ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

MAIN-CHAIN BENZOXAZINE PRECURSOR BLOCK COPOLYMERS

M.Sc. THESIS

Zeynep DELİBALLI

Department of Chemistry

Chemistry Programme

JUNE 2018

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ANA ZİNCİRDE BENZOKSAZİN BLOK KOPOLİMERİ

YÜKSEK LİSANS TEZİ

Zeynep DELİBALLI
509161249

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Doç. Dr. Barış Kışkan

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Zeynep Deliballı, a M.Sc student of ITU Graduate School of Science Engineering and Technology student ID 509161249, successfully defended the thesis entitled "MAIN-CHAIN BENZOXAZINE PRECURSOR BLOCK COPOLYMERS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assoc. Prof. Barış KIŞKAN** ....
İstanbul Technical University

Jury Members : **Prof. Dr. Yusuf YAĞCI** ....
Istanbul Technical University

Assoc. Prof. Binnur AYDOĞAN TEMEL..............................
Bezmialem University

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To my family,

FOREWORD

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ABBREVIATIONS

^{1}H-NMR	: Nuclear magnetic resonance spectroscopy
Bisphenol-A	: 4,4-Isopropylidenediphenol
Da	: Dalton
DSC	: Differential scanning calorimeter
FTIR	: Fourier transform infrared
GPC	: Gel Permeation Chromatography
HY	: Hydrogen containing compound
ROP	: Ring opening polymerization
TGA	: Thermogravimetric analyzer
MPBZ	: AB type main chain polybenzoxazine
PEA	: Polyetheramines

SYMBOLS

T_g	: Glass Transition Temperature
T_{max}	: The temperature for maximum weight loss.
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%.
Y_c	: Char yields at 800° C under nitrogen atmosphere.

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MAIN-CHAIN BENZOXAZINE PRECURSOR BLOCK COPOLYMERS

SUMMARY

In recent years, high performance polymers have gained much interest since they have applications commercially in different industry areas like aerospace, adhesives, electronic curcuits, and coatings. Most of the thermosets can be considered as High performance polymers because of their thermal and mechanical properties. Phenolics, epoxies, bismaleimides, cyanate esters, vinyl esters and polyimides are widely used thermosetting resin systems. However, traditional phenolic resins are the well-known members of the thermosetting family. Thermoset resins have numerous features such as good mechanical strength, dimensional stability, strength against many solvents, and flame resistance. However, they also have several drawbacks like being brittle, water adsortion and short shelf life etc. In the case of classical phenolic resins, the acid or base catalysts usually used for phenolic resin preparation, lead to corrosion on processing equipment. During polymerization, cured resins are influenced by volumetric shrinkage and release of side products. Recently, to overcome these kind of drawbacks, a new type of polymers have been developed; namely polybenzoxazines. Due to their superior features over traditional novolac and phenolic resins, polybenzoxazine has gained increasing interest as one of the valuable high performance polymeric material. They present features such as (i) near-zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazine based materials Tg is much higher than cure temperature, (iv) high char yield, (v) release of no toxic by-product during curing, and (vi) no strong acid catalysts required for curing. However, polybenzoxazines synthesized from the monomer precursors suffer from some shortcomings incluiding i) brittleness ii) need of quite high temperature for curing process and iii) poor film forming. To solve this problems, researchers study on two subjects; blending polybenzoxazines with other polymeric materials and modifying monomers with additional functionalities.

The Jeffamines, polyetheramines involve primary amines terminated polyether backbone. In general Jeffamines (polyethersmines) are used in the process of epoxy curing and they also serve stiff, impact-modified coatings, castings, and adhesives.

Block copolymers are advantageous and practicable in numerous application field where different kind of polymers are modified with each other to transform a material with hybrid features such as termoplastic elastomers. The block copolymers are a kind of polymer blend.

In this study, to modify benzoxazines, polyetheramine derivatives were used. In general polyetheramines are used in the process of epoxy curing and they also serve stiff, impact-modified coatings, castings, and adhesives. A new method for the preparation of block copolymers of polymeric benzoxazine precursors with polyetheramines by one-pot two-step or stepwise pathways is described. The method pertains to the use of simple chemicals such as 4-hydroxyaniline, formaldehyde and polyetheramines (Jeffamines). The structure and molecular weights of polymers were characterized by FTIR, ^{1}H NMR and GPC. Successful block copolymer formation was evidenced by the clear shift of the molecular weight of the block copolymer to the higher molecular weight region. Thermal properties of the polymers were also investigated by using DSC and TGA. Block copolymers were shown to undergo thermally activated curing by the ring opening polymerization of benzoxazine block. The thermal stability of the cured product drastically increased compared to the precursor polyetheramine.

ANA ZİNCİR BENZOKSAZİN BLOK KOPOLİMERLERİ

ÖZET

Son yıllarda, yüksek performanslı polimerler, havacılık, yapıştırıcılar, elektronik devreler ve kaplamalar gibi farklı endüstri alanlarında ticari olarak üretilebilmeleri nedeniyle büyük ilgi görmüştür. Yüksek performanslı polimerler, termal özellikleri nedeniyle "termoset" olarak da adlandırılır. Fenolikler, epoksiler, siyanat esterleri, vinil esterler ve poliimidler yaygın olarak kullanılan termoset reçine sistemleridir. Ancak geleneksel fenolik reçineler, thermoset ailesinin iyi bilinen üyelerindendir. Termoset reçinelerin sahip olduğu; iyi mekanik mukavemet, kürlendikten sonra boyutsal kararlılık, birçok çözücüye karşı mukavemet ve aleve dayanıklılık gibi birçok özellik fenolik reçinelerin özellikleridir. Ancak bu özelliklerle birlikte, kırılganlık ve kısa raf ömrü gibi çeşitli dezavantajları da vardır. Ayrıca genellikle fenolik reçine hazırlığı için kullanılan asit veya baz katalizörleri, deney ekipmanları üzerinde korozyona neden olurlar. Polimerizasyon esnasında reçineler hacimsel büzülme veya yan ürünlerin salınımını sıklıkla gösterebilir. Bu yan ürün salınımı maddenin şeklini ve yapısını bozabilir. Son zamanlarda, bu tür dezavantajların üstesinden gelmek için yeni tip polimerler geliştirilmiştir; polibenzoksazinler. Geleneksel novalak ve fenolik reçineler üzerindeki avantajlı özellikleri nedeniyle, polibenzoksazinler değerli, yüksek performanslı polimerik malzemelerden biri olarak büyük ilgi çekmiştir ve bu ilgi artmaya devam etmektedir.

Polibenzoksazinler üstün özellikler gösterirler; (i) kürleme sırasında sıfıra yakın hacimsel değişim gösterirler, (ii) su tutması sıfıra yakın ya da çok azdır, (iii) bazı polibenzoksazin esaslı malzemeler için (T_g) sertleşme sıcaklığından çok daha yüksek olabilmektedir, (iv) yüksek verimde yanma ürünü verirler, (v) kürlenme sırasında salınan yan ürünleri genellikle toksik değildir ve (vi) kürlenme için güçlü asit katalizörleri gerekli değildir. Bununla birlikte, monomer öncülerinden sentezlenen polibenzoksazinlerin bazı kusurları vardır; i) kırılganlık özelliği ii) kürleme için oldukça yüksek bir sıcaklığa ihtiyaç duyması ve iii) zayıf film oluşturması gibi. Bu nedenle, bu eksikliklerin üstesinden gelmek ve mevcut özellikleri geliştirmek için çeşitli stratejik yaklaşımlar önerilmiştir. Önerilen alternatif yollardan biri, farklı işlevlere sahip modifiye edilmiş monomerlerin sentezi ile ilişkiliyken, diğer yol, polimerlerin dolgu maddeleri veya liflerle harman edilmesi ile ilgilidir. Diğer bir başka önemli gelişme ise, uç zincire, ana zincire veya yan zincirli polibenzoksazinlere benzoksazin birimlerinin dâhil edilmesine dayanır. Tüm bu geliştirilen stratejiler benzoksaksazinlerin geleceği için umut vermiştir.

Benzoksazinler çözücülü ya da çözücüsüz ortamda sentezlenebilirler. Çözücülü ortamda benzoksazin sentezlenmesinin bazı dezavatajları vardır. Polimerizasyon yavaş ilerlemesi, yüksek miktarda çözücü maddeye gereksinim ve bazı durumlarda monomerlerin zayıf çözünürlüğü bu dezavantajlardandır. Ayrıca büyük miktarda çözücü kullanılması, artan ürün maliyetine yol açmakta ve çözücü reaksiyon sisteminden uzaklaştırlırken çevresel sorunlara yol açmaktadır. Bunlara ek olarak,

polar çözücüler oligomerik yan ürünlerin oluşumu üzerinde olumlu bir etkiye sahiptir, bu yüzden benzoksazin sentezinin verimini düşürürler. Bu sorunların üstesinden gelmek için bileşiklerinden eriyerek karışabildiği erime noktasında çözücüsüz metot geliştirilmiştir. Çözücüsüz sentetik yöntem, geleneksel yöntemlerle karşılaştırıldığında daha kısa reaksiyon süreleri sağlar ve daha az istenmeyen ara ürünler ve yan ürünler oluşur. Çözeltili sistemlerin getirdiği dezavantajları ortadan kaldırmak için geliştirilen başka bir yöntem ise, çözücü çiftleri kullanılarak çözücünün polaritesinin ayarlanmasıdır. 2: 1 (v: v) oranında Toluen / Etanol çiftinin, benzoksazin sentezinin çoğunda oligomer oluşumunu azalttığı saptanmıştır. Eritme tekniği ve Toluen: Etanol karışımları, benzoksazin sentezlerinin çoğu için iyi çalışır, ancak bazı sentezlerde, özellikle reaksiyon hızı ve amin çözünürlüğünün problemli olduğu durumlarda (örneğin, 4,4'-sülfonildianilin veya benzidin), çözelti sistemi yöntemi olarak yüksek kaynama noktasına sahip olan apolar çözücülerden oluşan sistem oluşturulmuştur. Bu teknik için iki temel neden vardır; birincisi, organik çözücülerdeki aminlerin zayıf çözünürlüğüdür ve diğeri ise diaminlerin formaldehit ile reaksiyonunun kararlı bir triazin jel yapısına neden olmasıdır. Bu tür çözücüler başlangıç maddelerinin çözünürlüğünü arttırır ve triazin jellerinin hızlı bir şekilde kırılmasını sağlar. Reaksiyonun sonunda monomer, hiç ya da sınırlı sayıda yan ürünle beraber oluşur.

Benzoksazin elde etme reaksiyonunda reaktanlar, diğer bir deyişle aldehit, amin ve fenolik öncüler fiziksel olarak karıştırılır, erime sıcaklığına kadar ısıtılır ve daha sonra reaksiyon istenen benzoksazin ürünü üretmek için yeterli bir sıcaklıkta gerçekleştirilir. Formaldehit bu sentezde kullanılmaz, çünkü kolayca buharlaşır ve stokiyometrisini çok hızlı kaybeder. Bu nedenle onun yerine prosedürde paraformaldehit kullanılır.

Genel olarak, monofonksiyonel benzoksazinlerin polimerizasyonuyla sadece ortalama molekül ağırlığı yaklaşık 1000 Da olan oligomerik yapılar üretilir. Monofonksiyonel monomerler, çapraz bağlanabilmelerine ve termoset üretebilmelerine rağmen, polimerizasyon sırasında dimerlerin, trimerlerin ve zincir reaksiyonundan etkilenen monomerlerin termal olarak ayrıştığı ve bu nedenle düşük molekül ağırlığına sahip polimerler elde edilir. Sorunun üstesinden gelmek ve yüksek molekül ağırlıklı polimer elde etmek için, difonksiyonel ve çok fonksiyonel benzoksazinler sentezlenmiştir. Bisfenol A ve benzeri difonksiyonel fenolik reaktifler klasik benzoksazin sentezinde fenollerle yer değiştirmiştir ve böylece difonksiyonel benzoksinler elde edilmiştir.

