T. R.

GEBZE TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

HIGH PERFORMANCE BENZOXAZINE THERMOSETS FROM MONOMERS HAVING PHENOLIC GROUPS AND ASYMMETRIC STRUCTURE

BAHAR GUMUS

A THESIS SUBMITTED FOR THE DEGREE OF

MASTER OF SCIENCE

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GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

YÜKSEK PERFORMANSLI TERMOSETLER OLARAK FENOLİK VE ASİMETRİK BENZOKSAZİN MONOMERLERİ SENTEZİ

BAHAR GÜMÜŞ
YÜKSEK LİSANS TEZİ
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DANIŞMANI
PROF. DR. FARUK YILMAZ

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SUMMARY

Benzoxazines are converted to novel polymeric resins by means of thermally activated ring-opening reactions. Polybenzoxazines have numerous advantageous properties such as good mechanical, dimensional and thermal stability, chemical and flame resistivity. Benzoxazine monomers offer enormous design flexibility since they consist of phenol, formaldehyde, and amine (aliphatic or aromatic). This property allows for overcoming some limitations of benzoxazine monomers due to high curing temperature (~200°C or higher), complication in processing and brittleness. In the present research, we improved thermal resistance of polybenzoxazine thermosets by asymmetric bisbenzoxazine monomer and functionalization with phenolic end groups.

Phenol functional benzoxazine monomer was synthesized in two-step strategy unlike traditional synthetic routes and molecular structure was investigated by FT-IR and ^{1}H-NMR spectral analysis. Because the phenol groups on this new monomer behave as a catalyst, low curing onset temperature as low as 95 °C was obtained, which avails in the industrial application. Furthermore, the phenol groups in this monomer provided additional crosslinking points during curing and thus presumably caused a 60% increase in the thermal resistance of polybenzoxazine, as evidenced by thermogravimetric analysis.

Herein, a synthetic strategy was developed to prepare a novel asymmetric bisbenzoxazine without using bisphenols or bisamines. Due to absence of diphenolic groups, the structures were cross-linked via shorter bonds, and the decomposable bonds were decreased leading to increase in thermal stability. Thermal polymerization and resistance was investigated by DSC and TGA analysis. High thermal resistivity which was aimed with the production of this material appeared at 900 °C with 70% the char yield.

Key Words: Benzoxazine, Polybenzoxazine, Thermoset, Phenolic Resin, Thermal Resistance, High Performance Polymer, Thermal Curing, Cross-linked Polymer.

ÖZET

Benzoksazinler ısıyla aktive olarak halka açılma reaksiyonuyla yeni gelişmiş polimerik reçinelere dönüşmektedir. Polibenzoksazinler yüksek mekaniksel, boyutsal ve ısısal kararlılık, kimyasal ve ısısal dayanıklılık gibi pek çok avantaja sahiptir. Benkzoksazin monomerlerinde başlangıç maddesi olarak fenol, formaldehit ve amin (alifatik ya da aromatik) kullanılması çok iyi bir dizayn esnekliği sunmaktadır. Bu özellik farklı fonksiyonel gruplar sayesinde benzoksazin monomerlerinin yüksek kürlenme sıcaklığı(~200 °C ya da daha yüksek), işleme zorluğu ve kırılganlık gibi bazı sınırlandırıcı özelliklerinin üstesinden gelinmesine imkân sağlamaktadır. Sunulan bu çalışmada, polibenzoksazin termosetlerinin ısısal dayanıklılıkları asimetrik bisbenzoksazin monomeri ve fenolik uç grup fonksiyonlanması ile geliştirilmiştir.

Fenol fonksiyonel benzoksazin monomeri geleneksel sentez yöntemlerinin dışına çıkılarak iki aşamalı olarak sentezlendi ve moleküler yapı tayini FT-IR ve ^{1}H-NMR spektrum analizleriyle gerçekleştirildi. Yeni monomerdeki fenol gruplarının katalizör gibi davranması sebebiyle, endüstriyel uygulamayı kolaylaştıran 95 °C'ye kadar düşük polimerleşmeye başlama sıcaklığı elde edilmiştir. Ayrıca bu monomerde bulunan fenol gruplarının, kürlenirken ek çapraz bağlantı noktaları oluşturarak polibenzoksazin termosetlerinde ısısal kararlılığı % 60'a kadar arttırdığı termogravimetrik ölçümlerle saptanmıştır.

Bu çalışmada bisfenol ya da bisamin türevleri kullanılmaksızın özgün asimetrik iki fonksiyonlu benzoksazin hazırlamak için sentetik bir strateji geliştirildi. Difenol gibi gruplar bulundurmadığından daha kısa bağlarla yapılar çapraz bağlandığından bu da bozulacak bağ sayısını azaltarak ısısal kararlılığa katkı sağlamıştır. DSC ve TGA analizleri ile ısısal polimerizasyon ve dayanıklılık araştırılmıştır. Bu malzemenin üretimi ile amaçlanan yüksek ısısal dayanıklılık ise 900 °C'de % 70 oranında kütlesini koruması ile ısısal analizler sonucu ortaya çıkmıştır.

Anahtar Kelimeler: Benzoksazin, Polibenzoksazin, Termoset, Fenolik Raçine, Isısal Dayanıklılık, Yüksek Performanslı Polimerler, Isısal Kürlenme, Çapraz-bağlı Polimer.

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LIST of ABBREVIATIONS and ACRONYMS

Abbreviations and Acronyms		**Explanations**
Bisphenol-A	:	2,2-bis(4-hydroxyphenyl)propane
DSC	:	Differential Scanning Calorimeter
FTIR	:	Fourier Transform Infra-Red
GPC	:	Gel Permeation Chromatography
GTÜ	:	Gebze Teknik Üniversitesi
H	:	Hour
^{1}H-NMR	:	Nuclear Magnetic Resonance Spectroscopy
MHz	:	Mega Hertz
ROP	:	Ring Opening Polymerization
Rt		Room temperature
Tg	:	Glass Transition Temperature
TGA	:	Thermogravimetric Analyzer

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1. INTRODUCTION

In 1940's, Cope and Holly synthesized benzoxazines the first time. The efficiency of polybenzoxazines has been distinguished much later [1]. Accordingly, there has been a massive research on new monomers to develop thermal and mechanical performance of polybenzoxazines. Overall they have been developed for 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 [2]-[11].

In a manner, polymeric benzoxazines are kind of processable and crosslinkable thermoplastics. By addition of heat, around 200 °C [12], [13] they can turn into thermosets via thermally activated ring opening polymerization. Then, the obtained resin may avail both properties of thermoplastic and thermosetting polymers. Novel curable precursors can be obtained from Mannich type condensation using difunctional phenols or amines [16], coupling reactions [17], Huisgen type click reaction [18], and polyesterification [14], [15].As a result, polybenzoxazines can be tailored in each chemistry which brings the desired characteristic properties for specific application fields.

In order to raise crosslinking points many experts produced new kind of benzoxazine monomers with functional groups [18]. On the other hand, the utilization of benzoxazine precursors has some challenges like difficulty in fabrication of films from monomers because of their powder form. Furthermore, liquid monomers are quite limited [20]. In particular low molecular weight of the network structure in mono-functional benzoxazine precursors causes brittleness. To overcome these problems, research efforts have been focused on the new synthesis strategies of linear benzoxazine polymers as curable precursors. For this reason, some properties of polybenzoxazines were determined indeed such as flexibility, high crosslinking capacity, processability, reductions in the vapor pressure during process, and fragility for cured end-structures.

In the first part of this thesis, bifunctional phenolic benzoxazine monomers were prepared by a two step procedure and employed in the production of highly resistive thermosetting polymers. As the phenol groups on the new monomer behaved like a catalyst, new benzoxazine monomer starts to polymerize at very low

temperature, 95 °C. This ability gives them easier application in the industrial field. Furthermore, the phenol groups in this monomers provided additional crosslinking points during curing thus presumably causes an increment in the thermal resistance of cured polybenzoxazine thermosets. Polybenzoxazine thermosets that is produced from the new ring opening polymerization are a lot more thermally stable than usual benzoxazine.

60% of its mass at 900 °C is conserved. This material will have potency for conversion to polyester and polycarbonate precursors through phenolic ends via polycondensation thus a new strategy may be developed for the synthesis of polymeric precursors with benzoxazine units in the main backbone.

In the second part of this thesis, asymmetric difunctional benzoxazine monomers were prepared without using bisphenols or bisamines and employed in the production of highly resistive thermosetting polymer. Due to absence of diphenolic groups, the structures were cross-linked via shorter bonds and thus the decomposable bonds were decreased leading to increase in thermal stability. The structure of the monomer was confirmed by FT-IR and ^{1}H-NMR spectral analysis. Curing behaviors of the monomer was investigated using differential scanning calorimetry. Thermal properties of the polybenzoxazine were also studied by thermogravimetric measurements. The char yield of this novel asymmetric difunctional benzoxazine was achieved around 70% at 800 °C which is a significantly high value compare to traditional polybenzoxazines.

2. THEORETICAL PART

2.1. Phenolic Resins

Phenol formaldehyde or phenolic resins are one of the primordial polymeric resins obtained from phenols and aldehydes by a condensation polymerization [21]. The contributing factors of the kind of this kind of phenolic resins are the molar ratio of the starting materials with acid or base (Figure 2.1). One type of them is termed as resols or one stage resins that are produced under alkaline conditions by using above equimolar amounts of the formaldehyde and phenol. Their curing mechanism is dependent only on heat. Another one is known as novalacs or two stage resins which is prepared under acidic conditions by using from below equimolar amount of formaldehyde to phenol [22].

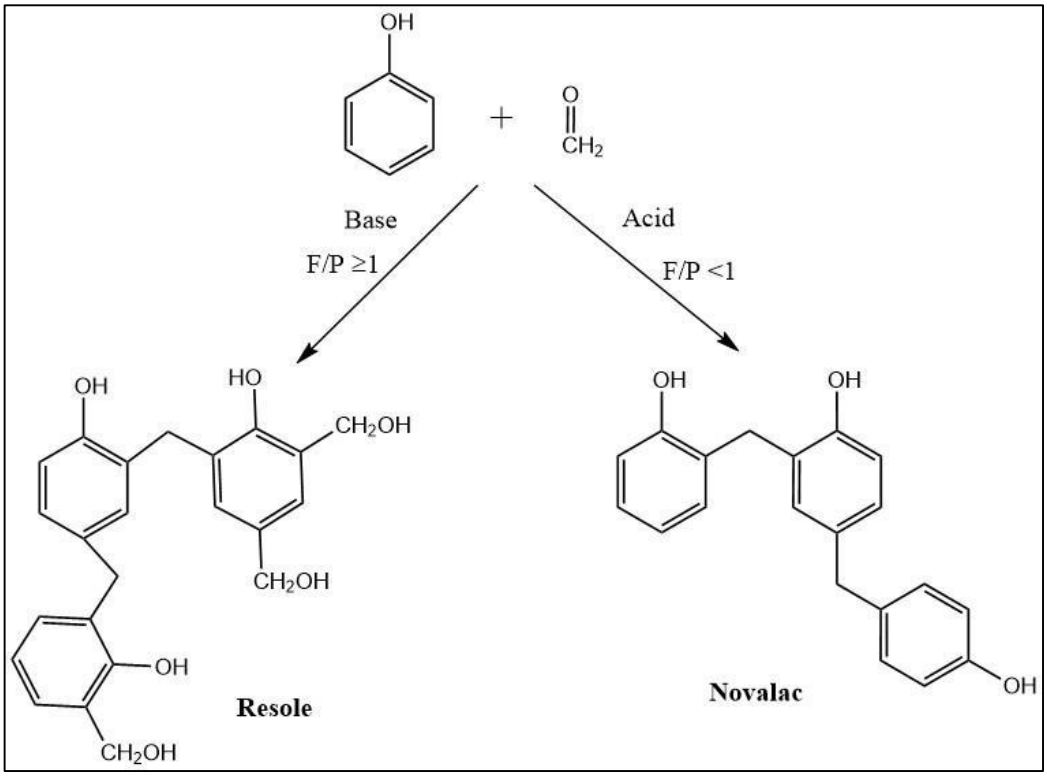


Figure 2.1: Reaction of phenol and formaldehyde.

