ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF THIOAMIDE CONTAINING POLYBENZOXAZINES BY WILLGERODT-KINDLER REACTION

M.Sc. THESIS

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Thesis Advisor: Assoc. Prof. Barış KIŞKAN

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TİYOAMİT İÇEREN POLİBENZOKSAZİNLERİN WILLGERODT-KINDLER REAKSİYONU İLE SENTEZİ

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Kamer BAYRAM, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 509171232, successfully defended the thesis entitled "SYNTHESIS OF THIOAMIDE CONTAINING POLYBENZOXAZINES BY WILLGERODT-KINDLER REACTION", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my husband and family,

FOREWORD

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June 2020 Kamer BAYRAM
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

Bz	**:** 1,3-Benzoxazine
Da	**:** Dalton
DCM	**:** Dichloromethane
DHC	**:** 3,4-Dihydrocoumarin
DMAc	**:** Dimethylacetamide
DMF	**:** Dimethylformamide
DSC	**:** Differential Scanning Calorimetry
FT-IR	**:** Fourier Transform Infrared
GPC	**:** Gel Permeation Chromatography
^{1}H-NMR	**:** Nuclear Magnetic Resonance Spectroscopy
HY	**:** Hydrogen Containing Compound
PA	**:** Polyamide
PBz	**:** Polybenzoxazine
ROP	**:** Ring Opening Polymerization
TGA	**:** Thermogravimetric Analyzer
THF	**:** Tetrahydrofuran
Th-amd-MonoBz-Bn	**:** Benzylamine based thioamide-benzoxazine
Th-amd-MonoBz-Fr	**:** Furfurylamine based thioamide-benzoxazine
Th-amd-DiBz-Bn	**:** Benzylamine based dithioamide-benzoxazine
Va-DiBenz	**:** Vanillin based Di-Benzoxazine

SYMBOLS

T_g	**:** Glass Transition Temperature
T_{max}	**:** Curing Maximum
T_{cure}	**:** Polymerization Temperature
$T_{5\%}$	**:** The Temperature of which the Weight Loss is 5%.
$T_{10\%}$	**:** The Temperature of which the Weight Loss is 10%.
T_c	**:** The Char Yield at 800 °C

LIST OF TABLES

LIST OF FIGURES

Page

SYNTHESIS OF THIOAMIDE CONTAINING POLYBENZOXAZINES BY WILLGERODT-KINDLER REACTION

SUMMARY

Advanced polymers are used in quite wide areas to increase our daily comfort. The processable and improvable structures of polymers have been the focus of interest for researchers, eventually fields of application in science, technology, and industry are increasing day by day.

The terms thermoplastic and thermoset determine by how a material can be processed under a changed temperature. Thermoplastic polymers can be melted at elevated temperatures and can be shaped and by heating can be reshaped according to the mold. Thermoset polymer becomes rigid when heated and it can not be reshaped by heating. Due to their cross-linked structure, they are insoluble in solvents. Phenol-formaldehyde, melamine-formaldehyde, urea-formaldehyde are some examples of thermoset materials.

Looking at the worldwide production in recent years, phenol-formaldehyde resins are among the most produced thermoset resins. Phenolic resins can be applied in many fields such as construction, adhesive industry, conductive polymers, aviation. The properties of phenolic resins such as heat and flame resistance, dimensional stability, high mechanical strength, resistance to solvents and low cost enable these resins to be used in these application areas. Phenol-formaldehyde resins are the first synthetic and commercially available thermoset polymer.

Benzoxazine resins termed as polybenzoxazines, have been developed to overcome the disadvantages of phenolic resins such as high curing temperatures, short shelf life, brittleness, by-product formation during curing and catalyst requirement. Polybenzoxazines, have become superior to traditional phenolic resins thanks to their near-zero volumetric changes during curing, low moisture absorption, no strong catalyst requirement during curing, no toxic by-products, high char yield properties. Another advantage is the easy synthesis of benzoxazine monomers using phenol, primary amines, and formaldehyde. The formation of polybenzoxazine is carried out by the ring-opening reaction occurring in the oxazine ring of the benzoxazine monomer. Although there are several oxazine isomers, including 1,2-, 1,3- and 1,4-, polybenzoxazines are synthesized from the 1,3-benzoxazine monomer. Because only 1,3-benzoxazine monomers are suitable for the ring-opening reaction.

The design flexibility of benzoxazines enables monomer synthesis with various functional groups. Polymers which are obtained from benzoxazine monomers with different functional groups may exhibit different physical and chemical properties, such as high efficiency, self-healing, shape-memory, etc.

As it is well known, thioamides, which are carboxylic acid derivatives, can be synthesized by the Willgerodt-Kindler reaction. In this study, the first examples of thioamide-containing benzoxazines were successfully produced by using the design flexibility of benzoxazine through the Willgerodt-Kindler reaction. In these syntheses, primarily phenolic mono and difunctional thioamides were obtained. Three different benzoxazine monomers were synthesized using the obtained phenolic thioamides and primary amines. In addition, while thioamides are obtained in these reactions, an environmentally friendly approach has been applied by using elemental sulfur, which is released as a by-product from the coal and petroleum industry. Then, the difunctional benzoxazine monomer containing phenolic thioamide and the main chain polybenzoxazine containing thioamide by Mannich type polycondensation were successfully synthesized.

This thioamide-containing polybenzoxazine exhibited good film-forming properties and flexible films were obtained. All starting phenolic reagents, benzoxazine monomers and polybenzoxazines obtained in this study were characterized by ^{1}H-NMR and FT-IR spectroscopy. Curing behavior and thermal stability of the compounds were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

TİYOAMİT İÇEREN POLİBENZOKSAZİNLERİN WILLGERODT-KINDLER REAKSİYONU İLE SENTEZİ

ÖZET

Günümüzde gelişmiş polimerler, yaşam konforumuzu artırmak için oldukça geniş alanlarda kullanılmaktadır. Polimerlerin geliştirilebilir ve modifiye edilebilir yapısı araştırmacılar için ilgi odağı olmuştur. Bu sayede bilim, teknoloji ve endüstride uygulama alanları gün geçtikçe artmaktadır.

Polimerler ısı karşısındaki davranışlarına göre; eriltilip tekrar şekil verilebiliyorsa termoplastik, eritilip tekrar şekillendirilemiyorsa termoset olarak adlandırılırlar. Poli(etilenteraftalat), poli(vinilklorür) termoplastik polimerlere örnek olarak verilebilir. Termosetler çapraz bağlı yapıları nedeniyle yeniden şekillendirme gösteremezken, çözücülerde çözünmez ve sert yapılıdırlar. Fenol-formaldehit, melamin-formaldehit, üre-formaldehit termoset polimerler örnekleridir.

Termoset reçineler sahip olduğu özellikler nedeniyle endüstride ve araştırmalarda ön plana çıkmıştır. Son yıllarda dünya çapında üretimlere bakıldığında fenol-formaldehit reçineler en çok üretilen termoset reçineler arasında yer almaktadır. Fenolik reçineler, inşaat, yapıştırıcı endüstrisi, iletken polimerler, devre kartları, havacılık gibi bir çok alanda uygulanabilmektedir. Fenolik reçinelerin; ısı ve alev dayanımı, boyutsal kararlılığı , yüksek mekanik mukavemeti, solventlere karşı direnci, düşük maliyet gibi özellikleri bu uygulama alanlarında kullanılmasını sağlamaktadır. Fenol-formaldehit reçineleri ilk sentetik ve ticari olarak piyasaya çıkmış termoset polimerdir.

Fenolik reçinelerin yüksek kürlenme sıcaklıkları, kısa raf ömrü, kırılganlıkları, kürlenme sırarsında yan ürün oluşturması, katalizör gereksinimi gibi dezavantajların üstesinden gelmek için (benzoksazin reçineleri) polibenzoksazinler geliştirilmiştir.

Polibenzoksazinler kürleme sırasında sıfır hacimsel değişim, düşük nem absorpsiyonu, kürleme sırasında güçlü katalizör gerektirmemeleri, toksik yan ürün oluşturmaması, yüksek kül verimi özellikleri sayesinde geleneksel fenolik reçinelerin önüne geçmektedir. Benzoksazin monomerlerinin fenol, primer aminler ve formaldehit kullanılarak kolaylıkla yapılan sentezi bir diğer avantajıdır. Polibenzoksazin oluşumu benzoksazin monomerinin oksazin halkasında meydana gelen halka açılma reaksiyonuyla gerçekleşir. 1,2- , 1,3- ve 1,4- olmak üzere çeşitli oksazin izomerleri bulunmasına rağmen, polibenzoksazinler 1,3- benzoksazin monomerinden sentezlenmektedir. Çünkü yalnızca 1,3-benzoksazin monomerleri halka açılma reaksiyonu için uygundur.

Benzoksazinlerin tasarım esnekliği, bize çeşitli monomer sentezi imkanı sağlamaktadır. Benzoksazin monomerlerin çeşitlendirilmesi kürleme sonrası elde edeceğimiz polimerlerde farklı kimyasal, fiziksel özellikler, verim artışı, akıllı malzemeler, kendini iyileştirebilen malzemeler üretmemizi sağlayabilir.

Bilindiği üzere, Willgerodt-Kindler reaksiyonu ile karboksilik asit türevi olan tiyoamidler sentezlenebilmektedir. Bu çalışmada Willgerodt-Kindler reaksiyonu ile benzoksazinin tasarım esnekliğinden faydalanarak tiyoamid içeren benzoksazinlerin ilk örneği başarıyla üretildi. Bu sentezlerde öncelikle fenolik mono ve difonksiyonel tiyoamidler elde edildi. Elde edilen fenolik tiyoamidler ile primer aminler kullanılarak üç farklı benzoksazin monomeri sentezlendi. Ayrıca bu reaksiyonlarda tiyoamidler elde edilirken, petrol ve doğalgaz endüstrisinde yan ürün (atık ürün) olarak açığa çıkan elementel sülfür kullanılarak çevre dostu bir yaklaşım uygulanmıştır. Daha sonra fenolik tiyoamid içeren difonksiyonel benzoksazin öncüsü, Mannich tipi polikondenzasyon ile tiyoamid içeren ana-zincir polibenzoksazin başarıyla sentezlendi.

Bu tiyoamid içeren polibenzoksazin, iyi film oluşturma özellikleri sergiledi ve esnek filmler elde edildi. Bu çalışmada elde edilen tüm başlangıç maddeleri, benzoksazin monomerleri ve polibenzoksazinler ^{1}H-NMR ve FT-IR spektroskopileri ile karakterize edildi. Bileşiklerin kürlenme davranışları ve termal kararlılıkları diferansiyel tarama kalorimetresi (DSC) ve termogravimetrik analiz (TGA) ile analiz edilmiştir.

1. INTRODUCTION

Polybenzoxazines as contender thermosets to classical phenolic resins gained much interest in the past decade. These polymers exhibit unusual properties stemming from their unique structure. A typical polybenzoxazine contains aminomethyl bridges between phenolic moieties and therefore several intra- and intermolecular hydrogen bonds are generated. Moreover, the phenolic nature of these materials brings about many properties already seen in phenol-formaldehyde resins. In general, most of the polybenzoxazines exhibit high thermal stability, char yield, glass transition temperatures, low water absorption, flammability and limited shrinkage during production from their corresponding monomers. Besides, low dielectric constants and resistance against corrosive chemicals are other benefits of these materials. Consequently, many different applications related to these properties were already put into practice in aerospace, automotive and electronic industries. Another appealing side of polybenzoxazines is their ease of synthesis from 1,3-benzoxazine monomers. Since, performing a simple heating procedure for 1,3-benzoxazines would give polybenzoxazines without using additives and/or curatives. However, the curing characteristics and temperature depend on the monomer structure.

A typical benzoxazine monomer is synthesized from a primary amine, a phenol and 2 equivalent formaldehyde. Therefore, by varying the amine and phenolic several different benzoxazines can be synthesized. In this line, many benzoxazines were synthesized with diverse functional groups. Among these groups, particularly, amides gained much interest due their hydrogen bonding ability. Thus, various amide containing benzoxazines were reported [1-4]. Although various amide functional benzoxazines were synthesized, thioamide based benzoxazine have never been reported.

2. THEORETICAL PART

2.1 Phenolic Resins

A wide variety of thermoset materials are used in different fields of the industry. Among these, phenol-formaldehyde resins, the first commercial thermosetting plastics synthesized from completely synthetic materials, have been used since the 1900s [5]. Leo Baekeland, ‘father of the phenolic resins’, developed these resins and published as a patent in 1907 [6,7].

Phenolic resins have applications in a broad range of industries such as aerospace, automotive, marine, electronic, insulation and commodity goods. These type of resins especially preferred in the aerospace industry due to their desirable properties like excellent heat resistance and low flammability. They emit low smoke, low toxic products during a fire. Moreover, phenolic resins are resistant against corrosion. Besides these properties, another reasons for their popularity and wide use is their synthesis from low cost chemicals [8].

Phenolic resins are produced through the condensation polymerization reaction of phenol and formaldehyde under acidic or basic conditions. To comprehend the variety of the convenient phenolic resins, it is necessary to understand how the reaction occurs between phenol and formaldehyde under acidic or basic conditions. In addition, the formaldehyde/phenol molar ratio has effect on the structure of final product as given in Figure 2.1 [9].

Resole type resins so-called heat reactive resins are manufactured by reacting phenol with a molar excess more than equimolar amount of formaldehyde (the phenol/formaldehyde molar ratio generally between 1/1.2 and 1/3) using a base catalyst such as sodium carbonate, ammonia in the presence of an alkaline solution. Since resole molecule contains reactive methylol groups, it can form easily large molecules only by heating and does not require addition of hardener or curing agent as shown in Figure 2.2. Therefore, they are termed/called single-step phenolic resins. [10,11].

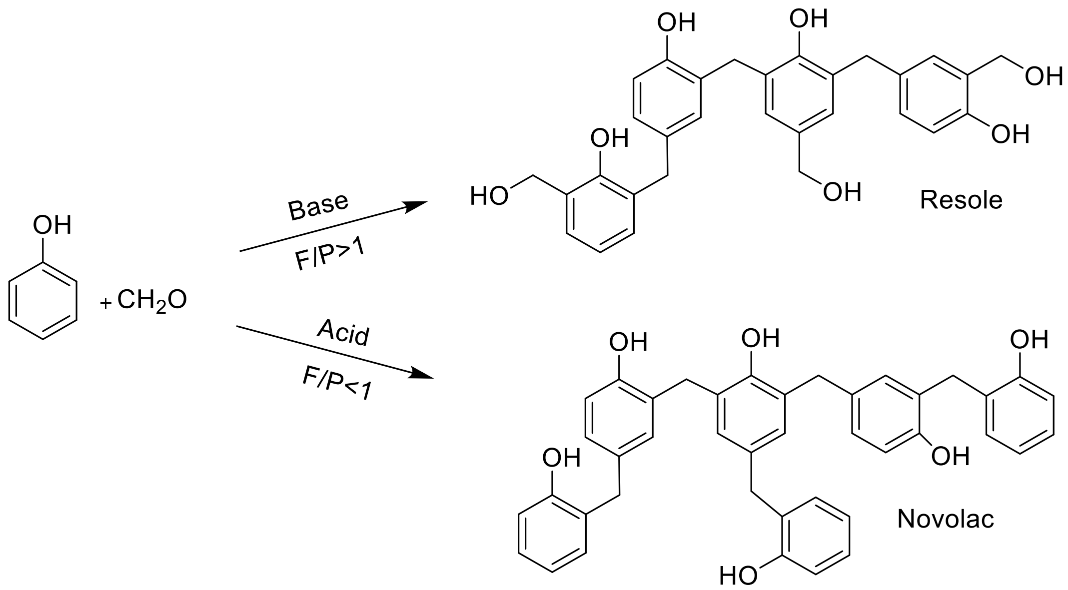


Figure 2.1 : Synthesis of resole and novolac.

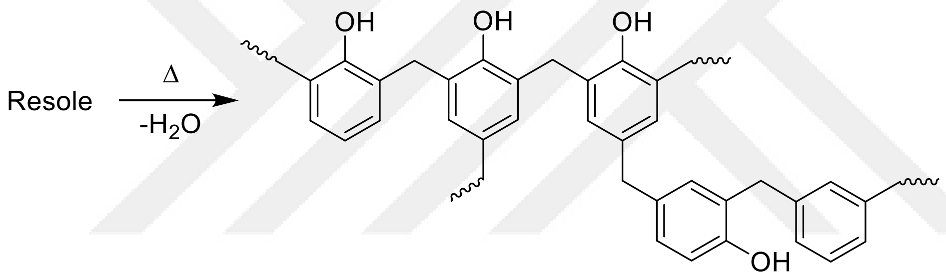


Figure 2.2 : Cross-linked structure of resole type phenolic resin.

In contrast to resole, novolac compounds are obtained in the presence of acid catalysts and the higher molar ratio of phenol than formaldehyde. The most frequently used catalysts are sulfuric, hydrochloric, toluene sulfonic acids (H_2SO_4, HCl, *p*-TSA). Novolac resins so-called two-stage phenolics, the reason why novolacs are called two-stage phenolics is that hardening takes place only with the addition of cross-linking agents. Novolac resins require a hardener in order to produce a crosslinking compound because they have no reactive methylol groups in its structure and need an additional source of methylene bridges. These are provided by cross-linking agents like hexamethylenetetramine (HMTA). The cross-linked structure of novolac is given in Figure 2.3 [5,8].

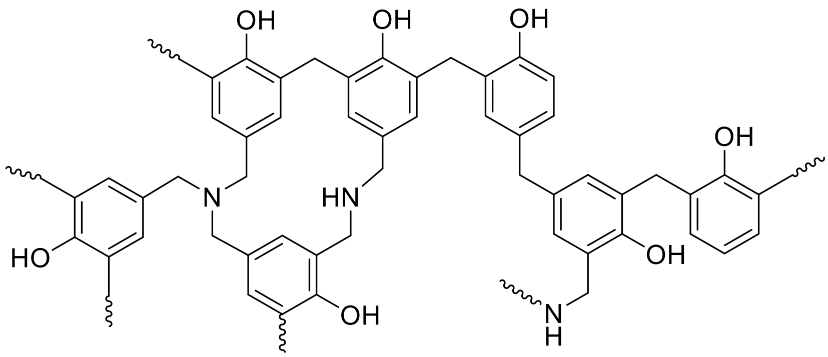


Figure 2.3 : Cross-linked structure of novolac type phenolic resins.

2.2 Benzoxazines

2.2.1 History of benzoxazine chemistry

Holly and Cope published the first article on the synthesis of benzoxazines in 1944 [12]. Later, in the 1950s and 1960s, Bruke *et al.* made significant contributions to the development of benzoxazine chemistry with several studies on low molecular weight benzoxazines [13-20].

