# THERMAL CHARACTERIZATION OF PHENOL AND BISPHENOL-A BASED POLYBENZOXAZINES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

SHAHLA BAGHERIFAM

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
POLYMER SCIENCE AND TECHNOLOGY

FEBRUARY 2009

Approval of the thesis:

# THERMAL CHARACTERIZATION OF PHENOL AND BISPHENOL A BASED POLYBENZOXAZINES

submitted by **SHAHLA BAGHERIFAM** in partial fulfilment of the requirements for the degree of **Master of Science in Polymer Science and Technology Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, **Graduate School of Natural and Applied Sciences**

Prof. Dr. Cevdet Kaynak
Head of Department, **Polymer Science and Technology**

Prof. Dr. Jale Hacaloğlu
Supervisor, **Chemistry Department, METU**

Prof. Dr. Ceyhan Kayran
Co-Supervisor, **Chemistry Department, METU**

**Examining Comitee Members:**

Prof. Dr. Jale Hacaloğlu
Chemistry Dept., METU

Prof. Dr. Ceyhan Kayran
Chemistry Dept., METU

Prof. Dr. Cevdet Kaynak
Metallurgical and Materials Engineering Dept., METU

Assoc. Prof. Dr. Göknur Bayram
Chemical Engineering, Dept., METU

Ast. Prof. Dr. Tamer Uyar
Material Science and Nanotechnology Institute
Bilkent University

Date: February 13, 2009

**I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.**

Name, Lastname: Shahla BAGHERIFAM

Signature:

# ABSTRACT

## THERMAL CHARACTERIZATION OF PHENOL AND BISPHENOL A BASED POLYBENZOXAZINES

Bagherifam, Shahla
Master of Science, Department of Polymer Science and Technology
Supervisor: Prof. Dr. Jale Hacaloğlu
Co-Supervisor: Prof. Dr. Ceyhan Kayran

February 2009 , 77 pages

Although, several researches on synthesis and characterization of benzoxazines and polybenzoxazines have appeared in the literature, detailed studies on thermal characterization are still limited. In this study, polymerization and thermal degradation mechanisms of benzoxazines were investigated via direct pyrolysis mass spectrometry. Benzoxazine monomers prepared by reactions of phenol or bisphenol-A with aniline or methyl amine were analyzed to investigate the effects of the structures of phenyl and amine groups on both polymerization and thermal degradation behaviours.

It has been proposed in the literature that polymerization of benzoxazines occurs by ring opening polymerization of oxazine ring; cleavage of O-$CH_2$ bond of the oxazine ring and attack of n-$CH_2$ group to phenol or bisphenol-A ring. However, the direct pyrolysis mass spectrometry analyses of polymerization and thermal degradation of benzoxazines pointed out that after the cleavage of O-$CH_2$ bond of the oxazine ring, polymerization proceeded through opposing pathways.

Strong evidences confirming coupling of $(CH_3)NCH_2$ or $(C_6H_5)NCH_2$ groups yielding dimers involving diamine linkages were detected. Polymerization of the dimer by the reactions with the corresponding monomers was proposed. In case of benzoxazines based on bisphenol-A, the results indicated polymerization of the dimer by coupling of both of the oxazine rings. On the other hand, polymerization of the dimer through the ethylene units (vinyl polymerization) in case of benzoxazine monomer based on phenol and methyl amine was also noted. For polybenzoxazines based on aniline another polymerization pathway involved attack of radicals generated by cleavage of the oxazine ring to aniline ring.

Multi-step thermal decomposition was observed for all the polybenzoxazines under investigation confirming the presence of units with different structures and stabilities.

**Keywords:** Benzoxazines, Polybenzoxazines, polymerization, thermal degradation, pyrolysis mass spectrometry

# ÖZ

## FENOLLÜ VE BİSFENOLLÜ POLİBENZOKSAZİNLERİN ISISAL OLARAK KARAKTERİZASYONU

Shahla Bagherifam
Yüksek Lisans, Polimer Bilim ve Teknolojisi Bölümü
Tez Yöneticisi: Prof. Dr. Jale Hacaloğlu
Ortak Tez Yöneticisi: Prof. Dr. Ceyhan Kayran

Şubat 2009, 77 Sayfa

Benzoksazinler ve polibenzoksazinlerin sentezi ve karakterizasyonu hakkında birçok çalışma yaygınlaştığı halde, literatürde, ısısal karakterizasyonu hakkındaki detaylı çalışmalar hala sınırlıdır.

Bu çalışmada, benzoksazinlerin polimerleşmesi ve ısısal bozunum mekanizmaları direkt piroliz kütle spekrometresi kullanılarak incelenmiştir. Fenol yada bisfenol-A'nın aniline yada metil amin reaksiyonları ile hazırlanan monomerleri, fenil ve amin gruplarının polimerizasyon ve ısısal bozunum davranışları üzerindeki etkisini incelemek için analiz edilmiştir.

