EFFECT OF AROMATIC BORONIC ACIDS ON THERMAL CHARACTERISTICS OF POLYBENZOXAZINE DERIVATIVES AND COMPOSITES

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EFFECT OF AROMATIC BORONIC ACIDS ON THERMAL CHARACTERISTICS OF POLYBENZOXAZINE DERIVATIVES AND COMPOSITES

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ABSTRACT

EFFECT OF AROMATIC BORONIC ACIDS ON THERMAL CHARACTERISTICS OF POLYBENZOXAZINE DERIVATIVES AND COMPOSITES

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Polybenzoxazines, a class of phenolics offering excellent mechanical and physical properties, have been developed to overcome the shortcomings of the traditional phenolic resins. These materials possess low water absorption, low melt viscosity, near-zero shrinkage upon curing and releasing no by-products. In addition, molecular design flexibility of benzoxazine monomers gives opportunity to adjust the properties of the polybenzoxazines according to the application area making them advantageous for various industrial and academic applications. Several methods such as preparation of alloys with other high performance polymers, hybridization with inorganics, designing of novel monomers and incorporation of additive compounds during curing process were employed to improve the performance of polybenzoxazines.

In this work, polybenzoxazines and polybenzoxazine composites involving aromatic boronic acid derivatives were prepared to improve thermal characteristics. The effect of aromatic boronic acids on thermal characteristics of polybenzoxazines were investigated. In the first part, benzoxazines based on phenol and aniline or/and 3-amino phenyl boronic acid were synthesized. The monomers were polymerized by using optimized curing program. In the second part, benzoxazine monomer based on phenol and 4-aminomethyl benzoate was synthesized. The monomer was cured with and without incorporation of various amounts of aromatic boronic acids (benzene-1,4-diboronic acid, 4,4′-biphenyldiboronic acid, or 3-hydroxyphenylboronic acid).

The structural and thermal characteristics of the benzoxazine monomers, polybenzoxazines and polybenzoxazine composites were analyzed by NMR, FTIR, DSC, TGA and DP-MS techniques. Improvement in the thermal characteristics were recorded by the incorporation of aromatic boronic acids either as an additive or as a reactant for the synthesis of the benzoxazine monomers.

Keywords: Polybenzoxazine, Aromatic Boronic Acid, Thermal Characterization, Direct Pyrolysis Mass Spectrometry

ÖZ

AROMATİK BORONİK ASİTLERİN POLİBENZOKSAZİN TÜREVLERİNİN VE KOMPOZİTLERİNİN ISIL ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİ

İpek, Halil
Doktora, Polimer Bilim ve Teknolojisi
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Fenolik reçinelerin üstün mekanik ve fizikesel özellikler gösteren bir sınıfı olan polibenzoksazinler, geleneksel fenoliklerin eksikliklerini kapatmak için geliştirilmiştir. Bu malzemeler, düşük su emilimi, düşük eriyik akmazlığı, kürleşme sırasında büzüşmeme ve yan ürün oluşturmama gibi yüksek performans özellikleri gösterirler. Ek olarak, benzoksazin monomerlerinin moleküler dizayn esnekliği polibenzoxazinlerin özelliklerini uygulama alanına göre ayarlama şansı verir ve polibenzoksazinleri çeşitli endüstriyel ve akademik uygulamalar için avantajlı kılar. Polibenzoksazinlerin performansını iyileştirmek için başka yüksek performanslı polimerler ile alaşımlama, anorganik maddeler ile hibritleştirme, yeni monomer dizaynı ve katkı maddeleri ile birlikte kürleştirme gibi yöntemler denenmiştir.

Bu çalışmada, yüksek çapraz bağ yoğunluğu elde edilerek daha iyi ısıl özellikler elde etmek amacıyla aromatic boronik asit içeren çeşitli polibenzoksazinler ve polibenzoksazin kompozitleri hazırlanmıştır. Üretilen benzoksazin polimerleri ve kompozitlerinin ısıl özellikleri incelenerek, aromatic boronik asit kullanımının polibenzoksazinlerin ısıl özelliklerine etkisine karar verilmiştir. Bu çalışmanın ilk kısmında, aniline ve 3-aminofenil boronik asit bazlı benzoksazinler sentezlenmiştir.

Sentezlenen monomerler, en yüksek ısıl özellik ve kül verimi elde edilen sıcaklık programı ile kürleştirerek polimerleştirilmiştir. Çalışmanın ikinci kısmında, 4-aminometil benzoate bazlı benzoksazin monomeri sentezlenmiştir. Sentezlenen monomer katkısız olarak ve çeşitli aromatik boronik asitler (benzen-1,4-diboronik asit, 4,4′-bifenildiboronik asit, 3-hidroksifenilboronik asit) ile katkılandırılarak kürleştirilmiştir.

Hazırlanan benzoksazin monomerlerinin, polibenzoksazinlerin ve polibenzoksazin kompozitlerinin yapısal ve ısıl özellikleri NMR, FTIR, DSC, TGA ve DP-MS teknikleri kullanılarak karakterize ve analiz edilmiştir. Sonuç olarak, aromatic boronik asitlerin, kürleşme sırasında katkı maddesi olarak ya da benzoksazin monomerinin sentezinde giren olarak kullanılmasıyla, polibenzoksazinlerin ısıl kararlılıklarını ve kül verimlerini iyileştirdiğine karar verilmiştir.

Anahtar Kelimeler: Polibenzoksazin, Aromatik Boronik Asit, Isıl Karakterizasyon, Direkt Piroliz Kütle Spektrometresi

To My Dear Family

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LIST OF ABBREVIATIONS

ABBREVIATIONS

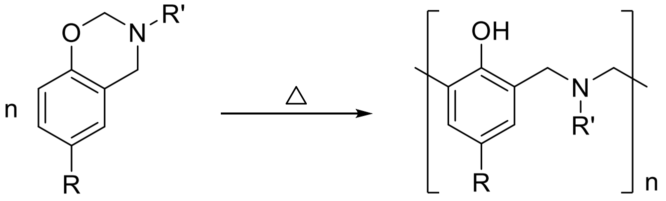
NMR	Nuclear Magnetic Resonance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
TGA	Thermal Gravimetric Analysis
DP-MS	Direct Pyrolysis Mass Spectrometry
BDBA	Benzene-1,4-diboronic acid
BPDBA	4,4′-Biphenyldiboronic acid
APBA	3-Aminophenyl boronic acid
HPBA	3-Hydroxyphenylboronic acid

CHAPTER 1

INTRODUCTION

Traditional phenolic resins are preferred materials in electronics, aerospace and other industries for their good heat resistance, low flammability, electrical insulation and dimensional stability. Yet, they have some disadvantageous properties such as brittleness, necessity of acid-base catalysts during synthesis and generation of hazardous by-products during curing.[1,2]

Polybenzoxazine, a class of phenolic resins, has low water absorption, offers low melt viscosity, near-zero shrinkage upon curing (Scheme 1.1) and releases no by-products. In addition to excellent thermal and mechanical properties, they have molecular design flexibility.



Scheme 1.1. Structure of benzoxazine monomer and polybenzoxazine

One of the important limitations for practical applications is the significantly high curing temperatures needed for ring opening polymerization of benzoxazines compared to that of the common industrial polymers. In addition, they have relatively low char yield. Even though they have several disadvantages, polybenzoxazines are preferred as the matrices for polymer composites due to their promising properties such as low cost, low water absorption, low dielectric constant, low melt viscosity, low shrinkage upon curing, relatively high thermal stability, molecular design flexibility and release of no by-products during synthesis.[3,4]

Thermal stability and char yield of the benzoxazine monomers vary depending on the structures of the selected amine and phenol and the number of functional groups on the benzoxazine monomer.[5] Functional groups with cross-linkable units can be introduced into the benzoxazine moiety to enhance the performance characteristics.

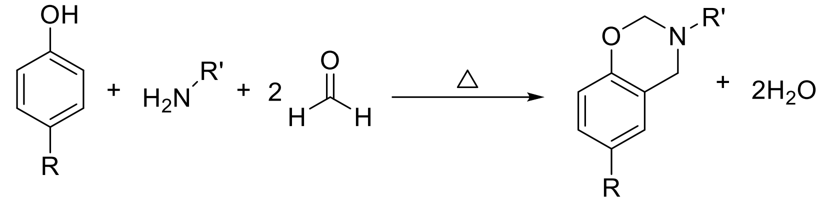
In addition, composites with various additives were prepared in several studies to improve the thermal stability and char yield of polybenzoxazines.[6] Also, reduction in the curing temperature is highly desirable for industrial applications.

Boron compounds generally used as additives for the thermal-resistant, ablation-resistant, and flame-retarded thermosetting resins, were used as additives in benzoxazine matrices in few studies.[7] These compounds can be added to both benzoxazine skeleton during monomer synthesis to obtain polymer containing boronic functionality and to monomer during curing process to obtain polymer composites.[8]

Recently, aromatic boronic acid derivatives were used with benzoxazine moieties and their properties were investigated.[9-15] Decrease in the curing temperature of the monomer was reported in the presence of aromatic boronic acid.[9] Polybenzoxazines with improved thermal stability and char yield were obtained due to the interactions of B-OH groups of aromatic boronic acids with OH groups of phenol units yielding a network structure. In addition, increase in flame retardancy[10] and polymerization rates[11] of polybenzoxazines were recorded by the use of aromatic boronic acids.

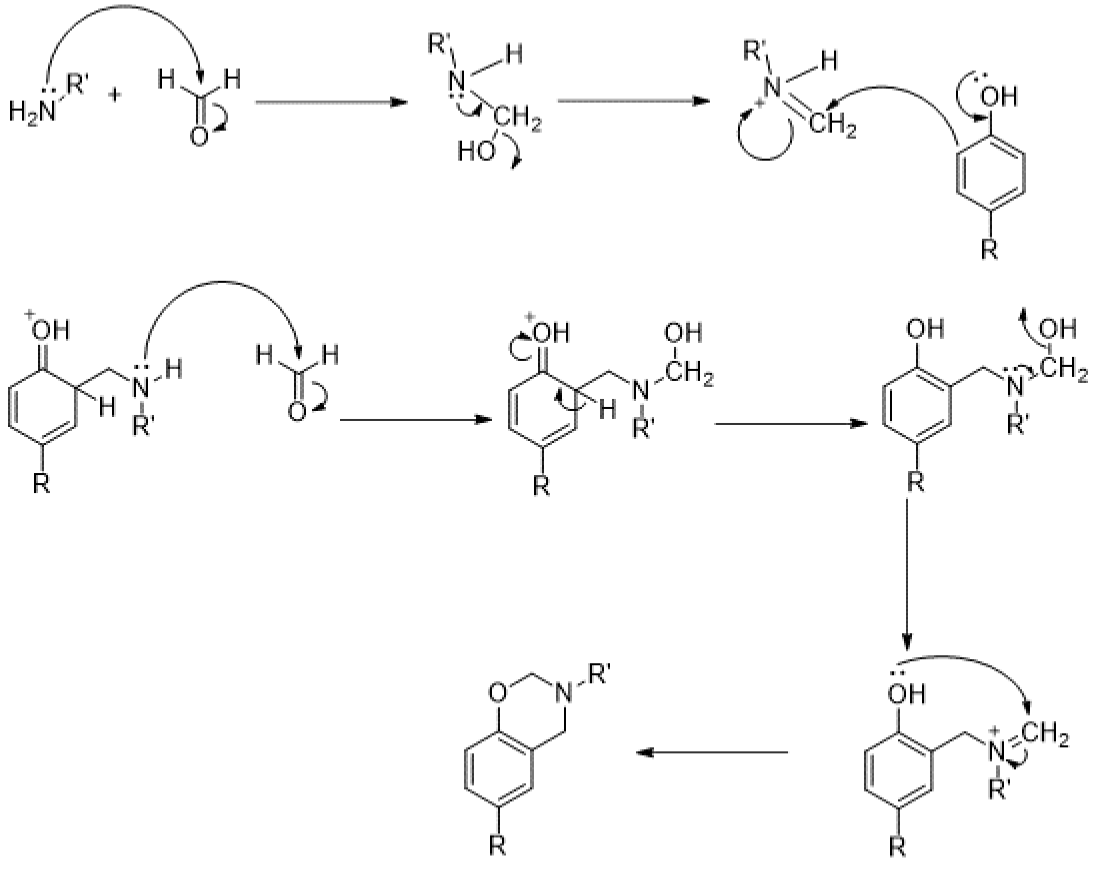
1.1. Benzoxazines

Benzoxazine is a molecule containing benzene ring fused to oxazine ring (six-membered heterocycle with a nitrogen atom and an oxygen atom). They are generally prepared with the Mannich reaction (Scheme 1.2) between a phenol derivative and an amine derivative (aliphatic or aromatic) in presence of formaldehyde either in solution or melt.[12]

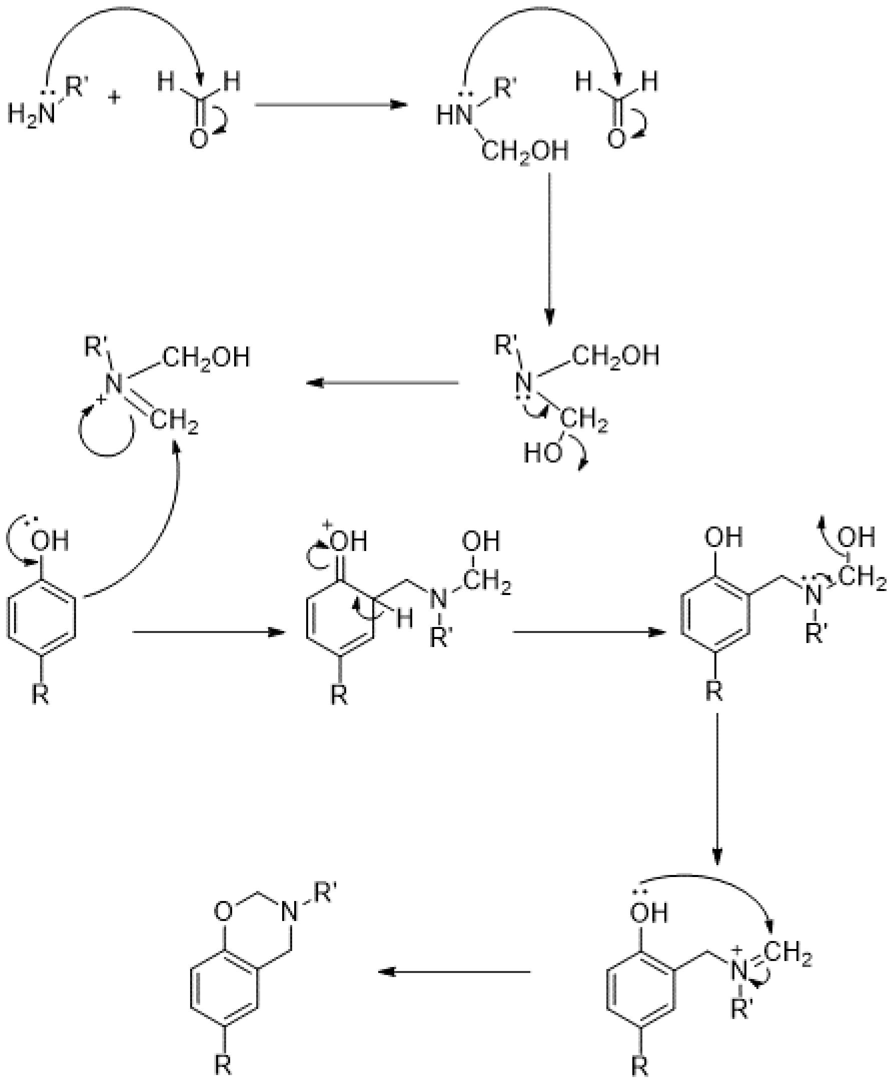


Scheme 1.2. Synthesis of benzoxazine monomer

Two possible reaction mechanisms based on secondary and tertiary iminium ions were suggested for the synthesis of benzoxazine monomers via Mannich reaction. These mechanisms were illustrated in the Scheme 1.3 and Scheme 1.4.[13]



Scheme 1.3. Suggested mechanism for the synthesis of benzoxazine monomer

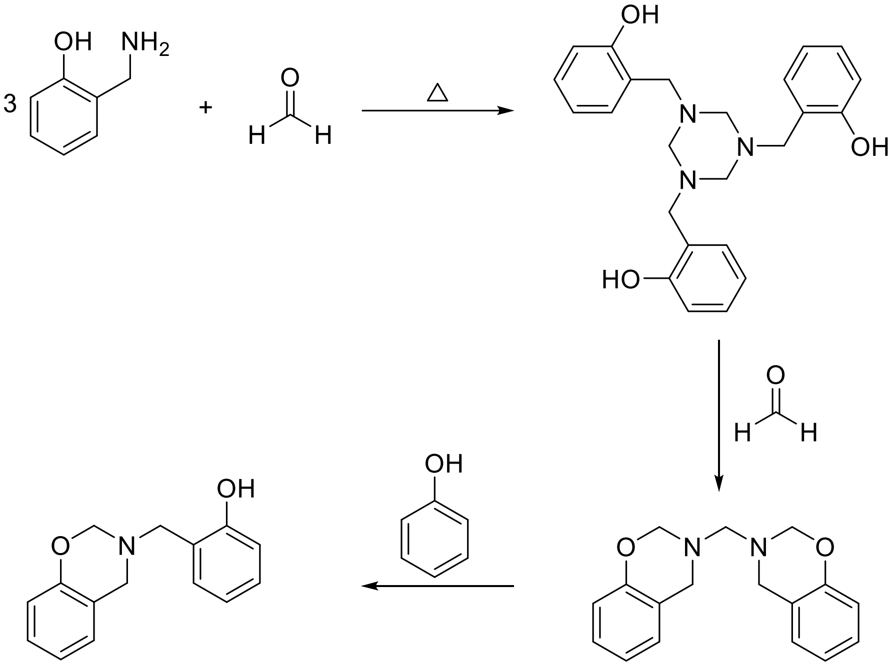


Scheme 1.4. Suggested mechanism for the synthesis of benzoxazine monomer

Benzoxazine monomers undergo ring-opening polymerization when heated without a catalyst to form network structures with high crosslinking density. Tendency of the ring opening process depends on the basicity of the nitrogen and oxygen on the oxazine ring.[14] During the multi-step curing process, thermally activated ring opening is achieved and the polymerization takes place without a catalyst by the attack of Mannich base generated to the phenol ring.[15]

1.1.1. History of Benzoxazines

The history of polybenzoxazines started with the first benzoxazine synthesis reported in 1944 by Holly and Cope with condensation reaction of formaldehyde and phenol with primary amines (Scheme 1.5).[16]



Scheme 1.5. The synthetic method of benzoxazines by Holy and Cope

In 1949, Burke et al. contributed to understanding of synthesis and structure of benzoxazines by reporting that oxazine ring reacts with free ortho positions of phenolic compounds to form Mannich bridge.[13] Riess et al. reported the high reactivity of ortho position of phenol and suggested the formation of iminium ion during the polymerization. They also studied the kinetics of monofunctional benzoxazines and found that high molecular weight linear polybenzoxazines cannot be yielded from monofunctional benzoxazines.[17]

In 1994, Ning and Ishida mentioned disadvantages of benzoxazine synthesis in solution system such as poor solubility of precursors, large amount of solvent, slow reaction rate, cost, environmental problems and processing problems due to residual solvent. They invented solventless synthesis method in melt state to overcome these disadvantages and popularized the benzoxazines in academic and industrial studies.[18]

1.1.2. Molecular Design Flexibility of Benzoxazines

Polybenzoxazines offer great molecular design flexibility unlike traditional phenolic resins. The possibility of selection of amine and phenol derivatives provides chance to design various benzoxazine monomers. Wide variety of benzoxazine monomers can be obtained with desired properties by using various amines and phenols having different substituents and functional groups.

Thus, it is possible to tune several properties of polybenzoxazines depending on the molecular structure. The design flexibility of benzoxazine monomers increases the potential of these materials for industrial and academic applications. For example, viscosity of polybenzoxazines can be adjusted by the use of long-chain alkyl or alcohol functionality.[19]

1.1.3. Improvement of Thermal Properties of Polybenzoxazines

Various types of polybenzoxazines were thermally analyzed in order to determine the effect of reactants on degradation behaviors of polybenzoxazines.[6] In order to improve thermal properties of polybenzoxazines loss of weak amine group at low temperatures may be avoided and functional groups that increase the cross-linking density may be introduced.

1.1.3.1. Stabilization of Amine Group

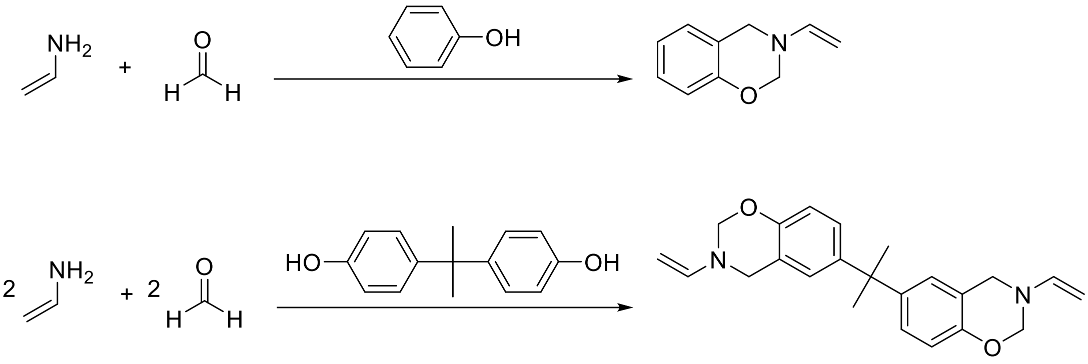
Decomposition of the polybenzoxazines is started by the loss of amine fragments.[20] In general, the aminomethyl, $-CH_2-NR-CH_2-$, group present in the benzoxazine structure as a dangling group decreases the thermal stability of the polybenzoxazines by being lost easily upon heating.[21] It was reported that the use of reactive amine groups improved thermal stability and char yield when compared to non-reactive amines. On the other hand, thermal properties were almost the same for polybenzoxazines obtained using different phenolic moieties. Thus, it can be concluded that thermal properties of polybenzoxazines mainly depend on only the type of the amine group. Allen et. al. prepared benzoxazines by reacting aliphatic diamines with different phenolic substitutions to observe the effect of diamine chain length on curing behaviors. They observed that increasing the diamine chain length increases the curing temperature of the benzoxazine monomers and decreases the reactivity of the monomer.[22]

Several studies were performed on the choice of the functional groups of the phenols and amines to improve the thermal stability and the char yield by delaying the evaporation of the dangling aminomethyl group. [23,24,25,26]

1.1.3.2. Using Functional Groups

The use of reactive functional groups in the monomer synthesis leads to polymers with void-free three dimensional networks having increased cross-linking density and improved thermal properties.[27]

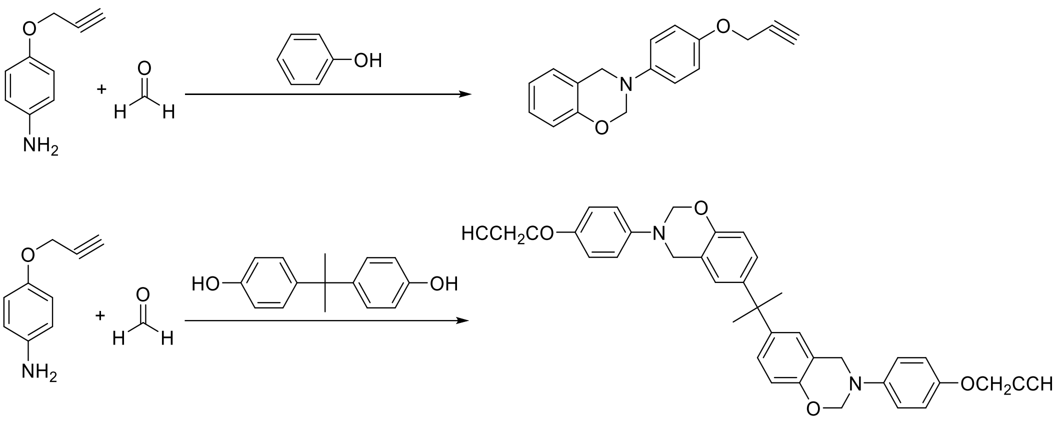
The allyl groups were employed to enhance the cross-linking density of polybenzoxazines. Benzoxazine monomers containing allyl group (Scheme 1.6) were prepared and DSC thermograms were analyzed. According to the exotherms obtained, higher thermal stability and constant storage moduli up to high temperatures were recorded.[28]



Scheme 1.6. Preparation of benzoxazine monomers containing allyl group

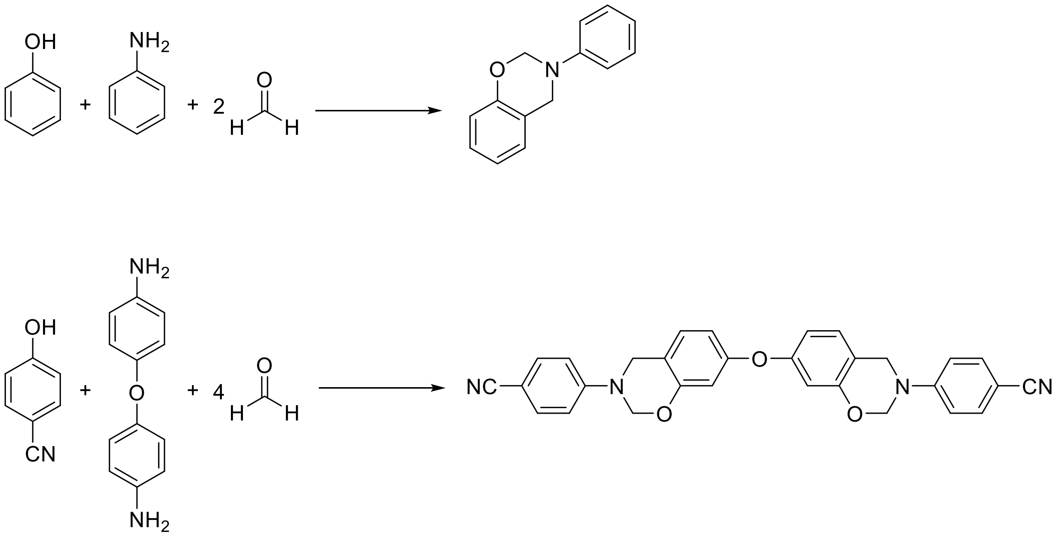
Chernykh et al. synthesized benzoxazine monomer with diacetylene group functionality. Addition of diacetylene functional group to benzoxazine structure lowered the polymerization temperature without using a catalyst. They also mentioned that alignment of benzoxazine groups in the melt directly affects the polymerization temperature.[29]

The propargyl group was also used as the cross-link site for polybenzoxazines and improved thermal stability and char yield (Scheme 1.7). Moreover, higher 5% and 10% weight loss temperatures, higher glass transition temperature and constant storage modulus up to 300℃ were obtained.[30]



Scheme 1.7. Preparation of benzoxazine monomers containing propargyl group

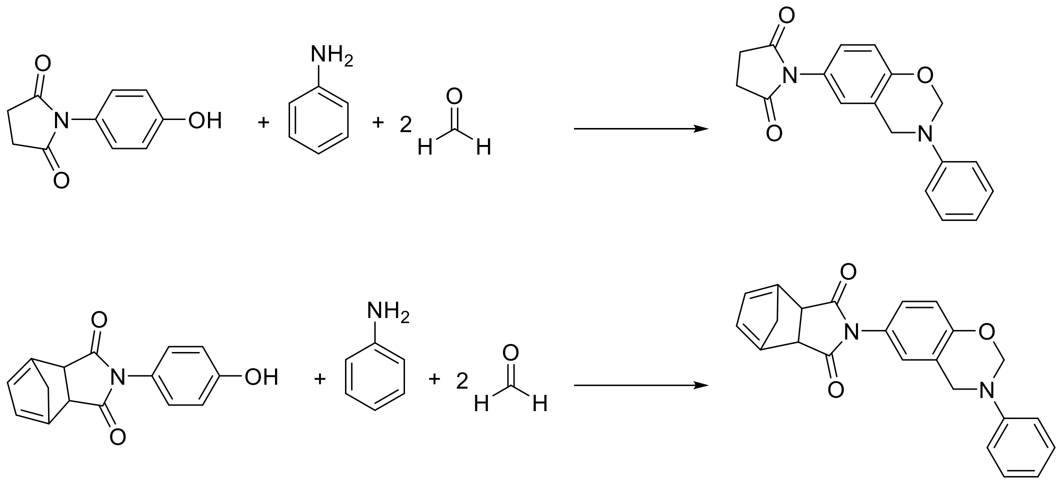
Polybenzoxazines functionalized with phenylnitrile and phthalatonitrile groups were also studied to improve thermal characteristics (Scheme 1.8).[27] DSC and FTIR analyses indicated lower curing temperatures, higher glass transition temperatures and higher thermal stability were obtained with phenylnitrile functional polybenzoxazines.



