ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ADVANCED THERMOSETS FROM SULFUR, RENEWABLE BENZOXAZINE AND IONONES VIA INVERSE VULCANIZATION

M.Sc. THESIS

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Chemistry Programme

JULY 2020

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TERS VULKANİZASYON YOLUYLA SULFUR, YENİLENEBİLİR BENZOKSAZİN VE İYONON'DAN GELİŞMİŞ TERMOSETLER

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To my wife,

FOREWORD

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ABBREVIATIONS

Bz : 1,3-Benzoxazine

Bisphenol-A : 4,4-Isoporpylidenediphenol

Da : Dalton

DSC : Differantial Scanning Calorimeter

FTIR : Fourier Transform Infrared Spectroscopy

GPC : Gel Permeation Chromatography

^{1}H-NMR : Nuclear Magnetic Resonance Spectroscopy

HY : Hydrogen Containing Compound

PBz : Polybenzoxazine

ROP : Ring Opening Polymerization

TGA : Thermogravimetric Analyzer

THF : Tetrahydrofuran

SYMBOLS

T_g : Glass Transition Temperature

T_{max} : Curing Maximum

T_{cure} : Polymerization Temperature

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

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

T_c : The char yield at 800 °C

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ADVANCED THERMOSETS FROM SULFUR, RENEWABLE BENZOXAZINE AND IONONES VIA INVERSE VULCANIZATION

SUMMARY

Polymers can be classified as thermoplastics and thermosets, considering their behaviour against heat. Thermoplastics show fluid-like behavior above a certain temperature and can be reshaped with heat. Examples of poly (ethylene terraftalate) - PET, poly (vinyl chloride) - PVC thermoplastic polymers. Thermosets, on the other hand, deteriorate without showing fluid properties above certain temperatures, and cannot be reshaped with heat due to their cross-linking. Naturally, they are not soluble nor mealeable. Some of the thermoset components are also called thermosetting resins. The main characteristic of tthese resins is that they require curing, when they undergo a molecular cross-linking process. Phenol-formaldehyde, melamine-formaldehyde, urea-formaldehyde resins are examples of thermosetting resins.

The most preferred and produced resin among thermoset resins are phenol-formaldehyde resins. Phenol-formaldehyde resins are used in the wood industry, construction, adhesive, conductive polymer structures, aviation industry. However, traditional phenolic resins have some drawbacks due to the need for catalysts during polymerization, limited shelf life, environmental and human health effects as a result of volitiles during their curing.

Polybenzoxazines overcome the disadvantages of classical phenolic resins. Features such as good thermal stability, low moisture absorption, high char yield, zero volumetric change during curing, low toxic substance release during curing, 100% atomic economics, no catalyst required, low cost, and benzoxasins are among the polymers.Polybenzoxazines found in industrial applications due to these features. For example, they are used in aviation industry, high performance electronic circuit boards, composite structures. Polybenzoxazines are synthesized from 1,3-benzoxazine monomers. In the structures of benzoxazines, there is a heterocyclic oxazine ring containing oxygen and nitrogen bondend with benzene ring . Although there are various benzoxazine monomers such as 1,2-, 1,4- benzoxazine, only 1,3- benzoxazine monomer is active for ring-opening polymerization.

Moreover, the design flexibility of benzoxazines allows to design various benzoxazines since there are many different amines and phenols present and suitable for the monomer synthesis. Hence, preoperties and chemistry of benzoxazines can be altered by selecting the reagents. By this way, many benzoxazines can be synthesized for different purposes such as fireproof products adsorbents for environmental problems, waste problems etc.

The synthesis of benzoxazines from natural products is also possible. Besides, by selecting plant based diphenols, the use of bisphenol A can be excluded.

On the other hand, the reactive nature of benzoxazines provides opportunities to merge polybenzoxazines with polysulfides via inverse vulcanization methods. It is known that high amounts of sulfur are produced as by-products during natural gas and oil production. Even though sulfur is used in chemical fertilizers and sulfuric acid production, 60 million tons of sulfur accumulates annually as waste. The benzoxazine chemistry allows to consume large amount of sulfurs by the stated method to form poly(benzoxazine-*co*-sulfide)s.

In this study, a terpolymeric system has been successfully synthesized with sulfur, terpene (ionone and carvone) and biological sources benzoxazine. Initially, benzoxazin monomer was synthesized from natural product such as vanillin and furfuryl amine. The structures of this synthesized polymeric precursor vanillin benzoxazine monomer were illuminated by ^{1}H NMR, FT-IR spectroscopic analysis. Then, by inverse vulcanization, a cross-linked system was obtained between the natural benzoxazine monomer and the terpene. Various samples of this terpolymeric material have been fabricated by changing the sulfur, vanilline benzoxazine and terpene mass ratios . It is known that sulfur-containing polymers show Li-S battery capacity. For our terpolymeric system, lithium-sulfur cell was also tested as cathode material property tests. Accordingly, over 400 mAh/g capacity more than 100 of cycles were observed for these materials.

TERS VULKANİZASYON YOLUYLA SULFUR, YENİLENEBİLİR BENZOKSAZİN VE İYONON’DAN GELİŞMİŞ TERMOSETLER

ÖZET

Doğal Polimerlerin kullanımı tarihsel süreç içerisinde Çin’de iplik üretiminden, güney ekvator bölgesinde doğal kauçuk olarak, Mezapotamya’da ise kıyafetler için koyundan elde edilen yün olarak kullanıldığını görmekteyiz. Zaman içerisinde gelişen kimya bilimi ve polimer kavramı bir çok bilim adamının dikkatini çekmeye başlamıştır. Polimerler, günümüz teknolojik alanlarında ve endüstriyel kullanım kolaylığı sayesinde çokça tercih edilmektedirler. Ayrıca istenilen özelliklerde sentezlenebilmesi ve kolay proseslerde üretilebilmesi gibi özellikleri sayesinde araştırma konularında oldukça ilgi odağı oluşturmaktadırlar. Dolayısıyla yüksek performanslı polimerler özelliklerinden dolayı günlük yaşamın içinde giderek artan şekilde yer edindiği görülmektedir.

Polimerler sıcaklıklara karşı gösterdikleri tepkiler göz önünde bulundurulduğunda, termoplastik ve termoset olarak ikiye ayrılmaktadırlar. Termoplastikler belirli bir sıcaklığın üzerinde akışkan davranış göstermektedirler ve ısı ile yeniden şekillendrilebilmektedirler. Poli(etilen teraftalat) - PET, poli(vinil klorür) - PVC termoplastik polimerlere örnektir. Termosetler ise belirli sıcaklıkların üzerinde akışkan özellik göstermeden bozulurlar, çapraz bağları nedeniyle ısı ile yeniden şekillendirilemezler. Çapraz bağlar olması çözünürlüğünün düşük olmasını neden olmaktadır. Termosetlere , aynı zamanda termoset reçine de denmektedir. Fenol-formaldehit, melamin-formaldehit, üre-formaldehit reçineleri termoset reçinelere örnektir.

Termoset reçineler arasında en çok tercih edilen ve üretilen reçine, fenol-formaldehit reçineleridir. Fenol-formaldehit reçineler başta odun endüstrisi olmak üzere, inşaat, yapıştırıcı, iletken polimer yapıları, havacılık endüstrisinde kullanılmaktadır. Fakat geleneksel fenolik reçineler, iyi termal ve mekanik özelliklerinin yanında, polimerizasyon sırasında katalizör gerekmesi, kısıtlı raf ömrü, çevresel ve insan sağlığını etkileyici yan ürün çıkarması gibi sebeplerle güncelliğini yitirmektedir.

Polibenzoksazinler ile klasik fenolik reçinelerin dezavantajlarının önüne geçilmiştir. İyi termal stabiliteye sahip olması, düşük nem absorbsiyonu, yüksek kül verimi, kürleme sırasında sıfır hacimsel değişim, kürleme sırasında düşük toksik madde salınımı, %100 atom ekonomik, katalizör gerekmemesi, düşük maliyet gibi özellikler polimerler arasında benzoksazinleri ön plana çıkarmaktadır. Bu özellikleri sayesinde endüstriyel uygulamalarda tercih edilmektedirler. Bu sayede havacılık endüstrisinde, yüksek performanslı elektronik devre kartlarında, kompozit yapılarda kullanılmaktadır. Polibenzoksazinler, 1,3- benzoksazin monomerlerinden sentezlenmektedirler. Benzoksazinlerin yapılarında, benzen ve oksijen ile azot atomu bulunan heterosiklik oksazin halkası bulunmaktadır. 1,2- ,1,4- gibi çeşitli benzoksazin monomerleri olmasına rağmen, 1,3- benzoksazin monomerinin halka açılma polimerizasyonu için aktif olduğundan dolayı kullanılmaktadır.

Benzoksazinlerin tasarım esnekliği, monomer sentezi sırasında kullanılan amin ve fenolü çeşitlendirmemizi sağlamaktadır. Türevlendirilmiş benzoksazin monomeri sayesinde elde ettiğimiz polimerler bize verimin artmasını, farklı kimyasal ve fiziksel özelliklere sahip polimerler elde etmemizi sağlayabilirler. Orto fonksiyonlu fenoller tercih edilirse daha yüksek verimde benzoksazin sentezi yapılırken, furfuril aminden sentezlenen benzoksazinler ise yüksek termal stabilite ve kömürleşme verimi sayesinde yanmaz ürün özelliğindedir.

Günümüzde karşılaştığımız çevresel sorunlar, atık problemleri, petrol bazlı ürünlerin kullanımının kısıtlanması gibi durumlar polimer kimyasını da "sürdürülebilirlik" çerçevesinde etkilemektedir. Ayrıca Benzoksazinler de bu çerçevede ele alındığında, tasarım esnekliğinin sayesinde doğal ürünlerden üretimi ön plana çıkmaktadır. Benzoksazin monomer sentezi sırasında kullanılan, fakat insan sağlığına zararı bulunan bisfenol A kullanımının önüne geçilmesi doğal ürünler sayesinde gerçekleşmektedir.

Doğal gaz ve petrol üretimi sırasında yüksek miktarlarda sülfür'ün yan ürün olarak ortaya çıktığını bilmekteyiz. Sülfür, kimyasal gübreler ve sülfürik asit üretiminde kullanılıyor olsa bile yılda 60 milyon ton sülfür atık tepeleri oluşturacak şekilde birikmektedir. Yapılan bilimsel çalışmalarda sülfür ve benzoksazin arasında ters vulkanizasyon yöntemi ile poli (benzoksazin *co*-sülfit) yapılar oluşturduğu göstermiştir.

Bu çalışmada, sülfür, terpen (iyonon ve karvon) ve biyo kaynaklardan üretilmiş benzoksazin ile terpolimerik bir sistem başarı ile sentezlenmiştir. Başlangıçta, doğal ürün olan vanilin ve furfuril amin'den benzoksazin monomeri sentezlenmiştir. Sentezlenen bu polimerik öncül vanilin benzoksazin için ^{1}H-NMR, FT-IR spektroskopik analizler ile yapıları aydınlatılmıştır. Daha sonra ters vulkanizasyon ile, sentezlenen vanilin benzoksazin monomeri ve terpen arasında, sülfür sayesinde çapraz bağlı bir sistem elde edilmiştir. Elde edilen bu terpolimerik sistem için, Sülfür, Vanilin benzoksazin ve Terpen oranları kütlece değiştirilerek çeşitli örnekler yapılmıştır. Sülfür içeren polimerlerin Li-S pil kapasitesi gösterdiği bilinmektedir. Yapmış olduğumuz terpolimerik sistem için de liyum-sülfür katot malzeme özelliği testleri yapılmıştır ve 100 şarj çevrimi için 400 mAh/g kapasite ölçülmüştür.

1. INTRODUCTION

Phenolic resins, resol and novalak type, have found a lot of use in the past century due to ease of production, low cost and industrial feasibility [1-3]. However, formaldehyde and by-product emissions that occur during the production of phenolic resin are major environmental concerns [4]. The outstanding advantages of benzoxazines offer us brilliant development opportunities to eliminate such disadvantages. For example, ring-opening polymerization of benzoxazines have 100% atomic economy, avoids the problems related to its formaldehyde by-product release. Besides, it is possible to reduce evaporation and cold flow by using it as main-side and end-chain precursors.

In addition to being similar to phenolic resins, benzoxazines are a new commercialized thermoset polymer thanks to its unique and excellent properties. High thermal stability, low water absorption, low combustion feature, high chemical resistance, low surface energy are some of prominent properties of these resins. Accordingly, benzoxazine resins found applicationsin extreme environments Such as aerospace, automotive, oil and high performance electronic components [5-8].

Another important feature of benzoxazines is versitality of the benzoxazine chemistry which bring about a huge molecular design flexibility. Unlike conventional phenolic resins, the release of by-products and formaldehyde during polybenzoxazine production (Figure 1.1) from benzoxazine monomers is limited and can usually occur during curing [9-12] . There have been studies to use polymeric benzoxazines as side and end chain precursors to reduce evaporation [13-15]. Hence, several benzoxazines can be designed by considering green chemistry requirements. Despite these features, in general, benzoxazines are still produced from fossil-based resources as many other monomers used in polymer chemistry.

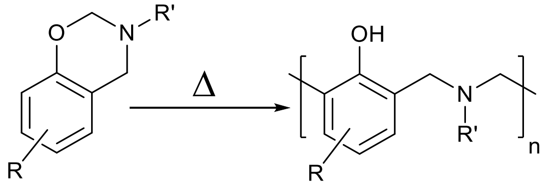

Figure 1.1 : Thermally activated polymerization of benzoxazine monomer.

