ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

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M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

BİYO BAZLI BİLEŞİKLERDEN AMİD İÇEREN POLİBENZOKSAZİNLERİN SENTEZİ VE KARAKTERİZASYONU

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MART 2024

Emine YILMAZ, a M.Sc. student of İTU Graduate School student ID 515211018, successfully defended the thesis/dissertation entitled “SYNTHESIS AND CHARACTERIZATION OF AMIDE CONTAINING POLYBENZOXAZINES FROM BIO-BASED COMPOUNDS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 04 February 2024
Date of Defense : 18 March 2024

To my beloved family and friends,

FOREWORD

First and foremost, I would like to express my sincere gratitude to my thesis advisor, Prof. Dr. Barış KIŞKAN, for his immense knowledge, guidance, and motivation. His guidance has always supported me throughout my Master's degree, my research, and the writing of this thesis. I would like to thank him very much for his support and patience during this process.

I would also like to thank Prof. Dr. Yusuf YAĞCI for his support of my research, continuous encouragement, and sharing his deep knowledge with great motivation. It was truly an honor for me to get a chance to work with him. I am deeply sorry for his loss and will remember him with love and great respect.

A special thanks to the members of Yağcı Group for all their help, support, and friendship. Particularly, Sevinç GÜLYÜZ, Zeynep ARSLAN, Zeynep DELİBALLI, Emirhan GENÇOSMAN, Dr. Kerem KAYA, Dr. Hüseyin Cem KILIÇLAR, Yüsra Bahar ÇAKIR, Sena ERMİŞ, Cansın Birsen BULDUM, and all others for their help during my experiments. We have worked in the laboratory together with pleasant experience, and I have benefited from their knowledge and experience.

I would like to express my gratitude to my dear friends Çiğdem Buse ORAL, Yıldız AYDIN, and Gamze AYDIN for stimulating discussions and all the good memories we shared during our undergraduate and graduate education.

Most importantly, none of this could have happened without my family. I must express my profound gratitude to my parents, Gülten YILMAZ, Bescet YILMAZ, my sister Elif YILMAZ YILDIRIM, my brother Emre YILMAZ, his wife Zeynep KORKMAZ YILMAZ, and my niece Evra YILDIRIM, for providing me during my education and for their endless support throughout my entire life. They encouraged me, and I owe a thank them for my success because of their constant support.

This study was performed under the supervision of Prof. Dr. Barış KIŞKAN to be presented as a master of science thesis in the chemistry-polymer science and technology department of Istanbul Technical University. Furthermore, the study was supported financially by the Istanbul Technical University Research Fund (Project No. TYL-2022- 44182).

We would also like to thank the TÜBİTAK Research Fund for their support in providing project 221Z183.

February 2024 | Emine YILMAZ
(Chemist)

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ABBREVIATIONS

ACN : Acetonitrile
BMI : Bismaleimide
B-a : Bisphenol-A
Bz : 1,3-Benzoxazine
Cou-Bz : Coumarine-Benzoxazine
Da : Dalton
DA : Diels-Alder
r-DA : Retro-Diels-Alder
DHC : 3,4-Dihydrocoumarine
DSC : Differential Scanning Calorimeter
EtOAc : Ethyl acetate
EtOH : Ethanole; ethyl alcohol
FFA : Furfurylamine
FTIR : Fourier Transform Infrared Spectroscopy
GPC : Gel Permeation Chromatography
HMTA : Hexamethylenetetramine
^{1}H-NMR : Nuclear Magnetic Resonance Spectroscopy
HY : Hydrogen Containing Compound
MCBP : Main Chain Benzoxazine Precursor
PA : Polyamide
PBz : Polybenzoxazine
PC : Polycarbonate
PET : Polyethyleneterephthalate
ROP : Ring Opening Polymerization
TGA : Thermogravimetric Analyzer
THF : Tetrahydrofuran

SYMBOLS

Tg	**:** Glass Transition Temperature
T_{max}	**:** Curing Maximum
T_{cure}	**:** Polymerization Temperature
$T_{5\%}$	**:** The temperature of which the weight loss is 5%.
$T_{10\%}$	**:** The temperature of which the weight loss is 10%.
T_c	**:** The char yield at 800 ^{O}C.

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SYNTHESIS AND CHARACTERIZATION OF AMIDE CONTAINING POLYBENZOXAZINES FROM BIO-BASED COMPOUNDS

SUMMARY

There are three classes of polymers, natural, semi-synthetic, and synthetic, depending on the formation. According to their response to heat, synthetic polymers are further divided into thermosets or thermoplastics. While thermoset materials are quite resistant to high temperatures, thermoplastic materials exhibit melting points, softening points and therefore become fluid. Polyethylenes, polypropylenes, polystyrenes and polycarbonates are in the thermoplastic polymers class, while silicone, phenol-formaldehyde resins, oxazolines, epoxies, bismaleimides (BMI), and unsaturated polyesters are in the thermoset polymers class.

Phenolic resins in the thermoset class stand out with their various properties. Also, the phenol-formaldehyde resins are remarkable in terms of being the first synthetic polymers synthesized. Phenolic resins have properties such as heat resistance, high mechanical strength, dimensional stability, high resistance to water, acids, and a variety of solvents, and flame resistance. Besides, while they burn, they produce little smoke. These resins are used in fields such as aerospace, computer, automotive and adhesives, electronics, conductive polymer structures.

Formaldehyde and phenol, or substituted phenol, are required for the synthesis of phenolic resins. There are different forms of phenol-formaldehyde resins. These are novolak and resol resins. In addition to certain molar ratios of formaldehyde and phenol, novolak-type resin is formed in the presence of an acid catalyst. In contrast, resol-type resin is obtained similarly according to the ratios and in the presence of a base catalyst. Apart from the relative molar ratios of phenol and formaldehyde, pH values are one of the other factors that affect this circumstance.

Phenolic resin research, which started at the beginning of the 20th century, shows the various positive properties of these resins, but also has some shortcomings. Brittleness, formation of by-products such as water and ammonia during curing, use of acid or base catalysts to prepare the resin that may cause corrosion of process equipment, and low shelf life can be shown as the shortcomings of these resins. A newly developed class of materials, known as polybenzoxazines, offers a solution to this problem.

In the past ten years, polybenzoxazines have emerged as an alternative to phenolic resins owing to their distinguishable features in comparison to many conventional resins. Polybenzoxazines are polymers of benzoxazine monomers, which are halogen-free compounds and they have properties such as; (i) stability against various chemicals and high temperatures, (ii) near-zero volumetric change during curing, (iii) good thermal stability and mechanical strength, (iv) high glass transition temperature (T_g), (v) low water uptake and dielectric constants, (vi) high char yield, (vii) no strong acid catalysts required for curing, and (viii) storage at room conditions, (ix) low toxicity. Also, from their corresponding monomers, polybenzoxazines are readily synthesized. Conventionally, polybenzoxazines can usually be synthesized using phenols, primary amines, and formaldehydes. Apart from this, there are also synthesis

methods used, yet classical synthesis is preferred due to reasons such as the easy availability of these required substances and the easy removal of by-products after synthesis. In this way, various benzoxazine monomers and polymers have been synthesized. Polybenzoxazines are employed as composites, blends, self-healing materials, and high-performance electronic circuit boards in industrial areas, particularly in the aerospace industry, because of their crucial features.

Despite the many advantages provided by benzoxazines, the fact that most of their monomers are still obtained from petroleum-based sources raises environmental concerns. Bisphenol-A, which is frequently used in the synthesis of benzoxazine, has carcinogenic properties as it mimics the estrogen hormone in humans, and therefore its use in food supply or storage containers is limited. Therefore, petroleum-based benzoxazines generate the need for new synthesis approaches, both to limit the use of bisphenol-A and its derivatives, as in the example given and because of their non-renewability and high cost. The trend towards bio-based benzoxazine syntheses obtained from natural sources has increased considerably in the last decade. The natural phenol sources essential for the synthesis of bio-based benzoxazine involve arbutin, cardanol, chavicol, coumarine, eugenol, resorcinol, and vanillin. Amines, which are another reactant required for the synthesis of benzoxazine, can be obtained from natural sources such as furfurylamine, chitosan, rosin, and agricultural by-products. Benzoxazines synthesized from natural sources attract interest because they offer a wide range of molecular design flexibility, low water absorption, low surface free energy, no or limited shrinkage during polymerization, high stability, and no by-product formation during polymerization.

Among all the research on substituents in benzoxazine molecules, amide-containing benzoxazines have gained interest in recent times since such structures provide renewable systems with lots of benefits. Coumarines are natural organic compounds obtained from plant sources such as tonka bean, vanilla grass, sweet wood chips, mullein, and sweet grass, and their use in the synthesis of benzoxazine makes these resins bio-based. Various advantages of coumarine include providing design flexibility for further expansion. Additionally, furfurylamines, which are synthesized from furfural, can also be used as an amine source in the synthesis of benzoxazine. The use of furfurylamine-based polybenzoxazines, which have excellent thermal stability, improved cross-linking ability, a high char yield, and self-destruction behavior, is gaining popularity. Apart from the properties of the reactants used for synthesis, the synthesis method is also significant. Bio-based and monofunctional benzoxazines can be synthesized both by the one-pot method and stepwise. Due to its minimal impact on reaction yield, this facilitates synthesis. The one-pot method retains both energy and time and can be preferred for renewable systems.

In this study, bio-based coumarine-benzoxazines were synthesized. 3,4-dihydrocoumarine (DHC) and furfurylamine (FFA), which is a primary amine, were used as reactants to synthesize phenolic amide through a ring-opening reaction. Afterward, the phenolic amides were reacted with formaldehyde and furfurylamine, and thus, amide-containing benzoxazines occurred. This reaction was done with two different methods, which are one-pot and stepwise methods. Furthermore, the monofunctional bio-based coumarine-benzoxazine reacted with bismaleimide (BMI) via the Diels-Alder reaction in order to give polybenzoxazine. Then, all monomers and polymer precursors were characterized by ^{1}H-NMR, ^{13}C-NMR, and FT-IR spectroscopies. Besides, the curing behaviors and thermal stabilities of the compounds were analyzed by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). As a consequence, polybenzoxazines, which are the new thermosetting resins, address concerns about the danger of depletion of natural resources and increasing oil prices, are used in a wide variety of fields, spanning from biomedical uses to composite materials and the aviation industry to adhesives, and are promising as renewables for the future.

BİYO BAZLI BİLEŞİKLERDEN AMİD İÇEREN POLİBENZOKSAZİNLERİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Oluşumuna bağlı olarak doğal, yarı sentetik ve sentetik olmak üzere üç polimer sınıfı vardır. Isıya tepkilerine göre sentetik polimerler ayrıca termosetler veya termoplastikler olarak ikiye ayrılır. Termoset malzemeler yüksek sıcaklıklara oldukça dayanıklı iken termoplastik malzemeler erime noktaları, yumuşama noktaları gösterir ve dolayısıyla akışkan hale gelir. Termoset polimerlere aynı zamanda termoset reçineler de denir. Polietilenler, polipropilenler, polistirenler ve polikarbonatlar termoplastik polimerler sınıfında yer alırken silikon, fenol-formaldehit reçineleri, oksazolinler, epoksiler, bismaleimidler (BMI) ve doymamış polyesterler termoset polimerler sınıfındadır. Kovalent olarak bağlı tekrarlayan birimler, termoset polimerlerin çapraz bağlı yapılarına yol açar. Bundan dolayı, yüksek sıcaklık veya reaktif bir çözücü karşısında çözünmez ve erimezler. Yüksek sıcaklıklar kovalent bağların kırılmasına neden olur, ancak buna rağmen termosetler akma özelliği göstermezler. Bundan dolayı, kovalent bağlarla oluşturulan çapraz bağlar termoset polimerlerin yapısını oluşturmaktadır.

Termoset sınıfında yer alan fenolik reçineler çeşitli özellikleriyle ön plana çıkmaktadır. Ayrıca fenol-formaldehit reçineleri sentezlenen ilk sentetik polimerler olması açısından dikkat çekicidir. Fenolik reçineler ısı direnci, yüksek mekanik mukavemet, boyutsal stabilite, suya, asitlere ve çeşitli solventlere karşı yüksek direnç ve alev direnci gibi özelliklere sahiptir. Ayrıca yanarken çok az duman çıkarırlar. Bu reçineler havacılık, bilgisayar, otomotiv ve yapıştırıcılar, elektronik, iletken polimer yapılar gibi alanlarda kullanılmaktadır.

Fenolik reçinelerin sentezi için formaldehit ve fenol veya sübstitüe edilmiş fenol gereklidir. Fenol-formaldehit reçinelerinin farklı formları vardır. Bunlar novolak ve resol reçineleridir. Formaldehit ve fenolün belirli molar oranlarına ek olarak, bir asit katalizörünün varlığında novolak tipi reçine oluşur. Bunun aksine, resol tipi reçine, oranlara göre ve bir baz katalizör varlığında benzer şekilde elde edilir. Fenol ve formaldehitin bağıl molar oranları dışında pH değerleri de bu durumu etkileyen diğer faktörlerden biridir.

20. yüzyılın başında başlayan fenolik reçine araştırmaları, bu reçinelerin çeşitli olumlu özelliklerinin yanı sıra bazı eksikliklerini de göstermektedir. Kırılganlık, kürleme sırasında su ve amonyak gibi yan ürünlerin oluşması, proses ekipmanlarının korozyonuna neden olabilecek reçineyi hazırlamak için asit veya baz katalizörlerin kullanılması ve raf ömrünün düşük olması bu reçinelerin eksiklikleri olarak gösterilebilir. Ayrıca, kürleme için gereken sıcaklıklar oldukça yüksektir. Polibenzoksazinler olarak bilinen yeni geliştirilen bir malzeme sınıfı bu soruna bir çözüm sunmaktadır.

Son on yılda polibenzoksazinler birçok geleneksel reçineye göre ayırt edici özellikleri nedeniyle fenolik reçinelere alternatif olarak ortaya çıkmıştır. Polibenzoksazinler halojen içermeyen bileşikler olan benzoksazin monomerlerinin polimerleridir ve şu özelliklere sahiptirler; (i) çeşitli kimyasallara ve yüksek sıcaklıklara karşı stabilite, (ii)

kürleme sırasında sıfıra yakın hacimsel değişim, (iii) iyi termal stabilite ve mekanik mukavemet, (iv) yüksek camsı geçiş sıcaklığı (T_g), (v) düşük su emme ve dielektrik sabitleri, (vi) yüksek kömür verimi, (vii) kürleme için güçlü asit katalizörlerine gerek olmaması ve (viii) oda koşullarında saklama, (ix) düşük toksisite. Ayrıca karşılık gelen monomerlerden polibenzoksazinler kolaylıkla sentezlenir. Geleneksel olarak polibenzoksazinler genellikle fenoller, birincil aminler ve formaldehitler kullanılarak sentezlenebilir. Bunun dışında kullanılan sentez yöntemleri de vardır ancak gerekli olan bu maddelerin kolay elde edilebilmesi ve sentez sonrası yan ürünlerin kolaylıkla uzaklaştırılması gibi nedenlerden dolayı klasik sentez tercih edilmektedir. Bu sayede çeşitli benzoksazin monomerleri ve polimerleri sentezlenmiştir. Polibenzoksazinler, önemli özellikleri nedeniyle endüstriyel alanlarda, özellikle havacılık endüstrisinde kompozit, karışım, kendi kendini onaran malzeme ve yüksek performanslı elektronik devre kartları olarak kullanılmaktadır.

Polibenzoksazin sentezi 1,3- benzoksazin olarak adlandırılan monomerler üzerinden katyonik halka açılma polimerizasyonu ile gerçekleşmektedir. Benzoksazinler, yapısında oksijen ve nitrojen atomu bulunduran heterosiklik altı üyeli bir oksazin halkası içerir ve bu oksazin halkası bir benzen halkasına bağlanır. Bu aromatik oksazinlerin 1,2-, 1,3- ve 1,4- olmak üzere çeşitli izomerleri bulunmaktadır. Polibenzoksazinlerin sentezi yalnızca 1,3-benzoksazinler ile gerçekleşir, bunun nedeni, yalnızca bu pozisyondaki türevler halka açılma polimerizasyonu için aktiftir.

Benzoksazinlerin sağladığı birçok avantaja rağmen monomerlerinin çoğunun hala petrol bazlı kaynaklardan elde edilmesi çevresel kaygıları artırmaktadır. Benzoksazin sentezinde sıklıkla kullanılan Bisfenol-A, insanlarda östrojen hormonunu taklit etmesi nedeniyle kanserojen özelliğe sahip olduğundan gıda tedariği veya saklama kaplarında kullanımı sınırlıdır. Bu nedenle petrol bazlı benzoksazinler, hem verilen örnekte olduğu gibi bisfenol-A ve türevlerinin kullanımını sınırlamak hem de yenilenememeleri ve yüksek maliyetleri nedeniyle yeni sentez yaklaşımlarına ihtiyaç duymaktadır. Doğal kaynaklardan elde edilen biyo bazlı benzoksazin sentezlerine yönelik eğilim son on yılda önemli ölçüde artmıştır. İlk kez kardanol bazlı benzoksazin sentezlenerek doğal kaynaklardan elde edilen biyo bazlı benzoksazin elde edilmiştir. Bu sentezde, terpendifenol ham madde olarak kullanılmıştır. Ticari polimerlerin su veya ısı direncini arttırmak amacıyla terpendifenol değerli bir katkı maddesi olarak önerilmiştir. Biyo bazlı ilk benzoksazin olan kardanol-benzoksazin sentezinden sonra, çeşitli sentezler de yapılmıştır. Çeşitli yenilenebilir kaynaklar araştırılmış ve bu kaynaklardan çeşitli polimer sistemleri geliştirilmiştir. Örnek olarak, bitkisel yağlar, selüloz, nişasta, kitosan, izosorbit verilebilir. Bu malzemeler endüstriyel olarak da tedarik edilebilmektedir. Biyo bazlı benzoksazin sentezi için gerekli olan doğal fenol kaynakları arasında arbutin, kardanol, katekol, kumarin, öjenol, resorsinol ve vanilin bulunur. Kaju fıstığının kabuk sıvısından elde edilen kardanol, yüksek mekanik performans, güçlü kimyasal direnç ve düşük dielektrik sabiti gibi özellikler gösterir. Ayrıca, katekol, midye yapışkan proteinlerinde bulunan katekolik bir amino asit olup yapışkanın güçlü, suya dayanıklı yapışmasından ve hızlı kürlenmesinden sorumludur. Akabinde, karanfil, tarçın, fesleğen, hindistan cevizi gibi çeşitli esansiyel yağlardan elde edilen öjenol, yapısal olarak sterik engellere sahiptir ve orto ve para olmak üzere her iki pozisyon da sentez için uygun değildir ve bu nedenle teorik olarak öjenol bazlı benzoksazinlerin polimerizasyonu zordur. Bu nedenle, öjenol bazlı benzoksazinler, performanslarını arttırmak için grafen oksit, karbon nanotüpler ve çok yüzlü oligomerik silseskioksan gibi nano dolgularla harmanlarak sentezlenebilmektedir. Diğer bir örnek olarak vanilin verilebilir. Vanilin, sarmaşık orkidesinden elde edilmekte olup sanayide kullanılan vanilinin büyük bir kısmı guaiakolden sentezlenmektedir. Aldehit grubu içermelerinden dolayı vanilin, benzoksazin monomerine fonksiyonel bir grup verir ve çapraz bağlanmayı arttırır. Benzoksazin sentezi için gerekli olan diğer bir reaktan olan aminler furfurilamin, kitosan, rosin gibi doğal kaynaklardan ve tarımsal yan ürünlerden elde edilebilmektedir. Doğal kaynaklardan sentezlenen benzoksazinler geniş yelpazede moleküler tasarım esnekliği, düşük su emme, düşük yüzey serbest enerjisi, polimerizasyon sırasında büzülmenin olmaması veya sınırlı olması, yüksek stabilite ve polimerizasyon sırasında yan ürün oluşmaması nedeniyle ilgi çekmektedir.