Klasik benzoksazinlerden elde edilen polibenzoksinlerin, kırılganlık ve yüksek kürlenme sıcaklıkları ile ilgili birkaç dezavantajı vardır. Bu sorunu çözmek için benzoksazinlerin diğer polimerik malzemelerle kombine edilmesi, özel monomerlerin veya benzoksazin temelli kompozitlerin oluşturulması gibi yeni stratejik yollar geliştirilmiştir.

Yukarıda bahsedildiği gibi benzoksazin monomerleri, fenoller, birincil aminler ve formaldehit ile sentezlenir ve bu sentez için kullanılabilecek birçok amin ve fenol vardır, bu nedenle benzoksazinler yüksek tasarım esnekliğine sahiptir. Benzoksazin monomerleri kumarin, allil, asetilen, nitril, propargil eter gibi farklı fonksiyonel gruplara sahip bileşikler ile modifiye edilebilirler. Polibenzoksazinlerin diğer polimerik malzemeler veya inorganik bileşikler ile modifiye edilmesi, havacılık uygulamaları gibi çeşitli amaçlar için tasarımlanmış polibenzoksazin materyalleri elde etmek için geliştirilmiş bir başka çözümdür.

Polibenzoksazinleri farklı polimerik malzemelerle kombine etmek, özelliklerini değiştirmek ve geliştirmek için avantajlı bir stratejidir. Çünkü, monomer öncüsünden hazırlanan polibenzoksazinler, pratik uygulama kullanımlarındaki bazı sınırlamalarla ilişkilidir. Monomerler genellikle tozdur ve ince filmlere işlenmesi oldukça zordur, bu nedenle, benzoksazinlerin geleneksel polimerler ile kombine edilmesi, bu işlenebilirlik problemine bir çözüm sağlayacaktır. İşlenebilirliği ve mekanik özellikleri geliştirmek için yeni polimerik temelli öncüller, ya yan zincir olarak ya uç zincir yada ana polimer zinciri olarak benzoksazin birimlerine dahil edilerek sentezlenmiştir.

Ana zincir polibenzoksazin öncülleri, polimerik malzemelerin çeşitli yararlarını sağlayacaktır. Bu strateji, iyileştirilebilir film ve elyaf hazırlıklarında çok yönlüdür ve tekrarlanan birim sayısı nedeniyle, bu polimerlerin artan termal ve mekanik dayanıklılığına yol açan yüksek çapraz bağlanma yoğunluklarına sahip termosetler oluşturabilmektedir.

Benzoksazin halkası, bozulmuş yarı- zincir yapısına sahiptir. Bu yapıda, azot benzen halkasının düzleminin üzerindeyken, azot ve oksijen arasındaki karbon ise benzen düzleminin üzerindedir. Bu konformasyon, halkanın belirli koşullarda halka açılması reaksiyonu vermesini sağlamaktadır. Ayrıca, hem oksijen hem de azot atomları güçlü baziktir ve bu nedenle ikisi de potansiyel katyonik polimerizasyon başlangıç yerine sahip olurlar. Benzoksazin halkası katyonik mekanizma ile açılmaya uygun hale gelir. Oksijenin, azottan daha elektronegatif olması nedeniyle tercih edilen polimerizasyon yeri olduğu düşünülmektedir.

Benzoksazinin halka açılımı, reaksiyon dengesinde elde edilen bir karbokatyon ve iminyum iyonunu üretmek için önerilmiştir. Polimerizasyon elektrofilik sübstitüsyon reaksiyonu gibi devam eder, karbokatyon bir elektrofil gibi davranır ve benzen halkasına saldırır. Genellikle fenol halkasının serbest orto ve para pozisyonunu tercih eder. İlerlemeye karşı karbokatyonun reaksiyonun ilerlemesinden sorumlu olması nedeniyle, ilerleme oranı iminyum iyonunun kararlılığından etkilenir.

Blok kopolimerler, termoplastik elastomerler gibi, farklı tipteki polimerleri, melez özellikleri olan bir malzemeye dönüştürmek için bir araya getirdiği için çok sayıda uygulama alanında avantajlıdır ve uygulanabilirdir. Blok kopolimerleri bir çeşit polimer harmanıdır ve atmosferik koşullarda kauçuk gibi davranırlar. İki veya daha fazla farklı polimer zincirini birleştirmek için kullanılabilirler. Birbirlerine uç kısımlarından eklenirler. Blok kopolimer sentezleme yöntemlerinden biri de kondenzasyon metodudur. Bu yöntemde, iki işlevli veya çok işlevli bileşenler arasında reaksiyon aşamalı olarak gerçekleşir. Su, alkol veya hidrojen gibi küçük moleküller reaksiyon sisteminden uzaklaştırılır ve en sonunda makromoleküler polimer oluşur. İki işlevli bileşikler kullanılarak doğrusal kondenzasyon polimerleri hazırlamak için iki temel yol vardır. İki yoldan birinde, iki farklı yan gruba sahip olan monomer kullanılır, bu yöntem AB tipi polikondensasyon olarak adlandırılır. Diğer yolda, benzer gruplara sahip olan ve birbirleriyle reaksiyona giren iki farklı monomer kullanılır ve bu yöntem de AABB tipi polikondenzasyon olarak adlandırılır.

Jeffaminler, polieteraminler, primer aminler ile sonlandırılmış polieter omurgasını içerirler. Ayrıca, Jeffaminlerin polimerik yapısı polietilen glikollere benzer, bu nedenle polieteraminler olarak da adlandırılırlar. Genel olarak, Jeffamines epoksi ile kürleme işleminde kullanılır ve aynı zamanda sert, darbeli modifiye kaplamaların, dökümlerin ve yapıştırıcıların yapımında da kullanılırlar. Bunlar, çeşitli çözücülerle uyumlu olabilen açık renk, hafif viskozite ve karıştırılabilir özelliklere sahiptir. Ayrıca, polietereaminlerin kısmi uzunluğu, yüzey nem emme yeteneğini ve sonuç olarak, yüzey elektriksel direncini kolayca değiştirebilir. Polipropilen Oksitler farklı moleküler ağırlıklara sahiptir ve bunlar monoamin, diamin ve triamin formundadır.

Jeffaminler, çapraz bağlama işlemi, zincir çoğaltıcı ve blok ve graft kopolimerleri ile modifiye edilmek için tercih edilir. Polieteraminler, monoaminler (M serisi), diaminler (D serisi) veya triaminler olarak farklı moleküler ağırlıklarda üretilir ve bu moleküler ağırlıklar 5.000 Da'ya ulaşabilir.

Bu çalışmada benzoksazinlerin modifiye edilmesi için polieteramin türevleri kullanılmıştır. Polimerik benzoksazin ön maddelerinin, tek potada, iki adımlı veya basamaklı yollarla polieteraminlerle blok kopolimerlerinin hazırlanması için yeni bir strateji tarif edilmektedir. Yöntem, 4-hidroksianilin, formaldehit ve polieteraminler (Jeffaminler) gibi basit kimyasalların kullanımına ilişkindir. Polimerlerin yapısı ve moleküler ağırlıkları FTIR, ^{1}H NMR, GPC ile karakterize edildi. Başarılı blok kopolimer oluşumu, blok kopolimerin molekül ağırlığının daha yüksek moleküler ağırlık bölgesine doğru kaymasıyla kanıtlanmıştır. Polimerlerin termal özellikleri de DSC ve TGA kullanılarak araştırıldı. Blok kopolimerlerin, benzoksazin bloğunun halka açılma polimerizasyonu ile termal olarak aktive edilmiş kürleme geçirdiği gösterilmiştir. Sertleşen ürünün termal stabilitesi, öncü polieteramine kıyasla büyük ölçüde artmıştır.

1. INTRODUCTION

Polybenzoxazines (PBZs) as contender to classical phenolic resins have numerous superior properties such as good mechanical strength, limited or no water absorption, dimensional and thermal stability, chemical and flame resistivity [1-3]. Moreover, their monomers, namely 1,3-benzoxazines (BZ), also have excellent storage life stability at room temperature. When BZ prepreg formulas analyzed over one year, they demonstrate slight change in differential scanning calorimetry (DSC) thermograms. Therefore, many resin producers established benzoxazine bearing formulations and these resins have found numerous applications as high performance materials in electronic circuit boards, composites, blends and alloys [4-7].

Polybenzoxazines are synthesized by thermaly ring-opening polymerization (ROP) of benzoxazine monomers. Typically, the polymerization takes place between 170–250 °C without using any catalyst or curative depending on the structure and purity of monomer (Figure 1.1) [8-10].

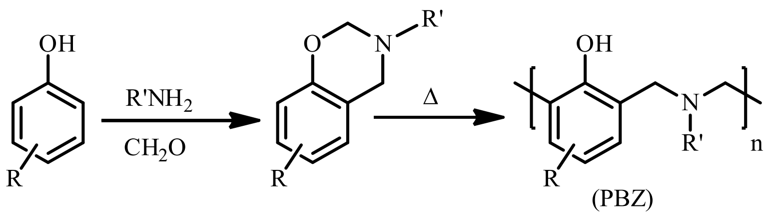


Figure 1.1 : Synthesis and polymerization of a benzoxazine monomer.

Purer monomers have higher curing temperatures then monomers containing phenolic residues, where these residues act as catalyst in the polymerization [11-16]. Another appealing aspect of the polybenzoxazines is their great molecular design flexibility unlike traditional phenolic resins. Simply, most of the benzoxazine monomers can be synthesized by using a derivative of phenol, a primary amine and formaldehyde (Scheme 1) [17]. Hence, various polybenzoxazines can be designed with tailored properties for desired applications [18-22]. For example, highly stiff polybenzoxazines can be obtained by using allyl, [23, 24] propargyl, [25] coumarine, [26, 27] or di-, tri-oxazine functional benzoxazines that allow extra crosslinking [28, 29]. For some specific applications, room temperature viscosity of the monomers can be decreased by selecting alcohol functional or long-chain alkyl amines in the synthesis to give essentially fluid benzoxazines important for moulding and similar uses [30, 31].

Apart from monomer synthesis, polymeric benzoxazine precursors were synthesized using various methods. For example, polycondensation of diamines and diphenols yields polybenzoxazine precursors with relatively high molecular weights and good film properties [32, 33]. Other polymer types such as polyesters, [34] polysiloxanes, [35, 36] polysulfones, [37] polyethers [38] were also synthesized from benzoxazines, successfully. Moreover, smart systems based on benzoxazines [39-42] as self-healing, [43-46] shape memory, [47] electro-responsive systems [48-50] etc. can even be designed by selecting suitable phenols and amines. Consequently, benzoxazine chemistry has high design capacity to obtain task specific benzoxazine monomers or polybenzoxazine precursors. Especially, polybenzoxazine precursors have huge potential in terms of applications since they have good film properties and can bear many features of general polymers. Thus, wide range of main-, side- and end-chain polybenzoxazine precursors were readily synthesized and used for different purposes [34, 51-57]. Obviously, each structural variation and the method used would reflect the characteristics of the polymer formed and modify the properties of the resulting polybenzoxazines. For example, flexible and tough materials could be produced from polybenzoxazine precursors selecting siloxanes or ethers as repeat units in the polymer [54]. The length of the siloxane or etheric chain in the polymeric benzoxazine precursors affected both toughness and thermal properties. Although, several polybenzoxazine precursors were reported, block copolymers of benzoxazines were scarcely been investigated and this subject has potential to combine the properties of two different polymer chains [38, 58]. In this study, we have shown that block copolymers of polybenzoxazine precursors can be synthesized using either in one-pot two-step or sequential synthetic pathways by selecting suitable aminophenols.

