ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ONE-POT SYNTHESIS OF AMIDE-FUNCTIONAL MAIN-CHAIN POLYBENZOXAZINE PRECURSORS

M.Sc. THESIS

Canan DURUKAN

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AMİT FONKSİYONLU ANA ZİNCİR POLİBENZOKSAZİNLERİN TEK-POTADA SENTEZİ

YÜKSEK LİSANS TEZİ

Canan DURUKAN

(509181276)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Yusuf YAĞCI

TEMMUZ 2020

Canan Durukan, a M.Sc. student of İTU Graduate School of Science Engineering and Technology 509181276, successfully defended the thesis entitled "ONE-POT SYNTHESIS OF AMIDE-FUNCTIONAL MAIN-CHAIN POLYBENZOXAZINE PRECURSORS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Yusuf YAĞCI** .....

İstanbul Technical University

Jury Members : **Assoc. Prof. Barış KIŞKAN** .....

Assoc. Prof. Binnur TEMEL .....

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To my beloved family and friends,

FOREWORD

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June 2020 Canan DURUKAN

(Chemist)

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ABBREVIATIONS

ROP	**:** Ring-Opening Polymerization
DHC	**:** 3,4-dihydrocoumarine
HMTA	**:** Hexamethylenetetramine
PO	**:** Propylene Oxide
EO	**:** Ethylene Oxide
PA	**:** Polyamide
PPA	**:** Polyphthalamide
Bz	**:** Benzoxazine
TGA	**:** Thermogravimetric Analysis
DSC	**:** Differential Scanning Calorimetry
GPC	**:** Gel-Permeation Chromatography
FT-IR	**:** Fourier Transform Infrared

SYMBOLS

T_g	: Glass Transition Temperature
$T_{5\%}$	: 5% Weight Loss Temperature
$T_{10\%}$	: 10% Weight Loss Temperature
T_c	: Char Yield at 800 °C
T_{max}	: Maximum Weight Loss Temperature Calculated

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ONE-POT SYNTHESIS OF AMIDE-FUNCTIONAL MAIN-CHAIN POLYBENZOXAZINE PRECURSORS

SUMMARY

Polymers are encountered in almost every aspect of modern life. People are likely in contact with at least one product that contains polymer; from water bottles to automobile tires. Polymer materials possess a wide range of characteristics that make them useful and practical for several applications. Nowadays, advanced polymer materials that exhibit special properties with different functions have attracted more attention. Even the more sophisticated technology uses polymers. For instance, water desalination membranes or artificial skin made from a silicone polymer.

Thermoplastics and thermosets are the two most important synthetic polymers in the field. Thermoset materials are a type of materials that are irreversibly hardened by curing of a solid or viscous liquid. On the contrary thermoplastic materials can be used several times as they can be re-melted. The main reason that thermoset polymers cannot be reused is that they have a highly cross-linked nature. That is the important feature of thermoset polymers that distinguish them from the other types including thermoplastics and elastomers. Besides much-used thermoset plastic materials such as a generic family of thermoset resins including polyesters, epoxy, vinyl esters, polyurethane resins, phenol- formaldehyde resins are also of great interest in the polymer industry. For their excellent mechanical and thermal resistance, phenolic resins are demanded in the growing industry of advanced polymer materials. Not only the traditional phenolic resins are the required members in polymer science but also polybenzoxazines have an important place in these types of polymers. Polybenzoxazines are a strong competitor in this field due to their superior properties. These are tailor-made synthetic polymers that exhibit excellent properties such as near-zero shrinkage, high glass transition temperatures, high char yield, low water absorption, good chemical resistance, good mechanical and thermal properties which make them a rival amongst their counterparts. These advanced material properties make them a perfect contender for several application areas such as electrochromic materials, self-healing materials, anti-corrosion coatings, shape memory materials, composite materials in the aerospace industry, environmental applications and textile applications.

Formaldehyde and a phenol or substituted phenol forms a reaction which results in phenolic resin. One of these synthetic thermoset resins, polybenzoxazines are similar to classical phenol-formaldehyde resins but their synthesis and polymerization proceed in a different manner. The polymerization reaction takes place via ring-opening polymerization. There is no need for any additive or catalyst during the polymerization process. Moreover, polybenzoxazines can easily be obtained from their monomer which comprises a 1,3-oxazine structure. There are derivatives of oxazine structures; 1,2-, 1,3- and 1,4-oxazine. In benzoxazine synthesis it is only used 1,3-oxazines because only they are active for ring-opening polymerization reactions. It is also

remarkable that the purification process is easy which makes it practical to eliminate the undesired by-products. Nevertheless, polybenzoxazines have some shortcomings such as difficulties in film and fiber formation and brittleness after curing process. To tackle these problems, several types of main-chain, side-chain, and end-chain polymers were synthesized. In addition to these, polybenzoxazines which comprise amide functionality have gained interest because of their structural advantage such as hydrogen bonding. Polyamides take an important place in other types of polymers as strong hydrogen bonding in their structure provides good mechanical and thermal properties. In the same vein, polybenzoxazines containing amide linkages in their structures have many hydrogen bonding interactions. There is previous research on the synthesis of different types of polybenzoxazines, amide linkage containing polybenzoxazines were rarely synthesized and with the one- pot strategy, this is an original approach that contributes to the field. In this novel approach, it was designed an amide functional polybenzoxazine starting from 3,4-dihydrocoumarines (DHC), which gives vast design flexibility for further applications.

In the scope of this study, main-chain polybenzoxazines containing amide linkages were successfully prepared in one-pot. Three different polymers were synthesized by reacting 3,4-dihydrocoumarine (DHC) and paraformaldehyde with 1,3-diaminopropane or 1,6-diaminohexane or Jeffamide D-900. The one-pot reaction proceeded through the combination of ring-opening of DHC with amines and subsequent Mannich and ring closure reactions in a cascade manner. The obtained polymer from Jeffamine exhibited good film forming properties and free standing flexible films were easily solvent casted on teflon plates. All polymeric precursors were characterized by spectroscopic analysis such including ^{1}H-NMR and FT-IR and their curing behavior and thermal stability were investigated by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA).

AMİT FONKSİYONLU ANA ZİNCİR POLİBENZOKSAZİNLERİN TEK-POTADA SENTEZİ

ÖZET

Polimerlere modern yaşamın hemen her alanında rastlanır. İnsanlar günlük hayatlarında polimer içeren ürünlerle en az bir defa da olsa mutlaka temas halindedirler; su şişelerinden otomobil lastiklerine bir çok alanda polimerlere rastlanır. Polimer malzemeler onları çeşitli uyulamalar için pratik ve kullanışlı hale getiren çok çeşitli özelliklere sahiptir. Günümüzde, farklı işlevlere sahip özellikler sunan gelişmiş polimerik malzemeler günden güne daha da fazla dikkat çekmekte ve bu alanda ilgi odağı olmaktadır. Daha karmaşık ve sofistike olan teknolojilerde bile polimer kullanımları yer alıyor. Örneğin, silikon polimerden yapılmış suni deri veya suyun tuzdan arındırılması uygulamalarında kullanılan membranlar için polimerler işlevselliğini korumaktadır.

Termoplastikler ve termosetler polimer kimyası ve teknolojisi alanındaki en önemli iki sentetik polimer grubunu oluşturur. Termoset malzemeler, ısıtıldığında sertleşen ve bu halini sonuna dek koruyan plastiklerdir. Katı veya yapışkan bir sıvının kürlenmesi ile geri dönüşü olmayan bir şekilde sertleşen bir malzeme türüdür. Termoset malzemeler polimerizasyon ve olgunlaşma süreçlerini tamamladıktan sonra çapraz bağlı güçlü bir yapı oluşturur, bu nedenle ısıya ve korozyona dayanımları oldukça yüksektir. Diğer bir taraftan termoplastik malzemeler tekrar eritilebildiklerinden bir kaç kez kullanılabilirler. Termoplastiklerde ikincil bağların zayıflaması veya kopması sonucu zincirlerin kayma-dönme hareketlerinden ötürü olıuşan elastik plastik deformasyonlar şekil değiştirme kabiliyetlerini açıklayan nedendir. Termoset polimerlerin tekrar tekrar kullanılamamasının temel nedeni, oldukça çapraz bağlı bir yapıya sahip olmalarıdır. Bu termoset polimerleri termoplastik ve elastomerlerden ayıran en önemli özelliklerdendir. Polyesterler, epoksi, vinil esterler, poliüretan reçineler, fenol formaldehit reçineleri gibi termoset reçineleri ailesinin önemli elemanları termoset plastik malzemelerde ve polimer endüstrisinde önemli yere sahip, büyük ilgi gören yapılardır. Mükemmel mekanik ve termal dayanımları dolayısıyla, her geçen gün daha da büyüyen polimerik malzemeler endüstrisinde fenolik reçineler oldukça revaçtadır. Fenolik reçineler yapıştırıcı, ısı izolasyonları, koruyucu kaplama gibi şeylerde oldukça yaygın kullanılır. Isı ve alev dayanımı, boyutsal kararlılık, yüksek mekanik mukavemet ve çeşitli çözücülere, asitlere ve suya karşı yüksek direnç gibi üstün özellikler gösterirler. Diğer reçinelerle kıyaslandığında yandığı zaman düşük duman yoğunluğuna sahiptir. Fenolik reçineler, maliyetlerinin düşük olması ve mukavemet ve dayanıklılık gibi avantajları nedeniyle termo-yapısal uygulamalar ve havacılık endüstrisi tarafından bu alanlarda ilgi görmektedir. Polimer biliminde yalnızca geleneksel fenolik reçineler rağbet gören üyeler değil, aynı zamanda polibenzoksazinler de bu alanda önemli bir yere sahiptir. Holly ve Cope, ilk polibenzoksazin sentezini 1940 yılında gerçekleştirmesine rağmen önemi ilerleyen

zamanlarda anlaşılmıştır. Polibenzoksazinlerin ısısal ve mekanik kararlılıkları gibi bazı özelliklerini arttırmak ve yeni özelliklerini ortaya koymak için özellikle ticari olarak daha ucuz olan, kolaylıkla hazırlanabilinen fenol, formaldehit ve birincil aminlerden yola çıkılarak farklı fonksiyonlara sahip monomerlerin hazırlanması sağlanmıştır. Ayrıca benzoksazin halkası üzerinde fonksiyonel grupların bulunması reaksiyon verimliliği açısından etkilidir. Polibenzoksazinler üstün özellikleri sayesinde bu alanda güçlü bir rakiptir. Bu polimerler sıfıra yakın büzülme, yüksek camsı geçiş sıcaklıkları, yüksek kömür verimi, düşük su tutma, iyi kimyasal direnç, kürleme sırasında toksik ürün oluşturmamaları, farklı fonksiyonel gruba sahip benzoksazin monomerlerinin sentez kolaylığı çeşitli uygulamalar için büyük bir kolaylık sağlamaktadır., sentezleri sırasında herhangi bir katkı madesi veya kataliz gerektirmemeleri, sahip oldukları iyi mekanik ve termal özellikler gibi elverişli ve performansı olumlu yönde etkileyen oldukça önemli özellikler sergileyen özel sentetik polimelerdir. Bu gelişmiş malzeme özellikleri onları elektrokromik malzemeler, kendi kendini iyileştiren malzemeler, korozyon önleyici kaplamalar, şekil hafızalı malzemeler, havacılık endüstrisindeki kompozit malzemeler, çevre uygulamaları ve tekstil uygulamaları gibi çeşitli uygulama alanları için klasik fenol-formaldehit reçinelerine mükemmel bir rakip haline gelmiştir.