Benzoksazin moleküllerindeki sübstitüentler üzerine yapılan tüm araştırmalar arasında, bu tür yapıların yenilenebilir sistemlere birçok fayda sağlaması nedeniyle, amid içeren benzoksazinler son zamanlarda ilgi görmüştür. Kumarinler tonka fasulyesi, vanilya otu, tatlı ağaç talaşı, sığırkuyruğu ve tatlı çim gibi bitki kaynaklarından elde edilen doğal organik bileşiklerdir ve benzoksazin sentezinde kullanılmaları bu reçineleri biyo bazlı hale getirmektedir. Kumarinin çeşitli avantajları arasında daha fazla genişleme için tasarım esnekliği sağlanması yer alır. Ayrıca furfuralden sentezlenen furfurilaminler de benzoksazin sentezinde amin kaynağı olarak kullanılabilmektedir. Mükemmel termal stabiliteye, geliştirilmiş çapraz bağlanma yeteneğine, yüksek kömür verimine ve kendi kendini yok etme davranışına sahip olan furfurilamin bazlı polibenzoksazinlerin kullanımı popülerlik kazanmaktadır. Sentez için kullanılan reaktanların özelliklerinin yanı sıra sentez yöntemi de önemlidir. Biyo bazlı ve tek fonksiyonlu benzoksazinler hem tek kap yöntemiyle hem de aşamalı olarak sentezlenebilir. Reaksiyon verimi üzerindeki minimum etkisi nedeniyle bu, sentezi kolaylaştırır. Tek kap yöntemi hem enerjiyi hem de zamanı korur ve yenilenebilir sistemler için tercih edilebilir.

Ayrıca, Diels-Alder (DA) reaksiyonu organik bileşiklerde en yaygın reaksiyonlardan biridir. Bu reaksiyon, 6 üyeli bir halka oluşturmak üzere bir konjüge dien ve bir dienofilin uyumu sonucu gerçekleşen $[4\pi + 2\pi]$ sikloadisyon reaksiyonudur. Retro-Diels-Alder reaksiyonu (rDA) ise Diels-Alder reaksiyonunun mikroskobik olarak tersidir ve bir siklohekseni bir dien ve dienofiline geri dönüştürür. Ayrıca, benzoksazin ana zincirleri Diels-Alder reaksiyonuna dâhil edilebilir. Literatürde furan veya maleimid zincirli benzoksazinlerle ilgili araştırmalar mevcuttur. Furan heterohalkasının sahip olduğu dienik yapı, Michael katılmaları, vinil reaksiyonları ve Diels-Alder (DA) siklo katılmaları gibi reaksiyonlarda kullanılmasına izin vermesi nedeniyle bu yapıları çekici kılmaktadır. Bu nedenle, sentezlenen biyo bazlı benzoksazin ile DA ve retro-DA reaksiyonlarına girme yeteneğine sahiptirler. Ayrıca, furan içeren benzoksazinler ve bismaleimidlerin kullanıldığı Diels-Alder reaksiyonları sonucunda; retro-DA reaksiyonu sayesinde nispeten düşük ayrışma sıcaklığı, kolay işlenebilirlik ve iyi alev geciktiricilik gibi özellikler sağlar. Bu özellikleri dolayısıyla, geri dönüştürülebilir ağlar, kendi kendini onaran malzemeler, kimyasal geri dönüşüm uygulamaları ve yüksek performanslı malzemeler dâhil olmak üzere çeşitli potansiyel uygulamalar sağlayabilir. Ek olarak, furan türevlerinin yenilenebilir kaynaklardan elde edilmesi de, furan/maleimid çiftinin sürdürülebilirliği ve yenilebilirliği gibi yaklaşımlara olanak sağlaması açısından dikkat çekicidir.

Bu çalışmada biyo bazlı kumarin-benzoksazinler sentezlendi. Birincil bir amin olan 3,4-dihidrokumarin (DHC) ve furfurilamin (FFA), bir halka açılma reaksiyonu yoluyla fenolik amidi sentezlemek için reaktanlar olarak kullanıldı. Daha sonra fenolik amidler formaldehit ve furfurilamin ile reaksiyona sokularak amid içeren benzoksazinler meydana geldi. Bu reaksiyon tek kap ve aşamalı yöntemler olmak üzere iki farklı yöntemle yapıldı. Ayrıca, tek işlevli biyo bazlı kumarin-benzoksazin, polibenzoksazin vermek üzere Diels-Alder reaksiyonu yoluyla bismaleimid (BMI) ile reaksiyona girdi. Daha sonra tüm monomerler ve polimer öncü, ^{1}H-NMR, ^{13}C-NMR ve FT-IR spektroskopileri ile karakterize edildi. Ayrıca bileşiklerin kürlenme davranışları ve termal stabiliteleri diferansiyel taramalı kalorimetre (DSC) ve termogravimetrik analiz (TGA) ile analiz edildi. Sonuç olarak, doğal kaynakların tükenmesi ve artan petrol fiyatları tehlikesine yönelik endişeleri gideren yeni ısıyla sertleşen reçineler olan polibenzoksazinler, biyomedikal kullanımlardan kompozit malzemelere ve havacılık endüstrisinden yapıştırıcılara kadar çok çeşitli alanlarda kullanılmaktadır ve gelecek için yenilenebilir enerji kaynakları olarak ümit vericidir.

1. INTRODUCTON

Phenolic resins, which are resol and novolak types, have been widely utilized in the past century. Some of the main reasons for their widespread use can be attributed to their low cost, ease of production, and industrial viability [1-3]. These materials have various desired features such as dimensional stability, resistance to various solvents, good mechanical strength, and flame retardance; nevertheless, they have several shortcomings such as brittleness, the use of acid or base catalysts to prepare the resin that can cause corrosion of processing equipment, the formation of by-products such as water, ammonia during curing, and low shelf life [4]. The development of benzoxazines and polybenzoxazines offers a solution to this problem. For instance, the curing of benzoxazine produces limited harmful by-products and does not require a catalyst [4, 5]. Additionally, they resolve the issues related to the release of formaldehyde by-products, which can typically take place during the curing process [6-9].

Benzoxazines, which are composed of a benzene ring and its fused oxazine, are considered the new class of thermosetting resins. Polybenzoxazines are polymers of benzoxazine monomers formed by ring-opening polymerization. The fact that they are halogen-free compounds allows them to protect their stability against high temperatures and various chemicals. In addition, they have low water absorption values, a high glass transition temperature (Tg), near-zero volume changes, high mechanical performance, and a very high char yield [10]. Benzoxazines can be used in many areas, such as aerospace, electronic packaging materials, transportation industry, composite material manufacturing, adhesives, and powder coating, owing to their unique features [11, 12].

In addition to the extraordinary properties of polybenzoxazines, the ease of synthesis of their corresponding monomers makes them tempting. Various methods are available for synthesizing benzoxazine, yet classical synthesis is commonly preferred. The availability of quite diverse phenols and amines and the ease of elimination of by-products after synthesis make classical synthesis preferable. According to this classical synthesis, benzoxazines can be easily synthesized with the reaction of phenol, formaldehyde, and amines [4]. The classical synthesis reaction with primary amines, phenols, and formaldehyde is shown in Figure 1.1.

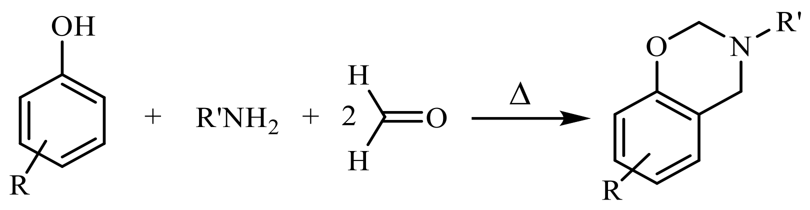


Figure 1.1: Classical benzoxazine synthesis reaction.

In spite of the many positive properties that benzoxazines provide, many of their monomers are still obtained from petroleum-based sources. The utilization of bisphenol-A and analogous compounds poses an issue for the production of conventional benzoxazines. Bisphenol-A is a chemical compound produced by the phenol and acetone's condensation reaction, and it is mostly used in the production of several plastics such as epoxy resins, polycarbonate, and polybenzoxazines. Also, bisphenol-A is a xenoestrogen that shows hormone-like properties and imitates the effects of estrogen in the body [13, 14]. Therefore, bisphenol-A poses a significant health hazard. For these reasons, studies on non-petroleum-based monomer synthesis in benzoxazines have proliferated in importance in recent years.

Petroleum-based benzoxazines give rise to a requirement for novel synthesis approaches owing to their non-renewable nature and high cost. Renewable, recyclable polymer materials are crucial for not only decreasing environmental pollution but also increasing the use of resources [15]. Therefore, bio-based benzoxazine syntheses are being developed. Numerous phenols and amines required for bio-based benzoxazine synthesis can be obtained from natural sources. The places where natural phenols are obtained can be stated as follows: arbutin, a plant from the Ericaceae family [16], cardanol, from the liquid found in cashew nut shells [17], chavicol, from basil oil or anise basil [18], coumarine, from tonka bean, deer tongue, sweet woodchip, or mullein [19], eugenol, from clove oil [20], resorcinol and pyrogallol, from tannic acid [21], and vanillin, from vanilla bean [22]. Amines are similarly obtainable from natural sources. These natural amines can be listed as follows too: furfurylamine synthesized from furfural [23], chitosan synthesized from chitin by deacetylation reaction [24], and rosin from pine trees [25]. These listed natural-origin phenols and amines have been used in benzoxazine syntheses with success. Thus, benzoxazine chemistry provides rich molecular design and therefore it is clear that environmentally friendly benzoxazine synthesis can be achieved [26].

Bio-based benzoxazines also have coumarine, which is a crucial natural source of phenol. Coumarines are naturally occurring heterocyclic compounds that are generally present in plants such as tonka beans, vanilla grass, the leaves of many cherry blossom trees, and sweet grass [19]. Namely, coumarines are readily accessible in nature. The importance of using coumarine in the synthesis of naturally sourced benzoxazine is that it assures a straightforward chemical reaction pathway in the synthesis. Furthermore, furfurylamine is also used for benzoxazine synthesis as the other biosource. Furfurylamine is derived from corncobs and wheat bran, which are agricultural by-products. It is synthesized from furfural industrially [27]. It is shown that utilizing furfurylamine increases the glass transition temperature (Tg), crosslinking density, and thermal stability [28].

Moreover, natural-origin benzoxazine syntheses can occur in a variety of ways, either in a one-pot or in multiple steps. There are synthesis steps that require three, four, five, or even more steps, but this is impractical for use during synthesis. In the field of benzoxazine synthesis, the one-pot method is, although not always, considered to be a more practical and environmentally friendly approach compared to the stepwise method. This is because the one-pot method allows for the direct synthesis of the product in one chemical reaction.

In this thesis, bio-based coumarine-benzoxazine monomers and polymers were synthesized in both one-pot and two-step approaches by using 3,4-dihydrocoumarine and furfuryl amine compounds. It has been shown that, in addition to the two-step synthesis method, the one-pot method can also be valid. Polybenzoxazines were obtained from monomers by curing and the Diels-Alder reaction. Since it is a monofunctional benzoxazine monomer, a low-molecular-weight oligomer was obtained after the Diels-Alder reaction and was characterized.

2. THEORETICAL PART

This section includes brief information about thermoset polymers, benzoxazines and their historical evolution, the synthesis of monofunctional and multifunctional benzoxazines, and the ring-opening polymerization of benzoxazines. Furthermore, a short introduction to coumarine-based benzoxazines and ring-opening polymerization of coumarines and bio-based benzoxazines from renewable sources is also the focus of this thesis.

2.1 Thermoset Polymers

Polymers are divided into three classes according to their occurrence in nature: natural, semi-synthetic, and synthetic. Based on how they react to heat, synthetic polymers are classified as thermosets or thermoplastics.

Thermoset materials can resist high temperatures without losing their mechanical and formal properties, whereas thermoplastic materials have low melting points. When heated initially, thermoplastics become soft, and when heated further, they become fluid. However, thermosets solidify at high temperatures and do not enter the regeneration cycle due to the formation of three-dimensional cross-links between the chains. Thermoplastic polymers include polyethylenes, polypropylenes, polystyrenes, and polycarbonates; and thermosetting polymers include silicone, phenol-formaldehyde resins, oxazolines, epoxies, and unsaturated polyesters. Examples of thermosetting materials such as epoxy and bismaleimide are shown in Figure 2.1.

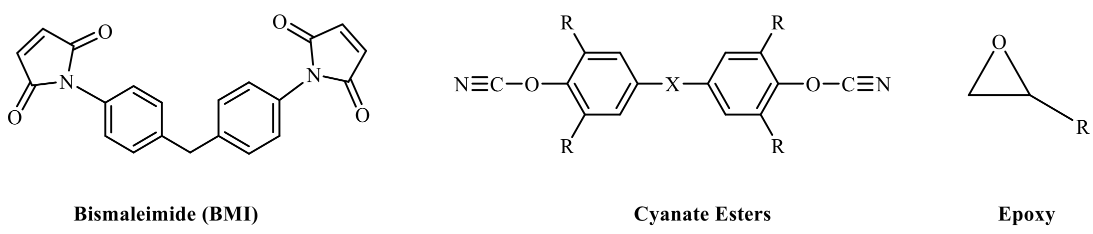


Figure 2.1 : Structures of thermoset materials.

Thermosets maintain their solid state after being heated, unless the chemical bonds are broken due to their cross-linked structure. The high degree of cross-linking in thermosets ensures that thermosets have higher physical and mechanical strength than thermoplastics. Even at high temperatures, they maintain their structure and strength. According to the stress-strain curve mechanically of thermosets, they exhibit hard and brittle properties [29].

2.1.1 Phenol-formaldehyde resins

Phenolic resins, which are thermosetting materials, are preferred in a wide variety of fields, such as the automotive, computer, and aerospace industries. These resins exhibit some properties: heat resistance, high mechanical strength, high resistance against various solvents, acids, and water, dimensional stability, and flame resistance. In addition to being flame-resistant, the amount of smoke it emits when burned is low, and it is low-cost. These properties of phenol-formaldehyde resins enable them to be used industrially and commercially, especially in the aerospace industry [7-10].

Phenol-formaldehyde resins are the first thermosetting plastics. Phenols and formaldehyde solutions react chemically to produce phenol-formaldehyde resins. They are composed entirely of synthetic materials [11].

Phenolic resin research began in the 20th century. Firstly, in 1872, the reaction of the tough, tar-resinous materials phenol and formaldehyde was reported by Adolf von Bayer. In 1894, according to the results of studies conducted under basic conditions by Lederer and Manasse, the stability of phenols was limited, and they were considered reactive intermediates, so their large-scale use was not developed. In 1902, Blumer obtained the first commercially available phenolic resin; however, the product was not successful on the market. Then, in 1907, Leo Baekeland succeeded in developing a controllable phenolic resin by reacting phenol with formaldehyde and received the Heat and Pressure Patent for phenolic resins [11-12]. Throughout his studies, he conceived of a reactor and named it the "Bakelizer." Originally calling his resin oxy-benzyl methyleneglycol anhydride, Baekeland subsequently registered the trademark under the name "Bakelite" [3]. The reactor Bakelizer is presented in Figure 2.2.

Figure 2.2: Bakelizer reactor.

2.1.2 Synthesis of phenol-formaldehyde resins

The reaction of phenol and formaldehyde forms two different resins: novolac and resol. A heat-reactive resol or a stable novolac may be formed [11, 13–14]. The formation of resol or novolac at the end of the reaction depends on the molar ratio between formaldehyde, phenol, and acid or base. In addition to that, there are other factors affecting the product, including temperature, pH values, and catalyst type. If an acid catalyst is used and the molar ratio of formaldehyde to phenol is less than 1, novolac is obtained. Conversely, if a base catalyst is used and the molar ratio of formaldehyde to phenol is greater than 1, resol is obtained [15]. It is obtained that type of catalyst, formaldehyde/phenol (F/P) molar ratio, and heat are the significant parameters to synthesize either novolac or resol. Furthermore, following the production of novolac and resol, hexamethylenetetramine (HMTA) is used to crosslink novolac, while heat is used to crosslink resol. The synthesis and synthesis conditions of novolac and resol-type phenolic resins are presented in Figure 2.3.

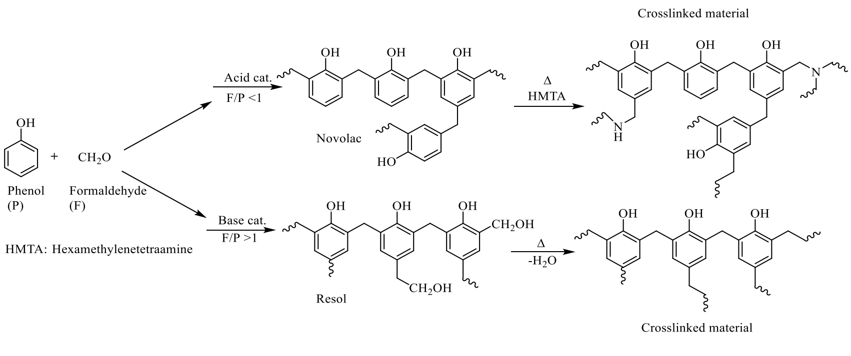


Figure 2.3: Synthesis of phenol-formaldehyde resins and cross-linked materials.

2.2 Benzoxazines

Benzoxazines are comprised of a six-membered heterocyclic ring containing both oxygen and nitrogen atoms, identified as an oxazine ring, and this oxazine ring is attached to a benzene ring. There are lots of benzoxazine monomer structures. Benzoxazine structures vary based on where the heteroatoms are located. Formaldehyde, phenolic derivatives, and primary amines can be combined to produce these resins easily [10]. The classical synthesis of benzoxazine from a phenol, formaldehyde, and an amine is represented in the Figure 2.4.

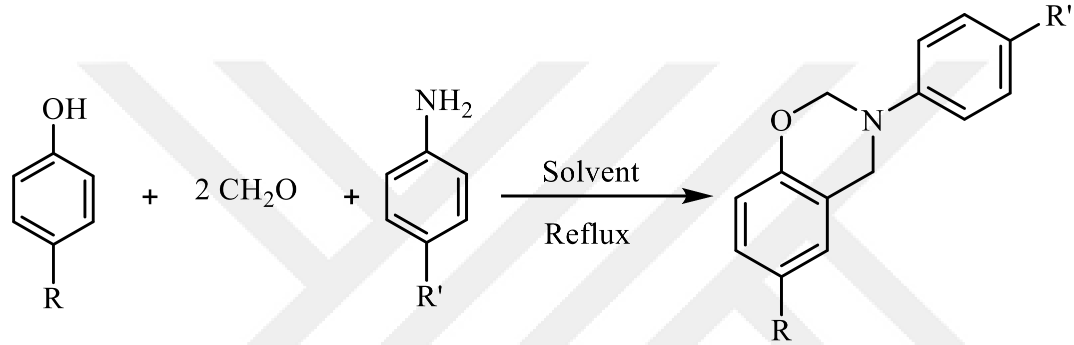


Figure 2.4: Classical synthesis of benzoxazine monomers.

