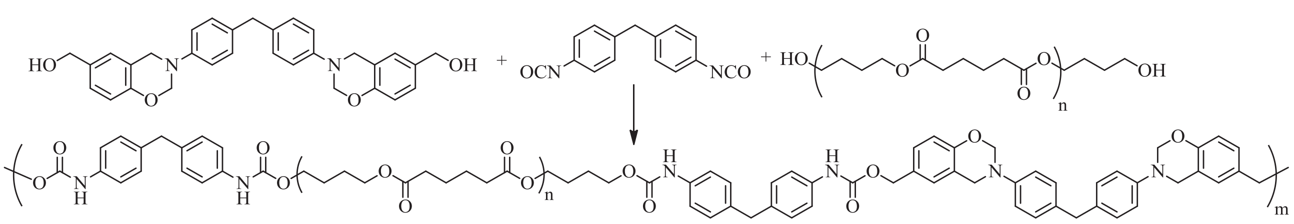
For further extending the concept, we have also described the synthesis of some other types of polyesters containing benzoxazine moieties in the main chain from diacid anhydrides and diol functional benzoxazine. Pyromellitic dianhydride and 4,4′-(hexafluoroisopropylidene) diphatalic anhydride were used as the dianhydride components to obtain desired carboxylic acid containing polyesters (see Scheme 6). The molecular weights of polymers were found to be between 5800 and 7000 Da. The film forming properties of corresponding polyesters were investigated and compared with conventional Pa (mono-functional benzoxazine from phenol and aniline) and carboxylic acid containing benzoxazine. The cured films showed enhanced thermal stability with respect to low molar mass analogous and a good flexibility possibly due to the presence of pentyl and ester groups in linear chain segments. Furthermore, hydroxyl and carboxylic acid groups promoted the adhesion of molecules to metals [30].

3.2. Polyurethane formation

The availability of the alcohol functional benzoxazine [17,31] and naphthoxazine [58] monomers has led to the development of new polybenzoxazine precursors. The initial application of the alcohol functionality concerned its use as initiator for the ring opening polymerization of ε-caprolactones in the presence of tinoctaate [58]. The potency of these type liquid monomers in various polycondensation reactions gave rise to a number of other main-chain polybenzoxazine precursors. For example, segmented polyurethanes consisting (PU) can readily be obtained from polyols and isocyanates. Even though, there have been some studies on the combination of polyurethanes and traditional phenolic resins, the procedures involved in situ addition of isocyanates during curing of the benzoxazine monomers. The first main chain type uretane linkage containing polynaphthoxazine precursors were synthesized by Yeganeh et al. by using NCO-terminal polyurethane prepolymers and a diol functional naphthoxazine. According to dynamic mechanical thermal analysis (DMTA) phase separation was observed, since two distinct T_g values for soft polyurethane and hard polynaphthoxazine segments were monitored. Moreover, mechanical analysis showed a considerable improvement in elongation property in comparison to neat polynaphthoxazine [59]. In another study, Baqar et al. made a contribution to poly(benzoxazine-*co*-uratene) concept by synthesizing diol functional bisbenzoxazine and using it with 4,4′-methylenediphenyldiisocyanate (MDI) to produce polyurethanes. The formation of urethane linkages was confirmed by model reactions (see Scheme 7). Superior thermal stability was



Scheme 6. Synthesis of polyesters containing benzoxazine moieties in the main chain from diacid anhydrides and diol functional benzoxazine.



Scheme 7. Synthesis of urethane linkage containing polybenzoxazine precursors.

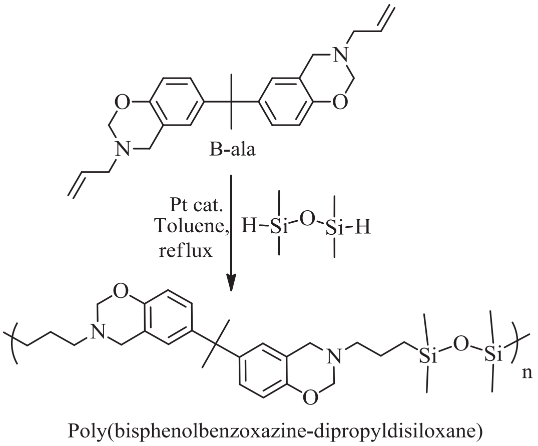
observed compared to previous approaches. Excellent mechanical integrity stemming from high tensile modulus and tensile strength due to the presence of polybenzoxazine as part of the main-chain was noted [60].