After these pioneering synthetic studies, benzoxazines were used in medicinal chemistry researches for a decade that is completely different from polymer chemistry. However, the synthesis of small benzoxazine oligomers for modifying epoxy resins was patented and published by Schreiber *et al.* in the 1970s. Following the first development of material by oligobenzoxazines, the first studies on cross-linked polybenzoxazines based on multifunctional benzoxazines were performed by Higginbottom et al. in 1980. Nevertheless, he did not state the properties of these polybenzoxazines in his patent [21].

Riese *et al.* discovered that high molecular weight linear polybenzoxazines could not be generated from monofunctional benzoxazine monomers. Because, monofunctional benzoxazines form only oligomers [22].

In his studies with various monomers, at the end of the polymerization, it has been indicated that the molecular weights of the polymerization are between hundreds and thousands.

The self-curable benzoxazine functional resins formulation were published in 1988 by Turpin and Thrane. They also defined the usage of multifunctional various phenols and amines as reactants/reagents for benzoxazine resins with small molecular weight [23].

Although studies on the discovery and synthesis of low molecular weight of benzoxazines were begun in the 1940s, after a long period of development, Ning and Ishida published the first study on defining the features of polybenzoxazines in 1994 [24].

Afterward, the potential and capabilities of polybenzoxazines have gained interest and still many studies are ongoing today.

2.2.2 Synthesis of benzoxazines

Benzoxazine monomers are synthesized usually by the reaction of phenols, primary amines, and formaldehyde solution or paraformaldehyde as starting reactants. This synthetic method can be performed in either solution or solventless methods.

The possible combinations of phenols and amines with various functionalities provide different types of benzoxazine monomers. Thus, these groups could affectthe curing process and the properties of resulting polybenzoxazines [25].

In this part, synthesis approaches of benzoxazine monomers have been discussed.

2.2.2.1 Synthesis of mono-functional benzoxazines

For the first research of a benzoxazine monomer, Holly and Cope [12] published the benzoxazine resulting from the reaction of primary amines with formaldehyde and substituted phenols via a condensation reaction.

This synthesis method of benzoxazine monomer proceeded with two stages in a solvent. First, adding an amine to formaldehyde at low temperatures resulted *N*,*N*-dihydroxymethylamine formation. Afterward this compound reacted with the hydroxyl group and ortho position of the phenol at high temperature, thereby oxazine ring formed. The first stage is a kind of Mannich Reaction and formation of Mannich base, the second stage is the reaction between phenol and Mannich base to give benzoxazine. It is clear that the phenol should have a vacant ortho-position otherwise, ring-closure is impossible [13,18].

The synthesis of 3,4-dihydro-2*H*-1,3-benzoxazine demonstrated in (Figure 2.4) and the plausible mechanism is as follow (Figure 2.5)

Figure 2.4 : Synthesis of of 3,4-dihydro-2*H*-1,3-benzoxazine.

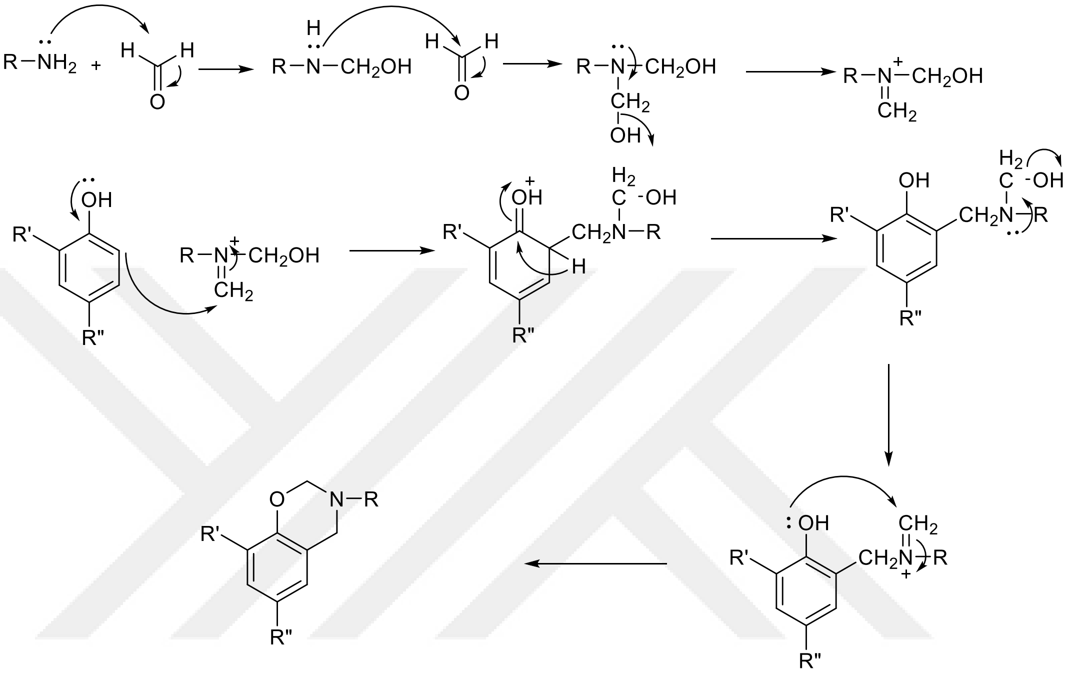


Figure 2.5 : Plausible mechanism of benzoxazine ring formation.

During the benzoxazine synthesis, triazines, oligobenzoxazines and aminoalkyl phenols are also produced due to side reactions. Especially, in the existence of acidic compounds a ring-opening reaction may occur (Figure 2.6) [16]. On the other hand, the amount of these side products can be decreased by blocking the para position of the used phenol and selecting non-acidic reagents. Moreover, the triazine formation can be controlled to some extent by arranging the solvent polarity. For example, triazine formation severely limited in the case of toluene/ethanol mixture (2:1, v/v).

As it is presented in the Figure 2.6, the ring-opening reaction of benzoxazine under acidic conditions generates the Mannich-bridge [26].

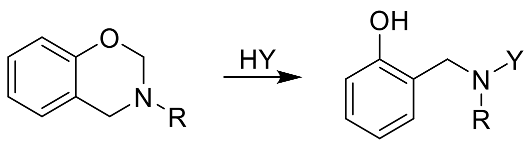


Figure 2.6 : Ring opening of benzoxazine in acidic medium.

The efficient solvent-free approach has been improved as a new alternative method to classical benzoxazine synthesis[27]. Since the synthetic method in a solvent can have some drawbacks, for instance, the requirement of a large volume of solvent, the low solubility of the starting reactants in a solvent, slow reaction rates, uncontrolled triazine formation.

Moreover, consuming organic solvents intensify the problems related to the environment. In addition, solvent residues in the final benzoxazine product could generate problems during curing stage, such as void formation in the polybenzoxazine molds or films.

As an alternative, solventless synthesis of benzoxazines are used to cope with the stated drawbacks. Solventless synthesis generally requires less reaction time and formation of side-products are reduced [27,28]. However, the solventless synthesis is limited to reagents that can be melted and miscible in each other. There are many different phenols and amines have high melting point and not miscible with each other.

2.2.2.2 Synthesis of bifunctional and multifunctional benzoxazines

In general, the polymerization process of monofunctional benzoxazines, depending on the structure, yield low molecular weight networks or oligomers that have molecular weight approximately 1000Da. The thermal dissociation in the reaction dominates chain propagation, therefore it is not possible to obtain high molecular weight polybenzoxazines by classical mono-benzoxazines [22].

In order to overcome this restriction, difunctional or multifunctional monomers have been dominated the practical applications. Although formation of oligomers to some extent can be observed for multifunctional benzoxazines, the majority of the final polybenzoxazine are large networks. There are several types of multifunctional benzoxazine monomers [24,29]. Among them, bisphenol-A based (BA-a resin) benzoxazines are extensively used for various application and this monomer can be synthesized by using bisphenol-A and primary amines (mostly aniline) either aromatic or aliphatic [30,31]. An example of this type is shown Figure 2.7.

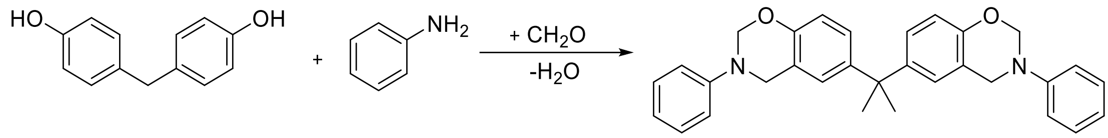


Figure 2.7 : Synthesis of bisphenol A- and methylamine- based benzoxazine.

Another type is diamine based bifunctional benzoxazines, which can be manufactured by the reaction of diamines (aromatic or aliphatic) with a monofunctional phenol having vacant ortho position. The example is given in Figure 2.8 [32].

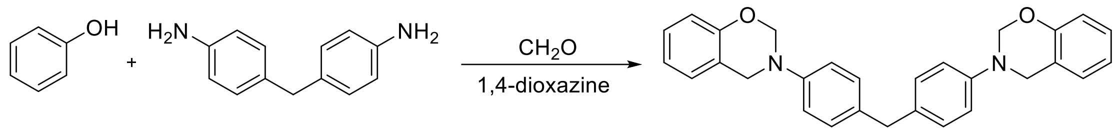


Figure 2.8 : Synthesis of DDM-based benzoxazine.

2.2.3 Ring opening polymerization mechanism of benzoxazines

Benzoxazines are polymerized through ring-opening polymerization with or without catalyst. The ring-opening polymerization method is a versatile route to obtain phenolic resins. Since, this approach requires self-polymerizable active monomers unlike classical pheol-formaldehyde production. Thus, many shortcomings of phenolic resin synthesis are alleviated like by-product formation, harsh acidic/basic catalyst requirements and formaldehyde emission during curing [25].

In terms of energy minimization, the preferred conformation of the benzoxazine ring is a distorted semi-chair structure. Although oxazine ring is a six membered chain, the close proximity of N and O atoms generate a ring strain. Moreover, the electronegativity of this heteroatom polarizes the N–CH_2–O bridge. Thus, benzoxazines can be polymerized through a ring-opening reaction under appropriate conditions. Literally, the ring strain and bond polarization are sufficient for a ring opening reaction at low temperature. Therefore, the ring-opening polymerization requires high temperatures such as 180–250 °C. On the other hand, the N and O atoms in the oxazine ring can be protonated by Bronsted acids or similarly Lewis acids can bind these atoms. Consequently, the ring strain and bond polarity increases to a certain level that even at room temperature ring opening takes place [30]. These findings clearly reveal that ring opening polymerization can be catalyzed by Bronsted acids and Lewis acids. These catalysts effectively reduce the ring opening polymerization temperatures. However, the final structure may differ from the uncatalyzed polybenzoxazines [33]. The mechanistic studies also revealed that the polymerization benzoxazines are a type of cationic ring opening polymerization and the N, O atoms stabilizes the cationic species during the polymerization process by their non-bonding electron pairs. The protonation of the 1,3-benzoxazine ring by the migration of the proton from N to O atom results formation of iminium ion intermediates [34]. Later on, the formation of such ionic species, proceed by electrophilic aromatic substitution as represented in Figure 2.9 [25,35,36].

The polymerization rate of benzoxazines is fast compared to condensation of phenol-formaldehyde but slow considering epoxides, due to the requirement of high energy to cleavage of the oxazine ring. Therefore, catalyzing the benzoxazine polymerization via acidic compounds is beneficial to both increase the polymerization rate and reduce the curing temperatures.Various catalysts (cationic, nucleophilic and radicalic) for the polymerization of benzoxazine precursors have been examined to decrease the curing temperature and time [37].

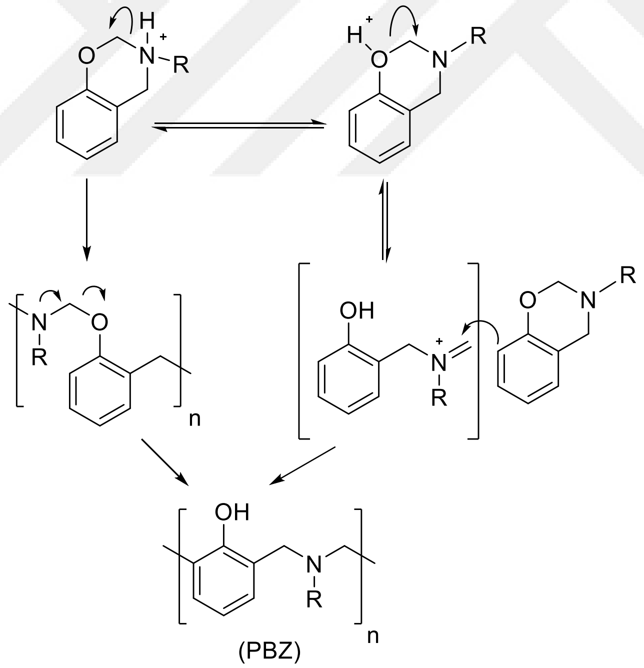


Figure 2.9 : Simplified polymerization mechanism of benzoxazines to give polybenzoxazines.

2.2.4 Properties of benzoxazine monomers and polybenzoxazines

The properties of polybenzoxazines differ according to the corresponding monomer, curing procedure, catalyst use. Because, the functionilites on the monomers could alter the final properties drastically. Moreover, curing procedure such as post curing, stepwise curing could have vast effect on the crosslinking density. Catalyst usage may change the final structure by increasing the aromatic ether formation as reported previously. Therefore, the properties of polybenzoxazine could be engineered by selecting suitable monomers, curing procedure and catalysts. However, a list of properties can be attributed to polybenzoxazine as general behavior of these materials.

-Forming no by-product during polymerization

-Near zero shrinkage upon polymerization process

-Good water resistance

-Heat resistance

-Low flammability

-High char-yields

-High modulus and glass transition temperature (T_g)

-Good thermal stability

-No need a strong acid catalyst or initiator for polymerization

-Wide range of raw materials with low cost

-Molecular design flexibility

-Good dielectric and mechanical properties

These characteristics render benzoxazine resins superior above conventional phenolics and epoxy resin in many applications [25].

Meanwhile, the polymerization process, volumes of thermoplastic and thermoset polymers tend to shrink. The shrinkage of polymers should be decreased to provide that it is effectively suitable for applications such as high-performance adhesive, coating, and sealant [38].

The volumetric shrinkage of thermosets range between 2% and 10%, besides thermoplastics show much more volumetric shrinkage [39,40]. Distinctively, benzoxazine resins with great mechanical entirety demonstrate almost zero volumetric shrinkage upon curing. Mostly, during many polymerizations, their volumetric changes differ about 1%. In fact; shrinkage occurs lightly in the volume of resin isothermal curing at high temperatures. According to the measurements of before and after polymerization at room temperature, there is a slight change in the densities and hence its volume changes. The advantage of the near-zero shrinkage precursors decrease the distortions optically in addition warping of final compound [41,42].

High water absorption is one of the typical disadvantage for many resins such as bismaleimide, epoxy, phenolic, polyester, polyimide resins. The feature of higher water absorptions is the result of the presence of polar groups in the resin structure. Even though polybenzoxazine resins comprise polar groups in every repeating unit, contrarily to expectancy, they resist to the water better than other resins and so their water absorption is lower [43-46].

While phenolic and epoxy resins provide water absorption between 3-20% of their volumes, benzoxazines show 1.3% at room temperature. While bisphenol-A based polymer was 1.9% in benzoxazines, aniline based polymer was 1.3%. The reason for this is the phenolic OH groups in the benzoxazine structure and the Mannich base effect low water absorption ensures a low dielectric constant [47].

One of the main features of benzoxazines is high char yield. When technological developments are considered, the use of materials with low flammability is increasingly preferred. Char reduces the diffusion of combustible gases from the flammable surface to inner parts of the material. Epoxy resins have char yields between 5% and 15%, conventional phenolic resins have 30-55% char yield. However, polybenzoxazines could yield 35-75% char, which could be considered as quite high, compared to many other polymers [48].

2.2.5 Alternative benzoxazine monomers

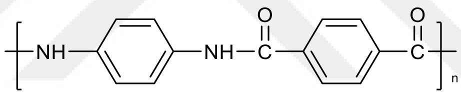
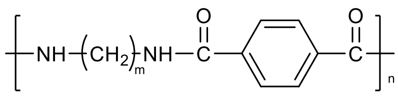
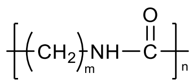
Although there are several different benzoxazines already reported in the literature, the scope of this thesis is limited to thioamide based systems. Therefore, this section focuses on amide containing benzoxazines and sulfur bearing benzoxazines.

2.2.5.1 Amide containing polybenzoxazines

Polyamides are preferred products among polymers due to their flame retardant properties, good thermal, chemical and mechanical resistance. The most common polyamides are poly(Ɛ-caprolactam) (known as Nylon-6) and poly(hexamethylene adipamide) (known as Nylon-6,6). Polyamides are classified as aliphatic class, semi-aromatic and fully aromatic (Table 2.1). Among the known polyamides, aromatics,, are highly priced and difficult to manufacture, shows high strength, flame and heat resistance properties and dimensional stability. Poly (m-phenylene isophthalamide) and poly (p-phenylene terephthalamide), known as Kevlar, have high tensile strength, high T_m value. Also, shows dimensional stability at room temperature. Their flame and heat resistance is high based on its aromatic structure and strong hydrogen bonds between polymer chains. Nylon-6 and Nylon-6,6, show good mechanical properties, high tensile strength, high impact strength and resistance to many solvents, good abrasion resistance is due to low friction factor [1].

Examples of semi-aromatic polyamides include polyptalamides (PPA), an important part of polyamides. They demonstrate high hardness and strength at high temperatures because their structures contain crystalline parts. They are higher in price compared to aliphatic amides.

Table 2.1 : Classes and structure of polyamides

Polyamide	Structure of Repeting Unit
Aromatic Polyamide	
Semi-Aromatic Polyamide	
Aliphatic Polyamide	

Combining thermoplastic polyamides with thermosetting benzoxazines, amide functional benzoxazines provide better film formation, dimensional stability and chemical resistance. As with polyamides, amide-containing polybenzoxazines provide mechanical and thermal advantages due to hydrogen bonds between phenolics, tertiary amine, carbonyl and amide -NH. Agag *et al.* synthesized primary amine-functional benzoxazine precursors [4] . They are synthesized as shown in the Figure 2.10 and are called poly (amide-benzoxazine), amide-linked as repeating units in the main chain. Excellent thermomechanical properties have been reported for these materials [49].