Benzoxazine resins possess several significant properties. These features include good mechanical strength, low water absorption, chemical resistance to acids or bases, high char yield, minimal or no shrinkage during curing, glass transition temperatures (*Tg*) higher than the curing temperature for some benzoxazines, and high service temperatures [30]. Benzoxazine represents a recently developed category of advanced thermosetting resins [31].

2.2.1 The historical evolution of benzoxazines

In 1944, Holly and Cope sythesized aromatic oxazines of low molecular weight, specifically 1,3-benzoxazine [32]. According to the research conducted by Burke between 1950 and 1965, small molecular-weight benzoxazines and their derivatives were synthesized, while the reactions of ortho or para positions with phenolic compounds were examined. It has been discovered that it mostly reacts from the ortho position rather than para, and Mannich Bridges are formed [33-40]. During the early 1970s, Schreiber, in his patent filings, described the production of small oligomers intended for modifying epoxy resin, although he did not provide detailed information about the properties of these oligomers [10, 41]. In the 1980s, Higginbottom enhanced the initial cross-linked polybenzoxazines using multifunctional benzoxazines; however, his patents did not elaborate on the properties of polybenzoxazines [42-44]. Riesse et al. discovered the formation of oligomers from monofunctional benzoxazines. According to studies on the reaction kinetics of oligomer formation, it was found that high-molecular-weight linear polybenzoxazines cannot be synthesized from monofunctional benzoxazines. Various research indicates that the molecular weights of the obtained polymers range approximately from one hundred to several thousand Dalton [45]. In 1988, Turpin and Thrane obtained a patent for their studies on a cathodic electrocoat resin that undergoes self-curing through the self-addition of oxazine [46]. The synthesis history of benzoxazines and polybenzoxazines dates back to the period between 1940 and 1994. The synthesis of low molecular weight benzoxazines began in the 1940s, followed by the first polymerization of benzoxazines in the 1970s and the synthesis of the first cross-linked polybenzoxazine in 1985. However, in 1994, the first research based on the properties of polybenzoxazines was indicated in studies conducted by Ning and Ishida [9, 41]. After these initial studies on polybenzoxazines, research has increased in recent years owing to their significant properties. The chemical, physical, mechanical, and thermal advantages of benzoxazines have made them a crucial candidate for use in various fields.

2.2.2 Properties of benzoxazines

Polybenzoxazines are advanced thermosets when compared to traditional novolac and resol-type phenolic resins. Polybenzoxazines not only improve the benefits of these classical novolac and resol-type phenolic resins but also handle their many shortcomings. Polybenzoxazines exhibit a number of unique properties, and these features lead to their unique applications. Phenolic resins are the materials of choice for a wide range of applications, from sophisticated uses in the aerospace sector to common commodities and building materials [1].

Benzoxazines have these properties [5, 47]:

- T_g (glass transition temperature) between 160 – 400 ^{O}C
- Near-zero volumetric change after the polymerization reaction
- Low water absorption
- Low toxicity

- Low cost
- Low thermal expansion coefficient
- Storage at room conditions
- High char-yield
- High flame retardancy
- Limited formation of toxic by-products during curing
- Do not requiring catalyst for curing
- Offering design flexibility for cross-linked polymers to be controlled, owing to benzoxazines molecular structure.

The physical and mechanical properties of certain high-performance thermosets are presented in Table 2.1.

Table 2.1: A comparison of the physical and mechanical characteristics between polybenzoxazines (PBz) and other commercial resins.

Property	PBz	Epoxy	Phenolics	Cyanate Esters	Bismaleimides (BMI)
Cure Temperature (˚C)	160–250	R.T.-180	150–190	180-250	220-300
Max. use Temperature (˚C)	130–280	180	200	150-200	~200
Cure shrinkage (%)	~ 0	>3	0.002	~3	0.007
T_g (˚C)	170–340	150–220	170	250-270	230-380
Elongation at break (%)	2.3–2.9	3–4.3	0.3	2-4	3
Tensile Strength (Mpa)	100–125	90–120	24–45	70-130	50-90

In addition to all these advantageous properties, benzoxazines also have some drawbacks. Examples of these characteristics include the possibility of the intermolecular hydrogen bonds breaking in cross-linked polybenzoxazines due to their high curing temperatures (160 ^{O}C or higher) or the potential for the product to be brittle. To overcome these disadvantages, it may be preferable to create composites or copolymerizations with polymerizable functional groups and suitable reinforcement systems. Among the new approaches of comparable significance are click chemistry, main-chain polymerization, and sustainable approaches. As a consequence, research focused on lowering curing temperatures and modifying polybenzoxazines is crucial to overcome these disadvantages and is highly significant for various applications [48].

2.2.3 Synthesis of benzoxazines

Benzoxazines are formed through the Mannich-like condensation of a phenol, formaldehyde, and an amine, resulting in the generation of bicyclic heterocycles [32, 34, 35, 39, 49-51]. The use of various amines, phenols, and aldehydes in benzoxazine synthesis provides the molecule with broad design flexibility [52]. Polybenzoxazines (PBzs) are produced from precursor molecules referred to as 1,3-benzoxazines easily [53-55]. Although various oxazine isomers other than 1,3-benzoxazines exist, only the 1,3-benzoxazine isomer is used in the synthesis of polybenzoxazines because of their active structures. 1,3-benzoxazines are polymerized by cationic ring-opening polymerization. The reaction for synthesizing benzoxazine, involving a primary amine, an appropriate phenolic compound, and formaldehyde, is illustrated in Figure 2.5 [23, 56-59].

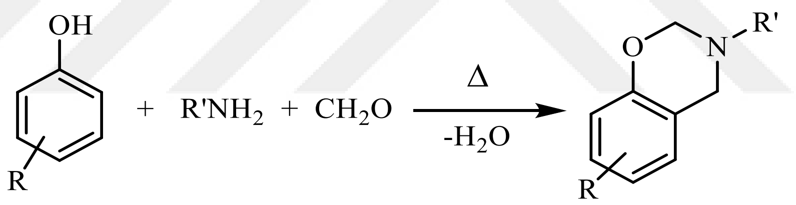


Figure 2.5: Synthesis of an 1,3-oxazine from a phenol, a primary amine, and a formaldehyde.

Both on the market and in natural types of phenols, amines, and aldehydes, various benzoxazine syntheses are quite possible. In addition to that, the synthesis process can be performed both easily and efficiently. The availability of different reactants expands the design possibilities of the product based on its intended use. Polybenzoxazines have a significant advantage due to this feature. For instance, the cross-linking density of polybenzoxazines can be increased when components such as allyl, propargyl, or coumarine are used. As another example, the toughness of polybenzoxazines can be modified when long-chain alkyl amines [60, 61] and amino alcohols [6, 57] are used in monomer synthesis.

The classical method of benzoxazine synthesis is reaction between phenol, formaldehyde and an amine. While solvent can be used during synthesis, solvent-free syntheses are also available [4]. X groups can be such as -CH_2, -$C(CH_3)_2$, -$C(CF_3)_2$, -C=O, -SO_2, and R groups can include -CH_3, -C_2H_5, and benzene. Also, R' groups can include such as -CH_3 or other aliphatic groups. In addition to influencing the curing process, these replacing groups may offer more polymerizable sites. Modifying the benzoxazine monomer through derivatization is a useful approach for achieving the desired features.

The first research in which benzoxazine monomers were synthesized was reported by Holy and Cope [32]. According to this study, primary amines, formaldehyde, and substituted phenols caused a condensation reaction. This synthesis procedure was carried out in two stages and a solvent medium. Later, it was found by Burke that the formed benzoxazine ring reacted with the ortho-position of the phenolic compound and formed a Mannich Bridge [34]. Here, the benzoxazine ring prefers the ortho position rather than the para position. According to the reaction mechanism, firstly, a *N*, *N*-dihydroxymethylamine derivative is formed from the reaction of amine and formaldehyde at low temperatures. Then, this formation reacts with the unstable hydrogen in the hydroxyl group at high temperature and the ortho-position of phenol to form the oxazine ring [62]. Accordingly, in the 1940s, Burke added para-substituted phenols, formaldehyde, and primary amine in molar ratios of 1:2:1, respectively, to synthesize 3,4-dihydro-1,3-2H-benzoxazines, and this synthesis has been reported [34]. The plausible reaction mechanism for the ring formation of benzoxazine is depicted in Figure 2.6.

Apart from this, alternatively, the formation of 3,4-dihydro-3,6-disubstituted-1,3-2H benzoxazine can also be shown in Figure 2.7. In this proposed mechanism, first of all, each reactant reacts in equal molar ratios, and as a result, the o-alkylaminomethyl-p-substituted phenol intermediate product is formed. Then, this intermediate product is converted into a 1,3-benzoxazine molecule by adding formaldehyde in a base catalyst environment.

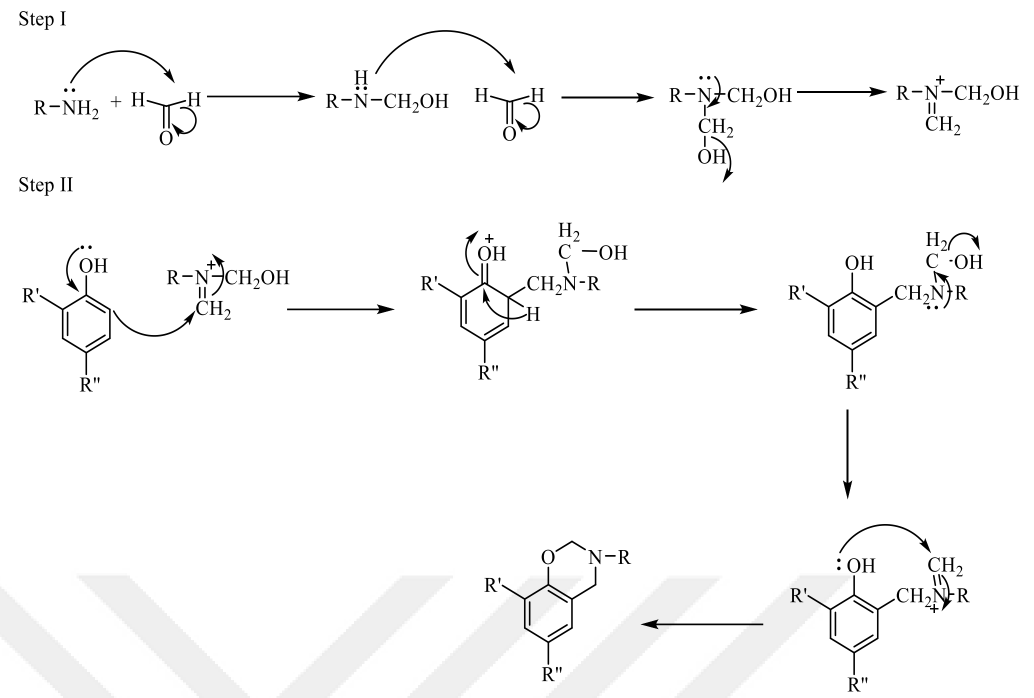


Figure 2.6 : The plausible reaction mechanism for ring formation of benzoxazine.

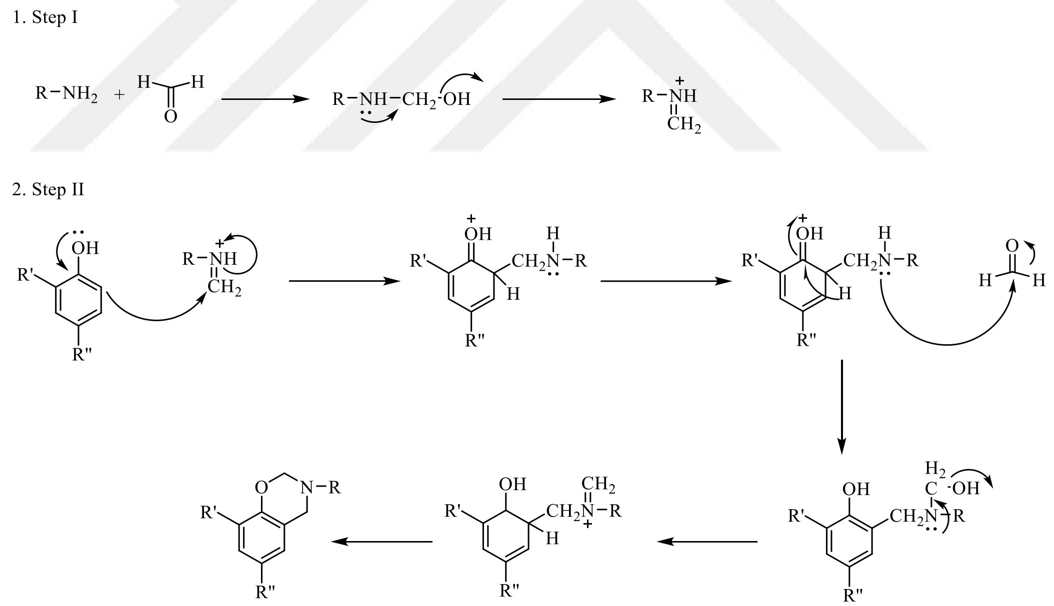


Figure 2.7 : An alternative mechanism for the formation of the benzoxazine ring.

In addition to the reactions that take place with a base catalyst, there are also ring-opening reactions in an acidic medium. It has been stated that benzoxazines cause ring-opening reactions when active hydrogen (HY) compounds such as carbazole, indoles, imides, aliphatic nitro compounds, naphthol, and phenol are used [63]. Hence, the ring opening of benzoxazine in an acidic environment gives rise to the formation of a Mannich Bridge, and small oligomers are formed at the end of the reaction [64]. The reaction showing the ring opening of benzoxazine in an acidic environment is presented in Figure 2.8.

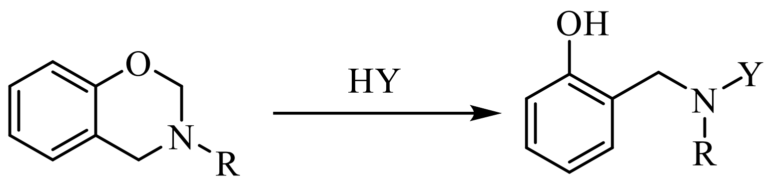


Figure 2.8 : The ring opening of benzoxazine in an acidic environment.

Furthermore, product yield is a critical factor in benzoxazine syntheses. The yield in benzoxazine synthesis typically ranges between 50 and 70%. Substituents related to phenol play a significant role in enhancing the efficiency of the synthesis. Multiple electron-donating substituents on phenols have the potential to cause further amino alkylation reactions [65]. Additionally, as mentioned earlier, reactions through the ortho position in phenols are more efficient due to the absence of para-attacks caused by the blocked para position. If the para position for electrophilic aromatic substitution is active, only dimers or oligomers will be formed instead of polymers.

On the other hand, there are some drawbacks to the synthesis methods of benzoxazines. These drawbacks can be listed as follows:

- Low reaction rate
- Low resolution of precursors
- Requires large amounts of solvent
- High cost of solvents
- Solvent can remain in the final product.

The method using solvent as the synthesis method can be used for nearly all types of benzoxazines. However, the need for a solvent-free method arose due to the drawbacks associated with using solvents. A novel, solvent-free synthesis in the molten state has been improved by Ishida et al. [66]. Improved reaction times and the creation of fewer undesirable intermediates and by-products are the main benefits of the solvent-free synthesis method compared to the traditional synthetic route [4]. Apart from this, in methods using solvents, by product formation can be reduced by using solvent pairs, which adjust the solvent polarity. For example, typically a 2:1 (v/v) (volume/volume) ratio is used with the toluene/ethanol solvent combination [67]. Besides, the ethyl acetate-ethanol 3:1 (v/v) ratio can be applied, particularly in green strategies.

2.2.4 Bifunctional and multifunctional benzoxazines

Monofunctional benzoxazine monomers have the ability to cross-link and form thermosets, but it has been observed that thermal decomposition of dimers, trimers, and monomers during polymerization negatively affects the chain reaction, resulting in low-molecular-weight polymers [68]. When monofunctional benzoxazines undergo polymerization, the outcome typically involves the formation of oligomeric structures with an average molecular weight of around 1000 Da. The synthesis of difunctional and multifunctional benzoxazines and thus the formation of high molecular weight polymers was carried out to solve this problem [41, 69]. Difunctional phenolic compounds, or bisphenol A (B-a), were used in these syntheses. Monomers with a bifunctional benzoxazine ring at both ends were obtained. As the reactants required for this synthesis, aniline and methylamine are utilized as amine sources [9, 70]. Examples of synthesized difunctional benzoxazine by using Bisphenol A (B-a), formaldehyde, and methylamine in solvent medium are presented in Figure 2.9.

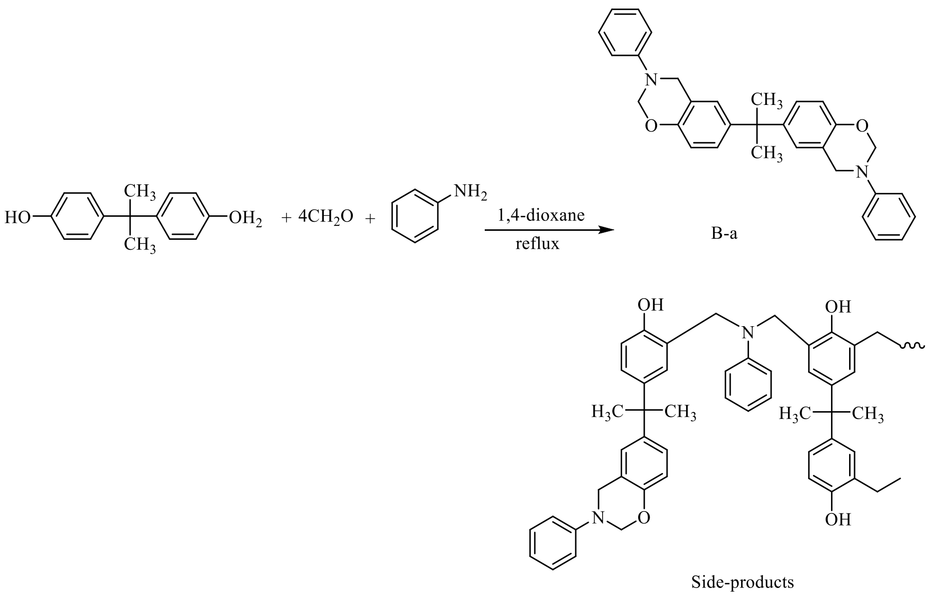


Figure 2.9 : Difunctional benzoxazine monomer synthesis.

Furthermore, there are other bisbenzoxazines synthesized by solvent-free medium. By combining the difunctional amine and the monofunctional phenol, or vice versa, difunctional benzoxazines can be formed. A list of difunctional monomers produced by the solvent-free approach is given in Figure 2.10.