The main problem with conventional benzoxazines is the use of bisphenol-A and related compounds during its production. Bisphenol-A creates a health problem by imitating the estrogen hormone in humans as reported in many hormonal system researches [16]. Therefore, non-petroleum based benzoxazine monomers are of interest in parallel to many other monomer synthesis topic.

While the concept of sustainability comes to the forefront everywhere in today's world, it has reached an important point in developing renewable materials in polymer chemistry. Within the framework of this concept, it is possible to choose and use environmentally friendly products in terms of the absence of by-products and pollution in the production processes of the materials [17-20].

Phenolics and related other aromatics that is required for the production of benzoxazines can be obtained from lignin, which is abundant in nature [21,22]. In addition, there are a lot of biomass-derived phenols other than lignin [23]. These phenols obtained from other natural sources can be synthesized by extracting from different plants such as eugenols [24-26], ferrulic and floretic acids [27,28], cardol and cardanols [29-31], arbutin [32], resveratrol [33], vanillin [34,35], gallic acid. Phenols of natural origin such as coumarines [36,37], chavicol [32], guaiacol and bisguaiacol F [38,39], diphenolic acids [40], catechol and resorcinols [41, 42] have been used successfully in benzoxazine syntheses. Likewise, amines can also be obtained from natural sources. Furfuryl amine [43], stearylamine [39], rosin based amines [44] were used as natural amine source in benzoxazine synthesis. It is obvious that eco-friendly benzoxazine synthesis can be made through the rich molecular design provided by the chemistry of benzoxazines [45].

Another appealing side of benzoxazine chemistry is related to the reactivity of benzoxazines against many other compounds such as aromatics, amines, alcohols and interestingly elemental sulfur [46-48]. The worlds’ sulfur production as side product of petroleum industry has a large volume and millions tons of sulfur is now considered as waste product. Thus, most of the sulfur is deposited as sulfur mountains on land. By taking the advantage of benzoxazine reactivity sulfur can be combined with this unique resin and novel materials can be synthesized.

In this thesis, the terpolymer system produced from renewable sources and waste product is designed by using the flexibility of benzoxazine. The synthesized terpolymeric system was used as a cathode material in the lithium-sulfur battery and showed a good charge/discharge capacity and exhibit a capacity of more than 400mAh/g over 100 cycles.

2. THEORETICAL PART

In this section, the general information about classical phenolic resins, benzoxazines, green chemistry and benzoxazines produced from natural products will be given.

2.1 Phenolic Resins History and Present Applications

Phenolic resins, are among the most used resins for a century, due to their important properties such as thermal stability, mechanical performance, resistance to various chemicals, acids and bases, fire resistance when exposed to low amounts of smoke and flames. These features enable them to be preferred among technology materials in the industry. In this way, these resins can be used to be suitable for thermo-structural applications in the aerospace industry, where they replace with polyimide-based systems and have rigid arrangements. Consequently, thanks to all these features, it is the most preferred resin after epoxy resins [3,4].

Natural polymers are based on the Stone Age from linen and hemp yarns, ropes and clothes. In the historical process, we see the use of natural polymers in many regions of the world, such as silk production in China, rubber in the southern equatorial region, products from sheep's wool in Mesapotamia [49].

By the 1900s, semi-synthetic and natural rubber were reported in organic chemistry. Natural Rubber was crosslinked with sulfur by Liedershoff and later developed by Goodyear, Hancock, and Thompson. Bakelite, the first synthetic thermoset polymer, also known as phenol-formaldehyde (PF) resin, was obtained in 1907 by Leo Henricus Arthur Baekeland. Synthetic polymer and plastic industry started with PF resin. Bakelite developed new techniques to control the condensation of phenol and formaldehyde and determined the steps of the reactions as A, B and C. A resin was produced by the reaction of phenol and formaldehyde with a miniature amount of formaldehyde in an acidic environment. Bakelite is named as novolak for this resin made in acidic medium. The pressure is required to move from steps A and B to step C. The fusible and linear novolak resin was converted into the C step in the mold by adding hexamethylenetetramine as the hardening agent.The reactor used the purpose was name as "bakalizer" (Figure 2.1). Although the resin was previously called oxylbenzyl methylene glycol anhydride, it was later called "bakelite" [50].

Figure 2.1 : Bakelizer.

2.1.1 Chemistry and curing

The design of the phenolic resin varies according to the mole ratios used in the synthesis of phenol and formaldehyde (Figure 2.2). When using a base catalyst such as NaOH, the amount of formaldehyde to phenol can vary by 3-4 moles. Novolak resin is obtained when using a smaller amount of formaldehyde against phenol in acid catalyst [51]. While NaOH is mostly preferred in resole production, organic bases such as Trimethylamine and Ammonia can be used as catalysts. In addition, resol produced with ammonia catalyst solutions enable higher molecular weight synthesis than other base-catalyzed products [52].

Polymerization in Novolak production is carried out using acid catalysts such as sulfuric acid, oxalic acid, hydrochloric acid, and phosphoric acid. Bisphenol F is the most manageable novolak and is carried out in the acid catalyst of excess large quantity of phenol and formaldehyde. As a result, formation of a mixture of isomers is inevitable and o,p’ isomer dominates, followed by p,p’ and o, o’ as the lowest (Figure 2.3).

Curing conditions and structural properties of resol and novolac resin are different from each other. Resols can be easily cured by acids, bases or heat treatment. In addition, anhydrides, esters, carbonates, amides can be used to cure these solutions [53].

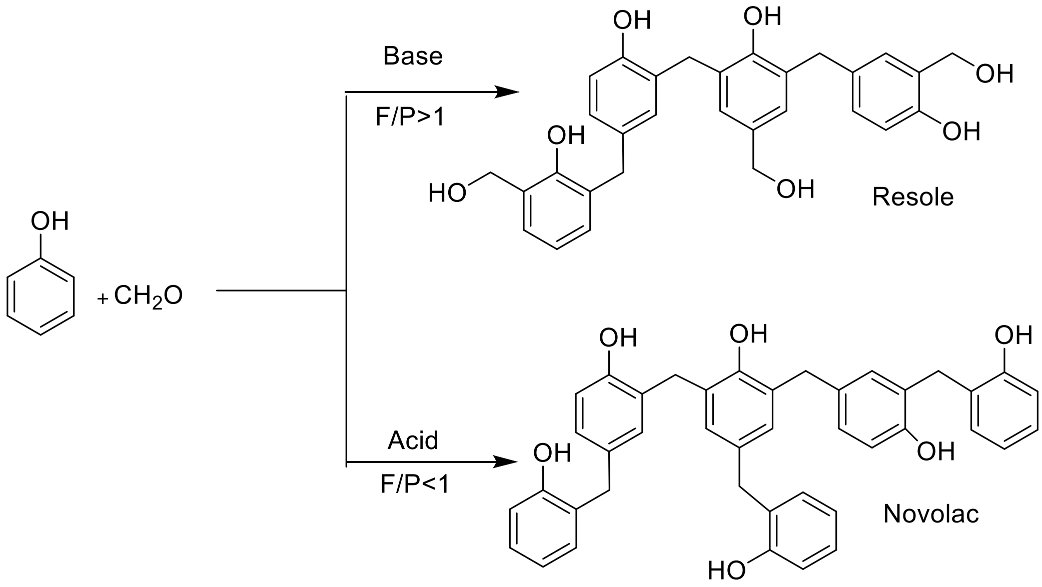

Figure 2.2 : Synthesis conditions and structures of resole and novolac.

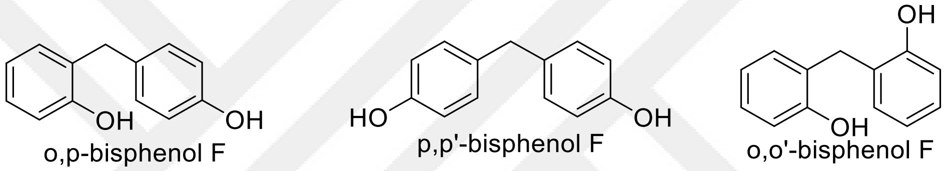

Figure 2.3 : The isomers of simplest novolac.

Hexamethylenetetramine (HMTA) is used as the most important activating agent for curing novolac resins (Figure 2.4). Apart from HMTA, other methods are mixing novalac resins with solvents, such as bismethylol phenolics, bisoxazolines, and bisbenzoxazines [54]. Resols are synthesis without a curing agent shown in Figure 2.5.

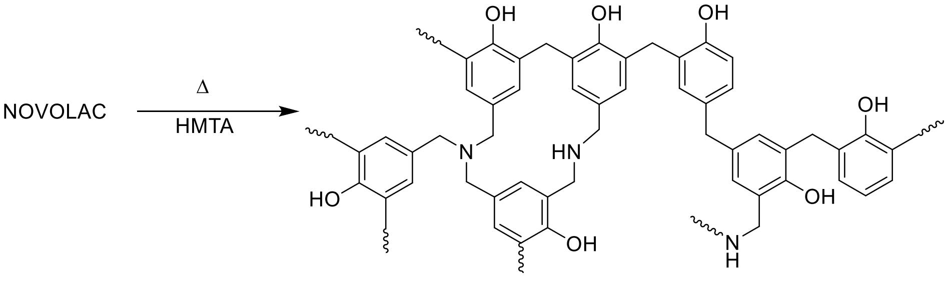

Figure 2.4 : The simplified structure for Novolac resin.

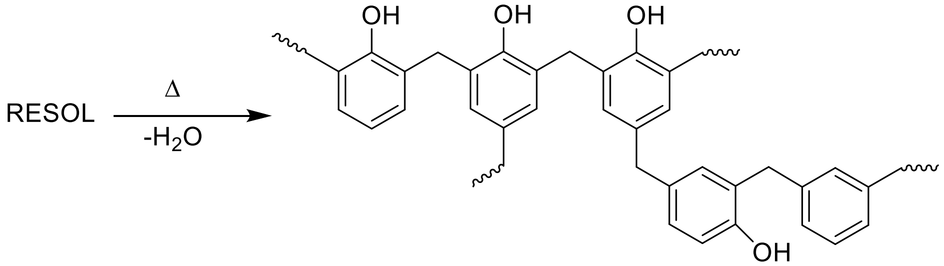

Figure 2.5 : Curing of Resol.

2.1.2 Present applications

Phenolic resins, which have had many applications over the past century, are now used in areas such as paper, fabric, organic or inorganic fibers. It has been used extensively in construction industries such as furniture laminates, flooring. In addition, PFs widely used in automotive industry such as, friction materials such as brake pads, disc pads, clutch pads. Due to its current use, research is actively ongoing. In addition, it can be used in composite materials; it is preferred in aircraft interiors, explosion protection, maritime transportation and defense applications.

The use of cashews, lignin, tannins and other renewable phenols is expected to increase gradually. Although the properties of modified phenolic resins produced from cashew and lignin have been compromised, researchers continue to use renewable resources [3].

2.2 Overwiev of Benzoxazines and Historical Background

The First synthesis of benzoxazines by Holly and Cope condensation of amine, formaldehyde and phenol dates back 60 years [55]. Burke *et al.* contributed to this low-molecular-weight benzoxazine chemistry in the 1950s [56,57]. Later, Schreiber studied the possibility of ring opening oxazines. He also showed that polybenzoxazines could replace phenolic resins for some applications. Reiss et al. also did their workstudied ring opening reaction of benzoxazines and on the oligomeric structures of the monofunctional benzoxazines via the Mannich Bridge was obtained [58]. Turpin and Thrane patented self-curing benzoxazines in 1988 [59]. Ning and Ishida published their work on lighting the properties of polybenzoxazines in 1994 [60]. After those pioneering works, benzoxazine chemistry found its way in polymer science as a separate topic under thermosettings.

Overcoming the deficiencies of phenolic resins was achieved with polybenzoxazines. In addition, having a wide range of features has expanded its usage in many field.

- Near-Zero Volumetric Change
- Low cost materials and Stable at room temperature
- %100 Atom economic
- Low Water Absorbtion

- Some Polybenzoxazines (PBz) their T_g is much higer than T_{cure}.
- High Char Yield
- No strong acid required for curing
- No toxic by-product

Physical and mechanical properties of epoxy, phenolic resin and polybenzoxazines are as in the Table 2.1.

Table 2.1 : Comparison of the properties of PBz, phenolic resins and epoxy resins.

Property	PBz	Phenolic Resin	Epoxy Resins
Cure Temperature (°C)	160-220	150-190	R.T.-180
Max.Use Temperature (°C)	130-180	200	180
Cure Shrinkage	~ 0	0.002	>3
T_g (°C)	170-340	170	150-220
Elongation /%)	2.3-2.9	0.3	3-4.3
Tensile Strength (Mpa)	100-125	24-45	90-120

2.2.1 Benzoxazine chemistry

Although there are different types of benzoxazines such as 1,2- 1,4- and 1,3-benzoxazines, only 1,3-isomers are polymerizable. The oxazine ring is a heterocycle with 6-atoms containing a nitrogen and an oxygen. The benzene ring is attached to the oxazine ring forming benzoxazines. 1,3-benzoxazines is the most common and most active among benzoxazines. Its polymerization occurs by cationic ring opening polymerization. Benzoxazine resins can be synthesized with a Phenol, Formaldehyde and primary amine (Figure 2.6). They contain groups X such as, CH_2, $C(CH_3)_2$, $C(CF_3)_2$, C=O, SO_2, and R' includes CH_3, C_2H_5, and benzene and, R group such as CH3 or other aliphatic groups. Any derivative of the bifunctional or monofuntional phenol and primary amine can be used. Examples of difunctional benzoxazines are shown in the Figure 2.7.

