ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ELECTROCHEMICAL MANIPULATION OF ADHESION STRENGTH OF POLYBENZOXAZINES ON METAL SURFACES: FROM STRONG ADHERING TO DISMANTLING

M.Sc. THESIS

Cansu AYDOĞAN

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİBENZOKSAZİNLERİN METAL YÜZEYLERE KUVVETLİ YAPIŞMA VE YÜZEYDEN AYRILMA ÖZELLİĞİNİN ELEKTROKİMYASAL OLARAK AYARLANMASI

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Cansu AYDOĞAN, **a M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **509111049**, successfully defended the **thesis/dissertation** entitled "**ELECTROCHEMICAL MANUPILATION OF ADHESION STRENGTH OF POLYBENZOXAZINES ON METAL SURFACES: FROM STRONG ADHERING TO DISMANTLING ''**,which she prepared after fulfilling the requirements specified in the associated legislations,

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To my family…

FOREWORD

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ABBREVIATIONS

^{1}H-NMR	**:** Nuclear magnetic resonance spectroscopy
Bisphenol-A	**:** 4,4-Isopropylidenediphenol
Da	**:** Dalton
DSC	**:** Differential scanning calorimeter
FTIR	**:** Fourier transform infrared
HY	**:** Hydrogen containing compound
MCBO	**:** Main-chain benzoxazine oligomer
MCBP	**:** Main-chain benzoxazine precursor
ROP	**:** Ring opening polymerization
TGA	**:** Thermogravimetric analyzer
CV	**:** Cyclic voltammetry
B-Ant –A	**:** Aniline based benzoxazine monomer
B-Ant –F	**:** Furfurylamine based benzoxazine monomer
B-Ant –Bn	**:** Benzylamine based benzoxazine monomer
PB-Ant-A	**:** Aniline based polybenzoxazine
PB-Ant-F	**:** Furfurylamine based polybenzoxazine
PB-Ant-B	**:** Benzylamine based polybenzoxazine

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Figure 4.19 : Derivative weight (%) of (a) PB-Ant-F (b) PB-Ant-Bn (c) PB-Ant-A31

ELECTROCHEMICAL MANUPILATION OF ADHESION STRENGTH OF POLYBENZOXAZINES ON METAL SURFACES: FROM STRONG ADHERING TO DISMANTLING

SUMMARY

Polybenzoxazine, has gained incremental interest as one of the precious high performance polymeric materials, due to their advantageous properties over the classical novolac and phenolic resins. They posses a number of outstanding characteristics such as, no requirement for harsh catalyst, long shelf lives, no generation of byproducts during curing, low water uptake, almost zero shrinkage in the course of curing. However, polybenzoxazines synthesized from the monomer precursors suffer from some demerits consisting of i) brittleness ii) need of quite high temperature for curing iii) poor film forming and proccesibility. Therefore, various strategic approaches were propounded to overcome these deficiencies as well as expand the existing properties. One of the alternative ways is associated with synthesis of modified monomers with different functionalities, while the other route is deal with blending with polymers or fillers and fibers. Another significant improvement is based on incorporating benzoxazine units at the end chain, main chain or side chain polybenzoxazines. Polybenzoxazine composites prepared by all strategies have reached quite promising performance.

It has been shown that, independently from the above strategies employed, monomer design approach has been repetitively used to incorporate desired functionalities to the end structure of polybenzoxazine thermosettings, since their molecular stucture provides immense design flexibility by means of using various phenolics, primary amines and formaldehyde.

Apart from straight forward synthesis of benzoxazines, another strinking feature is, their polymerization can easily be achieved in the absence of a catalyst at temperatures between *ca.* 160-250 °C depending on the functionalities on the monomer. Even much lower polymerization temperatures in special cases were reported. Mono-oxazine ring containing benzoxazine has a distorted semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. This heterocylic ring can easily undergo ring-opening reaction under specific conditions and the resultant polymer is a network comprised of phenolics and amine bridges as the structural motifs. Furthermore, as a result of both oxygen and nitrogen of the oxazine ring can behave as potential cationic polymerization initiation site thus the benzoxazine ring becomes very likely to open via a cationic mechanism.

It is known that polymers involving hydroquinone-quinone or similar redox couples have diverse applications ranging from electrical conductors, batteries, electrode coatings for sensors, catalysts for electrochemical reactions, antioxidants to reaction inhibitors On these bases, incorporation of quinone groups into the benzoxazine structure would be a great advantage by virtue of the redox cycle between quinone

hydroquinone couples. By this way, redox active polybenzoxazines can change the structural motif of itself simply using electrochemical stimulus, which meant that some properties of the polybenzoxazines can be altered in a cyclic manner between two distinct points. One of these properties is the adhesion of polybenzoxazines onto steel surfaces via attractions between phenolic hydroxyls and iron atoms. Quinone-hydroquinone conversions can effect the hydroxyl content on the structure of polybenzoxazines and the adhesive property could swing (oscillate) between two adhesion points.

Herein, we describe efforts to synthesize benzoxazine monomers possessing anthraquinone groups in the structure to generate corresponding polybenzoxazine networks by thermally active ring opening polymerization capable of changing adhesion property by external electrochemical stimulation.

For this purpose, using 1,5 dihydroxyanthraquinoe, paraformaldehyde and various amines, several anthraquinone based benzoxazines synthesized. Characterizations of three different monomoners were done by ^{1}H-NMR and FT-IR. Curing behavior of the monomers has been studied by DSC.Thermal properties of the cured polymers were investigated using TGA. The progress of the curing reaction was also monitored by IR . In addition, ^{13}C NMR was conducted for proving the polybenzoxazines. The redox behavior of these polymers is examinated by cyclic voltammetry. Furthermore, adhesion and dismantling properties of the polymers on the metal surfaces, in course of redox cycle, are demonstrated by adhesion test.

POLİBENZOKSAZİNLERİN METAL YÜZEYLERE KUVVETLİ YAPIŞMA VEYA YÜZEYDEN AYRILMA ÖZELLİĞİNİN ELEKTROKİMYASAL OLARAK AYARLANMASI

ÖZET

Polibenzoksazinler, üstün mekanik ve fiziksel özellikleri ile son yıllarda büyük ilgi uyandıran yüksek performanslı termoset fenolik reçinelerdir. Kürlenme sırasında hemen hemen hiç hacimsel değişime uğramayışları, düşük su absorbiyonu göstermeleri, yüksek yanma ürünü yüzdesi, kürlenme için asit katalizöre ihtiyaç duyulmaması, kürlenme sırasında yan ürün oluşturmamaları gibi özellikleri ile novalak ve resol tipi fenolik reçinelere alternatif olmuşlardır.

Birçok avantaj sağlayan özelliğinin yanı sıra, monomer öncülerinden sentezlenen saf polibenzoksazin kimyasının çeşitli dezavantajları da vardır. Film haline getirilememe, kırılganlık, işlenme güçlüğü, yüksek kürlenme sıcaklığı gibi özellikler polibenzoksazinlerin kullanılabilirliliğini sınırlanmaktadır.

Bu dezavantajların üstesinden gelebilmek için bilim adamları çeşitli stratejiler geliştirilmiştir; (i) çeşitli fonksiyonlu gruplarla modifiye edilmiş benzoksazin sentezi, (ii) polimerik benzoksazin sentezi, (iii) benzoksazinleri dolgu maddeleri, fiberler veya başka yüksek performanslı polimerlerle karıştırmak gibi yöntemler bu yaklaşımlara örnek olarak verilebilir.

Benzoksazin öncülleri ve onlardan meydana gelmiş çapraz bağlı polimerler bazı karakteristik özellikler göstermektedirler. Bunların başında, polimerizasyon sırasında düşük hacim kaybı gelmektedir. Tüm termoplastik ve termoset reçineler polimerizasyon süresince hacim kaybına uğrarlar. Düşük büzüşmeye (hacim kaybına) saip olan materyaller dahi %2-10 kadar hacim kaybederler, bu da benzoksazinlerin yapıştırıcı, kaplayıcı ve dolgu maddesi olarak kullanılmaları için sakıncalı bir durumdur.

Benzoksazinler ve polibenzoksazinler, yüksek derecede mekaniksel özellikleri yanında ± %1 kadar hacimsel değişiklik gösterirler. Yüksek sıcaklıklarda yapılan kürleme işleminde büzüşme çok az meydana gelirken, oda sıcaklığında küçük hacimsel değişiklikler oluşabilmektedir. Oda sıcaklığında bu iki türdeki sistemlerin birleştirilmesi idealdir.

Bunun dışında benzoksazinlerin ilgi çekici bir başka özelliği suyu çok çok az adsorplamalarıdır. Böylelikle düşük dielektrik sabitine sahip polimerlerin eldesi çok kolay olmaktadır.

Camsı geçiş sıcaklığı özelliği, polimerlerin termal kararlılıklarını etkileyen önemli bir faktördür. Yüksek camsı geçiş sıcaklıklarına sahip termosetlerin termal dayanıklılıkları, düşük camsı geçiş sıcaklığına sahip olanlara oranla daha yüksektir. Çapraz bağ yoğunluğunun artması kırılganlık ve yüksek camsı geçiş sıcaklıklarına, kırılganlığa neden olmaktadır.

Kömürleşme verimi, materyallerin yanabilirliklerini tespit etme konusunda gerekli bir parametredir. Kömürleşme verimi yüksek olan maddeler, düşük alev alma özellikleri sebebiyle tercih edilmektedirler. Benzoksazinler, çok sayıda hidroksil, tersiyer amin ve benzen gruplarına sahip olduklarından, yanmaya dayanıklı ve bu özellikleriyle de tercih edilen malzemelerdir.

Polibenzoksazinlerin işlenebilirliğini ve mekanik özelliklerini arttırmak için yapısında benzoksazin üniteleri içeren ana zincir, yan zincir veya uç zincir (telekelik) polimerler sentezlenmiştir.

Ana zincir polimerik benzoksazinlerin, molekül ağırlıkları benzoksazin monomerlerine oranla daha yüksektir. Bu da onlara kolaylıkla işlenebilme ve üstün mekanik özellikler sağlar. Ana zincirinde benzoksazin halkası içeren polibenzoksazinler çeşitli şekillerde elde edilebilirler. Lineer polimerlerin diaminler ve bisfenollerin reaksiyonu ile sentezlenmesi, ana zincir polimerik öncüllerin sentezindeki ilk yaklaşımdır. Bu yaklaşım ile oligomerik büyüklükte polimerler elde edilebilmektedir ($1000<M_n<10000$).

Bunun dışında poliester, poliamit, poliüretan oluşumu ile hidrosilasyon, Diels-Alder ve çıt-çıt reaksiyonları da lineer polimerlerin sentezlenmesinde kullanılan diğer kondenzasyon yöntemleridir.

Yan zincir öncül benzoksazin metodu, polimer ana zincirine benzoksazin gruplarının girmesiyle yüksek yoğunluklu ağsı yapılı polimer elde edilmesidir.Yan zincir öncül benzoksazin elde etmenin çeşitli yolları vardır. Çıt çıt kimyası ya da oksidatif yöntemle sentez bunlardan birkaçına örnek olarak verilebilir.

Benzoksazinin bağlı olduğu polimerik yapıların kürleme ile oluşan çağraz yapılarda işlenebilirliğe ve mekanik özelliklere katkı sağladığı görülmektedir. Zincir sonunda benzoksazin içeren ve çapraz bağlanabilen telekilik sentezi yöntemi sayesinde benzoksazinler polimerlere bağlanmıştır.Bu durumda polimerik yapı ana iskelet görevi görür. Böylece, telekilik polimerler termoplastik rol oynamakla beraber boyutsal kararlılılık, kimyasallara direnç ve ısıl dayanım gösterebilmektedirler.

Farklı başlangıç maddeleri kullanılarak esnek moleküler tasarıma sahip birçok uygulamada yer alan polibenzoksazinler sentezlenmektedir.

Kolay sentezinin yanında polibenzoksazinlerin göze çarpan özelliklerinden biri de polimerizasyonların monomer fonksiyonalitesine bağlı olarak 160-250°C derecede katalizörsüz gerçekleşmesidir.

Daha düşük sıcaklıklarda gerçekleşen polimerizasyonlara da rastlamak mümkündür. Benzoksazinlerin polimerizasyonu; heterosiklik halka açılma reaksiyonuyla gerçekleşir ve böylelikle fenolik gruplar ve amin köprülerini içeren ağsı yapılı polimerik bir yapı oluşur.

Benzoksazin halkası, bozulmuş yarı- zincir yapısındadır. Bu yapıda, azot benzen halkasının düzleminin üzerindeyken, azot ve oksijen arasındaki karbon ise benzen düzlemi üzerindedir. Bu konformasyon, halkanın uygun koşullarda halka açılması reaksiyonu vermesini sağlamaktadır. Bunun yanında, hem oksijen hem de azot atomları güçlü baziktir ki bu da onları potansiyel katyonik polimerizasyon başlangıç yerleri yapar ve benzoksazin halkası katyonik mekanizma ile açılmaya uygun hale gelir.