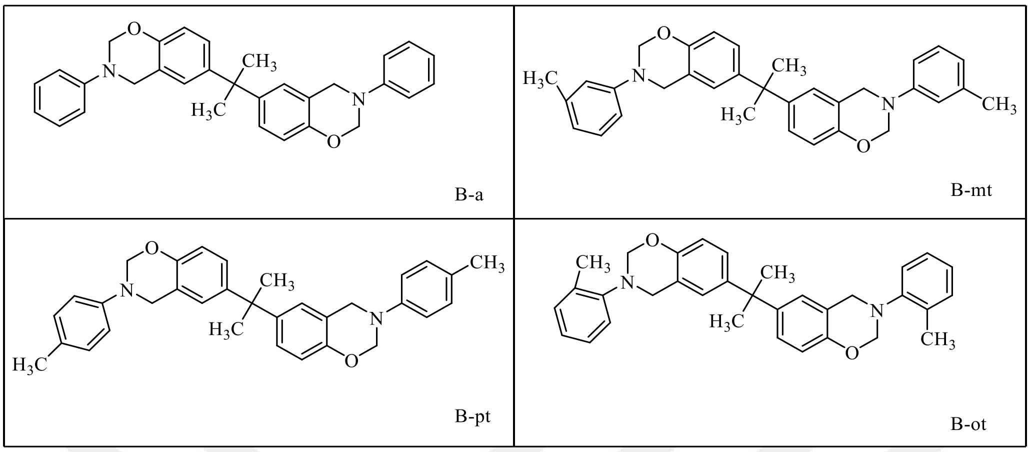


Figure 2.10 : Several difunctional benzoxazine monomers synthesized with solvent-free medium.

2.2.5 Ring opening polymerization of benzoxazines

The method of ring-opening polymerization is a versatile approach for obtaining phenolic resins. Unlike the conventional phenol-formaldehyde manufacturing process, this approach uses active monomers that can spontaneously polymerize [4]. It is essential to comprehend the mechanism of the polymerization reaction in the synthesis of benzoxazine. The benzoxazine monomers are thermally polymerized through cationic ring-opening polymerization (ROP) of oxazine rings [71-73]. In benzoxazine chemistry, the preferred conformation of a monooxazine ring is a distorted half-chair conformation. In this conformation, the nitrogen, which is located between the oxygen and nitrogen in the oxazine ring, is above the plane of the benzene ring, and the carbon is located below the plane of the benzene ring. Under some circumstances, this kind of six-membered ring can undergo a ring-opening reaction thanks to the ring strain that results from this molecular configuration. Furthermore, oxygen and nitrogen in the oxazine ring can be initiation sites for cationic polymerization due to their high basic properties, according to Lewis definition. Hence, the ring can be opened through a cationic mechanism [72, 74]. In other words, ring opening polymerization (ROP) occurs on cationic species because nitrogen and oxygen atoms can readily stabilize the cation. Although temperature values vary for some monomers, for most monomers, polymerization generally occurs at temperatures between 220 and 260 °C [75-77].

Ring opening polymerization reactions can be carried out with or without a catalyst. In acid catalyzed ring opening polymerizations, residual phenolic –OH groups act as cationic initiators [72, 77-79]. When an oxygen or nitrogen atom on a heterocycle is protonated, the bond breakage of O-CH_2-N can generate either an aryl aminomethyl repeat unit or an aryl ether, depending on whether a protonated atom is present. The application of heat causes a rearrangement of aryl ether units, leading to the formation of polybenzoxazine (PBz). The acid catalyzed synthesized polybenzoxazine is depicted in Figure 2.11.

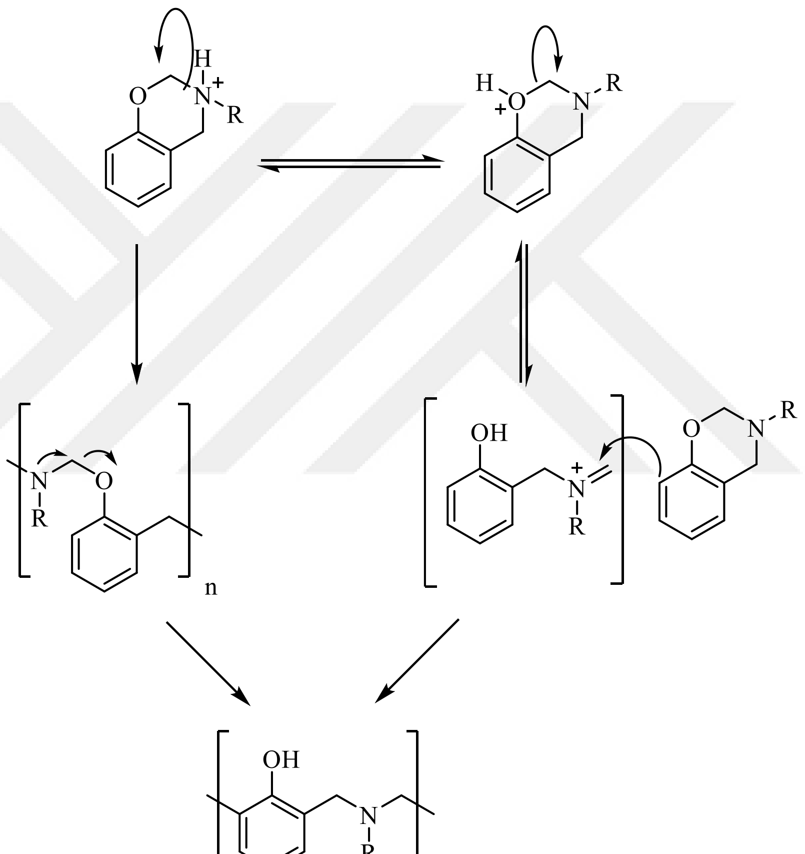


Figure 2.11 : Acid-catalyzed ring opening polymerization (ROP) of an 1,3-benzoxazine monomer.

Additionally, benzoxazine polymerization can easily occur without a catalyst. Nevertheless, the polymerization process typically demands elevated temperatures, posing a disadvantage in terms of energy consumption. Lower curing temperatures are needed. To address this challenge, the utilization of diverse catalysts has been tried, and successful results have been obtained. For example, when Lewis acids were applied, curing temperatures as low as 120-160 °C were achieved [72]. Catalysts such as PCl_5, $POCl_3$, $TiCl_4$, $AlCl_3$, and $FeCl_3$ are successful catalysts under curing conditions. Besides, the addition of solvents to these acids enhanced their effectiveness, enabling the opening of the oxazine ring to occur even at room temperature. Another example is that fourth period transition metals were able to reduce the onset of ring opening polymerization (ROP) temperatures in acetylacetonato complexes to 120 °C [80]. Therefore, Lewis acids act as highly active catalysts and frequently initiate ring-opening polymerization (ROP) during storage, leading to increased viscosity in formulations. Utilizing latent catalytic systems, which remain inert at specific temperatures but activate upon heating, this problem has been handled. Examples of latent catalysts for ROP are diamines [8, 81], thiols [82-86], toluene sulfonates [7], and colloidal sulphur [87, 88].

2.3 Bio-based Benzoxazines

Academic and industrial research focuses on developing a bio-based polymer using renewable organic raw materials and alternative sustainable processes [89, 90]. Similar to other petroleum-based polymer materials, benzoxazine resins have several challenges regarding environmental and ecological issues. These challenges include:

- Depletion of crude oil, the primary raw material for petroleum-based polymers, leading to increased prices.
- The numerous polymeric materials and issues associated with their disposal.
- The generation of toxic waste raises environmental concerns regarding the management of all waste materials.
- Acknowledgement that certain materials used in benzoxazine resins may pose health risks to humans [15, 91].

For instance, the production of bisphenol A, an industrial chemical used primarily in plastics since the 1950s, has experienced a significant increase as markets expanded. However, it has been determined that bisphenol-A, which is one of the raw materials and frequently used in the synthesis of benzoxazine, exhibits hormone-like properties that mimic estrogen. Therefore, its use in polymers is limited, especially for consumer products and food containers, because of its hazardous properties for human health [92, 93]. Thus, the development of non-petroleum-based, renewable, recyclable, and environmentally friendly polymer materials has gained enormous importance in an effort to prevent these ecological and economic issues that arise during the production of benzoxazine [15, 94-97].

In the past ten years, there has been a rise in interest in bio-based benzoxazines. On the other hand, the first bio-based benzoxazine was cardanol-based benzoxazine synthesized using terpenediphenol, a raw material derived from natural sources, according to the article published in early 1999 [58]. Excess phenol reacts with terpene compounds found in pine or orange rind to produce terpenediphenol. Terpenediphenol has been proposed as a valuable additive to enhance the water or heat resistance of commercial polymers. For example, according to Matsumoto *et al.*, who investigated the synthesis and properties of terpenediphenol-formaldehyde resin, terpenediphenol-formaldehyde resin was reported to have superior heat resistance, water resistance, and mechanical properties [58]. Therefore, the cured resin from terpenediphenol-based benzoxazine and epoxy resin is expected to have good heat resistance, water resistance, and mechanical properties [58, 94]. Nonetheless, this cardanol-based benzoxazine synthesis has increased the interest in benzoxazine synthesis from natural sources [15, 94].

In addition, many renewable resources, such as plant oils, cellulose, starch, chitosan, and isosorbide, have been investigated, and various polymer systems have been developed from these resources, and they can also be supplied industrially [98-101]. Plant oils are suitable both for the production of hydrophobic polymers and improvement of other natural hydrophilic biological resources such as carbohydrates and proteins. They are also utilized in the synthesis of reactive monomers that resemble petroleum-based counterparts [102, 103]. Furthermore, the most common polymer on earth is cellulose. One- or two-dimensional fiber materials in the nanoscale range can be produced from a variety of natural cellulose sources by applying the appropriate chemical and physical treatments. Some features of nanocellulose-based materials are: having a low carbon footprint; being sustainable; being recyclable; and being non-toxic [104]. Apart from that, chitosan is widely used in various industries such as biotechnology, food processing, pharmaceuticals, wastewater treatment, agriculture, and the textile industry, owing to its noteworthy properties such as strong biodegradability, solubility, biocompatibility, and minimal toxicity to mammalian cells [105-109].

Alternative phenolic compounds and amines have been utilized in research to develop bio-based polymers by polymerizing bio-based benzoxazine resins. Examples of phenolic -OH sources are cardanol, catechol, coumarine, diphenolic acid, eugenol, guaiacol, magnolol, resorcinol, terpenediphenol, urushiol, sesamol, and vanillin. In terms of amine sources, examples include dehydroabietylamine, chitosan, furfurylamine, jeffamine, and stearylamine. In addition, benzaldehyde and furfural are examples of renewable aldehyde sources [22, 23, 25-27, 56, 58, 110-130]. Cardanol is obtained from the shell liquid of cashew nuts. At an industrial level, cardanol is usually produced by heat treatment of cashew nut shell liquid, followed by decarboxylation of anacardic acid obtained by distillation [131]. The nature of cardanol has properties such as high mechanical performance, strong chemical resistance, and a low dielectric constant. Thus, it can play a significant role in the creation of several bio-based polymers, such as phenolic resin, benzoxazine, epoxy resins, and polyurethane, which are widely used in applications in the fields of elastomers, adhesives, and coatings [132]. The catechol structure of 3,4 dihydroxy-phenylalanine, namely 1,2-dihydroxybenzene, is a catecholic amino acid found in mussel adhesive proteins and is responsible for the strong, water-resistant adhesion and rapid curing of the adhesive. Catechol, which is a versatile adhesive molecule, can present strong and moisture-resistant adhesive features when incorporated into polymers [133, 134]. Polybenzoxazine containing catechol groups were compared to common benzoxazine monomers and were determined to increase lap shear adhesion strength by 53% and show tensile strength up to ∼2.61 MPa. The autocatalytic polymerization effect reduced the polymerization temperature in the presence of phenolic hydroxyl groups [135]. Condensation between phenol and levulinic acid yields diphenolic acid. Levulinic acid, which is believed to be an inexpensive platform chemical that can be generated on a large scale, can be commercially synthesized from waste biomass that contains a high percentage of cellulose [136, 137]. Eugenol is a guaiacol with an allyl chain substitution in its structure. It is obtained from several essential oils, especially clove, cinnamon, basil, nutmeg, and bay leaf. It is a colorless to pale yellow, aromatic, oily liquid. The ortho position is the preferred site for the ring opening polymerization of benzoxazines; nonetheless, there may be a few reaction potentials in the para position as well. However, eugenol is not suitable for either position since it has steric hindrances in its structure, and thus, in theory, polymerization of eugenol-based benzoxazines is difficult. Eugenol-based benzoxazines have been blended with nanofillers, such as graphene oxide, carbon nanotubes, and polyhedral oligomeric silsesquioxane, to enhance their performance [138-141]. Vanillin is extracted from the seed pods of *vanilla planifolia*, an ivy orchid native to Mexico. Vanillin can be produced both naturally and chemically. Also, most of the vanillin used in industry is synthesized from guaiacol. Alternatively, vanillin can be biosynthesized from lignin or other compounds such as eugenol, guaiacol, ferulic acid, and aromatic amino acids [22]. Vanillin, which is a renewable reactant for benzoxazine chemistry, contains an aldehyde group; hence, there is an increasing interest in vanillin. The aldehyde group, which is protected during synthesis, can also be utilized to react with other chemical groups or provide a functional group to the benzoxazine monomer. By giving the benzoxazine monomer a functional group, the aldehyde group in vanillin increases cross-linking. Research has shown that the char yield of benzoxazine-containing aldehydes is 68.4% at 800 °C [22, 142]. Benzoxazines produced from vanillin can be used in high-performance materials due to their properties.

Furthermore, furfurylamine is a significant renewable primary amine used in benzoxazine synthesis. Furfurylamine is synthesized from furfural. Furfural, excluding sugar, acetic acid, and ethanol, stands out as one of the earliest renewable compounds. Furfural is produced when various agricultural by-products, such as corncobs, wheat bran, oats, and sawdust, are processed with sulfuric acid or hydrochloric acid. This is because acid catalyzed dehydration of five carbon sugars, namely pentoses, results in furfural [143]. Furfurylamine has a characteristic amine smell and is a colorless to pale yellow liquid with a high boiling point. Liu *et al.* have introduced the furan ring into the benzoxazine chemistry, and furfurylamine has been extensively researched [23]. Furfural undergoes reductive amination to produce furfurylamines. It has been found that the catalysts that are effective for this reaction are assisted Ni catalysts, Raney Ni catalysts, and assisted Co catalysts [144]. The use of furfurylamine provides various advantages to benzoxazines. It leads to the conversion of the amine part of benzoxazine into renewable sources. Apart from that, polybenzoxazines based on furfurylamines are becoming more and more popular as polymers with strong thermal stability, a high char yield, enhanced cross-linking capability, and self-destruction behaviour [145].

Renewable phenols, amines, and aldehydes are listed and depicted in Table 2.2. These natural products are appropriate for the production of renewable benzoxazine synthesis.

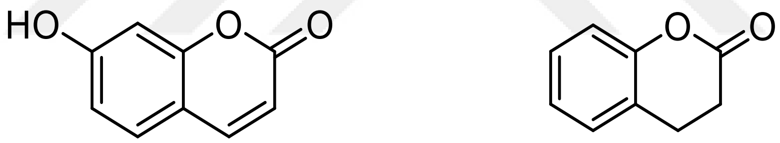
Table 2.2: Renewable, environmentally friendly phenols, amines and aldehyde.

Phenols	Amines	Aldehydes
Cardanol	Furfurylamine	Benzaldehyde
Catechol	Chitosan	Furfural
Coumarine	Jeffamine	-
Diphenolic acid	Cholesterol	-
Eugenol	Stearylamine	-
Guaiacol	-	-
Magnolol	-	-

Using naturally occurring renewable resources has several significant benefits and performance characteristics that affect the chemistry of benzoxazine. It addresses concerns about depletion of natural resources and rising oil prices. For instance, diphenolic acid and bisphenol A (B-a) could be substituted for one another owing to their structural similarities. It is also far less expensive commercially and, thus, provides ease of use [137]. The application of benzoxazine in the bio area offers wide molecular design flexibility that is facilitated by one-step and one-pot syntheses, allowing for the analysis of various molecules. Hence, bio-based benzoxazines are rapidly growing in that field. Benzoxazines in applications in the bio area have several advantages, such as low water absorption, low surface-free energy, absence of by-product generation during polymerization, no or limited shrinkage during polymerization, and high stability [15, 146, 147]. According to recent research, it has been determined that benzoxazine monomers have a wide spectrum of antiviral, anti-fungal, and anti-microbial impacts [148, 149]. Thanks to these unique properties, polybenzoxazines can be used in a wide variety of fields, spanning from biomedical uses to composite materials and from the aviation sector to adhesives.

2.3.1 Coumarine based benzoxazines

Coumarine is another renewable resource used for benzoxazine synthesis. Coumarines are a group of organic compounds that occur naturally. This group of organic compounds is classified according to their 1,2-benzopyrone structure. Coumarines, which are found in high amounts in various natural plant sources, in particular tonka beans, vanilla grass, sweet woodruff, mullein, sweet grass, deertongue, and the leaves of many cherry blossom trees, cassia cinnamon, and sweet clover, can be extracted from these natural plant sources [19]. Coumarine can be synthesized via various name reactions. An example of this is the Perkin reaction between salicylaldehyde and acetic anhydride [150]. There are several types of coumarine, such as 4-methylumbelliferone (MUM) and 7-hydroxycoumarine (umbelliferone, UM), and 3,4-dihydrocoumarine (DHC) and these derivatives are utilized in the production of benzoxazine. These derivatives of coumarine molecules are represented in Figure 2.12.



7-hydroxycoumarine (umbelliferone) 3,4-dihydrocoumarine

Figure 2.12 : Derivatives of coumarine molecule.

It was reported by Arza *et al.* that thermosetting materials synthesized with 7-hydroxycoumarine (umbelliferone), aniline, and paraformaldehyde have a char yield higher than 55%. According to the results, it was determined that this condition indicates efficient thermal stability [151]. When 7-hydroxycoumarine (umbelliferone) and 4-methylumbelliferone monomers were compared to one from phenol, it has found that 7-hydroxycoumarine (umbelliferone) benzoxazine had a comparatively low polymerization temperature of 220 °C [152]. Therefore, 7-hydroxycoumarine (umbelliferone) has a higher reactivity than 4-methylumbelliferone in polymerization reactions. Additionally, 3,4-dihydrocoumarine was used to synthesize amide-containing monophenol and bisphenol, bis-oxazine monomers, and main-chain polybenzoxazine precursors, which were converted to monooxazine [153]. Amide-functional benzoxazine resins are an appealing alternative to polybenzoxazine because of their structure, which is comparable to that of polyaromatic amide [154-156]. The importance of this work is that it is an approach to using the pyran ring of coumarine and also provides design flexibility for further expansion [15].