Formaldehit ve bir fenol veya sübstitüe edilmiş fenol, fenolik reçinelerin oluşumuyla sonuçlanan reaksiyonları oluşturmaktadır. Bu sentetik termoset reçinelerden biri olan polibenzoksazinler, klasik fenol-formaldehir reçinelerine benzerler ancak sentezleri ve polimerizasyonları farklı şekilde ilerler. Polimerizasyon reaksiyonları halka açılma polimerizasyonu yoluyla gerçekleşir. Polimerizasyon işlemi sırasında herhangi bir katkı maddesi veya katalizere gereksinim yoktur ki bu da bu malzemelerin üstün özelliklerinden biridir. Ayrıca polibenzoksazinler 1,3- oksazin yapısı içeren monomerlerinden kolayca elde edilebilirler. Oksazinlerin 1,2-, 1,3-, ve 1,4- olmak üzere türevleri mevcuttur. Ancak benzoksazin sentezinde 1,3-oksazin yapıları tercih edilir çünkü yalnızca bu yapı halka açılma polimerizasyonu için aktiftir. Reaksiyon sonrasında gereken saflaştırma işleminin kolaylığı da dikkat çekici bir özelliktir ki bu da istenmeyen yan ürünlerin ortadan kaldırılmasını kolaylaştırır ve pratik hale getirir.

Bunun yanı sıra, polibenzoksazin termosetlerin endüstriyel uygulamalarda kullanımını daraltan bazı sınırlamaları vardır. Polibenzoksazinlerin film ve lif oluşumundaki zorluklar ve kürleme işleminden sonra sahip oldukları kırılganlık gibi bazı eksiklikler mevcuttur. Bazı çalışmalar monomer fonksiyonlandırılması üzerinde ya da başka bir polimerleşebilen gruba ya da polimer zincirine bağlanması üzerinde yapılmıştır. Aynı zamanda polibenzoksazin kompozit çalışmaları da yapılarak dayanıklı yapılar elde edilmiştir. Ana zincirde, yan zincirde ya da uç kısımlarda benzoksazin içeren polimerler sentezlenmiştir ve klasik polibenzoksazinlerden daha iyi sonuçlar vermiştir. Bisfenol ve bisaminlerin formaldehit varlığında Mannich kondenzasyonu genel benzoksazin sentezini oluşturmaktadır ve bu yapıların elde edilmesinde kullanılmıştır. Ana zincir polimerik benzoksazinlerin, molekül ağırlıkları benzoksazin monomerlerine oranla daha yüksektir. Bu da onlara kolaylıkla işlenebilme ve üstün mekanik özellikler sağlar. Ana zincirinde benzoksazin halkası içeren polibenzoksazinler çeşitli yollarla elde edilebilirler. Düz zincir polimerlerin diaminler ve bisfenollerin reaksiyonu ile sentezlenmesi, ana zincir polimerlerin sentezinde kapsamında gerçekleştirilen ilk yaklaşımlardandır. Bu yaklaşım ile oligomerik büyüklükte polimerler elde edilebilmektedir. Bunun dışında poliester, poliamit, poliüretan oluşumu ile hidrosilasyon, Diels-Alder da lineer polimerlerin sentezlenmesinde kullanılan diğer kondenzasyon yöntemleridir. Yan zincir öncül

benzoksazin metodu ise, polimer ana zincirine benzoksazin gruplarının girmesiyle yüksek yoğunluklu ağsı yapılı polimer elde edilmesidir.Yan zincir öncül benzoksazin elde etmenin çeşitli yolları vardır. Esnek moleküler tasarıma sahip ve birçok uygulamada yer alan polibenzoksazinler, farklı başlangıç maddeleri kullanılarak sentezlenmektedir. Kolay sentezinin yanında polibenzoksazinlerin göze çarpan özelliklerinden biri de polimerizasyonların monomer fonksiyonalitesine bağlı olarak 160-250°C derecede katalizörsüz gerçekleşmesidir. Sahip oldukları safsızlıklar sayesinde halka açılma sıcaklıkları optimize olmaktadır. Diğer bir deyişle, aşırı olmamak kaydıyla, elde edilen yapının orta düzeyde safsızlık içermesi, halka açılma sıcaklığının çok yüksek olmasını engeller. Polibenzoksazinlerin bu davranışları diferansiyel taramalı kalorimetre yöntemi ile gözlemlenmektedir.

Yapılarında amit işlevselliği içeren polibenzoksazinler, hidrojen bağı gibi yapısal avantajları sayesinde ilgi kazanmıştır. Poliamitler, yapılarındaki güçlü hidrojen bağı gibi yapısal bir avantaja sahiptirler. Yapılarındaki bu güçlü hidrojen bağı sayesinde iyi mekanik ve termal özellikler gösterdiklerinden diğer polimer türleri arasında önemli yer tutarlar. Naylon sözcüğü poliamit lifleri için kullanılan genel bri ifade olarak kabul edilmiştir. Kimya ve endüstri anlamında çok geniş bir kullanım alanına sahiptir. Bu sebeplerden dolayı, yapılarında amit bağlantıları içeren polibenzoksazinlerin bir çok hidrojen bağı etkileşimi mevcuttur. Farklı polibenzoksazin tiplerinin sentezi hakkında daha önce çeşitli araştırmalar yapılmış olup, bu bağlantıları içeren polimerlerin sentezi için kullanılmış tek pot stratejisi bu alana katkıda bulunan özgün bir yaklaşımdır. Bu yeni yaklaşım daha sonraki uygulamalar için geniş tasarım esnekliği sağlayan 3,4-dihidrokumarinlerden (DHC) başlayarak amit fonksiyonlu polibenzoksazinlerin tasarımını içermektedir.

Bu çalışma kapsamında, amid bağlantıları içeren ana zincirli polibenzoksazinlerin sentezi tek-pota yöntemiyle başarılı bir şekilde gerçekleştirilmiştir.. 3,4-dihidrokumarin (DHC) ve paraformaldehit, 1,3-diaminopropan veya 1,6-diaminohekzan veya Jeffamin D-900 ile reaksiyona sokularak üç farklı polimer sentezlenmiştir. Tek pota reaksiyonu, DHC'nin halka açılmasının aminler ve bunu izleyen Mannich ve halka kapanma reaksiyonlarının kademeli bir şekilde bir araya getirilmesiyle ilerlemiştir. Jeffamine'den elde edilen polimer, iyi film oluşturma özellikleri sergilemiş ve serbest duran esnek filmler, teflon plakalar üzerine uygulanmış ve esnek film elde edilmiştir. Elde edilen tüm polimerler, ^{1}H-NMR ve FT-IR gibi spektroskopik analizlerle karakterize edilmiş ve kürlenme davranışları ve termal kararlılıkları, diferansiyel tarama kalorimetresi (DSC) ve termogravimetrik analiz (TGA) ile araştırılmıştır.

1. INTRODUCTION

Polybenzoxazines attract considerable interest in polymer and materials chemistry as a consequence of their unique characteristics in particular; high thermal stability, low water absorption, high char yields and glass transition temperatures, chemical resistance, and good mechanical performance as they are introduced as a contender to traditional phenolic resins [1-3]. For this reason, this is a mature field that is being spun out into various applications specifically including in the aerospace industry, in which high performance materials are demanded. There is a clear advantage in the preparation of polybenzoxazines that they can easily be synthesized from their 1,3-benzoxazine monomers. The polymerization of these monomers usually can be conducted without the need of any catalyst or additive at temperatures around 160-250 °C, which is also contingent upon the functionalities of benzoxazines [4-7]. The polymerization reaction progresses as the C–O bond in the N–CH_2–O bridge is cleaved during the ring-opening reaction of oxazine [8, 9]. (Figure 1.1)

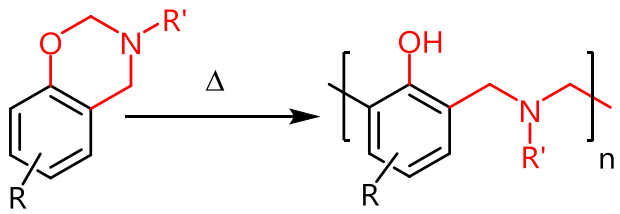


Figure 1.1: Polymerization of a benzoxazine monomer to produce polybenzoxazine.

The phenolic impurities coming from the benzoxazine monomers initiate the ring-opening polymerization (ROP) by protonating either the N or O atom of the oxazine ring, in spite of the fact that the ROP is considered to be a non-catalytic process. The C–O bond is subsequently cleaved in order to produce a carbocation which promptly attacks to the aromatic region of the nearby benzoxazine via Friedel-Crafts reaction [10, 11]. On the contrary, in case of a very pure benzoxazine monomer, polymerization takes place at higher temperatures since in that case there is lack of phenolic residues and the ROP temperature of such a monomer could raise nearly as much as 60 °C when it is compared to a regularly obtained similar benzoxazine [12].

Besides the easy polymerization process, another significant advantage of polybenzoxazines is that their monomers have synthetic design flexibility as a standard synthesis is based upon any type of convenient phenolic, primary amine and formaldehyde. Therefore it is efficacious even if the type of the phenols and amines is changed and in this way it would be obtained a considerable number of benzoxazines and several different commercially available reagents already exist. This presents some practical advantages. Thereby, the method enables it to originate a large monomer library in the scope of possible applications [13-18]. The literature has gradually broadened for the purpose of introducing different functionalities of polybenzoxazine end-groups. For instance, allyl, alkyl, carbonyl, alcohol, carboxyl, coumarine, propargyl, amide and sulfone containing monomers were efficiently synthesized [13, 19-32]. Main-chain, side-chain, and end-chain polybenzoxazine precursors were also produced by using reactions such as Mannich type polycondensation, polyesterification, carbon-carbon couplings, free-radical polymerization as an alternative to different types of monomer designs [33-45]. In addition to these, amide functional benzoxazines have attracted great deal of attention due to their structural similarity to benzanilides. Polyamides are recognized as being one of the most important class of polymers since they have a remarkable feature of strong hydrogen bonding which is responsible for the good mechanical and thermal properties. By the same token, polybenzoxazines containing amide linkage in their structure possess many hydrogen bonding interactions between phenolic –OH, carbonyl, tertiary amine, and amide–NH functionalities [46-49]. Several different approaches were utilized to produce amide functional benzoxazines for taking the advantage of amide functionality. Formerly, primary amine functional benzoxazine synthesis were endeavoured to be able to use them in classical amidation reactions. Nevertheless, the main downsides of the straightforward synthesis of amine functional benzoxazines obtained by using phenols and amines with the arrangement of stoichiometry, are the complicated side reactions occurring during the synthesis and the formation of triazine, aminomethylol, or uncontrolled oligomerizations. On this ground; primary amine functional benzoxazines were synthesized by the sequential synthesis pathway with the help of protective groups. Such a strategy successfully resulted in the desired benzoxazine with an amide functionality, by reacting these amine functional benzoxazines with the acid chlorides [50, 51]. Nonetheless, a challenging problem which arises in this method is that it requires minimum four step

synthesis and additional purification processes are needed which are impractical. For this reason, acid halides and aminophenols were used to obtain amide functional phenols as hydroxybenzamides to minimize the number of reactions. Ultimately, different primary amines and formaldehyde were reacted with these amide functional phenols namely hydroxybenzamides to produce amide functional benzoxazines, and a vast majority of benzoxazines containing amide linkages were synthesized [46-52]. On the other side, the need for the use of aminophenols and acyl halides turn out to be a handicap because the synthetic diversity of amide functional benzoxazines are limited. A new and original approach was developed for obtaining amide functional benzoxazines by using the starting reagent 3,4-dihydrocoumarines (DHC). Primary amines were reacted with DHC to attain phenols containing amide linkage for performing an advanced benzoxazine synthesis [53]. Despite the fact that it was yielded the desired products, unavoidable formation of triazines as by-products caused yields to be relatively low. However, this synthetic route establishes a groundwork for a potential main-chain polybenzoxazine synthesis. Based on the successful results, this thesis aims to contribute to the literature with the one-pot synthesis of main-chain poly(benzoxazine-amide) precursors by taking advantage of DHC chemistry, with a successful and versatile approach [54].