2. THEORETICAL PART

2.1 Brief Historical Backround of 1,3-Benzoxazine Chemistry

Among aromatic oxazines 1,3-benzoxazines were first synthesized in 1946s by Holy and Cope using aldehydes and hydroxy aromatic amines (Figure 2.1) [59]. After a few years, Burke synthesized several benzoxazine derivatives using phenolic compounds and also discovered that the benzoxazine ring gives reaction favourably with the ortho positions of the ring with the phenolic compounds and creates a Mannich Bridges. Thus, these studies revealed that by using different phenols and amines derivatives, various benzoxazines can be obtained. Initial studies about benzoxazines were focusing on medicinal properties of these molecules since 1,3-benzoxazines exhibited anti-carcinogenic effects against some tumors [60]. Although, there are modern studies based on medicinal properties of benzoxazines, these molecules still need to pass the stages to be an approved medicine. Apart from medicinal chemistry approach, the importance of benzoxazines in polymer chemistry was recognized much later maybe due to the high stability of oxazine ring. Thermally polymerizable character was first reported in a German patent in 1973 and in 1984, ring-opening polymerization of benzoxazines was reported by Reiss et al [61]. Moreover, the properties of benzoxazine resins were first investigated by Ishida et al. and after these pioneering studies superior features of these materials attracted many researches in the field of high performance materials [10, 62, 63]. Nowadays, the research interest for benzoxazine and related polymers is stadely growing in the field of polymer chemistry and many papers and patents are being published annually, reflecting the importance of this area.

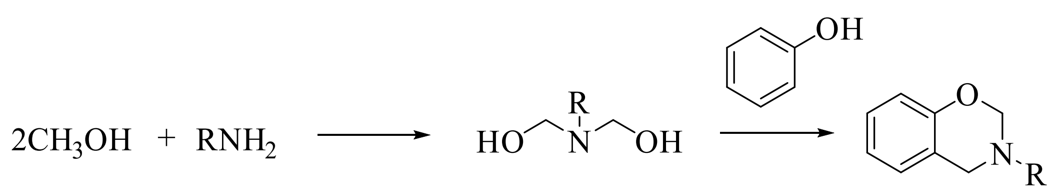


Figure 2.1 : Synthetic procedure for benzoxazine synthesis.

2.1.1 Properties of benzoxazine monomers and polybenzoxazines

Polybenzoxazines are member of curable phenolic resin family. The basic reason of improving these polymers is combining the thermal features and flame dilatory of phenolic composites with the mechanical performance and molecular structure of sophisticated epoxy systems [64]. The polybenzoxazines achieve many deficiencies of conventional novolac and resole-type phenolic resins, meanwhile it protects their benefits. Polybenzoxazines composites are anticipated to substitute conventional phenolics, polyesters, vinyl esters, epoxies, cyanate esters and polyimides in numerous aspects. The molecular structure of polybenzoxazines presents magnificent design flexibility that permits properties of the crosslinked polymer to be controlled for specific requirements of a broad array of particular necessities.

The resin allows progress of new applications by utilizing some of their unique properties like [63, 65]:

- Almost zero volumetric change after polymerization reaction
- Low water absorption
- For some polybenzoxazines, Tg much higher than cure temperature
- Low cost materials
- High char-yield
- Low coefficient of thermal expansion
- Low viscosity
- Storage in room conditions
- Leaving limited toxic by-products during curing

The ring-opening polymerization of these new polymers happens with either almost zero shrinkage or even with a light expansion on curing process. It is suggested that the volumetric stretching of the benzoxazines is usually owing to the result of molecular packing affected through inter and intramolecular hydrogen bonding.

When the benzoxazines are compared with the other known improved monomers and spiro ortho compounds, it is thought that this kind of polymers have an increased potential for structural applications [66]. Because of releasing the lowest heat during curing and having flame proof property, polybenzoxazines are prefered by aerospace endustry for matrices nowaday.

2.1.2 Synthesis of benzoxazine monomers

There are many studies about synthesis of novel benzoxazines. Hence, many articles have been published in this context. The first work about benzoxazines which was made by Holy and Cope, the benzoxazine reaction carried out in a solvent with two steps in the procedure [59]. The synthesis of benzoxazine monomers was performed in a solvent, based on Mannich condensation by amine and formaldehyde at decreased temperatures to generate a kind of *N,N*-dihydroxymethylamine. After this step, the formed compound gives reactions with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the increased temperature yielding the benzoxazine. The preparation of 3,4-dihydro-1,3-2H-benzoxazine was proposed by Burke in a single step from *p*-substituted phenol, formaldehyde and primary amine in a molar ratio of 1:2:1, respectively. The plausable synthesis mechanism is demonstrated in Figure 2.2 [67].

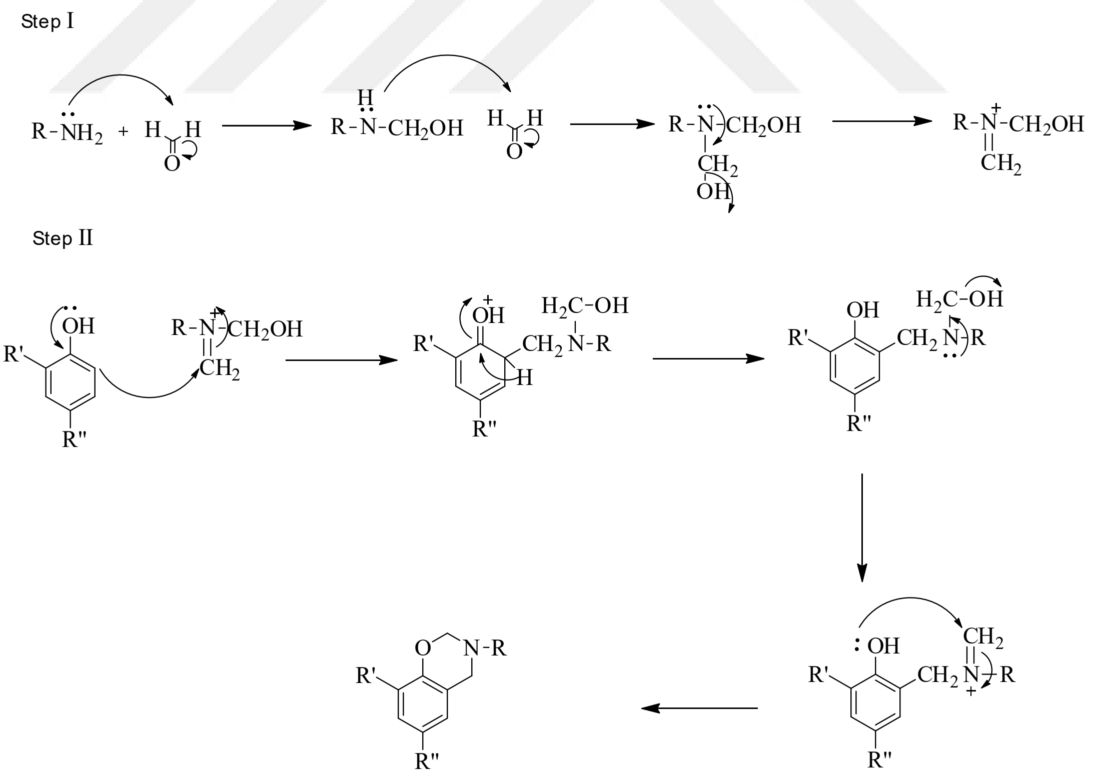


Figure 2.2 : Probable mechanism of benzoxazine ring formation.

Alternatively, benzoxazine ring formation mechanism of 3,4-dihydro-3,6-disubstituted-1,3-2H-benzoxazine was also presented in Figure 2.3.

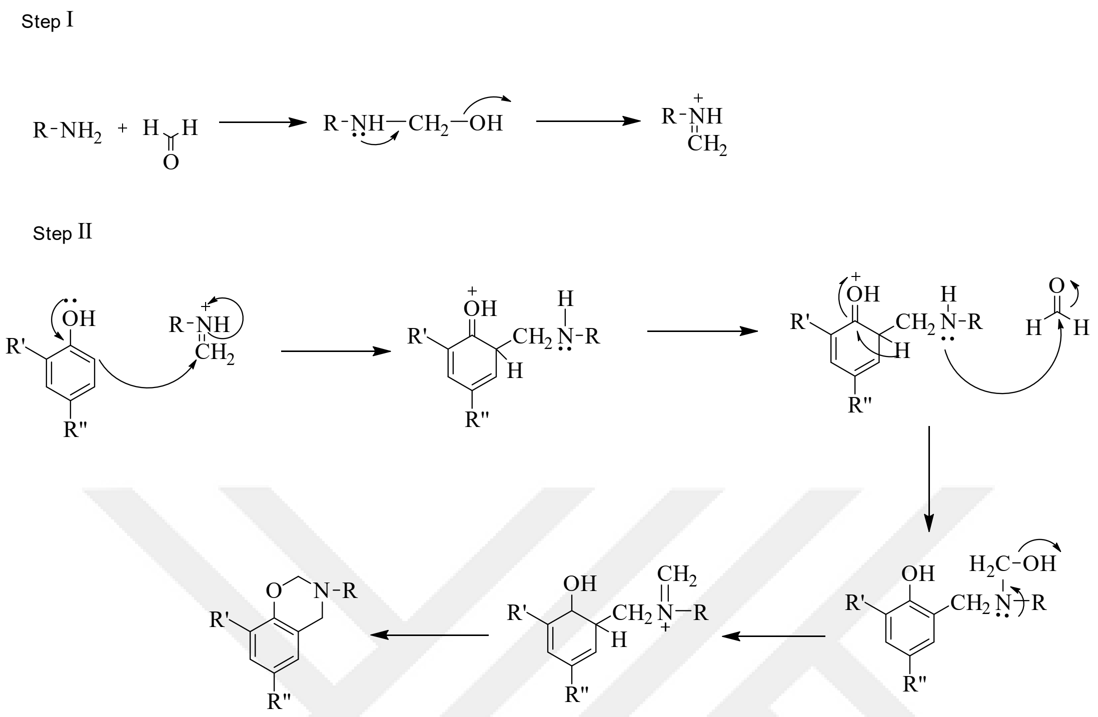


Figure 2.3 : Alternative benzoxazine ring formation mechanism.

Subsequent ring opening of oxazine may occur during the synthesis with the existence of compounds including active hydrogen (HY) such as imides, indoles, carbazole, naphtol and aliphatic nitro compounds even phenol which is also one of reactants for the synthesis of monomer and small oligomers may be generated as by products [68]. The ring opening of benzoxazine in acidic medium forms compunds having Mannich bridges as represented in Figure 2.4 [69].

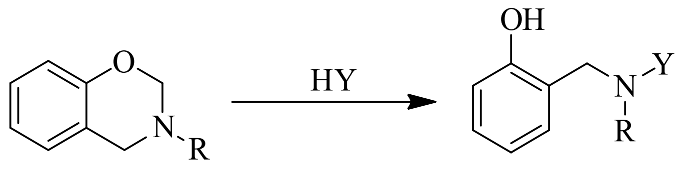


Figure 2.4 : Formation of the Mannich bridge via ring opening of benzoxazine.

Substituent on the phenolic component is important to reduce the side products. If phenolic reagent has more than one reactive ortho and para positions, another aminoalkylation reaction might take place resulting in side-products. Therefore, blocking the other reactive sites on phenols increase the yield drastically. For example, non-functional phenols may give benzoxazines around 55–65%, para blocked phenols (*p*-cresol) increases the yields up to 90%. Moreover, the basisty of the used primary amine affects the product type hence the yield. Aromatic amines with strong electron withdrawing groups make the reaction sluggish. [70]

The solvent also lead to change the formation of benzoxazine and affect the yield of product. Using solvent in benzoxazine reactions has several drawbacks such as slow reaction rate, and poor solubility of precursors. Beside, using large amount of solvent lead to increasing cost of products and causing environmental problems when removing solvent from the reaction system. Moreover, polar solvents have positive effect on the formation of oligomeric side products thus reduce the yield of benzoxazine synthesis. For overcoming these disadvantages, Ishida *et al.* used solventless synthesis in melt state [71] where components are miscible in melt phase. Unlike traditional methods, solventless synthetic method supplies improved reaction times and fewer undesirable intermediates and by products are occured [72]. Another method is to arrange the polarity of solvent by using solvent couples. Toluene/Ethanol couple in 2:1 (v:v) ratio was found to reduce the oligomer formation for most of benzoxazine synthesis [73].