3.3. Polyamide formation

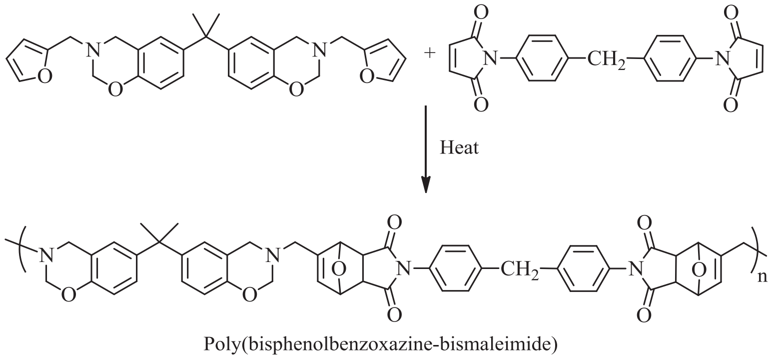
Polyamides are a unique family of thermoplastics with their natural flame retardancy, thermal and chemical resistances and excellent mechanical properties. Agag et al. have recently reported a synthetic approach for the preparation of poly(amide-benzoxazine) polymers in order to combine the thermoplastic and thermosetting natures of polyamide and polybenzoxazine, respectively. They synthesized a primary amine-bifunctional benzoxazine (P-ddm-NH_2) and reacted with adipoyl and isophthaloyl dichloride in dimethylacetamide as solvent in the presence of triethylamine to prepare both aliphatic and aromatic poly(amide-benzoxazine)s. The thermally activated crosslinking behavior of these main chain polymers was studied by DSC and FT-IR. The aliphatic (poly(diphenylmethanebenzoxazine-adipamide)) showed slightly lower exothermic peak compared to aromatic poly(diphenylmethanebenzoxazine-phtalamide) due to the flexible aliphatic chains. The cured polymers exhibited good thermal stability indicating the applicability of poly(amide-benzoxazine)s as high performance materials [61].

3.4. Hydrosilation reaction

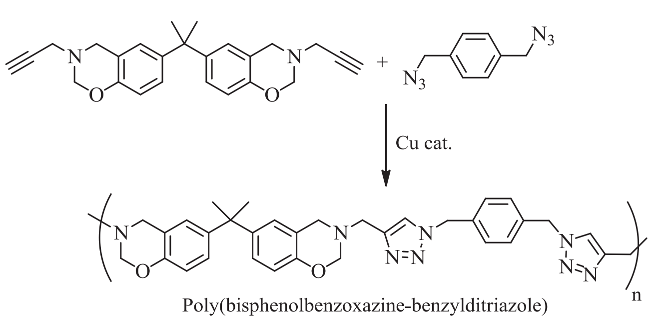
Recently, we have demonstrated that polysiloxanes containing benzoxazine moieties in the main chain can be prepared by Pt-catalyzed hydrosilylation reaction between tetramethyldisiloxane and diallyl functional benzoxazines (Scheme 8). Although moderate yields were attained, the chain growth was limited and only oligomers were formed probably due to inhibition or poisoning of some catalyst by amino groups on benzoxazine structure. Nevertheless, the process was found to be highly selective as ring opened oxazine structures were not detected which is a common problem encountered in the synthesis of main-chain polybenzoxazine precursor using Mannich type polycondensation. Moreover, the products exhibited the properties of both siloxane and benzoxazine segments where benzoxazine units were used for creating crosslinked network and siloxane segments introduced flexibility.



Scheme 8. Synthesis of disiloxane containing polybenzoxazine precursor.



Scheme 9. Synthesis of main-chain polybenzoxazine precursor via Diels–Alder reaction.



Scheme 10. Synthesis of main-chain polybenzoxazine precursor via [3 + 2] click reaction.

The transparent thin precursor films were easily obtained by solvent casting method and then cross-linked by thermal treatment. Final cured polymers exhibited much more thermal stability than those of the structurally similar low-molecular weight analogous. The enhanced thermal stability was attributed to the presence of siloxane units [62].

