ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

BENZOXAZINE BASED MACROMOLECULAR ARCHITECHTURE

Ph.D. Thesis by
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Department : Chemistry

Programme : Chemistry

SEPTEMBER 2009

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Date of submission : 01 July 2009
Date of defence examination: 25 September 2009

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SEPTEMBER 2009

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BENZOKSAZİN ESASLI MAKROMOLEKÜLER MİMARİ

DOKTORA TEZİ

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Tezin Enstitüye Verildiği Tarih : 01 Temmuz 2009
Tezin Savunulduğu Tarih : 25 Eylül 2009

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EYLÜL 2009

FOREWORD

I would like to dedicate this thesis to my daughter Bilge Yağmur Kışkan, my wife Füsun Şeyma Kışkan and my parents that they are the meaning of my life. Also, I would like to express my deep appreciation and thanks for my advisor Prof. Dr. Yusuf Yağcı who supported and trusted me during my work. And the most important thing that he taught how to do good science and publish the results.

Finally, I would like to thank my past and current laboratory collegues for all their help.

This work is supported by ITU Institute of Science and Technology.

July 2009 MSc. Barış KIŞKAN

TABLE OF CONTENTS

Page

ABBREVIATIONS

ATBN : Amine terminated butadiene acrylonitrile rubber
ATRP : Atom transfer radical polymerization
B-a : Bisbenzoxazine
BZPOSS : Benzoxazine containing polyhedral oligomeric silsesquioxane
CAPRO : 6-Aminocaproic acid
CQ : Camphorquinone
DGEBA : Diglycidyl ether of bisphenol A
DMAc : Dimethylacetamide
DMPA : 2,2'-Dimethoxy-2-phenylacetophenone
DODEC : Dodecylamine
DOPO : Dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide
DOPO-Gly : Glycidyl phosphinate
DSC : Differential scanning calorimetry
EPO732 : Commercial name of a flexible epoxy resin
FT-IR : Fourier transform infrared
GPC : Gel permiation chromatography
HPM : *N*-(4-Hydroxyphenyl) malemide
H-POSS : Hydrosilane functionalized polyhedral oligomeric silsesquioxane
HTBD : Hydroxyl terminated polybutadiene
IPDI : Isophorone diisocyanate
IPN : Inter penetrating network
ITX : Isopropyl thixanthone
MIB : Benzoxazine with maleimide group
MMA : Methyl methacrylate
MMT : Montmorillonite
NMR : Nuclear magnetic resonance
NOB : *p*-Hydroxyphenylnadimide derived benzoxazine
P-a : *N*-Phenyl-3,4-dihydro-2*H*-1,3-benzoxazine
P-ala : 3-Allyl-3,4-dihydro-2*H*-1,3-benzoxazine
PBO : (2,2'-(1,3-Phenylene)-bis(4,5-dihydro-oxazoles))
PC : Polycarbonate
PCL : Poly(ε-caprolactone)
PGE : Phenyl glycidyl ether
PHEN : *p*-Phenetidine
POSS : Polyhedral oligomeric silsesquioxane
PP-a : Poly(*N*-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine)
PU : Polyurethane
SEC : Size exclusion chromatography
St : Styrene
THF : Tetrahydrofuran
TMAN : 2,4,6-Trimethylaniline
TPHT : 1,3,5-Triphenylhexahydro-1,3,5-triazine
TX : Thioxanthone

LIST OF TABLES

Page

LIST OF FIGURES

Page

BENZOXAZINE BASED MACROMOLECULAR ARCHITECTURE

SUMMARY

Polybenzoxazine is a newly developed phenolic system, having a wide range of interesting features and has the capability to overcome several shortcomings of conventional novolac and resole type phenolic resins. These materials 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. The molecular structure of polybenzoxazines offers enormous design flexibility which allows tailoring the properties of the cured materials for wide range of applications. Different synthetic strategies for the preparation of benzoxazine monomers and blends, their polymerization reaction mechanisms, and the structure property relationships of the cured materials have been studied by various research groups. But, pure polybenzoxazine based polymers also suffer number of disadvantages, in terms of (i) high curing temperature (~ 200°C or higher), (ii) difficulty in processing and (iii) brittleness. To properly address these issues and overcome the associated disadvantages, several researchers have attempted various strategies, such as (i) preparation of modified monomers with additional functionality, (ii) synthesis of novel polymeric precursors and (iii) by blending with a high performance polymer or filler and fibers. Polybenzoxazines prepared from the monomers precursor are associated with some limitations on their use in practical applications. The monomers are usually powder and processing into thin films is rather difficult. Addition of elastomeric materials to brittle resins is a well known approach to improve the ductility. But while improvement in ductility of benzoxazine may be achieved using this approach, it sacrifices the intrinsic advantages of thermosetting resins. To improve the process ability 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 cross-linked network structure formed from polymer and polymerization of benzoxazine, will exhibit enhanced mechanical property while retaining the beneficial properties of polybenzoxazine. Cross linkable telechelics with benzoxazine moiety at the chain end. In this approach, benzoxazine ring has been anchored to the end of a polymer. Here a polymeric structure act as back bone structure, which are end capped with benzoxazine. Telechelics with relatively large molecular weight oligomers possess thermoplastic like properties, while allowing later cross linking for dimensional stability, chemical resistance, and high temperature stability.

Thermally curable benzoxazine ring containing polystyrene macromonomers were synthesized and characterized. 1,4-Dibromo-2,5-bis (bromomethyl)benzene and 1,4-dibromo-2-(bromomethyl)benzene were used as initiators in atom transfer radical polymerization (ATRP) of styrene. The resulting polymers were used in combination with 3-aminophenylboronic acid hemisulfate, for a Suzuki coupling.

The obtained polymers, with amino groups in the middle or end of the chains, were reacted with formaldehyde and phenol to yield benzoxazine ring-containing macromonomers. In addition to the glass transtion temperature of polystyrene segment observed at ca. 105ºC their differential scanning calorimetry (DSC) exhibit an exotherm at ca. 276^{o}C corresponding to the oxazine thermal polymerization. Both macronomers undergo thermal cure with the formation of thermosets having polystyrene segments.

Addition to telechilic strategy a novel naphthoxazine ring containing poly(ε-caprolacton) (PCL) was synthesized and characterized. For this purpose, first hydroxyl functional naphthoxazine, namely 2-(1*H*-naphtho [1,2-e][1,3] oxazin-2-yl) ethanol (N-a-OH) was prepared by the reaction of 2-naphthol, ethanolamine and methanal either in bulk or in dioxane as solvent at 110 ºC. Subsequently, N-a-OH was used as the initiator for the stannous-2-ethylhexanoate catalyzed living ring opening polymerization of ε-caprolactone. The gel permeation chromatography (GPC), fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) studies revealed that low poly dispersity PCL with naphthoxazine functionality at the end of the chain was obtained. The resulting PCL macro monomer undergoes thermal curing in the presence of low molar mass benzoxazine (P-a) at various temperatures with the formation of thermo sets having PCL segments. Curing behavior of the monomer and polymers has also been studied DSC.

For main chain precursors we have synthesized high molecular weight poly(etheresters) (PEE) containing benzoxazine units in the main chain by the diol functional monomer first was synthesized using bisphenol A, formaldehyde and 2-(2-amino-ethoxy) ethanol. Polycondensation of the resulting benzoxa-zine diether diol (B-Etherdiol) with adipoyl chloride and terephthaloyl dichloride in the presence of triethylamine resulted in corresponding PEE with molecular weights of 34,000 Da. These polymers consist of benzoxazine units, formed cross linked network. Here, presence of polyester introduced flexibility in the resulting polymer. These reactive poly (etherester) films can be further cross linked thermally which could enhance the application of polybenzoxazines. Transparent flexible films were obtained by the solvent casting method. Structures of the precursor diol monomer and the resulting PEEs are confirmed by FT-IR ^{1}H-NMR analysis. Curing behavior of both the monomer and polymers has also been studied by DSC. Thermal properties of the cured polymers are also investigated by thermo gravimetric analysis (TGA). For side chain benzoxsazine containing polymers.

A novel acetylene monomer containing benzoxazine group was synthesized and polymerized with [(norbornadiene)rhodium(I) chloride]$_2$ ([(nbd)RhCl]$_2$) to give the corresponding polymer. The effect of triethylamine as co-catalyst in the polymerization was investigated. The spectral and thermal analysis confirmed the presence of benzoxazine functionality in the resulting polymer. It is shown that polyacetylene containing benzoxazine side groups undergoes irreversible *cis-trans* isomerization and thermally activated curing in the absence of any catalyst forming polyacetylene thermoset with high thermal stability.

BENZOKSAZİN ESASLI MAKROMOLEKÜLER MİMARİ

ÖZET

Polibenzoksazinler, ilginç bir çok özellikleri ile novalak ve resol tipi fenolik reçinelerine daha üstün gelen yeni geliştirilmiş fenolik sistemlerdir. Bu malzemeler (i) kürleme sırasında hemen hemen hacimsel değişime uğramayışı (ii) düşük su absorpsiyonu (iii) bazı polibenzoksazinler için T_g (camsı geçiş sıcaklığı) kürlenme sıcaklığından yüksek oluşu (iv) yüksek yanma ürünü yüzdesi (v) kürleme için asit gerektirmemesi (vi) kürleme sırasında yan ürün oluşturmaması gibi özellikler gösterirler. Polibenzoksazinlerin moleküler yapıları kürlenmiş malzemelerin özelliklerini farklı uygulamalar için geniş bir aralıkta değiştirme imkanı tanır. Benzoksazin monomerleri ve karışımları, polimerizasyon mekanizmaları, kürlenmiş malzemelerin yapı özellik ilişkileri çeşitli araştırma grupları tarafından araştırılmıştır. Fakat saf polibenzoksazin kimyasının (i) yüksek kürleme sıcaklığı (~ 200°C veya üstü), (ii) işleme zorluğu ve (iii) kırılganlık gibi dezavantajları vardır. Bu dezavantajların üstesinden gelmek için birçok araştırmacı değişik stratejiler denemiştir. (i) Çeşitli fonksiyolu gruplarla modifiye edilmiş benzoksazin sentezi, (ii) polimerik benzoksazin sentezi, (iii) dolgu maddeleri, fiberler veya başka yüksek perfrmanslı polimerlerle karıştımak denenmiştir.

Fonksiyonlandırılmış monomerlerden hazırlanan polimerler bazı sınırlamalarla karşılaşmıştır, örneğin, monomerler genellikle toz halindedir, film haline getirmek oldukça zordur. Kırılgan reçinelere elastomerik malzemeler katmak iyi bilinen bir yöntemdir. Fakat bu yöntemde kırılganlık azaltılırken, fenolik reçinelerin geleneksel özellikleri kaybolmaktadır. Polibenzoksazinlerin işlenebilirliğini ve mekanik özelliklerini geliştirmek için yapısında benzoksazin üniteleri içeren yan zincir, ana zincir veya telekilik polimerler sentezlenmiştir. Kürleme ile oluşacak çapraz bağlı yapılarda benzoksazinin bağlı olduğu polimerik yapıların işlenebilirliğe ve mekanik özelliklere katkısı beklenmiştir. Zincir sonunda benzoksazin içeren çapraz bağlanabilen telekilik sentezi yaklaşımı ile benzoksazinler bu polimerlere bağlanmıştır. Polimerik yapı ana iskelet görevi yapmaktadır. Böylece, telekilik polimerler termoplastik rol oynamakta ama, boyutsal karalılık, kimyasallara direnç ve ısıl dayanım gösterebilmektedirler.

Bu amaca yönelik benzoksazin içeren polistirenler sentezlenmiştir. Bunun için 1,4-dibromo-2,5-bis(bromometil)benzen ve 2-bromo-1,4-bis(bromometil)benzen ATRP (Atom Transfer Radical Polymerization) başlatıcısı olarak kullanılmıştır. Ele geçen polimer 3-aminofenil boronik asit hemisülfat ile Suzuki eşleşme reaksiyonuna sokulmuştur. Böylece, zincir sonunda veya ortasında amino grubu içeren polimerler elde edilmiştir. Bu polimerler paraformaldehit, fenol ile reaksiyona sokularak benzoksazin içeren makromonomerler sentezlenmiştir. DSC (Differential Scanning Calorimeter) çalışmaları 105°C' daki polistirene ait T_g dışında 276°C' de oksazinin halka açılma ekzotermini de göstermiştir. Her iki makromonomer kürlenebilmiş ve

polistiren segmentleri içeren termosetler elde edilmiştir. Telekilik stratejisine ek olarak, naftoksazin uç gruplu poli(ε-kaprolakton) (PCL) sentezlenmiştir. Bunun için 2-(1*H*-nafto[1,2-e][1,3]oksazin-2-il)etanol (N-a-OH) 2-naftolün, etanolamin ve paraformaldehit reaksiyonundan elde edilmiştir. Bu bileşik kalay-2-hekzanoat katalizörü eşliğinde ε-kaprolaktonun yaşayan polimerizasyonunda başlatıcı olarak kullanılmıştır. GPC (Gel Permeation Chromatography), FT-IR (Fourier Transform Infra Red), NMR (Nuclear Magnetic Resonance) çalışmaları düşük polidispersite indeksli naftoksazin sonlu PCL elde edildiğini göstermiştir. PCL monofonksiyonlu benzoksazin (P-a) varlığında çeşitli sıcaklıklarda termosetler oluşturmuştur. Başlatıcının ve PCL nin kürlenme davranışları DSC ile izlenmiştir.

Ana zincirde benzoksazin içeren polimerler için yüksek molekül ağırlıklı poli(estereter)ler (PEE) sentezlenmiştir. Bunun için önce diol fonksiyonlu benzoksazin monomeri bisfenol A, paraformaldehit ve 2(2-aminoetoksi) etanol kullanılarak sentezlenmiştir. Trietilamin varlığında bu monomerin (B-eterdiol) tereftaloil klorür ve adipoil klorürle kondenzasyon reaksiyonları yaklaşık 34,000 Da ağırlığında PEE vermiştir. Böylece, bu polimerler kürlenebilen benzoksazin ünitelerinden oluşmuştur. Ester eter üniteleri sonuç polimere esneklik vermek için seçilmiştir. Kürlenebilir poli(estereter) filmleri polibenzoksazinlerin uygulamalarını geliştirmektedir. Diol monomerinin ve PEElerin yapıları FT-IR, NMR analizleri ile termal özellikleri DSC ve TGA (Thermogravimetric analysis) ile analizlenmiştir.

Yan zincirde benzoksazin içeren polimerler için asetilen içeren benzoksazin sentezlenmiştir. Bu monomer [norbornadienrodyum(I) klorür]$_2$ katalizörü ile polimerleştirilmiştir. Trietilamin ko-katalizör olarak kullanılmıştır. Spektral ve termal analizler ile polimer incelenmiş yapının benzoksazin içeren poliasetilen olduğu gösterilmiştir. Termal analizler polimerde tersinmez cis-trans izomerisayon göstermiştir. Sonuçta katalizör gerektirmeden kürlenebilen poliasetilen termosetleri ele geçirilmiştir. Bu termosetler klasik poliasetilenlerden termal olarak daha gelişmiş özellik göstermiştir.

1. INTRODUCTION

Phenolic resins are widely used in industry for various applications, from construction materials to high technology aerospace industry. Though several desirable properties, such as good mechanical strength, dimensional stability, resistance against various solvents and flame, are characteristics of the phenolic resins, a number of short-comings are also associated with these materials. For example, they are brittle, have poor shelf life, acid or base catalysts are often used for the preparation of resin, which corrode the processing equipments, and they release by-products (such as water, ammonia compounds during curing) which sometimes affect the properties of cured resins by forming micro voids. To overcome these problems recently a new type of addition-cure phenolic system, polybenzoxazines, has been recently developed. They have gained immense interest in the field of polymer research because they have the capability to exhibit such properties which are the combination of thermal and flame retardance properties of phenolics along with mechanical performance and molecular design flexibility. Although the benzoxazines were first synthesized in 1940s [1], the potential of polybenzoxazines has been recognized only recently [2]. The molecular structure of polybenzoxazines offers enormous design flexibility which allows the properties of the cured materials to be tailored for wide range of applications. These newly developed resins possess unique features, namely (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazine based materials Tg much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, (vi) release of no by-products (even non-toxic) during curing [3]. Though several researchers have reported different synthetic methodologies of many benzoxazine containing monomers, blends, composites, and their cure reactions and properties, no extensive and critical review is available solely devoted to these materials. A special section has been dedicated to describe the recent trend to incorporate benzoxazine groups into macromolecular chains.

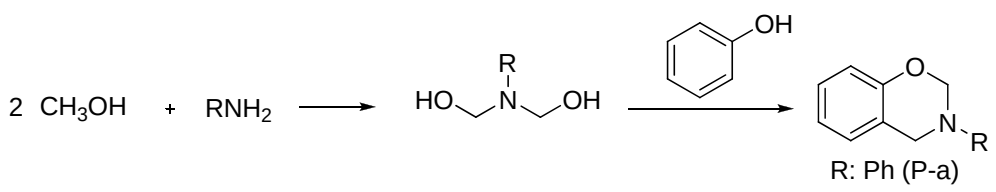
2. THEORETICAL PART

2.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution method or solventless method. Using various types of phenols and amines, having different substitution groups attached, various types of benzoxazine monomer can be synthesized. These substituting groups can provide additional polymerizable sites and also affect the curing process. In order to obtain polymeric materials, with desired properties, by tailoring the benzoxazine monomer with different functionality and a wide variety of monomers can be synthesized by using appropriate chosen phenol and amine. In this section synthesis of different benzoxazine monomers have been discussed.

2.1.1 Mono-functional benzoxazine monomers

Condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers was reported. According to the reported procedure, this reaction was performed in a solvent in two-steps. It was found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and forms a Mannich bridge [4]. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an *N*,*N*-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and *ortho* position of the phenol at the elevated temperature to form the oxazine ring [5] (Reactions 2.1).



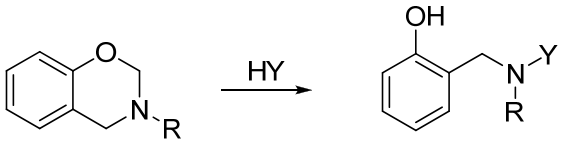
(2.1)

As an example, to prepare 3,4-dihydro-3-cyclohexyl-6-*t*-butyl-1,3,2H-benzoxazine, Two procedures were employed [4]:

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 [6-8].

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) [9] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [2] is shown below in reaction 2.2.



(2.2)

The benzoxazines derived from a strongly basic amine and a less acidic phenol found to be more stable in the hot alcohols [10]. 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 [11]. A significantly higher yield obtained when the benzoxazine derived from phenol having an *ortho* substituent.

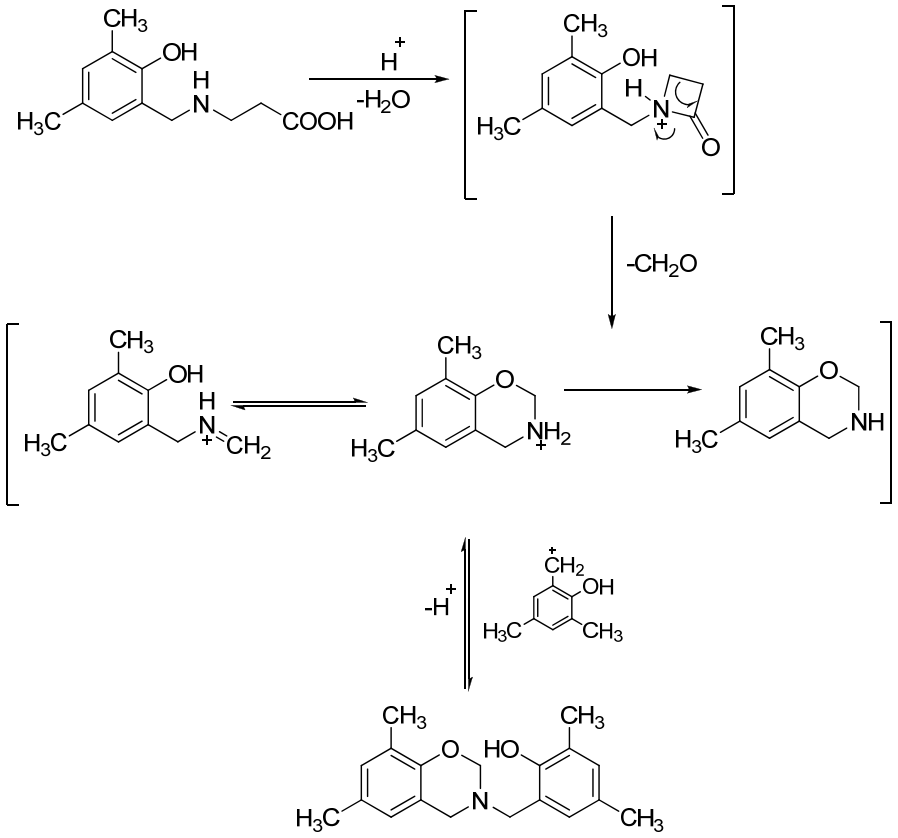
The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, 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 [12].

The reaction mechanism and kinetics of this solventless synthesis were proposed [13]. 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.

Although most of the benzoxazines were synthesized by using phenol, formaldehyde and primary amines as starting compounds several other synthetic strategies were also reported. To synthesize 3,4-dihydro-2*H*-1,3-benzoxazine, Firstly [14] *N*-(2-hydroxy-3,5-dimethylbenzyl)-aminopropanoic acid was synthesized via the Mannich reaction between 2,4-dimethylphenol, aqueous formaldehyde, and 3-aminopropanoic acid in ethanol. This amino acid was allowed to react in 96% sulfuric acid at room temperature. After neutralization, 3-(2-hydroxy-3,5-dimethyl)benzyl-3,4-dihydro-6,8-dimethyl-2*H*-1,3-benzoxazine was obtained. The reaction steps are shown in Scheme 3. In this method, the alkylating agent arises from acid-induced deamination of the phenolic Mannich base. Thus, the variety of substituent on the N-3 position of the benzoxazine ring is limited. Benzoxazine can also be obtained by heating the mixture of 2,4-xylenol and hexamethylenetetramine (3:4:1 mole) at 135°C for 2 h in air. The reaction of 1 mole of 2-hydroxybenzylamine with 2 moles of formaldehyde produces bis-(3,4-dihydro-2*H*-1,3-benzoxazine-3-yl)-methylene.

Some 3,4-dihydro-2*H*-1,3-benzoxazines with substituents on C-2 or C-4 such as, 2,2-dibenz-1,3-oxazine, were also synthesized, by the reactions of salicylamines(o-hydroxybenzylamine) with glyoxal or -diketones in methanol at a temperature lower than 20 °C [15].



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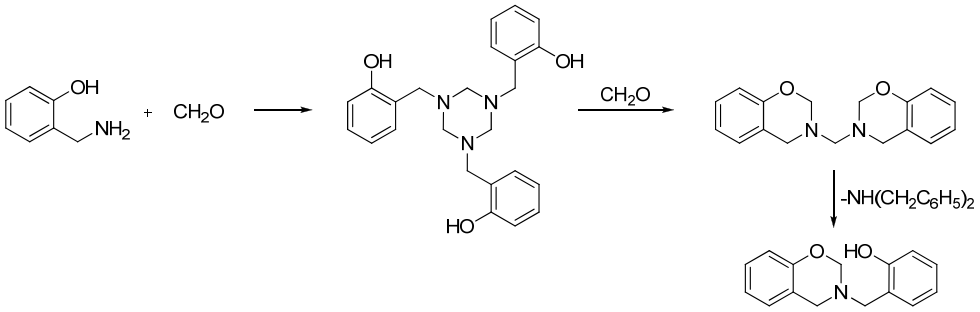
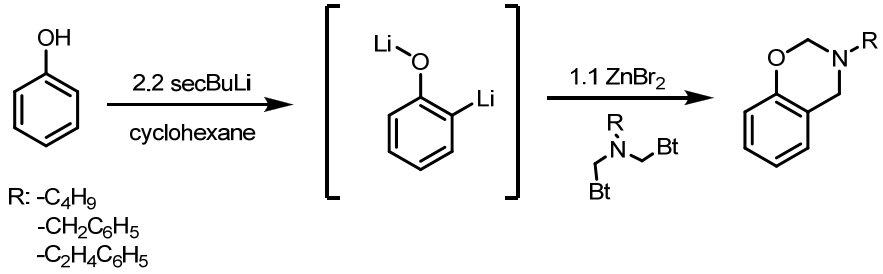


(2.4)

Another method to synthesize benzoxazines is directed *ortho*-metalation methodology. This offers a predictable and widely applicable synthetic strategy for the regiospecific construction of heterocyclic compounds [16]. 3,4-Dihydro-2*H*-1,3-benzoxazines were synthesized by directed *ortho*-lithiation of phenols and by side-chain lithiation of substituted phenols, respectively, in one-pot by reacting with *N*,*N*-bis[(benzotriazol-1-yl)methyl]amines as 1,3-biselectrophile synthons (reaction 2.5) [17].



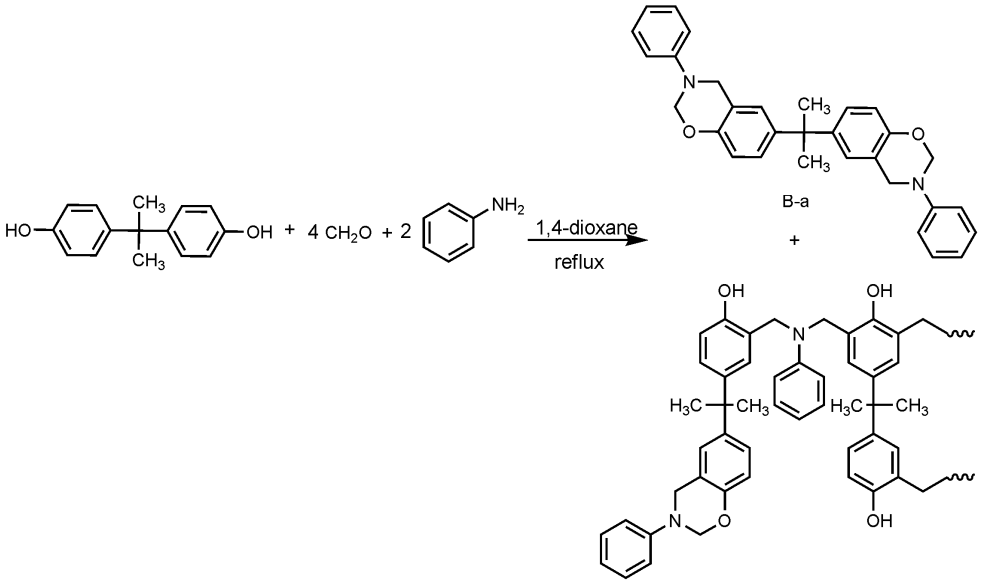
(2.5)

2.1.2 Di-functional and 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. 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 [18]. 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 [19]. To overcome this limitation, a new class of difunctional or multifunctional benzoxazine monomers [20] 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 precursor was synthesized using bisphenol-A, formaldehyde and methyl amine in different solvents and referred as B-m, (see Table 2.1) as a reference to two of its original ingredients: bisphenol-A and methylamine. 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 [21, 22] 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 ^{1}H-NMR measurements. The overall synthetic procedure is shown in reaction 2.6. 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.



(2.6)

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 [23].

Solventless method was successfully employed for synthesis of a series of difunctional monomers listed in Figure 2.1 [22-26].

2.1.3 Step-wise controlled synthesis of dimers and oligomers

To properly understand the structures of benzoxazines and the polymers formed due to the ring opening polymerization, several model oligomers (dimers, trimers, tetramers etc.) were synthesized using a controlled step-wise route [27-30] and the synthetic strategy is shown in reaction 2.7. From in-depth characterizations of these model benzoxazine oligomers by ^{1}H-NMR, ^{13}C-NMR and FT-IR spectroscopy a pseudo cyclic structure based on stable –OH---N intramolecular hydrogen bonding and OH---O intramolecular hydrogen bonding has been proposed and the possibility of helical structure formation in the longer chain benzoxazine oligomers has been predicted.

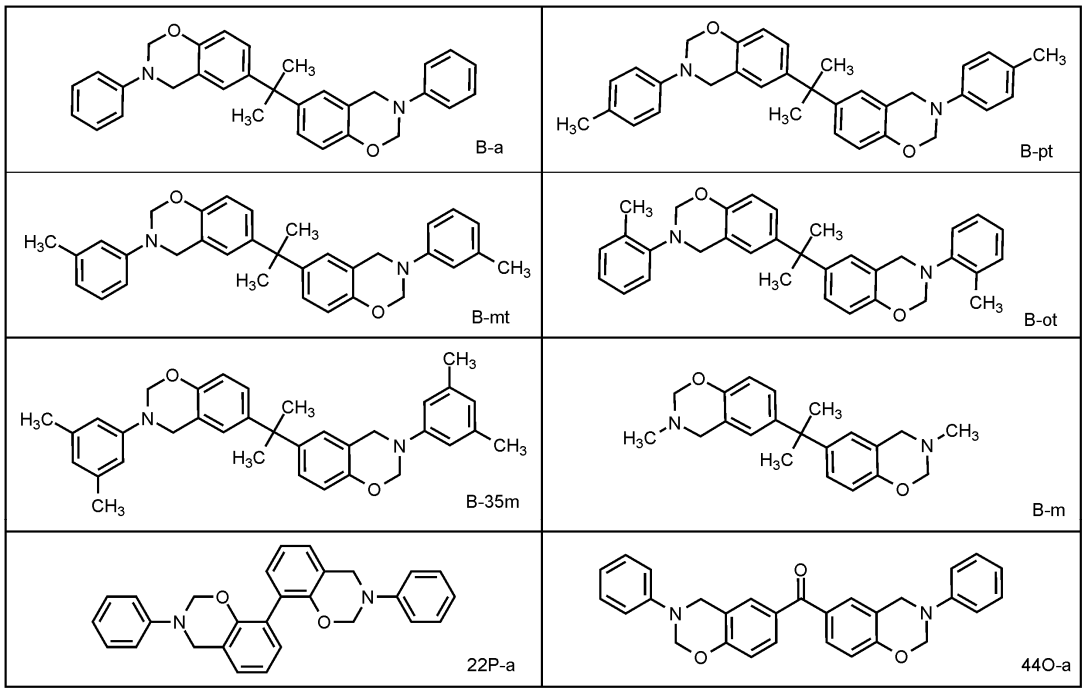
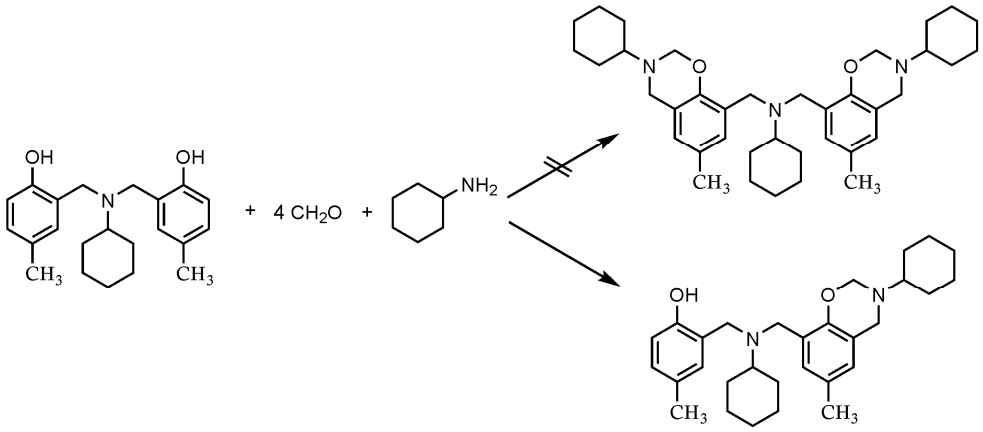


Figure 2.1 : Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer

It was demonstrated how the stereo-structure of the reactant molecule plays an important role to control the reaction and synthesized an asymmetric product, which was not expected when considering the chemical formula of the reactants [31]. The major disadvantages of the typical polybenzoxazines are their brittleness and the high cure temperature needed to the ring opening polymerization. To address the issues related to the enhancement of the performance of polybenzoxazines are highly challenging. Two major approaches are generally considered: (1) by preparing specially designed novel monomers, or (2) by blending with a high-performance polymer or filler and fiber.

Despite their usual thermal stability, the side functional groups R of the Mannich bridge, $-CH_2-NR-CH_2-$, were found to be the weakest points of the cross-linked network structures. Thermal decomposition study of the polybenzoxazines revealed that they decompose by loss of amine fragments [32]. Therefore "end-capping" to these functionalities by another polymerizable group was promising strategy to stabilize the Mannich bridge, with the expectation of further improvement of the thermal stability of the polybenzoxazines.

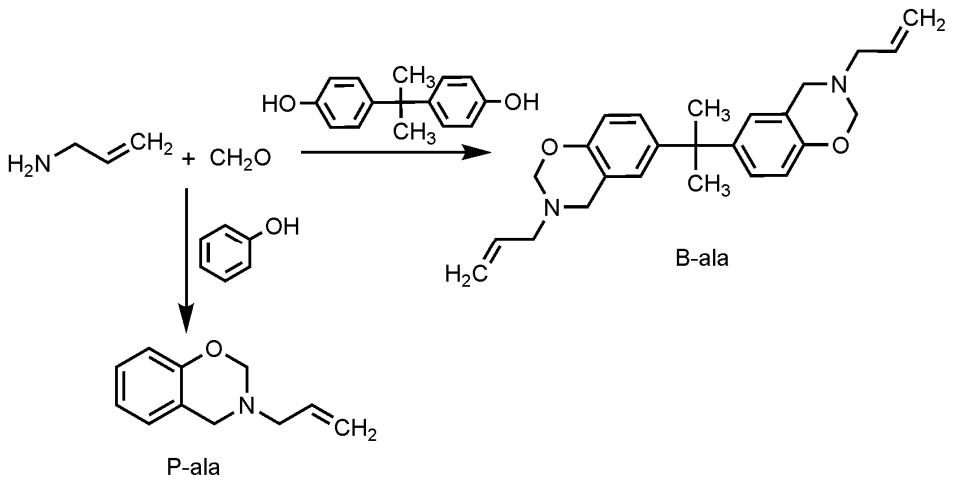


(2.7)

As per approach one, introduction of ethynyl or phenyl ethynyl [33, 34], nitrile [35], propargyl [36] etc. groups, which can offer additional cross-linking site during polymerization, was found to acceptable choice for this purpose. According to the second approach, mechanical and thermal properties of polybenzoxazines can be improved by the preparation of copolymers, polymer alloys, composites, and polymer-clay nanocomposites.

2.1.4 Allyl containing monomers

The main advantage of the allyl group [37,38] is that not only it provides additional crosslinkable sites, it can be easily be cured at temperature lower than acetylene groups. Allyl-containing monomers have attracted much attention because they are used as reactive diluents of bismaleimides to improve the toughness of the cured resin. Ishida also reported [12] the preparation of an allyl-containing benzoxazine monomer, 3-phenyl-3,4-dihydro-8-allyl-2*H*-1,3-benzoxazine, from allylphenol, aniline, and paraformaldehyde. A similar benzoxazine monomer based on allylphenol was reported for sillylation of allyl group to enhance the interface between the matrix and glass or carbon fiber in fiber-reinforced polybenzoxazine [39]. Also, similar bifunctional allylphenol-derived polybenzoxazine was reported [40]. Because of the absence of activated *ortho* position to the phenolic hydroxyl group, these allylphenol-based benzoxazine monomers, however, are considered to be difficult to polymerize through ring-opening and are not a good candidate for preparing high performance polybenzoxazines. The synthetic approaches adopted for 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 are shown below in reaction 2.8 [41].

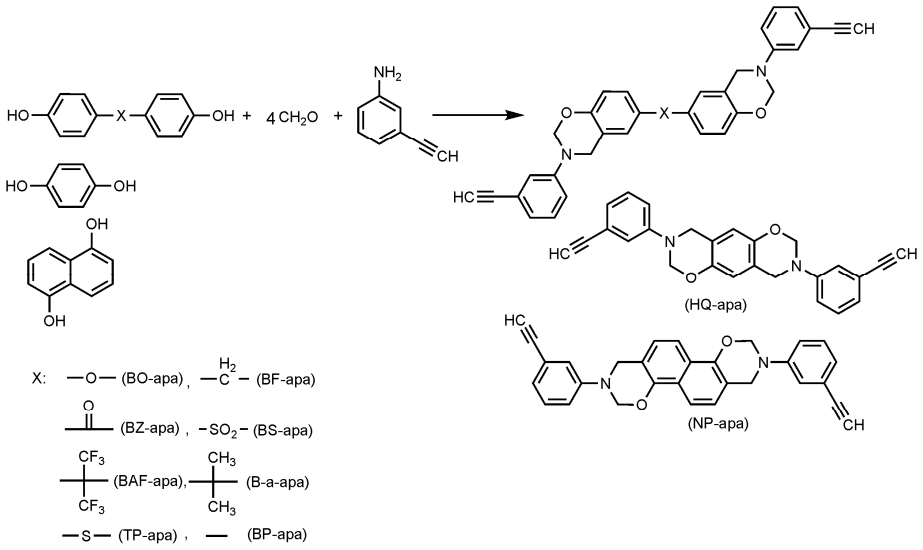


(2.8)

It was reported that benzoxazines containing allyl group can polymerize at temperatures below 150°C. However, this polymerization occurring at low temperature was not from the benzoxazine ring-opening reaction, but from the allyl group and high temperature above 250°C was still needed to complete the polymerization of benzoxazine rings. Synthesis of a series of allyl group containing mono-functional benzoxazine monomers, where the allyl group is attached with nitrogen and derived from cresol and allyl amine by solventless method has been reported and the effect of these allyl groups on polymerization reaction and the performance enhancement of the cured polymers at high temperature have been reported [42].

2.1.5 Acetylene containing monomers

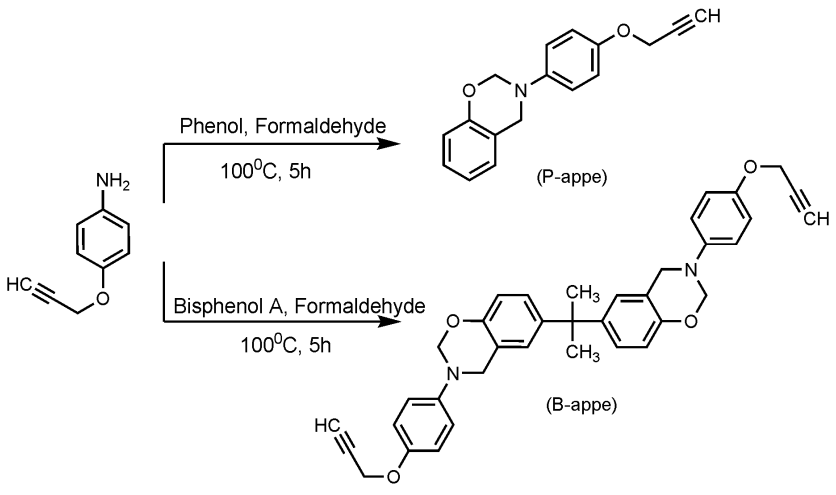
The synthesis of easily processable benzoxazine monomers with acetylene functionality has been reported [43]. It has been observed that the high thermal stability of the polybenzoxazines derived from this class of monomers is a combined result of polymerization of acetylene terminal functional group and oxazine ring-opening polymerization. Most of the mono-functional monomers were synthesized by the general solvent method whereas the multifunctional monomers were by solventless method. The synthesis of various difunctional monomers is depicted in reaction 2.9.



