İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF BENZOXAZINE-SULFONES AS PRECURSORS FOR THERMALLY STABLE THERMOSETS

M. Sc. Thesis by
ÇAĞATAY ALTINKÖK

Department : Chemistry

Programme : Chemistry

JANUARY 2011

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Date of submission : **20 December 2010**
Date of defence examination: **28 January 2011**

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Doç. Dr. Mesut Kaçan (TU)

JANUARY 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ISISAL KARARLI TERMOSETLER İÇİN BENZOKSAZİN-SÜLFON BAŞLANGIÇ MADDELERİNİN SENTEZİ VE KARAKTERİZASYONU

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(509091035)

Tezin Enstitüye Verildiği Tarih : **20 Aralık 2010**
Tezin Savunulduğu Tarih : **28 Ocak 2011**

Tez Danışmanı : **Prof. Dr. Yusuf YAĞCI (İTÜ)**
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Doç. Dr. Mesut KAÇAN

OCAK 2011

FOREWORD

I would like to thank all the people who support me and made this study possible. It is a pleasant opportunity that I express my gratitude to all of them.

First of all, I would like to thank my supervisor Prof. Dr. Yusuf Yağcı for his help and support in the graduation thesis study and for being such a decent and fine instructor.

I also owe a debt of gratitude to Asst. Prof. M. Atilla Taşdelen for her kind guidance and help during the experiments.

I wish to deeply thank to past and current members of Yagci Lab for all their help, support and friendship. In particular, Dr. Demet Göen Çolak, Dr. Binnur Aydoğan, Dr. Barış Kışkan Dr. Yasemin Yüksel Durmaz, Res Asst. Burçin Gacal, Kübra Demir, Cemil Dizman, Manolya Kukut, Halime Cengiz, Alev Tüzün, Zeynep Beyazkılıç, Serdar Okçu, Hande Çelebi, Bahadır Gacal, Elif L. Şahkulubey, Mustafa Uygun, Selim Beyazıt and Deniz Tunç with all of you, it has really been a great pleasure.

I wish to express my special gratitude to Muhammet Ü. Kahveci and Res Asst. Ali Görkem Yılmaz for their support, encouragement and patience.

I also thank to my best friend Gökhan Açık for her kind support, help, encouragement and significantly always beeing next to me.

Finally, I acknowledge to my brother Çağdaş Altınkök, my mother and my father for their support, patience and encouragement throughout my education.

Thank all of you very much…

January 2011 ÇAĞATAY ALTINKÖK

Chemist

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ABBREVIATIONS

^{1}H-NMR : Nuclear magnetic resonance spectroscopy
FT–IR : Fourier transforms infrared spectroscopy
DSC : Differential scanning calorimetry
GPC : Gel permeation chromatography
Tg : Glass transition temperature
B-ala : 6,6'-(Propane-2,2-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3] oxazine)
Bisphenol–A : 4, 4'- isopropylidenediphenol
PSU : Polysulfone
TGA : Thermal gravimetric analysis
DMF : *N*,*N*-dimethylformamide
K_2CO_3 : Potassium carbonate
PEE : Poly(ether esters)

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LIST OF SYMBOLS

$R^{\bullet}$ **:** Radical
PI **:** Photoinitiator
M **:** Monomer
λ **:** Wavelength

SYNTHESIS AND CHARACTERIZATION OF BENZOXAZINE-SULFONES AS PRECURSORS FOR THERMALLY STABLE THERMOSETS

SUMMARY

Polybenzoxazines are class of thermosetting resins that can be used in many fields such as electronics and aerospace industries because they have a good combination of several pre-eminent features. They exhibit nearly zero shrinkage upon curing, thermal stability, chemical resistance, low water absorption; for some polybenzoxazines Tg is much higher than cure temperature and no strong acid catalysts are required for curing. The synthesis of polybenzoxazines can be done easily by thermally activated ring opening of the corresponding benzoxazine without generating any byproducts. 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 high curing temperature (~ 200°C or higher), difficulty in processing and 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.

Polysulfones are a family of high performance thermoplastic materials with chemical inertness, excellent oxidative, thermal and hydrolytic stability, as well as mechanical strength and film forming properties. This desirable combination of properties and their availability makes polysulfones as attractive materials for the manufacture of commercial membranes and biomedical applications such as gas separation, pervaporation, hemodialysis, nano/ultrafiltration, cell culture, drug delivery, bioartificial, fuel cells, and so on.

In this study, we synthesized poly(benzoxazine-co-sulfone) to combine two different polymers in a single structure. First a monomer sulfonylbisoxydianiline was obtained according to a modified procedure described in the literature. Then the characterization of the synthesized monomer was performed by ^{1}H-NMR and FT-IR analysis. After the monomer diamino functional monomer was prepared properly, it was used in conjunction with bisphenol-A and paraphormaldehyde in convenient conditions to synthesize the poly(benzoxazine-co-sulfone) polymer. This polymer was characterized by H-NMR, FT-IR, DSC and TGA measurements.

ISISAL KARARLI TERMOSETLER İÇİN BENZOKSAZİN-SÜLFON BAŞLANGIÇ MADDELERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Polibenzoksazinler, ilginç bir çok özellikleri ile novalak ve resol tipi fenolik reçinelerine daha üstün gelen yeni geliştirilmiş fenolik sistemlerdir. Bu malzemeler kürleme sırasında hemen hemen hacimsel değişime uğramayışı düşük su absorpsiyonu bazı polibenzoksazinler için Tg (camsı geçiş sıcaklığı) kürlenme sıcaklığından yüksek oluşu yüksek yanma ürünü yüzdesi kürleme için asit gerektirmemesi kürleme sırasında yan ürün oluşturmaması gibi özellikler gösterirler. Polibenzoksazinlerin sentezi herhangi bir yan ürün oluşturmadan, benzoksazinlerin termal aktiflenmesi sonucu halka açılarak meydana gelebilir. Benzoksazin monomerlerinin hazırlanması için çeşitli sentetik yollar, polimerizasyon mekanizmaları ve kürlenmiş maddelerin yapısal özellikleri birçok grup tarafından araştırılmıştır. Ancak saf polibenzoksazin temelli polimerler birkaç dezavantaja sahiptir. Yüksek kürleme sıcaklığı(200^{o}C veya daha üst sıcaklıklar), işleme güçlüğü ve kırılganlıkları bunlardan birkaçıdır. 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.

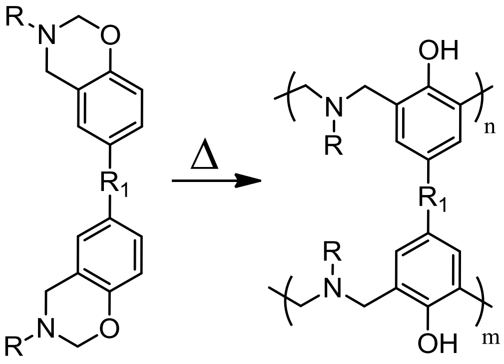
Polisülfonlar, kimyasal reaksiyonlara karşı dayanıklılığı,mükemmel oksidatif özelliği, termal ve hidrolitik dayanıklılığı ayrıca mekanik sağlamlığı ve film haline getirilebilme özellikleri ile yüksek performanslı termoplastik maddelerinin bir üyesidir. Bu eşsiz özelliklerin birleşimi ile birlikte, ticari membranlar, gaz ayrımı, hemodiyaliz, nano/ultra filtreler, hücre kültürü, ilaç uygulamaları, yakıt hücreleri ve bunun gibi birçok ticari membranların üretilmesi için ilgi çekici maddelerdir.

Bu çalışmada iki farklı polimer, poli(benzoksazin-*ko*-sülfon) sentezlenerek tek bir yapı altında toplanmıştır. Öncelikle, sülfonilbisoksidianilin monomeri literatürde tanımlanan prosedüre göre elde edildi. Daha sonra sentezlenen monomerin karakterizasyonu ^{1}H-NMR ve FT-IR ile yapıldı. Diamin fonksiyonlu monomer hazırlandıktan sonra, bisfenol-A ve paraformaldehit kullanılarak uygun koşullarda poli(benzoksazin-*ko*-sülfon) elde edildi. Polimer, H-NMR, FT-IR, DSC, TGA ve GPC ölçümleriyle karakterize edildi.

1. INTRODUCTION

The interest in 1,3-benzoxazine chemistry is growing rapidly due to many unique properties of benzoxazines and their resins. They have various advantages in comparison to other types of thermosets such as phenolic, epoxy, bismaleimide, or cyanate ester resins. These extraordinary properties of benzoxazines can be listed as near zero volumetric change upon curing, no strong acid catalysts or additives requirement for curing, high thermal stability, good mechanical performance, low water absorption and high char yield of the cured products. Additionally, another attractive feature of benzoxazine chemistry is the preparation of monomers from inexpensive, commercially available phenols, primary amines, and formaldehyde, easily. By varying the starting phenols and amines a wide range of molecular design flexibility can also be achieved.

The polymerization of these monomers is a thermally induced ring opening polymerization which can be accomplished without any initiator or curative yielding polybenzoxazine networks and this can be considered as a green process since no toxic by-product is released. (Reaction 1.1)



(1.1)

Despite unique properties and ease of preparation, polybenzoxazines suffer from processibility due to powder structure of monomers and brittle nature of their networks. Hence, a wide range of study dealing with the improvements in this issue has been published including synthesis of new monomeric or polymeric benzoxazine precursors. So the active concept in benzoxazine resin research is based on the synthesis of telechelic, linear or side chain polymers containing a benzoxazine moiety. Such new polymers provide solubility, processability, and also offer the ability to prepare good quality films from benzoxazines without distorting the beneficial properties of polybenzoxazines like superior mechanical property.