Melt technique and toluene:ethanol mixtures work well for most of benzoxazine synthesis, but in some synthesis especially where reaction rate and amine solubility is problematic (for example, 4,4'-sulfonyldianiline or benzidine) nonpolar solvents having high boiling point as an intrinsic solution method was established. There are two different essential reasons for this tecnique. The first one is poor solubility of amines in organic solvents and the other one is the reaction of diamines with formaldehyde caused a stable triazine gel structure. These kind of solvents enhance the solubility of starting materials and lead to rapid breakage of triazine gels. In the end of reaction, monomer formation occurs correspondingly without and limited side reactions [74].

Another approach is multistep synthesis of benzoxazines. There are two methods under this approach. The first route is based on ortho-lithation of phenolic reagent and then reacting the intermadiatite with a suitable benzotriazole using $ZnBr_2$ catalyst. However, low yields and problems in isolation of the benzoxazines have limited usage of this approach [75]. The second route involves the use of 2-hydroxybenzaldehyde or structurally similar compounds as phenolic reagents. Imine formation between the aldehyde and amino compound is the first stage, followed by reduction to form 2-

hydroxybenzylamines, and finally ring closure is accomplished by using formaldehyde. This methodology is especially useful when the starting reagents possess groups that do not tolerate the Mannich reaction [76].

2.1.3 Bifunctional and multi-functional benzoxazines

Generally, polymerization of monofunctional benzoxazines produce only oligomeric structures having average molecular weight approximately 1000 Da. Although, monofunctional monomer are capable of crosslinking and produce thermosets, it was revealed that during polymerization thermal dissociation of dimers, trimers and monomers adversely affect chain reaction, and therefore polymers with low molecular weights could be obtained [77]. In order to overcome the problem and obtain high molecular weigth polymers, di- and multifunctional benzoxazines were synthesized [10, 78]. Bisphenol A and similar difunctional phenolic reagents were replaced with phenols in the classical benzoxazine synthesis and difunctional benzoxaines were obtained. The resultant monomers consisted of difunctional benzoxazine ring having at two end sides of the molecules.

Inherently, aniline and methylamine is preferred as amine source and the obtained polybenzoxazines from these monomers exhibited the similar properties [63, 79] The synthesis of these bisbenzoxazines is depicted in (Figure 2.5).

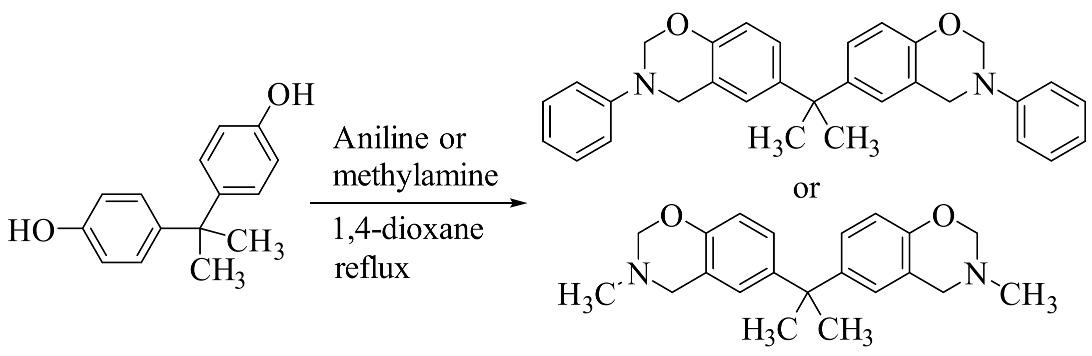


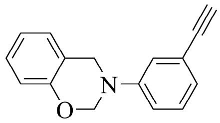
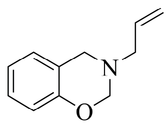
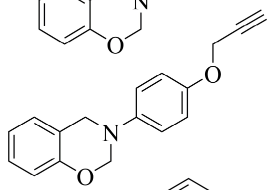
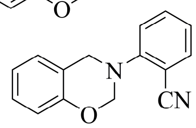
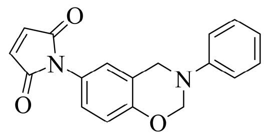
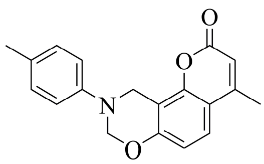
Figure 2.5 : Synthesis of bifunctional benzoxazines.

The curing of bisbenzoxazines was examined with regard to cure kinetics via DSC. It was observed that the curing of benzoxazine precursors is an auto-catalyzed reaction, however when vitrification is started, autocatalysis ends. Beside, afterwards diffusion starts to control the procedure of curing [80].

2.1.4 Modifying benzoxazine monomers with various functional groups

Polybenzoxazines from classic benzoxazines have a few disadvantages related to the brittleness and high curing temperatures. For solving this issue new strategic ways have been developed such as combination of benzoxazines with other polymeric materials, generating specific monomers or composites which are based benzoxazine. Benzoxazine monomers are synthesid from phenols, primary amines and formaldehyde and there several available amines and phenols therefore this chemistry has high design flexibilty [2, 61, 77, 81, 82]. Thereby, benzoxazine monomers can be modified with compounds having different functional group like coumarin, allyl, acetylene, nitrile, melaimide, allyl, propargyl ether. (Table 2.1.) The selected functional groups can be used to arrange the toughness of final polybenzoxazines. Also, extra crosslinking units can be incooperated into the monomers allowing more rigid and thermally stable thermosets.

Table 2.1 : Benzoxazine monomers having various functionalities

Functional Monomers	
Acetylene functionalized monomers (Ph-apa)	
Allyl functionalized monomers (P-ala)	
Phenyl propargyl functionalized monomers	
Nitrile functionalized monomers	
Maleimide functionalized monomers	
Coumarine-containing benzoxazine	

2.2 Ring Opening Polymerization of Benzoxazines

Understanding the chemical structure of oxazine ring of benzoxazine is important in order to analyse the ring opening polymerization mechanism. Mono-oxazine ring including benzoxazine has a amorphous semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, in return, above and below the benzene ring plane. With helping it's conformation which was explained above, this ring having six member exposes ring-opening reaction under specifical circumstances. Furthermore, by the reason of their high basicity (by Lewis description) of both oxygen and nitrogen of the oxazine ring can play like potential cationic polymerization initiation site and converts the ring very likely to open by a cationic mechanism [13, 83]. After energy minimization estimates, by the reason of its increased negative charge distribution, it is anticipated that the oxygen might be used the polymerization site (O, -0.311; N, -0.270).

2.2.1 Polymerization of benzoxazines with acid catalyzed

The ring opening polymerization of the benzoxazine proceeds via a cationic mechanism [84, 85] It has been stated that 3,4-dihydro-2H-1,3-benzoxazine presents ring/chain tautomerism with protonation, through migration of the proton from the nitrogen to the oxygen atom, consequently generate iminium ions in the chain form by Mcdonagh and Smith [71]. The reaction of electrophilic substitution pursues this ring opening polymerization is depicted (Figure 2. 6) [86].

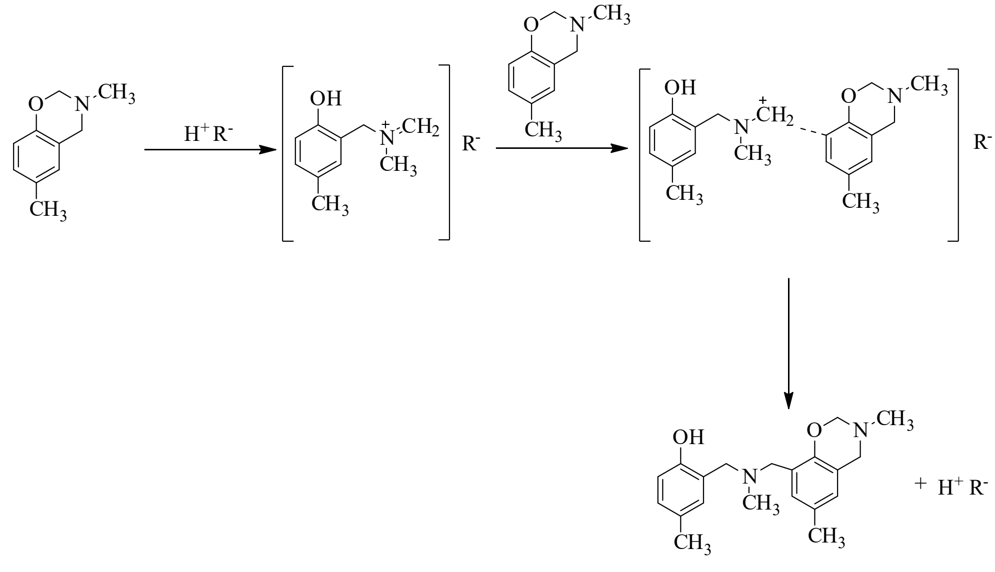


Figure 2.6 : Acid catalyzed ring opening polymerization of 1,3-benzoxazine.

As showed above, this polymerization mechanism does not affect the pKa of the acid catalyst, however the pKa affects the structure of the polymerization intermediate. With helping strong acid catalyst, benzoxazines transform to polybenzoxazine at low temperatures following ring opening polymerization. The intermediate was suggested to be an iminium ion. If weak acid catalyst is prefered instead of strong acid catalyst, in the starting of polymerization, reaction rate would decrease.

2.2.2 Thermal polymerization of benzoxazine monomers

The ring- opening of benzoxazine is proposed to generate a carbocation and an iminium ion which were obtained in equilibrium of reaction. Polymerization continues like electrofilic substitution reaction. The carbocation behaves like a electrophile and attacks to the benzene ring. It prefers the free ortho and para positions of the phenol ring. Propagation rate affects from the stability of the iminium ion, cause carbocation is liable for the propagation.

To describe thermal polymerization of benzoxazines, many researchers have suggested different mechanism (Figure 2.7).

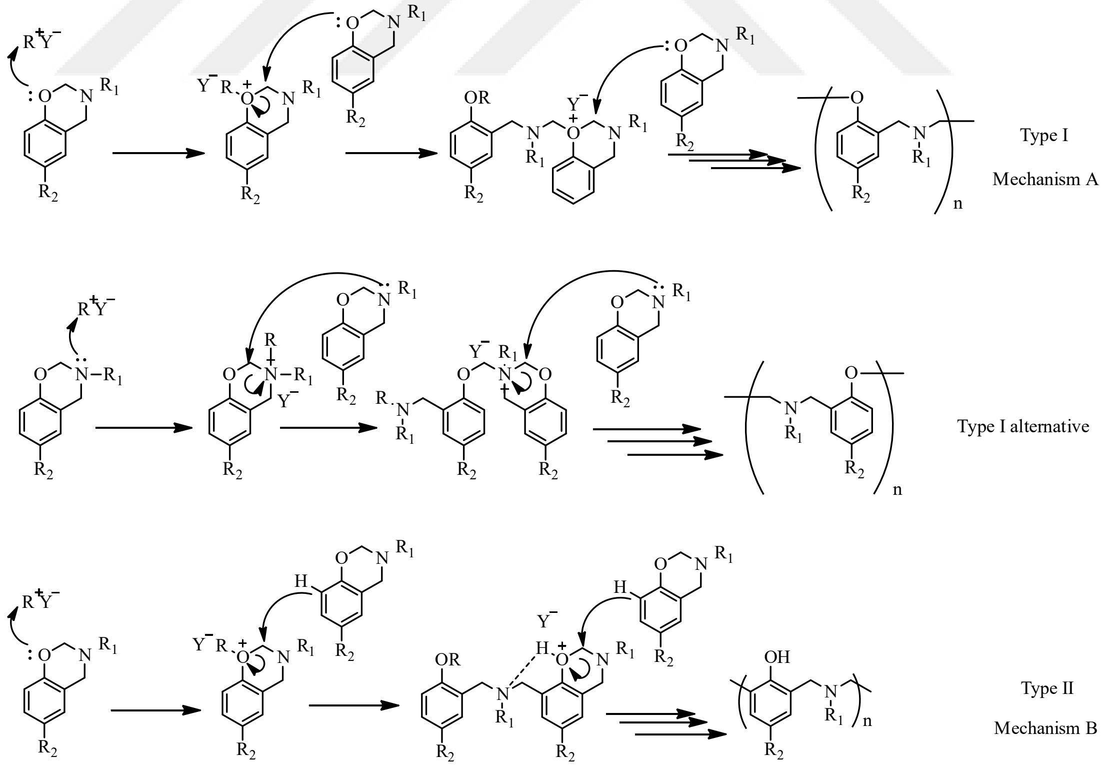


Figure 2.7 : Proposed mechanisms for thermal polymerization of benzoxazines.