Benzoksazin polimerizasyonu, literatürde öne sürüldüğü üzere, oksazin halkasındaki O-$CH_2$ bağının kırılması ve n-$CH_2$ grubunun fenol veya bifenol-A halkasına saldırmasıyla gerçekleşen halka açılma polimerizasyonu şeklindedir. Fakat, benzoksazin polimerizasyonunun ve ısısal bozunumunun direkt piroliz kütle spektrometre analizleri oksazin halkasındaki O-$CH_2$ bağının kırılmasından sonra polimerizasyonun zıt yönlerde gerçekleştiğini göstermiştir.

Güçlü delillerin onayladığı, $(CH_3)NCH_2$ veya $(C_6H_5)NCH_2$ gruplarının çiftleşmesinin diamin bağlantıları içeren dimerleri oluşturduğu tespit edilmiştir. İlgili monomerlerin reaksiyonları ile oluşan dimerlerin polimerizasyonu sunulmuştur. Bisfenol-A bazlı benzoksazinlerin durumunda, sonuçlar dimerin polimerizasyonun her iki oksazin halkasının çiftleşmesi ile oluştuğunu göstermiştir. Diğer yandan, fenol ve metil amin bazlı benzoksazin durumunda dimer polimerizasyonunun etilen birimlerince(vinil polimerizasyonu) gerçekleştirildiği belirtilmiştir. Aniline bazlı polibenzoksazinler için oksazin halkasından anilin halkasın kırılmasıyla oluşturulan radikallerin saldırısını içeren diğer polimerizasyon yolları gözlemlenmiştir.

İnceleme altındaki bütün polibenzoksazinler için farklı yapı ve kararlılıktaki birimlerin varlığını doğrulayan çok basamaklı ısısal ayrışımlar gözlemlenmiştir.

**Anahtar Kelime**: benzoksazinler, polibenzoksazinler, ısısal bozunum, piroliz kütle spektrometresi

To My Precious Mom and Dad
For their endless support

To My Dear Advisor
For always being there for me

To my fiance
For his encouragement.

# ACKNOWLEDGEMENTS

This research was made possible by the efforts and support of some people. First of all I would like to express my science appreciation to my advisor, Prof. Dr. Jale Hacaloğlu for her guidance, support and patience during this study. I wish also to express my profound gratitude to my co-advisor, Prof. Dr. Ceyhan Kayran for her advice.

I would also like to thank Ass. Prof. Dr. Tamer Uyar(UNAM – Bilkent University), for synthesis of my monomers.

I am so grateful to my father for always having my back. I could never have succeeded all of this without his moral support.

A word of appreciation is due to my dear fiancé for his understanding, encouragement and patience.

I wish to thank my friend, Tuğba Orhan for her kindness help for Turkish translation.

# Table of Contents

Chapters

# List of figures

# List of tables

# List of schemes

# CHAPTER 1

# INTRODUCTION

## 1.1. Benzoxazines

Polymers that can deal successfully in high-temperature engineering environments are termed *high-performance polymers.* Developments of high performance thermosetting resins continue receiving considerable interests of researchers especially for their wide applications in microelectronics and aerospace industries. Many of the established thermoplastics are not capable to tolerate high-temperature, so recent researches have focused on modification or synthesis of polymer structures which involve thermally stable and/or resonance-stabilized systems such as aromatic groups [1].

Phenolic resins include any of the various synthetic thermoseting resins obtained by reactions of phenols with simple aldehydes. They are applicable polymers that exhibit higher thermal stability than others [2]. Phenolic resin was the first totally synthetic coating material [3]. Because of their relatively low cost and dimensional stability, the resole type resins are still largely used in the industry of polymeric materials. Polybenzoxazines, a new class of phenolic resins with a similar main chain structure, have been developed to be more useful over conventional resins. They have some additional advantages, such as no release of volatiles during cure and no need for harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties and molecular design flexibility and low melt viscosity [2].

Polybenzoxazines are a type of thermosetting phenolic resins that have been developed over the last decade for electronics, and aerospace applications [2].

Aromatic oxazines were first synthesized in 1944 by *Holly and Cope* through Mannich reaction from phenols and formaldehyde, and amines. According to the reported procedure, this reaction was performed in a solvent in two-steps [4].

In 1950s to 1960s, *Burke* and coworkers found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and Mannich bridge is generated. Later, benzoxazine were also produced as the intermediate in the synthesis of novalac resins. The heat cured polymers derived from benzoxazine were first achieved by *Schreiber* [5].

*Reiss* and his co-workers worked on the polymerization of monofunctional benzoxazines in present or absent of phenol as an initiator. This procedure was lead to produce linear polymers under 4000 molecular weight [6].

Recently, the development of the benzoxazine-based phenolic resins has attracted significant attention. This attention causes to the synthesis of polybenzoxazines with quite good thermal and mechanical properties. They not only have the characteristics of traditional phenolic resins such as good flame retardancy and chemical resistance, but also unique characteristics that are not found in the traditional phenolic resins such as low moisture absorption, low shrinkage during polymerization, low dielectric constant and melt viscosity, no need for harsh catalysts, high thermal stability, good mechanical properties, excellent electrical properties and molecular design flexibility. These characteristics make this type of polymers as high performance polymers [7, 8].