Polysulfones (PSU), another high performance polymer family, known to have good toughness and stability at high temperatures. They show high strength and stiffness even at elevated temperatures, high continuous use and heat deflection temperatures, excellent resistance to hydrolysis by acids and bases, and good dimensional stability and the highest service temperature of all melt-processable thermoplastics [1].

Combination of polybenzoxazine and polysulfones structures could be important for extending properties of polybenzoxazines for various applications. In this study, we presented the synthesis of poly(benzoxazine-*co*-sulfones) precursors via condensation polymerization of suitable sulfone containing diamine and diphenols. A structure of the obtained product was characterized by spectroscopic and thermal analyses successfully.

2. THEORETICAL PART

2.1 General Methods for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are simple heterocycles and easily prepared from inexpensive and commercially available phenol, p-formaldehyde and amine (aliphatic or aromatic) either by employing solution or solventless methods. In order to synthesis of polymeric compounds with desired properties, by tailoring the benzoxazine monomer with various functionality and a wide variety of monomers can be synthesized by using appropriate starting materials. For example, presence of electron withdrawing functional groups (-COOH, -CN) with amine was found to be responsible for reduction in yields. In addition, it is hard to synthesize benzoxazine monomers containing free phenolic -OH groups employing conventional method [2].

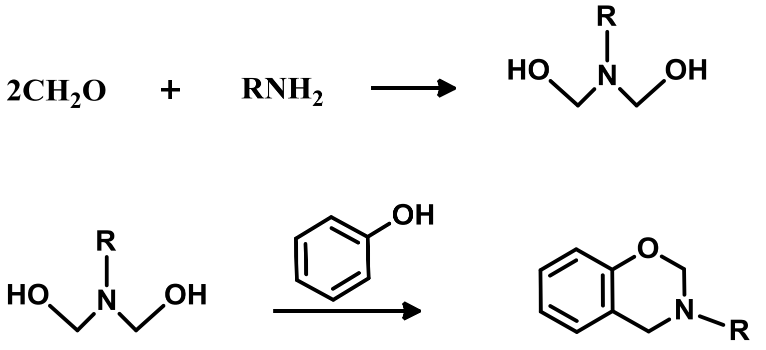
2.1.1 Preparation of mono-functional benzoxazine monomers

Condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of mono-functional benzoxazine monomers were first reported by Holly and Cope [3]. According to their procedure, this reaction was performed in a solvent through two-steps. Then, Burke explored that the benzoxazine ring reacts 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 changeable hydrogen of the hydroxyl group and ortho position of the phenol at the high temperature to form the oxazine ring [5].(Reactions 2.1.)

For example, to prepare 3,4-dihydro-3-cyclo-hexyl-6-t-butyl-1,3,2H-benzoxazine, Burke [6] followed two different procedures.

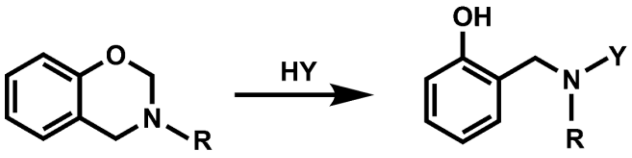
For the first procedure, cyclohexylamine was mixed formaldehyde in dioxane. After addition of *p*-butyl phenol the mixture was refluxed for 2 h. Upon cooling to room temperature, a crystalline product was obtained, which was then recrystallized from 95% ethanol with 78% yield.

For the second procedure, paraformaldehyde was first dissolved in warm methanolic KOH solution. Subsequently, 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 with 92% yield. Synthesis of a *p*-cresol based benzoxazine by using aniline, formaldehyde and *p*-cresol as starting materials in dioxane has been reported [7-9].



(2.1)

During the monomer synthesis, ring opening reaction of benzoxazine 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) [10] may exist and they need to be considered in advance. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [11] is shown below in equation (2. 2.)



(2.2)

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 disadvantages, Ishida et al. developed a *solventless synthesis* in the melt state [12, 13]. In this procedure, 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 [14]. In this connection, it should be pointed out that formaldehyde is not typically used as it evaporates easily and lose stocihiometry quickly. 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.

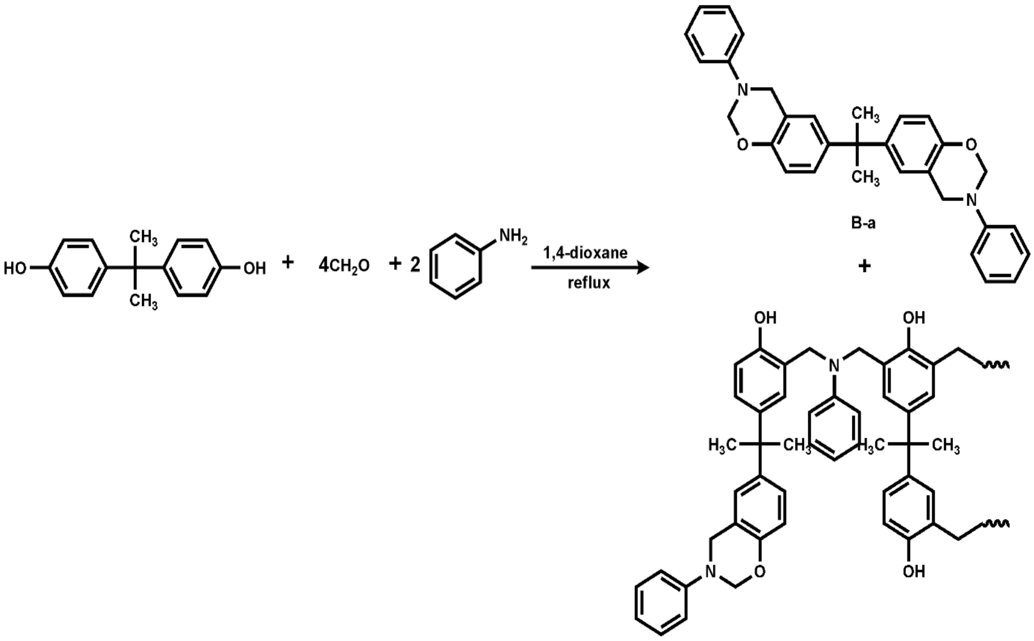
Recently, novel variation of solution method was applied for successful synthesis of benzoxazine monomer by using high boiling point nonpolar solvents [15]. There are two main reasons for this: first, the starting phenol, has poor solubility in common organic solvent used as the ordinary benzoxazine synthesis; and second, the reaction of diamines with formaldehyde afforded a stable triaza gel structure, which was difficult to be broken by phenols. All these retard the desired monomer formation. To overcome this difficulty, a new method was developed by using high boiling point nonpolar solvents such as xylenes or dichlorobenzene at higher reaction temperature (130 °C). These solvents increased the solubility of phenols and accelerated the breakage of triaza gel by phenols. As a consequence, monomer formation proceeded smoothly without generating significant side reaction as the solvents are nonpolar. All the monomers were easily soluble in common polar and nonpolar solvents, such as dimethylsulfoxide, dimethylformamide, dioxane, ethyl acetate, chloroform and tetrahydrofuran.

2.1.2 Preparation of multi-functional benzoxazine monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Under mild polymerization conditions, chain growth can terminate at the dimer length due to hydrogen bond formation at the growth front [16, 17]. To overcome this limitation, a new class of difunctional or multifunctional benzoxazine monomers [18, 19] have been developed, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by NMR, FT-IR and SEC.

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

Similar type of difunctional benzoxazine was prepared using aniline instead of methyl amine [20-22] and the pure monomer was referred as bisbenzoxazine (B-a) and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a analyzed by ^{1}H-NMR measurements. The overall synthetic procedure is shown in Eq. 2.4. To achieve successful processing, cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors is an auto-catalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process afterwards.



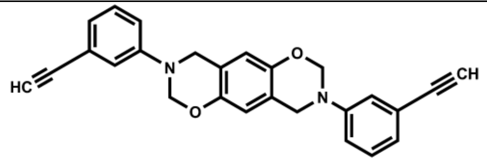
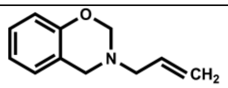
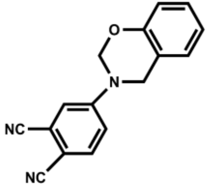
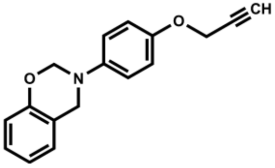
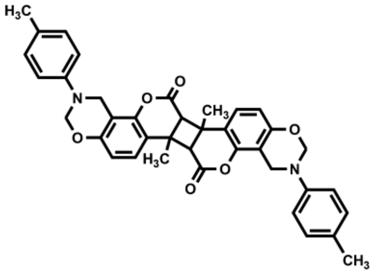
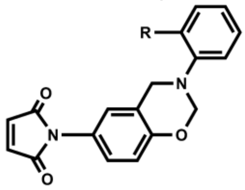
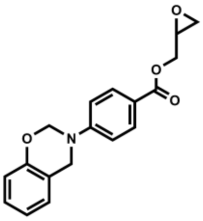
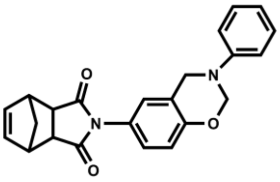
(2.3)

The synthesis of bisbenzoxazine monomer 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].