2.2.3 Photoinitiated polymerization of benzoxazine monomers

3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (P-a) which is a monofunctional benzoxazine monomer, was investigated from the point of its photoinitiated ring-opening cationic polymerization with initiators diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate as by Kasapoglu et al. [64]. In this work, researhers found out that the synthesized polymer structure is dependent on the ring opening of the protonated monomer either at the oxygen or nitrogen atoms. Besides, free radical assisted cationic polymerization of benzoxazines was examined in this study. The polymerization can be obtained at much higher wavelengths and carbon centered radicals were oxidized to form carbocations. Figure 2.8 shows the photopolymerization of benzoxazine monomers.

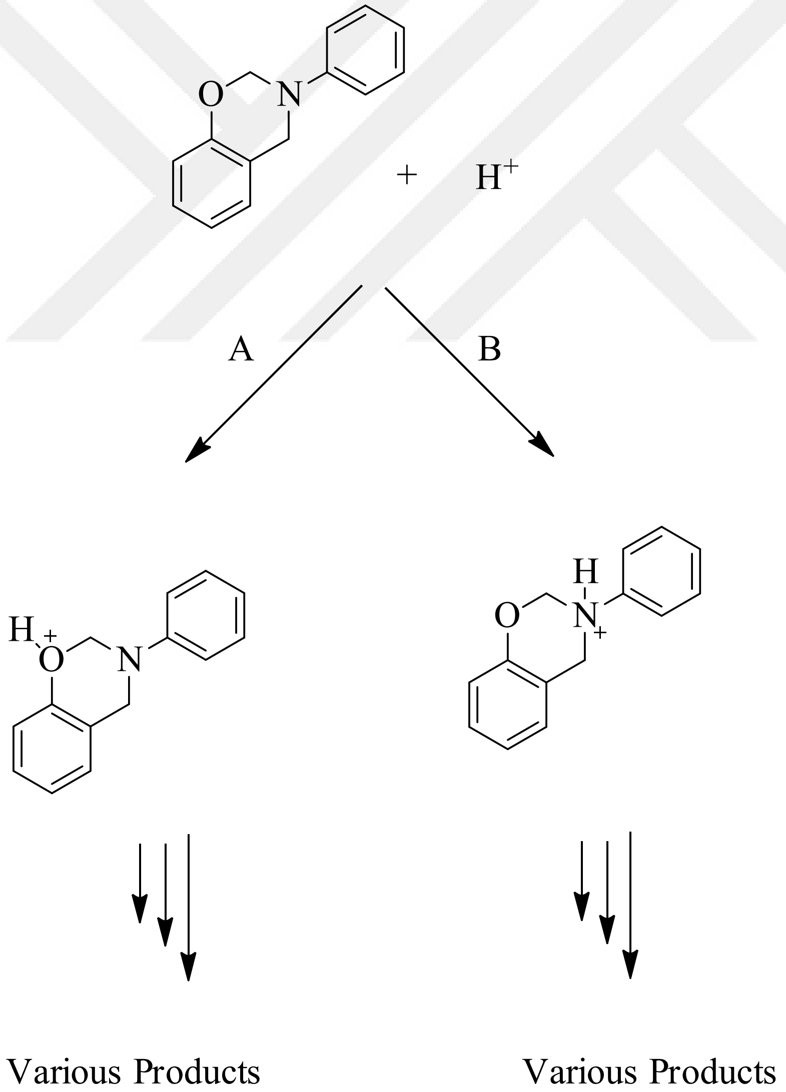


Figure 2.8 : Photopolymerization of benzoxazine monomers.

2.3 Modifying of Benzoxazine Monomers with Other Materials

2.3.1 Blends and composites of benzoxazine

As mentioned above, several solutions have been suggested involving monomer combination, forming benzoxazine mixtures and generating linear benzoxazine polymers for overcoming some of the drawbacks of polybenzoxazines, such as brittleness and high curing temperature. Modifying polybenzoxazines with other polymeric materials or inorganic compounds is another solution to obtained designed polybenzoxazine materials for various purposes such as aerospace applications. Therefore, several materials were mixed with benzoxazine as rubber [62, 87-89], polycarbonate [90, 91], poly (ε-caprolactone) [92, 93], polyurethane [94, 95], epoxy resins [96, 97], composites including phosphorous [82, 98] and kaolin [99, 100]. Their thermal properties (e.g., degradation, char yield, T_g) and mechanical properties (such as storage modulus, flexural modulus, flexural strength etc) enhanced after compositions. In order to satify aerospace inductry criteria benzoxazines were also mixed with carbon fibers and carbon nantubes. The prepared composites from these formulations exhibited very high T_g (over 250 °C), char yields (over 60%) and flame retardancy [101].

2.3.2 Preparation of polymers with benzoxazine moieties

Combining polybenzoxazines with different polymeric materials is an advantageous strategy to alter and improve their features. Because, polybenzoxazines prepared from the monomers precursor are associated with some limitations on their use in practical applications. The monomers are usually powder and processing into thin films is rather difficult. Therefore, combining benzoxazines with conventional polymers would provide a solution to this processibility problem. To improve the processibility and mechanical properties novel polymeric based precursors have been synthesized by incorporating benzoxazine units either as side chain or as end chain or in main chain of polymer. Polymers modified with benzoxazines are poly (p-vinylphenol) (Figure 2.9a) [102] , poly (ε-caprolactone) (Figure 2.9b) [103] and poly (methyl methacrylate) (Figure 2.9c) [104]. Below, polymeric benzoxazines is discussed further under the subject of benzoxazine precursors.

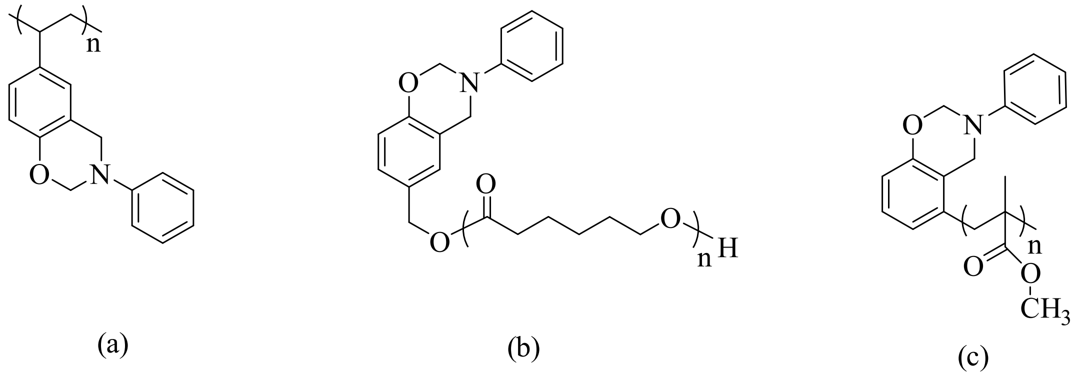


Figure 2.9 : Typical benzoxazine functional polymers.

2.4 Benzoxazine Procursors

2.4.1 Main-chain benzoxazine functional procursors

As mentioned above, benzoxazines can be incooporated into classical polymers. Main-chain polybenzoxazine precursors would provide several benefits of polymeric materials. This strategy is versitile in curable film and fiber preparations and due to the number of repeat units these polymers can generate thermosets with high crosslinking densities leading to increased thermal stability and mechanical durability. The first main-chain type benzoxazine polymers was synthesized by Liu et al. using 4,4'-methylenebis 2,6-dimethylaniline bisphenol-A, and formaldehyde [72]. In pursuit of Liu and coworkers, an improved work about generating an AABB-type linear polymer with benzoxazine rings in the main chain by formation of high molecular weight main chain benzoxazine polymers via the polycondensation of diamines and bisphenols was presented by Takeichi et al. [33] and Chernykh et al. [32] (Figure 2.10).

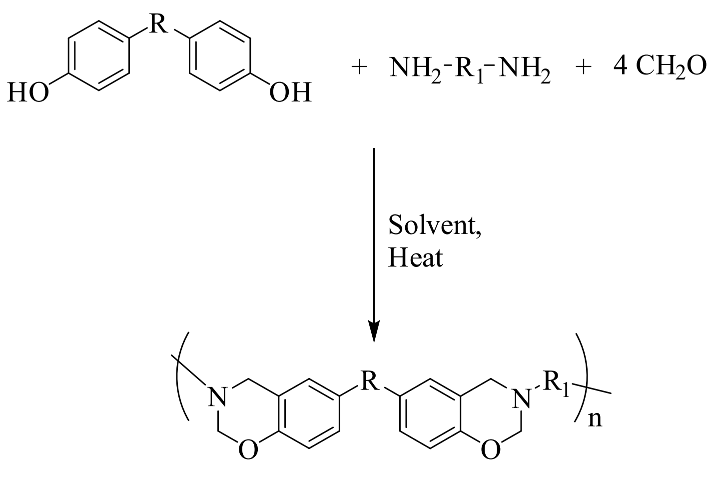


Figure 2.10 : AB-type linear polymer.

Apart from Mannich type main-chain polybenzoxazines, other condensation polymerization techniques were also used to obtain polyester, polyether, polysiloxane etc. type polybenzoxazine precursors. However, in these polymerization special difunctional benzoxazines are required such as dially, dialcohol containing bisbenzoxazines [1].

2.4.2 Side-chain benzoxazine functional procursors

Incorparation of benzoxazine monomers into a polymer backbone as a side chain is another strategic pathway to attain a highly dense network and solve the processibility problem of classical benzoxazine monomers. Curing numerous benzoxazine monomers lead to crosslinking in polymer chains. Many different side chain benzoxazine polymers were reported and some of the important polymers is illustrated in Figure (2.11).

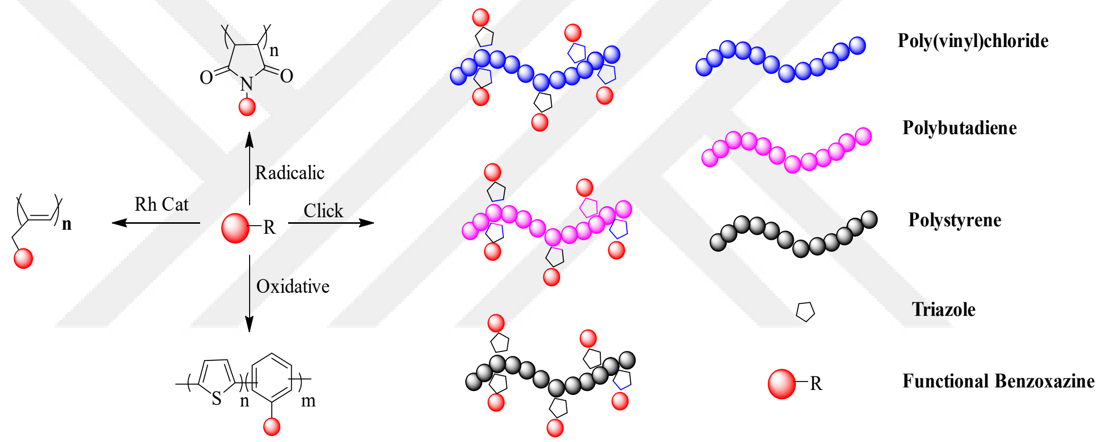


Figure 2.11 : A strategy to obtain side-chain polymer.