(2.9)

2.1.6 Propargyl ether containing monomers

Propargyl ether group, as a thermally reactive end capping agent, has attracted much attention because these monomers can be synthesized in high yield with low cost, in contrast to ethynyl-containing monomers which the preparation procedure is in low yield and high price [44]. Novel benzoxazine monomers containing a propargyl ether group have been prepared as the cross-linkable functional group according to reaction 2.10 and obtained novel polybenzoxazines with attractive thermal properties [36]. The ring-opening polymerization of oxazine ring and cross-linking of propargyl ether group occurred at almost the same temperature range, at 230°C for mono-functional and 249°C for bifunctional monomer. Polybenzoxazines derived from these monomers exhibited significantly improved thermal properties than the typical polybenzoxazines.



(2.10)

2.1.7 Nitrile containing monomers

Development of high performance phthalonitrile functional polybenzoxazines was another attempt taken to achieve highly thermal stable resin [35]. It was expected that side functionality, phthalonitrile, would contribute to the cross-linked network formation by its own polymerization. This attempt was taken because nitrile group reacts during pyrolysis of polyacrylonitrile. It has been reported that this thermal polymerization can be initiated by nucleophilic species that attack nitrile groups and form active species $-C^{+}=N^{-}$. The active species continue the reaction with the neighboring nitrile group and a ladder like polymer is formed with tetrahydronaphthiridine ring structure [45]. Benzoxazines with one or more nitrile functionalities of the following structures were synthesized. Figure 2.2 represents several phenyl nitrile containing benzoxazine monomers.

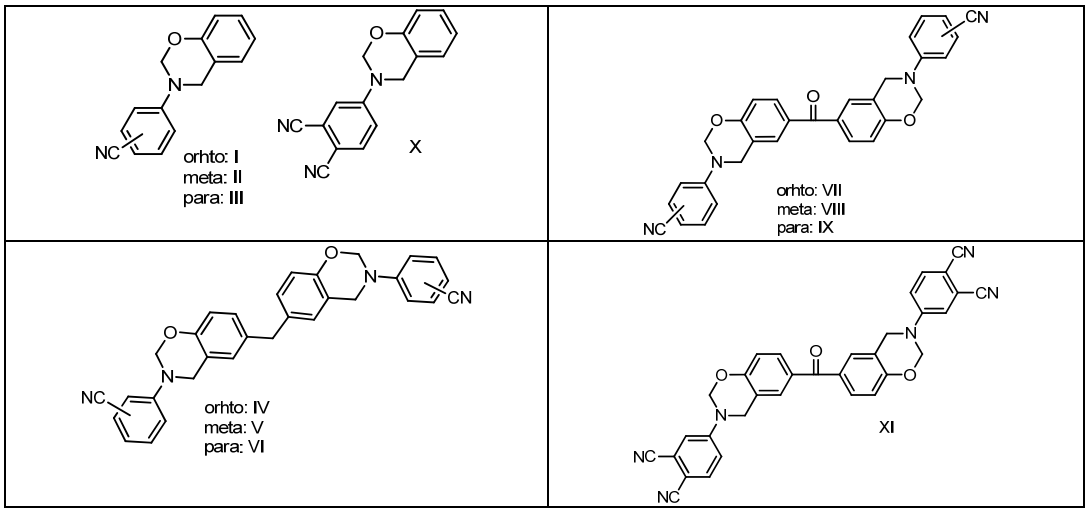


Figure 2.2 : Phenylnitrile containing benzoxazine monomers.

Notably, the polymers obtained from monomers with two –CN groups exhibited better thermal properties [46].

2.1.8 Meleimide & norbornane containing monomers

Benzoxazine compound with a maleimide pendant (HPM-Ba) was prepared to achieve attractive processing and thermal properties. It was prepared from *N*-(4-hydroxyphenyl) malemide (HPM), formaldehyde and aniline in dioxane medium and the yield was 30%. Another reported method is using 1,3,5-triphenylhexahydro-1,3,5-triazine (TPHT). The reaction was performed through solventless synthesis route where TPHT, aniline and paraformaldehyde was mixed together and heated at 150°C for 1.5 h. The yield of the final product, HPM-Ba, after washing and

precipitation was 70% [47, 48]. Similarly, mono-functional benzoxazine with norborane functionatility, NOB, was synthesized [49] using *p*-hydroxyphenylnadimide, p-formaldehyde and aniline in DMF (dimethyl formamide) at 90°C. Also, nitrile group containing maleimide benzoxazine was synthesized to further improve thermal properties of polybenzoxazine resin [50]. The structures of benzoxazine monomers having malemide and norbornane functionality are shown at Figure 2.3.

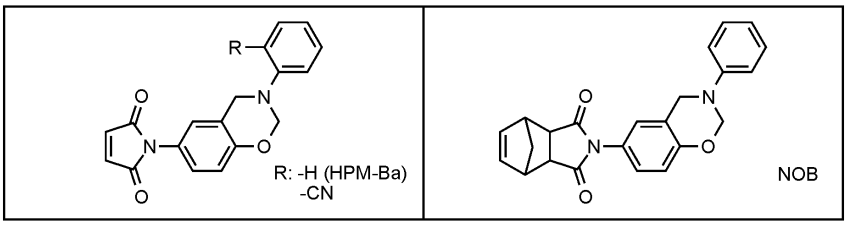


Figure 2.3 : Maleimidyl and norbornyl functional benzoxazines.

2.1.9 Adamantane containing monomers

The synthesis of adamantyl modified benzoxazine monomers (Figure 2.4) of the following structure from 4-(1-adamantyl)-phenol, formaldehyde and aniline (or methylamine) in dioxane were reported [51,52].

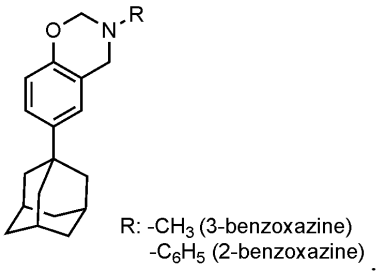
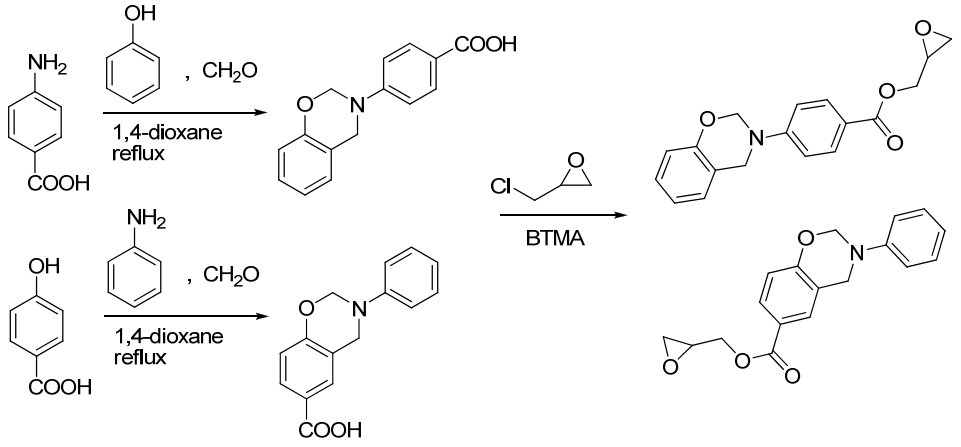


Figure 2.4 : Adamantyl functional benzoxazine.

It was expected that the rigid structure of the adamantane will hinder the chain mobility (boat anchor effect) and substantially the thermal properties of the resulting polymer, including the glass-transition temperature and decomposition temperature would be enhanced, especially for poly(6-adamantyl-3-methyl-3,4-dihydro-2*H*-1,3-benzoxazine) (poly(3-benzoxazine). In the poly(6-adamantyl-3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine) (poly(2-benzoxazine) system, however, the opposite result for the glass-transition temperature was observed and explained by lowering of cross-linking density. As the phenyl group was bulkier than the methyl group, the movement of the molecular chain was hindered between bridging points during the curing process; this resulted in a lower cross-linking density [51,52].

2.1.10 Epoxy containing monomers

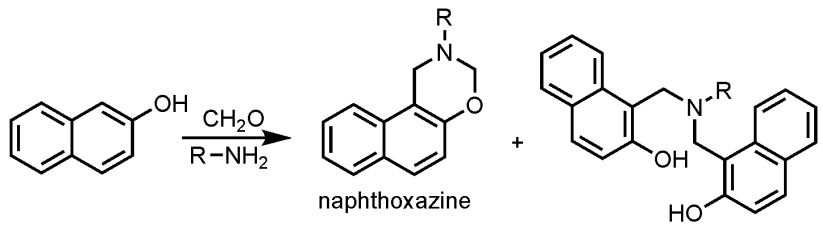
Synthesis and polymerization of glycidylic derivatives of benzoxazines obtained from aniline and 4-hydroxybenzoic acid and from phenol and 4-aminobenzoic acid (reaction 2.11) was reported [53]. By introducing epoxy groups into the molecular structure of benzoxazine, another attractive way of improving the thermal stability and glass-transition temperatures of the resulting polybenzoxazines was achieved.



(2.11)

2.1.11 Naphthoxazine monomer

When benzene ring is replaced by the naphthalene, the corresponding oxazine becomes naphthoxazine. Naphthoxazines were synthesized employing the similar strategy, *i.e.*, reaction of napthol, formaldehyde and primary amines. But along with it alkylaminomethyl-2-napthol also formed as by-product as shown in the reaction 2.12 [9].



(2.12)

R: methyl, benzyl, cyclohexyl, n-butyl

Solvent, temperature and basicity of amine play important roles upon the yield of the corresponding naphthoxazine monomer formation. Difunctional amines like *p*-phenylenediamine when reacted with formaldehyde and napthol (1:4:2 molar ratio) it produced 2,2'-*p*-phenylene-bis-(2,3-dihydro-1*H*-napth[1,2-e]-*m*-oxazine) (2Na-a). Several other difunctional naphthoxazines were also synthesized from dihydroxynapthalene, formaldehyde and primary amines (Figure 2.5) [54-57].

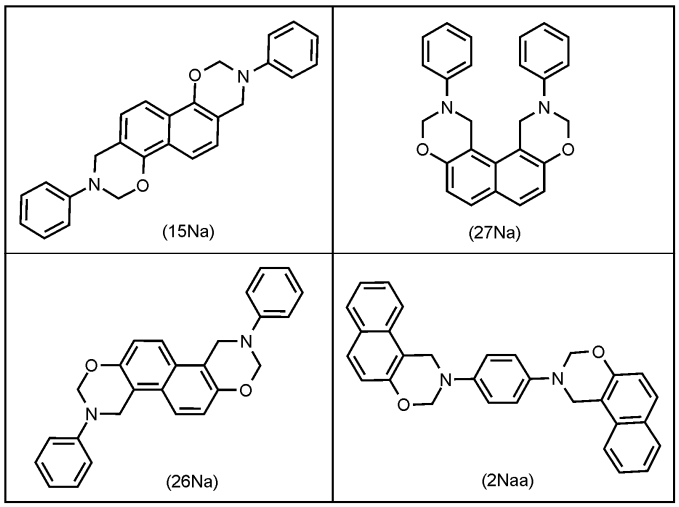


Figure 2.5 : Difunctional naphthoxazine.

Apart from naphthoxazine some fluorinated benzoxazine [58-60] and furan containing benzoxazine [61] have also been reported in the literature.

2.2 Combination of Polybenzoxazines with Other Polymeric Materials

As stated previously, several approaches to overcome some of the shortcomings of polybenzoxazines, such as mechanical properties, high curing temperature and low process ability, have been proposed. These include modification of the monomer, preparation of polymer blends and composites, hybridization with inorganic materials and chemical incorporation of benzoxazine structure into polymers. The first approach which concerns the modification of monomer in the synthesis step has been discussed in detail in the previous section. The described methods allow the possibility of preparation of a wide range of monomers with additional functionalities if not to meet completely targeted properties but at least to improve. In the following section, we will discuss the combination of polybenzoxazines with the other polymeric and inorganic materials.

2.2.1 Preparations of blends and composites

2.2.1.1 Rubber modified polybenzoxazine

One of the successful approaches to overcome the inherent brittleness of the thermosets is modifying by rubber [62]. The toughening mechanism may be involved cavitations of rubber particles, followed by plastic deformation of the matrix. Through cavitations is not alone the considerable source of toughening, yet its importance on the plastic deformation of the matrix has been widely recognized [63,

64]. Two mechanisms for the plastic deformation induced by rubber particles have been proposed: (i) shear yielding of matrix between the neighboring rubber particles and (ii) plastic void growth of the matrix surrounding the particle. It has also been identified that, the role of the rubber particles in the matrix phase is to relieve the constraint in front of crack tips by rubber cavitations, which triggers the formation of shear bands [65]. Various morphological parameters, such as particle size, particle size distribution, and matrix to particle adhesion, play important roles in toughening [66-69]. Therefore, the liquid rubber, which is commonly used for epoxy modifications, is thought to be appropriate due to its low viscosity and its polarity can easily be monitored by changing the ratio of polybutadiene and acrylonitrile. The polarity control of additives is important because polarity effects the distribution of rubber in the matrix. It has been reported that the phase separation of rubber and matrix is necessary and the size of distributed rubber particle has to be $10^2 \sim 10^3$ nm to obtain substantial improvement in toughness.

Polybenzoxazine was modified with amine-terminated butadiene acrylonitrile rubber (ATBN) and with carboxyl-terminated butadiene acrylonitrile rubber (CTBN) in order to improve its mechanical properties. Rubber modification of polybenzoxazine was carried out by adding liquid rubber to a molten benzoxazine monomer (bisphenol-A based difunctional benzoxazine) at 120°C with mechanical stirring. The molten mixture was then cast in a silicon rubber open mold and cured at a well defined curing cycle. In this particular investigation, the formulation of ATBN and CTBN series were varied from 0-3 wt %.

In another investigation, hydroxyl terminated polybutadiene (HTBD) rubber, having various epoxy content, was used as the toughening modifier [69]. As the epoxidized polybutadiene rubber can undergo copolymerization with the hydroxyl groups, produced upon ring opening of benzoxazine, and thus can be chemically grafted into the matrix network [70], a toughened composite with a higher compatibility was obtained. Melt mixing method was used to obtain rubber-modified polybenzoxazine.

Preparation of hydroxyphenylmaleimide (HPM) and ATBN-modified polybenzoxazine by mixing benzoxazine monomer (B-a), HPM and ATBN in melting state, followed by film casting and curing have been reported [71].

2.2.1.2 Polycarbonate blends with polybenzoxazine

Due to the relatively high toughness and the capability of intermolecular hydrogen bond formation with polybenzoxazine main chain, polycarbonate (PC) was chosen as blending material to improve the toughness of polybenzoxazines [72]. The driving force that results in the miscibility of the PC/benzoxazine blend in the entire composition range is the interaction between the hydroxyl groups of polybenzoxazine and the carbonyl groups of the PC. A solution blending method was employed for the preparation of all the blend samples. The solutions of the purified benzoxazine monomer which is based on *p*-cresol and aniline, 3-benzyl-3,4-dihydro-6-methyl-2*H*-1,3-benzoxazine (abbreviated as *p*-Ca), and PC were blended at room temperature to form a homogeneous mixture with the aid of chloroform and a transparent yellow solution was obtained. The solvent in the blended mixture was first evaporated in an ambient environment until most of the solvent was driven off, followed by removal of the residual solvent and moisture in a vacuum oven at room temperature for at least 48 h. The sample obtained above was isothermally polymerized in an air-circulated oven at 180°C for various periods of time. It should be noted that phase separation occurs with the increase of PC content [73].

2.2.1.3 Poly(ε-caprolactone) blends with polybenzoxazine

Though poly(ε-caprolactone) (PCL) possesses very low T_g (-55°C), its thermal stability is much higher compared to the other low T_g modifiers. This unique property makes PCL a potential candidate for blending with polybenzoxazine to achieve easy possibility and improved thermal properties. Apart from that, as intermolecular hydrogen bonding between hydroxyl groups of polybenzoxazine main chain and the carbonyl groups of PCL may form, it can enhance the miscibility of PCL with polybenzoxazine [74-76].

Preparation and characterizations of PCL- polybenzoxazine (PB-a) blends by melt blending process was reported by Ishida and Lee. Different concentrations of PCL were added to B-a at 120°C. After through mixing, a clear homogeneous mixture obtained. This mixture was then step cured in a compression molder after degassing.

Blends of B-a with PCL by casting from chloroform solution at room temperature followed by removal of solvents by drying in a vacuum oven at 60°C for 2 d was

prepared [76]. A melt blending method was applied to prepare PB-a/PCL blends from B-a and PCL.

Solution blending method was used a to obtain B-m / PCL blends having different compositions where THF used as solvent [77].

2.2.1.4 Polyurethane (PU) blends with polybenzoxazine

Good abrasion resistance, outstanding oil resistance, excellent low-temperature flexibility, and extraordinary processibility make polyurethane (PU) elastomers (which are the family members of segmented polymers where soft segments derived from polyols and hard segments from isocyanates and chain extenders) as one of the most attractive class of elastomers. They also exhibit the widest variety of hardness and elastic moduli that just fill in the gap between plastics and rubbers. In another words, they have the potential to tailor the materials with characteristics of either high modulus or good elasticity. However, low resistance to moisture and hydrolysis, low resistance to polar solvents, and poor thermal stability are some limitations associated with these elastomers. Generally, the acceptable thermal durability for PUs ranges from 80 to 90°C, and the thermal degradation of PUs occurs at ca. 200°C [78]. The phenolic hydroxyl groups present in the polybenzoxazine have a strong capability for reacting with PUs or their prepolymers with terminal reactive -NCO groups, which draws the motivation to prepare PU/ polybenzoxazine blends [79, 80].

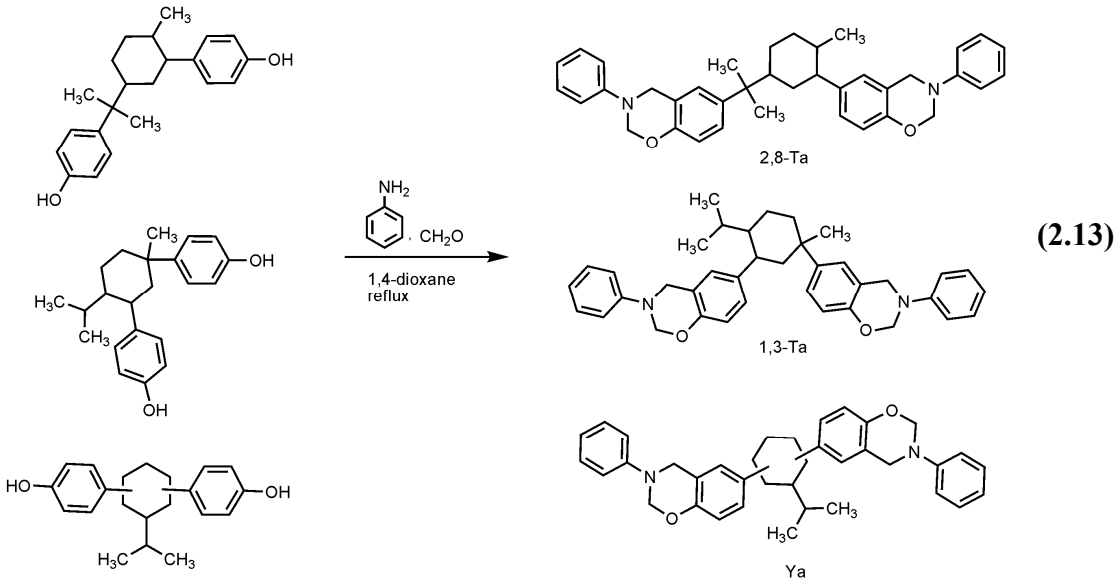
Poly(urethane-benzoxazine) films were prepared by solution blending method where the PU prepolymer was mixed with various amount of a benzoxazine monomer, B-a, in THF and followed by casting on glass plates and curing by thermal treatment [81].

Inter Penetrating Networks (IPN) of PU/ PB-a was prepared by mixing B-a with PU in warm *N,N*-dimethylacetamide (DMA). The mixture was procured at 120°C for 1 h and was coated into a preheated Teflon mould at 180°C. The mould was then kept in a vacuum oven at 120°C for 2 h and then cured at 200°C for 2 h [82].

A melt blending technique was used for alloying polybenzoxazine with PU and epoxy [83].

2.2.1.5 Epoxy blends with polybenzoxazine

The benzoxazines were first copolymerized with an epoxy resin in order to modify their performance [84]. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization led to significant increase in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness.Copolymers from polybenzoxazines and epoxy resins were also designed keeping in mind that the ring opening reactions of benzoxazines produces phenolic hydroxyl groups, which can react with epoxy resins and provide additional cross-linking points into the matrix offer a network structure [85]. Samples containing 50 mol % B-a and 50% DGEBA (diglycidyl ether of bisphenol A) was prepared and cured in a mold in the oven using the curing condition of 150°C/1 h + 170°C /1 h + 190°C /2 h + 200°C/2 h + 220°C/2 h. As it is reported that terpenediphenol-formaldehyde resin possesses superior heat resistance, water resistance, and mechanical properties, terpenediphenol based benzoxazine monomers were synthesized (reaction 2.13) and cured blend samples containing 50 mol% DGEBA and 50 mol% benzoxazine monomers were prepared employing the above mentioned cure conditions [86].



(2.13)

The molding compounds were prepared by hot roll-kneading of a mixture of 50 phr (per hot roll-kneading) Ya, 50 phr OCNE (*o*-Cresol novolac-type epoxy resin) wax and 100 phr fused silica. Test pieces of the molding compounds were prepared by

compression molding at 190°C for 20 min after preheating to required moldability for compression molding. All test pieces were postcured at the same cure conditions to complete the cure reactions, and they were used for the various measurements. Copolymers of chain extended epoxy (40 mol%) with benzoxazine (bisphenol A and aniline based) (60 mol%) were prepared using a solutiong mixing method in acetone and investigated the effects of molecular weight of the added epoxy resins [87].

2.2.1.6 Phosphorous containing blends with polybenzoxazine

Organo-phosphate compounds have attracted attention for their use as flame retardant polymers. Two different routes were suggested for the preparation of flame retardant polymers. [88,89] (1) modified novalac resins with benzoxazines were copolymerized with a glycidyl phosphinate, (2) modified novalac resins with benzoxazines were cured with isobutyl bis(glycidylpropylether) phophine oxide (IHPOGly) as cross-linking agent. Mixtures of novolac resin, diglycidylethers and PPh_3 were made by dissolving the components in acetone and then evaporating the solvent at room temperature under a vacuum. The resin was placed into a 60 x 40 x 0.5 mm mold and compression molded at 180°C for 2 h under 0.1 Mpa pressure. Post-curing was carried out at 220°C for 5 h.

Three approaches had been applied to obtain flame-retardant benzoxazines [90]. In the first approach, a novel phosphorous containing dopotriolbenzoxazine was copolymerized with a commercial benzoxazine [6,6-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazineyl) methane (F-a)] or diglycidyl ether of bisphenol A (DGEBA). In the second case, the element phosphorus was incorporated into benzoxazine via curing reaction of dopotriol and F-a. In the third approach, dopo reacted with benzoxazine to incorporate the element phosphorus (Figure 2.6).

2.2.1.7 Clay-polybenzoxazine composites

Smectite clays became good candidates for the preparation of organic–inorganic nanocomposites because they can be broken down into nanoscale building blocks and act as reinforcing phase in organic–inorganic hybrid nanocomposites [91, 92]. Designing and creation of new materials from polymer and layered silicates composites has become extremely interesting in the field of research, because they typically exhibit properties far superior to those of separate components and are capable of achieving the recent technological requirements. Thus, the general

perception that clays act as low cost fillers in polymers has been changed because of their ability to enhance the properties of the final materials.

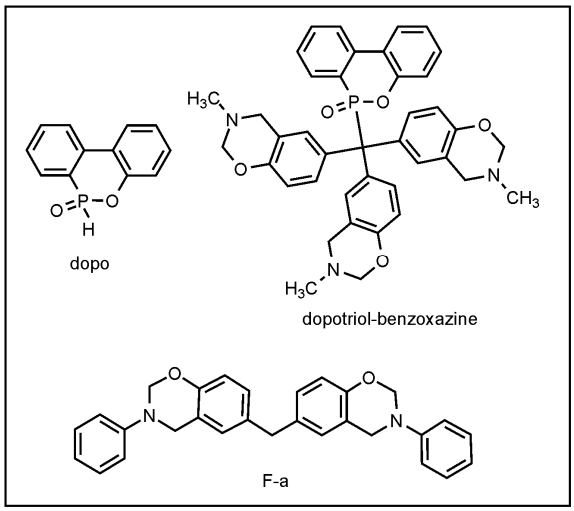


Figure 2.6 : Flame retardant materials.

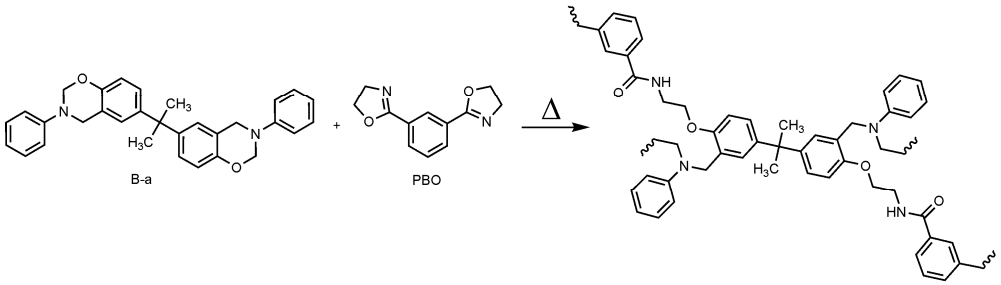
A nanocomposite composition comprising clay and an effective amount benzoxazine monomer, oligomer and/or polymer was developed. The presence of benzoxazines in the clay resulted in an at least about 5% increase in the spacing between platelets of the clay. In another study, the polybenzoxazine–clay hybrid nanocomposites have been prepared from a polybenzoxazine precursor (B-a) and organically modified montmorillonite (OMMT), as a type of layered silicates. OMMTs were prepared by surface treatment of montmorillonite (MMT) by octyl, dodecyl or stearyl ammonium chloride. In the melt of B-a OMMT was mixed by using a mechanical stirrer at 100°C, where small amount of methylene chloride was added to achieve better dispersion. The mixture was then heated at 120°C for 2 h to remove solvents, followed by film casting on glass plates. Then film was cured by step wise increase of heating up to 230°C.

Poly(urethane-benzoxazine)-clay hybrid nanocomposites (PU/P-a-OMMTs) were prepared [93] from an *in situ* copolymerization of a polyurethane (PU) prepolymer and a mono-functional benzoxazine monomer, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a), in the presence of an organophilic montmorillonite (OMMT), by solvent method using DMAc. OMMT was prepared by the cation-exchange reaction between Na^+ cation and dodecyl ammonium chloride. In the OMMT suspension in DMAc a solution of Pa in DMAc was added at 60°C. To this solution PU prepolymer

was added with continuous stirring. The homogeneous solution was cast on a glass plate followed by thermal treatment for curing.

Another type of organically modified montmorillonite was prepared by ion-exchange reaction between Na^+-montmorillonite and various protonated amines [94]. The amines used as the modifying agent were dodecylamine (DODEC), 6-aminocaproic acid (CAPRO), 4-amino-*N*,*N*-dimethyl aniline dihydrochloride (ANDAD), *p*-phenetidine (PHEN) and 2,4,6-trimethylaniline (TMAN). Mixtures of 3 wt % OMOM with benzoxazine monomers were prepared by using solvent, binary solvent and non-solvent systems. All samples were cast on aluminium foil surface, and solvents were allowed to evaporate and then cured at 230 °C for 90 min.

For preparation of nanocomposites, OMMT was mixed with B-a and PBO (2,2'-(1,3-phenylene)-bis(4,5-dihydro-oxazoles)) in their melt state (reaction 2.14) [95].



(2.14)

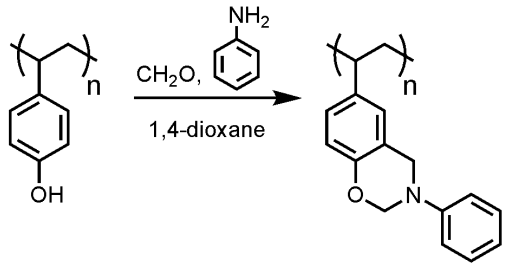
Carbon fiber, glass fiber and natural fiber have been used to develop high performance fiber reinforced polybenzoxazine composites and reported their properties [96-98]. They also investigated the use of $CaCO_3$ as filler [99]. The preparation of titania-polybenzoxazine as organic inorganic hydrid material by using sol-gel process was reported [100].

2.3 Preparation of Polymers with Benzoxazine Moieties

Regarding chemical linking of polybenzoxazines with the other conventional polymers the macromonomer technique was followed. The benzoxazine groups are introduced by initiation of a selected polymerization or synthesizing benzoxazines from amino or phenol functional prepolymers. In the former case, the propagating species should be unreactive towards the benzoxazine ring and N and O hetero atoms.

2.3.1 Benzoxazine functional polystyrene

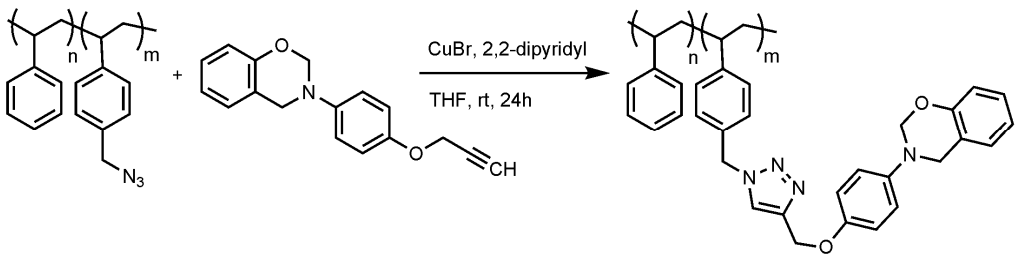
Poly(*p*-vinylphenol) (Poly(VP)) based benzoxazine was prepared from Poly(VP), formaline, and aniline (reaction 2.15). The curing behavior of the benzoxazine with the epoxy resin and the properties of the cured resin were investigated.



(2.15)

Consequently, the curing reaction did not proceed at low temperatures, but it proceeded rapidly at higher temperatures without a curing accelerator. The reaction induction time or cure time of the molten mixture from Poly(VP) based benzoxazine and epoxy resin was found to decrease, compared with those from conventional bisphenol A based benzoxazine and epoxy resin. The curing reaction rate of Poly(VP) based benzoxazine and epoxy resin increased more than that of conventional bisphenol A based benzoxazine and epoxy resin. The properties of the cured resin from neat resins and from reinforced resins with fused silica were evaluated. The cured resins from Poly(VP) based benzoxazine and epoxy resin showed good heat resistance, mechanical properties, electrical insulation, and water resistance compared to the cured resin from VP and epoxy resin using imidazole as the catalyst.

More recently, copper catalyst 1,3-cycloaddition reaction (named as "Click Reaction") was used to synthesize side-chain benzoxazine functional polymers [101]. This route has the unique feature of being quantitative and at the same time preserving the benzoxazine ring structure. The benzoxazine groups have been shown to readily undergo thermal ring opening reaction to form cross-linked polymer networks (reaction 2.16).

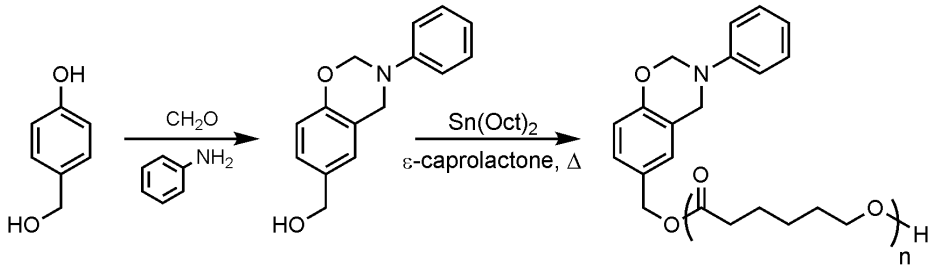


(2.16)

2.3.2 Benzoxazine functional poly(ε-caprolactone)

A novel benzoxazine ring-containing PCL was synthesized. For this purpose, first hydroxyl functional benzoxazine was prepared. Subsequently, this benzoxazine was used as the co-initiator for the stannous-2-ethylhexanoate ($Sn(Oct)_2$) catalyzed living ring-opening polymerization of CL. The synthesis of the initiator and benzoxazine ring-containing PCL are shown in reaction 2.17.

These authors also prepared porous polybenzoxazine materials by using this macronomer together with bisbenzoxazine [102]. Films were cast and thermally cured, which resulted in the nanoscale microphase separation of these two dissimilar blocks. Then, the labile PCL constituent was removed selectively through hydrolysis using $NaHCO_3$, which created nanoporous morphology.

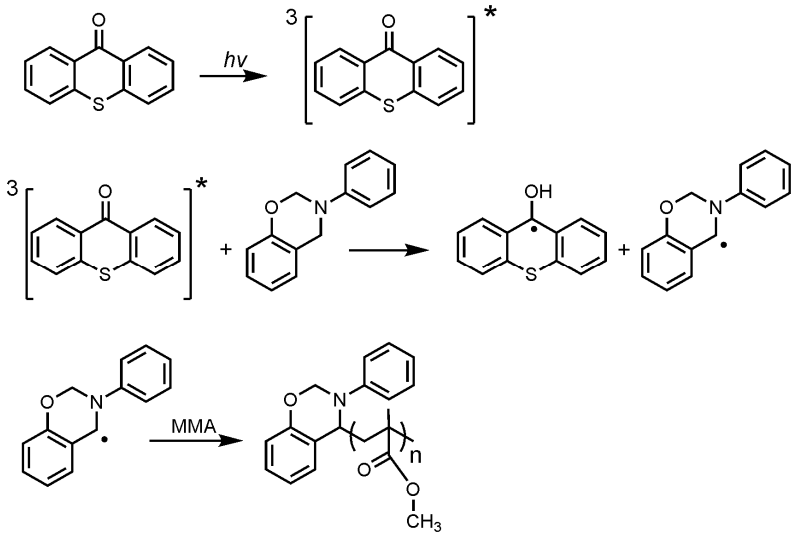


(2.17)

2.3.3 Benzoxazine functional poly(methyl methacrylate)

It is well known that photosensitized aromatic carbonyl compounds in conjunction with hyrodgen donors can readily initiate free radical polymerization of appropriate olefinic monomers. Among various hydrogen donors tertiary amines were found to be the most suitable co-initiators. Depending on the substituents, dialkyl aniline derivatives are also used in these systems. Besides the oxazine ring, benzoxazines possess substituted dimethyl aniline groups in the structure. It seemed, therefore, appropriate to test whether they would also act as hydrogen donor in photoinitiated free radical polymerization using aromatic carbonyl sensitizers. Accordingly, free radical polymerization of methyl methacrylate (MMA) was demonstrated [103].

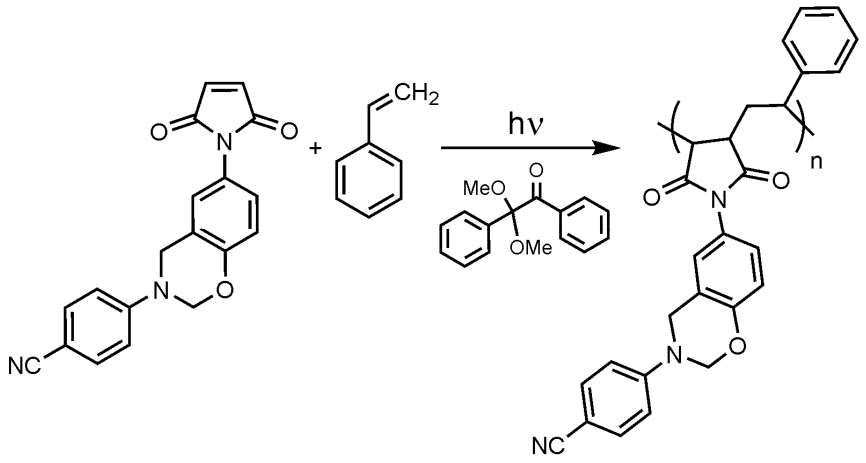
Polymerization was initiated upon irradiation at $\lambda > 350$ nm in CH_2Cl_2 solution containing benzoxazine (P-a) and one of the following photosensitizers: benzophenone (BP), thioxanthone (TX), isopropyl thixanthone (ITX), chlorothioxanthone (CTX) and camphorquinone (CQ) (reaction 2.18). The postulated mechanism is based on the intermolecular reaction of excited photo-sensitizer with the tertiary amino moiety of ground state benzoxazine and subsequent hydrogen abstraction reaction. The resulting aminoalkyl radicals initiate the polymerization. The possibility of deep curing using described photo-initiating system followed by the thermal ring opening of the incorporated benzoxazine groups was also demonstrated.



(2.18)

2.3.4 Alternating maleimide copolymers with pendant benzoxazine groups

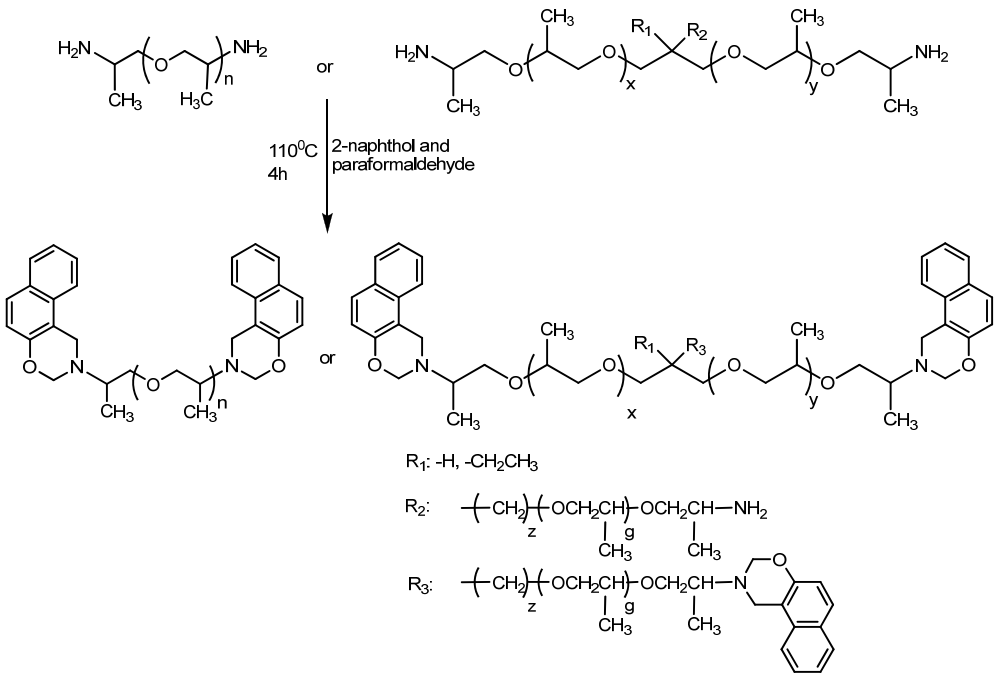
It was recently reported that alternating copolymers of maleimide-benzoxazine with styrene (St) can readily be prepared by photo-induced radical polymerization at room temperature using 2,2'-dimethoxy-2-phenylacetophenone (DMPA) as photo-initiator (reaction 2.19). The photochemical method was deliberately chosen so as to preserve the benzoxazine ring structure. Copolymers' compositions and the monomer reactivity ratios suggested the alternating nature of the copolymerization. These polymers underwent cross-linking through the thermal ring opening reaction of pendant benzoxazine groups [104].



