

**İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY**

**SYNTHESIS AND CHARACTERIZATION OF THERMALLY CURABLE  
BENZOXAZINE BASED POLYMERS BY THIOL-ENE REACTIONS**

**M. Sc. Thesis by  
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**Department : Chemistry**

**Programme : Chemistry**

**JUNE 2010**



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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**TİYOL-EN REAKSİYONLARI İLE ISISAL OLARAK KÜRLEŞEBİLEN  
BENZOKSAZİN YAPILI POLİMELERİN SENTEZİ VE  
KARAKTERİZASYONU**

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## FOREWORD

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## ABBREVIATIONS

<b>DMPA</b>	: 2,2-dimethoxy-2-phenylacetophenone
<b>IR</b>	: Infrared Spectrophotometer
<b><sup>1</sup>H-NMR</b>	: Nuclear Magnetic Resonance Spectroscopy
<b>FT-IR</b>	: Fourier Transform Infrared Resonance
<b>DSC</b>	: Differential Scanning Colorimetry
<b>DMA</b>	: Dynamic Mechanic analyzer
<b>Tg</b>	: Glass Transition Temperature
<b>B-ala</b>	: 6,6'-(propane-2,2-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazine)
<b>Bisphenol-A</b>	: 4, 4'- isopropylidenediphenol
<b>SEC</b>	: Size exclusion chromatography
<b>B-a</b>	: 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine)
<b>COI</b>	: Coinitiator
<b>TGA</b>	: Thermal gravimetric analysis
<b>GPC</b>	: Gel Permeation Chromatography
<b>UV</b>	: Ultra-violet
<b>THF</b>	: Tetrahydrofuran
<b>St</b>	: Styrene
<b>NaSO<sub>4</sub></b>	: Sodium Sulfate



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## LIST OF SYMBOLS

<b>R</b>	: Radical
<b>PI</b>	: Photoinitiator
<b>M</b>	: Monomer
$\lambda$	: Wavelength



# **SYNTHESIS AND CHARACTERIZATION OF THERMALLY CURABLE BENZOXAZINE BASED POLYMERS BY THIOL-ENE REACTIONS**

## **SUMMARY**

Polybenzoxazines-based materials have an increasing concern as a new phenolic system because of their noteworthy properties that can be used in many fields, such as electronics and aerospace industries. These attractive properties include low water absorption, thermal stability and dimensional stability. Therefore, polybenzoxazines overcome several short-coming of conventional novolac and resole-type phenolic resins characterized with brittleness, poor shelf life, usage of acid or base catalysts, release of by products, formation of micro voids during curing. Furthermore, the molecular structures of benzoxazine provide enormous design flexibility by using various starting materials and so these molecular structures can be tailored for specific applications.

Thiol-ene chemistry have been studied over the last century and extensively to be used in polymer science including modification of polymers and surfaces. In this system, many types of enes and thiols can be combined into thiol-ene networks. Moreover, one of the advantageous characteristics of thiol-ene system is its correspond insensitivity to oxygen inhibition in reaction conditions.

In this study, modification of chemical structure and investigation of curing behaviours of polybenzoxazine were aimed by using photoinitiated thiol-ene reaction and subsequent thermal curing. First, the diallyl functional monomer, 6,6'-(propane-2,2-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3] oxazine) (B-ala), was synthesized through the Mannich and ring closing reaction of 4,4'-isopropylidenediphenol (bisphenol A), formaldehyde and allylamine. Then B-ala was polymerized with difunctional thiol compound upon irradiation. The possible mechanism for formation of polymer involves addition of thiyl radical formed photochemically to allyl group of the benzoxazine monomer (B-ala) and consequent hydrogen abstraction from thiol compound leading to a chain reaction. The aim is to improve toughness and mechanical properties of conventional polybenzoxazines and gain more flexible forms of such materials. The structures of the products are characterized by various analysis including DMA, DSC, TGA and IR analysis.



# **TİYOL-EN REAKSİYONLARI İLE ISISAL OLARAK KÜRLEŞEBİLEN BENZOKSAZİN YAPILI POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU**

## **ÖZET**

Polibenzoksazin temelli malzemeler, günümüzde sahip olduğu ilgi çekici özelliklerinden dolayı elektronik ve uçak sanayileri gibi birçok alanda kullanılmaktadır. Düşük su absorplamaları, ısıl kararlılıkları ve kimyasal dayanımları benzoksazin yapıli maddelerin bahsedilen önemli özellikleri arasında yer almaktadır. Bu yüzden polibenzoksazinler genenekselsel Novalac ve resol tipindeki fenolik reçinelerin kırılğanlık, kısa raf ömrü, asit ve baz katalizörü kullanımı, kürlenme esnasında mikro boyutlarda boşlukların oluşumu gibi sorunlarını gidermektedir. Ayrıca çeşitli başlangıç madderi kullanılarak, benzoksazinlerin moleküler şekilleri müthiş derecede elastik yapıya sahip olmaktadır ve birçok uygulama alanında kullanılmak üzere bu moleköl şekilleri istenilen hale getirilmektedir.

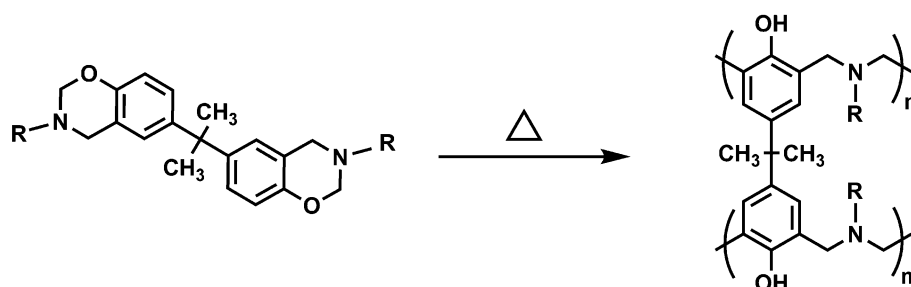
Tiyol-en kimyası ile yüzyılı aşkın bir süredir çalışılmaktadır ve polimerik yapıların ve yüzeylerin modifikasyonunu içeren polimer ile ilgili araştırmalarda yaygın olarak kullanılmaktadır. Dahası tiyol-en sisteminin öne çıkan yararlı özellikleri arasında oksijen varlığından etkilenmemeleri ve birçok -en monomerine uygulanabilir olmaları yer almaktadır.

Bu çalışmada, fotokimyasal yoldan başlatılan tiyol-en reaksiyonu ile polibenzoksazinlerin modifikasyonu ve kürlenme davranışlarını incelemek amaçlanmıştır. İlk olarak 6,6'-(propan-2,2-diil)bis(3-allil-3,4-dihidro-2H-benzo[e][1,3] oksazin) (B-ala) Mannich ve 4,4'-izopropilidendifenol (bisfenol A), formaldehit ve allil aminin halka kapanma reaksiyonu vasıtasıyla sentezlenir. Daha sonraki aşamada, B-ala difonksiyonlu tiyol bileşiği ile ışıkla uyarılarak polimerleştirildi. Oluşan bu polimer için olası mekanizma fotokimyasal olarak oluşturulan tiyil radikalinin benzoksazin monomerinin allil grubuna katılması ve yeni oluşan radikalın başka bir tiyol molekülünden hidrojen koparmasını içermektedir. Gelenekselsel polibenzoksazinlerin kırılğanlıklarını ve mekanik özelliklerini iyileştirmek ve bu materyallerin daha esnek formlarını elde etmek amaçlanmıştır. Ürünlerin yapıları DMA, DSC, TGA ve IR ölçümleri ile karakterize edilmiştir.



## 1. INTRODUCTION

Benzoxazine-based novel thermoset phenolics have an increasing concern in the field of polymer research, in recent decades. Indeed, the attraction of polybenzoxazines is originated from their advantageous properties that overcome several deficiencies of conventional Novolac and resole-type phenolic resins including brittleness, poor shelf life, usage of acid or base catalysts, release of by products, formation of micro voids during curing process [1]. Furthermore, the attractive properties of benzoxazine based materials involve low water absorption, nearly zero shrinkage upon curing [2, 3], thermal stability [4-6] and chemical resistance [7].

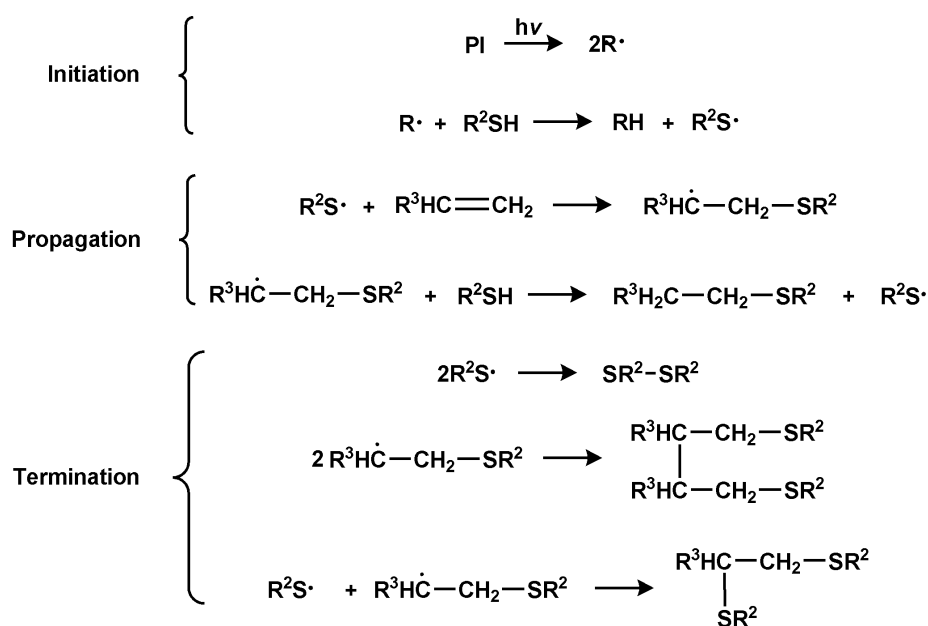


**Figure 1.1:** Thermally activated ring-opening polymerization of bisbenzoxazines.

Formations of polybenzoxazines networks are usually driven by thermally activated ring-opening of the corresponding benzoxazines without any catalyst and without generation of any by-products (Figure 1.1) [8-12]. Benzoxazine monomers are basically synthesized by the reaction between phenol, formaldehyde and amine (aliphatic or aromatic) [13]. Therefore, the molecular structures of benzoxazine provide enormous design flexibility by utilization of various starting materials [14-19]. Although this way allows preparation of tailor-made polybenzoxazines for specific applications by a variety of processes there are some drawbacks and limitations of simple polybenzoxazine materials due to their characteristics including brittleness and need of high cure temperature. In order to overcome these quandaries, the properties of polybenzoxazines can be improved with various pathways. For example, allyl-, acetylene-, nitrile-, propargyl-functional benzoxazine can be synthesized to offer additional cross-linking site for thermal curing [5, 20-22] and the

mechanical and thermal properties of polybenzoxazines can be modified by the preparation of copolymers, polymer alloys, composites, polymer-clay nanocomposites [23-30]. Alternatively, the usual drawbacks of benzoxazine-based materials can be overcome by employment of thiol-ene chemistry in modification of these materials [31-34].