The demand of phenolic resins is fairly high because of wide application in so many industrial applications such as aerospace technology, microelectronics, biomaterials, etc.

2.2. General Approaches for Synthesis of Benzoxazine Monomers

As a novel type of phenolic resins, benzoxazine monomers are connected through the formation of a cyclic structure from the phenolic hydroxyl to the ortho position [O–CH2–N(R)–CH2–] rather than a methylene [–CH2–] bridge that is associated with traditional phenolics [23]-[26] They are commonly synthesized from phenolic materials (bisphenols or novolak), primary amines, and formaldehyde either by applying solution method or solvent free method. Miscellaneous derivatives of benzoxazine monomers can be prepared by using appropriately chosen phenol and amine. In order to get the desired properties on polymeric materials is a head start to differentiate the substituents of phenol and primary amine which can supply more polymerizable sites affecting the process of curing. In this part of the thesis, synthesis approaches of mono-functional and bifunctional benzoxazine monomers have been discussed.

2.2.1. Synthesis of Mono-Functional Benzoxazine Monomers

Well-defined mono-functional benzoxazines were first synthesized in 1940s as mentioned above by achieving condensation reaction of primary amines with formaldehyde and substituted phenols [1]. They obtained this monomer in a solvent method with two stage procedure. After then, Burke reported that the benzoxazine ring reacts advantageously with the free ortho positions of a compound and constructs a Mannich Bridge [27], [28]. The synthesis method of the Mannich reaction for benzoxazine happens in a solvent by two stages. Firstly, N,N-dihydroxymethylamine derivative forms by adding amine to formaldehyde at lower temperatures. Secondly, the oxazine ring proceeds by reaction of crude product and the labile hydrogen of the hydroxyl group and ortho position of the phenol at the high temperature [28] (Figure 2.2)

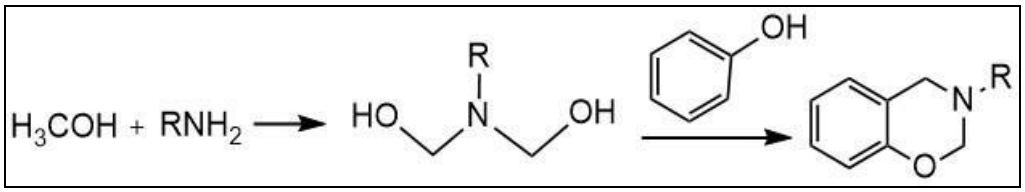


Figure 2.2: Synthesis of benzoxazine.

For instance, Burke [27] followed two procedures to synthesize 3, 4-dihydro-3-cyclo-hexyl-6-t-butyl-1, 3, 2 H-benzoxazine:

As a first procedure, cyclohexylamine and formaldehyde were dissolved in dioxane. Then, of *p*-butyl phenol was added into the mixture for refluxing 2 h. A crystalline product was obtained upon cooling to room temperature. For further purification, it was recrystallized from 95% ethanol and yielded as 78%.

As a second procedure, paraformaldehyde was first dissolved in a warm solution of KOH/methanol. Subsequently, cyclohexylamine was added in small portions while the solution was cooling down. Then, 4-*t*-butylphenol was also added into the obtained mixture and waited until room temperature was arrived. The final product was recrystallized from 95% ethanol and yielded 92%. Synthesis of a *p*-cresol based benzoxazine from formaldehyde, aniline, and *p*-cresol in dioxane has been reported [29], [30].

Ring opening reaction mechanism of some benzoxazines are due to active hydrogen (HY) containing compounds such as indoles, naphthol, imides, carbazole, and aliphatic nitro compounds [31]. Small oligomers are also observed as by-product. Figure 2.3 presents the arrangement of the Mannich-bridge caused by the ring opening of benzoxazine under acidic conditions (HY) [32]

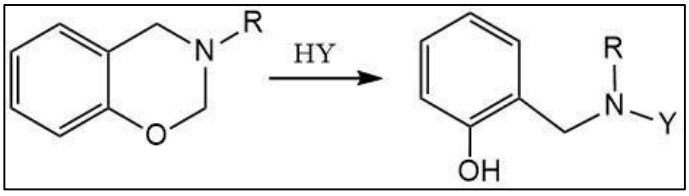


Figure 2.3: Ring opening of benzoxazine under acidic conditions.

Functional groups of the benzoxazines are responsible from the ring stability. Another aminoalkylation reaction was caused by multiple ortho positions in the

starting product. To use of ortho substituted phenols for derived benzoxazines increased the yield of the product [33].

This procedure has some challenges such as the slow reaction rates, requiring large amount of solvent for the synthesis, and in some circumstances, use of hardly soluble precursors. Additionally, process problems of the polybenzoxazines may appear with the solvent residue in the reaction medium. Solventless synthesis method in the melt state was improved as an alternative way to solvent method [34]. Liu reported the reaction kinetics and mechanism of this method [35]. To produce the desired benzoxazine, this typical procedure was followed in sequence all of the starting materials such as aldehyde, amine and phenolic precursors are mixed together, heated to their melting temperature, and kept at the temperature for a long period to assure completion of the reaction. At this point, mostly paraformaldehyde was preferred instead of formaldehyde, which would easily evaporate and lose stoichiometry quickly. Benzoxazine monomers can be easily designed by choosing the derivatives of phenols and amines for tailoring the properties of polybenzoxazines. This synthetic method is more useful than traditional methods considering that less impurities and by-products will be available.

2.2.2. Synthesis of Multi-functional Benzoxazine Monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Under mild polymerization conditions, chain growth can terminate at the dimer length due to hydrogen bond formation at the growth front [23], [36]. To overcome this limitation, a new class of difunctional or multifunctional benzoxazine monomers [29], [37] have been developed, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by NMR, FT-IR and SEC.

The solvent polarity is significant to obtain mainly the desired composition of the products. This reaction route has a few simple steps and can often results in various phenolic structures with design flexibility. The same procedure was followed

starting with aniline instead of methyl amine to produce similar type of difunctional benzoxazine [37]-[39] and the pure monomer was referred as bisbenzoxazine (B-a) and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a were analyzed by 1H-NMR measurements. The overall synthetic procedure is shown in Figure 2.4. To achieve successful processing, cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors is an auto-catalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process afterwards.

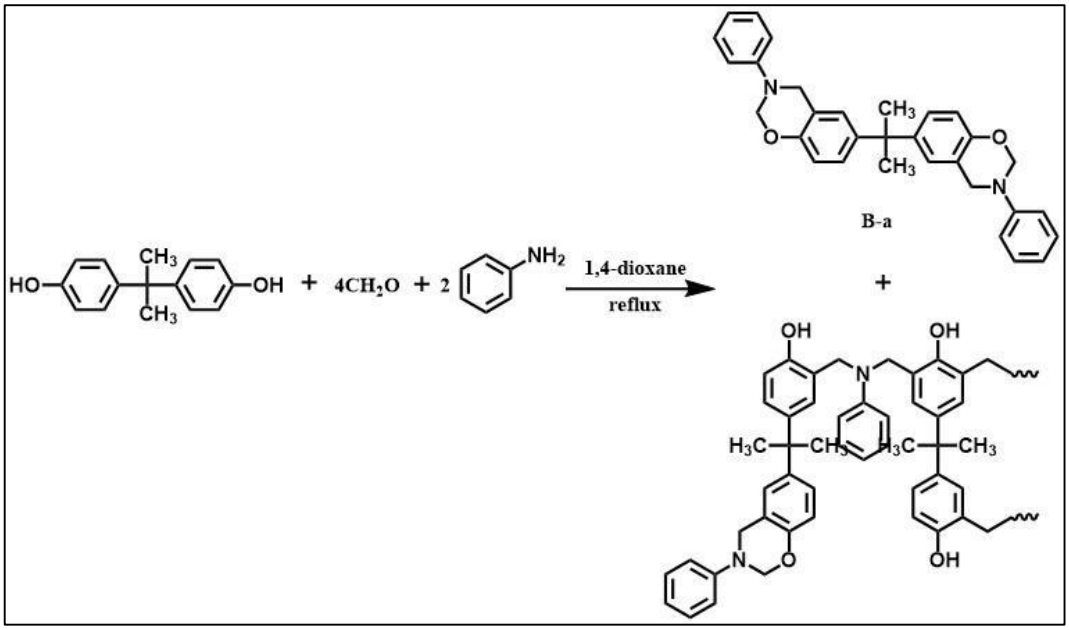


Figure 2.4: Synthetic pathway of B-a and oligo-B-a.

Brunovska et al. reported [40] the synthesis of bisbenzoxazine monomer in high char yield by the solventless method. They used 1,3,5 triphenyl(alkyl) hexahydro-1,3,5 triazine, paraformaldehyde and bisphenol A as starting materials.

2.2.3. Synthesis of Benzoxazine Monomers Having Different functionality

Regular benzoxazine monomers have some limitations such as the brittleness that can cause poor processability and the elevated temperature needed for the completion of the ring opening polymerization. Three main approaches are developed to remove these limitations:

- Synthesizing benzoxazines with special functional groups such as acetylene [41], allyl [13], [42], nitrile [43], [44], propargyl [45], alcohol [5], [17], norbornane [46], coumarin [7], epoxy [47], and maleimide [46] (Table 2.1).These modifications can increase the crosslinking and post-modifiable points.
- Preparing conventional polymers with benzoxazine moieties as repeating units. They can construct external crosslinks by curing partially or fully (Table 2.2).
- Producing main-chain benzoxazine precursors.

The major advantage of the benzoxazines is the design flexibility by choosing a wide range of different starting materials for desired application areas.

Table 2.2.: Some Examples of Polymers with Benzoxazine Moieties.