Ishida and his colleagues studied on thermal degradation of a series of polybenzoxazines based on bisphenol-A and various aliphatic amines. They used Thermo Gravimetric Analysis – Fourier Transform Infrared (TGA-FTIR) and Gas Chromatography – Mass spectrometry (GC-MS) techniques [8]. Ishida proposed that the Mannich base in polybenzoxazines plays an important role in the thermal degradation of polybenzoxazines. He worked on effect of hydrogen bonding on the degradation mechanism of benzoxazines. In addition, in 1997 he also studied on the aniline based polybenzoxazines under both inert and oxidative environments [2].

*Takeichi* and *Agag* added proparyl and allyl groups to benzoxazines to obtain higher glass transition temperature and higher thermal stability. In 2005 *Liu* and his co-worker researched on furfurylamine as a raw material to form Mannich bridge networks in the polymerizations of polybenzoxazines which increased the cross-linking densities and thermal stability. They also exhibited high glass transition temperatures above 300ºC, high char yields, and low flammability with limited oxygen index values of 31 [9]. Recently, 2007, *Emanuela Calo* et al synthesized a novel cardanol based, a well known renewable organic resource, benzoxazine as a pre-polymer which is used to produce bio-composites containing high percentage of renewable materials [10].

It has been shown that glass transition temperature (Tg) of PB-a (6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) are 150 ºC which is not high enough for the use in a harsh condition. The thermal properties of polybenzoxazines can be improved mainly by two ways. One is the modification of the monomer structure and the other is the preparation of alloys with highly thermally stable materials, such as polyimide[4]. In fact, these new materials combine the thermal properties and the mechanical performance of advanced composites. For this reason, the polybenzoxazines show better physical and mechanical properties compared to those of the conventional phenolic and epoxy resins.

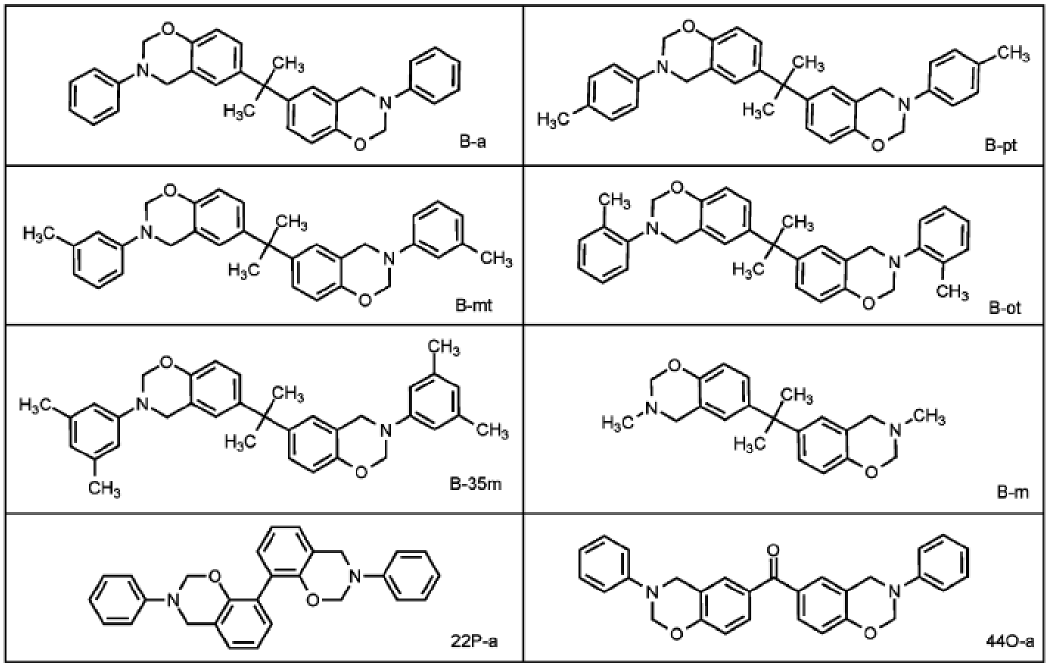
Although polybenzoxazines were classified as high performance polymers, there are some disadvantages on their use in practical application. For instance the monomers are usually powder so processing into thin films is difficult. Additionally, because of the low molecular weight of the network structure the formed polymers are brittle. To overcome these problems benzoxazine structures can be combined with conventional polymers [6]. Yagcı and coworkers suggested a macromonomer method generating polybenzoxazines with polymer segments and good mechanical properties by using Atom Transfer Radical Polymerization (ATRP) and Ring Opening Polymerization (ROP) methods [11].

### 1.1.1. Synthesis and reactions

Researches has recognized that, in order to obtain thermal stability, the presence of aromatic and heterocyclic ring structures in the polymer main chain is necessary [12]. It was shown that the thermal stability increases as the number of aromatic rings increases [13]. Benzoxazines are readily synthesized, either in solution or by a melt-state reaction using a combination of a phenolic derivative, formaldehyde, and a primary amine (Scheme 2-1) [4].