2.1.3 Synthesis of benzoxazine monomers with different functional groups

The chemistry of benzoxazine synthesis exhibit a wide range of molecular design flexibility by using suitable starting materials. Therefore, molecular structure can be tailored for specific applications [24-30]. It is possible that benzoxazine monomers are diversified by using many functional groups. Synthesis of allyl, acetylene, propargyl ether, nitrile, maleimide, norbornane, coumarin, epoxy groups containing benzoxazine monomers have a part in several research. (structures are shown in Table 2.1).

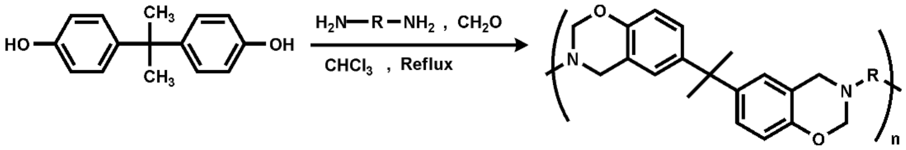
Table 2.1: Benzoxazine monomers with various functionalities.

Benzoxazine monomers	
 Acetylene-containing benzoxazine [31]	 Allyl-containing benzoxazine [32]
 Nitrile-containing benzoxazine [33]	 Propargyl ether-containing benzoxazine [34]
 Coumarin-containing benzoxazine [35]	 Maleimide-containing benzoxazine [36]
 Epoxy-containing benzoxazine [37]	 Norbornane containing benzoxazine [36]

2.1.4 Synthesis of main chain type benzoxazine polymers

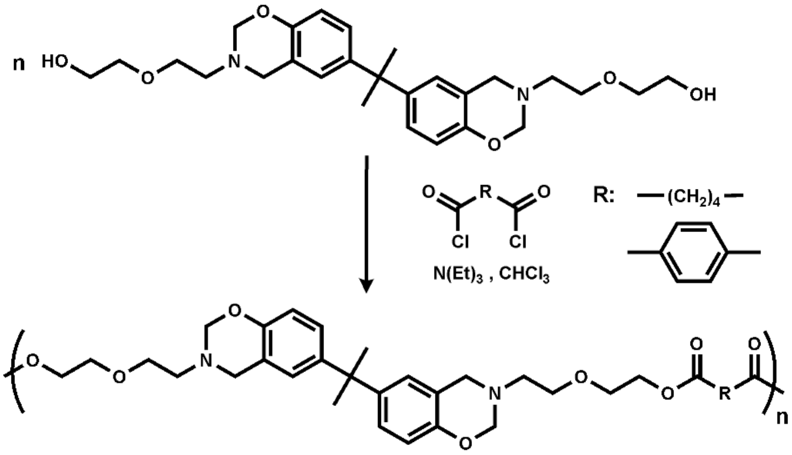
The view of oligomeric benzoxazine resins containing oxazine ring in the main chain was first reported by Liu and Ishida [11]. Then the same research group published more detailed work about the effect of water, solvents, catalyst, ratio of reactants and temperature [14].

Takeichi et al. [38] and Ishida and coworkers [39] have independently reported a synthetic approach for the preparation of polymers containing benzoxazine moieties in the main chain. According to their research high-molecular weight polybenzoxazine precursor was synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde. The critical problems in this polymerization are that the preparation of such main-chain benzoxazine precursor polymers are low molecular weight and crosslinking arising from the Mannich reactions of multiple functional groups. The choice of the right conditions for a Mannich reaction is important for achieving high yields with a minimum by product. In this type of Mannich polymerization, partially ring-opened structures were also observed. But, the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, whereas polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability.



(2.4)

Yagci and Ishida have synthesized high molecular weight poly (etheresters) (PEE) containing benzoxazine units in the main chain by diol functional monomer and was first synthesized using bisphenol A, formaldehyde, and 2-(2- aminoethoxy) ethanol [40]. 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. These polymers consist of benzoxazine units, formed crosslinked network. Here, presence of polyester introduced flexibility in the resulting polymer. These reactive polyether ester films can be further crosslinked thermally which could enhance the application of polybenzoxazines. The cured PEE exhibited good thermal stability and the toughness induced by the soft etherester. This synthetic strategy may open new pathways to prepare the other conventional thermoplastic elastomers those can be thermally cured in the absence of any catalyst leading to materials with improved properties.



(2.6)

It was reported that polysiloxanes containing benzoxazine moieties in the main chain can be prepared by hydrosilylation reaction between tetramethyldisiloxane and benzoxazine structurally equipped with allyl groups [41]. Siloxane segments introduce flexibility and transparent thin precursor films were easily obtained by casting the precursor solution on Teflon plate. The benzoxazine groups were shown to readily undergo thermally activated ring-opening reaction in the absence of added catalyst to form cross-linked polymer network. The polymers cured in this way exhibited much more thermal stability than those of the structurally similar low-molecular weight analogous. The enhanced thermal stability was attributed to the presence of siloxane units.

Different types of benzoxazine based main-chain polymeric precursors have been described in Figure 2.1 [42].

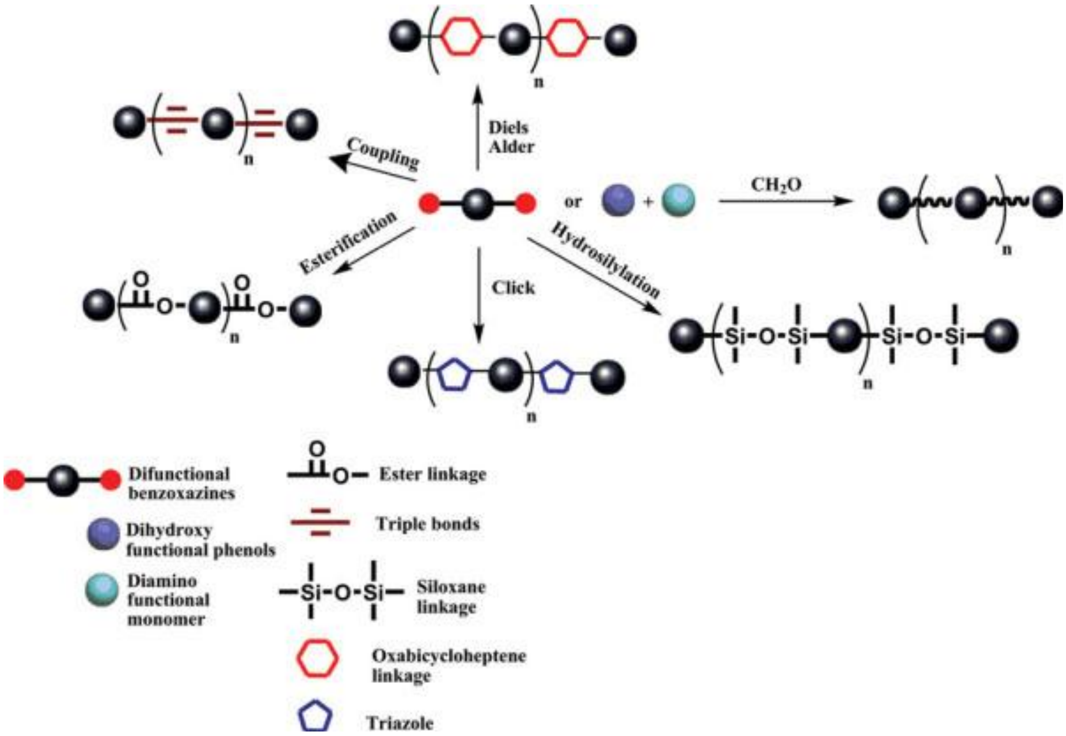


Figure 2.1 : Main applications of main-chain benzoxazines.

2.1.5 Synthesis of side chain type benzoxazine polymers

Side-chain polymeric method is a path to incorporate benzoxazine groups into a polymer backbone to achieve a highly dense network. Curing of many repeating benzoxazine units resulted in crosslinking of polymer chains. There are various synthetic methods to obtain side chain polymers. The side-chain polymeric benzoxazine precursor was prepared by oxidative polymerization 3-phenyl-3,4-dihydro-2H-benzo[e][1,3] oxazine (P-a) in the presence of thiophene (Th) with ceric ammonium nitrate [43]. 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. Some include postpolymer modification like click chemistry or polymerizing suitable molecules (Figure 2.2) [42].

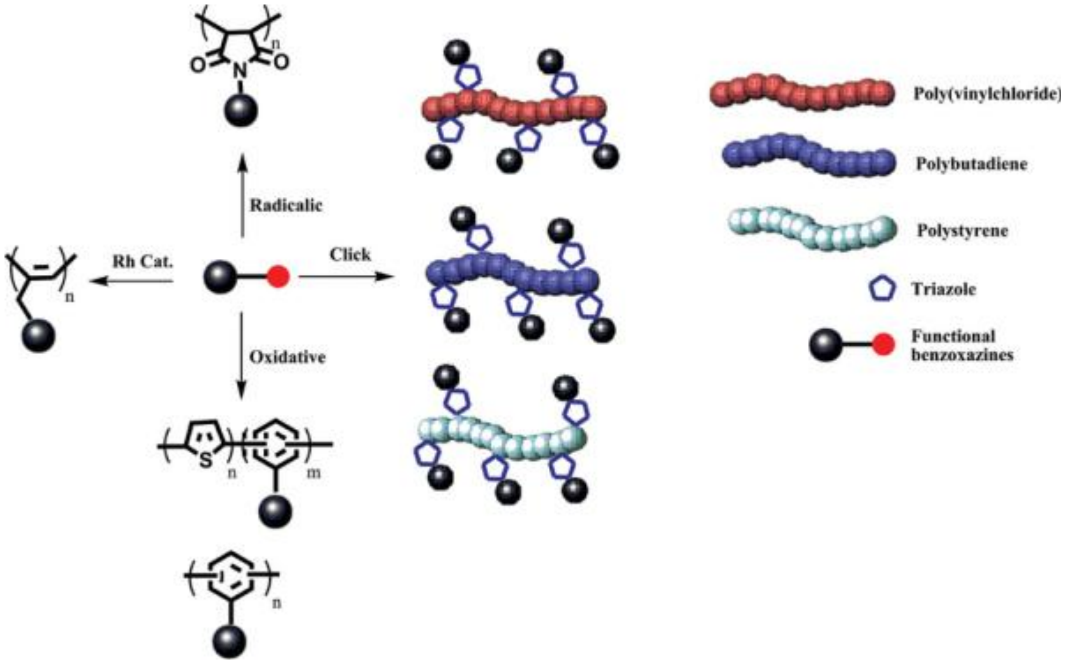


Figure 2.2 : Applications of side-chain benzoxazines.