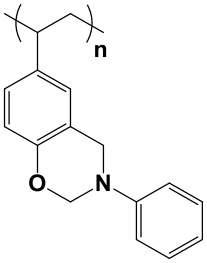
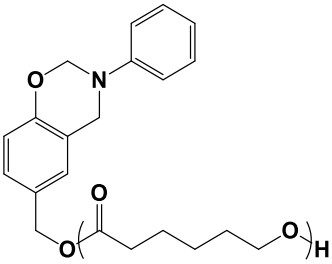
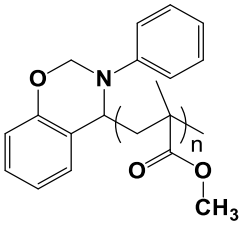
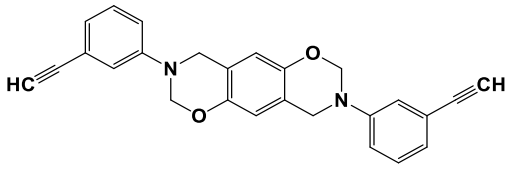
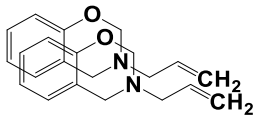
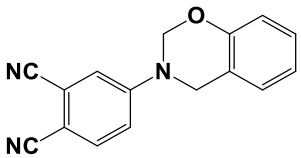
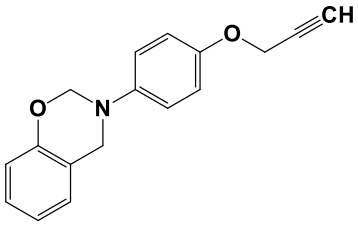
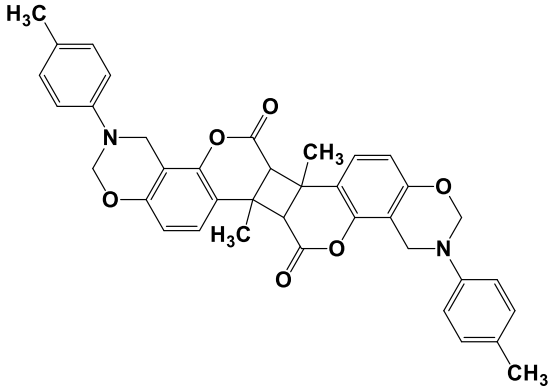
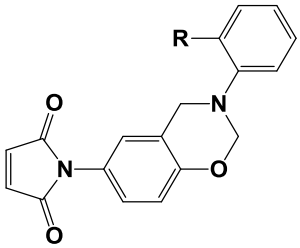
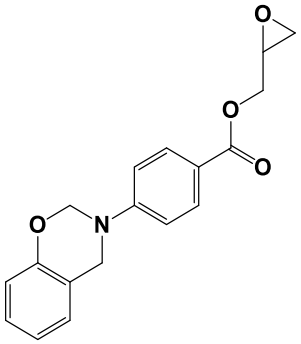
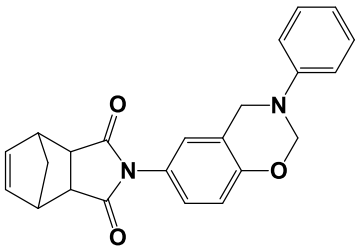
Examples of Polymers with Benzoxazine Moieties		
		
benzoxazine functional polystyrene [48]	benzoxazine functional poly (ε-caprolactone)[49]	benzoxazine functional poly (methyl methacrylate)[50]

Table 2.1: Different Functional Benzoxazine Monomers.

Benzoxazine Monomers	
 Acetylene containing benzoxazine [41]	 Allyl-containing benzoxazine [42]
 Nitrile-containing benzoxazine [43]	 Propargyl-ether-containing benzoxazine [45]
 Coumarine-containing benzoxazine [7]	 Maleimide-containing benzoxazine [46]
 Epoxy-containing benzoxazine [47]	 Norbornane-containing benzoxazine [46]

2.3. Historical Outlook of Polybenzoxazines

High performance polymeric materials are interesting to study because of their research and development programs in the world. There are plenty of polymer types that have been subject of a variety of research which ended with useful applications. But most of those polymers cause some problems during the process of production to application. It is either too difficult to synthesize and derive or some hazardous chemicals come out during the reactions. Or final products might have some problems. For instance, one common type of polymer, phenolic resins are thermally very stable, however they decrease their mechanical structure. They are cheap and easy to produce but they require alkali environment and there are a lot of hazardous leftover substances [51]. Polybenzoxazines are an alternative to phenolic resins because they possess most of the properties of phenolic resins and they are more advantageous to derive, have less hazardous chemical products, possess high mechanical resistance, higher thermal stability compared to known polymers, durable against solvents, acids, and base, creates low smoke when exposed to fire and loses almost no volume during curing process [26], [52].

Because of those properties of polybenzoxazines they are potential replacements of phenolic resins, polyesters, vinyl esters, epoxies, cyanate esters, and polyimides. Benzoxazines are synthesized around 1940's [1], [27]. Chemistry of benzoxazine is studied as organic chemistry in 1950 and 1960's [52], [31]. Studies on polybenzoxazine continued after its anti-cancer effect is investigated [53]. Anti-cancer properties weren't enough to use them in medicine but studies still continue [54]. These molecules are used for the modification of epoxy resins in 1970's [55]. This study is the first use of this substance in material science. Cross-linked polybenzoxazines are developed for the first time in 1980's [56]. At the same time Riese and his friends investigated reaction kinetics during formation of benzoxazine oligomer by usually using single functional benzoxazine monomer and he showed that high molecular weight polybenzoxazines cannot be produced from single functional benzoxazines [57]. After their potential material properties are recognized, Ning and Ishida introduced their first basic scientific results in 1994. In this study results showed that polybenzoxazines can compete with phenolic resins [23], [29].

As a result, this study became a new important study area where universities and research groups are making research about.

The basic reason that polybenzoxazines are important is their complex hydrogen bonds and amino methyl bridges in its structure. Almost all of the known forms of hydrogen bonds (intramolecular OH⋯OH, OH⋯N 6 membered hydrogen bond and OH⋯π relations) exist in polybenzoxazines. Molecular modellings, X-Rays, solid state proton NMR, and FTIR studies supported both intramolecular and external molecule hydrogen bonging formation [58]-[61]. In basic synthesis methods of polybenzoxazines, benzoxazine monomer is heated directly to the temperatures around 180–250 °C. Monomer is exposed to ring opening polymerization and insoluble polymer is attained (Figure 2.5). This polymerization can be catalyzed with Lewis acids and produce polymers at lower temperatures respectively [9], [62].

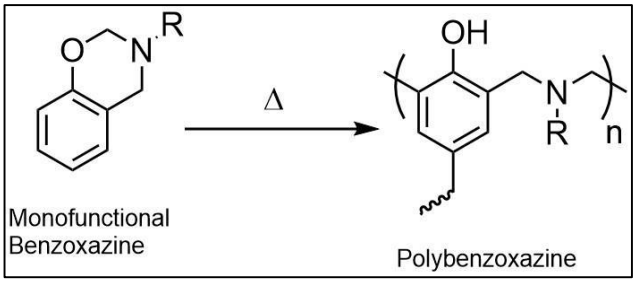


Figure 2.5: Polybenzoxazine synthesize.

Synthesize of monomers are attained by phenols, primary amins and formaldehydes. Some other methods are tried yet this is the simplest one [63]-[67]. However, some monomer structures are not attained by this method. For this reason, some alternative methods needed. Some of those methods closes rings by reduction and produces Schiff base or using amine instead of triazines. By Schiff method, benzoxazines that contains free phenols are synthesized [68].

In this thesis by using Schiff method an asymmetric and functional group containing benzoxazine monomer is produced and added to the literature. Benzoxazine monomers that have a single oxazine in its structure but can react with phenol functions at two ends are very useful for most of the polymerization methods. Two functional and asymmetric structured benzoxazine monomers are transformed to a thermoset in this study for the first time. Polybenzoxazines that is produced by

this method are important due to their high number of cross-link points which makes them more thermally stable.

2.3.1. Ring Opening Polymerization of Benzoxazines

The reaction mechanism of ring opening polymerization in benzoxazine resins are recommend by several attempts that begins with the construction of the linear chain and goes on with branching and crosslinking [69]. Polymeric chains build up networking structure while the molecular weight increases. Polybenzoxazines have a distinctive polymerization system for crosslinking. They don't need any curing catalyst at high temperature and release by-products.

Benzoxazines, consisting of six-membered heterocyclic rings, have irregular chair structures with ring strain that polymerize by ring-opening at elevated temperatures. The elevated temperature is necessary for cleavage of the heterocyclic bond rather than epoxides. The monofunctional benzoxazines commonly induce linear (or perhaps branched) polymers with low molecular weights except having reactive benzene rings for producing crosslinked polybenzoxazines [70]. Furthermore, multiple functionality on the benzoxazine monomers cause to more crosslinked polybenzoxazines [29].

Ring-opening polymerization of benzoxazine by heat occurs via cationic mechanism with or without the use of an initiator. A labile proton initiator, such as phenol, leads to a phenolic structure in polybenzoxazine whereas a nonlabile proton initiator, like Lewis acid, forms arylether. Considering the aryl ether does not have good thermal stability, it turns into the phenolic structure at high temperatures (Figure 2.6).

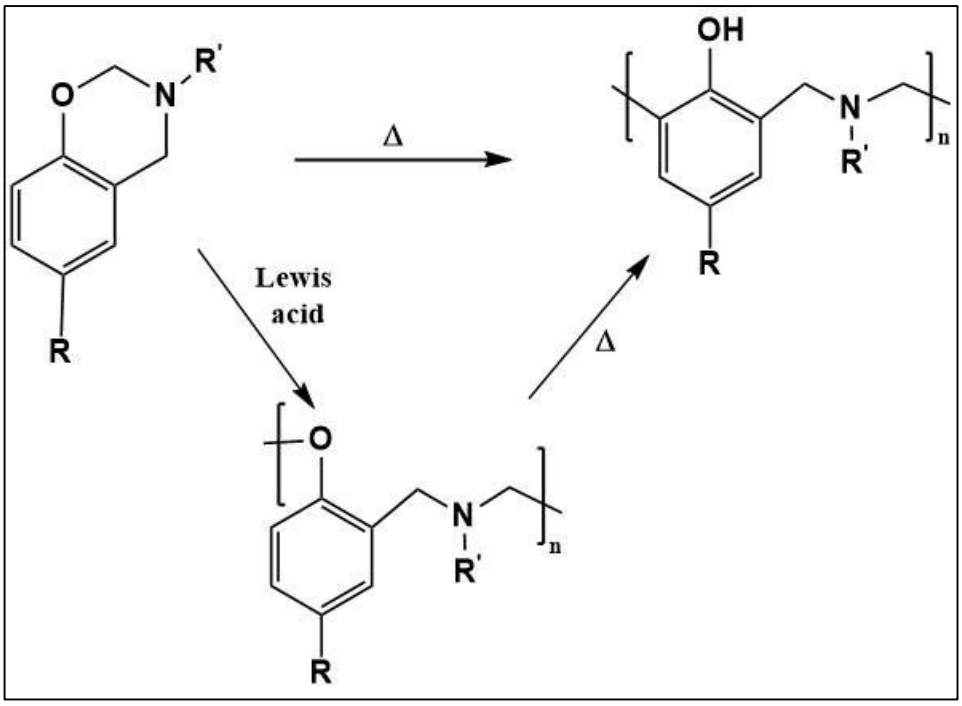


Figure 2.6: Ring opening polymerization of benzoxazine by heat or acid.

As the benzoxazine monomer ordinarily comprises cationic initiator residues, such as phenolic reactants or oligomers, the polymerization is still achieved by heating the benzoxazine monomer. Furthermore, the recently obtained phenolic materials have importance on initiation resulting in an auto-catalyzed polymerization system [71]. For enlarging of polymer chains, the reactive terminal end of a polymer attends to cyclic structures through ionic propagation. The temperature range between 160-220 °C is essential for the polymerization rate which related to heating process. [29]. A gel can be formed quickly, if there is no initiator or catalyst.

Ring opening polymerization is an attractive area due to their reaction mechanism in resin chemistry. These polymerization reactions are mostly affected by cyclic precursors having functional groups and the ring size [72]. Benzoxazines, heterocyclic rings, can mainly generate the different structures of the polymers such as linear or crosslinked depending on the reaction proceeding at the *ortho* and additional *para* positions. In polymerization, the most reactive site is the ortho position to the hydroxyl group on the aromatic ring. Furthermore, para and meta positions are also reactive sites but their reactivities are quite less than ortho positions. These multiple reactive sites limit the perfect linear chains on polymer development from monofunctional bezoxazines.