2. THEORETICAL PART

This section includes a brief synopsis about thermosettings and introduction to benzoxazine chemistry, its historical development, synthesis of benzoxazines, ring-opening polymerization of these monomers, the resemblance of polybenzoxazines to novolak systems. Moreover, a short introduction about the main-chain polybenzoxazines and imine containing polymeric materials are also provided regarding the focus of this thesis.

2.1 Thermoset Materials

Since the production of the first man-made synthetic polymer named Bakelite, which was synthesized by Leo Baekeland, there is increased development of polymeric materials. These synthetic polymers can be classified into two major categories; thermoplastics and thermosets.

Thermoset materials are a type of materials that are produced by using polymers joined together by chemical bonds, bringing in a highly crosslinked polymer structure. The highly crosslinked nature in thermoset materials is responsible for the high mechanical and physical strength compared to thermoplastics or elastomer materials. The significant feature that distinguishes thermosets from thermoplastics and elastomers is the presence of the crosslinked-network.

Besides, thermosets cannot tolerate repeated heating cycles as thermoplastics can. When they are initially heated, they soften and flow for molding. In the case of reheating, thermosets undergo degradation.

On the other hand, they retain their strength and shape even when they are heated. Thermosets exhibit elasticity and chemical resistance and it is relatively easy for them to cure. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. As long as the chemical bonds are not destroyed, thermosets remain in the solid state as they are cross-linked structures.

Glass transition temperature (Tg) of thermosets cannot be defined easily as they become rubbery over a narrow range.

Epoxy, polyurethane, silicone, phenolic and urea-formaldehyde resins and cross-linkable polyimides are common examples of thermosetting polymers.

Themosets such as phenol-formaldehyde, epoxy and urea-formaldehyde resins and polyamides evolve their significant features through their cross-linking nature [55].

2.2 Historical Development And Properties Of Benzoxazine Resins

It has been more than 60 years since it has first been mentioned about benzoxazines. The synthesis of benzoxazine was first reported by Holy and Cope in 1944 [56] In the 1950s and 1960s, there were significant contributions to the essential understandings of benzoxazine chemistry [57-64]. For the development of a coating system, it was then produced cross-linked polybenzoxazines derived from multifunctional benzoxazines. Moreover, today there are still immense developments in the synthesis and the utilization of polybenzoxazines in various advanced applications in the industry such as high technology applications in the electronics and aerospace industry. Polybenzoxazines are contenders to classical phenolic resins that are synthesized via traditional condensation reactions. In terms of tailor-made synthetic polymers, benzoxazine resins can be adapted to various properties such as mechanical and physical properties as there is vast design flexibility of benzoxazine monomers. Polybenzoxazines have advanced material properties as; favorable mechanical, electrical, chemical, and thermal characteristics that make them an excellent candidate for possible applications in the relevant areas. Among the unique properties polybenzoxazines have, there are near-zero shrinkage, glass transitions even higher than curing temperatures, high char yield, low water absorption due to intramolecular hydrogen bonding, storage stability and flame resistance . The property of limited shrinkage, which is achieved during the production of polybenzoxazines, comes from the nature of the ring opening polymerization, that benzoxazines go through over a cationic mechanism. The release of toxic by products during the curing process of polybenzoxazines is limited as there is no need for the use of extra additive or catalyst for this process.

In the last decade, polybenzoxazines were developed as an advanced material as an

alternative to classical phenolic resins due to their superior properties as mentioned above. While thermoset resins exhibit a shrinkage of about 2-10% [65-67] and thermoplastics even higher, benzoxazine resins exhibit almost zero-shrinkage during the polymerization [68-70].

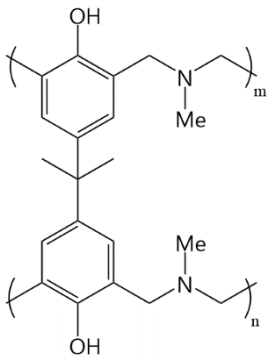
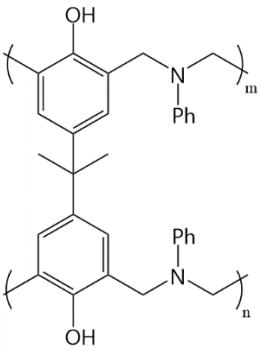
The benefit of using zero-shrinkage materials is that it helps the prevention of optical distortion and warping of composite material. There is usually a 1% volume change of the monomers during the polymerization process. The resin shrinks slowly when it is isothermally cured at gradually increasing temperature. The shrinkage can be decided according to the results of the measurements that are performed at room temperature before and after the polymerization.

The water absorption is dependent on the polar groups that resins have. To give an example, bismaleimide, epoxy, polyester, vinylester, phenolic and polyimide resins have higher water uptake when it is compared to other resins. The water absorption of epoxy and phenolic resin is around 3-20% by weight [71-74]. Polybenzoxazines also comprise polar groups in their structure such as phenolic -OH and Mannich base, -CH_2NCH_2. Contrary to expectations, polybenzoxazines exhibit low water uptake, unlike other resins. Phenols and amines that contain more hydrophobic groups can be used in order to decrease the water absorption. When the water absorption is about 1%, the change in the dielectric constant is around 1%. Hence, low water absorption is benign to attain a decrease in the dielectric constant of the polymer. For example, water absorption of bisphenol-A and aniline-based polybenzoxazine is about 1.9%, while bisphenol-A and methylamine-based polybenzoxazine has 1.3% water absorption by weight in water [75].

Since there is rapid development in technology and there are more strict regulations, non-flammable materials have gained great interest in both industry and academia. For the minimization of burning, inherently high char forming materials are rather preferred. Therefore, in the application of flame-resistant materials, polymers with high char yield are chosen, as the char decreases the rate of diffusion of the flammable. It is observed that many polymers have low char yield when the remained weight is analyzed under Nitrogen at 800 ^{o}C. Whilst epoxy resins usually have a char yield of about 5-15%, traditional phenolic resins have char yields around 30-55%. Nonetheless, traditional phenolic resins constitute the groups with the highest char yield. Although there is not a direct relation between char yield and benzene content, char formation is

usually enhanced by the increased number of benzene groups. Even though polybenzoxazines possess the high meaning of aromatic groups, they have even higher char yields than conventional phenolic resins. Moreover, different functional groups lead to different heat release capacities for the characteristics of flammability.

Table 2.1: Some properties of cross-linked polybenzoxazines versus phenolic and epoxy resins.

Property	**PolyBA-m Benzoxazine** 	**PolyBA-a Benzoxazine** 	**Epoxy**	**Phenolic**
Tensile Properties				
Modulus (GPa)	4.3	5.2	2.7	3.8
Strength (MPa)	44	64	59	48
Elongation at break (%)	1.0	1.3	4.5	1.8
Flexural Properties				

Modulus (GPa)	3.8	4.5	2.9	
Strength (MPa)	103	126	119	
Strain at break (%)	2.6	2.9	4.5	
Impact Strength (J/m, 3.2 mm thick)	31	18	32	17
Dynamic Mech. Properties				
G' at R.T. (GPa)	1.8	2.2		
G' at 50°C above T_g (MPa)	<4.5	2.2		
Density				
Monomer (g/cm^3)	1.159	1.200	1.16	
Polymer (g/cm^3)	1.122	1.195	1.26	1.28

Thermal Properties				
Glass transition temperature (T_g) (^oC)	180	170	165	170
Cure shrinkage (%)		2.9/0	4.5	
Water Absorption (% at R.T.)				
24 h	0.17	0.11	0.12	0.23
7 days	0.40	0.28	0.62	
120 days	1.15	0.98	1.8	

2.3 Synthesis Of Benzoxazines

The core concept of benzoxazine chemistry stands up to the synthesis of the resin with the constituents such as phenolic derivative, formaldehyde and a primary amine [76]. Benzoxazine monomer is a type of an oxazine ring structure, which is attached to a benzene ring. It is possible to obtain various benzoxazine structures depending on the position of the heteroatoms (Figure 2.1). 1,3-benzoxazines are widely used since they are the active species for the polymerization of benzoxazine molecules via cationic ring-opening polymerization [76].

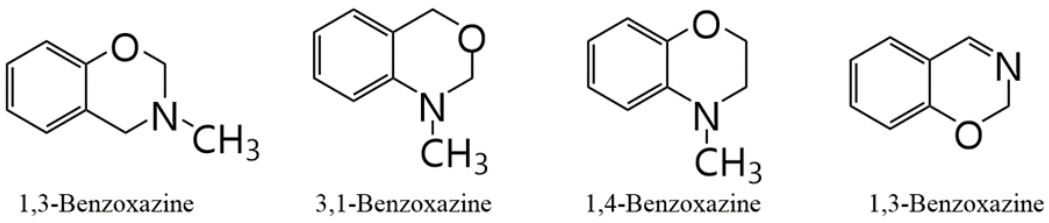


Figure 2.1: Several structures of benzoxazine molecules.

In the 1940s, it was elucidated that the benzoxazine ring primarily reacts with the ortho positions of a phenolic structure, which subsequently forms a Mannich bridge. Monofunctional amine, formaldehyde and phenol react to give a Mannich condensation reaction which produces a classical benzoxazine monomer (Figure 2.2). Along with heating up to 160-220 ^{o}C benzoxazine monomer goes through a ring-opening polymerization [77].