Scheme 1.8. Preparation of benzoxazine monomers containing nitrile group

In another study, methylol substituted phenols and aromatic amines were used to obtain the benzoxazine monomers. Formation of void and condensation side products were inhibited by the use of methylol as the functional group. As a consequence, the polybenzoxazines with higher degree of crosslinking and thus, improved thermal properties were yielded.[31]

Polybenzoxazines with higher char yield and glass transition temperature were obtained by employing maleimide and norbornane functional groups (Scheme 1.9).[32] Furthermore, improved crosslinking density and thermal stability were obtained by addition of nitrile functional group to the benzoxazine monomers with maleimide functionality. The resulting polybenzoxazine also showed good mechanic properties with improved processability.[33]



Scheme 1.9. Preparation of benzoxazine monomers containing maleimide and norbornane groups

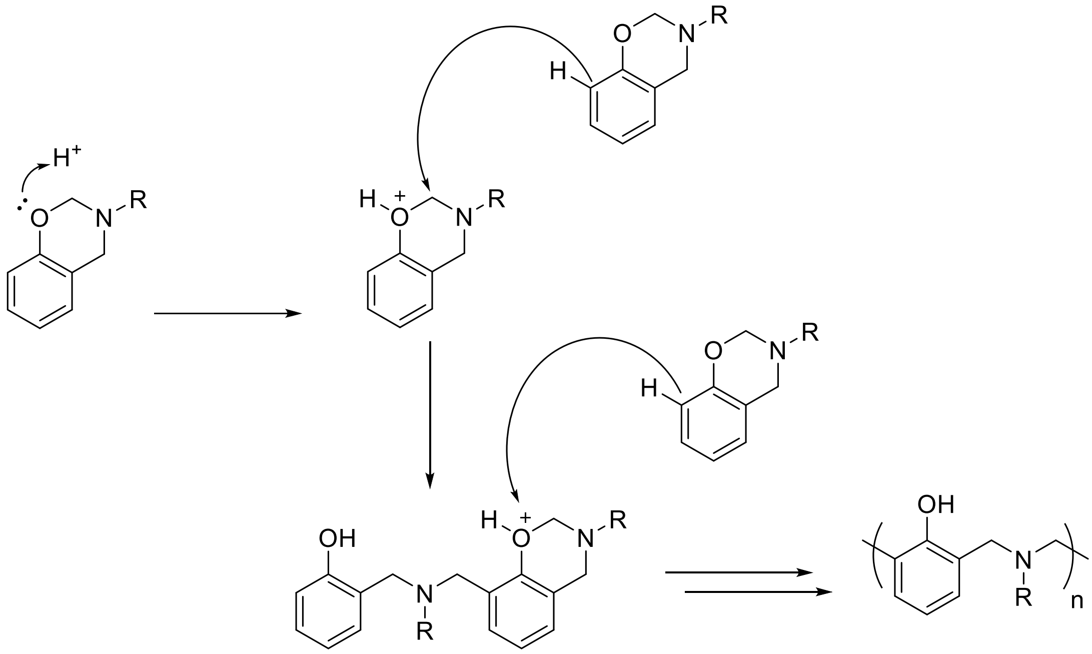
1.1.4. Polymerization Mechanism of Benzoxazines

The benzoxazine molecule consists of a six-membered heterocyclic ring, containing N and O atoms, fused to a benzene ring. Polymerization of benzoxazine monomers proceeds by opening this heterocyclyic ring. Either thermal curing or photopolymerization can be used for the polymerization of benzoxazines.[4]

1.1.4.1. Thermal Polymerization of Benzoxazines

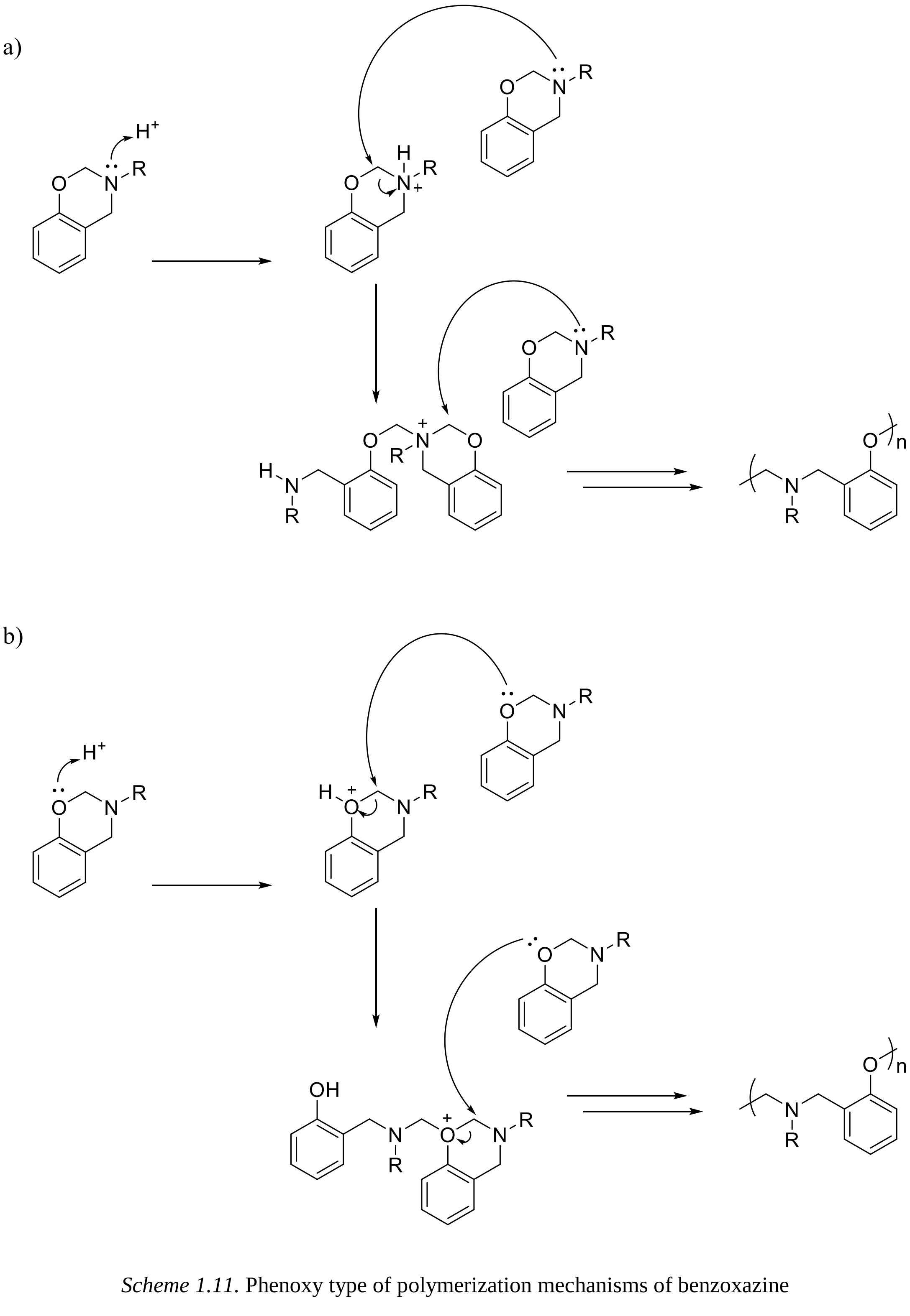
Due to the ring strain of the oxazine ring, benzoxazine molecule has the tendency for ring-opening polymerization. Therefore, benzoxazine monomers are generally polymerized at high temperatures with or without use of a catalyst. Also, it was observed that it is possible to decrease the curing periods and increase the polymerization rate by the use of catalysts.

Several polymerization pathways were explained as competing with each other during the curing process of benzoxazines. Oxazine ring may be opened to produce Mannich base and propagation may proceed over benzene ring which is highly reactive towards the Mannich base to proceed the thermal polymerization yielding the phenolic type polybenzoxazine (Scheme 1.10). Ortho positions of phenolic compounds were mentioned as preferred positions for benzoxazines to react.[34]



Scheme 1.10. Phenolic type of polymerization mechanism of benzoxazine

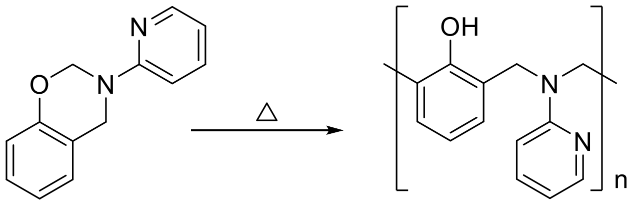
According to the Lewis definition, nitrogen and oxygen atoms, having high basicity, in the oxazine ring may also be initiation sites to yield reactive Mannich bases.[34] In the second proposed mechanism for the ring opening polymerization (Scheme 1.11), nitrogen and oxygen with high negative charge distribution attack to the oxazine ring to form Mannich bases ready to react with other monomers. Also, propagation of the thermal polymerization was occured by the attacks of the nitrogen and oxygen atoms to the produced Mannich bases.



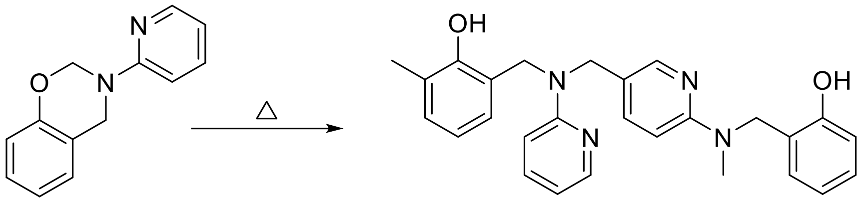
Scheme 1.11. Phenoxy type of polymerization mechanisms of benzoxazine

In the studies performed by our research group, polymerization mechanism of polybenzoxazines were analyzed by using Direct Pyrolysis Mass Spectrometry technique and additional reaction pathways were suggested. First possibility is the heterocyclic ring opening followed by $-NH_2$ groups attack to ortho and para positions of phenol and pyridyl ring. (Scheme 1.12).[35]

a) Attack to phenyl ring

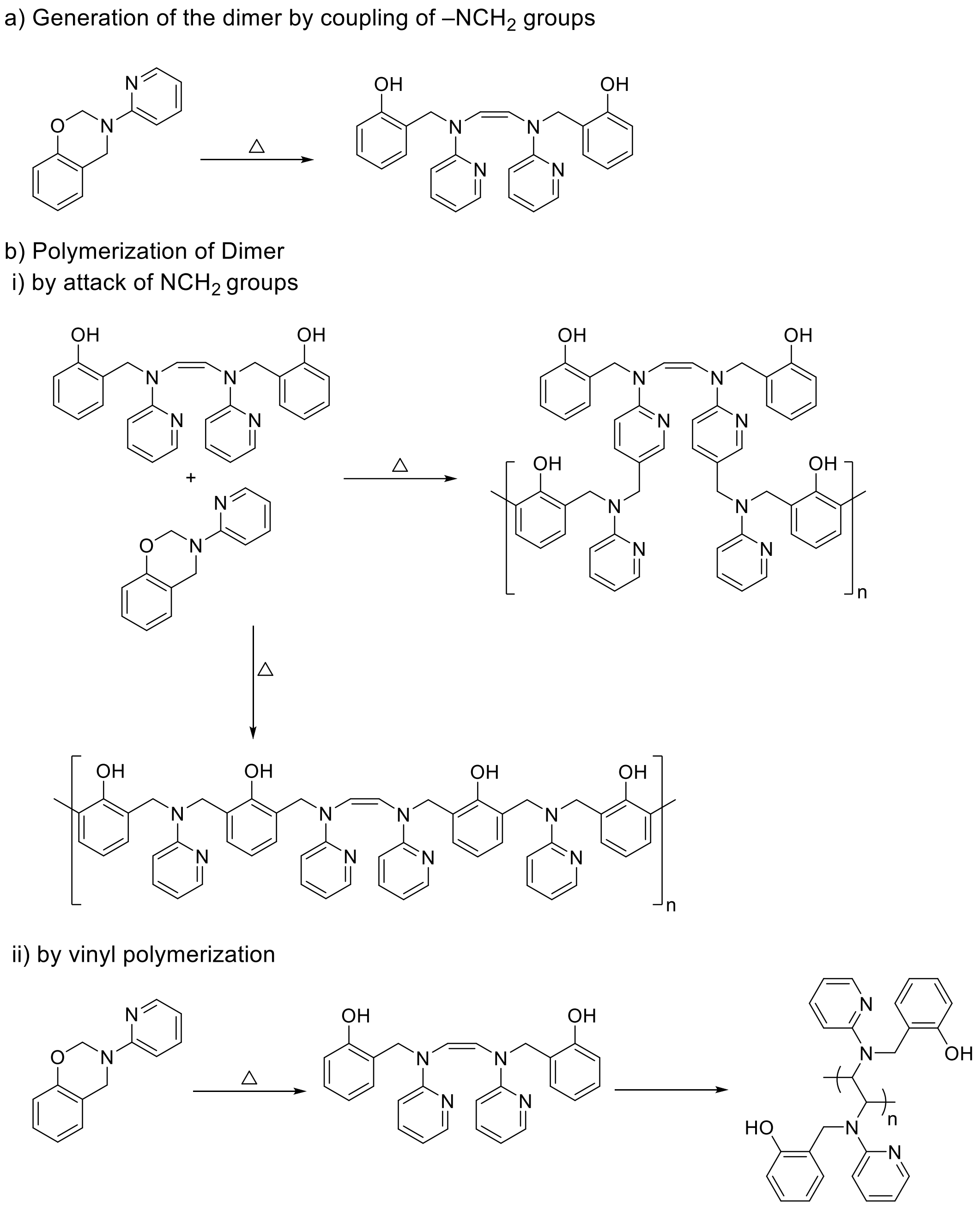


b) Attack to pyriydyl ring



Scheme 1.12. Ring opening polymerization of benzoxazines

Another possible pathway was the vinly polymerization of the dimer formed by the coupling of $-NH_2$ by the attack of $-NH_2$ to the phenol and/or pyridine ring (Scheme 1.13).

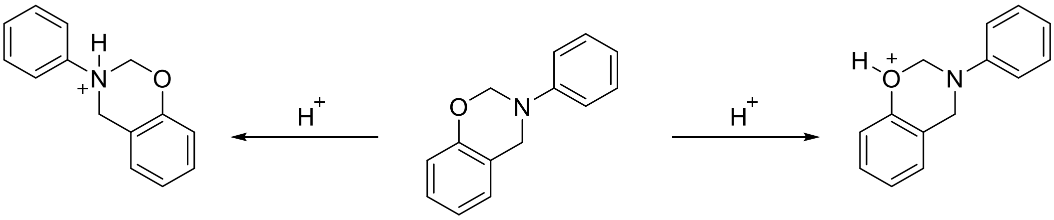


Scheme 1.13. Polymerization of benzoxazines based on dimer formation

Due to the different polymerization pathways explained above, it was expected to obtain polybenzoxazines with heterogeneous and cross-linked structures which was approved by thermal and degradation analyses.[36]

1.1.4.2. Photopolymerization of Benzoxazines

Kasapoğlu et. al. studied the photo-initiated ring opening polymerization of benzoxazines by the use of photosentisizers. They reported the protonation of monomers at oxygen and nitrogen atoms leading to ring opening photopolymerization (Scheme 1.14).[37]



Scheme 1.14. Ring opening polymerization of benzoxazines by radical sources

1.1.5. Characterization Studies

Several techniques are used for the characterization of benzoxazine monomers and corresponding polymers such as nuclear magnetic resonance spectroscopy, fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis and mass spectrometry.

1.1.5.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) spectroscopy is a very common characterization technique used for the prediction of the structure of the benzoxazine monomers. Oxazine ring contains two CH_2 groups which show characteristic resonances in ^1H NMR spectrum. CH_2 group between phenyl and amine group, Ph-CH_2-N(R)-, has resonance frequency in the region 3.8-4.8 ppm. CH_2 group between oxygen atom and amine group, -O-CH_2-N(R)-, has resonance frequency in the region 4.7 and 5.7 ppm. ^{13}C NMR gives characteristic resonances for these methylene carbons in the regions

79-84 ppm and 49-59 ppm, respectively.[38] For polybenzoxazines with cross-linked structures, due to low solubility, solid state NMR has to be used.[39]

1.1.5.2. Fourier Transform Infrared Spectroscopy (FTIR)

Benzoxazine monomers show various characteristic peaks in the IR spectra and polymerization can be proved based on the changes in these peaks. The peak at around 1500 cm^{-1} attributed to disubstituted benzene ring shifts to 1490 cm^{-1} confirming the polymerization and formation of trisubstituted benzene ring. Another characteristic peak of benzoxazine monomer is at around 950 cm^{-1} due to oxazine ring. This band disappears when the polymerization is completed pointing out opening of the oxazine ring.[40]

1.1.5.3. Differential Scanning Calorimetry (DSC)

During polymerization of benzoxazine monomers, due ring opening of oxazine ring, an exothermic differential scanning calorimetry curve is observed. This exotherm is generally detected in the temperature region of 200-250℃ for pure samples. The exothermic peak temperatures for polymerization decrease for impure monomer samples involving raw materials or catalysts.[41]

1.1.5.4. Thermogravimetric Analysis (TGA)

Thermal properties of polybenzoxazines are widely investigated by thermogravimetric analysis. Thermal stability, char yield and rate of degradation can be analyzed by this technique.

1.1.5.5. Direct Pyrolysis Mass Spectrometry

Direct pyrolysis mass spectrometry (DP-MS) is a technique in which compounds are heated under vacuum and fragmented. This technique is used to analyze degradation behavior and decomposition mechanism of materials. The high vacuum system, favors vaporization of high molecular weight molecules. In addition as degradation products are removed from the heating region immediately, secondary reactions are prevented. In addition, DP-MS technique has high sensitivity, high reproducibility, requires only small amount of sample and it can detect unstable thermal degradation products rapidly.[42]

1.1.6. Polybenzoxazine Composites

Benzoxazine resins are high performance phenolic resins offering various advantages to be employed in advance composites. There are several studies in which composites of polybenzoxazines were prepared and characterized. Polybenzoxazines were reinforced with carbon nanotubes (CNT) to obtain high performance polybenzoxazine/CNT composites, but improvements in properties were not yielded due to the poor dispersion of CNT in polybenzoxazine matrix. Wang et. al. functionalized carbon nanotubes with benzoxazine structures to enhance the interaction between polybenzoxazine matrix and the additive to overcome this problem. As a result, they obtained nanocomposites with better electrical and mechanic properties.[43]

Addition of phenolic composites containing carbon fibers (CF) as an additive improved some properties such as mechanical properties, ablation resistance and flame retardancy.[44] Polybenzoxazines and composites with better ductility, strength and modulus were yielded upon addition of carbon fibers. Fiber length was effective in the extent of improvement.

Polybenzoxazine composites were also prepared by incorporation of clay into the matrix. Polybenzoxazine-montmorillonite (MMT) nanocomposites were prepared by addition of MMT to the polybenzoxazine based on bisphenol A and aniline.[45] A low temperature shift of the exothermic polymerization peak was reported in DSC analysis indicating that MMT was acting as a catalyst for the ring opening process.

Polyhedral oligomeric silsesquioxane (POSS) was another reinforcement material used with polybenzoxazines.[46] Addition of POSS to a polymer matrix provided various properties such as monodispersity, high temperature stability, low density, lack of trace material and increased cross-linking.

In the studies performed with polybenzoxazine/POSS composites, improved thermal and mechanical properties were reported due to improved cross-linking due to functional groups on POSS.[47] In addition, as the number of functional groups on benzoxazine moieties was increased the interactions between matrix and the additive also increased. As a result, higher decomposition and glass transition temperatures were observed for these samples.

Composites having magnetic properties were prepared by the addition of magnetite (Fe_3O_4) nanoparticles to the polybenzoxazine matrix with functionalities such as carboxylic acids to interact with nanomagnetite.[33] It was reported that magnetic properties were protected during curing and thermal stability was improved due to the use of nanomagnetite.

Boronic compounds were also used to enhance thermal and mechanical properties of polybenzoxazines.[48] Recently, both academic and industrial studies were performed to investigate the effect of boronic compounds on the properties of polymers and composites of benzoxazines. As discussed before, one of the limitations of polybenzoxazines is the high curing temperatures required for ring opening polymerization of monomers compared to the industrial polymers. Reduction in the curing temperature of the monomers and enhancement in the thermal properties of the polybenzoxazines were reported by the use of boronic compounds. Boron can be used either in the benzoxazine monomer skeleton or in the polybenzoxazine resin as the additive.[48]

1.2. Boronic Compounds

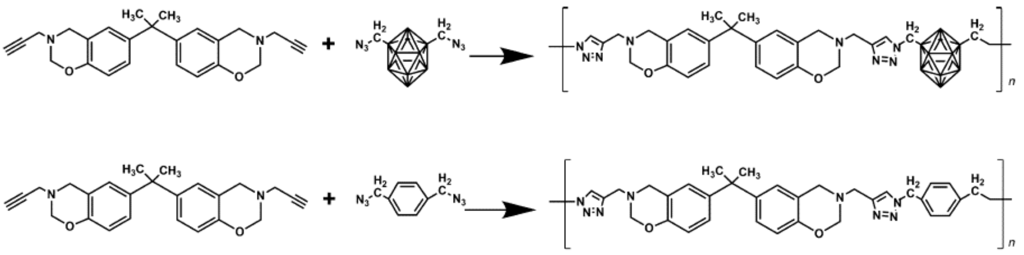
Boron element is mostly used to improve thermal properties by providing resistance to oxidation synergistically. Thermal resistant, ablation resistant and flame retardant materials can be obtained by the use of boronic compounds.[8] Zinc borate and borophospate were used to enhance flame retardancy of polypropylene matrix.[49] Char yield of phenolic resins were increased by employing boron carbide to form phenol borate and benzyl borate.[50] It was reported that thermal stabilities of phenolic resins can be enhanced by using the antioxidative properties of boron containing compounds

1.2.1. Use of Boronic Compounds in Benzoxazine Resins

Several properties of benzoxazine resins can be changed by the use of additives to prepare polybenzoxazine composites according to the application area and various additives were employed for this purpose. Yet, use of boronic compounds with benzoxazine resins appeared only in few studies in the literature.

Huang and Ishida introduced hexagonal boron nitrides as the fillers to the polybenzoxazine resins. Addition of boron nitride improved the thermal conductivity of benzoxazine resins making them applicable for electronic packaging. [51] They also reported that boron nitride acted as the inhibitor during the ring opening process.

Huang et. al. used icosahedral carboranes, carbon containing boron cluster, in the benzoxazine main chain and obtained enhanced thermal stability due to the cage structure of carboranes (Scheme 1.15).[52]



Scheme 1.15. Use of icosahedral carborane with benzoxazines

Hyperbranched polyborates (Figure 1.1) were also prepared to modify benzoxazine. Excellent thermal resistance and improved toughness were observed due to hyperbranched structure. Moreover, it was found that hyperbranched polyborates can catalyze the polymerization due to the presence of phenolic groups promoting ring opening process.[53]

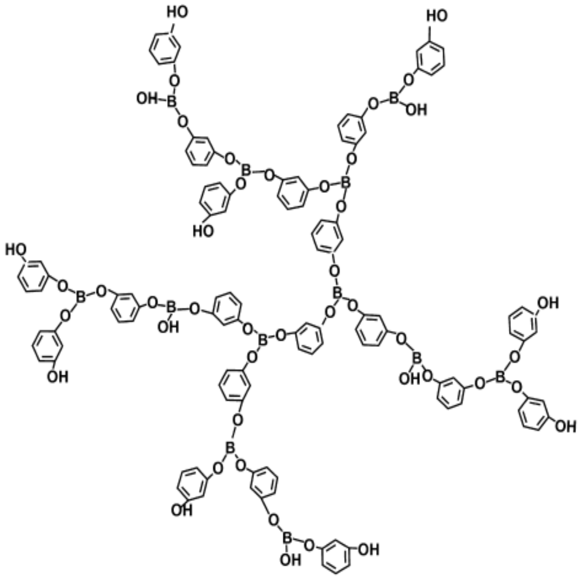


Figure 1.1. Structure of hyperbranched polyborates

Liu et. al. prepared hyperbranched polyborazines (Figure 1.2) using boron trichloride and *p*-phenylene diamine to enhance thermal properties of polybenzoxazines. High performance benzoxazine resins with improved char yield and thermal stability and lower curing temperatures were reported.[54]

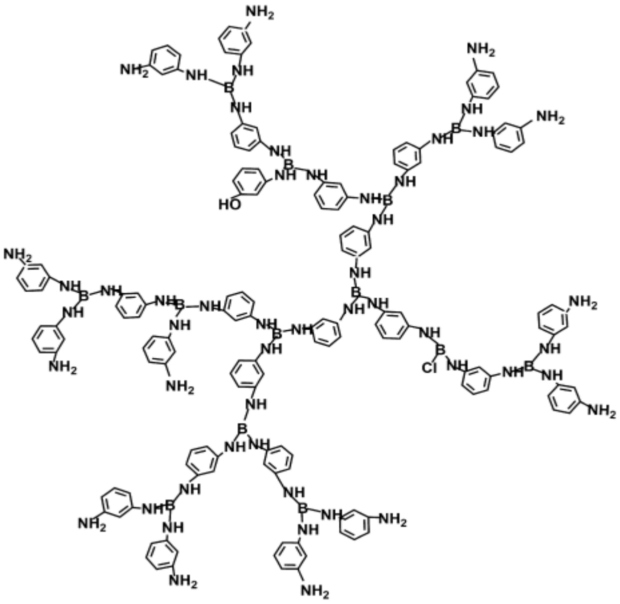


Figure 1.2. Structure of hyperbranched polyborazines

In another study, hyperbranched polyresorkinol borate was used as an additive.[55] Decrease in the curing temperature, increase in thermal stability and improvement in mechanical properties were reported.