The purity of benzoxazine is responsible from arrangement of the polymerization rate and temperature. The curing temperature can rise up to high purity. In addition, elevated temperatures need shorter time for the ring opening polymerization of the benzoxazine [73]. Besides the purity of monomer, steric hindrance and electronic properties of its surrounding groups also affect the rate of ring-opening polymerization [74].

The environmental issues are obtained with the starting materials of the benzoxazine. On the other hand, the release of the formaldehyde, phenol and amine derivatives at ring opening polymerization process is quite lower than the regular phenolic resins. Plus, conventional phenolic resins expose water molecule as byproduct, however any water molecule is observed during polybenzoxazine formation.

2.3.1.1. ROP mechanisms of Benzoxazines

The mechanism of ring-opening polymerization of benzoxazine [70], [75]-[80] is assumed by many researchers and some of them are placed in Figure 2.7. The formation of the by-product is quite complex and because of that an accurate mechanistic explanation for polybenzoxazine formation is complicated. Phenolic-type Mannich polymer and nonphenolic arylether-type Mannich base polymer can be generated from same monomer depending on the initiation mode [78]. As mentioned above under thermal curing, the arylether polymer converts into the phenolic polybenzoxazine with Mannich base in traditional polybenzoxazines [80]. For last stage, it is still unclear that why it takes place early on mono-substituted benzoxazines exactly.

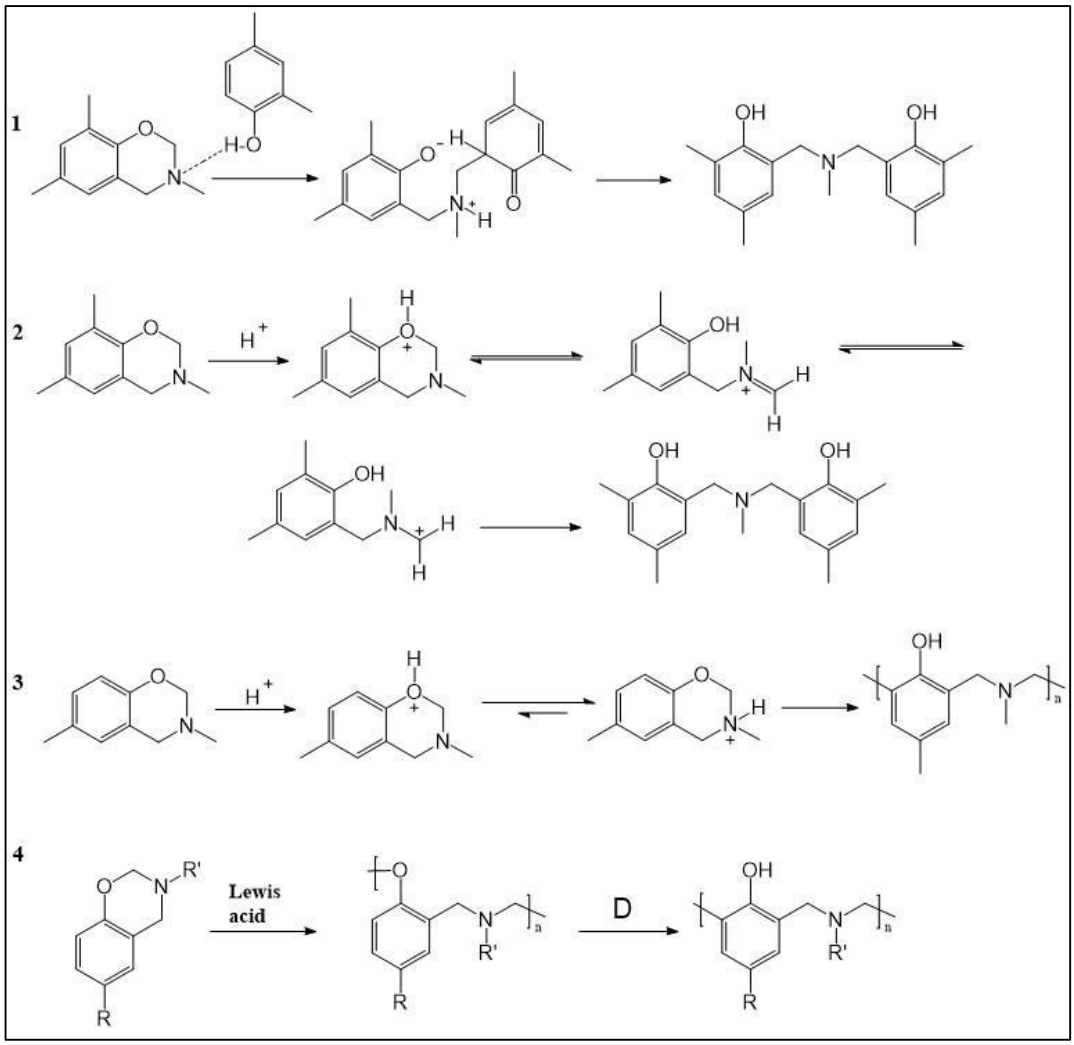


Figure 2.7: Assumed ring opening mechanisms of benzoxazine.

Benzoxazine molecule performs reverse Mannich reaction (Figure 2.8). At the initiation reaction, intermolecular hydrogen bonded intermediary complex is formed by approaching of phenol to benzoxazines [81]. In this complex, electrons of nitrogen atom shifts to hydroxyl group of phenol.

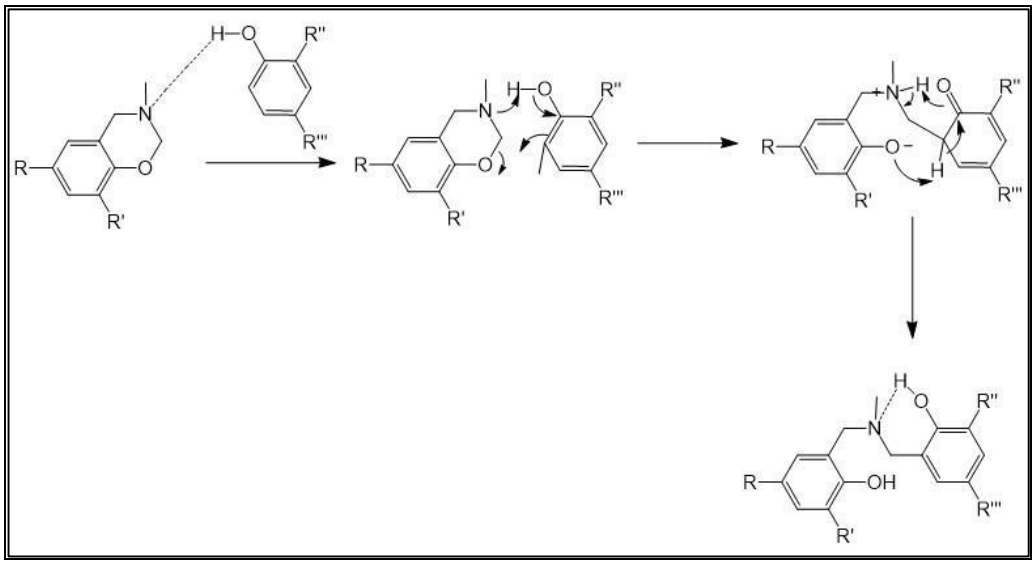


Figure 2.8: Ring opening mechanism of benzoxazine.

During curing of benzoxazine, chain propagation and intra-molecular six-membered ring hydrogen bonding competes each other [82], [83]. Because of this difficulty, mono-functional benzoxazines form short linear polybenzoxazine chains with low molecular weight. So that using a blend partner polymer, which forms hydrogen bond, presents synergism in polybenzoxazine preparation and increases the *T*g comparing to pure components.

The active sites on the benzene ring of benzoxazine behave in varying degrees of reactivity. Although this rich reactivity complicates the polymerization mechanism, it causes regioselectively improvement of mechanical and thermal properties. For example, a methyl substitution on aniline in benzoxazine synthesis increases the *T*g value for 75 ºC [84], [85].

Bond breaking mechanism is started by heat and the heat shows external increase because of more bond formation with additional crosslinking points. This energy release causes an exothermic peak which is due to the stability of the obtained cured product.

3. EXPERIMENTAL PART

3.1. Materials

3.1.1. Solvents

All of the solvents such as ethanol, chloroform, toluene, diethyl ether, n-hexane, dimethylsulfoxide, and methanol were supplied from Merck and used without further purification.

3.1.2. Chemicals

2,5-Dihydroxybenzaldeyde (alfa aesar, 98%), 2,4-dihydroxybenzaldehyde (alfa aesar, 98%), 4-aminophenol (merck, 99%), sodium borohydrate (merck, 98%), paraformaldehyde (alfa aesar, 97%), sodium hydroxide (merck, 99%), allylamine (alfa aesar, 98%) and aniline (merck, 99,5%) were used as received.

3.2. Characterization

3.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with $Si(CH_3)_4$ as an internal standard, operating a Varian UNITY INOVA 500 MHz instrument.

3.2.2. Fourier Transform Infrared Spectrophotometer (FT-IR)

The FTIR spectra of the monomers and cured monomers were recorded on a Perkin Paragon 1000 Spectrometer.

3.2.3. Differential Scanning Calorimeter (DSC)

Under Nitrogen flow (20 ml min^{-1}), curing temperatures of the polymers were recorded on a Pelkin Elmer DSC 8500 instrument.

3.2.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was determined on a Mettler Toledo TGA/SDTA 851 instrument and the heating rate was 10 °C min^{-1} from room temperature to 900 °C under nitrogen atmosphere.

3.3. Synthesis of Benzoxazine Monomers Having Phenolic End Groups via Two-Step Procedure

A phenolic OH-containing benzoxazine, which cannot be directly prepared from phenol, aminophenol, and formaldehyde by traditional one step procedures, has been successfully prepared by a two-step procedure.