Yagci and coworkers were synthesized a new side-chain polymer (polyvinylchloride) functionalized by benzoxazine by using click chemistry, which is a way of obtaining side-chain polymers [105]. In this method, about 10% of chloro groups of polyvinylchloride were transformed to azido groups by using NaN_3 in *N,N*-dimethylformamide. Independently, in the previous stage, propargyl benzoxazine was synthesized by a ring closure reaction using *p*-propargyloxy aniline, paraformaldehyde, and phenol. In the end, azidofunctionalized polyvinylchloride was modified with propargyl benzoxazine (Figure 2.12).

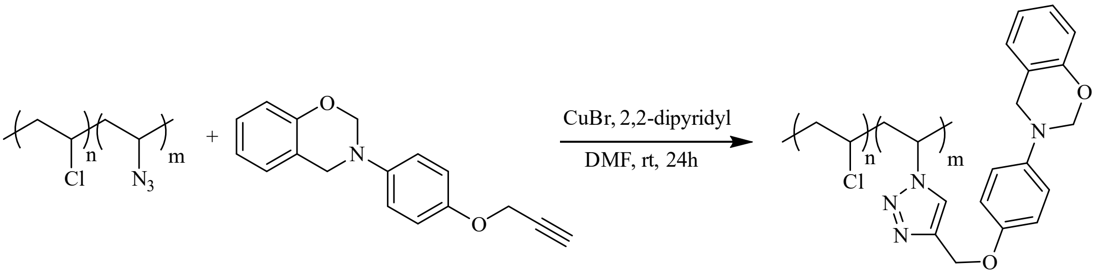


Figure 2.12 : Synthesis of benzoxazine functional PVC.

2.5 Block Copolymers

Block copolymers are advantageous and practicable in numerous application field where different kind of polymers are combined each other to transform a material with crossbreed features such as termoplastic elastomers. Indeed, the block copolymers are a kind of polymer blend. They act like rubber at athmospheric conditions. However they can be given shape by the reason of the existence of the glassy areas which behave like physical crosslinks at high temperatures. If a water soluble polymer combine with an insoluble polymer, an amphiphilic block copolymer occurs. This can be evaluated as a solution. The block copolymer that occurs end of combination, shows different characteristic features from the polymers which are used for integration.

To make combining two or more different polymer chains can be used. They are added at their end points. While block copolymers which include two or more polymers are called linear block copolymers, including two or more block copolymers that combined a common branch spot are called starblock copolymers. Different kind of block copolymers are shown at Figure 2.13.

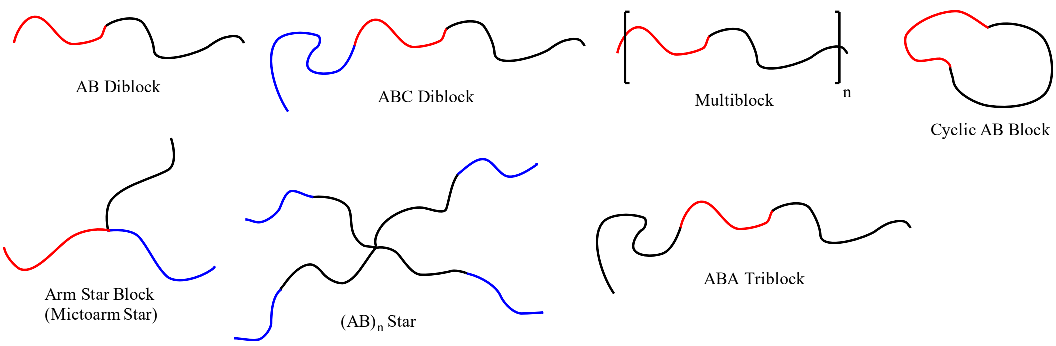


Figure 2.13 : Block copolymer structures.

2.5.1 Synthesis of block bopolymer

In all around the world, researchers use mostly two techniques for synthesis block copolymer; anionic polymerization and controlled radical polymerization. Anionic polymerization, the senior method, is still preferred in the endustrial production of block copolymer. Sometimes cationic polymerization can be also preferred when polimerize monomers cannot be adapted to anionic polymerization [106].

2.5.1.1 Anionic polymerization

Anionic polymerization is a superior tecnique for preparing special, well-designed block copolymers. In order to synthesis well-designed block copolymers, especially for anionic method, reagents must be high pure. To avoid impurities, high vacuum distillation tecniques are used. In the lab conditions, obtaining polydispersities $Mw=Mn < 1.05$ by anionic polymerization. Furthermore, preparing many significant types of block copolymers like SBS-type thermoplastic elastomers (S = polystyrene, B =polybutadiene) and pluronic amphiphilic copolymers, this tecnique is preferred [107].

2.5.1.2 Living radical polymerization

The biggest contribution of synthesis of block copolymer is enabling new methods to develop. The most important one is living radical polymerization. The basis of living radical polymerization tecnique is constituting an equilibrium between a small fraction of growing free radicals and a large majority of unexplored species. Free radicals which were produced, like traditional polymerization method, propagate and terminate the polymerization, even though small fraction of radicals handicap premature termination. Atom transfer radical polymerization (ATRP) is the most used and preferred method for synthesizing block copolymers. In this tecnique, the radicals are produced via a reversible redox reaction and catalysed by a transition metal complex [108].

2.5.1.3 Other methods

To prepare block copolymers including a vinyl ether block, or polyisobutylene, sequential living cationic polymerization is used. The range of polymerizing monomers via this method may be slightly restricted, therefore this cationic method is used only in detected situations [109-111]

Ring opening metathesis polymerization (ROMP) has been used for constructing blocks from cyclic olefins, particularly polynorbornene [106].

Other block copolymerization methods are condensations, namely “Polycondensations”. In these methods, reactions occur stepwise between bifunctional or polyfunctional components. Small molecules like water, alcohol, or hydrogen are removed from the reaction system and at last, macromolecular polymer is formed. There are two fundamentally pathways to prepare linear condensation polymers with using bifuctional compounds. In one of the two pathways, monomer having two different side-groups is used, this method is called AB type polycondensation. In the other pathway, two different varied monomers which have similar groups and give reaction with each other. This second method is callled AABB type. If polyfunctional compounds which enable to obtain branched, hyperbranched, or crosslinked condensation polymers, are wanted to use, same prosedure can be applied.

AB type is the polycondensation of hydroxycarboxylic acid is shown at Figure 2.14.

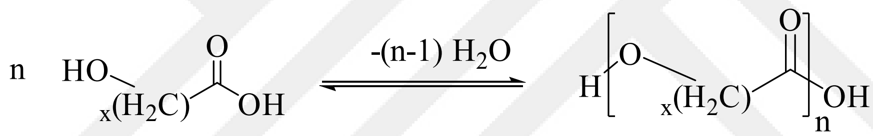


Figure 2.14 : AB type polycondensations.

2.6 Properties of Jeffamines

The Jeffamine, polyetheramines include with primary amines terminated polyether backbone. Beside, polymeric structure of Jeffamines look like to the polyethylene glycols. Therefore, one of their name is polyether amines. Basis of polyether backbone depend on propylene oxide, ethylene oxide, or both blended propylene oxide and ethylene oxide.

In general Jeffamines are used in the process of epoxy curing and they also serve stiff, impact-modified coatings, castings, and adhesives. They have light color, slight viscosity and mixable property which lead to be compatible with various of solvents. Besides, partial length of the polyethereamines can readily modify the surface moisture absorption ability and, consequently, the surface electrical resistivity. Polypropyleneoxides have different molecular weights and they are in the form of monoamine, diamines, and triamines. Eventually, Jeffamines are prefered for crosslink process, chain replicator, and modifiying with block and graft copolymers. Polyethereamines are generated in different molecular weights as monoamines (M-series), diamines (D series), or triaminesand this molecular weights can be reach at 5.000 Da. Jeffamines provide flexibile design to polymers having many kind of molecular weight, various amines and oxides.

2.6.1 Polypropyleneoxide amines (Jeffamines) D series

They belong to Jeffamine diamines family with ED Series. The D-series compounds are polyoxypropylene diols having amines in both two end sides. Their structure (Figure 2.15) and their molecular properties (Table 2.2) are shown.

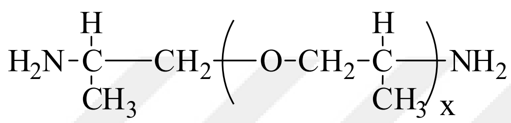


Figure 2.15 : Jeffamine D Series

Table 2.2 : Molecular Properties of Jeffamine D Series

Jeffamine Product*	X	Approximately Molecular Weight (Da)
D-230	2-3	230
D-400	5-6	400
D-2000	33 (Avarage)	2000
D-4000	68 (Avarage)	4000

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Chemicals

Paraformaldehyde (Aldrich, 95.0-100.5%): Paraformaldehyde was used as received.

p-aminophenol (Merck, ≥99%): p-aminophenol was used as received.

Jeffamine D-2000: Jeffamine D-2000 was used as received.

Jeffamine D-2000: Jeffamine D-2000 was used as received.

Toluene (Merck, ≥99%): Toluene was used as received.

Ethanol (EtOH, Carlo Erba, ≥99.9%): Ethanol was used as received.

Methanol (MeOH, Aldrich, 99.8%): Methanol was used as received.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

All ^1H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ or DMSO-d_6 with $Si(CH_3)_4$ as an internal standard.

3.2.2 Infrared spectrophotometer (FT-IR)

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

3.2.3 Differential scanning calorimeter (DSC)

Differential Scanning Calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC from 30 °C to 320 °C with a heating rate of 10 $°C.min^{-1}$ under nitrogen flow. A typical DSC sample was 2–5 mg in a 30 μL aluminum pan.

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 performed 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 TSKgel 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 main-chain benzoxazine precursor (MPBz)

Paraformaldehyde (0.87 g, 0.029 mol) and 4-aminophenol (1.5 g, 0.014 mol) were dissolved in 40 mL toluene and 20 mL ethanol mixture, in a 150 mL flask equipped with a reflux condenser and a magnet for stirring. The solution was refluxed for 24 h at ca. 110° C temperature. After reflux, the flask was cooled to r.t. and the content was filtered using an ordinary filter paper to remove solid particles. The clear solution was concentrated under vacuum, and then precipitated in 250 mL of methanol containing 2–3 mL salty water. The polymer was filtered, washed with water and methanol, dried in a vacuum chamber at ambient temperature for 48 h to obtain brown powdery solid. (Yield ≈ 68 %)

3.3.2 Synthesis of poly(benzoxazine-co-etheramine) (MPBz-co-PEA)

Paraformaldehyde (0.87 g, 0.029 mol) and 4-aminophenol (1.5 g, 0.014 mol) were dissolved in 40 mL toluene and 20 mL ethanol mixture, in a 150 mL flask equipped with a reflux condenser and a magnet for stirring. The solution was refluxed for 24 h at ca. 110° C temperature. The whole mixture was magnetically stirred at ambient temperature for 24 hours. Then, Jeffamine D-4000 (1.8 g) (or Jeffamine D-2000) and extra paraformaldehyde (0.1 g, 0.014 mol) was admixed. The solution was again refluxed for 3 hours at ca. 110° C. After reflux, the reaction mixture was filtered through an ordinary filter paper, concentrated, and finally precipitated in 250 mL of deionized water. The polymer was filtered under vacuum, washed with copious amount of water, and dried in a vacuum chamber at ambient temperature for 48 h to obtain brownish solid with a quantitative yield.

4. RESULTS AND DISCUSSION

Initially, AB type main-chain polybenzoxazine (MPBz) prepolymer was synthesized using a slightly modified procedure reported by Takeichi et al [112]. In this synthesis p-aminophenol and formaldehyde was reacted in a molar ratio of 1:2 (Figure 4.1). Ishida and Low reported non-polar solvent mixtures for the synthesis of benzoxazine monomer with high yields and purity [113]. Moreover, toluene:ethanol (2:1, v/v) binary system was found to reduce gelation and increase molecular weight of main-chain polybenzoxazine prepolymers [73]. Therefore, we applied nonpolar solvent method by using toluene:ethanol system. The purpose of MPBz synthesis is to produce a scaffold for further reactions and p-aminophenol was selected deliberately, since the prepolymer is expected to possess a free phenol and amino group as end-chains. This way, polybenzoxazine prepolymer can be modified from end-chains and further reactions over phenolic group with polyetheramines and formaldehyde would yield ultimate block copolymers (Figure 4.1).