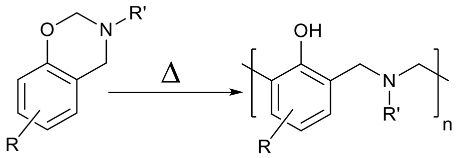

Figure 2.6 : Synthesis of polybenzoxazine from benzoxazine monomer.

Having little solvent in benzoxazines increases impurity. As a result, the purification is very difficult. If you have obtained a pure benzoxazine monomer, it should look crystal. By the polymerization of benzoxazines, polybenzoxazines have a cross-linked and amorphous structure.

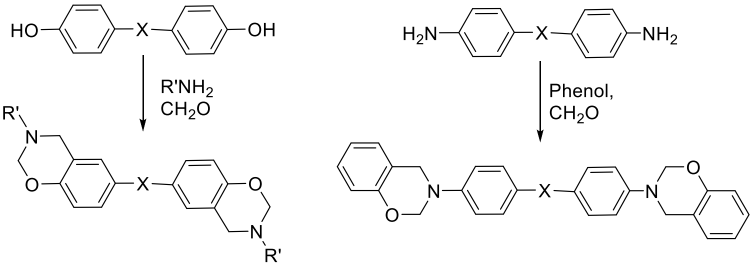

Figure 2.7 : Monomeric type difunctional benzoxazine resins based on bisphenol and monoamine, or diamine and phenol.

Compared to epoxy resins, bismaleimides, cyanate esters and polyimides, benzoxazine resins are used more because they have superior properties. Curing of benzoxazines at high temperature may cause fragility due to the breaking of the intermolecular H-bond in cross-linked benzoxazines. In addition, due to the some chemicals is harmful for human body such as Bisphenol A at synthesize of Pbzs (Figure2.7), from natural and sustainable by-products has important role to synthesize Pbzs [61].

2.2.2 Synthesize of benzoxazine monomers

Benzoxazines can be synthesized in solution medium or solvent-free using phenol, formaldehyde, and amine (may be aliphatic or aromatic). Various types of benzoxazine monomers can also be produced with different substituent groups. These substituents can increase polymerization sites for the benzoxazine monomer and affect the curing process.

2.2.2.1 Synthesize of monofunctional benzoxazine monomer

Polybenzoxazines from Mmonofunctional benzoxazines mostly have a low molecular weight (500-2000Da) and linear structure. Therefore, such benzoxazine monomers provide structurally limited utility in polymers [58].

Synthesis of benzoxazine monomers obtained Holy & Cope by condensation reaction with primary amine, formaldehyde and substituted phenols [55]. They performed these reactions in a solvent in two stages. Burke first found that the benzoxazine ring reacted with the free ortho position of the phenolic compound and formed the Mannich Bridge

[57] (Figure 2.8). With the Mannich Condensation reaction for the synthesis of monofunctional benzoxazine, amine is added to the low temperature formaldehyde; the N, N-dihydroxymethylamine derivative is formed. Here, hydrogen and ortho position react due to the hydroxyl group instability. By increasing the temperature, the benzoxazine monomer is obtained by adding Phenol [62].

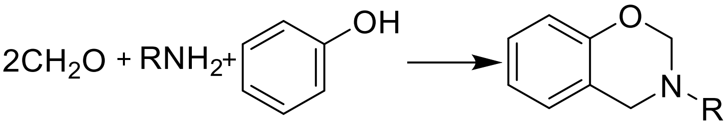

Figure 2.8 : Synthesis of 3,4-dihydro-2H-1,3benzoxazine.

In the presence of active hydrogen (HY) compounds such as naphthol, indoles, carbazole, imides, and aliphatic nitro compounds, and phenol, it has been shown to open to the public in their reactions with benzoxazines. The result is small oligomers as a by-product [56]. The structure of the Mannich Bridge in the acidic environment of opening the benzoxazine ring is shown in Figure 2.9.

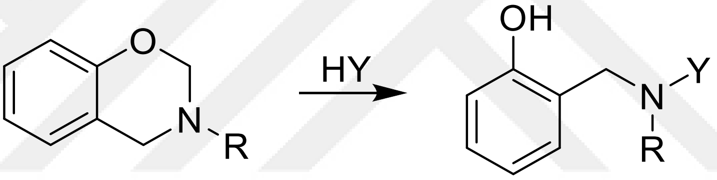

Figure 2.9 : Ring opening of acidic medium.

2.2.2.2 Synthesis of difunctional benzoxazine monomer

Monofunctional benzoxazines give an oligomeric structure with an average molecular weight of 1000 Da when cured with phenol. For this reason, no material could be obtained as the high molecular weight linear structure was prevented by the thermal decomposition of the monomer by chain formation reaction in benzoxazines [58]. Hemvichian K. et al. observed that at the temperatures at which the Mannich Reaction took place, the reduction of reactivity was related to the hydrogen bond. Ishida and colleagues have overcome this limitation by developing new functional or multi-functional benzoxazine monomers. They observed that these benzoxazines, dimers and high oligomers in resin started curing in phenolic material with ring-opening reactions [63]. The monomer was synthesized using bisphenol-a, formaldehyde, and methylamine in different solvents, these resulting monomers have a benzoxazine ring structure that functions at both ends of bisphenol-A (Figure 2.10).

The difunctional monomers made by the solvent-free method are as listed at Figure 2.11. Difunctional benzoxazines can be prepared with various combinations such as difunctional amine and monofunctional phenol or monofunctional amine and difunctional phenols.

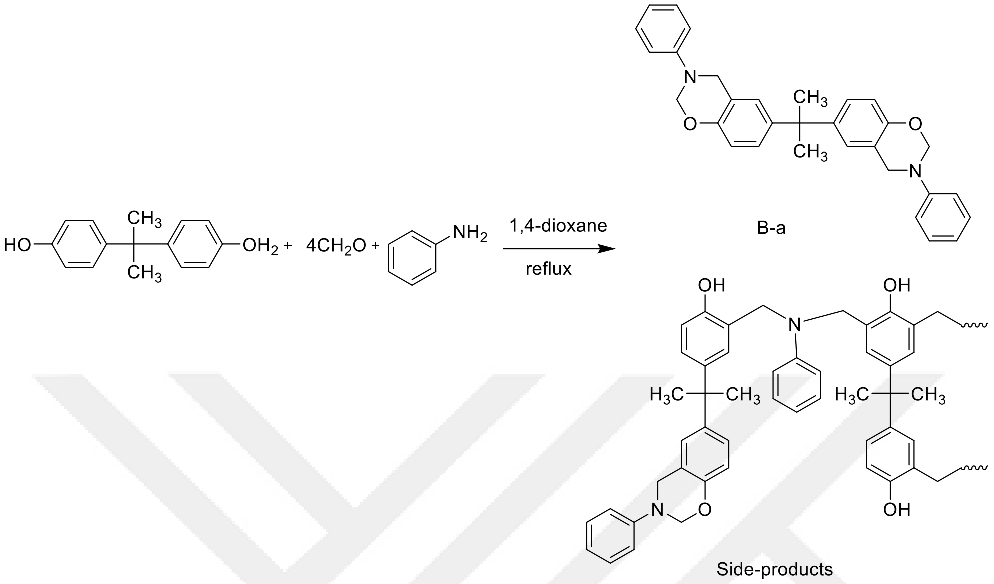

Figure 2.10 : Bisphenol-A and aniline based benzoxazine monomer.

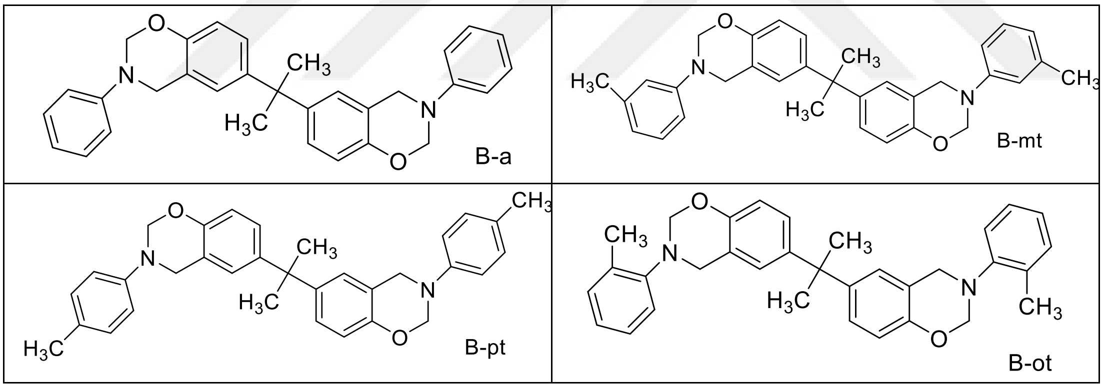

Figure 2.11 : Solventless method for synthesis of a some difunctional benzoxazine monomers.

2.2.2.3 Allyl containing benzoxazine monomers

Allyl groups provide advantages such as providing additional crosslinking, being able to be cured at lower temperatures for acetylene groups, increasing the hardness of cured resin [64]. It is reported by Ishida that it is prepared from a benzoxazine monomer containing 3-phenyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine, alylphenol, aniline and paraformaldehyde. In the bifunctional allylphenol derivative polybenzoxazines reported by Pei *et al*., These benzoxazines are thought to be difficult to polymerize by ring-opening due to the lack of active ortho position to the phenolic hydroxyl group. Agag and Takeichi synthesized benzoxazine monomers modified with allyl groups using these synthetic methods [65]. Synthesis of allyl containing monomers are shown at Figure 2.12.

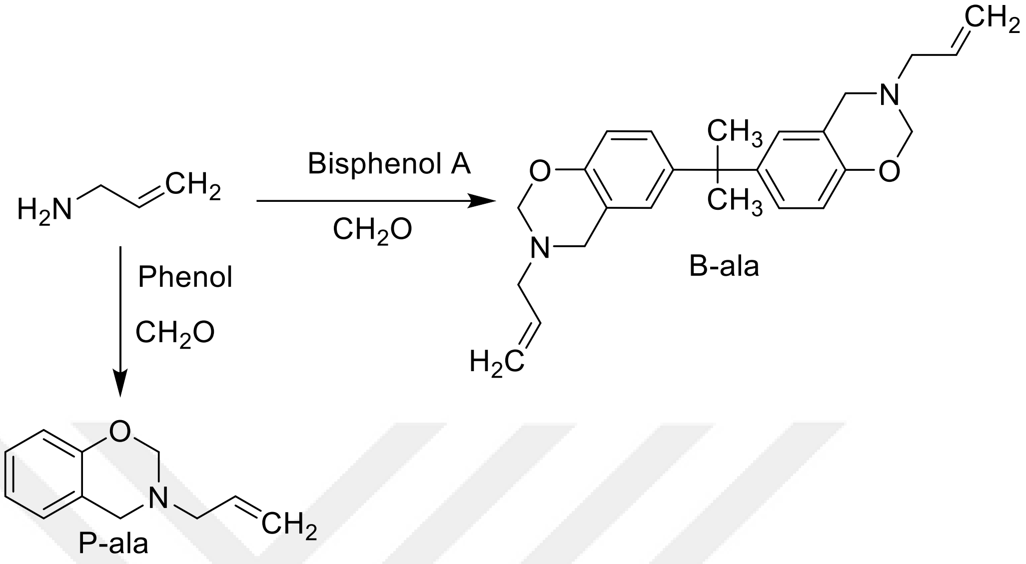

Figure 2.12 : Synthesis of allyl containing monomers.

Polymerization at low temperatures such as 150 °C does not trigger ring opening in benzoxazines. Mainly, allyl groups polymerize under such temperatures. In order for the benzoxazine ring to also polymerize, polymerization should be done over 250 °C [66].

2.2.2.4 Polymerization mechanism of benzoxazines

Understanding the structure of the oxazine ring is crucial to clarify the mechanism in the polymerization,reactions of benzoxazines. In the X-ray crystallographic illumination of the benzoxazine sample containing the monoxazin-ring structure, it was observed that the conformation of the oxazin ring is in the half-chair structure. In this way, thanks to the position of the ring, it is easier to perform a ring-opening reaction under special conditions. Polymerization and opening of the ring is seen as both oxygen and nitrogen due to its high basicity, which are cationic polymerization initiation sites. Moreover, in contrast to the water producing condensation polymerization of phenolic resins, water is not released in the ring opening polymerization of benzoxazines [67].

Burke *et al*. Demonstrated that the free ortho and para zones of the 1,3-dihydrobenzoxazine with phenol, the aminoalkylation in the ring-opening reaction of the benzoxazines, formed the Mannich base bridge structure with the free ortho position [62]. Preferably, it is seen in lesser para position. The intermolecular hydrogen bond describes,its preference for the ortho position. During the kinetics of monofunctional benzoxazines with 2,4-di-tert-butylphenol catalyst, Riese et al. found that the activity of the ortho position is high [58]. Benzoxazines are generally polymerized by thermal curing and without catalyst. The polymerization mechanisms of benzoxazines have not been fully elucidated despite years of studies [68].