Hidrokinon-kinon veya benzer redoks ciftleri içeren polimerler; elektrik iletkenleri, piller, sensörler için elektrot kaplamalar, elektrokimyasal reaksiyonlar için katalizör

vb.birçok uygulamada kullanılmaktadır. Bu bağlamda benzoksazin yapısına kinon gruplarının girmesi hidrokinon-kinon redox döngüsü dolayısıyla büyük yarar sağlayacaktır. Böylelikle elektroaktif hale gelen polibenzoksazinlerin elektrokimyasal bir uyaranla yapısal motifleri değişebilmektedir.

Bu özelliklerden bir tanesi fenolik hidroksil ve demir atomları arasındaki etkileşim dolayısıyla elektrokimyasal uyaranla polibenzoksazinlerin çelik yüzeye yapışıp yüzeyi bırakmasıdır. Kinon-hidrokinon dönüşümü polibenzoksazin yapısındaki hidroksil içeriğini etkileyecek çelik yüzeye yapışma özelliği de buna bağlı olarak değişkenlik gösterecektir.

Bu çalışma, bir kinon türevi olan antrakinon grubuna sahip benzoksazin monomerlerinin sentezi, ısısal halka açılma reaksiyonu ile polimerizasyonu ve oluşan ağsı yapılı polibenzoksazinlerin elektrokimyasal özellikleri ile birlikte dışardan etki eden elektrokimyasal uyaran ile değişen yapışkanlık özelliği üzerine yoğunlaşmıştır.

Bu amaçla 1,5 dihidroksiantrakinon, paraformaldehit ve çeşitli aminlerle, benzoksazin bazlı antrakinon monomerleri sentezlenmiştir. Ardından termal yolla polimerizasyonları gerçekleştirilmiştir. Sentezlenen 3 farklı monomerin yapıları FT-IR ve ^{1}H-NMR ile karakterize edilmiştir.

Karakterizasyonları yapılan monomerlerin kürlenme davranışları diferansiyel taramalı kalorimetri (DSC) cihazı ile incelenmiştir. Kürlenmiş polimerlerin ısısal özellikleri de termogravimetrik analizler (TGA) ile doğrulanmıştır.Böylelikle farklı amin bileşikleri kullanılarak elde edilen polimerlerin termal özellikleri karşılaştırılarak yorumlanmıştır.

Buna ek olarak 180^{o}C den 210^{o}C dereceye kadar aşamalı olarak kürlenen örneklerin FT-IR analizleri yapılarak oluşan polimerik yapı doğrulanmıştır.

Ayrıca 210^{o}C derecede kürlenmiş örneklerin ^{13}C NMR'ına bakılarak yapı tekrar karakterize edilmiştir. Bunun dışında örmeklerin elektroaktif özellik gösterdiğinin kanıtı için, 2 saat 180^{o}C derecede kürlenen üç farklı monomere elektrokimyasal işlem uygulanarak örneklerin redoks özellikleri incelenmiştir. Polimerlerin siklik voltametri ile indirgeneme yükseltgenme özelliği gösterdiği kanıtlanıp potansiyelleri ölçülmüştür.

Polimerlerin redox döngüsü sırasında metal yüzeye yapışıp bırakma özelliği de yapışma testi uygulanarak kanıtlanmıştır.

1. INTRODUCTION

Polybenzoxazines are a rapid progressing thermosetting resins that obtain a number of enchanting superiorities in contrast with other sort of thermosets for instance phenolic, epoxy, bismaleimide, or cyanate ester resins. Low water uptake, near zero shinkage upon polymerization, high glass transition temperature, high char yield are some of unique features of these newly developed materials[1]. Furthermore, the polymerization of benzoxazine monomers occur through thermally induced mechanism without any initiator or catalyst. These numeruous exceptional properties of benzoxazines are deal with the presence of inter-and the intermolecular hydrogen bonds in the network architecture [2]. There has been lots of labors to synthesize new monomers for enhancing the properties of polybenzoxazines profiting by design flexibility of benzoxazine monomers as a consequence of usage cheap and commercially available phenols, primary amines and formaldehyde [3-5].

Eventhough polybenzoxazines exhibit a variety of facinating behaviors, pure polybenzoxazine-based polymers have number of handicaps in terms of (i) high curing temperature (200 ^{o}C or higher), (ii) difficulty in processing and (iii) poor mechanical strength (brittless).

Recent synthetic advances provide promising strategies to combine this chemistry with classical polymers. Many different end chain, main chain, or side chain polybenzoxazine prepolymers were synthesized by various research groups overcoming problems associated with the processability of brittle polybenzoxazines. Blending benzoxazines with polymers or fillers and fibers was also proposed as an alternative route to reach desired ultimate performances.

It is expected that, the cross-linked network structure formed from polymer and polymerization of benzoxazine, will exhibit amplified mechanical properties while keeping the beneficial properties of polybenzoxazine [6].

Redox active polymers consisting of hydroquinone/quinone units play a vital role in a wide range areas such as electron transfer and energy conservation systems [7]. When

incorporated into benzoxazines, the redox cycle between hydroquinone/quinone couples would make these compounds particularly useful as electroactive thermosets. Some properties of the polybenzoxazines can, thus, be changed in a cyclic manner between two distinct points by electrochemical stimulus. Electrochemical reduction converts quinone groups into hydroquinone moieities so that the strong binding affinities of phenolic hydroxyl groups of anthrahydroquinone moiety in the cured polymers promotes adhesion on the metal surface [8].

2. THEORETICAL PART

2.1 General Pathway for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are typically synthesized using primary amines with formaldeyde and phenolic derivatives. Numerous types of benzoxazines can be obtained by varying amine and phenolic compounds. Substituton groups of these phenol and amines may offer additional polymerize sites which also influence the curing structure. On account of obtaining polymeric materials with desired properties by tailoring the benzoxazine monomer with different functionality and enormous number of monomers can be synthesized via utilizing appropriate chosen phenol and amine. In this part of the thesis synthesis of different benzoxazine monomers have been discussed [9] (Figure 2.1).

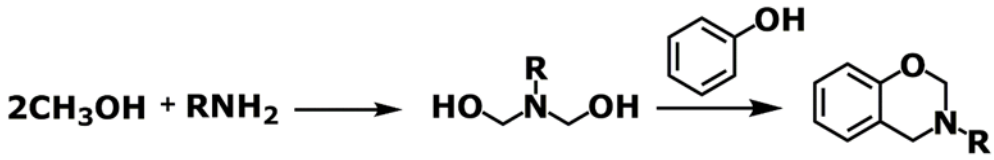


Figure 2.1 : Synthetic procedure for benzoxazine synthesis.

2.1.1 Mono functional benzoxazine monomers

Cope and Holly [8] were firsty reported the synthesis of well-defined benzoxazine monomers by condensation reaction of primary amines with formaldehyde and phenol. According to this procedure, the reaction carried out in a solvent with two steps. The following years, Burke found that the benzoxazine ring reacts preferably with the free ortho positions of a phenolic component and forms a Mannich bridge [7]. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the high temperature to form the oxazine ring. The preparation of 3,4-dihydro-1,3-2H-benzoxazine was proposed by Burke in a single step from p-substituted phenol, formaldehyde and primary amine

in a molar ratio of 1:2:1, respectively. The probable mechanism is demonstrated in Figure 2.2 [9].

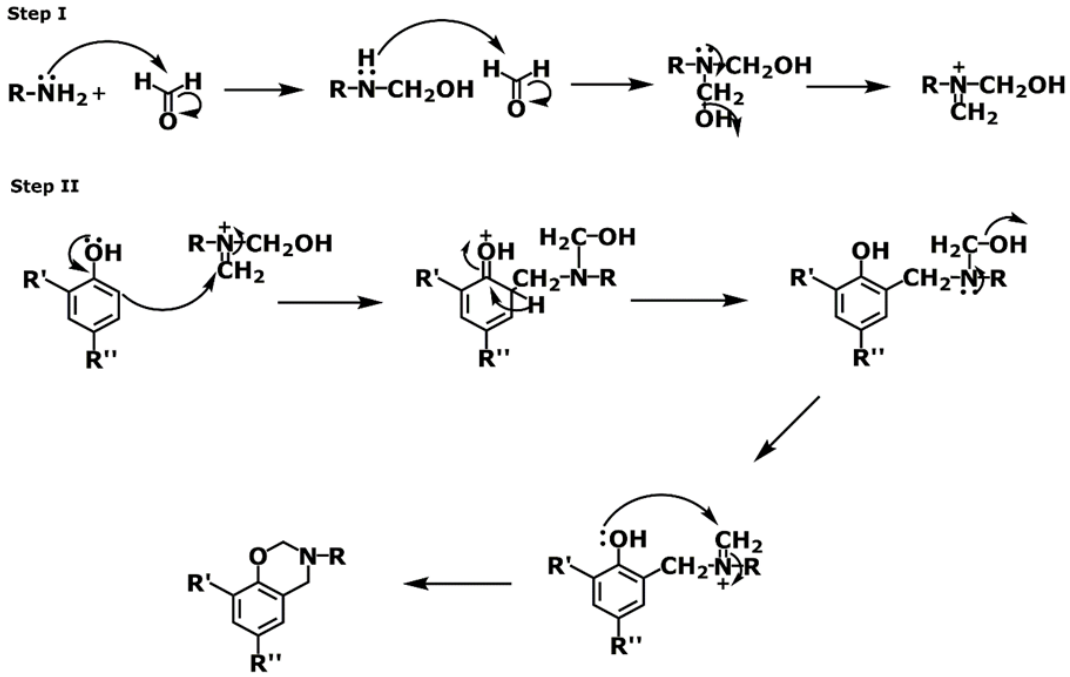


Figure 2.2 : Probable mechanism of benzoxazine ring formation

Alternatively, the mechanism of 3,4-dihydro-3,6-disubstituted-1,3-2H-benzoxazine formation was also showed in Figure 2.3. In the first step, *o*-alkylaminomethyl-*p*-substituted phenol is generated as intermediate by an equimolar reaction of every reactant. Then, the intermediate are converted to 1,3-benzoxazine via addition of formaldehyde in the existence of a basic catalyst [10].

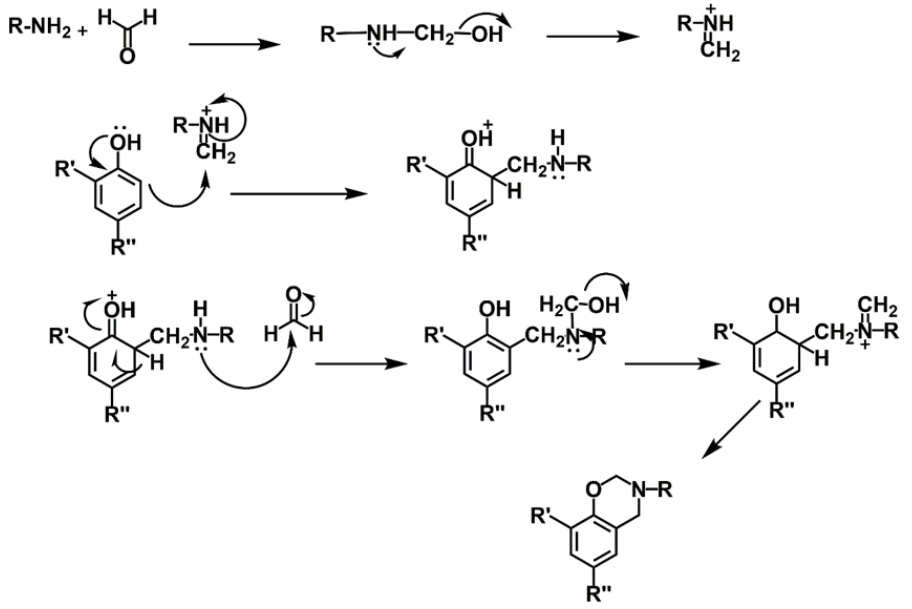


Figure 2.3 : Alternative benzoxazine ring formation mechanism.

It has been reported that for some benzoxazines, the ring opening occurs existence of compounds including active hydrogen (HY), for instance imides, indoles, carbazole, naphtol and aliphatic nitro compounds even phenol (which is also one of the reactants for the synthesis) and small oligomers generated as by products [11]. Mannich bridge formation owing to the ring opening of benzoxazine in acidic medium is illustrated in Figure 2.4.

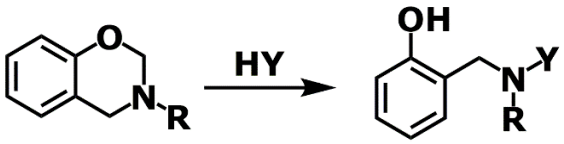


Figure 2.4 : Mannich bridge formation through ring opening of benzoxazine.

Substituent on the benzoxazine ring play critical role the stability of the ring. If there is more than one reactive ortho position in the initial product may lead to another aminoalkylation reaction. Ortho substituent having phenols increase the yield corresponding to the product [12].