2.1.6 Ring opening polymerization of benzoxazines

To understand the polymerization reaction mechanism of benzoxazines, an understanding of the chemical structure of its oxazine ring is very important. A single crystal X-ray crystallographic study detect that mono-oxazine ring containing benzoxazine is a distorted semi-chair structure, with the nitrogen and carbon, between oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six-membered ring to undergo ring-opening reaction

under specific conditions. In addition, due to their high basicity (by Lewis definition) both oxygen and nitrogen of the oxazine ring can act as potential cationic polymerization initiation site and makes the ring very likely to open via a cationic mechanism [44, 45]. The electron charge calculation after energy minimization predicts that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270).

2.1.6.1 Thermal polymerization of polybenzoxazines

Benzoxazine undergoes ring opening polymerization during thermal curing（Figure 1.1）. It has been proposed that, the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which in equilibrium [46]. Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and para position of the phenol group. The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Though, several authors have proposed different mechanism of thermal curing of benzoxazine, however, the mechanism is not well established.

2.1.6.2 Photo-initiated polymerization of benzoxazine

The ring-opening cationic polymerization of a benzoxazine, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa), with onium salts, such as diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate as initiators, investigated by Kasapoglu et al. [47]. In this work, both direct and indirect activations by using radical sources and photosensitizers were reported. The complex structure of the resulting polymers was formed due to the simultaneous ring-opening process of the protonated monomer either at the oxygen or nitrogen atoms. The phenolic mechanism also contributed, but its influence decreased with decreasing monomer concentration. Free radical promoted cationic polymerization of benzoxazines was also considered. In this case, the polymerization can be performed at much higher wavelengths and carbon-centered radicals formed from the photolysis of 2,2-dimethoxy-2-phenylacetophenone, were oxidized to produce carbocations. These carbocations are capable to initiate benzoxazine polymerizations. Figure 2.3 describes the photopolymerization of benzoxazine.

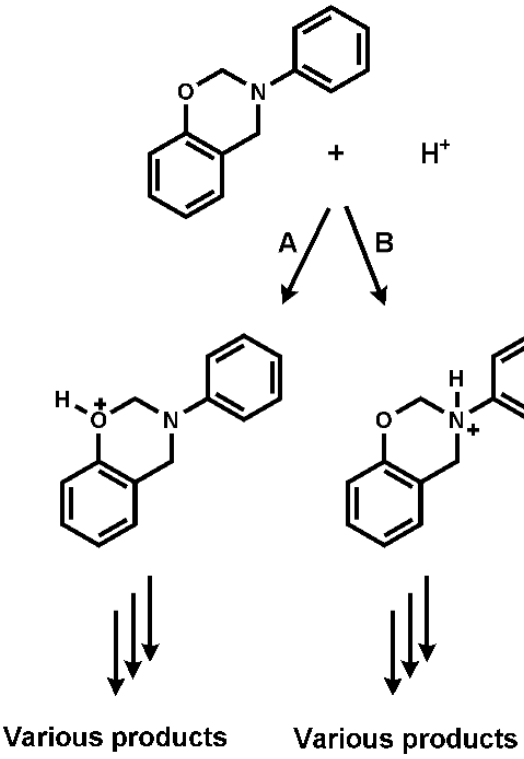
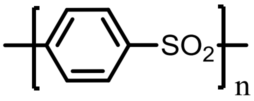


Figure 2.3 : Photopolymerization of benzoxazines.

2.2 Polysulfones

Polysulfones are a family of engineering thermoplastics with excellent high temperature properties. The simplest aromatic polysulfone, poly (p-phenylene sulfone) does not show thermoplastic behavior, melting with decomposition above 500 °C. Hence, to obtain a material capable of injection molding in conventional machines, the polymer chain is made more flexible by incorporating ether links into the backbone [48].



(2.7)

The structures and glass transition temperatures of several commercial polysulfones are listed in Table 1.30. The polymers have different degrees of spacing between the p-phenylene groups and thus have a spectrum of glass transition temperatures which determine the heat-distortion temperature (or deflection temperature under load), since the materials are all amorphous.

The first commercial polysulfone was introduced in 1965 by Union Carbide (Table 2.2A). This material, now known as Udel, has a continuous-use temperature of 150 ^{o}C and a maximum-use temperature of 170 ^{o}C, and it can be fabricated easily by injection molding in conventional machines. In 1967, Minnesota Mining and Manufacturing (3M) introduced Astrel 360, an especially high performance thermoplastic, which requires specialized equipment with extra heating and pressure capabilities for processing. ICI’s polyether sulfones, introduced in 1972 Victrex and polyethersulfone 720P are intermediate in performance and processing. In the late 1970s, Union Carbide introduced Radel, which has a higher level of toughness. Note that all of the commercial materials mentioned in Table 2.2 may be described as polysulfones, polyarylsulfones, polyether sulfones, or polyaryl ether sulfone [49].

In principle, there are two main routes to the preparation of polysulfones: (1) polysulfonylation and (2) polyetherification.

Polysulfonylation reactions are of the following general types:

$$\begin{gathered}
H{-}Ar{-}H \quad + \quad ClSO_2{-}Ar'{-}SO_2Cl \xrightarrow[\text{Catalyst}]{\text{Friedel-Crafts}} \left(Ar{-}SO_2{-}Ar'{-}SO_2 \right)_n \quad + \quad HCl \\
H{-}Ar{-}SO_2Cl \longrightarrow \left(Ar{-}SO_2 \right)_n \quad + \quad HCl
\end{gathered} \tag{2.8}$$

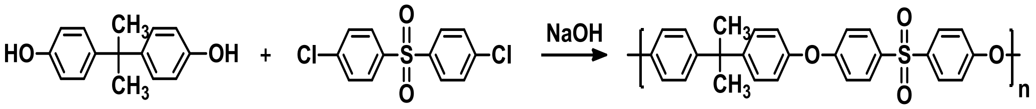
The Ar' and/or Ar' group(s) contain an ether oxygen, and if Ar=Ar’, then identical products may be obtained by the two routes.

In the polyetherification route the condensation reaction proceeds by reactions of types

$$\begin{gathered}
HO{-}Ar{-}OH \quad + \quad Cl{-}Ar'{-}Cl \xrightarrow{\text{NaOH}} \left(O{-}Ar{-}O{-}Ar' \right)_n \quad + \quad NaCl \\
HO{-}Ar{-}Cl \xrightarrow{\text{NaOH}} \left(O{-}Ar \right)_n \quad + \quad NaCl
\end{gathered} \tag{2.9}$$

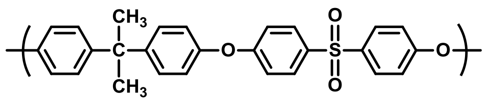
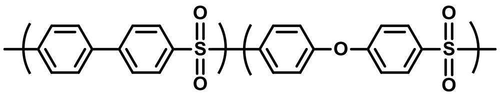
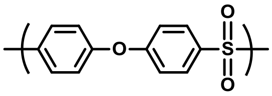
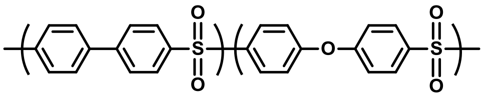
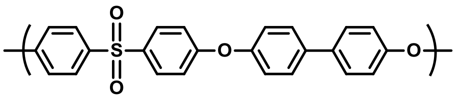
The Ar and/or Ar' group(s) contain sulfone groups, and if Ar=Ar, then identical products may be obtained by the two routes.

Polyetherification processes form the basis of commercial polysulfone production methods. For example, the Udel-type polymer (Union Carbide) is prepared by reacting, 4,4'-dichlorodiphenylsulfone with an alkali salt of bisphenol A. The polycondensation is conducted in highly polar solvents, such as dimethylsulfoxide or sulfolane.



2.10

Table 2.2: Commercial polysulfones

Type of Structure	Tg (^{o}C)	Trade Name
A 	**190**	**Udel (Union Carbide)**
B 	**285**	**Astrel (3 M Corp.)**
C 	**230**	**Victrex (1C1)**
D 	**250**	**Polyether-Sulfone 720 P (1CI)**
E 	—	**Radel (Union Carbide)**

2.2.1 Properties of polysulfones

In spite of their linear and regular structure, the commercial polysulfones are amorphous. This property might be attributed to the high degree of chain stiffness of polymer molecules that make crystallization difficult. Because of their high in-chain aromaticity and consequent high chain stiffness, the polymers have high values of T_g, which means that the processing temperatures must be above 300^{0}C.