3.3.1. Synthesis of 2-((4-hydroxyphenylamino)methyl)benzene-1,4-diol

In a dry 50 ml round bottom flask, 2,5-dihyroxybenzaldehyde (2 gr, 14.4mmol) and 4-aminophenol (1.5 gr, 14.4 mmol) were dissolved with 60 ml of ethanol by addition of catalytic amount of sulphuric acid. After refluxing for 5 h at 72 °C in argon atmosphere, the red mixture was cooled to room temperature and 1 equivalence of $NaBH_4$ (0.54 gr, 14.4 mmol) was added in small portions. The obtained solution was further mixed for 3 h. When the reduction completed, it was concentrated to 20 ml and 40 ml of distilled water was added and washed with 120 ml of diethyl ether three times. It was dried over $MgSO_4$ and after evaporation of solvent, brown precipitate was obtained. For further purification, column chromatography was used with 3:1 ratio hexane:ethylacetate as an eluent solution. White color of benzylamine (2-((4-hydroxyphenylamino) methyl)benzene-1,4-diol) was yielded around 45%. (M_W:231,25 g/mol)

3.3.2. Synthesis of 3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol

In a 100 ml round-bottom glass flask, 2-((4-hydroxyphenylamino) methyl)benzene-1,4-diol (1.5 gr, 6.5 mmol) and paraformaldehyde (0.39 gr, 13 mmol) was dissolved with 75 ml of toluene:ethanol (2:1) mixture and equipped with

a condenser and magnetic stirrer. After refluxing for 18 h at 102 °C, the reaction solvent was removed and crude product was precipitated in ether. The precipitate was separated by using centrifuge. The purification step was completed by precipitating the organic layer in hexane. 90% yield of black solid benzoxazine [3-(4-hydroxyphenyl)-3,4-dihydro-2Hbenzo[e][1,3]oxazin-6-ol] was synthesized. (M_W:243,26 g/mol)

3.4. Synthesis of Allylic Asymmetric Bisbenzoxazine Monomer via Two Step Procedure

3.4.1. Synthesis of 2-((phenylamino)methyl)benzen-1,4-diol

2,5-Dihydroxybenzaldehyde (3 gr, 21.7 mmol) and aniline (2.02 gr, 21.7 mmol) were refluxed with 90 ml of ethanol in a 100 ml round bottom flask under argon atmosphere at 72°C for 5 h. The obtained imine as red color was reduced with sodium borohydrate (0.82 gr, 21.7 mmol) for 3 h. The solution was concentrated to 30 ml and extracted with 180 ml of diethyl ether for 3 times after addition of 60 ml of distilled water. It was dried adding magnesium sulphate and its solvent was evaporated was in a rotary evaporator. 2-((phenylamino)methyl)benzene-1,4-diol having dark red color was synthesized with a yield of 83%. (M_W:215,25 g/mol)

3.4.2. Synthesis of (3-allyl-8-phenyl-2,3,4,7,8,9-hexahydrobenzo[1,2-e:4,5-e']bis([1,3]oxazine))

In a 500 mL round bottom flask, benzylamine (3.95 gr, 18 mmol), allylamine (1.05 gr, 18 mmol) and paraformaldehyde (1.66 gr, 55 mmol) were dissolved in 270 ml of ethanol: toluene (1:2) mixture under argon atmosphere. The reaction mixture was stirred at 102 °C for 18 h. The solvent was evaporated under vacuum and the black product was dissolved in chloroform. The solution was washed five times with 0.1 M sodium hydroxide (NaOH) aqueous solution. The organic phases were dried with magnesium sulphate. It was concentrated to 10 mL by evaporating under vacuum and precipitated in 200 mL of hexane. The resulting product was purified by using column chromatography with silica gel as an internal standard and mixture of

hexane: ethyl acetate (3: 1) as a mobile phase and dark brown product was obtained (Yield: 30%) (M_W:308,37 g/mol)

4. RESULTS and DISCUSSION

4.1. Benzoxazine Monomers Having Phenolic End Groups

To increase the thermal stability of polybenzoxazine it was aimed to obtain new benzoxazine monomer by using different synthesis methods. At the first part of this study one function benzoxazine was prepared that carries phenol group at two ends. With the traditional routes, benzoxazine synthesize is obtained as result of Mannich condensation of amine, phenol and formaldehyde. However, functioning of the two ends of the benzoxazine requires two step methods as it is presented in this thesis. Additionally, thermal ring opening reaction of this new benzoxazine monomer was observed and attempts were made obtaining polycarbonate by condensation.

4.1.1. Synthesis of 3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol

Imine that was formed upon condensation of 2,5-dihydroxybenzaldehyde and 4-aminophenol under argon atmosphere was reduced by sodium borohydrate. Reaction mixture reacted with formaldehyde to benzoxazine synthesis after it was extracted with ether and ethanol. Once obtained reaction mixture was precipitated in hexane, benzoxazine monomer that carries phenol at two ends was synthesized as single ring (Figure 4.1)

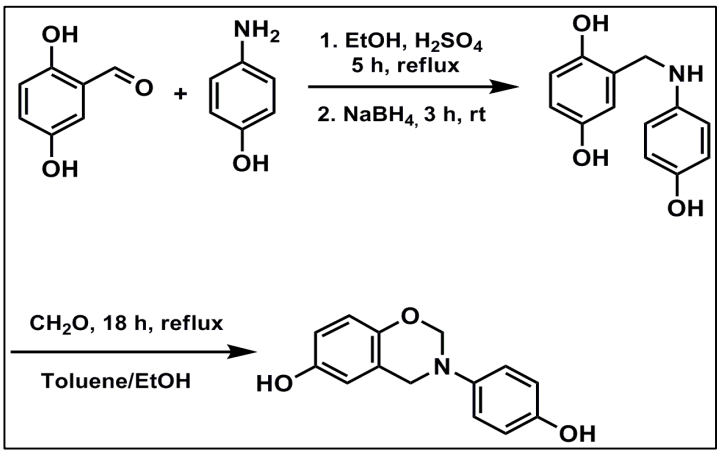


Figure 4.1: Synthetic pathway used in the preparation of benzoxazine having phenolic end groups.

4.1.2. Characterization of 3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol

The molecular structure of this novel benzoxazine bearing phenolic end groups [3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol] was determined by ^{1}H NMR measurements. As shown in Figure 4.1, the characteristic peaks of benzoxazine, O-CH_2-N (1) and Ph-CH_2-N (2), were observed at 5.17 and 4.40 ppm, respectively. The signals of phenolic OH was placed at 8.84 and 8.91 ppm, indicating that aimed benzoxazine monomer structure that carries phenol groups at two ends formed.

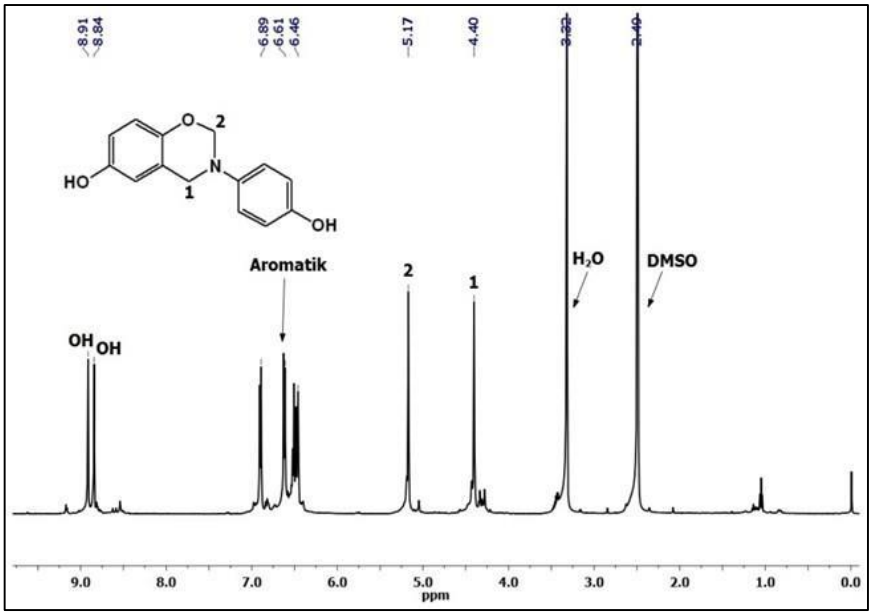


Figure 4.2: ^{1}H-NMR spectrum of benzoxazine having phenolic end groups.

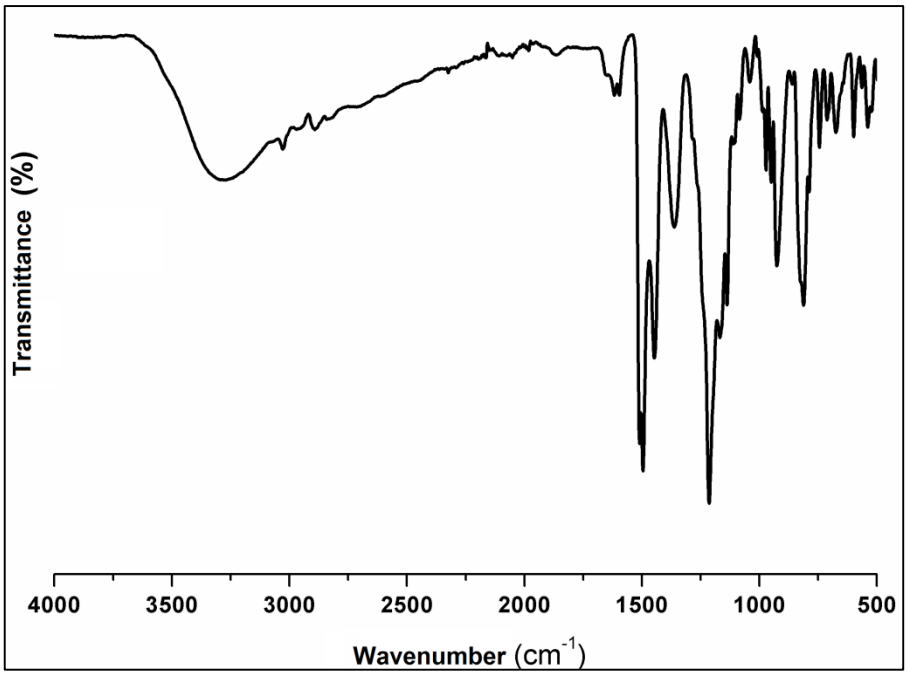


Figure 4.3: IR spectrum of benzoxazine having phenolic end groups.

The IR spectrum of benzoxazine having phenolic groups is shown in Figure 4.3. 1350 cm^{-1} and 1240 cm^{-1} are typical benzoxazine peaks and 3400 cm^{-1} belongs to hydoxide groups.

4.1.3. Thermal Polymerization of 3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol

Thermal polymerization behavior of benzoxazine monomer [3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol] that carries phenol at two ends was monitored by curing at different temperatures (Figure 4.4).

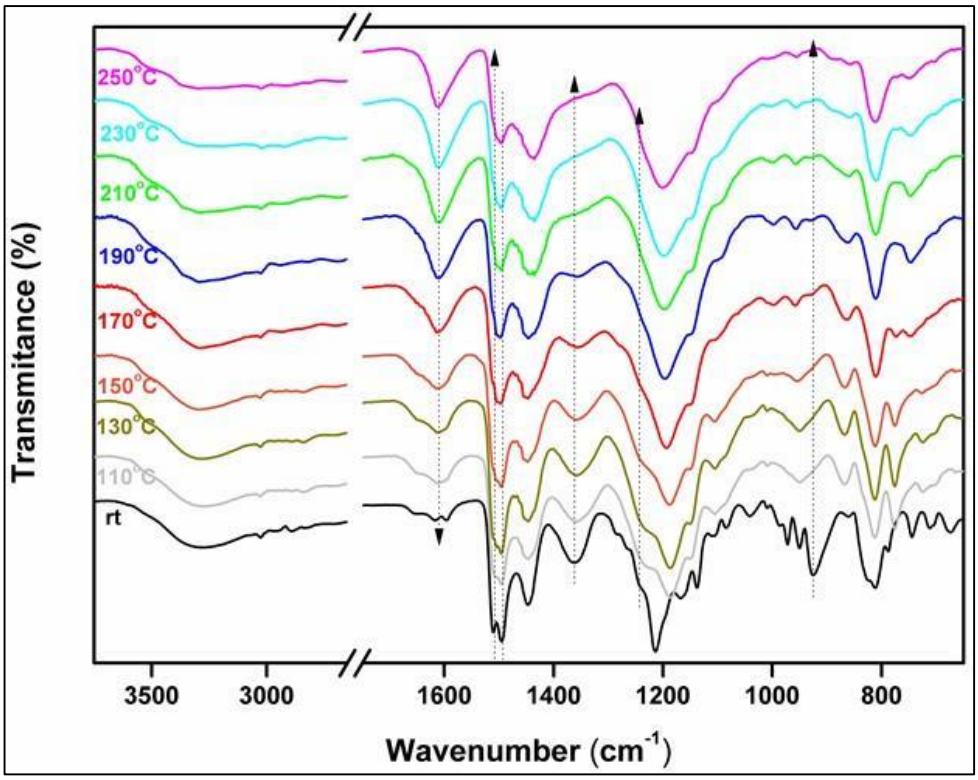


Figure 4.4: FT-IR spectra of phenol functional benzoxazine which cured different temperatures.