Benzoxazines are bicyclic heterocycles. These monomers contain oxazine ring which opens during thermal polymerization and form a phenolic structure in acidic medium as shown in Scheme 2-1. During the polymerization, benzoxazines are produced by thermally activated ring-opening reaction to form a Mannich base bridge [14].
Polymerization takes place through the ring opening of the cyclic monomers by heat treatment in the absence of a catalyst and without producing harmful byproducts during the cure process [7]. The presence of different functional groups in the structure makes polybenzoxazines more suitable for many applications. Some typical benzoxazine monomers are 3-phenyl-3,4- dihydro-2H-1,3-benzoxazine (P-a) and 6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) (B-a), and polymer of B-a (PB-a).

Recent researches have developed a new class of difunctional or multifunctional benzoxazine monomers yielding the ring opening reactions during curing to produce phenolic materials which initiated by dimers and higher oligomers in the resin composition (Scheme 1-1) [4].



**Scheme 1-1: Chemical structure of multifunctional benzoxazine monomers.**

The knowledge of mechanisms of curing and thermal degradation of polybenzoxazines and the effect of functional groups are very important for determination of the application areas and the strategies for modifications of the monomers and polymers.

## 1.2. Thermal degradation

Thermal degradation of polymeric materials is an important issue from both the academic and the industrial viewpoints. Organic polymers are more suitable to thermal degradation than inorganic materials. Organic polymers can cleave by thermal, oxidative or radical means. Thermal degradation process is affected by various parameters such as environment of degradation, types of additives and the structure of the polymer. The structure of the polymer can be affected by the molecular weight, degree of crosslinking, the structures of the end groups and the substituents [2].

The chemical reactions involved in thermal degradation lead to changes in physical and optical properties relative to the initially specified properties. Thermal degradation generally involves changes of the molecular weight and molecular weight distribution. The thermal degradation study of polymers may be difficult since the polymers fragment to a large number of decomposition products during pyrolysis [15].

### 1.2.1. Mechanism of thermal degradation of polymers

Thermal degradation of polymers is molecular weight deterioration because of overheating. At high temperatures the components of the long polymer backbone can begin to separate (molecular scission) and react with one another to change the properties of the polymer. Indeed significant thermal decomposition can occur at temperatures much lower than those at which mechanical failure takes place. Thermal degradation can take place through different reaction pathways such as depolymerization, random chain scission, side group elimination and oxidation [16, 17].

- Depolymerization

Depolymerization corresponds to depropagation of the polymer chain. Under thermal effects, the end of polymer chain separates and generates a free radical with low activity [17]. Then according to the chain reaction mechanism, the polymer loses monomers one by one. This unzipping process produces mainly monomer and low molecular weight oligomers. However, the molecular chain doesn’t change a lot in a short time period. Thermal degradation of polystyrene, poly(methyl metacrylate) take place by depolymerization reactions [18].

- Random chain scission

Statistical or random cleavage occures when the bond energies involved in the polymer are comparable and there is no intermolecular rearrangements which yield to produce molecules with different structures than that of the monomer. The chain backbone will break down randomly. These cleavages can take place at any position of the chain backbone . Therefore, the molecular weight will decrease rapidly. Because of forming new free radicals, monomer formation is not likely during random chain scission processes[17] . Thermal decomposition of poly(ethyleneoxide) (PEO) is an example for random chain scission mechanism[19].

- Side group elimination

Elimination of side chains is generally two-step pyrolysis. By this way, groups that attached to the polymer backbone by weak bonds are eliminated first [17]. During the heating process, the side groups are stripped off before the decomposition of the main chain. For example the thermal degradation of polyvinyl acetate and polyvinychloride, PVAc occur in two steps; lose of side groups occurs in the first step and decomposition of the main chain takes place in the second step. PVC eliminates HCl in the temperature range 100-120$^{o}$C [20].

- Oxidation of the polymer

Oxidation of a polymer surface in the presence of oxygen or ozone is facilitated by radiant energy such as UV or artificial light. This process may be nonfree radical process involving intermolecular exchange reactions. This process is often the most significant component of weather degradation of polymers. [17].

### 1.2.2. Analysis of thermal degradation

The common methods used to investigate thermal characteristics of polymers, such as thermal stability, thermal degradation products and mechanism, are *Thermogravimetric Analysis* (TGA), *Differential thermal analysis* (DTA), *differential scanning calorimetry* (DSC) and pyrolysis [21].

### 1.2.2.1. Thermal gravimetric analysis, TGA

TGA is a type of testing that is performed on samples to determine the weight loss as a function of temperature. For a better interpretation, as many weight loss curves look similar, derivative weight loss curves are used to investigate the point at which weight loss is most apparent.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine thermal stability, degradation temperatures, absorbed solvent residues and moisture content, the level of inorganic and organic components in the materials, decomposition points of explosives. TGA can be coupled to Fourier transform infrared spectroscopy, (TGA-FTIR) or mass spectrometry (TGA-MS). The TGA-FTIR gives useful information about the types and functionalities of the degradation products according to fingerprints. [15]. Coupling of the technique with mass spectrometry brings further advantages such as sensitivity. In TGA-MS, reaction gases transfer to the mass spectrometer. As the transfer rate is high and the transfer time is short, a real-time-temperature correlation of decomposition products is obtained. [22].