Thiol-ene chemistry has considerably high attention in many applications including modification of polymers [33, 35-39] and surfaces [40-42], preparation of bioconjugated polymers [43, 44], synthesis of star polymers [45], dendrimers [46], dental materials [47, 48] etc. Thiol-ene reactions can be initiated either photochemically at ambient temperature or thermally [49-52]. The main advantage of thiol-ene process is that the polymerization can be occurred in the presence of oxygen. Moreover, it has also many other advantages including rapid polymerization rates and significantly versatility in vinyl monomer (ene-monomer) units. Thiol-ene system is fundamentally based on a step-growth process that forms highly uniform crosslinked networks [32]. The general mechanism of thiol-ene photopolymerization is shown in Figure 1.2. The thiol-ene polymerization mechanism progresses via propagation and chain transfer steps after initiation step. In the termination step, as shown in Figure 1.2, there are three possibilities including bimolecular coupling of radical species.



**Figure 1.2 :** The general mechanism of thiol-ene photopolymerization.



In this study, a bisbenzoxazine-based ene-monomer, diallyl benzoxazine (B-ala), and a difunctional thiol compound, 1, 2-ethanedithiol, were utilized in photoinduced thiol-ene reaction to prepare thermally curable benzoxazine polymers as precursor film with the aim of improving benzoxazine properties. Subsequently, the precursor films are thermally cured. The films were thermally and mechanically characterized before and after curing process by DMA, DSC, TGA and IR spectroscopy.



## **2. THEORETICAL PART**

### **2.1 Polybenzoxazines**

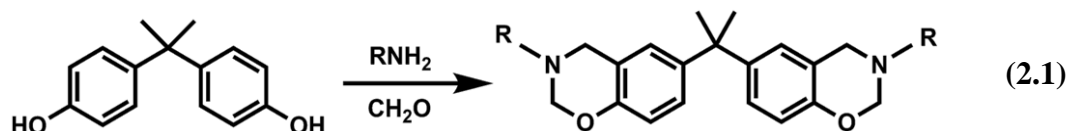
Benzoxazine-based materials has recently been developed as a new type phenolic system in order to overcome various short-comings of conventional phenolic resins. Phenolic resins are presented in many industrial application and products such as fiber reinforced composites, resistant coatings, glass fiber and widely used aerospace industry. Although these systems have significant features that including high strength level of thermal and mechanical behaviour, flame retardance and resistance against various solvents, there are some noticeable problems. For instance, these conventional materials are brittle, have poor shelf life, acid or base catalysts are often used for the preparation of resin. Using of catalysts in this case leads to corrode the processing equipments, release by products (such as water, ammonia compounds) and formation of micro voids during curing.

First synthesis of benzoxazines was found by Holly and Cope in 1940s by using condensation reaction of primary amines with formaldehyde and phenol [53]. But the using of potential benzoxazines has been recognized recently. So these materials have an increasing concern in many applications due to the fact that become a new type of thermoset phenolic resins with attractive features. Polybenzoxazines exhibit (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazines  $T_g$  much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, (vi) release of no toxic by-product during curing.

#### **2.1.1 Synthesis of Benzoxazine Monomers**

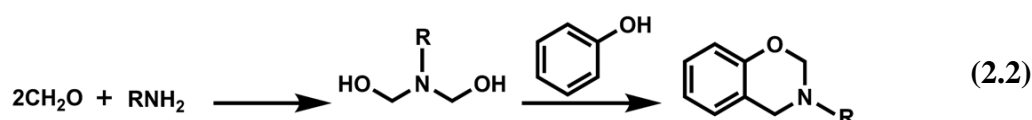
Benzoxazine is a single benzene ring coupled to oxazine ring system forming six-membered heterocycle containing one oxygen atom and a nitrogen atom. This oxazine ring system can exhibit a number of possible isomeric benzoxazines depending on the relative positions of the two heteroatoms of oxazine ring system and 1,3-benzoxazine is the kind of isomer used for polymerization.

Benzoxazine monomers can easily be synthesized from phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials (Eq. 2.1) [54]. Moreover, they exhibit molecular design flexibility with using variety of phenolic compound and amines. By this way several kinds of benzoxazine monomers with different substituting groups which have long shelf life and relatively low viscosities are obtained as using in desired many application. As a result, various polymeric products can be formed by these substituted groups of additional polymerizable sites.



### 2.1.1.1 General pathway of synthesis of benzoxazine monomers

As of now, many chemical methodologies about synthesis of mono-functional benzoxazine monomers have been found and published by various investigations. To synthesize of well-defined benzoxazine monomers, Holly and Cope [53] first reported the condensation reaction of primary amines with formaldehyde and substituted phenols. According to their study, this reaction was performed in a solvent in two-steps. Then, it is found by Burke that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge [55]. The synthetic method of the Mannich condensation for benzoxazine synthesis in a solvent proceeds with two steps. In the first step, amine compound adds to formaldehyde at lower temperatures to form an *N,N*-dihydroxymethylamine derivative. Then to form the oxazine ring, *N,N*-dihydroxymethylamine derivative reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature in the last step (Eq. 2.2) [56].



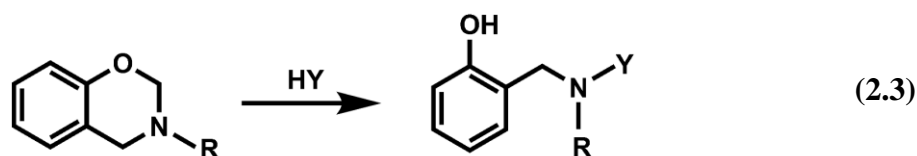
As an example, to prepare 3,4-dihydro-3-cyclohexyl-6-t-butyl-1,3,2H-benzoxazine,

Two procedures were employed [55]:

Cyclohexylamine was mixed formaldehyde in dioxane. After addition of p-t-butyl phenol the mixture was refluxed for 2 h. Upon cooling to room temperature, a crystalline product was obtained, which was then recrystallized from 95% ethanol and the yield was 78%.

Paraformaldehyde was dissolved in warm methanolic KOH solution. The solution was cooled during the portion-wise addition of cyclohexylamine. After the addition of 4-t-butylphenol, the resulting solution was cooled to room temperature and the product was recrystallized from 95% ethanol and the yield was 92%. Synthesis of a p-cresol based benzoxazine by using aniline, formaldehyde and p-cresol as starting materials in dioxane has been reported [8, 57, 58].

It has been observed that for some benzoxazines, the ring opening occurs in the presence of compounds with active hydrogen (HY), such as naphthol, indoles, carbazole, imides, and aliphatic nitro compounds even phenol (which is also one of the starting compound for synthesis) [59] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [60] is shown in Eq. 2.3



The benzoxazines derived from a strongly basic amine and a less acidic phenol found to be more stable in the hot alcohols [61]. Substituent on the benzoxazine ring affects the stability of the ring. The presence of more than one reactive ortho position in the initial product may lead to another aminoalkylation reaction [62]. A significantly higher yield obtained when the benzoxazine derived from phenol having an ortho substituent.

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins.

To overcome these shortcomings, solventless synthesis in the melt state was developed [54].

The reaction mechanism and kinetics of this solventless synthesis were proposed [63]. In a typical synthesis, the reactants, i.e., aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. In this connection, it should be pointed out that formaldehyde is not typically used as it evaporates easily and lose stoichiometry quickly. Instead, paraformaldehyde is used. The choice for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and by products.

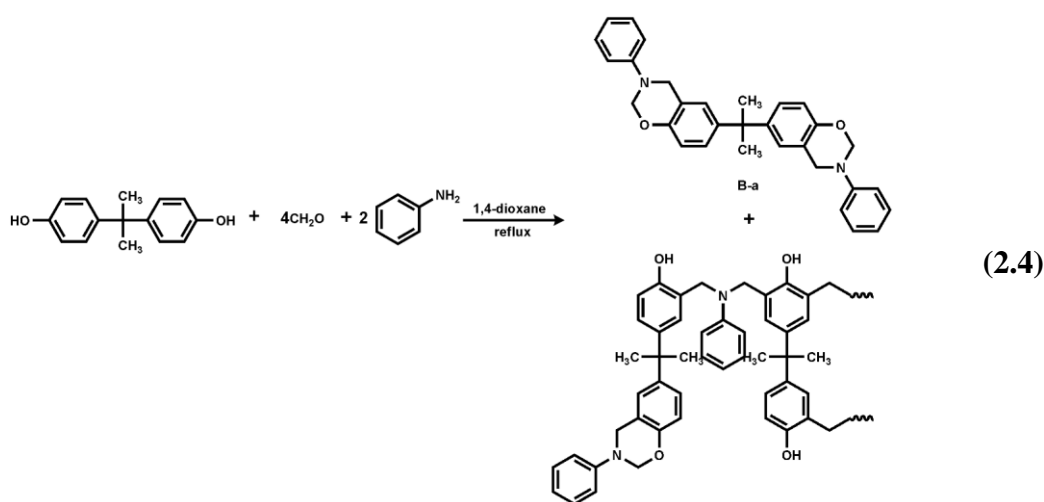
#### **2.1.1.2 Synthesis of di-functional and multifunctional benzoxazine monomers**

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high molecular weight linear structures were unobtainable [64]. Actually, there is no convincing evidence reported for the thermal dissociation theory, though it was mentioned in the literature. Moreover, it was reported that the reduction of reactivity is due to the hydrogen bonding formation. Such phenomenon was observed in the temperature range below where reverse Mannich reaction occurs in benzoxazine chemistry [65].

To overcome this limitation, a new class of difunctional or multifunctional benzoxazine monomers [66] 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 the 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.

It was observed that, the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.

Similar type of difunctional benzoxazine was prepared using aniline instead of methyl amine [27, 67] and the pure monomer was referred as B-a and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a analyzed by <sup>1</sup>H-NMR measurements. The overall synthetic procedure is shown in Eq. 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.



The synthesis of 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3]oxazine) (B- a) in high yield by the solventless reaction process using 1,3,5 triphenyl(alkyl) hexahydro-1,3,5 triazine, paraformaldehyde and bisphenol A has been reported [68].

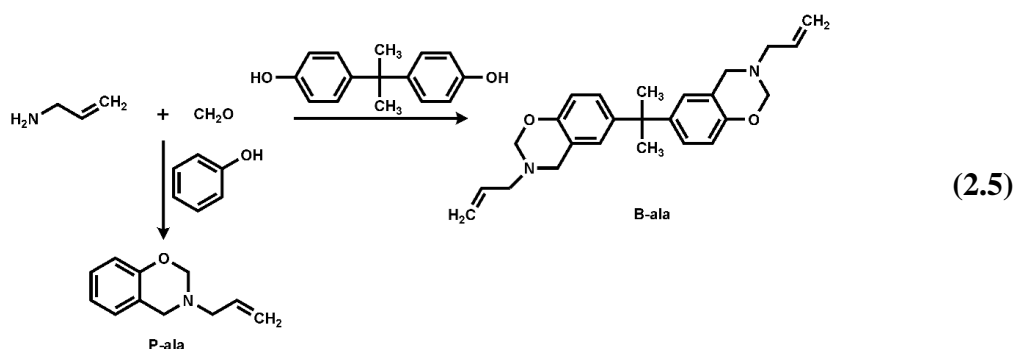
### 2.1.1.3 Synthesis of benzoxazine monomers with different functional groups

The chemistry of benzoxazine synthesis exhibit a wide range of molecular design flexibility by using suitable starting materials. Therefore, molecular structure can be tailored for specific applications [14-19, 69]. It is possible that benzoxazine monomers are diversified by using many functional groups. Synthesis of allyl, acetylene, propargyl ether, nitrile, maleimide, norbornane, coumarin, epoxy groups

containing benzoxazine monomers have a part in several research. (structures are shown in Table 2.1)

#### 2.1.1.4 Allyl containing monomers

In this study, allyl containing benzoxazine monomer was employed. There are two main advantages of the allyl group [70, 71]. It provides additional crosslinkable sites and can be easily be cured at a temperature lower than acetylene groups. In order to improve the toughness of the cured resin, they are used as reactive diluents of bismaleimides. Thus, allyl-containing monomers have attracted much attention. In the past about preparation of an allyl-containing benzoxazine monomers many study are to be found. For instance, Ishida also reported [54] that 3-phenyl-3,4-dihydro-8-allyl-2*H*-1,3-benzoxazine was prepared from using allylphenol, aniline, and paraformaldehyde. To develop the interface between the matrix and glass or carbon fiber in fiber-reinforced polybenzoxazine, a similar benzoxazine monomer based on allylphenol was reported for silylation of allyl group [72]. Also, similar bifunctional allylphenol-derived polybenzoxazine was reported [73]. However, these allylphenol-based benzoxazine monomers are considered to be difficult to polymerize through ring-opening and are not a good candidate for preparing high performance polybenzoxazines because they do not have activated *ortho* position to the phenolic hydroxyl group. Then, the preparation of two novel benzoxazine monomers modified with allyl groups (i) 3-allyl-3,4-dihydro-2*H*-1,3-benzoxazine and (ii) bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) isopropane (Eq 2.5) have been adopted [34].