The use of coumarine in the synthesis of benzoxazine ensures that these resins are bio-based. After polymerization, these bio-based benzoxazines showed high thermal stability. Additionally, polymerization temperatures decreased. Coumarines offer a straightforward chemical reaction pathway for the benzoxazine synthesis. Its reaction yield is quite high [56, 87]. These emerging properties are remarkable and can be used in various potential applications such as flame retardant or fire-resistant materials. Being bio-based also allows it to compete with petroleum-based resins [157, 158]. As a result, there is superb potential for the synthesis of bio-based benzoxazines by using coumarines.

2.3.2 Ring opening reactions of coumarines

Research and synthesis of coumarines and their derivatives are emphasized. Since coumarines are used in a wide variety of areas due to both their renewable nature and their substantial properties. The reaction of the diethyl ester of 2-oxo-2H-1-benzopyran-3-phosphonic acid as an acceptor in the Michael reaction with the anion derived from nitromethane as a nucleophile has been studied. Apart from that, the reaction has been carried out in the presence of KF as a deprotonating agent using esters and amides of 2 oxo-2H-1-benzopyran-3-carboxylic acid. This former reaction was carried out in the presence of KF and ethanol solvent conditions. The diethyl ester of coumarine-3-phosphonic acid has also been found to give products similar to those obtained in reactions with other 3-substituted coumarines [159]. Initially, in the former reaction, nitromethane is added to coumarine via the 1,4-addition reaction. Then, a solvent molecule attacks the carbonyl group of this ring, and the lactone ring opens. Ethanol, the solvent molecule, acts as the nucleophilic agent at this stage of the reaction.

The latter reaction, namely coumarine with CH_3NO_2, has been carried out in the presence of nucleophiles other than ethanol, such as the amines Et_3N, piperidine, and $PrNH_2$. The proposed reaction mechanism is depicted in Figure 2.13.

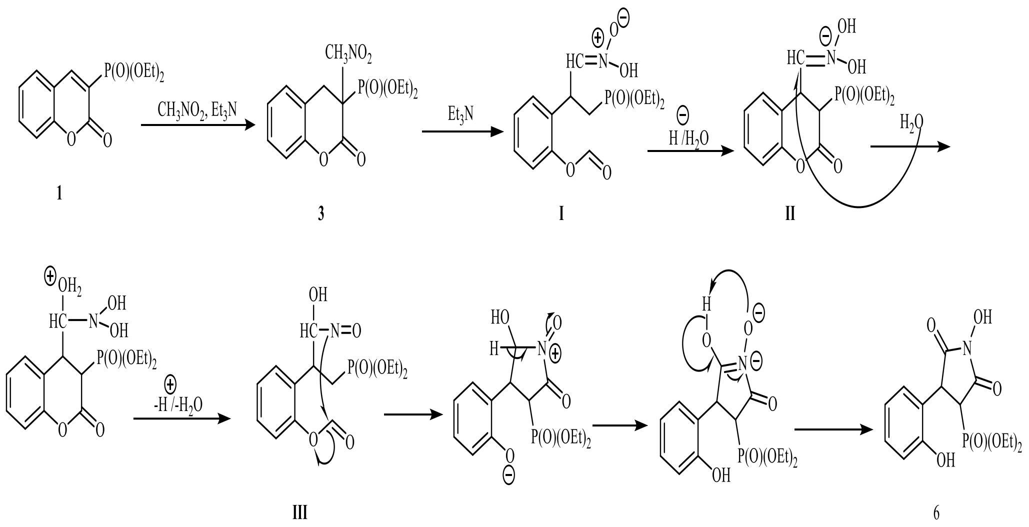


Figure 2.13 : Proposed ring-opening reaction mechanism of coumarine.

According to the mechanism of this reaction, these amines also serve as bases in the nitromethane addition in the first stage [160]. Firstly, the amine attacks the carbonyl group of the Michael addition product, leading to the opening of the lactone ring. The Michael addition product is an intermediate. In other words, in the first step, a base-catalyzed tautomeric transformation occurs, which will yield nitronate I, which is typical for nitro compounds with the H-C-NO_2 group. After that, structure diethyl (3-(nitromethyl)-2-oxochroman-3-yl)phosphonate molecule is produced by acid-catalyzed hydrolysis of the iminium ion II needed for the Nef reaction. Subsequently, the reaction continues with the nitrogen atom attacking the carbonyl group, leading to the simultaneous formation of the new pyrrolidin ring as the lactone ring opens [160, 161]. As a result, coumarine, a pyrrolidin derivative, can be readily obtained by the ring-opening reaction and with a high yield. Coumarines are frequently used in medical and chemical applications.

Also, there is another reaction example that shows the ring-opening reaction of coumarine, which is between coumarine and amine. According to this reaction mechanism, 3,4-dihydroxycoumarine, or, in other words, (2-chromanone), reacts with dimethylamine to give the product hydroxyamide (5a). Under specific reaction time and room temperature circumstances, it can be quantitatively transformed to benzyloxyacetamide (5b) by treating it with sodium hydride and benzyl bromide. Then, this acetamide (5b) can be converted to the o-triflyl derivative 6c in a four-step sequence starting with basic hydrolysis, resulting in the product phenylpropionic acid

(5c). These reactions are achieved at very high yields. Afterward, the resulting compound 5c can be converted to carbamate 6a by adding CuCl and EtOH in a solution and via the Curtius sequence. In the final step, the catalytic hydrogenation of product 6a can offer a quantitative yield of carbamate 6b. Reactions of this compound with phenyltriphlylamide and Et_3N provide the desired triflate 6c [162, 163]. Consequently, due to this reaction with 3,4-dihydroxycoumarine (2-chromanone), the desired product could be obtained in high yield and used for its intended purpose. The reaction mechanism of this reaction example is shown in Figure 2.14.

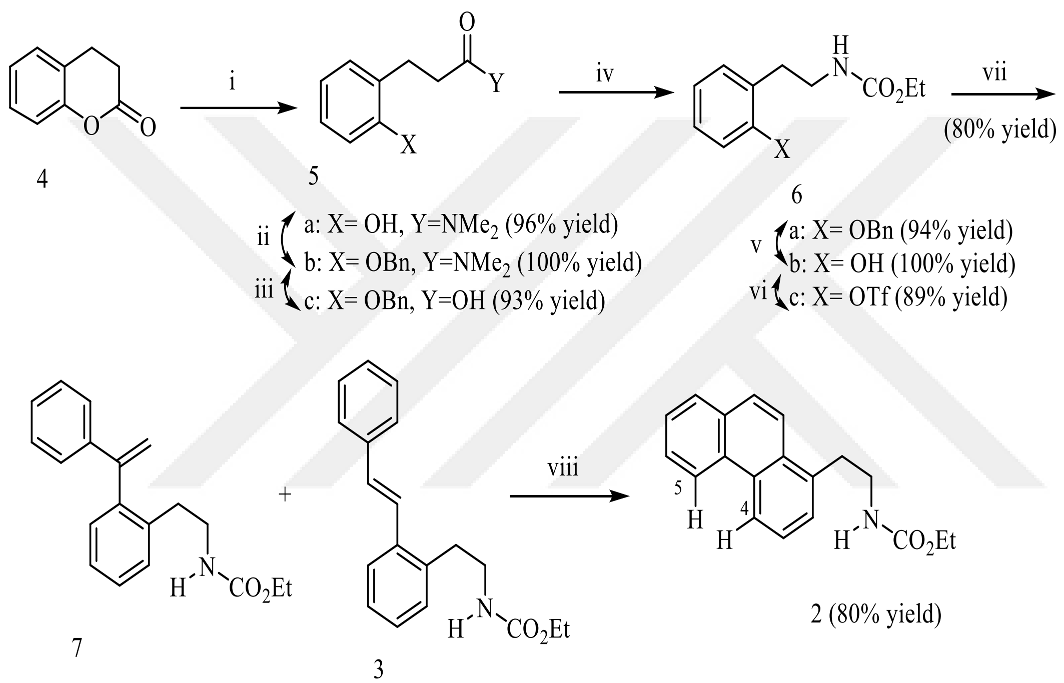


Figure 2.14 : Example reaction mechanism of ring-opening reaction of coumarine with amines.

There is another example showing ring-opening reactions of coumarines with amines. This example is related to the isolation and identification of components of spider toxins, especially naturally occurring spider toxins. The characterization of these toxins is determined by a diverse range of compounds formed with a new structure containing a phenolic group in addition to a polyamine moiety [164, 165]. In this kind of synthesis, 3,4-dihydrocoumarine is used as the phenolic substrate. The ring-opening reaction between 3,4-dihydrocoumarine and bis(Boc)-protected spermidine is shown in Figure 2.15.

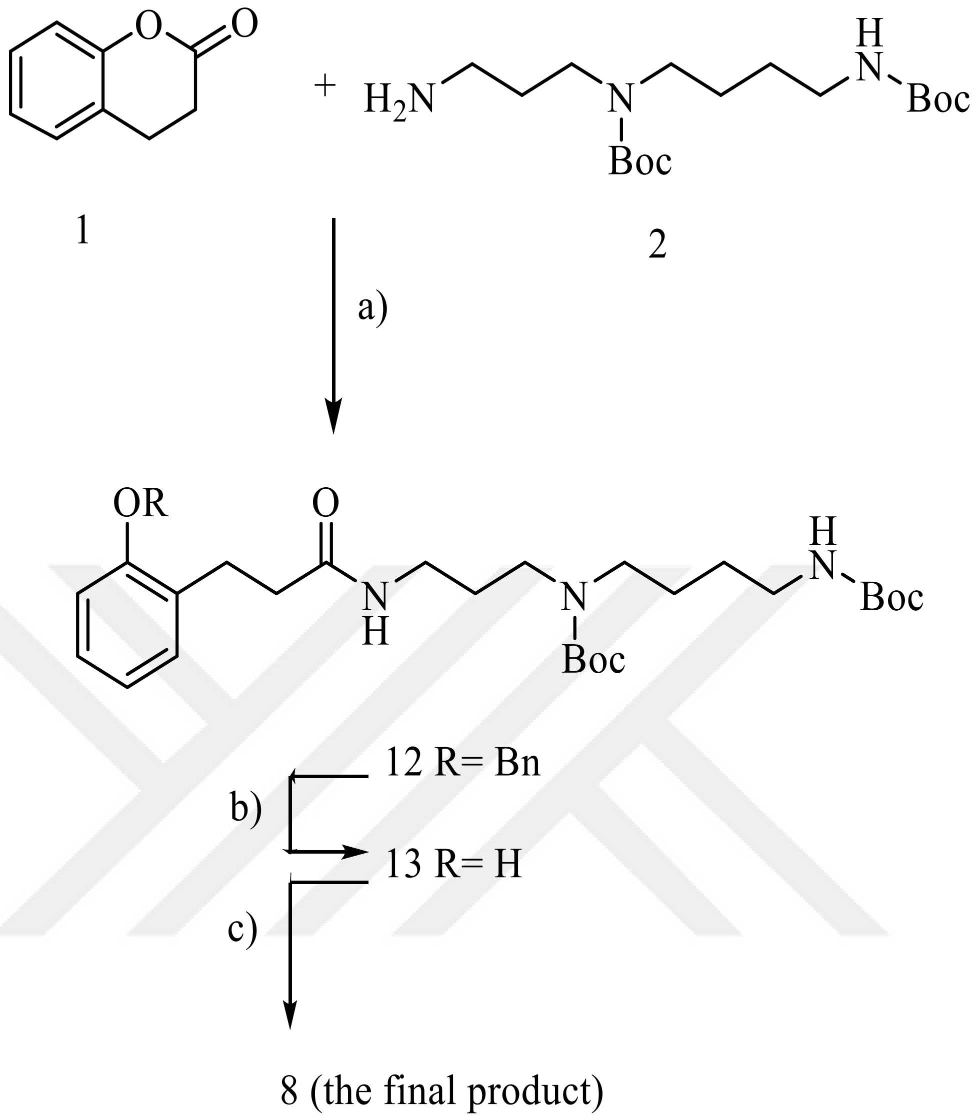


Figure 2.15 : The ring-opening reaction between 3,4-dihydrocoumarine and bis(Boc)-protected spermidine.

According to this procedure, the final product was synthesized by the aminolysis of 3,4-dihydrocoumarine. It has been proven that the amides might be prepared more effectively by directly acylating the primary amines. Thus, after treating the bis(Boc)-protected spermidine 2 with 1, the amide 13 was produced in 96% yield. Finally, the amine 8 was obtained when the Boc groups were eliminated [166]. In summary, ring-opening reactions of coumarines with amines can be utilized in a wide variety of areas, in particular with bio-based systems due to their unique properties.

2.4 Diels-Alder Reactions in Polybenzoxazines

The formation of unsaturated six-membered rings by the reaction of a conjugated diene and an alkene, namely, dienophile, is known as the Diels-Alder reaction. The process is also known as "cycloaddition" since it results in the development of a cyclic product through a cyclic transition state. In other words, the Diels-Alder reaction is [4+2]-cycloaddition from 4 π-electrons of the conjugated diene and 2 π-electrons of the dienophile, namely, an alkene or alkyne. The stability of σ and π bonds, which are bonds between atoms, is different according to their energies; the σ bond is more stable than the π bond, and therefore, as a result of these reactions, σ bonds are obtained instead of π bonds. Diels-Alder reactions are one of the most widely used reactions in organic chemistry and are crucial reactions owing to being stereospecific. The Diels-Alder reaction was discovered in 1928 by Otto Diels and Kurt Alder, and its name derives from their names [167]. Then, Otto Diels and Kurt Alder won the Nobel Prize because of their discoveries in 1950 [168].

Furthermore, the thermally reversible feature is another significant property of the Diels-Alder (DA) reaction. These reactions, which can be controlled by temperature, are the decomposition of the cyclic product and are called Retro-Diels-Alder (rDA) [169]. The Diels-Alder reaction is microscopically reversed by the retro-Diels-Alder reaction (rDA), which starts with a cyclohexene and ends with a diene and dienophile [170, 171]. The Diels-Alder reaction is a member of the class of "click" reactions, which are characterized by their extreme versatility, high efficiency, and excellent selectivity [172]. The general mechanism of Diels-Alder and retro Diels-Alder reactions is depicted in Figure 2.16.

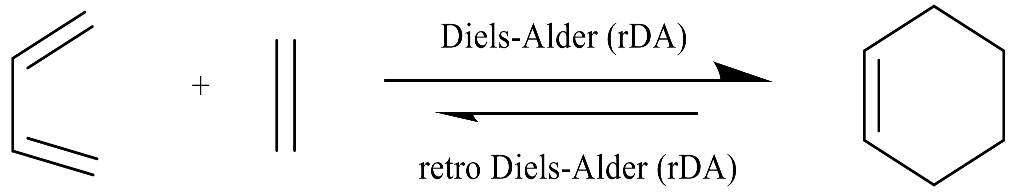


Figure 2.16 : General mechanism of Diels-Alder (DA) and retro Diels-Alder (rDA) reactions.

Moreover, benzoxazine main chains can be included in the Diels-Alder reaction. There is research in the literature related to benzoxazines with furan or maleimide chains

[173]. Furans are easily accessible due to their widespread nature as an organic family or compound [174, 175]. The dienic structure of the furan heterocycle is its most appealing structural feature since it allows it to be used in reactions such as Michael additions, vinyl reactions, and Diels-Alder (DA) cycloadditions. Hence, they possess the capability to undergo DA and retro-DA reactions with synthesized bio-benzoxazine [176].

In addition, DA reactions using furan-containing benzoxazines and bismaleimides provide features such as relatively low decomposition temperature through the retro-DA reaction, easy processability, and good flame retardancy. Therefore, recyclable networks can provide a variety of potential applications, including self-healing materials, chemical recycling applications, and high-performance materials [176-179]. In summary, obtaining furan derivatives from renewable resources is noteworthy in that it enables approaches such as sustainability and edibility of the furan/maleimide couple.

3. EXPERIMENTAL PART

3.1 Materials

3,4-Dihydrocoumarine (DHC) (Alfa Aesar, 99%), furfurylamine (Acros Organics, Thermo Scientific Chemicals 99%), paraformaldehyde (Sigma-Aldrich, 95%), 1,1’- (Methylenedi-4,1-phenylene)bismaleimide (BMI) (Sigma-Aldrich, 95%), sodium hydroxide (Isolab, ≥99%), magnesium sulfate ($MgSO_4$, VWR Chemicals, 98%), acetonitrile (ACN, Lab- Scan 99.9%), ethyl acetate (EtOAc, Carlo Erba, ≥99.9%), chloroform ($CHCl_3$, Riedel-de Haën, ≥99.5%), ethanol (EtOH, J.T.Baker, 96%), methanol (MeOH, Sigma-Aldrich, ≥99.8%), tetrahydrafuran (THF, Riedel-de Haën, ≥99.9%), diethyl ether (DEE, Riedel-de Haën, ≥99.8%), acetone (Carlo Erba >99.8%) were 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)

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

3.2.3 Differential scanning calorimeter (DSC)

Differential Scanning Calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC from 30 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 of N-(furan-2-ylmethyl)-3-(hydroxyphenyl)propanamide

3,4-dihydrocoumarine (3.00 g, 0.020 mol), and furfurylamine (1.94 g, 0.020 mol) were dissolved in acetonitrile (160 mL) in a 250 mL round-bottomed flask. Then, the solution was refluxed at 85 ^{O}C for 24 h. After, the solution was cooled to room temperature (R.T.) and filtered with an ordinary filter paper to remove any solid. Afterward, acetonitrile was evaporated by using a rotary evaporator and the remaining brownish oily liquid was dried in a vacuum at R.T. for 48 h in order to remove any solvent residue. The compound was obtained as cream colored solid (Yield: 93.02%).

3.3.2 Synthesis of monofunctional benzoxazine monomer by stepwise method

N-(furan-2-ylmethyl)-3-(hydroxyphenyl)propanamide (0.6 g, 0.00245 mol), which is the first step product, furfurylamine (0.238 g, 0.0245 mol) were mixed in 20 mL of ethyl acetate-ethanol mixture (3:1, v/v) in a 50 mL flask. Then, paraformaldehyde (0.147 g, 0.0049 mol) was added to this solution. The content was refluxed for 72 h at 80^{O}C. After cooling the reaction content to room temperature, the solution was filtered with an ordinary filter paper in order to remove any solid. Then, the ethyl acetate-ethanol mixture was removed by using a rotary evaporator. Afterward, the remaining oily crude product was dissolved in chloroform ($CHCl_3$), and this solution was washed with 1 M NaOH solution (3 x 50 mL), and then was neutralized with deionized water (3 x 50 mL). The chloroform solution was dried with anhydrous $MgSO_4$ (*ca.* 10 g) and left for 15 min. prior to filtering the solids. After filtration, the chloroform was completely removed by using a rotary evaporator, and the remaining yellowish oily liquid was dried in a vacuum at room temperature (R.T.) for 24 h and obtained as a yellowish solid. The yield was calculated as 45.58 %.