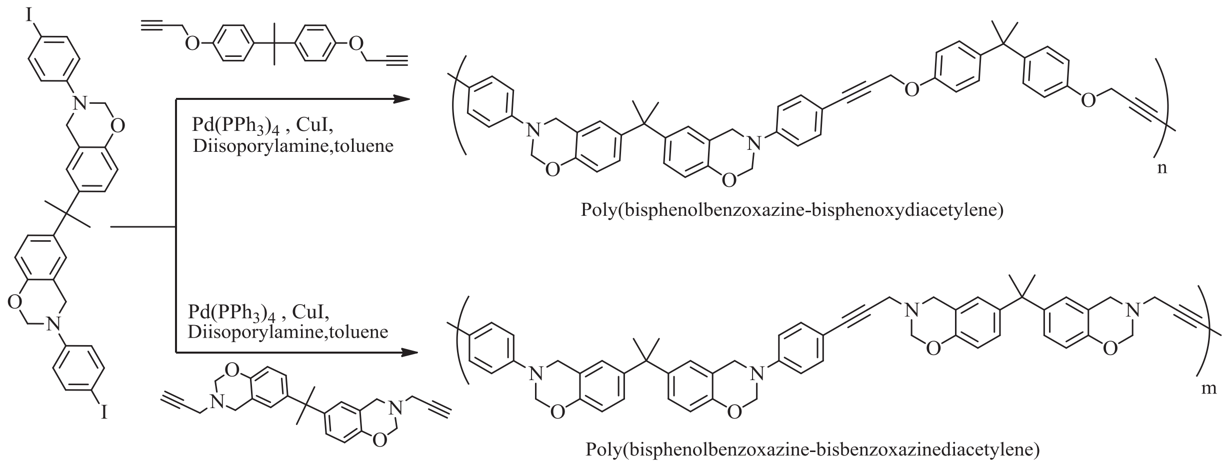
Similar improvement in the thermal stability was also reported polyhedral oligomeric silsesquioxane (POSS) and polybenzoxazine composites [63–66]. In a following study, we have described the chain extension of main chain benzoxazine-siloxane oligomers by cyclic siloxanes in the presence of tetrabutylammonium hydroxide (TBAH) as catalyst through the anionic polymerization route. By such chain extension, the thermal stability of poly(bisbenzoxazine-dimethylsiloxane)s (PBDMS) were increased due to the increasing fraction of siloxane units in the main chain [67].

3.5. Diels–Alder reaction

The Diels–Alder (DA) reaction, one of the most useful reactions in modern chemistry, is an efficient [4 + 2] cycloaddition reaction, in which an unsaturated group, a dienophile combines with a 1,3-diene in a concerted fashion to form a six-membered ring [68,69]. It has been successfully and widely adapted to macromolecular chemistry for the construction of different kinds of polymers [70]. Also, DA chemistry has been used as an alternative click chemistry to Huisgen Type 1,3-cycloadditions [71]. Recently, Chou and Liu applied this strategy for the synthesis of a high-molecular-weight polymer containing reactive benzoxazine groups in the main chain using bis(3-furfuryl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane and bismaleimide (see Scheme 9). They reported that the crosslinking of the final polymer is moderately complex due to the simultaneous retro Diels–Alder reaction and ring-opening polymerization. Therefore, decrease in molecular weight and increase in polydispersity was observed during thermal curing. However, the resultant polymer showed comparatively good thermal and mechanical properties [72].

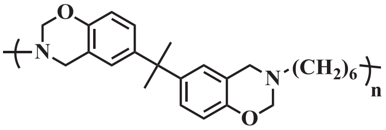
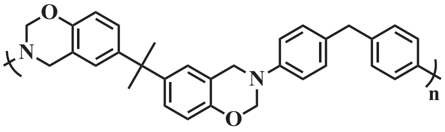
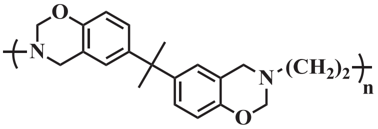
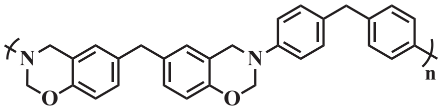
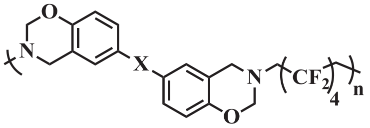
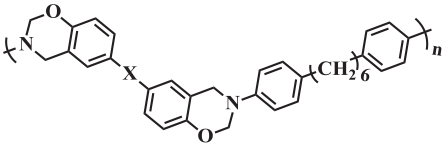
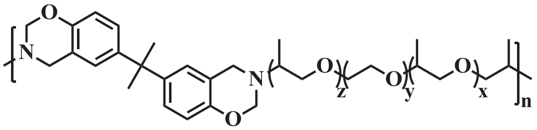
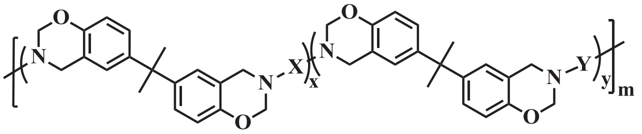
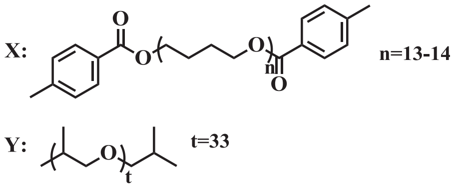
3.6. Click reaction