Commercial polymers generally resist aqueous acids and alkalis but are attacked by concentrated sulfuric acid. Being highly polar, the polymer is not dissolved by aliphatic hydrocarbons but dissolves in dimethyl formamide and dimethyl acetamide.

In addition to the high heat-deformation resistance, the polymers also exhibit a high degree of chemical stability. This has been ascribed to an enhanced bond strength arising from the high degree of resonance in the structure. The polymers are thus capable of absorbing a high degree of thermal and ionizing radiation without cross-linking.

The principal features of commercial polysulfones are their rigidity, transparency, self-extinguishing characteristics, exceptional resistance to creep, especially at somewhat elevated temperatures, and good high-temperature resistance [50].

Polysulfones are among the higher-priced engineering thermoplastics and so are only considered when polycarbonates or other cheaper polymers are unsuitable. In brief, polysulfones are more heat resistant and have greater resistance to creep, whereas polycarbonates have a somewhat higher Izod and tensile impact strength besides being less expensive.

In many fields of use polysulfones have replaced or are replacing metals, ceramics, and thermosetting plastics, rather than other thermoplastics. Since commercial polysulfones can be injection molded into complex shapes, they avoid costly machining and finishing operations. Polysulfones can also be extruded into film and foil. The latter is of interest for flexible printed circuitry because of its high temperature performance.

Polysulfones have found widespread use where good dimensional stability at elevated temperatures is required and fabrication is done by injection molding. Some products made from polysulfones are electrical components, connectors, coil bobbins, relays, and appliances operating at high temperatures (e.g., hair driers, fan heaters, microwave ovens, lamp housings and bases).

Polysulfones are transparent (though often slightly yellow), have low flammability (limiting oxygen index typically 38), and burn with little smoke production.

2.2.2 Limitations of polysulfones

Polysulfones have some of limitations. One of them is environmental stress crack resistance. Environmental stress crack resistance is not chemical degradation where a chemical reaction takes place changing the structure such as hydrolysis or ozone attack in rubbers. Actually, polysulfones has excellent chemical resistance in that it is not attacked by aqueous acids and bases or by oxygen and ozone. Environmental stress, cracking is a breakdown of physical structure due to a combination of applied stress, temperature and an aggressive chemical environment [51]. In general, the aggressive environments for polysulfone are the organic ketones, esters, aromatic hydrocarbons and certain chlorinated hydrocarbons. Resistance to environmental stress cracking is difficult to predict and testing in the actual environment of use is recommended. Use of glass fiber filled polysulfones is the best solution to this deficiency.

The second limitation of polysulfone is notch sensitivity. All polymers have some degree of notch sensitivity. The polycarbonates are outstanding in having very bad notch sensivity. The notch sensitivity of polysulfones can be overcome by proper part design that is by using generous radii or fillets to prevent stress concentration.

The weather resistance of polysulfone is poor. The high degree of resonance that imparts many beneficial properties also makes it a strong UV absorber. This results in poor weather resistance and makes the conventional means for improvement, UV absorbers, and defective. The best means for improving the weather resistance of polysulfone is through painting or electroplating [51].

2.2.3 Applications of polysulfones

Udel polysulfone can be fabricated by melt processing techniques available for thermoplastics, injection molding, extrusion and thermoforming [51]. Table 2.3 lists examples of early application areas and end uses for polysulfones [51].

Table 2.3: Industrial application of polysulfones

Aircraft & Aerospace

Passenger service units
Luggage rack bulk heads
Astronauts’ outer face mask shields

Automotive

Steering column units
Relay insulators
Pistons in load leveler

Appliances

Coffee makers
Humidifiers
Hair dryer components
Hot lather dispensers
Steam iron components
Egg cookers
Clothes steamers
Hot chocolate dispensers
Water heater dip tubes
Microwave oven components

Electrical & Electronic

Integrated circuit carriers
Connectors
Coil bobbins
Capacitor film
TV components
Brush holders
Terminal blocks
Business machine components
Printed circuit boards
Alkaline battery cases

Medical – Surgical

Respirator parts
Nebulizers
Dialysis components
Instruments
Sterilizable packages
Hospital feeding trays

Processing Equipment

Milking machine components
Ball valves
Steam table trays
Membranes for reverse osmosis
Microfiltration
Peterson separator candles

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Reagents for synthesis of monomer

Bis(4-chlorophenyl) sulfone (Sigma-Aldrich98%) : It was used as received.

Paraformaldehyde (powder, J.T.Baker, 95%) : It was used as received.

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

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

Potassium carbonate (Carlo Erba 99%) : It was used as received.

4-amino phenol (Merck, 99%) : It was used as received.

3.1.2 Solvents

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

Diethylether (Sigma-Aldrich) : It was used as recieved.

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

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

Chloroform (Sigma) : It was dried with P_2O_5 and distilled from CaH_2.

3.2 Equipments

3.2.1 ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.2 Infrared spectrophotometer (IR)

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

3.2.3 Differential scanning calorimeter (DSC)

Differential scanning calorimeter (DSC) was performed on a Perkin Elmer Diamond DSC with a heating rate of 10 oC min-1 under nitrogen flow.

3.2.4 Thermal gravimetric analyser (TGA)

Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 ºC min under nitrogen flow.

3.2.5 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation Methods

3.3.1 Synthesis of monomer

The monomer 4,4'-((sulfonylbis(4,1-phenylene))bis(oxy))dianiline was synthesized according to a modified procedure described in the literature. Thus, into a 100 ml, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer was placed 0.025 mol of bis(4-chlorophenyl) sulfone, 0.053 mol of 4-aminophenol, 60 ml of dry DMF, and 40 ml of dry toluene. Then 0.079 mol of K_2CO_3 was added to the mixture and the reaction mixture was heated to 140 ^{0}C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165^0C by removing more toluene and kept at the same temperature for 21 h. The resulting reaction mixture was cooled and poured into water. Then 100 ml of %5 NaOH was added to the mixture, filtered and washed with hot water. The crude mixture was washed repeatedly with a 5% NaOH solution, water, and finally, hot methanol. The obtained product was dried in a vacuum oven.

3.3.2 Synthesis of polymer

4,4'-((Sulfonylbis(4,1-phenylene))bis(oxy))dianiline (2.3 mmol, 1 g), bisphenol A (2.3 mmol, 0.52 g) or 4,4'-(perfluoropropane-2,2-diyl)diphenol(2.3 mmol,0.67 g), paraformaldehyde(9.2 mmol, 0.276g) were dissolved in 40 ml chloroform in a 100 mL three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser ,a thermometer. The reaction temperature was then raised to 110 ^{0}C in an oil bath. The reaction time is 6 h for obtain polymer. The reaction mixture was filtered and then liquid phase was concentrated and precipitated in methanol.

4. RESULTS AND DISCUSSION

Nucleophilic aromatic substitution reaction of 4-amino-1-phenol with bis(4-chlorophenyl)sulfone in the presence of anhydrous potassium carbonate in DMF resulted in sulfonylbisoxydianiline (Figure 4.1) [52]. The structure of the prepared diamine was characterized by ^{1}H-NMR and FT-IR spectrometers.

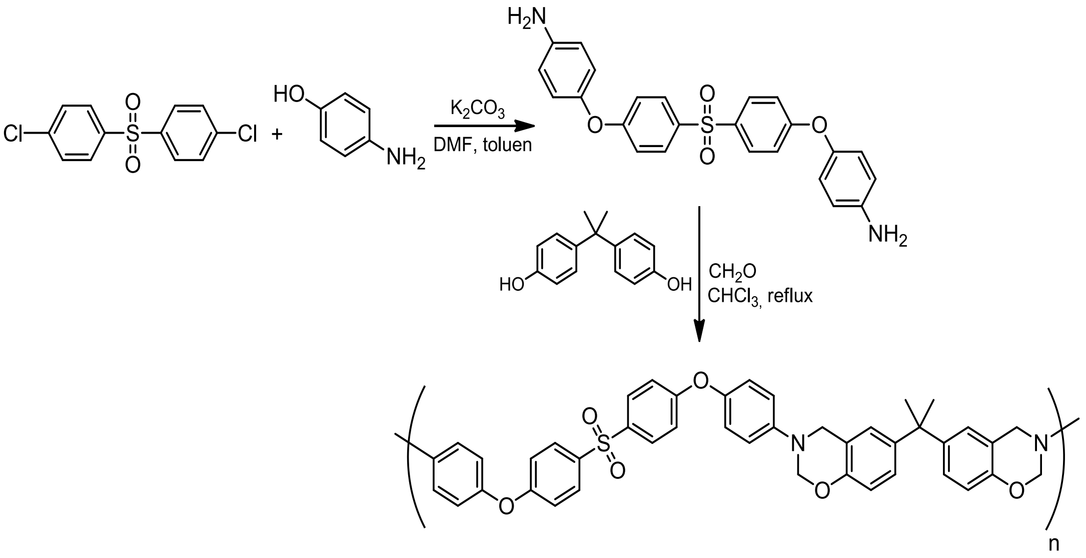


Figure 4.1 : Synthesis of (benzoxazine-co-sulfone)

^{1}H-NMR spectrum of sulfonylbisoxydianiline features NH_2 protons at 5.12 ppm and aromatic protons between 7.86-6.58 ppm (Figure 4.2). Moreover, IR spectra of sulfonylbisoxydianiline reveals NH_2 stretching vibrations at 3457, 3367 cm^{-1}, Ar-H stretching vibrations at 309, 3045 cm^{-1}, aromatic overtones between 1927-1871 cm^{-1}, NH_2 scissoring at 1622 cm^{-1}, sp^2 C-O stretching at 1233 cm^{-1}, S=O stretching vibrations at 1311 (asym.) and 1140 (strong, sym.) and additionally para-disubstituted benzene mode can be seen at 870, 831 cm^{-1}(Figure4.3).