It has been observed as a result of research that the use of acid catalyst in the improvement of benzoxazines diminish the induction time and increases the reaction rate (Figure 2.13). Strong acids, weak carboxylic acids, phenols have been studied by Ishida and Rodriguez for polymerization. In ring opening polymerization with weak acid, such as carboxylic acid, they have shown that weak acid acts as a catalyst with an auto-accelerator. On the contrary, such an effect is not seen when using strong acid [69]. Initiators such as PCl_5, PCl_3, $POCl_3$, $TiCl_4$, $AlCl_3$ and MeOTf are polymerization initiators that render high Tg and high char yield.

Studies have shown that, besides anionic and radical initiators, cationic initiators can be used in ring-opening polymerization of benzoxazine, the reaction continues through the cationic mechanism. Research by McDonagh and Smith [24] identified that with the immigration of the proton from nitrogen to the oxygen atom, 3,4-dihydro-2H-1,3-benzoxazine tautomerism protonated. In this way, the chain forms iminium ions . As shown in the Figure 2.13, the formation of iminium ions by oxygen atom protonation, the ring-opening mechanism Ishida and Dunkers have shown [69].

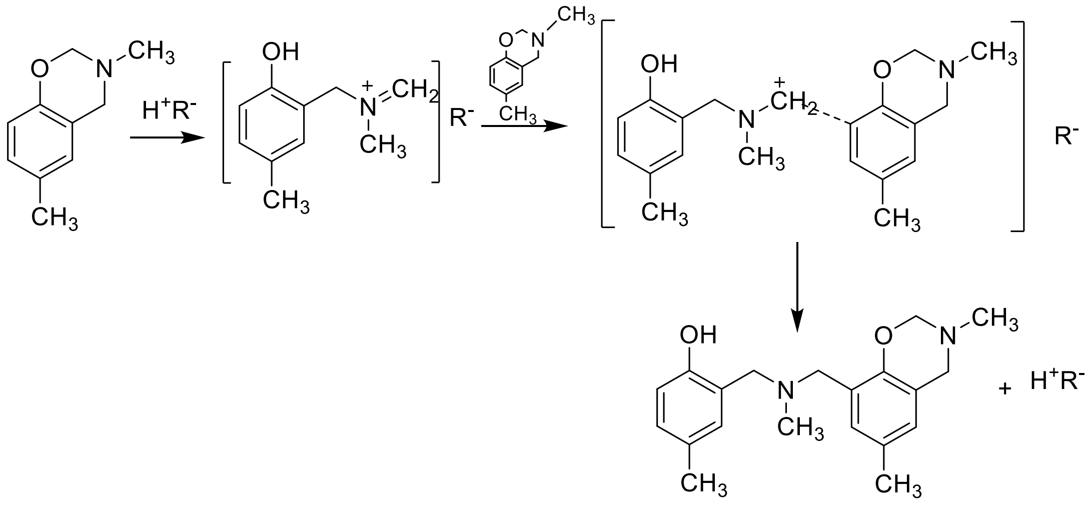

Figure 2.13 : Acid catalyst ring opening polymerization of 3,4-dihydro-2H-1,3-benzoxazine.

After the ring opening of benzoxazine monomer with strong acids, such as trifluoroacetic acid, benzoxazine monomers turn into polybenzoxazine at low temperatures. Iminium ion has been proposed as an intermediate product. This intermediate provides the presence of trifluoroacetic acid because it can give the stability of the intermediate because it provides the counter ion in ionic form instead of the covalent form. If a weak acid were used as the catalyst, like sebacic acid, polymerization would be slow at the start of the reaction.

Pure benzoxazines can be cured at 160-170 °C without catalyst. Curing can be done in the presence of phenol. Sequentially ring opening and Mannich bridge formation are back-to-back reactions. During these reactions, while the benzoxazine ring is spent, the formation of trisubstituted benzene ring should occur simultaneously. This situation is illuminated with FTIR. Then termination in ring-opening reactions takes place. In the polymerization initiated with PCl_5, Wang and Ishida found 3 different mechanisms in their results with 3,4-dihydro-2H-1,3 benzoxazines with different monooxazine rings. They showed that different polymeric structures were obtained according to the substitutions in the benzene ring (Figure 2.14) [68].

To receive a cross-linked polybenzoxazine, thermal polymerization of bifunctional or multifunctional benzoxazines can be performed. Cross-linked polymers with high T_g and degradation density are obtained because of thermal polymerization. In the Figure 2.15, polymeric structures of the monofunctional and bifunctional benzoxazines are shown as a result of curing [65].

Bi-functional benzoxazine synthesis can also be made with bisphenol- A based monomer, dimers, and small oligomers. Free phenolic hydroxyl groups in the structure of dimers and oligomers act as initiators for cross-linking. Carbocation and iminium ion in the starting phase of the ring-opening reaction of bisphenol-A based benzoxazine are as shown in the Figure 2.16.

Polymerization, continuing by electrophilic displacement between the carbocation and the benzene ring, happens in the free ortho and para positions of the phenol group. In this reaction, carbocation is responsible for propagation. Therefore, the stability of the iminium ion influences the propagation step.

In curing reactions, it was found to be different in kinetic studies performed above and below T_g. Vitrification increases the viscosity of the system, at a temperature below

T_g, and affects the hardening kinetics. In the Figure 2.17, the cationic mechanism of the B-a monomer can be seen by the thermal polymerization method.

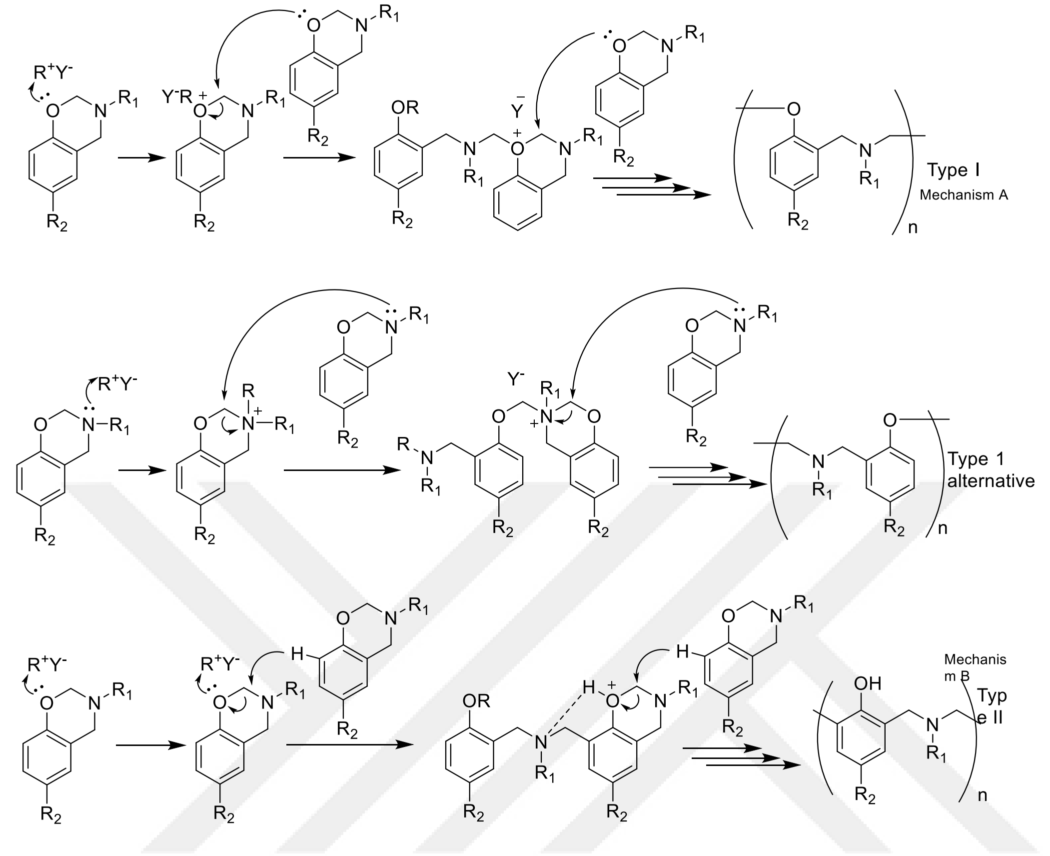

Figure 2.14 : Cationic ring opening polymerization of 3,4-dihydro-2H-1,3 benzoxazines Type I and Type II.

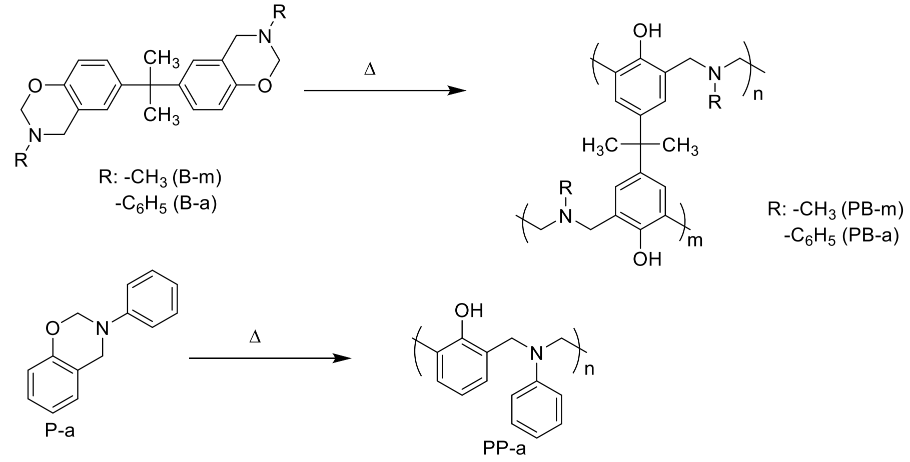

Figure 2.15 : Curing of monofunctional and difunctional benzoxazine.

Carbocation with aniline ortho position has been observed in solid State 15N NMR, studies where there is an electrophilic displacement reaction. Due to the electron-donating nitrogen structure of aniline, it enables ortho and para positions to perform electrophilic displacement reaction by carbocation. In Figure 2.18, we can see this structure.

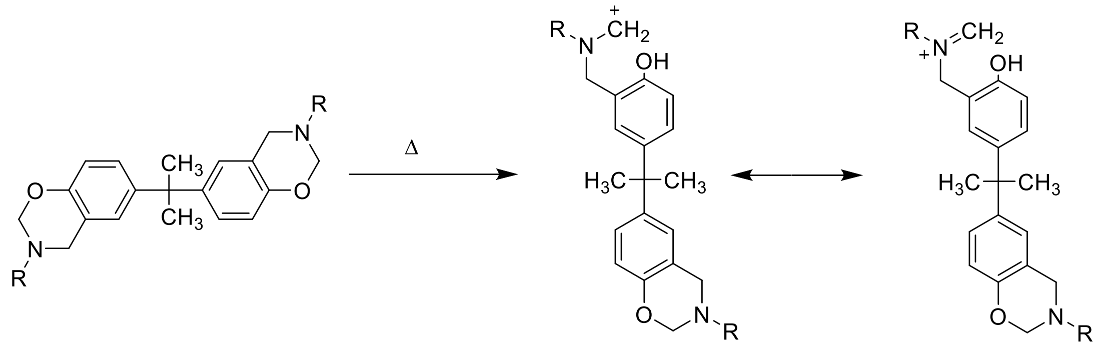

Figure 2.16 : Initiation of ring opening polymerization of benzoxazines.

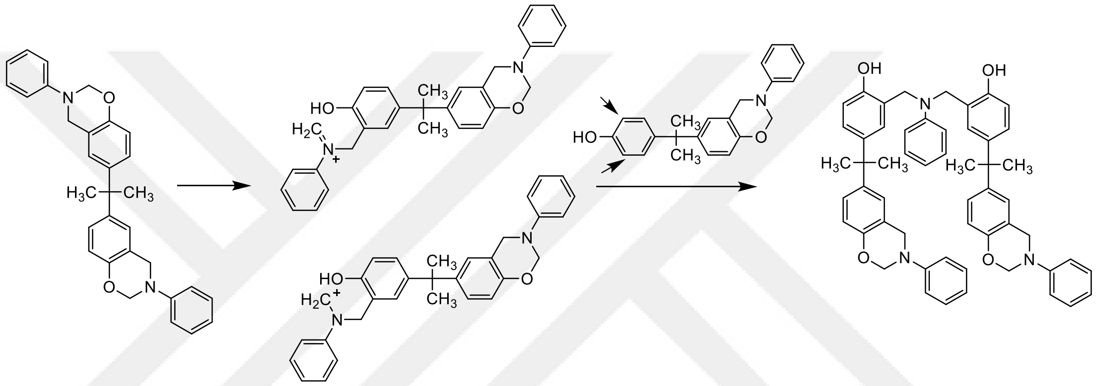

Figure 2.17 : Thermal polymerization of B-a through cationic mechanism.