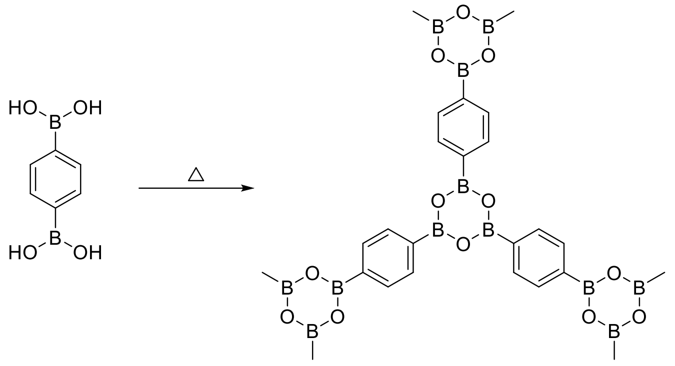
1.2.2. Use of Boronic Acids in Benzoxazine Resins

Boronic compounds were used in the synthesis of benzoxazine monomers to produce boron containing benzoxazine resins. For this purpose, borates were prepared by using bisphenol-A and boric acid in the Mannich reaction with aniline and formaldehyde. Generation of boron containing benzoxazine monomers was confirmed by FTIR analyses. The characteristic peaks of oxazine ring and B-O-C linkage were detected at 980 and 1330 cm^{-1} respectively. Thermogravimetric analysis (TGA) indicated increase in thermal stability and char yield upon boron introduction to benzoxazine skeleton. Liu et. al. produced boron containing polybenzoxazine by reacting formaldehyde, phenol and 4,4-diaminodiphenylmethane in presence of boric acid.[10] They reported increase in thermal stability and flame retardency due to synergic effect of boron and nitrogen.

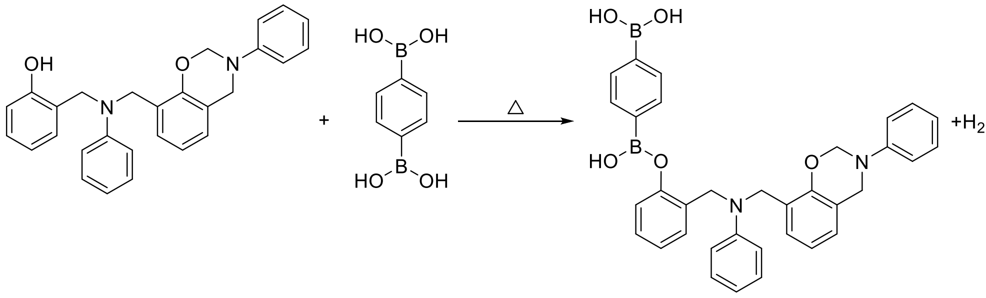
Wang and coworkers reported stable boronate ester network by condensation of hydroxyl groups of boronic acid and phenolic groups. Thermal properties and the processability of benzoxazine resins were improved as the amount of phenyl boronic acid added was increased due to increased cross-linking density. Furthermore, it was found that phenolic boronic acid acted as catalyst for the polymerization process.[11] The thermal stability and char yield were increased in presence of aromatic monoboronic acid due to the interactions between B-OH groups and phenolic hydroxyl and ester groups forming a network structure.[9]

In a recent study conducted in our research group, 1,4-benzene diboronic acid (BDBA) was added to polybenzoxazine matrix based on phenol and aniline. Different amounts of BDBA was mixed with as-synthesized and pure benzoxazine monomers. After the curing process, it was observed that more efficient interactions between benzoxazine and BDBA molecules were obtained when as-synthesized benzoxazine monomer was used as the matrix. Curing of the purified benzoxazine monomer mostly yielded boroxine network formation (Scheme 1.16).[56]

a) Generation of boroxine network



b) Interaction of aromatic diboronic acid with benzoxazine dimer



Scheme 1.16. Boroxine network formation and diboronic acid-dimer interaction

1.3. Aim of Study

In this study, our aim was to investigate the effect of aromatic boronic acids on thermal characteristics of polybenzoxazine derivatives and composites. For this purpose, novel benzoxazine polymers and composites containing aromatic boronic acids were prepared and characterized. Improved thermal characteristics were expected due to the contribution of condensation and transesterification reactions of boronic hydroxy groups to the crosslinking. Benzoxazine monomers with aromatic boronic acid precursors (3-amino phenyl boronic acid) were synthesized and polymerized. Also, polybenzoxazine composites were prepared by introduction of aromatic boronic acids (benzene-1,4-diboronic acid, 4,4′-biphenyldiboronic acid, 3-hydroxyphenylboronic acid) in various amounts during curing process of benzoxazine monomer having ester functionality.

Structural characterization studies were performed by Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR) and Mass Spectrometry (MS) techniques. Thermal characteristics were investigated by Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA) and Direct Pyrolysis Mass Spectrometry (DP-MS) techniques.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

Phenol (99.5%), paraformaldehyde, 4-aminobenzoic acid, benzene-1,4-diboronic acid, 4,4′-Biphenyldiboronic acid, 3-aminophenyl boronic acid, 3-hydroxyphenylboronic acid, thionyl chloride, sodium hydroxide and chloroform were supplied by Sigma Aldrich Co. Aniline, hexane, ethyl acetate and $MgSO_4$ were purchased from Merck. All chemicals were used as received without further purification.

2.2. Characterization Techniques

2.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Bruker AC250 (250.133 MHz) spectrometer was used for the NMR analysis in which tetramethylsilane (TMS) was used as the internal standard and $CDCl_3$ was used as the solvent.

2.2.2. Infrared Spectrophotometer (ATR-FT-IR)

Thermo Scientific Nicolet IS10 Spectrometer with 4 cm^{-1} resolution was used to perform ATR-FT-IR analysis of the solid samples.

2.2.3. Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA)

Perkin Elmer STA6000 instrument was used to perform DSC and TGA analysis. Solid samples (5-10 mg) were heated with a rate of 10℃/min under nitrogen atmosphere.

2.2.4. Direct Pyrolysis Mass Spectrometry (DP-MS)

Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 15-1500 Da coupled to a direct insertion probe was used for the direct pyrolysis mass spectrometry (DP-MS) analyses of the samples (0.010 mg) in flared quartz sample vials. Heating rate of the samples was 10℃/min while recording 70 eV EI mass spectra, at a rate of 1 scan/s. The step-wise curing of the monomers, pyrolysis of the polymers and polymer composites were also investigated by the mass spectrometer while samples were heated to 650℃ inside the MS recording the mass spectra continuously. Argon was used as the collision gas and reproducibility of the experiments were tested by repeating all analyses at least twice. The precursor ions were selected and the mass spectra recorded at the temperature where the ion yields were maximized were analyzed. Single ion evolution profiles of the abundant and/or characteristic ions were analyzed.

2.3. Synthesis

2.3.1. Synthesis of Benzoxazine Based on Phenol and Aniline, Bz

Benzoxazine monomer was synthesized according to the literature method by reacting phenol, aniline and paraformaldehyde via solventless method.[22] The mixture of phenol (0.470 g, 5 mmol), aniline (0.460 g, 5 mmol) and paraformaldehyde (0.300 g, 10 mmol) was heated at 110 °C for 2 h. Subsequently, the viscous liquid was cooled to about 50 °C and 30 mL chloroform was added to the mixture gradually. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH aqueous solution (3 mol/L) and distilled water. The chloroform solution separated as the organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The light orange residue was fractionated by silica gel column chromatography using hexane/ethyl acetate mixture as an eluent to obtain benzoxazine monomer, Bz, as a yellow solid.

2.3.2. Synthesis of Benzoxazine Based on Phenol and 3-Aminophenyl Boronic Acid-Aniline Mixture, Bz-50APBA

Phenol (0.470 g, 5 mmol) and paraformaldehyde (0.300 g, 10 mmol) were introduced to the mixture of 3-amino phenyl boronic acid (APBA) (0.343 g, 2.5 mmol) and aniline (0.230 g, 2.5 mmol). The mixture was heated to reflux at 110 °C for 3 hours. Subsequently, the viscous liquid was cooled to about 50 °C and 30 mL chloroform was added to the mixture gradually. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH aqueous solution (3 mol/L) and distilled water. The chloroform solution was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was fractionated to obtain benzoxazine monomer, Bz-50APBA, by silica gel column chromatography using hexane/ethyl acetate mixture (3:1) as an eluent.

2.3.3. Synthesis of Benzoxazine Based on Phenol and 3-Aminophenyl Boronic Acid, Bz-100APBA

The mixture of phenol (0.470 g, 5 mmol), 3-amino phenyl boronic acid (APBA) (0.685 g, 5 mmol) and paraformaldehyde (0.300 g, 10 mmol) were mixed and heated at 110 °C for 3 hours. Subsequently, the viscous liquid was cooled to about 50 °C and 30 mL chloroform was added to the mixture gradually. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH aqueous solution (3 mol/L) and distilled water. The chloroform solution separated as the organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was fractionated by silica gel column chromatography using hexane/ethyl acetate mixture (3:1) as an eluent to obtain brown benzoxazine monomer Bz-100APBA.

2.3.4. Polymerization of Benzoxazines Based on Phenol and Aniline and/or 3-Aminophenyl Boronic Acid

Benzoxazine monomers based on phenol and aniline or 50 % aniline and 3-amino phenyl boronic acid mixture or 3-amino phenyl boronic acid were cured with optimized temperature program by heating for 1 hour at 175, 200 and 225°C in a vented oven to obtain brown colored polymers (PBz, PBz-50APBA and PBz-100APBA).

2.3.5. Synthesis of 4-Aminobenzoate

4-aminobenzoic acid (1.37g, 10 mmol) was dissolved in 30 mL methanol. The mixture was stirred at room temperature for an hour. Then, the mixture was cooled to 0℃ and thionyl chloride (2.93g, 25 mmol) was added dropwise. The mixture was heated to reflux at 90℃ for 24 hours and the solvent was removed under reduced pressure. Ethyl acetate (30 mL) was added over the residue and the solution was poured into a separatory funnel, washed three times with saturated $NaHCO_3$ aqueous solution and distilled water, respectively. The organic phase was dried over anhydrous MgSO4 and the solvent was removed under reduced pressure to obtain 4-amino benzoate. 4-amino benzoate was obtained as a yellow solid.

2.3.6. Synthesis of Benzoxazine Based on Phenol and 4-Aminobenzoate

A mixture of phenol (0.470 g, 5 mmol), 4-aminobenzoate (0.815 g, 5 mmol) and paraformaldehyde (0.300 g, 10 mmol) was heated to reflux at 130 °C for 2 hours.

Subsequently, the viscous liquid was cooled to 50℃ and 30 mL chloroform were gradually introduced into the flask. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH solution (3 mol/L) and distilled water. The chloroform solution was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. The residue was fractionated by silica gel column chromatography over silica gel using hexane: ethyl acetate mixture (3:1) as the eluent to obtain pure benzoxazine monomer, Pab. Pab was obtained as a pale-yellow solid.

2.3.7. Polymerization of Benzoxazine Based on Phenol and 4-Aminobenzoate

Benzoxazine monomer based on phenol and 4-aminobenzoate was cured using the optimized temperature program by heating for 1 hour at 150, 175 and 200°C in a vented oven. A reddish brown colored polymer (PPab) was obtained.

2.3.8. Preparation of Polybenzoxazine Composites PPab/BDBA

Benzoxazine monomer, Pab, and 1,4-benzene diboronic acid (BDBA) was mixed in different ratios (5, 10, 15 wt%) and mixture dissolved in 5 mL of chloroform by using ultrasonic bath. Obtained solution was casted on a glass plate and dried under reduced pressure to obtain 5, 10, 15 wt% Pab/BDBA samples. The dried samples were cured step-wise by heating for 1 hour at 150, 175 and 200 °C in a vented oven to obtain transparent reddish brown polybenzoxazine composites (PPab/5BDBA, PPab/10BDBA and PPab/15BDBA).

2.3.9. Preparation of Polybenzoxazine Composites PPab/BPDBA

Benzoxazine monomer, Pab, and 4,4′-Biphenyldiboronic acid (BPDBA) was mixed in different ratios (5, 10, 15 wt%) and mixture dissolved in 5 mL of chloroform by using ultrasonic bath. Obtained solution was casted on a glass plate and dried under reduced pressure to obtain 5, 10, 15 wt% Pab/BPDBA samples. The dried samples were cured step-wise by heating for 1 hour at 150, 175 and 200 °C in a vented oven to obtain reddish brown polybenzoxazine composites (PPab/5BPDBA, PPab/10BPDBA and PPab/15BPDBA).

2.3.10. Preparation of Polybenzoxazine Composites PPab/HPBA

Benzoxazine monomer, Pab, and 3-hydroxyphenylboronic acid (HPBA) was mixed in different ratios (2.5, 5, 7.5, 10 wt%) and mixture dissolved in 5 mL of chloroform by using ultrasonic bath. Obtained solution was casted on a glass plate and dried under reduced pressure to obtain 2.5, 5, 7.5, 10 wt% Pab/HPBA samples. The dried samples were cured step-wise by heating for 1 hour at 150, 175 and 200 °C in a vented oven to obtain transparent reddish brown polybenzoxazine composites (PPab/2.5HPBA, PPab/5HPBA, PPab/7.5HPBA and PPab/10HPBA).

CHAPTER 3

RESULTS AND DISCUSSION

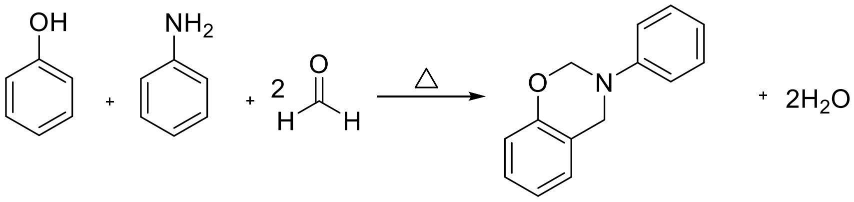
3.1. Polybenzoxazines Based on Aniline and 3-Aminophenyl Boronic Acid

Benzoxazine monomers were prepared by reacting aniline and 3-amino phenyl boronic acid (APBA) with phenol in presence of formaldehyde. The monomers were polymerized by curing and characterized. The thermal characteristics of these polymers were investigated to understand the effect of boronic acid on thermal characteristics of polybenzoxazines. Structural characterization studies were performed by using NMR, FTIR and MS techniques. Thermal characteristics of polybenzoxazine samples were determined by employing DSC, TGA and DP-MS techniques.

Thermal stability and char yield of the polybenzoxazines based on aniline involving boronic acid functional groups were improved compared to the polybenzoxazines based on aniline confirming the enhanced crosslinked structure generated by the condensation reactions of B-OH groups with OH groups of phenol and self-condensation reactions.

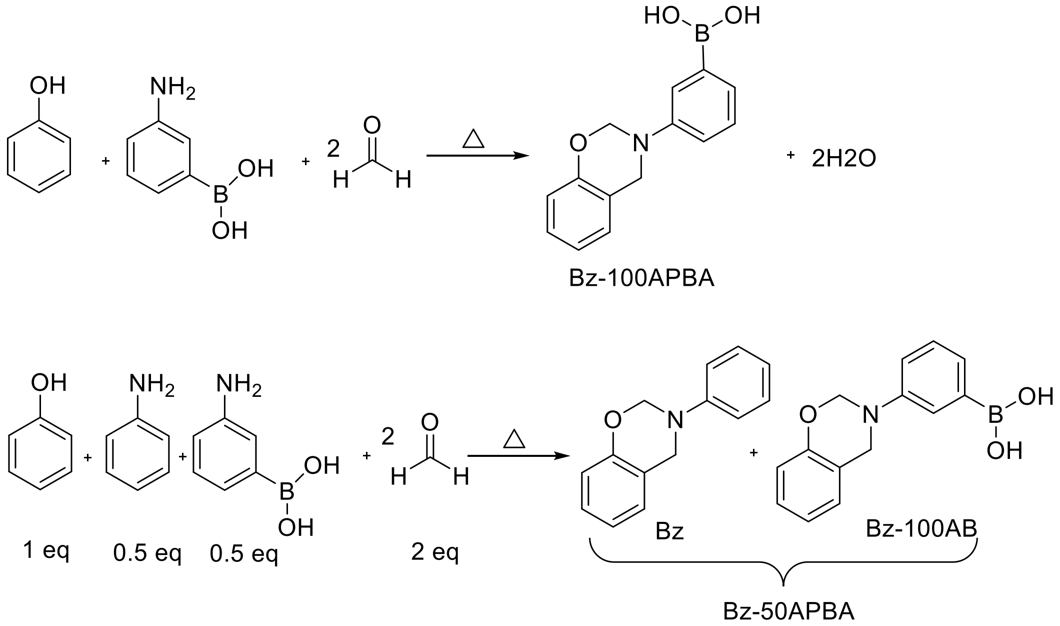
3.1.1. Synthesis of Benzoxazine Monomers

Benzoxazine monomer based on aniline was synthesized by reacting aniline, phenol and formaldehyde according to literature methods without using solvent (Scheme 3.1).[57]



Scheme 3.1. Synthesis of benzoxazine based on phenol and aniline

The same procedure was modified by the replacement of aniline with 3-amino phenyl boronic acid (APBA) in 50 and 100% ratios (Scheme 3.2). As a result, benzoxazine monomer samples based on pure aniline (Bz), aniline-APBA mixture (Bz-50APBA) and pure APBA (Bz-100APBA) were obtained.



Scheme 3.2. Synthesis of Bz-50APBA and Bz-100APBA benzoxazine monomers

NMR spectrum of pure Bz-100APBA monomer were recorded and analyzed for characterization (Figure 3.1). 1H NMR ($CDCl_3$, δ ppm): 7.12 (s, 1H), 7.10 (s, 1H), 6.82-7.03 ppm (m, 8H), 5.39 (s, 2H), 4.64 (s,2H).

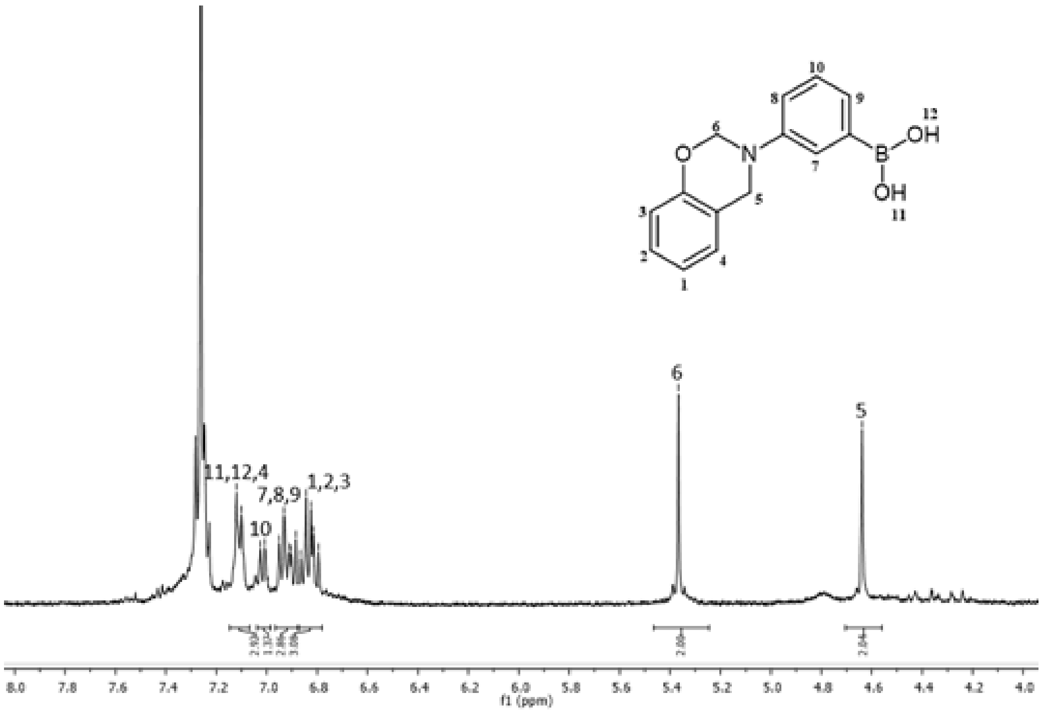
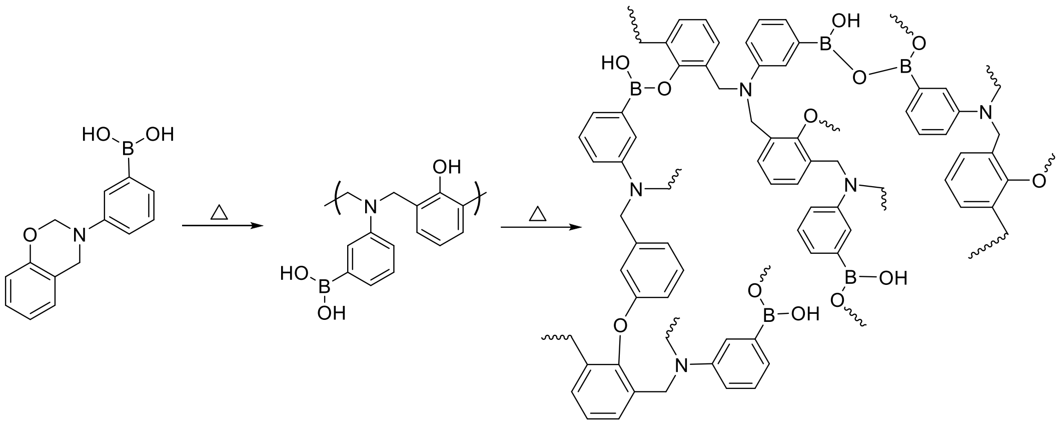


Figure 3.1. Proton NMR spectrum of Bz-100APBA monomer

The proton NMR spectrum of the monomer based on 3-amino phenyl boronic acid shows strong resonances at 4.64 and 5.39 ppm corresponding to the characteristic methylene protons (H5 and H6) of Ar-CH$_2$-N and O-CH$_2$-N of the oxazine ring, respectively. The resonance signals at 6.82, 6.87, 6.90, 7.03, 7.10 and 7.12 are associated with the protons of OH groups of boronic acid and aromatic rings.

3.1.2. Preparation of Polybenzoxazines

Benzoxazine monomers based on phenol and 3-amino phenyl boronic acid (Bz-100APBA) or 50% aniline and 50% 3-amino phenyl boronic acid (Bz-100-APBA) were heated step-wise with determined curing temperature program (1 hour heating at each temperature of 175, 200 and 225 °C) in a vented oven. Brown colored polymers were obtained. FTIR, DSC, TGA and DP-MS techniques were used for the characterization of the polymers. Possible cross-linked structure generated during curing process is shown in Scheme 3.3.[58]



Scheme 3.3. Crosslinking during polymerization of Bz-100APBA monomer

The step-wise curing program used for polymerization of the monomers was optimized by comparing thermal stabilities and char yields of various PBz-100APBA polymers prepared by applying the two and three step curing temperature programs to the Bz-100APBA monomer. TGA curves of PBz-100APBA polymers obtained by employing different two step and three step curing programs are given in Figure 3.2.

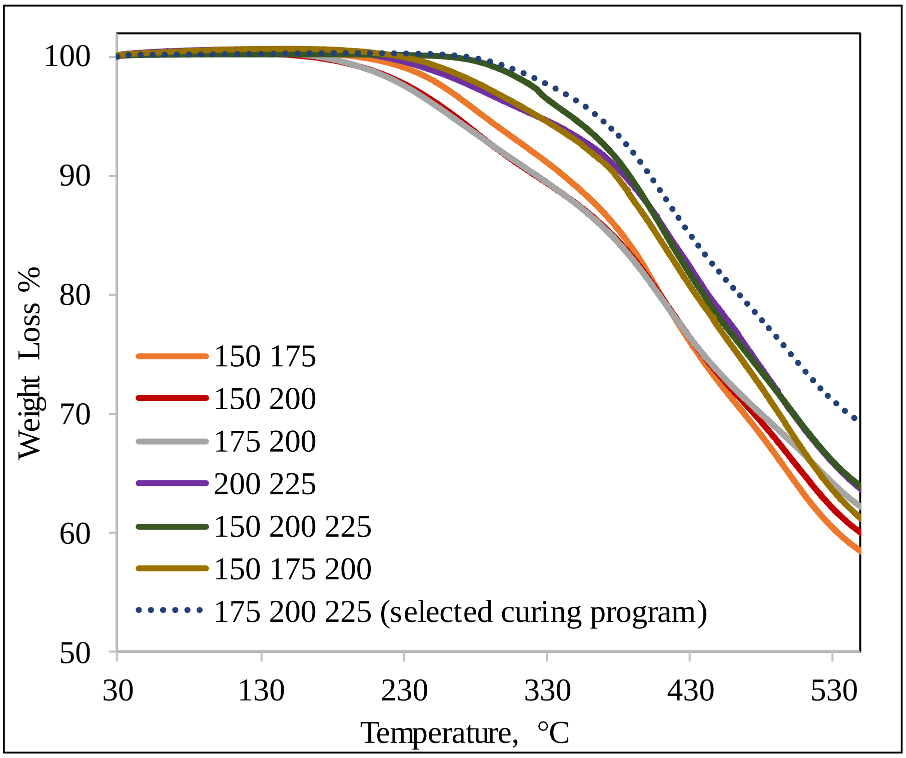


Figure 3.2. TGA curves different temperature programs applied to Bz-100APBA

As explained before, during the thermal polymerization of benzoxazine monomers, various polymerization pathways compete with each other propagating different type of polymer chains. Moreover, these chains may interact with each other to form crosslinkages. Type of growing polymer chains and amount of crosslinkages determine the thermal stabilities and the char yields of the polybenzoxazines. Therefore, optimized curing program is the temperature program promoting the growing of the polymer chain type yielding highest thermal characteristics and offering the highest interactions with other chains.