Another beneficial approach for the preparation of main-chain benzoxazine containing polymers is [3 + 2] Huisgen type click reaction [73–76]. The usage of this type click reaction in polybenzoxazine chemistry was first reported from the authors' laboratory for the synthesis of benzoxazine functional polystyrenes [77]. Commonly used commercial polymers such as polyvinylchloride



Scheme 11. Synthesis of main chain polybenzoxazine precursors using Sonogashira coupling.

Table 1
Chemical structures of polycondensates from benzoxazines.

Chemical structure	Ref.
 **Poly(bisphenolbenzoxazine-hexane)**	[33,35]
 **Poly(bisphenolbenzoxazine-diphenylmethane)**	[33]
 **Poly(bisphenolbenzoxazine-ethane)**	[33]
 **Poly(methylenediphenolbenzoxazine-diphenylmethane)**	[43]
 **X: $C(CF_3)_2$** **Poly(hexafluorobisphenolbenzoxazine-octafluorobutane)** **X: $C(CH_3)_2$** **Poly(bisphenolbenzoxazine-octafluorobutane)**	[44]
 **X: $C(CF_3)_2$** **Poly(hexafluorobisphenolbenzoxazine-diphenylhexane)** **X: $C(CH_3)_2$** **Poly(bisphenolbenzoxazine-diphenylhexane)**	[44]
 **x+z y** **Poly(bisphenolbenzoxazine-jeffamine600) 3.6 9.0** **Poly(bisphenolbenzoxazine-jeffamine900) 6.0 12.5** **Poly(bisphenolbenzoxazine-jeffamine2000) 6.0 39**	[45]
  **X:Y** **TBox100 100:0** **TBox50 50:50** **TBox0 0:100**	[46]

(*continued on next page*)

Table 1 (*continued*)