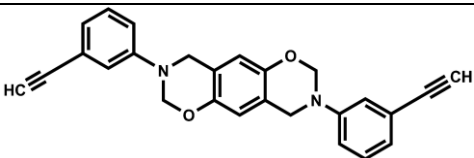
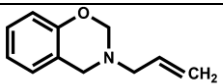
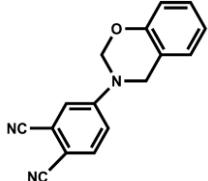
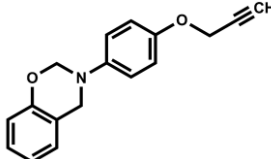
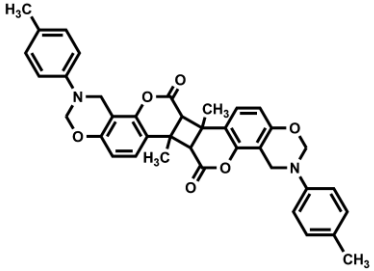
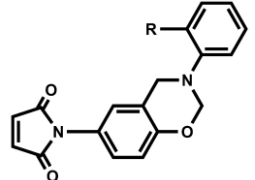
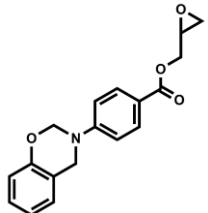
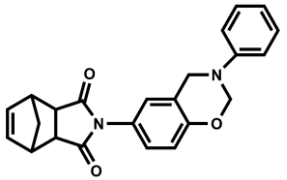


According to a report, allyl-containing benzoxazine monomers can polymerize at temperatures below 150 °C. However, this polymerization occurring at low temperature was not from the benzoxazine ringopening reaction, but from the allyl



group and a high temperature above 250 °C was needed to complete the polymerization of benzoxazine rings.

**Table 2.1:** Benzoxazine monomers with various functionalities.

Benzoxazine monomers	
	
Acetylene-containing benzoxazine [74]	Allyl-containing benzoxazine [34]
	
Nitrile-containing benzoxazine [21]	Propargyl ether-containing benzoxazine [22]
	
Coumarin-containing benzoxazine [75]	Maleimide-containing benzoxazine [76]
	
Epoxy-containing benzoxazine [77]	Norbornane containing benzoxazine [76]

### 2.1.1.5 Polymeric Benzoxazine Precursors

Most of benzoxazine-based studies were related to the polybenzoxazines prepared from precursor monomers until recently. This conventional method brings with some limitations on their use in practical applications. The monomers synthesized by various procedure are usually powder and processing into thin films is rather difficult. As a result of the short molecular weight of the network structure, the polymers prepared with these monomers have brittle form. Several strategies were aimed in order to enhance toughness and other mechanical properties. Addition of elastomeric segments to brittle resins is a common method to develop the ductility. For example, the addition of poly(urethaneimide) polyurethane reduced glass transition temperature ( $T_g$ ) and the cured product exhibited elastomer characteristics

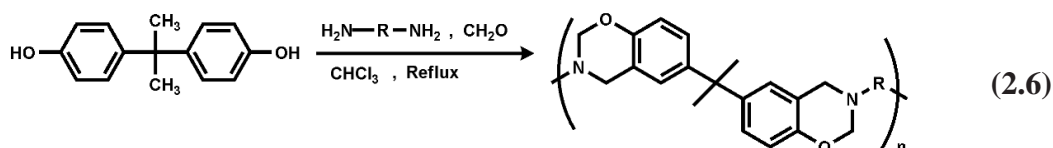
[78]. Instead of polyurethane using of poly(imide-siloxane) was known as other similar approach. . In that case, they took advantage of two structurally different segments present in the polymeric additive, that is, toughening polybenzoxazine with polysiloxane segment while maintaining polybenzoxazine T<sub>g</sub> with polyimide segment [24]. To improve the processibility and mechanical properties, novel polymeric-based precursors have been synthesized by incorporating benzoxazine units either as side chain or as end chain or in main chain of polymer. It is expected that the crosslinked network structure formed from polymer and polymerization of benzoxazine, will exhibit enhanced mechanical property while retaining the beneficial properties of polybenzoxazine. Polymeric precursors offer the ability to prepare a varnish with low solid content that forms good quality films.

### ***Main-Chain Precursors***

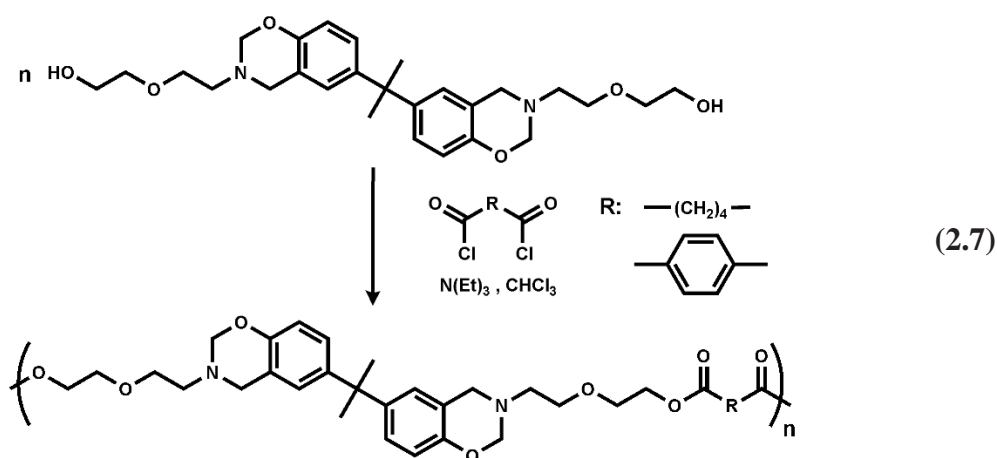
The view of oligomeric benzoxazine resins containing oxazine ring in the main chain was first reported by Liu and Ishida [60]. Then the same research group published more detailed work about the effect of water, solvents, catalyst, ratio of reactants and temperature [63].

Takeichi et al. [79] and Ishida and coworkers [80] have independently reported a synthetic approach for the preparation of polymers containing benzoxazine moieties in the main chain. According to their research high-molecular weight polybenzoxazine precursor was synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (Eq. 2.6). The critical problems in this polymerization are that the preparation of such main-chain benzoxazine precursor polymers are low molecular weight and crosslinking arising from the Mannich reactions of multiple functional groups. The choice of the right conditions for a Mannich reaction is important for achieving high yields with a minimum by product. In this type of Mannich polymerization, partially ring-opened structures were also observed. But, the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, whereas polybenzoxazine from longer aliphatic diamine had higher elongation at

break. The viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability.

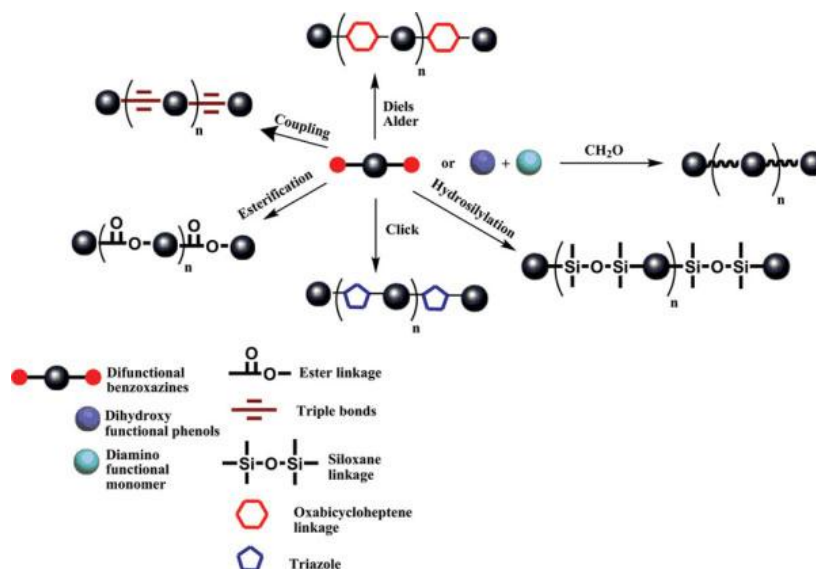


Yagci and Ishida have synthesized high molecular weight poly (etheresters) (PEE) containing benzoxazine units in the main chain by diol functional monomer and was first synthesized using bisphenol A, formaldehyde, and 2-(2- aminoethoxy) ethanol [81]. Polycondensation of the resulting benzoxazine dietherdiol (B-Etherdiol) with adipoyl chloride and terephthaloyl dichloride in the presence of triethyl amine resulted in corresponding PEE with molecular weights of 34,000 Da (Eq. 2.7). These polymers consist of benzoxazine units, formed crosslinked network. Here, presence of polyester introduced flexibility in the resulting polymer. These reactive polyether ester films can be further crosslinked thermally which could enhance the application of polybenzoxazines. The cured PEE exhibited good thermal stability and the toughness induced by the soft etherester. This synthetic strategy may open new pathways to prepare the other conventional thermoplastic elastomers those can be thermally cured in the absence of any catalyst leading to materials with improved properties.



It was reported that polysiloxanes containing benzoxazine moieties in the main chain can be prepared by hydrosilylation reaction between tetramethyldisiloxane and benzoxazine structurally equipped with allyl groups [82]. Siloxane segments introduce flexibility and transparent thin precursor films were easily obtained by casting the precursor solution on Teflon plate. The benzoxazine groups were shown to readily undergo thermally activated ring-opening reaction in the absence of added catalyst to form cross-linked polymer network. The polymers cured in this way 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.

Different types of benzoxazine based main-chain polymeric precursors have been described in Figure 2.1.