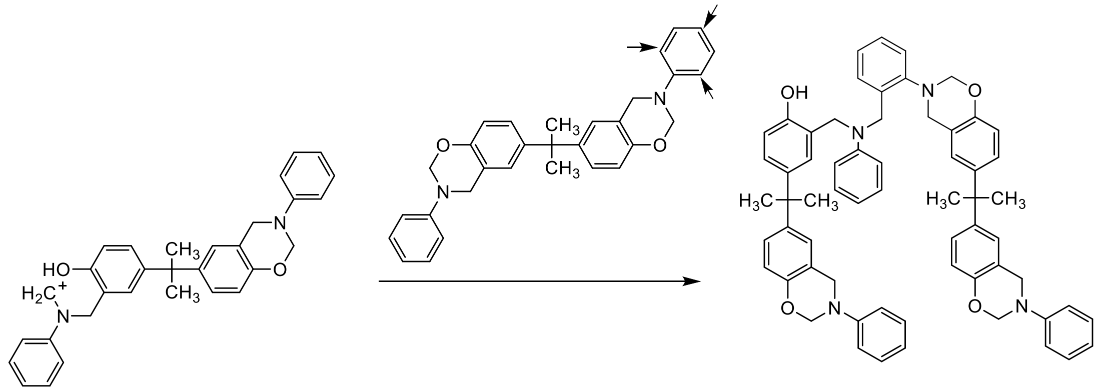

Figure 2.18 : Electrophilic substitution reaction of aniline moiety.

2.2.2.5 Properties of benzoxazines

Thanks to the unique properties of benzoxazines compared to other polymers, it provides many applications, application areas and development areas.

Hydroxyl groups are known to provide water absorption to a polymer. Contrary to this situation, although there is a hydroxyl group in benzoxazines, such as phenolin OH, Mannich base, oppposite to expectation, it shows low water absorption. Therefore, compared to polyester, vinyl ester, phenolic, epoxy, bismaleimide and polymide resins, it provides an advantage to benzoxazines. In order to reduce the water absorption of benzoxazines, it is possible to derivative monomers with hydrophobic phenol and amine. Since the water absorption rate is directly related to the dielectric constant, low water absorption gives us an advantage. In terms of the application of the materials, the difference between dry T_g and wet T_g should be low.

Thermoset resins show more shrinkage than thermoplastics [70,71]. Thermoset resins shrink approximately 2-10%. Contrary to thermoset and thermoplastics, benzoxazine resins show zero shrinkage [72,73]. High performance adhesives are the use of expanding polymers that are ideal for sealants and coatings. On the contrary, it is important to use polymeric materials with zero shrinkage to prevent bending of composite materials. Monomers show 1% change after polymerization. It is observed that the volume of resins decreased slightly during isothermal curing at rising temperature. However, minor changes are observed between the volume before polymerization and the volume after polymerization.

The crosslinked benzoxazines display glass transition temperatures ranging from 170 to 340 ^{0}C, which allows us to design polymer with zero T_g for benzoxazines. If there are many active sites in benzoxazines and the active areas react in polybenzoxazines where the benzene rings are abundant, T_g continues to increase than the polymerization temperature T_{cure}, if the polymerization mechanism allows the chain to be rearranged in its motion.

Fireproof product designs are very important in today's industries. To reduce combustion, it is necessary to use materials with a high char yield. This highlights polymers with high char yield. However, most polymers have low char yield such as epoxy resins 5-15%, phenolic resins 30-55%. Benzoxazines, on the other hand, have a high char yield with a rate of 35-75%. This can be observed by increasing the content of phenolic groups. According to Walter and Lyon, benzoxazines can be good flame retardants by their nature [74].

2.3 Green Chemistry

Designs can be made with the "Green Chemistry" concept to reduce or eliminate the use and production of hazardous materials [75]. Innovation, planning, design concept, and systematic comprehension are important for green chemistry. To provide this concept, using the twelve principles of green chemistry are the rules that help chemists sustainability goal [76].

The twelve principles mentioned below are the criteria that can be used for sustainable design of green chemistry [77].

1. Prevention: Waste prevention is more important than waste formation or cleaning.

2. Atom Economy: These methods should be designed to maximize the inclusion of all materials used in chemical processes as output in the final product.

3. Less Hazardous Chemical Synthesis: As far as possible, methodologies should be designed to use and produce substances that are less harmful to the environment and human health.

4. Designing Safer Chemicals: Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5. Safer Solvents and Auxiliaries: The use of auxiliary substances such as solvents, separation agents should be made as harmless or selected as possible.

6. Design for Energy Efficiency: The energy requirements and economic effects of chemical processes such as ambient temperature and pressure should be minimized.

7. Use of Renewable Feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives: Uses for derivatization such as blocking groups, protection groups, modifying groups should be minimized or avoided if possible, since these steps may require additional reagents or produce waste.

9. Catalysis: Catalytic regents are superior to stoichiometric agents.

10. Design for Degradation: Products obtained as a result of chemical reactions should not be transformed into harmless decomposition products, products should be designed so as not to remain in the environment.

11. Real-Time Analysis for Pollution Prevention: Analytical methodologies need to be further developed to allow for real time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention: Substances used in chemical processes should be designed and selected to prevent substance emissions, explosions and fires.

Achieving molecular sustainability at the green chemistry approach has enabled it to be applied in almost all industrial sectors. There are many economical applications in sectors such as aviation, automobile, cosmetics, electronics, energy, household products, medicine, agriculture.

It has been observed that green chemistry reduces the probability of causing negative results for human and environment and it is economically profitable. That is, we are very likely to be designed to reduce chemicals such as chemical hazard, toxicity, explosion, flammability, or depletion of the ozone layer. In short, it is necessary to realize a design in accordance with the twelve principles [76].

Framework of Green Chemistry

The green chemistry concept can be summarized in 3 ways:

1. Designs chemical life cycle.

2. Designs to reduce the nature and internal hazards of chemical products and processes.

3. Continues to work systematically within the framework of green chemistry principles and designs.

2.4 Renewable Resourced Based Benzoxazine

Benzoxazine studies based on renewable resources have been increasing day by day [78]. Today, there are difficulties in petroleum-based polymers. The same is true for benzoxazine resins. There are environmental concerns regarding the chemicals used in the elimination or production of such polymeric materials. Substances such as bisphenol a, which are widely used in the production of benzoxazins, are known to be destructive to human health. Since bisphenol-A mimics the hormone estrogen in humans, its use in food supplies or storage containers is restricted [16]. Within the framework of the concept of 'sustainability', renewable and recyclable polymer material studies gain importance to minimize pollution as well as increase resource utilization [8].

Looking at all these studies, benzoxazines can be produced from natural sources, such as terpenediphenol with the reaction between phenol and terpene obtained from pine or orange peel [79]. The most abundant renewable resource is cellulose. It can be used to increase char yield by modifying with the side chains of benzoxazines. Pure cellulose remains 4% at 800 °C in an inert atmosphere, but when modified with Benzoxazine, a 50% ratio is observed.

Many benefits and performances are provided by the use of natural and renewable materials in polymers and benzoxazines. The depletion of natural resources and the negativities in the prices of petroleum products are overcome. Diphenolic acid, similar to bisphenol A, can be produced from cellulose-rich waste products with high amounts of phenol and levunilic acid. These products are commercially available as well as cheaper than bisphenol-A [80].

The environmental effects of chemical use, recycling at the end of its life cycle, problems that may occur during use should be taken into consideration as much as possible. In this concept, environmentally friendly and natural benzoxazines can be obtained from phenols produced from leaf, root, or plant seed [81].

Where the natural phenols extracted; Cardanol is from the shell liquid of cashews [82], Arbutin is from ericaceae family plant [83], Chavicol is from basil oil or aniseed basil [84], eugenol is from clove oil [26], resorcinol and pyrogallol are from tannic acid [85], and vanillin is from vanilla bean [35]. Furfurylamine is synthesized from furfural [86], chitosan is obtained from chitin [87], rosins are produced from pines [44]. As we have seen, due to the large number of plant-derived phenols and amines, it can be used to reduce the environmental effects of benzoxazines. Furthermore, natural materials can provide unique chemical properties that are difficult to imitate benzoxazines produced from synthetic materials.

Renewable phenols, amines and aldehydes are listed in the below. The natural products that are listed can use for produce to renewable benzoxazine synthesis (Table 2.2).

It is known that coumarin-based benzoxazines heals themselves [88]. They can extracted from natural plant sources, notably in high concentration such as tonka bean, vanilla grass, sweet woodruff, mullein, sweet grass, cassia cinnamon, sweet-clover, deertongue, and the leaves of many cherry blossom tree [89]. The coumarin derivative compounds used by benzoxazines are 7-hydroxycoumarin (umbelliferone, UM) and 4- methylumbelliferone.

Table 2.2 : Renewable phenols, amines and aldehyde.

Phenols		Amines	Aldehyde
Arbutin	Vanilin	Furfurylamine	Benzaldehyde
Cardanol	Coumarine	Chitosan	
Catechol	Diphenolicacid	Rosin	
Chavicol		Cholesterol	
Eugenol		Stearylamine	
Resorcinol			

Vanillin can extracted from vanilla bean [35]. However, most of the vanillin used in the industry is chemically synthesized from guaiacol. While they can also be synthesized from lignin, they can be synthesized from biosynthesis with the help of a fungus or bacteria, such as eugenol, guaicol, ferrulic acid [90]. Vanilla-based benzoxazines have an aldehyde group from vanillin. We see that aldehyde group increases cross-linking by providing a functional group to the benzoxazine monomer At the studies, char yield of aldehyde containing benzoxazine observed 68,4% at 800^0C. It is known that the char yield of the polymerized vanillin benzoxazine is 55.3% higher than the aniline containing polybenzoxazine is 36%. Due to the furan ring from vanillin, vanilin-furfurilamin benzoxazine , T_g is 270 °C and the char yield is 65%. The reason for this is the electrophilic substitution at the furan ring [91]. As indicated, the polybenzoxazines made of vanillin have high Tg and char yields, which provide flame retardant properties and also indicate that high performance materials can be developed.

In addition, Liu *et al.* directed the benzoxazine amine portion from furfuril amine to renewable sources [86]. Furfural, where furfuril amine is synthesized, is one of the oldest known renewable chemicals, except ethanol, acetic acid and sugar. Furfurilamines can be synthesized by reduction of furfural. They are also used in the synthesis of furfurilamine, herbicide, pesticide, pharmaceuticals. Furfuryl amine-based polybenzoxazines emerge as polymers with high crosslink abilities, good thermal stability, high char yield and self- estinguishing behavior [92].

2.5 Inverse Vulcanization

Every year more than 70 million tons of petroleum products elemental sulfur emerges as an unwanted by-product. They are used in the production of chemicals in the form of sulfur, sulfuric acid, fertilizer, vulcanization of natural synthetic rubbers [93]. Despite all these areas of use, "excess sulfur problem" has arisen because the supply is more than demand. With the increasing request for energy, this problem will gradually grow. A lot of work is being done today to expand the use of sulfur. Its use as a cathode material for rechargeable batteries, such as lithium - sulfur (Li-S) [94] and sodium - sulfur (Na-S) systems [95]. Additionally, since sulfur rich materials show transparency in the IR region, it is an example for use in the production of IR optical materials [96]. From this point of view, it is very interesting to use low-cost sulfur for materials.

While regular vulcanization represents the process of creating durable material by adding a small amount of sulfur to the natural rubber, inverse vulcanization refers to the reaction of a large amount of sulfur and a small amount of additives, usually with diene. At high temperature, the sulfur ring is cleaved, forming sulfur cross-linked structures with a diene (Figure 2.19). The materials produced in this way provide convenience such as being produced with elemental sulfur without the need for harmful organic solvents. Molten sulfur acts as a reaction solvent, monomer, and initiator. Despite the cross-linked structures of thiopolymers, the reversibility of sulfur-sulfur bonds also provides vitrimer behavior, allowing recycling and repair.

In the light of sulfur chemistry, it is an option to prepare high sulfur-containing polybenzoxazines with inverse vulcanization chemistry to extend the applications of benzoxazine-based systems (Figure 2.20).

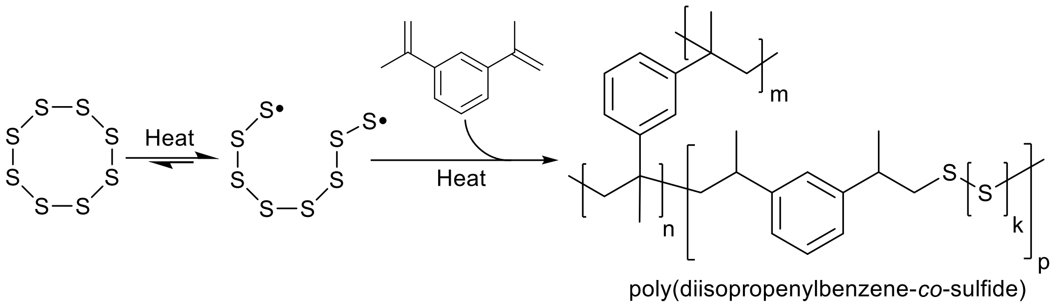

Figure 2.19 : Inverse vulcanization mechanism.

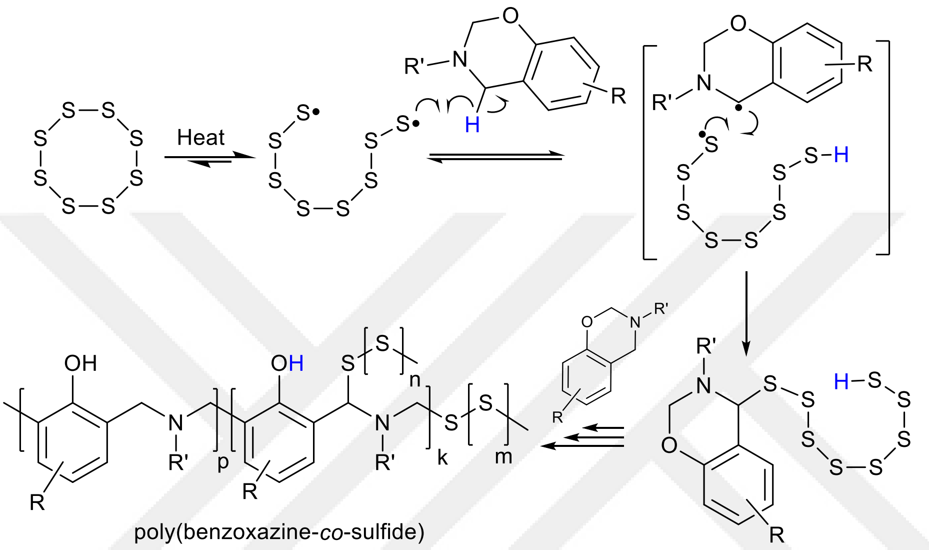

Figure 2.20 : Reaction between elemental sulfur and benzoxazine monomers to produce a poly(benzoxazine-co-sulfide).