As a result, three-step curing program, heating at 175, 200 and 225 °C for an hour, was selected as the optimized curing program yielding a polymer with highest thermal stability and char yield (Tmax was 572°C and char yield was about 65 % at 650°C) for the thermal polymerization of Bz-100APBA. Same curing program was also applied for the polymerization of Bz and Bz-50APBA monomers.

FTIR spectra are used to follow the disappearance of the characteristic peaks of the monomer and formation of characteristic peaks of the polymer to confirm polymerization of benzoxazines. In addition, the functional groups present in the benzoxazine structures were investigated. The peaks at around 1600-1350 cm^{-1} are related to C-C stretching vibrations of the ring. The aromatic C-H bending modes of benzene are recorded in the region 1300-1000 cm^{-1}.

Generally, absorption peaks at around 1485 cm^{-1} is typical for di-substituted benzene ring, 1375 cm^{-1} corresponds to CH_2 wagging, 1230 cm^{-1} corresponds to Ar-O-C anti-symmetric stretching, 1030 cm^{-1} corresponds to C-O-C symmetric stretching and 820 cm^{-1} is assigned to C-N-C symmetric stretching vibrations. The peak obtained at around 940 cm^{-1} is characteristically obtained for the benzoxazines due to the vibration modes of an oxazine ring.

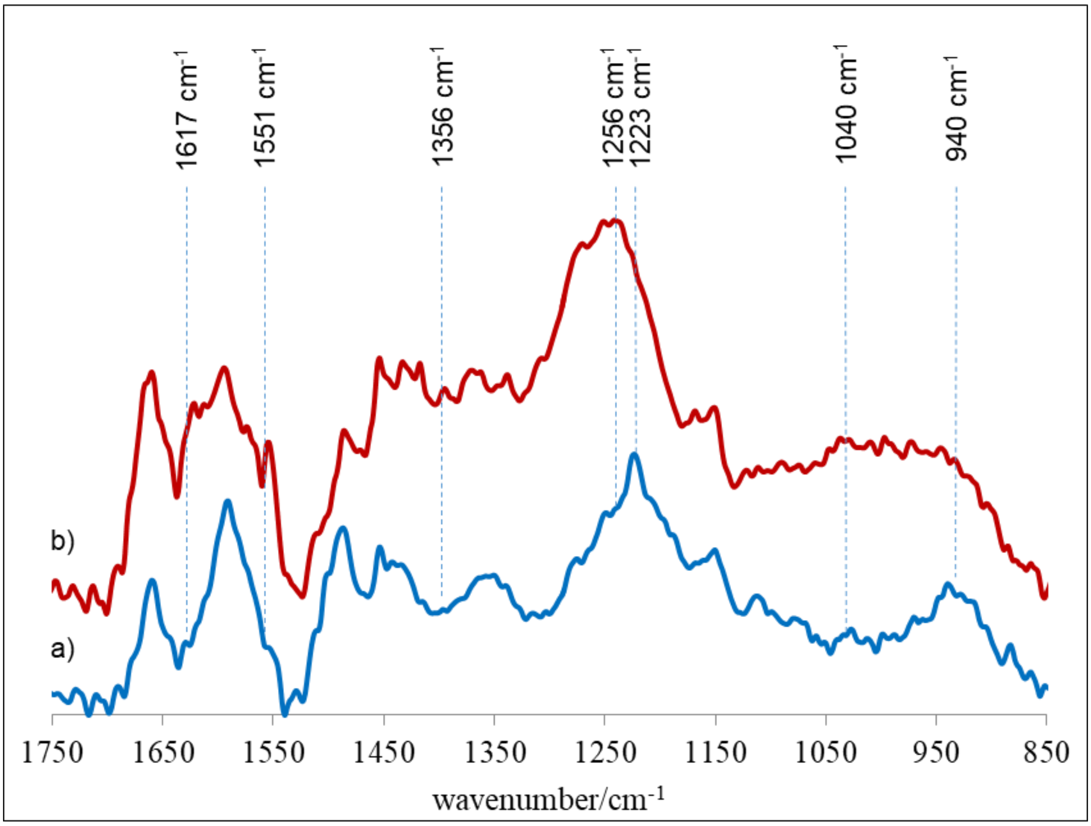


Figure 3.3. FTIR spectra of a) Bz-100APBA monomer and the b) PBz-100 polymer

Comparison of the FTIR spectra of the monomer and the polymer indicated disappearance of the characteristic peaks confirming the completion of the polymerization. The vibration modes of oxazine ring, symmetric stretching vibration peak of C-O-C of oxazine ring and di-substituted benzene ring at around 940, 1223 and 1485 cm^{-1} were disappeared, respectively (Figure 3.3). Moreover, new peaks were appeared at 1256 cm^{-1} assigned to Ar-O-C asymmetric stretching vibration, at 1551 cm^{-1} due to the presence of phenolic hydroxy groups and at 1617 cm^{-1} typical for the tri-substituted benzene ring which were also evidences for the completion of the ring-opening polymerization during curing process. In addition, the peaks at 1040 and 1356 cm^{-1} are assigned to the B-C and B-O-C stretching vibrations indicating the interactions of boronic acid functional groups.

3.1.3. Thermal Analysis

Differential scanning calorimetry (DSC) analysis is used to determine the temperature region where the exothermic peak related to ring opening polymerization of the benzoxazine monomer takes place. The disappearance of this peak indicates that the polymerization is completed. The DSC curve of the Bz-100APBA monomer (Figure 3.4) showed a weak exothermic peak starting at around 190°C and maximizing at above 234°C due to ring-opening polymerization of oxazine ring. The disappearance of this exothermic peak in the DSC curve of polybenzoxazines and polybenzoxazine composites involving variable amounts of aniline and APBA confirmed polymerization of the Bz-100APBA monomer by the applied curing program.

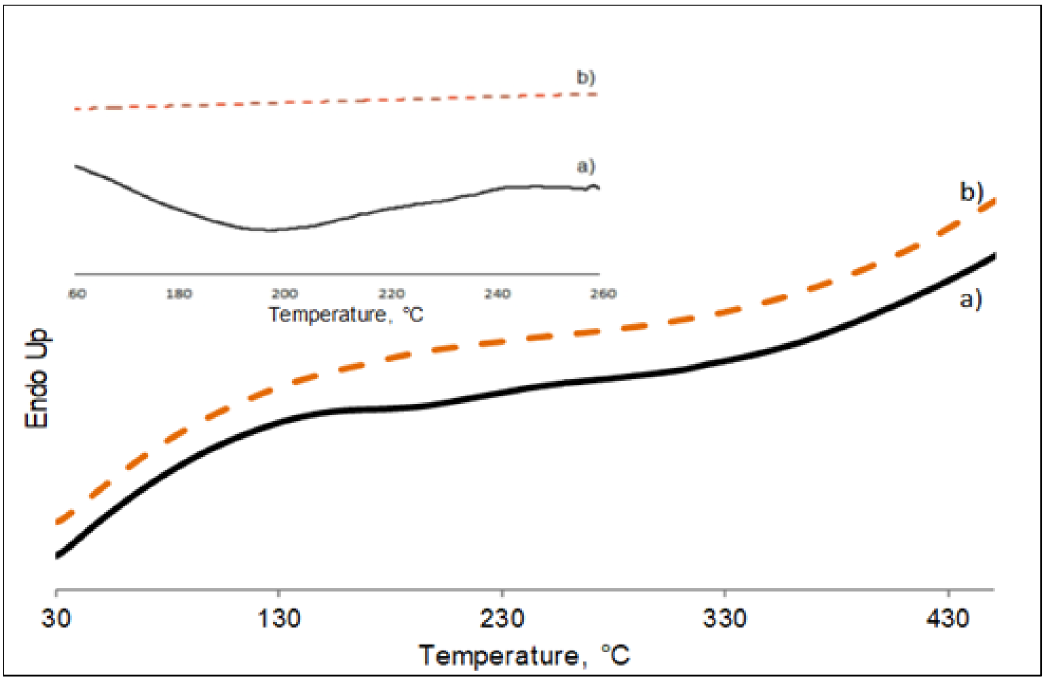
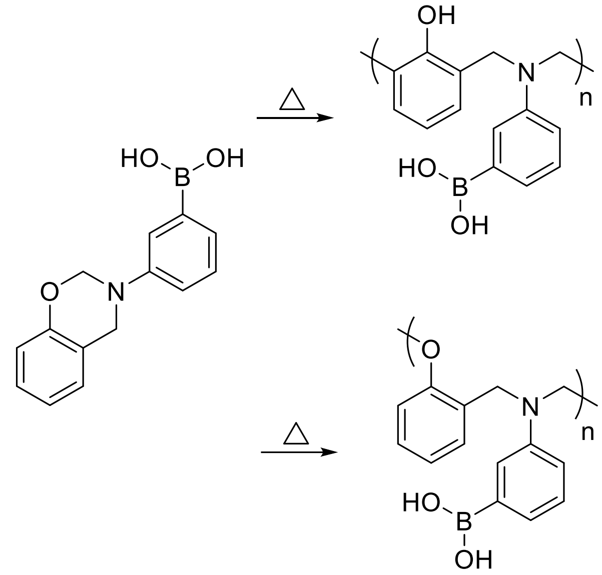


Figure 3.4. DSC curves of a) Bz-100APBA monomer and the b) PBz-100 polymer

Broad exothermic peak may be regarded as an evidence for polymerization occurring in a wide temperature region due to various polymerization pathways competing with each other during complex polymerization mechanism.

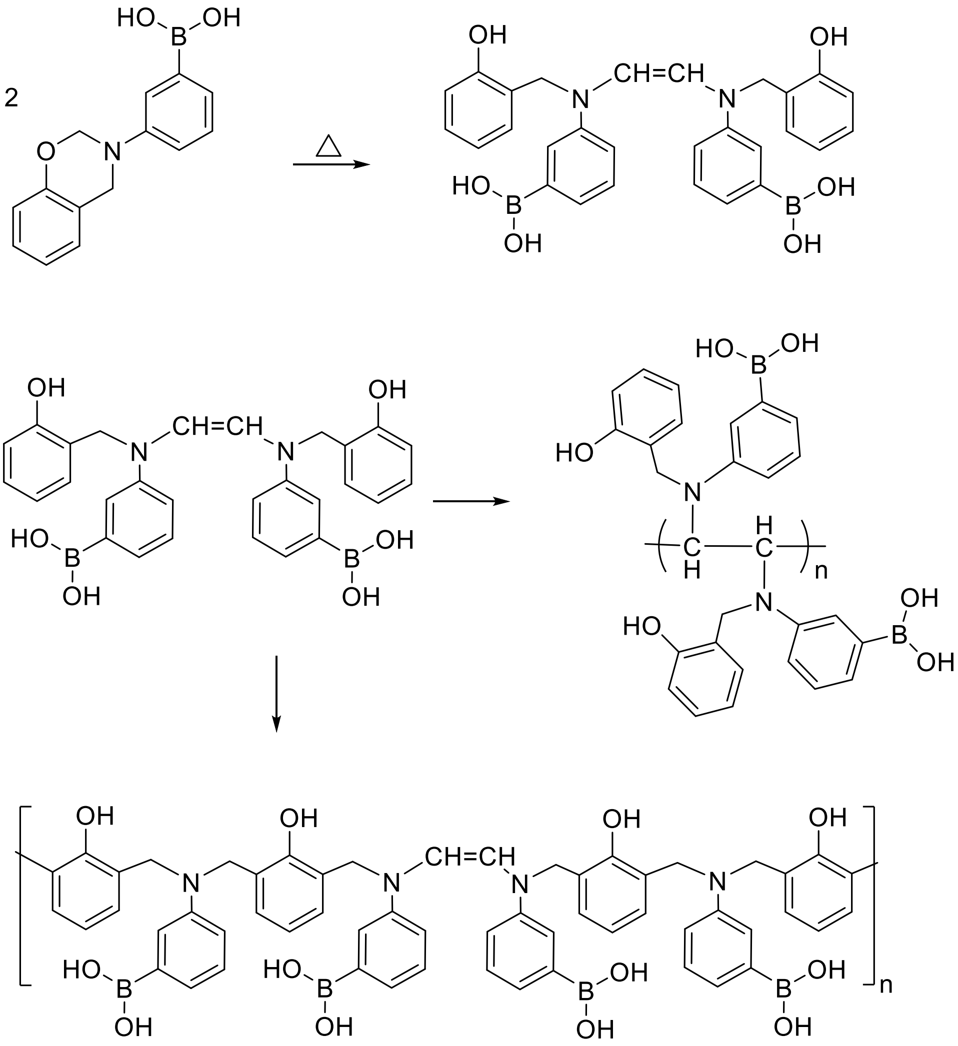
As explained before, phenolic and phenoxy types of polymerization pathways (Scheme 3.4) were expected to proceed during the curing process of Bz-100APBA monomer. The heterocyclic ring opening followed by attack of -NCH_2 groups to mainly para positions of either phenol or aniline rings may contribute to the complex polymerization mechanism of benzoxazines.



Scheme 3.4. Ring opening polymerization of Bz-100APBA

Moreover, the dimers may be produced by the coupling of -NCH_2 groups during ring opening. Benzoxazine monomers may attack to the dimers to start and propagate the polymerization. Alternatively, dimers may undergo vinyl polymerization as shown in Scheme 3.5.

Various polymer chains formed during the thermal polymerization having interactions with each other to form thermosetting network. By the addition of the boronic acid functionality, further interactions due to reactions of boronic hydroxyl groups were expected to improve the crosslinking.



Scheme 3.5. Generation and polymerization of benzoxazine dimers

Thermogravimetric analysis can be used for investigation of thermal decomposition characteristics such as thermal stability and char yield. Moreover, thermal degradation pathways and decomposition temperatures of the chains with different thermal stabilities can be determined. The TGA curves of the polymer samples involving 3-amino phenyl boronic acid (APBA) indicated again a multi-step decomposition as in the case of polybenzoxazine based on aniline, yet, the char yield was increased significantly (Figure 3.5). The temperature at which 5 wt% of the polymer decompose, T_5, was also increased when 3-amino phenyl boronic acid (APBA) was used.

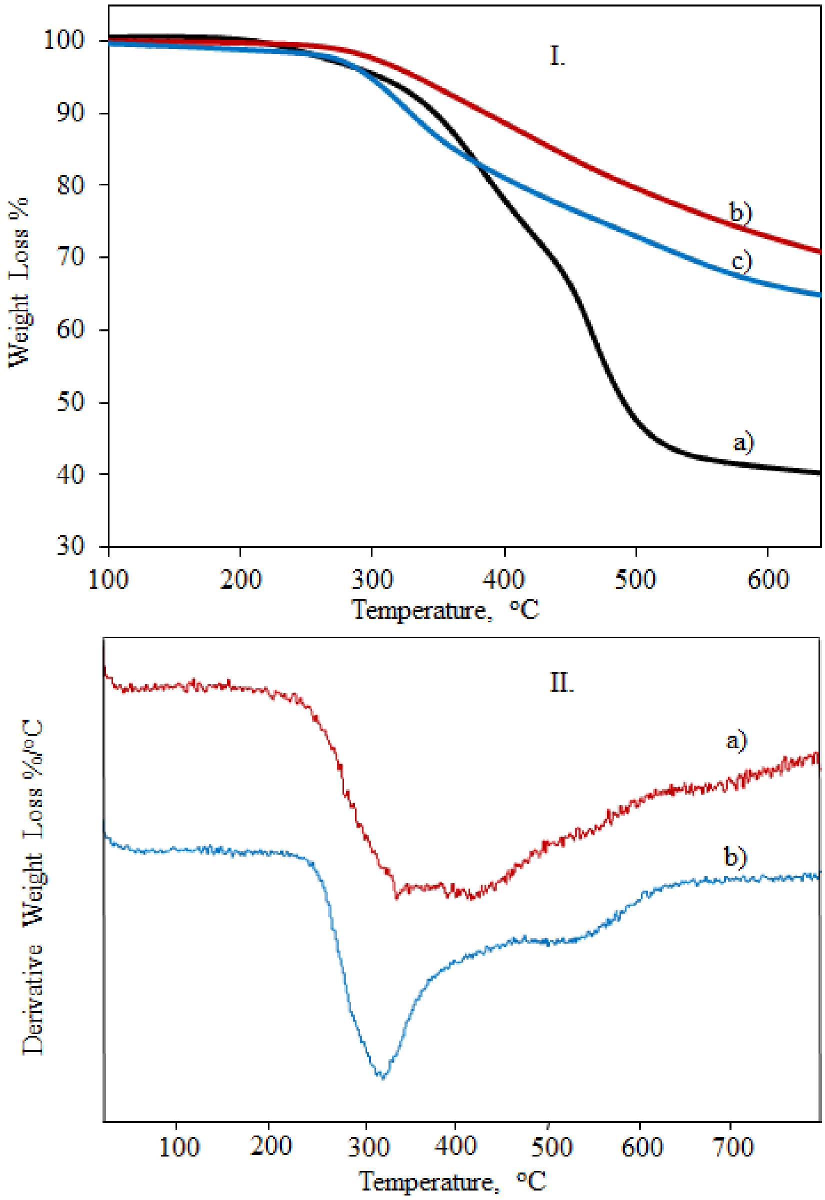


Figure 3.5. I. TGA curves of a) Bz, b) Bz-50APBA and c) Bz-100APBA monomers, II. DTA curves of a) PBz-50APBA and b) PBz-100 polymers

It was indicated that the decomposition of polybenzoxazines based on aniline mainly occurs in three steps, the first being loss of aniline, the second being degradation of the polymer backbone formed by attack of -NCH_2 groups to ortho and para positions of phenol and aniline rings and the final step being decomposition of phenolic network generated upon loss of aniline units.[20]

The use of 50 % or 100% 3-amino phenyl boronic acid increased both thermal stability and char yield significantly being more pronounced for PBz-50APBA. The char yield of PBz based on aniline was 40 % and increased to 70 and 65 % for PBz-50APBA and PBz-100APBA, respectively (Table 3.1). This behavior may be associated with condensation reactions of boronic acid groups yielding network structures. It may be thought that if the condensation reactions between B-OH groups and hydroxyl groups of benzoxazine took place, the final step of degradation related to decomposition of phenolic network should shift to higher temperatures. On the other hand, if self-condensation reactions between B-OH groups took place then the loss of aromatic amine groups should occur at lower temperatures, and thus, thermal decomposition should be initiated at lower temperatures.

Table 3.1. *T_5, Tmax and char yields of PBz, PBz-50APBA, PBz-100APBA polymers*

Sample	**T_5, °C**	**T_{max}, °C**			**char yield at 650 °C**
		Step 1	Step 2	Step 3	
PBz	306	263	389	471	40%
PBz-50APBA	333	303	452	578	70%
PBz-100APBA	298	269	441	572	65%

As there are two B-OH functional groups on each APBA molecule, the number of moles of B-OH groups is equal to the number of moles of phenolic hydroxyls for the polymer based on 50 % mixture of aniline and 3-amino phenyl boronic acid, PBz-50APBA. However, the number of moles of B-OH groups is twice of that of phenolic hydroxyls for the polybenzoxazine based only on 3-amino phenyl boronic acid, PBz-100APBA. Therefore, the probability of self-condensation reactions was increased noticeably for PBz-100APBA.

The lower thermal stability and char yield of PBz-100APBA compared to PBz-50APBA indicated that the improvement in thermal stability due to the net-work structure generated by self-condensation reactions was limited compared to the net-work structure generated by condensation reactions between boronic acid and phenolic hydroxyl groups.

The total ion current, TIC, (the variation of total ion yield as a function of temperature) curves and the pyrolysis mass spectra at the maximum of the peaks present in the TIC curves of the polybenzoxazine samples are shown in Figure 3.6. The TIC curves of the samples showed more than one peak indicating either a multi-step degradation mechanism and/or presence of chains with different thermal stabilities. The use of APBA as the aromatic amine derivative shifted both initial and final steps of thermal decomposition to higher temperatures.

The base peak in the pyrolysis mass spectra of PBz and PBz-50APBA at initial and moderate temperatures was at 93 Da that can be associated with $C_6H_5NH_2$ and C_6H_5O or C_6H_4OH. On the other hand, the base peak observed in the pyrolysis mass spectra of PBz-100APBA at initial and moderate temperatures was at 77 Da due to C_6H_5 (Figure 3.6).

Peaks at 107, 179, 193 and 207 Da were attributed to $HNC_6H_5CH_3$ or $HOC_6H_4CH_2$, $C_6H_5CHCHC_6H_4$, $C_6H_5CHCHC_6H_4CH_2$ and $C_6H_5CHCHC_6H_4CH_2CH_2$ respectively, pointing out that thermal degradation was started by loss of aromatic amine group similar to what was detected for polybenzoxazine based on phenol and aniline for which thermal decomposition was started by loss of aniline.

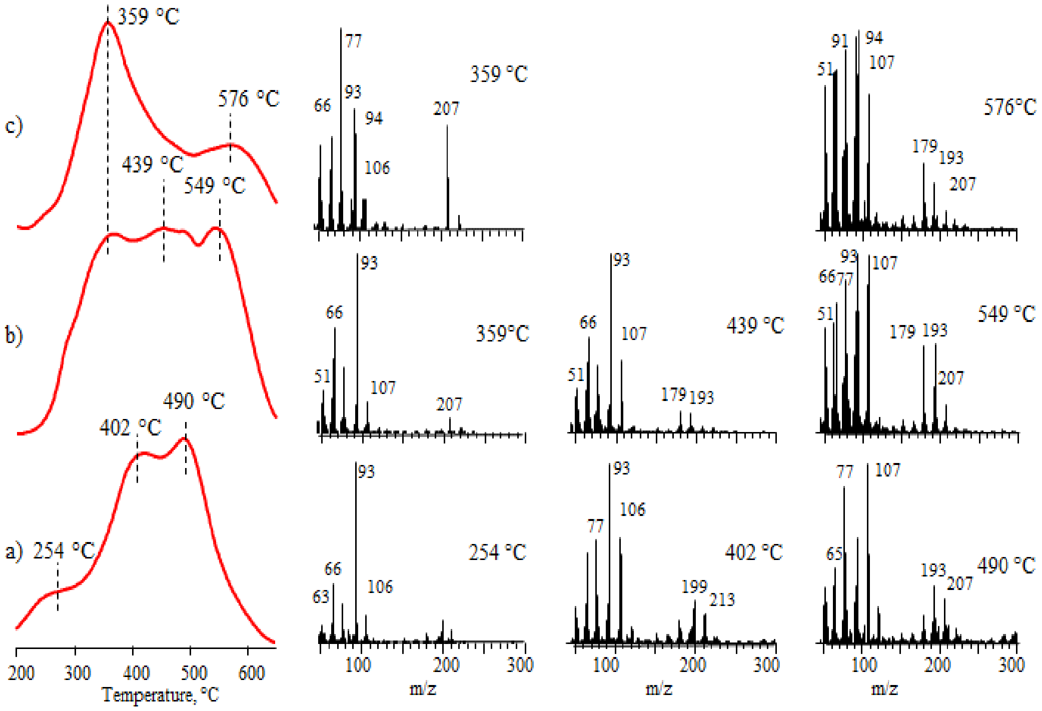


Figure 3.6. Total ion current curves and mass spectra of a) PBz, b) PBz-50PBA and c) PBz-100APBA

Single ion evolution profiles of characteristic and/or abundant products, namely $C_6H_5NH_2$ (93 Da), C_6H_5 (77 Da), C_6H_5OH (94 Da), $C_6H_5NHCH_3$ or $C_6H_4OHCH_2$ (107 Da), $C_6H_5NH_2B(OH)_2$ or $C_6H_4OHCH_2NHCH_3$ (137 Da), $C_6H_5CHCHC_6H_4CH_2$ (193 Da) and C_7H_7 (91 Da) detected during the pyrolysis of PBz, PBz-50APBA and PBz-100APBA are given in Figure 3.7. Thermal decomposition products of PBz-50APBA were detected in three regions; below 400, in the temperature region 400-500°C and above 540 °C. On the other hand, degradation of PBz-100APBA took place mainly in two regions, below 400°C and above 560°C. The loss of C_7H_7 (91 Da) fragment associated with unsaturated aromatic units, was observed at around 588 and 616°C, for PBz-50APBA and PBz-100APBA respectively, at noticeably higher temperatures than the region the same fragments lost during the pyrolysis of PBz. This behavior may be associated with crosslinking of the phenolic backbone in the presence of 3-amino phenyl boronic acid.

The relative yields of the decomposition products lost at initial stages were increased, whereas, the relative yields of the unsaturated units were decreased for PBz-100APBA compared to PBz-50APBA. The decrease in the relative yields of the unsaturated units was in accordance with the lower char yield observed for PBz-100APBA during TGA analysis. It may be thought that the condensation reactions between B-OH groups and hydroxyl groups of benzoxazine generated a crosslinked structure shifting the final stage of degradation to higher temperatures. On the other hand, self-condensation reactions resulted in cross-linking of the aromatic amine units shifting the initial step of thermal decomposition to high temperature regions (Figure 3.7). As the extent of self-condensation reactions increased, the aniline units became bulkier. As a consequence, the relative yields of the products lost at initial stages of pyrolysis also increased.

The thermogravimetric analyses of polymer samples prepared with 3-amino phenyl boronic acid pointed out significant increase in thermal stability and char compared to the polymer prepared using aniline. In addition, higher decomposition temperatures were observed for polymer samples involving 3-amino phenyl boronic acid as amine derivative. These results confirm our hypothesis on formation of cross-linked structures generated by condensation reactions of B-OH groups with hydroxyls of benzoxazines shifting decomposition of phenolic backbone to higher temperatures or self-condensation reactions of B-OH groups shifting initial step of thermal degradation to high temperatures.