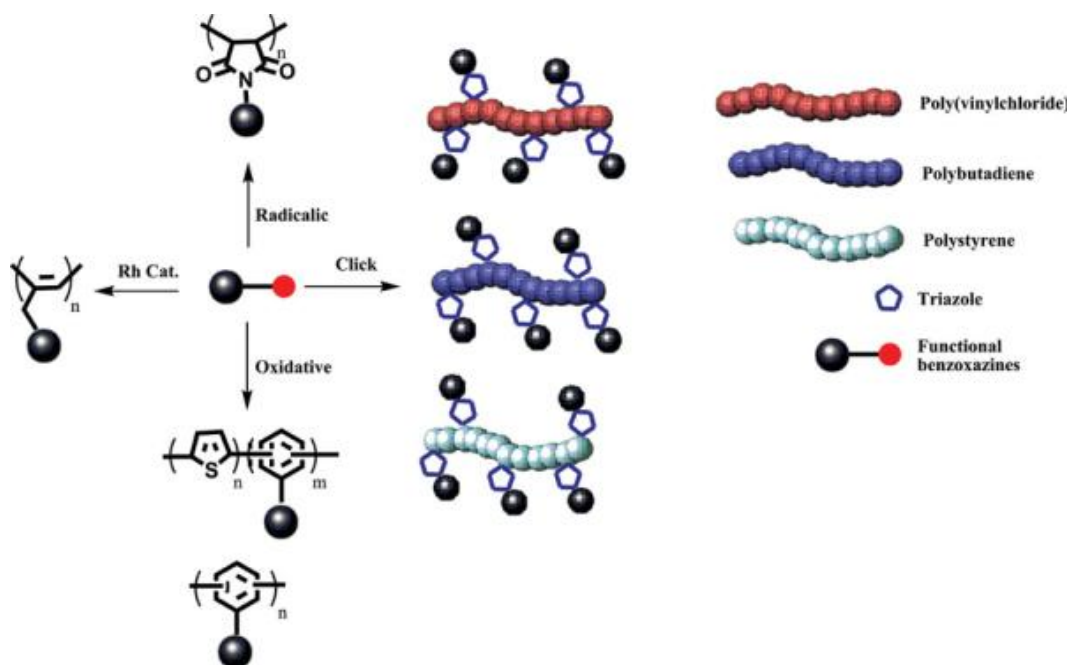


**Figure 2.1 :** Main applications of main-chain benzoxazines.

### *Side-Chain Precursors*

Side-chain polymeric method is a path to incorporate benzoxazine groups into a polymer backbone to achieve a highly dense network. Curing of many repeating benzoxazine units resulted in crosslinking of polymer chains. There are various synthetic methods to obtain side chain polymers. The side-chain polymeric benzoxazine precursor was prepared by oxidative polymerization 3-phenyl-3,4-dihydro-2H-benzo[e][1,3] oxazine (P-a) in the presence of thiophene (Th) with ceric ammonium nitrate [83]. The resulting polymers exhibit conductivities around  $10^{-2}$  S  $\text{cm}^{-1}$  and undergo thermal curing at various temperatures. The partially ring-opened

structure which was formed during the oxidative polymerization affects the thermal curing behavior of the polymers. The cured products exhibited high thermal stability but lower conductivity than those of the precursors. Some include postpolymer modification like click chemistry or polymerizing suitable molecules (Figure 2.2).



**Figure 2.2 :** Applications of side-chain benzoxazines.

### 2.1.2 Ring Opening Polymerization of Benzoxazines

To understand the polymerization reaction mechanism of benzoxazines, an understanding of the chemical structure of its oxazine ring is very important. A single crystal X-ray crystallographic study detect that mono-oxazine ring containing benzoxazine is a distorted semi-chair structure, with the nitrogen and carbon, between oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six-membered ring to undergo ring-opening reaction under specific conditions. In addition, due to their high basicity (by Lewis definition) both oxygen and nitrogen of the oxazine ring can act as potential cationic polymerization initiation site and makes the ring very likely to open via a cationic mechanism [11, 84]. The electron charge calculation after energy minimization

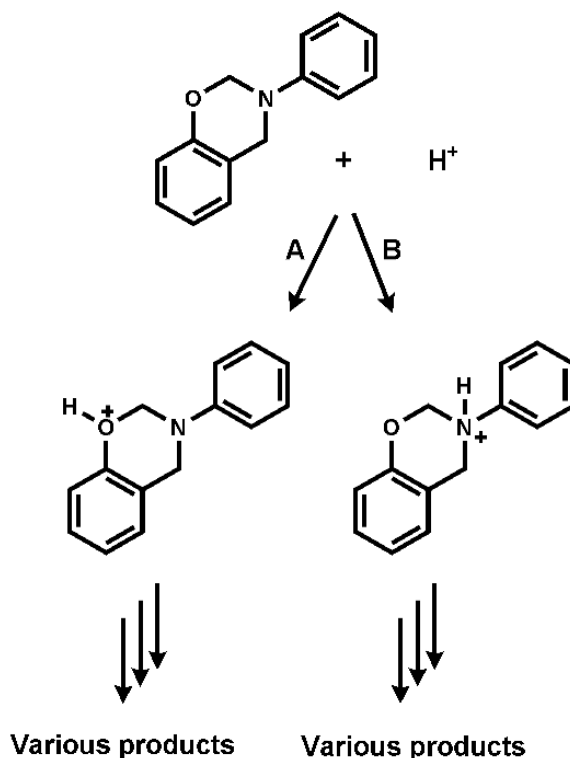
predicts that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270).

### **2.1.2.1 Thermal polymerization of polybenzoxazines**

Benzoxazine undergoes ring opening polymerization during thermal curing (Figure 1.1). It has been proposed that, the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which in equilibrium [85]. Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and para position of the phenol group. The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Though, several authors have proposed different mechanism of thermal curing of benzoxazine, however, the mechanism is not well established.

### **2.1.2.2 Photo-initiated polymerization of benzoxazine**

The ring-opening cationic polymerization of a benzoxazine, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa), with onium salts, such as diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate as initiators, investigated by Kasapoglu et al. [12]. In this work, both direct and indirect activations by using radical sources and photosensitizers were reported. The complex structure of the resulting polymers was formed due to the simultaneous ring-opening process of the protonated monomer either at the oxygen or nitrogen atoms. The phenolic mechanism also contributed, but its influence decreased with decreasing monomer concentration. Free radical promoted cationic polymerization of benzoxazines was also considered. In this case, the polymerization can be performed at much higher wavelengths and carbon-centered radicals formed from the photolysis of 2,2-dimethoxy-2-phenylacetophenone (DMPA), were oxidized to produce carbocations. These carbocations are capable to initiate benzoxazine polymerizations. Figure 2.3 describes the photopolymerization of benzoxazine.



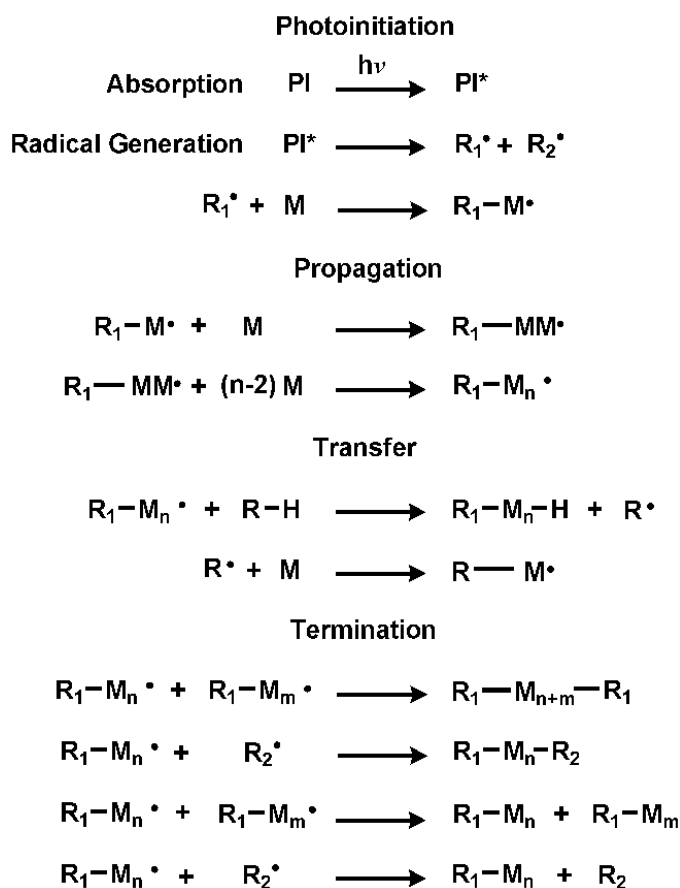
**Figure 2.3 :** Photopolymerization of benzoxazine.

## 2.2 Photopolymerization

Photoinitiated polymerization has been widely used in the electronics industry for etching, microlithography, in paper industry for printing or in polymer industry for curing processes as well as several other applications. These commercial needs lead to a increased interest of chemists in understanding the mechanisms of polymer photoinitiation, in order to improve the efficiency of the initiating systems (initiator and sensitizer), to adapt existing systems to a broader range of monomers, solvents and polymerization types, and to gain more control of the initiation process.

### 2.2.1 Photoinitiated Free Radical Polymerization

Photoinitiated free radical polymerization consists of photoinitiation, propagation, chain transfer, and termination (Figure 2.4). Particularly, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light [86].



**Figure 2.4 :** General photopolymerization mechanism.

Photoinitiation involves absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit. Repeated addition of monomer units to the chain radical produces the polymer backbone (propagation).

Chain transfer also takes place, that is, growing chains are terminated by hydrogen abstraction from various species (e.g., from solvent) and new radicals capable of initiating other chain reactions are formed.

Finally, chain radicals are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.



### 2.2.1.1 Absorption of light

Photochemistry is concerned with chemical reactions induced by optical radiation [87-89]. The radiation is most often ultraviolet (200–400 nm) or visible (400–800 nm) light but is sometimes infrared (800–2500 nm) light.

The absorption of a photon of light excites the electrons of a molecule. The stability of bond of compound is reduced by electronic excitation, under this circumstance, lead to its dissociation.

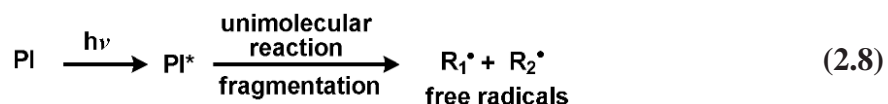
Chromophoric groups defined as having functional group which show high absorbency. For example, phenyl rings or carbonyl groups take place in this groups. The energy causing excitation,  $E$ , is described by  $E=hc/\lambda$  where  $h$  is Planck's constant,  $c$  is the speed of light, and  $\lambda$  is the wavelength of the exciting light. Light absorption is described by  $A= \epsilon Cl$ , where  $\epsilon$  is the molar absorptivity (extinction coefficient),  $C$  is the concentration of the species, and  $l$  is the light path length.

### 2.2.1.2 Initiators for free radical photopolymerization

Most of photoinduced reactions are carried out by using photoinitiators in order to generate radicals. A photoinitiator is a molecule that absorbs energy of radiation, and consequently initiates polymerization. Photoinitiators are generally divided into two classes according to the process by which initiating radicals are formed. *Type I* photoinitiators and *Type II* Photoinitiators.

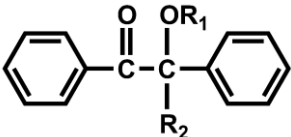
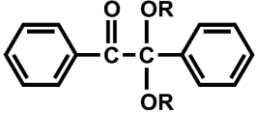
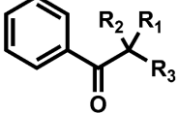
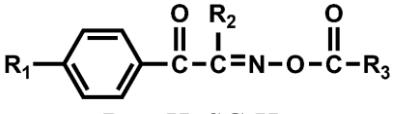
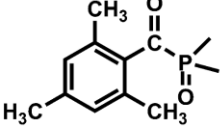
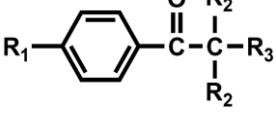
#### *Type I Photoinitiators: Unimolecular Photoinitiators*

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in Eq. 2.8 are termed “*Type I* photoinitiators”. This process is termed homolytic cleavage or direct fragmentation. The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction.



There are many photoinitiators which are classified as most efficient *Type I* photoinitiators, and are termed as benzoin ether derivatives, benzil ketals, hydroxylalkylphenones,  $\alpha$ -aminoketones and acylphosphine oxides. Examples of them are given in the Table 2.2 [90-93].