3. EXPERIMENTAL

3.1 Materials

4,4-Isopropylidenediphenol (bisphenol A) (Aldrich, 97%), paraformaldehyde (Acros, 96%), allylamine (Aldrich, 98%), vanillin (Alfa Aesar, 99%), furfurylamine (Sigma Aldrich, 99%) sulfur (S_8, colloidal powder, reagent grade, Aldrich), sodium hydroxide (Acros, >97%), sodium sulfate (Acros, 99%), diethyl ether (Aldrich, ≥98%), tetrahydrofuran (THF, VWR Chemicals, 99.7%), chloroform (Carlo Erba, 99,9%) and chloroform-d ($CDCl_3$, 99.8 atom % D), 4-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2-one(β-Ionone, Sigma-Aldrich, 96%), (R)-(-)-Carvone (Sigma-Aldrich, 98%) were used as received.

3.2 Characterization

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer Diamond DSC under a scanning rate 10 °C. min^{-1} covering temperatures 30 – 320 °C. The ^1H NMR spectra of the products were measured at room temperature in $CDCl_3$ or DMSO-d6 with $Si(CH_3)_4$ using a 500 MHz NMR (Agilent NMR System VNMRS). The Fourier Transform infrared (FTIR) spectroscopy measurements were recorded as 20 scans using a Perkin-Elmer FTIR Spectrum One spectrometer. Thermogravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA at a heating rate 10 °C.min^{-1} from 50 to 900 °C under the nitrogen.

Electrodes were prepared by hand milling of 80 wt % of poly(Va-Bz_{15}-S_{70}-$ionone_{15}$) and 20wt % of conducting agent (Ketjen black) in a mortar and used directly as cathode. Swagelok type cells were assembled in an Ar-filled glovebox. 1M LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) salt and 0.5 M $LiNO_3$ (lithium nitrate) additive containing 1,3-dioxolane (DOL) dimethoxoxymethane (DME) (1:1, v:v) solvent was used as electrolyte. Lithium metal foil was used as both reference and counter electrodes. All electrochemical measurements were performed by using Biologic VMP-3 galvanostat/potentiostat in a voltage range of 1.8-3.0 V (vs. Li/Li^+). Cyclic voltammetry (CV) test was carried at a scan rate of 0.1 mV/s. Galvanostatic charge/discharge measurement was performed at a current density of C/5. Electrochemical impedance spectroscopy (EIS) test was performed in the frequency range from 1 MHz to 10 mHz with a voltage amplitude of 5 mV with a two-electrode SwagelokTM cells where lithium metal was used as both working and reference electrode. The experimental data were fitted by an EC-lab software created ZFit.

3.3 Synthesis

3.3.1 Synthesis of vanilline-benzoxazine (Va-Bz)

In a 500 ml round bottom flask, 4-Hydroxy-3-methoxybenzaldehyde (20g, 0,13mol), furfurylamine (12,8 g, 0,13 mol), paraformaldehyde (7,8 g, 0,26 mol) was dissolved in 250 ml chloroform. The mixture was magnetically stirred under reflux at 61 °C for 24h. The resulting product was extracted with 0.1 N sodium hydroxide (500 mL). Then, to neutralize the solution, chloroform solution was washed with distilled water (250 mL) for two times. The solution was dried with anhydrous Na_2SO_4 and filtered. Chloroform was evaporated on rotary. Than the product was dried under vacuum at 60 °C for 24 h. (yield 57%)

3.3.2 Synthesis of allyl functional bisbenzoxazine (B-ala)

In a 250 mL round bottomed flask, allyamine (15.4 g, 0.270 mol) was dissolved in 1,4-dioxane (100 mL), and the solution was cooled in an ice bath. Paraformaldehyde (16.2 g, 0.540 mol) was added portion wise to this solution during 10 min. Then, bisphenol A (30.8 g, 0.135 mol) was added to the solution, and the mixture was refluxed for 24 h. The solvent was evaporated using a rotary evaporator. The resulting oily product was dissolved in diethyl ether (150 mL) and extracted with 0.1 N sodium hydroxide for various times to remove unreacted bisphenol A. Then, to neutralize the solution, diethyl ether solution was washed with distilled water (50 mL) for two times. The solution was dried with anhydrous Na_2SO_4 and filtered. Diethyl ether was evaporated under vacuum, and the remaining oily product was dissolved in MeOH (15 mL). Water was added drop by drop into MeOH solution until it became turbid, and then the solution was refrigerated (4 °C). The precipitated sticky mass was obtained by decantation of MeOH and washing with excess water. The product was dried under vacuum at 60 °C for 24 h (yield 61%).

3.3.3 Inverse vulcanization of Va-Bz and ionones to produce terpolymer (poly(benzoxazine-sulfide-β-ionone or (R)-carvone))

A general procedure for the preparation of the terpolymer is as follows: To a 20 mL ordinary glass test tube, equipped with a magnetic stir bar, sulfur, B-ala or Va-Bz and β-ionone or carvone were added in various amounts (see table 4.1). The content of the tube was heated up to 185 °C with vigorous stirring in an oil bath. In the first 2 min. a clear orange solution is formed and became transparent yellow subsequently. Then, the color of the solution changed to brown black after 10 min. The overall reaction time was 30 min. in total. After cooling the tube down to room temperature, the product was collected by gently breaking the glass tube.

4. RESULT AND DISCUSSIONS

By combining polybenzoxazines with suitable polymers or compounds, the advanced material design is due to the reactive nature of the benzoxazine monomer, as well as the ring opening reaction of the oxazine ring. This reaction has two major steps and proceeds over cationic species. The last step is electrophilic substitution, which allows benzoxazines to react with suitable aromatics and heteroatoms [97, 98]. However, in the case of reaction of sulfur and benzoxazines, according to the proposed mechanisms, the reaction proceeds over a radical mediated process which was named as sulfur radical transfer and coupling (SRTC) [48, 99]. At the beginning of this reaction, sulfur radicals form by thermally induced homolytic cleavage of S–S bonds of S_8. Then, radical transfer occurs from oligosulfide to oxazine ring by hydrogen abstraction from either Ar–CH_2–N or O–CH_2–N bridges. The abstracted hydrogen generates a thiol group at the chain end of oligosulfide that ultimately reacts with oxazine to trigger the cationic ring-opening polymerization (Figure 2.19). Thus, it can be concluded that the whole reaction proceeds over simultaneous radical and cationic pathways. Furthermore, It is known from previous studies that the reaction of thiols with benzoxazines is effective even at room temperature. Hence, thiols are considered as great catalyst in ring-opening reactions [100, 101] . First, the benzoxazine monomer was synthesized from renewable sources, namely vanillin [102] and furfurylamine (Figure 4.1) [35]. Two different methods for synthesis, as in solvent and solventless, were realized with high efficiency. On the other hand, for comparison, a difunctional monomer synthesis consisting of bisphenol A and allylamine (B-ala) was made as a model monomer see in Figure A.1.

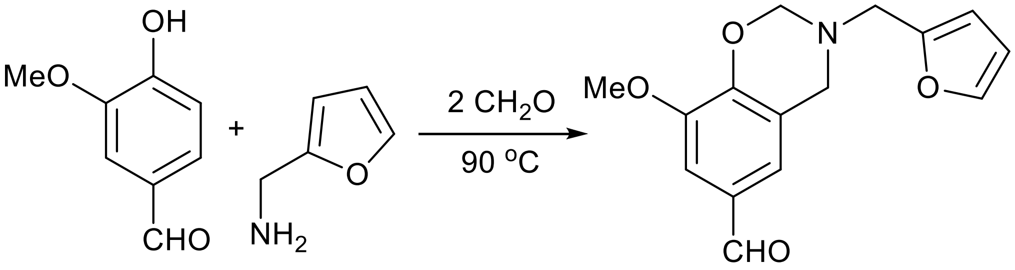

Figure 4.1 : Synthesis of vanillin based benzoxazine monomer (Va-Bz).

The structures of Va-Bz and B-ala were spectrally illuminated by ^{1}H-NMR and FTIR analysis Figure A.2 and Figure A.3. In the study, terpolymeric systems were obtained at 180 ^{0}C for 30 minutes by mixing different mass ratios (Table 4.1) Va-Bz / S8 / β - ionone or (R) -carvone in a reaction tube and teflon mold (Figure 4.2).

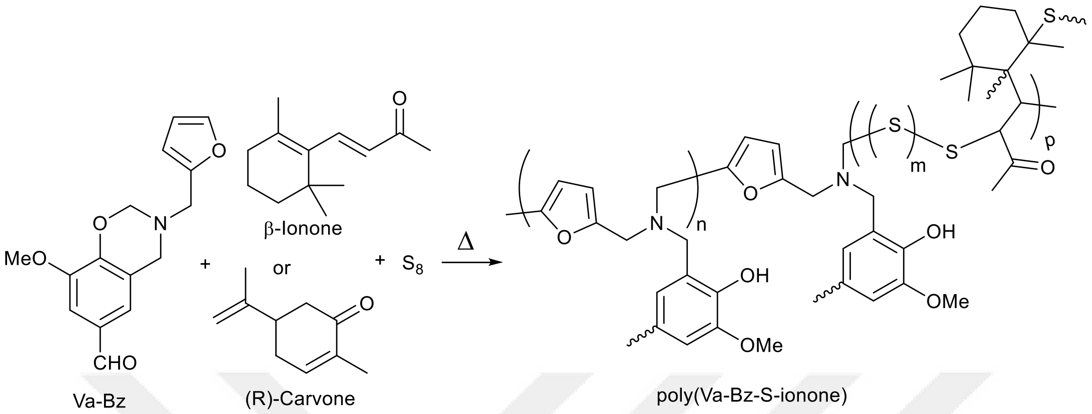

Figure 4.2 : Synthesis of terpolymer poly(Va-Bz-S-ionone or -carvone) via inverse vulcanization of Va-Bz and β-ionone or (R)-carvone.

In the synthesized terpolymeric system, polymers are named poly (Va-Bza-Sb-iononec or carvonec) and a, b, c correspond to the mass ratios in the mixture. As a result, it could be easily synthesized from a waste product with bio-sourced monomers in a test tube to obtain the desired advanced material. Ionones are aromatic compounds in essential oils derived from rose oil [103]. β-ionone is an important fragrance for perfumery. Besides, carvone is found in natural in essential oils such as in the seeds of caraway, spearmint, and dill [104].

Table 4.1 : Synthesis of poly(Va-Bz-S-ionone)s using Va-Bz or B-ala and β-ionone and sulfur at various mixing ratios.

Sulfur (%)	Va-Bz (%)	B-ala (%)	β-Ionone (%)
20	40	40	40
30	30	30	40
40	20	20	40
50	10	10	40
70	15	15	15
20	40	40	40

Polymer was mostly cross-linked from the synthesized Va-Bz, sulfur and ionone. However, proton nuclear magnetic resonance characterization was performed for some soluble polymer samples. The high sulfur content reduced the possibility of crosslinking. Therefore, the insoluble terpolymeric system was synthesized by using low amounts of sulfur. By selecting a relatively low amount of sulfur containing poly (Va-Bz$_{30}$-S$_{30}$-ionone$_{40}$), polybenzoxazin and ionon proton signals are easily detected (Figure 4.3). As seen in Figure 4.3, double bond decreases due to the bonding between sulfur and ionone and double bond protons disappear at 6.12 and 7.28ppm. In addition, the peaks of the –N – CH$_2$ – O bridge of the Oxazin ring disappeared at the end of the reaction. The aldehyde proton peak of Va-Bz at 9.82 ppm (Figure 4.3 b) also disappeared after thermal treatment indicating the polymerization of benzoxazine also proceeds over aldehyde carbon [42]. Here, it should be noted that the integration ratios of the peaks in Figure 4.3 c do not agree well with the ideal proposed terpolymer structure since the polymerization is uncontrolled and polysulfide, polysulfide-co-ionone, polybenzoxazine, segments may be formed in a complex order and the final terpolymer structure is most probably branched or hyperbranched.