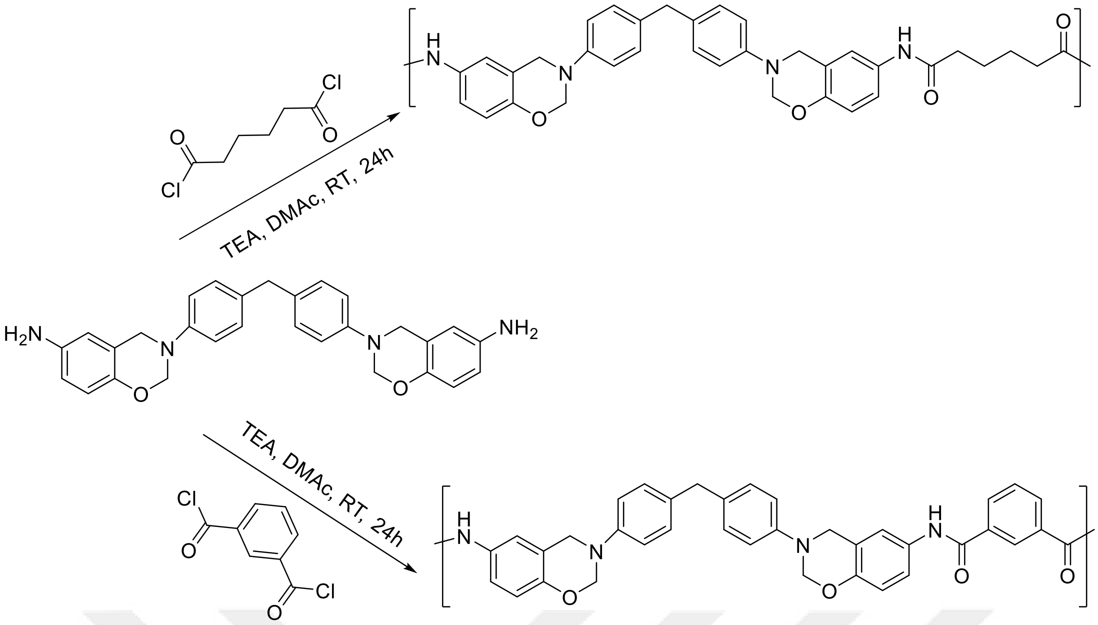


Figure 2.10 : Preparation of aliphatic and aromatic MCBP poly(amide-benzoxazine).

Moreover, 3,4-Dihydrocoumarines (DHC) were used to obtain amide containing polybenzoxazines both as in monomeric and polymeric forms. DHC was selected as masked phenol and reacted with aniline and 3-hydroxyaniline to synthesize mono and diphenolic amides in high yields to use in the subsequent syntheses (Figure 2.11). Then, the intermediate phenolics were successfully converted to amide containing benzoxazines. This study disclosed that DHC is a convenient compound to design several different amide containing benzoxazines by altering the amines either in the ring-opening of DHC or benzoxazine synthesis stages [1].

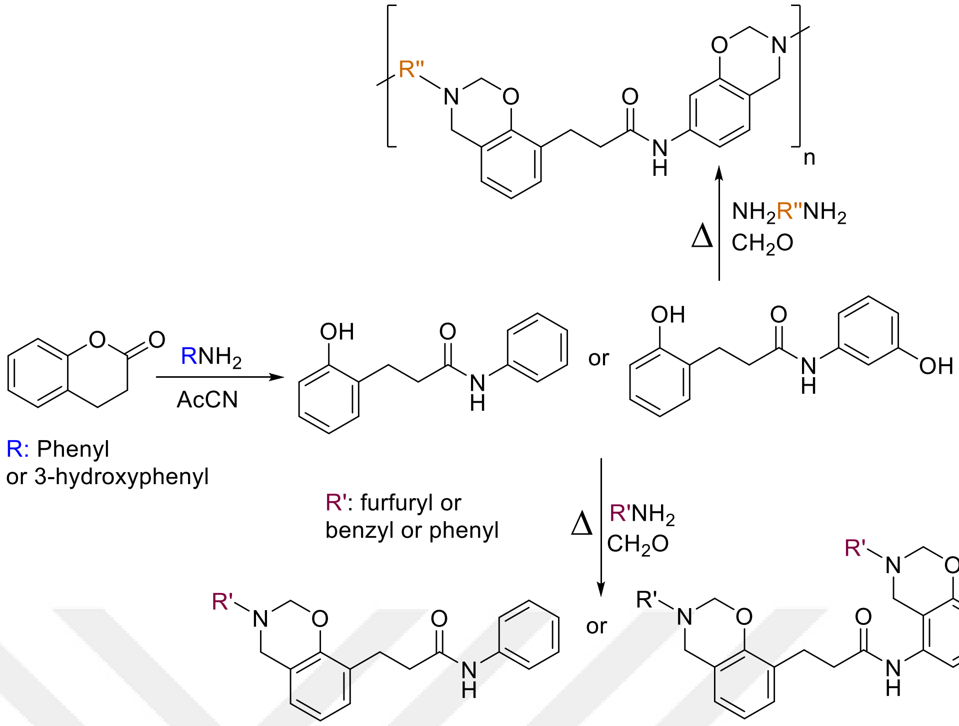


Figure 2.11 : Preparation of mono and di-functional benzoxazines and main-chain polybenzoxaine.

2.2.5.2 Sulfur containing polybenzoxazines

Sulfur is the third most abundant element in the world among waste products. Today, although sulfur use is used in the production processes of sulfuric acid, fertilizer, vulcanization natural synthetic rubbers, it causes deposits in the form of sulfur peaks as a result of excess supply problem. Inverse vulcanization consists of a compound reaction containing high amounts of sulfur and diene (Figure 2.12) . Elemental sulfur is processed in a molten state, as well as forming a radical S with heat. Thanks to the ability of the radical S atom to react to the double bonds, they form the C-S covalent bond by attacking the double bonds in the benzoxazine monomer. Since it acts as a molten sulfur reaction solvent, it eliminates the need for harmful organic solvents. At the same time, polybenzoxazine is formed by ring opening. Thus, polysulfides form copolymers and stabilize with polybenzoxazine bridges. Sulfur based material can be developed by using this system for inverse vulcanization with various vinyl monomers [50,51].

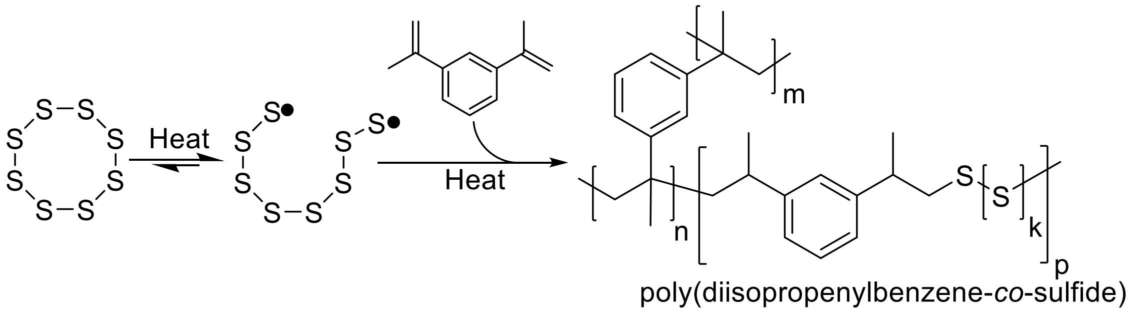


Figure 2.12 : The mechanism of inverse vulcanization.

2.3 Thioamides

Thioamides, the type of carboxylic acid derivate are formed the replacement of the oxygen with sulfur in the amide . Many unique properties of thioamides are related to two active centers in their structure. These are the unshared electrons in the nitrogen atom and the localized electrons on the thiocarbonyl group. The mesomeric effect is observed in thioamides because of the delocalization of π electrons and instability of unshared electrons in nitrogen and sulfur atoms. Thus, the single carbon-nitrogen bond results barrier to the rotation [52].

In addition, the NH proton is more acidic and provides a strong hydrogen bond, the sulfur (C=S–NH) bond weakly accept hydrogen bonds compared to the corresponding amide [53].

Thioamides are involved as intermediates in the synthesis of five- and six-membered heterocyclic structures. Moreover, they exhibit a wide variety of significant biological activity for instance antithyroid, antioxidant, antibacterial, anticancer, etc. They are still being researched in many fields such as polymer synthesis, materials science, biochemistry. Due to their excellent functional and synthetic applicability, various approaches are continuously improving in different industrial areas [54,55].

2.3.1 Synthesis of thioamides

Many synthetic methods have been published in the literature for the synthesis of thioamides since the late nineteenth century [53].

The most common method to prepare thioamides is based on simple thionation of the corresponding amides with the help of tionating reagents, tetraphosphorous decasulfide (P_4S_{10}), or Lawesson's reagent. The thioacylation of amines, the thiolysis of aromatic or nitriles or iminium salts, and a Friedel Crafts type reaction of thioacyanates are the alternative routes to produce thioamides [52].

Willgerodt-Kindler reaction is one of the earliest process to generate different types of thioamides. Surprisingly, this reaction has not gained much attention until the end of the 20th century.Conrad Willgerodt discovered the Willgerodt reaction in 1887. In this reaction, the initial compound ketone, rearrange to produce amide or the ammonium salt of the carboxylic acid (Figure 2.13a) [56].

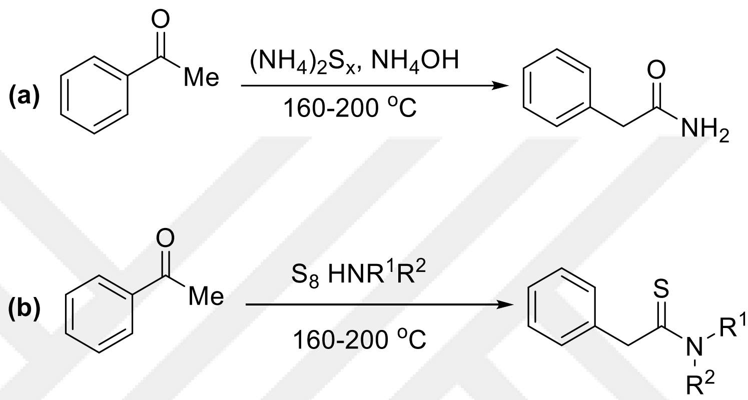


Figure 2.13 : The Willgerodt reaction (a), The Kindler modification (b)

Afterward, in 1923, the modification of Willgerodt reaction was introduced by Karl Kindler.This modified reaction includes usage of a secondary amine, ketone or aldehyde and elemental sulfur under thermal conditions to provide the thioamide (Figure 2.13b) [57]. Consequently, it can be stated that the components of classical Willgerodt-Kindler reaction are elemental sulfur, ketone or aldehyde, and an amine (or ammonia).

The Willgerodt–Kindler reaction has termed as "one-pot, three-component process for the synthesis of synthetically useful (thio)amides". With a wide variety of initial reagents (aldehydes and primary/secondary amides), and the ease and commercial availability of those compounds give the possibility for preparing many various thioamide compounds. In addition, advantageously, the thioamides easily convert to the carboxylic acids or thioesters . When the reaction is performed by using arylalkyl ketone, can be assumed as an auto-redox process, by favour of the reduction of ketone, and oxidation occurs at the terminal carbon [58,59]. The carbonyl migration is less efficient in a longer carbon chain, so it results in low yield. Thus, it is estimated that the optimum alkyl chain extent is not much than two or three carbon atom [53].

In 1989, Carmack and co-workers indicated the plausible mechanism for the Willgerodt–Kindler reaction (Figure 2.14) after their studies immense researches [60].

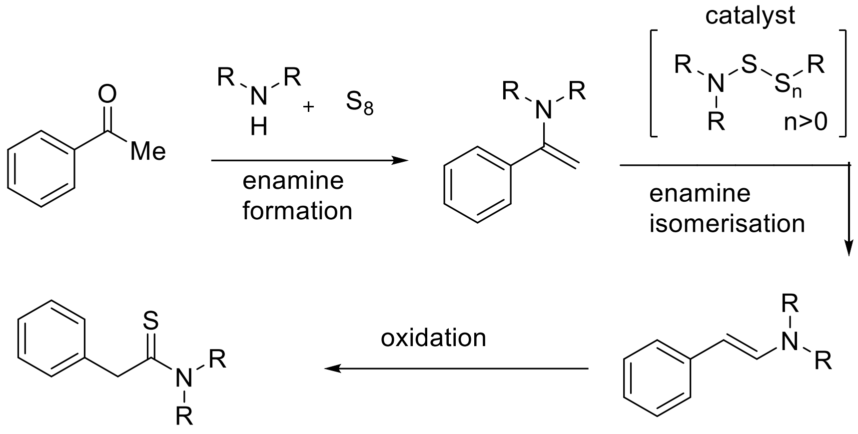


Figure 2.14 : The mechanism of the Willgerodt-Kindler reaction [60].

The conventional Willgerodt-Kindler reaction had some drawbacks for this reason the researchers tried to improve conditions to produce easily and safely thioamide derivatives.

Kanbara and co-worker utilized base catalyst (sodium sulfide nonahydrate) $Na_2S.9H_2O$ to remove the drawbacks of the Willgerodt-Kindler reaction, and improved the reaction conditions successfully (Figure 2.15). If the reaction of benzaldehyde, aniline with sulfur occurs under conventional Willgerodt-Kindler reaction conditions, it results in a yield of 15%, while using a $Na_2S.9H_2O$ catalyst results in a yield of 66% [61].

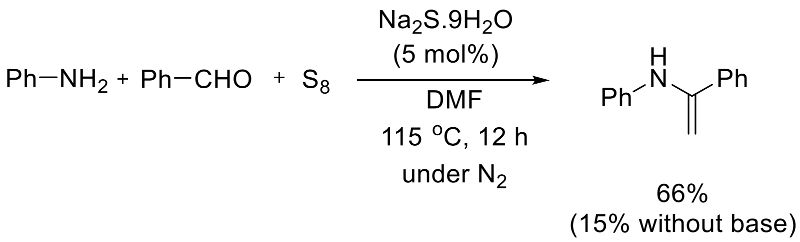


Figure 2.15 : The Willgerodt-Kindler reaction with catalyst.

As presented in Table 2.2, the reactions of benzaldehyde, aniline, and elemental sulfur easily progressed with the addition of base catalyst $Na_2S.9H_2O$ and the yield increase [61].

Table 2.2 : The effect of catalyst in Willgerodt-Kindler reaction of aniline with benzaldehyde.[a]

Entry	Base	Reaction time (h)	Yield[b] (%)
1	$Na_2S.9H_2O$,1 mol%	12	55
2	$Na_2S.9H_2O$, 5 mol%	4	32
3	$Na_2S.9H_2O$, 5 mol%	12	66
4	$Na_2S.9H_2O$, 10 mol%	12	83
5	$Na_2S.9H_2O$, 15 mol%	12	91
6	$Na_2S.9H_2O$, 20 mol%	12	88

[a]Reaction conditions : aniline (6 mmol), benzaldehyde (4 mmol) and sulfur (5 mmol) in DMF (4mL) at 115 °C.

[b]Isolated yield.

2.3.2 Synthesis of polythioamides

In recent years, sulfur-containing polymers have attracted attention increasingly due to their characteristics like self-healing ability, high refractive indices, low dispersion, electrochemical features, etc. [62].

As one kind of the sulfur containing polymeric compounds, polythioamide is a novel class of polymer which includes −C(=S)NH− repeating unit and exhibits great refractivity, metal coordination capability, and luminescence character. However, characterization and synthesis of polythiamides were researched rarely compared to polyamides [63].

Polythioamides can be produced, from the polycondensation type reaction of dithioesters with diamines, but at the end of reaction removal of harmful side product methanethiol is quite challenging. Consequently, this is limiting the study and applicability of the polythioamides prepared by this method [63,64].

In 2001, Kanbara et al. reported the reaction process of polythioamides through the Willgerodt–Kindler reaction, it occurs between dialdehydes and diamines in the presence of sulfur at 115 °C (Figure 2.16). Since this method is applicable to a wide variety of commercially available dialdehydes and diamines, it serves the production of polytioamides derivatives [65].

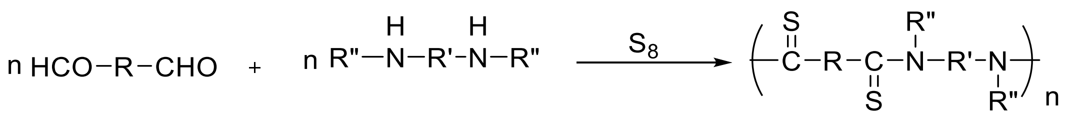


Figure 2.16 : Synthesis of poly(thioamide).

In recent past, some researchers have used multicomponent polymerizations (MCPs) technique to generate sulfur containing polymeric compounds with good efficiency, mild conditions, and high atom economy [62]. In 2015, Li *et al*. reported the multicomponent polymerizations technique, to provide the polythioamide directly and conveniently with usage of elemental sulfur, aliphatic diamines, aromatic diynes without catalyst, in a high yields [66].

3. EXPERIMENTAL PART

3.1 Materials

Aniline (Merck, 99.5%), Sulfur (S_8, colloidal powder, reagent grade, Aldrich), Paraformaldehyde (Acros, 96%), Benzylamine (Merck, ≥99%), Furfurylamine (Fluka, ≥98%), Sodium hydroxide (Acros, >97%), Ethyl acetate (EtOAc, Merck, ≥99.5%), o,o′-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Sigma-Aldrich, Jeffamine® ED-900, St. Louis, MO, USA), 4-aminophenol (*p*-aminophenol Merck, ≥99%), 4-hydroxybenzaldehyde (Merck, ≥98%), 1,6-diaminohexane (Fluka), 4-Hydroxy-3-methoxybenzaldehyde (Vanillin) (Alfa Aesar, 99%), Tetrahydrofuran (THF, VWR Chemicals, 99.7%), Ethanol (EtOH, Aldrich, ≥99.5%), Toluene (Carlo Erba, 99.5%), Chloroform ($CHCl_3$, Carlo Erba, 99,9%), Sodium sulfide nonahydrate (Carlo Erba), N,N-Dimethylformamide (DMF, Merck), Magnesium sulfate anhydrous (Aldrich, ≥99.5%), chloroform-d ($CDCl_3$, 99.8 atom % D) were used as received.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

The ^1H-NMR measurements were recorded at room temperature in $CDCl_3$ or DMSO-d_6 with $Si(CH_3)_4$ as an internal standard, using a 500 MHz NMR (Agilent NMR System VNMRS).

3.2.2 Infrared spectrophotometer (FT-IR)

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

3.2.3 Differential scanning calorimeter (DSC)

Differential scanning calorimetry (DSC) was carried out on a Perkin Elmer Diamond DSC with a heating rate of 10 °C.min^{-1} under nitrogen flow, covering temperatures of 30-320 °C.