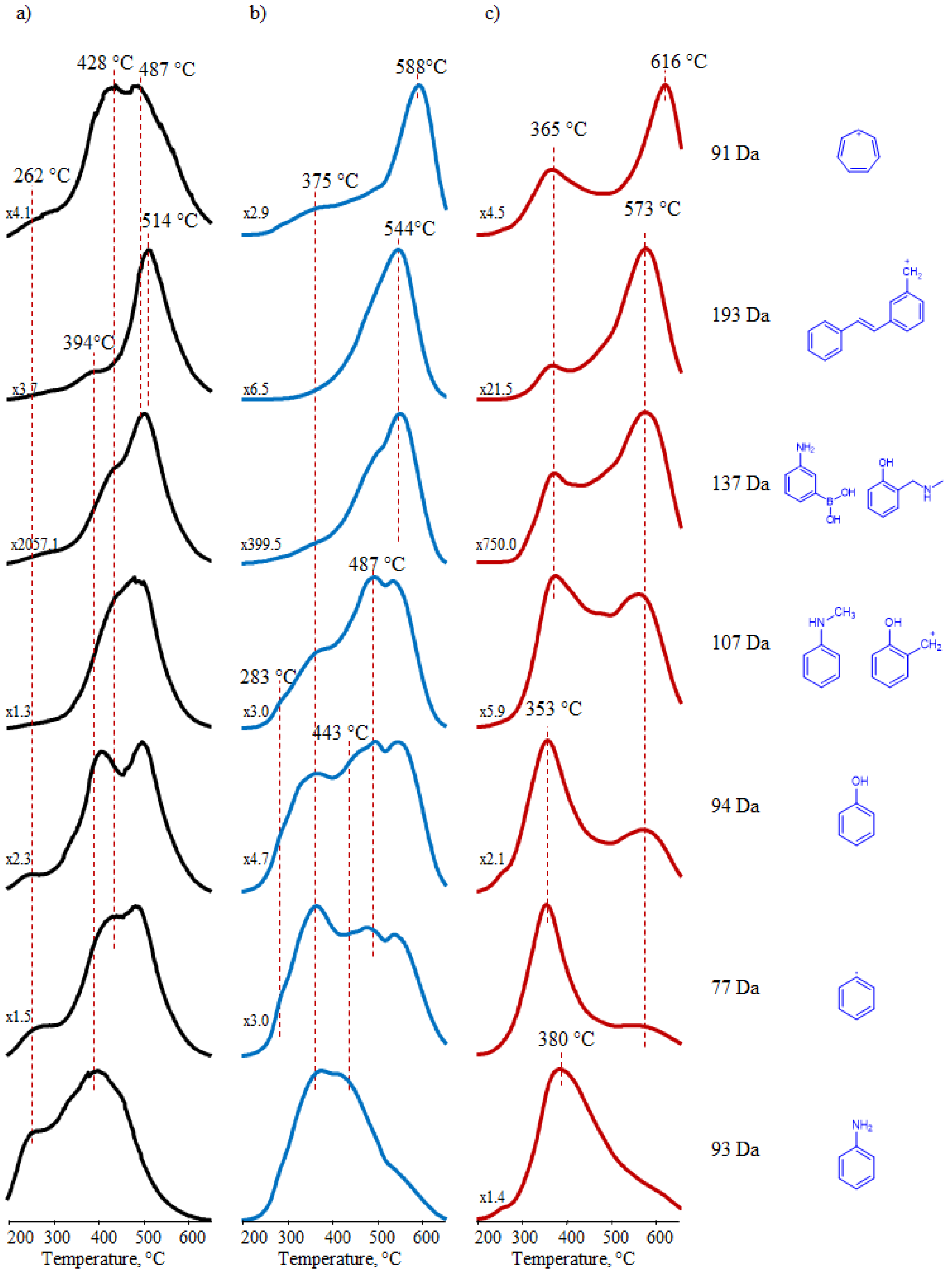


Figure 3.7. Single ion evolution profiles of a) PBz, b) PBz-50PBA and c) PBz-100APBA

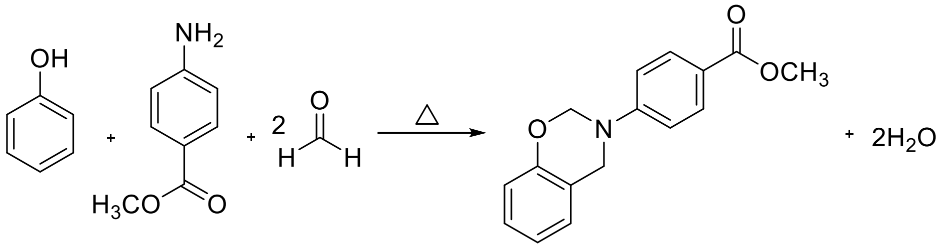
3.2. Polybenzoxazine Based on 4-aminomethylbenzoate (PPab) / Aromatic Boronic Acid Composites (BDBA, BPDBA, HPBA)

A benzoxazine monomer, (Pab), having ester functionality was synthesized using 4-aminomethyl benzoate as the amine derivative. The benzoxazine obtained was cured to obtain polybenzoxazine with highly crosslinked structure enhanced by the contribution of transesterification reactions in addition to the condensation reactions. Moreover, aromatic boronic acids were added to the reaction medium during the curing process to obtain polybenzoxazine composites with further improved crosslinking structure. Benzene-1,4-diboronic acid (BDBA), 4,4′-Biphenyldiboronic acid (BPDBA) and 3-hydroxyphenylboronic (HPBA) acid were used as the aromatic boronic acid derivatives to produce the polybenzoxazine composites with improved crosslinking and thermal properties.

It has been determined that both thermal stability and char yield were increased as the amount of boronic acid incorporated was increased. The enhanced thermal properties were related to the condensation reactions of B-OH groups of boronic acid having interacting with hydroxyl groups of polybenzoxazine and ester groups on the aniline linkages. Structural and thermal characterization of the monomers and the polymers were investigated by utilizing NMR, FTIR, DSC, TGA and DP-MS techniques.

3.2.1. Synthesis of Benzoxazine Monomer, Pab

Phenol and 4-aminomethyl benzoate were reacted in presence of formaldehyde to produce benzoxazine monomer having ester functional group via solventless method as shown Scheme 3.6.[59]



Scheme 3.6. Synthesis of benzoxazine based on phenol and 4-aminomethyl benzoate

^{1}H and ^{13}C NMR spectra of the benzoxazine monomer, Pab, are depicted in Figure 3.8. The proton NMR spectrum of the benzoxazine monomer (Pab) showed strong resonances at 3.89 ppm due to methoxy group, 4.59 and 5.39 ppm corresponding to the methylene protons (C1 and C2) of Ar-CH_2-N and O-CH_2- N of the oxazine ring, respectively.

The resonance signals obtained in ^{1}H NMR spectrum in the range of 6.88-7.08 ppm are typical for the phenyl ring. Thus, the chemical shifts at 6.83 ppm (2H, H5 and H6), 6.96 ppm (1H, H7), 7.06 ppm (2H, H10 and H14), 7.08 ppm (1H, H4) were assigned to the aromatic protons. The resonances at 49.69 ppm in the ^{13}C NMR spectrum corresponds to methoxy carbon (C1, methoxy). Signals at 51.87 (C9), 77.83 (C10), 115.85 (C6, C7), 117.24 (C13), 120.65 (C16), 121.98 (C3), 122.30 (C12), 126.88 (C15), 128.18 (C14), 131.40 (C4, C5), 151.82 (C8), 154.33 (C11) and 166.96 ppm (C2) were assigned to the resonances of the carbons indicated.

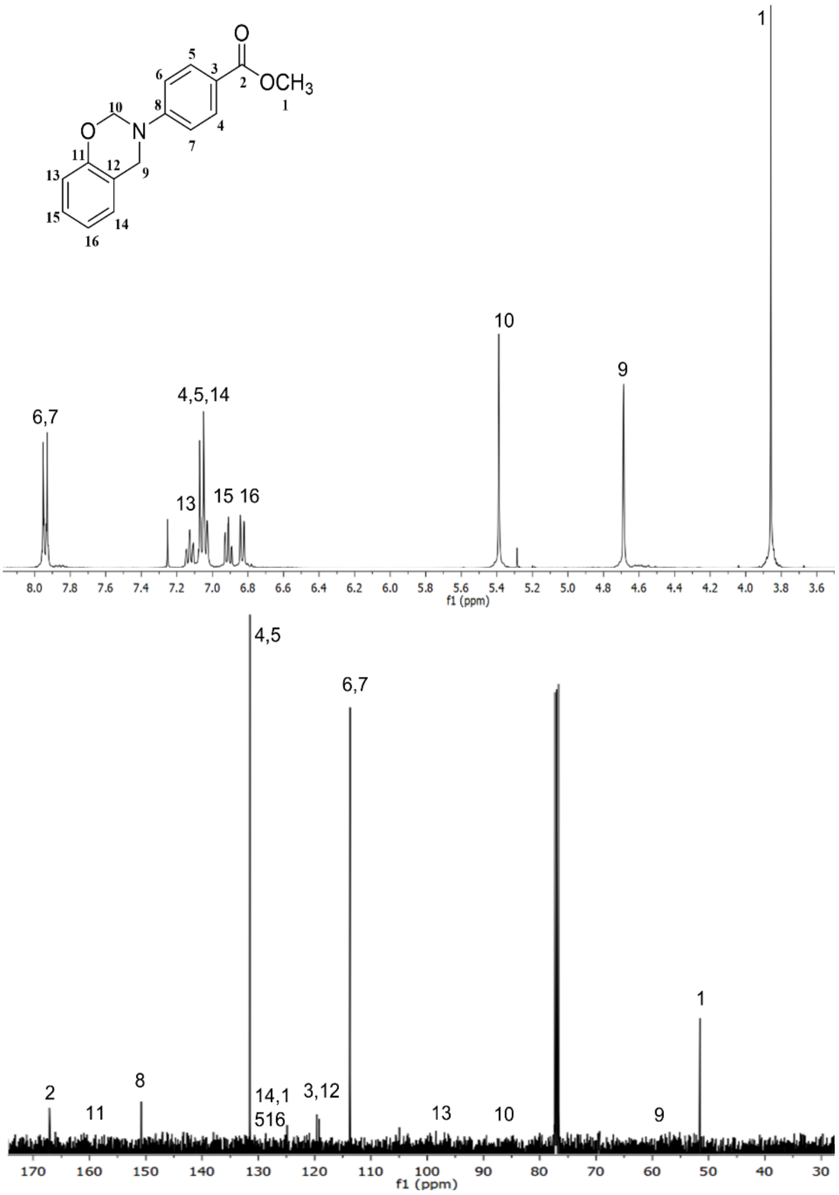


Figure 3.8. ^{1}H and ^{13}C NMR spectrum of Pab monomer

Benzoxazine monomer, Pab, was also characterized by DP-MS technique (Figure 3.9) Mass spectrum of Pab showed a peak at 269 Da corresponding to the molecular mass of the benzoxazine monomer. Also, strong peaks due to fragments $CH_2NC_6H_4COOCH_3$ (163 Da), $CH_2NC_6H_4CO$ (132 Da), NC_6H_4CO (120 Da), $OC_6H_4CH_2$ (106 Da) and the base peak at 78 Da due to C_6H_6 supported the assigned structure.

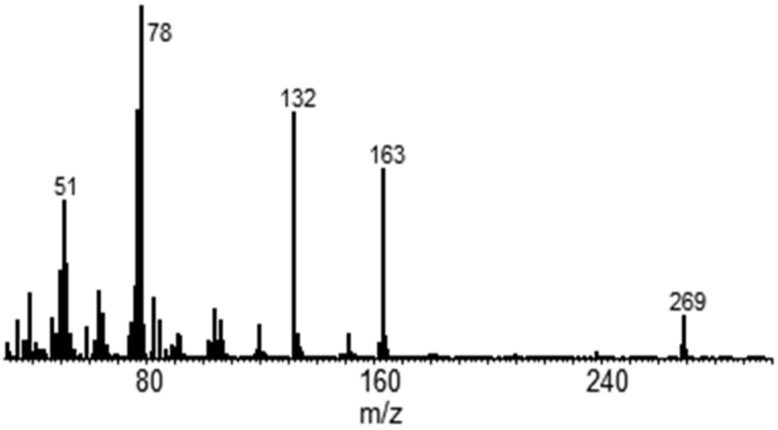
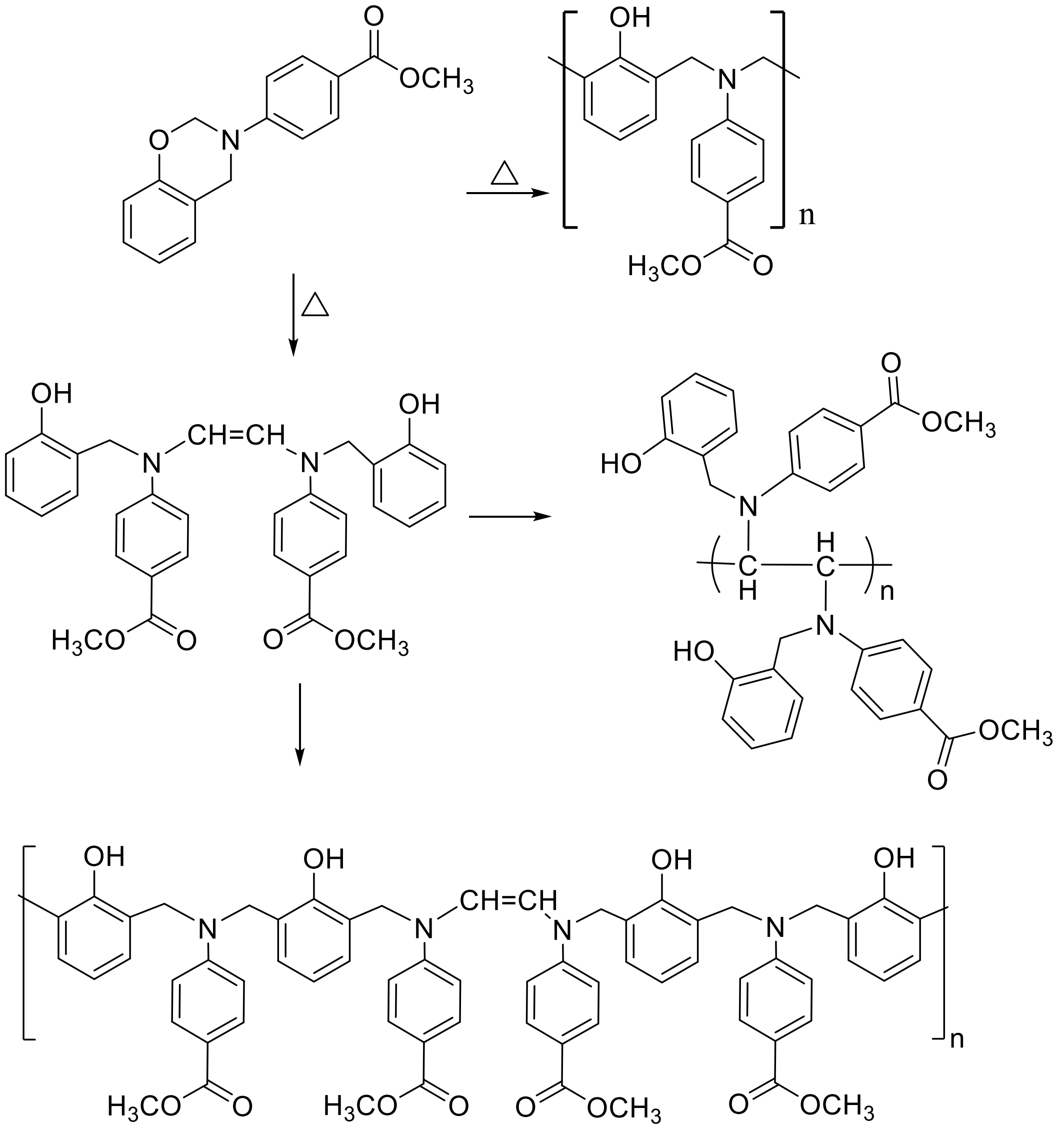


Figure 3.9. Mass spectrum of Pab monomer

3.2.2. Preparation of Polybenzoxazine, PPab

Benzoxazine monomer, Pab, based on phenol and 4-aminomethyl benzoate was polymerized by step-wise curing using the selected temperature program (at 150, 175 and 200 °C for 1 h each in a vented oven) yielding highest thermal stability and char yield among the several two step and three step programs tested. Polymerization process may follow various reaction pathways (Scheme 3.7) resulting in different polymer chains with benzoxazine body.



Scheme 3.7. Polymerization pathways of Pab monomer

The aromatic C-H in plane bending and out-of-plane deformation modes of benzene and its derivatives are observed in the region 1250-1050 and 900-700 cm^{-1} regions respectively. The asymmetric and symmetric stretching vibrations of C–N–C located at 1120 cm^{-1}, the characteristic mode of benzene with an attached oxazine ring appeared at 936 cm^{-1}, the symmetric and asymmetric stretching vibrations of C–O–C were obtained around 1030 and 1220 cm^{-1} and the peak corresponding to the ortho substituted benzene ring are detected around 1572 cm^{-1}.

In Figure 3.10, the FTIR spectra of the monomer (Pab) and the polymer (PPab) are given. The disappearances of the peaks around 936, 1175 and 1220 cm^{-1} due to characteristic mode of benzene with an attached oxazine ring, the stretching vibrations of C-N and C-O bonds respectively (Figure 3.10). Appearance of peaks at 1273 and 1572 cm^{-1} pointed out presence of phenolic hydroxyl groups and tri-substituted benzene ring confirming the completion of oxazine ring-opening reaction during curing at this stage.

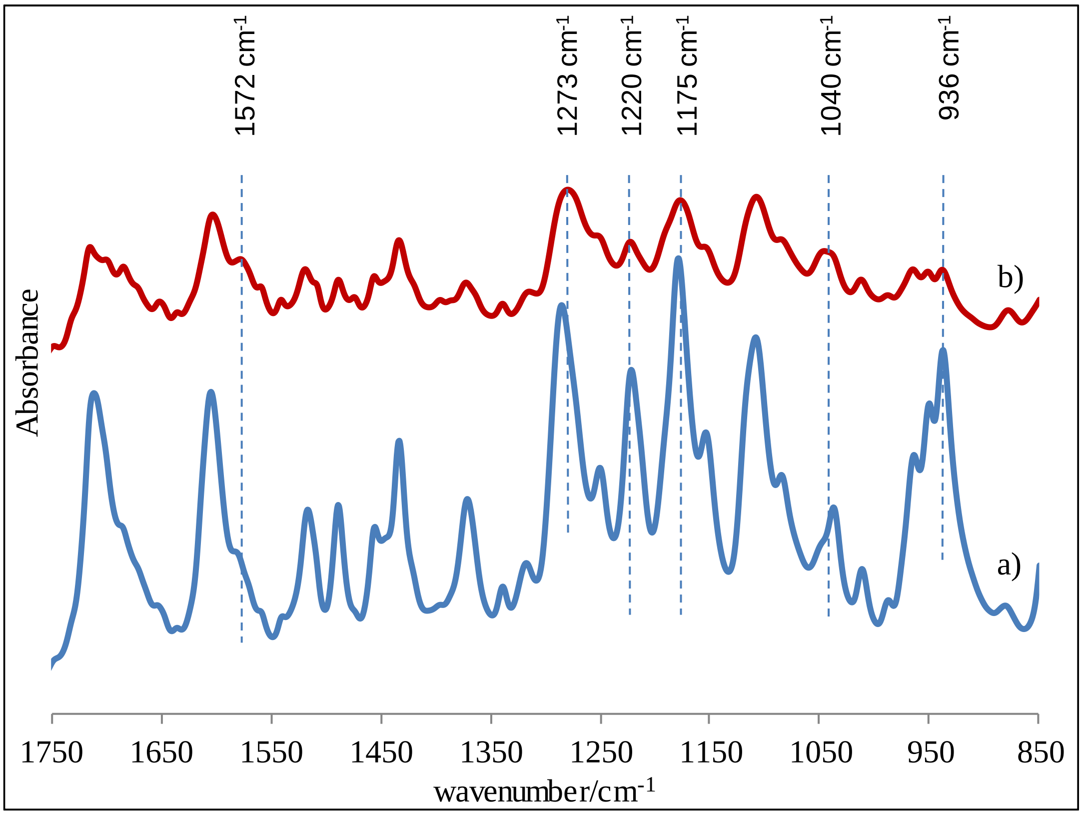


Figure 3.10. FTIR spectra of a) Pab monomer and b) PPab polymer

Ring opening polymerization of benzoxazine monomer, Pab, was also confirmed by the DSC analysis. The exothermic ring opening polymerization peak at about 240°C in the DSC curve of Pab monomer was disappeared in the DSC curves of the polymer, shown in Figure 3.11, which is another evidence for the completion of the polymerization by the applied curing program.

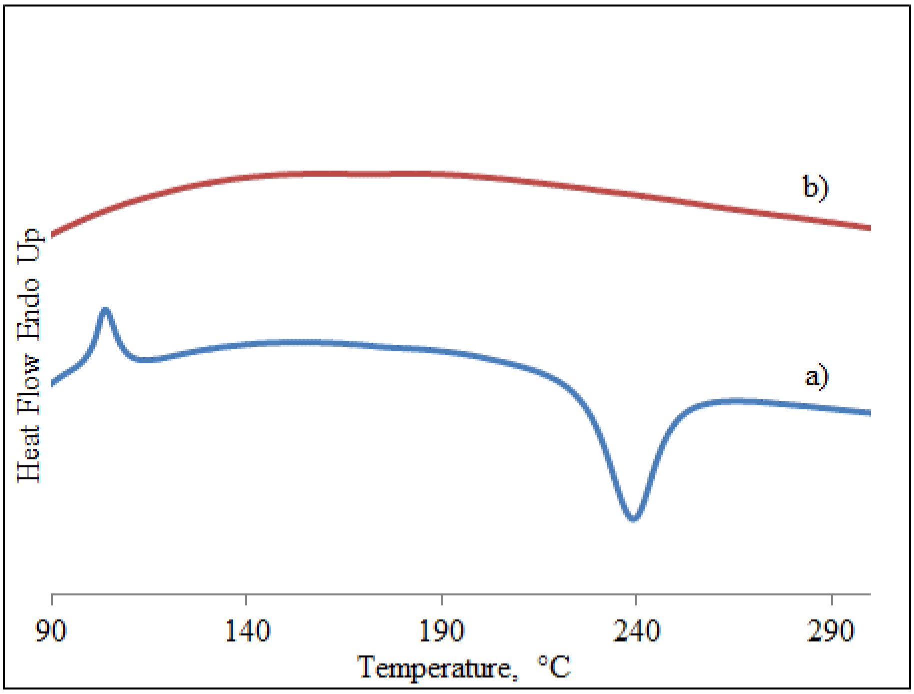
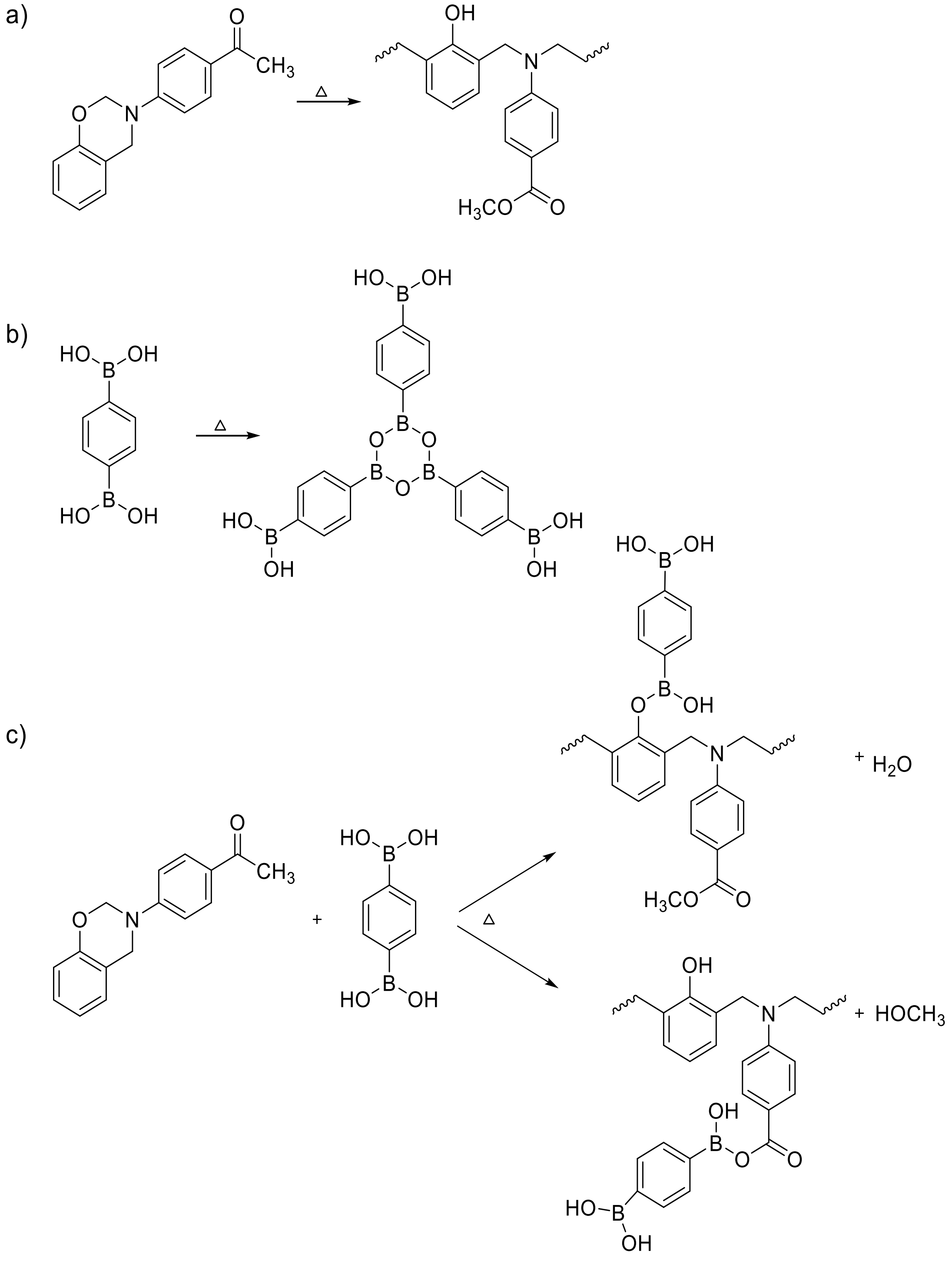


Figure 3.11. DSC spectra of a) Pab monomer and b) PPab polymer

3.2.3. PPab/BDBA Polybenzoxazine Composites

Different amounts of benzene-1,4-diboronic acid (BDBA) was mixed with benzoxazine monomer (Pab) and cured together to obtain PPab/HPBA polybenzoxazine composites with improved thermal properties. It was aimed to obtain enhanced cross-linked network structure due to condensation reactions between hydroxyl groups on diboronic acid and hydroxyl groups on polybenzoxazine and/or ester groups on the aniline linkages. FTIR, DSC, TGA and DP-MS techniques were applied for the characterization of the polybenzoxazine composites. Possible reactions of Pab monomer and BDBA are shown in Scheme 3.8.



Scheme 3.8. Interactions during curing process of PPab/BDBA composites

3.2.3.1. Preparation and Characterization of PPab/BDBA Composites

Mixtures involving benzoxazine monomer and 5, 10, and 15 wt% BDBA in 5 ml of chloroform were cast on glass plate. The films obtained after drying under vacuum, were cured step-wise at 150, 175 and 200 °C for 1 h each in a vented oven. Transparent reddish brown polybenzoxazine/BDBA composites (PPab/5BDBA, PPab/10BDBA and PPab/15BDBA) were obtained.[59]

FTIR analyses were employed for the characterization of PPab/BDBA composites. FTIR spectra of Pab monomer, PPab polymer and PPab/15BDBA polymer composite are shown in Figure 3.12. Characteristic peaks of oxazine ring obtained at 936, 1173 and 1220 cm^{-1} were disappeared in FTIR spectra of PPab and PPab/BDBA composite supporting the ring opening polymerization process was ended.