(2.19)

2.3.5 Naphthoxazine functional poly(propylene oxide)

Thermally curable naphthoxazine-functionalized polymers were synthesized by the reaction of linear (Diamines) and branched (Triamines) poly(propylene oxide)s (Jeffamine series) having various molecular weights, with *p*-formaldehyde, and 2-naphthol (see reaction 2.20). Properties and morphologies of the products before and after curing were investigated [105].



(2.20)

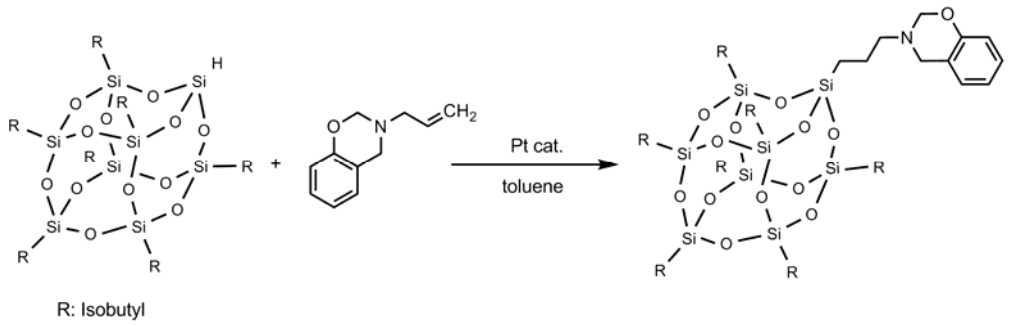
2.3.6 Benzoxazine functional polyhedral oligomeric silsesquioxane (POSS)

Recently, a novel class of organic-inorganic hybrid materials has been developed containing *Polyhedral Oligomeric Silsesquioxane* (POSS) [106-110] which contains an inorganic Si_8O_{12} core surrounded by eight hydrocarbon substituents, or seven of

them plus a functional group. The unique and well-defined structure of POSS moiety provides the possibility of preparing hybrid materials with interesting structures. Several reports during last few years have reported the synthesis and characterization of mono-substituted POSS derivatives.

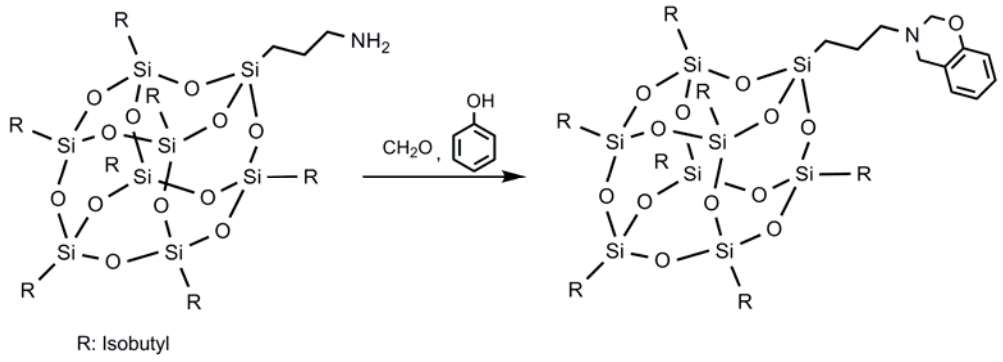
Synthesis of benzoxazine monomer containing a POSS moiety (BZPOSS) by two different routes has been reported as described below:

i) Benzoxazine-POSS (BZ-POSS-1) was synthesized from the reaction of hydro-silane functionalized POSS (H-POSS) and allyl functional benzoxazine (3: 4 molar ratio) in toluene in presence of a Pt catalyst at 80 °C under nitrogen atmosphere (reaction 2.21).



(2.21)

ii) Another structurally similar macromonomer was synthesized from the reaction of primary amine terminated POSS, phenol and paraformaldehyde in THF medium at 90 °C (reaction 2.22).

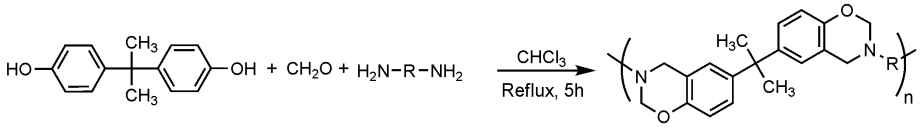


(2.22)

2.4 Polymeric Benzoxazine Precursors

2.4.1 Main-chain precursors

High molecular weight polybenzoxazine precursors can be synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (see reaction 2.23).



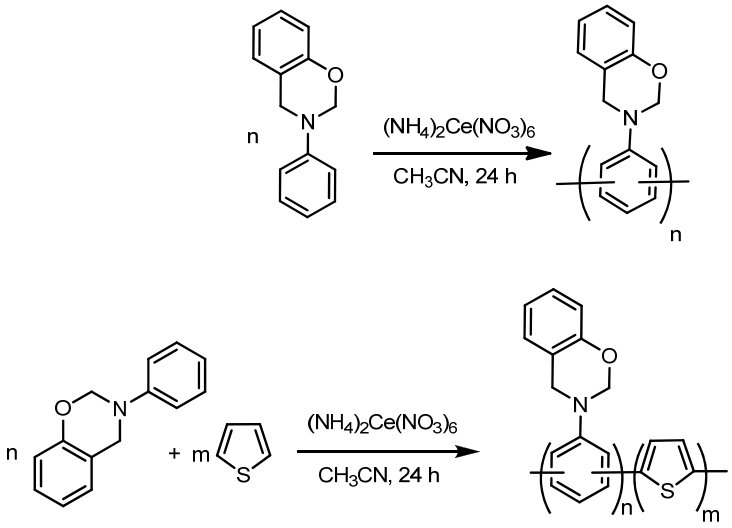
(2.23)

The possibility of the preparation of polymers containing oxazine ring in the main chain was discussed before. Later, more detailed work on the effect of water, solvents, catalyst, ratio of reactants and temperature was reported by the same research group. The major problems associated with the preparation of such main-chain benzoxazine precursor polymers were low molecular weight and cross-linking arising from the Mannich reactions of multiple functional groups. The choice of the right conditions for a Mannich reaction is critical for achieving high yields with the minimum of side reactions. 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 precursor solution was cast on glass plate, giving transparent and self-standing precursor films, which was thermally cured up to 240^{o}C to give brown transparent polybenzoxazine films. The toughness of the cross-linked 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, while 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 [111,112].

2.4.2 Side-chain precursors

The only reported side-chain polymeric benzoxazine precursor is based on polyphenylene structure. Soluble and thermally curable conducting high molecular

weight polybenzoxazine precursors were prepared by oxidative polymerization 3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3] oxazine (P-a) alone and in the presence of thiophene (Th) with ceric ammonium nitrate in acetonitrile (reaction 2.24). The resulting polymers exhibit conductivities around 10^{-2} S 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 [113].



(2.24)

2.5 Reaction Mechanism of Ring Opening Polymerization of Benzoxazine

To understand the polymerization reaction mechanism of benzoxazines, understanding of the chemical structure of its oxazine ring is very important. A single crystal X-ray crystallographic study revealed that the preferential conformation of a mono-oxazine ring containing benzoxazine is a distorted semi-chair structure, with the nitrogen and the carbon between the 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 the oxygen and the 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 [114,115]. 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).

The ring opening reaction of the benzoxazine was first reported . In the reaction of 1,3- dihydrobenzoxazine with a phenol, having both *ortho* and *para* position free, it was found that aminoalkylation occurred preferentially at the free *ortho* position to form a Mannich base bridge structure, along with small amount reaction at *para* position. To explain this *ortho* preferency formation of a intermolecular hydrogen-bonded intermediate species was proposed. High reactivity of the *ortho* position was also observed when following the kinetics of mono-functional benzoxazines with 2,4-di-*tert*-butylphenol catalyst. The typical method of polymerization of benzoxazine monomers is thermal curing without using any catalyst [21]. It should be emphasized that the polymerization mechanism of benzoxazine resins is still not well established.

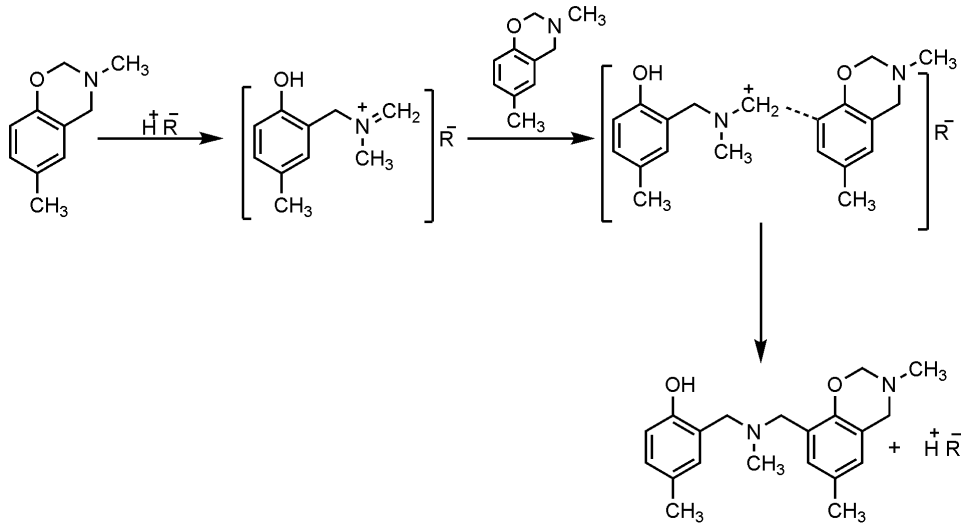
2.5.1 Cationic polymerization of benzoxazine

2.5.1.1 Acid catalyzed polymerization of benzoxazine

Some investigations on catalyst assisted benzoxazine curing showed that the presence of catalysts influence to reduce the induction time and accelerate the reaction rate [116]. However, no significant polymerization was observed below 100 °C. Various acids ranging from strong acids to weak carboxylic acids to phenols have been surveyed as catalyst for this type of polymerization reaction. It has been observed that polybenzoxazines cured with strong carboxylic acids were inferior to those cured with weak carboxylic acids [117]. Several initiators, such as PCl_5, PCl_3, $POCl_3$, $TiCl_4$, $AlCl_3$ and MeOTf, were also reported as effective catalyst for polymerization which provides polybenzoxazines with high T_g and high char yield.

From the investigations on use of various cationic, anionic and radical initiators it has been proposed that the ring opening polymerization of the benzoxazine proceeds through a cationic mechanism [118,119]. 3,4-dihydro-2*H*-1,3-benzoxazine exhibits ring/chain tautomerism when protonated, by migration of the proton from the nitrogen to the oxygen atom, and thereby produce iminium ions in the chain form was reported [11]. Ring opening mechanism by protonation of the oxygen atom to form an iminium ion, followed by electrophilic aromatic substitution, as shown below in reaction 2.25 was proposed [117].

But this mechanism does not take into account the effect of the pKa of the acid, which controls the structure of the reactive intermediate. The effects of strong and weak carboxylic acids and phenols as catalysts on curing 3,4-dihydro-3,6-dimethyl-2*H*-1,3-benzoxazines to polybenzoxazines has been described. The curing reaction was monitored *in situ* by using Fourier transform infrared (FT-IR) spectroscopy. The IR bands, used to evaluate the curing reaction, were (i) 1050 cm^{-1}, representative of the oxazine ring, (ii) 813 cm^{-1}, associated with 1,2,4 substitution of the monomeric benzene, and (iii) 1030 cm^{-1} , attributed to the methyl rocking on the *para* position of the benzene ring and used as an internal standard.



(2.25)

In the presence of strong organic acid, such as trifluroacetic acid, benzoxazine monomer converts to polybenzoxazine immediately at low temperatures after ring opening. The formation of the iminium ion as intermediate was proposed, because trifluoroacetic acid can provide a counter ion, capable of existing in the ionic form rather than the covalent form and can give stability of the intermediate. As the curing temperature increases, side reactions also took place, which also leads to curing. But when weak acid, sebacic acid, was used as catalyst, the polymerization reaction was slow in the early stage of the reaction. The ring opening polymerization of benzoxazines when catalyzed by a weak carboxylic acid was proposed to be an auto-accelerated reaction, where aminomethyl ester species were initially formed as intermediate. At the beginning of the reaction a covalently bonded aminomethyl species existed in equilibrium with the iminium ion form of the intermediate. This explains the large difference seen in the early stages of the reaction. Since the reaction of this intermediate with another benzene ring to form the aminomethylene

bridge was occurring very slowly catalyst was consumed but could not be regenerated. As the dielectric constant of the medium increased through the appearance of hydroxyl groups due to the ring opening, the equilibrium shifted toward the reactive carbocation form. Thus, the consumption of trisubstituted benzene was accelerated by this shift in the equilibrium. Then, electrophilic aromatic substitution occurred and regenerated the acid catalyst. This explains how the pKa value of the organic acid effects the polymerization of benzoxazine. In the early stages of the reaction, the acids, having pKa in the range of 0.70-4.43, provide a stable counterion for the intermediate iminium cation where as adipic acid and the acids with higher pKa values do not provide support for the iminium ion and this factor influence the reaction.

When pure benzoxazine was cured without catalyst at 160 and 170°C, the curing may be catalyzed by phenols, which can be formed by the ring opening from trace impurities. The ring opening and the Mannich bridge formation were consecutive reactions, whereby the consumption of one benzoxazine ring and one trisubstituted benzene ring should be occurred simultaneously. This is reflected in the in the FT-IR study of the early part of the reaction. In the later stages the ring opening reaction occurred by termination.

Based on the results obtained from PCl_5 initiated polymerization of different mono-oxazine ring containing substituted 3,4-dihydro-2*H*-1,3-benzoxazines, three different mechanisms were proposed and explained the dependency of formation of different polymeric structures on the number and the position of substitutions in the benzene ring of the monomer [115]. The structures of four types of investigated monomers, pC-m, 24DMP, 235TMP and 345TMP, are shown in Figure 2.7.

^{1}H-NMR, ^{13}C-NMR and FT-IR study of the polymers obtained from the PCl_5 initiated polymerization of the above mentioned monomers revealed that (i) the polymers having Mannich base phenoxy-type structure (Type I) forms by polymerization of from 24DMP-m and 235TMP-m monomers, (ii) the Mannich base phenolic-type structure (Type II) polymer produce from pC-m monomer, and (iii) the mixed polymers result from 345TMP-m monomer, with the phenoxy type (Type I) as the major component.

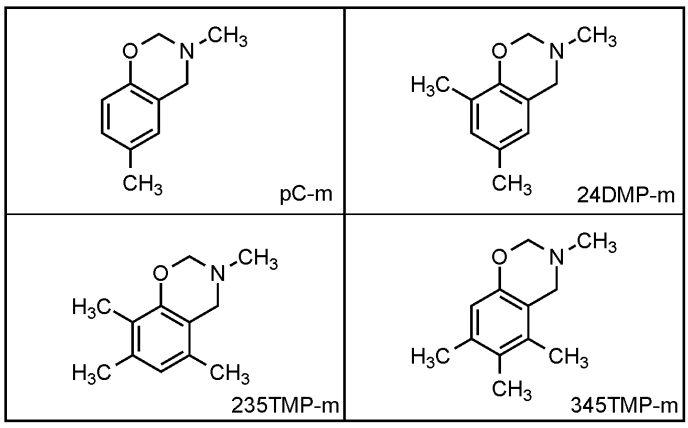
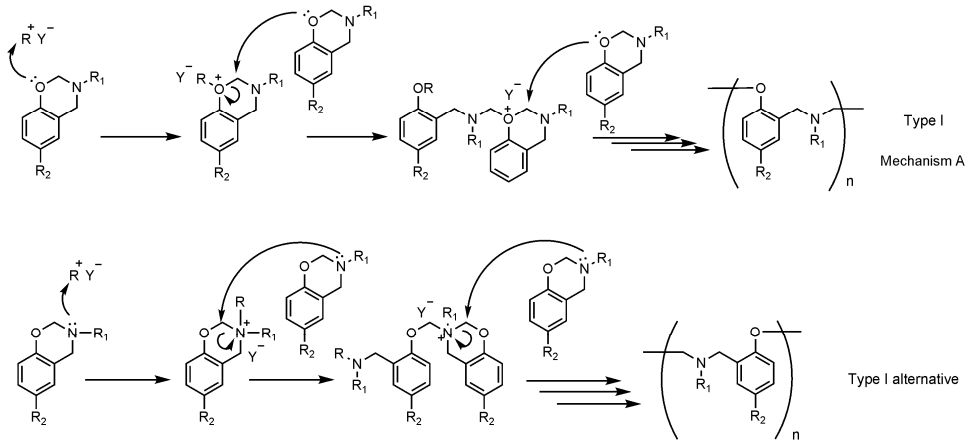


Figure 2.7 : Methyl substituted benzoxazines.

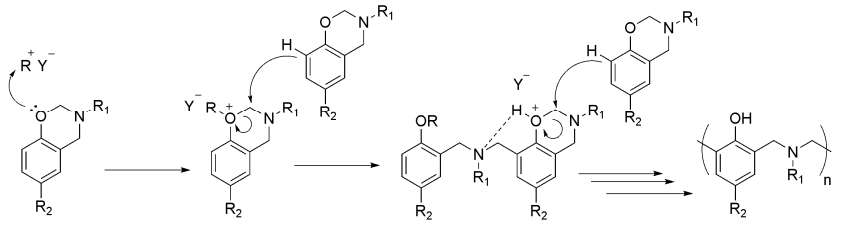
These results demonstrate how the change of the position of substitute of the benzene ring affects the nature of the resulting polymers. The proposed reaction mechanisms are shown in reaction 2.26 and 2.27 [115].



(2.26)

Reaction 2.26 illustrates the mechanism of formation of Type I polymer, having the Mannich base phenoxy-type structure, from 24DMP-m and 235TMP-m monomers. It was proposed that the oxygen on the oxazine ring acts as the initiation site and due to the attack of a cationic initiator (H^+) cyclic tertiary oxonium ion intermediate form. The polymerization then proceeds via the insertion of the monomers through the reaction between the intermediate and the oxygen of another oxazine ring and results the formation of Mannich base phenoxy-type (Type I) polybenzoxazine structure. An alternative polymerization route for Type I structure formation was also suggested as shown in reaction 2.32, which is similar to the mechanism A, but in this case N acts as the initiation and as well as propagation sites. The formation of Mannich base phenolic-type structure (Type II) polymer from pC-m monomer was explained by assuming that upon initiation by a cationic initiator, the propagation proceeds by the

incorporation of monomers through the reaction of the unobstructed *ortho* position of benzene and eventually produces a Mannich base phenolic-type (Type II) polymer. This proposed mechanism is illustrated as mechanism B in reaction 2.27.



(2.27)

Moreover, in this case, the monomers propagate via reasonably stable carbocations, *i.e.*, the intermediate oxonium cation is stabilized by intramolecular hydrogen bonding, which could lead to high-molecular weight polymer formation. It has been observed that the polymer, having highest molecular weight, was formed from pC-m amongst these four type monomers.

In case of 345TMP major polymerization proceeds via mechanism A (formation of Type I polymer), the unobstructed *ortho* position on the benzene ring also partially participate in the polymerization through mechanism B, resulting a small portion of the phenolic type (Type II) polymer structure formation. Quantitative analysis by NMR of two different polymer structures revealed a 9:1 ratio for the Mannich base phenoxy-type (Type I) and the Mannich base phenolic-type (Type II) polybenzoxazines.

It was also mentioned that polybenzoxazine structure via thermal curing can also be thought of as the Type II polymer structure which can be generated through mechanisms similar to mechanism B.

Phenols (trace amount of which may present as impurity) with free *ortho* positions can act as initiators in the oligomerization of benzoxazine compounds. It can be speculated that at elevated temperatures, the self dissociation of the benzoxazine ring can produce free phenol structures and also initiate the ring opening reaction.

2.5.1.2 Photoinitiated polymerization of benzoxazine

The photoinitiated ring-opening cationic polymerization of a mono-functional benzoxazine, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a), with onium salts such as diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate as initiators was investigated [120]. In this work, both direct

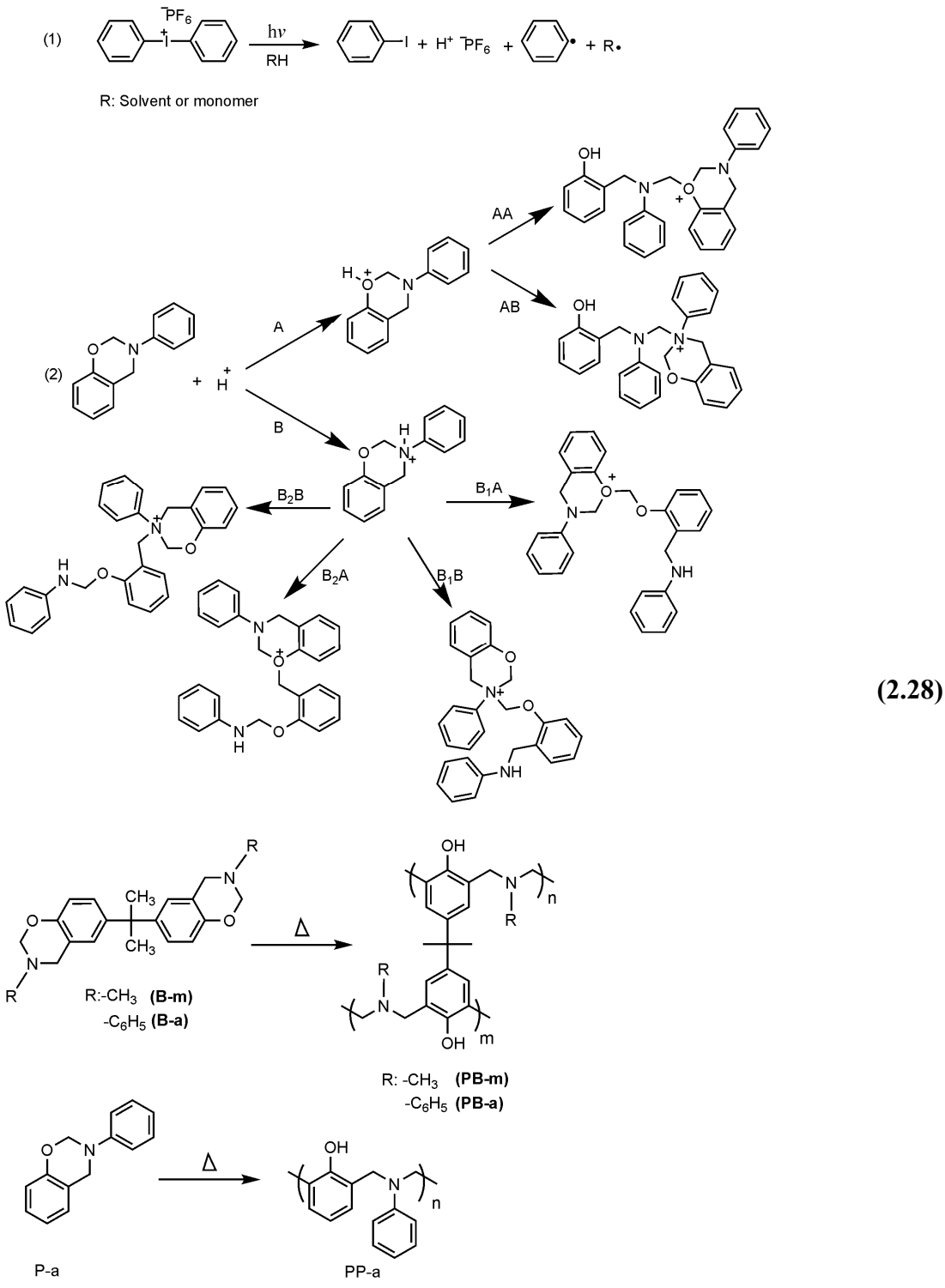
and indirect activations by using radical sources and photosensitizers were reported. ^{1}H-NMR and FT-IR study revealed the complex structure of the resulting polymers which was related to the simultaneous ring-opening process of the protonated monomer either at the oxygen or nitrogen atoms. The phenolic mechanism also contributed, but its influence decreased with decreasing monomer concentration. Free radical promoted cationic polymerization of benzoxazines was also examined. 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. Reaction 2.28 describes that after addition of a proton (or carbocation) to the either heteroatom (oxygen or nitrogen) yields oxonium or ammonium cations, respectively. For the next step, several probable routes were proposed by which polymerization can proceed and produce different polymeric structures.

2.5.2 Thermal polymerization of benzoxazines

A cross-linked network structured polybenzoxazines, with higher T_g and degradation temperature, can be obtained when difunctional or multifunctional benzoxazines undergo polymerization. The polymeric structures form due to curing of mono-functional and difunctional benzoxazines are shown below in reaction 2.28. Obviously, difunctional benzoxazines derived from diamines are expected to undergo similar cross-linking.

In the DSC thermogram of a mono-functional benzoxazine, P-a, a sharp exotherm was observed with onset and maximum temperatures of the exotherm at 202 and 230°C respectively, corresponding to the ring-opening polymerization. The amount of exotherm for P-a was 62 cal/g. In case of difunctional benzoxazine, B-a, DSC showed an exotherm on with onset at ca. 223°C and maximum at 249°C corresponding to the ring-opening polymerization of benzoxazine. The amount of exotherm for B-a was 79 cal/g.

It has been observed that during synthesis of a difunctional benzoxazine (from bisphenol A, formaldehyde and methyl amine) not only bisphenol-A based benzoxazine (B-m) monomer forms as major product but also dimers and small oligomers form by the subsequent reactions between the rings and *ortho* position of bisphenol A hydroxyl groups.

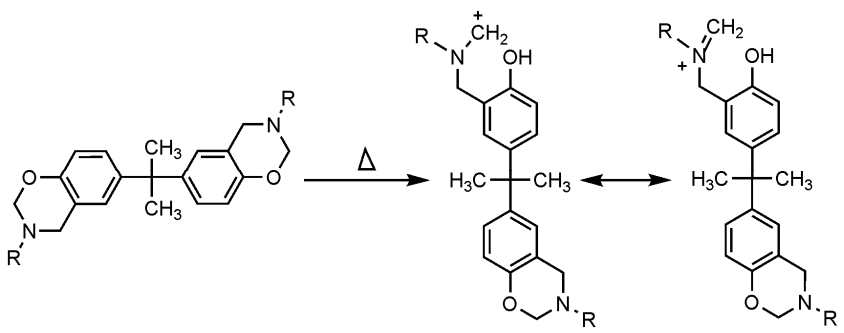


(2.28)

These free phenolic hydroxy structure containing dimers and oligomers trigger the monomer to be self-initiated towards polymerization and cross-linking reactions. Attempts have been taken to understand the cure mechanism and kinetics of the

thermal curing of mono and difunctional benzoxazines utilizing DSC, FT-IR, DMA, ^{13}C and ^{15}N solid sate NMR spectroscopic measurements [121-127].

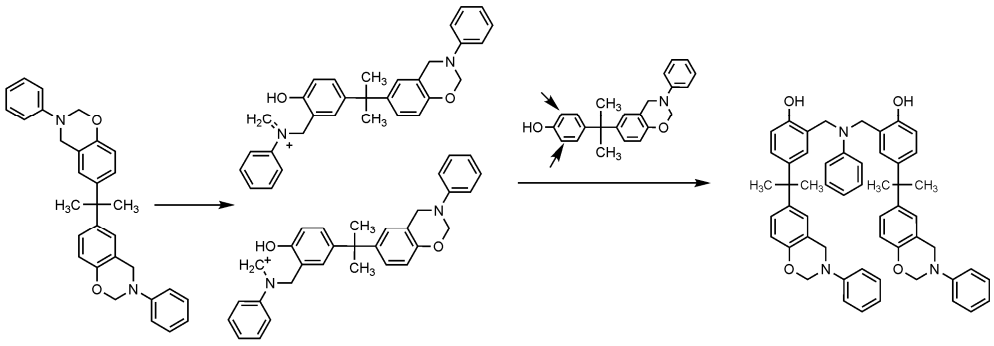
It has been proposed that, the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which exist in equilibrium (reaction 2.29). Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially 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. Further, the reactivity of the equilibrium pair depends on the basicity of the amine group. The more basic the amine, with more the free electron density of the nitrogen, has the capability to stabilize more the positive charge of the iminium ion. If the iminium ion is more stable, the equilibrium shifts toward it, causing lowering in propagation rate. If the iminium ion is unstable, the equilibrium will be shifted toward the carbocation, resulting in a higher propagation rate.



(2.29)

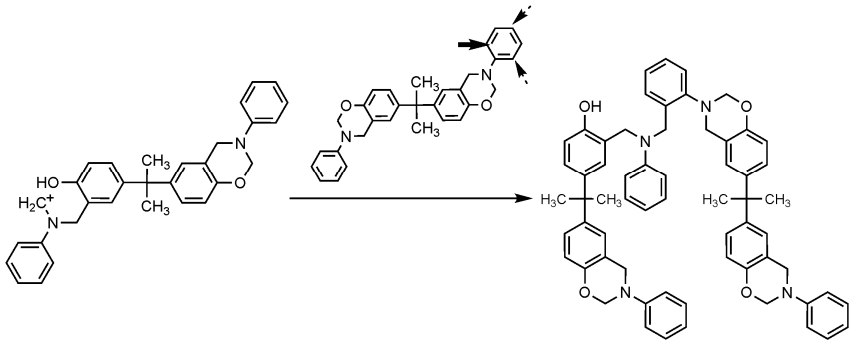
It should be noted that since the propagation reaction involves chain transfer to a benzene ring temperature should have a great impact on the rate of propagation. Kinetic study indicated that in the early stages of polymerization, the reaction may be relatively independent of the cure temperature. As the reaction proceeds, the temperature effect on propagation becomes more evident in the reaction kinetics.

Curing reactions at two different temperatures, below and above T_g temperature, demonstrate that the kinetics are significantly different for the two cure temperatures. Vitrification occurs sooner at higher cure temperature than the lower cure temperature, especially below the T_g. As vitrification causes a large increase in the viscosity of the system, at the reaction becomes largely diffusion-controlled, and greatly affect the curing kinetics. Reaction 2.30 illustrates the thermal polymerization of B-a through cationic mechanism.



(2.30)

Solid State ^{15}N-NMR study identified the formation of a structure generated possibly due to the electrophilic substitution reaction between *ortho* position of the aniline and carbocation. Similar to phenol, the electron donating nature of nitrogen of the aniline makes its *ortho* and *para* position as possible sites for electrophilic substitution with the carbocation. The formation of this structure is shown in reaction 2.31 [121].



(2.31)

2.6 Properties of Polybenzoxazines and Their Blends and Composites

2.6.1 Properties of polybenzoxazines

A typical polybenzoxazine, prepared from mono-functional 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a), exhibit T_g at 146 and 161°C, obtained from maximum of loss modulus and the maximum of tan δ respectively of DMA results. The storage modulus decreases sharply at about 110°C. From TGA profile it was observed that, its 5 and 10% weight loss temperatures were 342 and 369°C, respectively and char yield was 44%.

A comparative investigation on several physical properties of polybenzoxazines (PB-a and PB-m), prepared by thermal curing of difunctional B-a and B-m monomers, has been reported [70]. They exhibit high T_g and significantly higher tensile moduli

than both phenolics and epoxies at the same time maintain adequate tensile strength and impact resistance.

From the DMA study of these cured polybenzoxazine materials; it has been observed that they possess the characteristic features of cross-linked thermosetting materials. The PB-a has a higher storage modulus in the glassy region than the PB-m, as observed from their respective room-temperature values of 2.2 and 1.8 GPa. The glass transition temperature of the PB-m (180°C), however, is significantly higher than that of the cured PB-a material (150°C), as determined from the maxima of the loss spectrum. As the presence of high free volumes responsible for lowering of T_g, it was postulated that the PB-a might contain a greater free volume than the PB-m. The crosslink density of cured PB-a was estimated of about 1.1 x 10^{-3} mol/cm^3 where as that of PB-m was not able to be determined, because the torque in the plateau region dropped below the minimal sensitivity of the transducer. But as the storage modulus was at the level of the PB-a plateau and still decreased at its last measurable point, it was assumed that the PB-m has an even lower crosslink density than the PB-a.

For these polybenzoxazines the concentration of network chains is significantly lower than is typically seen in cross-linked epoxides. Though the polybenzoxazines posses low cross-linking density, they exhibit higher T_gs. The intra and intermolecular hydrogen bonding in the network of the polybenzoxazines and the cured materials are responsible for low crosslink density [128,129]. However, these hydrogen bindings are sufficiently strong to confine segmental mobility and contribute rigidity in the glassy state, which would normally be expected only from a much tighter network structure. In this connection it should be pointed out that the higher value of storage modulus of PB-a than that of PB-m should not be explained from the crosslink density point of view. According to many authors for epoxy resins, the crosslink density has little or no influence on stiffness or rigidity in the glassy state [130-132]. Free volume, chain interaction, and intermolecular packing influence the small strain properties of a material in its glassy state, including the modulus. Hydrogen bonding should decrease the flexibility of a cross-linked network as it hinders rotational isomeric configurational changes and other segmental motion of chain. Thus, the higher glassy modulus of PB-a indicate that the hydrogen bonding is more prevalent in the PB-a than in the PB-m (see reaction 2.31 for the structure).

The reported values of notched Izod impact strengths for PB-a and PB-m are 18 and 31 J/m, which are higher than for these phenolic materials (~ 17 J/m) and similar to epoxy resins (~ 32 J/m). Because of the difference in the crosslink densities the lower value of impact strengths for PB-a than PB-m was expected. A more highly cross-linked material behaves in a more brittle manner because high cross-linking lowers segmental mobility.

Generally, intermolecular packing, free volume, molecular architecture, and molecular weight between cross-links influence the large-strain glassy state properties, namely tensile strength and elongation at break. Higher free volume tends to enhance the mobility of network segments under load to increase ultimate elongation. PB-a exhibits brittle fracture at a higher strain than PB-m. PB-a possesses superior tensile strength and elastic modulus than those of PB-m, which indicate that the regularity and perfection of the network formed for the PB-a are superior to those of the PB-m network. These two materials exhibit near zero shrinkage due to curing at about 200 °C where as typical epoxy resins show higher cure shrinkage. One possible explanation might be the relieving of ring strain during the ring opening polymerization of benzoxazines. However, the ring strain alone can not explain the near zero volumetric shrinkage. Chain conformation influenced by strong intramolecular hydrogen bonding is also an important factor for the volumetric expansion. It has been observed that the volumetric expansion coefficients for PB-a and PB-m are competitive with that of epoxides and the values are listed in Table 2.1 [133, 134].

Table 2.1: Volumetric expansion coefficient values of polymers obtained from difunctional benzoxazine and epoxy resins

Polymer	Volumetric expansion coefficient (cm^3/ cm^3-°C)
PB-a	1.7×10^{-4}
PB-m	2.1×10^{-4}
Epoxy resin	$1.7 - 2.8 \times 10^{-4}$

It has been observed that, after 600 days in water at room temperature PB-a absorbs water up to 1.9%, where as PB-m up to 1.3% by weight and the former material absorbs water at a slower rate. Despite the presence of hydrophilic phenolic and tertiary amine groups polybenzoxazines do not absorb water as much as do phenolic

or epoxy resins. The mode of sorption of water of these materials was determined by plotting the log of the amount of the amount of water vs. logarithmic time, which indicated the occurrence of a very near- Fickian Manner. The rate of diffusion of PB-m (diffusion coefficient= 4.9 x 10^2 cm^2/s) is higher than that of PB-a (diffusion coefficient= 3.6 X 10^2 cm^2/s).

For epoxy-amine systems the rate of water transport in the networks is governed by polymer-water interactions and is inversely related to the extent of intermolecular hydrogen bonding was reported [135]. The presence of inter- and intramolecular hydrogen bonding within the polybenzoxazine systems, which shield the hydroxyl groups (present abundantly in the network) from interaction with water molecules is the probable main cause for the low water diffusivities and saturation contents of the polybenzoxazines. The lower diffusion rate of PB-a, despite of its higher overall absorption, than that of PB-m is consistent with their finding that, diffusivity decreases with hydrophilicity.

The dielectric constant value of PB-a is 3.6 and has only a slight dependence on frequency, at temperatures below approximately 120°C. It decreases less than 3% as the testing frequency increases from 428 Hz to 1 MHz. Thus, the polybenzoxazine not only has a lower electrical capacitance than other thermosetting materials (for conventional phenolic resins dielectric constant is 4.8-5 and for epoxides 3.7-4) but also is less sensitive to the changes in frequency. The change of loss factor with temperature shows the B-a material withstands electrical power loss at least as well as epoxies, which have loss factors that are typically between 0.01 and 0.08.

As the relaxation process of PB-a begins at about near T_g (150°C) the dielectric properties of the resin begin to deteriorate. Even so, the polybenzoxazine material appears to possess excellent electrical performance up to service temperatures (150°C for B-a) beyond those of most other polymer resins.

In another paper it has been reported that DMA analysis of polybenzoxazines from B-m (synthesized from bisphenol A and methyl amine) shows T_g at 215°C when the sample was cured at 210°C [6].

A systematic study of thermal and mechanical properties for a series of polybenzoxazines, based upon alkyl substituted aryl amines, has been reported.

Difunctional bisphenol A based benzoxazines monomers were synthesized from different methyl substituted amines.

The curing of these monomers was performed by following the step profile: 140°C for 30 min, 160°C for 30 min, 170°C for 45 min, 180°C for 45 min, 190°C for 75 min, and 200°C for 90 min. The substitution on different positions show pronounced effect on polymerization. Due to the activation of *ortho* and *para* positions on the pendent ring by placing electron-donating alkyl substituent groups on one or both *meta* positions, the oxazine ring-opening polymerization occurs at lower temperatures. In addition, significant numbers of arylamine Mannich bridges and methylene bridges were formed during the cure of these monomers [24]. DSC results showed that, B-a-ot exhibits the lowest glass transition temperature of 114°C and comparatively lower extent of reaction in this material is possibly due to the lower basicity and greater steric hindrance of the arylamine. B-a and B-pt showed T_g at 168 and 158°C, respectively where as B-mt and B-35x exhibit at 203 and 205°C after the initial cure. BA-a and BA-pt after curing an additional 30 min at 240°C, exhibit the final T_g at 209 and 238°C, respectively. Further curing at higher temperatures did not increase the T_g of these materials appreciably.