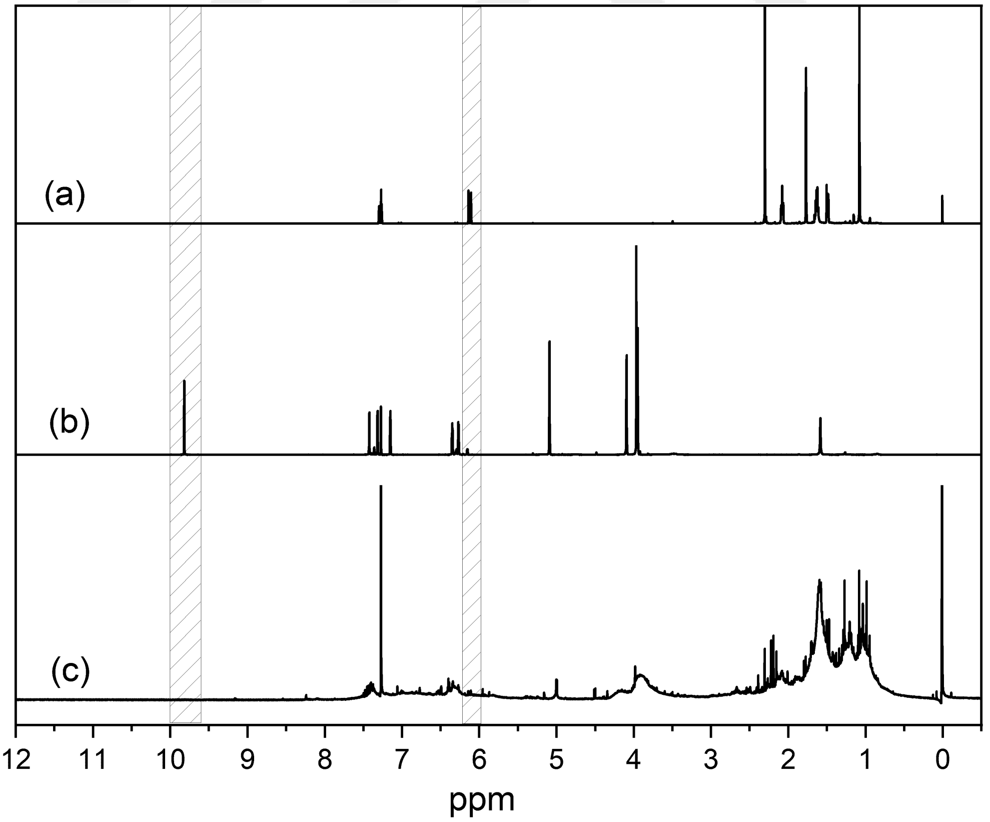

Figure 4.3 : Overlaid ^{1}H NMR spectra of β-ionone (a), Va-Bz (b) and poly(Va-Bz$_{30}$-S$_{30}$-ionone$_{40}$).

As seen from the FTIR results, the oxazin ring and ionon double bonds in the corresponding terpolymers with two different sulfur ratios and Va-Bz provide evidence. The consumption of conjugated double bonds of ionone depending on sulfur amount can easily be traced by carbonyl band of the ketone group. As seen from the FTIR results, the oxazin ring and ionon double bonds in the corresponding terpolymers with two different sulfur ratios and Va-Bz provide evidence. The consumption of conjugated double bonds of ionone depending on sulfur amount can easily be traced by carbonyl band of the ketone group. In Figure 4.4, the IR of poly (Va-Bz$_{40}$-S$_{20}$-ionone$_{40}$) has two different ketone carbonyl at 1672 cm^{-1} and a minor shoulder at 1710 cm^{-1} corresponding to conjugated and non-conjugated ketones, respectively. In the polymer made using 20% sulfur, double bonds were not consumed, and conjugated ketone bonds are observed in FTIR spectra at 1672 cm^{-1}. In Figure 4.4 b FTIR spectrum, it is seen that 50% sulfur consumes ionon double bonds. The typical ketone band for unconjugated carbonyl is at 1711 cm^{-1}. This leads to an isolated ketone structure. The peaks seen at 3400cm^{-1} belong to the phenolic -OH of polybenzoxazines in terpolymeric samples. The oxazine ring band in Figure 4.4 at 948 cm^{-1} disappeared after curing, proving polymerization under certain conditions.

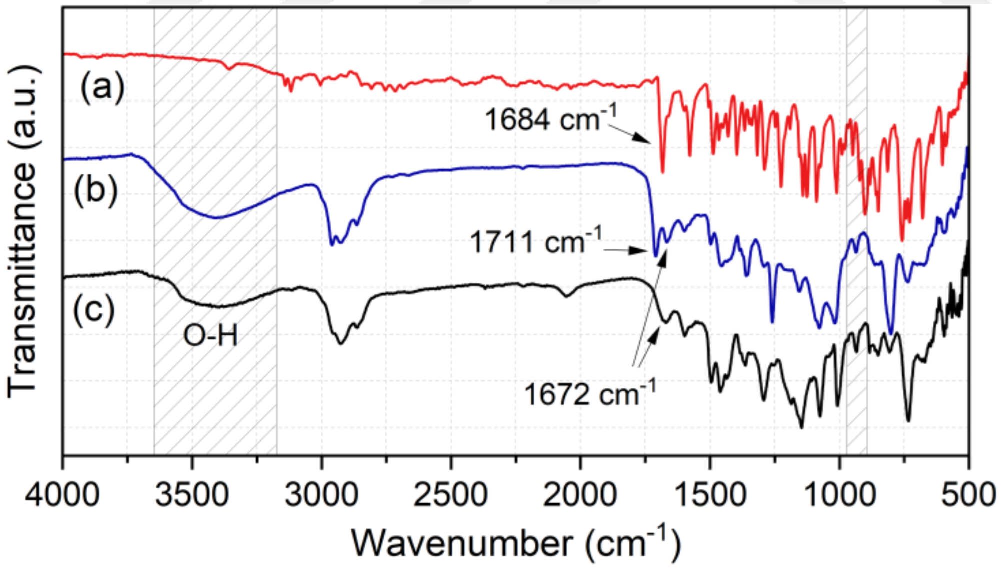

Figure 4.4 : Overlaid FTIR spectra of Va-Bz (a), poly(Va-Bz$_{10}$-S$_{50}$-ionone$_{40}$) (b), poly(Va-Bz$_{40}$-S$_{20}$-ionone$_{40}$) (c).

Apart from β -ionone, (R)-carvone was attempted to synthesize terpolymer. Contrary to β - ionic terpolymeric systems, low molecular weight oily products were formed in experiments with carvone. As a result, studies did not continue due to the carvon's unstable terpolymeric mold and incompatibility. For all mixing ratios given in the

Table of B-ala, a completely cross-linked system is obtained by fully incorporating allyl functionality and inverse vulcanization. In addition, it appears that the mixture with B-ala with β -ionone cannot adequately dissolve sulfur at the reaction temperature, seen as a heterogeneous mixture at Figure A.4. On the contrary, with the Va-Bz monomer, molten sulfur and ionone can be dissolved and homogeneous products can be obtained easily. Since Poly (Va-Bz$_{40}$-S$_{20}$-ionon$_{40}$) is an insoluble sample, it could be molded as a film and triangularly shape (Figure 4.5).

Figure 4.5 : Images of poly(Va-Bz$_{40}$-S$_{20}$-ionone$_{40}$) as mold (a) and film (b).

As seen in Figure 4.6, Va-Bz melting endotherm is 117 °C and maximum curing temperature is 202 ^{0}C. By adding sulfur to Va-Bz, ring opening polymerization was reduced to 175 ^{0}C (Figure A.5). Besides, the melting endotherm of sulfur can be easily detected by DSC at 110 °C, as one or more endotherms, depending on the sulfur allotropes. As seen in Figure 4.6 (c), a slight melting endotherm is observed for poly (Va-Bz$_{10}$-S$_{50}$-ionon$_{40}$) where sulfur feed rate is 50%, while in the sample Poly (Va-Bz$_{40}$-S$_{20}$-ionon$_{40}$) (Figure 4.6 (b)) all sulfur was consumed by Va-Bz and β -ionone and no melting endotherm was observed. The DSC results show that a homogeneously dispersed sulfur-containing terpolymer will only be slightly below 50% by mass. The DSC results show that a homogeneously dispersed sulfur-containing terpolymer will only be little below 50% by mass. In addition, in the DSC analysis of cross-linked terpolymers, seen in Figure 4.6, evaporation of sulfur-based compounds at high temperatures between 210-270 °C is seen as irregular endotherms (Figure A.5).

Poly (Va-Bz40-S20-ionone40) was chosen to measure thermal stability because it has a low amount of polysulfide content and a completely crosslink structure. The reason for choosing this sample is that, in samples with a low content of sulfur, sulfur is found to be homogeneus and form a unsoluble sample. The degradation temperatures for T5%, T10% of poly(Va-Bz40-S20-ionone40) are as 277, 302°C. These values can be attributed to polysulfide degradation due to the relatively weak S–S bond. According to the derivative TGA, our terpolymeric system shows two different Tmax values, 311 and 384°C. These Tmax values observed are based on the amine and phenol degredation in polybenzoxazines and the carbonyl degradation of the ionone. The char yield of the sample terpolymer is 43% at 800°C (Figure 4.7). Char yield can be considered as a competitor to classical benzoxazines.The furan and aldehyde content provided additional cross-linking increased the thermal stability of Va-Bz.

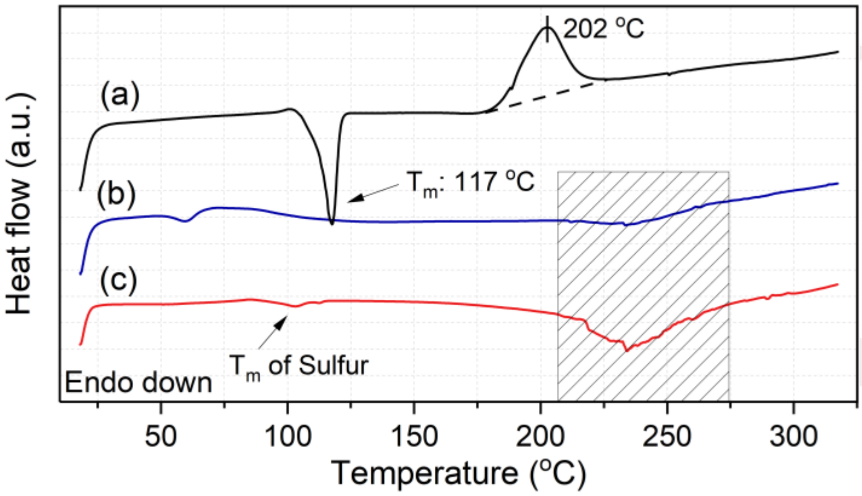

Figure 4.6 : Overlaid DSC traces of Va-Bz (a), poly(Va-Bz$_{40}$-S$_{20}$-ionone$_{40}$) (b), poly(Va-Bz$_{10}$-S$_{50}$-ionone$_{40}$) (c).

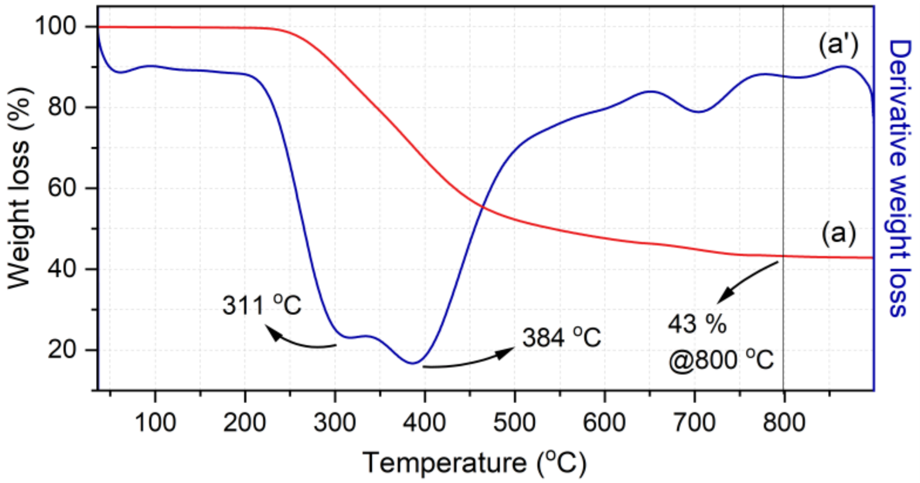

Figure 4.7 : TGA (a) and derivative TGA (a’) of poly(Va-Bz$_{40}$-S$_{20}$-ionone$_{40}$).

Sulfur rich polymers are good candidates for cathode materials for lithium-sulfur battery applications. Besides, in previous studies, poly (benzoxazin-co-sulfur) s produced by inverse vulcanization were used as cathode materials for Li-S batteries and showed good capacity life [105]. Therefore, for poly (Va-Bz_{15}-S_{70}-$ionon_{15}$), the highest sulfur content among our syntheses, cyclic voltammetry, charge-discharge cycle, and electrochemical impedance spectroscopy (EIS) measurements were made as Li-S cathodes.