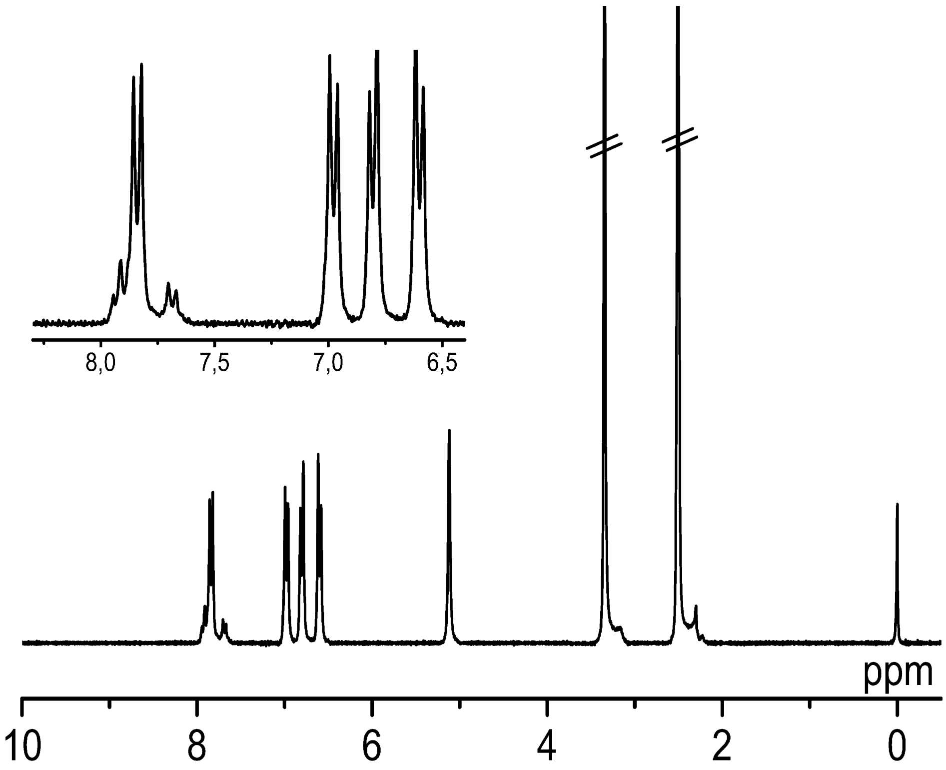


Figure 4.2 : ^{1}H-NMR spectrum of sulfonylbisoxydianiline

Condensation polymerization of sulfonylbisoxydianiline and bisphenol-A in the presence of formaldehyde resulted in poly(benzoxazine-co-sulfone) (See Figure 4.1). This method can also be coined as Mannich polymerization and has been independently reported by Takeichi and Ishida *et.al.* In this type of polymerization partially ring-opened structures were also observed by these authors [53, 54]. But, the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors. The structure of polymer confirmed by ^{1}H NMR spectrum. The O-CH$_2$-N and O-CH$_2$-Ar protons of oxazine emerge at 4.84 and 3.49 ppm, respectively. Additionally, due to partial ring-opened structure, phenolic OH protons can be seen as overlapped on the O-CH$_2$-N protons of oxazine at 4.95 ppm (See Figure 4.4). Moreover, IR spectra of the polymer reveals aromatic C-H stretching vibration at 3063 cm^{-1}, C-H aliphatic stretching at 2953,2912 cm^{-1}, CH$_2$ deformation band at 1387 cm^{-1}, S=O stretching vibrations at 1320 cm^{-1} (asym.) and 1149 cm^{-1} (strong, sym.), sp^2 C-O stretching at 1240 cm^{-1} and additionally 1,2,4-trisubstituted benzene mode at 934, *p*-disubstituted benzene mode at 834, 872 cm^{-1} (Figure4.3).

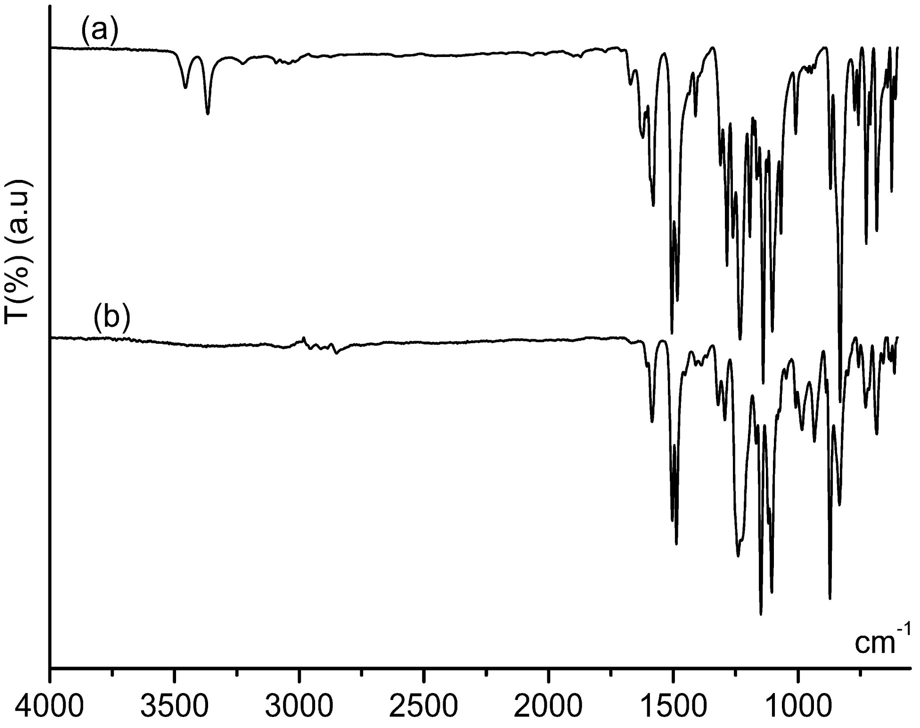


Figure 4.3 : FT-IR spectra of sulfonylbisoxydianiline and poly(benzoxazine-*co*-sulfone)

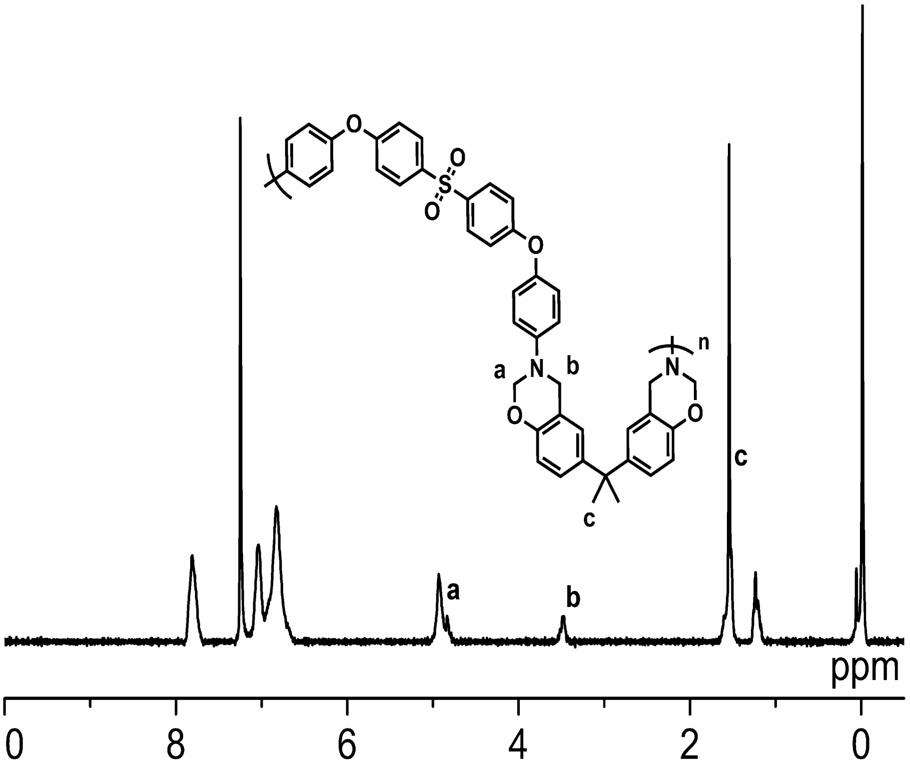


Figure 4.4 : ^{1}H-NMR spectrum of poly(benzoxazine-*co*-sulfone)

It is well known that thermally activated ring opening polymerization of 1,3 benzoxazines is an exothermic process which have maximums at around 200-250 °C depending on the functionalities of the benzoxazines. DSC thermogram the polymer shows an exotherm with an onset at 277 ^{o}C. Notably, a decrease in the ring opening temperature of benzoxazine structures is observed due to the phenolic moieties (Figure 4.5).