Amongst this series of materials B-mt possess highest mechanical property, with storage modulus 1.78 GPa at 28°C and the plateau modulus is 11.9 MPa at 265°C. This is much higher than other polybenzoxazines, which showed definable rubbery plateaus. In addition, it was quite stable in the rubbery region since no void forming was observed even after 2 h at temperatures above 260°C, whereas many polybenzoxazines used to undergo degradation and weight loss soon after reaching temperatures above T_g. B-mt is one of the few polybenzoxazines which shows such a large window of thermal stability in the rubbery region.

When thermogravimetric analysis was employed to determine the thermal stability of these materials three major events were observed. Ishida and coworkers analyzed the evolved gases to determine the nature of these weight loss events and also proposed degradation mechanism [136]. The first event near 310 °C was due to the breakage of Mannich bridge in the phenolic Mannich bridge network which produced free aniline via a deamination reaction, along with some *N*-methyl anilines by deaminomethylation. During second event at about 400°C, the breakup of the isopropylidene linkage of the bisphenol A occurred. The primary weight loss

products were aniline and various phenolic species. Finally the last weight loss, centered near 460 °C, was attributed to the degradation of char, with release of traces of phenolic and significant amount of substituted benzene compounds. The *meta* substituted materials, B-mt and B-35x, achieved the highest thermal stability and showed a different weight loss behavior where the first weight-loss event was absent. For BA-35x a new peak appeared at 350°C, which was due to the release of amine. It was proposed that, these two materials possess such a polymeric structure which is not a pure phenolic Mannich bridge network but contain additional arylamine Mannich bridge network and various methylene bridges similar to those in a phenolic network [137].

Two difunctional polybenzoxazines, 22P-a PBZ and 440-a PBZ, were prepared by curing the benzoxazine monomers, 8,8'-bis(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine)

22P-a, and 6,6'-bis(2,3-dihydro-3-phenyl-4*H*-1,3-benzoxazinyl) ketone, abbreviated as 44O-a, respectively [25] . T_gs of these polybenzoxazine materials increase linearly without showing the ultimate value with the increase of postcure temperature. Although 440-a PBZ cured at 316°C for 1 h exhibited T_g of 410°C, it slowed decomposition starting at 300°C accompanied by weight loss. The high T_g may be due to secondary reactions involving bisphenolic methylene bridge formation and some other unknown structures. Therefore, the recommended postcure temperature was 290°C rather than 316°C. As the T_g's of the 440-a PBZ are always higher than the cure temperatures applied (T_g was 365°C at postcure temperature 300°C), it provides a great advantage in processibility. There are only a few thermosetting polymers that exhibit such behavior [138]. The T_g higher than T_{cure} behavior might be due to cross-linking reaction, which is not completely quenched in the glassy sate and surpasses the curing temperature.

DMA results of the samples cured at 180°C indicate that further curing at higher temperature was necessary by showing the increase of G' and G" after the α transition (T_g). But this behavior disappeared when the samples were cured at higher temperature (ca 240°C). The storage moduli at room temperature of these polymers are approximately 2.0 GPa.

The TGA of the 22P-a PBZ (cured at 240°C) and 440-a PBZ (cured at 290°C) indicate that they start decomposing at 200°C in both air and nitrogen, followed by

oxidation in air at 550-600°C. The high char yield of 440-a PBZ makes it a good candidate for the precursors of carbon-carbon composites.

It has been reported that, incorporation of several transition metal salts (2 mol%) results improvement of the char yield of the polybenzoxazines by 10-20%. The metal salts initiate the ring opening but do not catalyze the polymerization and promote the carbonyl group formation during polymerization [139].

Degradation of polybenzoxazines (derived from different phenols and amines) by UV radiation has been reported and degradation mechanism has been proposed [140-142].

2.6.1.1 Properties of polybenzoxazines with additional functionalities

The incorporation of several other functionalities can influence the curing behavior of benzoxazine. Obviously, this would result different microstructure and consequently the thermal and mechanical properties of the cured products. In the following section, the effect of different functional groups on the properties of both precursor benzoxazine monomers and the corresponding polymers will be described.

For the benzoxazine with acetylene group. The non isothermal DSC thermograms of Ph-apa resins show that oxazine ring opening polymerization exotherm overlaps with acetylene polymerization exotherm at the temperature range of 220-235°C. However, Ph-apc exhibited two well resolved exotherms for both processes (i) the sharp exotherm at 230°C for the benzoxazine polymerization, and (ii) the broad exotherm at 350°C was because of the acetylene polymerization. These assignments were supported by the FT-IR studies of the polymerization of this compound. It was also reported that polymerization of disubstituted arylacetylenic monomers occurs at the higher temperature of 350 °C, as identified by DSC [143].

Char yield of polybenzoxazines from purified acetylene functionalize benzoxazine monomers were 5-10% lower than the char yield of resins from as-synthesized monomers, as determined from TGA. Very high char yield of 80 wt % was achieved for this type of polybenzoxazines. The high char of these polymers are due to introduction of another polymerizable functional group, acetylene, by which a more cross-linked network structure forms due to polymerization. The char yield of the analogous compound (B-a) containing aniline instead of 3-aminophenylacetylene is 32 wt %. Side phenyl groups present in the structure of polybenzoxazines from

unfunctionalized monomers (B-a) can easily be volatilized during thermal degradation. Linking these weak groups by introducing polymerizable acetylene group contributed to improve the thermal stability of these materials.

These polybenzoxazines exhibit very high glass transition temperatures (T_g) ranging from 320 to 370°C and high values of shear modulus (G'), up to 2.3 GPa, as determined by the DMA.

For benzoxazine with propargyl ether functional group. In the DSC runs for the monomers with propargyl group, P-appe, the exotherm, starting at 191°C with a maximum 235°C, indicate the ring opening polymerization and cross-linking of propargyl group took place within the same temperature range. The appearance of another exotherm, starting at 325°C with maximum at 341°C, is due to the degradation of cross-linked structure. For bifunctional benzoxazine with propargyl group, B-appe, the similar behavior was observed. From DMA results revealed that the T_g of these polymers were increased by about 100-140°C and the storage moduli were maintained constant up to ~100°C higher temperature than the typical unfunctionalized polybenzoxazines. Excellent thermal stability of these polymers, as reflected from TGA results, were due to the prevention of aniline derivatives from volatilization as a degradation product by anchoring the aniline component in the network structure through cross-linking by the propargyl ether groups [36]. The char yield of these polymers were also increased by ca. 22-29%.

For benzoxazine with allyl group. DSC investigations reveled that, for 3-allyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-ala) the thermal curing of the allyl group occurred first, showing an exotherm with the onset temperature at 145°C with exotherm peak at 207°C, followed by the ring-opening of the oxazine ring, which was appeared as second exotherm, having onset at 225°C with maximum at 260°C. The total amount of exotherm of P-ala was 84 cal/g. DSC thermograms after each cure for P-ala was showed that the first exotherm for the cross-linking of allyl groups disappeared after curing at 200°C and the second exotherm decreased with the increasing cure temperature and disappeared after 240°C.

On the other hand, P-alp (3-phenyl-3,4-dihydro-8-allyl-2*H*-1,3-benzoxazine) showed only one exotherm, the onset of which was at 241°C and maximum at 263°C, without showing any exotherm at lower temperature range for to the thermal cure of the allyl group. The amount of exotherm was 20 cal/g, much smaller than P-ala. The

difficulty of the radical polymerization of the allyl phenyl group is due to the stability of the radical [174]. In case of P-alp, the *ortho* position, the primary reaction site to form phenolic Mannich bridge structure via the ring-opening polymerization, is blocked by allyl group. Therefore, this exotherm at high temperature might be due to the cleavage of the oxazine ring that leads to degradation [24].

The curing of of a bifunctional allyl-containing benzoxazine, B-ala (bis(3-allyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane), was investigated and compared with the typical bifunctional benzoxazine, B-a. When the DSC plots of B-a showed an exotherm with onset at ca. 223°C with maximum at 249°C corresponding to the ring-opening polymerization of benzoxazine, B-ala exhibited an unsymmetrical broad exotherm with the onset at 145°C and maximum at 265°C corresponding to both the cross-linking of allyl group and the ring-opening polymerization of benzoxazine. The heat of polymerization for B-a was 79 cal/g and that for B-ala was 127 cal/g. Thermal polymerization of N-allyl group is known to occur at lower temperature. In the case of P-ala, it was considered that the thermal polymerization of allyl group occurred first, followed by the ring-opening polymerization of benzoxazine at slightly higher temperature than P-a. The shift of the ring-opening polymerization to higher temperature range was due to the restricted mobility of P-ala because of the polymerization of allyl group.

A significant increase in T_g was observed due to the introduction of allyl groups in the monomers. For example, when the typical polybenzoxazine, PP-a (from mono-functional benzoxazine without acetylene group), exhibited the T_g at 146°C, that for PP-ala was shifted to as high as 285°C. Since the introduced allyl groups provide additional cross-linking sites into polybenzoxazine, the rigidity of the polymer backbone was increased with cross-linking density, and hence the damping was significantly decreased. However, for PP-alp, the T_g was as low as 107°C. The poor thermo-mechanical properties for PP-alp were due to its low cross-linking density which arises from the difficulty in the polymerization of the monomer as described above. Bifunctional polybenzoxazines, PB-ala (with acetylene side group) and PB-a (without acetylene side group), showed similar behavior exhibiting T_gs at 298 and 154°C respectively, indicating the beneficial effect of additional cross-linking offered by the introduction of allyl group as another cross-linkable site.

TGA showed that for PP-ala and PB-ala, the thermal stability was improved compared to the cured samples of the corresponding benzoxazines without allyl functionality (PP-a and PB-a). This was inferred from their increase in 5 and 10% weight loss temperatures. Notably, these temperatures were decreased for the benzoxazines possessing allyl group on the phenyl ring (PP-alp). The observed increase for PP-ala and PB-ala was due to the prevention of amines from volatizing at the initial stages of the degradation because of the additional cross-linked structure. The char yields of PP-a PP-ala and PP-alp were almost the same (~44%) [41].

For benzoxazine with nitrile functional group. Phenylnitrile- and phthalonitrile-functional benzoxazines and their copolymers possess high thermal stability because terminal phthalonitrile group introduce extra cross-linking in the network structure. It was reported that, the *ortho* nitrile group in the *ortho*-phenyl nitrile functional benzoxazine is more reactive during polymerization than *meta* and *para*- nitrile analog. TGA-FTIR analysis revealed that some portion of the nitrile groups present in the monomer undergoes cross-linking reaction during curing and the rest react during char formation and results in high char yields. These highly cross-linked materials also possess higher T_g in the range of 275 to 300°C and T_g which is higher than T_{cure}. The neat phthalonitrile benzoxazine resins have high melting point (160°C) and higher melt viscosity than unfunctionalized benzoxazines, whereas phenylnitrile mono-functional benzoxazines are viscous liquids at room temperature with viscosity 6 x 10^5 Pa s and 1 Pa s at 80°C.

For benzoxazine with maleimide & norbornane functional group. Benzoxazine monomers with imide functionalities, maleimide (MIB) and norborane (NOB) showed improved thermal properties. The DSC and FT-IR studies of maleimide containing monomer, HPM-Ba, revealed that polymerizations occurs in two stages in the temperature range from 120 to 250°C (i) polymerization of C=C bonds of maleimide group at about 150°C by free radical mechanism, and (ii) the ring opening polymerization of oxazine at about 230°C. DSC thermograms of MIB and NOB showed benzoxazine polymerization occurred at 213 and 261°C, respectively. In case of NOB the cross-linking reaction of nadimide group proceeds via reverse Diels-Alder reaction at higher temperature ca 271°C. The char yields and T_g of the benzoxazine based polymers has also been increased due to incorporation of these

additional functionalities, since they improve the network structure by providing extra cross-linking [49].

For benzoxazine with adamantine functional group. Polymers obtained by thermal curing of benzoxazines with adamantine functional group exhibited different Tg values depending on the substituents on the benzoxazine ring. The lower T_g noted with poly(2-benzoxazine) was attributed to the presence of bulkier phenyl group in the structure which causes hindrance in the molecular chain movement in the network structure. Due to the same reason, poly(3-benzoxazine) possesses higher cross-linking density and also higher decomposition temperature. However, due to the incorporation of adamantane group into the polybenzoxazine backbone, the crosslink density of these polymers becomes lower than that of unmodified polybenzoxazines, which reflects as the comparatively lower char yield of adamantane functionalized polymers. Interestingly, they show high decomposition temperature. In Table 2.2 thermal properties of polybenzoxazines prepared from different benzoxazine monomers are listed.

2.6.1.2 Properties of rubber-modified polybenzoxazine

It has been reported that stress intensity factor, K_{Ic}, was increased when polybenzoxazine was modified with amine terminated butadiene acrylronitrile rubber (ATBN) or with carboxyl-terminated butadiene acrylronitrile rubber (CTBN) [65]. For toughening polybenzoxazine with liquid rubber, the particle size and the content of rubber dissolved in matrix phase are the main factors of the toughness improvement. Improvement of toughness is shown better by ATBN than CTBN and the trend of change of K_{Ic} values with the rubber content was different in both the cases. The K_{Ic} of polybenzoxazine increased from 0.6 $MP.m^{1/2}$ to 1.8 $MP.m^{1/2}$ with the increase of rubber content. Due to the highly cross-linked nature of the structure, the crack propagation rate is very fast for neat polybenzoxazine. However, a rough fracture surface, which may cause multiple crack initiation, was observed in both CTBN and ATBN modified systems. In addition, several different features were observed in the morphologies of CTBN- and ATBN-modified cases. It has been observed that the flexural strength of the ATBN-modified polybenzoxazine was increased with increasing rubber content, but decreased slightly for CTBN-modified polybenzoxazine.

The flexural strength of polybenzoxazine increased slightly or was maintained, and its flexural modulus decreased up to 2.4 GPa as rubber content increased.

From DSC study of the cure reaction of CTBN and ATBN modified systems; it was observed that cure peak temperature decreased with the increase of rubber content. By acting like an acid catalyst. CTBN helps the ring opening and this effect results the decrease of cure temperature. But ATBN, an amine terminated rubber, acts as a stabilizer of the ring-opened compound and helps to reduce the cure temperature. The T_g was also found decrease with the increase of CTBN and ATBN concentration [81]. It has been reported that when polybenzoxazine modified with hydroxy phenylmalemide (HPMI) and/ or ATBN, the incorporation of ATBN causes lowering of onset and the maximum exotherm of the ring opening of benzoxazine to 180°C and 216°C respectively, whereas for HPMI those values were 160°C and 200°C [71]. Viscoelastic measurements showed that the incorporation of HPMI increased the T_g and the storage modulus compared to that of the unmodified polybenzoxazine and ATBN modified polybenzoxazines.

Table 2.2: Thermal properties of benzoxazines

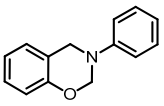
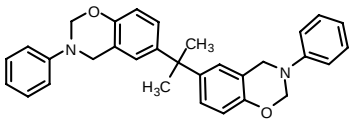
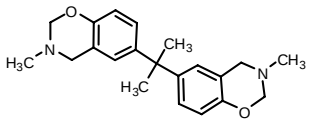
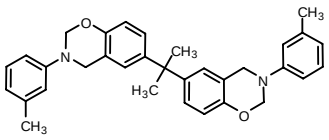
Monomers	T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (%)	Reference
 (P-a)	146	342	369	44	[41,70]
 (B-a)	150	310	327	32	[41,70]
 (B-m)	180	-	-	-	[41]
 (B-mt)	209	350	-	31	[144]

Table 2.2 : (continued) Thermal properties of benzoxazines

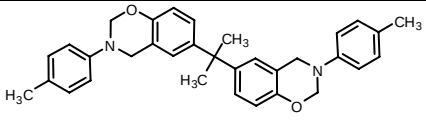
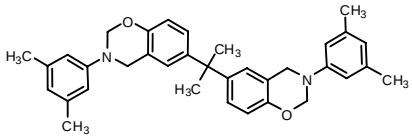
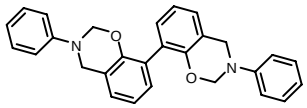
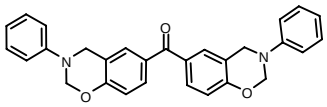
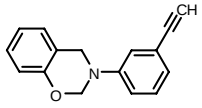
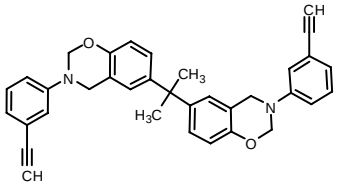
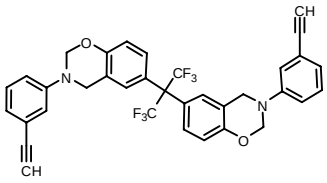
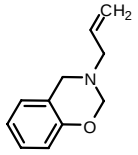
 (B-pt)	158	305	-	32	[144]
 (B-35x)	238	350	-	28	[144]
 (22P-a)	200	250	260	45	[25]
 (44O-a)	340	290	370	65	[25]
Acetylene functionalized monomers					
 (Ph-apa)	329	491	592	81	[43]
 (B-apa)	350	458	524	74	[43]
 (B-af-apa)	368	494	539	71	[43]
Allyl functionalized monomers					
 (P-ala)	285	348	374	44	[41]

Table 2.2 : (continued) Thermal properties of benzoxazines

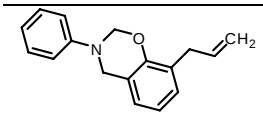
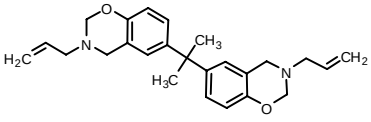
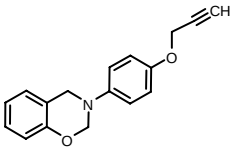
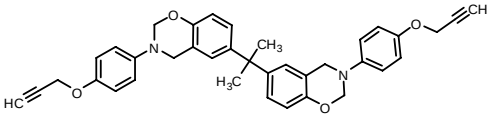
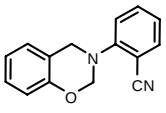
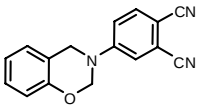
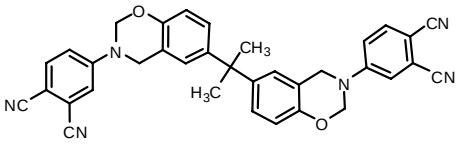
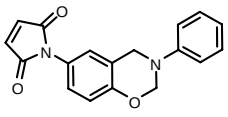
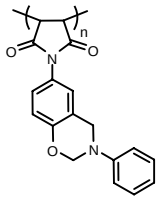
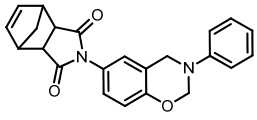
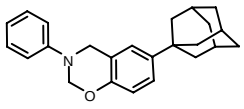
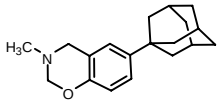
 (P-alp)	107	288	356	45	[41]
 (B-ala)	298	343	367	28	[41]
Phenyl propargyl functionalized monomers					
 (P-appe)	249	362	400	66	[36]
	295	352	388	66	[36]
(B-appe) Nitrile functionalized monomers					
 (I)	175	332	371	60	[35]
 (x)	278	450	560	76	[46]
 (IV)	300	423	468	68	[46]
Malemide functionalized monomers					
 (MIB)	252	375	392	56	[49]

Table 2.2 : (continued) Thermal properties of benzoxazines

 (HPM-BaI)	204	330	366	49	
 (NOB)	>250	365	383	58	[49]
Adamantane functionalized monomers					
 (2-benzoxazine)	109	335	365	24.2	[51]
 (3-benzoxazine)	189	399	439	30.8	[51]

TGA thermograms indicated that these modifications did not increase the thermal stability remarkably. However, thermal stability was slightly decreased with incorporation of ATBN whereas the incorporation of HPMI into PB-a or into ATBN modified PB-a thermal stability slightly increased

It has also been observed that the incorporation of HPMI into ATBN-modified polybenzoxazine improved the thermal and mechanical properties of the materials.

AFM study was employed to investigate the hydroxyl-terminated polybutadiene rubber modified polybenzoxazine. Both the dissolved rubber and phase-separated rubber were found to facilitate the energy dissipation upon mechanical deformation, yet the later was appeared to be much more effective, as only 40% of extra damping was observed from the former compared with 80% from the latter.

2.6.1.3 Polycarbonate (PC)-modified polybenzoxazine

From DSC analysis polycarbonate (PC) was found to be completely miscible with the cured polybenzoxazine resin, which was reflected by the presence of a single glass-transition temperature and the disappearance of the PC melting behavior in the DSC thermograms of PC-polybenzoxazine blends. Ishida and Lee concluded that, the main reason for this miscibility of PC in the PC-polybenzoxazine blend is the hydrogen-bonding interaction, which occurs between the hydroxyl groups of polybenzoxazine and the carbonyl groups of the PC. It was observed that hydrogen-bonding of carbonyl groups did not occur until 1 h of curing at 180°C, because of the existence of rather stable intramolecular hydrogen bonding within the flexible polybenzoxazine main chain at an early stage of curing. The content of hydrogen-bonded carbonyls gradually increased after prolonged heating because the hydroxyl groups became more accessible to the mobile PC chains after gelation. Moreover, both the fraction of hydrogen-bonded carbonyls of PC and the strength of the hydrogen-bonded hydroxyl groups of polybenzoxazine were greater in the blends with a lower PC concentration. DSC experiments revealed that due to the addition of PC modifier, the ring-opening and polymerization reactions became slow at an early curing stage and a lesser extent of polymerization was observed in the blend with a higher percentage of PC. For this reason the exothermic peak of the polymerization shifted toward a higher temperature and the glass transition temperatures of PC blends appeared to be lower than the predicted values from the Fox equation.

2.6.1.4 Properties of polycaprolactone (PCL)-modified polybenzoxazine

FT-IR investigation of PCL- polybenzoxazine blends, with a wide range of compositions, indicated the existence of hydrogen bonding between hydroxyl groups of polybenzoxazines and carbonyl groups of PCL [74]. DSC results of various PCL-polybenzoxazines blends revealed that the addition of PCL delays the polymerization reaction, which was reflected by the appearance of onset and peak temperatures of benzoxazine exotherms at higher temperatures as more PCL added into the benzoxazine monomers. The T_g's of the blends, with PCL concentrations greater than 55%, were located in the range of PCL T_g, whereas the blends with a PCL content less than 33% exhibited final T_g's in the benzoxazine range. The T_gs of the blends were increased continuously with increasing concentration of PCL till 33wt %. This is due to the fact that in presence of PCL, higher polymerization conversion

occurred, which was supported by FT-IR results. The addition of PCL improved the flexural properties of the blends and as well as thermal properties. Phase separation, thermal properties and morphological features of PCL- polybenzoxazine blends were also been reported [76,77].

2.6.1.5 Properties of polyurethane-polybenzoxazine

Poly(urethane-benzoxazine) films were prepared by blending the PU prepolymer with a benzoxazine monomer, B-a, (derived from bisphenol A). The PU prepolymer was blended with various amount of B-a in THF and followed by thermal treatment. It was believed that the cross-linking between -NCO of the PU prepolymer and phenolic OH, from ring-opening polymerization of B-a, and the allophanate formation via the intermolecular reaction of the PU prepolymer construct the main structures of the PU/B-a composite. The transparent nature of the cured PU/B-a films suggested the good compatibility between PU and B-a components. Only one T_g of all the PU/B-a films, from their viscoelastic properties, indicated that no phase separation in poly(urethane-benzoxazine) occurred due to the *in situ* polymerization. T_g was increased with the increase of B-a content. Elasticity characteristics with a good elongation with excellent reinstating behavior was exhibited by the films containing less than 15% of B-a, while those containing more than 20% of B-a exhibited plastic characteristics.

The films possessed excellent resistance to organic solvents such as THF, DMF, and NMP. Compared with PU these films showed an improvement in thermal stability. The decomposition temperature of PU/B-a films increased with the higher B-a content.

But, FT-IR study of the PU/ polybenzoxazine based IPN indicated that there was no apparent graft reaction occurred between the two components during IPN formation. SEM and TEM studies showed that although PU/ polybenzoxazine IPN film was transparent, phase separation occurs to a certain level regardless of the composition [82]. It was concluded that the structure of PU significantly influenced the B-a monomer distribution in PU network and subsequently affected the ring opening polymerization. The B-a monomers were well distributed in a noncompact PU network and with the increase of the degree of cross-linking this distribution of monomers was probably disturbed. During the thermal polymerization, rearrangement of B-a oligomers was hindered, resulting from the hydrogen bonding

between the renascent hydroxyl groups of PB-a and the PU segments. The higher the cross-linking degree of the PU network, the more difficult becomes such an interaction. The size of the PB-a network was decreased with increasing cross-linker in the PU composition.

2.6.1.6 Properties of epoxy-polybenzoxazine

For the improvement of the mechanical and water resistance properties of the cured resins from benzoxazine compounds and epoxy resins, terpendiphenol-based benzoxazines were synthesized and their curing with epoxy resins were investigated. It has been observed that the curing reaction did not proceed below 150°C, but it proceeded quantitatively without curing accelerators above 180°C. The cured resins derived from terpendiphenol-based benzoxazines and epoxy resins exhibited higher T_g, because of the hindrance of molecular chain mobility by the rigid and bulky cyclohexane ring from terpen backbone. The cured resins showed superior heat resistance, electrical insulation, and specially water resistance properties compared with the epoxy resins cured by bisphenol A type Novalac resin or B-a.

Appearance of two exotherms in the DSC plots of binary mixture of benzoxazine and epoxy resins was due to the existence of at least two reactions: (i) curing reaction among benzoxazine monomers was the reason for the first exotherm, at the temperature range of about 240-250°C, (ii) the second exotherm was attributed to the reaction between benzoxazine and epoxy resins, which occurred at temperatures of about 290-300°C [145].

Curing behavior of an epoxy resin and benzoxazine resin was described. The epoxy rings opened when they reacted with the hydroxyl groups that resulted from the ring opening of benzoxazines, and construct a network structure. For blends with equal functionality of oxirane to oxazine, the ring opening of benzoxazine and the partial curing of epoxy with hydroxyl functionalities was indicated by a single exotherm at temperatures of about 240°C in DSC thermograms. For the blends with higher molar ratio of epoxy, the homopolymerization of the residual epoxy resins with secondary hydroxyl groups, resulting from the ring opening of epoxide, [146] was observed by the second exotherm appears at 300°C in the DSC plot.

For better understanding of the curing behavior of the epoxy resins by bisphenol A based benzoxazine the curing reaction of model reactions of phenyl glycidyl ether

(PGE) and a mono-functional benzoxazine, P-Ca, (synthesized from *p*-cresol, formaldehyde and aniline) was investigated. Curing reaction at different temperatures were monitored by using ^{13}C-NMR spectroscopy, which confirmed that the phenolic hydroxyl groups produced by the ring opening of P-Ca reacted rapidly the epoxy groups of PGE at higher temperature, especially above 190°C, without a catalyst. It was postulated that the tertiary amine group produced by ring opening of benzoxazine accelerated the reaction. For another set of curing reactions with DGEBA and bisphenol A based benzoxazine (B-a) was carried out to compare the curing behavior of DGBA with bisphenol A type Novalac hardener. It was observed that epoxy resin cured by B-a possess higher T_g (175°C) along with superior heat resistance, water resistance and electrical insulation to those of the epoxy cured by BisA-N.

The effects of epoxy concentrations on the properties of benzoxazine-epoxy copolymers have been extensively studied. The effect of molecular weight epoxy resins in epoxy-benzoxazine was also reported. Epoxy resins having different molecular weights were synthesized by the chain extension of glycidyl ether of bisphenol A with bisphenol A and tetrabromobisphenol A. Copolymers having higher crosslink density and T_g were resulted due to the incorporation of epoxy into the polybenzoxazine network. The reduction of T_g with increasing molecular weight due to reduced crosslink density, whereas a marginal increase in storage modulus with chain extension was observed from DMTA studies. TGA results indicated that the samples were stable up to 300°C. Copolymerization with epoxy in fact causes reduction of char yields compared with pure polybenzoxazine, but chain extension caused slightly increase in the char yield. Increasing molecular weight between epoxy groups by chain extension of bisphenol-A and tetrabromobisphenol A has afforded copolymers with reduced crosslink density, improved storage modulus, reduced glass transition temperature and a slight increase in the char yield.

Comparative study of the properties of polybenzoxazine alloying with urethane prepolymer and epoxy resins was reported. According to their report the toughness of polybenzoxazine was effectively improved by alloying with isophorone diisocyanate (IPDI)-based urethane prepolymers (PU) or with flexible epoxy (EPO732). The flexural testing and dynamic mechanical analysis revealed that due to the addition of more flexible molecular segments in the polymer hybrids, the toughness of the alloys

of the rigid polybenzoxazine and the PU or the EPO732 systematically increased with the amount of either toughener. The curing temperature of the benzoxazine resin (B-a) at about 225°C shifted to higher value when the fraction of B-a in alloy decreased. Interestingly, Tg of the B-a/PU alloys was significantly higher (Tg beyond 200°C) than those of the parent resins, *i.e.*, 170°C for BA-a and-70°C for PU, whereas decreases of the Tg was observed as the content of epoxy fraction increased. Furthermore, the degradation temperature of the B-a/PU alloys was improved with the presence of the PU, though the opposite trend was observed in the B-a/EPO732 systems. The char yield of both alloy systems was steadily enhanced with the increased benzoxazine content because the char yield of the polybenzoxazine was inherently higher than that of the two tougheners.

2.6.1.7 Polybenzoxazines with flame retarding properties

Modified novolac resins with benzoxazine rings was synthesized and copolymerized it with glycidyl phosphinate (DOPO-Gly). From DTA results showed that modulus, cross-linking densities and T_gs of the blends decreased with increasing DOPO-Gly content. The reason of this trend may be the presence of bulky DOPO group, which decrease the cross-link density and appear to be less able to restrict segmental motions. These phosphorylated resins showed high char yield, which increases with increasing phosphorous content. This also indicates that their flame retardancy would be high. The thermal stabilities of DOPO-benzoxazine-novolac resins are relatively poor compared to the phosphorous free benzoxazine-novolac resins, because phosphorous DOPO group degrades at relatively low temperatures. The burn tests (UL-94) of these materials indicate that, novolac modified benzoxazines are V-1 materials where as high phosphorous content polymers belong to V-0 category.

When novolac resins with benzoxazine rings cured with isobutyl bis(glycidylpropylether) phosphine oxide) (IHPOGly), they produce flame retardant polymers of V-0 grade. Thermo-gravimetric analysis of these materials showed that, the temperature of 5% weight loss decreases with increase of phosphorous content and char yields were around 20%. The phosphorous containing materials showed higher T_gs, because of the presence of strong polar P=O group.

2.6.1.8 Clay-polymer composite

Polybenzoxazine-clay (B-a-OMMT) [39] and poly(urethane-benzoxazine)-clay (PU/P-a-OMMT) nanocomposites with various compositions were prepared. It has been observed that due to the catalytic effect of OMMT, the ring opening temperature of benzoxazines was reduced for these composites compared to the pristine polymer. T_g's and char yield of these hybrid materials were also higher and increased with increasing OMMT content. The initial decomposition temperatures (5% and 10% weight loss temperatures) were enhanced by hybridizing with OMMT. In the case of Pu/P-a- OMMT composites, the tensile strength and modulus increased, while the elongation decreased with the increase of OMMT loading. Due to the addition of OMMT, the solvent resistance was also improved. This may be because of the layered silicate structures in OMMT which acts as a protecting wall and prevents solvents to penetrate into the nanocomposites.

TGA of the polybenzoxazine-OMOM composites were prepared and it was indicated that the char yield of the composites is greater than that of polybenzoxazines (except for MOM-dodecylamine-polybenzoxazine, which may undergo some decomposition during curing). The heat resistance of these composites has been improved.

In case of PBO-Bz-OMMT composites, the inclusion of OMMT decreases the curing temperature and increases T_g and the storage modulus of these nanocomposites was maintained up to higher temperatures was reported.

2.6.1.9 Boron nitride-polybenzoxazine composites

To develop highly conductive molding compounds for electronic packing applications boron nitride filled polybenzoxazines were prepared. These materials exhibited a very high conductivity along with high and stable mechanical strength up to 200°C with a high T_g of ca. 220°C and a very low water absorption property [147,148]. Specific heat capacity of boron nitride filled polybenzoxazines has been investigated by using temperature modulated differential scanning calorimetry (TMDSC) and it was observed that filler loading is the critical factor that can change the heat capacity of the composite. A linear relationship between the composite heat capacity and filler loading was found out [149]. During investigation of the inter-phase of boron nitride-polybenzoxazine, it has been observed that the boron nitride surface inhibits curing of benzoxazine coatings in the interfacial region. DMA results

indicated a slightly higher activation enthalpy of the glass transition process, as well as slightly higher T_g for the cured composite specimens [150].

2.7 Telechelic Polymers

Telechelic polymers are defined as macromolecules that contain two reactive end-groups that have the ability to react selectively with another molecule. Depending on the functionality, telechelics can be classified as mono-, di-, tri-, and multifunctional telechelics (polytelechelics) [151]. Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Moreover, star and hyper-branched or dendric polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. Various macromolecular architectures obtained by the reactions of telechelics are represented in Figure 2.8. The end group functionality designates the polymerization pathways. When end groups are bifunctional (*eg*, vinyl groups) they yield graft copolymers or networks; such telechelic polymers are called macromolecular monomers, macromonomers. Telechelics can be synthesized by conventional radical polymerization in two ways: End groups can be controlled using large concentration of functional initiator, or polymerization can be conducted in the presence of suitable transfer agents. Controlled radical polymerization is another way to synthesize telechelics. Control of chain ends was traditionally accomplished using living ionic polymerization techniques. However, recently controlled living radical polymerization provided the possibility to synthesize well-defined telechelic polymers with controlled functionality with radical routes. Atom transfer radical polymerization, stable free radical mediated polymerization (SFRP), also called as nitroxide mediated polymerization (NMP), and reversible addition fragmentation chain transfer polymerization (RAFT) are useful for preparation of various telechelics.

Addition to radical routes, the synthesis of telechelics by ring opening has attracted great interest. The end groups are introduced by initiation, end capping, or transfer reactions. Telechelics can be obtained from cyclic ethers, cyclic acetals, cyclic sulfides, cyclic amines, lactones, siloxanes, oxazolines in various methods. For example, polymerization of ε-caprolactone by suitable alcoholates simply yields telechelic polymers

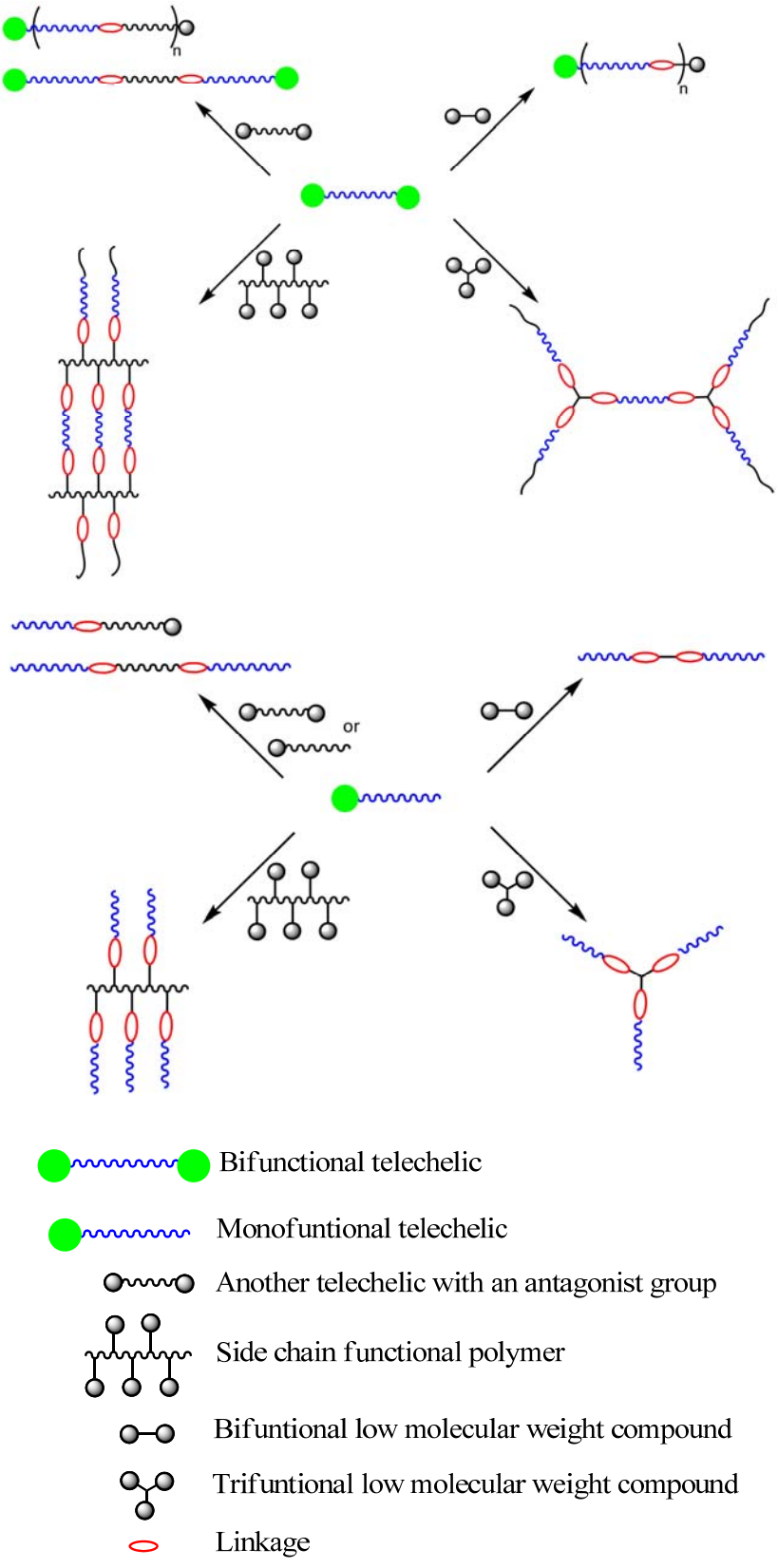


Figure 2.8 : Reactions of telechelics for various structures

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Monomers

Styrene (St, 99.0%, Aldrich)

It was vacuum distilled over calcium hydride just before use.

ε-Caprolactone (ε-CL, 99.0%, Aldrich)

It was vacuum distilled over calcium hydride.

Terephthaloyl dichloride (99.0%, Alfa Aesar)

It was was recrystallized from hexane.

Adipoyl chloride (98.0%, Acros)

It was used as received.

3.1.2 Solvents

N,*N*-Dimethyl formamide (99.0 %, Aldrich)

It was used as received.

1,4-dioxane (≥99.0%, Sigma-Aldrich)

It was used as received.

Tetrahydrofuran (THF, 99.8%, J.T.Baker)

(a) It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

(b) For use in the chemical reactions, it was dried and distilled over benzophenone-sodium.