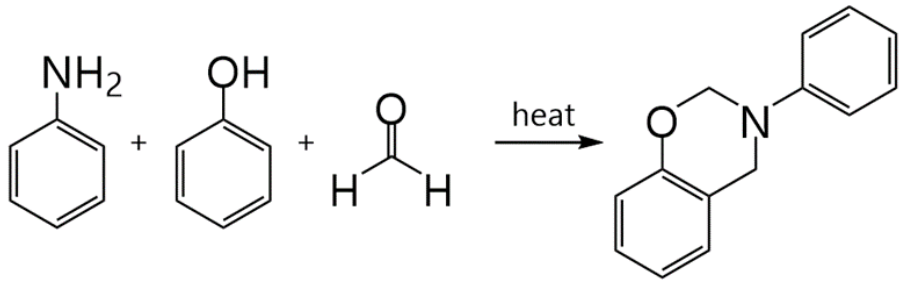


Figure 2.2: Classical synthesis of benzoxazine monomer from aniline, phenol and the resulting product.

In recent years, there has been considerable interest in the utilization of a diamine and difunctional phenolic compound that leads to the formation of main-chain linear polymers with an oxazine ring [76].

Monofunctional and difunctional benzoxazines have some drawbacks that monofunctional benzoxazines generate small oligomers instead of strong in structure and crosslinked polymers, and branching as a result of the synthesis from difunctional monomers. To circumvent these problems, the main-chain polybenzoxazine approach, which results in better crosslinked structure and thermal properties, has been developed. As has been previously reported in the literature, many main-chain polybenzoxazines have been developed until today. Main-chain polybenzoxazines also ease the film-forming process through their higher molecular weight [77].

2.4 Ring Opening Polymerization Of Benzoxazines

The ring strain that oxazine structures have is the helping parameter for benzoxazine structures to undergo a ring-opening polymerization reaction under limited conditions. A highly basic characteristic of both oxygen and nitrogen of the oxazine ring provides the ring to be easily opened with a cationic mechanism. (Figure 2.3) As for the polymerization of benzoxazine monomers, it is usually not needed any kind of catalyst or additive at temperatures around 160-250 ^{o}C. During the cationic ring-opening of an oxazine structure, it is cleaved N-CH_2-O bridge and C-O [78, 79]. Besides, this ring opening generates free phenolic -OH groups and there is also a tertiary amine group from the initial structure. Therefore, the most important aspect is that polybenzoxazines have intermolecular and intramolecular hydrogen bonding and most of the properties are determined by this hydrogen bonding. Although polybenzoxazines have too many phenolic -OH groups, water absorption is limited due to this hydrogen bonding. (Figure 2.3)

Even though the ring opening polymerization reaction of benzoxazines does not require any catalyst or additive, the phenolic impurities that were obtained during the benzoxazine synthesis are rather beneficial to have moderate ring opening polymerization temperature because it causes the ring opening by protonating either the N or O. Nonetheless, the ring opening polymerization temperature automatically increases in case of very pure monomers.

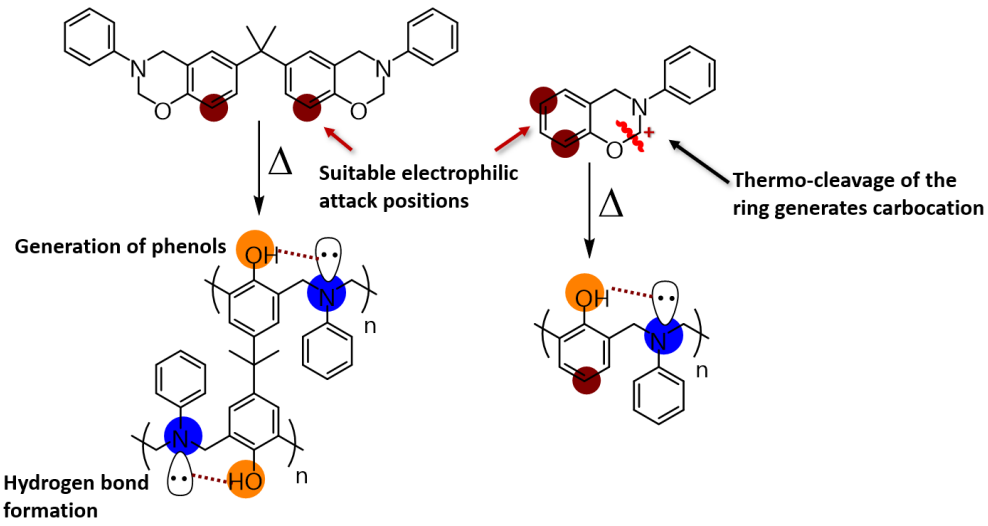


Figure 2.3: ROP mechanism of benzoxazines.

2.5 Comparison of Phenolic Resins and Polybenzoxazines

Polybenzoxazines can eliminate several drawbacks of classical phenol-formaldehyde resins; resole and novolac, as it was mentioned previously. Furthermore, traditional phenol-formaldehyde resins have many similarities with polybenzoxazines. The synthesis conditions and the mole ratio of the phenol/formaldehyde are determinant about the structure of the obtained phenolic resin [80]. (Figure 2.4) For instance, resole, a base catalyzed formaldehyde resin, is made with a formaldehyde/phenol ratio of greater than one; usually around 3-4. Differently, novolac (or novolak) resin is obtained if the molar ratio is less than 1.

It should also be pointed out that paraformaldehyde can also be used in lieu of formaldehyde. Nevertheless, paraformaldehyde is not often used in resin formulations since its cost is higher compared to the aqueous solution of formaldehyde [80].

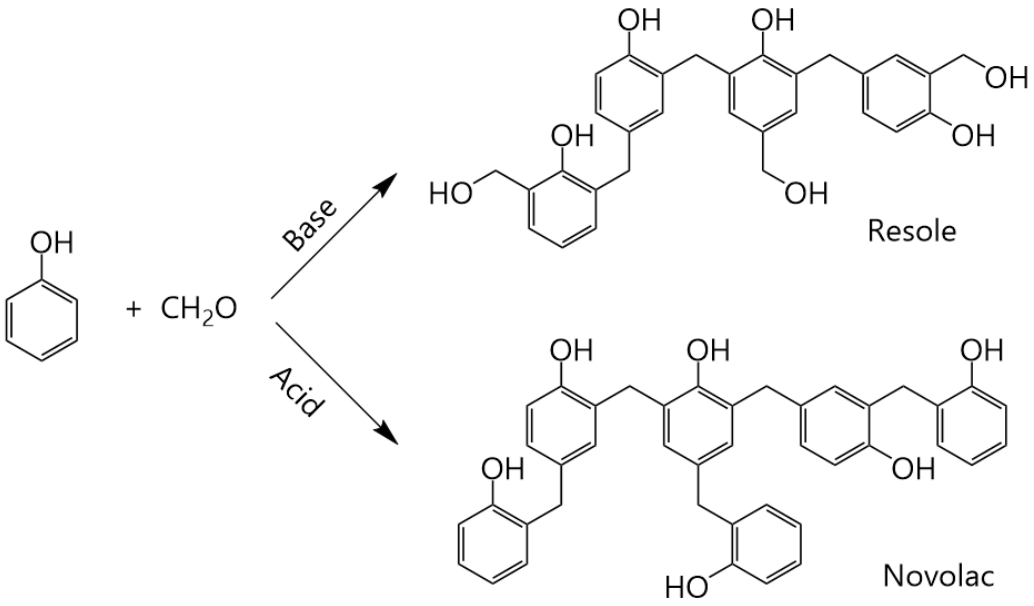


Figure 2.4: Synthesis of resol and novolac.

The obtained resol structures differ based on reaction conditions. It is obtained a mixture of methylol phenols, the residual quantity of free phenol, oligomers, and formaldehyde as the constituents of the resole under the conditions of low temperature which is around 60^{o}C and pH around 9 [81, 82]. Nonetheless, methylol phenol condensation reaction takes place under 60^{o}C and it causes prepolymer formation. That

being said, sodium hyroxide (NaOH) is frequently used as a base catalyst in this production. In addition to that, ammonia and trimethylamine can also be used as a functional catalyst. It is noteworthy that the ammonia has a considerably different effect than the other bases because it is then formed azomethine groups (–CH=N–) among the products [80]. This imine functionality is also the reason for the yellowish color of resoles. Not only resoles but also the cured novolacs obtained by using hexamethylenetetramine (hexa or HMTA) as a hardener have similar color. Also, when ammonia is used as a catalyst in the production of resoles, it is reached higher average molecular weight.

Correspondingly, polymerization of novolac resins is carried out by using acid catalysts such as sulfuric acid, hydrochloric acid, phosphoric acid and oxalic acid. As a result of this process, the obtained polymer is a thermoplastic and it is needed to use a curing agent or a hardener to attain a thermoset polymer. For that case, hexamethylenetetramine is used as a hardener and it forms methylene and dimethylene amino bridges at the temperatures greater than 90 ^{o}C.

Theoretically, every phenol is connected to each other by methylene bridges, which results in a single molecule and a total crosslinked system when the molar ratio meets one. For this reason, it is needed a crosslinking agent to obtain a hardened novolac, and it also explains why resoles have a molar ratio for the formulation of more than 1.

Considering that these two resole and novolac structures have some particular differences, the curing conditions of these resins are also mutually different. Resoles can easily be cured with the use of some acids, bases, or thermal treatment. Regarding the curing mechanism of this type of resins, it is fairly complicated and it could have not been completely elucidated although many model compounds including dimethylol phenols and its derivatives have been utilized to clarify the curing mechanism [80]. On the contrary, novolac type resin demands the use of hexamethylenetetramine as a hardener and curing agent. There are also other methods used for the curing process of novolacs such as blending novolacs with some oxazoline derivatives, resoles or difunctional benzoxazines. Nonetheless, hexa is considerably practical and usually more favored for the curing of novolacs. Since it is encountered with a crosslinking of the resulting product, it is also difficult to explicate the exact mechanism for the curing of this resin type. The findings concerning some reactions of HMTA with some phenolic oligomers outline that there are some probable

intermediates in this process [83-87]. (Figure 2.5) [88] presents a recognized curing mechanism of novolac together with hexamethylenetetramine that is comprised of two stages. Firstly, benzoxazines and benzyl amines occur and the amount of each intermediate is dependent on the unoccupied ortho and para positions. As a second step in the curing mechanism, initial intermediates decompose, oxidize or go through some other reactions to form methylene bridges among phenolic rings as well as the methyl phenol, benzaldehyde, imines, amides and several amines. (Figure 2.6) At the initial curing stage, not only benzoxazine and benzyl amine intermediates are formed but also triazine, ether type and diamine type structures are generated [88].