IR spectra of uncured and completely or partially polymerized states of phenol ended benzoxazine that was heated for 5 min. at 110 °C, 130 °C, 150 °C, 170 °C, 190 °C, 210 °C, 230 °C and 250 °C was seen in Figure 4.4. Presence of O-H absorption band at 3300 cm^{-1} retains as getting thicker as the temperature increases. Absorption band at 1609 cm^{-1} indicates new dense aromatic structures formed as a result of ring opening reaction of benzoxazine starts to appear after 110 °C. Bands at 1512 and 1495 cm^{-1} which indicates two and three substitutions of benzene ring also expand as the temperature increases. Typical benzene peak which is bonded with oxazine out plane at 935 cm^{-1}, absorbances of asymmetric Ar-O-C at 1245 cm^{-1} and CH_2 fluctuation at 1364 cm^{-1} disappears completely after oxirane ring in benzoxazine opens at 110 ^{o}C.

The absorbance that is usually observed around 1478 cm^{-1} in IR spectrum that is caused by four substitutions benzene ring formation in usual polybenzoxazine, is not absorbed during curing of phenol ended benzoxazine. Morever, it is observed that the band that indicates 1, 2, 4-three substitutions of phenyl at 1495 cm^{-1} decreases and yet does not disappear. This behavior indicates formation of a new 1, 2, 4-three substitutions phenyl of benzoxazine ring as it is marked in Figure 4.5.

Nitrogen bridge that opens in benzoxazine ring with the heat, maintain its three substitutions benzene existence by linking phenols at the end of the monomers that exist before the ring opens, instead of linking to newly formed phenol as it is seen in typical benzoxazines.

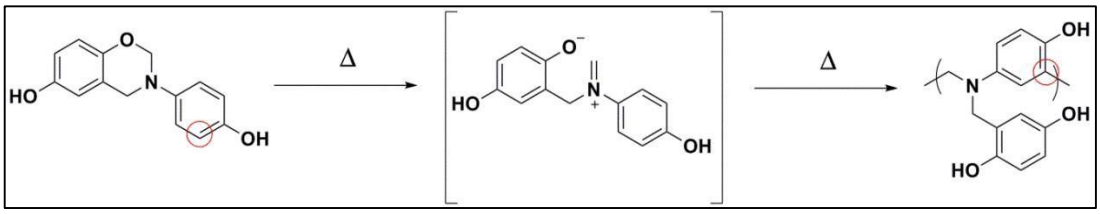


Figure 4.5: Probable mechanism of polybenzoxazine formation.

DSC thermograms of uncured and completely or partially polymerized states of phenol ended benzoxazine that was heated for 5 min. at 110 °C, 130 °C, 150 °C, 170 °C, 190 °C, 210 °C, 230 °C and 250 °C is seen in Figure 4.6. Benzoxazine monomer, to which heat is not applied, presents 2615 J/g exotherm that starts from 95 °C and reaches to a maximum at 193 °C. In this study phenol ended benzoxazine production aims to decrease polymerization temperature compared to usual benzoxazine because of catalyst effect of hydroxyl group on ring opening It is also known that para position hydroxyl, which is an electron donating group increases reactivity by supporting Zwitter ion production during polymerization. Maximum of this exotherm is observed as 194 °C and heat 375 J/g after being cured for 5 min. at 110 °C. As the curing temperature increases maximum value of exotherm increases and heat decreases as it is expected.

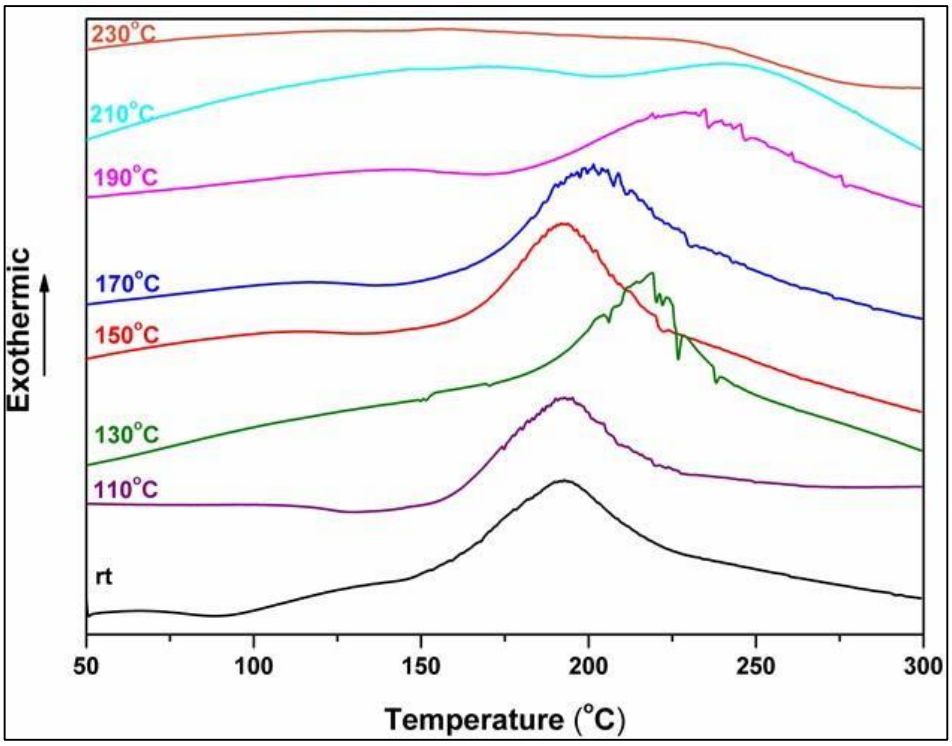


Figure 4.6**:** DSC thermogram of phenol functional benzoxazine cured different temperatures.

TGA thermogram in Figure 4.7 of cured polybenzoxazine shows that 60% of the substance still exists at 900 °C which shows that thermal stability of cured polybenzoxazine is high. 5% of weight loss is observed at 302 °C and 10% of weight loss is at 356 °C is observed.

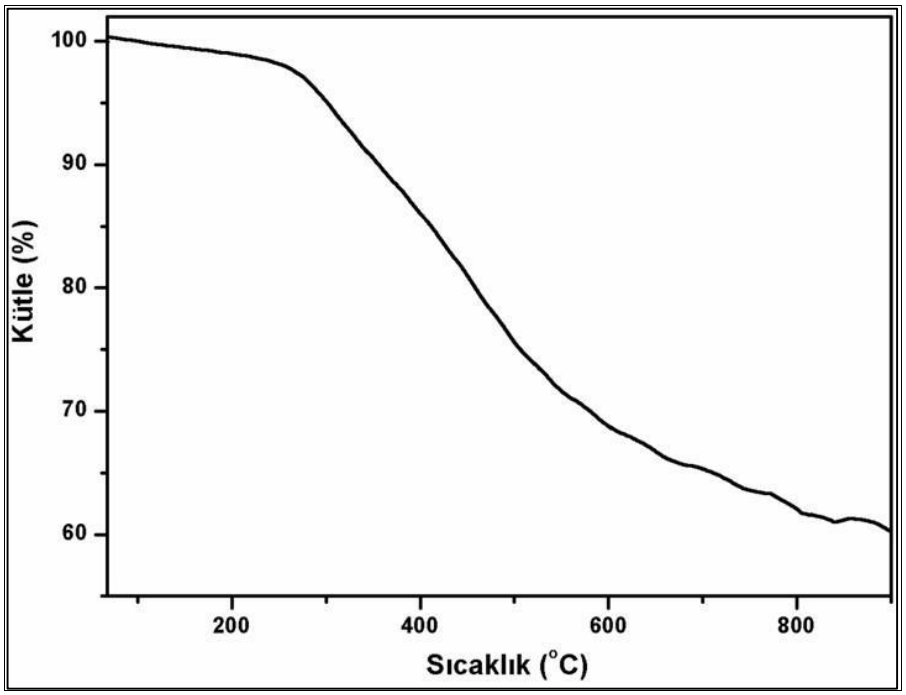


Figure 4.7: TGA thermogram of the curing benzoxazine at 250 °C for 5 mins.

4.1.4. Condensation of 3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo [e][1,3]oxazin-6-ol

At the last part of this study, phenol ended benzoxazine and terephthaloyl chloride reaction was tested. It is aimed it to transform to pioneer polymer that contains benzoxazine in the main chain (Figure 4.8). 3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol was dissolved in THF and then pyridine was added with 6:1 ratio. Afterwards terephthaloyl chloride was put with 1:1 ratio to the reaction mixture slowly at 0 ° C. Afterwards, brown precipitate was observed. The reaction mixture that was kept at room temperature for two days was filtered and then attempted to be precipitated in methanol. After having been kept for a day, cloudy precipitate was separated via centrifuge and GPC measurements of this substance were taken. No polymeric structure was found in GPC measurements.

In this reaction DMF is used as a solvent in the same conditions however undissolved solid substance was observed. No polymeric structure was found in filtrate. Triethylamine was used to alter the pH of the medium conduct but again undissolved solid substance was formed.

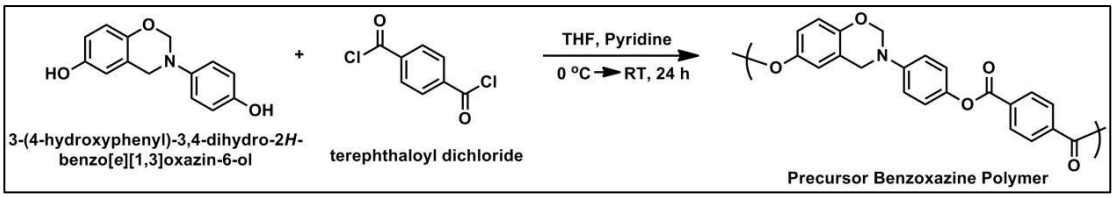


Figure 4.8: Synthesis of precursor benzoxazine monomer.

4.2. Asymmetric Bifunctional Benzoxazine Monomer

At the second part of this thesis, bifunctional benzoxazine monomer was synthesized out of the traditional procedures. Additonally, thermal ring opening reaction of this new benzoxazine monomer was investigated and thermal stability of the obtained polybenzoxazine was examined using FT-IR, DSC, and TGA measurements.

4.2.1. Synthesis of Allylic Asymmetric Bifunctional Benzoxazine Monomer via Two-Step Procedure

Imine that was obtained from condensation of 2,5-dihydroxybenzaldehyde and aniline under argon atmosphere was reduced by sodium borohydrate. The red crude product reacted with formaldehyde and allyl amine to benzoxazine synthesis after it was extracted with ether and distilled water. It was purified by using column chromatography and then precipitated in hexane.