Diethyl ether (≥ 99.0%, J.T. Baker)

It was used as received.

Toluene (99.9%, Acros)

It was used as received.

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

n-Hexane (99.0%, Aldrich)

It was used as received.

Chloroform (≥99%, Aldrich)

It was used as received.

Dichloromethane (≥99%, J.T. Baker)

It was used as received.

Acetic acid (99-100%, Merck)

It was used as received.

Dimethyl sulfoxide (DMSO) (≥99.5%, Sigma)

It was used as received.

Ethanol (≥99.5%, Aldrich)

It was used as received.

3.1.3 Other chemicals

Paraformaldehyde (powder, 95%, Sigma-Aldrich)

It was used as received.

Phenol (loose crystals, ≥99.0%, Sigma-Aldrich)

It was used as received.

3-Aminophenylboronic acid hemisulfate (Acros)

It was used as received.

2,2-bipyridine (bpy) (≥99%, Sigma-Aldrich)

It was used as received.

Copper(I) bromide (CuBr) (≥98.0%, Sigma-Aldrich)

It was used as received.

Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (99%, (Aldrich)

It was used as received.

1,4-Dibromo-2,5-dimethylbenzene (98%, Aldrich)

It was used as received.

2,5-dibromotoluene (98%, Aldrich)

It was used as received.

2,5-Dibromotoluene (99%, Acros)

It was used as received.

N-bromosuccinimide (NBS) (99%, Acros)

It was used as received.

Ethanolamine (99%, Acros)

It was used as received.

β-naphthol (≥98.0%, Fluka)

It was recrystallized from water.

Aniline (≥99.5%, Sigma-Aldrich)

It was distilled before usage.

Sodium hydroxide (Granulated, ≥ 98%, Merck)

It was used as received.

Sodium sulfate (≥ 99.0 %, Merck)

It was used as received.

Triethylamine (≥99%, Aldrich)

It was dried with NaOH pellets and distilled.

2-(2-aminoethoxy)ethanol (98%, Acros)

It was used as received.

4,4'-Isopropylidenediphenol (97%, Aldrich)

It was used as received.

Stannous 2-ethyl-hexanoate (stannous octoate) (~95%, Aldrich)

It was used as received.

Acetic anhydride (≥99%, Sigma-Aldrich)

It was used as received.

[(norbornadiene)rhodium(I) chloride]$_2$ [(nbd)RhCl]$_2$ (≥98%, Fluka)

It was used as received.

Propargyl bromide (~80 volume % in toluene, Fluka)

It was used as received.

HCl (37%, Sigma-Aldrich)

It was used as received.

1,4-Dibromo-2,5-bis(bromomethyl) benzene and 1,4-dibromo-2-(bromomethyl) benzene

They were prepared by bromination of methyl groups of 2,5-dibromo-*p*-xylene or 1,4-dibromotoluene, respectively, using *N*-bromosuccinimide.

3.2 Objectives Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H-NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

3.2.2 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.3 UV-visible spectrophotometer

UV-Visible spectra were recorded on a Shimadzu UV-1601 UV-visible spectrophotometer.

3.2.4 Fluoresans spectrophotometer

Fluoresans spectra were obtained on a Perkin Elmer LS 50 Luminesans spectrometer.

3.2.5 Gel-permeation chromatography (GPC)

a) Gel permeation chromatography analyses were performed with a set up consisting of a Waters 410 Differential Refractometer, a Waters 515 HPLC Pump and an apparatus equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular 515 weights were calculated on the basis of a calibration curve recorded with mono disperse polystyrene standards.

b) Gel permeation chromatography analyses were measured on a Shimadzu system equipped with a SCL 10A system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV detector and both a PSS Gram30 and a PSS Gram1000 column in series, whereby N, N-dimethyl acetamide with 5 mmol LiCl was used as eluent at 1mL/min flow rate and the column oven was set to 60°C. The molecular weight and the molecular weight distribution of the prepared polymers were calculated by using poly(methyl methacrylate) standards.

c) Gel permeation chromatography instrument equipped with a Waters 1515 pump and Waters styragel column (HT4) utilizing DMF containing 5mM NH_4PF_6 at a flow rate of 0.5 ml/min and the column oven set to 50°C.

3.2.6 Differential scanning calorimeter (DSC)

Differential scanning calorimeter was performed on a Perkin Elmer Diamond DSC with a heating rate of 10°C min^{-1} under nitrogen flow.

3.2.7 Thermal gravimetric analysis (TGA)

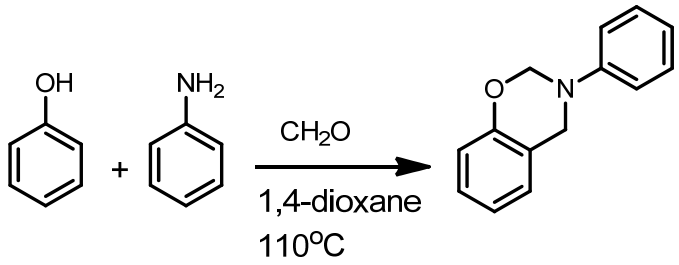
TGA was carried out on Perkin Elmer Diamond TA/TGA with a heating rate of 10°C min^{-1} under nitrogen flow.

3.3 Synthesis

3.3.1 Synthesis of monofunctional benzoxazine monomer (P-a)

The general procedure is as follows; 18.6 g (0.2 mol) aniline is added slowly to the flask containing 12.0 g (0.4 mol) *p*-formaldehyde, keeping the temperature below 10°C in ice bath. The mixture is stirred for 10 min, 18.8 g (0.2 mol) phenol is added to the mixture. Then the flask heated up to 110°C for one and half an hour. The content of the flask is dissolved in ethyl ether. The ether solution was washed several times with 1 N sodium hydroxide solution and de-ionized water, respectively.

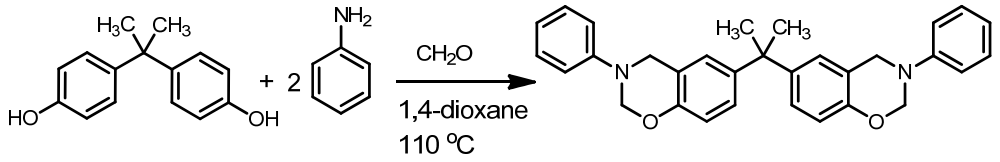
Organic layer was dried with anhydrous sodium sulfate and diethyl ether was evaporated to yield light yellow viscous liquid. Solid product was formed after applying vacuum at 50°C in 24 h. (Yield: 65%)



(3.1)

3.3.2 Synthesis of difunctional bisbenzoxazine (B-a)

Synthesis of bisbenzoxazine was performed as follows [306]; to 100 mL of 1,4-dioxane, aniline (40.0 mmol, 3.72 g), 4,4'-Isopropylidenediphenol (40.0 mmol, 9.13 g), and *p*-formaldehyde (160 mmol, 4.80 g) were added and refluxed for 3 days. The reaction mixture was filtered and 1,4-dioxane was evaporated under vacuum. Resulting oily product was dissolved in chloroform and washed five times with 40 mL 0.1 N sodium hydroxide aqueous solution and distilled water, respectively. Then, the chloroform solution was dried with anhydrous sodium sulfate. Removal of solvent by evaporation afforded orange yellow oil. (Yield: 60%)



(3.2)

3.3.3 Synthesis of ATRP initiators

1,4-Dibromo-2,5-bis(bromomethyl)benzene (1a), was prepared by bromination of methyl groups of 2,5-dibromo-p-xylene using *N*-bromosuccinimide in CCl_4. 6.2 g (0.025 mol) 2,5-dibromo-p-xylene, 9.26 g (0.52 mol) *N*-bromosuccinimide and 0.1g benzoyl peroxide were dissolved in 20mL CCl_4. The solution was maintained at reflux temperature for 4 h. After that time the solution was filtered. The succinimide was washed with a supplementary amount of CCl_4 and finally with a little quantity of CH_2Cl_2. The combined organic solutions were washed several times with water and than dried over $MgSO_4$. The solvent was removed by rotary evaporator. The product was purified by passing through a silicagel column using diethyl ether as eluent.

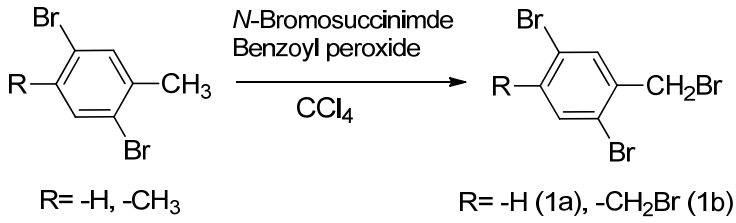
Finally, the product was obtained as white crystals after recrystallizing twice from benzene. 1,4-Dibromo-2-(bromomethyl)benzene (1b) was prepared in a similar way with (1) from 1,4-dibromotoluene.

1,4-Dibromo-2,5-bis(bromomethyl)benzene (1a) and 1,4-dibromo-2-(bromomethyl) benzene (1b) were prepared by bromination of methyl groups of 2,5-dibromo-*p*-xylene or 1,4-dibromotoluene, respectively, using NBS.

1(a): ^{1}H-NMR ($CDCl_3$): δ = 4.5 (s, 4H, CH_2), 7.65 (s, 2H, aromatic); white crystals, m.p. (DSC): 159-160^{o}C. Anal. ($C_8H_6Br_4$): Calc. C 22.78; H 1.43. Found C 22.52; H 1.35

1(b): ^{1}H-NMR ($CDCl_3$): δ = 7.58 (s, 1H, Ar*H* -3-position), 7.43-7.40 (d, 1H, Ar*H* -5 position), 7.28-7.26 (d, 1H, Ar*H* -6 position), 4.51 (s, 2H, C*H*$_2$Br); white crystals, m.p. (DSC): 94-95^{o}C.

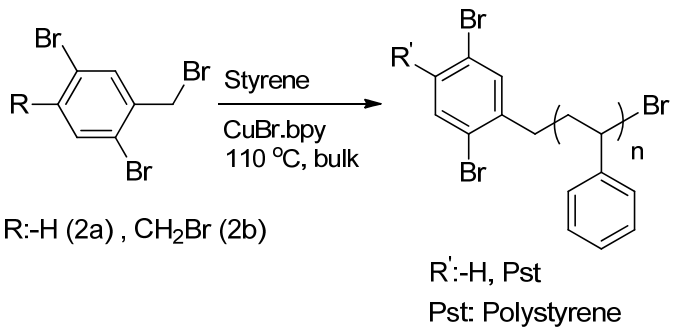
Anal. ($C_7H_5Br_3$) Calc. C 25.57; H 1.53. Found C 25.63; H 1.73



(3.3)

3.3.4 General procedure for atom transfer radical polymerization

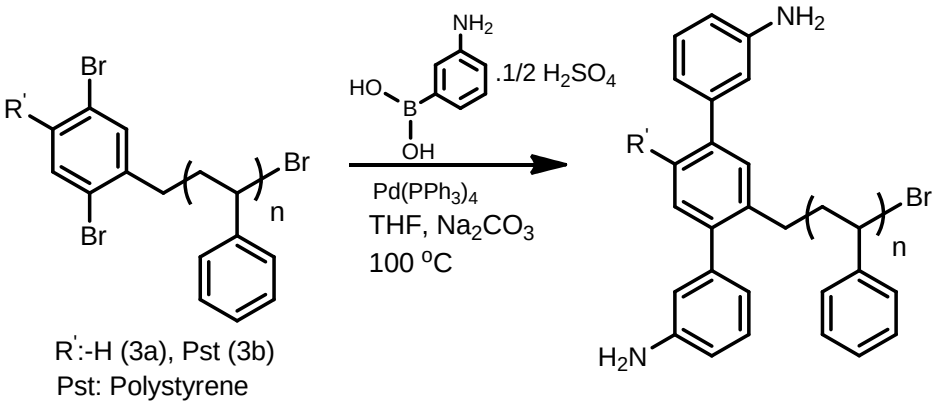
A round-bottom flask equipped with a magnetic stirrer and a lateral neck with tap was used. The system was evacuated and back-filled with dry nitrogen several times. The catalyst (CuBr), ligand (bpy), initiator (1a or 1b), and styrene were introduced under an inert atmosphere. The flask was placed in an oil bath warmed at 110°C and stirred at that temperature for a given time, after which the reaction was stopped and the mixture was diluted with tetrahydrofuran and finally poured into a ten-fold excess of methanol. The solid was collected after filtration and dried in an oven at 40°C and at reduced pressure overnight. The polymers were purified by passing through a silica gel column using tetrahydrofuran as eluent and re-precipitated in methanol.



(3.4)

3.3.5 General procedure for the synthesis of amino functional polymers by Suzuki Coupling

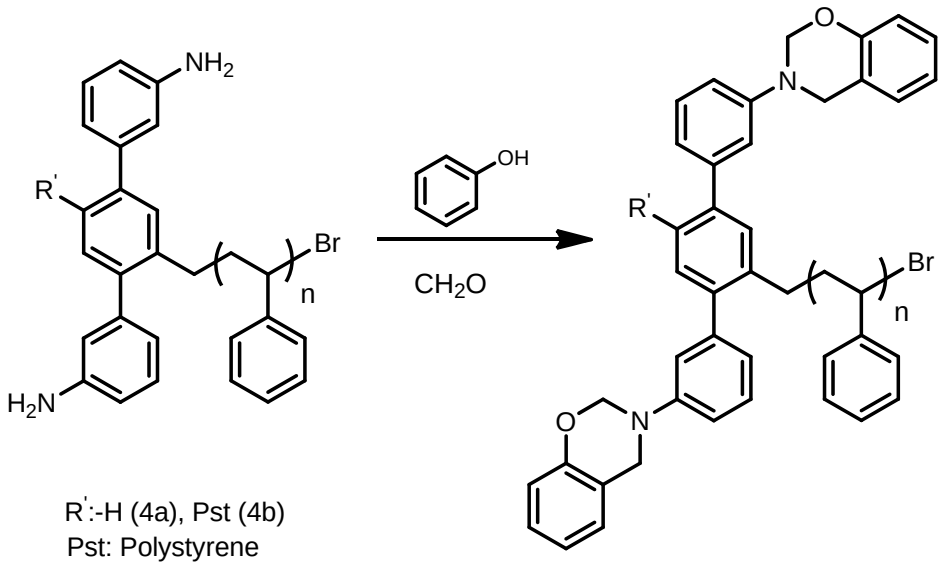
A 100 mL three-necked round bottom flask equipped with a condenser, a rubber septum, a nitrogen inlet-outlet and a magnetic stirrer was charged with 1M $NaHCO_3$ (10 mL) and THF (15 mL). The mixture was previously bubbled with nitrogen over a period of 30 minutes and refluxed under nitrogen for 4 h. A 20 mL three-necked round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.208 mmol of polymer (2a or 2b), 0.174g (1.04 mmol) 3-aminophenylboronic acid hemisulfate and 0.01 g (0.008 mmol) of $Pd(PPh_3)_4$. The solvent mixture (4 mL) was introduced with a syringe through the septum. The mixture was refluxed under nitrogen for 4 days, maintaining vigorous stirring and with the exclusion of oxygen and light. The amino-functionalized polymers (3a or 3b) were separated by precipitation in methanol, filtrated, washed several times with water for the removal of inorganic salts and dried. Further purification was performed by passing the polymers through a silicagel column using THF as eluent and re-precipitated in methanol.



(3.5)

3.3.6 Synthesis of benzoxazine functional macromonomers

Solid phenol (10 g, 0.106 mol) was placed in a 100 mL round-bottom flask containing a magnetic stirring bar. The flask was heated and after complete melting of the phenol crystals, the polymer with amino functions, 3b, (0.2 g, 0.05 mmol) and paraformaldehyde (0.3 g, 0.01 mol) were added to the flask. A yellow solution was obtained. The solution was stirred at 110ºC for 2 h, then cooled to room temperature. Tetrahydrofuran (10 mL) was added to the flask. The resulting polymer was precipitated in excess (200 mL) methanol and then filtered. The solid polymer was dissolved in dichloromethane, washed with 0.1N NaOH solution two times and neutralized with distilled water. Dichlorometane was evaporated to concentrate the polymer solution. The solution was re-precipitated in methanol (200 mL), and filtered. Solid polymer (4b) was dried under vacuum before analysis. The same method applied for the synthesis of 4a.



(3.6)

R':-H (4a), Pst (4b)
Pst: Polystyrene

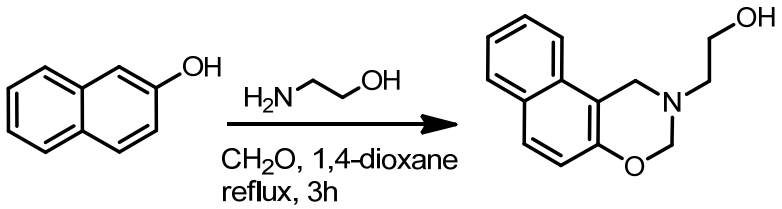
3.3.7 General procedure for synthesis of 2-(1*H*-Naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH)

A 100 mL round-bottomed flask, equipped with magnetic stirrer and a reflux condenser, placed in ice bath, was charged with paraformaldehyde (0.03 mol) and ethanolamine (0.015 mol). 2-Naphthol (0.015 mol) was subsequently added to the mixture. The flask is then placed in an oil bath which is heated to 110°C and the mixture was maintained at that temperature for three hours. At the end of the reaction the mixture was diluted with dichloromethane and by means of a separatory funnel. The organic layer was washed successively several times with 0.1 N NaOH and

diluted AcOH solution. Then organic phase was neutralized with distilled water. Organic layer was dried with anhydrous Na_2SO_4 and dichloromethane was evaporated to yield 2-(1*H*-Naphtho [1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH). Yield: 56%. The same synthetic procedure in dioxane as a solvent gave the same product with a relatively lower yield (49%).

^{1}H-NMR ($CDCl_3$): δ = 2.57 (broad s, 1H, OH), 3.00 (t, 2H, CH_2), 3.73 (t, 2H, CH_2), 4.34 (s, 2H, CH_2), 4.94 (s, 2H, CH_2), 7.00-7.04 (d, 1H, aromatic -3-position), 7.32-7.39 (t, 1H, aromatic -7-position), 7.45-7.51 (t, 1H, aromatic -6-position), 7.58-7.61 (d, 1H, aromatic -5-position), 7.63-7.67 (d, 1H, aromatic -4-position), 7.75 (d, 1H, aromatic -8-position).

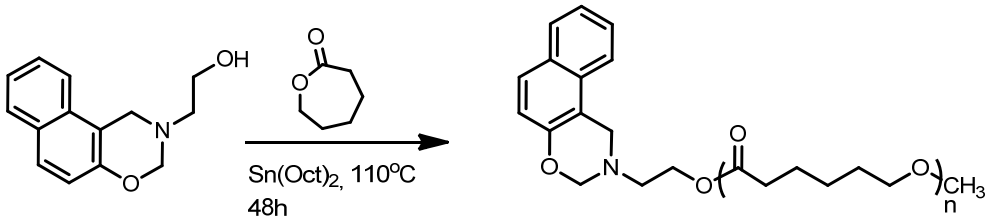
IR (neat): 3370 cm^{-1} (O-H stretch), 3059 cm^{-1} (aromatic C-H stretch), 1750-1909 cm^{-1} (aromatic overtones), 1224 cm^{-1} (aromatic C-O stretch), 1072, 1038 cm^{-1} (C-O stretch), 940 cm^{-1} (aromatic ring mode) Anal. ($C_{14}H_{15}NO_2$) Calc. C 73.34; H 6.59, N 6.11 Found C 72.16; H 6.22, N 6.63.



(3.7)

3.3.8 General method for preparation of poly(ε-caprolactone) with the 2-(1*H*-Naphtho[1,2-e][1,3]oxazin-2-yl)-ethoxy end group (PCL-N-a)

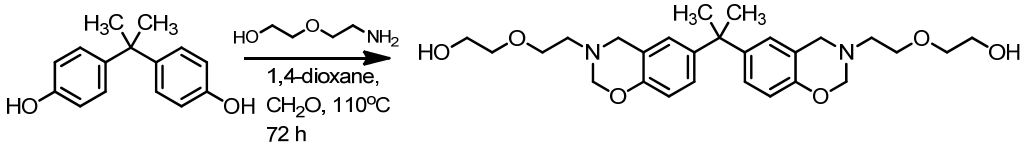
N-a-OH (0.001 mol) , monomer (ε-CL) (0.02 mol) and stannous octoate (2.5x10^{-6} mol), were added under nitrogen in previously flamed and nitrogen-purged schlenk tube equipped with magnetic stirrer. The ε-CL polymerization was carried out in bulk at 110°C. After 48 h, the polymerization was terminated by cooling the tube to the room temperature, then diluted with CH_2Cl_2 and poured into 10-fold excess of cold methanol. The polymer with naphthoxazine end group was collected after filtration and drying at room temperature in a vacuum for 2 days. (Yield: 96%)



(3.8)

3.3.9 Synthesis of diol containing bisbenzoxazine (B-etherdiol)

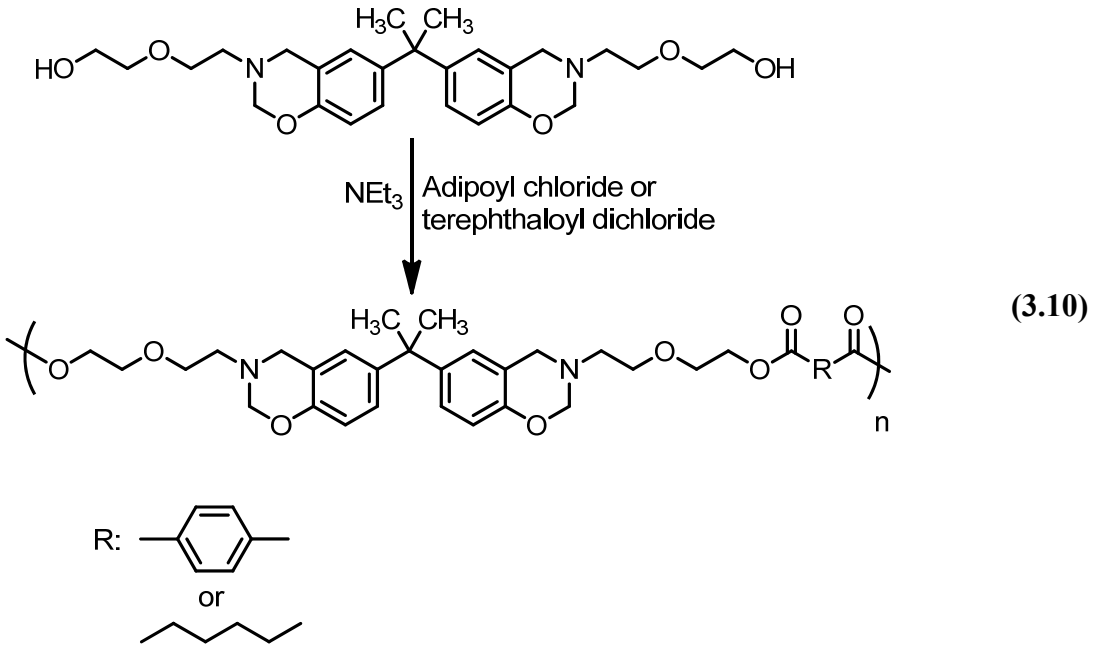
Synthesis of B-etherdiol was performed as follows. To 100 mL of 1,4-dioxane, 2-(2-aminoethoxy)ethanol (40.0 mmol, 4.20 g), 4,4′-isopropylidenediphenol (40.0 mmol, 9.13 g) and paraformaldehyde (160 mmol, 4.80 g) were added and refluxed for 3 days. The reaction mixture was filtered and 1,4-dioxane was evaporated under vacuum. Resulting oily product was dissolved in chloroform and washed five times with 40 ml 0.1 N NaOH aqueous solution and distilled water, respectively. Then, the chloroform solution was dried with anhydrous sodium sulfate. Removal of solvent by evaporation afforded orange-yellow oil. (Yield: 60%)



(3.9)

3.3.10 Polyetherester synthesis

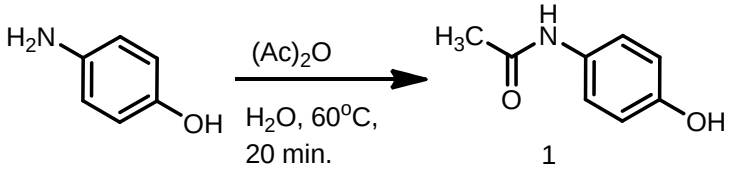
In a dry 100 mL round bottom flask equipped with a Claisen head with a calcium chloride drying tube and a rubber septum were placed 30 mL of chloroform, B-etherdiol (1 g, 2,05 mmol) and 5 mL of triethylamine. The mixture was cooled with an ice bath and a nitrogen stream was maintained by needles through septum. Then, 30 mL chloroform solution of terephthaloyl dichloride (0,42 g, 2,06 mmol) (or adipoylchloride) was added portion-wise via syringe. After addition of diacidchloride, the mixture was stirred for 3 h at ambient temperature and refluxed for 1 h. The cooled solution was washed three times with 40 mL of distilled water. The chloroform solution was dried with $MgSO_4$, filtered and concentrated under vacuum. The polymer was precipitated in 200 mL of methanol (diethylether was used in adipoylchloride case), filtered and dried under vacuum overnight. (Typical yield ca. 55%, Molecular weights of polymers; PEE-BA= M*n*: 33.400, PDI (polydispersity): 4.37, PEE-BT= M*n*: 33.700, PDI (polydispersity): 1.36)



(3.10)

3.3.11 Preparation of *N*-(4-hydroxphenyl)acetamide (1)

A suspension of *p*-aminophenol (15.3 g, 140 mmol,) in water (50 mL) was taken into a 250 mL flask. Acetic anhydride (14.2 mL, 150 mmol,) was added to this solution. The mixture was heated at 60^{o}C with vigorous stirring until formation of clear solution. After about 20 minutes, the solution cooled to ambient temperature and the crude product was filtered and washed with deionized water. Crude solid was recrystallized from water to yield white crystals. (Yield: 80%, mp: 169ºC)

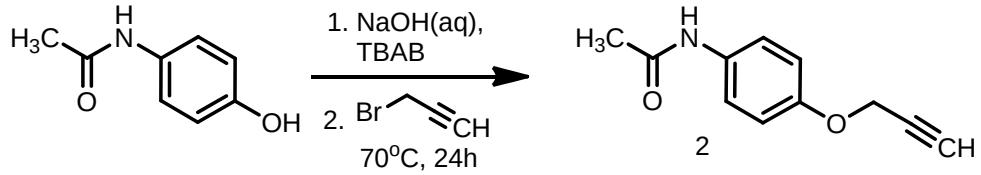


(3.11)

3.3.12 Preparation *N*-(4-(prop-2-ynyloxy)phenyl)acetamide (2)

In a 250 mL flask, of *N*-(4-hydroxphenyl)acetamide (8.1 g, 50 mmol) was dissolved in 100 mL of 0.4 N NaOH. The mixture was heated at 70°C until a clear solution was formed. To this solution, tetrabutylammonium bromide (1.6 g, 5 mmol,) was added as a phase transfer catalyst. A solution of propargyl bromide (6.5 g 55, mmol) in 50 mL of toluene was added portion wise to the solution. The mixture was kept stirring at 70°C for 24 h. Then it was cooled to afford solid. In addition, the toluene layer was separated and washed repeatedly with water. Evaporating toluene afforded extra solid. The crude product was dissolved in 1,4-dioxane and precipitated in water (ca.

200 mL) , then filtered, and washed repeatedly with copious amount of water. (Yield: 94%)

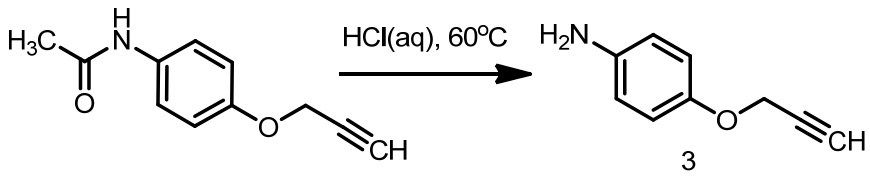


(3.12)

TBAB: Tetrabutylammonium bromide.

3.3.13 Preparation of *p*-propargyloxy aniline (3)

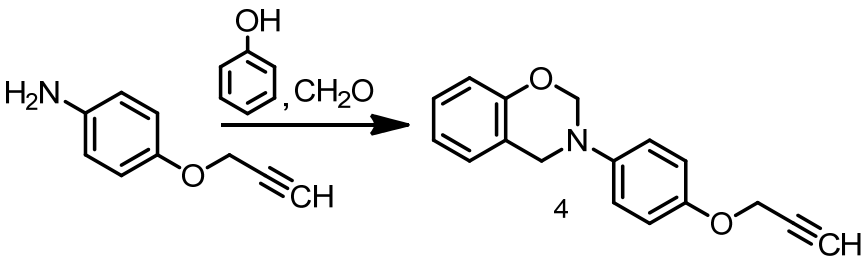
In a 250 ml flask, *N*-(4-(prop-2-ynyloxy)phenyl)acetamide (8,5 g, 45 mmol) was dissolved in ethyl alcohol (70 mL) and HCl (36%, 70 mL) was added. The mixture was stirred at 60 ^{o}C for 3 h. After neutralizing with aqueous sodium hydroxide, the solution was extracted with chloroform, and the organic layer was dried over anhydrous $MgSO_4$. Evaporation of chloroform gave a yellowish brown viscous product. The crude product was purified by distillation under reduced pressure (bp: 95°C, 10 mmHg) to afford a colorless and highly viscous liquid, which crystallized into yellowish white crystals after a while in the flask (Yield: 75%, mp: 49-50°C).



(3.13)

3.3.14 Preparation of 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2*H*-benzo[e][1,3]oxazine (4)

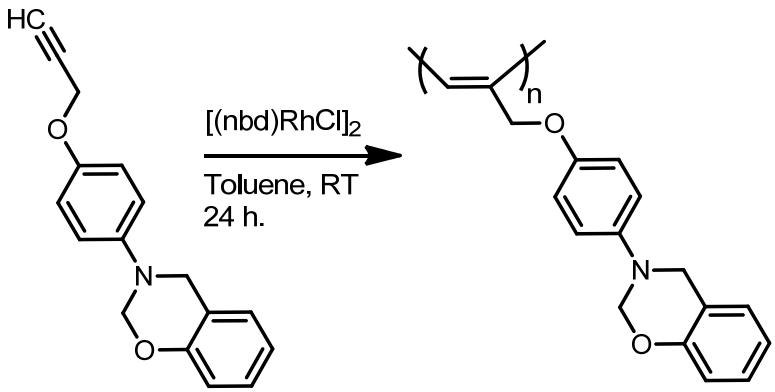
In a 250 mL flask, paraformaldehyde (1.9 g, 63 mmol) in 100 mL of dioxane was cooled by ice bath. To this solution, p-propargyloxy aniline (34 mmol, 5 g) in 25 mL of dioxane was added portion-wise. The solution was kept stirring for 15 min below 5°C. Thereafter, a solution of phenol (3.3 g, 35 mmol,) in 25 mL of dioxane was added. The solution was refluxed at 110°C for 6 h. Removal of the solvent in a rotary evaporator gave a viscous residue that was dissolved in 100 mL of diethylether and washed several times with 1 N sodium hydroxide solution and finally with distilled water. Then, the ether solution was dried with anhydrous sodium sulfate, followed by evaporation of ether under vacuum to afford pale yellow viscous fluid. (Yield: 60%)



(3.14)

3.3.15 Polymer synthesis

Into a 20 mL Schlenk tube with a sidearm was added 0.85 mmol of propargyl benzoxazine. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the sidearm. Toluene (3 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving $[(nbd)RhCl]_2$ (10 μmol) in 2 mL of toluene with 1 drop of triethylamine, which was transferred to the monomer solution using a syringe. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The mixture was then diluted with 3-5 mL of toluene and the solution filtered for insoluble products. Then the solution was added drop wise to methanol (100 mL) under stirring. The precipitate was collected by filtration and dried under vacuum at room temperature to a constant weight. The polymeric product was isolated as powder with a moderate yield (26%). Additionally, the insoluble product was obtained with an 18% yield. (Note: Polymerization without co-catalyst yielded 25% soluble and 16% insoluble products)



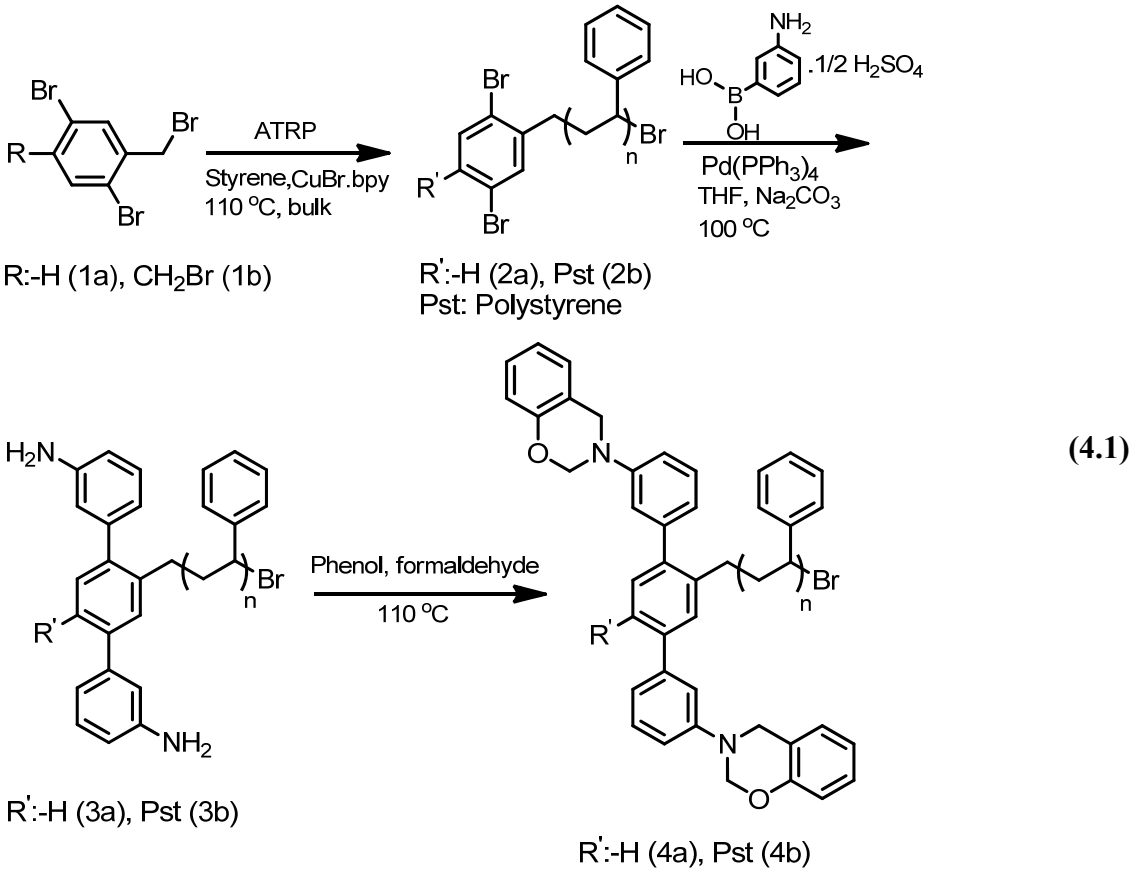
(3.15)

4. RESULTS AND DISCUSSIONS

The molecular structure of polybenzoxazines offers enormous design flexibility which allows tailoring the properties of the cured materials for wide range of applications. Different synthetic strategies for the preparation of benzoxazine monomers and blends, their polymerization reaction mechanisms, and the structure property relationships of the cured materials have been studied by various research groups. But, pure polybenzoxazine based polymers also suffer number of disadvantages, in terms of (a) high curing temperature (~ 200°C or higher), (b) difficulty in processing and (c) brittleness. To overcome those disadvantages, several researchers have attempted various strategies, such as (a) preparation of modified monomers with additional functionality, (b) synthesis of novel polymeric precursors and (c) by blending with a high performance polymer or filler and fibers. The monomers are usually powder and processing into thin films is rather difficult. Addition of elastomeric materials to brittle resins is a well known approach to improve the ductility. But while improvement in ductility of benzoxazine may be achieved using this approach, it sacrifices the intrinsic advantages of thermosetting resins. To improve the processability 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 cross-linked network structure formed from polymer and polymerization of benzoxazine, will exhibit enhanced mechanical property while retaining the beneficial properties of polybenzoxazine.

By using Atom Transfer Radical Polymerization, a functional end group can easily be incorporated in a linear polymer by varying the initiator. By this method end-chain or mid-chain functional telechelics can be synthesized. The macromonomer method is proposed for obtaining polybenzoxazines with polystyrene groups. As it will be shown below benzoxazine type macromonomers can easily be prepared from amino functional telechelics which were obtained via combination of ATRP and

Suzuki coupling. First, ATRP initiators were synthesized and subsequently used in ATRP of styrene to yield dibromophenyl functional polymers (Reaction 4.1).



(4.1)

Table 4.1 : Conditions and results of ATRP of styrene using initiators 1 and 2 in the presence of CuBr/bpy complex

Initiator (mol/L)	Time (min)	Yield (%)	M_n (GPC)	M_n (Theoretical)	M_n (^{1}H-NMR)	M_w/M_n	Polymer
1[a] (0.10)	45	41	4265	4150	4180	1.19	2b
2[b] (0.15)	60	27	2182	1850	1860	1.25	2a

[a] bulk, 120°C, [I]/CuBr/bpy = 1/2/6
[b] bulk, 120°C, [I]/CuBr/bpy = 1/1/3
[c] Determined by GPC

It should be noted that while the bromomethyl groups are effective for ATRP initiation of styrene, the bromine atoms directly connected to the benzene ring are preserved for further coupling reactions. Thus, Suzuki coupling with boronic acid amino compound in the presence of a $Pd(PPh_3)_4$ catalyst yielded respective amino telecehelics. Subsequently, these polymers were converted to benzoxazine macromonomers following the general synthetic pathway shown in reaction 4.1.

In this connection it should be pointed out that during the benzoxazine ring closure process we have encountered formation of by-products arising from the additional Mannich reactions.

In figure 4.1, ^{1}H-NMR spectrum of the product clearly reveals that instead of benzoxazine ring formation aminomethyl linkages between polymer backbones are formed.