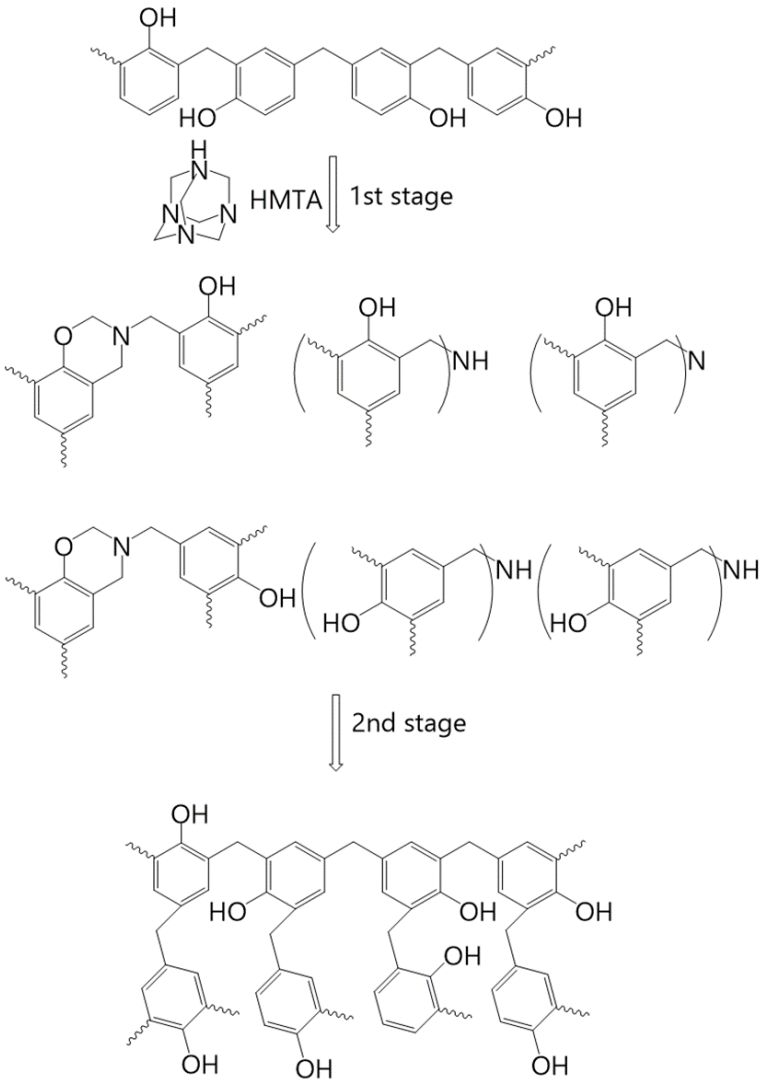


Figure 2.5: Curing of novolac with HMTA.

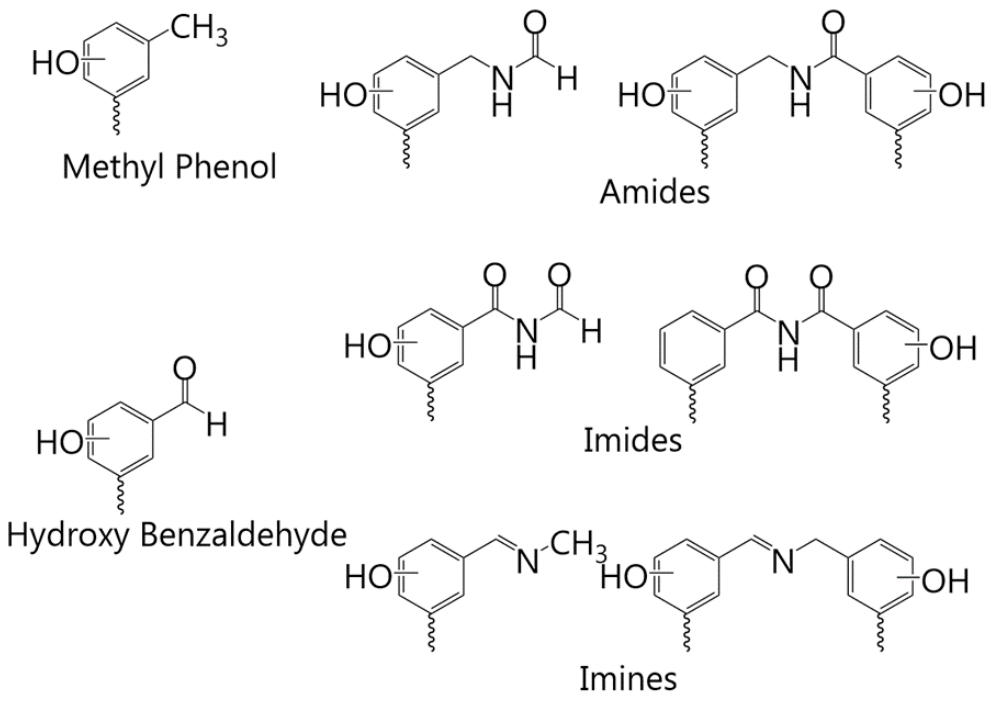


Figure 2.6: Some other reaction products in the curing mechanism of novolac.

One of the other intriguing and promising phenolic type resins is polybenzoxazines, which are sort of polyaminophenols. These phenol formaldehyde resins are a contender to those classical resol and novolac systems and have gained a particular interest among the considerable amount of literature. Their structures resemble phenolic resins and hence there are lots of similar properties. At the same time, polybenzoxazines have individual building blocks consisting of $-CH_2-NR-CH_2$ and phenolic -OH that are adjacent to each other. Moreover, polymer chains are immensely impacted by the inter and intramolecular hydrogen bonding created among these groups, which is exceptional for traditional phenolic systems. This remarkable structure of polybenzoxazines is the underlying reason their superior characteristics mentioned in the previous sections, such as; near-zero shrinkage, high mechanical performance, high glass transition temperature and char yields, besides chemical resistance. Another crucial point is that polybenzoxazines have low water absorption despite their phenolic nature as a result of hydrogen bonding. To sum up, because of their attractive properties, polybenzoxazines have established a presence especially in the industry of high performance materials, composites, electronics and aerospace.

2.6 Main-chain Polybenzoxazine Precursors

A typical benzoxazine monomer is synthesized from petroleum-based phenols, amines and formaldehyde that is carried through the Mannich reaction. Thermally activated ring opening of the benzoxazine structure results in the polymerization of 1,3-benzoxazine [89] and cross-linked polybenzoxazine is obtained. As it is the case for all thermosetting resins, cross-linked polybenzoxazines are brittle [77]. The propagation of the polymer chains and the intramolecular hydrogen bond formation compete, which leads to the branching of the structure [77]. It was hypothesized that these branches can be the cause of low temperature degradation. To tackle these problems, main-chain polybenzoxazine approach was developed leading to more adaptable cross-linked benzoxazine polymers and enhanced thermal properties.

Main-chain polybenzoxazines are a type of benzoxazine polymers that contain benzoxazine repeat units in their backbone. There have been several studies in this growing body of literature for the main-chain polybenzoxazine precursors. For instance, some preliminary work was carried out in the early 1990s that Liu et al. [77] synthesized main-chain polybenzoxazine precursor by using 2,6-dimethylaniline bisphenol-A and formaldehyde. The subsequent studies in this scope comprise the effect of solvent, water, the ratio of the reactants, catalyst and temperature, that was again carried out by the same research group [2, 90]. Thereafter, this approach stated by Takeichi and Ishida without dependence on the previous studies as an easy path for yielding main chain precursors comprising benzoxazine sections in the main chain (Figure 2.7) [42, 44, 91]. Many studies have been published on this approach by altering the phenols and the diamines to perform this strategy for producing precursors that are used in several application areas [77, 92]. To obtain a polymer with high number-average molecular weights, high yields, and a limited by products, it should be chosen optimum conditions for the Mannich reaction. For instance, when it is used $CHCl_3$ as a solvent in the reaction, it is attained a molecular weight of around 2000 g mol^{-1}, while the use of solvents such as 1,4-dioxane and toluene leads to an insoluble crosslinked structures. It should be noticed that choosing toluene/ethanol mixture as a solvent couple in the reaction confers an advantage because it results in soluble polymeric precursors with quite high molecular weights around 20,000 Da [42]. Also, polybenzoxazines with higher molecular weights possess higher toughness after they

are cured in comparison to the precursors obtained from monomers with relatively low molecular weights.

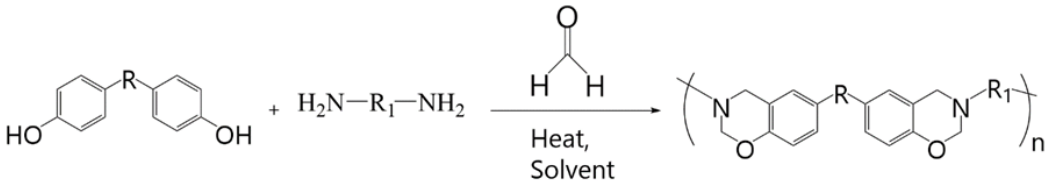
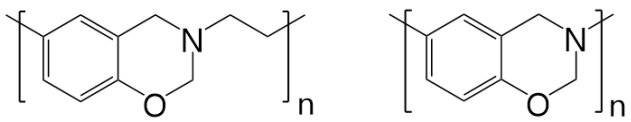
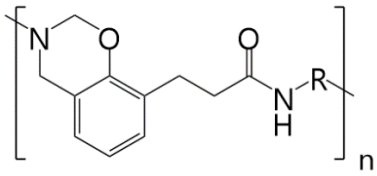
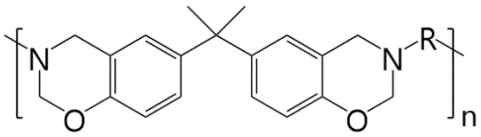
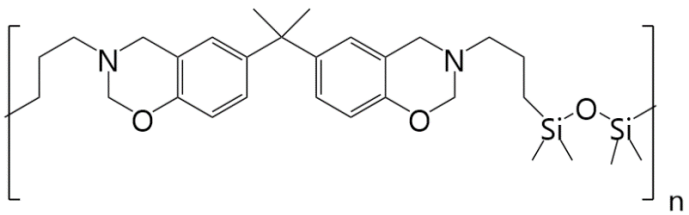
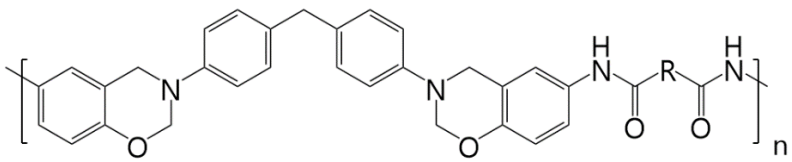


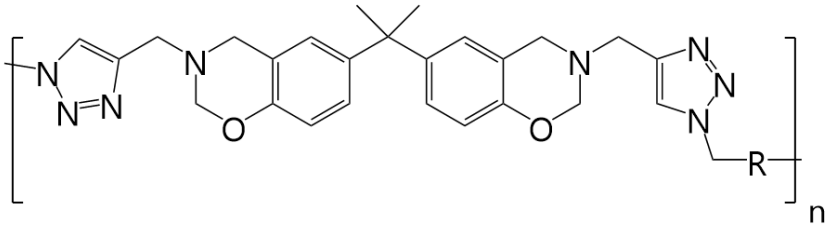
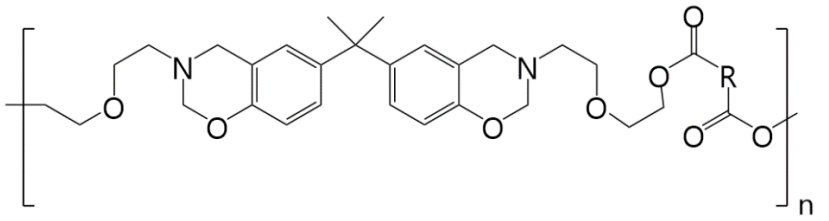
Figure 2.7: Typical synthesis for main-chain polybenzoxazine.