3.2.4 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C min^{-1} under nitrogen flow.

3.2.5 Gel-permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were taken on a TOSOH EcoSEC GPC system equipped with an auto sampler system, a temperature controlled pump, a column oven, a refractive index (RI) detector, a purge and degasser unit and TSK gel superhZ2000, 4.6 mm ID × 15 cm × 2 cm column. Tetrahydrofuran was used as an eluent at flow rate of 1.0 mL min^{-1} at 40 °C. Refractive index detector was calibrated with polystyrene standards having narrow molecular-weight distributions. Data were analyzed using Eco-SEC Analysis software.

3.3 Synthesis

3.3.1 Synthesis of mono-functional thioamide (MonoHyroxythioamide)

In a 100 mL round-bottom flask, aniline (1.6763 g, 18 mmol), elemental sulfur (0.7696 g, 24 mmol), Na_2S (0.14048 g, 1.8 mmol) were mixed with 15 mL DMF. Then 4-hydroxybenzaldehyde (1.4654 g, 12 mmol) was added into mixture under nitrogen gas. The reaction mixture was stirred at 120 °C for 8 h under nitrogen. After reflux, the flask was cooled to room temperature, then the solution was poured into water. It was kept in a refrigerator for 2 days. The orange crystalline precipitate was obtained. The obtained solid was separated by filtration. Dried in a vacuum for 2 days at 50 °C temperature.

The purification procedure is as follows : solid was dissolved in ethyl acetate (100 mL) to remove unreacted sulfur. Since, sulfur is not soluble in ethyl acetate. Then, unreacted sulfur was separated by filtration. Ethyl acetate was removed by using a rotary evaporator and the orange crystalline product was obtained (Figure A.6). Dried in a vacuum for 2 days at 50 °C temperature. (Yield: 55 %)

3.3.2 Synthesis of di-functional thioamide (DiHydroxythioamide)

In a 100 mL round-bottom flask, 4-aminophenol (1.9643 g, 18 mmol), elemental sulfur (0.7696 g, 24 mmol), Na_2S (0.14048 g, 1.8 mmol) were mixed with 15 mL DMF. Then 4-hydroxybenzaldehyde (1.4654 g, 12 mmol) was added into mixture under nitrogen gas. The reaction mixture was stirred at 120 °C for 8 h under nitrogen. After reflux, the flask was cooled to room temperature then the solution was poured into water. It kept in a refrigerator for 24 h .The orange crystalline precipitate was obtained. The precipitate was separated by filtration. Dried in a vacuum for 2 days at 50 °C temperature. After drying, the solid was dissolved in ethyl acetate (100 mL) to remove unreacted sulfur. Since, sulfur is not soluble in ethyl acetate. Then, unreacted sulfur was separated by filtration. Ethyl acetate was removed by using a rotary evaporator and the orange crystalline product was obtained. Dried in a vacuum for 2 days at 50 °C temperature. (Yield:~59 %)

3.3.3 Synthesis of thioamide based mono-benzoxazine (Th-amd-MonoBz-Bn)

Monofunctional phenolic thioamide, 4-hydroxy-*N*-phenylbenzothioamide (0.5458 g, 2.38 mmol), benzylamine (0.2551 g, 2.38 mmol), paraformaldehyde (0.1429g, 4.76 mmol) were dissolved in 15 mL of toluene/ethanol (2:1, v/v) in a 100 mL round-bottom flask. The reaction mixture was refluxed at 100 °C temperature for 24 h. The solvent was evaporated using a rotary evaporator. The resulting product was dissolved in chloroform (50 mL) and extracted with 1 M sodium hydroxide for five times. Then, to neutralize the solution chloroform solution was washed with distilled water (250 mL) for three times. The solution was dried with anhydrous $MgSO_4$ and filtered. Chloroform was evaporated under vacuum. The product was dried in a vacuum oven at 50 °C temperature for 24 h. (Yield: 85 %)

3.3.4 Synthesis of thioamide based mono-benzoxazine (Th-amd-MonoBz-Fr)

Monofunctional phenolic thioamide, 4-hydroxy-*N*-phenylbenzothioamide (1.01 g, 4.4 mmol), furfurylamine (0.43 g, 4.4 mmol), paraformaldehyde (0.27 g, 8.8 mmol) were dissolved in 30 mL toluene/ethanol mixture (2:1, v/v) in a 100 mL round-bottom flask. The reaction mixture was refluxed at 100 °C temperature for 24 h. The solvent was evaporated using a rotary evaporator. The resulting product was dissolved in chloroform (50 mL) and extracted with 1 M sodium hydroxide for five times. Then, to neutralize the solution chloroform solution was washed with distilled water (250 mL) for three times. The solution was dried with anhydrous $MgSO_4$ and filtered. Chloroform was evaporated under vacuum. The product was dried in a vacuum oven at 50 °C temperature for 24 h. (Yield: 32%)

3.3.5 Synthesis of thioamide based di-benzoxazine (Th-amd-DiBz-Bn)

In a 100 ml round-bottom flask, difunctional phenolic thioamide, 4-hydroxy-*N*-(4-hydroxyphenyl)benzothioamide (1.500 g, 6.14 mmol), benzylamine (1.3157 g, 12.3mmol) and paraformaldehyde (0.7374 g, 25 mmol) were dissolved with 30 mL mixture of toluene/ethanol (2:1, v/v). The reaction mixture was refluxed at 100 °C temperature for 24 h. The solvent was evaporated using a rotary evaporator. The resulting product was dissolved in chloroform (50 mL) and extracted with 1 M sodium hydroxide for five times. Then, to neutralize the solution chloroform solution was washed with distilled water (250 mL) for three times. The solution was dried with anhydrous $MgSO_4$ and filtered. Chloroform was evaporated under vacuum. The product was dried in a vacuum oven at 50 ° C temperature for 24 h. (Yield: 67%)

3.3.6 Synthesis of main-chain poly(thioamide-benz-PPEO)

Difunctional benzoxazine thioamide containing monomer (2.37 g, 9.6 mmol), Jeffamine ED-900 (8.68 g, 9.6 mmol) and paraformaldehyde (1.16 g, 38 mmol) were dissolved in 75 mL mixture of toluene/ethanol (2:1, v/v) in a 250 ml round-bottom flask equipped with a reflux condenser and a magnet for stirring. The solution was refluxed for 24 h at 100° C temperature. After reflux, the flask was cooled to room temperature and, solvent was removed using a rotary evaporator under reduced pressure. After cooling the room temperature, oily product was obtained. Mass of obtained polymer was 11.32 g.

Film preparation; to obtain a typical polybenzoxazine film, 1 g of main-chain polybenzoxazine precursor was dissolved in 10 mL of DCM and charged into a Teflon mold (2 cm width, 5 cm length, 0.5 cm depth). The molds were kept at room temperature for 72 h to remove the DCM. Then, the films were heated at 120 ° C for 10 min. for the removal of solvent residues in an ordinary oven. Then, molds were gradually heated up to 180-200 ° C and cured for 0.5 h. After curing, a dark-orange, transparent, and flexible crosslinked films with a smooth surface was obtained.

3.3.7 Synthesis of vanillin di-benzoxazine (Va-DiBenz)

In a 500 ml round-bottom flask, 4-Hydroxy-3-methoxybenzaldehyde (vanillin) (30g, 0.197 mol), 1,6 diaminohexane (11.457g, 0.0986 mol) and paraformaldehyde (11.842 g, 0.394 mol) were dissolved in 250 ml chloroform. The mixture was magnetically stirred under reflux at 61 ° C for 24 h. The resulting product was extracted with 0.3 M sodium hydroxide for five times (1000 mL). Then, to neutralize the solution, chloroform solution was washed with distilled water (500 mL) for three times. The solution was dried with anhydrous Na_2SO_4 and filtered. Chloroform was evaporated on rotary. Then the product was dried under vacuum at 40 °C for 24 h. (Yield: 36)

3.3.8 Synthesis of main-chain polybenzoxazine precursor (1,6-diaminohexane)

1,6-diaminohexane (20 mmol, 0.2324 g), sulfur (5 mmol, 0.160 g) were dissolved with 10 mL DMAc in round bottom flask under nitrogen gas 20 min. at room temperature. Then vanillin benzoxazine (20 mmol, 0.937g) was dissolved with 7 mL DMAc and then added into the mixture. The mixture was magnetically stirred under nitrogen gas and reflux at 100 °C for 6h. After reflux, the flask was cooled to room temperature. Then solution was poured into methanol dropwise, and kept in a refrigerator for 24 h. The solvent was filtered on the crucible and the polymer washed with cold methanol. The polymer was dried at ambient temperature in a vacuum chamber for 24 h to obtain an orange colored polymer. After drying, the solid was dissolved in 20 ml DMF to remove unreacted sulfur. Since, sulfur is not soluble in DMF, but obtained polymer soluble in DMF.Then the solution was filtered, after that the polymer changed the color to dark reddish solid.

3.3.9 Synthesis of main-chain polybenzoxazine precursor (jeffamine ED900)

Jeffamine ED-900 (2 mmol , 1.8g), sulfur (5 mmol, 0.160g) were dissolved with 10 mL DMAc in round-bottom flask under nitrogen gas 20 min. at room temperature. Then vanillin benzoxazine (2 mmol, 0.937g), was dissolved with 7 mL DMAc and then added into the mixture. The mixture was magnetically stirred under nitrogen gas and reflux at 100 °C for 6 h. After reflux, the flask was cooled to room temperature. Then solution was poured into methanol dropwise, and kept in a refrigerator for 24 h. The solvent was filtered on the crucible and the polymer washed with cold methanol. The polymer was dried at ambient temperature in a vacuum chamber for 24 h to obtain an orange colored polymer. After drying, the solid was dissolved in 20 ml DMF to remove unreacted sulfur. Since, sulfur is not soluble in DMF, but obtained polymer soluble in DMF. Then the solution was filtered and orange product was obtained.

4. RESULT AND DISCUSSION

Several polybenzoxazines containing amide linkages have already been synthesized successfully. In these studies, different synthetic approaches were used ranging from the use of amino functional benzoxazines to amide bearing phenols [2,4,67]. Alternatively, amide functional phenols were obtained by the ring opening of dihydrocoumarines for the synthesis of benzoxazines [1]. On the other hand, thioamide based benzoxazines has never been reported for this class of polybenzoxazines. As well known, thiomamides have recently become a very important functional group in organic synthesis and polymer chemistry. Especially, in recent years, the Willgerodt–Kindler reaction has received high interest and many applications in synthetic polymer chemistry. Because, this reaction utilizes elemental sulfur as a reagent and sulfur is considered as waste product. Any process that converts sulfur into useful materials are now considered as potential sustainable chemistry.

Elemental sulfur is the by product of coal and petroleum industry, and as stated can be used efficiently in Willgerodt-Kindler reaction. In a worldwide, more than 60 million tons of elemental sulfur are produced annually. Hence, to use sulfur in both organic synthesis and polymer synthesis could be an important issue for environmental purposes. Besides, sulfur is a cheap chemical and it can even be considered as waste product. So advanced materials from sulfur would reduce the prices of polymeric materials definitively.

Initially, our approach was to synthesize thioamide bearing main-chain polybenzoxazines by the Willgerodt-Kindler reaction via one-pot method. For this attempt, difunctional vanillin benzoxazine was synthesized by the reaction of 4-hydroxy-3-methoxybenzaldehyde (vanillin), 1,6-diaminohexane, paraformaldehyde in chloroform. The synthesis pathway of the benzoxazine (Va-DiBenz) is demonstrated in Figure 4.1. The obtained benzoxazine was characterized by ^{1}H-NMR, FT-IR.

In Figure A.1, the ^{1}H-NMR spectrum of the Va-Dibenz clearly reveals the characteristic proton signals of oxazine ring at 5.05 ppm (N-C**H**$_2$-O) and at 4.06 (Ar-C**H**$_2$-N). Moreover, the aldehyde functionality can be observed by the signal at 9.81

ppm, which is typical for aldehyde protons. Besides, the proton signal related to -OC**H3** appears at 3.94 ppm. The detailed proton signal assignments for the Va-DiBenz is visible in Figure A.1.

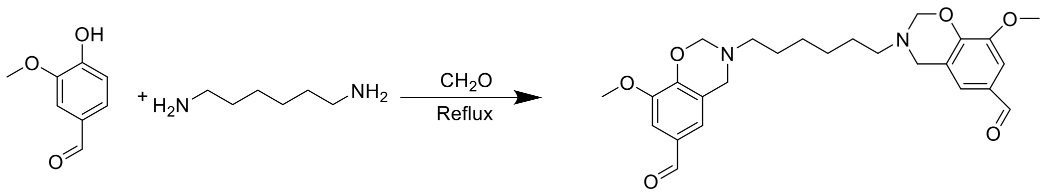


Figure 4.1 : Synthesis of vanillin based dibenzoxazine (Va-DiBenz)

The structure of Va-DiBenz was further supported by FT-IR analysis. In Figure A.2, the C-O-C oxazine mode is clearly visible at 930 cm^{-1}. As reported previously, this band is characteristic for benzoxazines and can even be used to trace the ring opening of oxazine ring. Moreover, the carbonyl C=O stretching vibration is detectable as a intense band at 1680 cm^{-1} evidencing the preservation of aldehyde functionality during the synthesis of Va-DiBenz. And typical aromatic C=C stretching vibrations can be seen between 1485-1580 cm^{-1}. Additionally, the aldehyde C-H stretching vibration band is clearly visible at ca. 2820 cm^{-1}.

Subsequently, Va-DiBenz was used to obtain thioamide group containing main-chain polybenzoxazine. The one-pot synthesis of main-chain polybenzoxazine was tried through the reaction of Va-DiBenz, 1,6-diaminohexane in presence of elemental sulfur in dimethyl acetamide (DMAc) solvent and also the same procedure was applied by changing the amine source with jeffamine ED-900 (Figure A.3).

However, the expected product could not be obtained in both attempts, due to extensive ring-opening of benzoxazines. The elemental sulfur acts as a reagent for the oxazine ring to trigger the ring opening of oxazine. The major reason of the uncontrolled ring opening is possibly due to sulfur radical transfer and coupling (SRTC) reaction (shown Figure A.4). Alternatively, this reaction can be coined as inverse vulcanization of benzoxazines [51,68].

Depending on the reaction conditions, insoluble products were produced because of the crosslinking reactions of benzoxazines and sulfur. However, we still could isolated some soluble parts and according to ^{1}H-NMR analysis benzoxazine functionalities almost completely lost as seen in Figure A.5.

The gel permeation chromatography (GPC) analysis of the soluble part revealed that only oligomers could be obtained (seen Table A.1). This means this methodology is generating somehow oligomers or low molecular weight polymer but we could not preserve the oxazine structure.

In order to overcome the problems associated with the one-pot Willgerodt-Kindler reaction and high reactivity of sulfur against benzoxazine, we have synthesized thioamide-containing phenolics as reagents to be used in benzoxazine synthesis. The phenolics were synthesized according to catalytic Willgerodt-Kindler reaction to increase the activity of sulfur in this reaction. 4-hydroxybenzaldehyde reacted with aniline in presence of elemental sulfur under nitrogen gas at 120 °C in DMF and additionally Na_2S was used as catalyst. Other attempts without catalyst did not yield enough thioamides. Moreover, we have also recognized that preventing the oxidation by inert atmosphere has vast importance to limit the amount of side reactions. Under the reported conditions the orange crystalline solid, mono-functional thioamide (4-hydroxy-*N*-phenylbenzothioamide) was obtained (seen Figure 4.2(a) and Figure A.6). Then, with the similar procedure, di-functional thioamide (4-hydroxy-*N*-(4-hydroxyphenyl)benzothioamide) synthesis was achieved from 4-hydroxybenzaldehyde and 4-aminophenol and the reaction proceed in presence of elemental sulfur at 120 ° C in DMF (seen Figure 4.2 (b)).

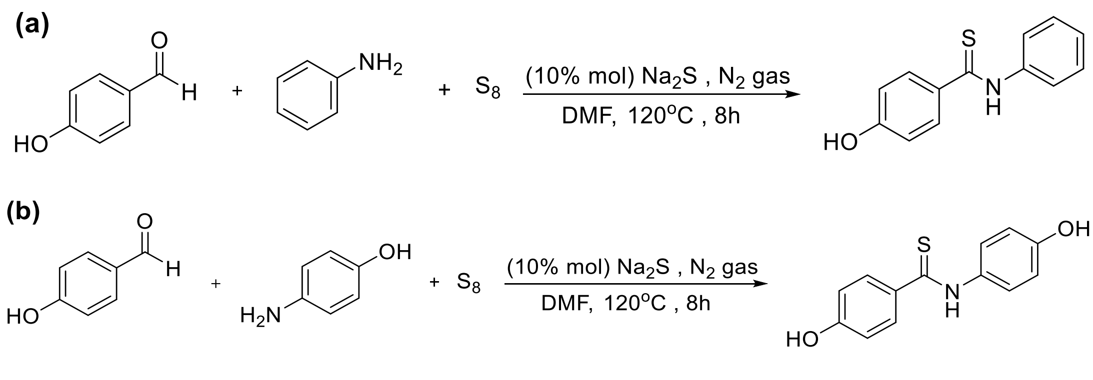


Figure 4.2 : Synthetic pathway of Willgerodt-Kindler reactions for phenolic thioamides.

The spectral characterizations of two different thioamides were performed using ^{1}H-NMR spectroscopy. As the results of ^{1}H-NMR spectroscopy, the characteristic peaks of thioamides structures were seen in Figure A.7 and Figure A.8. The proton signals related to amide -NH appear at 11.40 ppm and the phenolic -OH is detectable at 10.08

ppm. Similar peaks can be observed for the di-functional thioamide as -NH at 11.20 ppm, -OH at 10.03 ppm and 9.50 ppm.

Furthermore, FT-IR spectra of these compounds show stretching vibration band of N–H and O–H bands around 3300 cm^{-1}, C-O and C=S bands at 1170-1230 cm^{-1}, respectively (Figure A.9).

After the successful synthesis of phenolic thioamides, we used these compounds in classical benzoxazine syntheses and monofunctional and difunctional benzoxazine monomers-containing thioamide groups were obtained with a relatively good yields.

For the benzoxazines syntheses, we chose benzyl amine, furfuryl amine as amine sources (Figure 4.3). We did not prefer to use aniline because in the case of the usage of aniline the structure could be rigid and solubility problems could be encountered, which eventually would limit the spectral characterization. The abbreviations for the synthesized benzoxazine monomers are as follows: Benzylamine based benzoxazine is Th-amd-MonoBz-Bn, furfurylamine based benzoxazine is Th-amd-MonoBz-Fr and difunctional benzylamine based is Th-amd-DiBz-Bn.