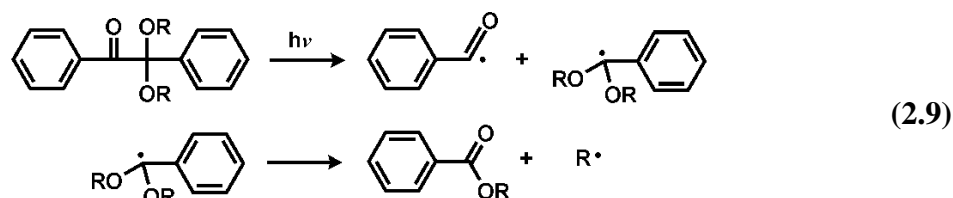
**Table 2.1** : Main Type I photoinitiators for free radical polymerization.

Photoinitiators	Structure	$\lambda_{\max}$ (nm)
Benzoin ethers	 <p style="text-align: center;"> <math>R_1 = \text{H, alkyl}</math>  <math>R_2 = \text{H, substituted alkyl}</math> </p>	323
Benzil ketals	 <p style="text-align: center;"> <math>R = \text{CH}_3, \text{C}_3\text{H}_7, \text{CH}_2</math> </p>	365
Acetophenones	 <p style="text-align: center;"> <math>R_1 = \text{OCH}_3, \text{OC}_2\text{H}_5</math>  <math>R_2 = \text{OCH}_3, \text{H}</math>  <math>R_3 = \text{C}_6\text{H}_5, \text{OH}</math> </p>	340
Benzyl oximes	 <p style="text-align: center;"> <math>R_1 = \text{H, SC}_6\text{H}_5</math>  <math>R_2 = \text{CH}_3, \text{C}_6\text{H}_{13}</math>  <math>R_3 = \text{C}_6\text{H}_5, \text{OC}_2\text{H}_5</math> </p>	335
Acylphosphine oxides	 <p style="text-align: center;"> <math>R = \text{C}_6\text{H}_5 \text{ or } \text{OCH}_3</math> </p>	380
Aminoalkyl phenones	 <p style="text-align: center;"> <math>R_1 = \text{SCH}_3, \text{morpholine}</math>  <math>R_2 = \text{CH}_3, \text{CH}_2\text{Ph or C}_2\text{H}_5</math>  <math>R_3 = \text{N}(\text{CH}_3)_3, \text{morpholine}</math> </p>	320

***Benzil Ketals***

In this study photoreaction was carried out with a type of benzyl ketals that called as DMPA. Benzilketals are another important class of photoinitiators developed for free radical vinyl polymerization. Benzilketals exhibit higher thermal stability than benzoin compounds due to the absence of thermally labile benzylic hydrogen. The most prominent member of this class is the commercially used 2,2- dimethoxy-2-phenyl-acetophenone (DMPA). Indeed, this initiator shows an excellent efficiency in photopolymerizations and is at the same time easy to synthesize. Other benzilketals are also suitable initiators but do not reach the price performance ratio of DMPA.

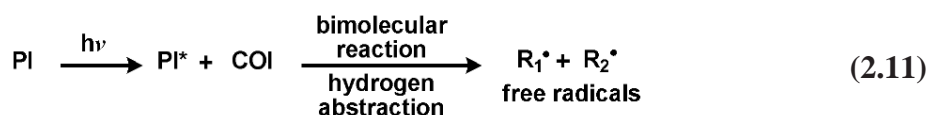
Like benzoin ethers, benzilketals undergo  $\alpha$ -cleavage whereby a benzoyl radical and a dialkoxybenzyl radical is formed (Eq. 2.9). Although the benzoyl radicals are, as explained earlier, vigorously reacting with olefinic bonds of vinyl monomers, dialkoxybenzyl radicals were found to be of low reactivity. Actually, one of seven dialkoxy benzyl radicals formed is found to be incorporated into the polymer chain during the photopolymerization of methyl methacrylate initiated by DMPA. However, to what extent this portion of dialkoxy benzyl groups is caused by termination instead of initiation remains unclear. Dimethoxybenzyl radicals undergo a fragmentation yielding methyl radicals [94, 95] which act as additional initiating species in radical vinyl polymerization [96].



### *Type II Photoinitiators: Bimolecular Photoinitiators*

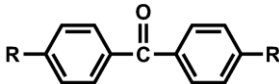
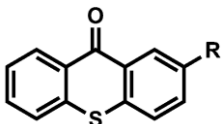
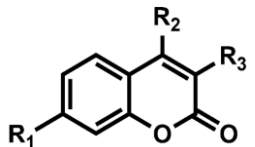
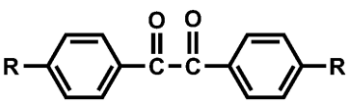
When certain compounds absorb light leading to excited state molecules, they do not undergo Type I reactions because their excitation energy is not high enough for fragmentation (i.e., their excitation

energy is lower than the bond dissociation energy). The photoinitiator that absorbs the light and a co-initiator that serves as a hydrogen or electron donor. The excited state photoinitiator interacts with the coinitiator (COI), to generate initiating radicals in a bimolecular reaction as shown in Eq. 2.11, the initiating system is termed a “Type II Photoinitiator”.



*Type II* photoinitiators including benzophenones, thioxanones, benzyls, and ketocoumarins are listed in Table 2.3

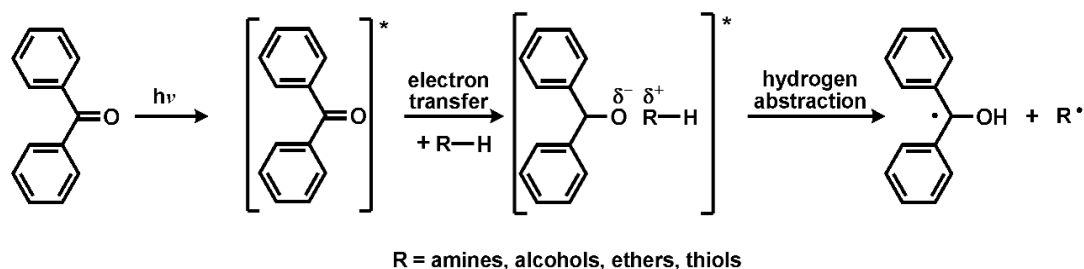
**Table 2.2 :** Type II free radical photoinitiators.

Photoinitiators	Structure	$\lambda_{\max}$ (nm)
Benzophenones	 R = H, OH, N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , C <sub>6</sub> H <sub>5</sub>	335
Thioxanthenes	 R = H, Cl, isopropyl	390
Coumarins	 R <sub>1</sub> = N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , N(CH <sub>3</sub> ) <sub>2</sub> R <sub>2</sub> = CH <sub>3</sub> , cyclopentane R <sub>3</sub> = benzothiazole, H	370
Benzils	 R = H, CH <sub>3</sub>	340

In Type II systems, radicals are generated by two distinct pathways: hydrogen abstraction and photo-induced electron transfer process

### ***Hydrogen abstraction***

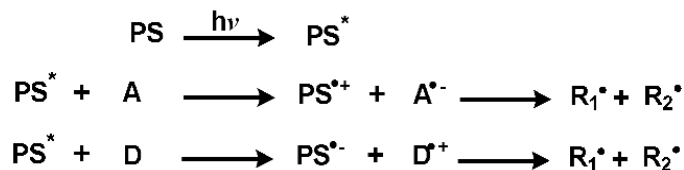
Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (Figure 2.5) When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.



**Figure 2.5 :** Photo-induced free radical formation upon irradiation of benzophenone in the presence of hydrogen donor

### *Photoinduced electron transfer reactions and subsequent fragmentation*

Photoinduced electron transfer is a more general process which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds (sensitizer) can act as either an electron donor with the coinitiator as an electron acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (Figure 2.6)



**Figure 2.6 :** Free radical generation by photosensitization

### **2.3 Thiol-ene Polymerization**

The thiol-ene polymerization, which dated to the late 1930s, is an efficient method for the rapid production of films and thermoset plastics of thiol and ene-compounds with extraordinary physical and mechanical properties. This advantageous polymerization method has been employed in many applications including modification of polymers and surfaces [33, 35-39], bioconjugated polymers [43, 44], synthesis of star polymers [45], dendrimers [46] and disaccharides [97].

The polymerization of functional thiols and ene monomers is proceed via a step growth radical addition mechanism initiated either thermally or photochemically. In

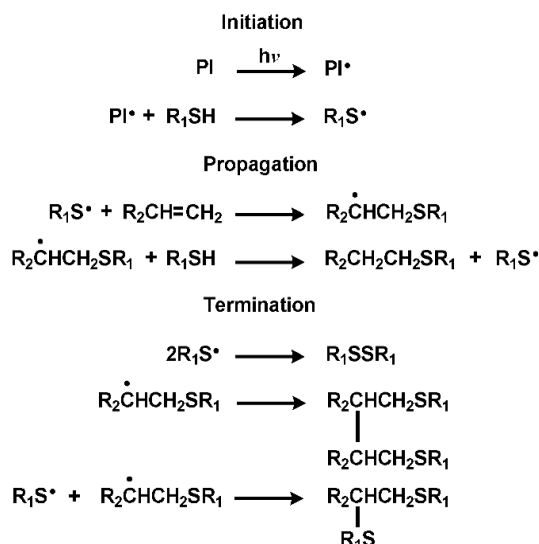
this work, special attention has been devoted on photoinitiated mode of thiol-ene reactions. The polymerization of thiol-ene mixture is initiated by generating of radical centers. Photoinitiation of the radical centers is widely effective method in thiol-ene polymerization reactions to produce films and thermoset plastics with noteworthy mechanical and physical properties. Thiol-ene addition reaction was discovered as early as 1905 by Posner [98] and since then the reaction mechanism, polymerization kinetics, and monomer reactivities were extensively investigated, and two excellent reviews were published by Jacobine [99] and Woods [100]. The major advantage of photoinitiated thiol-ene polymerization is that the system is not affected by air which is a serious problem in traditional free-radical polymerization. Moreover the polymerization carried out in air atmosphere almost as rapidly as in an inert atmosphere. Any type of ene monomer can react with a functional thiol in free-radical polymerization process. In various applications, materials can be tailored in order to require any combination of properties. Hence the reactions between a multifunctional monomer and multifunctional thiol are part of an attractive and versatile method that can be used for the preparation of adhesives, sealants, and coatings by using UV light.

### **2.3.1 Photoinitiated Thiol-Ene Polymerization**

Thiol-ene systems are generally polymerized by a free-radical chain process [99] with initiation, propagation and termination steps as shown in Figure 2.7.

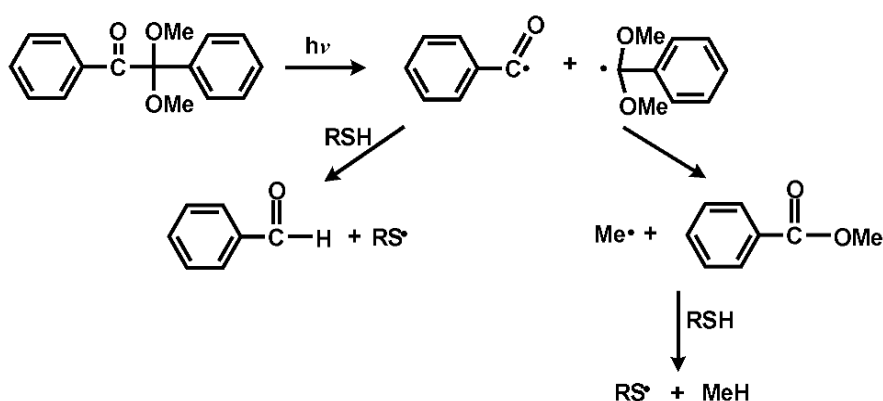
Initiation step contains the treatment of a thiol with photoinitiator, upon irradiation yielding a thiyl radical,  $RS\cdot$ . Propagation process has two step involving first addition of the thiyl radical to the C-C double bond and a subsequent hydrogen abstraction of a thiol group by a carbon-centered radical to give a thiyl radical. Termination step occurs by radical-radical coupling.