Within using solvent for stynthesis, large amount of solvent is used and also reaction rate is slow, in some circumtances, the poor solubility of the precursors are the major drawbacks related with this method. Furthermore, using an organic solvent promote the cost of the products and causes enviromental problems. Moreover, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these limitations, solventless synthesis in the melt state was developed.

The reactants, i.e, aldehyde, amine and phenolic precursors are mixed together physically, heated to their melting temperature and then continued at a temperature sufficient to generate desired benzoxazine product. Formaldehyde is not used in this synthesis, because it evaporates easily and loses stoichiometry rapidly. Instead, paraformaldehyde is used for this procedure. Solventless synthetic method have been a good alternative to traditional synthetic method because of improved reaction times and fewer unwanted intermediates and by products [13].

2.1.2 Difunctional and multifunctional benzoxazine monomers

Only oligomeric structures with average molecular weight around 1000 Da generated via curing monofunctional benzoxazine with phenol. It was observed that, the thermal

dissociation of monomer competed with chain propagation reaction since high molecular weight structures were'nt obtainable so that materials could'nt be made from this pathway[14]. Ishida and coworkers [15, 16] developed an original method to solve the problem and obtain high molecular weight polymers. This strategy comprised a new class of difunctional or multifunctional benzoxazine monomers and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition.The precursor was formed by bisphenol A, formaldehyde and methylamine and the fundemantal component of the resulting products consisted of a monomer with difunctional benzoxazine ring at two end sides of bisphenol A. The remainder of the composition was a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as determined by NMR, FTIR and SEC.

It was proved that, the composition of the products is depend on the polarity of the solvent. This synthetic method includes a few simple steps and can easily provide different phenolic structures with wide design flexibility. Using aniline inreplacement of methylamine, a similar benzoxazine monomer was synthesized [17, 18] and it was named as B-a (Figure 2.6b) (bisphenol A and aniline) and oligomers were oligo B-a. Preparation procedure is demonstrated in Figure 2.5.

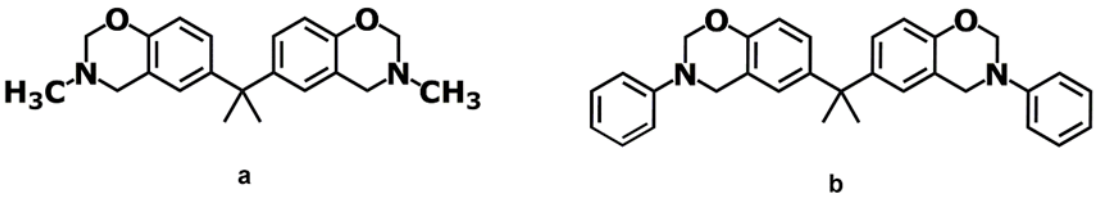
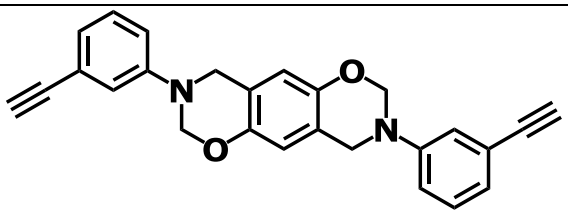
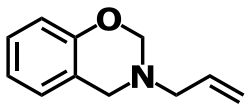
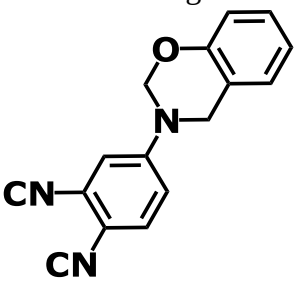
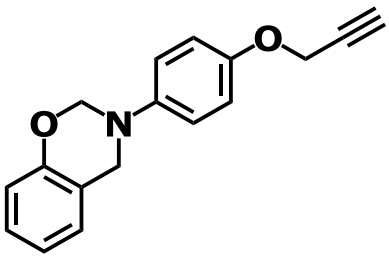
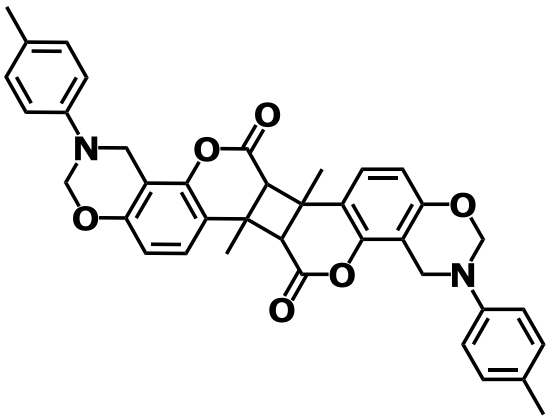
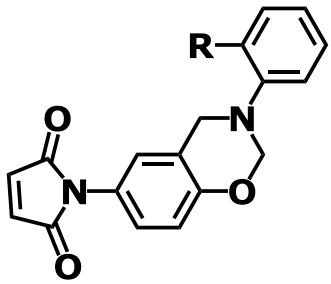
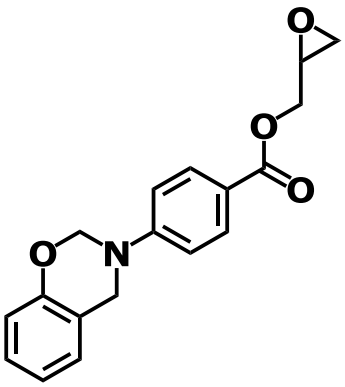
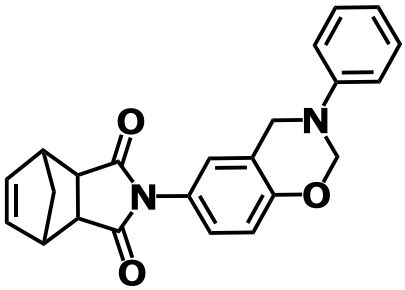


Figure 2.5 : Synthesis of typical functional benzoxazine monomers.

2.1.3 Synthesis of benzoxazine monomers with different functional groups

Pure benzoxazines have some limitations and drawbacks related to brittleness and high curing temperatures. To overcome this problems new strategies have been adopted like incorporation of benzoxazine in poymer chains and synthesis of benzoxazine based composites or alloys also synthesis of benzoxazine monomers with additional functionality. By taking advantage of design flexibility of benzoxazine monomers from judiciously chosen various type of starting materials, benzoxazines can be tailored for a wide range application fields [6, 14, 19-21]. Hence, a series of benzoxazine monomers containing different functional groups such as allyl, acetylene, propargyl ether, nitrile, maleimide, coumarin,epoxy were synthesized. (See Table 2.1.)

Table 2.1: Benzoxazine monomers with different functionalities

Benzoxazine Monomers	
 Acetylene-containing benzoxazine	 Allyl-containing benzoxazine
 Nitrile-containing benzoxazine	 Propargyl-ether- containing benzoxazine
 Coumarin-containing benzoxazine	 Maleimide-containing benzoxazine
 Epoxy-containing benzoxazine	 Norbornane-containing benzoxazine

2.1.3.1 Preparations of blends and composites

As stated previously, several approaches to overcome some of the shortcomings of polybenzoxazines, such as mechanical properties, high curing temperature and low process ability, have been proposed which include monomer modification, forming of polybenzoxazine blends and composites. The first method in terms of the modification of monomers has been examinated in the previous section. In this section, combination of polybenzoxazines with the other polymeric and inorganic materials will be discussed. Here some of the examples of blending materials with polybenzoxazines such as rubber [22-25] , polycarbonate [26, 27] , poly (ε-caprolactone) [28, 29] , polyurethane [30, 31] , epoxy resins [32, 33] , phosphorous containing compounds [21, 34] and clay [35, 36] .

2.1.3.2 Preparation of polymers with benzoxazine moieties

Blending materials with polybenzoxazines is a beneficial concept to enhance their properties. Moreover, preparing polymers containing benzoxazine moieties in their chains is another route. A macromonomer technique was applied for chemical linking of polybenzoxazines with other conventional polymers.The benzoxazine groups are introduced by initiation of a selected polymerization or synthesizing benzoxazines from amino or phenol functional prepolymers. In the previous case, the propagating species should be unreactive towards the benzoxazine ring and N and O hetero atoms. Benzoxazine functionalized poly(p-vinylphenol) (Figure 2.6a) [37] , poly (ε-caprolactone) (Figure 2.6b) [38] and poly (methyl methacrylate) (Figure 2.6c) [39] were presented.

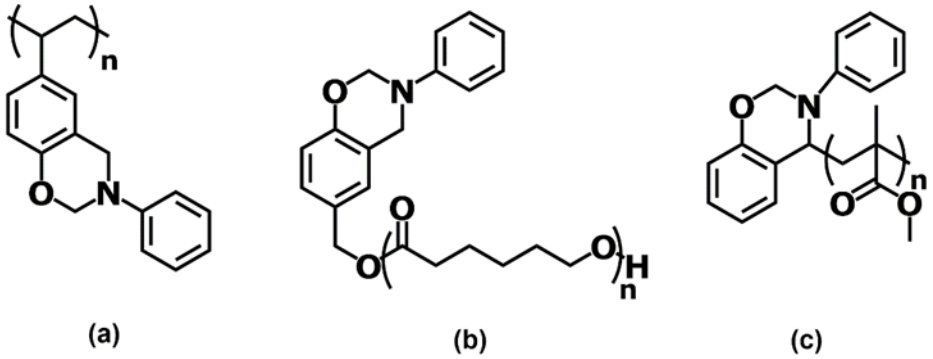


Figure 2.6 : Benzoxazine typical functional polymers.

2.1.4 Polymeric benzoxazine precursors

2.1.4.1 Main-chain precursors

As stated earlier, mono-functional benzoxazines lead to small oligomers upon polymerization and do not produce structurally strong, cross-linked polymers, unless they are combined with groups that polymerize in non-benzoxazine chemistry. These precursors are also brittle as a result of the low molecular weight of the network structure, and casting films from them is difficult on account of being powdery for most of them. New approaches were developed to overcome these limitations. One of the important ones is main-chain benzoxazine precursors strategy, which leads to more ductile cross-linked polybenzoxazines and improved thermal properties. Liu et al. [40] were the first to prepare main-chain type benzoxazine precursors using 4,4'-methylenebis(2,6-dimethylaniline), bisphenol-A, and formaldehyde, later Takeichi et al. [41] and Chernykh et al.[42] published detailed studies of the synthesis of high molecular weight MCBP through the polycondensation of diamines and bisphenols to produce an ABAB-type linear polymer with benzoxazine rings in the main chain (Figure 2.7).

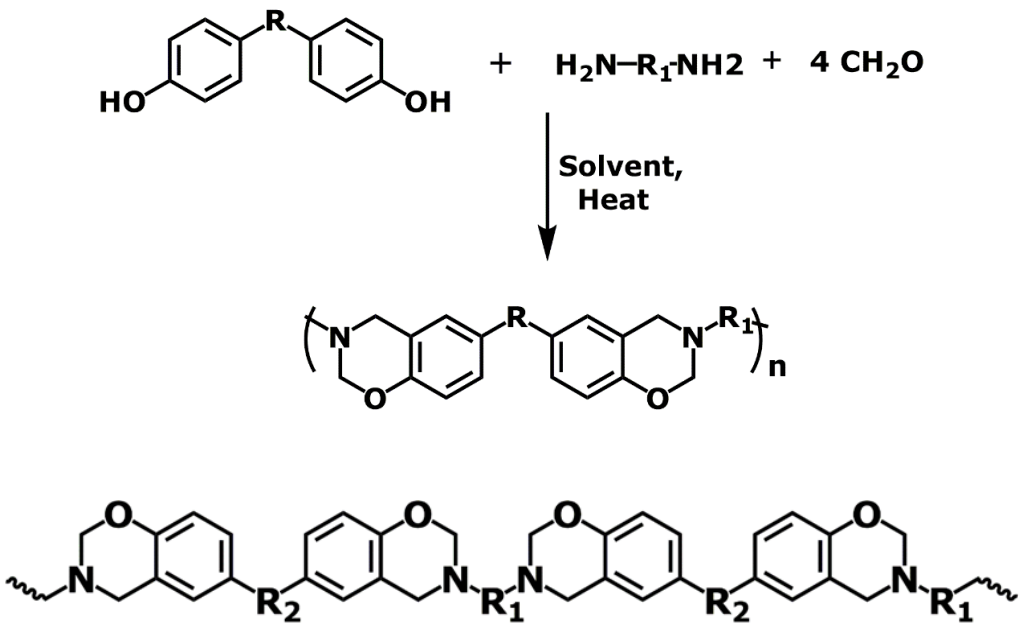


Figure 2.7 : ABAB-type linear polymer with benzoxazine rings in the main chain.

2.1.4.2 Side-chain precursors

Side chain polymer strategy is a way to incorporate benzoxazine groups into a polymer backbone to achieve a highly dense network. Curing of many repeating benzoxazine units resulted in crosslinking of polymer chains. In the course of time, material scientist have developed various methods to obtain side chain polymers. Some of them are postpolymer modification like click chemistry or polymerizing suitable molecules (Figure 2.8).