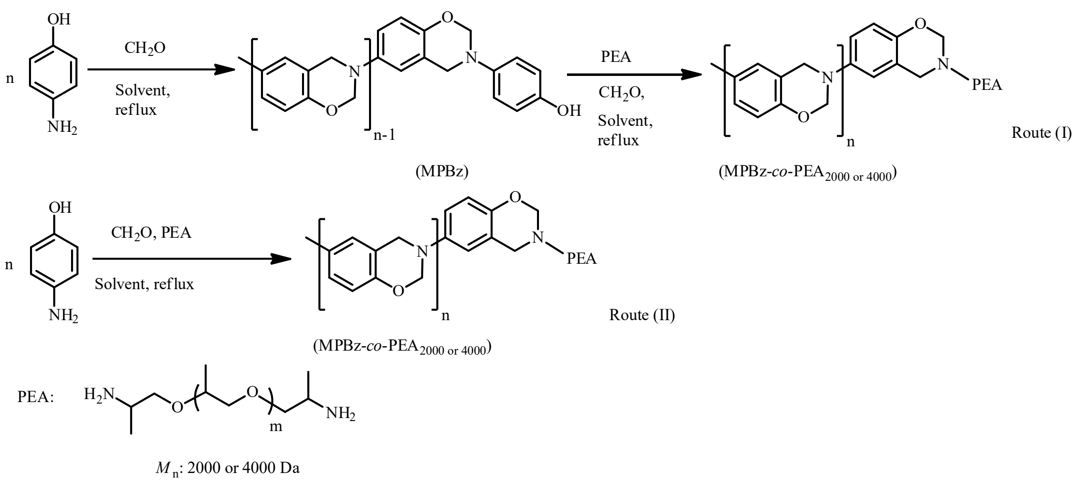


Figure 4.1 : Sequential or one-pot two step synthesis of MPBz-co-PEA2000 or 4000.

For this purpose, MPBz was reacted with two different commercially available polyetheramines (PEA), namely Jeffamine D-2000 and D-4000, having molecular weights approximately 2000 and 4000 Da, respectively. In addition to the sequential approach block copolymer formation was also performed with one-pot two-step manner which would essentially yield identical copolymers and eliminate additional separation step for MPBz. The block copolymer abbreviated as MPBz-co-PEA_{2000} and MPBz-co-PEA_{4000} according to molecular weights of the used PEAs.

Block copolymer formations were monitored by using gel-permeation chromatography (GPC). The number average molecular weight of MPBz was measured as 1364 Da which is in accordance with the literature [112]. After the copolymerization with Jeffamine D-2000 and D-4000 the molecular weights increased up to 3150 and 6160 Da, respectively in complete accordance with that of the precursor polymers indicating that one MPBz and one PEA were connected from end-chains (Table 4.1). Although, PEA has two amino groups at its two ends, the MPBz-PEA-MPBz polymer was not detected from GPC chromatogram. And the observed narrow molecular weight distribution also supports the hypothesis of one MPBz connected with one PEA and no additional chain extension was noted.

Table 4.1 : Molecular weight characteristics of MPBz and its copolymers.

Polymer	M_n^a	M_w^a	M_w/M_n^a
MPBz	1364	1466	1.08
MPBz-*co*-PEA$_{2000}$	3150	3346	1.06
MPBz-*co*-PEA$_{4000}$	6160	6641	1.08

[a]Determined by GPC according to polystyrene standards

The structure of the MPBz and MPBz-co-PEA polymers was confirmed by FTIR and ^{1}H NMR spectroscopies. Figure 4.2 shows the FTIR spectra of the copolymers and main-chain precursor. The characteristic IR bands of benzoxazines were detected for MPBz at 1230 cm^{-1} (asymmetric stretching of C–O–C) and at 1375 cm^{-1} (CH_2 wagging). Additionally, typical absorptions attributed to the tri-substituted benzene ring at 1498 cm^{-1} and out of plane bending of C–H at 927 cm^{-1} were observed, evidencing the presence of the oxazine ring in the backbone of the polymers [114]. Moreover, aromatic C–H stretching vibration band is visible at 3026 cm^{-1}. Similarly, identical IR bands can be observed for both MPBz-co-PEA polymers disclosing the oxazine ring preservation after copolymerization reactions. Apart from oxazine IR bands, etheric C–O stretching vibration of PEA block is visible as a strong band at 1084 cm^{-1} providing further evidence for the copolymer formation.

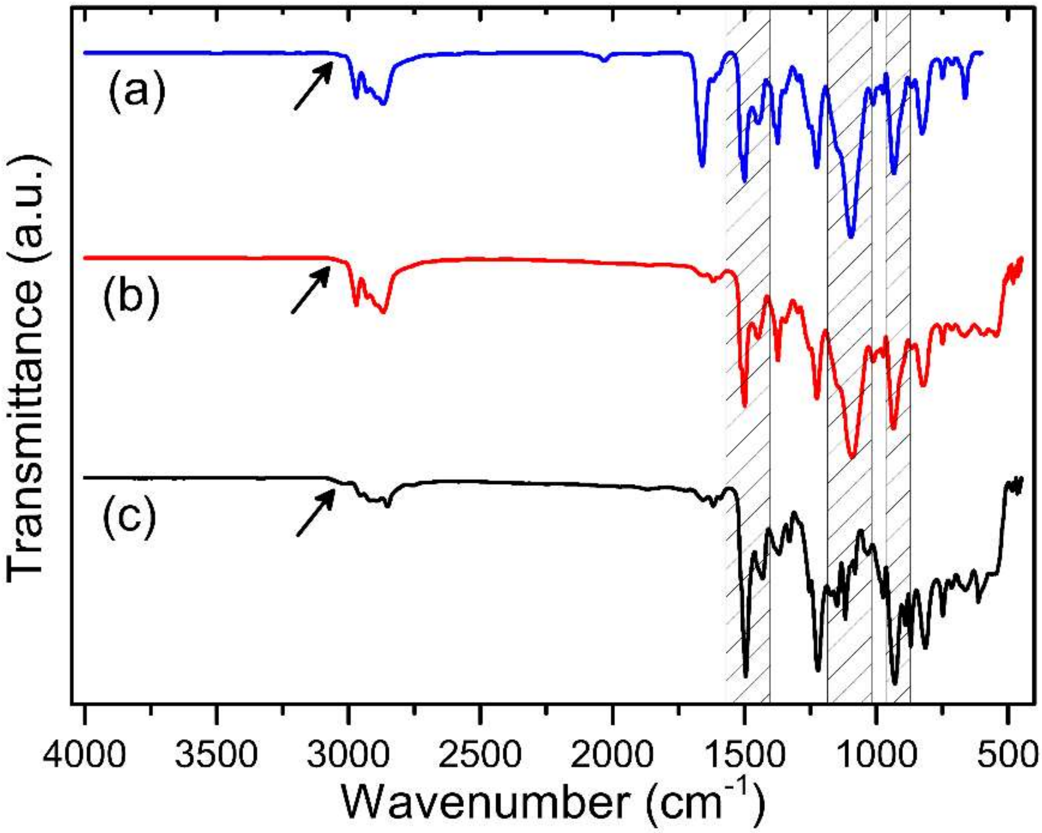


Figure 4.2 : FT-IR spectra of MPBz-co-PEA4000 (a), MPBz-co-PEA2000 (b), and MPBz (c).

The ^1H NMR spectrum of MPBz, shown in Figure 4.3, displayed the typical NMR peaks attributed to methylene protons of oxazine ring (O–CH_2–N at 5.19 ppm and Ar–CH_2–N at 4.42 ppm). The aromatic protons produced signals between 6.58–6.88 ppm. The ^1H NMR spectrum of MPBz-co-PEA_{2000} shown in Figure 4.3. Similar proton signals related to benzoxazine ring appear at 5.17 ppm for O–CH_2–N and at 4.41 for Ar–CH_2–N clearly indicate that oxazine ring preserved under copolymerization conditions. Moreover, aromatic protons slightly shifted between 6.61–6.87 ppm. Proton signals related to PEA block appear at 3.40–3.46 ppm for O–CH_2–CH_2, at 3.34 ppm for O–CH_2–CH_2–, at 1.01 ppm for branching –CH_3 groups. Methylene group attached to oxazine amino group is also visible at 2.97 ppm showing the linkage between PEA and MPBz in according with the literature [45]. It should be noted that synthesis of main-chain polybenzoxazine prepolymers is a kind of polycondensation reaction and the ring-closed ratio is around 85–95% according to the literature due to the nature of the polymerization [32, 33, 52, 73, 112, 115]. Therefore, peak areas for oxazine protons do not fit well in the NMR spectra.

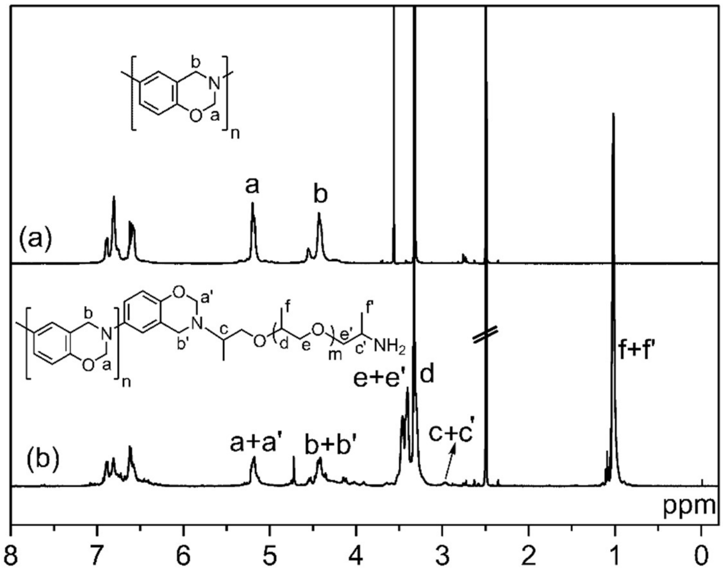


Figure 4.3 : NMR spectra of MPBz (a) and MPBz-co-PEA2000 (b).

The ROP temperatures of benzoxazines generally lay between 170-260 °C depending on the structure. Figure 4.4 shows the overlaid DSC profiles of MPBz and its copolymers. The curing of MPBz has an onset at 195 °C, end-set at 296 °C and the curing maximum at 257 °C, indicating that ring-opening process occurs in abroad temperature range, ca. 100 °C. Moreover, DSC thermogram of MPBz shows an endotherm between 123–147 °C, which may be related to evaporation of small molecule residues. These values were affected after connecting PEA to MPBz, the onset temperatures decreased in the range of 3–5 ˚C (Table 4.2) and temperature interval of whole ring-opening process dropped from 100 to 80 °C. However, the end-set and curing maximum temperatures reduced ca. 24 and 16 °C, respectively. The decrease in curing temperature can be explained as the effect of amino groups at the chain end of the block copolymer, since amines are known to catalyse ROP of benzoxazines [8, 116]. Moreover, the amount of exotherm gradually reduced with increasing PEA chain length due to the its contribution as an extra mass.

Table 4.2 : DSC[a] characteristics of MPBz and its copolymers under N_2 environment.