There are several ways for initiating thiol-ene polymerization including the excitation of a diarylketone followed by hydrogen transfer [101], the excitation of an aryl aliphatic ketone followed by  $\alpha$ -bond cleavage [52, 101] and the direct excitation of the thiol followed by a lysis of the sulfur-hydrogen bond [102].



**Figure 2.7 :** General mechanism of thiol-ene reactions.

In this investigation, thiol-ene polymerization was initiated by the excitation of cleavage photoinitiator. Upon irradiation dimethoxyphenyl acetophenone (DMPA) give a benzoyl radical and a tertiary carbon radical as shown in Figure 2.8. The tertiary carbon radical occurs a methyl radical and methyl benzoate. The methyl and benzoyl radicals may insert into a carbon– carbon bond directly or abstract a hydrogen from a thiol group. Initiation with the cleavage photoinitiator is more efficient than hydrogen-transfer (abstraction) photoinitiators such as BP because the quantum yield for the production of reactive radicals is higher [32].


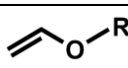
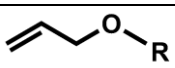
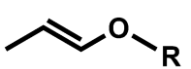
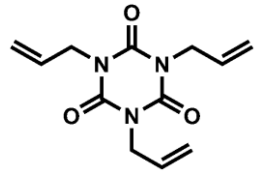
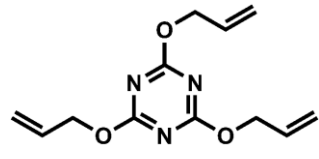

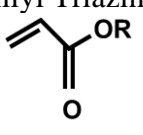
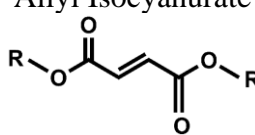
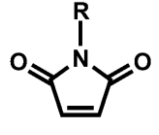
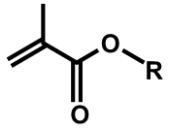
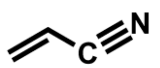
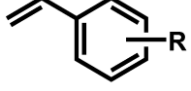
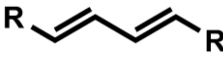
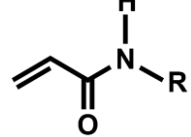


**Figure 2.8 :** Initiation of thiol-ene photopolymerization by utilization of DMPA as photoinitiator.

### 2.3.2 Suitable Compounds for Thiol-ene Reactions

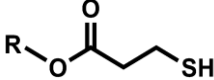
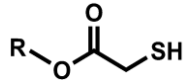
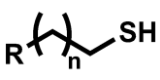
The major feature of thiol-ene photopolymerization is that almost any type of ene can participate (structures are shown in Table 2.4) [32]. General thiol compounds used in thiol-ene photoinitiated polymerization are shown in Table 2.5. A wide type of enes employ as suitable compounds, containing diversely-substituted olefinic bond. However in the radical thiol-ene reaction reactivity can vary quite based on the chemical structure of the ene and thiol compounds.

**Table 2.3 :** General structures of typical ene monomers used in thiol-ene polymerizations.

Ene monomers		
		
Norbornene	Vinyl Ether	Allyl Ether
		
Propenyl Ether	Allyl Triazine	Allyl Isocyanurate
		
Alkene	Acrylate	Unsaturated Ester (UPE)
		
Maleimide	Methacrylate	Acrylonitrile
		
Styrene	Diene	N-Vinyl Amide



**Table 2.4 :** General structures of three basic types of thiol compounds used in thiol-ene polymerizations

Thiol compounds		
 Alkyl 3- mercaptopropionate	 Alkylthioglycolate	 Alkyl thiol

Hoyle and coworkers have reported general ene reactivity with three typical thiol types (alkyl 3-mercaptopropionates, alkyl thioglycolates, and alkylthiols) under radical conditions. According to their studies, reactivity follows that order: norbornene > vinyl ether > propenyl > alkene  $\approx$  vinyl ester > *N*-vinylamide > allyl ether  $\approx$  allyl triazine  $\approx$  allyl isocyanurate > acrylate > *N*-substituted maleimide > acrylonitrile  $\approx$  methacrylate > styrene > conjugated diene. With the exception of norbornene, methacrylates, styrenes and conjugated dienes, the ene reactivity decreased with decreasing electron density of the carbon-carbon double bond. The rates of free-radical addition of thiols to norbornene are exceptionally rapid due to a combination of the significant relief of ring strain upon addition of a thiyl radical across the carbon-carbon double bond and the subsequent rapid hydrogen-abstraction rate of a thiol hydrogen by the carbon-centered radical. In contrast to, the low reactivity of methacrylates, styrenes and conjugated dienes is due to the relatively high stability of the intermediate carbon-centered radicals leading to low hydrogen abstraction rates from RS-H in the second stage of the propagation step.



### **3. EXPERIMENTAL WORK**

#### **3.1 Materials and Chemicals**

##### **3.1.1 Reagents for Synthesis of Ene-Monomer**

*4,4'-isopropylidenediphenol (Aldrich, 97%)* : 4,4'-isopropylidenediphenol was used as received.

*Paraformaldehyde (Acros, 96%)* : Paraformaldehyde was used as received.

*Allyl amine (Merck, >98%)* : Allyl amine was used as received.

*Sodium hydroxide (Acros, >97%)* : Sodium hydroxide was used as received.

*Sodium sulfate (Acros 99%)* : Sodium sulfate was used as received.

*1,2-ethanedithiol (Merck, 99%)* : 1,2-ethanedithiol was used as received.

##### **3.1.2 Solvents**

*Methanol (Technical)* : Methanol was used for the precipitation of polymers without further purification.

*Diethylether (Sigma-Aldrich)* : Diethylether was used as received.

*1,4-dioxane (Aldrich, 99%)* : 1,4-dioxane was used as received.

*N,N-dimethyl formamide (DMF, Merck, 99.8%)* : *N,N*-dimethyl formamide was used as received.

*Toluene (Aldrich 99%)* : Toluene was dried with calcium chloride and distilled over sodium wire.

*Chloroform (Sigma )* : Chloroform was dried with P<sub>2</sub>O<sub>5</sub> and distilled from CaH<sub>2</sub>.

##### **3.1.3 Photoinitiator**

*2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba)* : DMPA was used as received.

## **3.2 Equipments**

### **3.2.1 Photoreactor**

Photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350 nm was used for photopolymerization of formulations containing DMPA which absorbs around 350 nm.

### **3.2.2 $^1\text{H}$ Nuclear magnetic resonance spectroscopy ( $^1\text{H}$ -NMR)**

$^1\text{H}$ -NMR spectra of 5–10 % (w/w) solutions in  $\text{CDCl}_3$  with  $\text{Si}(\text{CH}_3)_4$  as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

### **3.2.3 Infrared spectrophotometer (IR)**

FT-IR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer via attenuated total reflectance (ATR) technique with 4 scans for each sample.

### **3.2.4 Differential Scanning Calorimeter (DSC)**

Differential scanning calorimeter (DSC) was performed on a Perkin Elmer Diamond DSC with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under nitrogen flow.

### **3.2.5 Thermal Gravimetric Analyser (TGA)**

Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of  $10\text{ }^\circ\text{C min}$  under nitrogen flow.

### **3.2.6 Dynamic Mechanical Analyser (DMA)**

Dynamic viscoelastic measurements were conducted on Perkin Elmer dynamic mechanical analyzer model DMS6100 at 1 Hz at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$ .

### **3.2.7 Gel permeation chromatography (GPC)**

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns ( $\text{G2000H}_{\text{HR}}$ ,  $\text{G3000H}_{\text{HR}}$  and  $\text{G4000H}_{\text{HR}}$ ), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were

456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min<sup>-1</sup> at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

### 3.3 Preparation Methods

#### 3.3.1 Synthesis of 6,6'-(propane-2,2-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) (B-ala)

In a 250 mL flask, allyamine (30.8 g, 0.54 mol) was dissolved in 200 ml of 1,4-dioxane at room temperature. The solution was cooled in an ice bath, followed by portion-wise addition of paraformaldehyde (32.5 g, 1.08 mol) during 10 min of stirring in an ice bath. Then, bisphenol A (61.6 g, 0.27 mol) was added to the cooled solution. The temperature was raised and refluxed for 24 h. After removal of 1,4-dioxane under vacuum, the resulted crude product was purified by dissolving in 200 mL of diethyl ether and washing various times with 0.1 N sodium hydroxide, and finally two times with distilled water. Pale yellowish oily product was obtained after drying with NaSO<sub>4</sub>, filtering and evaporating diethyl ether. The oily viscous product was dissolved in 20 ml of MeOH; water was added to this solution until it became turbid and then the mixture was refrigerated. The precipitated sticky mass was obtained after decantation and subsequently washing with water. The mass was dried under vacuum at 60 °C for 24 h to afford solid (Yield: % 62). The <sup>1</sup>H NMR spectrum of B-ala is as follows: δ (CDCl<sub>3</sub>) 6.94 (dd, *J* = 8.3 and 2.1 Hz, 2H, Ar*H*); 6.79 (dd, *J* = 2.0 Hz, 2H, Ar*H*); 6.67 (dd, *J* = 8.3 Hz, 2H, Ar*H*); 5.89 (multiplet, 2H, CH<sub>2</sub>=CH-); 5.23 (dd, *J* = 12.2 and 1.5 Hz, 2H, CH=CH<sub>2</sub>); 5.17 (dd, *J* = 5.3 and 1.3 Hz, 2H, CH=CH<sub>2</sub>); 4.82 (s, 4H, N-CH<sub>2</sub>-O); 3.93 (s, 4H, Ar-CH<sub>2</sub>-); 3.37 (d, 4H, CH<sub>2</sub>=CH-CH<sub>2</sub>-); 1.58 (s, 6H, -CH<sub>3</sub>).

#### 3.3.2 Preparation of Precursor Films [pre-P(B-ala-DTE)] by Photo-induced Thiol-ene Reaction

Typical procedure for preparation of the precursor films is as follows: B-ala (1.0 g, 2.6×10<sup>-3</sup> mol), 1,2-ethanedithiol (214 μL, 2.6×10<sup>-3</sup> mol) and photoinitiator DMPA (6.7 mg, 2.6×10<sup>-5</sup> mol, 1 % equiv of thiol reagent) were dissolved in a minimal

amount of the solvent, chloroform, required to dissolve the photoinitiator. For preparation of flexible films, the mixture was placed equally into Teflon® plates and exposed to light continuously at room temperature for 6 hours in a Rayonet merry-go-round photoreactor in which the sample was surrounded by a circle of 16 lamps emitting light nominally at 350 nm. The light intensity at the location of the sample was measured by a Delta Ohm model HD-9021 radiometer ( $I = 0.5 \text{ mW}\cdot\text{cm}^{-2}$ ).