3.3.3 Synthesis of monofunctional benzoxazine monomer by one-pot method

A representative procedure is as follows: 3,4-dihydrocoumarine (3 g, 0.020 mol) and furfurylamine (3.9330 g, 0.040 mol) were mixed in 150 mL chloroform in a 250 mL round-bottomed flask. The content was refluxed for 24 h at 85 ^{O}C. Afterward, paraformaldehyde (2.43 g, 0.080 mol) was added to the reaction mixture and refluxed for a further 12 h. Then, the mixture was cooled to room temperature and chloroform was removed by using a rotary evaporator. Then, the remaining oily crude product was dissolved in chloroform ($CHCl_3$), then, this solution was washed with 1 M NaOH solution (3 x 100 mL), and then was neutralized with deionized water (3 x 100 mL). The chloroform solution was dried with anhydrous $MgSO_4$ (*ca.* 10 g) and left for 15 min. After that, the mixture was filtered and chloroform was removed through a rotary evaporator. Afterward, the remaining product was dried in a vacuum at room temperature (R.T.) for 24 h and obtained as a yellowish viscous solid. Thereafter, the product was dissolved in ~3 mL tetrahydrafuran (THF) and was precipitated in diethyl ether. The compound was dried under vacuum at R.T. and obtained as a white solid (yield: ~40%).

3.3.4 Synthesis of main-chain polybenzoxazines by Diels-Alder reaction

A representative procedure is as follows: In a 50 mL round-bottomed flask, 1,3-benzoxazine (0.511 g, 1 mol) and 1,1’- (methylenedi-4,1-phenylene) bismaleimide (BMI) (0.5 g, 1 mol) were added and dissolved in 10 mL THF. This content was refluxed for 24h at 50 ^{O}C. Afterward, the mixture was cooled the room temperature. Then, the content was precipitated with 25 mL of methanol and 2 mL of Nacl-water mixture and the mixture was filtered and dried in a vacuum at room temperature overnight. The obtained product was yellowish solid. The yield was calculated as 85.71 %.

4. RESULTS AND DISCUSSIONS

3,4-Dihydrocoumarines (DHC), which are naturally derived six-membered aromatic lactones, tend to undergo ring-opening reactions and thus, particularly in the formation of esters, serve as precursors in medicinal chemistry [180, 181]. Furthermore, for the synthesis of amide functional phenolics, 3,4-dihydrocoumarines are an applicable choice as reagents. A primary or secondary amine can readily initiate a ring-opening reaction without the need for a catalyst [162, 166, 182, 183]. The yield of the reaction is quite high. The vast design flexibility can be fulfilled by this reaction in order to obtain various different phenolics with amide functionality. This reaction is also known as the aminolysis reaction. The ring-opening reaction of 3,4-dihydrocoumarine with amines to form an amide is represented in Figure 4.1.

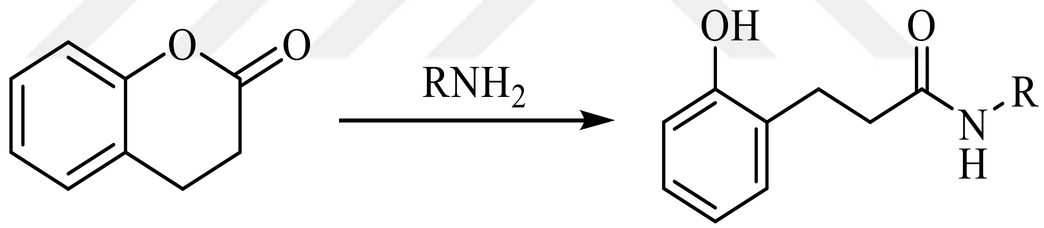


Figure 4.1 : Ring-opening reaction of 3,4-dihydrocoumarine with amines to form an amide.

In addition, furfurylamine is a renewable and low-cost resource and can be produced from various agricultural by-products [117, 184]. In other words, furfurylamine is a renewable platform for benzoxazine synthesis owing to the presence of an amine group [120, 184-188]. Therefore, this furan structure facilitates an increase in the cross-linking density and charring capability of the resulting thermosets [189, 190].

In this study, our approach was to synthesize bio-based benzoxazine monomers and main-chain polybenzoxazine precursor by using renewable resources, which are 3,4-dihydrocoumarine and furfurylamine, with two different approaches: stepwise and one-pot methods. Initially, 3,4-dihydrocoumarine (DHC) was selected as a natural phenol source and reacted with natural furfurylamine to synthesize the phenolic amide compound with quite high yield, and this synthesized compound was the reagent for benzoxazine monomer synthesis. The reaction of DHC with furfurylamine was performed in acetonitrile (CH_3CN) solvent, and then the solid compound was acquired with ~93% yield. The reaction between the DHC and furfurylamine in the solvent condition is presented in Figure 4.2.

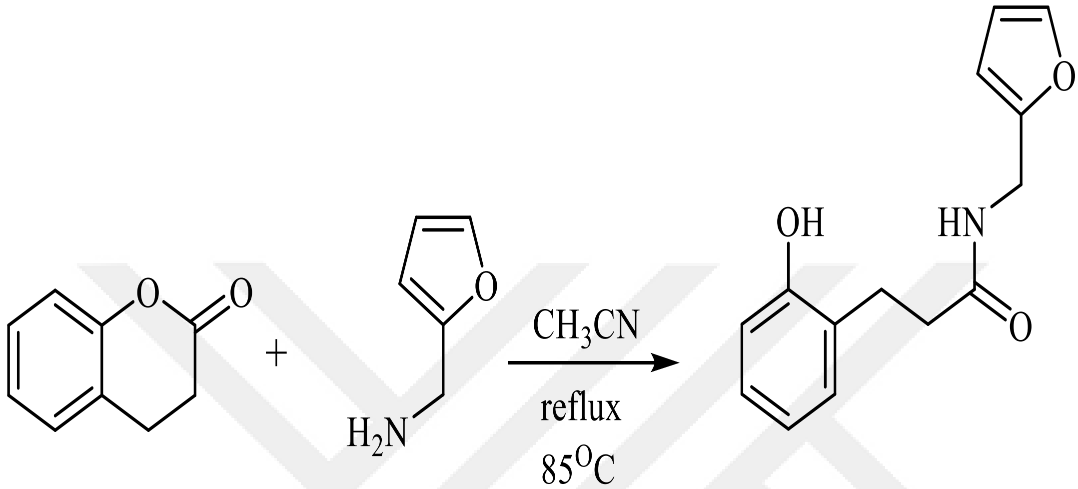


Figure 4.2 : Synthesis of DHC-furfurylamine.

The achievement of the synthesis was obviously unveiled by the spectral analysis of phenolic amide. The obtained compound was abbreviated as DHC-furfurylamine. The chemical structure of DHC-furfurylamine was evaluated by ^{1}H NMR and FT-IR spectral analysis. The ^{1}H NMR spectrum of DHC-furfurylamine is depicted in Figure 4.3. Also, all peaks including solvent peaks and water residue are represented in the Figure 4.3.

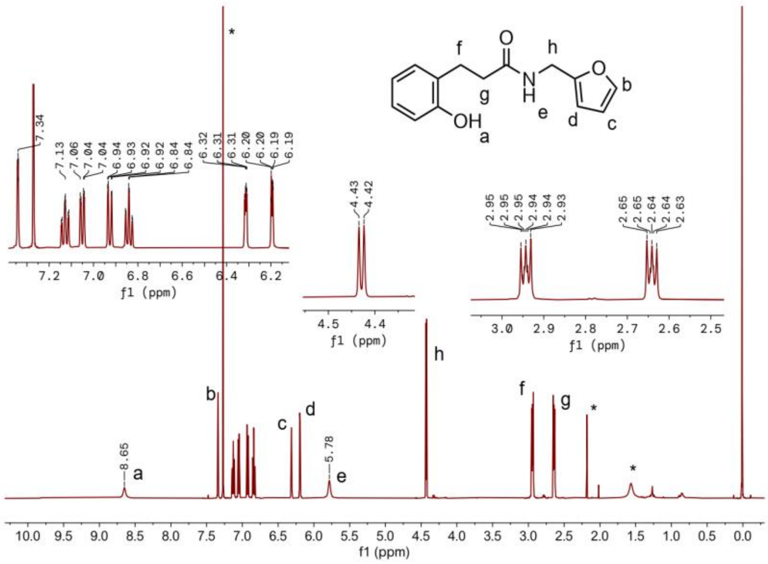


Figure 4.3 : [1]H-NMR spectrum of DHC-furfurylamine (*Indicates solvent peaks and water residue).

The [1]H NMR spectrum of DHC-furfurylamine shows characteristic peaks such as 4.42 ppm (NH-CH_2) of the ring-opened structure. Moreover, the amide proton appears at 5.78 and the hydroxyl proton also visible at 8.65 ppm. In addition, the structure of DHC-furfurylamine which is the reagent for the coumarine-benzoxazine (Cou-Bz) monomer, was illuminated through the FT-IR analysis. The FT-IR spectrum of DHC-furfurylamine is illustrated in Figure 4.4.

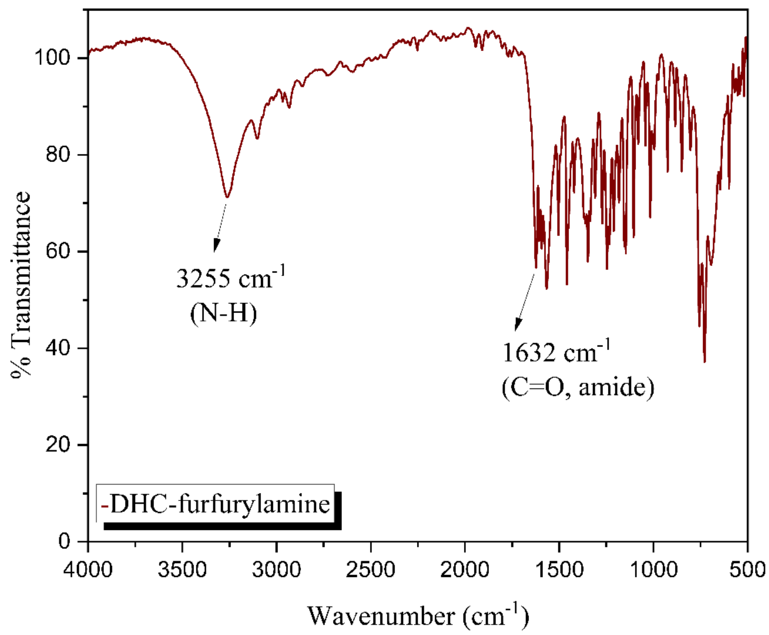


Figure 4.4 : FT-IR spectrum of DHC-furfurylamine.

The FT-IR spectrum of this compound displays the amide carbonyl and stretching vibration band of N-H and O-H bands. In Figure 4.4, the FT-IR spectrum, the stretching vibration bands of amide N-H (3255 cm^{-1}) merged with Phenolic O-H, and amide C=O (1632 cm^{-1}) bands provide evidence of a ring-opened structure.

Following the production of phenols containing amide linkages, benzoxazine monomers were synthesized through the classical synthesis approach, which includes phenol, formaldehyde, and an amine. 3,4-dihydrocoumarine and furfurylamine were used as biosources for the coumarine-benzoxazines. 3,4-dihydrocoumarine was selected as a phenol source, furfurylamine was selected as an amine source, and paraformaldehyde was used in this synthesis. These monomers were synthesized both sequentially and by one-pot methods. Firstly, in the stepwise method, the reaction was performed in chloroform, acetonitril, and toluene:ethanol (2:1, v/v) solvents separately. Even though each solvent provides the product, in chloroform, better analysis results were acquired. However, this solvent was changed to an ethyl acetate:ethanol (3:1, v/v) solvent pair in order to provide the green chemistry principles. Also, benzoxazine monomers with high yields and purity have reportedly been achieved with the use of non-polar solvent combinations [52]. It has also been discovered that gelation can be diminished and the molecular weight of main-chain polybenzoxazine prepolymers can be increased using the toluene:ethanol (2:1, v/v) binary system [67]. Hence, by using the ethyl acetate:ethanol (3:1, v/v) solvent pair, the DHC-furfurylamine reagent was reacted with furfurylamine and paraformaldehyde in a molar ratio of 1:1:2. The benzoxazine monomer was obtained as a monofunctional coumarine-benzoxazine. The monofunctional Cou-Bz synthesis reaction between DHC-furfurylamine, furfurylamine and paraformaldehyde is presented in Figure 4.5.

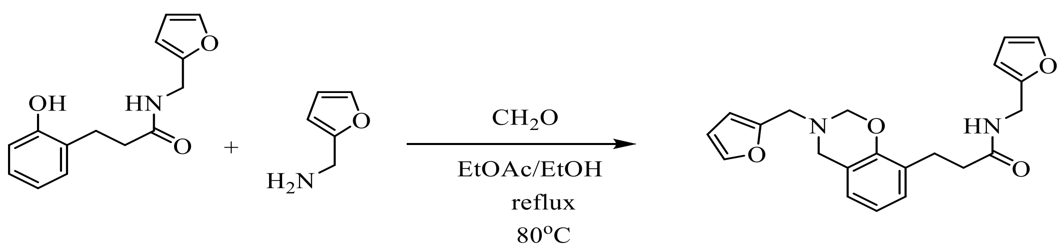


Figure 4.5 : The monofunctional Cou-Bz synthesis.

In the one-pot method, the reaction between 3,4-dihydrocoumarine and furfurylamine was performed at 85 °C in chloroform for 24h in order to complete the ring-opening reaction. Afterward, paraformaldehyde was added to the mixture under reflux for another 12 h to form the benzoxazine ring. The obtained compounds were abbreviated as Cou-Bz in both stepwise and one-pot methods. The monofunctional Cou-Bz synthesis one-pot reaction is depicted in Figure 4.6.

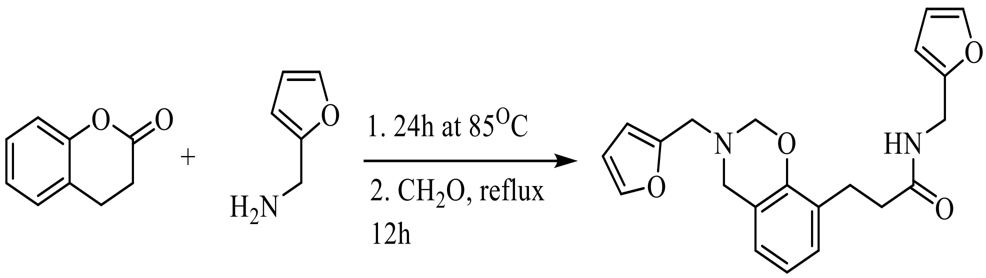


Figure 4.6 : The one-pot synthesis of monofunctional Cou-Bz monomer.

The chemical structures of the synthesized stepwise and one-pot benzoxazine monomers were confirmed by ^{1}H NMR and FT-IR spectral analysis. The ^{1}H NMR spectrum of the stepwise coumarine-benzoxazine monomer presented in Figure 4.7 shows the characteristic peaks of the monomer. Then, the ^{1}H NMR spectrum of the one-pot coumarine-benzoxazine monomer represented in Figure 4.8.

In Figures 4.7 and 4.8, the proton signals at 4.89, 4.44 ppm (O-CH_2-N), and 4.00, 3.99, and 3.89 ppm (Ar-CH_2-N) are evidence of the existence of the oxazine rings in the monomer. Figure 4.9 represents the ^{13}C NMR of the coumarine-benzoxazine. In that spectrum, the peaks at 77.3, 77.0, and 76.7 ppm are attributed to the carbons on (N-CH_2-O), and 48.2 ppm is assigned to the (Ar-CH_2-N) carbons of the oxazine ring. The characteristic peaks are matched with each other; hence, both methods are available.

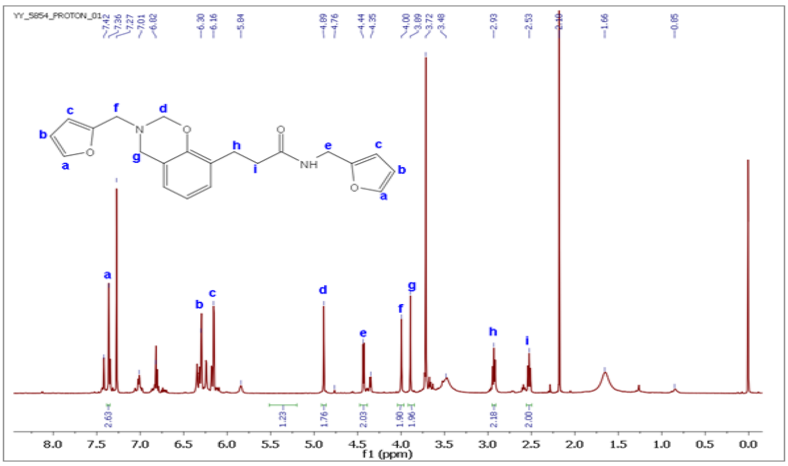


Figure 4.7 : ^{1}H-NMR spectrum of stepwise Cou-Bz monomer.

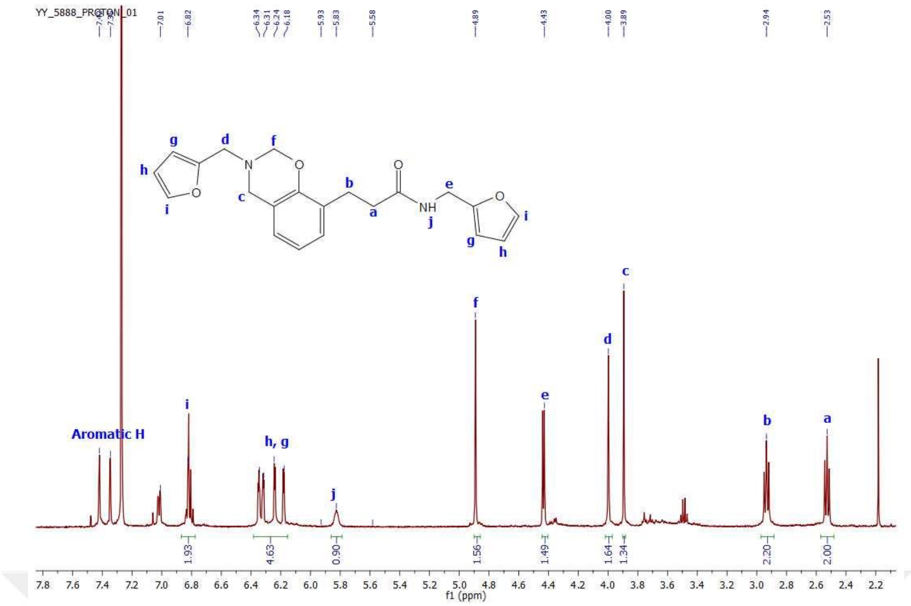


Figure 4.8 : ^{1}H-NMR spectrum of one-pot Cou-Bz monomer.