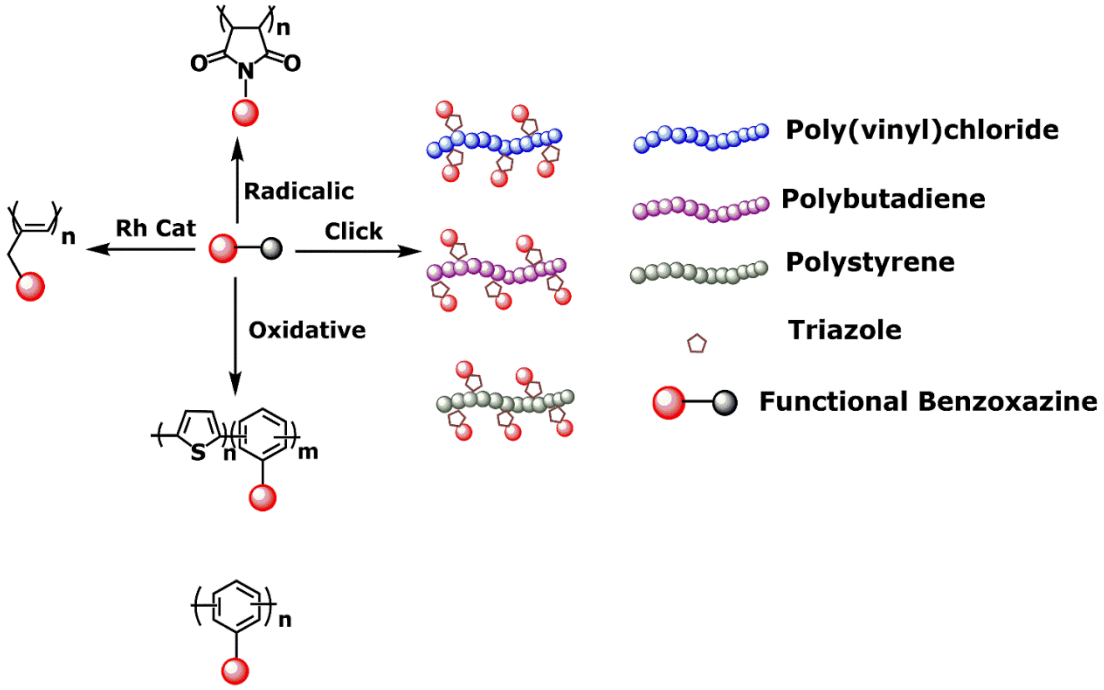


Figure 2.8 : Side chain polymer strategy to incorporate benzoxazine groups into a polymer.

2.2 Ring Opening Polymerization

To figure out the polymerization reaction mechanism of benzoxazines, an understanding of the chemical structure of its oxazine ring is essential. A single crystal X-ray crystallographic study determine that mono-oxazine ring containing benzoxazine is a distorted semi-chair structure, with the nitrogen and carbon, between oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six-membered ring to undergo ring-opening reaction under specific conditions. Besides, due to their high basicity (by Lewis definition) both oxygen and nitrogen of the oxazine ring can act as potential cationic polymerization initiation site

and makes the ring very likely to open via a cationic mechanism [43, 44]. The electron charge calculation after energy minimization predicts that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270).

2.2.1 Thermal polymerization of benzoxazines

The ring-opening initiation of benzoxazine has been suggested that brings about a carbocation and an iminium ion which exist in equilibrium. This carbocation attacks to the benzene ring as an electrofile preferring the free ortho and para position of the phenol group. The stability of the iminium ion notably effects the propagation rate by reason of carbocation is responsible for propagation step (Figure 2.9). There are several attempts proposing different mechanisms of thermal polymerization of benzoxazines [44].

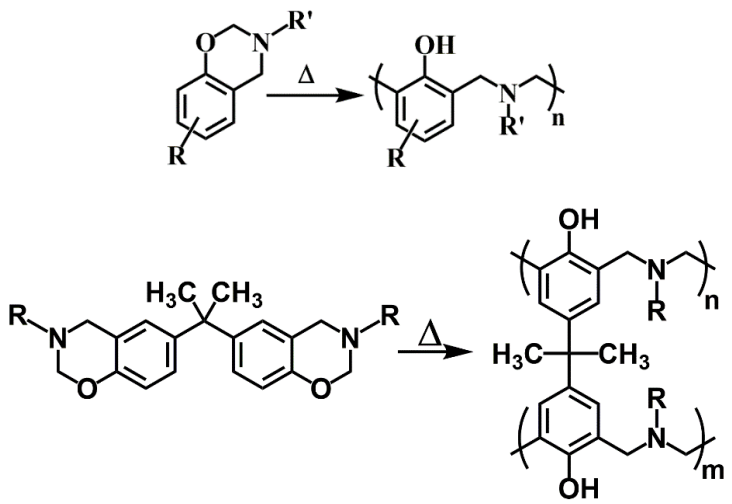


Figure 2.9 : Thermally induced ring opening polymerization of benzoxazine monomers.

2.3 Electrochemical Oxidation-Reduction Reaction

An electrochemical reaction occurs via transferring electrons between a molecule of the substrate and the electrode. Electrons are always transferred singly and the substrate is converted to an intermediate with an unpaired electron. Transformation of this reactive immediate to the final product includes a sequence of bond forming or bond cleaving reactions and frequently further single electron transfer steps. The complete electrochemical reaction vessel is composed of an anode and a cathode. Only one of these electrodes, the working electrode, is involved with the chemical reaction

of interest, oxidation at the anode or reduction at the cathode. The second electrode is the counter electrode and usually some simple inorganic reaction takes place here, for instance hydrogen evolution if this is a cathode or oxygen evolution if this is an anode. Ionised salt solution fills the space between the anode and cathode and charge passes by emigration of ions through the solution.

Electrochemical reactions include a solvent and electrolyte system having as small resistance as possible between the anode and cathode. Alcohol–water and dioxan water mixtures can be used as protic solvents and and the electrolyte may be any soluble salt, an acid or a base. Protons are depleted at the cathode and generated at the anode therefore a buffer wil be needed to maintain a permanent pH throughout the reaction. Also, aprotic solvents such as acetonitrile and dimethylformamide used for numerous reactions [45]. In aprotic solvents, the supporting electrolyte is usually a tetra-alkylammonium fluoroborate or perchlorate. Perchlorate salts are dissuasive for usage due to the possibility that traces of perchlorate in the final product may cause an explosion.

2.3.1 Quinone /hydroquinone redox reaction

The oxidation of hydroquinone (or l,4 dihydroxybenzene) and the reduction of 1,4-benzoquinone are well known redox reactions in organic electrochemistry [46].

Among various types of quinone involving in redox reactions, hydroquinone/ quinone is one of the most substantial; indeed hydroquinone is a phenol molecule with two hydroxyl group (—OH) bonded directly to an aromatic hydrocarbon group, in para positions, Figure 2.10, and redox reactions of phenols have been investigated for a long time and numerous experiments have been reported [47].

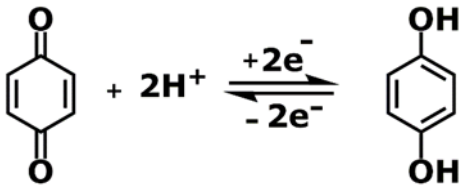


Figure 2.10: Hydroquinone quinone reaction

The reduction route of the quinone/hydroquinone is very complicated and depends on the media. In dry, neutral, aprotic media hydroquinone/quinone molecules shows two cathodic chemically reversible waves which correspond to the formation of Q^{*-} and Q^{2-} respectively; instead in protic media such as water, specific mechanistic issues

arise in quinone redox reactions. Water may act as proton acceptor along with OH^- and the basic components of any buffers used. Water may also behave as a proton donor along with $H_3O^+$and acidic components of any buffers used. In the case of the quinone/hydroquinone system, there are two electron and two proton transfer sequence, and the microscopic mechanistic pathway has been investigated by electrochemical methods long ago [48].

2.4 Adhesion Property of Anthraquinones by External Electrochemical Stimulation

Quinone-hydroquinone couples are the typical examples of redox systems and the research on the electrochemical behavior of these compounds has been rapidly expanding in recent years [49].

It has also been proved that metal ions interact with hydroquinones with σ-bonding to the oxygen atoms and/or through π-bonding to the carbocyclic ring. Based on these interactions, hydroxyl and carboxylic acid groups increase the adhesion of molecules to metals. With the acknowledgment that quinone/hydroquinone derivatives play very important roles in redox systems, quinones and their derivatives appear to be promising candidates as their adhesion behavior on various metal surfaces [8].

Various compounds having anthraquinone functionality can undergo to interact with metal compounds to result in adhesion of the anthraquinone compounds to the metal surface. This adhesion process is obtained because of the interaction of the phenolic groups within anthrahydroquinone with metal atoms. Because of the cyclic reduction-oxidation behavior of anthraquinone compounds, the adhesion of anthraquinone to metal surface can be manipulated by external stimulation

Oxidation of hydroquinone to quinone causes in disappearance of OH groups (in anthraquinone) to ketones, which results in dismantling of the coated surface, as ketone groups are incapable of establishment of adhesion to metal surfaces. The oxidation process can be realized, for instance, by applying electrochemical method as the external stimulation.

In the case of polybenzoxazines having anthraquinone groups, it is expected that , the strong binding affinities of phenolic hydroxyl groups of anthydroquinone moiety in the cured polymers would improve adhesion on the metal surface. The generality of

this electrochemical method is demonstrated by initial results on platinum electrodes as well as steel plates.

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Solvents

Solvents we used are given below:

Chloroform ($CHCl_3$,VWR, 99,2%): Chloroform was used as received.

Diethyl ether (J.T. Baker): Diethyl ether was used as received.

Ethanol (Merck, 99,9%): Ethanol was used as received.

1,4 dioxane (Riedel-deHaen,99,5%): 1,4 dioxane was used as received.

Toluene (AnalaR Normapur): Toluene was used as received.

3.1.2 Chemicals

Chemicals we used are given below:

Bisphenol A(2,2-bis(4-hydroxyphenyl)propane, Acros, 97 %): It was used as received.

Paraformaldehyde (Aldrich, 95,0- 100,5 %):It was used as received.

Benzylamine (Merck): Benzylamine was used as received.

Aniline: Aniline was distilled before used.

Furfurylamine (Fluka, ≥ 99%): Furfurylamine was used as received.

1,5 dihyroxyanthraquinone tech. (Alfa Aesar, 90%): It was used as received.

Sodyum hydroxide (Acros, >97%): It was used as received.

Anhydrous magnesium sulphate (Alfa Aesar, 99.5%): It was used as received.

Tetrabutylammonium hexafluorophosphate (Sigma Aldrich, ≥ 99%): It was used as received.

Acetonitrile (Sigma Aldrich, 98 %): Acetonitrile was used as received.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR spectra of all samples were recorded in chloroform, using a Agilent VNMRS 500 MHz instrument.

^{13}C CP-MAS NMR experiments were acquired on a Bruker DMX 300WB (7 T) spectrometer using a 4 mm zirconia rotors spinning at the MAS frequency of ν_{MAS} = 11 kHz. Cross polarization transfers were performed using adiabatic tangential ramps, the contact time was t_{CP} = 3 ms, recycle delay was 3 s and Spinal64 decoupling was applied during signal acquisition. The FIDs were subjected to an exponential multiplication (EM) function with a line broadening value of 40 Hz prior to Fourier transform.

3.2.2 Infrared spectrophotometer (FT-IR)

The FTIR spectra are recorded at Perkin Elmer Spectrum One with an ATR accessory (ZnSe, Pick Miracle Accessory) and cadmium telluride (MCT) detector .

3.2.3 Differential scanning calorimeter (DSC)

DSC measurements were performed on Perkin-Elmer Diamond DSC with a heating rate of 15°C min^{-1} under nitrogen flow.

3.2.4 Thermal gravimetric analysis (TGA)

TGA measurements were performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10°C min^{-1} under nitrogen flow (200 mL min^{-}).

3.2.5 Cyclic voltammetry

Single scan cyclic voltammogram of monomers and polymers were recorded in 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$)/ acetonitrile (ACN) solution. For this experiment, Pt foil electrode was used as the working electrode. Monomers were dissolved in $CHCl_3$ and drop casted on Pt electrode. Resulting CVs were recorded in $Bu_4N^+PF_6^-$ /ACN electrolyte system. Then, to explore the redox behavior of polymers, freshly prepared Pt electrodes stored in the oven for 3 hours at 180 ºC. Single scan CVs of resulting polymers were also investigated with the same conditions used for the monomers.

3.3 Synthesis

3.3.1 Synthesis of B-Ant-A based bisbenzoxazine monomer

1,5 Dihydroxyanthraquinone (8,32 mmol, 2g), aniline (0.01 mol ,5,5g), paraformaldehyde (0.03 mol,1 g) were dissolved in a mixture of ethanol-toluene (1:2, v/v, 150 ml) in a 250 ml round bottom flask and refluxed overnight. The reaction mixture was filtered off, the solvent was evaporated under vacuum. Resulting product was dissolved in diethylether and washed with 0,1 N NaOH aqueous solution and distilled water, for many times. Then the solution was dried with anhydrous magnesium sulfate,the solvent were removed by evaporation under vacuum.Yield (% 44).