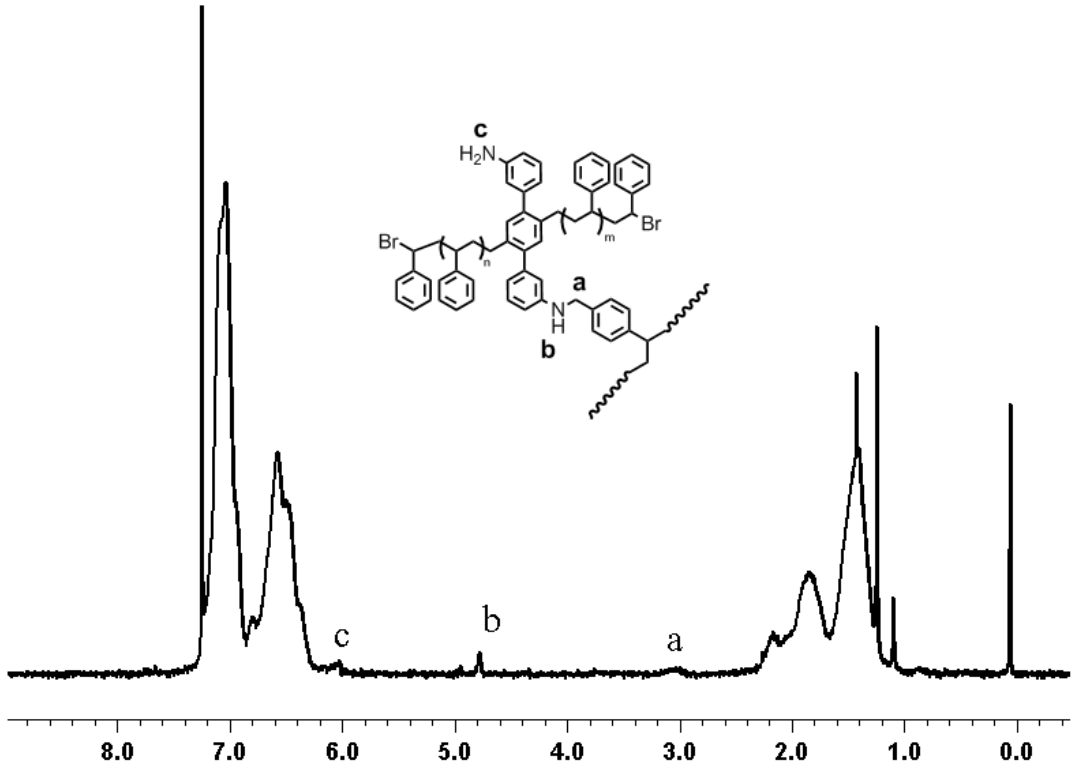


Figure 4.1 : ^{1}H-NMR spectrum of the aminomethyl linked polystyrene.

depending on the structure of the respective ATRP initiator, end-chain functional or mid-chain functional polymers were formed. As the functionalized polystyrene was intended to be used in further modification reactions, the conditions of ATRP (high concentration of initiator 0.1 M and low reaction time 45-60 minutes) were chosen to obtain a low molecular weight polymer, combined with a satisfactory conversion and polydispersity (Table 4.1).

In the case of the preparation of low molar mass benzoxazine derivatives, such by-products and partially ring opened oligomers can easily be removed by washing the crude products with NaOH solution. In order to recognize competing side reactions we have performed a control experiment in which conventional benzoxazine formation was achieved from phenol, aniline and paraformaldehyde in the presence

of commercial nonfunctional polystyrene sample. Indeed, the inspection of the ^{1}H-NMR spectrum of the isolated polystyrene indicated various additional Mannich reaction on the aromatic ring of the polystyrene backbone (Figure 4.2).

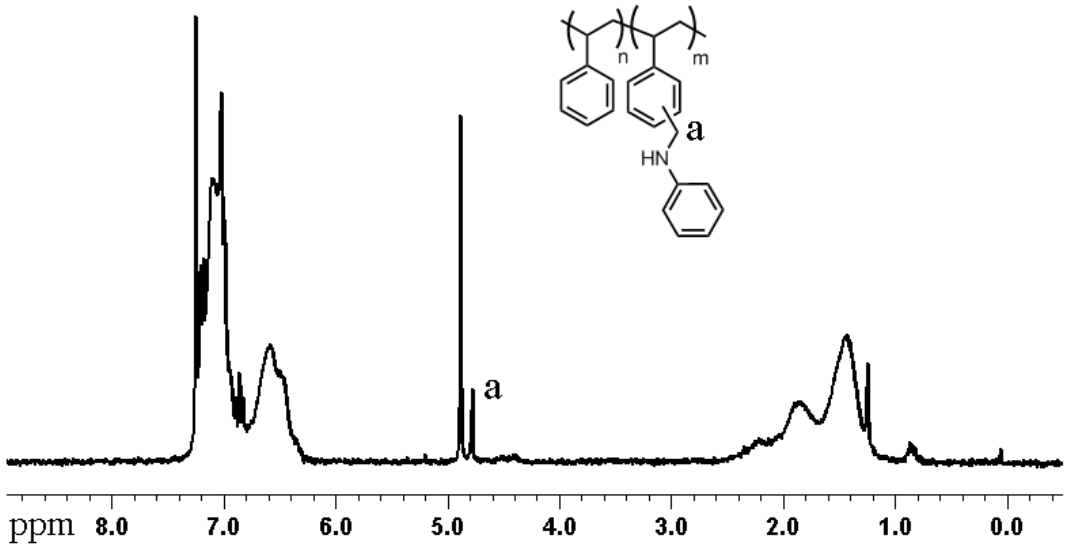


Figure 4.2 : ^{1}H-NMR spectrum of the product obtained from the control experiment.

Thus the conventional method was slightly modified and interactions of the amino functions with aromatic groups of the polystyrene backbone were prevented by using bulk phenol as both reactant and solvent. By this way, side reactions on the polymer backbone were eliminated and benzoxazine macromonomers readily obtained.

The structure of benzoxazine macromonomers, carrying polystyrene groups, was investigated by spectral methods (FT-IR and ^{1}H-NMR). In IR spectra of the macromonomers, the disappearance of the characteristic absorption bands at 3453 and 3376 cm^{-1} which they are the asymmetric and symmetric vibration modes of the amino groups is clearly noted. The absorption bands at 1225 cm^{-1} corresponds to an aromatic C–O streching frequency as in phenols and 944 cm^{-1} can be attributed to a C–O–C cyclic acetal vibrational mode as in oxazine ring (see figure 4.3 and 4.4)

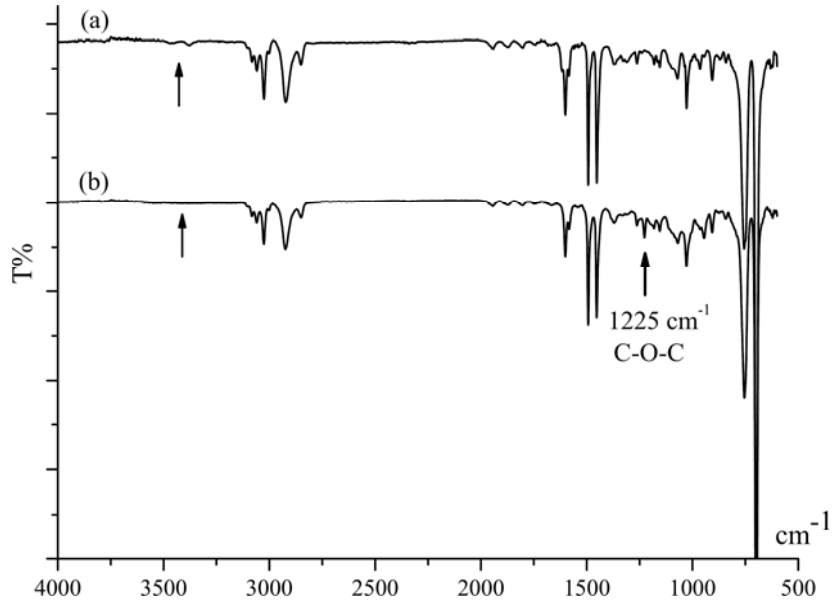


Figure 4.3 : FT-IR spectra of benzoxazine-functional polystyrene 4b (a) and amino- functional polystyrene 3b (b).

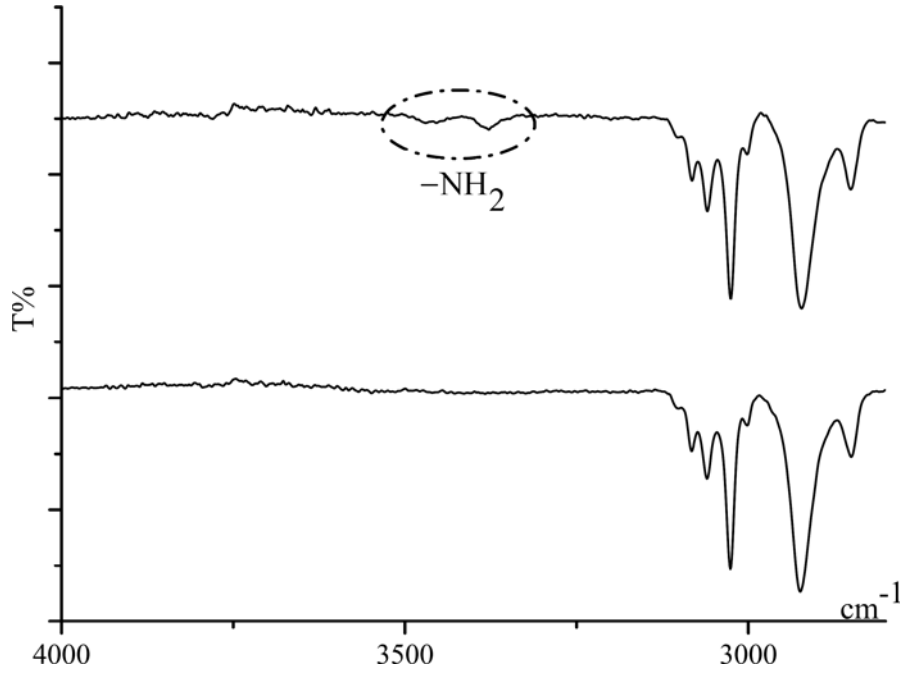


Figure 4.4 : Expanded FT-IR spectra of 4000-2800 cm^{-1} (a) 3b and (b) 4b.

In IR spectra of the end chain macromonomers reveal the characteristic absorption bands at 3453 and 3376 cm^{-1} which they are the asymmetric and symmetric vibration modes of the amino groups. After benzoxazine formation reactions those bands were disappered. Both end chain and mid-chain amino-macromonomers converted to benzoxazines as FT-IR shows (see figure 4.5 and 4.6 also vide infra figure 4.3 and 4.4).

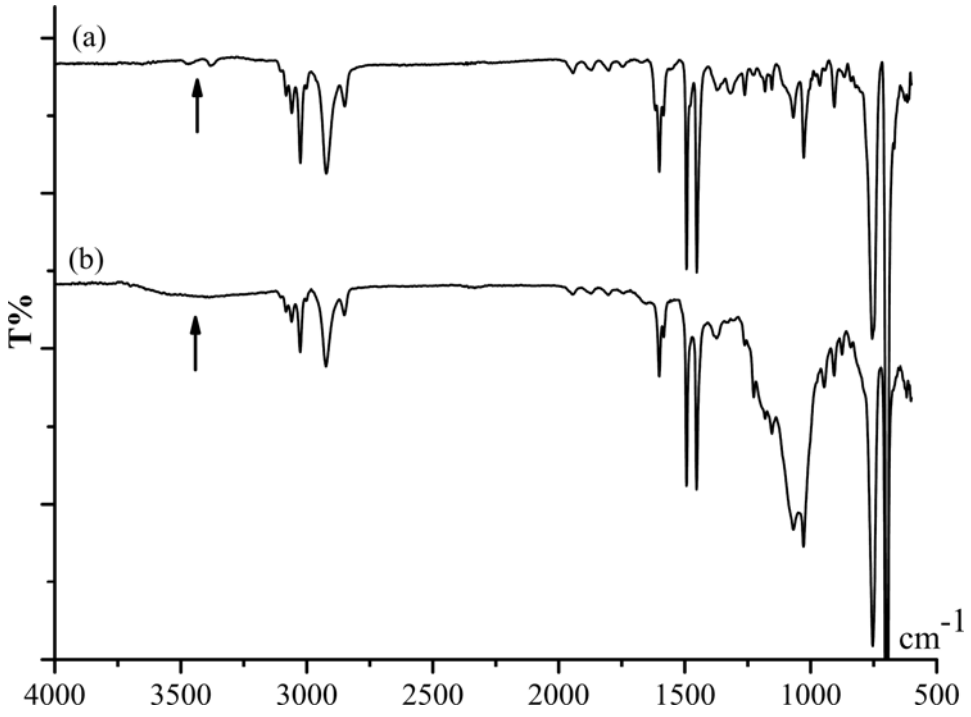


Figure 4.5 : FT-IR spectra of amino-functional polystyrene, 3a (a) and benzoxazine-functional polystyrene, 4a (b).

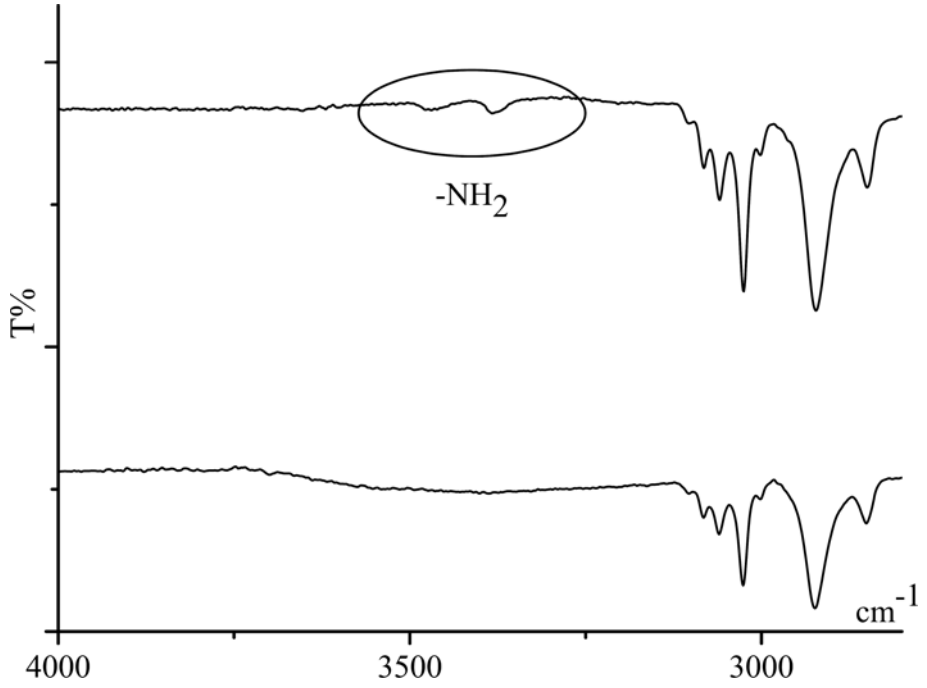


Figure 4.6 : Expanded FT-IR spectra of 4000-2800 cm-1 (a) 3a and (b) 4a.

The conversion of amino groups into benzoxazines was further confirmed by ^{1}H-NMR spectroscopy (Figure 4.7 and 4.8).

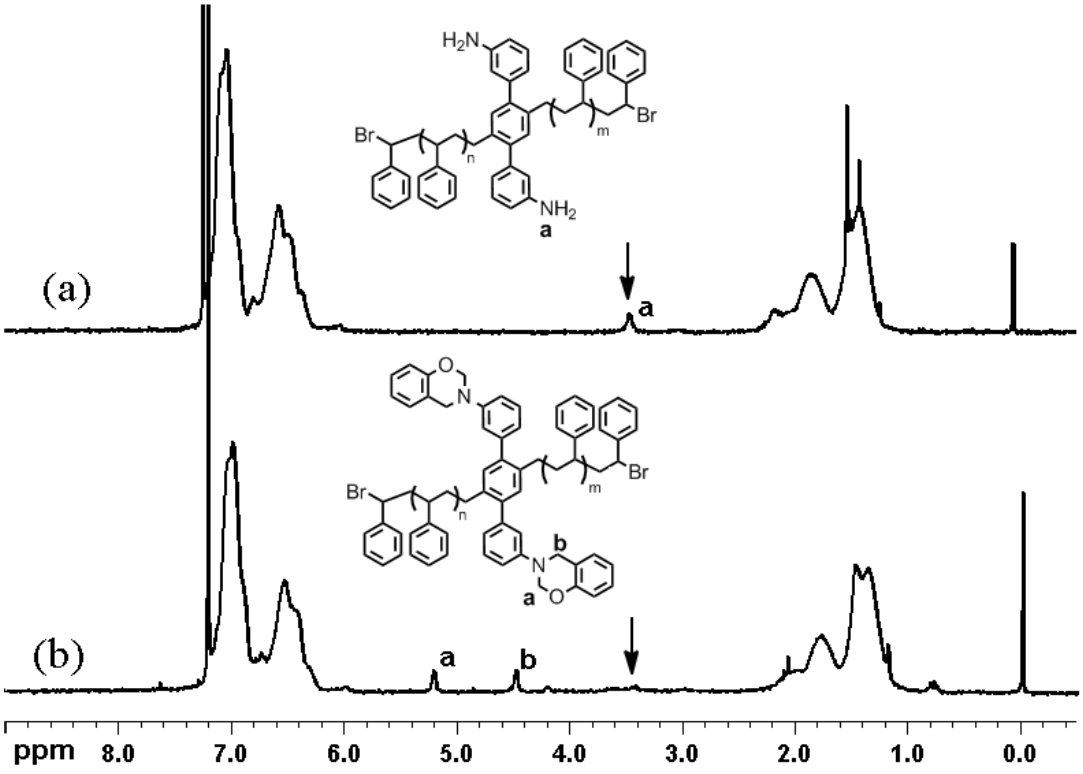


Figure 4.7 : ^{1}H-NMR spectra of 3b (a) and 4b (b).

The characteristic protons originating from the polystyrene chains appear in both spectra. Additionally, amino protons of the telechelic polymer (3b) appear at 3.47 ppm as was confirmed by their disappearance with D_2O exchange. The ^{1}H-NMR spectrum of benzoxazine functional PSt macromonomer exhibits two broad signals in the range of 5.2 and 4.5 ppm corresponding to $-CH_2$ protons of benzoxazine ring, i.e. Ar-C*H*$_2$-N and –O-C*H*$_2$-N, respectively. Moreover, one can observe the disappearance of the amino functionality at 3.47 ppm due to its consuming in benzoxazine synthesis.

The curing behavior of the macromonomers was examined by DSC. Figure 4.9 shows typical DSC thermogram of the macromonomer, 4b. An exotherm was observed in the first run for both macromonomers corresponding to the ring opening polymerization in addition to the glass transition (ca. 105ºC) of the polystyrene segment. The dissapearance of the exotherm in the second run was another indication for the ring opening process. Notably, both macromonomers became insoluble after thermal treatment. The onset and maximum of curing, and the amount of exotherms were collected in Table 4.2.

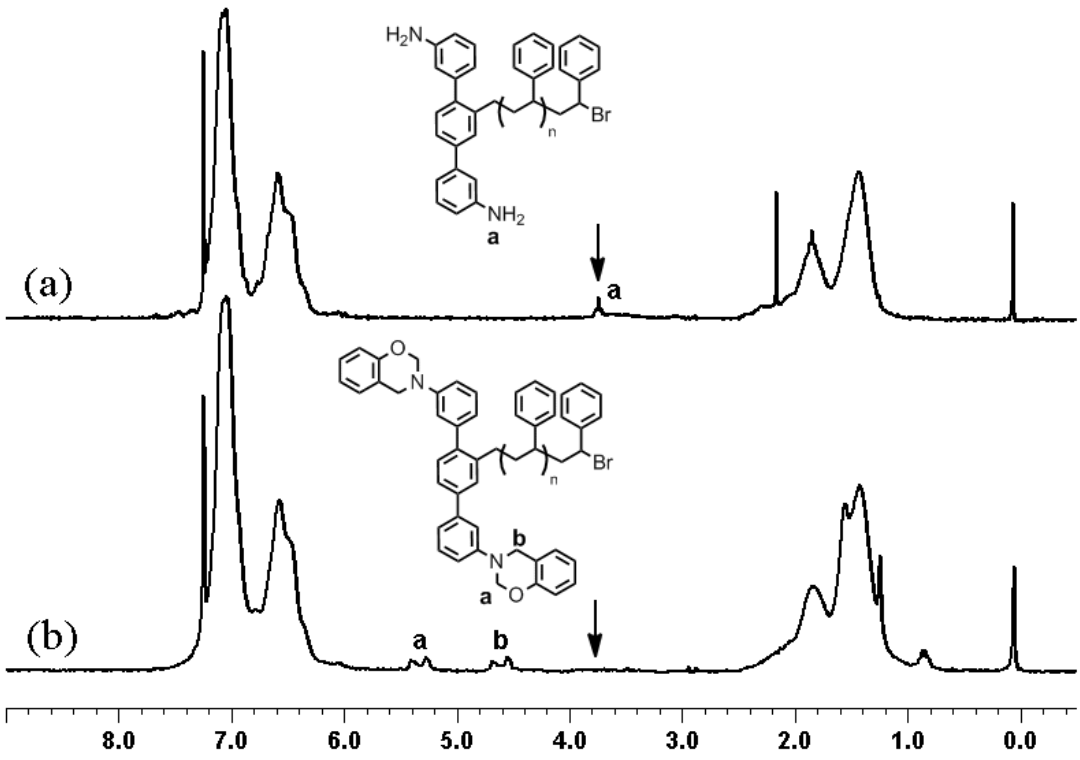


Figure 4.8 : ^{1}H-NMR spectra of 3a (a) and 4a (b).

As can be seen from the table, the polymerization of the macromonomer 4b, occurs at higher temperature than that of the macromonomer 4a, because benzoxazine rings of 4a and 4b have to encounter another benzoxazine ring for polymerization but due to restricted mobility of the benzoxazine rings of 4b compared to 4a, results in an increase at the cure temperature.

Benzoxazine type macromonomers were prepared via ATRP and coupling reactions as candidates for high-performance thermosetting application.

In this connection another telechlic synthesis was also achived. Instead of benzoxazines, naphthoxazines were used to incoorporate curable moeity as end chain of poly(ε-caprolactone). Tin octoate, $Sn(O(O)CCH(C_2H_5)C_4H_9)_2$, in short $Sn(Oct)_2$, is the most widely used initiator to synthesize designed polymers based on PCL [152].

Table 4.2 : DSC characteristics of benzoxazine macromonomers

Macromonomer	Onset of Curing (°C)	Maximum Curing Temp. (°C)	Amount of Exotherm (cal/g)
4b	244.6	271.1	2.08
4a	231.8	258.1	1.48

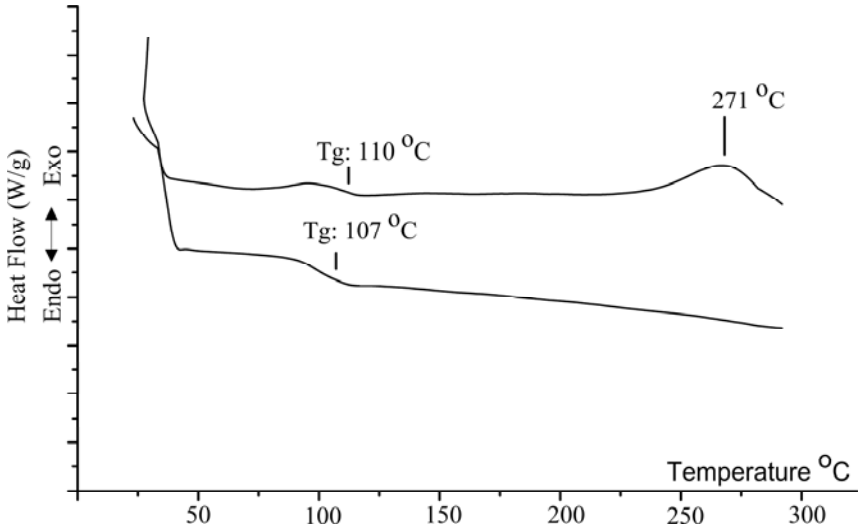
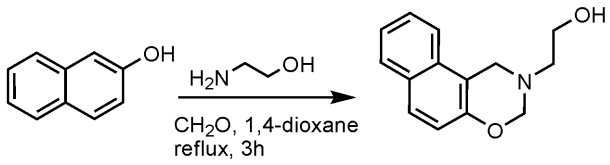


Figure 4.9 : DSC curves of benzoxazine-functional polystyrene 4b (a) first and (b) second run 30-300°C.

In particular when used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, linear and star-shaped block copolymers or networks can be obtained via corresponding alkyl octoate formation. In view of the reported role of hydroxyl groups as initiators of the ring-opening polymerization, the 2-(1*H*-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol (N-a-OH) is expected to produce polymers containing a naphthoxazine group on one end of the chain.

It is well known that benzoxazine or naphthoxazine monomers can easily be prepared from primary amines, and phenols or naphthols with formaldehyde. The synthesis of the initiator is shown in reaction 4.2. In this connection it should be pointed out that benzoxazine type initiators can also be synthesized by following the same strategy. However, attempts to synthesize the corresponding initiator resulted in the formation of side products. Thus the initiator was obtained only with a very low yield. Moreover, as it will be shown below, photochromophoric naphthalene ring present in N-a moiety gives possibility for the structural characterization of the intermediates at the various stages by using spectroscopic methods.



(4.2)

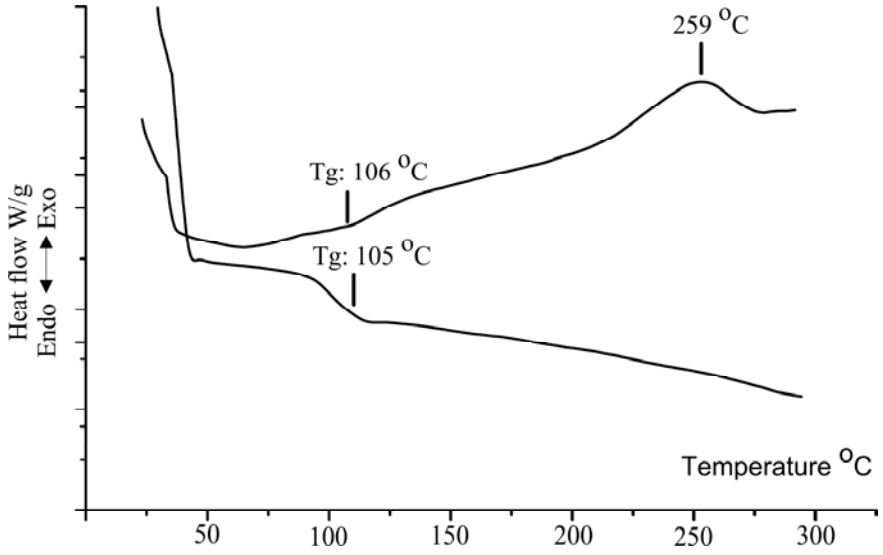


Figure 4.10 : DSC curves of benzoxazine-functional polystyrene 4a (a) first and second run 30-300°C.

The structure of the initiator was confirmed by elemental analysis as well as spectroscopic investigations. The FT-IR spectrum contains characteristic C-O (primary alcohol), Ar-O, aromatic overtones, aromatic C=C, and O-H bands at 1038, 1225, 1750-1909, 3059 and 3370 cm^{-1}, respectively (Figure 4.11).

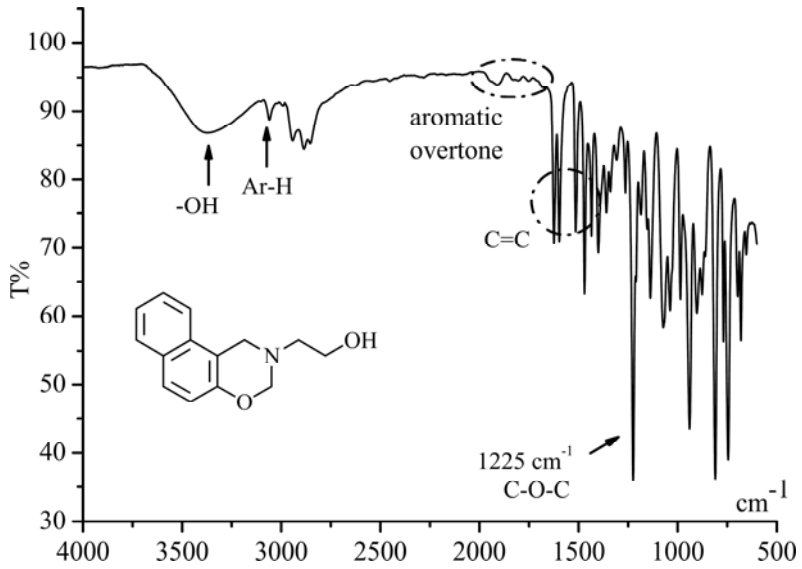


Figure 4.11 : FT-IR spectrum of 2-(1*H*-naphtho[1,2-e][1,3]oxazine-2-yl)-ethanol.

The ^{1}H-NMR spectrum recorded in $CDCl_3$ evidenced resonance signals of protons of relative intensities corresponding to the number and type of protons (Figure 4.12).

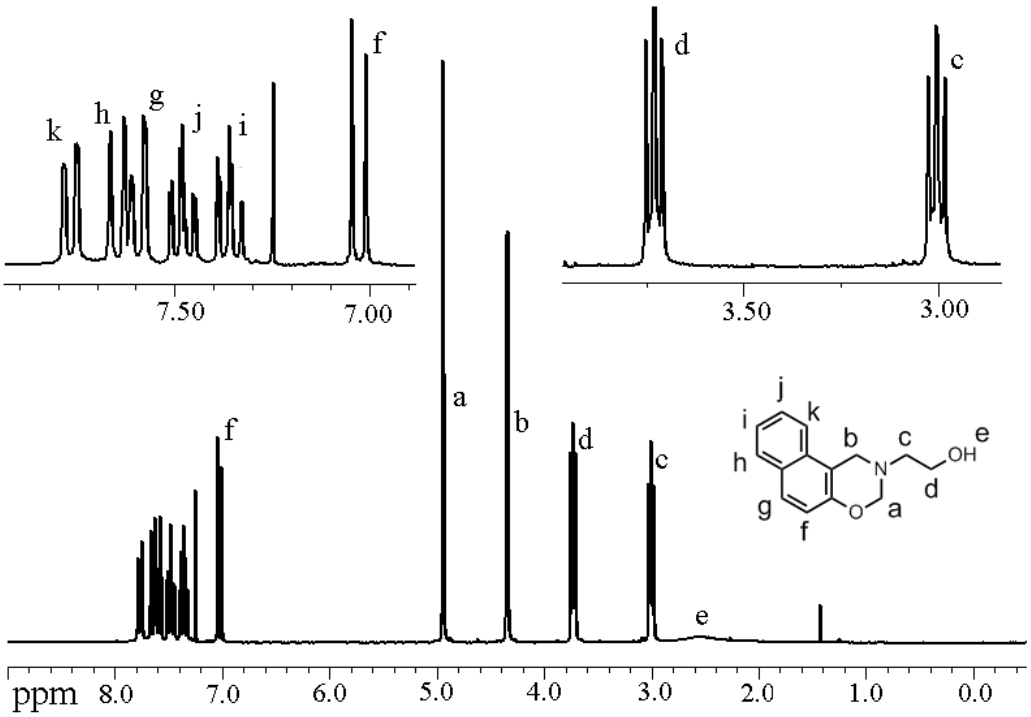
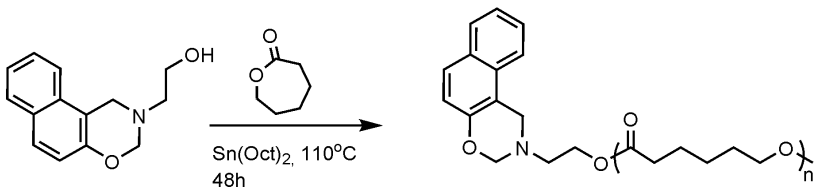


Figure 4.12 : [1]H-NMR spectrum of 2-(1*H*-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol.

The synthesis of naphthoxazine macromonomer of PCL (PCL-N-a) depicted in reaction 4.3, involved the reaction of N-a-OH with ε-caprolactone (ε-CL) in the presence of stannous octoate catalyst.



(4.3)

The results of the polymerization are given in Table 1. In our experiments, the amount of $Sn(Oct)_2$ catalyst was delibaretly kept low so as to prevent side-reactions such as intra- and inter-molecular transesterification.

Table 4.3 : Conditions and results of ROP of ε-caprolacton[a]

PCL	[N-a-OH]/[CL]	M_{nHNMR}	M_{nGPC} [b]
P1	1/20	5790	7020
P2	1/30	7830	9890

[a]T=110ºC, bulk, 48 h, $Sn(Oct)_2 = 2.5x10^{-6}$ mol
[b]Determined by GPC against PS standards

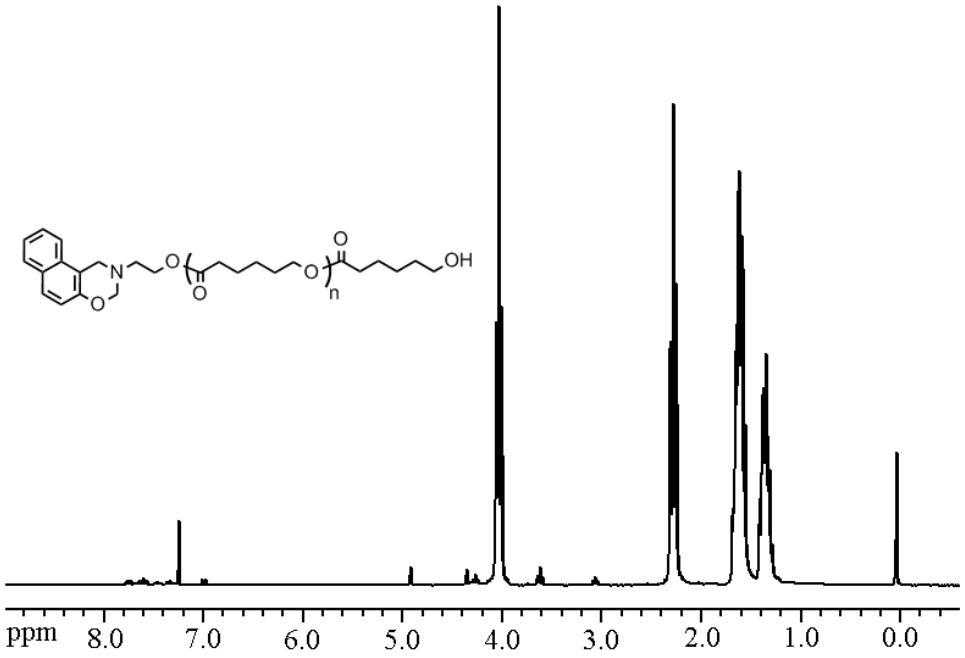


Figure 4.13 : ^{1}H-NMR spectrum of PCL-N-a.

As can be seen from Table 4.3, there is some discrepancy between the measured and H^{1}-NMR calculated $\overline{M}_n$ values. It is known that the true Mn determined for PCL is lower than tha calculations when polystyrene standards are used for GPC. Similar observation was made by Su et al for the benzoxazine functional PCL. In Figure 4.13 the ^{1}H-NMR spectra of the polymer can be found not only the specific signals of PCL but also absorptions relating to the naphthoxazine.

For example, the characteristic peaks of an oxazine ring can clearly be seen at 4.93 ppm (N-C*H*$_2$-O) and 4.35 ppm (Ar-C*H*$_2$-N), in addition to the aromatic protons of naphthyl group appearing at between 6.98-7.77 ppm.

A more detailed vision the figure 4.13 and 4.6-3.9 ppm interval reveals the end hydroxyl group proton in NMR spectrum (see figure 4.14 and 4.15).

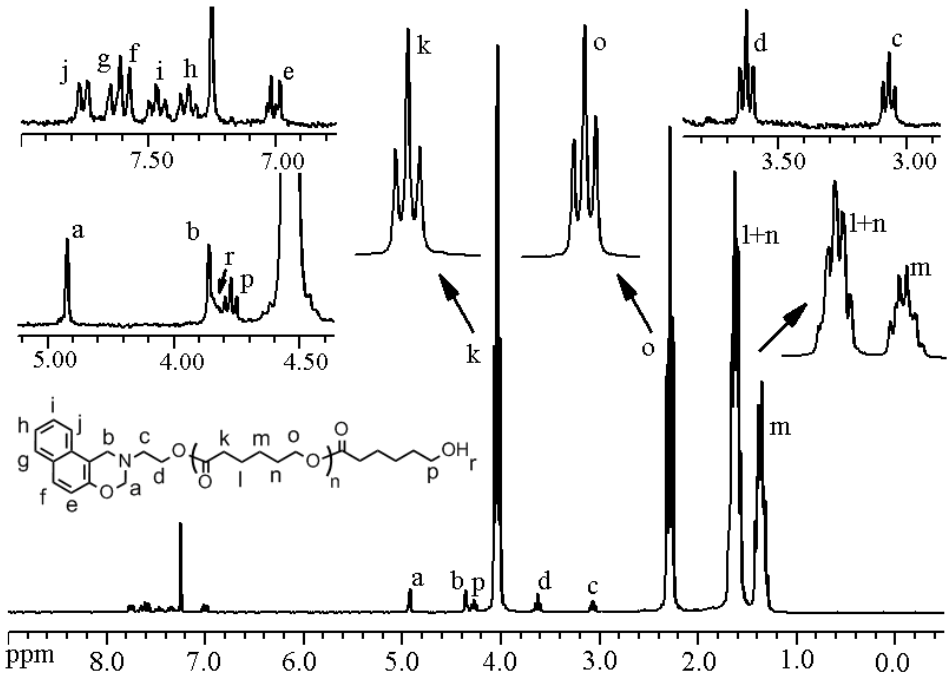


Figure 4.14 : Detailed vision the ^{1}H-NMR spectrum of PCL-N-a.

Incorporation of naphthoxazine groups was further evidenced by FT-IR spectral measurements. Figure 4.16 shows the FT-IR spectra of PCL without (neat) (a) and with (b) naphthoxazine end group.

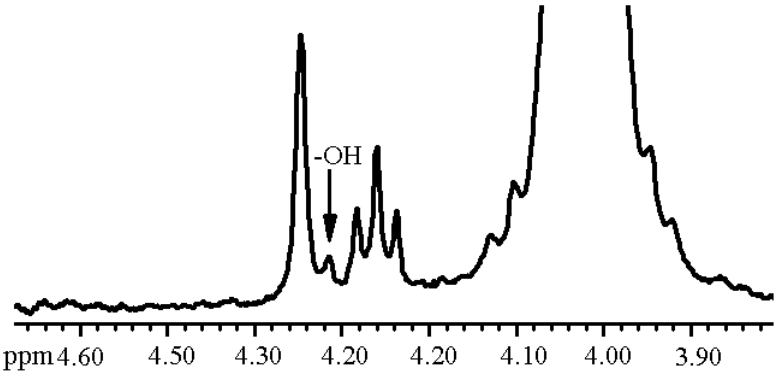


Figure 4.15 : 4.6-3.9 ppm interval of the ^{1}H-NMR of PCL-N-a.

It can be seen that spectrum (b) contains aborption bands at 1625 and 1594 cm^{-1} (C=C aromatic vibrations) and 806 cm^{-1} (aromatic C-H out of plane deformation bands) characteristic of naphthoxazine groups which were not present in the spectrum (a). Notably, CH_2 wagging of the oxazine ring are not detectable probably due to the relatively high molecular weight of the polymers.