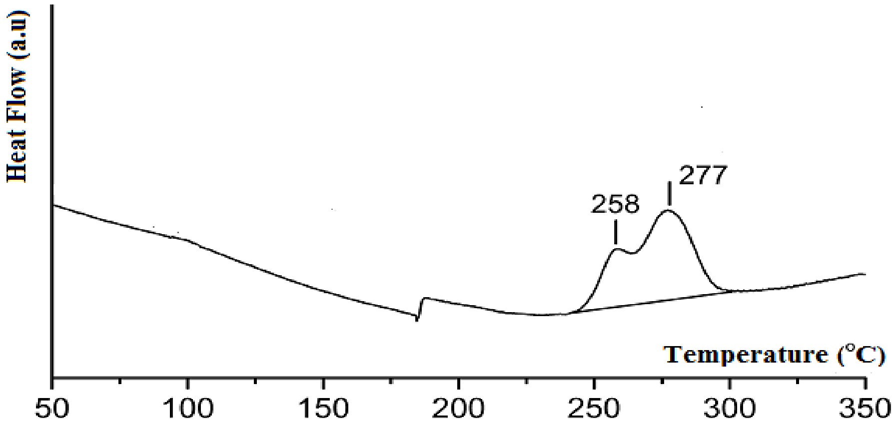


Figure 4.5 : Ring opening temperature of poli(benzoxazine-*co*-sulfone)

The degradation temperatures T5%, and T%10 of the cured oligo(benzoxazine-co-sulfone) is lower than cured neat poylsulfone which can be possibly attributed to Mannich base cleavage of the benzoxazine units. On the contrary, the degradation steps presented in Figure 6 reveals that the cured oligo(benzoxazine-co-sulfone) has higher initial and maximum degradation temperatures. It is quite likely that the sulfone and additional aromatic groups present in the structure prevent volatilization during heat exposure since the dissociation energy of the C-S bond (ΔH = 272 kJ/mol) is higher than that of the C-C bond (ΔH = 251 kJ/mol).

However, the weight lost becomes more significant for the cured oligo(benzoxazine-*co*-sulfone) at temperatures above ~550 ºC which may correspond to the formation and evaporation of sulphur-containing pyrolysis products such as SO_2. Moreover, the cured poly(benzoxazine-*co*-sulfone) has better char yield than neat polysulfone and comparable char yield to classical polybenzoxazine derived from P-a.

Table 2.4: Thermal Properties of the cured oligo(benzoxazine-*co*-sulfone), polysulfone and polybenzoxazine

Polymer	**$T_{5\%}$ (°C)**	**$T_{10\%}$ (°C)**	**T_{max} (°C)**	**Char (%) at 800 °C**
Polysulfone	356	431	524	21
Polybenzoxazine	293	342	398	35
Cured poly(benzoxazine-*co*-sulfone)	345	378	425	26

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

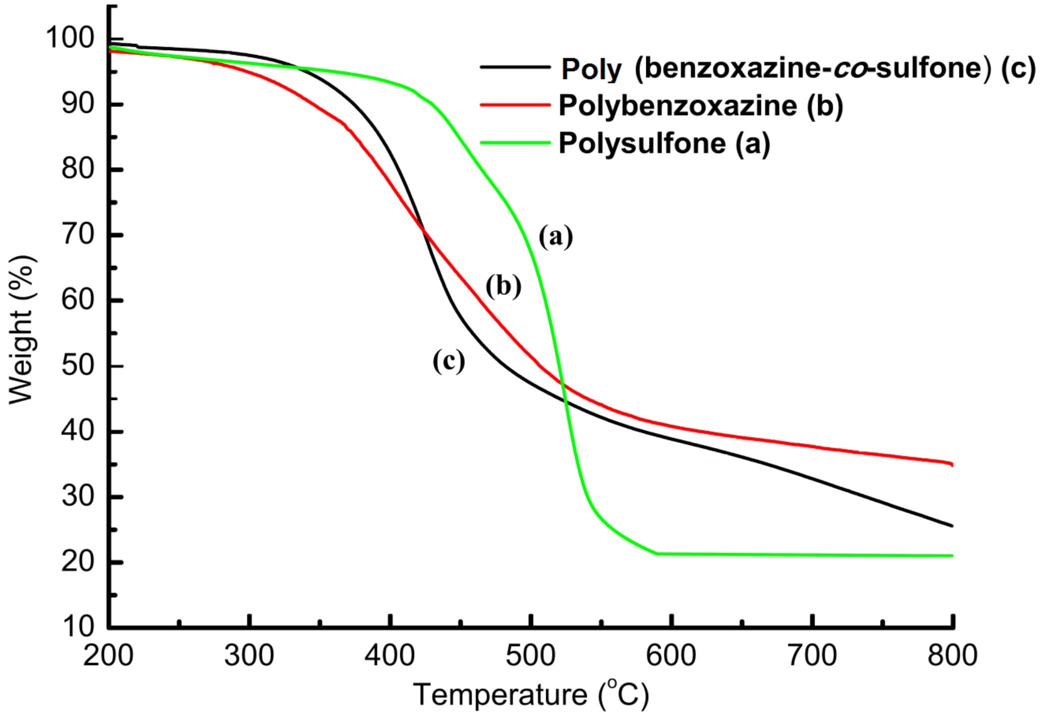


Figure 4.6 : TGA thermograms of poly(benzoxazine-co-sulfone), polysulfone and polybenzoxazine

The moleculer weight of polymer (Mn= 2960) is lower than expected value, suggesting that obtained polymer may have significantly different hydrodynamic volume compared to polystyrene calibration standards. The broad moleculer weight distribution evidences that the polymer was obtained via a step growth mechanism (Figure 4.7). Moreover, the broad molecular weight distribution of the polymer observed may be related to the type of polymerization emploed. Step-growth polymerization usually yields polymer with broader molecular weight distribution compare to the those obtaned by chain polymerization.

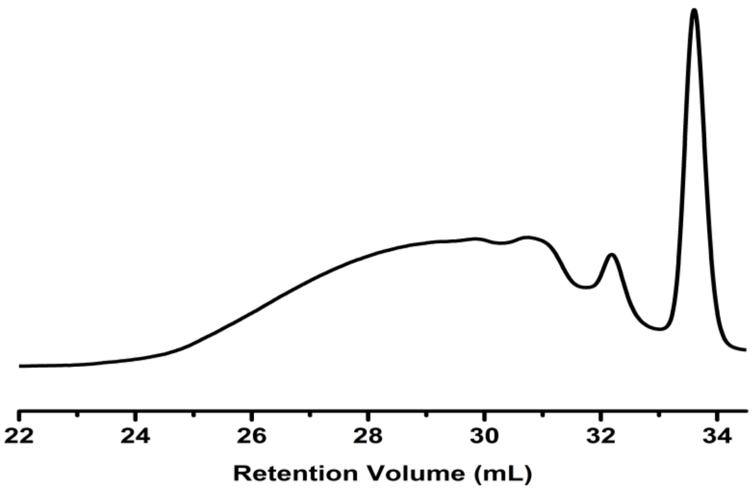


Figure 4.7 :GPC chromatogram of poly(benzoxazine-*co*-sulfone)

5. CONCLUSION

This study demonstrates that combination of the rigid aromatic sulfone structure enhances the thermal properties of polybenzoxazines which may lead to wider usage in various applications, particularly those needs high thermal stability. Herein, we have synthesized poly(benzoxazine-*co*-sulfone) precursor via condensation polymerization of suitable sulfone containing diamine and diphenols which was characterized by spectroscopic, chromatographic and thermal analyses methods successfully. Differencial scanning calorimetry studies reveal that incorparation of aromatic sulfone moieties into benzoxazine structures dramatically increases the thermal stability of benzoxazine polymers. The ring openinng temperature of the benzoxazine functinalty shifts from 200-250 ^{o}C to around 280 ^{o}C. Further investigations releated to thermal properties of the resulting polymers shows incorporation of sulfone groups improves thermal stability.

REFERENCES

[1] **Olabisi, O.**, *Handbook of thermoplastics*. 1997: CRC.

[2] **Pilato, L.**, *Phenolic resins: A century of progress*. 2010: Springer Verlag.

[3] **Holly, F.W. and Cope, A.C.**, 1944. Condensation products of aldehydes and ketones with o-aminobenzyl alcohol and o-hydroxy-benzylamine, *Journal of the American Chemical Society*, **66**, 1875-1879.

[4] **Burke, W.J.**, 1949. 3,4-dihydro-1,3,2h-benzoxazines. Reaction of p-substituted phenols with n,n-dimethylolamines, *Journal of the American Chemical Society*, **71**, 609-612.

[5] **Burke, W.J., Bishop, J.L., Glennie, E.L.M., and Bauer, W.N.**, 1965. A new aminoalkylation reaction . Condensation of phenols with dihydro-1,3-aroxazines, *Journal of Organic Chemistry*, 30, 3423-3427.

[6] **Burke, W.J.**, 1949. 3,4-dihydro-1,3,2h-benzoxazines. Reaction of p-substituted phenols with n,n-dimethylolamines, *Journal of the American Chemical Society*, **71**, 609-612.

[7] **Ning, X. and Ishida, H.**, 1994. Phenolic materials via ring-opening polymerization - synthesis and characterization of bisphenol-a based benzoxazines and their polymers, *Journal of Polymer Science Part a-Polymer Chemistry*, **32**, 1121-1129.

[8] **Ning, X. and Ishida, H.S.**, 1994. Phenolic materials via ring-opening polymerization of benzoxazines - effect of molecular-structure on mechanical and dynamic-mechanical properties, *Journal of Polymer Science Part B-Polymer Physics*, **32**, 921-927.

[9] **Kimura, H., Matsumoto, A., Hasegawa, K., Ohtsuka, K., and Fukuda, A.**, 1998. Epoxy resin cured by bisphenol a based benzoxazine, *Journal of Applied Polymer Science*, **68**, 1903-1910.

[10] **Burke, W.J., Kolbezen, M.J., and Stephens, C.W.**, 1952. Condensation of naphthols with formaldehyde and primary amines, *Journal of American Chemical Society*, **74**, 3601-3605.