### 1.2.2.2. Pyrolysis

Pyrolysis is an analytical technique to convert a nonvolatile complex material into smaller volatile molecules by heating in an inert atmospheric or vacuum. As thermal stability depends on relative strengths of the molecular bonds, thermal decomposition of an original sample, under the same pyrolysis conditions, always occurs in reproducible way, shows unique characteristics and is a fingerprint of the sample. The technique is also used as a preprocessing step to convert high molecular weight molecules to lower molecular weight ones that can be easily detectable. Pyrolysis temperature is an important factor that determines product distribution. At relatively low temperatures, degradation may be too slow to be analytically useful. On the other hand, at very high temperatures, degradation may be too extensive, yielding only very small and nonspecific products. Another important factor that affects the products distribution is the heating rate. At high heating rates, thermal degradation is more selective. Thus the pyrolysis temperature and heating rate should be strictly controlled to ensure the reproducibility.

Pyrolysis (Py) can be coupled to FTIR, (Py-FTIR) gas chromatography (Py-GC), gas chromatography-mass spectrometry (Py-GC-MS) or directly to mass spectrometry (Py-MS). Among these various analytical pyrolysis techniques, Py-GC-MS or Py-MS have several advantages such as sensitivity, reproducibility, minimal sample preparation and speed of analysis. Pyrolysis mass spectrometry techniques find application in several industrial, technological and research areas. Analysis are widely applied in the field of polymer science and include determination of molecular weight distribution, fingerprint patterns for polymer identification, sequences of monomeric units, the branching, cross-linking, end groups, copolymer structure and identification of additives or impurities present. [17].

In the Py-GC-MS technique, the gas chromatography column separates thermal degradation products before the analysis by the mass spectrometer. This process occurs generally by three steps:

a) Thermal degradation of sample
b) Ionization of thermal degradation products
c) Detection of all separated compounds by MS

In the case of direct pyrolysis–MS thermal degradation takes place inside the mass spectrometer and pyrolyzed compounds are transferred rapidly to the ionization source.

Direct pyrolysis by mass spectrometer takes place by four steps:

a) Thermal degradation of sample
b) Ionization of thermal degradation products
c) Fragmentation of ionization parts

d) Detection of all ions by MS

The high vacuum condition of the direct Py-MS technique favours vaporization which allows the analysis of higher molecular weight. In addition, the high vacuum system causes the removal of the degradation products from the heating zone immediately, thus, the condensation and secondary reactions are avoided [17].

### 1.2.2.3. Mass spectrometry

A mass spectrometer is an analytical technique that converts a gaseous, liquid or solid sample into gas phase ions that can be separated according to mass to charge ratios by application of external electric and magnetic fields or by flight times in order to investigate the characteristics of the individual molecules. Vacuum is needed in mass spectrometers to avoid scattering and collisions, to remove sample from the mass spectrometer after the analysis, to avoid secondary reactions that may take place as the ions are very reactive and short-lived.

The pressure inside the mass spectrometer must be roughly in the range from$10^{-5}$ to $10^{-8}$ torr (less than a billionth of an atmosphere). The three essential functions of a mass spectrometer, and the associated components, are:

- **The Ion Source**: In this section a small sample of a compound is ionized, usually to cations by loss of one or more electron. Some common ion sources are electron impact, EI, chemical ionization, CI, field ionization, atmospheric pressure ionization API, fast atom bombardment, FAB, matrix assisted laser desorption, MALDI, and electron spray, ES.
- **The Mass Analyzer:** The ions are separated according to the ratio of mass to charge. For this purpose a magnetic, quadrupole, time-off-flight, ion trap or cyclotron analyzer is used.
- **The Detector:** The separated ions are then detected and tallied in this part and the resulting information is stored and analyzed in a computer. [23].

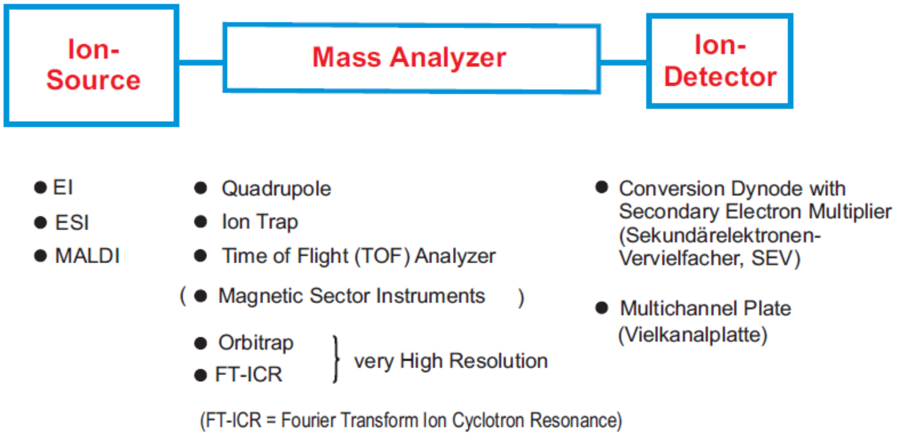


**Figure 1-1 : General scheme of a mass spectrometer [23].**

## 1.3. Aim of work

Although, several researches on synthesis and characterization of benzoxazines and polybenzoxazines have been appeared in the literature, detailed studies on thermal characterization is still limited. The mechanisms of curing, thermal degradation and crosslinking are among the most important research areas for investigation of modifications and application areas of these compounds. Most of the researches on thermal characterization is focused on TGA studies that can only give information on thermal stability and weight loss.