### **3.3.3 Curing of B-ala and pre-P(B-ala-DTE) Films by Heat**

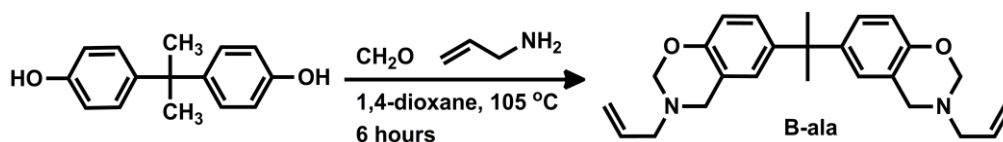
Films of bisallyl benzoxazine were prepared by solvent casting of B-ala (50% w/v in DMF) over Teflon® plates. Curing of both B-ala and pre-P(B-ala-DTE) films was performed stepwise at 80 °C for 5 h and 110 °C for 3 h, and then at 160, 180, and 200 °C for 2 h each in an air oven. The films then were postcured at 240 °C for 1 h resulted in transparent brown films.

## 4. RESULTS AND DISCUSSION

Photo-induced thiol-ene reactions have been employed in the synthesis of thermally curable benzoxazine based materials. For this purpose, allyl functional bizbenzoxazine was synthesized and used as ene-monomer in thiol-ene reactions.

### 4.1 Synthesis of B-ala and Its Thiol-ene Polymerization

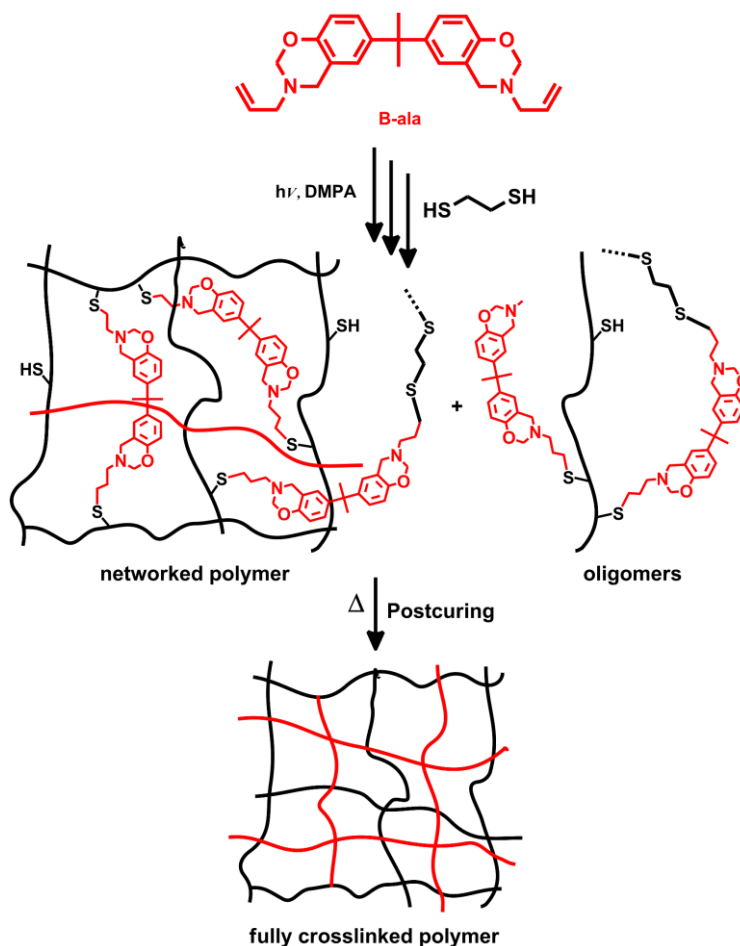
Allyl functional benzoxazine, B-ala, was synthesized through the Mannich and ring closing reaction between 4,4'-isopropylidenediphenol (bisphenol A) and allylamine in the presence of formaldehyde (Figure 4.1) [34].



**Figure 4.1** : The synthetic strategy for preparation of B-ala.

The thiol-ene reaction of B-ala as an ene-monomer and 1,2-ethanedithiol as a thiol compound was initiated by a typical free radical photoinitiator, DMPA (Figure 4.2). Under UV irradiation DMPA generates alkoxybenzyl and benzoyl radicals by  $\alpha$ -cleavage. Both radicals can abstract labile hydrogens from certain compounds such as thiols leading to formation of thiyl radicals (Figure 2.7). Then, the thiyl radicals react and couple with ene-monomers readily and form polymeric materials when at least difunctional reactants are used. In the case of 1,2-ethanedithiol and B-ala, one would expect a linear polymer as a result of polycondensation-like reactions since both thiol and B-ala contained two functional units. However, a soft and partially crosslinked (insoluble) polymeric material was obtained due to the complex mechanism of the thiol-ene reactions. First, abstractable hydrogen atoms of B-ala might cause new active sites on the propagating chains and, in turn, branching [103]. Second, the free radicals and the heat released during the reaction can also yield networked structure. It should be noted that major part of the film after the thiol-ene

reaction still contained benzoxazine rings utilized in the subsequent thermal curing. Therefore, upon heating the film became more rigid and tough due to ring opening of the unreacted benzoxazine rings.



**Figure 4.2 :** Generation of thermally curable benzoxazine based film [pre-P(B-alaDTE)] by photo-induced thiol-ene reaction and its thermal curing.

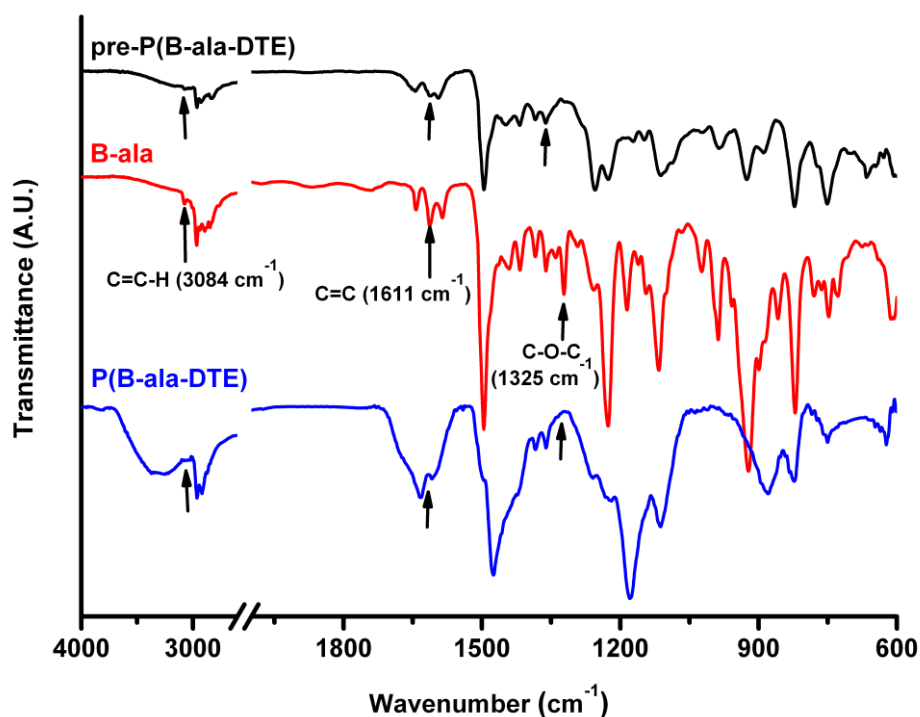
## 4.2 Characterization of B-ala and pre-P(B-ala-DTE)

### 4.2.1 FT-IR Investigation

The chemical structures of both the ene-monomer and the polymers obtained were confirmed by FT-IR spectroscopy. The spectra of free B-ala, the polymeric film obtained by the photo-induced thiol-ene reaction [pre-P(B-ala-DTE)] and the cured film [P(B-ala-DTE)] are shown in (Figure 4.3). Pure monomer exhibited its characteristic absorption bands located at  $3084 \text{ cm}^{-1}$  (stretching of  $=\text{C-H}$ ) and  $1611 \text{ cm}^{-1}$  (stretching of  $\text{C}=\text{C}$ ) due to the allyl group (Figure 4.3a). Additionally, the band



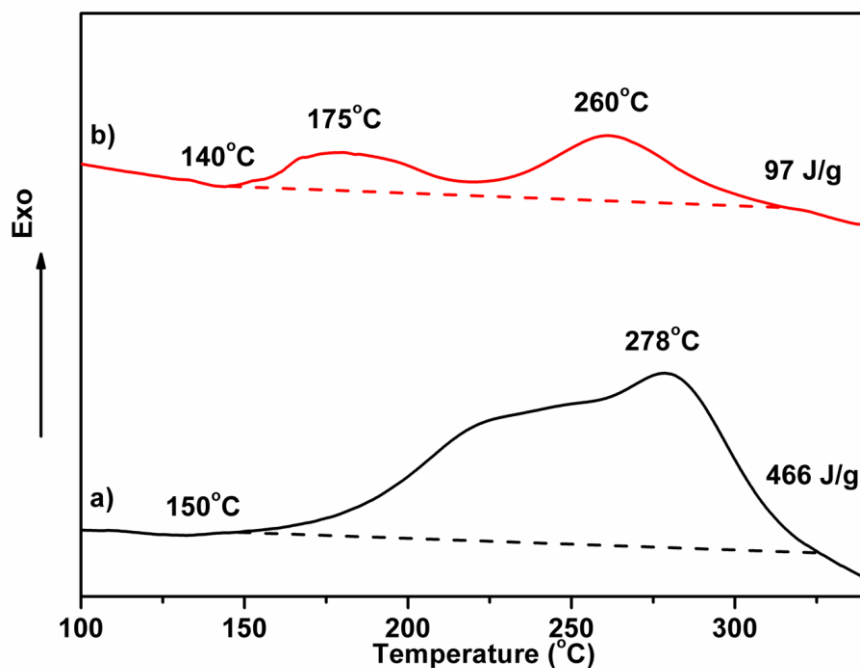
corresponding to the C-O-C oxazine ring mode was also observed at  $1325\text{ cm}^{-1}$ . The absorptions originated from allyl groups disappeared after the thiol-ene reaction (Figure 4.3b) while absorption band corresponding to the C-O-C oxazine ring disappeared after postcuring (Figure 4.3c)



**Figure 4.3** : FT-IR spectra of B-ala, pre-P(B-ala-DTE) and P(B-ala-DTE).

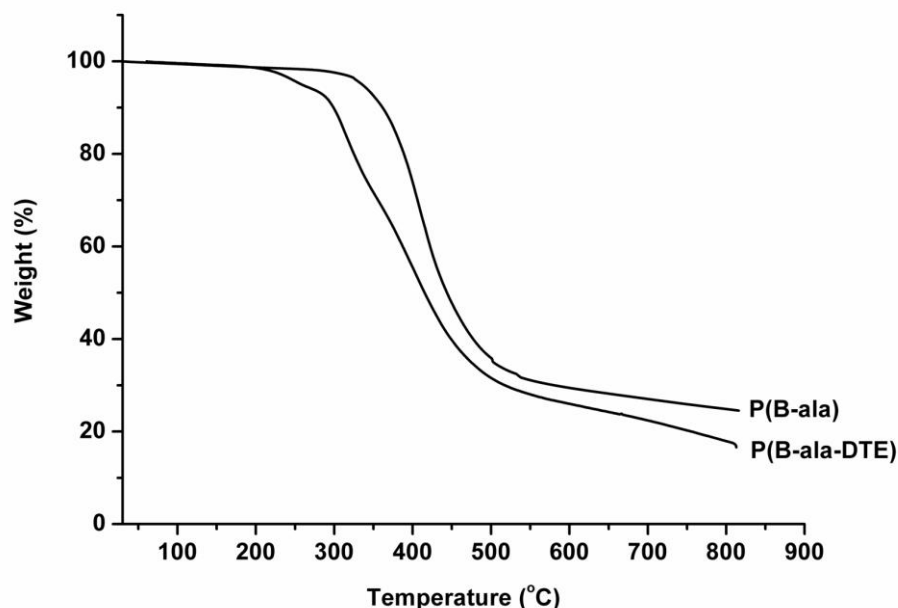
#### 4.2.2 Thermal Analysis of B-ala and pre-P(B-ala-DTE)

Thermal postcurings of both pure B-ala film and the film obtained by the thiol-ene reaction were monitored by DSC investigations. A typical unsymmetrical broad exotherm corresponding to both thermal cure of the allyl groups and the ring opening of the oxazine rings was observed during the curing of pure B-ala film. The onset temperature and peak were at  $150\text{ }^{\circ}\text{C}$  and  $278\text{ }^{\circ}\text{C}$  respectively (Figure 4.4) [34]. On the other hand, two exotherms were observed on thermogram of pre-P(B-ala-DTE) (Figure 4.4b). The first exotherm with onset temperature at  $140\text{ }^{\circ}\text{C}$  and exotherm maximum at  $175\text{ }^{\circ}\text{C}$  was attributed to thermal cure of the residual allyl groups; while the second exotherm with onset at  $225\text{ }^{\circ}\text{C}$  and peak at  $260\text{ }^{\circ}\text{C}$  was due to the ring-opening polymerization of benzoxazine moieties.