In other words, the cured form of these types of benzoxazine resins commonly exhibits better mechanical, thermal and electric properties in contrast to cured monomeric benzoxazines. The core reason behind this characteristic is that the main chain type precursors have higher chemical crosslinking densities [91, 93]. The problems that were addressed for obtaining such kind of benzoxazine precursors were that the low molecular weight and the functional groups react to give a Mannich reaction, which results in a cross-linking structure. Therefore, finding the optimum conditions for a Mannich reaction is crucial to have a high molecular weight precursor with relatively fewer side reactions [2].

Some examples of studied main-chain polybenzoxazines are shown in Table 2.2.

Table 2.2: Some Examples for Main-chain Polybenzoxazine Precursors.

Polymer	Ref.
	[33]
	[54]
	[44, 91]
	[94, 95]
	[51]

	[43, 96]
	[96, 97]

Various approaches have been put forward for further studies regarding the main-chain type polybenzoxazines. For instance, one of the previous studies includes the synthesis of non-fluorinated main -chain polybenzoxazines that were synthesized via Ullmann coupling. In that study, it was aimed to generate polybenzoxazines that exhibit improved glass transition temperature, thermal electric properties and low water absorption [36]. Other studies include the utilization of polybenzoxazines with different type of thermosets as a blend to attain a novel type of polybenzoxazines consisting benzoxazine repeating units in their main-chain. It has also been reported preparation of biobased main-chain benzoxazine polymers composing aliphatic segments as well as a study in which it has been taken advantage of the function of biobased compounds to reinforce the processability of the petroleum-based structures [89, 98].

2.6.1 As a type of polyetheramines: jeffamines

Jeffamines that are frequently used in the synthesis of main-chain polybenzoxazine precursors are a type of polyetheramines. They are highly versatile chemical structures that contain primary amino groups connected to the end of a backbone of polyether and this backbone is usually based upon propylene oxide [PO], ethylene oxide [EO], or a mixture of ethylene oxide and propylene oxide. These polyether based amines

enhance the properties of polymers such as toughness and flexibility. They are typically three types of jeffamines which are monofunctional, difunctional and trifunctional amines and the type of these amines are dependent on the main polyether backbone structure. However, recently some other types such as polytetramethylene glycol based jeffamines were also developed. They are managed low viscosity and light-colored. In case it is favored a higher reactivity of the curing system, then it is used D- types of jeffamines which are diamines. If it is wanted a very strong hardness of the product, then it is favorably used T- types of jeffamines which are trifunctional polyetheramines and provide greater crosslinking. Some other types result in reduced swelling and moisture uptake. In a nutshell, these types of polyetheramines are used in various applications including in epoxy resins as a hardener for curing and thus creating more rigid structures, as well as in coatings and adhesives.

2.7 Amide Polymers

The poly(ε–caproamide) was the first polyamide synthesized in history. At the end of the 1880s, it was obtained by heating ε –aminocaproic acid. It has then been studied on the development of the synthesis of various polyamides. Until the first preparation of PA (polyamide) 6,6, it has been published several patents for this study. Hence, it has then been introduced quite interesting characteristics of these new materials in the textile industry as fibers. During World War II, these materials have even been an alternative to silk as the development in the industry of PA 6,6 and PA 6 has been rapidly increased. They have been started to be used in the manufacture of parachutes and tires.

Polyamides (PA) are types of polymers involving amide repeat linkage in the polymer backbone. The repeating units in the molecular chain are linked together by amide groups [–C(=O)–NH–]. Amongst covalent linkages, amide linkages are the most commonly used linkages as it is one of the most important and popular chemical bonds in nature; peptides and proteins, as well as in a vast majority of organic molecules, polymers and materials. Amide linkage is recognized as widely considered to be one of the most used structures in the applications in several industries not only in the textile industry but also in adhesives, extruded films [99].

There is a vast amount of literature on the synthesis of polyamides however as per usual they are synthesized via condensation polymerization of monomers, typically by

the reaction of a diacid and diamine. Nomenclature of these amide polymers emanates from the number of carbon atoms included in the diamine followed by the number of carbon atoms on the diacid. (Figure 2.10) Moreover, nylons that are significantly important on commercial terms are attained in two fundamental ways. One of these processes is the polycondensation of difunctional monomers which results in AABB type polymers (Figure 2.8) and the other one is the ring-opening polymerization of lactams that are AB types (Figure 2.9).

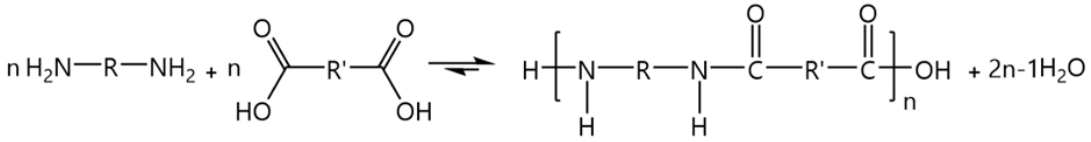


Figure 2.8: Synthesis of AABB type polyamides from a diamine and a diacid.

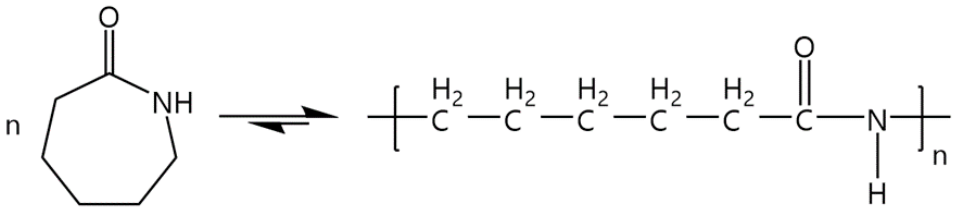


Figure 2.9: Synthesis of AB type polyamides from ε–caprolactam.

Polyamides are an important cluster of synthetic polymers and they can be divided into three categories, so-called aliphatic, semi-aromatic, and aromatic. (Table 2.3) Aliphatic polyamides are less costly and easier to produce than the aromatic polyamides that are also called as aramids. Aramids exhibit better resistance towards the flame, chemical and heat and improved dimensional stability.

The most known manufactured polyamides are frequently called nylons and these are in the group of aliphatic polyamides.

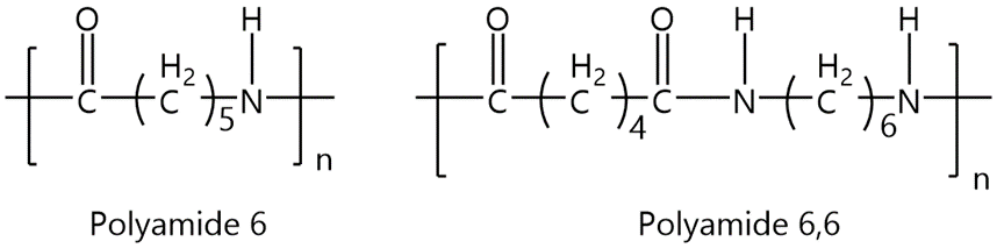


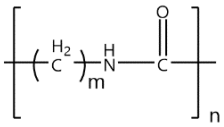
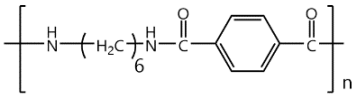
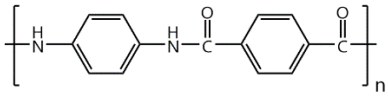
Figure 2.10: Nomenclature of polyamides.

One of the most important aromatic polyamides is poly(p-phenylene terephthalamide), also known as Kevlar and poly(m-phenylene isophthalamide) is also another significant example for this class. The strong hydrogen bonds between the aramid chains and the aromatic structure contribute tensile strength, high melting points and distinguished flame, heat and solvent resistance.

Semi-aromatic type polyamides, polyphthalamides (PPAs), are semi-crystalline thermoplastic resins and they are melt-processable that are obtained by the condensation of an aliphatic diamine such as hexamethylene diamine with terephthalic acid or isophthalic acid. Typically, the aromatic part consists of repeating units of at least 55 molar % in the polymer chain. The association of aliphatic and aromatic groups eventuates in the reduction of moisture absorption and this leads to dimensional changes and stabilized characteristics. Hence, the performance gap between aliphatic nylons and highly expensive polyaramids is being filled by the PPAs. They introduce high strength and stiffness at high temperatures. On the other hand, these resins are much more expensive than aliphatic amides and it is harder to process them because of their higher melting point. They are sometimes mixed with aliphatic polyamides such as nylon 6,6 to enhance processability and reduce the cost.

One of the major classes of manufactured thermoplastics is aliphatic polyamides and they are much more preferred than fully aromatic polyamides in the production-wise and they are amorphous. The two most significant aliphatic polyamides are poly(hexamethylene adipamide) so-called Nylon 6,6 and polycaprolactam (Nylon 6). They both exhibit distinguished mechanical properties such as high flexibility, high tensile strength, decent resilience and high toughness. Both types introduce high melting points and glass transition temperatures that provide a basis for good mechanical characteristics even at high temperature conditions.

Table 2.3: Some classes of polyamides with their structures.

Aliphatic Polyamide	**Semi-Aromatic Polyamide**	**Aromatic Polyamide**
		

All things considered, polyamides are highly important commercial polymeric materials in the industry possessing excellent properties with significant total world consumption of principal polymers. They have several application areas including in the textile industry as a fiber, adhesives, automotive industry, electrical insulation, engineering plastics and biodegradable polymer production, due to their superior characteristics such as high strength, elasticity, abrasion resistance, shape-holding properties, dyeability [100]. As a result of all these advantages, polyamides are very favorable polymers with high performance.

3. EXPERIMENTAL PART

3.1 Materials

3,4-Dihydrocoumarine (DHC) (Alfa Aesar, 99%), o,o′-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Sigma-Aldrich, Jeffamine® ED-900), paraformaldehyde (Aldrich, 95.0−100.5%), acetonitrile (ACN, Merck, 99.9%), ethanol (EtOH, Aldrich, ≥99.5%), methanol (MeOH, Sigma-Aldrich, ≥99.8%), (diethyl ether (DEE, VWR Chemicals, ≥99.5%), toluene (Carlo Erba, 99.5%) and acetone (Carlo Erba, >99.8%) were used as received.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

The ^{1}H NMR spectra were taken from Agilent VNMRS 500 MHz machine. The deuterated solvents were used as a reference and chemical shifts were recorded in ppm units using tetramethylsilane as an internal standard. All samples were measured at 298 K.

3.2.2 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded by using PerkinElmer FTIR Spectrum One spectrometer.