Few studies on thermal degaradation products involved pyrolysis GC-MS and TGA-FTIR analyses. Yet, with the use of classic techniques secondary reactions during heating can not be eliminated and only stable degradation products can be detected. Thus, the data obtained can not be used to investigate thermal degradation mechanism.

In this study, our first aim is to investigate the processes taking place during the curing of a number of benzoxazine monomers prepared by reactions of phenol and bisphenol-A with aniline and methyl amine. The second aim is to study the thermal degradation behaviour, namely the mechanism and the decomposition products and the crosslinking processes of the polybenzoxazines prepared by curing of the benzoxazine monomers. The effect of the phenol and the amine groups, especially polymerizable functional groups on polymerization and thermal degradation mechanism will be investigated by direct pyrolysis mass spectrometry.

# CHAPTER 2

# EXPERIMENTAL

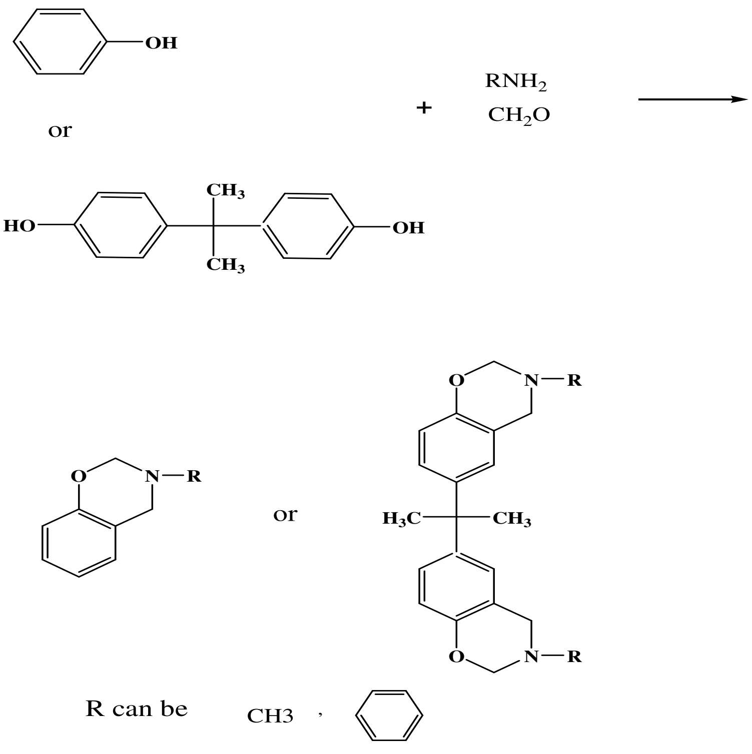
## 2.1. Materials and synthesis

Materials which are used in this study were benzoxazines are prepared by reactions of phenol or bisphenol-A and methylamine or aniline and formaldehyde. The monomers based on phenol and methyl amine, Ph-m, based on phenol and aniline, Ph-a, based on bisphenol-A and methylamine, BA-m and based on bisphenol-A and aniline BA-a and the corresponding polybenzoxazines were synthesized and characterized by Dr.Tamer Uyar as described in the literature. The procedure followed to synthesize the benzoxazine monomers and polymers were explained in detail in the literature [4,7]. The mechanism of formation of benzoxazine monomers is shown in Scheme 2-1.