**Figure 4.4 :** DSC profiles of a) pure B-ala film and b) pre-P(B-ala-DTE) during their postcuring.

Thermal stabilities of the films were investigated by TGA under nitrogen atmosphere. The comparative TGA thermograms of P(B-ala-DTE) and P(B-ala) are shown in Figure 4.5. The results are summarized in Table 4.1 The 5 and 10% weight loss temperatures ( $T_{5\%}$  and  $T_{10\%}$ ) for P(B-ala) are 334°C and 363°C, respectively. Incorporation of linear alkyl groups into the polybenzoxazines decreases aromatic content of the materials and so their thermal stabilities [81]. Therefore, the  $T_{5\%}$  and  $T_{10\%}$  for P(B-ala-DTE) were as low as 255°C and 300°C, respectively. Moreover, the similar fashion was observed when char yields of P(B-ala) (25%) and P(B-ala-DTE) (17%) at 800 °C were compared (Figure 4.5).



**Figure 4.5 :** TGA thermograms of P(B-ala) and P(B-ala-DTE).

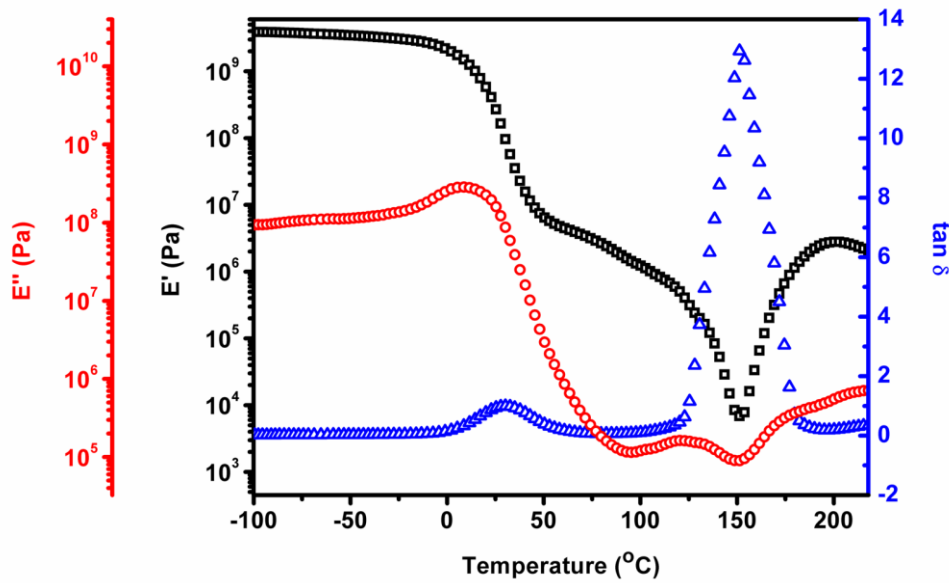
**Table 4.1 :** Thermal properties of benzoxazine polymers.

Polymer	$T_g$ (°C)		Weight-Loss Temp. (°C)		Char Yield (%)
	$E''$	$\tan \delta$	$T_{5\%}$	$T_{10\%}$	
pre-P(B-ala-DTE)	12 and 123	30 and 151	-	-	-
P(B-ala-DTE)	150 and 255	170 and 245	255	300	17
P(B-ala)	276	298	334	363	25

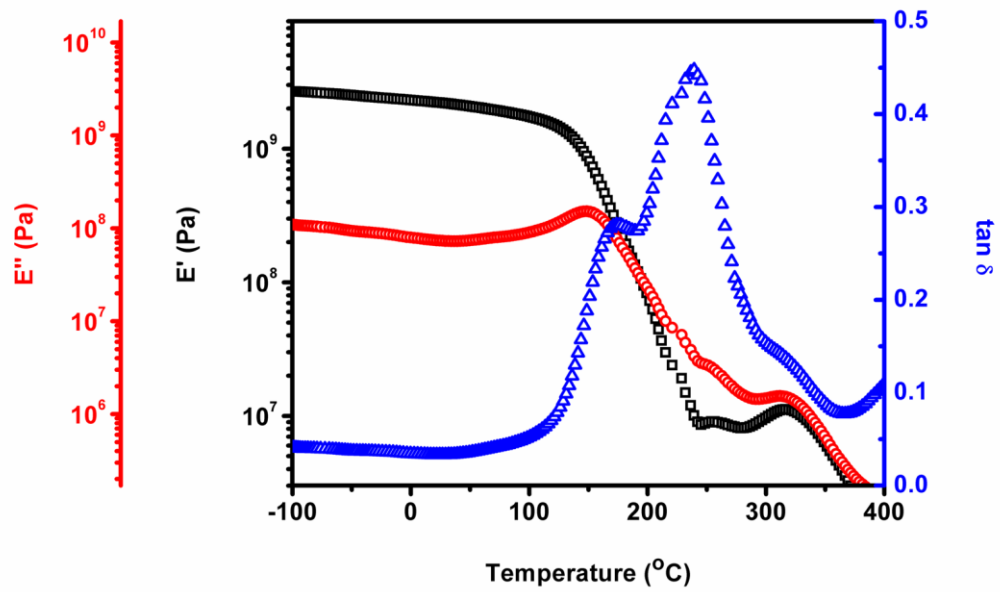
#### 4.2.3 Dynamic mechanical analysis of pre-P(B-ala-DTE) and P(B-ala-DTE)

Dynamic mechanical analysis of pre-P(B-ala-DTE) and P(B-ala-DTE) were examined along with the typical polybenzoxazine P(B-ala). Figure 4.6 – 4.8 show the temperature dependence of the storage modulus, loss modulus and  $\tan \delta$  for pre-P(B-ala-DTE), P(B-ala-DTE), P(B-ala), respectively. The  $T_g$ s are summarized in Table 1. For the precursor polymer, pre-P(B-ala-DTE), two  $T_g$ s were observed at 12°C and 123°C from the maximum of loss modulus and 30°C and 151°C from the maximum of  $\tan \delta$ . The storage modulus decreased sharply at ca. 2°C and 115°C. According to these results, it could be assumed that the polymer obtained by thiol-ene reaction, pre-P(B-ala-DTE), was not completely crosslinked and still contained

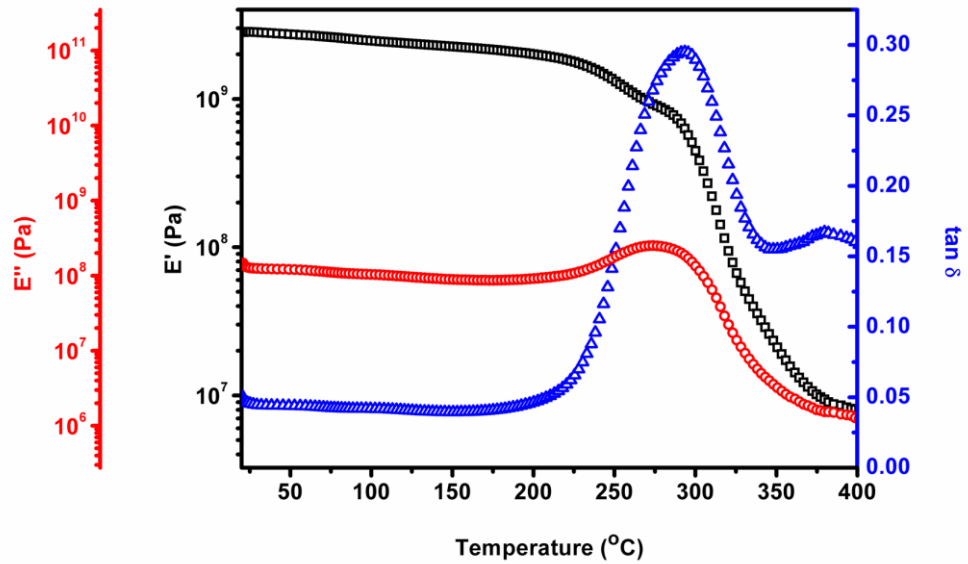
some linear oligomeric parts. The presence of these linear oligomeric structures was proved by GPC and considered above in detail. Thermal curing of pre-P(B-ala-DTE) resulted in ring opening polymerization of the benzoxazine moieties and increased the rigidity of the polymer by the increase of cross-linking density. As a result, two  $T_g$ s were determined for P(B-ala-DTE) at 150°C and 255°C from the maximum of loss modulus and 170°C and 245°C from the maximum of  $\tan \delta$ . The storage modulus was maintained up to much higher temperatures and started to decrease at 140°C and 315°C. Therefore, the first  $T_g$  disappeared since the linear oligomeric parts of precursor polymer was completely crosslinked by heating while a new  $T_g$  appeared around 250°C owing to the crosslinking of benzoxazine moieties. The typical polybenzoxazine, P(B-ala), exhibited only one  $T_g$  at relatively higher temperature, 276°C from the maximum of loss modulus and 298°C from the maximum of  $\tan \delta$ . The storage modulus started to decrease at ca. 280°C. The lower  $T_g$  for P(B-ala-DTE) compared to P(B-ala) may be attributed to the presence of cross-linked parts of pre-P(B-ala-DTE), leading to a lower cross-linking density.



**Figure 4.6 :** Dynamic mechanical spectra of pre-P(B-ala-DTE) polymerized at  $\lambda > 350$  nm for 6 h in air: (■)  $E'$ , (●)  $E''$  and (△)  $\tan \delta$ .



**Figure 4.7 :** Dynamic mechanical spectra of P(B-ala-DTE) polymerized at 240°C for 1 h in air: (□)  $E'$ , (○)  $E''$  and (△)  $\tan \delta$ .



**Figure 4.8 :** Dynamic mechanical spectra of P(B-ala) polymerized at 240°C for 1 h in air: (□)  $E'$ , (○)  $E''$  and (△)  $\tan \delta$ .



## 5. CONCLUSION

In conclusion, we synthesized thermally curable benzoxazine based polymers by using photoinitiated thiol-ene polymerization. We proposed a possible mechanism for formation of polymer involving addition of photochemically formed thiyl radical to allyl group of the benzoxazine monomer (B-ala) and consequent hydrogen abstraction from thiol compound leading to a chain reaction. Flexible thin films were formed during the thiol-ene polymerization on Teflon® plates and obtained precursor films were further cross-linked by thermally activated ring opening reaction of the benzoxazine groups present in the main chain. The thermal and mechanical properties of polymers were investigated by DSC, TGA and DMA. The cured P(B-ala-DTE) exhibited comparable flexibility induced by the alkyl groups compared to the typical polybenzoxazine P(B-ala).





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## **CURRICULUM VITAE**



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