[11] **Liu, J. and Ishida, H.**, in *A new class of phenolic resins with ring-opening polymerization, the polymeric materials encyclopedia*, J.C. Salamone, Editor. 1996, CRC Press: Florida. p. 484-494.

[12] Ishida, H., U.S. Patent, Editor. 1996.

[13] **Brunovska, Z., Liu, J., and Ishida, H.**, 1999. 1, 3, 5-triphenylhexahydro-1, 3, 5-triazine-active intermediate and precursor in the novel synthesis of benzoxazine monomers and oligomers, *Macromolecular Chemistry and Physics*, **200**, 1745-1752.

[14] **Liu, J.**, 1994. Ph. D. Thesis, case western reserve university, cleveland oh.

[15] **Agag, T., Jin, L., and Ishida, H.**, 2009. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4'-diaminodiphenyl sulfone-based benzoxazine monomer, *Polymer*, **50**, 5940-5944.

[16] **Hemvichian, K., Laobuthee, A., Chirachanchai, S., and Ishida, H.**, 2002. Thermal decomposition processes in polybenzoxazine model dimers investigated by tga-ftir and gc-ms, *Polymer Degradation and Stability*, **76**, 1-15.

[17] **Ning, X. and Ishida, H.**, 1994. Phenolic materials via ring opening polymerization: Synthesis and characterization of bisphenol a based benzoxazines and their polymers, *Journal of Polymer Science Part A: Polymer Chemistry*, **32**, 1121-1129.

[18] **Wang, Y.X. and Ishida, H.**, 2002. Development of low-viscosity benzoxazine resins and their polymers, *Journal of Applied Polymer Science*, **86**, 2953-2966.

[19] **Ning, X. and Ishida, H.**, 1994. Phenolic materials via ring opening polymerization of benzoxazines: Effect of molecular structure on mechanical and dynamic mechanical properties, *Journal of Polymer Science Part B: Polymer Physics*, **32**, 921-927.

[20] **Ishida, H. and Rodriguez, Y.**, 1995. Curing kinetics of a new benzoxazine based phenolic resin by dsc, *Abstracts of Papers of the American Chemical Society*, **210**, 273-PMSE.

[21] **Kimura, H., Matsumoto, A., Sugito, H., Hasegawa, K., Ohtsuka, K., and Fukuda, A.**, 2001. New thermosetting resin from poly(p-vinylphenol) based benzoxazine and epoxy resin, *Journal of Applied Polymer Science*, **79**, 555-565.

[22] **Wang, Y. and Ishida, H.**, 2002. Development of low viscosity benzoxazine resins and their polymers, *Journal of Applied Polymer Science*, **86**, 2953-2966.

[23] **Brunovska, Z., Liu, J.P., and Ishida, H.**, 1999. 1,3,5-triphenylhexahydro-1,3,5-triazine - active intermediate and precursor in the novel synthesis of benzoxazine monomers and oligomers, *Macromolecular Chemistry and Physics*, **200**, 1745-1752.

[24] **Ghosh, N.N., Kiskan, B., and Yagci, Y.**, 2007. Polybenzoxazines - new high performance thermosetting resins: Synthesis and properties, *Progress in Polymer Science*, **32**, 1344-1391.

[25] **Nair, C.P.R.**, 2004. Advances in addition-cure phenolic resins, *Progress in Polymer Science*, **29**, 401-498.

[26] **Riess, G., Schwob, J.M., Guth, G., Roche, M., and Laude, B.**, in *Advances in polymer synthesis*, B.M. Culbertson and J.E. McGrath, Editors. 1985, Plenum Press: New York. p. 27–49.

[27] **Riess, G., Schwob, J.M., and Guth, G.**, 1984. Ring-opening polymerization of benzoxazines - a new route to phenolic resins, *Abstracts of Papers of the American Chemical Society*, **188**, 85-Poly.

[28] **Espinosa, M.A., Galia, M., and Cadiz, V.**, 2004. Novel phosphorilated flame retardant thermosets: Epoxy-benzoxazine-novolac systems, *Polymer*, **45**, 6103-6109.

[29] Schreiber, H. 2 255 504; 1973: German Patent.

[30] Schreiber, H. 2 323 936, 1973.: German Patent.

[31] **Kim, H.J., Brunovska, Z., and Ishida, H.**, 1999. Synthesis and thermal characterization of polybenzoxazines based on acetylene-functional monomers, *Polymer*, **40**, 6565-6573.

[32] **Agag, T. and Takeichi, T.**, 2003. Synthesis and characterization of novel benzoxazine monomers containing allyl groups and their high performance thermosets, *Macromolecules*, **36**, 6010-6017.

[33] **Brunovska, Z. and Ishida, H.**, 1999. Thermal study on the copolymers of phthalonitrile and phenylnitrile-functional benzoxazines, *Journal of Applied Polymer Science*, **73**, 2937-2949.

[34] **Agag, T. and Takeichi, T.**, 2001. Novel benzoxazine monomers containing p-phenyl propargyl ether: Polymerization of monomers and properties of polybenzoxazines, *Macromolecules*, **34**, 7257-7263.

[35] **Kiskan, B. and Yagci, Y.**, 2007. Thermally curable benzoxazine monomer with a photodimerizable coumarin group, *Journal of Polymer Science Part A: Polymer Chemistry*, **45**, 1670-1676.

[36] **Ishida, H. and Ohba, S.**, 2005. Synthesis and characterization of maleimide and norbornene functionalized benzoxazines, *Polymer*, **46**, 5588-5595.

[37] **Andreu, R., Espinosa, M.A., Galia, M., Cadiz, V., Ronda, J.C., and Reina, J.A.**, 2006. Synthesis of novel benzoxazines containing glycidyl groups: A study of the crosslinking behavior, *Journal of Polymer Science Part a-Polymer Chemistry*, **44**, 1529-1540.

[38] **Takeichi, T., Kano, T., and Agag, T.**, 2005. Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets, *Polymer*, **46**, 12172-12180.

[39] **Chernykh, A., Liu, J.P., and Ishida, H.**, 2006. Synthesis and properties of a new crosslinkable polymer containing benzoxazine moiety in the main chain, *Polymer*, **47**, 7664-7669.

[40] **Kiskan, B., Yagci, Y., and Ishida, H.**, 2008. Synthesis, characterization,, and properties of new thermally curable polyetheresters containing benzoxazine moieties in the main chain, *Journal of Polymer Science Part a-Polymer Chemistry*, **46**, 414-420.

[41] **Kiskan, B., Aydogan, B., and Yagci, Y.**, 2009. Synthesis, characterization, and thermally activated curing of oligosiloxanes containing

benzoxazine moieties in the main chain, *Journal of Polymer Science Part A: Polymer Chemistry*, **47**, 804-811.

[42] **Yagci, Y., Kiskan, B., and Ghosh, N.**, 2009. Recent advancement on polybenzoxazine—a newly developed high performance thermoset, *Journal of Polymer Science Part A: Polymer Chemistry*, **47**, 5565-5576.

[43] **Kiskan, B., Yagci, Y., Sahmetlioglu, E., and Toppare, L.**, 2007. Preparation of conductive polybenzoxazines by oxidative polymerization, *J. Polym. Sci. Part A: Polym. Chem.*, **45**, 999-1006.

[44] **Wang, Y.X. and Ishida, H.**, 1999. Cationic ring-opening polymerization of benzoxazines, *Polymer*, **40**, 4563-4570.

[45] **Wang, Y.X. and Ishida, H.**, 2000. Synthesis and properties of new thermoplastic polymers from substituted 3,4-dihydro-2h-1,3-benzoxazines, *Macromolecules*, **33**, 2839-2847.

[46] **Russell, V.M., Koenig, J.L., Low, H.Y., and Ishida, H.**, 1998. Study of the characterization and curing of benzoxazines using c-13 solid-state nuclear magnetic resonance, *Journal of Applied Polymer Science*, **70**, 1413-1425.

[47] **Kasapoglu, F., Cianga, I., Yagci, Y., and Takeichi, T.**, 2003. Photoinitiated cationic polymerization of monofunctional benzoxazine, *Journal of Polymer Science Part a-Polymer Chemistry*, **41**, 3320-3328.

[48] **Cheremisinoff, N.**, *Condensed encyclopedia of polymer engineering terms*. 2001: Butterworth-Heinemann.

[49] **Chanda, M. and Roy, S.**, *Industrial polymers, specialty polymers, and their applications*. 2008: CRC.

[50] **Peinemann, K. and Nunes, S.**, *Membranes for life sciences*. 2007: Wiley-VCH Verlag GmbH.

[51] **Seymour, R.**, *"Polyether ketones, polysulfones, and polyphenylene sulfide" chapter 17, in engineering polymer sourcebook,*. 1990: McGraw-Hill Companies.

[52] **Mehdipour-Ataei, S.**, 2005. Novel thermally stable poly(sulfone ether ester imide)s, *European Polymer Journal*, **41**, 91-96.

[53] **Chernykh, A., Liu, J., and Ishida, H.**, 2006. Synthesis and properties of a new crosslinkable polymer containing benzoxazine moiety in the main chain, *Polymer*, **47**, 7664-7669.

[54] **Takeichi, T., Kano, T., Agag, T., Kawauchi, T., and Furukawa, N.**, 2010. Preparation of high molecular weight polybenzoxazine prepolymers containing siloxane unites and properties of their thermosets, *Journal of Polymer Science Part A: Polymer Chemistry*, **48**, 5945-5952.

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