Figure 4.8 a demonstrates the CV measurement of the poly(Va-Bz_{15}-S_{70}-$ionone_{15}$) performed at a scan rate of 0.1 mV/s. The profile displayed a representative signature of sulfur oxidation and reduction phenomena with two main reduction peaks situated at around 2.3 V and 2 V vs Li/Li^+. Those peaks correspond to the reduction of sulfur chain first into long-chain polysulfides (Li_2Sn ($6 < n < 8$) followed by mid- and short-chains (Li_2Sn ($2 < n < 6$) leading the formation of Li_2S (the least sulfur reduction specie), respectively. The subsequent anodic peaks located at around 2.35 vs Li/Li^+ were attributed to the re-oxidation of Li_2S to long chain polysulfides and sulfur. After the first cycles, the shifts of current peaks can be observed towards higher voltage values related to the rearranging of sulfur particles from the original sites to more energetic sites. The first galvanostatic charge discharge profiles of the electrode cycled at C/5 current density (1 C = 1674 mA/g means the current applied to the cell reached the theoretical capacity value in 1 h) is shown in Figure 4.8 b. As observed with CV profile, the cycling curve depicted characteristic staircase voltage profiles of Li-S cells in which upper discharge plateau (2.3 V vs Li/Li^+) corresponds to the reduction of long chain polysulfide followed by longer plateau located at 2.0 vs Li/Li^+ to further reduction of the polysulfides. 1040 mAh/g discharge and 1034 mAh/g charge capacities were obtained at the first cycle leading almost 100 % of initial Columbic efficiency. Even though the first couple of cycles a fast capacity decay was observed, latter a sustained capacity values around 400 mAh/g was achieved over 70 of cycles (Figure 6c). Electrochemical properties were further investigated by means of C- rate performance at varying current densities (C/5, C/2, C, 2C, 5C, 10C). As expected, relatively higher current densities let lower capacity values in which the cell displayed around 470 mAh/g, 350 mAh/g, 240 mAh/g and 50 mAh/g discharge capacities at C/2, 1 C, 2 C, 5 C and 10 C, respectively. When the cell was set backed to C/5 current density, it covered most of its capacity and more than 400 mAh/g capacity values were obtained over 100 of cycles that is consistent with the Figure 4.8 c.

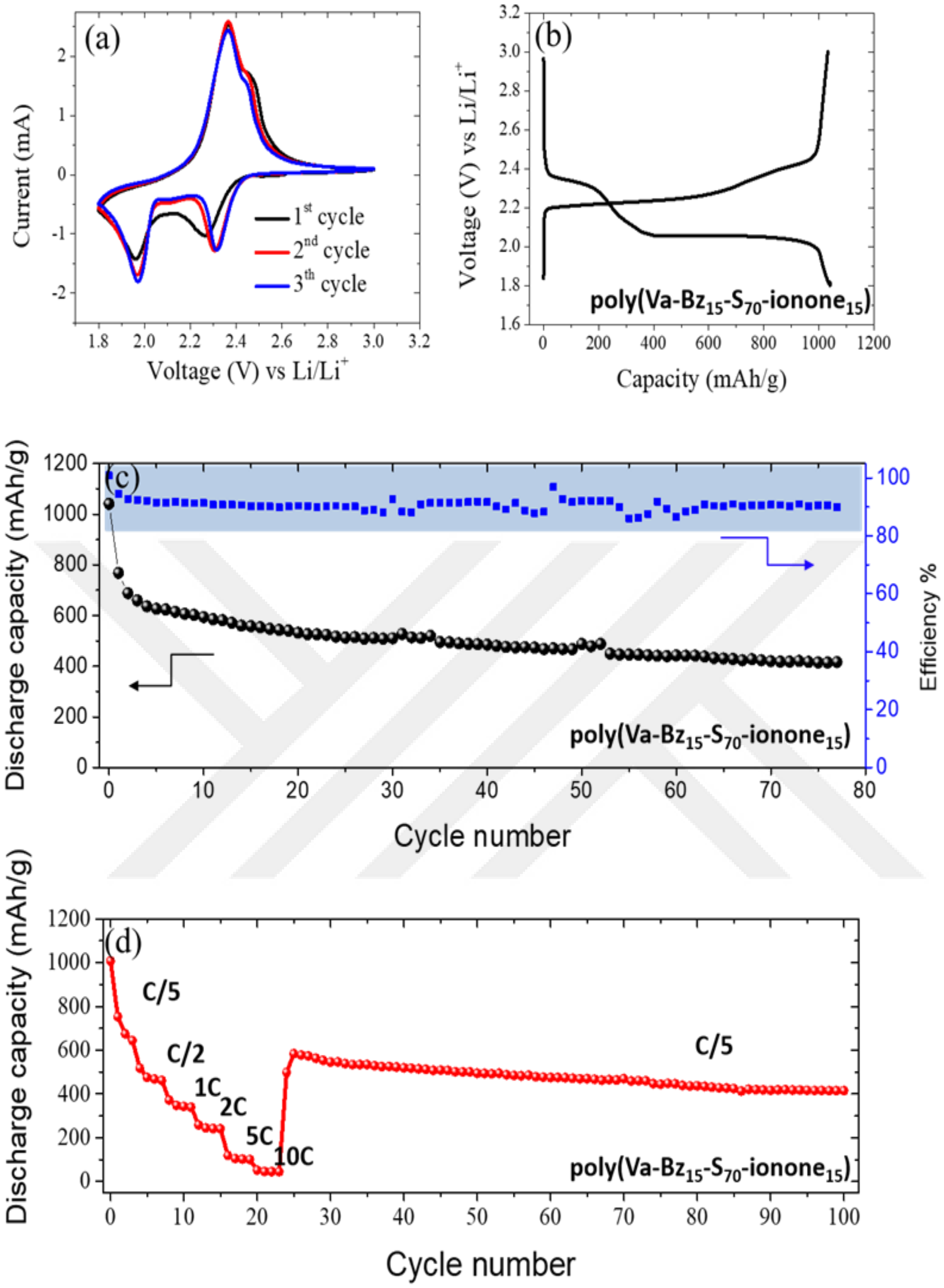

Figure 4.8 : (a) CV measurement of poly(Va-Bz_{15}-S_{70}-$ionone_{15}$) at a scan rate of 0.1 mV/s, (b) first galvanostatic discharge-charge profile cycled at C/5 current density, (c) cycling performance of poly(Va-Bz_{15}-S_{70}-$ionone_{15}$) cycled at C/5 and (d) C-rate performance of poly(Va-Bz_{15}-S_{70}-$ionone_{15}$).

5. CONCLUSION

Bio-derived monomer, sulfur and waste product can easily be combined to form a terpolymer in a test tube. Renewable benzoxazine monomer synthesized with vanillin and furfurilamine, selected to be combined with ionone and sulfur. With inverse vulcanization, sulfur, ionone and benzoxazine monomer provided the formation of a terpolymer. During terpolymer synthesis, sulfur atoms triggered ring-openning of the benzoxazine monomer to form polymers by sulfur radical transfer and coupling (SRTC). The procedure is simple and can be completed in ca. 30 min. by a melt process. Besides, our polymer sample with high sulfur contentof %70 showed more than 100 cycles over 400 mAh / g capacity as Li-S battery cathode. Electrochemical impedance spectroscopy (ESI) studies were used to gain more insight into lithium storage mechanism before and after cycling where sharp capacity decay at the first couple of cycles could be associated with the trapping of Li ions into polymeric network. Apparently, this green chemical approach relies on a simple procedure and low cost bio-sourced chemicals allowing a useful design for fabrication Li−S cathode in one-pot.

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APPENDICES

APPENDIX A: Supporting information of results and discussion.

APPENDIX A

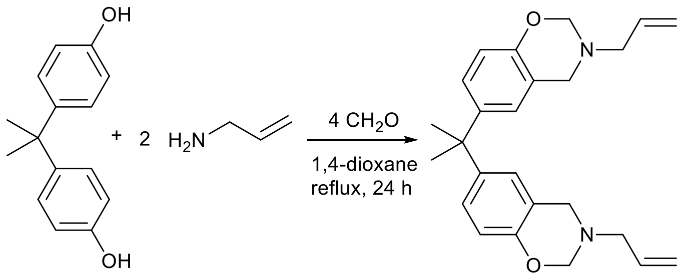

Figure A.1 : Synthesis of bisphenol A based benzoxzine monomer (B-ala).

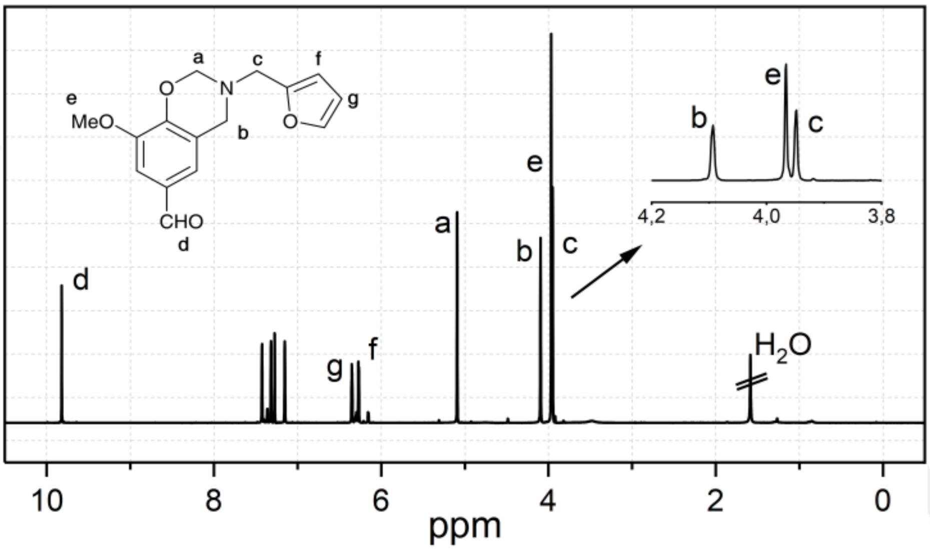

Figure A.2 : ^{1}H NMR spectrum of Va-Bz monomer.

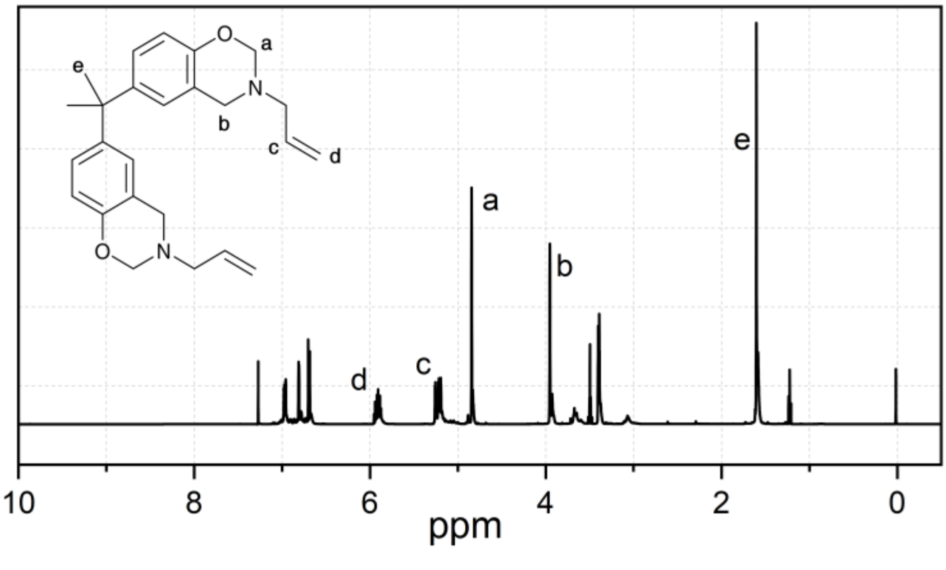

Figure A.3 : ^{1}H NMR spectrum of Ba-ala monomer.

Figure A.4 : Image of molded poly(B-ala-S-ionone).

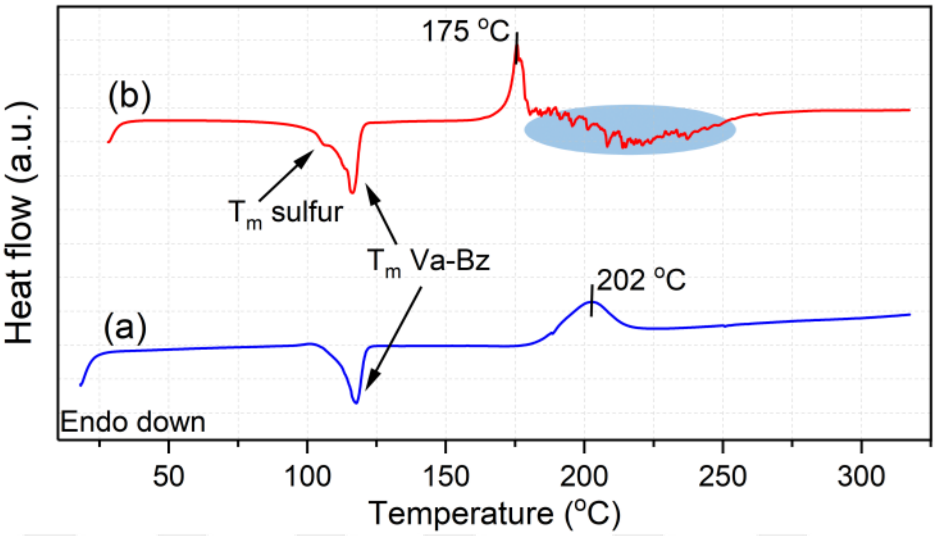

Figure A.5 : Overlaid DSC thermograms of Va-Bz (a) and Va-Bz/sulfur mixture (60:40, w/w).

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- **Bayram, O., Kiskan, B., Demir, E., Demir-Cakan, R., Yagci, Y..** (2020). Advanced Thermosets from Sulfur and Renewable Benzoxazine and Ionones via Inverse Vulcanization, *ACS Sustainable Chemistry & Engineering*, ***8***(24), 9145-9155.

- **Bayram. O.**, Kiskan B., Yagci Y., 2019, Combining Benzoxazine and Sulfur Chemistries for Advanced Materials (poster presentation), **VII. International Baekeland Symposium, October 15-18, 2019, Tarragona, Spain.**