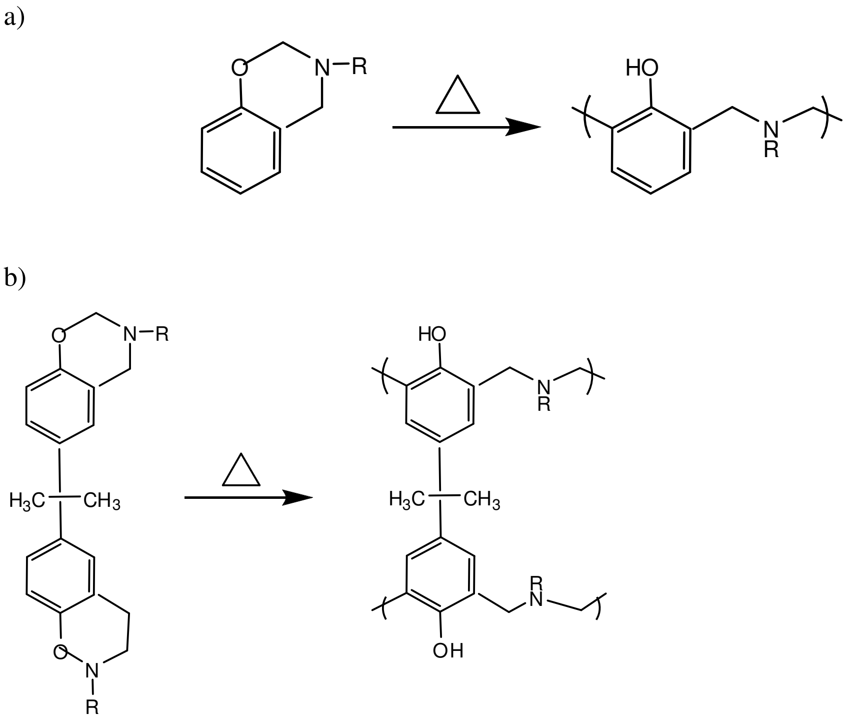
The benzoxazine monomers were cured by applying a stepwise curing program to obtain polybenzoxazines. The curing programs and types of polymer produced during the curing and the proposed polymerization mechanisms are shown in Table 2-1 and 2-2 and Scheme 2-2 respectively.

**Table 2-1 : Curing temperature program of polybenzoxazines monomers.**

| Benzoxazine sample | Curing Temperature Programs |
|---|---|
| Bisphenol A + Aniline | 0.5 hr at 160, 180, and 200 °C and 1.5 hr at 210°C |
| Phenol +Aniline | 0.5 hr at 160, 170, and 180 °C and 1.5 hr at 190°C |
| Bisphenol A + Methylamine | 0.5 hr at 160, 180, and 200 °C and 1.5 hr at 210°C |
| Phenol + Methylamine | 0.5 hr at 160, 180, and 200 °C and 1.5 hr at 210°C |



**Scheme 2-1: Synthesis of benzoxazines [4].**



**Scheme 2-2 : Synthesis of polybenzoxazines by ring opening reaction.**

**Table 2-2 : Types of polymers produced during curing of benzoxazines monomers.**

| Name | Polymer |
|---|---|
| PPh1-m | Polybenzoxazine based on phenol and methylamine, type 1 |
| PPh1-a | Polybenzoxazine based on phenol and aniline, type 1 |
| PBA1-m | Polybenzoxazine based on bisphenol-A and methylamine, type 1 |
| PBA1-a | Polybenzoxazine based on bisphenol-A and aniline, type 1 |
| PPh2-m | Polybenzoxazine based on phenol and methylamine, type 2 |
| PPh2-a | Polybenzoxazine based on phenol and aniline, type 2 |
| PBA2-m | Polybenzoxazine based on bisphenol-A and methylamine, type 2 |
| PBA2-a | Polybenzoxazine based on bisphenol-A and aniline, type 2 |
| PPh3-m | Polybenzoxazine based on phenol and methylamine, type 3 |
| PPh4-a | Polybenzoxazine based on phenol and aniline, type 4 |
| PBA4-a | Polybenzoxazine based on bisphenol-A and aniline, type 4 |

## 2.2. Thermal characterization

TGA technique was used in order to understand the degradation kinetics of the polymers by using a *2950 TGA HR V5.4A*, (Department of Macromolecular Science and Engineering, Case Western Reserve University) under nitrogen atmosphere, by Dr. Tamer Uyar. The temperature was increased to 850 °C at a heating rate of 10 °C/min. The TGA curves obtained for PPh-m, PPh-a, PBA-m and PBA-a are given in Figure 2-1.

### 2.2.1. Direct pyrolysis mass spectrometry

The Benzoxazine monomers and polymers were pyrolyzed separately. DP-MS analyses were carried out by using *Waters Quattro Micro GC Mass Spectrometer* with a mass range 10 – 1500 Da. EI (electron impact) ion source was coupled to a direct insertion probe. 70 eV EI mass spectra, at a rate of 1 scan/s, were continuously recorded during the pyrolysis. Deep capillary quartz tubes were used as sample containers.