3.3.2 Synthesis of B-Ant-Bn based bisbenzoxazine monomer

1,5 Dihydroxy anthraquinone (8,32 mmol, l,2 g) , benzylamine (0,016 mol,1815 ul) , paraformaldehyde (0.03 mol, 0,99g) and 1,4 dioxane (150 ml) added to 250 ml round bottom flask and refluxed overnight. The reaction mixture was filtered off and 1,4 dioxane was evaporated under vacuum. Resulting product was dissolved in diethylether and extracted with 0,1 N NaOH aqueous solution and distilled water, for many times. Then the solution was dried with anhydrous magnesium sulfate, filtered, solvents were removed by evaporation under vacuum.Yield (%66).

3.3.3 Synthesis of B-Ant-F based bisbenzoxazine monomer

In a 250 ml round bottomed flask 1,5 dihydroxy anthraquinone ($8.32x10^{-3}$mol, 2.01g), furfurylamine (0.015 mol, 1482 ul), paraformaldehyde (0.03mol, 0.99g) and 1,4 dioxane (150 ml) were added and heated to 110^{o}C with refluxing for overnight. After cooling to room temperature, the reaction mixture was filtered off and 1,4 dioxane was evaporated under reduced pressure. Resulting product was dissolved in diethylether and extracted with 0,1 N NaOH aqueous solution and distilled water for many times.Then the organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum.Yield (% 58)

4. RESULTS AND DISCUSSION

As stated previously, functional benzoxazine monomers with complex structures can easily be prepared by using appropriate phenol or amine in the modified Mannich reaction. Thus, the desired antraquinone-benzoxazine monomers were readily obtained from 1,5-dihydroxyanthraquionone, primary amines and formaldehyde. (Figure 4.1).

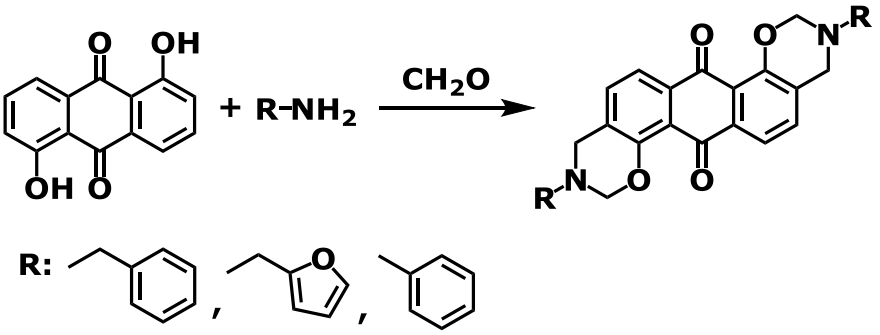


Figure 4.1: Synthesis of anthraquinone based bisbenzoxazines.

The basis of polymerization of benzoxazines relies on the benzoxazine ring structure having distorted semi–chair conformation. Therewith, the formed ring strain from this molecular structure assists six–membered ring to undergo ring–opening reaction under thermal conditions with a mechanism through two main pathways. The first step is the heterolytic cleavage of the C–O bond of the oxazine yielding a carbocation. Subsequent attack of the corresponding carbocation to either the *ortho* or *para* position of the neighbor aromatic ring, which can be considered as a kind of Friedel–Crafts reaction. Thus, cross-linked structures can easily be obtained even using mono-functional benzoxazines with free *ortho* and *para* positions on the phenolic structure. Due to the nature of the reaction mechanism, aromatic ketonic species can survive under this conditions and similarly quiononic structure could be preserved. And the FT-IR spectra of cured monomers reveals the ketonic carbonyl at a range between 1670-1685 cm^{-1}.

The structure of the monomers were confirmed by spectral analysis. As can be seen from Figures 4.2–4.4, the ^{1}H-NMR spectra of the monomers exhibit the specific

signals of benzoxazine ring. Notably, the two broad signals in the range of 4.9 and 3.7 ppm corresponding to –CH_2 protons of benzoxazine rings are revealed.

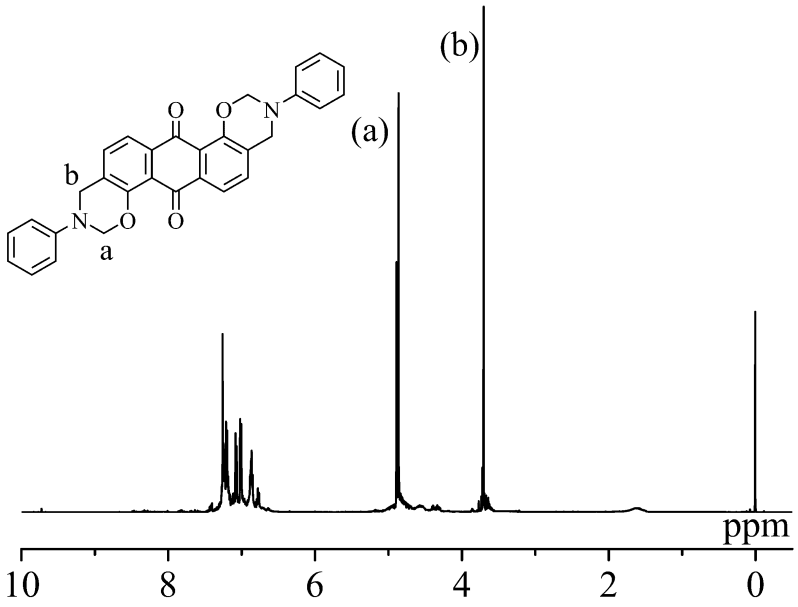


Figure 4.2: ^{1}H NMR spectrum of B-Ant-A

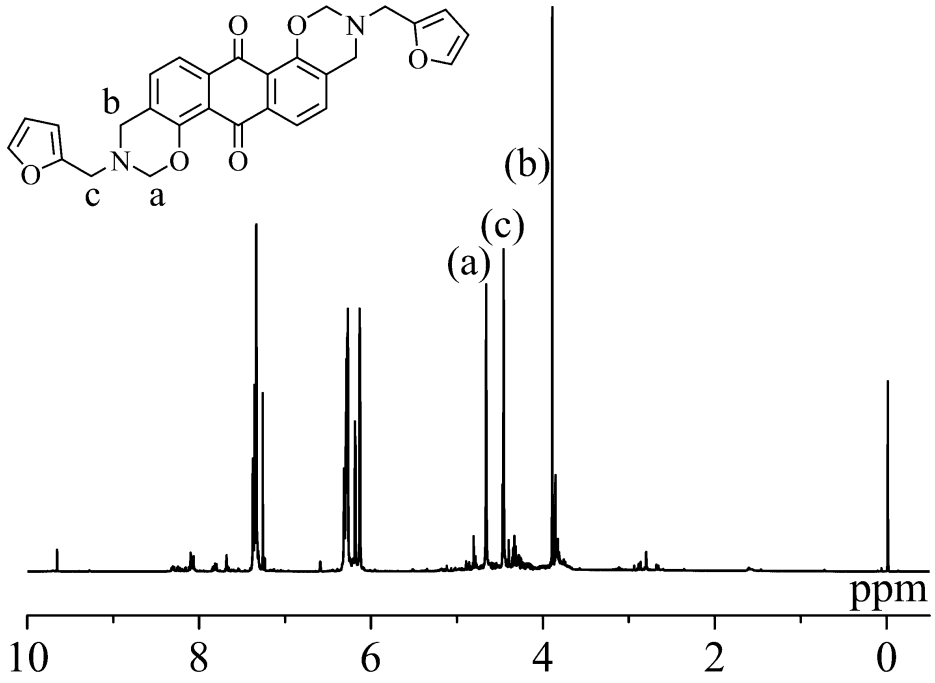


Figure 4.3: ^{1}H NMR spectrum of B-Ant-F.

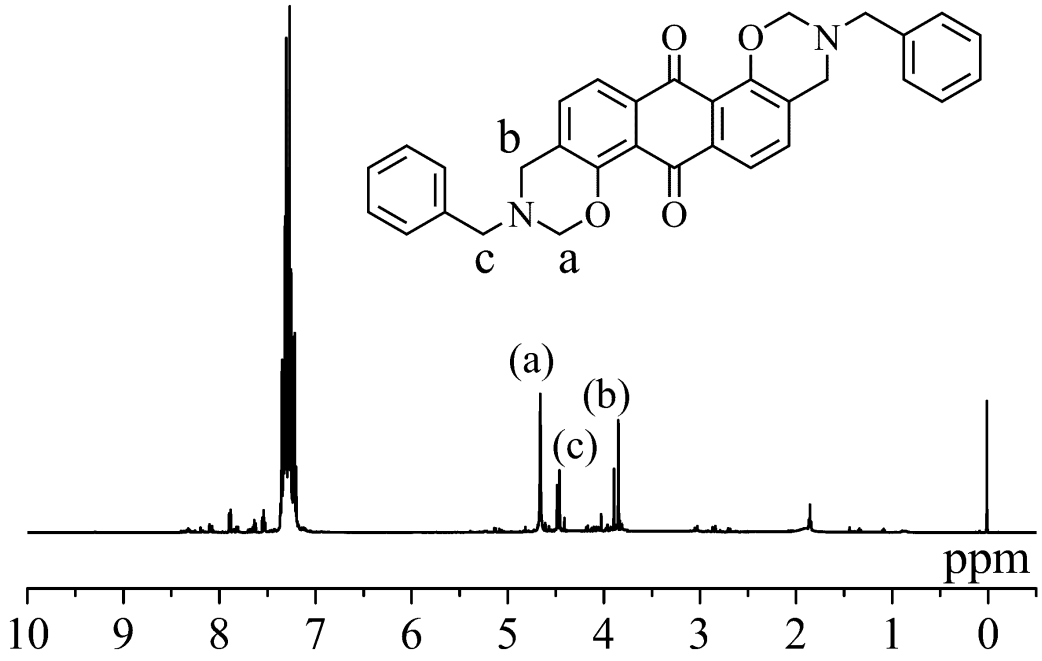


Figure 4.4 : ^{1}H NMR spectrum of B-Ant-Bn.

In Figure 4.5, the important bands of infra–red absorptions of benzoxazines observed at 932 and 1496 cm^{-1} can be attributed to the tri-substituted benzene ring and the peak at 1229 cm^{-1} is assigned to the asymmetric stretching of C–O–C group of oxazine ring.

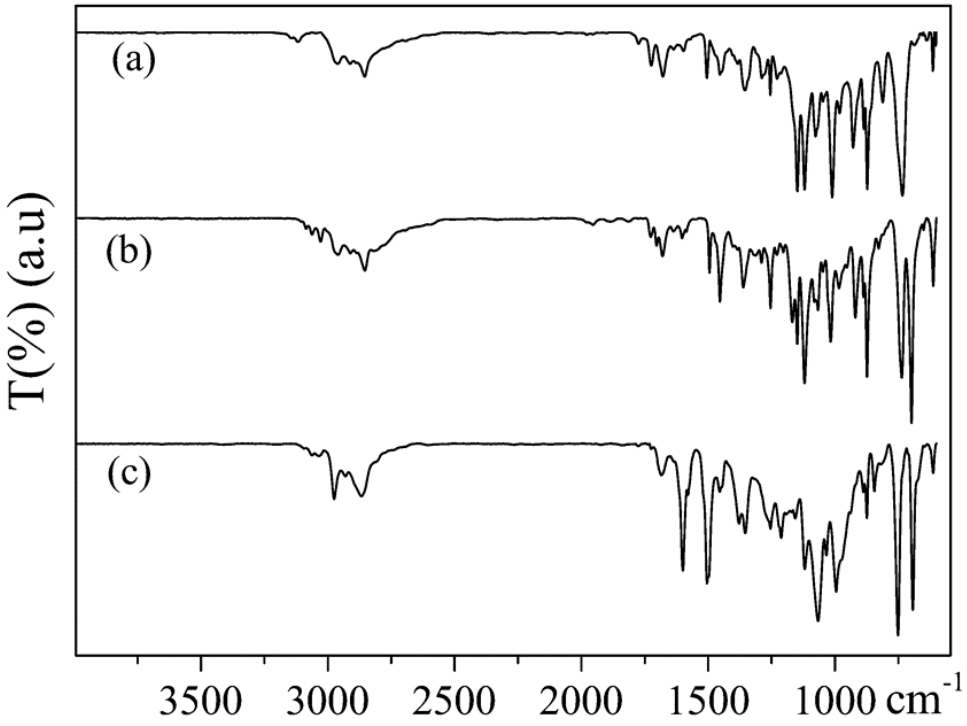


Figure 4.5: FT-IR spectra of B-Ant-F (a), B-Ant-Bn (b), B-Ant-A (c)

A detailed view of region below 1700 $cm^{-1}$of Figure 4.5 is demonstrated in Figure 4.6.