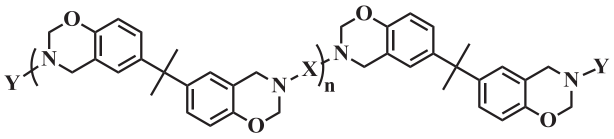
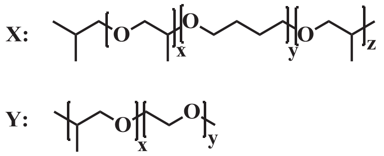
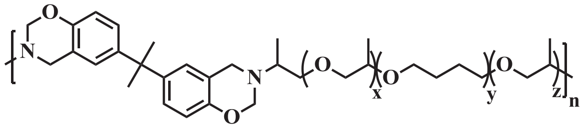
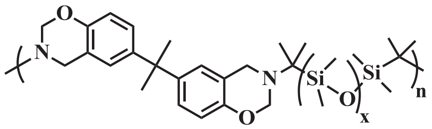
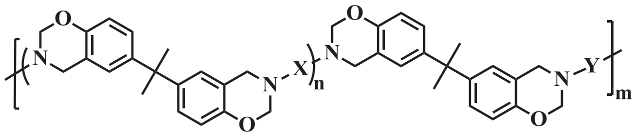
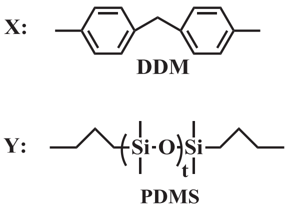
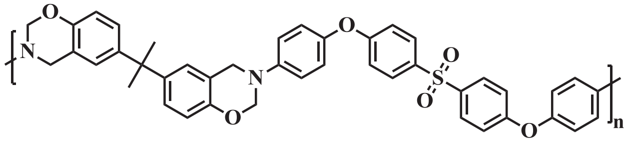
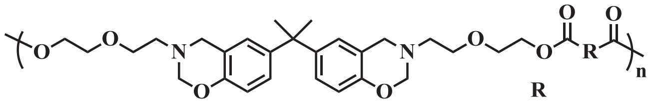
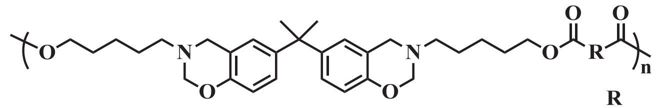
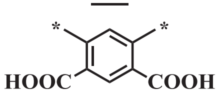
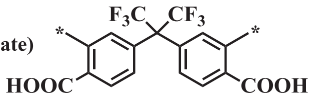
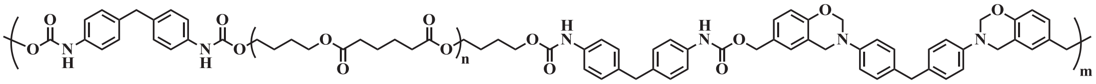
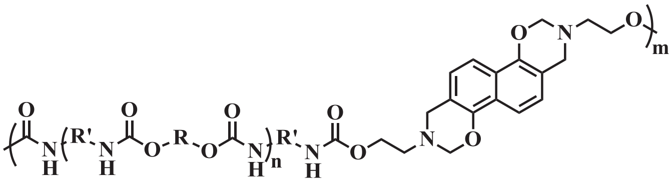
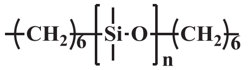
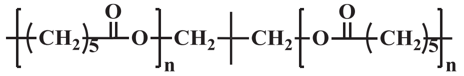
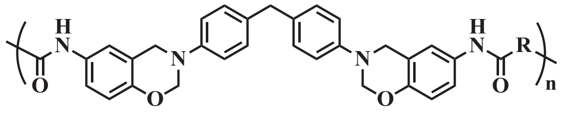
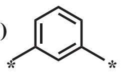
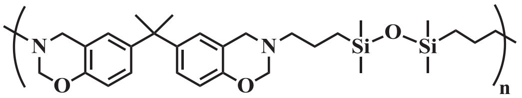
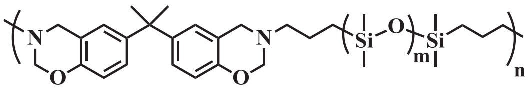
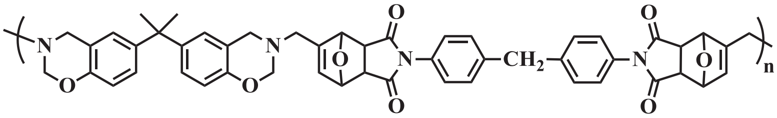
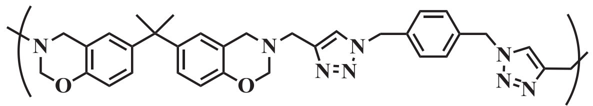
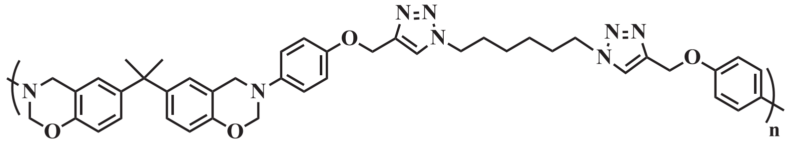
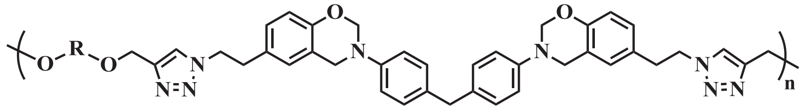
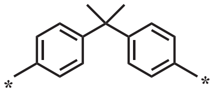
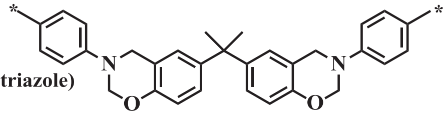
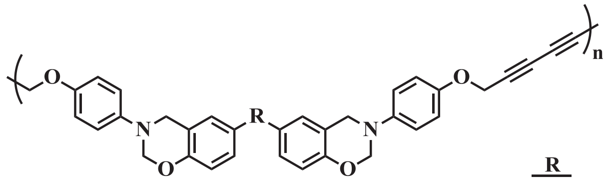
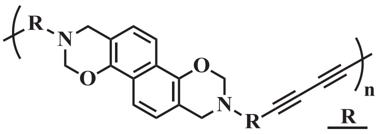
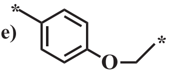
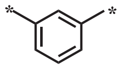
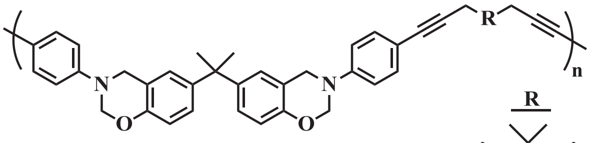
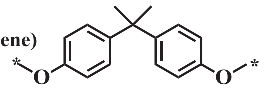
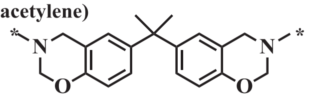
Chemical structure	Ref.
 **Poly(bisphenolbenzoxazine-jeffamines)**  	[47]
 **Poly(bisphenolbenzoxazine-jeffamine)**	[47]
 **Poly(bisphenolbenzoxazine-dimethylsiloxane)**	[48]
  PDMS(%) **PBaDDM28-b-PDMS** 72 **PBaDDM45-b-PDMS** 55 **PBaDDM54-b-PDMS** 46 **PBaDDM61-b-PDMS** 39	[49]
 **Poly(bisphenolbenzoxazine-sulfonylbis(phenoxybenzene))**	[55]
 R **Poly(bisphenoldiolbenzoxazine-adipate)** $-(CH_2)_4-$ **Poly(bisphenoldiolbenzoxazine-phthalate)** 	[31]