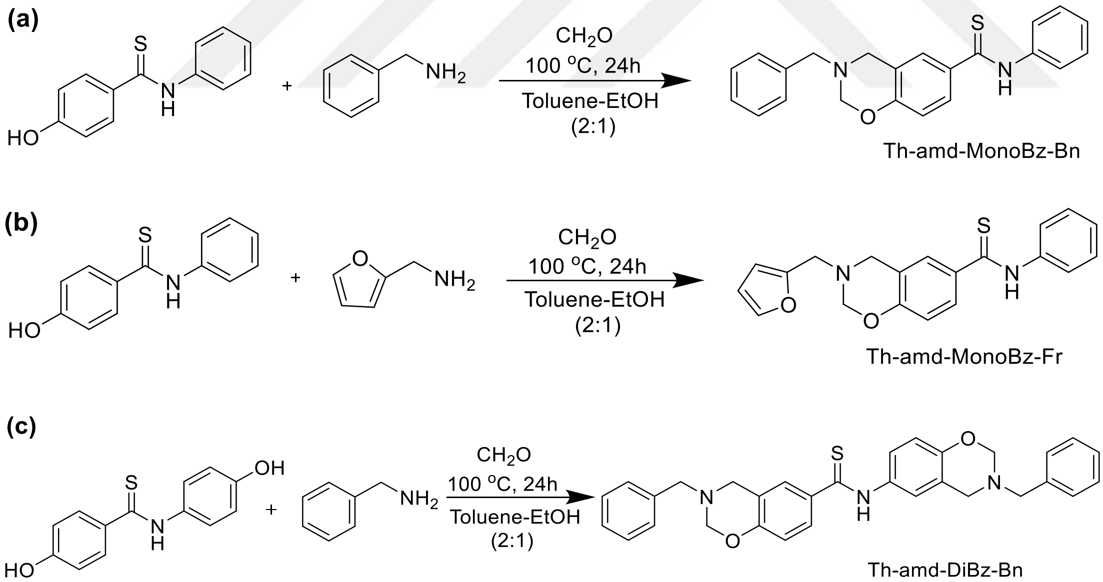


Figure 4.3 : Synthesis of Th-amd-MonoBz-Bn (a), Th-amd-MonoBz-Fr (b), Th-amd-DiBz-Bn (c).

All there benzoxazine monomer were characterized by using NMR and FTIR spectroscopies. In Figure 4.4, the ^{1}H-NMR spectrum of Th-amd-MonoBz-Bn clearly exhibit the characteristic oxazine ring proton signals as 4.94 ppm (for N-C**H**$_2$-O), 3.97 ppm (for Ar-C**H**$_2$-N) and 3.86 ppm (benzylic -C**H**$_2$-N). Besdides these peaks the thioamide -N**H** is detectable at 11.47 ppm evidencing the preservation of thioamide functionality after the benzoxazine synthesis. Similar NMR peaks can also be observed for both Th-amd-MonoBz-Fr and Th-amd-DiBz-Bn. In Figure 4.5, the oxazine signals appear at 4.91 ppm, 3.99 ppm and 3.85 ppm for N-C**H**$_2$-O and Ar-C**H**$_2$-N, benzylic -C**H**$_2$-N respectively, which the spectrum belongs to Th-amd-MonoBz-Fr. In addition, the thioamide –N**H** is visible at 11.49 ppm. In Figure 4.6, two types of oxazine signals appear at 4.94, 4.87 ppm for N-C**H**$_2$-O and 3.96, 3.90 ppm for Ar-C**H**$_2$-N, respectively. Because, the Th-amd-DiBz-Bn is an asymmetric difunctional monomer and naturally two different magnetic environment present over oxazine rings for this monomer. The peak related to benzylic proton emerges at 3.86 ppm. Likewise, the characteristic peak for thioamide –NH is visible at 11.28 ppm.

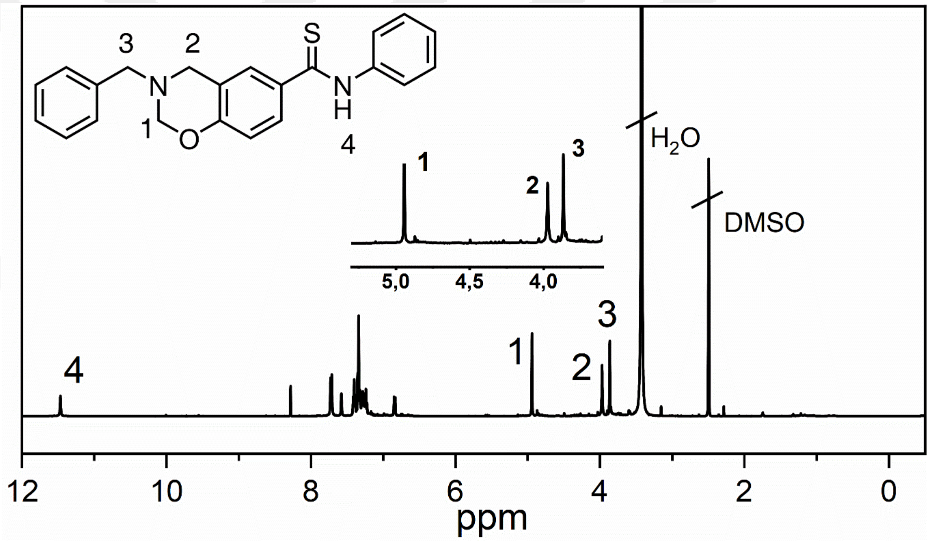


Figure 4.4 : ^{1}H-NMR spectrum of Th-amd-MonoBz-Bn.

The overlaid FT-IR spectra of the resulting benzoxazines are presented in Figure 4.7. In the IR spectra, the characteristic absorption bands of the benzoxazines ring emerg at 920-940 cm^{-1}. These bands are related to both oxazine ring bending mode and out of plane bending vibration of the benzene ring that is attached to the oxazine ring. The aromatic C-H stretching vibrations are visible at *ca.* (3001–3118 cm^{-1}) and aromatic C=C at *ca.* (1441–1600 cm^{-1}), CH$_2$ wagging at *ca.* (1360 cm^{-1}) N-H stretching vibrations of thioamide group is visible at *ca.* (3300 cm^{-1}).

Accordingly, these results further support the successful syntheses of thioamide containing benzoxazines.

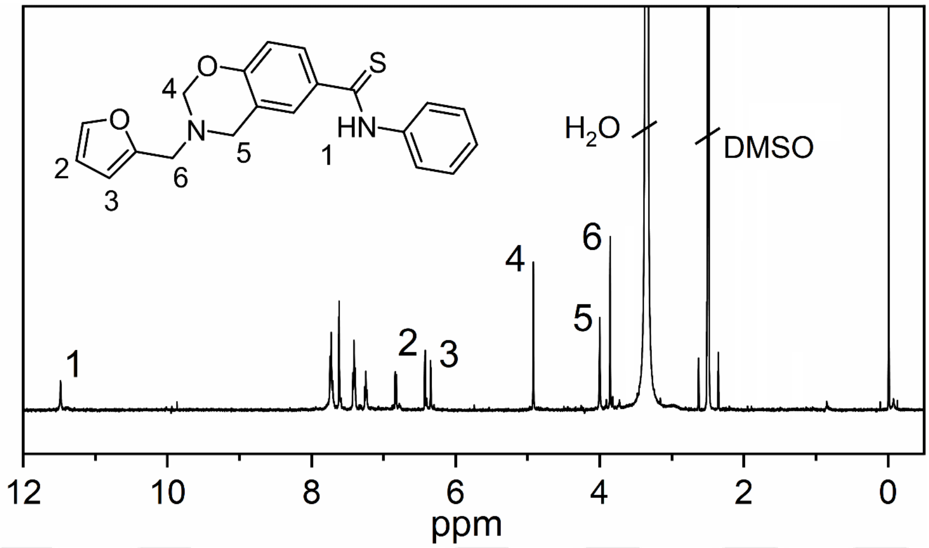


Figure 4.5 : ^{1}H-NMR spectrum of Th-amd-MonoBz-Fr.

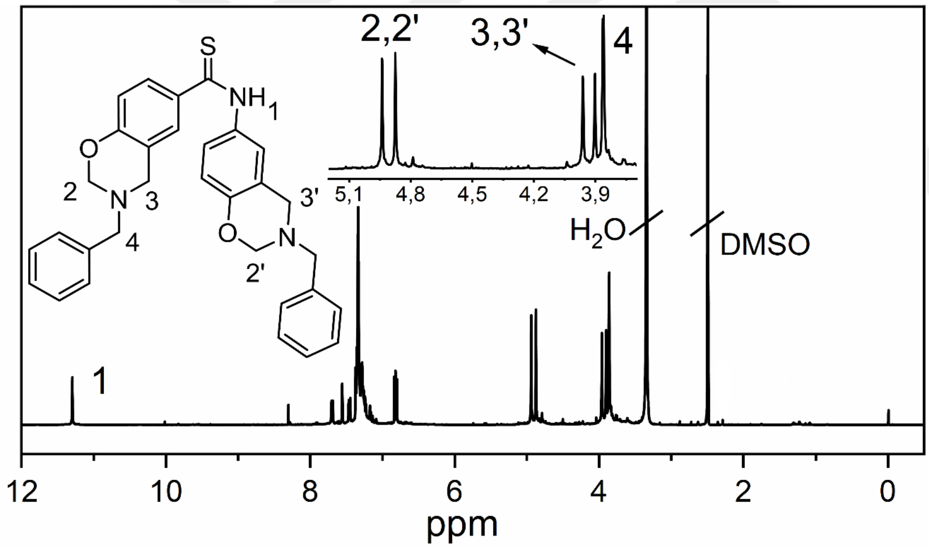


Figure 4.6 : ^{1}H-NMR spectrum Th-amd-DiBz-Bn.

Typically ring-opening polymerization temperature range of 1,3-benzoxazines state between 180-260 °C based on the functionalities present on the benzoxazines. Furthermore, these thioamide-containing benzoxazine monomers are thermally curable. This thermal curing was traced by using DSC under nitrogen gas and using a heating rate of 10 °C min^{-1}. The exotherms related to the ring-opening polymerization reactions are clearly visible in DSC analysis (Figure 4.8).

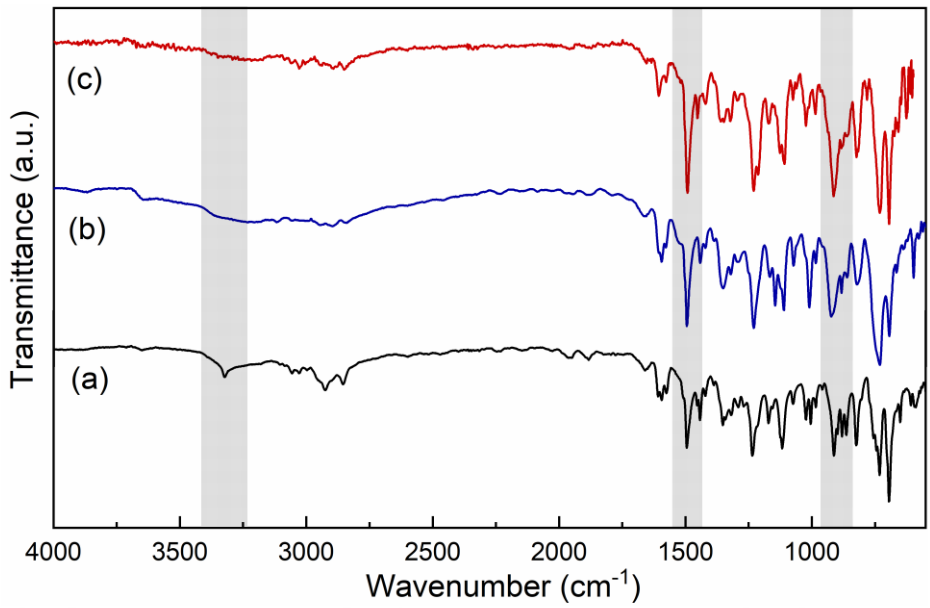


Figure 4.7 : FT-IR spectra of benzoxazines Th-amd-MonoBz-Bn (a) Th-amd-MonoBz-Fr (b), Th-amd-DiBz-Bn (c).

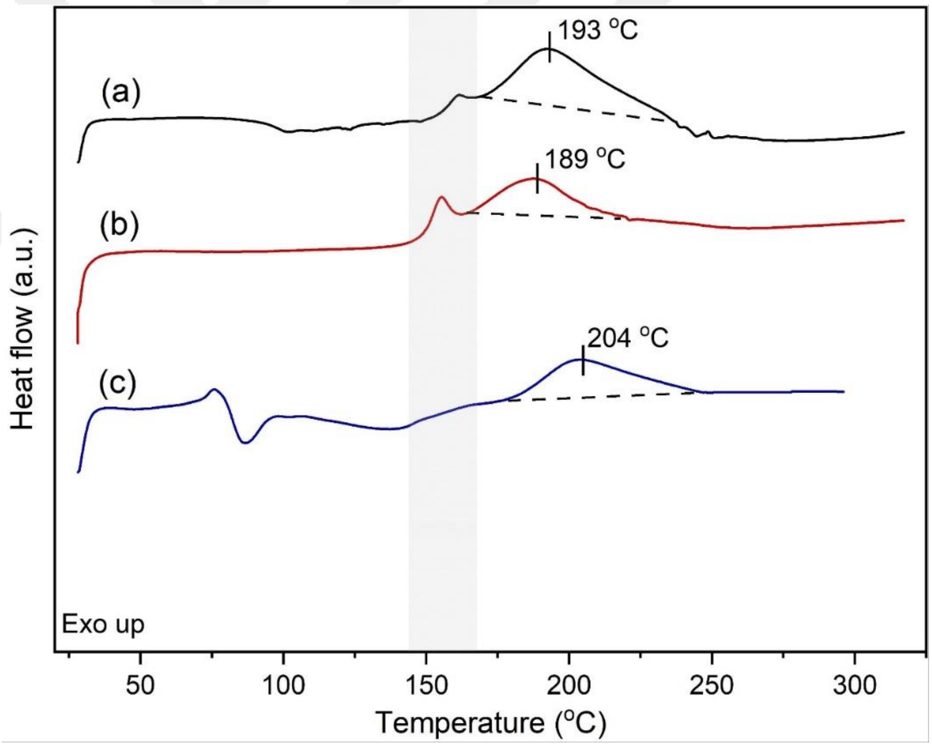


Figure 4.8 : DSC thermogram of thioamide based benzoxazine monomers Th-amd-MonoBz-Bn (a), Th-amd-MonoBz-Fr (b), Th-amd-DiBz-Bn (c).

The data collected from DSC are tabulated in Table 4.1. Th-amd-MonoBz-Bn displays a curing exotherm that have an onset at 172°C and the curing maximum at 193 °C with 88.01 j/g exotherm enthalpy. The curing exotherm of Th-amd-MonoBz-Fr benzoxazine has an onset at 165 °C and a maximum at 188 °C with 65.77 j/g exotherm enthalpy. The curing exotherm of Th-amd-DiBz-Bn show an onset at 186 °C and a maximum at 204°C with 57.07 j/g exotherm enthalpy in Figure 4.8.

Table 4.1 : DSC characteristics of benzoxazines under N_2 environment

Benzoxazine Monomer	Curing on-set (°C)	Curing end-set (°C)	Curing maximum (°C)	Curing exotherm (J/g)
Thio-BnBz	172	238	193	-88.01
Thio-FurBz	165	220	188	-65.77
Thio-DiBnBz	180	241	204	-57.07

DSC analyses were performed under nitrogen stream (20 mL/min.) with a 10 °C/min. heating rate.

As seen in the DSC results three of these monomers have relatively low ring-opening temperatures when compared to classical benzoxazines. Many classical benzoxazines have curing temperatures more than 220 °C. The reason for such cure temperature decrease can be explained by the labile C=S bond. In the literature, there are reports that C=S bond can be broken under harsh conditions to generate –SH. As well known, thiols can even trigger ring opening of oxazines at room temperature and even below. Therefore, the possible in-situ generation of thiols over thioamides effectively catalyzes the ring opening polymerization of these monomers. This effect was also tested by designing a DSC experiment. In this experiment, the thioamide based benzoxazine was used as catalyst for the classical monofunctional benzoxazine and it was demonstrated that the maximum curing temperature of monofunctional benzoxazine dropped down by 28 °C (as seen Figure 4.9).

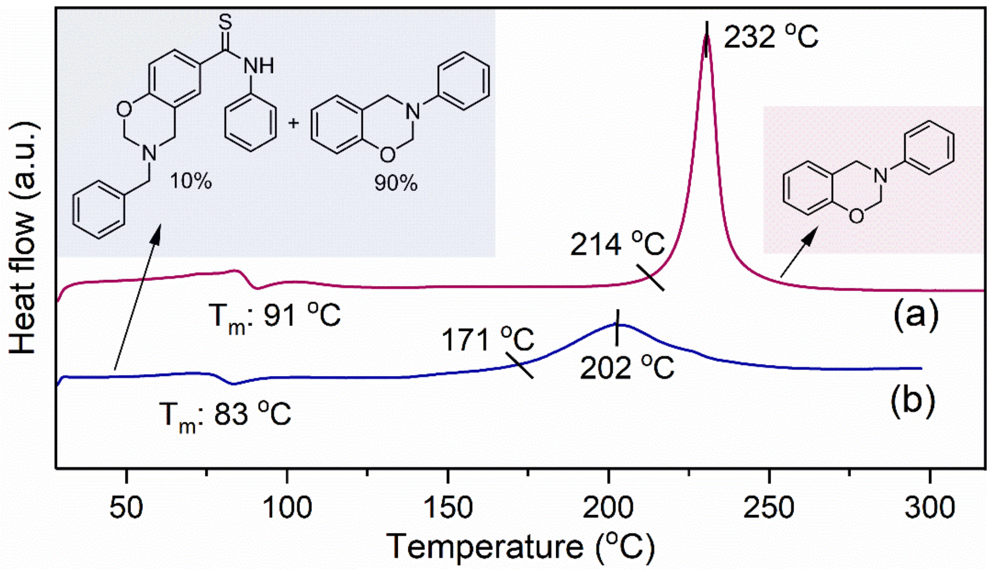


Figure 4.9 : DSC thermogram of mixture of Th-amd-MonoBz-Bn and monofunctional classic benzoxazine monomer.

Although the thiol formation proposal requires further support, at this stage the explanation of cure temperature is accordance with many papers related to catalytic polymerization of benzoxazines [69-72].