3.2.3 Differential scanning calorimeter (DSC)

Calorimetric studies were carried out on a PerkinElmer Diamond DSC using N_2 as a purge gas at a scanning rate of 10 ºC/min from 20 to 320 °C.

3.2.4 Thermogravimetric analysis

Thermal stability studies were performed on PerkinElmer Diamond TA/TGA with a heating rate of 10 ºC/min under nitrogen flow.

3.2.5 Gel permeation chromatography (GPC)

Molecular weights were determined by gel permeation chromatography (GPC). The measurements were carried out on a TOSOH EcoSEC GPC system equipped with an autosampler system, a temperature controlled pump, a column oven, a refractive index (RI) detector, a purge and a degasser unit, and a TSKgel superhZ2000, 4.6 mm i.d. × 15 cm × 2 cm column. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL/min at 40 °C. The refractive index detector was calibrated with polystyrene standards having narrow molecular weight distributions. Data were analyzed using Eco-SEC Analysis software.

3.3 Syntheses

3.3.1 Synthesis of poly(DHC-Bz-hexylamide)

In a 250 ml round-bottomed flask, 1,6-diaminohexane (3.137 g, 0.026 mol) was dissolved in acetonitrile (75 ml). 3,4-dihydrocoumarine (4 g, 0.026 mol) was dissolved apart in 25 ml acetonitrile and this was added to a solution as one third by the hour. The whole mixture was magnetically stirred under reflux at 80 °C for 24 hours. After cooling the solution, acetonitrile was evaporated using a rotary evaporator. The resulting product was dissolved in 75 ml toluene-ethanol (2:1) and mixed with paraformaldehyde (1.561 g, 0.052 mol). After the mixture was stirred at 100-105 °C under reflux for 12 h, the mixture was concentrated under vacuum with a rotary evaporator. The concentrated solution was precipitated in diethyl ether. After decantation of diethyl ether, the remaining product was dried under vacuum at 30 °C for 48 h, resulting a orangy solid.

3.3.2 Synthesis of poly(DHC-Bz-propylamide)

In a 250 ml round- bottomed flask, 1,3-diaminopropane (2 g, 0.026 mol) was dissolved in acetonitrile (75 ml). 3,4-dihydrocoumarine (4 g, 0.026 mol) was dissolved apart in 25 ml acetonitrile and this was added to a solution as one third by the hour. The whole mixture was magnetically stirred under reflux at 30°C until all the adding is done. When the insertion is done, the reaction temperature was risen to 80°C for 24 h. After cooling the solution, acetonitrile was evaporated using a rotary evaporator. The resulting mixture was dissolved in 75 ml toluene-ethanol (2:1) and mixed with paraformaldehyde (1.561 g, 0.052 mol). After the mixture was stirred at 100-105 °C

under reflux for 12 h, the mixture was concentrated under vacuum with a rotary evaporator. The concentrated solution was precipitated in diethyl ether. After the decantation of diethyl ether, the remaining product was dried under vacuum at 30 °C for 48 h, resulting in a yellowish solid.

3.3.3 Synthesis of poly(DHC-Bz-jeffamide)

In a 250 ml round-bottomed flask, jeffamine D-900 (11.7 g, 0.013 mol) was dissolved in 75 ml of acetonitrile and 3,4-dihydrocoumarine (2 g, 0.013 mol) was dissolved apart in 25 ml of acetonitrile and this was added to a solution as one third by the hour. The whole mixture was magnetically stirred at 30°C overnight and the temperature was risen to 80°C to be stirred for 24 h. After cooling the solution, acetonitrile was evaporated using a rotary evaporator. Paraformaldehyde (0.78 g, 0.026 mol) was added into a mixture that was dissolved in a mixture of 50 mL of toluene and 25 mL of ethanol in a 250 mL flask equipped with a reflux condenser and a magnet for stirring. The solution was refluxed for 12 h at ca. 105 °C. The clear solution was concentrated under vacuum and then precipitated in 250 mL of diethyl ether. Ethyl ether was decantated and the polymer was washed with diethyl ether, then dried in a vacuum chamber at ambient temperature for 48 h to obtain a transparent oily product.

3.4 Film preparation

To obtain polybenzoxazine film, 1 g of main-chain polybenzoxazine precursor poly(DHC-Bz-jeffamide) was dissolved in 10 mL of acetone, charged into a Teflon mold. The solvent was evaporated at room temperature for 3 days. Subsequently, the film was subjected to a heat treatment at 120 °C for 10 min. in an ordinary oven for removal of solvent residues and then it was gradually heated up to 180 °C and was cured for 0.5 h. After curing, dark orange, transparent and flexible cross-linked film with a smooth surface was obtained.

4. RESULTS AND DISCUSSION

DHCs prone to react with amines at benign conditions without catalyst requirement (Figure 4.1) [101, 102]. Correspondingly, ring-opening reactions of DHC gained interest especially in medicinal chemistry to synthesize amide precursors where mild and non-catalytic conditions are preferred to meet the requirements of green chemical synthesis [103]. More specifically, DHCs are suitable reagents for the preparation of amide functional phenolics at room temperature quantitatively or with high yields. Therefore, such phenolics can be prepared without a significant effort to select suitable amines.

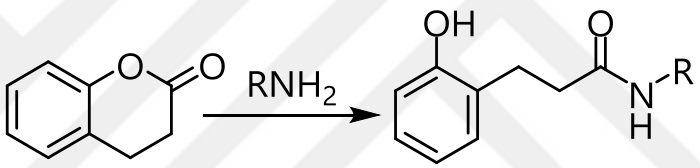


Figure 4.1: Ring-opening aminolysis of DHC to form a phenolic amide.

The presence of several different commercially available amines provides a vast design capacity to obtain phenolics to further use for benzoxazine synthesis. Besides, ring-opening aminolysis of two moles of DHC with one mol of difunctional amine in a medium having 4 moles of formaldehyde would also trigger concomitant Mannich and ring-closure cascade reactions to form 1,3-oxazines. Hence, main-chain polybenzoxazines with amide linkages would eventually be synthesized under such a condition. Accordingly, DHC was reacted with three different diamines and paraformaldehyde and polybenzoxazines precursors with different molecular weights were obtained successfully (Figure 4.2).

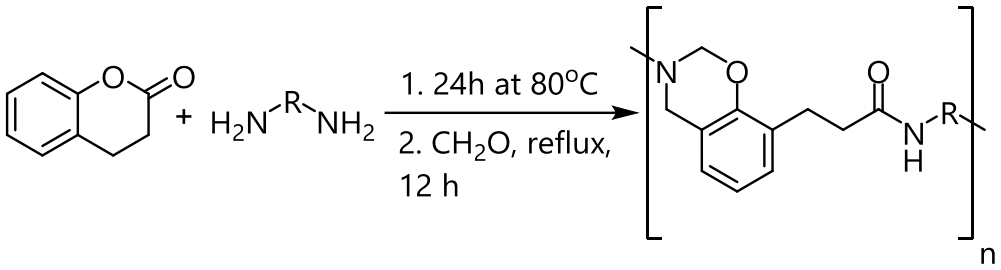


Figure 4.2: One-pot synthesis of amide linkage containing main-chain polybenzoxazine precursor

The reaction between DHC and diamines was performed at 80 °C in both CH_3CN and toluene-ethanol mixture (v/v, 2:1) for 24 h to complete the ring-opening aminolysis reaction and then, paraformaldehyde was added into the mixture under reflux for further 12 h to form benzoxazine ring. 1,3-Diaminopropane, 1,6-diaminohexane and Jeffamine® ED-900 were selected as diamines to arrange the flexibility of the main-chain polybenzoxazine precursor. The obtained polymers were abbreviated as poly(DHC-Bz-propylamide), poly(DHC-Bz-hexylamide) and poly(DHC-Bz-jeffamide), respectively.

The chemical structures of the polybenzoxazine precursors were evaluated by ^{1}H NMR and FT-IR spectral analysis. In Figure 4.3, the ^{1}H NMR spectra of poly(DHC-Bz-hexylamide) and poly(DHC-Bz-jeffamide) were presented. It should be noted that poly(DHC-Bz-propylamide) was insoluble in common solvents facilitating NMR characterization. The characteristic oxazine proton signals at 4.96, 4.84, (O–CH_2–N) and 4.05, 3.94 ppm (Ar–CH_2–N) provide clear evidence of the formation of benzoxazine on the poly(DHC-Bz-jeffamide) and poly(DHC-Bz-hexylamide), respectively. Moreover, the triplet peaks at 2.61, 2.58 ppm (–CH_2–NH) and 2.47, 2.40 ppm (Ar–CH_2–) also verify the ring-opening of DHC. Besides, in Figure 4.3 (b), the peak at 2.68 ppm indicates that poly(DHC-Bz-hexylamide) contains an end-chain primary amine. FT-IR spectra of the main-chain polybenzoxazines disclose the formation of amide functionality and oxazine ring. (Figure 4.4) The stretching vibration bands of aromatic C–H (3136–3038 cm^{-1}) and aromatic C=C (1461–1598 cm^{-1}) bonds, the out of plane bending of aromatics and oxazine ring vibrations of C–H bonds (925–941 cm^{-1}) can be considered as convincing spectral evidence for the formation benzoxazine moieties. Besides, stretching vibrations of amide carbonyl group is clearly visible at ca. 1630–1653 cm^{-1} and amide N–H with water residue emerges ca. 3288–3313 cm^{-1}. Moreover, Figure 4.4 exhibits strong C–O stretching

vibration of poly(propylene glycol) segment at 1100 cm^{-1}. Apart from spectral characterization, molecular weights (Mn) and polydispersity index (PDI) of the polymers are determined as ca. 4600 Da, 1.3 for poly(DHC-Bz-hexylamide) and ca. 3000 Da, 1.2 for poly(DHC-Bz-hexylamide) by using GPC. These spectral and chromatographic data confirm the successful synthesis of amide functional main-chain polybenzoxazines.

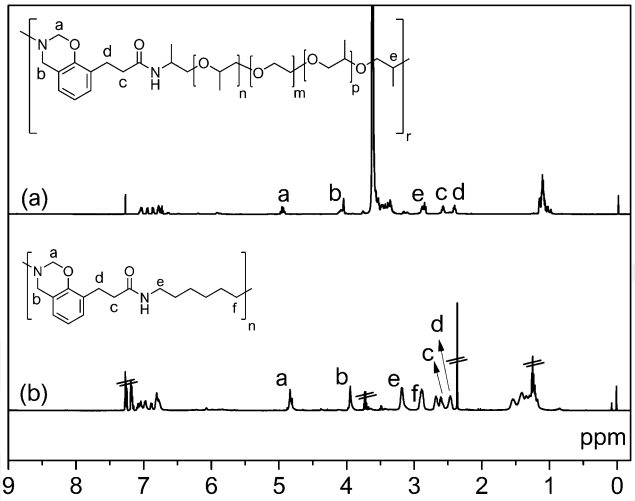


Figure 4.3: ^{1}H NMR spectra of poly(DHC-Bz-jeffamide) (a) and poly(DHC-Bz-hexylamide) (b).