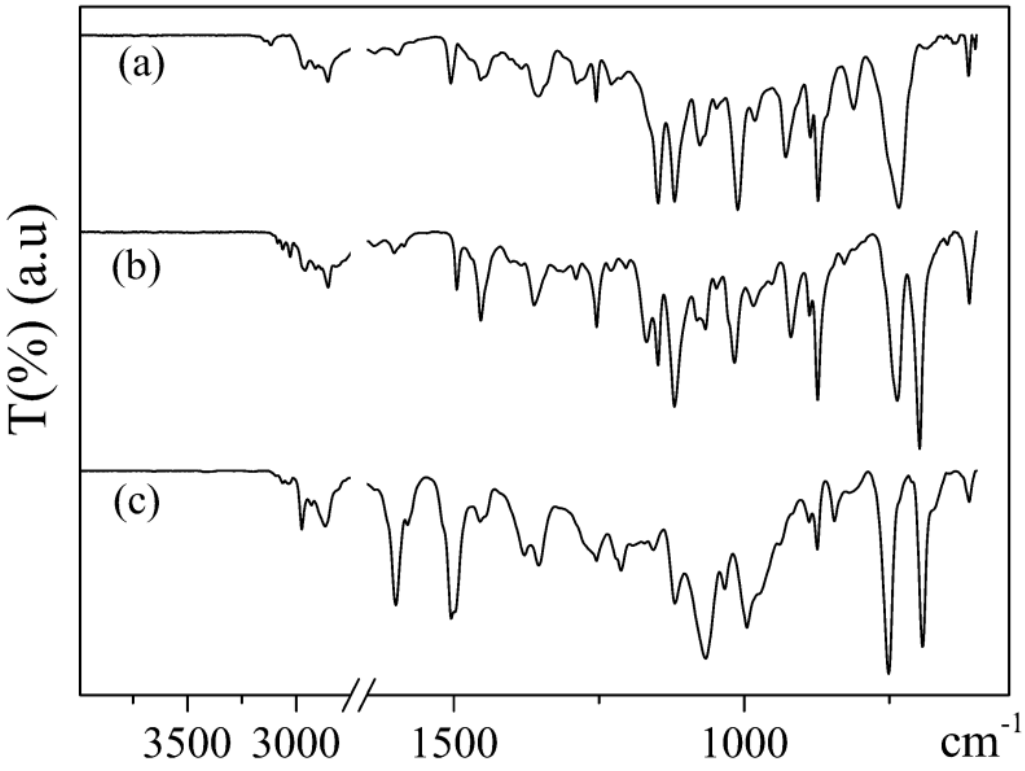


Figure 4.6: FT-IR spectra of B-Ant-F (a), B-Ant-Bn (b), B-Ant-A (c).

It is well known that 1,3–benzoxazines and related polymeric precursors can be cured by thermally–activated ring–opening polymerization and the exothermic process can be monitored using differential scanning calorimetry (DSC). The curing maximum vary from 160 to 250 °C, depending on the functionalities present on the benzoxazines or related polymeric precursors. In some cases, even curing temperatures below 160 °C was also reported. Figure 4.7. shows the overlaid DSC profiles of anthraquinone-benzoxazines. It is clear that the monomers are curable and the curing temperature vary between 180–230 °C. In detail, an exotherm belonging to B-Ant-A is detected having an onset of polymerization reaction at 221 °C with a maximum at 227 °C. On the other hand, the exotherm of B-Ant-Bn has a maximum at 195 °C; also, B-Ant-F shows an exothermic peak starting from 170 °C and reaching its maximum at 181 °C. B-Ant-F and B-Ant-Bn monomers exhibited an endotherm right after the end-set temperatures showing that some volatile compounds are formed or sublimation occured at that temperature. However, benzoxazine coated Pt electrodes were treated

at 180 ºC, which is even below the maximum cure temperature. Thus, possible side product formation during thermal treatment can be discarded. (See Table 4.1)

Table 4.1. DSC characteristics of antraquinone monomers

Benzoxazine	Maximum Curing Temperature (°C)	On-set (°C)	End-set (°C)	Curing ΔH (J/g)
B-Ant-A	229	221	234	-118
B-Ant-Bn	196	170	230	-111
B-Ant-F	181	170	202	-107

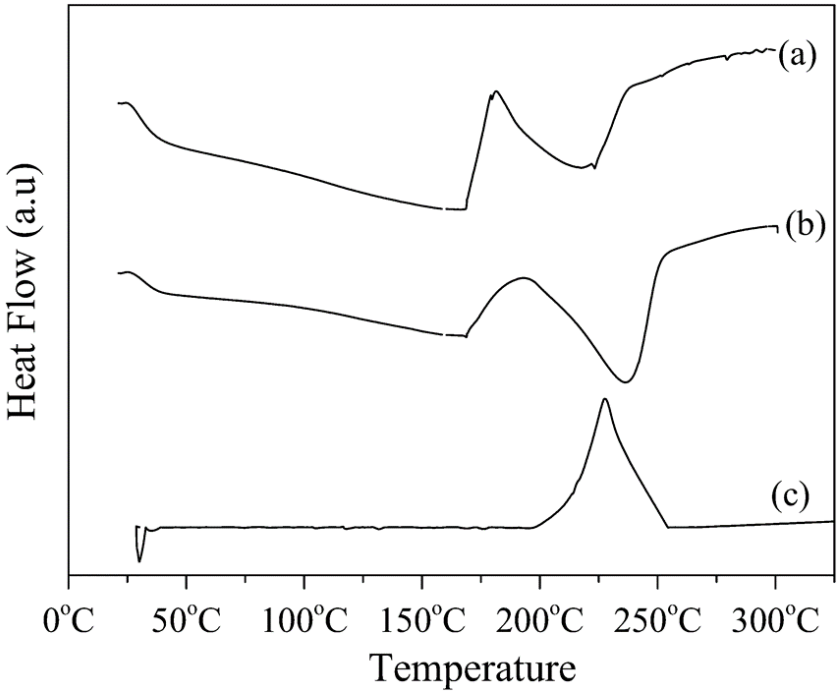


Figure 4.7: DSC thermograms of B-Ant-F (a), B-Ant-Bn (b), B-Ant-A (c).

The polymerization of benzoxazines occurs in response to the benzoxazine ring structure having distorted semi–chair conformation. The ring strain created from this molecular structure assists six–membered ring to undergo ring–opening reaction under thermal conditions with a mechanism through two main pathways. The first step is the heterolytic cleavage of the C–O bond of the oxazine yielding a carbocation. Subsequent attack of the corresponding carbocation to either the *ortho* or *para* position of the neighbor aromatic ring, which can be considered as a kind of Friedel–Crafts reaction. Thus, cross-linked structures can easily be obtained even using mono-functional benzoxazines with free *ortho* and *para* positions on the phenolic structure. Due to the nature of the reaction mechanism, if the benzoxazine monomer contain

aromatic ketonic moieties in the structure, these groups can survive under curing condition. Indeed, the FT-IR spectra of cured monomers reveals the ketonic carbonyl in the range between 1670-1685 cm^{-1} indicating the preservation of the quiononic structure (Figure 4.8, 4.9).

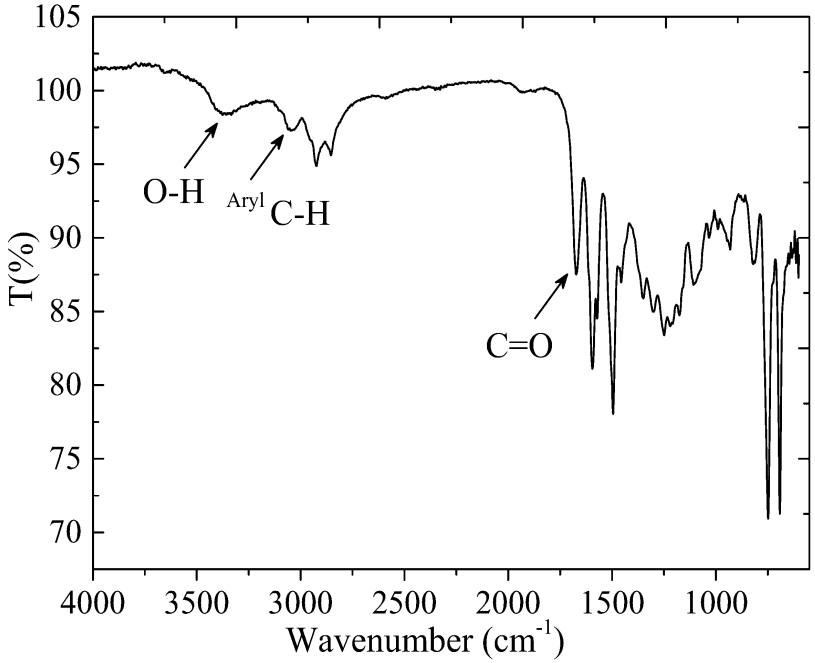


Figure 4.8: FT-IR spectrum of cured B-Ant-A.

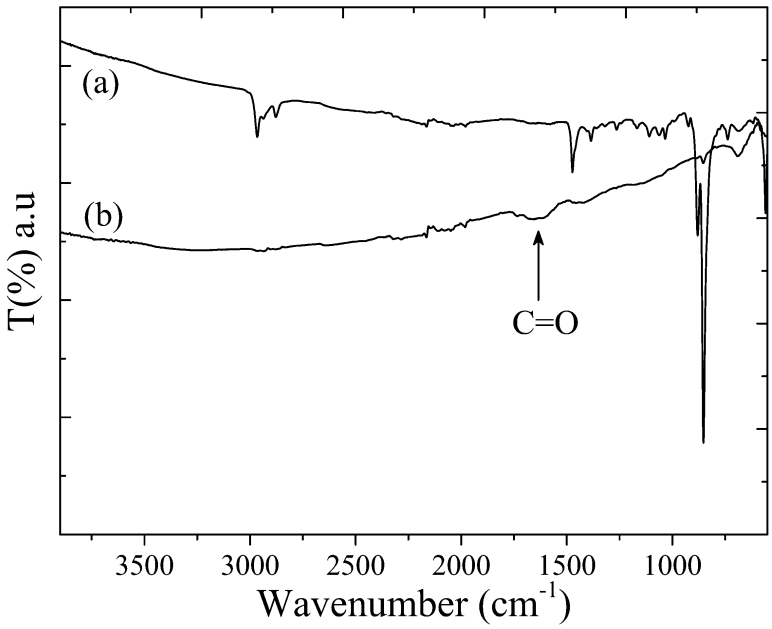


Figure 4.9: FT-IR spectra of electrochemically oxidized PB-Ant-A (a) and pristine PB-Ant-A (b).

Moreover, the progress of the curing reaction was monitored by IR and the each cure stage, from 120 to 210 °C, is shown in Figure 4.10.

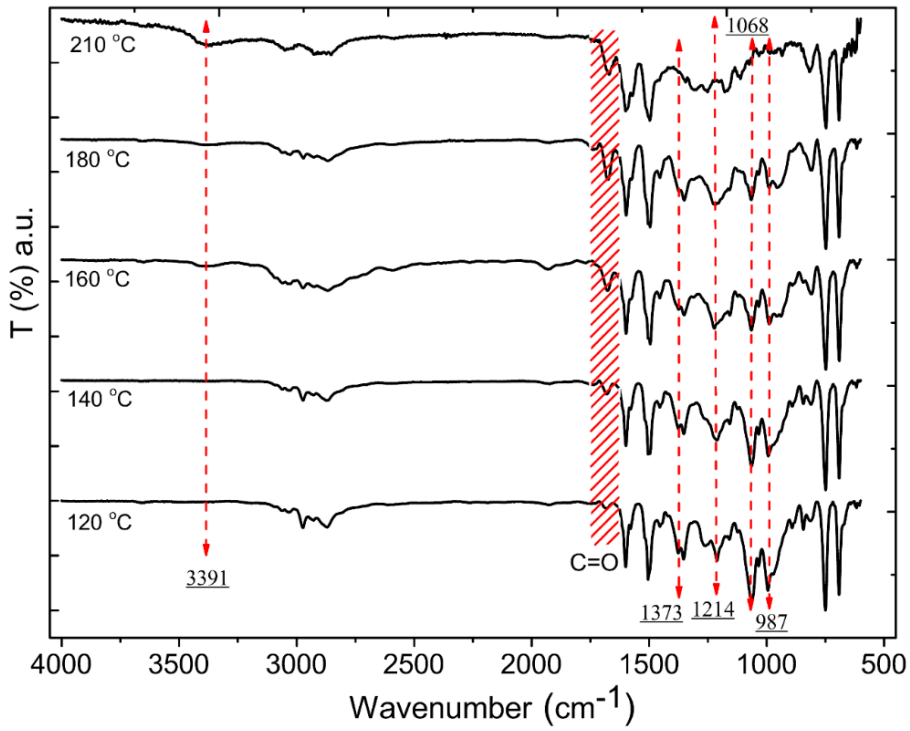


Figure 4.10 : FT-IR spectra of B-Ant-A at different temperatures.