Table 1 (*continued*)

Chemical structure	Ref.
 R **Poly(bisphenoldiolbenzoxazine-pyromellitate)**  **Poly(bisphenoldiolbenzoxazine-hexafluorodiphthalate)** 	[30]
 molar percent of polyol I-0 0 I-10 10 I-20 20 I-30 30 I-40 40	[60]
 R **TPUNZ1**  $-(CH_2)_6-[Si(CH_3)_2-O]_n-(CH_2)_6-$ **TPUNZ2**  $-[(CH_2)_5-C(=O)-O]_n-CH_2-C-CH_2-[O-C(=O)-(CH_2)_5]_n-$ **TPUNZ3** $-[(CH_2)_4-O]_n-$ **R':** $-(CH_2)_6-$	[59]
 R **Poly(diphenylmethanebenzoxazine-phtalamide)**  **Poly(diphenylmethanebenzoxazine-adipamide)** $*-C_4H_8-*$	[61]
 **Poly(bisphenolbenzoxazine-dipropyldisiloxane)**	[62]
 **Poly(bisphenolbenzoxazine-siloxane-dipropyldisiloxane)**	[67]
 **Poly(bisphenolbenzoxazine-bismaleimide)**	[72]

(*continued on next page*)

Table 1 (*continued*)

Chemical structure	Ref.
 **Poly(bisphenolbenzoxazine-benzylditriazole)**	[38]
 **Poly(bisphenolbenzoxazine-phenoxymethylheptylditriazole)**	[39]
 **R** **poly(methylenedianilinebenzoxazine-bisphenoxyditriazole)**  **poly(methylenedianilinebenzoxazine-bisbenzoxazineditriazole)** 	[39]
 **R** **Poly(bisphenolbenzoxazine-phenoxydiacetylene)** **$C(CH_3)_2$** **Poly(benzophenonebenzoxazine-phenoxydiacetylene)** **CO**	[36]
 **R** **Poly(naphthalenebisbenzoxazine-phenoxydiacetylene)**  **Poly(naphthalenebisbenzoxazine-phenyldiacetylene)** 	[36]
 **R** **Poly(bisphenolbenzoxazine-bisphenoxydiacetylene)**  **Poly(bisphenolbenzoxazine-bisbenzoxazinediacetylene)** 	[37]

[78] and polybutadiene [79] were also modified with side chain benzoxazine groups through this click reaction. Endo and co-workers used this approach to prepare main-chain polybenzoxazine precursors having 1,2,3-triazole junctions and high-molecular weights by using diacetylene functional benzoxazines to couple with diazido monomers [38] (see Scheme 10).

This strategy has attracted attention because of the important features of click reaction including high yields, selectivity and high atom economy bringing about high efficiency. Chernykh et al. also reported other examples of high molecular weight main-chain benzoxazine prepolymers having different structural motifs [39]. For instance, they synthesized an azido and a propargyl functional benzoxazines separately in order to incorporate benzoxazines in every repeat unit of the corresponding polymer. The molecular weights of the polymers were found to be between 20,000 and 40,000 Da indicating effectiveness of the click reaction in

Table 2
Molecular weights of main chain benzoxazine polycondensates, and thermal, mechanical properties of their crosslinked polymers.