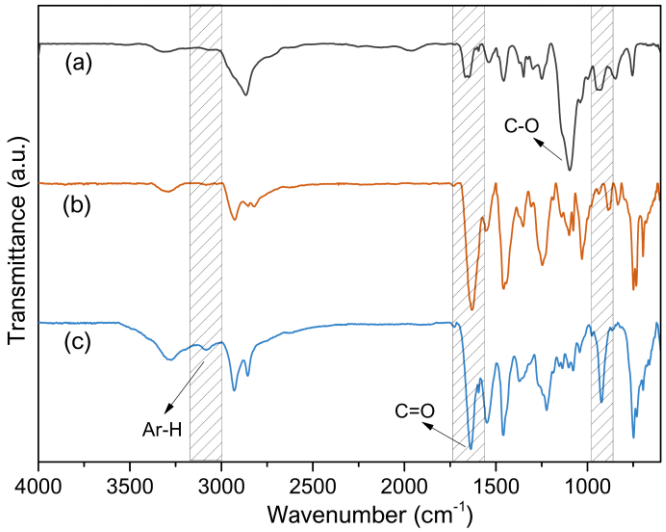


Figure 4.4: The overlaid FTIR spectra of poly(DHC-Bz-jeffamide) (a), poly(DHC-Bz-hexylamide) (b) and poly(DHC-Bz-propylamide) (c).

As stated, polybenzoxazines can be synthesized by ring-opening polymerization (ROP) of benzoxazines at temperatures between 160 and 260 °C. The polymerization of these monomers is exothermic and can be monitored easily by differential scanning calorimetry (DSC). Figure 4.5 and Table 4.1 show the DSC results of poly(DHC-Bz-

propylamide), poly(DHC-Bz-hexylamide) and poly(DHC-Bz-jeffamide). Accordingly, all the precursors are curable and exhibit broad curing exotherms starting from 168 °C for hexylamide, 172 °C for Jeffamide and 185 °C for propylamide based precursors. These on-set values are relatively low compared to the curing temperatures of classical benzoxazine monomers. The main reason for low on-set temperatures might be the presence of some ring-opened oxazine repeat units. Since, it is well-known that unreacted phenols in a benzoxazine formulation could catalyze the ROP and reduce the curing temperatures [7, 104]. Moreover, the precursor poly(DHC-Bz-propylamide) that synthesized from shorter amine exhibits the largest amount of exotherm among the three examples because of the reason for having more oxazine mass per repeat unit. Conversely, poly(DHC-Bz-jeffamide) has the smallest amount of exotherm due to the large Jeffamide units per oxazine ring. Therefore, it could be concluded that the amount of exotherm of a polymeric benzoxazine precursor is directly proportional to the mass ratio of oxazine ring per total mass of the related precursor. However, this generalization may not count for the two types of different main-chain precursors due to functional group effects. And also, without considering the structure, the success of the ring-closure reaction to form oxazine rings on the precursor would affect the extent of exotherm. In general, around 10% of ring-opened oxazine units remain on the polymer backbone in a classical main-chain polybenzoxazine synthesis [44]. However, the ring closure ratio of poly(DHC-Bz-jeffamide) was calculated as ca. 77 % by using integration ratios from proton NMR spectroscopy. This result could be expected since the synthesis of poly(DHC-Bz-jeffamide) basically should include two successive stages as ring-opening of DHC and oxazine formation.

Table 4.1: DSC[a] characteristics of amide functional polybenzoxazine precursors.

Polymer	**$T_{on\text{-}set}$ (°C)**	**$T_{end\text{-}set}$ (°C)**	**$T_{max.}$ (°C)**	**Enthalpy (j/g)**
Poly(DHC-Bz-propylamide)	185	265	222	-122
Poly(DHC-Bz-hexylamide)	168	241	201	-56
Poly(DHC-Bz-jeffamide)	172	257	212	-49

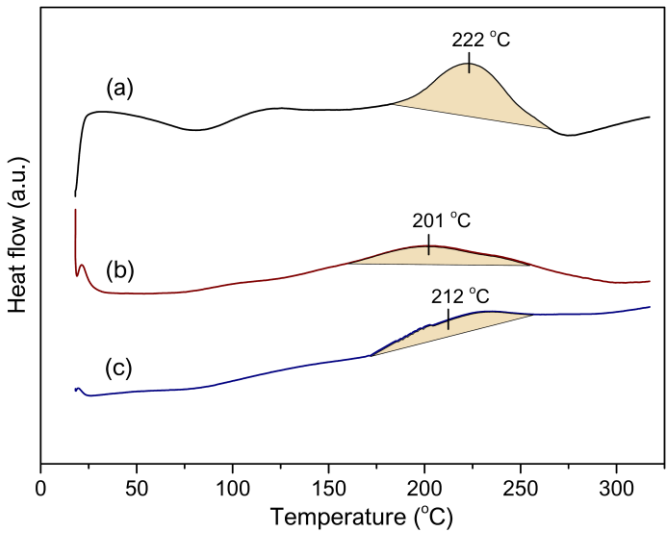


Figure 4.5: DSC thermograms of poly(DHC-Bz-propylamide) (a), poly(DHC-Bz-hexylamide) (b) and poly(DHC-Bz-jeffamide) (c).

Film fabrication from benzoxazine monomers is complicated especially for mono-functional ones. Because casting films from powdery monomers are usually difficult and the formed films are generally brittle as a result of insufficient molecular weight and inflexible polybenzoxazine network. Thereupon, combining benzoxazines with polymeric structures to obtain main- or side-chain polybenzoxazine precursors emerged as a solution for film formation difficulties with exploited additional benefits stemming from the polymeric nature. Accordingly, processable, curable and flexible polybenzoxazine thermoplastics were synthesized by Mannich condensation reaction. Similarly obtained precursors reported in this study were solvent casted in Teflon molds and, after evaporating the solvent, cured at 180 °C for 30 min. to get flexible transparent films (Figure 4.6). It should be noted that the films of poly(DHC-Bz-propylamide) and poly(DHC-Bz-hexylamide) could not be casted due to their limited solubility. Conversely, the films of poly(DHC-Bz-jeffamide) were prepared easily as the polypropylene glycol and polyethylene glycol blocks on the precursor immensely contribute to the overall solubility.

Figure 4.6: Images of cured poly(DHC-Bz-jeffamide) films.

Thermostabilities of the cured precursors were characterized by using thermal gravimetric analysis (TGA). TGA thermograms and their derivatives are displayed in Figures 4.7A, 4.7B and the associated thermal properties are tabulated in Table 4.2. The initial degradation temperatures, $T_{5\%}$ and $T_{10\%}$, of the samples differ in the order of the chain length of the diamine. Shorter chains have lower initial degradation temperatures than longer Jeffamine chain probably due to the amine degradation of polybenzoxazines where the temperature of this type of decomposition generally lie between 160 °C and 300 °C via C–N cleavage [105-107]. In poly(DHC-Bz-propylamide) and poly(DHC-Bz-hexylamide) the amino groups per repeat unit are much higher than the poly(DHC-Bz-jeffamide) and thus amine degradation might be severe in these polymers. In Figure 4.7B (a') and (b'), the derivative thermograms clearly exhibit this behavior as downward bands. Conversely, the T_{max} values and char yields of the short chain precursors are significantly higher than Jeffamide based precursor due to the number of aromatics per repeat units. Moreover, it is well-known that large polyether units prone to degrade rapidly at such high temperatures. For example, pristine Jeffamines generally have char yields below 1% at 800 °C even under non-oxidizing conditions such as N_2 or Ar atmosphere.

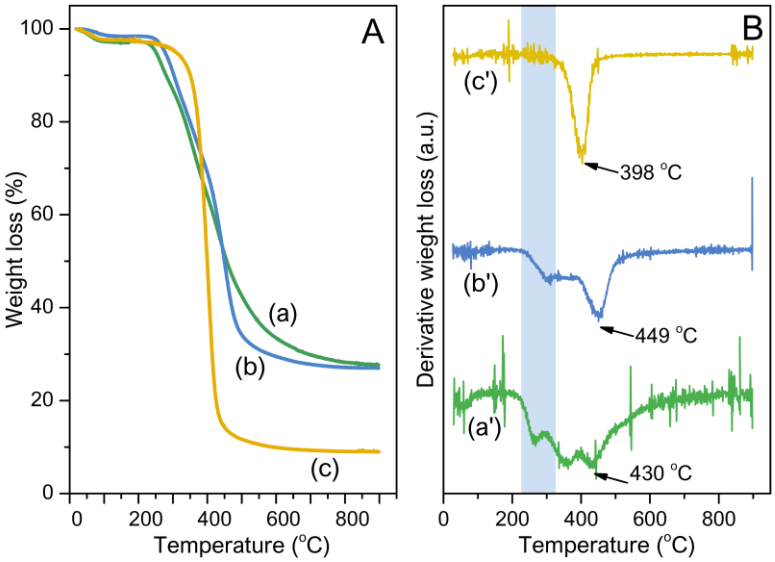


Figure 4.7: TGA thermograms (A) and their derivative curves (B) of cured precursors poly(DHC-Bz-propylamide) (a), (a'), poly(DHC-Bz-hexylamide) (b), (b') and poly(DHC-Bz-jeffamide) (c), (c').

Table 4.2: Thermal properties of the cured[a] polybenzoxazine precursors.

Cured precursor	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_c (%)	T_{max} (°C)
Poly(DHC-Bz-propylamide)a	250	280	28	430
Poly(DHC-Bz-hexylamide)a	276	303	27	449
Poly(DHC-Bz-jeffamide)a	307	351	9	398

5. CONCLUSION

In this study, amide repeat unit containing main-chain polybenzoxazine precursors with different chain lengths were synthesized in one-pot starting from readily available and relatively cheap paraformaldehyde, 3,4-dihydrocoumarine (DHC), 1,3-diaminopropane, 1,6-diaminohexane and jeffamine D-900. The polymeric precursors were obtained through cascade ring-opening aminolysis of DHC with the selected amines, Mannich reaction and ring-closure to form oxazine rings with amide linkages. One of the polymeric precursors exhibited good film forming ability and the casted films were flexible after curing at 180 °C. The study reveals the potential of DHC and related compounds to be used as precursors for several different amides containing main-chain polybenzoxazines in one-pot by selecting suitable diamines. Accordingly, this method has a vast design capacity for this specific type of polybenzoxazines and can be broadened according to specific application needs.

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CURRICULUM VITAE

Name Surname **:** Canan Durukan

Place and Date of Birth **:** İstanbul / 23.09.1993

E-Mail **:** cnndurukan@gmail.com

EDUCATION

- **B.Sc.** **:** 2017, Yıldız TechnicalUniversity, Faculty of Arts and Sciences, Department of Chemistry
- **High School** : FMV Ayazağa Işık High School

PUBLICATIONS AND PRESENTATIONS ON THE THESIS:

- **Durukan, C., Kiskan B., Yagci Y. (2019).** One-pot synthesis of amide-functional main-chain polybenzoxazine precursors. *Polymers*, *11*(4), 679.