The thermostability of cured benzoxazine specimens were measured with the thermogravimetric analysis (TGA) under N_2 flow (20 mL/min.). TGA analysis and the important points of thermal properties are presented in Figure 4.10 and Table 4.2 correspondingly. All the obtained benzoxazines are comparable with classical mono and difunctional benzoxazines. Generally monofunctional benzoxazines have char yield around 30-40 % difunctional have char yield around 50 %.

The thermal behavior differences between these monomers can explained by attributing their structures. There is a vast thermal stability divergence when Th-amd-MonoBz-Bn and Th-amd-MonoBz-Fr are compared. The major reason is related to the furan functionality. As reported in the literature, during the curing of benzoxazines furan groups also participate these curing reactions and generate extra crosslinking. A monofunctional but furan containing benzoxazine can even act, as a difunctional benzoxazine. In the related TGA thermogram (Figure 4.10) similar phenomenon is observed and the thermal stability of Th-amd-MonoBz-Fr is close to Th-amd-DiBz-Bn.

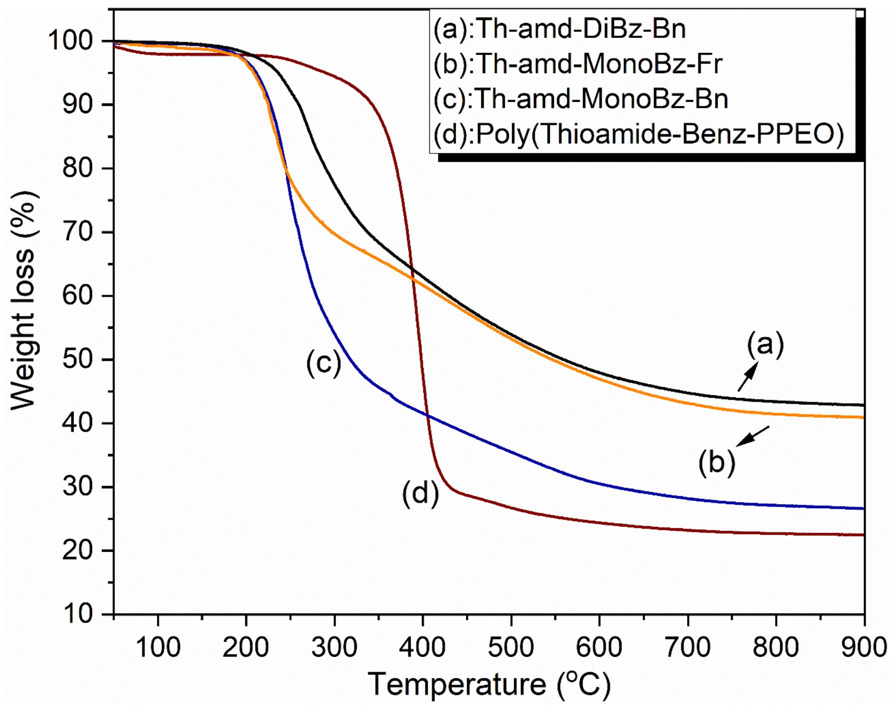


Figure 4.10 : TGA traces of cured Th-amd-DiBz-Bn (a),Th-amd-MonoBz-Fr (b), Th-amd-MonoBz-Bn (c), Poly(Thioamide-Benz-PPEO) (d).

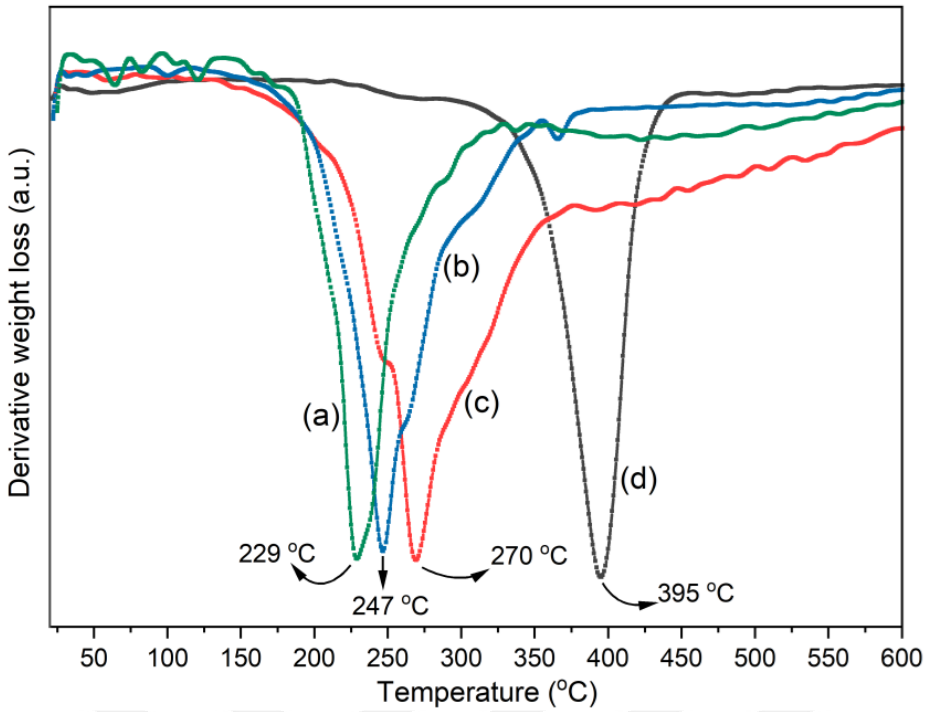


Figure 4.11 : Derivative TGA of cured Th-amd-DiBz-Bn (a), Th-amd-MonoBz-Fr (b), Th-amd-MonoBz-Bn (c), Poly(Thioamide-Benz-PPEO) (d).

Table 4.2 : Thermal properties of the cured benzoxazines Th-amd-DiBz-Bn (a), Th-amd-MonoBz-Fr (b), Th-amd-MonoBz-Bn (c), Poly(Thioamide-Benz-PPEO) (d).

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	T_c (%)
Thio-DiBnBz	236	259	265	43
Thio-FurBz	208	225	225	41
Thio-BnBz	212	228	247	27
Poly(Thioamide-Benz-PPEO)	290	343	395	23

$T_{5\%}$: The temperature for which the weight loss is 5% .

$T_{10\%}$: The temperature for which the weight loss is 10% .

T_c : The char yield at 800 °C under nitrogen atmosphere.

T_{max} : The temperature for maximum weight loss extracted from derivative TGA graph in the Figure 4.11.

The synthesis of main-chain polybenzoxazines can be performed via Mannich reaction through diphenol and diamines. The condensation reaction eventually yields oligo or polybenzoxazine precursor ready to cure. These polymeric benzoxazines have high film forming ability and processability unlike monomeric benzoxazines. Therefore, we used diphenolic thioamide as a reagent to obtain main-chain thioamide containing polybenzoxazines. Besides thioamide 1,6-diaminohexane and jeffamineED900 were selected as diamine reagents for the synthesis. As known, these type of Mannich polymerization could generate too much triazine during the synthesis that lead to gelation. Therefore, controlling the reaction condition is crucial for this type of polymerization. It was found that toluene:ethanol mixture in 2:1 (v/v) reduce the triazine formation drastically. Hence, we selected this solvent couple in our synthesis. The overall process is given in Figure 4.12.

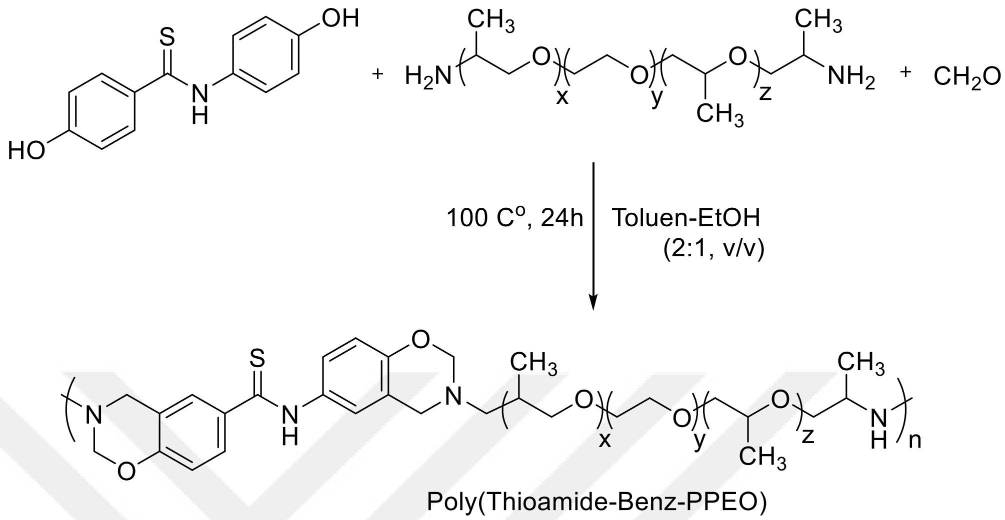


Figure 4.12 : Synthesis of thioamide containing main-chain Poly(Thioamide-Benz-PPEO) .

Two different main-chain polybenzoxazines were obtained. However, the solubility of the polymer synthesized from 1,6-diaminohexane was limited and due to uncontrolled gelation the characterization of this polymer is omitted. On the other hand, the polymers obtained from jeffamine ED-900 were soluble and spectral characterization could be performed. Accordingly, the ^{1}H-NMR spectrum of the Poly(Thioamide-Benz-PPEO) is digitized as Figure 4.13. The characteristic peaks related to oxazine ring is clearly detectable at 4.97 and 4.90 ppm for N-C**H**$_2$-O and 4.08 and 4.01 for Ar-C**H**$_2$-N. Notably, in the main-chain structure two different types of benzoxazine occurs during the synthesis due to the asymmetry of the used thioamide. Moreover, the preservation of thioamide structure can be supported by the peak belongs to thioamide –N**H** proton at 11.25 ppm.

Similarly, the structure can be further supported by FT-IR in Figure 4.14. The typical C-O-C oxazine bending is detected at 940 cm^{-1}. The band stemming from C-O stretching vibration of ether bonds is evidencing the incorporation of jeffamine in the polymer. Apart from these two major bands, the thioamide –NH stretching vibration band can be observed at ca. 3300 cm^{-1}.

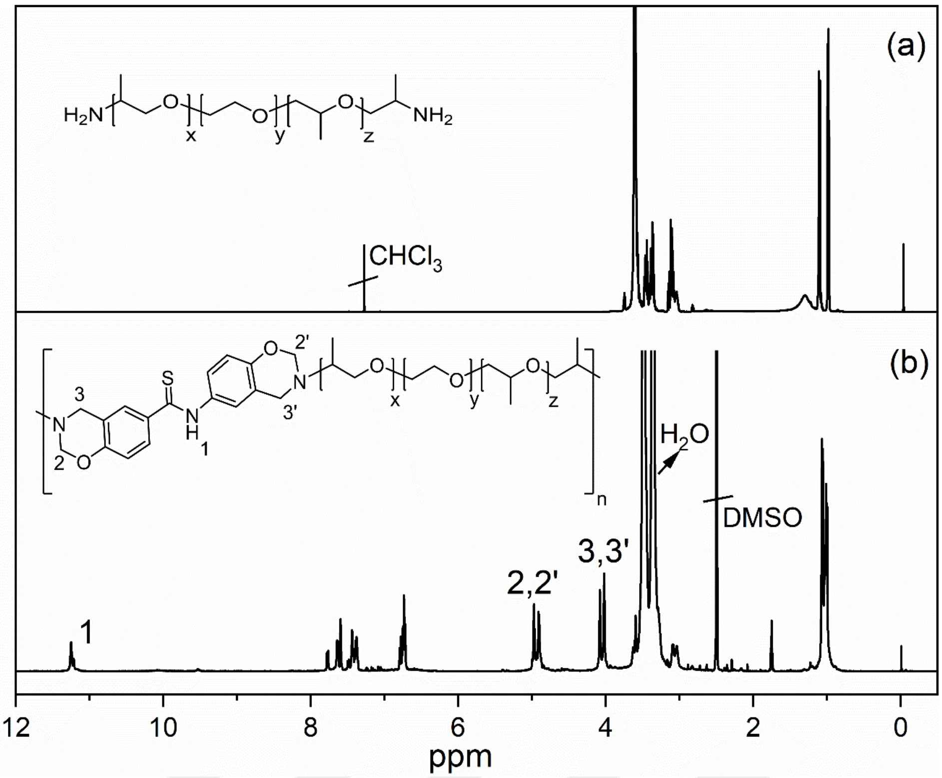


Figure 4.13 : ^{1}H-NMR spectrum of main-chain Poly(Thioamide-Benz-PPEO)

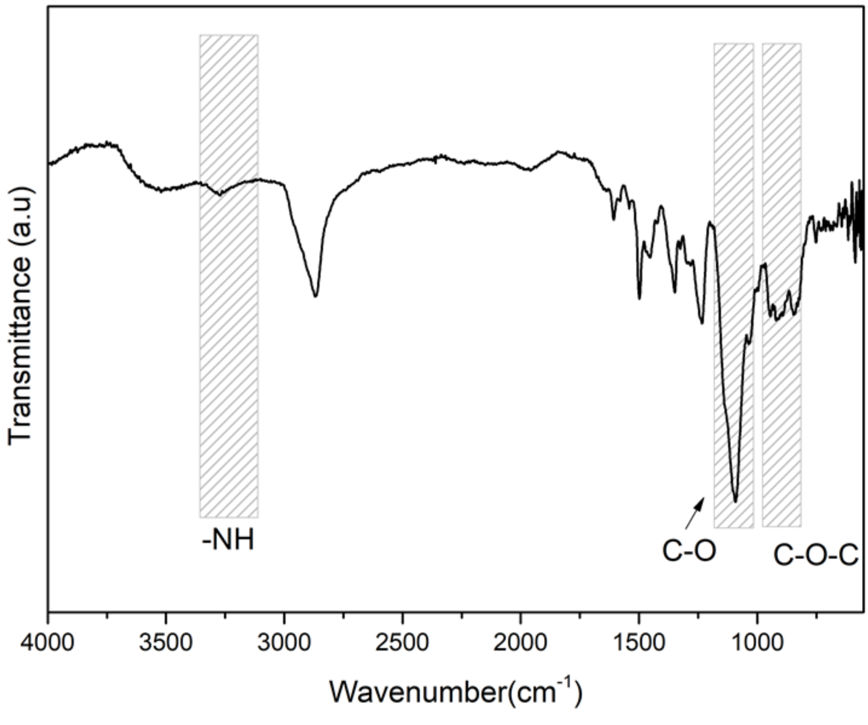


Figure 4.14 : FT-IR spectrum of main-chain Poly(Thioamide-Benz-PPEO).

Besides spectral characterization of the polymeric precursor, a GPC analysis was also performed in order to quantify the molecular weight of the polymer. Accordingly, the GPC analysis revealed that the M_n is 2299 Da and M_w is 5218 Da.(Table 4.3). Here, it should be noted that the jeffamine ED-900 has a molecular weight of *ca*. 900 Da, however according the GPC used for this study the molecular weight is found as *ca*. 600 Da. Therefore, it can be concluded that the molecular weight of Poly(Thioamide-Benz-PPEO) is probably much larger than 2299 Da.

Table 4.3 : Molecular weight of Poly(Thioamide-Benz-PPEO).

	M_n	M_w	M_w/M_n
Polymer precursor	2299	5218	2.27

As stated, the main-chain polybenzoxazines has high film abilities according to the previous studies. Thus, we also prepared films of Poly(Thioamide-Benz-PPEO) by using solvent casting method. A concentrated solution (a fluid like honey) of the precursor was poured into Teflon molds. After evaporating the solvent at room temperature, the remaining solvent residues were removed under vacuum. Then, the films were cured in an ordinary oven with a stepwise curing procedure. Flexible thermosetting films were easily removed from the molds (Figure 4.15).

Figure 4.15 : The visual images of cured Poly(Thioamide-Benz-PPEO).

The presence of the oxazine ring can also be supported by DSC analysis since benzoxazine are curable and exhibit an exotherm during ring opening. Hence, a DSC analysis (Figure 4.16) of Poly(Thioamide-Benz-PPEO) was performed and a clear exotherm is detected as a broad band starting from ca. 175 °C with a maximum at 211°C. As stated previously, the thioamide functionality has a sort of catalytic effect on curing of benzoxazines and this effect is again visible for the main-chain polymer.

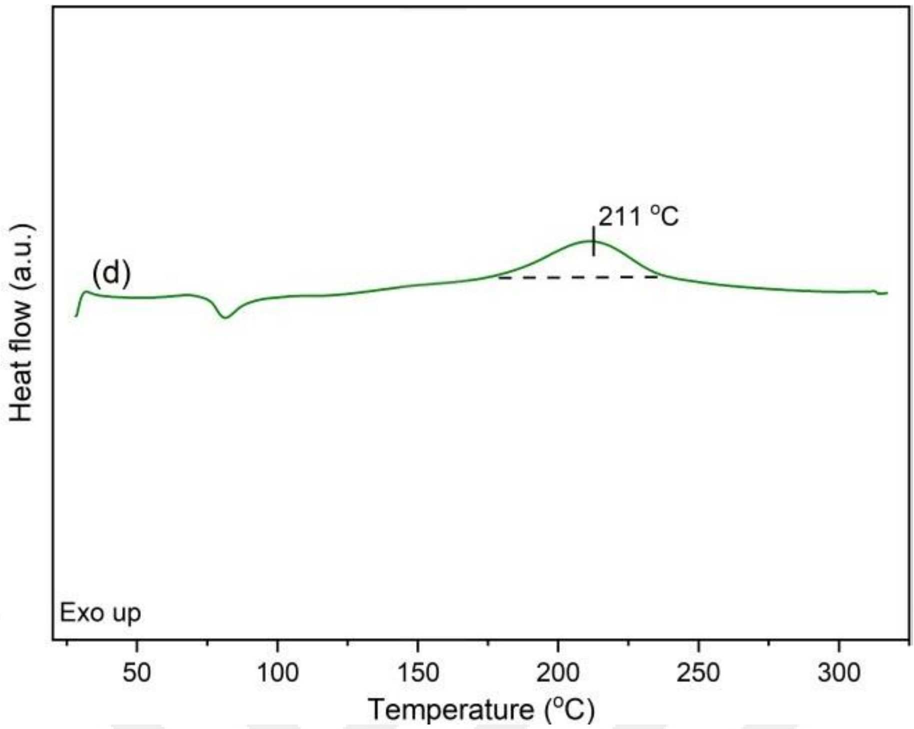


Figure 4.16 : DSC thermogram of Poly(Thioamide-Benz-PPEO).

Table 4.4 : DSC characteristic of Poly(Thioamide-Benz-PPEO).