Polymers	M_n	PDI	Thermal properties			Mechanical properties					
			T_{max} (°C)	$T_{5\%}$ (°C)	T_c (%)	E' (GPa)	T_g (E'') (°C)	T_g (tan δ) (°C)	E (MPa)	σ_b (MPa)	ε_b (%)
Poly(bisphenolbenzoxazine-hexane)	3300	3.0	242	302	18	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-hexane)	2358	3.7	244	301	30	1.8	247	260	2000	65	4.1
Poly(bisphenolbenzoxazine-ethane)	2571	2.4	217	282	35	2.4	249	259	3300	58	2.4
Poly(bisphenolbenzoxazine-diphenylmethane)	2232	3.0	236	341	54	2.4	228	238	3500	87	4.1
Poly(methylenediphenolbenzoxazine-diphenylmethane)	1527	1.7	247	346	55	1.9	–	213	–	–	–
Poly(hexafluorobisphenolbenzoxazine-octafluorobutane)	6645	2.7	260	322	50	1.8	–	180	–	–	–
Poly(bisphenolbenzoxazine-octafluorobutane)	7329	3.3	256	332	20	2.0	–	227	–	–	–
Poly(hexafluorobisphenolbenzoxazine-diphenylhexane)	13,332	2.7	225	377	50	2.0	–	164	–	–	–
Poly(bisphenolbenzoxazine-diphenylhexane)	6476	2.56	230	347	30	2.0	–	160	–	–	–
Poly(bisphenolbenzoxazine-jeffamine600)	–	–	246	285	18	9.5	-19	–	–	–	–
Poly(bisphenolbenzoxazine-jeffamine900)	–	–	247	324	15	2	-40	–	–	–	–
Poly(bisphenolbenzoxazine-jeffamine2000)	–	–	255	350	17	12	-45, 0	–	–	–	–
TBox100	14,800	3.3	231	–	–	–	–	-43(DSC)	–	–	–
TBox50	15,430	2.8	224	–	–	–	–	-52(DSC)	–	–	–
TBox0	41,360	2.7	228	–	–	–	–	-56(DSC)	–	–	–
Poly(bisphenolbenzoxazine-jeffamines)	6400	2.3	237	–	–	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-jeffamine)	10,700	2.4	230	–	–	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-dimethylsiloxane)	3000	1.9	223	324	44	0.5	225	238	3.2	49	3.1
PBaDDM28-*b*-PDMS	4560	2.31	–	290	23	–	–	–	–	–	–
PBaDDM45-*b*-PDMS	7800	2.52	–	310	37	–	–	–	–	–	–
PBaDDM54-*b*-PDMS	6840	2.34	270	320	49	–	–	–	–	–	–
PBaDDM61-*b*-PDMS	7730	2.86	–	335	47	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-sulfonylbis(phenoxybenzene))	2600	2.18	258, 276	345	26	–	–	–	–	–	–
Poly(bisphenoldiolbenzoxazine-adipate)	33,400	4.37	250	248	22	–	–	–	–	–	–
Poly(bisphenoldiolbenzoxazine-phthalate)	33,700	1.36	243	288	36	–	–	–	–	–	–
Poly(bisphenoldiolbenzoxazine-pyromellitate)	5800	1.54	251	301	32	–	–	–	–	–	–
Poly(bisphenoldiolbenzoxazine-hexafluorodiphthalate)	5900	2.45	246	285	27	–	–	–	–	–	–
I-0	–	–	248	280	53	–	–	–	2358	78	4
I-10	–	–	252	300	44.3	–	–	–	737	40	12
I-20	–	–	256	293	35	–	–	–	517	32	16
I-30	–	–	258	287	27.5	–	–	–	54	13	73
I-40	–	–	259	285	17.5	–	–	–	18	3	109
TPUNZ1	–	–	200	-	18	–	–	–	137 ± 1	22 ± 1	22 ± 1
TPUNZ2	–	–	200	-	12	–	–	–	56 ± 2	19 ± 1	70 ± 2
TPUNZ3	–	–	200	-	11	–	–	–	39 ± 2	16 ± 2	63 ± 2
Poly(diphenylmethanebenzoxazine-phtalamide)	–	–	245	347	57	–	236	–	–	–	–
Poly(diphenylmethanebenzoxazine-adipamide)	–	–	236	259	41	–	169	–	–	–	–
Poly(bisphenolbenzoxazine-dipropyldisiloxane)	1700	1.70	228	351	58	–	-	–	–	–	–
	2530	1.72	249	356	61	–	-	–	–	–	–
	–	1.70	247	361	61	–	-	–	–	–	–
Poly(bisphenolbenzoxazine-siloxane-dipropyldisiloxane)	8200	1.58	250	375	7	–	-	–	–	–	–
	8080	1.53	269	425	9						
Poly(bisphenolbenzoxazine-bismaleimide)	19,000	1.81	200	390	52	5.2	–	–	907	31	3.7
Poly(bisphenolbenzoxazine-benzylditriazole)	14,400	4.37	254.7	315	–	–	–	–	–	–	–
	19,400	2.56									
	14,800	7.28									
	27,700	2.19									
Poly(bisphenolbenzoxazine-phenoxymethylheptylditriazole)	25,900	1.9	235	324	42	–	–	–	–	–	–
Poly(methylenedianilinebenzoxazine-bisphenoxyditriazole)	32,600	1.9	251	323	-	–	–	–	–	–	–
Poly(methylenedianilinebenzoxazine-bisbenzoxazineditriazole)	47,900	2.1	242	331	51	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-phenoxydiacetylene)	21,000	1.91	185, 260	367	59	–	–	–	–	–	–
Poly(benzophenonebenzoxazine-phenoxydiacetylene)	25,000	1.96	–	401	70	–	–	–	–	–	–
Poly(naphthalenebisbenzoxazine-phenoxydiacetylene)	14,000	1.53	–	379	72	–	–	–	–	–	–
Poly(naphthalenebisbenzoxazine-phenyldiacetylene)	–	–	–	409	68	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-bisphenoxydiacetylene)	2330	1.6	205, 270	342	58	–	–	–	–	–	–
Poly(bisphenolbenzoxazine-bisbenzoxazinediacetylene)	3497	1.3	214, 272	329	61	–	–	–	–	–	–