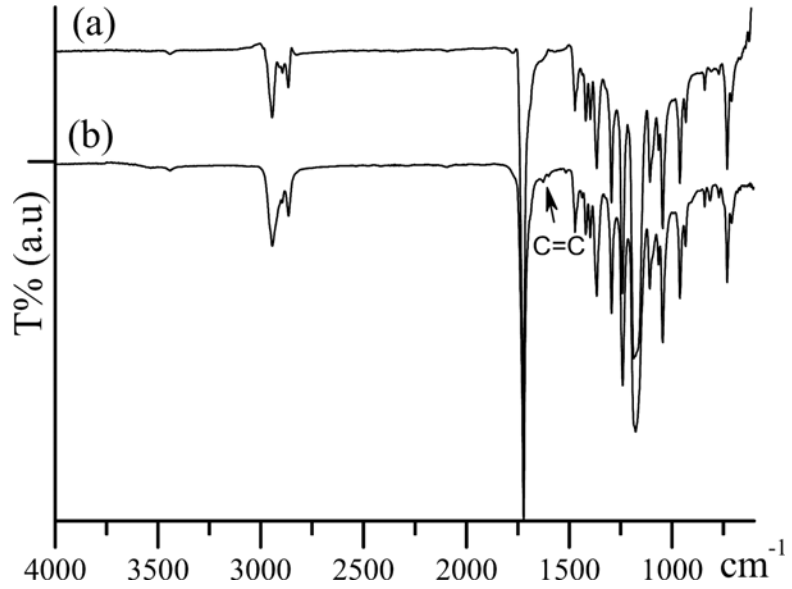


Figure 4.16 : FT-IR spectra of PCL without (neat) (a) and with (b) naphthoxazine end group.

GPC traces recorded with the macromonomer by using RI and UV detectors are shown in Figure 4.17. The dual detection provided a clear evidence for incorporation of the naphthoxazine group into polymer chain since PCL is transparent at the wavelength (335 nm) of the UV detector.

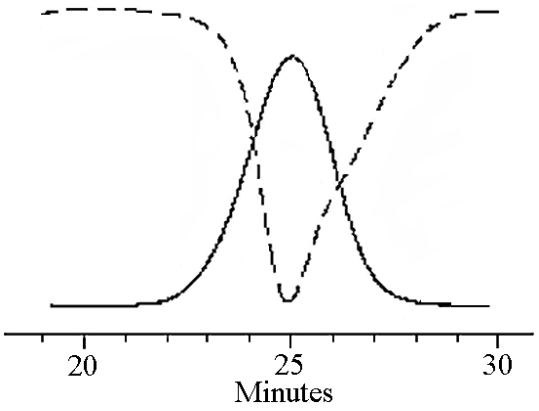


Figure 4.17 : GPC traces of PCL with naphthoxazine end group.

Figure 4.18, shows the fluorescence excitation and emission spectra of the naphthoxazine macromonomer in chloroform at room temperature. Because of the fact that only one naphthoxazine groups is present at the polymer chain end, rather weak signals were observed. However, both spectra show the vibration structures of the naphtalene chromophore indicating that naphthoxazine groups were conserved under the polymerization conditions.

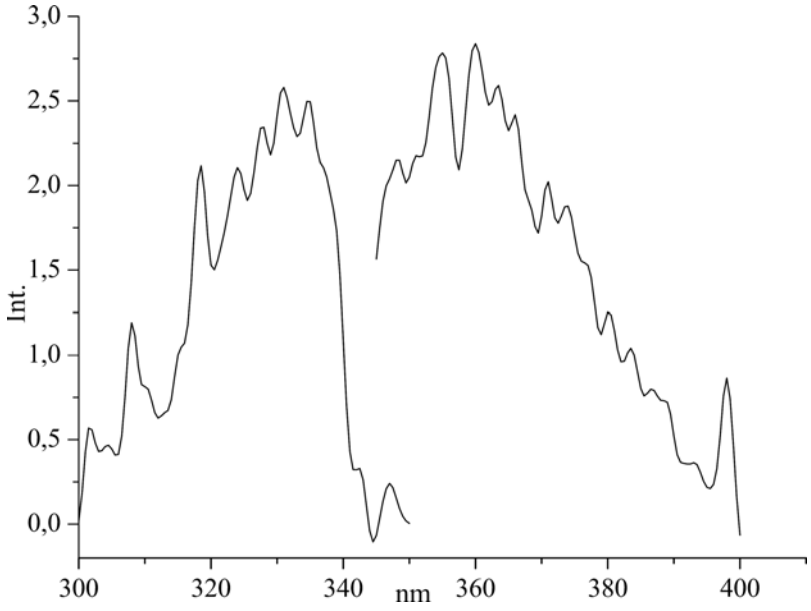


Figure 4.18 : Fluorescence excitation and emission spectra of the naphthoxazine macromonomer in chloroform.

As stated previously naphthoxazine groups are expected to undergo ring opening polymerization on heating in a similar manner to benzoxazine monomers. In figure 4.21, DSC traces of the related naphthoxazine is shown. Because of the polymeric nature, the ring opening process could not be monitored neither by the disappearance of the benzoxazine mode in IR spectrum nor by the exothermic peak observed in DSC thermograms. In this connection, it should be pointed out that the benzoxazine functional PCL macromonomers also do not exhibit the exotherms that observed with low molecular weight benzoxazines. However, ^{1}H-NMR and FT-IR investigations confirm the ring opening of the naphthoxazine groups. In the NMR spectrum of the PCL-N-a after 1 h at 200ºC, the disappearance of the benzoxazine ring and broadening of aromatic peaks belonging to naphtyl group are clearly observed (Figure 4.19).

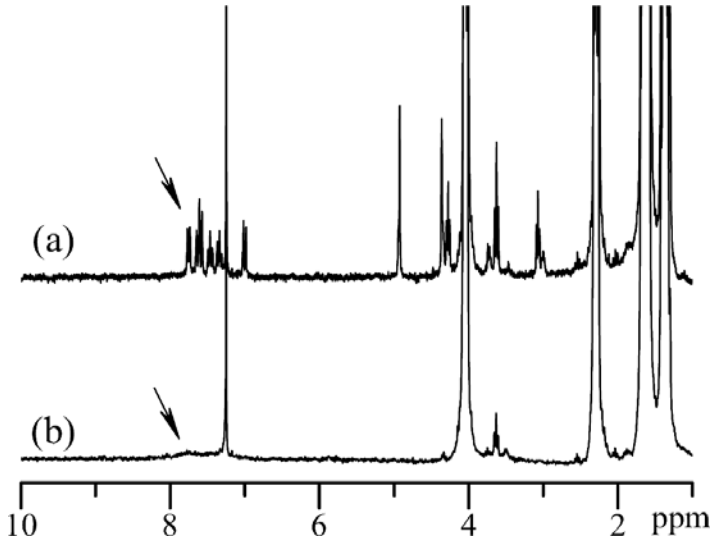


Figure 4.19 : ^{1}H-NMR spectra of (a) PCL-N-a and (b) cured PCL-N-a.

As can be seen from the FT-IR spectrum of the cured PCL-N-a, aromatic C-H stretching vibrations of naphthyl group at 3060 cm^{-1} are evidencing incorporation of naphthoxazine groups (Figure 4.20 (a)).

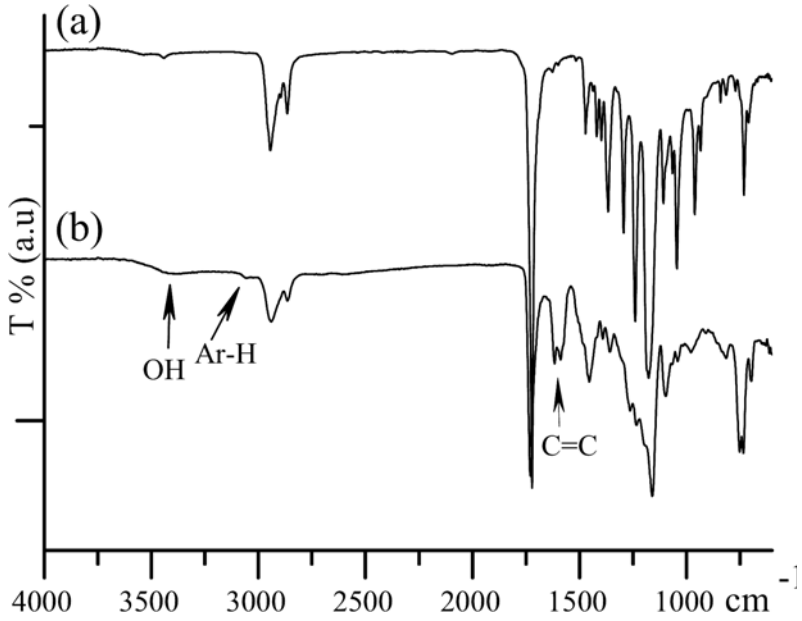


Figure 4.20 : FT-IR spectrum of the curedd PCL-N-a (a) and thermally polymerization macromonomer in the absence of added benzoxazine (b).

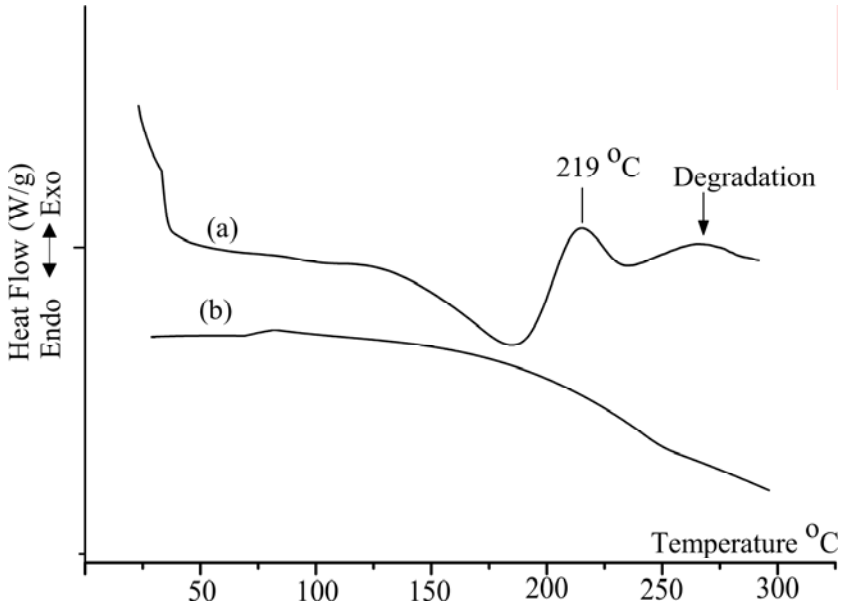


Figure 4.21 : DSC traces of the 2-(1*H*-naphtho[1,2-e][1,3]oxazin-2-yl)-ethanol (a) first and (b) second run.

We have also studied the curing behavior of the blends. DSC thermograms of the benzoxazine monomer (P-a)/(PCL-N-a) blends for various PCL-N-a concentrations are shown in Figure 4.22 (see Reactions 2.1 or 3.1 for the structure of P-a). (a) 100% PCL with (b) 75% PCL N-a, 25% P-a, (c) 50% PCL N-a, 50% P-a; (d) %25 PCL N-a,75% P-a; (e) 100% P-a. Only one exhotermic peak was found for all concentrations which are similar to the benzoxazine monomer and its blend with neat PCL [74, 75]. However, the curing exothermic peak shifts toward a higher temperature as the concentration of PCL-N-a increases. As both the onset and peak temperatures appear at higher temperatures as more PCL macromonomer is added into the benzoxazine monomer, the ring opening polymerization can be considered as delayed process.

Even though the macromonomer also contains naphthoxazine end groups, the concentration of polymerizable groups is diluted with by PCL component and it becomes more difficult to develop the network structure. Similar trend was also observed with the neat PCL blends. It was shown that the cured products of such blends exhibit hydrogen bond formation between the hydroxyl groups of polybenzoxazine and the carbonyl groups of PCL. In our case, in addition to such interactions, PCL segments are chemically bound to the network since naphthoxazine groups also polymerize during the thermal process. Indeed, treatment of the cured product with THF and dichloromethane, which are known as solvents for PCL did not remove any polymer.

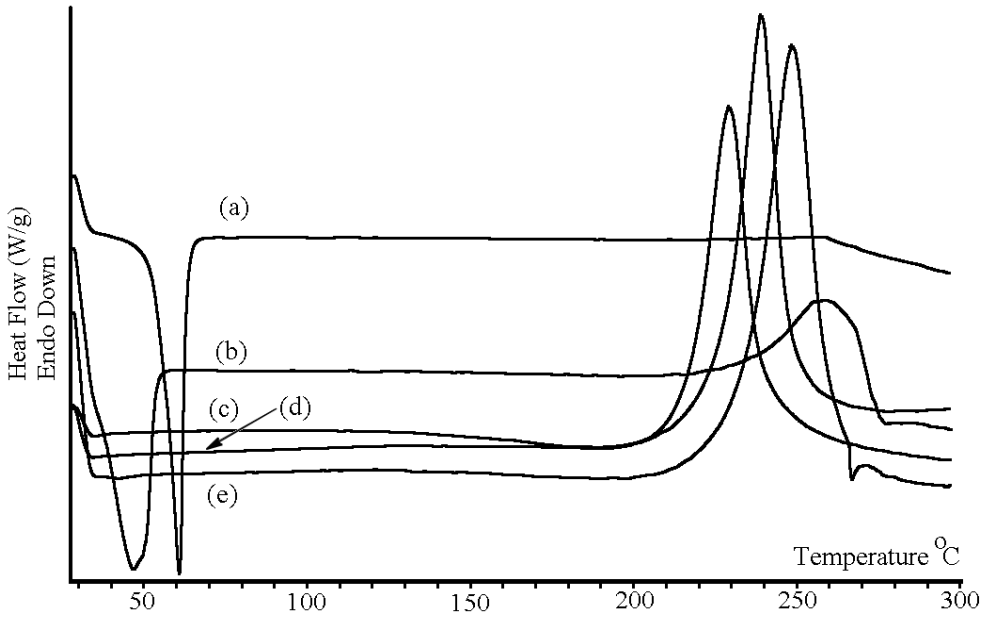
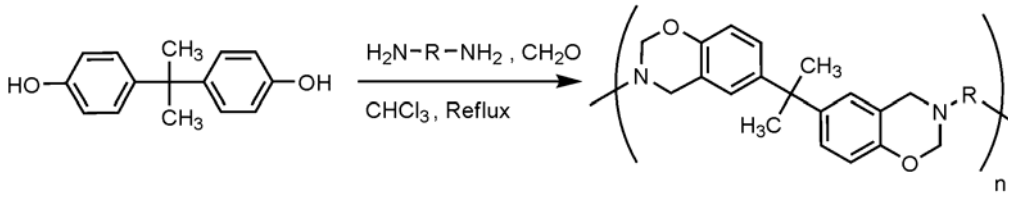


Figure 4.22 : DSC thermograms of the benzoxazine monomer (P-a)/ (PCL-N-a) blends for various PCL-N-a concentrations.

Moreover, the IR spectra of this product exhibited characteristic carbonyl band at 1728 cm^{-1} indicating successful incorporation of PCL segments. When this spectrum is compared with that of the thermally polymerized macromonomer in the absence of added benzoxazine (*vide antre*, Figure 4.20 (b)) OH band shifts appeared at 3374 cm^{-1}. In the spectrum aromatic C-H stretching vibration is also noted.

Naphthoxazine type PCL macromonomers were prepared via ring opening polymerization of ε-CL using $Sn(Oct)_2$ alkyl octoate formation. Such prepared narrowly distributed macromonomers undergo thermal ring opening polymerization. When used in conjunction with conventional benzoxazine monomers, the cured products contain chemically incorporated PCL segments which may significantly influence physical and mechanical properties.

Concept of oligomeric benzoxazine resins where oxazine rings are in the main chain and experimental study was reported. Very recently, more detailed studies of a synthetic approach for the preparation of polymers containing benzoxazine moieties in the main chain was independently reported. In this approach, polybenzoxazine precursors were prepared by benzoxazine ring forming reaction in a step-wise manner using bisphenol A, bifunctional amine and formaldehyde (4.4).



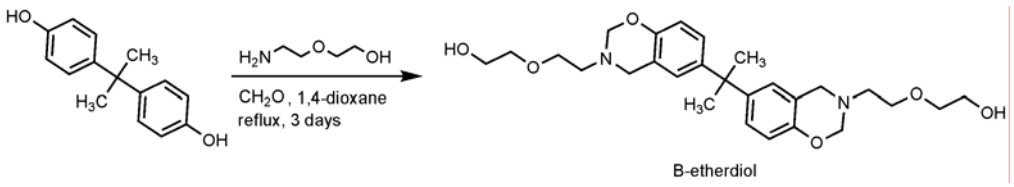
(4.4)

As reported, transparent thin films were easily prepared by solvent casting of the solutions of the resulting polymers. The films retained their shape after thermal curing.

Aiming at expanding their industrial applicability, it seemed appropriate to prepare a family of highly flexible benzoxazine polycondensates, tailored to meet different requirements, depending on the specific application. Our working concept is based on creating polymeric backbones integrating segments that induce molecular flexibility, on one hand, and that comprise thermally curable benzoxazine moieties, on the other hand.

This part of the thesis describes synthesis and characterization of polyetheresters containing benzoxazine moieties in the main chain and differing in the segments with two components, namely adipoyl and terephthaloyl groups. These polymers consist of benzoxazine units which create cross-linked network and impart the polybenzoxazine properties, while the etherester units form the soft segments along the backbone.

The polyester family is extremely large and, depending on the nature of monomers, exhibits an enormous variety of structures, architectures, properties, and, therefore, applications. Thus, synthesis of suitable monomers for esterification is required to tailor polyester properties. In our work, we selected amino ethanol containing oxyethylenic spacer group as the primary amine component in the benzoxazine ring forming reaction to introduce flexible ether groups in the final benzoxazine polyester. Hence, diol containing benzoxazine was synthesized as the monomer for the subsequent polyesterification process by reacting 4,4′-isopropylidenediphenol, 2-(2-aminoethoxy)ethanol, and paraformaldehyde, as shown in reaction 4.5. In this connection, it should be pointed out that the attempts to synthesize the corresponding benzoxazine diols by using either ethanolamine or 3-amino-1-propanol were either failed or produced negligible amounts of the products.



(4.5)

The structure of the diol monomer, successfully prepared from 2-(2-aminoethoxy)ethanol, was confirmed by spectral and thermal analysis. As can be seen from Figure 4.23 the ^{1}H-NMR spectrum of the monomer exhibits not only the specific signals of the benzoxazine ring, but also chemical shifts that belong to the alkyl chain and hydroxyl groups. Notably, while the two signals at 4.8 and 4.0 ppm corresponds to –C***H*****$_2$** protons of benzoxazine ring, methyl protons of the isopropylidene group at 1.6 ppm (singlet, 6*H*). Alkyl protons of the ethoxyethanol group resonate at 3.0 ppm (triplet, -N-C***H*****$_2$**, 4*H*), 3.6 ppm (triplet, HO-C***H*****$_2$**, 4*H*), 3.7 ppm (broad triplet, O-C***H*****$_2$**, 8*H*), and the O*H* protons at 3.7 ppm.

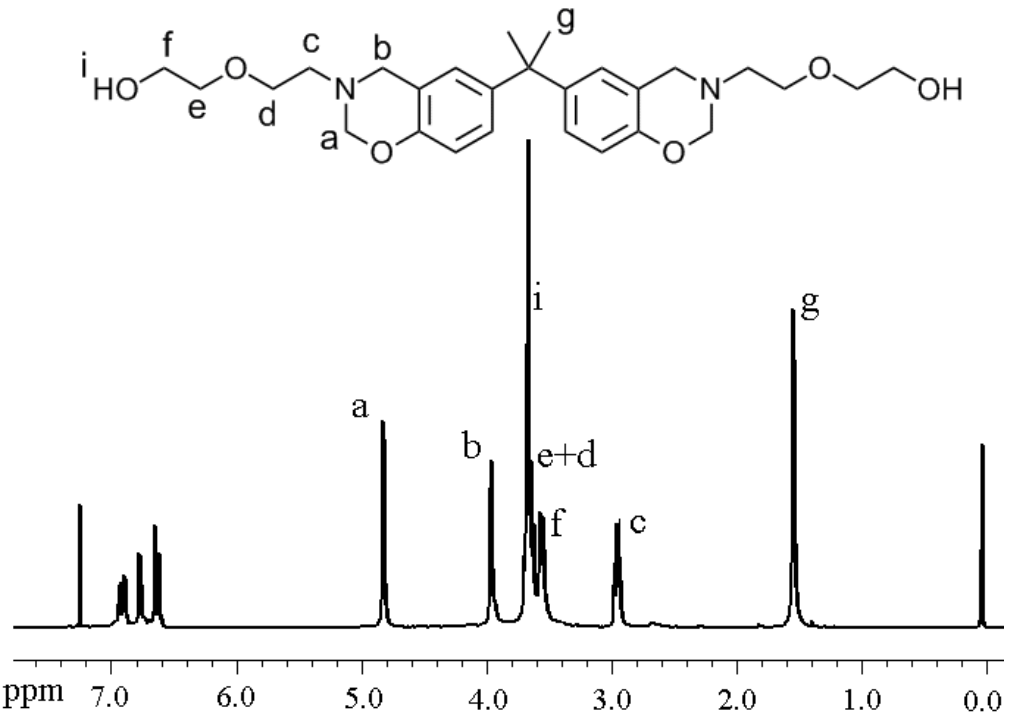


Figure 4.23 : ^{1}H-NMR spectrum of the B-etherdiol.

It is known that hydrogen and deuterium nuclei are very different in their magnetic properties. Thus it is possible to distinguish between them by NMR spectroscopy with the help of a chemical reaction in which a covalently bonded hydrogen atom is replaced by a deuterium atom, or vice versa. In Figure 4.24, ^{1}H-NMR and its D_2O exchange spectra of the monomer are overlaid. Sharp decrease of the intensity of the

O*H* proton at 3.7 ppm and the appearance of the *H*OD proton signal at 4.8 ppm are clearly detected.

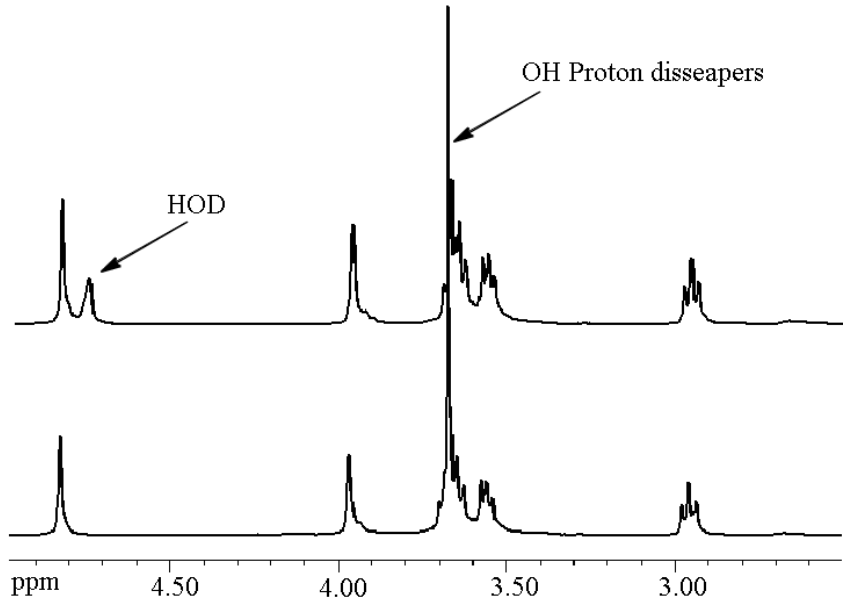


Figure 4.24 : ^{1}H-NMR and its D_2O exchange spectra of diol containing benzoxazine (B-etherdiol).

Moreover, the FT-IR spectrum of the monomer further evidences the expected structure. As can be seen from Figure 4.25, in addition to the band corresponding to the C-O-C oxazine ring mode at 1390 cm $^{-1}$ and aromatic C-H stretching vibration at 3002 cm^{-1} , the O-H and C-O (aliphatic ether and primary alcohol) stretching bands at 3391 cm^{-1}and 1120, and 1059 cm^{-1}, respectively, were noted. Furthermore, the band at 931 cm^{-1} is the mode that arises from the benzene ring to which oxazine ring is attached.

It is known that 1,3-benzoxazines exhibit exothermic ring opening reaction around 200-250ºC, which can be monitored by DSC. The thermogram presented in Figure 4.26 reveals a ring opening exotherm with an onset at 180ºC and a maximum at 202ºC, and 74.6 J/g as the exothermic energy. Notably, a degradation process begins after 247ºC. According to TGA studies of monomer majority of weight loss is observed between 240- 300 °C which also observed in poly(vinylalcohol) (PVA) as water elimination. So this degradation can be attributed to water elimination and also water triggered formation of other volitiles such aldehydes and ketones as observed in PVA degradation.

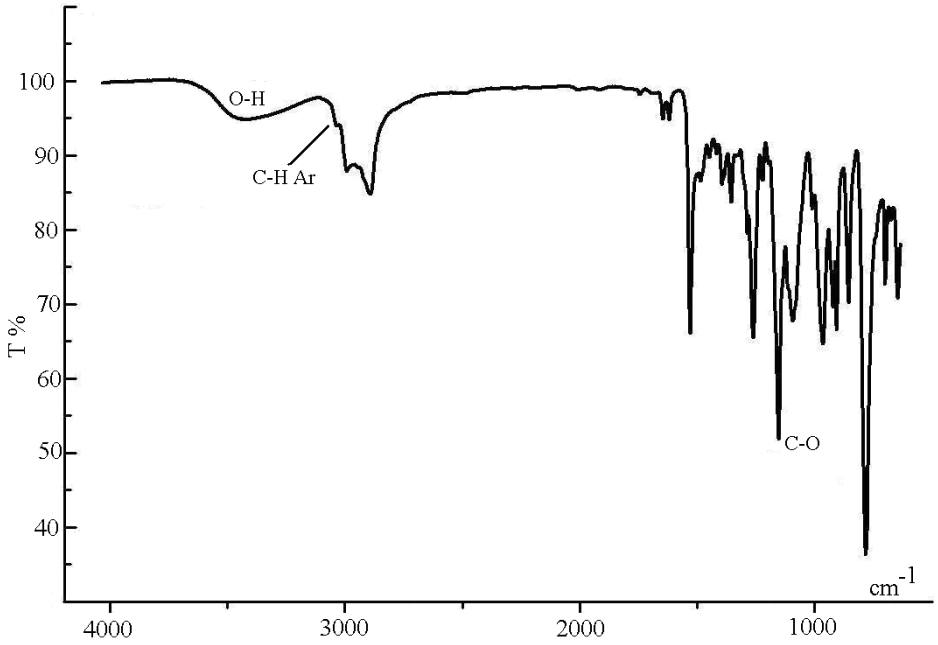


Figure 4.25 : FT-IR spectrum of diol containing benzoxazine (B-etherdiol)

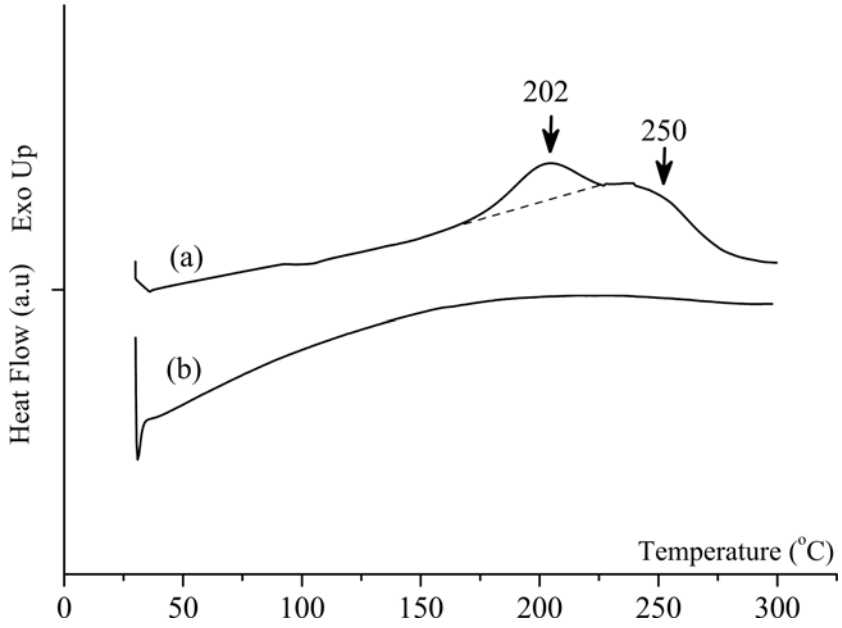
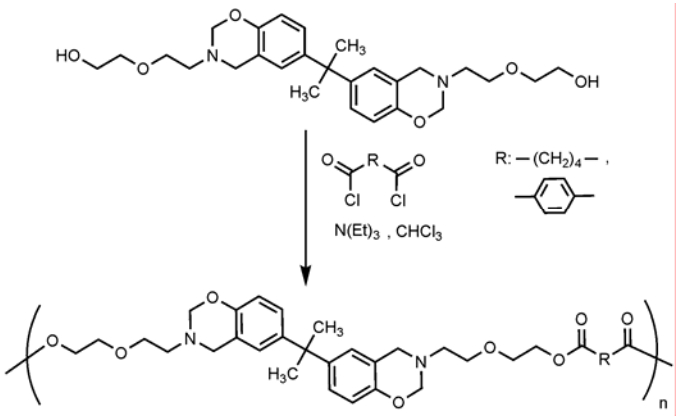


Figure 4.26 : DSC thermogram of diol containing benzoxazine (B-etherdiol) (a) first run, (b) second run.

Polyesters can be obtained by a wide range of reactions, the most important being polyesterifications between diacid chlorides and diols or their derivatives. Adipoyl chloride and terephtalolyl dichloride were used as the diacid chloride components to obtain desired polyetheresters. The polymerization reactions were achieved by using excess triethyl amine to trap the released HCl. This is an important provision for the conservation of the benzoxazine ring as acids readily react with benzoxazines resulting in ring opening (reaction 4.6).



(4.6)

The ^{1}H-NMR spectra for both polyetheresters were measured to confirm the structures. The ^{1}H-NMR spectrum of the polyetherester, derived from adipoylchloride (PEE-BAd), shown in Figure 4.27, indicated the characteristic peaks assigned to methylene protons of the oxazine ring at 4.8 and 4.0 ppm. Moreover, the polyester formation was evidenced by the shift of the signal from 3.6 ppm, corresponding to HO-CH_2 protons that appeared in the spectrum of the monomer (see Figure 4.22), to 4.2 ppm. Aliphatic protons of propane-2,2-diyldiphenolic structure appears at 1.6 ppm with aliphatic protons of adipoyl group. Also, the protons of CH_2-C=O ester emerge at 2.3 ppm are further evidencing the formation of ester bond.

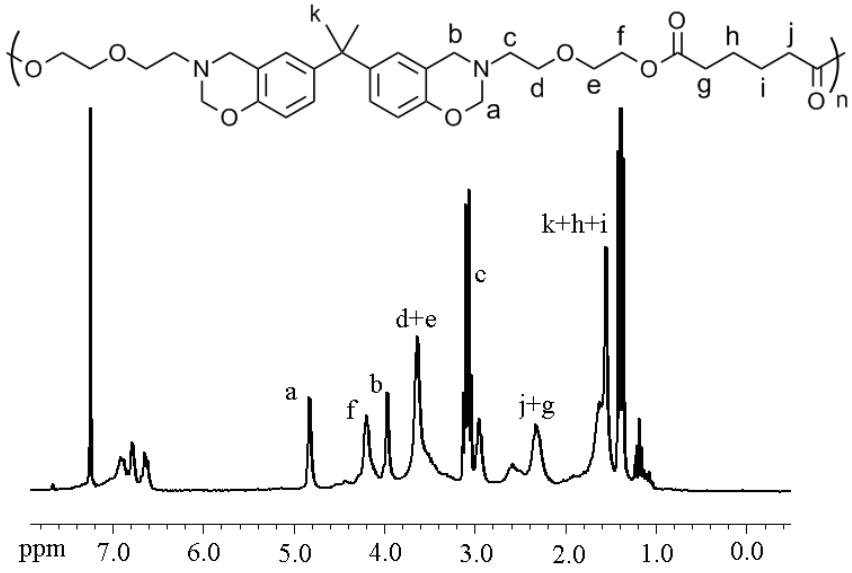


Figure 4.27 : ^{1}H-NMR spectrum of PEE-BA.

The structure of the polyetheresters was also confirmed by FT-IR. Figure 4.29 shows the IR spectra of the polyetheresters. The characteristic carbonyl stretching vibrations

were observed at 1721 cm^{-1} and 1730 cm^{-1} for PEE-BA and PEE-BT, respectively. In addition, the respective aromatic C-H stretching vibrations of the polyesters at 3014 cm^{-1} and 3046 cm^{-1} are noted. Also, C-O vibration modes of ether and ester linkages, and benzene ring mode frequencies related to benzoxazine are detectable between 1017 and 1260 cm^{-1}, and 900 - 933 cm^{-1}, respectively.

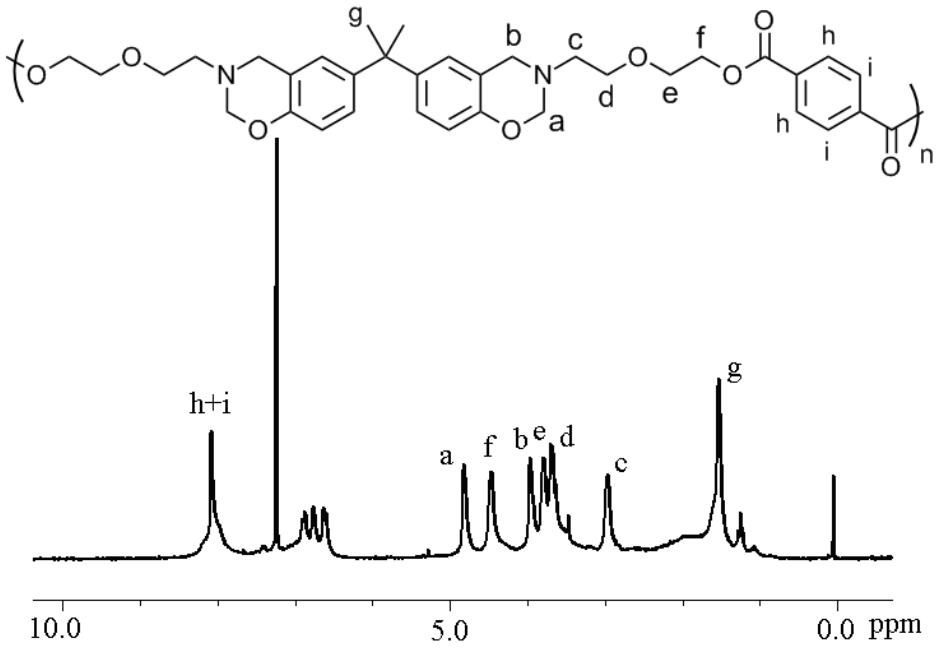


Figure 4.28 : ^{1}H-NMR spectrum of PEE-BT

DSC was used for characterizing the curing behavior of the polyetheresters (Figure 4. 30). As stated previously, benzoxazine groups are expected to undergo ring opening polymerization. This exothermic event was detected for both polymers. PEE-BA exhibited an onset at 215ºC and a maximum at 250ºC with 105 J/g of exotherm energy. Similarly, for PEE-BT, the onset of the exotherm started at about 210ºC with a maximum at 243ºC, and 95 J/g as the heat of polymerization. Expectedly, both polymers resembled almost the same thermal properties as they are structurally similar and every repeating unit contains one benzoxazine unit. The slight difference observed for the amount of exotherm is probably due to the difference of the molecular weights, and aliphatic and aromatic nature of the adipoyl and terephthaloyl components.

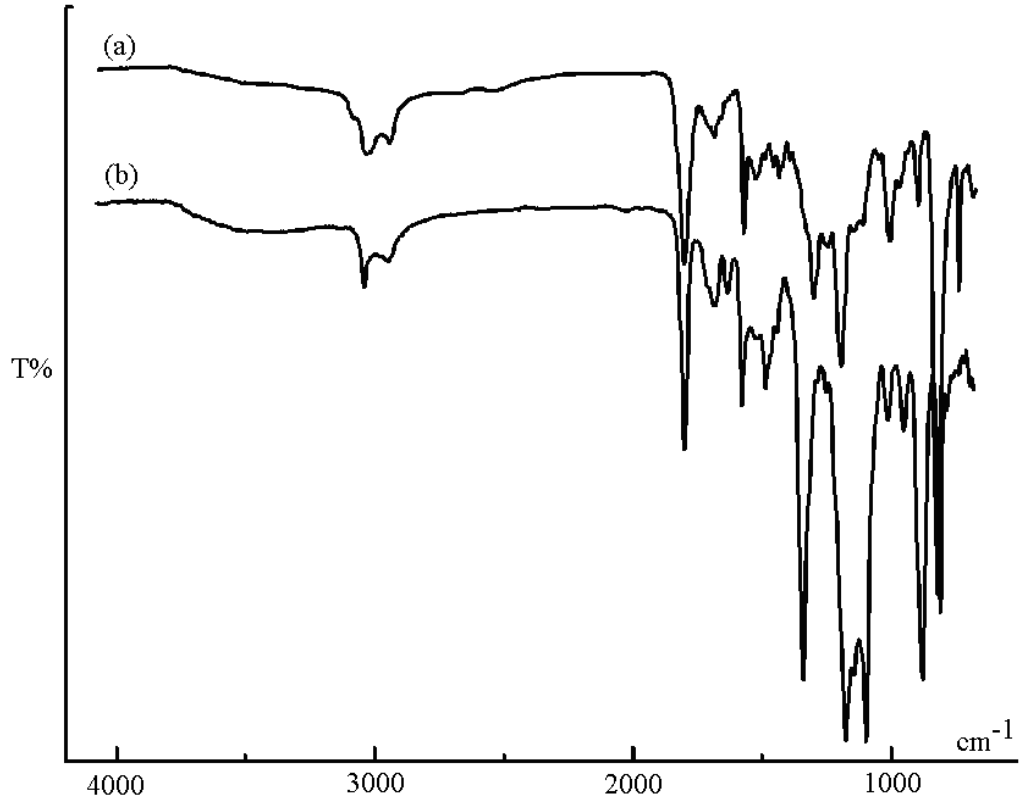


Figure 4.29 : IR spectra of the polyetheresters.