Polymer	Curing on-set (°C)	Curing end-set (°C)	Curing maximum (°C)	Curing exotherm (J/g)
MPBz	195	296	257	–137.5
MPBz-*co*-PEA$_{2000}$	192	272	241	– 45.7
MPBz-*co*-PEA$_{4000}$	190	275	242	–30.4

[a]DSC analyses were performed under N_2 stream (20 mL/min.) with a 10 °C/min. heating rate

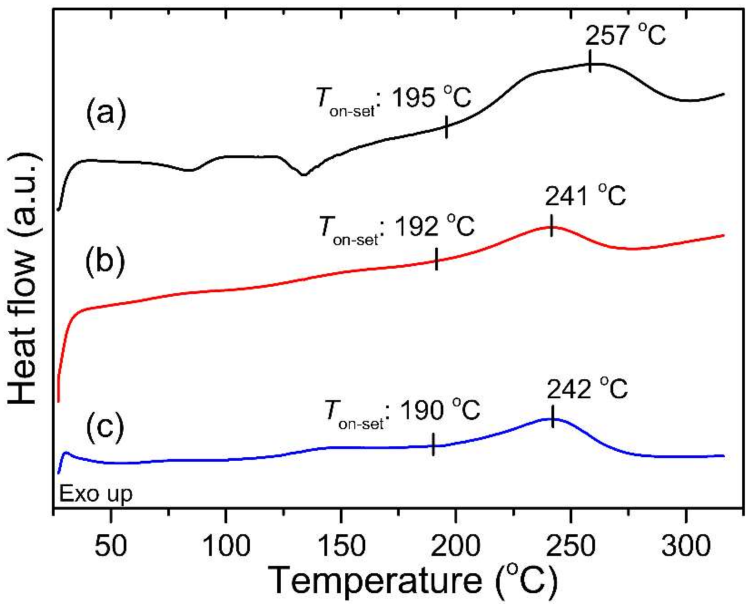


Figure 4.4 : DSC thermograms of MPBZ (a), MPBZ-co-PEA2000 (b), MPBZ-co-PEA4000 (c).

Apart from DSC behaviours of MPBz-co-PEA polymers, there are physical differences between cured MPBz and MPBz-co-PEAs. The cured MPBz has a macroporous structure and shows elastic behaviour. The MPBz network can be squeezed easily by hand and turns back to its original shape. Conversely, MPBz-co-PEA_{2000} network is more stiff than cured MPBz in non-porous form (Figure 4.5).

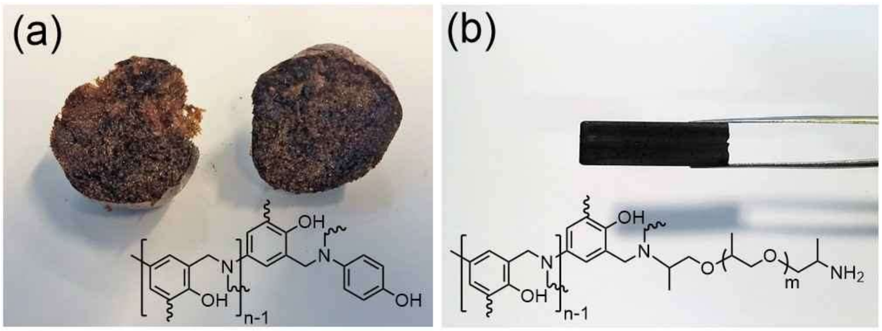


Figure 4.5 : Images of cured MPBz (a), and MPBz-co-PEA_{2000} (b)

The gaseous, presumably formed as by-products during ROP of MPBz block and captured by PEA block, is more slowly released which prevents pore formation. Thermal stabilities of the MPBz and its copolymers were investigated by thermo-gravimetric analysis (TGA) under N_2 flow (200 mL/min.). The TGA curves of cured MPBz, MPBz-co-PEA_{2000}, MPBz-co-PEA_{2000} and PEAs (D-2000 and D-4000) are shown in Figure 4.6 and the results are tabulated in Table 4.3. Moreover, derivatives of TGA curves are displayed in Figure 4.7. All the cured MPBz and its copolymers

polymers exhibited better char yields, $T_{5\%}$, and $T_{10\%}$, than PEAs. Accordingly, all the PEAs almost completely vaporized after 425 °C and only 0.02% remained at 800 °C. With the all polymers studied, the cured MPBz displayed the highest char as 67% due to the quantity of benzoxazines in per mass sample. Initial degradations of the cured MPBz-co-PEA_{2000} and MPBz-co-PEA_{4000} have identical temperatures at $T_{5\%}$, and relatively close values at $T_{10\%}$ probably owing to the thermal stability of the ether linkages. Non-functional PEAs also showed comparable initial degradation temperatures and the ether cleavage reaches to their maximum at ≈377 °C supporting the thermal stability of ether linkages. Interestingly, there are two Tmax values for the cured MPBz and the derivative TGA is a broad curve. Although this polymer has high char yield, the first Tmax value is between $T_{5\%}$ and $T_{10\%}$ temperatures and a rapid degradation is observed at initial stages. Conversely, only one Tmax is recorded at 400 °C when the same structure connects to PEA chain. Obviously, benzoxazine units significantly improves the char yield of bare PEA in accordance with previous reports. Another important point is the dependence of char yields on the molecular weight of PEA block. As seen in overlaid TGA curves, incorporation of each 2000 Da PEA unit results in the approximately 20 % decrease of the char yield. However, the initial and maximum degradation temperatures are not affected by the chain length of PEA.

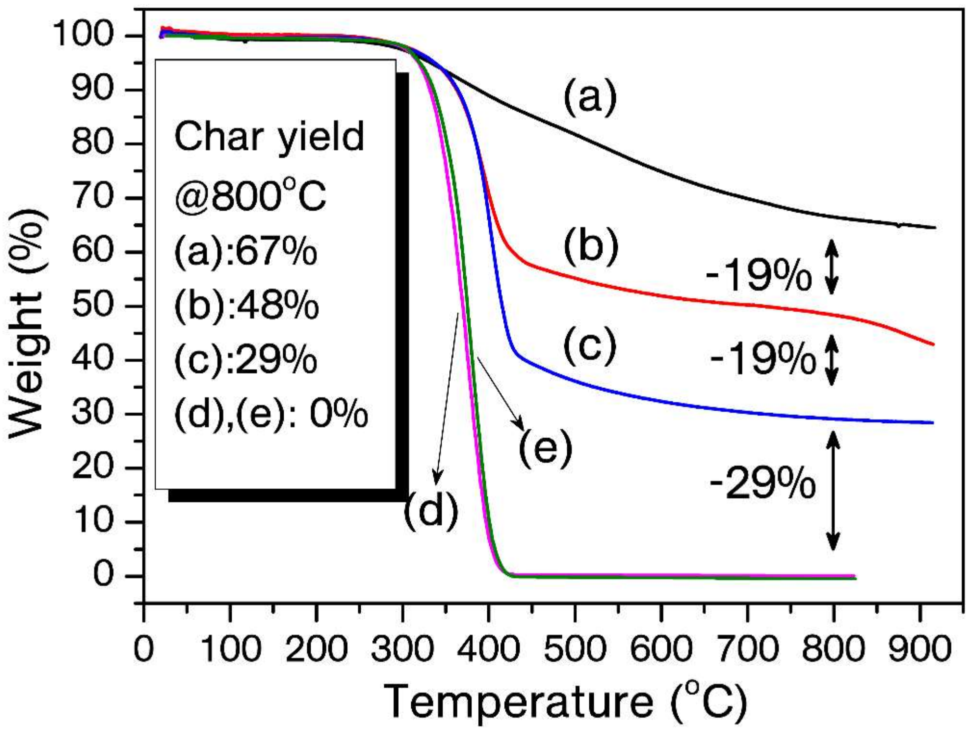


Figure 4.6 : TGA traces of cured MPBz (a), MPBz-co-PEA2000 (b), MPBz-co-PEA4000 (c) and pristine PEA (D-2000) (d), PEA (D-4000) (e).

Table 4.3 : Thermal characteristics of cured MPBz and its cured copolymers determined by TGA

Polymer	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Y_c (%)
Cured[a] MPBz	339	389	358, 533	67
Cured[a] MPBz-*co*-PEA$_{2000}$	339	363	393	48
Cured[a] MPBz-*co*-PEA$_{4000}$	339	363	401	29
PEA (D-2000)	319	332	376	≈0
PEA (D-4000)	319	334	377	≈0

[a]Curing was performed in TGA at 240 °C for 15 min. under N_2 stream (200 mL/min.)
$T_{5\%}$: The temperature for which the weight loss is 5%
$T_{10\%}$: The temperature for which the weight loss is 10%
T_{max}: The temperature for maximum weight loss extracted from figure 4.7.
Y_c: Char yields at 800 °C under nitrogen atmosphere

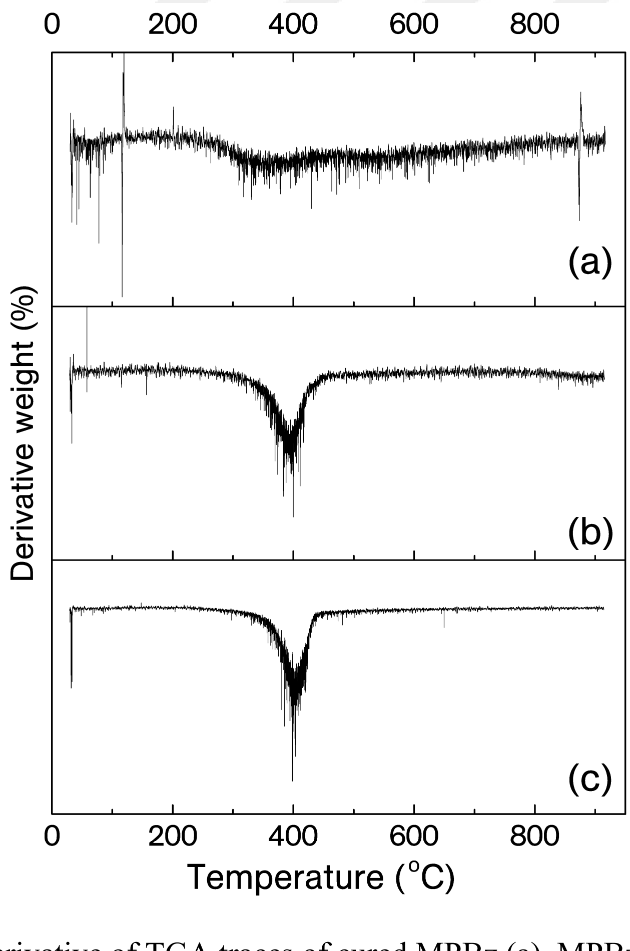


Figure 4.7 : Derivative of TGA traces of cured MPBz (a), MPBz-co-PEA2000 (b) and MPBz-co-PEA4000 (c).

5. CONCLUSION

In conclusion, we have demonstrated that block copolymers of polybenzoxazines with polyetheramines can be synthesized from main-chain polybenzoxazines either in one-pot two-step or stepwise pathways. The synthetic methodology described here is relatively easy, which can be achieved by using simple and commercially available chemicals such as 4-hydroxyaniline, formaldehyde and polyetheramines (Jeff amines) by a straightforward process. In this context, the design flexibility of benzoxazine chemistry can provide a vast number of different possible block copolymers giving opportunity to further extend the described approach for the fabrication of thermally stable materials. As demonstrated, copolymerization of MPBz with jeffamines has a drastic impact on the physical behaviours compared to pristine MPBz. Apparently, the porous structure of MPBz can easily be converted to smooth films. Also, thermal stability of jeffamines significantly increased in the copolymer form as one can expect from the contribution of benzoxazines. Consequently, the most appealing part of this strategy is its simplicity and low cost of the chemicals that can be converted into advanced materials using the conditions outlined here in one-pot.

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CURRICULUM VITAE

Name Surname : Zeynep DELİBALLI

Place and Date of Birth : İstanbul / 16.08.1991

E-Mail : zeynepdeliballi@gmail.com

EDUCATION

- **B.Sc.** : 2016, İstanbul Tecnical University, Faculty of Sience and Letters, Chemistry Department
- **M.Sc.** : 2018, İstanbul Tecnical University, Facultyof Sience and Letters, Chemistry Department

PUBLICATIONS, PRESENTATIONS ON THE THESIS:

- **Deliballı, Z., Kışkan, B., Yağcı, Y.** 2018. Main-chain Benzoxazine Precursor Block Copolymers , *Polymer Chemistry*, 9(2), 178-183.
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