E': Storage modulus.
E: Tensile modulus (Young's modulus).
σ_b: Tensile strength.
ε_b: Elongation at break.

preparation high molecular weight main chain benzoxazine polymers. Reportedly, the resultant polymers exhibited typical benzoxazine polymerization exothermic peak with maximums ranging from 230 °C to 250 °C and high thermal stabilities. Additionally, a low temperature exotherm was observed and it was attributed as the thermal coupling of the residual propargyl and azide end groups as evidenced by model reactions [39].

3.7. Coupling reaction

Using oxidative coupling reaction diacetylene containing polybenzoxazine prepolymers were synthesized from corresponding propargyl functionalized benzoxazine monomers in the presence of a copper catalyst. Unexpectedly, ring opening polymerization temperature of these obtained polybenzoxazine precursors were reduced drastically. This behavior was attributed to the topological properties of the diacetylene system. Moreover, polymers showed considerably high thermal stability and high char yields which were around 72% at 800 °C. The initial thermal decomposition by 5% observed at > 400 °C, is quite high compared to polybenzoxazines derived from classical mono and difunctional monomers [36]. Another alternative method for acetylene containing polybenzoxazine precursors is related to the use of Sonogoshira coupling reaction. An aryl halide functional benzoxazine, namely diiodobisbenzoxazine (DIBB), was synthesized and further reacted with diacetylene bisether and diacetylene bisbenzoxazine in the presence of $Pd(PPh_3)_4$ catalyst, CuI as co-catalyst and diisopropylamine (Scheme 11). Compare to the general Sonogoshira type polymers, relatively lower yields and molecular weights were attained. This behavior was attributed to the low polymerization temperature. The temperature was deliberately kept lower than that applied in usual Sonogashira reactions so as to prevent ring opening of oxazines [37].

4. Structure–property relationship

In previous sections, various synthetic methods to prepare polymeric benzoxazine precursors via condensation reactions were presented and discussed in detail. These polybenzoxazines combine several preeminent features required for high performance polymers and possess good prospects for application in several areas. The structures of the polycondensates from benzoxazines and their important physical properties such as thermal properties (e.g., degradation, char yield, T_g) and mechanical properties (such as storage modulus, flexural modulus, and flexural strength) are tabulated in Tables 1 and 2, respectively Using these data structure–property relations can be revealed and advantages or disadvantages of each system can be identified to select proper structures for various applications. It is anticipated that with the persistent development of the new methods, the feasibility of producing such hybrid materials for high technology applications will soon be insight.

5. Conclusions

In this paper, we have provided various approaches to prepare polymeric benzoxazines by well-known condensation reactions. Although each approach has advantages and disadvantages, it is clear that they will increase the design flexibility of benzoxazine-containing main chain polymers and can satisfy the demands of polybenzoxazine based thermosets such as flexibility, processability, lowering curing temperature, and improving thermal stability and mechanical properties. Investigations on structure–property relations suggest that the beneficial effect of polymeric nature afforded by the related polymer will provide a wider usage of polybenzoxazines as high performance thermosets in specific applications. Further, owing to the inimitable properties of these hybrid materials, polycondensation method indeed stimulates new techniques for the production of future generation materials.

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