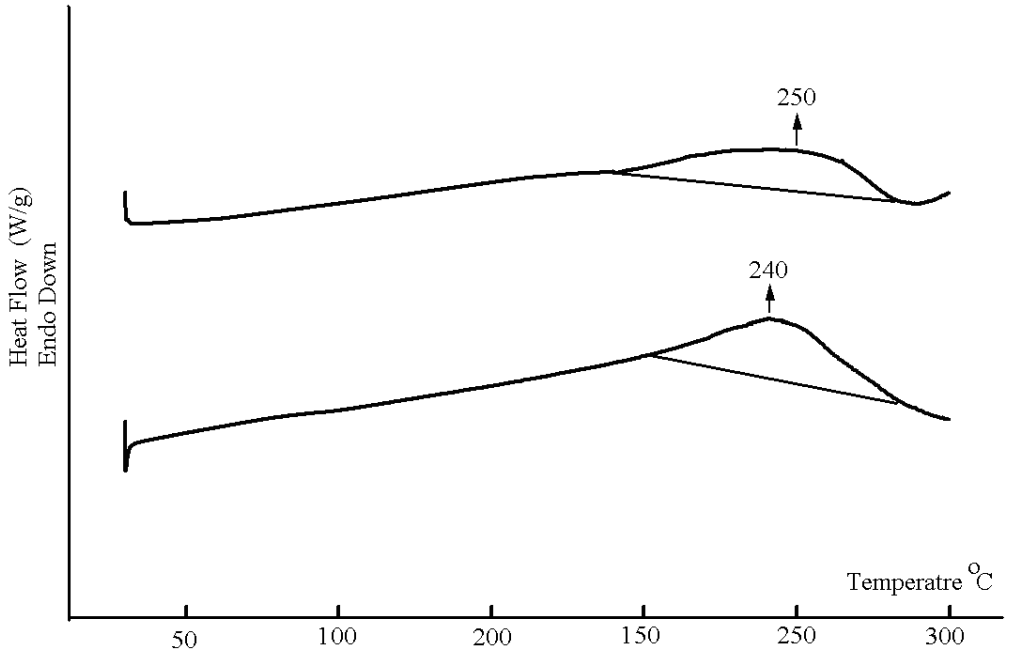


Figure 4.30 : DSC traces of the polyetheresters (a) adipoyl (b) terephthaloyl derivatives.

However, the thermal stabilities of the PEEs were not similar. The comparative TGA is illustrated in Figure 4.30 and the results are summarized in Table 4.4.

Table 4.4 : Thermal properties of the cured polyetheresters (PEE-BT and PEE-BA) and low-molecular weight benzoxazine (P-a)

Polymer	$T_{5\%}$ (ºC)	$T_{10\%}$ (ºC)	T_{max} (ºC)	Y_c (%)
Cured P-a	298	346	421	34
PEE-BA	248	278	397	22
PEE-BT	288	328	386	36

$T_{5\%}$: The temperature for which the weight loss is 5%
$T_{10\%}$: The temperature for which the weight loss is 10%
Y_c: Char yields at 800°C under nitrogen atmosphere

PEE-BT exhibited higher thermal stability because of the additional aromatic group content imparted by the terephthaloyl group. This stability is also comparable with that of the cured mono-functional aniline derived benzoxazine (P-a cured) (see Reactions 2.1 or 3.1 for the structure of P-a). Interestingly, the char yield of cured PEE-BT is even higher than that of cured P-a. This enhancement in the thermal stability can again be attributed to additional aromatic groups and also to the increase in the cross-linking density due to the extension of the network.

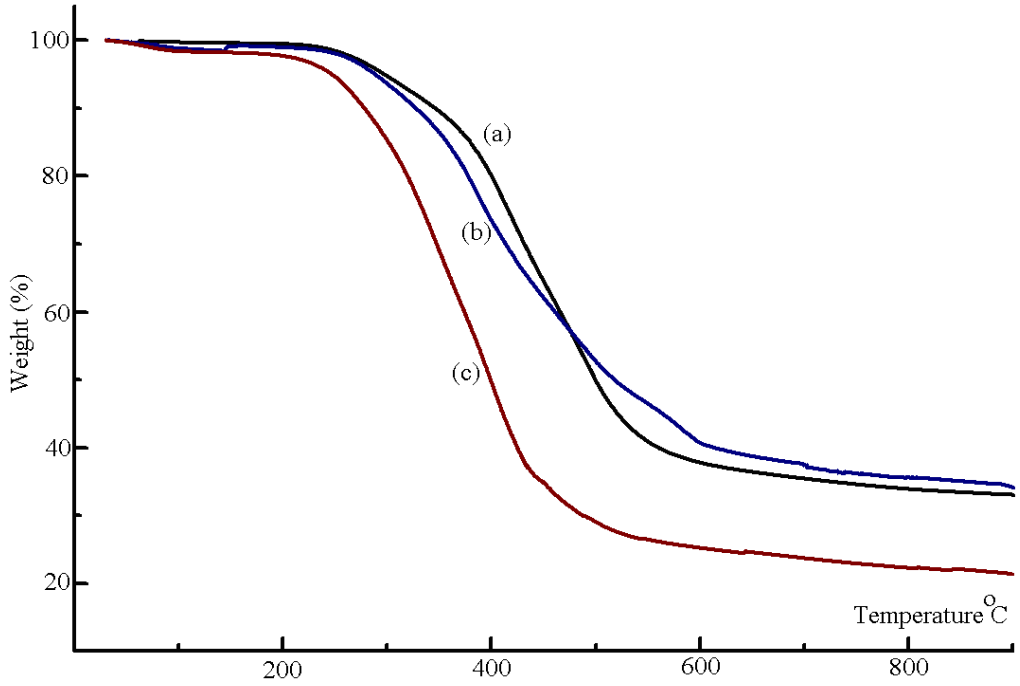


Figure 4.31 : TGA thermograms of (a) cured P-a, (b) cured PEE-BT, (c) cured PEE-BA.

The film forming property and flexibility of the polyetheresters were also demonstrated. For this purpose, free standing films were prepared by solvent casting of the polymers from chloroform solutions on Teflon plates. As can be seen from Figure 4.32, the PEE-BA film is completely bendable without any problem. After

gradual heat treatment between 100-240°C, a cured film retained its size and shape and but its flexibility was reduced.

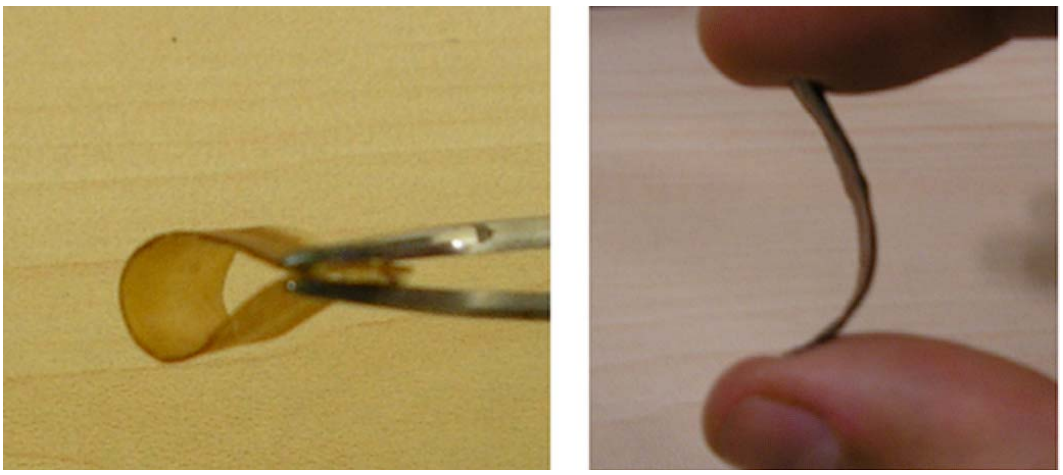


Figure 4.32 : Thin film photographs of (a) PEE-BA, (b) cured PEE-BA

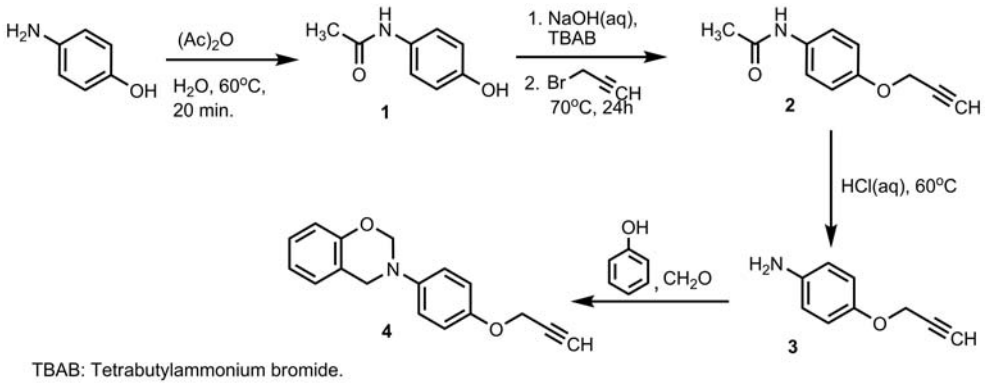
We have been able to synthesize polyetheresters containing benzoxazine moieties in the main chain. Two kinds of polyetheresters with the molecular weights of ca. 34.000 Da have been synthesized by polycondensation of benzoxazine diether diol with adipoyl chloride and terephataloyl chloride in the presence of triethylamine. Transparent flexible thin films were easily obtained by the solvent casting method. These reactive polyetherester films can be further cross-linked thermally which could enhance the application of polybenzoxazines. The cured polyetheresters exhibited good thermal stability and the toughness induced by the soft etherester. This is the first study on the benzoxazine type polycondensate and the synthetic strategy presented here may open new pathways to prepare the other conventional thermoplastic elastomers that can thermally be cured in the absence of any catalyst leading to materials with improved properties.

Considerable attention has been devoted to the incorporation of benzoxazines as a thermally reactive group into the backbone of conventional polymers. In these cases, polymers contain higher number of benzoxazine units per chain and upon curing the polymer segments chemically anchored to the network. However, the preparation of the corresponding side chain polymers has scarcely been dealt with. The only previous report concerns the preparation of side-chain benzoxazine polymers from poly(*p*-hydroxy styrene by applying usual benzoxazine synthesis. It is known that transition metal catalyzed polymerization of substituted acetylenes has been subject of substantial interest, owing to the unique physical and chemical characteristics of

the materials thus obtained. Accordingly, significant amount of research effort is directed to design and prepare catalyst systems to polymerize acetylene derivatives. Among those catalysts, rhodium polymerizes substituted acetylenes like phenylacetylene, *N*-propargylamides, *N*-propargylcarbamates, propiolic esters efficiently initiate the polymerization through an insertion mechanism. The resulting polymers are stereo-regular with generally *cis-transoidal* main chain structures, which give rise to helical conformations. Another important feature of the rhodium catalyst is related to its tolerance to various solvents and functional groups. For example, protic solvents as amines, alcohols, and even water can be used for such polymerization systems [153-160].

In this study, propargyl ether group containing benzoxazine was synthesized and polymerized with Rh catalyst alone and in the presence of triethylamine co-catalyst to yield helical polymers with thermally curable side chain benzoxazines. The structures of the intermediate compounds, monomer and the resulting polymers were characterized. The thermal properties of the cured structures were also investigated and compared with that of typical polybenzoxazines.

Propargyl benzoxazine was selected as thermally reactive and transition metal catalyst polymerizable monomer, which was prepared according to the modified procedure described by Agag and Takeichi (Reaction 4.7).



(4.7)

TBAB: Tetrabutylammonium bromide.

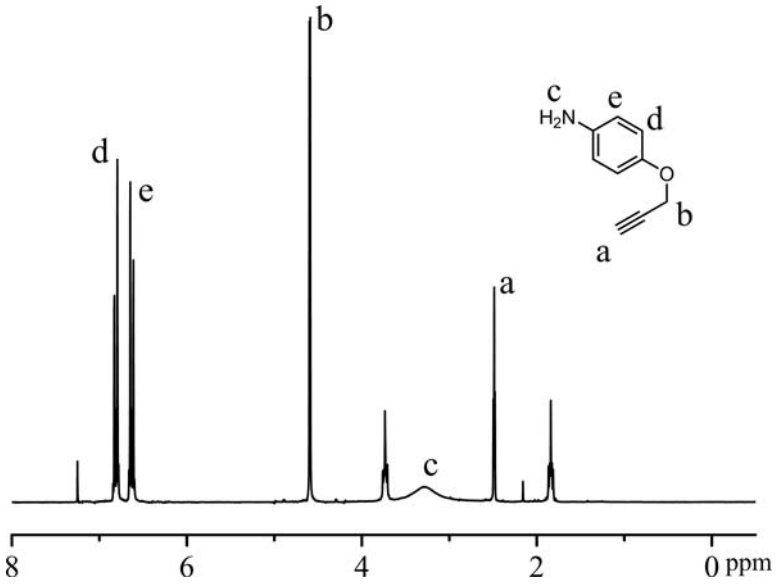
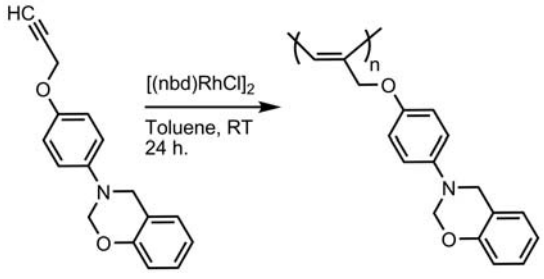


Figure 4.33 : ^{1}H-NMR spectrum of 4-(prop-2-ynyloxy)aniline

Instead of starting with 4-nitrophenol, we have used 4-aminophenol and protected amino group as amide. After eterification reaction between phenolic OH and propargyl bromide. Acidic hydrolysis yielded the expected amine (4-(prop-2-ynyloxy)aniline). In Figure 4.33 the ^{1}H-NMR spectrum reveals the successive synthesis of the required amine. Classical benzoxazine synthesis method was used to obtain propargyl benzoxazine.

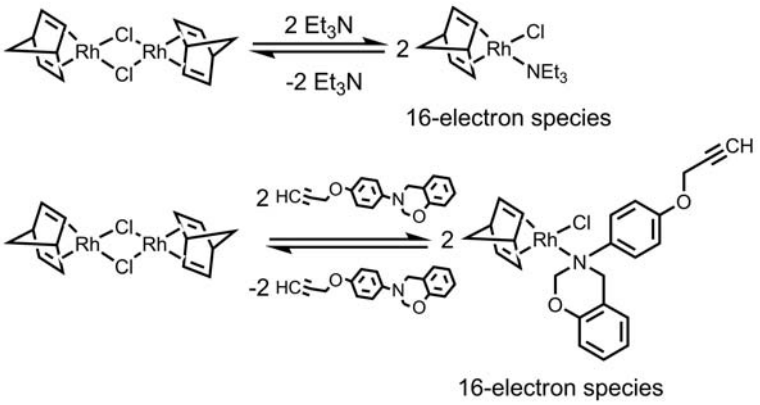
Propargyl benzoxazine is expected to yield polymers upon transition metal catalyst polymerization as it contains terminal acetylene group in its structure (reaction 4.8). The Rh-catalyzed reaction in toluene proceeded smoothly at ambient temperature for 24 h and gave the expected light gray poly(acetylene benzoxazine) (PBA), after precipitation in MeOH. In this reaction, Rh (I) was selected as the polymerization catalyst due to its widespread use in related polymerizations.



(4.8)

Although moderate yields were attained, limited chain growth was occurred. This is probably due to the partial activity of the $[(nbd)RhCl]_2$ as catalyst in the polymerization. It is demonstrated that this catalyst does not display a good catalytic

activity by itself. However, in the presence of Et_3N as co-catalyst, its catalytic activity considerably increases by the loss of symmetry of the 2,5-norbornadiene ligand in the initiating species with the formation of a 16-electron Rh complex [(nbd)Rh(Et_3N)Cl]. In our case, trisubstituted amine structure present in the propargyl benzoxazine would presumably act as co-catalyst (reaction 4.9). The results of polymerizations in the absence and presence of triethylamine are given in Table 4.5. The pronounced effect of triethylamine in the molecular weight is noted.



(4.9)

Table 4.5 : The results of polymerizations in the absence and presence of triethyl amine

Polymer	Co-catalyst	Yield (%)	M*n*	PDI
PBA-1	Et_3N	26	3450	2,56
PBA-2	—	25	<1000	—

Polymerizations were performed under N_2 at ambient temperature for 24 h

The chemical structure of the PBA obtained was confirmed by both FT-IR and ^{1}H-NMR spectral analysis. In the FT-IR spectrum (Figure 4.34), the disappearance of the acetylenic ≡C-H and C≡C stretching vibrations at 3290 cm^{-1} at 2121 cm^{-1}, respectively, was clearly noted. Additionally, the observation of C=C stretching vibration bands at 1674 cm^{-1} indicates the formation of polyacetylene backbone. The remaining bands of the benzoxazine group, such as aromatic C=C stretching vibrations and C-O-C symmetric and asymmetric vibrations etc. are detected from the FT-IR.

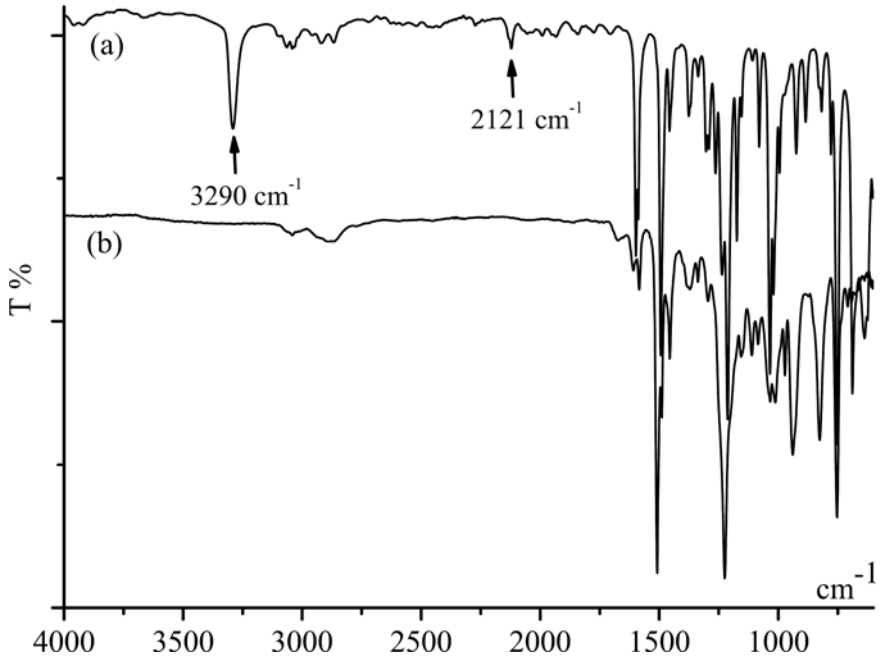


Figure 4.34 : FT-IR spectra of propargylbenzoxazine(a) and PBA-1 (b).

Further analysis of PBA-1 via ^{1}H-NMR (Figure 4.35) showed the disappearance of ≡C-*H* at 2.5 ppm after polymerization. Additionally, appearance of =C-*H* proton at 6.2 ppm indicates the polyacetylene formation with *cis* conformation. As far as the subsequent use of the resulting polymer (PBA) in thermal curing is concerned, the effect of Rh catalyst polymerization reaction on the stability of benzoxazine ring was an important issue. Thus, O-CH_2-N and Ar-CH_2-N protons of the oxazine structure appearing at 5.1 and 4.2 ppm, respectively, clearly indicates the retention of the benzoxazine ring during the polymerization reaction. Spectral characteristics of the compounds are tabulated in Table 4.6.

However, after polymerization in the presence of triethylamine, some insoluble products (PBA-2, see Table 4.5) were formed, which was still containing oxazine ring as confirmed by FT-IR and DSC analysis. It should also be mentioned that phenolic OH stretching vibrations are detectable in the FT-IR spectra of insoluble PBA-2, which is evidencing the presence of ring opened benzoxazine structures in the polymer.

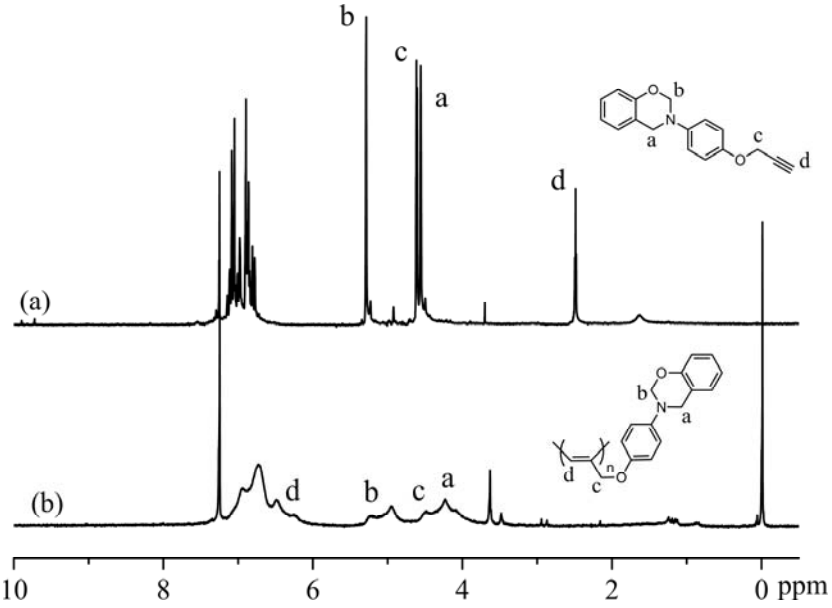


Figure 4.35 : ^{1}H-NMR spectra of propargylbenzoxazine (1) and PBA-1 (2).

Table 4.6 : Spectral characterization of propargyl benzoxazine and PAB-1

Compound	^{1}H-NMR δ (ppm)	^{13}C-NMR δ (ppm)	FT-IR ν (cm^{-1})	UV λ_{max} (nm)
Propargyl Benzoxazine	2.48 (t, *J* = 2.4, 1H), 4.55 (s, 2H), 4.61 (d, *J* = 2.3, 2H), 5.29 (s, 2H), 6.78-7.14 (aromatics, 8H)	51.0, 56.3, 75.4, 78.9, 80.5, 114.4, 116.9, 120.4, 120.8, 126.8, 127.9, 128.5, 143.2, 152.9, 154.4	3290, 3094, 3060, 3036, 2919, 2867, 2121, 1598, 1494, 1213, 1035,1020, 924, 885, 818, 752	244
PAB-1	4.23 (broad s, 2H), 4.48 (broad s, 2H), 4.95 (broad s, 2H), 6.26 (broad s, 1H), 6.48-6.95 (aromatics, 8H)	21.1, 25.6, 50.6, 67.9, 69.7, 80.2, 115.5, 116.8, 120.0, 120.8, 126.7, 127.8, 129.4, 142.3, 153.4, 154.3	3041, 2937, 2893, 1584, 1508, 1489, 1456, 1225, 1034, 1012, 972, 939, 826, 753	242

The absorption spectrum of the PBA-1 is shown in Figure 4.36. PBA-1 displayed a strong band of the phenyl chromophore at 242 nm. Little absorption was observed in the long wavelength region, suggesting the polymer possesses a short persistence length of backbone conjugation and lack of enough stereo-regularity. It was previously reported that the electronic absorption of a polyacetylene chain increases with its stereoregularity. Moreover, the steric requirements of aromatic substituents may enforce a planar conformation of polyacetylene backbone, which allows better

conjugation of the alternating double bonds and hence makes the polymer absorptive in the longer wavelength region. In our case, however, such steric effect is not valid and as a consequence longer wavelength absorption is not detected.

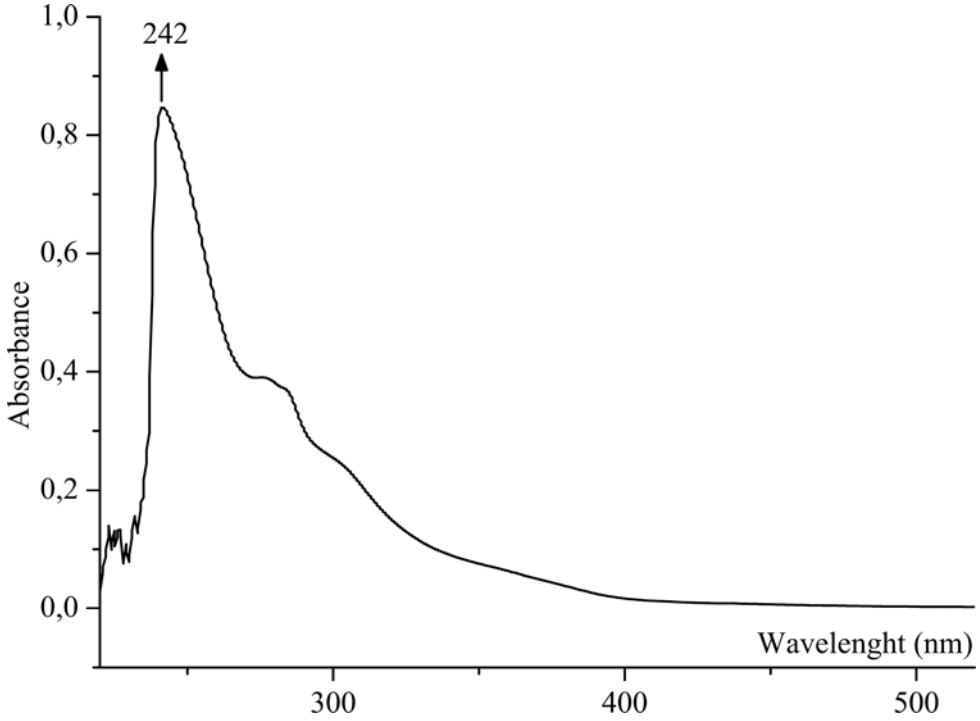
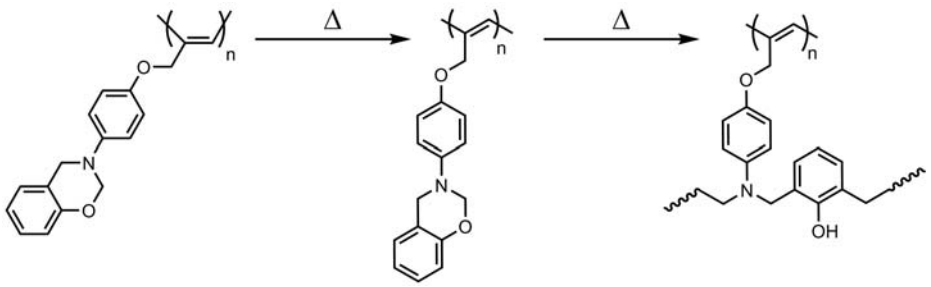


Figure 4.36 : UV-VIS spectrum of PBA-1 in chloroform.

The ring strain of oxazine allows benzoxazines to undergo ring-opening polymerization under thermally activated reaction conditions. Because of the multifunctional nature, PBAs were expected to form cross-linked networks upon heating (reaction 4.9).



(4.9)

The thermally activated cure behavior of PBAs and precursor propargyl monomer were studied by Differential Scanning Calorimetry (DSC) and the results are summarized in Table 4.7. In Figure 4.37, the non-isothermal DSC thermograms of PBA, first (a) and second runs (b), are plotted. As can be seen from Figure 4.36a, the polymer exhibits a glass transition temperature (T_g) at 104°C. The exothermic peak

with a maximum of 221°C was assigned to the ring opening polymerization of benzoxazine moieties. It is known that the helical structure is deformed by external stimuli such as heat and polar solvents. In the thermogram the *cis*-to-*trans* isomerization of the polymer; starting from ca.140°C with a maximum at 170°C is detectable. Further heating results in the conversion to a random coil structure. In the second run, however, no thermal transition is observed (Figure 4.36b). The fixed random coil form retains its configuration after crosslinking.

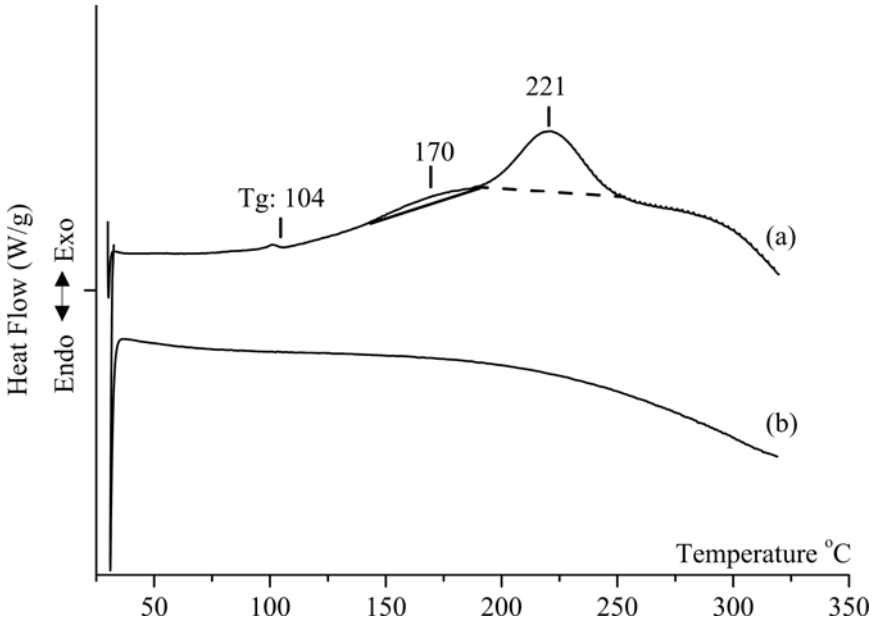


Figure 4.37 : DSC curves of PBA-1 (a) first and (b) second run 30-320ºC.

In Figure 4.38, DSC thermograms of propargyl benzoxazine (a), PBA-1 (b), PBA-2 (c) are overlaid. The maximum curing temperatures of PBA-1 and PBA-2 are less than that of propargyl benzoxazine. This behavior can be attributed to neighboring effect of any ring opened benzoxazine. When phenolic structures, formed from the partial ring opening, are in close proximity, they trigger further ring opening process and reduce the curing temperature. In another words, partially ring opened structures play a catalytic role in the curing process. Consequently, the maximum curing temperature of PBA-2 is lower than PBA-1. This behavior also accounts for the onset curing temperature and heat exotherm. The broad exothermic interval observed in the case of PBA-2 (Figure 4.38, curve c) may be due the irreversible *cis*-to-*trans* transition merged with and/or hidden beneath the latter ring opening exotherm. DSC characteristics of PBA-1, PBA-2 and propargylbenzoxazine are expressed in table 4.7.

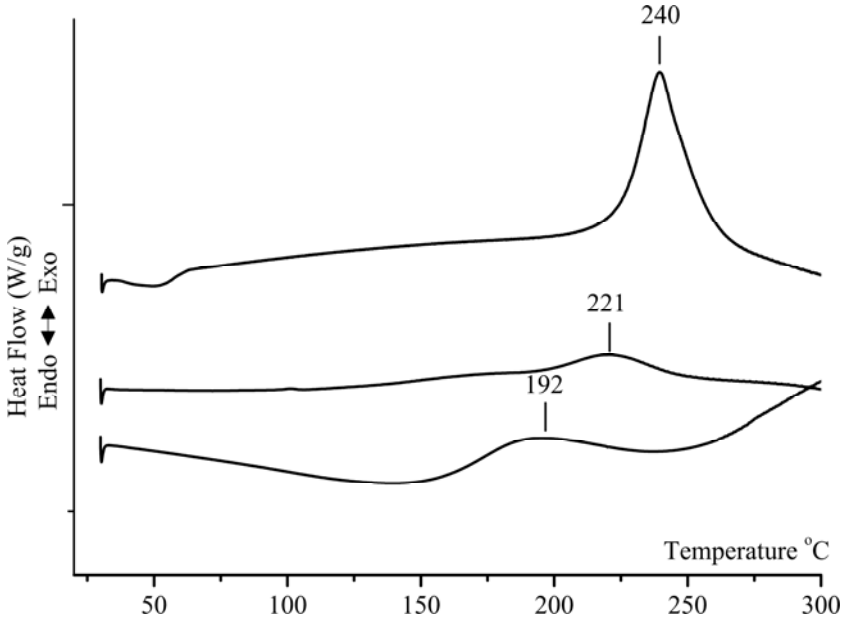


Figure 4.38 : DSC curves of propargylbenzoxazine (a) PBA-1 (b) and PBA-2 (c) 30-300°C.

Thermal stability of the cured PBA was investigated by thermal gravimetric analysis (TGA) under nitrogen exposure. The TGA and derivate profiles of cured propargyl benzoxazine (a), (a^d) and cured PBA (b), (b^d), respectively are shown in Figure 4.39 and the results are summarized in Table 4.8. It can be seen that the char yield at 800°C of the cured PBA is significantly higher than cured propargyl benzoxazine.

Table 4.7 : DSC characteristics of PBA-1, PBA-2 and propargylbenzoxazine

Polymer	Tg (°C)	Isomerization Onset (°C)	Isomerization Maximum (°C)	Onset of curing (°C)	Maximum Curing (°C)	Heat of Exotherm (j/g)
Propargyl Benzoxazine	—	—	—	225	240	772
PBA-1	104	140	170	188	221	130
PBA-2	—	—	—	162	192	222

DSC experiments were performed with a heating rate of 10 °C min under nitrogen flow.

This behavior can be attributed to the constructive effect of the molecular weight on the thermal stability which may be explained in terms of more favored intramolecular besides intermolecular cross-linking. However, the initial weight loss temperature of cured PBA is slightly lower than the cured propargyl benzoxazine.

Table 4.8 : TGA analysis of cured propargylbenzoxazine and PBA-1

Cured Product	$T_{5\%}$[a] (ºC)	$T_{10\%}$[b] (°C)	T_d max. (°C)	Y_c[c] at 800°C (%)
Propargyl Benzoxazine	348	386	414	55
PBA-1	330	371	380	65

TGA analysis were performed with a heating rate of 10 ºC min under nitrogen flow (200ml/min)
[a]$T_{5\%}$: The temperature for which the weight loss is 5%
[b]$T_{10\%}$: The temperature for which the weight loss is 10%
[c]$T_{max.}$: Maximum weight loss temperature.
[d]Y_c: Char yields

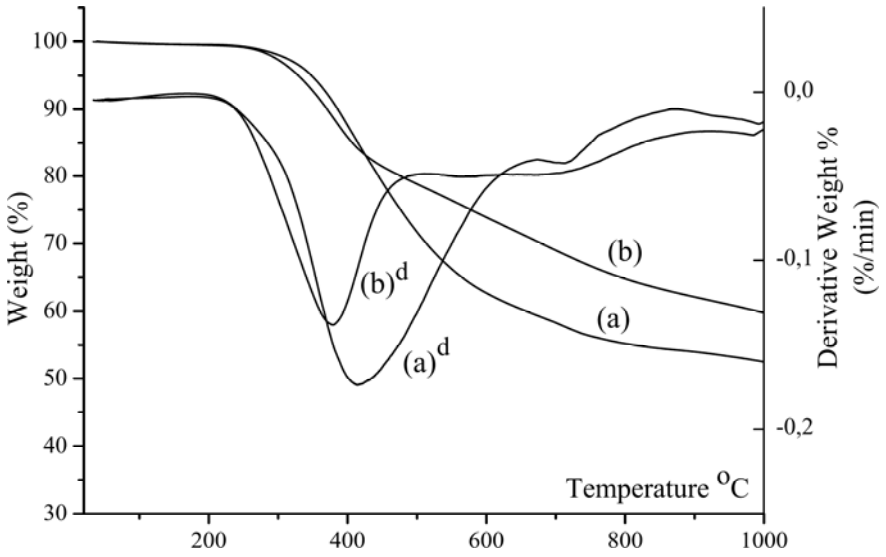


Figure 4.39 : TGA thermograms and their derivatives of cured propargylbenzoxazine (a), (a^d) and cured PBA-1 (b), (b^d).

We have synthesized and polymerized benzoxazine based acetylene monomer to obtain thermally activated self-curable polymers. Upon heating benzoxazine acetylene polymers undergo irreversible cis-trans isomerization followed by random coil formation and finally intra- and intermolecular curing.

5. CONCLUSION

In this thesis we have discussed about the polymeric precursors and telechilics of benzoxazines. Benzoxazine attracted the attention of polymer scientists after 1994 when the synthesis of the polybenzoxazine by cross-linking bifunctional benzoxazine monomer through a ring-opening reaction mechanism and identified the benefits this family of compounds can offer compared to the conventional novolac or resole or epoxy resins was reported. Though benzoxazine based materials possess several advantages, they have not yet became very attractive to the industries. To improve the mechanical properties and processibility several strategies have been reported including (i) synthesis of benzoxazine monomers with additional functionality, (ii) blending of benzoxazines with polymers (iii) benzoxazine based composites or alloys. However, all of these approaches are also associated with some limitations. In case of polymeric precursors and telechilics, though the polymeric chain contributes towards the improvement of mechanical property and processibility of the resulting polymer. According to this approach, we anchored benzoxazine ring to the end of a polymer. Here a polymeric structure act as back bone structure, which are endcapped with benzoxazine. Telechelics with relatively large molecular weight oligomers possess thermoplastic-like properties, while allowing later cross-linking for dimensional stability, chemical resistance, and high-temperature stability. A unique synthetic route was reported in this thesis for synthesis of a macromonomer where benzoxazine ring was anchored to the polysterene polymer. Using Atom Transfer Radical Polymerization (ATRP) to synthesize dibromophenyl terminated polystyrene, followed by Suzuki coupling reaction amino functional polymer was prepared. These amino functional polymers were when reacted with phenol and paraformaldehyde to produce benzoxazine functionalized polystyrene macromonomer. In the literature it was reported that the miscible blends of polybisbenzoxazine (PB-a) and poly(ε-caprolactone) (PCL) can be prepared by an in situ curing reaction of benzoxazine in the presence of PCL. The miscibility was attributed to the intermolecular hydrogen bonding between the hydroxyl groups of PB-a and the carbonyl groups of PCL. On the basis of this information, we have

synthesized naphthoxazine ring-containing PCL macromonomers. Thermosets of polybenzoxazines with covalently bonded PCL segments were formed, when PCL macromonomers cured with conventional benzoxazine monomers. Such prepared narrowly distributed macromonomers undergo thermal ring opening polymerization. When used in conjunction with conventional benzoxazine monomers, the observed properties of physical mixing can be attained with additional benefits of covalent attachment.

Concept of oligomeric benzoxazine resins where oxazine rings are in the main chain was reported. Synthetic approach for the preparation of polymers containing benzoxazine moieties in the main chain have been independently reported. In both cases high-molecular weight polybenzoxazine precursor was synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde. The major problems associated with the preparation of such main-chain benzoxazine precursor polymers are low molecular weight and cross-linking arising from the Mannich reactions of multiple functional groups. As a solution to this problem we have synthesized high molecular weight poly(etheresters) (PEE) containing benzoxazine units in the main chain by using diol functional monomer which was synthesized from bisphenol A, formaldehyde and 2-(2-aminoethoxy) ethanol. 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. Upon thermal treatment these polymers formed cross-linked network. Here, presence of polyester introduced flexibility in both precurser polymers and crosslinked network.

Side chain polymer strategy is another concept that ultimately lead to highly dense network; due to the presence of benzoxazine structure in every repeating unit. We therefore have synthesized and polymerized benzoxazine based acetylene monomer. Upon heating, benzoxazine acetylene polymers undergo irreversible cis-trans isomerization followed by random coil formation and finally intra- and intermolecular ring opening reactions to form such crosslinked polymers with high crosslinking densitiy.

Future direction of research in this area should be towards the development of benzoxazine based materials with better processibility, low curing temperature and

good mechanical strength. We believe the pioneering studies reported in the thesis will contribute to achieved new pathways in the future.

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