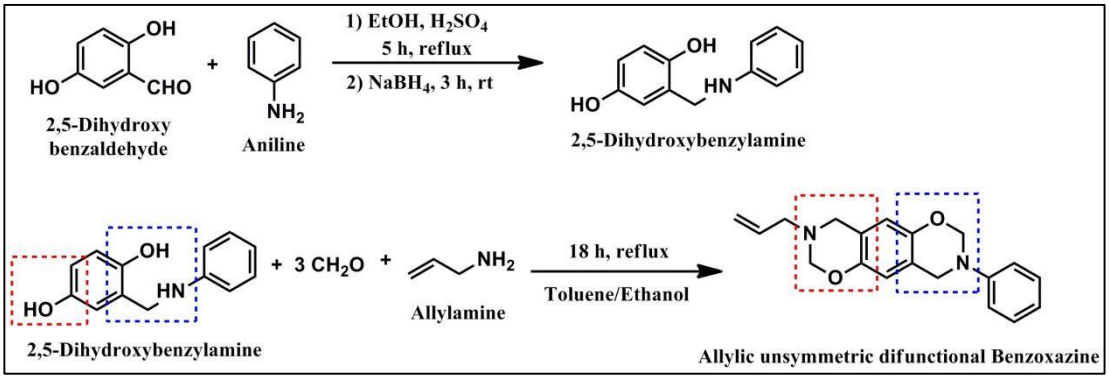


Figure 4.9: Synthesis of allylic asymmetric bifunctional benzoxazine.

4.2.2. Characterization of Allylic Asymmetric Bifunctional Benzoxazine Monomer

Figure 4.10 shows ^{1}H-NMR spectrum of this asymmetric benzoxazine monomer. The peaks which are located in 4.53, 4.54, and 5.32, 5.34 ppm show the existence of two different benzoxazine rings. The allyl groups evidenced by the peaks at 5.88, 6.50 and 6.53 ppm. In addition, aromatic peaks are well-demonstrated on the ^{1}H-NMR spectrum in the range of 6.82-7.21 ppm. For structural characterization, the IR spectrum of the obtained novel benzoxazine is given in Figure 4.11.

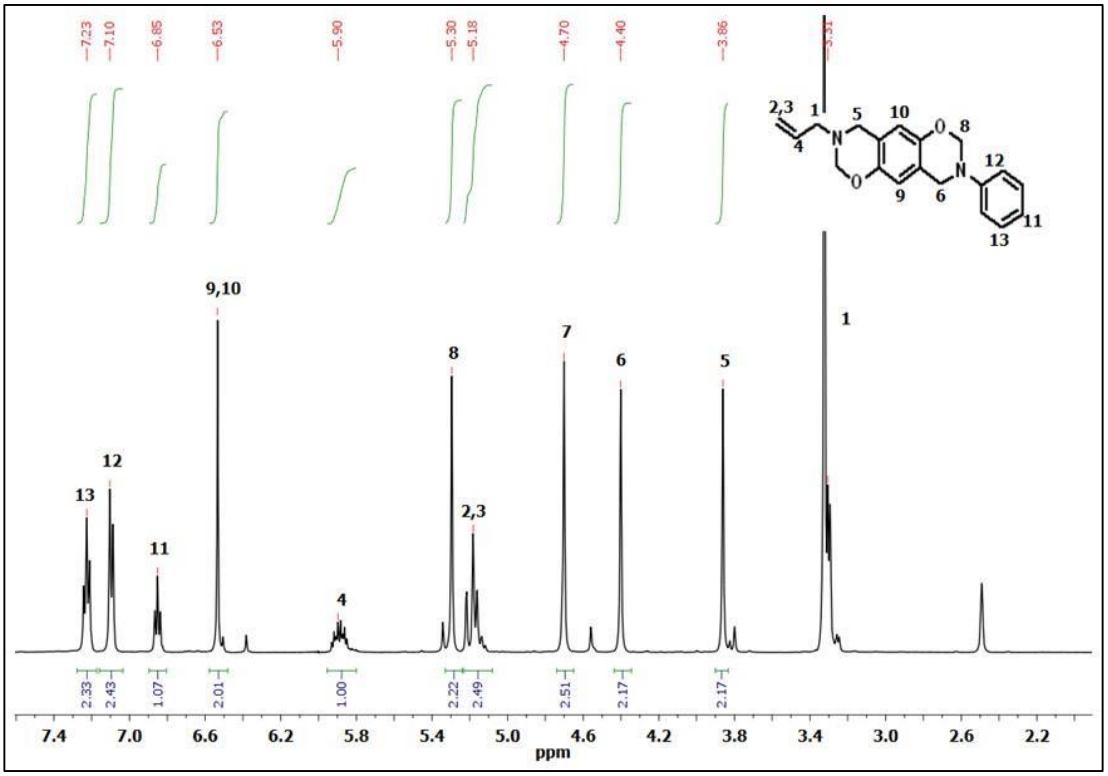


Figure 4.10: ^{1}H-NMR spectrum of allylic asymmetric bifunctional benzoxazine monomer (DMSO- d^{6}).

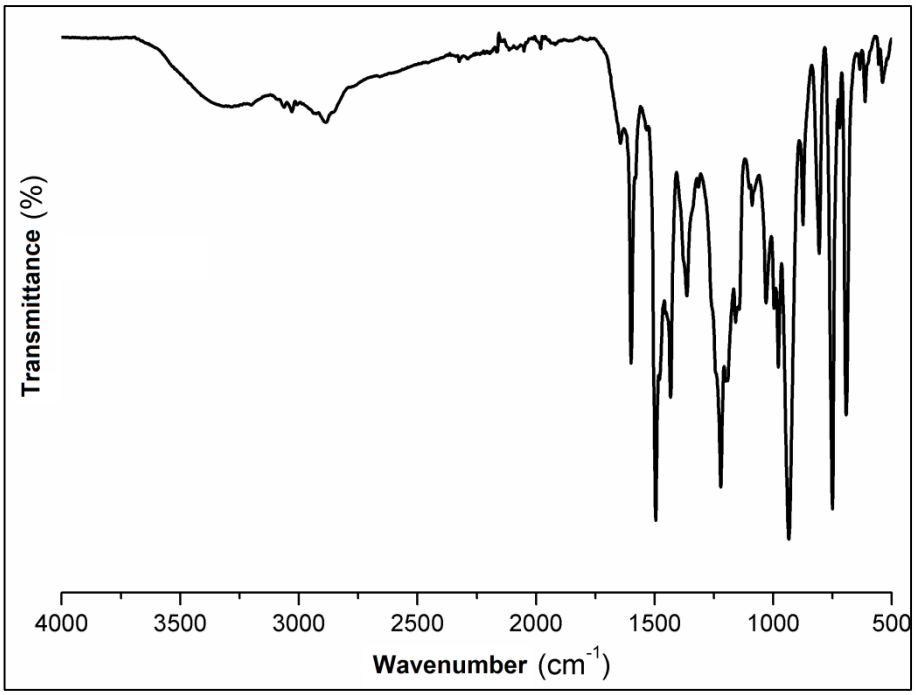


Figure 4.11: IR spectra of asymmetric bifunctional benzoxazine monomer.

4.2.3. Thermal Polymerization of Allylic Asymmetric Bifunctional Benzoxazine Monomer

Figure 4.12 presents the IR spectra of asymmetric bisbenzoxazine after accumulative curing at each temperature for 5 min. Phenolic structure comes out by thermal ring opening reactions, so O-H absorption started to increase from 180 ^{o}C to 220 ^{o}C. As the intensity of the 1476 cm^{-1}peaks decreased by increasing of the polymerization temperature, intensity of four substituted benzene ring is disappeared after 220 ^{o}C. 875 cm belongs to five substituted benzene ring. It is decreased at 180 ^{o}C, despite increasing the temperature it is still existed by becoming thicker. This behavior shows the presence of five substituted phenyl which is associated with oxazine-nitrogen bridge which formed upon opening of the benzoxazine ring. At 933 cm^{-1}, as the temperature increases typical out of plane C-H bending that belongs to benzoxazine ring reduces and disappears when 220 ^{o}C is reached. Asymmetric Ar-O-C at typical 1245 cm^{-1} and CH_2 fluctuation absorbance change at 1364 cm^{-1} that belong to benzoxazine are observed in the spectrum.

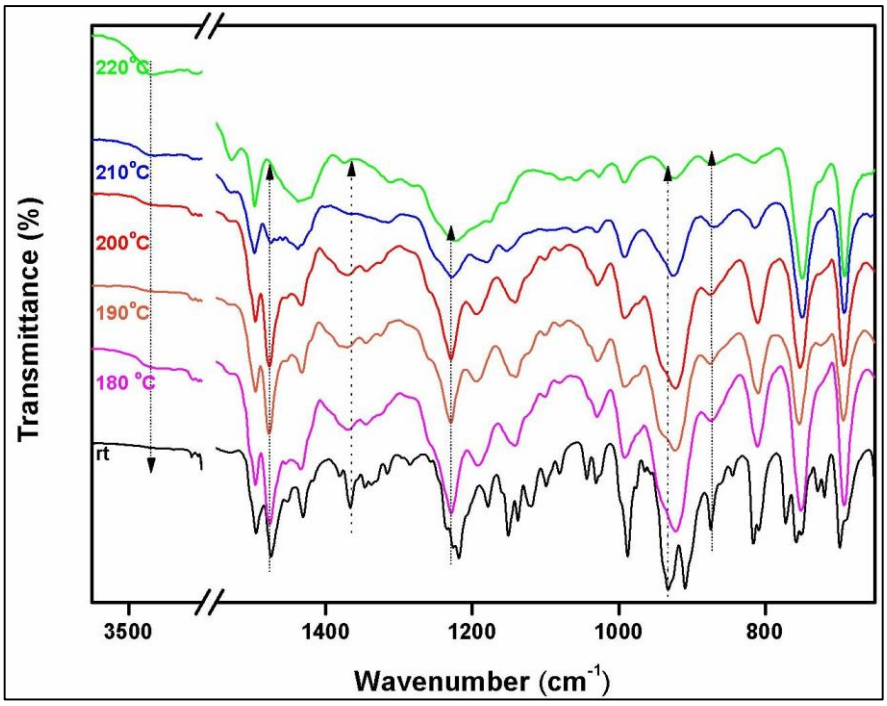


Figure 4.12: FT-IR spectrum of allylic asymmetric bifunctional benzoxazine cured different temperatures.

When the spectra are enlarged (Figure 4.13) to examine thermal behavior of allyl group in the asymmetric benzoxazine, it is observed that C-H stretching absorbance band at 3006 cm^{-1} went down to 210 ^{o}C and completely disappeared at 220 ^{o}C. C=C streching peak at 1639 cm^{-1} decreases heating from 180 ^{o}C and merges with absorbance of dense aromatic structures in the formation of polybenzoxazine at 1643 cm^{-1}. According to these observations, it can be concluded that polymerization of allyl group and ring opening reaction start at the same temperatures and again end at the same temperatures.