	Curing on-set (°C)	Curing end-set (°C)	Curing maximum (°C)	Curing exotherm (J/g)
Polybenzoxazine	178	239	211	-74.40

DSC analyses were performed under nitrogen stream (20 mL/min.) with a 10 °C/min. heating rate.

Apart from DSC analysis, to provide a better thermal behavior profile for the Poly(Thioamide-Benz-PPEO) a TGA analysis was also performed. Accordingly, the cured polymer exhibited better thermal stability compared to monomeric thioamide benzoxazines especially in terms of initial degradation and maximum weight loss temperatures (Figure 4.10). This behavior is due to the presence of jeffamine moiety and reported previously in other studies. It is known that the incorporation of jeffamines in benzoxazine structure ameliorates the initial degradation temperatures but does not increase the char yield. Conversely, in general, jeffamines cause reduction in char yield for many benzoxazine samples. Our results are in accordance with the previous studies [1,73-75]. The results of TGA and derivative TGA (Figure 11) is tabulated in Table 4.2.

5. CONCLUSION

In this thesis, the first example of thioamide based benzoxazines by combining Willgerodt-Kindler reaction with benzoxazine chemistry is achieved. Interestingly, the thioamide group behaves as a self-catalytic system to reduce the ring opening polymerization of benzoxazines. It is anticipated that this catalaytic behavior stems from the cleavage of π-bond of thiocarbonyl group thus generating thiols. It is well known that thiols are considered as effective catalysts for benzoxazine curing. Moreover, in this thesis, we managed to use elemental sulfur in the syntheses. By this way, the sulfur as a waste product of petroleum industry and coal industry has found another application. In this study, three different types of novel thioamide containing benzoxazines were synthesized and characterized. The thermal characterization of their cured product also revealed that thermal stabilities of the polybenzoxazines derived from these monomers are comparable with classical polybenzoxazines from mono- and di-functional benzoxazines. Besides monomeric benzoxazines, main chain polybenzoxazines bearing thioamide moieties were also obtained by using classical Mannich type polyconsensation. The polybenzoxazine precursors exhibited excellent film properties. Cured films of these main chain polybenzoxazines are highly flexible and self-standing. The advantage of this strategy is the simplicity of the process and use of low cost of the chemicals. Consequently, a novel type of polybenzoxazines is now reported with this thesis. The studies detailed in this thesis could open new routes and inspire strategies for the development of polybenzoxazine with further beneficial properties.

REFERENCES

[1] **Kaya, G., Kiskan, B. and Yagci, Y.** (2019). Coumarines as masked phenols for amide functional benzoxazines, *Polymer Chemistry*, ***10***(10), 1268-1275.

[2] **Sun, L., Zhang, K., Min, C., Liu, Y., Wang, Y., Zhang, J., Li, S.** (2018). Synthesis, characterization and structural thermally rearrangement of ortho-amide functional benzoxazine containing acetylene group, *Thermochimica Acta*, ***668***, 1-8.

[3] **Zhang, K. and Ishida, H.** (2015). Smart synthesis of high-performance thermosets based on ortho-amide-imide functional benzoxazines, *Front. Mater.*, **2**, 1.

[4] **Agag, T., Arza, C. R., Maurer, F. H. J. and Ishida, H.** (2010). Primary Amine-Functional Benzoxazine Monomers and Their Use for Amide-Containing Monomeric Benzoxazines, *Macromolecules*, ***43***(6), 2748-2758.

[5] **Dodiuk, H. and Goodman, S., H.** (2013). *Handbook of thermoset plastics*, San Diago, CA : Elsevier.

[6] **Baekeland, L., H.** (1909). The Synthesis, Constitution, and Uses of Bakelite, *Journal of Industrial and Engineering Chemistry*, ***1***(3), 149-161.

[7] **Baekeland, L.** (1914). The invention of celluloid, *The Journal of Industrial and Engineering Chemistry*, ***6***(2), 90-91.

[8] **Frollini, E., Silva, C. and Ramires, E.** (2013). Phenolic resins as a matrix material in advanced fiber-reinforced polymer (FRP) composites, In J. Bai (Eds.), *Advanced Fibre-Reinforced Polymer (FRP) composites for structural applications* (1st ed., pp.7-43), Cambridge : Woodhead Publishing.

[9] **Pilato, L.** (2010). *Phenolic Resins: A Century of Progress*. Berlin, Heidelberg : Springer-Verlag.

[10] **Gardziella, A., Pilato, L. A. and Knop, A.** (2013). *Phenolic resins: chemistry, applications, standardization, safety and ecology*. Berlin, Heidelberg : Springer Science & Business Media.

[11] **Allen, D. J. and Ishida, H.** (2001). Thermosets: Phenolics, Novolacs, and Benzoxazine, In K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilschner, E. J. Kramer, S. Mahajan, P. Veyssière (Eds.), *Encyclopedia of Materials: Science and Technology* (1st ed., pp. 9226-9229), Oxford : Elsevier.

[12] **Holly, F. W. and Cope, A. C.** (1944). Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine, *Journal of the American Chemical Society*, ***66***(11), 1875-1879.

[13] **Burke, W. J.** (1949). 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of p-substituted phenols with N, N-dimethylolamines, *J. Am. Chem. Soc.*, ***71***, 609.

[14] **Burke, W. J. and Weatherbee, C.** (1950). 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of Polyhydroxybenzenes with N-Methylolamines, *J. Am. Chem. Soc.*, ***72***(10), 4691-4694.

[15] **Burke, W. J. and Stephens, C. W.** (1952). Monomeric products from the condensation of phenol with formaldehyde and primary amines, *J. Am. Chem. Soc.*, ***74***(6), 1518-1520.

[16] **Burke, W. J., Kolbezen, M. J. and Stephens, C. W.** (1952). Condensation of Naphthols with Formaldehyde and Primary Amines, *J. Am. Chem. Soc.*, ***74***(14), 3601-3605.

[17] **Burke, W. J., Murdock, K. C. and Ec, G.** (1954). Condensation of Hydroxyaromatic Compounds with Formaldehyde and Primary Aromatic Amines, *J. Am. Chem. Soc.*, ***76***(6), 1677-1679.

[18] **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 *The Journal of Organic Chemistry*, ***30***(10), 3423-3427.

[19] **Burke, W., Smith, R., P. and Weatherbee, C.** (1952). N, N-bis-(hydroxybenzyl)-amines: synthesis from phenols, formaldehyde and primary amines1, *Journal of the American Chemical Society*, ***74***(3), 602-605.

[20] **Burke, W. J., Glennie, E. M. and Weatherbee, C.** (1964). Condensation of Halophenols with Formaldehyde and Primary Amines1, *The Journal of Organic Chemistry*, ***29***(4), 909-912.

[21] **Ishida, H.** (2011). Overview and historical background of polybenzoxazine research. In H. Ishida, T. Agag (Eds.), *Handbook of benzoxazine resins* (1st ed., pp. 3-81). Oxford : Elsevier.

[22] **Riess, G., Schwob, J. M., Guth, G., Roche, M., Lande, B.** (1985). *Advances in Polymer Synthesis*, New York : Plenum.

[23] **Turpin, E. T. and Thrane, D. T.** (1988). United States Patent No.471925. Retrieved from Scopus.

[24] **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***(6), 1121-1129.

[25] **Ghosh, N. N., Kiskan, B. and Yagci, Y.** (2007). Polybenzoxazines—New high performance thermosetting resins: Synthesis and properties, *Progress in Polymer Science*, ***32***(11), 1344-1391.

[26] **Liu, J. and Ishida, H.** (1996). A New Class of Phenolic Resins with Ring-Opening Polymerization. In J. Liu, H. Ishida (Eds.), *The Polymeric Materials Encyclopedia* (pp. 484-494). Florida : CRC Press.

[27] **Ishida, H.** (1996). United States Patent No.5543516. Retrieved from Scopus.

[28] **Liu, J.** (1995). *Characterization, Reaction Mechanism and Kinetics of 3,4-Dihydro-2H-1,3-benzoxazine and its Polymers*. Cleveland, OH.

[29] **Wang, Y. X. and Ishida, H.** (2002). Development of low-viscosity benzoxazine resins and their polymers, *Journal of Applied Polymer Science*, ***86***(12), 2953-2966.

[30] **Ishida, H. and Rodriguez, Y.** (1995). Curing Kinetics of a New Benzoxazine-Based Phenolic Resin by Differential Scanning Calorimetry, *Polymer*, ***36***(16), 3151-3158.

[31] **Kimura, H., Taguchi, S. and Matsumoto, A.** (2001). Studies on new type of phenolic resin (IX) curing reaction of bisphenol A-based benzoxazine with bisoxazoline and the properties of the cured resin. II. Cure reactivity of benzoxazine, *Journal of Applied Polymer Science*, ***79***(13), 2331-2339.

[32] **Liu, J., Agag, T. and Ishida, H.** (2011). Main-chain type benzoxazine oligomers: a new concept for easy processable high performance polybenzoxazines. In J. Liu, T. Agag, H. Ishida (Eds.) *Handbook of Benzoxazine Resins*, (1st ed., pp.355-362) Oxford : Elsevier.

[33] **Wang, Y. X. and Ishida, H.** (1999). Cationic ring-opening polymerization of benzoxazines, *Polymer*, ***40***(16), 4563-4570.

[34] **McDonagh, A. F. and Smith, H. E.** (1968). Ring-chain tautomerism of derivatives of o-hydroxybenzylamine with aldehydes and ketones, *J. Org. Chem.*, ***33***(1), 1-8.

[35] **Dunkers, J. and Ishida, H.** (1999). Reaction of benzoxazine-based phenolic resins with strong and weak carboxylic acids and phenols as catalysts, *J. Polym. Sci. Part A: Polym. Chem.*, ***37***(13), 1913-1921.

[36] **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***(8), 2839-2847.

[37] **Ishida, H. and Rodriguez, Y.** (1995). Catalyzing the Curing Reaction of a New Benzoxazine-Based Phenolic Resin, *Journal of Applied Polymer Science*, ***58***(10), 1751-1760.

[38] **Wang, J., Liu, W. and Feng, T.** (2017). Furan-Based Benzoxazines. In, H. Ishida and P. Froimowicz (Eds.), *Advanced and Emerging Polybenzoxazine Science and Technology* (1st ed., pp.533-567) Amsterdam : Elsevier.

[39] **Russell, J.** (1993). Cure shrinkage of thermoset composites, *Society of Aerospace Material and Process Engineers*, ***24***(2).

[40] **Dong, J. P., Chiu, S. G., Hsu, M. W. and Huang, Y. J.** (2006). Effects of reactive low-profile additives on the volume shrinkage and internal

pigmentability for low-temperature cure of unsaturated polyester, *Journal of applied polymer science*, ***100***(2), 967-979.

[41] **Ishida, H. and Low, H. Y.** (1997). A study on the volumetric expansion of benzoxazine-based phenolic resin, *Macromolecules*, ***30***, 1099.

[42] **Liu, X. and Gu, Y.** (2002). Study on the volumetric expansion of benzoxazine curing with different catalysts, *Journal of Applied Polymer Science*, ***84***(6), 1107-1113.

[43] **Maggana, C. and Pissis, P.** (1999). Water sorption and diffusion studies in an epoxy resin system, *Journal of Polymer Science Part B: Polymer Physics*, ***37***(11), 1165-1182.

[44] **Lee, S.-B., Rockett, T. and Hoffman, R.** (1992). Interactions of water with unsaturated polyester, vinyl ester and acrylic resins, *Polymer*, ***33***(17), 3691-3697.

[45] **Gellert, E. and Turley, D.** (1999). Seawater immersion ageing of glass-fibre reinforced polymer laminates for marine applications, *Composites Part A: Applied Science and Manufacturing*, ***30***(11), 1259-1265.

[46] **Ghosh, S., Klett, R., Fink, D., Dwivedi, K., Vacik, J., Hnatowicz, V., Cervena, J.** (1999). On the penetration of aqueous solutions into pristine and radiation damaged polyimide, *Radiation Physics and Chemistry*, ***55***(3), 271-284.

[47] **Ishida, H. and Allen, D. J.** (1996). Physical and mechanical characterization of near-zero shrinkage polybenzoxazines, *Journal of Polymer Science Part B-Polymer Physics*, ***34***(6), 1019-1030.

[48] **Walters, R. N. and Lyon, R. E.** (2003). Molar group contributions to polymer flammability, *J. Appl. Polym. Sci.*, ***87***, 548.

[49] **Agag, T., Arza, C. R., Maurer, F. H. J. and Ishida, H.** (2011). Crosslinked polyamide based on main-chain type polybenzoxazines derived from a primary amine-functionalized benzoxazine monomer, *Journal of Polymer Science Part A: Polymer Chemistry*, ***49***(20), 4335-4342.

[50] **Bayram, O., Kiskan, B., Demir, E., Demir-Cakan, R., Yagci Y.** (2020). Advanced thermosets from sulfur, renewable benzoxazine and ionones via inverse vulcanization, *ACS Sustainable Chemistry & Engineering*. ***8***, 9145-9155.

[51] **Arslan, M., Kiskan, B. and Yagci, Y.** (2016). Combining Elemental Sulfur with Polybenzoxazines via Inverse Vulcanization, *Macromolecules*, ***49***(3), 767-773.

[52] **Jagodziński, T. S.** (2003). Thioamides as useful synthons in the synthesis of heterocycles, *Chemical reviews*, ***103***(1), 197-228.

[53] **Priebbenow, D. L. and Bolm, C.** (2013). Recent advances in the Willgerodt–Kindler reaction, *Chemical Society Reviews*, ***42***(19), 7870-7880.

[54] **Pathare, S. P., Chaudhari, P. S. and Akamanchi, K. G.** (2012). Sulfated tungstate: An efficient catalyst for synthesis of thioamides via Kindler reaction, *Applied Catalysis A: General*, ***425***, 125-129.

[55] **Kale, A. D., Tayade, Y. A., Mahale, S. D., Patil, R. D., Dalal, D. S.** (2019). Willgerodt-Kindler reaction at room temperature: Synthesis of thioamides from aromatic aldehydes and cyclic secondary amines, *Tetrahedron*, ***75***(41), 130575.

[56] **Willgerodt, C.** (1887). Ueber die Einwirkung von gelbem Schwefelammonium auf Ketone und Chinone, *Berichte der deutschen chemischen Gesellschaft*, ***20***(2), 2467-2470.

[57] **Kindler, K.** (1923). Studien über den mechanismus chemischer reaktionen. Erste abhandlung. Reduktion von amiden und oxydation von aminen, *Justus Liebigs Annalen der Chemie*, ***431***(1), 187-230.

[58] **Carmack, M.** and **Spielman, M.**, (1949) *Organic Reactions*, New York : Wiley.

[59] **Dauben, W. G., Ciula, R. P. and Rogan, J. B.** (1957). Mechanism of the Willgerodt Reaction. Studies with 1-Tetralones1, *The Journal of Organic Chemistry*, ***22***(4), 362-365.

[60] **Carmack, M.** (1989). The willgerodt-kindler reactions. 7. The mechanisms, *Journal of heterocyclic chemistry*, ***26***(5), 1319-1323.

[61] **Okamoto, K., Yamamoto, T. and Kanbara, T.** (2007). Efficient synthesis of thiobenzanilides by Willgerodt-Kindler reaction with base catalysts, *Synlett*, ***2007***(17), 2687-2690.

[62] **Cao, W., Dai, F., Hu, R. and Tang, B. Z.** (2019). Economic Sulfur Conversion to Functional Polythioamides through Catalyst-Free Multicomponent Polymerizations of Sulfur, Acids, and Amines, *Journal of the American Chemical Society*, ***142***(2), 978-986.

[63] **Sun, Z., Huang, H., Li, L., Liu, L., Chen Y.** (2017). Polythioamides of high refractive index by direct polymerization of aliphatic primary diamines in the presence of elemental sulfur, *Macromolecules*, ***50***(21), 8505-8511.

[64] **Mutlu, H., Ceper, E. B., Li, X., Yang, J., Dong W., Ozmen M. M., Theato P.** (2019). Sulfur chemistry in polymer and materials science, *Macromolecular rapid communications*, ***40***(1), 1800650.

[65] **Kanbara, T., Kawai, Y., Hasegawa, K., Morita, H., Yamamoto T.** (2001). Preparation of polythioamides from dialdehydes and diamines with sulfur by the Willgerodt–Kindler type reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, ***39***(21), 3739-3750.

[66] **Li, W., Wu, X., Zhao, Z., Qin, A., Hu R., Tang, B. Z.** (2015). Catalyst-free, atom-economic, multicomponent polymerizations of aromatic diynes, elemental sulfur, and aliphatic diamines toward luminescent polythioamides, *Macromolecules*, ***48***(21), 7747-7754.

[67] **Zhang, K. and Ishida, H.** (2015). Smart Synthesis of High-Performance Thermosets Based on ortho-Amide–Imide Functional Benzoxazines, *Frontiers in Materials*, ***2***(5).

[68] **Lin, H. K. and Liu, Y. L.** (2018). Sulfur Radical Transfer and Coupling Reaction to Benzoxazine Groups: A New Reaction Route for

Preparation of Polymeric Materials Using Elemental Sulfur as a Feedstock, *Macromolecular Rapid Communications*, ***39***(8), 1700832.

[69] **Gorodisher, I., DeVoe, R. J. and Webb, R. J.** (2011). Catalytic Opening of Lateral Benzoxazine Rings by Thiols, T. Agag and H. Ishida (Eds.) *Handbook of Benzoxazine Resins*, (1st ed., pp.211-234). Amsterdam : Elsevier.

[70] **Semerci, E., Kiskan, B. and Yagci, Y.** (2015). Thiol reactive polybenzoxazine precursors: A novel route to functional polymers by thiol-oxazine chemistry, *European Polymer Journal*, ***69***, 636-641.

[71] **Musa, A., Kiskan, B. and Yagci, Y.** (2014). Thiol-benzoxazine chemistry as a novel Thiol-X reaction for the synthesis of block copolymers, *Polymer (United Kingdom)*, ***55***(22), 5550-5556.

[72] **Beyazkilic, Z., Kahveci, M. U., Aydogan, B., Kiskan, B., Yagci Y.** (2012). Synthesis of polybenzoxazine precursors using thiols: Simultaneous thiol–ene and ring-opening reactions, *J. Polym. Sci. Part A: Polym. Chem.*, ***50***(19), 4029-4036.

[73] **Durukan, C., Kiskan, B. and Yagci, Y.** (2019). One-Pot Synthesis of Amide-Functional Main-Chain Polybenzoxazine Precursors, *Polymers*, ***11***(4), 679.