Expectedly, the bands corresponding to the oxazine and substituted benzene rings at 1373, 1214, 1068 and 987 cm^{-1} decrease and finally dissapear with increasing temperature. Ultimately, polybenzoxazine resins exhibiting a redox capability through hydroquinone-quinone transformation can readily be obtained by thermally activated curing of the corresponding monomer (Figure 4.11).

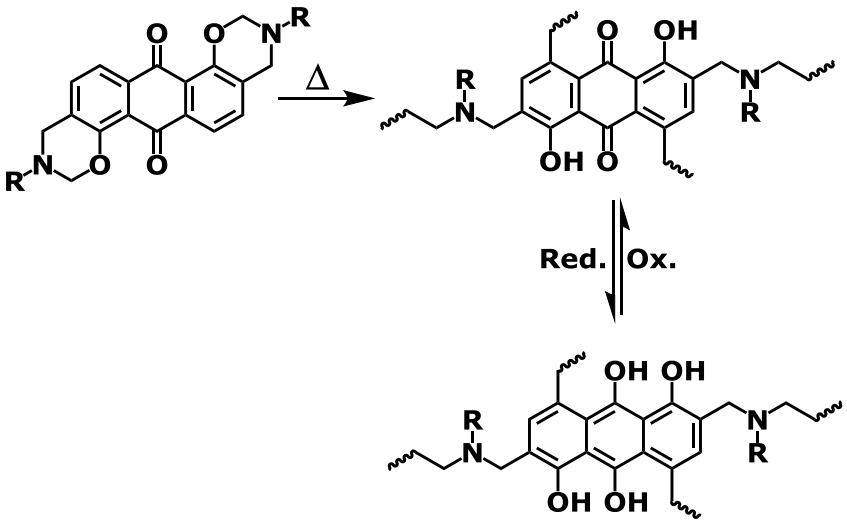


Figure 4.11: Thermally induced ring-opening polymerization of anthraquinone-benzoxazines and subsequent redox process.

In order to prove that the ring-opened materials are truly polybenzoxazines and discard possible thermal degradation during the curing process, solid state NMR was conducted (Figure 4.12).

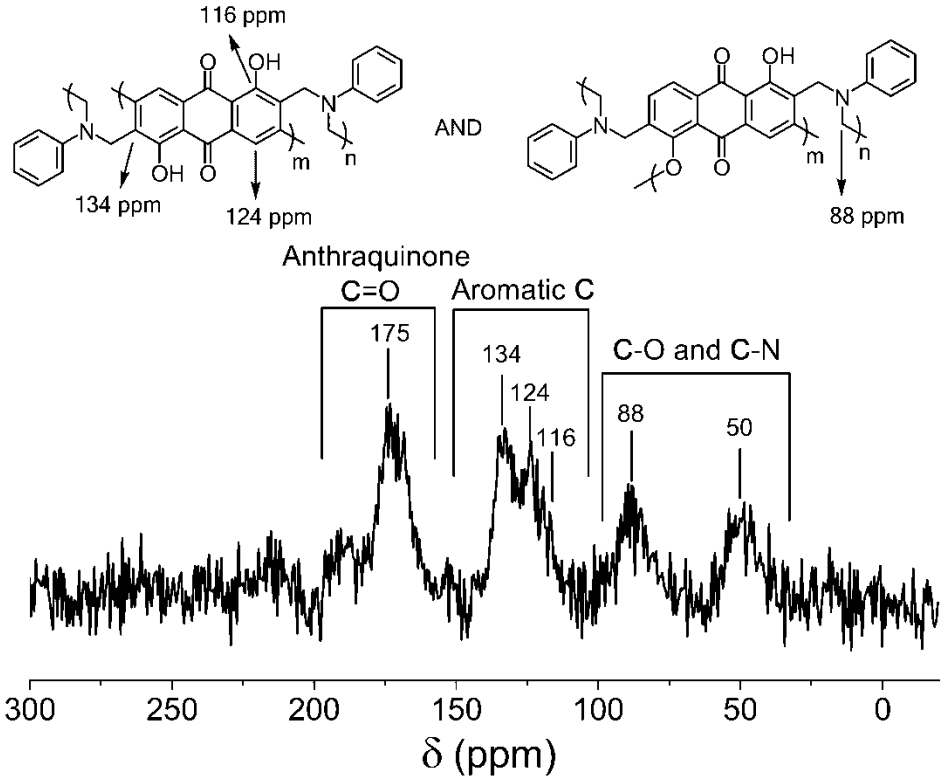


Figure 4.12: ^{13}C NMR of PB-Ant-A

According to the NMR results, two types of polybenzoxazine structures are present in the final product. (Figure 4.13).

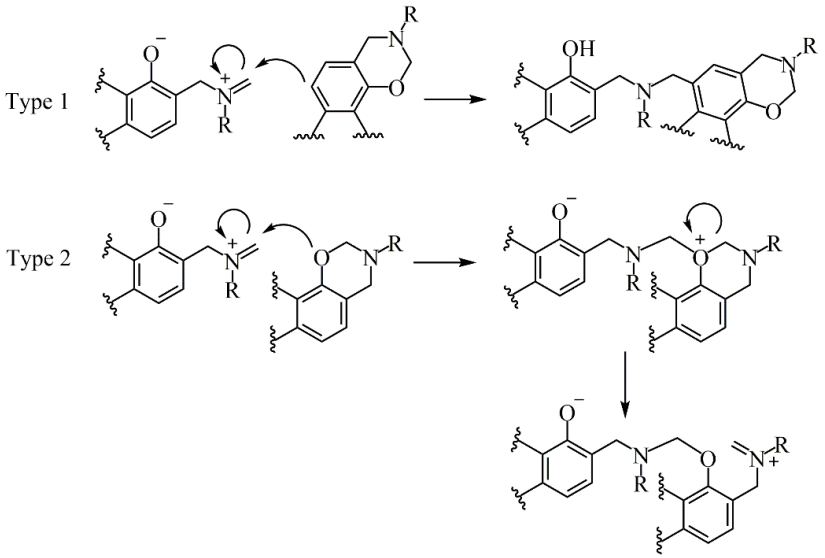


Figure 4.13: Plausible mechanism for polymerization of benzoxazine monomer producing two different types of polybenzoxazine

The first structure has free phenolic hydroxyl groups as a result of Friedel-Crafts reaction. The second phenoxy ether type structure is formed by the attack of imine intermediate to the phenolic oxygen. Similar reactions were previously reported by Wang et. al.[44, 50] briefly illustrates the mechanism of the formation of the two types of the polymers

The electroactivity of the monomers and resulting polymers was investigated by cyclic voltammetry. As illustrated in Figure 4.14, while aniline, benzyl and furfuryl based benzoxazines have oxidation peaks at around 1.5 V, all peaks were irreversible and all oxidations dissappear in the CV s of polymers. While the reduction behaviors of monomers compared to polymers (Figure 4.15), in the negative side there is a significant change in the reduction peaks from -0.5 V to -1 V.

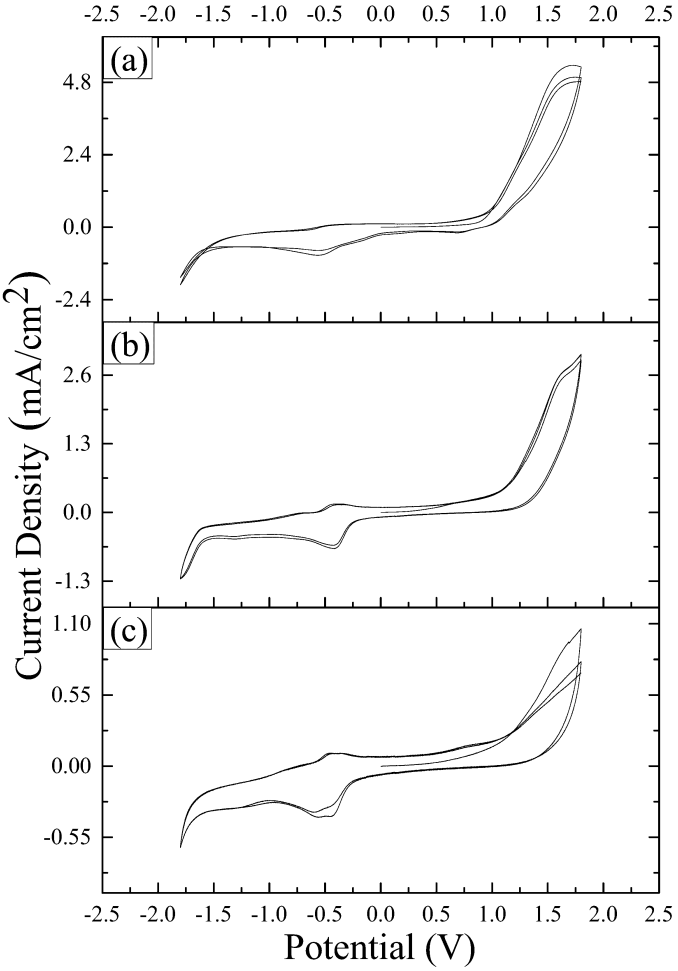


Figure 4.14: Single scan cyclic voltammogram of monomers (B-Ant-A (a), B-Ant-Bn (b), and B-Ant-F (c) based benzoxazines) in 0.1 M Tetrabutylammo-onium Hexafluorophosphate($NH_4^+PF_6^-$)/Acetonitrile (ACN) solution at a scan rate of 100 mV/s.

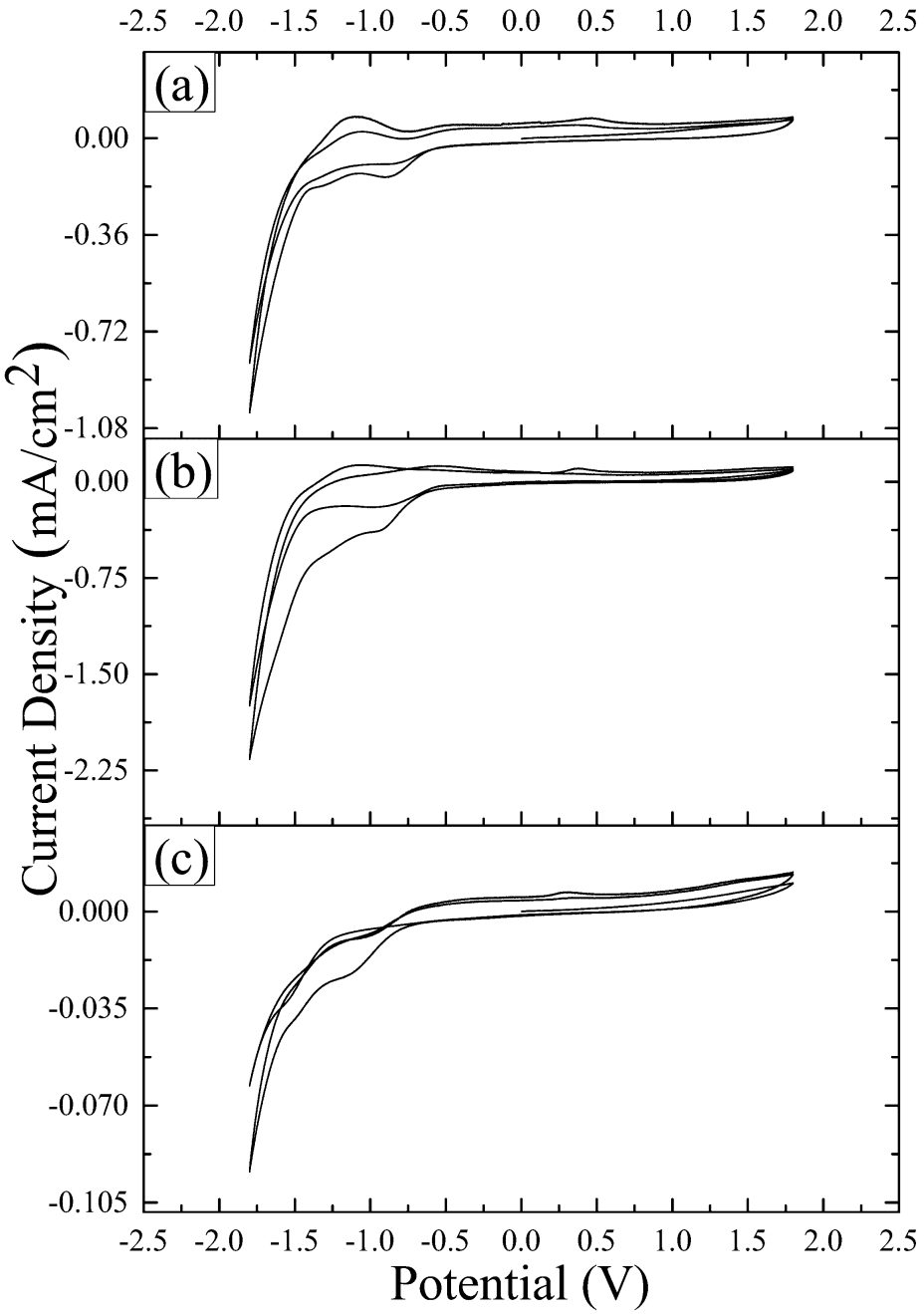


Figure 4.15: Single scan cyclic voltammogram of polymers PB-Ant-A (a), PB-Ant-Bn (b), and PB-Ant-F (c) based polybenzoxazines) in 0.1 M ($NH_4^+PF_6^-$)/ ACN solution at a scan rate of 100 mV/s.