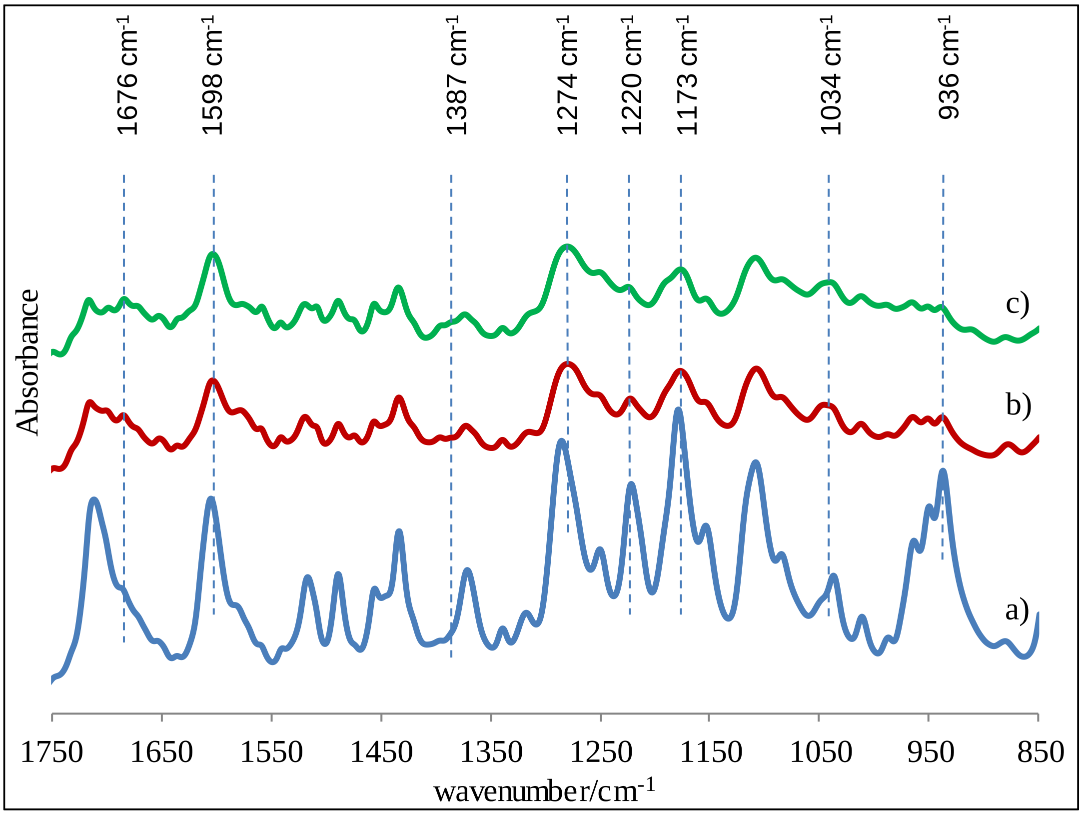


Figure 3.12. FTIR spectra of a) Pab monomer, b) PPab polymer and c) PPab/15BDBA composite

Appearance of peaks at 1274 and 1598 cm^{-1} pointed out presence of phenolic hydroxyl groups and tri-substituted benzene ring respectively also confirming the completion of oxazine ring-opening reaction during curing at this stage. Strong bands in the FTIR spectrum of PPab/BDBA composite at around 1676, 1387 and 1034 cm^{-1} were observed due to B-O-H, B-O-C and B-C stretching vibrations of the composite network structure obtained by the condensation and transesterification reactions between hydroxy groups of BDBA and hydroxy and/or ester groups of Pab during curing.

3.2.3.2. Thermal Analysis of PPab/BDBA Composites

DSC curves of the prepared PPab/BDBA composites are given in Figure 3.13. The exothermic ring opening polymerization peak at about 240 °C in DSC curve of Pab monomer was disappeared in the DSC curves of the polymer and its composites involving 5, 10 and 15 wt% BDBA confirming the polymerization of the samples by the applied curing program. The disappearance of the endothermic boiling point peak of BDBA in the DSC curves of the samples involving BDBA can be regarded as an evidence for interactions of BDBA with hydroxyl and/or ester groups present in the structure.

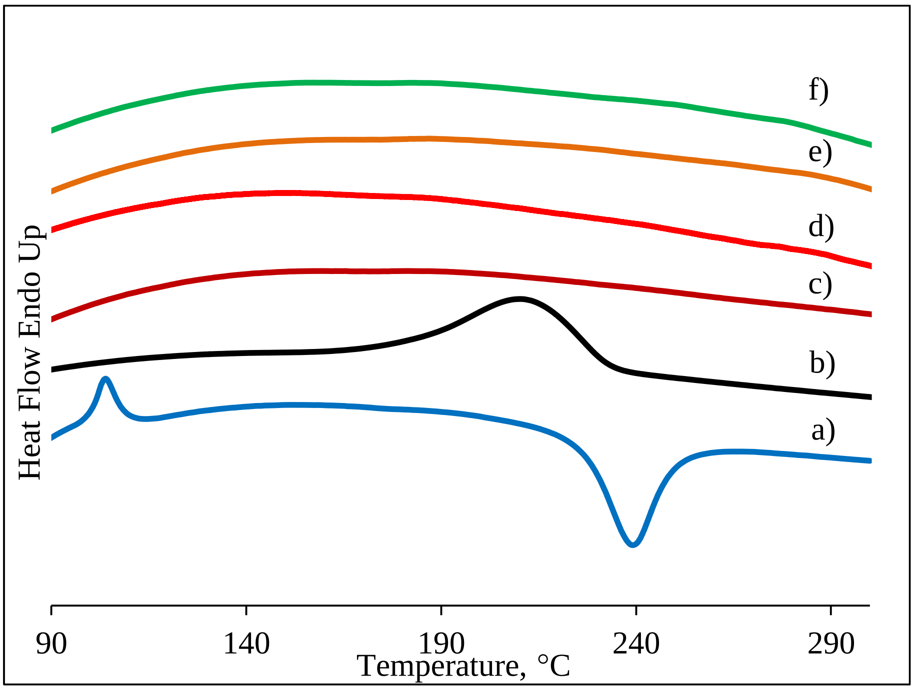


Figure 3.13. DSC curves of a) Pab monomer, b) BDBA, c) PPab polymer, d) PPab/5BDBA, e) PPab/10BDBA and f) 15BDBA

The TGA curve of PPab, depicted in Figure 3.14, revealed a multi-step decomposition. The first step in the TGA curve of BDBA was associated with evaporation of BDBA. The second step at relatively high temperatures was associated with degradation of boroxine net-work generated during the heating process. These steps cannot be differentiated in the TGA curves of the composites involving BDBA and again considered as evidence for the interactions of BDBA with hydroxyl and/or ester groups present in the structure.

The increase in the char yield of polymer composites was directly proportional to the amount of BDBA introduced. However, when the amount of BDBA in the composite exceeded 10wt%, TGA curve showed deviation from linearity at low temperatures. This behavior can be explained by the evaporation of excess BDBA unused in the condensation and transesterification reactions.

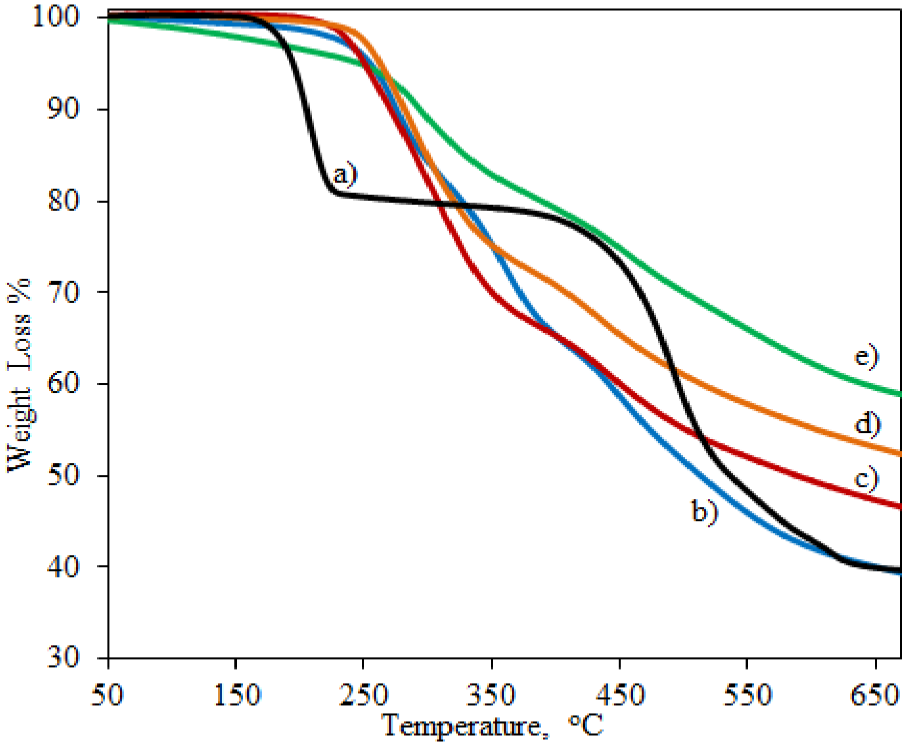


Figure 3.14. TGA curves of a) BDBA, b) PPab polymer, c) PPab/5BDBA, d) PPab/10BDBA and e) 15BDBA

No noticeable improvement was recorded for the thermal stability and char yield of PPab when compared to those of polybenzoxazine based on phenol and aniline, PBz. T_5 and char yield of PPab were 255 °C and 40%. The corresponding values were 306 °C and 40.1% for PBz. This behavior may be explained by having ester group in the para position of aniline blocking the chain growing even if ester groups contribute to the crosslinking.

More significant increase in the char yields was detected with PPab/BDBA composites compared to the PBz/BDBA composites with same amounts of additives. Char yields of composites involving 5, 10 and 15% BDBA were 45, 51 and 58%, respectively. Thus, it may be concluded that the improvement in thermal characteristics of the composites based on 4-aminobenzoate were more significant compared to the ones based on aniline confirming the enhanced crosslinking by the interactions of B-OH and ester groups.

Table 3.2. T_5, Tmax and char yields of PPab, PPab/5BDBA, PPab/10BDBA and PPab/15BDBA

Sample	**T_5, °C**	**T_{max1}, °C**	**T_{max2}, °C**	**T_{max3}, °C**	**Char Yield at 650 °C**
PPab	255	249	345	435	40%
PPab/5BDBA	251	231	-	437	45%
PPab/10BDBA	263	242	-	434	51%
PPab/15BDBA	247	271	-	423	58%

The total ion current, TIC, curves and the pyrolysis mass spectra at the maximum of the peaks present in the TIC curves of the PPab polybenzoxazine and PPab/BDBA composites are given in Figure 3.15. The TIC curves of all the samples showed more than one peak indicating either a multi-step degradation mechanism and/or presence of chains with different thermal stabilities.

The TIC curve of PPab showed an intense peak at around 264 °C and broad overlapping peaks with maxima at around 365 and 479 °C. The base peak at 120 Da was readily associated with $H_2NC_6H_4CO$ and other intense peaks obtained at 151, 92 and 65 Da were attributed to $H_2NC_6H_4COOCH_3$, $H_2NC_6H_4$ and C_5H_5, respectively. Generation of these peaks points out that thermal degradation was started by the loss of 4-amino benzoate. This behavior was similar to what was detected for polybenzoxazine based on phenol and aniline, PBz, for which thermal decomposition was started by loss of aniline.[20] In addition, peaks indicating elimination of phenol and unsaturated hydrocarbons were mainly detected at elevated temperatures again as in case of PBz.

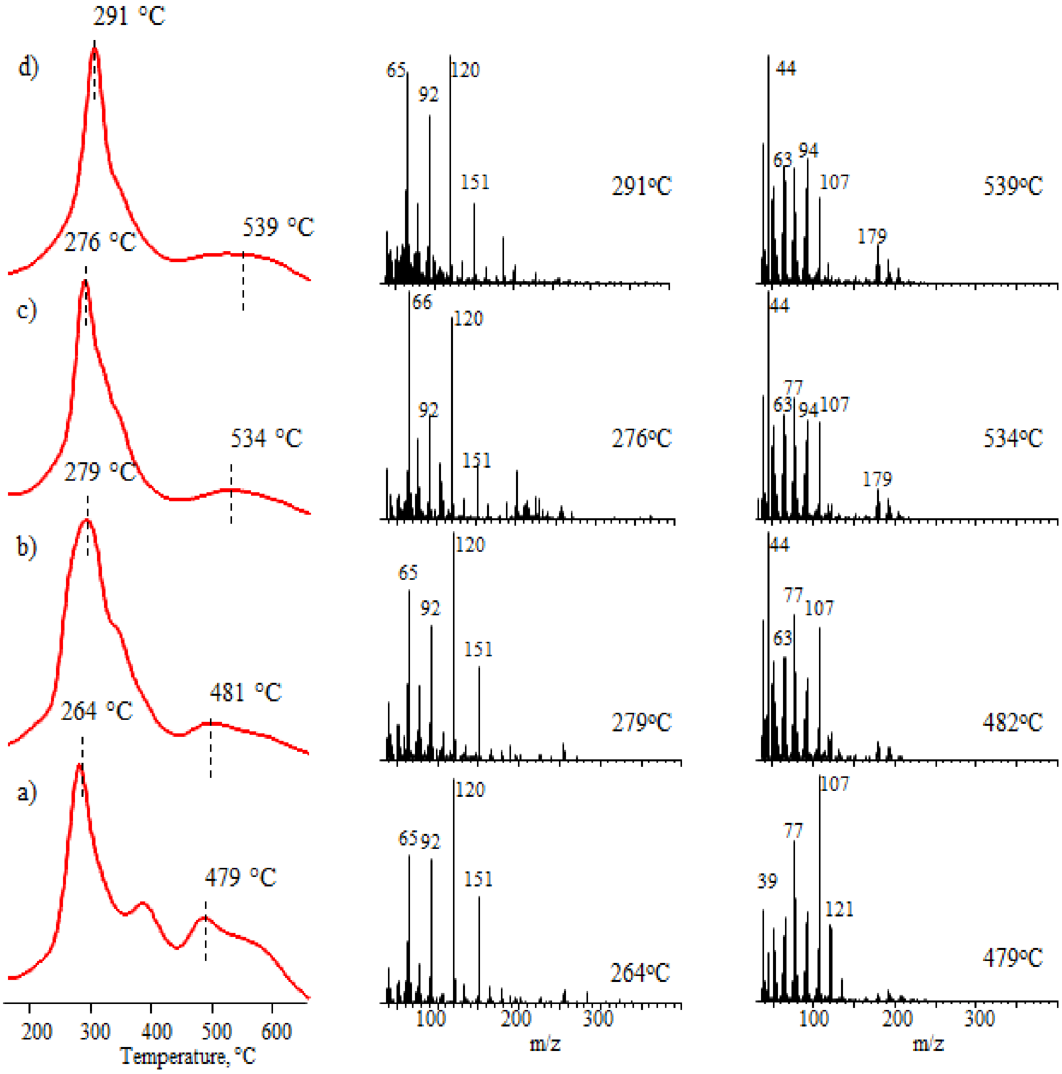


Figure 3.15. Total ion current curves and mass spectra of a) PPab, b) PPab/5BDBA, c) PPab/10BDBA and d) PPab/15BDBA

Upon addition of BDBA, the low temperature peak in the TIC curve of polybenzoxazine was slightly shifted to high temperature region and the peak at around 365 °C was almost totally disappeared. In our previous studies, decompositions of units formed by attack of -NCH_2 groups to ortho and para positions of phenol and aniline rings were detected at moderate temperatures. It may be thought that the interaction of BDBA with benzoate units inhibited attack of -NCH_2 groups to ortho and para positions of aniline ring due to steric hindrance.

The mass spectra recorded at peak maxima also showed some differences. The relative intensities of the peaks at m/z 107 and 121 Da associated with $HOC_6H_4CH_2$ and HOC_6H_4CHNH fragments respectively were decreased noticeably, while those at 32, 44 and 179 Da attributed to CH_3OH, BO_2H and $C_6H_4CHNC_6H_4$ and/or $C_6H_5C_2H_2C_6H_4$ were increased significantly. In addition, new peaks indicating generation of boroxine network and units due to interactions of hydroxyl groups of BDBA with ester groups present in benzoxazine were detected.

Single ion evolution profiles of characteristic fragments of polybenzoxazine, namely, $H_2NC_6H_4CO$ (120 Da), $CH_3OCOC6H_3(NH_2)CH{=}NC_6H_4COOCH_3$ (312 Da), monomer (269 Da), $CH_3NHC_6H_4COOCH_3$ (165 Da), C_6H_5OH (94 Da) and C_7H_7 (91 Da) are shown in Figure 3.16. Among these, 165 and 312 Da fragments may also be associated with $HOBOC_6H_4B(OH)_2$ and $(C_6H_5BO)_3$ respectively. Significant increases in their abundances with the increase in the amount of BDBA (mixed with the monomer just before curing) supported these assignments. In addition, 269 Da fragment, may also be attributed to $OBOCOC_6H_4NHCH_2C_6H_4OH$ fragment, that may be generated by trans-esterification reactions between hydroxyl groups of BDBA and ester groups present in the structure of polybenzoxazine.

On the other hand, 370 Da fragment detected upon addition of BDBA may be associated with $BC_6H_4B(OH)OCOC_6H_4N(CH_2)CH_2C_6H_4OH$ in accordance with the proposed trans-esterification reaction. Significant increase in the relative abundance of CH_3OH (32 Da) supported this proposal.

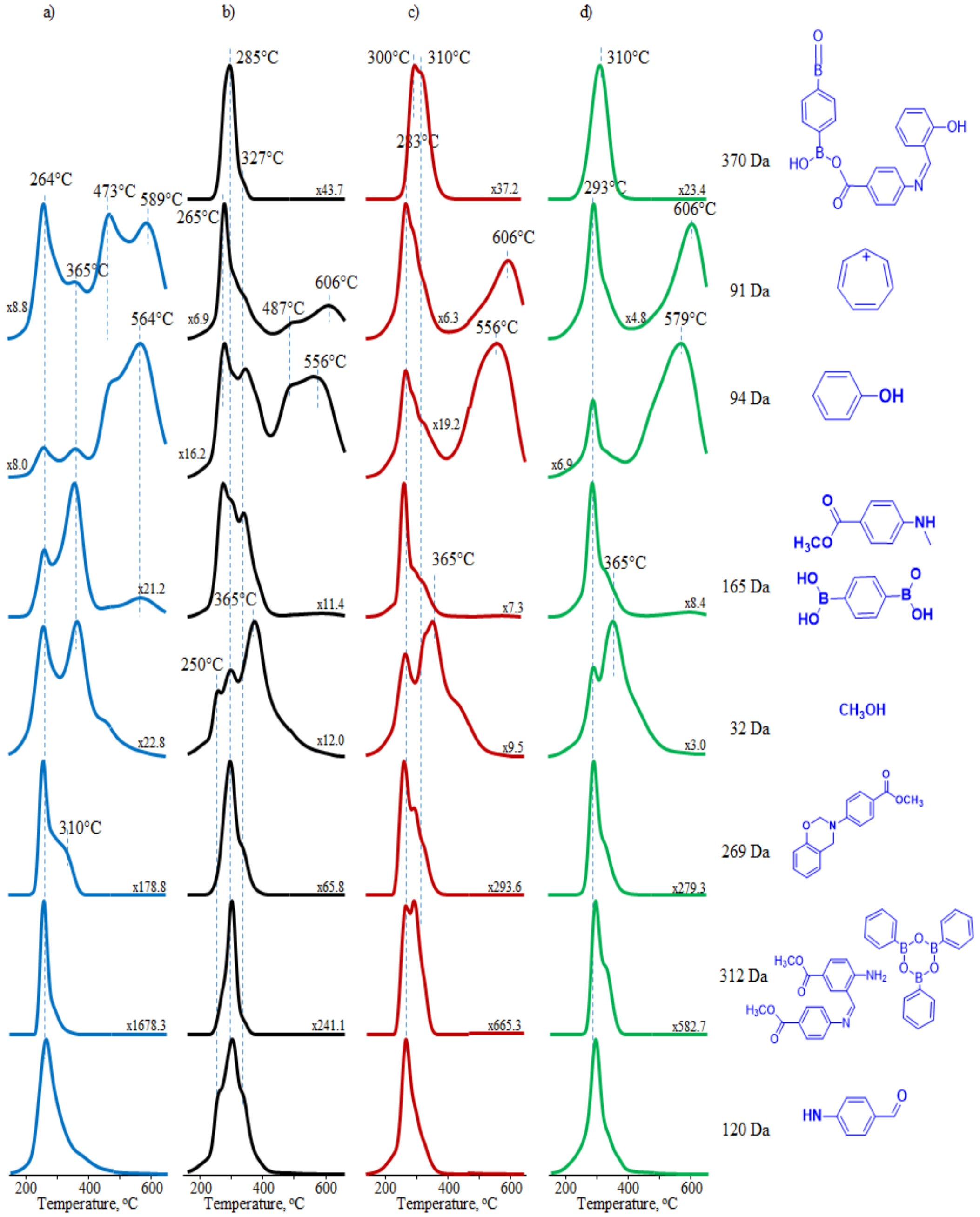


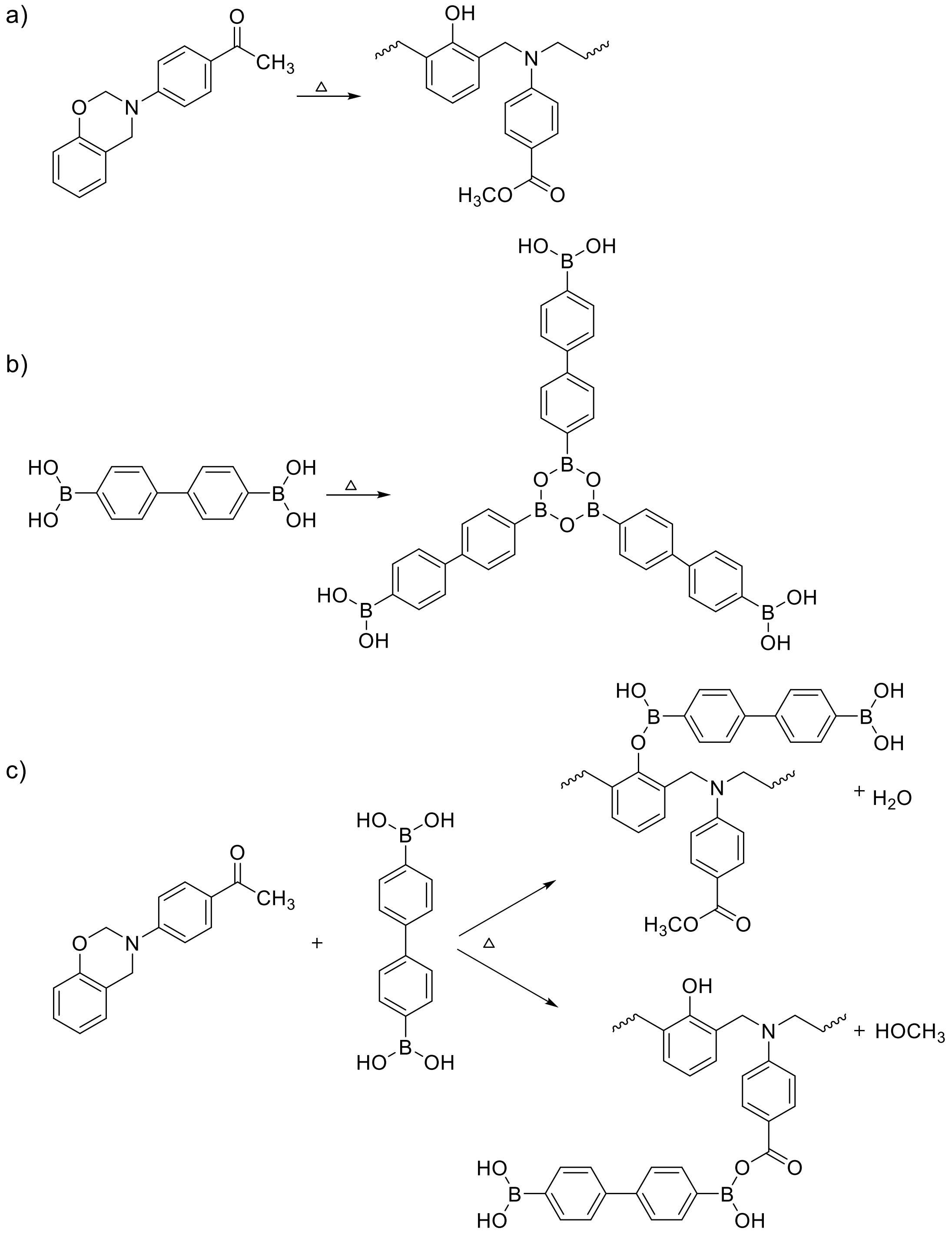
Figure 3.16. Single ion evolution profiles of a) PPab, b) PPab/5BDBA, c) PPab/10BDBA and d) PPab/15BDBA

It is clear that thermal decomposition of PPab and its composites involving BDBA started again by loss of aromatic amine group. Yet, its elimination was shifted to high temperature regions as the amount of BDBA was increased. It may be thought that the interactions of BDBA with ester groups of aromatic amines not only inhibited attack of NCH_2 groups to aniline groups but also caused retardation of their elimination during pyrolysis. It may further be proposed that upon loss of aromatic amine groups, coupling of radicals generated thermally more stable unsaturated and crosslinked chains and higher char yield.

Polybenzoxazines based on phenol and 4-amino benzoate, PPab, and its composites involving various amounts of 1,4-benzenediboronic acid, BDBA, were prepared and characterized.[59] Direct pyrolysis mass spectrometry analyses revealed a complex degradation mechanism starting by loss of 4-aminobenzoate groups. Incorporation of BDBA shifted initial step of thermal degradation to higher temperatures. Elimination of BDBA in the temperature region where 4-aminobenzoate groups lost and generation of fragments that may be associated with units involving PPab and BDBA confirmed the interaction of BDBA mainly with OCH groups of the monomer. Loss of boroxine again in the same temperature region pointed out generation of boron network linked to aromatic amines. As the amount of BDBA, increased the thermal stability and the relative yields of unsaturated units increased.

3.2.4. PPab/BPDBA Polybenzoxazine Composites

4,4′-Biphenyldiboronic acid (BPDBA) was also mixed and cured with benzoxazine monomer, Pab, in order to obtain polybenzoxazines showing further improved thermal stability and char yield due to formed linkages with biphenyl body as a result of condensation and transesterification interactions between functional groups of Pab monomer and BPDBA. FTIR, DSC, TGA and DP-MS analyses were applied for characterization of the polybenzoxazine composites. Possible interactions of PPab and BPDBA are depicted in Scheme 3.9.