[74] **Kiskan, B. and Yagci, Y.** (2014). Self-healing of poly (propylene oxide)-polybenzoxazine thermosets by photoinduced coumarine dimerization, *Journal of Polymer Science Part A: Polymer Chemistry*, ***52***(20), 2911-2918.

[75] **Yildirim, A., Kiskan, B., Demirel, A. L. and Yagci, Y.** (2006). Synthesis, characterization and properties of naphthoxazine-functional poly(propyleneoxide)s, *European Polymer Journal*, ***42***(11), 3006-3014.

APPENDICES

APPENDIX A: Supporting information of result and discussions.

APPENDIX A

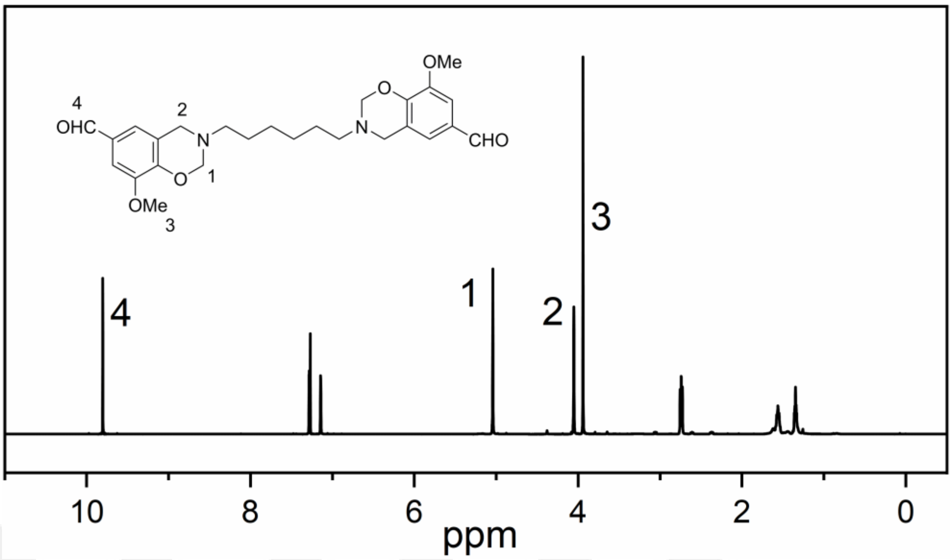


Figure A.1 : ^{1}H-NMR spectrum of vanillin di-benzoxazine monomer (Va-DiBenz).

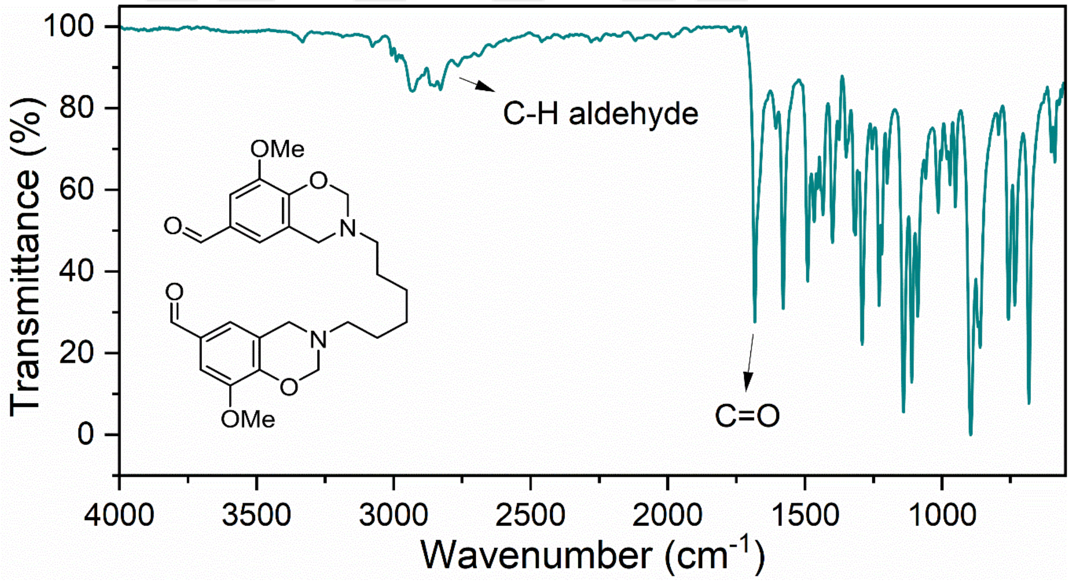


Figure A.2 : FT-IR spectrum of vanillin di-benzoxazine monomer (Va-DiBenz).

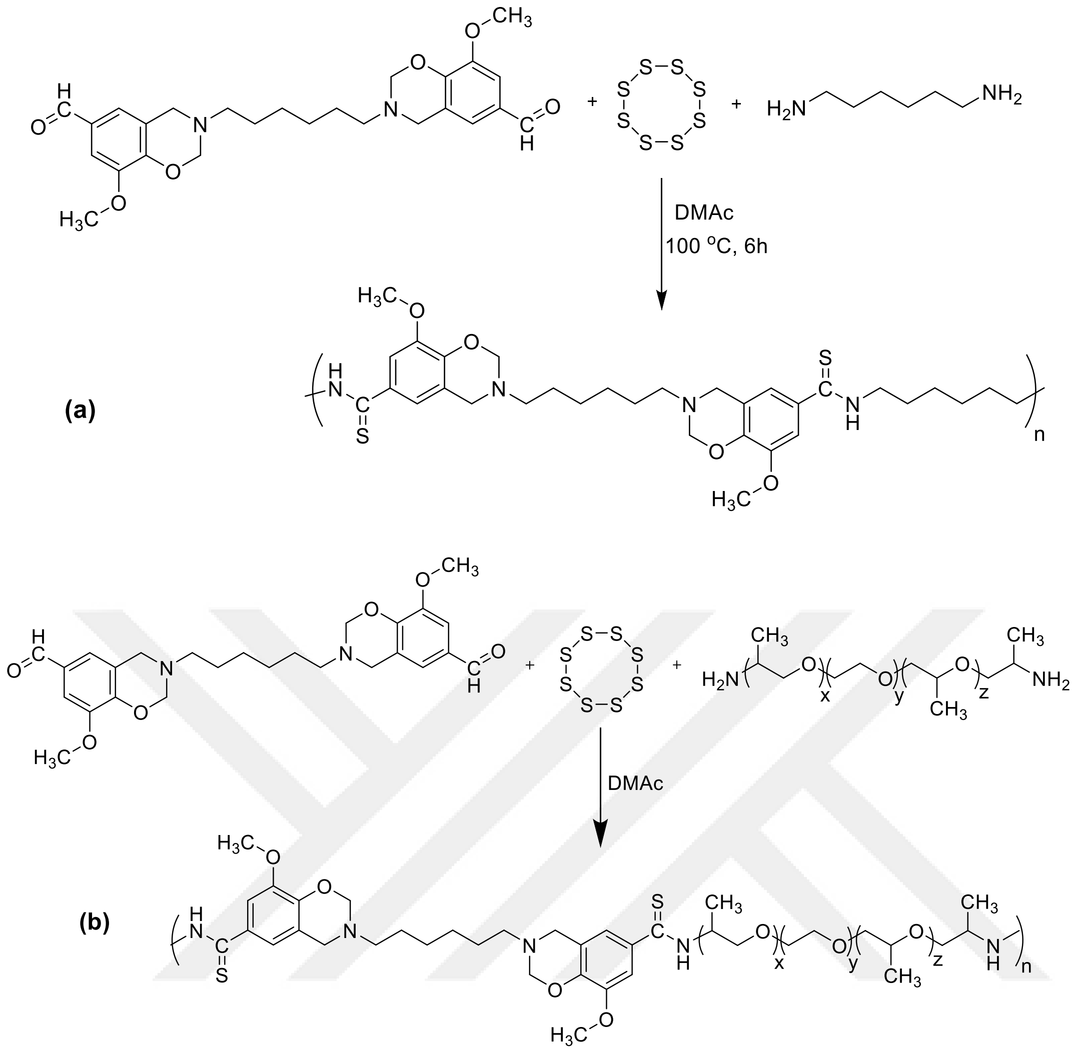


Figure A.3 : Willgerodt-Kindler reaction of Va-DiBz with (a) 1,6-diaminohexane, (b) Jeffamine-ED900, x+z≈6, y≈12.5

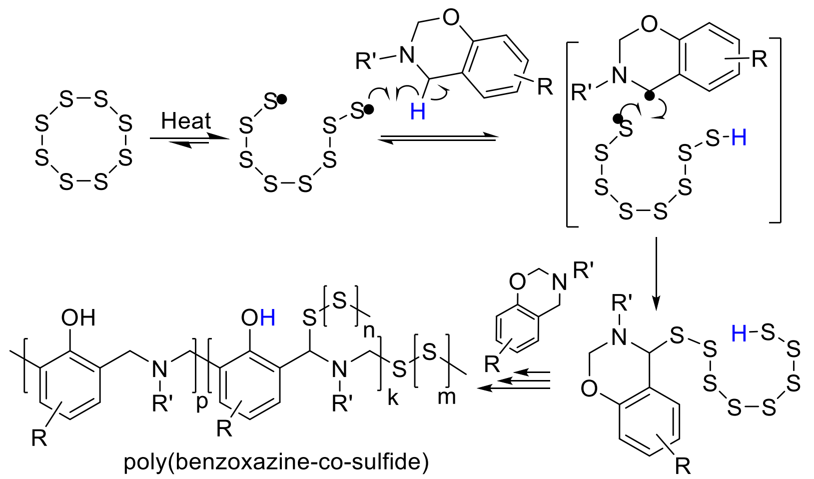


Figure A.4 : The reaction between elemental sulfur and benzoxazine monomer to give polysulfide-*co*-benzoxazines.

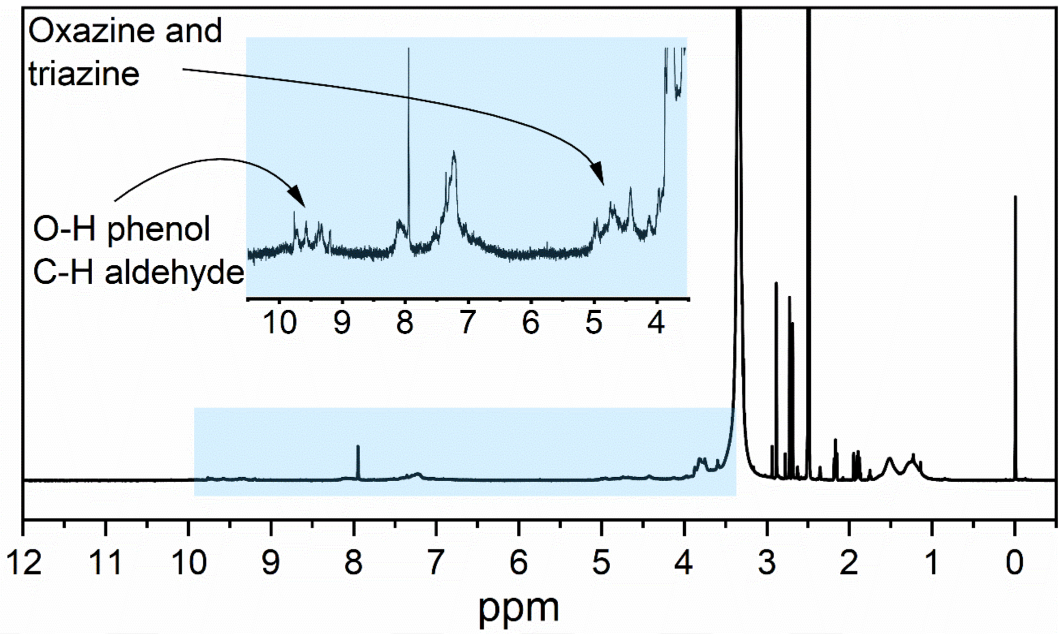


Figure A.5 : ^{1}H-NMR spectrum of expected product (amine source: jeffamine ED-900)

Figure A.6 : The image of the product mono-functional thioamide.

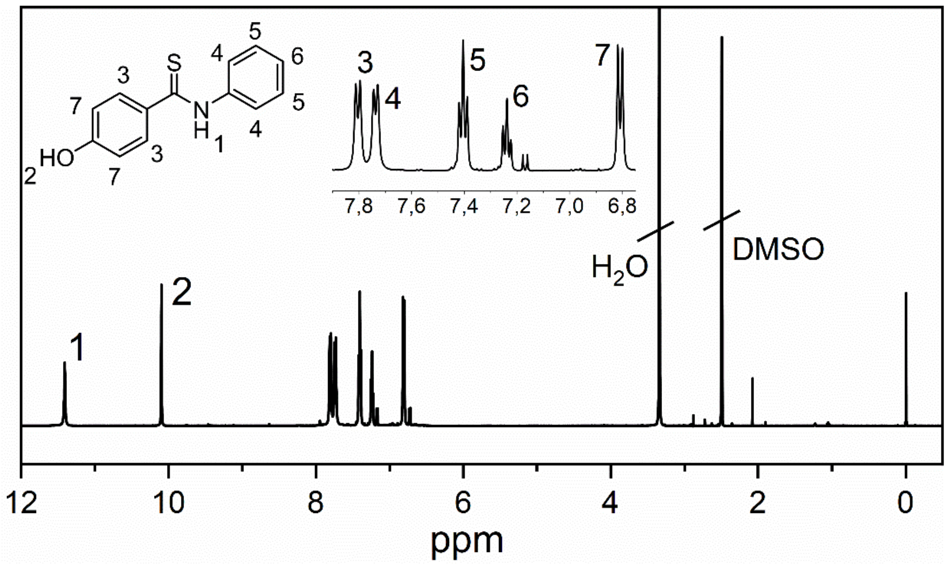


Figure A.7 : ^{1}H-NMR spectrum of mono-functional thioamide.

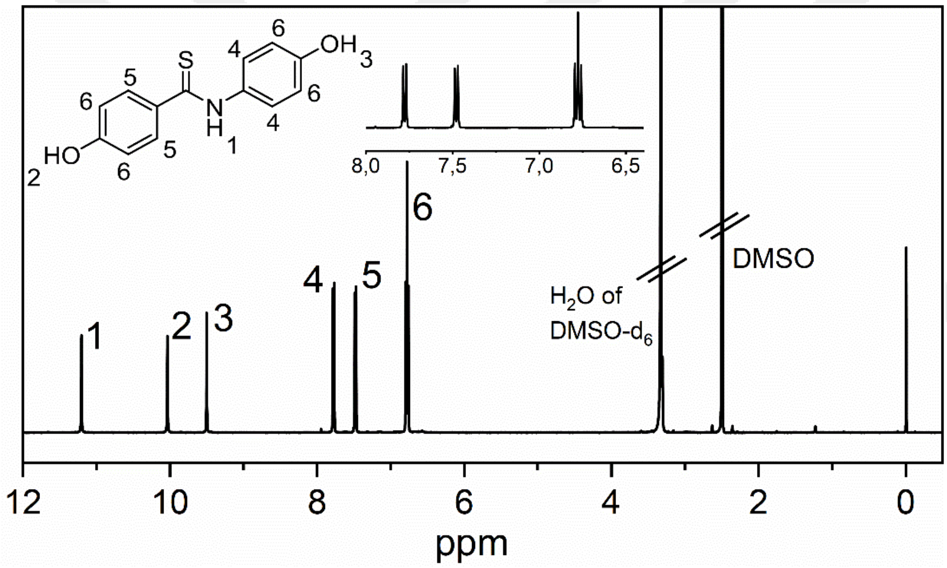


Figure A.8 : ^{1}H-NMR spectrum of di-functional thioamide.

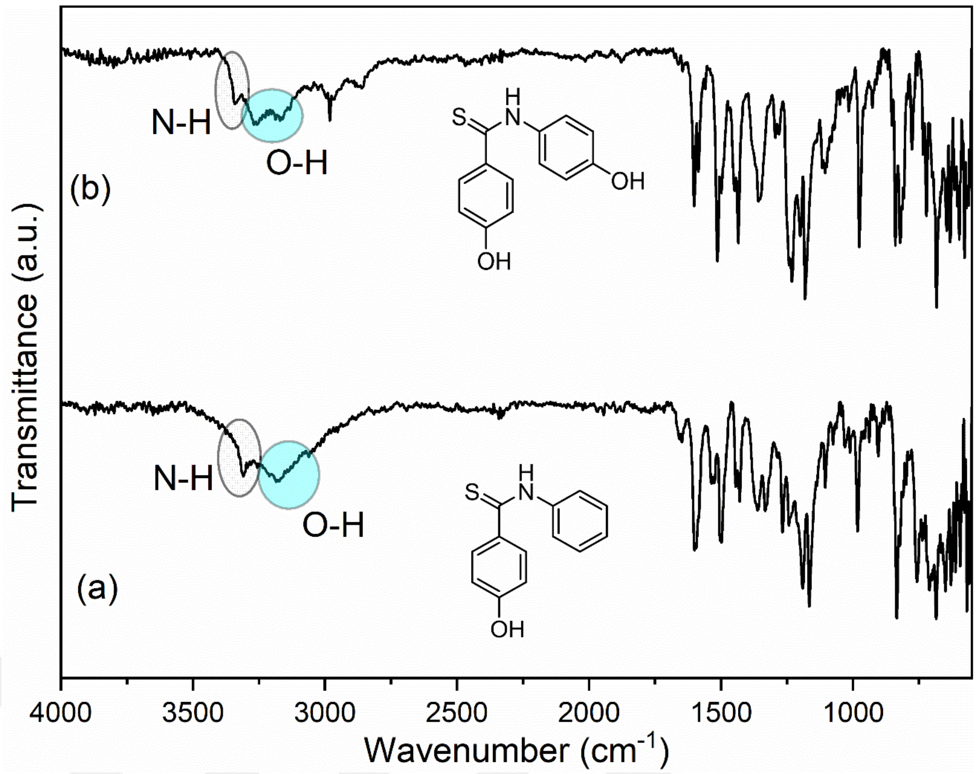


Figure A.9 : FT-IR spectra of thioamides.

Table A.1 : Molecular weight of expected product.

	M_n	M_w	M_n/M_w
Soluble precursor	1284	2521	1.963

Determined by GPC according to polystyrene standards.

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PUBLICATIONS AND PRESENTATIONS ON THE THESIS:

- **Bayram K.,** Kiskan B., Yagci Y. 2019 : Modification of Polybenzoxazines for Advanced Materials by Kindler Reaction (oral presantation), **VII International Baekeland Symposium, October 15-18, 2019, Tarragona, Spain.**
- **Bayram K.,** Kiskan B., Yagci Y., 2020, Synthesis of Thioamide Containing Polybenzoxazines by Willgerodt-Kindler Reaction (to be submitted).