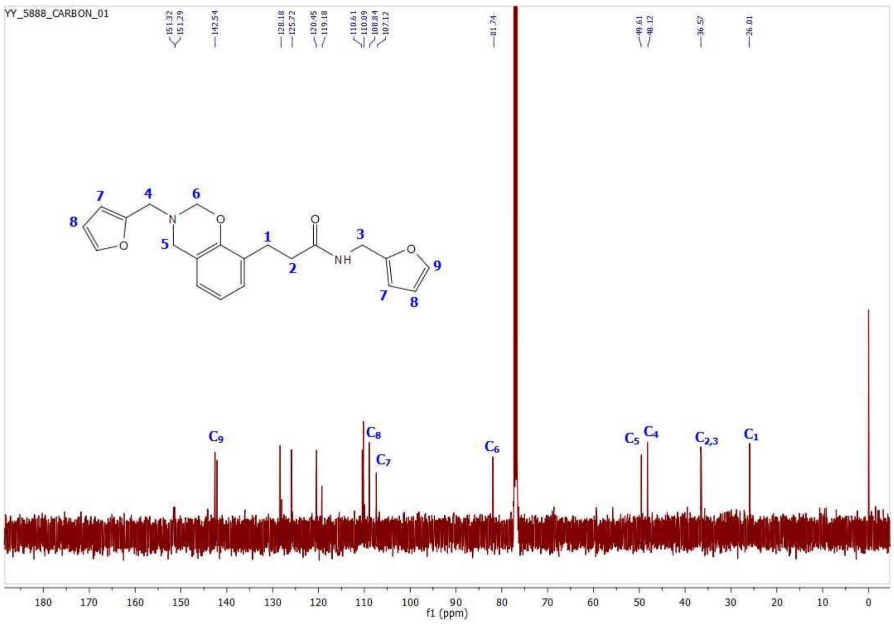


Figure 4.9 : ^{13}C NMR spectrum of one-pot Cou-Bz monomer.

The FT-IR spectra of Cou-Bz by stepwise and one-pot methods are illustrated in Figure 4.10. The FT-IR spectrum presented in Figure 4.4 provides that 1632 cm^{-1} shows the amide structure, and 3255 cm^{-1} shows the N-H bond in DHC-furfurylamine. Figure 4.10 represents the one-pot and stepwise coumarine-benzoxazine (Cou-Bz) monomers at 1647 cm^{-1} for amide and at 3255 cm^{-1} N-H band. Therefore, these results verify the successful synthesis of amide containing biobased benzoxazines.

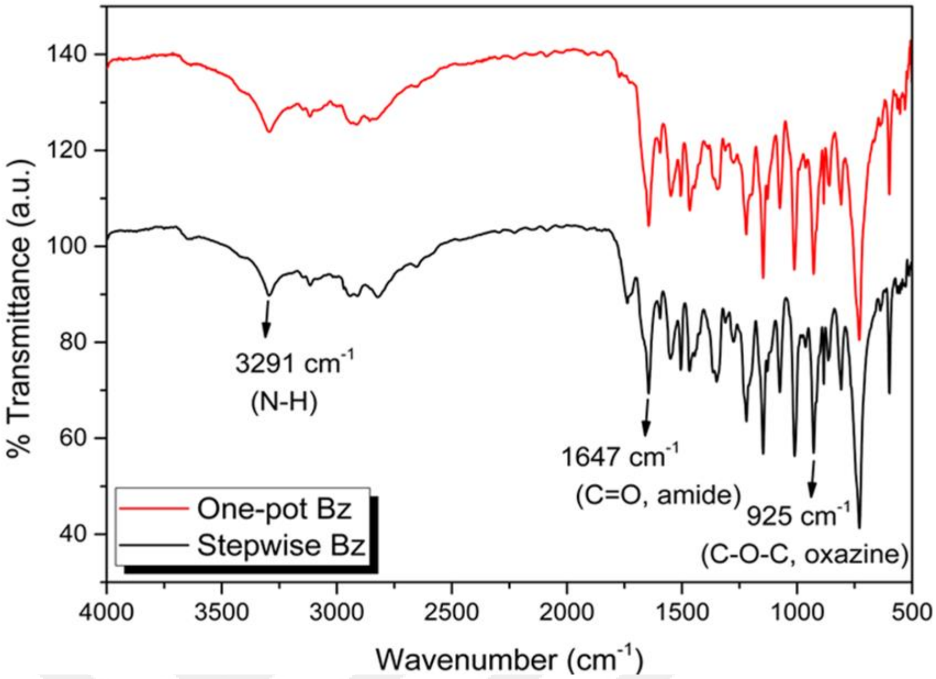


Figure 4.10 : FT-IR spectra of one-pot and stepwise Cou-Bz monomers.

Depending on the functional groups present, benzoxazines can have a wide range of ring-opening polymerization temperatures, usually between 160 and 260°C. Because benzoxazines undergo exothermic polymerization, ring-opening polymerization can be observed by differential scanning calorimetry (DSC). Figure 4.11 presents the DSC results of coumarine-benzoxazines with different heating rates. By this way, the activation energy of the synthesized coumarine based benzoxazine was calculated by using the Kissinger-Ozawa method. The well-known Kissinger and Ozawa techniques, which are modifications of the Arrhenius equation, may be used to calculate the activation energy of the polymerization of benzoxazine monomers with the use of DSC [191]. The techniques rely on heating samples at many distinct heating rates, such as 5, 7.5, 10, 12.5, and 15 ◦C/min, in order to determine the reaction peak temperature [192, 193]. The calculation of activation energy (E_a) is explained according to Kissinger and Ozawa methods. Initially, according to the Kissinger method, E_a can be calculated by equation (1) as follows:

$$ln(\beta / T^2_p) = ln(AR/Ea) - E_a /RTp \qquad (4.1)$$

Where β:heating rate, A: the frequency factor, T: the maximum temperature of the exotherm, R: the gas constant, and E_a :the activation energy. The E_a can be calculated from the slope of ln(β/Tp 2) against 1/Tp if a good linear relationship is obtained.

Additionally, the activation energy can be calculated by the Ozawa method too (equation 2):

$$\ln\beta = -\,1.052\ E_a / RT_p + C \qquad (4.2)$$

Where c: constant. The slope of the plot ln(β) against 1/Tp gives the activation energy. Typically, the activation energies of benzoxazines lie between 100 and 160 kJ/mol. The activation energy of the coumarine-benzoxazine is 108 and 99 kJ/mol, according to the Kissinger-Ozawa methods, respectively. The activation energies calculated through the Kissinger-Ozawa methods respctively, are represented in Figure 4.12. These results are at the low end of benzoxazine activation energy because of the possible catalytic effect of amide NH. The catalytic effect of amide NH has been shown in previous reports in the literature, and the obtained result from the kinetic study aligns well with the previous reports. Figure 4.13 shows the conversion of the coumarine-benzoxazine monomer. Depending on the heating rate, the full conversion can be attained at *ca.* 230 ^{O}C. Thus, both stepwise and one-pot synthesized monomers DSC analyses demonstrate that both monomers are thermally curable and display DSC characteristics.

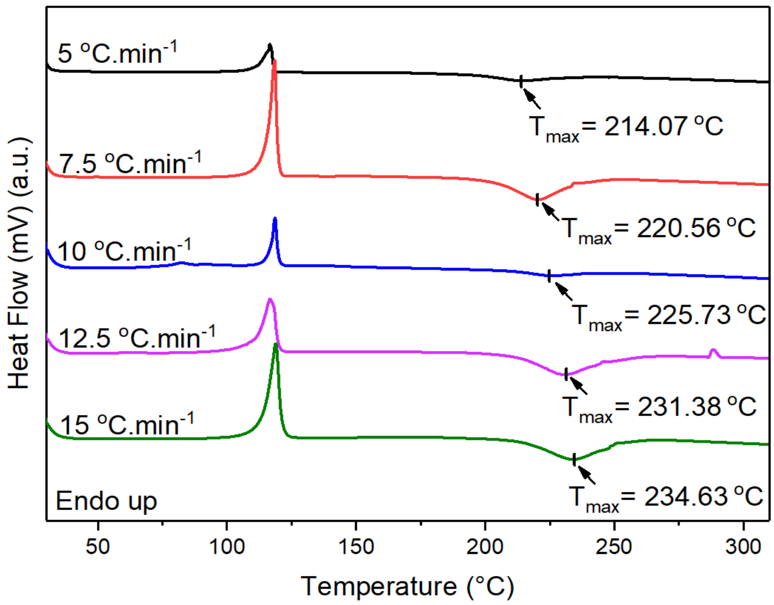


Figure 4.11 : DSC Thermograms of Cou-Bz with different heating rates (5 ^{o}C.min^{-1}, 7.5 ^{o}C.min^{-1}, 10 ^{o}C.min^{-1}, 12.5 ^{o}C.min^{-1}, 15 ^{o}C.min^{-1}).

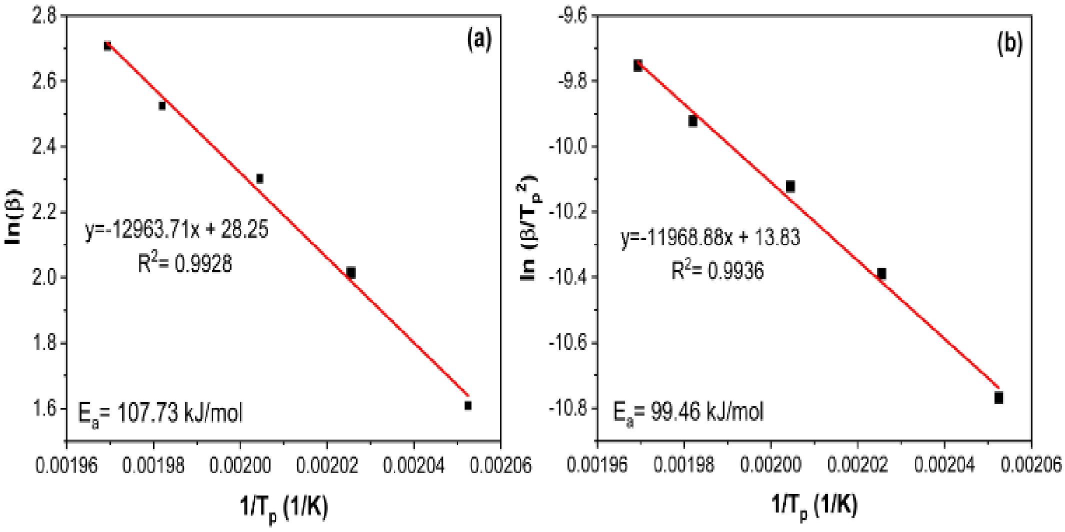


Figure 4.12 : DSC curves Cou-Bz at different heating rates and the graphs of Ozawa (a) and Kissinger (b) methods for the calculation of Ea using non-isothermal data.

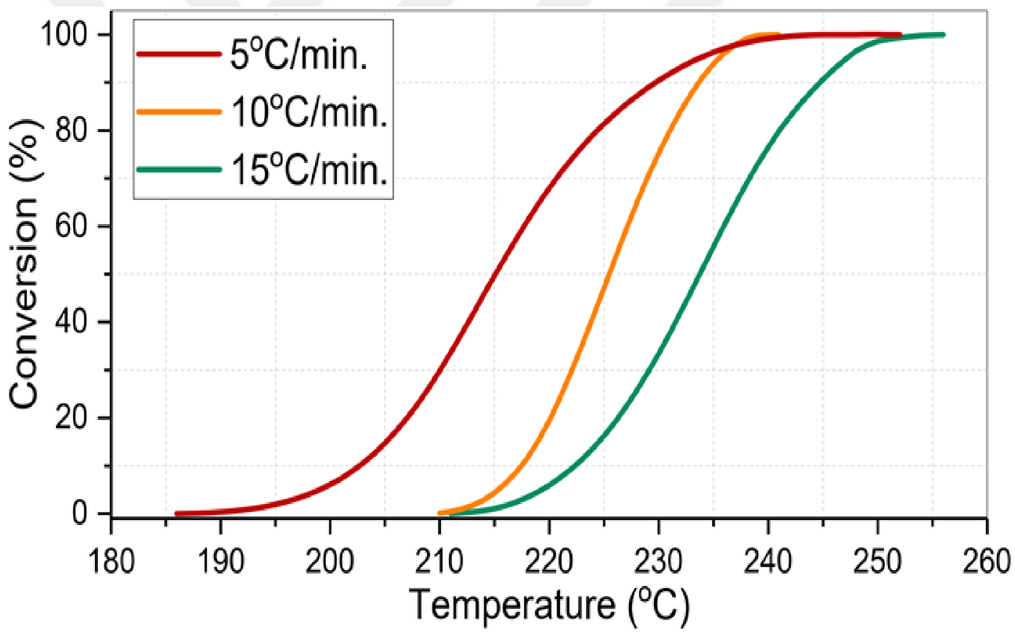


Figure 4.13 : Conversion graph of coumarine-benzoxazine monomer.

In the case of thermal stability for cured coumarine-benzoxazine monomer, thermogravimetric analyzer (TGA) analysis was performed under nitrogen gas. TGA thermograms and related thermal properties are represented in Figures 4.14, 4.15, and Table 4.1, respectively. In terms of initial degradations, polybenzoxazines from the stepwise method, monofunctional benzoxazines, and one-pot monofunctional benzoxazines show the same values at $T_{5\%}$; at $T_{10\%}$, the stepwise method is lower than the one-pot method; and at T_{max} values, both of them have two different temperatures and are close to each other. Besides, the char yield at 800 °C, one-pot, is higher than the stepwise method. According to TGA results, the char yield of monofunctional bio-based benzoxazines is as high as with classical benzoxazines.

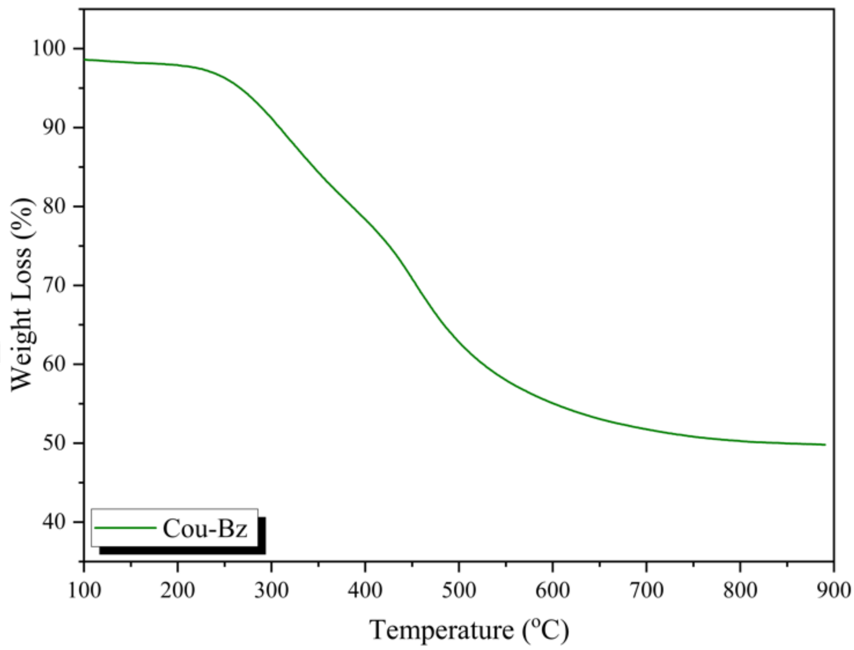


Figure 4.14 : TGA thermogram of coumarine-benzoxazine (Cou-Bz).

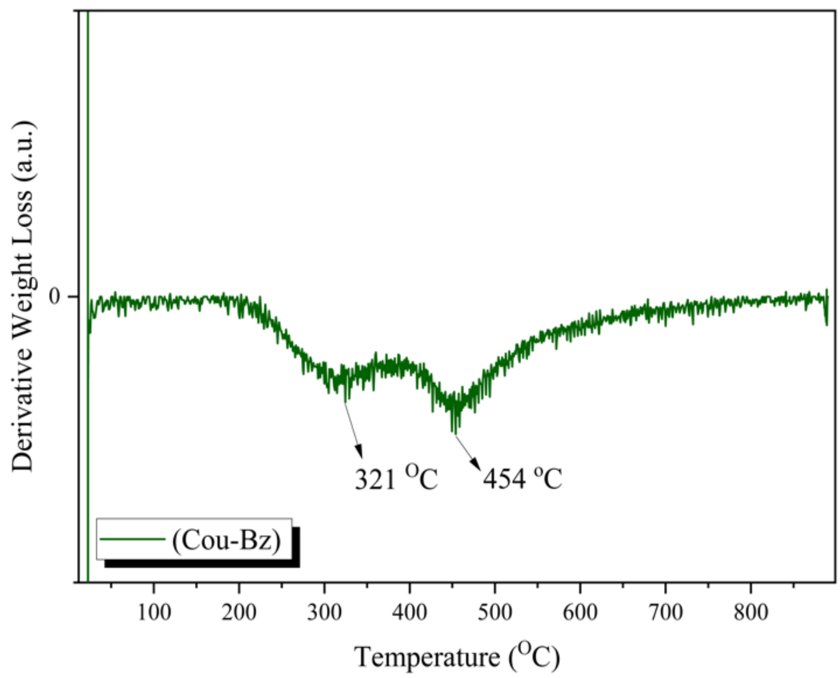


Figure 4.15 : Derivative TGA of cured coumarine-benzoxazine (Cou-Bz).

Table 4.1 : Thermal properties of the cured coumarine-benzoxazine (Cou-Bz).

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_c (%)	T_{max} (°C)
Coumarine-benzoxazine	231	254	40	321
Coumarine-benzoxazine	231	254	40	454

Subsequently, synthesized benzoxazines polymerized through the Diels-Alder reaction by using bismaleimides in order to obtain main-chain polybenzoxazine. The reaction between the synthesized benzoxazine and bismaleimide in a 1:1 molar ratio was performed at 50 °C in tetrahydrofuran (THF). The polybenzoxazine was obtained after 12h. The synthesis reaction between Cou-Bz and bismaleimide is presented in Figure 4.16. The obtained main-chain polybenzoxazine is abbreviated as Cou-Bz-BMI.

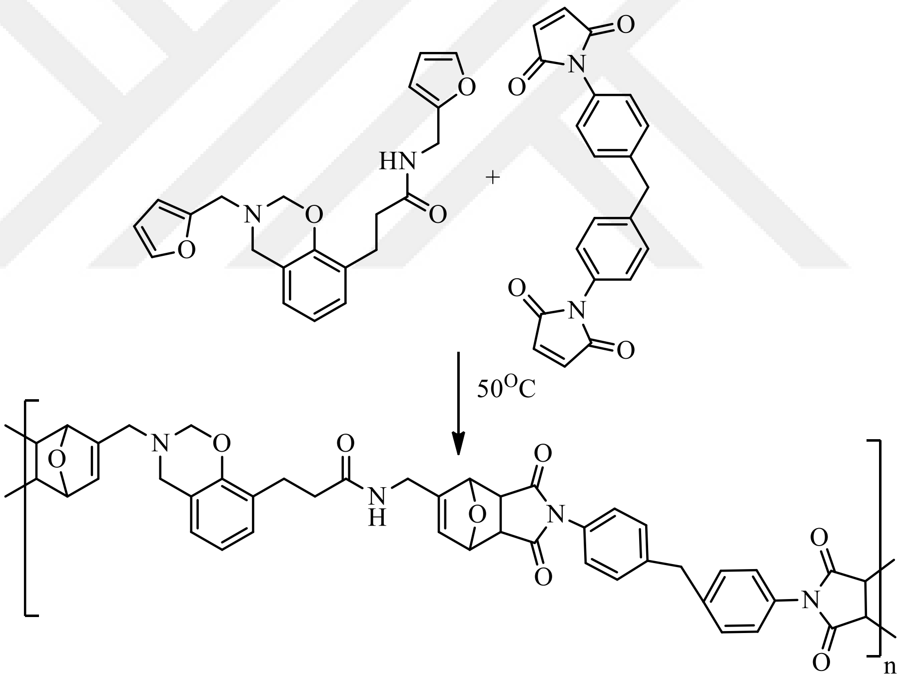


Figure 4.16 : Diels-Alder Reaction between Cou-Bz and BMI.