Scheme 3.9. Interactions during curing process of PPab/BPDBA composites

3.2.4.1. Preparation and Characterization of PPab/BPDBA Composites

Benzoxazine monomer, Pab, was dissolved in 5 ml of chloroform and BPDBA was added to the mixture to prepare 5, 10, and 15 wt% BPDBA including samples. The mixture was poured on a glass plate and dried under reduced pressure. Step-wise curing program was applied by heating 1 h at each temperature of 150, 175 and 200 °C in vented oven. Brown polybenzoxazine/BDBA composites (PPab/5BPDBA, PPab/10BPDBA and PPab/15BPDBA) were obtained.

FTIR analyses were performed for characterization of the Pab/BPDBA composites. FTIR spectra of Pab monomer, PPab polymer and PPab/15BPDBA polymer composite are given in Figure 3.17.

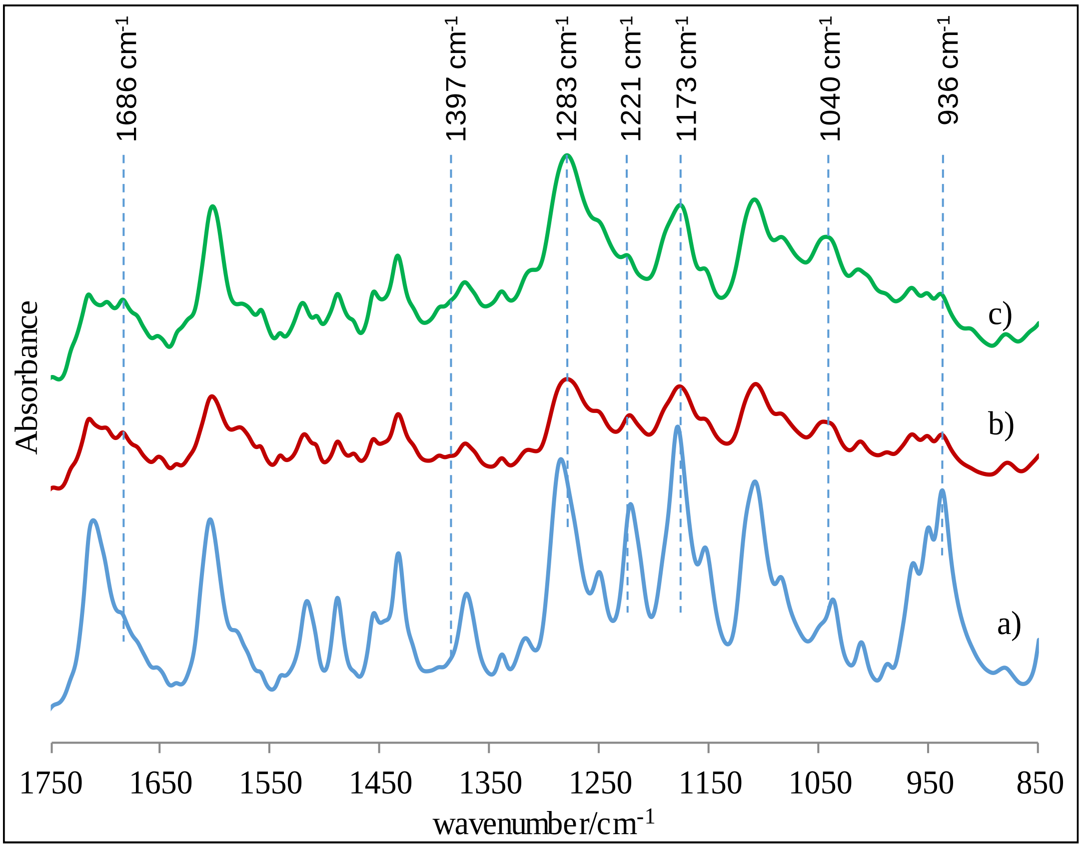


Figure 3.17. FTIR spectra of a) Pab monomer, b) PPab polymer and c) PPab/15BPDBA composite

In addition to the characteristic peaks mentioned previously, due to polybenzoxazine body, strong bands at around 1686, 1397 and 1040 cm^{-1} corresponding to the B-O-H, B-O-C and B-C stretching vibrations were detected. Presence of these peaks confirm the network structure obtained by the condensation and transesterification reactions yielding cross-linkages between functional groups of PPab and BPDBA during polymerization.

3.2.4.2. Thermal Analysis of PPAB/BPDBA Composites

As in the case of PPab/BDBA composites, the exothermic peak corresponding to the ring opening polymerization process at about 240 °C in DSC curve, shown in Figure 3.18, of Pab monomer was disappeared confirming the curing process is completed for all PPab/BPDBA samples (5, 10 and 15 wt% BPDBA).

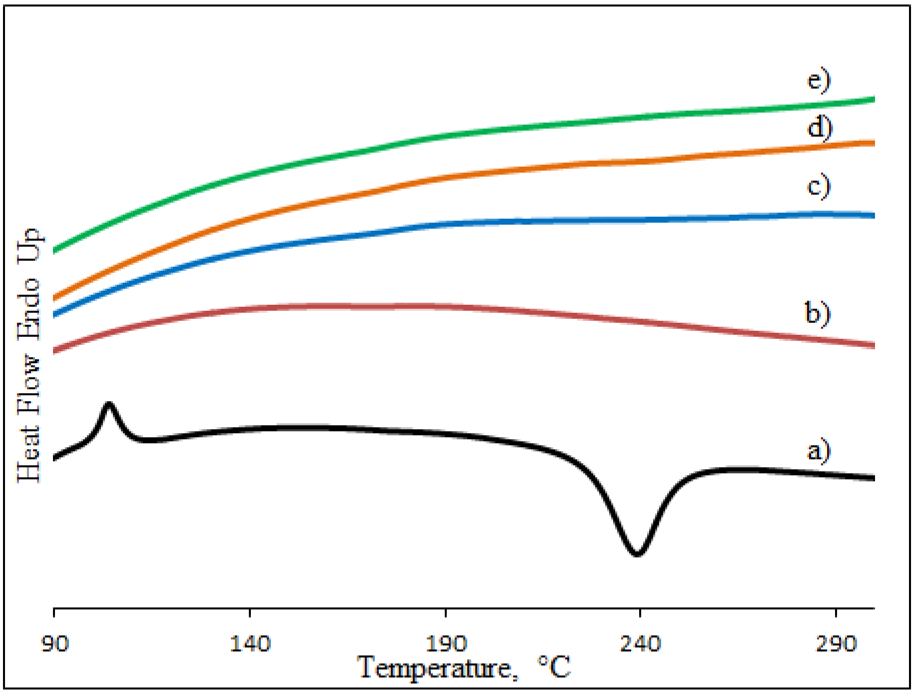


Figure 3.18. DSC curves of a) Pab monomer, b) PPab polymer, c) PPab/5BPDBA, d) PPab/10BPDBA and f) PPab/15BPDBA

The TGA curve of PPab and PPab/BPDBA composites (Figure 3.19) showed a multi-step decomposition due to a complex degradation mechanism. Char yield and thermal stabilities of the prepared PPab/BPDBA composites showed further improvement compared to PPab/BDBA composites confirming the effect of formation of cross-linkages with biphenyl body.

Char yield of the polymer composites was directly proportional to the BDBA ratio incorporated. Weight loss was observed at lower temperatures for the PPab/BPDBA, although higher char yield was obtained. This behavior may be explained by evaporation of excess BPDBA.

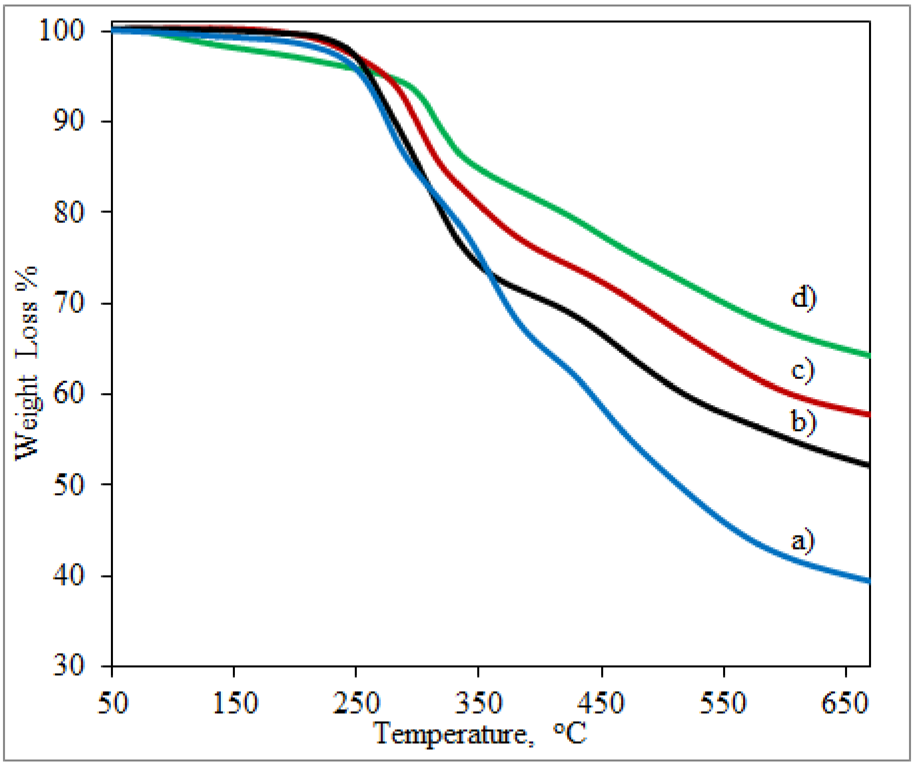


Figure 3.19. TGA curves of a) PPab polymer, b) PPab/5BPDBA, c) PPab/10BPDBA and d) PPab/15BPDBA

Thermal stability and char yield of PPab/BPDBA was determined to be higher than those of PPab and PPab/BDBA. T_5 and char yield of PPab were 255 °C and 40% and the corresponding values were 247 °C and 58% for PPab/15BDBA. Incorporation of BPDBA leaded to significant improvement in the char yields and thermal stabilities.

Char yields of composites involving 5, 10 and 15% BPDBA were 52, 58 and 64%, respectively (Table 3.3). These values were recorded as 45, 51 and 58% for 5, 10, 15% BDBA involving PPab composites. T_5 of prepared BPDBA composites were also improved and recorded as 261, 271 and 277 °C for PPab/5BPDBA, PPab/10BPDBA and PPab/15BPDBA, respectively. Thus, further improvement in the thermal properties was obtained by diphenyl cross-linkages (formed by BPDBA) when compared to phenyl cross-linkages (formed by BDBA).

Table 3.3. *T_5 and char yields of PPab, PPab/5BPDBA, PPab/10BPDBA and PPab/15BPDBA*

Sample	T_5, °C	Char Yield at 650 °C
PPab	255	40%
PPab/5BPDBA	261	52%
PPab/10BPDBA	271	58%
PPab/15BPDBA	277	64%

The total ion current curves and pyrolysis mass spectra at the maxima of the peaks present recorded during the pyrolysis of PPab and PPab/BPDBA composites are given in Figure 3.20. The TIC curves of all the samples showed more than one peak associated with multi-step degradation mechanism and/or presence of chains with different thermal stabilities. PPab showed an intense peak at around 265 °C and peaks at around 371 and 477 °C. Upon incorporation of BPDBA, maximum of the first peak at 265 °C was shifted increased up to 281 °C and maximum of the peak obtained at 477 °C was increased up to 583 °C while no significant improvement was observed for the peak at around 371 °C. This behavior can be explained by the interaction of BPDBA with benzoate units hindering sterically the attack of $-NCH_2$ groups to ortho and para positions of aniline ring. In addition to the increase in the evolution temperature, intensity of the peak at high temperature region was increased as the amount of BPDBA introduced BPDBA was increased.

The base peak was at 120 Da corresponding to the evolution of $H_2NC_6H_4CO$ for PPab. In the presence of BPDBA, the base peak was recorded at 154 Da that may be related to the $C_6H_5C_6H_5$ fragment. Other intense peaks at 151, 92 and 65 Da were associated with the $H_2NC_6H_4COOCH_3$, $H_2NC_6H_4$ and C_5H_5. Detection of these peaks may be regarded as an evidence for the thermal degradation starting by the loss of 4-amino benzoate as observed for PPab. Likewise, mass spectra of PPab/BPDBA composites indicated thermal decomposition was started evolution of amino groups. Yet, this process took place at elevated temperatures confirming increase in thermal stability. Also, evolution of phenol and unsaturated hydrocarbons was observed at elevated temperatures, as expected, leading to increase in the char yield.

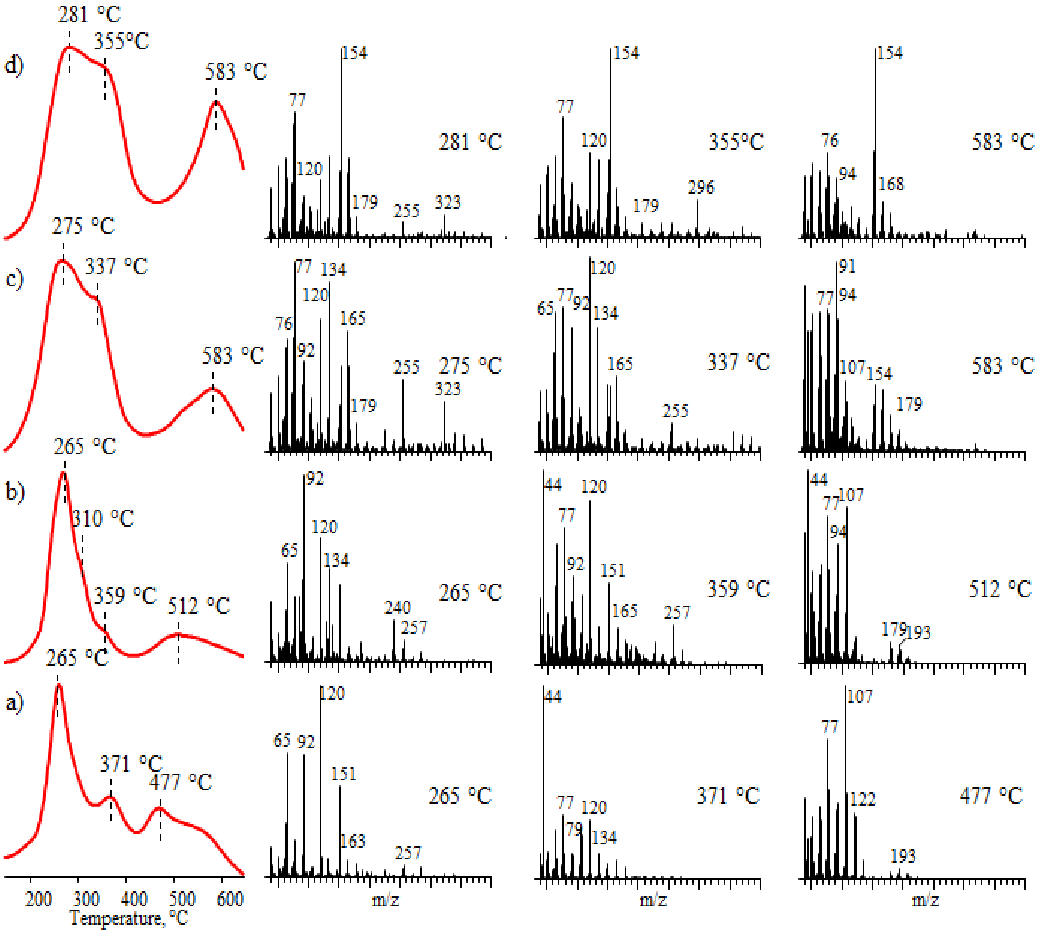


Figure 3.20. Total ion current curves and mass spectra of a) PPab, b) PPab/5BPDBA, c) PPab/10BPDBA and d) PPab/15BPDBA

Single ion evolution profiles of PPab and PPab/BPDBDA composites showed characteristic fragments of polybenzoxazines. These fragments are C_7H_7 (91 Da), C_6H_5OH (94 Da), $HOC_6H_4CH_2$ (107 Da), $H_2NC_6H_4CO$ (120 Da) and $H_2NC_6H_4COOCH_3$ (151) shown in Figure 3.21. Significant increases in the evolution temperatures of $H_2NC_6H_4CO$ (120 Da) and $H_2NC_6H_4COOCH_3$ (151) fragments confirm the delayed elimination of amino groups upon addition of BPDBA leading to the improvement in the thermal stability.

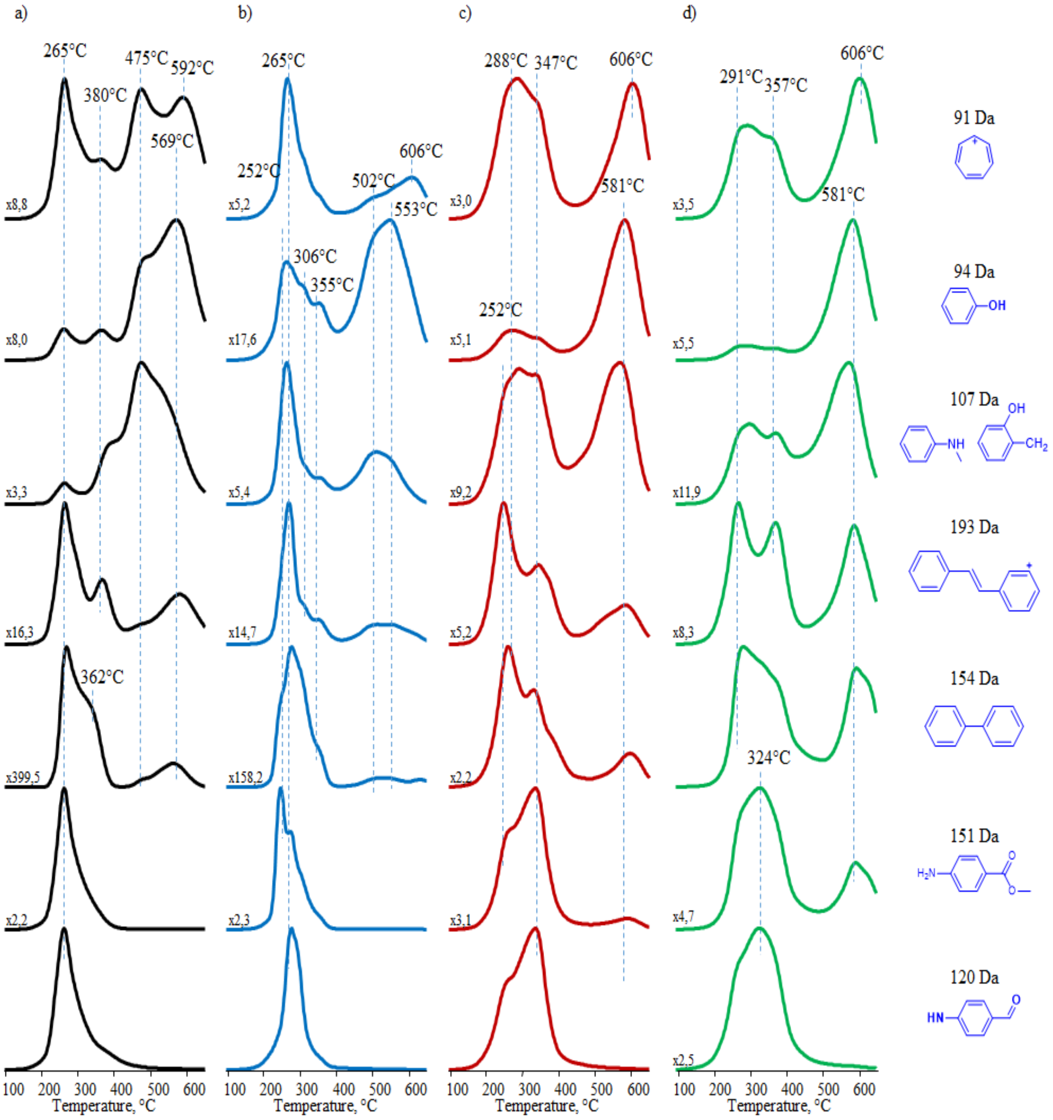


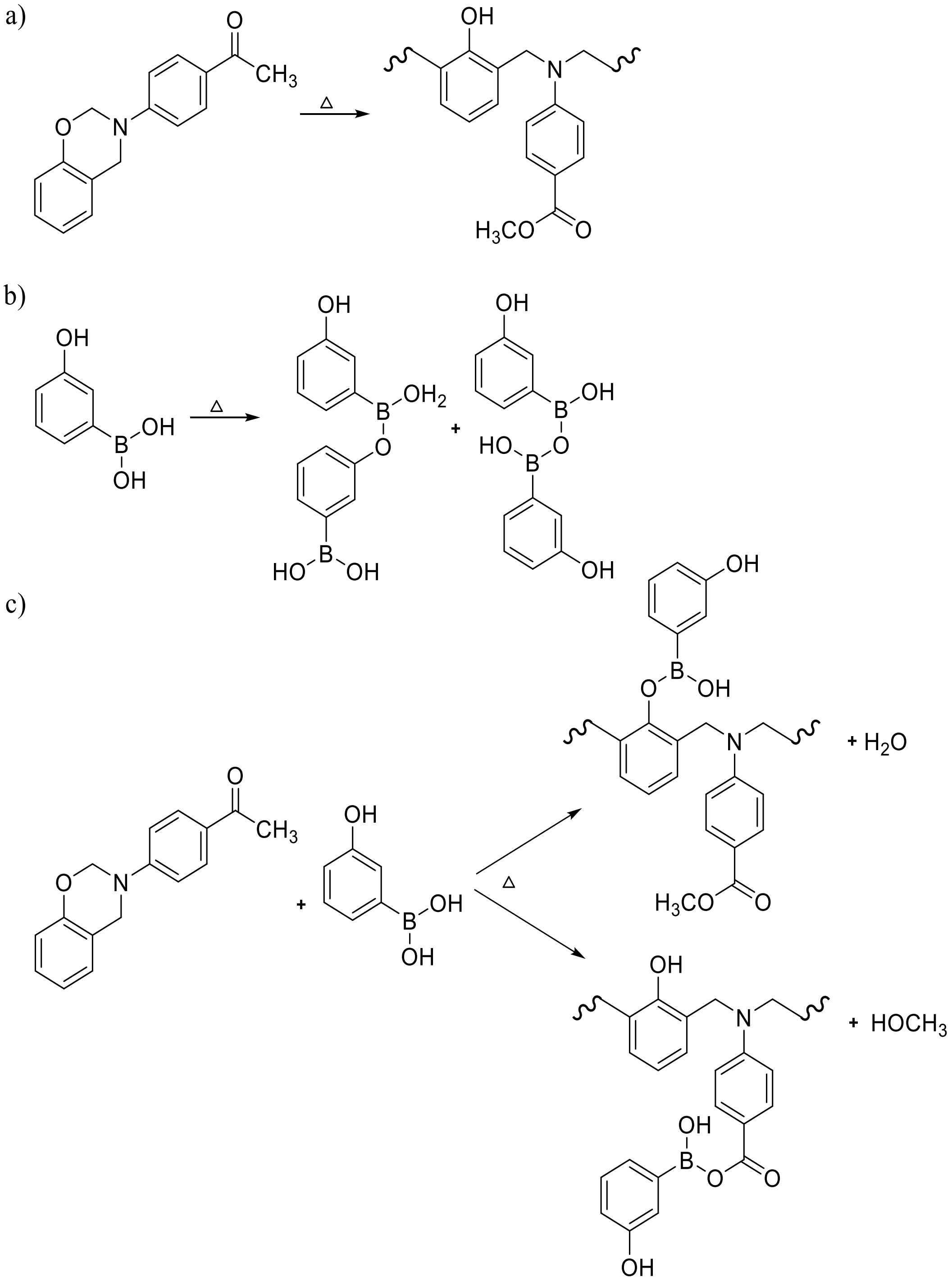
Figure 3.21. Single ion evolution profiles of a) PPab, b) PPab/5BPDBA, c) PPab/10BPDBA and d) PPab/15BPDBA

Moreover, the relative intensities of the peaks at 91 Da (C_7H_7), 154 Da ($C_6H_5C_6H_5$) and 193 Da ($C_6H_4CHNC_6H_4CH_2$) were increased significantly in the pyrolysis mass spectra of the composites. This behavior is explained by the presence of the phenolic groups at elevation temperatures without decomposition to increase the char yield and the stability.

Thermal decomposition of PPab and its BPDBA was started again by elimination of aromatic amine group. Evolution temperature of amino group was shifted to high temperature regions as the amount of BPDBA in the sample was increased. BPDBA was also contributed to cross-linking formation as in the BDBA case with higher degree due to biphenyl linkage body.

3.2.5. PPab/HPBA Polybenzoxazine Composites

3-Hydroxyphenylboronic acid, (HPBA), was introduced to the benzoxazine moiety, Pab, in various amounts and PPab/HPBA polybenzoxazine composites were prepared by stepwise curing in vented oven.[60] Thermal properties of obtained polymer composites were analyzed to determine the effect of addition of HPBA on the thermal stability and char yield of the polybenzoxazine. The improvements in thermal characteristics were associated with condensation reactions of hydroxyl groups of polybenzoxazine and ester groups on the aniline linkages yielding a highly cross-linked structure. FTIR, DSC, TGA and DP-MS techniques were applied to supply characterization information for the polybenzoxazine composites. Possible interactions of Pab monomer and HPBA are shown in Scheme 3.10.



Scheme 3.10. Interactions during curing process of PPab/HPBA composites

3.2.5.1. Preparation and Characterization of PPab/HPBA Composites

Mixtures involving benzoxazine monomer, Pab, and 2.5, 5, 7.5 and 10 wt % 3-hydroxyphenylboronic acid in 5 ml of chloroform were cast on glass plate. The films obtained after drying under vacuum, were cured step-wise at 150, 175 and 200 °C for 1h each in a vented oven. Transparent reddish brown polybenzoxazine/3-hydroxyphenylboronic acid composites (PPab/2.5HPBA, PPab/5HPBA, PPab/7.5HPBA and PPab/10HPBA) were obtained.

The FTIR spectra of the Pab monomer, PPab polymer and PPab/10HPBA are shown in Figure 3.22. The peaks in the region 1600-1400 cm^{-1} are assigned to C-C stretching vibrations in aromatic compounds.