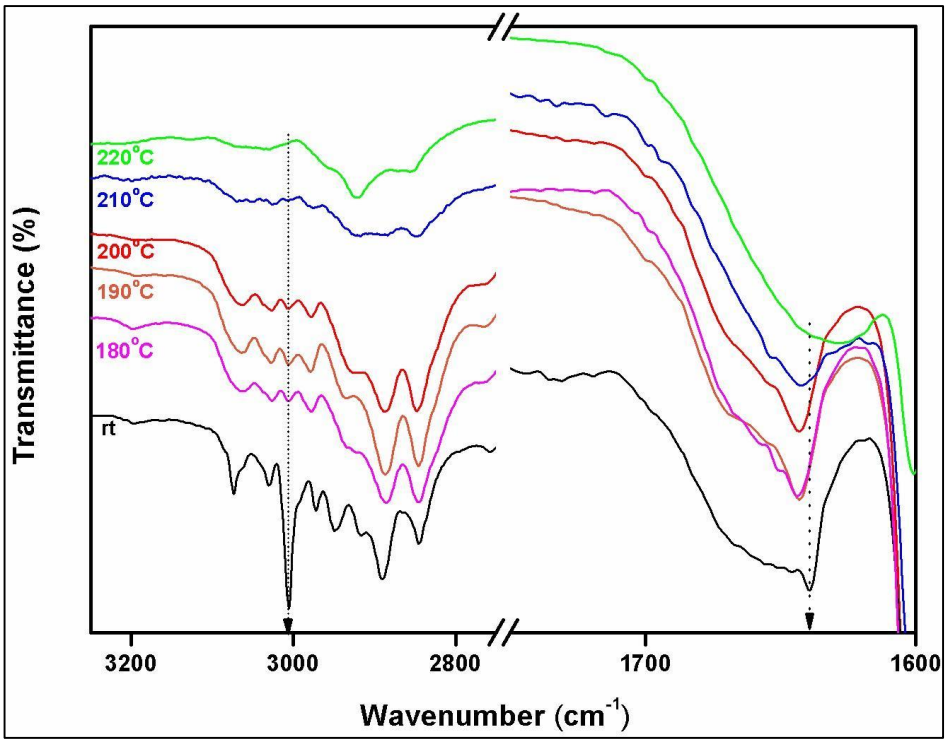


Figure 4.13: IR spectra of the polymerization of allylic groups on the asymmetric benzoxazine.

Figure 4.14 shows the DSC thermograms of the asymmetric bisbenzoxazine which are uncured, half-cured, or fully-cured at room temperature, 180 °C, 190 °C, 200 °C, 210 °C and 220 °C for 5 mins. The uncured monomer showed an exotherm (301 j/ g) starting from 201 °C and reaching a maximum at 231 .The exotherm is rapidly decreasing at heated samples. Polybenzoxazine is fully formed curing around 220 °C.

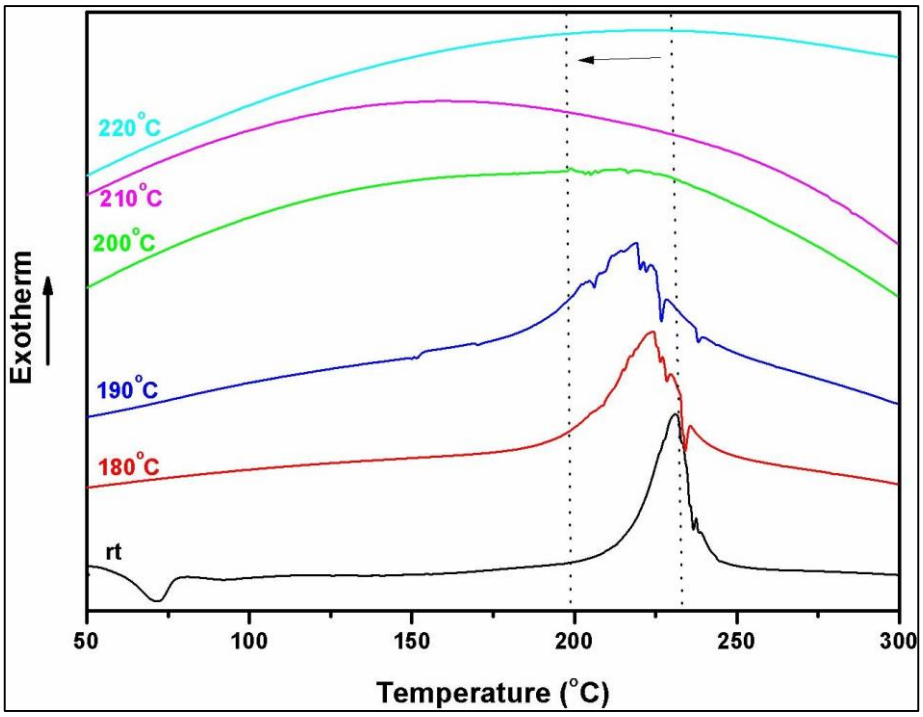


Figure 4.14: DSC thermograms of the heating asymmetric bifunctional benzoxazine at different temperatures.

Polybenzoxazines which are prepared with the ring opening polymerization of asymmetric benzoxazine monomer was able to form more rigid structures than symmetric one. Since asymmetric benzoxazines do not have diphenolic structure, bonds connect cross-links with shorter ties. Thus, it is able to contribute to thermal stability by reducing the number of disordered bonds. Besides, the new functional monobenzoxazine monomer with potency of cross-linkable groups such as ally and propargyl also increases the performance of termosetting resin.

The probable structure of the polybenzoxazine is given in Figure 4.15. It is obtained from the ROP mechanism of the asymmetric bisbenzoxazine and the curing of the allylic groups.

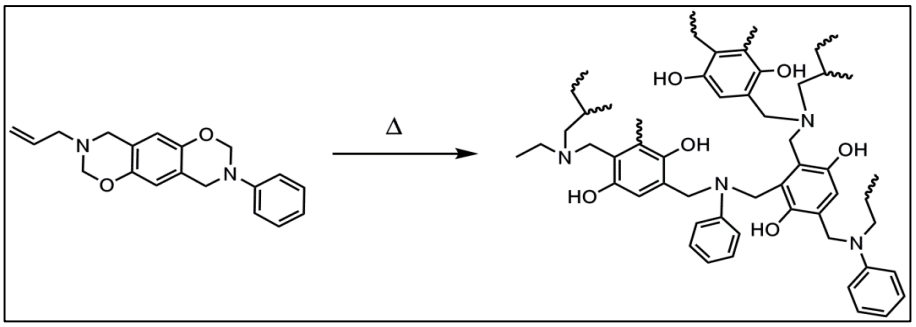


Figure 4.15: The probable structure of the polybenzoxazine which is obtained from asymmetric bisbenzoxazine.

Figure 4.16 presents the TGA thermogram of the polybenzoxazine formed by curing asymmetric benzoxazine monomer at 220 °C for 5 min. Thermal degradation started at 280 °C and decelerated after 500 °C. High number of crosslinking sites are responsible for the thermal stability. At 900 °C, the char yield of this thermoset is 70% which a significantly high value compared to traditional polybenzoxazines. The 5% and 10% degradation temperature of the polybenzoxazine were 331 °C and 371 °C, respectively.

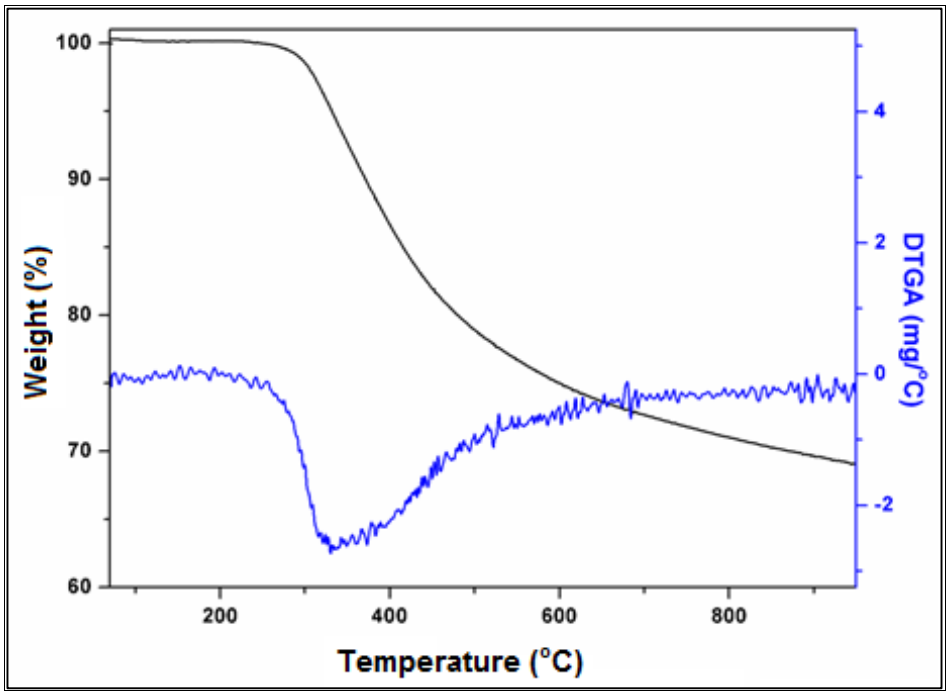


Figure 4.16: TGA thermogram of the curing allylic asymmetric bifunctional benzoxazine at 220 °C for 5 mins.

5. CONCLUSION

In this study, two new benzoxazine monomers were prepared and their behavior was investigated to facilitate industrial applications of polybenzoxazine that have recently been recognized as a superior among phenolic resins. There are studies about monomeric benzoxazines such as using catalysts to decrease polymerization heat and making structural changes. It was known that phenolic structures show catalytic behavior, however, single stage synthesis method does not allow phenol function in monobenzoxazine. In this thesis, benzoxazine monomer that contains phenolic groups at two ends [3-(4-hydroxyphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol] was synthesized and characterized for the first time by using two stage synthesis method. Plausible structure of polybenzoxazine thermoset is presented in the light of the observations of structural changes that occured during thermal curing. It was observed that new benzoxazine monomer starts to polymerize at very low temperature, particularly 95 °C, as evidenced by thermal analysis. The purpose of producing phenol ended benzoxazine in this study is to emphasize the catalytic effect of the hydroxyl group on the ring opening. Polybenzoxazine thermosets produced from the new ring opening polymerization are a lot more thermally stable than usual benzoxazine, conserving as high as 60% of its initial mass at 900 °C.

Bifunctional benzoxazine monomers are often used to increase molecular weight of polybenzoxazine thermosets. However, so far in usual single staged synthesis methods, two staged benzoxazines that is in symmetrical structure starting from diphenol or diamine are synthesized. In this thesis two-functional asymmetric has been prepared for the first time by a two-stage synthesis method to increase thermal performance. During gradual thermal curing of this monomer, behaviors of oxazine ring and allylic group are examined and possible polybenzoxazine structure is presented. It is observed that polymerization starts around 201 °C and ends around 250 °C. High thermal resistivity which was aimed with the production of this material was appeared at 900 °C and 70% the char yield as observed in thermal analysis.

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BIOGRAPHY

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APPENDICES

Appendix A: Publications/Presentations On The Thesis:

Gumus B., Sennik B., Kiskan B., Yilmaz F., Demir K., (2015), "High Performance Benzoxazine Thermosets from Monomers with Phenolic End Groups", Thermosets 2015, Berlin, Germany, 16-18 Semptember 2015, 192-195.

Gumus B., Sennik B., Kiskan B., Yilmaz F., Demir K., (2015) "Synthesis and Characterization of Novel Asymmetric Bisbenzoxazine", 11th International Conference on Advanced Polymers via Macromolecular Engineering (APME 2015), Yokohama, Japan, 18-22 October 2015, 1-1.

Gumus B., Sennik B., Yilmaz F., Kiskan B., Demir K., (2015) "High Performance Benzoxazine Thermosets from Monomers with Functional Groups", Material Science and Polymer Engineering, Dubai, United Arab Emirates, 26-28 November 2015, 00-01.