Quinone-hydroquinone transformation generates a cycle between tetrahydroxy and dihydroxy aromatic structures. It is well known that, phenolic hydroxyl groups promote the adhesion of molecules to metals. Using quinone-hydroquinone cycle generates two different adhesion strength since the number of phenolic hydroxyls doubles in reduced form and this structure has high adhesion strentght on steel surfaces. The oxidized form of the polybenzoxazine resins showed a drastic decrease

in adhesion and simply dismantled from the surface of the steel specimen. The adhesion values, the photographs and an illustration of dismantling of the polybenzoxazine resins are presented in Figure 4.16, Table 4.2 and Figure 4.17, respectively.

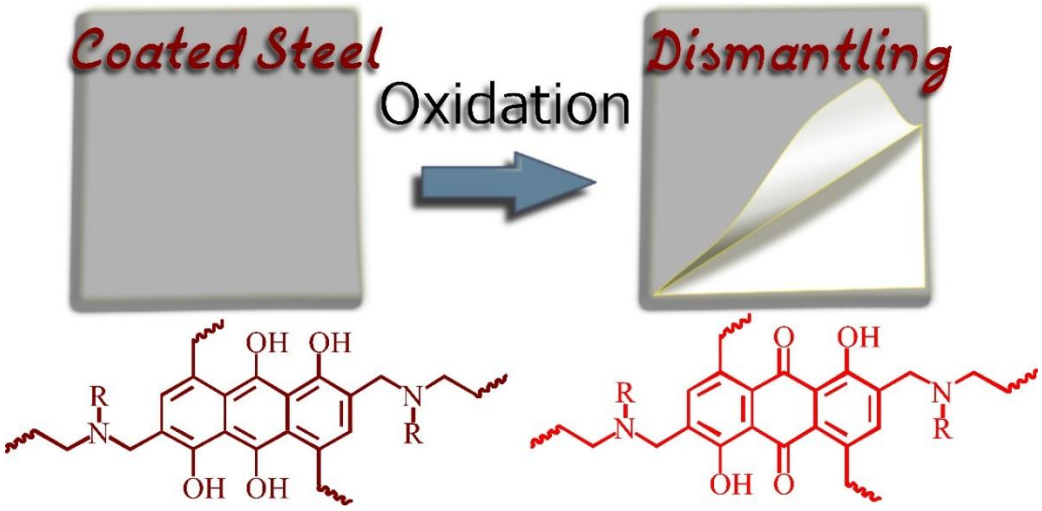


Figure 4.16: Cartoon representation of reduced polybenzoxazine coated on steel, oxidized and dismantled

Table 4.2. Adhesion data of thermally cured benzoxazines

Polymer	Reduced form	Oxidized form
PB-Ant-A	5B	0B
PB-Ant-Bn	5B	0B
PB-Ant-F	5B	0B

Standard tests for measuring adhesion by tape test[51] were carried out on stainless steel plates (5 cm X 5 cm). Polymers were prepared using the same procedure described for Pt foil electrode. All polymers are well adhered and durable versus adhesion tests.

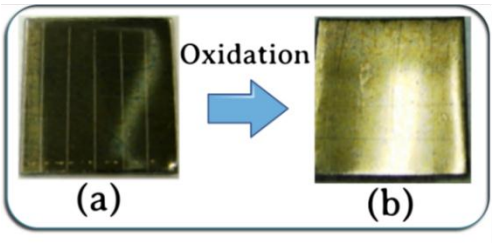


Figure 4.17: The photographes of reduced PB-Ant-A coated on steel (a), oxidized and dismantled (b)

In order to confirm the proposed redox mechanism, electrochemical studies were combined with FTIR spectral analysis. Thus, monomer films were prepared on stainless steel (5cm X 5cm) electrodes by spray processing and then polymerized at 180 ^{o}C similar to the Pt electrodes. Resulting polymers were subjected to the constant potential at -0.3 V for 20 hours to reduce the carbonyl bonds in the polymer backbone to –OH units. Although the initial current was 3 μA, it was drastically decreased to 0.5 μA after 20 h reduction. FTIR spectra of the polymer films before and after reduction were recorded. The concurent appearance of While a new peak at 2965 cm^{-1} and disappearance of the carbonyl peak at 1655 cm^{-1} clearly confirms the successful redox process (see Figure 4.9). When the reduced polymer films were subjected to oxidation at +1.8 V, dismantling of film was observed in a matter of seconds due to the oxidation of the polymer resulting in the formation of ketone moieties.

Thermogravimetric behavior of the cured polybenzoxazines were investigated by TGA under nitrogen atmosphere. The TGA and derivative thermal gravimetry (DTG) profiles are shown in Figure 4.18 and 4.19, respectively.

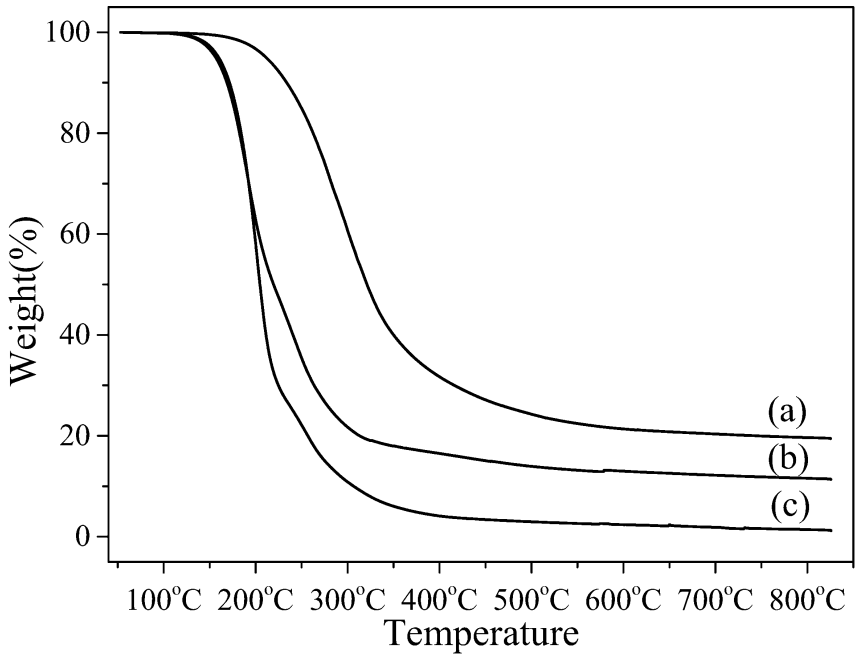


Figure 4.18: TGA curves of PB-Ant-A (a), PB-Ant-F(b), PB-Ant-Bn (c).

DTG curves of benzyl and furane II yl based polybenzoxazines exhibit peaks at 192 °C, 200°C and inflection points at 240 °C, 254 °C, respectively. However, aniline based polybenzoxazine showed a peak at relatively higher temperature, 296 °C,

indicating a different degradation pathway than that of benzyl and furan derivatives. (Figure 4.19)

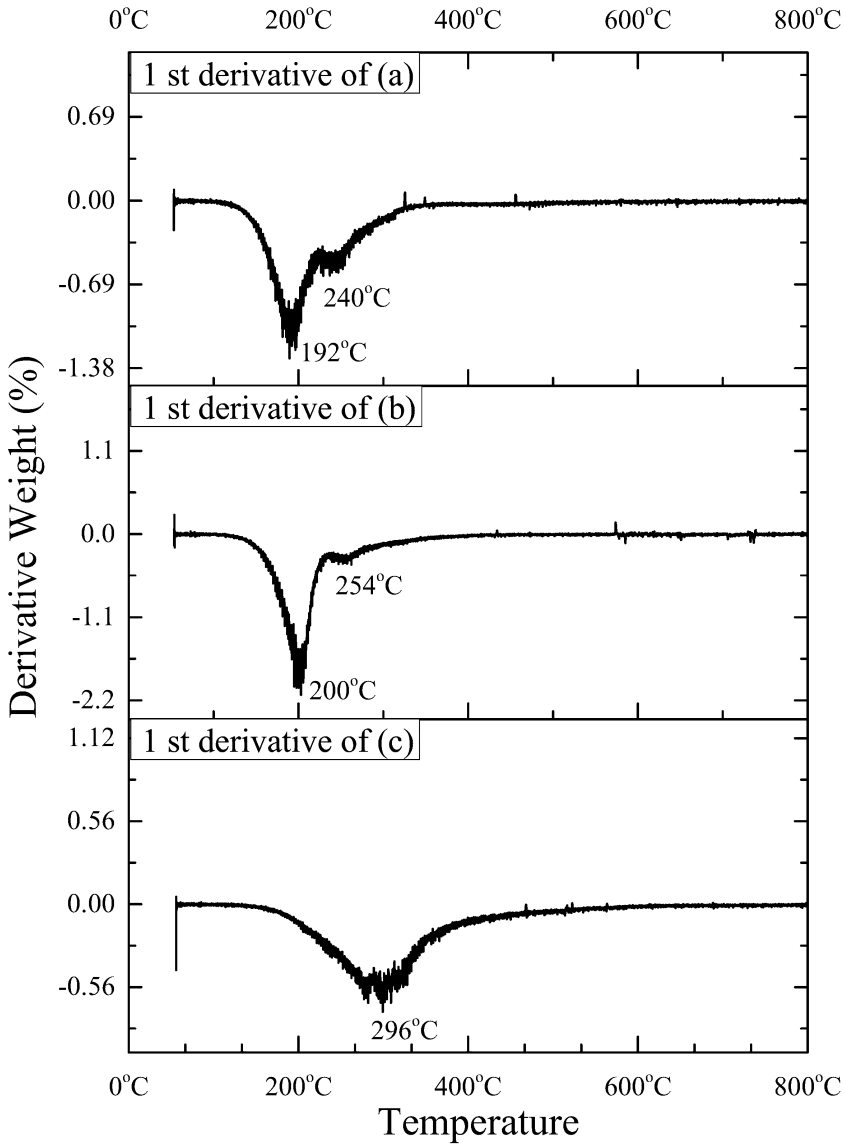


Figure 4.19: Derivative weight (%) of (a) PB-Ant-F (b) PB-Ant-Bn (c) PB-Ant-A

Thermal characteristics are also summarized in Table 4.3. It can be seen that aniline functional anthraquinone based polybenzoxazine shows significantly higher thermal stabilty than the other two polybenzoxazines. Moreover, furane II yl based polybenzoxazine has higher char yield compared to benzyl based benzoxazine. The differences observed in their thermal stability can be explained by the aromatization of the furan groups. This phenomenon is well known and reported in carbonization studies of furans [52, 53].

Table 4.3. Thermal properties of the anthraquinone based polybenzoxazine

Polymer[a]	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Char yield (%) at 800°C
PB-Ant-A	211	233	296	19
PB-Ant-Bn	159	171	200	1
PB-Ant-F	156	168	192	11

[a]Curing was performed in TGA at 220 °C for 15 min. under N_2 stream (200 mL/min.)

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

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

Y_c: Char yields at 800 °C under nitrogen atmosphere

T_{max}: The temperature for maximum weight loss.

5. CONCLUSION

It has been demonstrated that adhesion of anthraquinone based polybenzoxazine thermosets on metal surfaces can be manipulated effieciently by electrochemical redox process. The method relies on the electrochemically driven hydroquinone-quinone redox couple. The strong binding affinities of phenolic hydroxyl groups on the metal surface can be increased by increasing the number of phenolic hydroxyls via reduction of anthraquinone moieties in the cured polymers, which promotes adhesion drastically. Furthermore, electrochemical oxidation converts reduced groups into quinone moieties resulting in the dismantling of the coated films. Consequently, this work is very appealing due to its very simple design and manupulation of adhesion property supported by convincing electrochemical and adhesion test data. And it is anticipated that the approach can be applied in recycling processes of polybenzoxazine coated steels.

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PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Aydogan, C.,** Kışkan, B., Hacioglu, S.,Toppare , L., Yağcı, Y., 2013,Synthesis and Characterization of Electroactive Benzoxazine Base Anthraquinones :From Strong Adhering to Dismantling ,*IUPAC*, August 11- 16 ,2013, İstanbul, Turkey
- **Aydogan, C.,** Kışkan, B., Hacioglu, S.,Toppare , L., Yağcı, Y., 2014, Electrochemical Manupilation of Adhesion Strength of Polybenzoxazines on Metal Surfaces :From Strong Adhering to Dismantling (to be submitted)