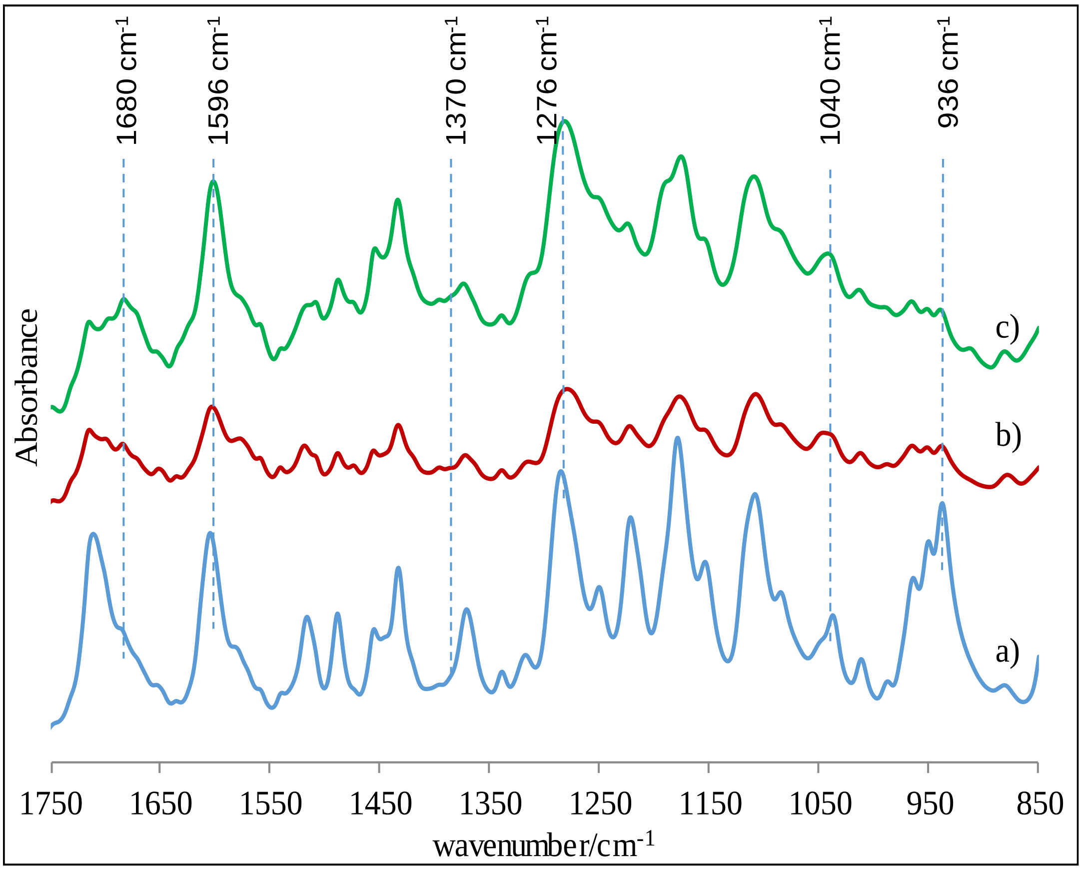


Figure 3.22. FTIR spectra of a) Pab monomer, b) PPab polymer and c) PPab/10HPBA composite

The characteristic peaks of the oxazine ring attached to a benzene ring recorded at 936 cm^{-1} was disappeared in the IR spectra of PPab and PPab/10HPBA indicating that the polymerization was completed (Figure 3.22). The FTIR spectrum of PPab/10HPBA showed characteristic B-O-H, B-O-C and B-C stretching vibrations at 1680, 1370 and 1040 cm^{-1} which confirmed the interactions of B-OH groups with functional groups of bezoxazines.

3.2.5.2. Thermal Analysis of PPab/BPDBA Composites

The exothermic ring opening polymerization peak in DSC curve of Pab monomer observed at around 240°C was disappeared in the DSC curves of the polymer and its composites involving 2.5, 5, 7.5 and 10 wt% HPBA supporting the polymerization of the monomer and samples involving various amounts of HPBA by the applied curing program (Figure 3.23).

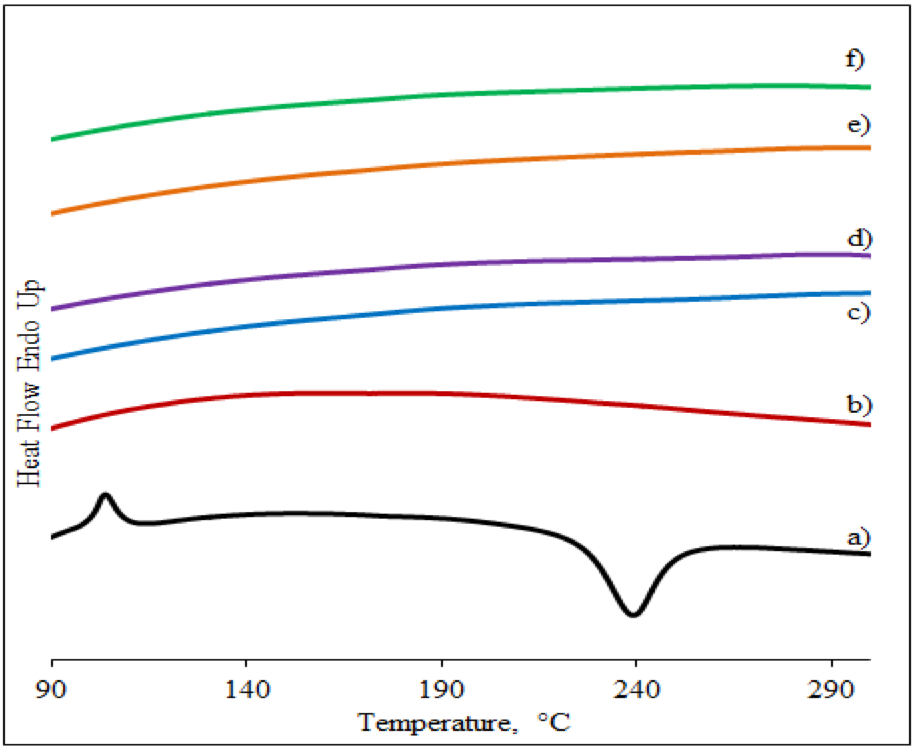


Figure 3.23. DSC curves of a) Pab, b) PPab, c) PPab/2.5HPBA, d) PPab/5HPBA, e) PPab/7.5HPBA and f) PPab/10HPBA

The TGA curve of PPab revealed a multi-step decomposition with T_5 and char yield values 255°C and 40 % respectively. PPab/HPBA composites also showed multistep degradation mechanism and improved thermal characteristics (Figure 3.24). Thermal stabilities and char yields of PPab/HPBA composites were determined to be higher than that of PPab. T_5 value of the composites showed slight increase upon incorporation of HPBA. Char yield of the composites showed improvement proportional to the amount of HPBA introduced. The char yields of the composites involving 2.5, 5, 7.5 and 10 % HPBA were 54, 58, 60 and 66 % respectively at 650°C (Table 3.4).

Table 3.4. *T_5 and char yields of PPab polymer and PPab/HPBA composites*

Sample	**T_5, °C**	**Char Yield at 650 °C**
PPab	255	40%
PPab/2.5HPBA	272	54%
PPab/5HPBA	276	58%
PPab/7.5HPBA	271	60%
PPab/10HPBA	279	66%

These behaviors may be regarded as an indication for the interactions of functional groups of PPab and HPBA yielding a network structure as expected.

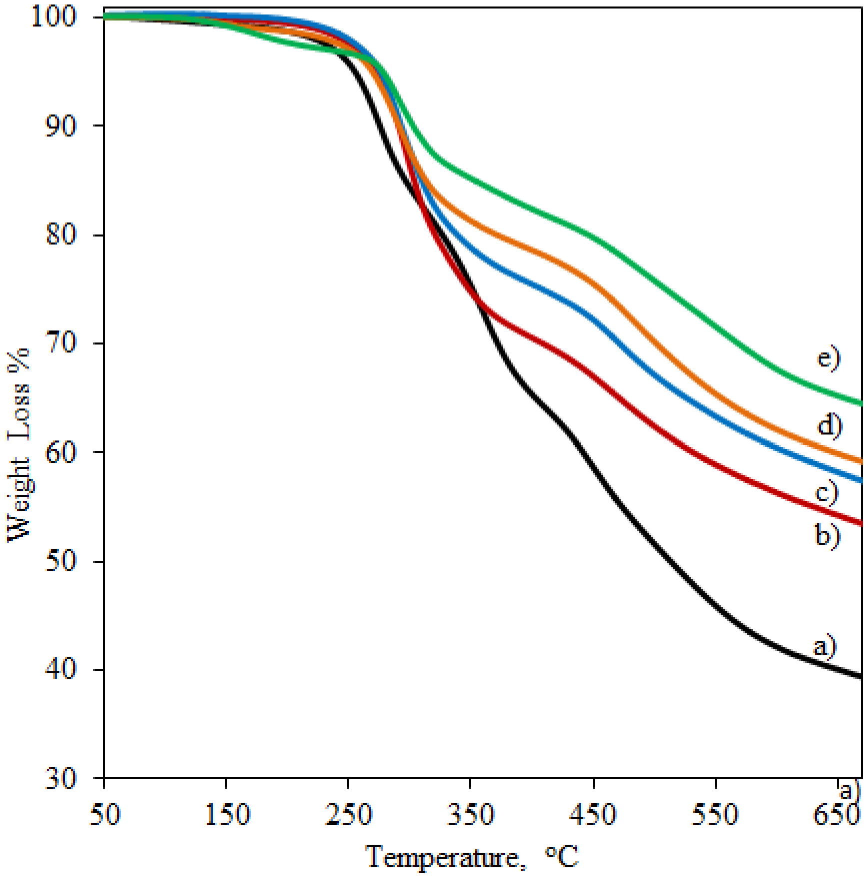


Figure 3.24. TGA curves of a) PPab, b) PPab/2.5HPBA, c) PPab/5HPBA, d) PPab/7.5HPBA and e) PPab/10HPBA

The total ion current curves, TIC, (the variation of total ion yield as a function of temperature) and the pyrolysis mass spectra at the maximum of the peaks present in the TIC curves of the PPab polymer and PPab/HPBA composites are shown Figure 3.25. The TIC curves of all the samples showed more than one peak indicating a multi-step degradation mechanism and/or presence of chains with different thermal stabilities, in accordance with TGA results. The TIC curve of PPab showed an intense peak at around 263°C and broad overlapping peaks with maxima at around 370 and 470°C. A low temperature peak appeared in the TIC curve upon addition of HPBA. This peak shifted to lower temperatures as the amount of HPBA added was increased. It was previously mentioned that vaporization of excess amount of boronic acid compounds was observed at low temperatures. Thus, it may be associated with vaporization of the residual HPBA not interacted with the monomer and/or polymer.

In DP-MS studies, the base peak in the mass spectrum of PPab recorded at 263 °C was at 120 Da due to $H_2NC_6H_4CO$. Other intense peaks at 65, 92, 107, 151 and 193 Da were associated with C_5H_5, $H_2NC_6H_4$, $HOC_6H_4CH_2$, $H_2NC_6H_4COOCH_3$ and $C_6H_4CHNC_6H_4CH_2$ fragments, respectively. The relative intensities of the peaks at m/z 91 Da (C_7H_7), 107 Da ($HOC_6H_4CH_2$) and 193 Da ($C_6H_4CHNC_6H_4CH_2$) were increased significantly in the pyrolysis mass spectra of the composites.

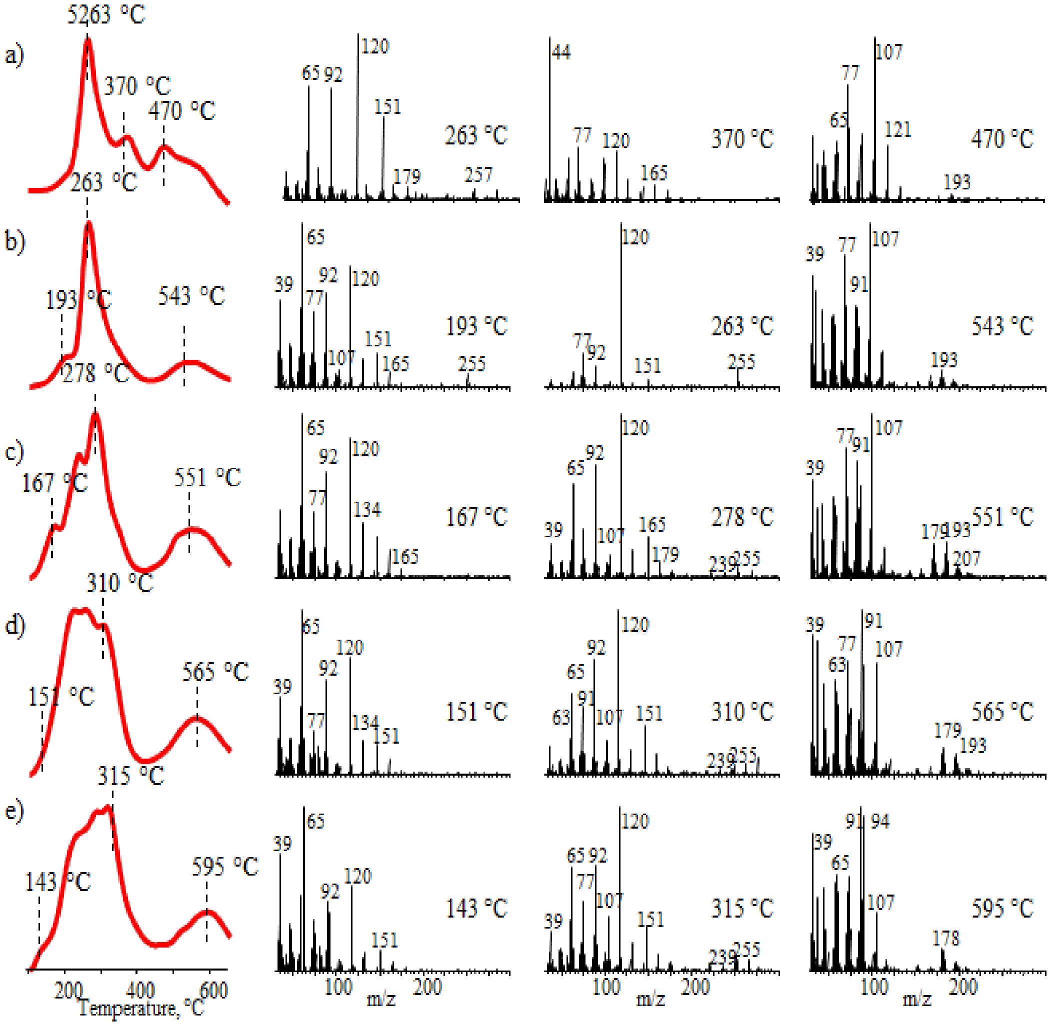


Figure 3.25 Total ion current curves and mass spectra of a) PPab, b) PPab/2.5HPBA, c) PPab/5HPBA, d) PPab/7.5HPBA and e) PPab/10HPBA

In our previous studies, we determined that thermal decomposition of polybenzoxazine based on aniline took place mainly in three regions. The first step involves loss of aniline group, the second step is related to decomposition of polymer chains generated by attack of NCH_2 groups to ortho and para positions of aniline ring and the last step is related to degradation of crosslinked structure generated during synthesis and/or early stages of pyrolysis.[20]

Upon addition of HPBA, the yield of the characteristic products of polybenzoxazine were maximized at around 315°C, at noticeably higher temperatures than those detected for the neat polymer. In addition, the second step of thermal degradation of PPab at around 370°C was totally disappeared. It may be thought that the interactions of HPBA with benzoate units inhibit the attack of $-NCH_2$ groups to ortho and para positions of aniline ring due to steric hindrance. It is clear that thermal decomposition of PPab and its composites involving HPBA (Figure 3.26) also started by loss of aromatic amine group generating $H_2NC_6H_4CO$ (120 Da), $H_2NC_6H_4COOCH_3$ (151 Da), $C_6H_4OCH_2CH_2NC_6H_4COH$ (239 Da), $C_6H_4OCH_2CH_2NC_6H_4COOH$ (255 Da). Yet, the process was recorded at noticeably higher temperatures.

Single ion evolution profiles of abundant fragments $HOC_6H_4CH_2$ (107 Da), $C_6H_4CHNC_6H_4CH_2$ (193 Da), C_6H_5OH (94 Da), C_7H_7 (91 Da) and $H_2NC_6H_4$ (92 Da) are also shown in Figure 3.26. It may be thought that the generation of network structure was enhanced by the interactions of HPBA with ester groups of the aromatic amines. These interactions may cause the retardation of their elimination during pyrolysis.

The peak at 239 Da can also be associated with $HOC_6H_4BOCOC_6H_4NH$ which may be regarded as an evidence for the condensation and esterification reactions between hydroxyl groups of HPBA and functional groups present in benzoxazine. Significant increase in its intensity is recorded with the increase in the amount of HPBA supported this proposal. The final step of thermal degradation related to decomposition of the unsaturated aromatic groups was detected at significantly higher temperatures compared to that of PPab; unsaturated aromatic groups were eliminated at 470°C and 595°C during the pyrolysis of PPab and PPab/HPBA10, respectively.

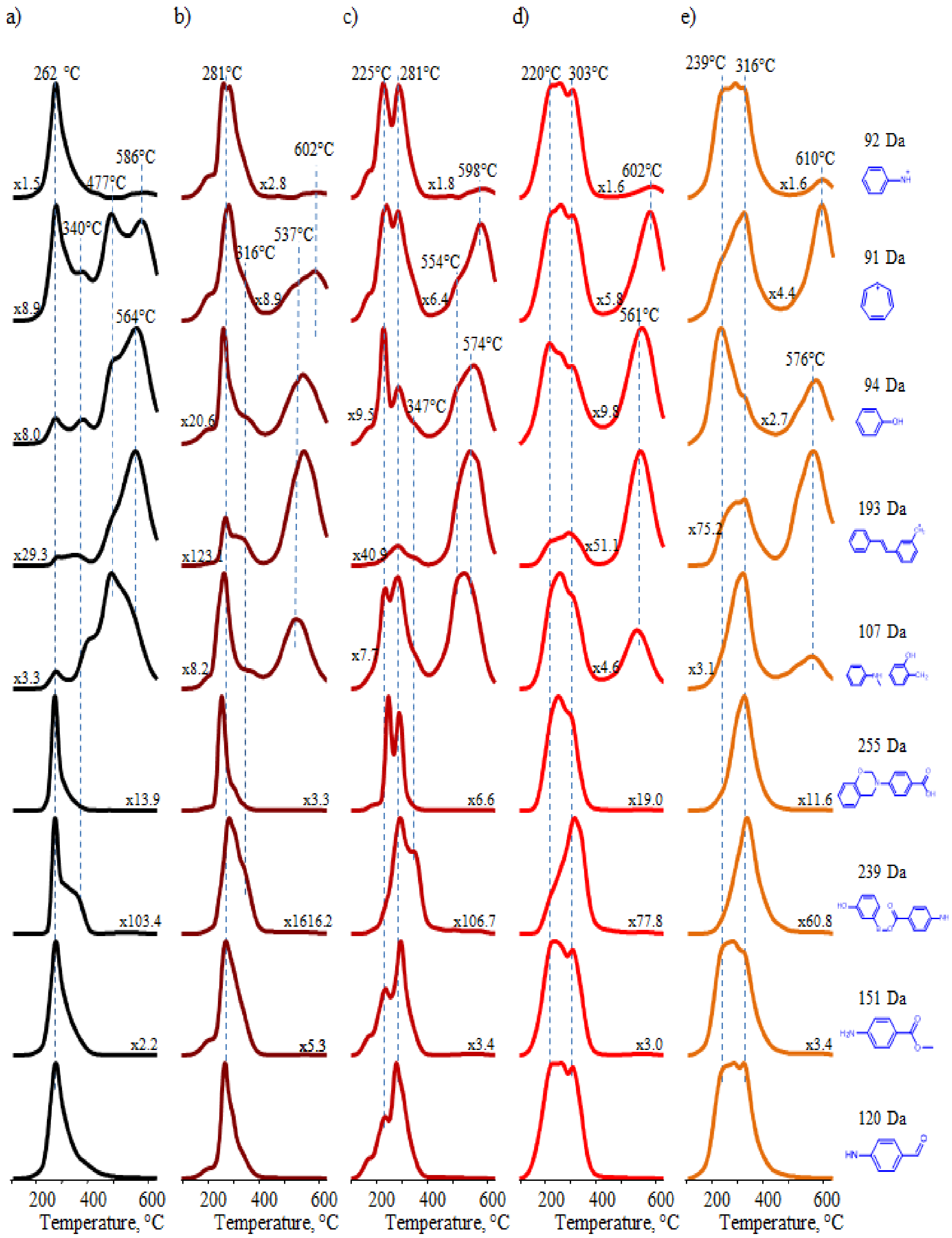


Figure 3.26. Single ion evolution profiles of a) PPab, b) PPab/2.5HPBA, c) PPab/5HPBA, d) PPab/7.5HPBA and e) PPab/10HPBA

Upon incorporation of HPBA, degradation of PPab/HPBA composites also started by loss of aniline and thermal degradation was shifted to higher temperatures. Increase in the char yield and the relative yields of the unsaturated units was recorded as the amount of HPBA increased.[60] These behaviors confirmed the enhanced network structure grown by the interactions of functional groups Pab and HPBA. Thus, more stable and cross-linked polybenzoxazine composites were produced with high char yield.

CHAPTER 4

CONCLUSION

In this work, various polybenzoxazines and polybenzoxazine composites involving aromatic boronic acid derivatives were prepared. The effect of aromatic boronic acids on thermal characteristics benzoxazine polymers and composites were investigated. In the first part of this work, benzoxazine monomer based on phenol and aniline or/and 3-amino phenyl boronic acid were prepared. The monomers were polymerized by using the optimized temperature program yielding highest char yield and thermal properties. In the second part of the work, benzoxazine monomer based on phenol and 4-aminomethyl benzoate was prepared. The monomer was used with and without incorporation of various aromatic boronic acid derivatives (benzene-1,4-diboronic acid, 4,4′-biphenyldiboronic acid, or 3-hydroxyphenylboronic acid). The structural and thermal characteristics of the benzoxazine monomers, polybenzoxazines and polybenzoxazine composites were analyzed by using NMR, FTIR, DSC, TGA and DP-MS techniques.

Polymerization of benzoxazines based on phenol and aniline or aniline derivatives is generally obtained by the ring opening of oxazine ring to form Mannich base reactive to the mainly ortho and para positions of phenol and aniline ring. Also, generation of dimers may be produced to contribute to the complex polymerization mechanism.

Aniline and/or its derivatives are eliminated during the curing process to form unsaturated linkages. Attack of NCH_2 groups to attack the aniline ring and interactions between the chains are found to be related with the substituents and functional groups on aniline compounds. These interactions determine the extent of cross-linking and thus the thermal stability and char yield of the polybenzoxazines.

Polybenzoxazines and polybenzoxazine-aromatic boronic acid composites showed complex degradation mechanisms starting by the loss of aniline groups. At early stages of pyrolysis process (around 300°C), amino groups are eliminated to form unsaturated chains. At high temperature regions (at around 500°C), these unsaturated chains with cross-linked structure were decomposed.

The use of aniline derivative with boronic acid functionality provided improvement in crosslinking density due to the condensation reactions of B-OH groups with hydroxy groups of benzoxazines. As a result, decomposition of phenolic backbone was shifted to higher temperatures. T_5 and char yields of the prepared polybenzoxazines are shown in Table 4.1.

Table 4.1. *T_5 and char yields of PBz, PBz-50APBA and PBz-100APBA*

Sample	**T_5, °C**	**Char yield at 650 °C**
PBz	306	40%
PBz-50APBA	333	70%
PBz-100APBA	298	65%

Composites of ester functionalized benzoxazine showed enhanced cross-linked structure compared to benzoxazine based on phenol and aniline due to condensation and transesterification reactions of ester groups in addition to the condensation reactions of hydroxy groups. Therefore, improved thermal stability and char yield was obtained due to enhanced cross-linked structure. T_5 and char yields of the prepared benzoxazine polymer and composites are shown in Table 4.2.

Table 4.2. *T_5 and char yields of PPab, PPab/15BDBA, PPab/15BPDBA and PPab/10HPBA*

Sample	**T_5, °C**	**Char Yield at 650 °C**
PPab	255	40%
PPab/15BDBA	247	58%
PPab/15BPDBA	277	64%
PPab/10HPBA	279	66%

Various aromatic boronic acid derivatives including benzene-1,4-diboronic acid, 4,4′-biphenyldiboronic acid and 3-hydroxyphenylboronic acid were introduced as additive compounds to the polybenzoxazine with ester functionality. Further improvement was recorded in the thermal characteristics of prepared polybenzoxazine-aromatic boronic acid composites. This behavior is explained by the increase in the extent of network structure due to the contribution of the B-OH groups of additives to the condensation and transesterification reactions. Improvement in thermal stabilities and increase in char yields were recorded upon incorporation of aromatic boronic acid either as an additive or as a reactant for the synthesis of the benzoxazine monomers.

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PUBLICATIONS

1. İpek H. and Hacaloğlu J. "The effect of 3-hydroxyphenylboronic acid on thermal characteristics of polybenzoxazine based on phenol and 4-aminomethylbenzoate" submitted, (2019)

2. İpek H. and Hacaloğlu J. "Synthesis and analysis of thermal characteristics of polybenzoxazine based on phenol and 3-Amino phenyl boronic acid", Journal of Polymer Science: Polymer Chemistry, 57(15), 1711-1716 (2019)

3. İpek H. and Hacaloğlu J. "The effect of aromatic diboronic acid on characteristics of polybenzoxazine based on phenol and 4-aminomethylbenzoate", Journal of Polymer Research, 25(12), 263-270 (2018)

4. İpek H. and Akdag A. "Enantioselective oxidation of thioanisole to metyl phenyl sulfoxide by chiral compounds bearing N-Cl bond", Phosphorus, Sulfur, and Silicon and the Related Elements, 190(8), 1285-1293 (2015)

5. Özkut M.İ., İpek H., Karabay B., Cihaner A. and Önal A.M. "Furan and benzochalcogenodiazole based multichromic polymers via a donor-acceptor approach", Polymer Chemistry, 4, 2457-2463 (2013)

INTERNATIONAL CONFERENCE PROCEEDINGS

1. 255th American Chemical Society National Meeting, Polybenzoxazine based on phenol and m-amino phenyl boronic acid. 18-22 March 2018, New Orleans, USA. (Oral Presentation)

2. 254th American Chemical Society National Meeting, Effect of aromatic boronic acid on characteristics of polybenzoxazine based on phenol and p-amino methyl benzoate 20-24 August 2017, Washington DC, USA. (Poster Presentation)

NATIONAL CONFERENCE PROCEEDINGS

1. 29th National Chemistry Congress, Aminometil Benzoat Bazlı Polibenzoksazin Özelliklerine Aromatik Boronik Asit Etkisi. 10-14 September 2017, Ankara, Turkey. (Poster Presentation)

2. 2nd National Organic Chemistry Congress, Kiral Sülfoksitlerin kiral N-Klorosüksinimid Türevi ile Eldesi. 24-26 September 2014, Ankara, Turkey. (Poster Presentation)

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