The chemical structures of the main-chain polybenzoxazine were evaluated by ^{1}H NMR and FT-IR spectral analysis. The ^{1}H-NMR spectrum of the Cou-Bz-BMI is illustrated in Figure 4.17. According to the ^{1}H-NMR spectrum, the characteristic oxazine proton signals at 5.5, 5.3 (O-CH_2-N), and 3.71 ppm (Ar-CH_2-N) provide clear evidence of the formation of benzoxazine on the structure. Also, the peaks at 4.1 and 3.9 ppm (CH_2) stem from 2,5-dihydrofuran, proving that the aromaticity of furan has ceased to exist. Also, the ^{13}C NMR spectrum of Cou-Bz-BMI main-chain polybenzoxazine is illustrated in Figure 4.18.

In Figure 4.18, the ^{13}C NMR spectrum, the peaks at 175.23, 174.32 ppm show the carbonyl (C=O), 80.78, 80.41, and 80.03 ppm (O-CH_2-N) oxazine. Moreover, peaks at 75.19 and 74.82 ppm (CH_2) show that they are coming from 2,5-dihydrofuran, however, not from the aromatic one.

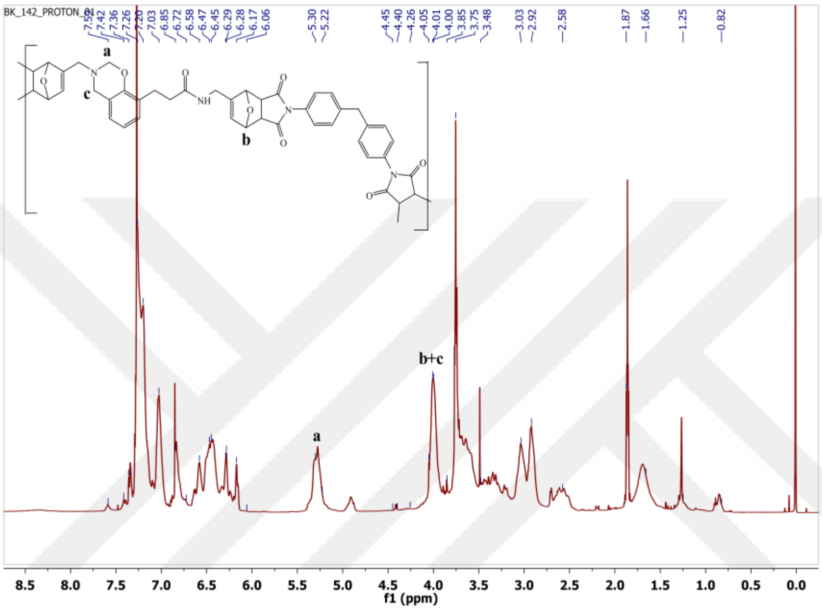


Figure 4.17 : ^{1}H NMR Spectrum of Cou-Bz-BMI main-chain polybenzoxazine.

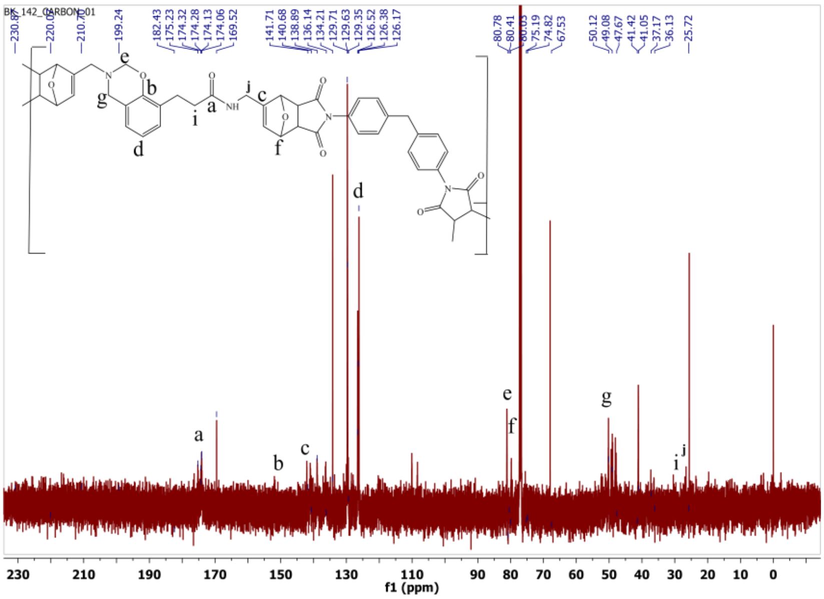


Figure 4.18 : ^{13}C NMR Spectrum of Cou-Bz-BMI main-chain polybenzoxazine.

The FT-IR spectrum of Cou-Bz-BMI is depicted in Figure 4.19. The FT-IR spectrum also gives evidence for the formation of the corresponding main-chain polybenzoxazine structure in Figure 4.19. The stretching vibrations of C=O (1710 cm^{-1}) aromatic C-H (3000-3050 cm^{-1}), and N-H (3400 cm^{-1}) can be considered strong proof supporting the suggested structure.

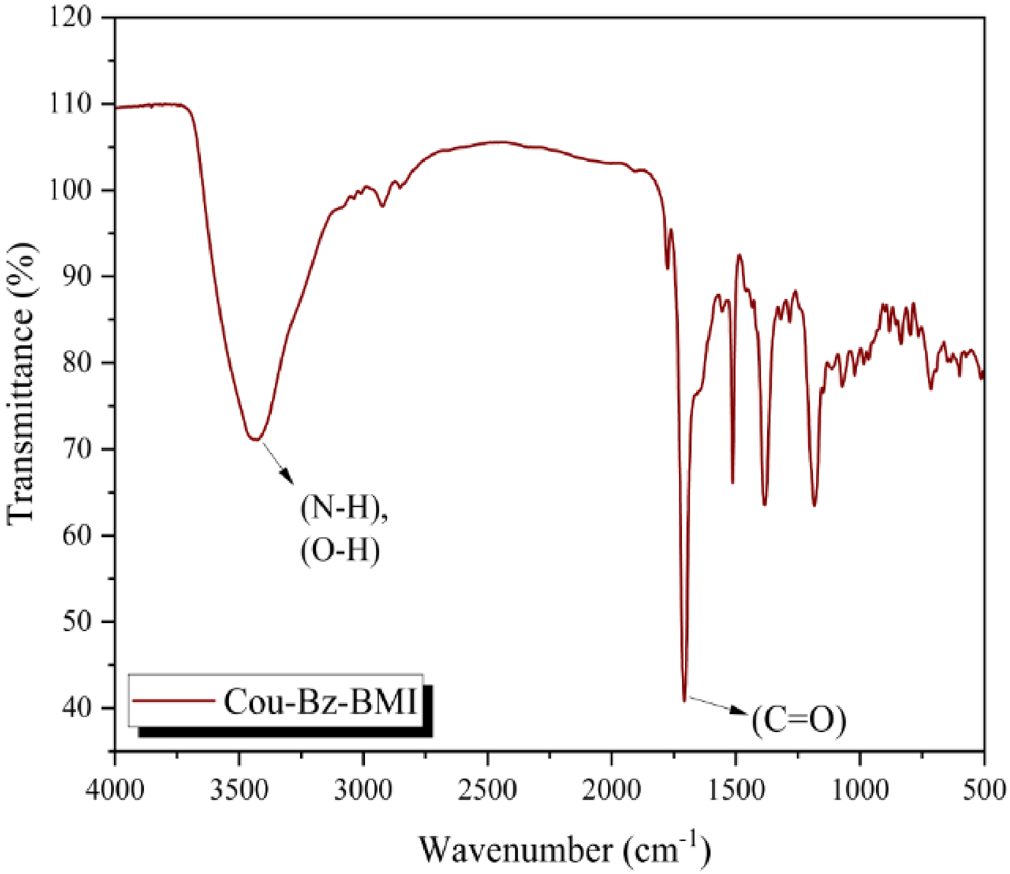


Figure 4.19 : FT-IR spectrum of Cou-Bz-BMI main-chain polybenzoxazine.

Furthermore, thermal behaviors were traced by using DSC under nitrogen gas and using a heating rate of 10 °C min^{-1}. Figure 4.20 represents the exotherms related to the polymerization via the Diels-Alder reaction of Cou-Bz-BMI in the DSC analysis and the conversion of this compound. The 93 °C represents the retro Diels-Alder (rDA) temperature. The T_{max} value was found to be 191 °C. It is also seen that the conversion occurs at 225 °C at a rate of 10 °C min^{-1}.

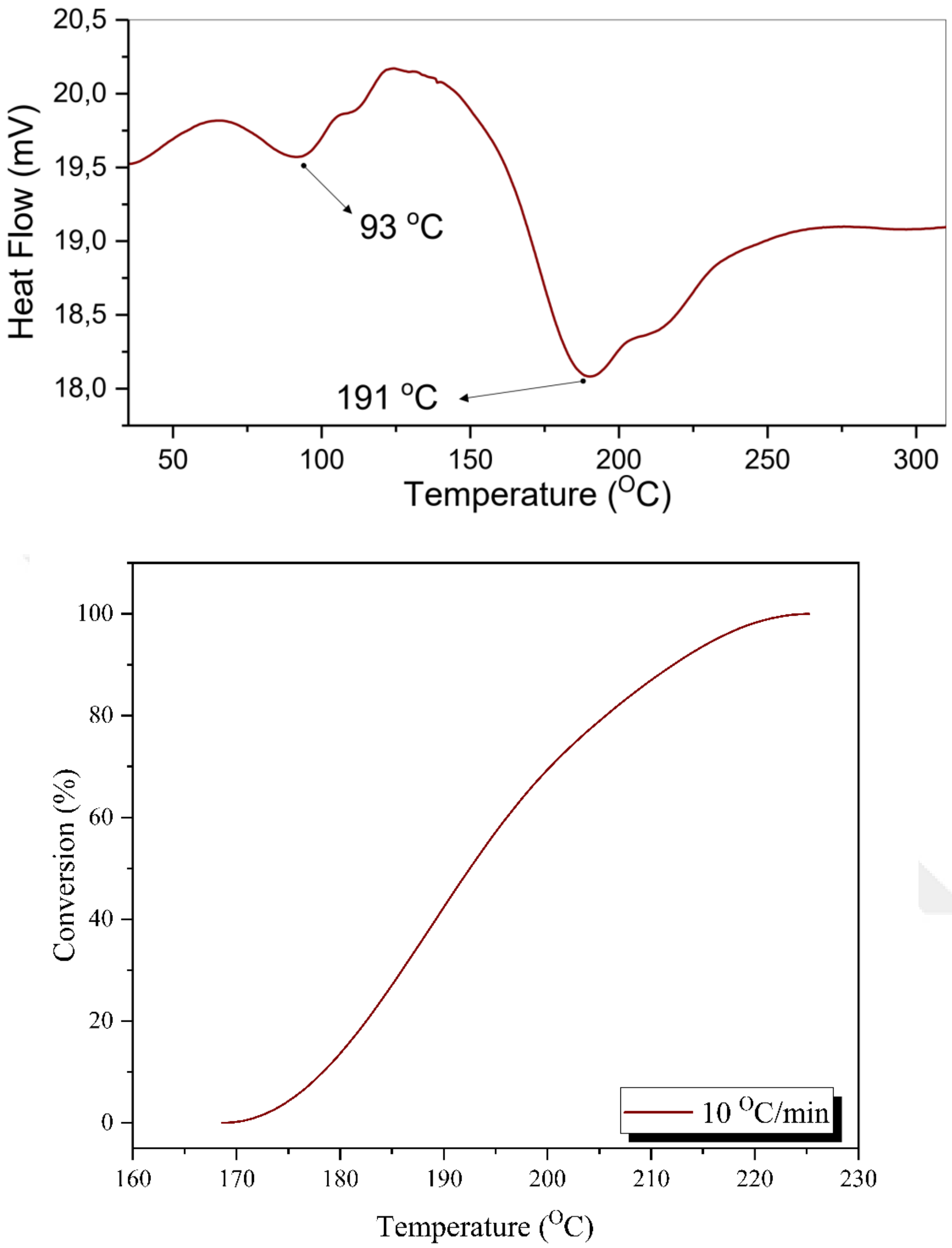


Figure 4.20 : DSC thermogram and conversion of Cou-Bz-BMI.

The molecular weight of the main-chain polybenzoxazine was analyzed using gel permeation chromatography (GPC). The GPC data is presented in Table 4.2. In general, monofunctional benzoxazines have a small number of repeating units and, hence, low molecular weights. The main reason for this situation is the continuous reaction circle of benzoxazines, such as ring-opening reactions and Friedel-Crafts reactions. In other words, there are a variety of reactions during the polymerization of benzoxazines, and thus, their molecular weights cannot be very high. Even though, according to Table 4.2, there are no larger macromolecules, oligomers are formed and provide the main-chain polybenzoxazine characteristics.

Table 4.2 : GPC data of Cou-Bz-BMI.

Polymer	M_n	M_w	M_w/M_n
Cou-Bz-BMI	1,014 Da	2,017 Da	1.989

The thermostability of Cou-Bz-BMI before curing and after curing main-chain polybenzoxazine specimens was measured with thermogravimetric analysis (TGA) under nitrogen flow. TGA analysis and the significant points of thermal properties are presented in Figure 4.21, Figure 4.22, and Table 4.3, respectively.

The degradation temperatures for $T_{5\%}$ and $T_{10\%}$ of Cou-Bz-BMI before curing are 123 °C, 280 °C, and those of Cou-Bz-BMI after curing are 260°C, 312 °C. Also, at T_{max} values, Cou-Bz-BMI before curing has two values of 260 and 452 °C, and Cou-Bz-BMI after curing is 452 °C. Moreover, in general, the char yield of monofunctional benzoxazines is around 30–40%. The obtained char yields are 43% and 51%, respectively, and it has been shown that the biobased main-chain polybenzoxazine was successfully synthesized.

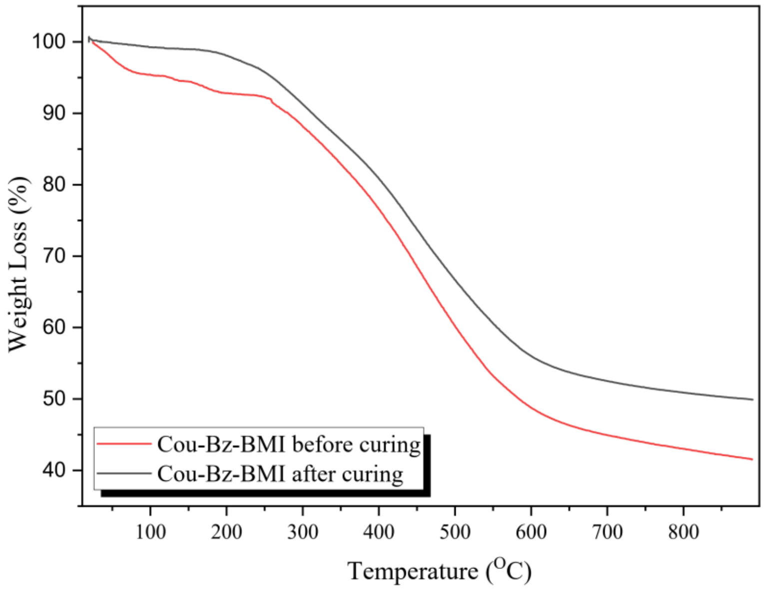


Figure 4.21 : TGA thermogram of Cou-Bz and BMI of Diels-Alder reaction.

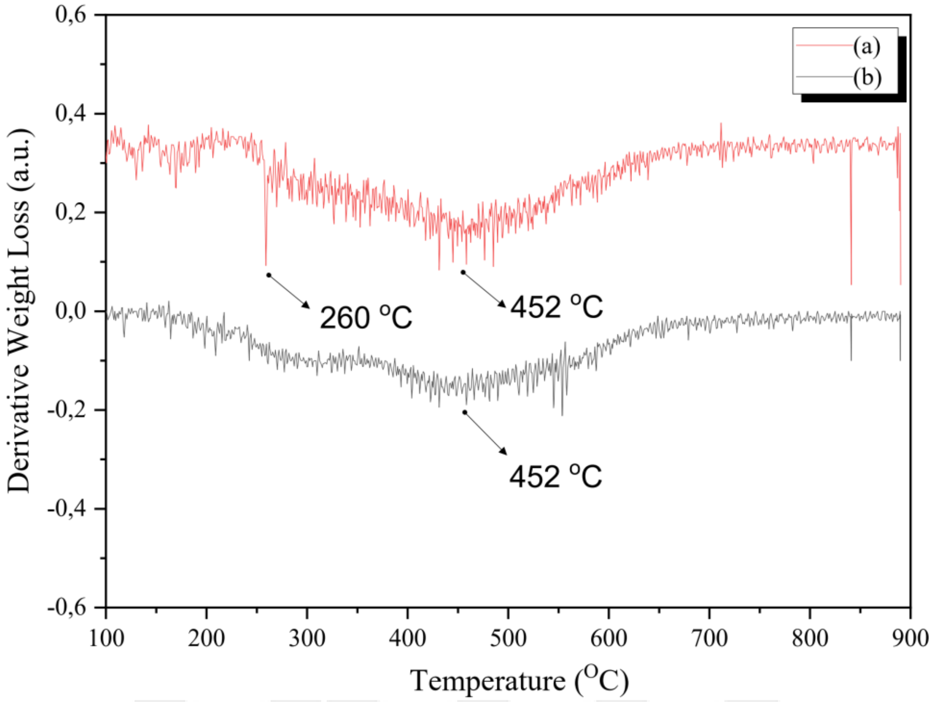


Figure 4.22 : Derivative TGA of Cou-Bz-BMI before curing (a), and Cou-Bz-BMI after curing (b).

Table 4.3 : Thermal properties of the cured and un-cured Cou-Bz-BMI.

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_c (%)	T_{max} (°C)
Cou-Bz-BMI before curing	123	280	43	260-452
Cou-Bz-BMI after curing	260	312	51	452

5. CONCLUSION

In conclusion, in this work, a novel, straightforward, and sustainable methodology is presented for the synthesis of a highly bio-based benzoxazine monomer by using 3,4-dihydrocoumarine and furfurylamine. Monofunctional benzoxazines are successfully synthesized both sequentially and one-pot. The ring-opening reaction of DHC and furfurylamine, provides the required amide-containing phenolics in quite high yields. The subsequent reactions with furfurylamine yielded the monofunctional bio-based benzoxazines through one-pot and stepwise routes. Furthermore, main-chain polybenzoxazines were successfully synthesized from monofunctional coumarine-benzoxazines with bismaleimides via the Diels-Alder reaction. Based on the thermal analysis, the synthesized benzoxazines were observed to be capable of curing, and their polymers exhibited thermal stability comparable to that of classical benzoxazine monomers. The research reveals that 3,4-dihydrocoumarine (DHC) is an appropriate compound for designing benzoxazines containing amide groups, either in the ring-opening of 3,4-dihydrocoumarine or during benzoxazine synthesis stages, because of its natural properties. Therefore, this approach provides a straightforward synthesis for these specific coumarine based benzoxazines, offering significant design flexibility and potential for future advancements.

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