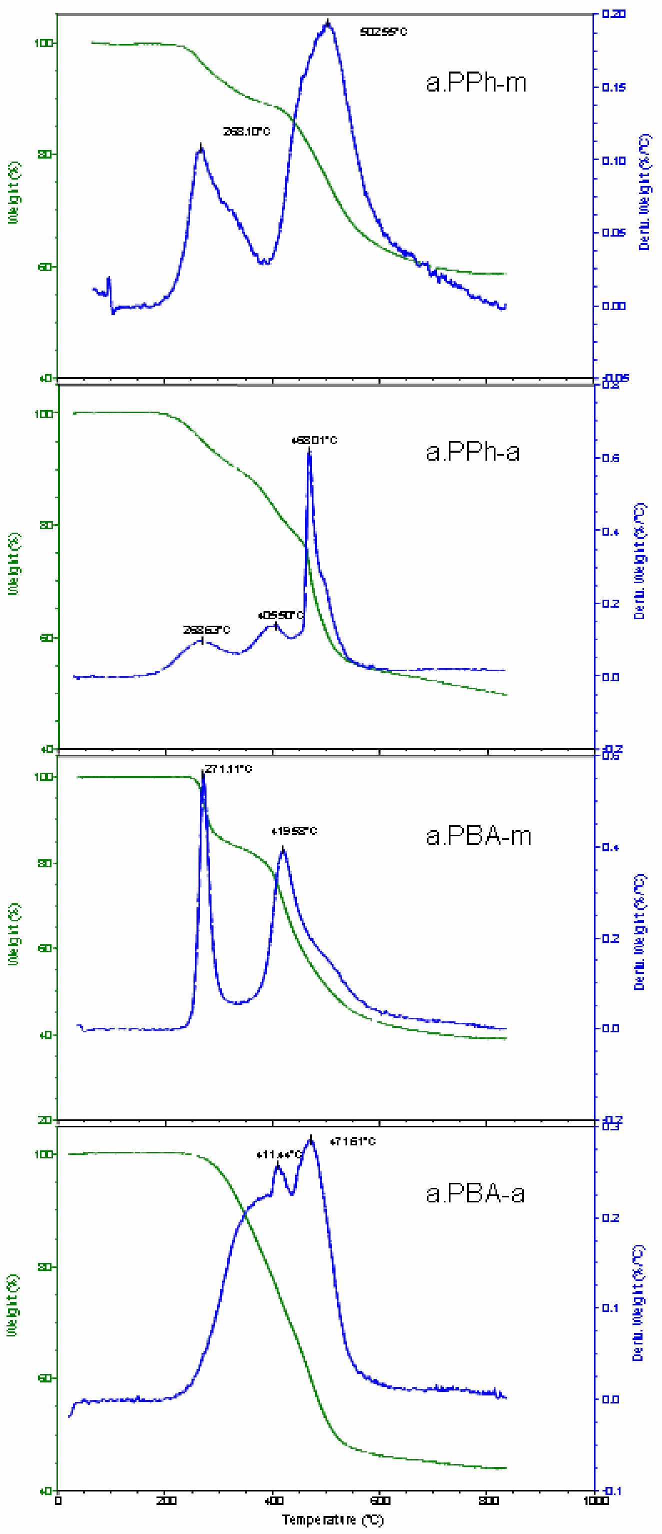


Figure 2-1 : TGA curves of the polybenzoxazines.

During the pyrolysis of the benzoxazine monomers and polymers the temperature was increased to 50 ºC at a rate of 5ºC /min., then it was raised to 650 ºC at rate of 10 ºC/min and finally kept at 650 ºC for 5 additional minutes.

In order to investigate the curing behaviour of benzoxazine monomers, the monomers were heated inside the mass spectrometer by applying the same step-wise curing program used for the synthesis of the polymers in an oven. In order to control the extent of evaporation of the monomers under the high vacuum conditions of the mass spectrometer, two different heating rates were used. In the first case, the temperature was increased at a rate of 10 ºC/min to each step, in the second case, a flash heating program for raising the temperature to threshold values was applied.

In order to determine whether the polymerization of the monomers occurred under high vacuum conditions of the mass spectrometer during the curing process or not, the samples were further heated to 650 °C at a rate of 10 ºC, when the curing program was completed.

After the pyrolysis, the total ion curves (TIC), the variation of total ion yield as a function of temperature and single ion evolution profiles (single ion pyrograms) and pyrolysis mass spectra of the samples were analyzed by a special software program called *Mass lynx V4.1* copyrighted by Waters Cooperation.

All DP-MS analyses were performed at least twice in order to ensure reproducibility. Furthermore, curing experiments were also repeated using recrystallized monomers in methanol in order to eliminate the effects of presence of oligomers and/or polymers that might have been produced during the transport or storage.

### 2.2.2. Data Analysis

For the analyses of curing and thermal behaviour of the samples, the mass spectra recorded at the maximum of the peaks present in the TIC curve were analyzed first. In the first step, all intense and characteristic peaks in the mass spectra of the monomers were identified and a fragmentation pattern for each monomer was proposed.

In the next step, all intense and characteristic peaks in the pyrolysis mass spectra of the polymers were identified. The trends in the evolution profiles were used to classify the products according to the source of generation to determine whether it was generated during pyrolysis or during the dissociative ionization processes in the mass spectrometer. Products were grouped considering the similarities in their evolution profiles and then taking into account probable thermal degradation processes and classical fragmentation pathways for organic compounds during ionization, curing and thermal degradation mechanisms were proposed [25].

# CHAPTER 3

# RESULTS AND DISCUSSION

Polymerization and thermal degradation of benzoxazines based on phenol or bisphenol-A, and two different Mannich bases methyl amine and aniline were investigated by direct pyrolysis mass spectrometry technique. Furthermore, the effect of different functional groups on polymerization and thermal degradation and crosslinking processes were studied for each benzoxazine.

## 3.1. Polymerization and thermal degradation of benzoxazine based on phenol and methyl amine

In order to investigate the polymerization and thermal degradation mechanisms of benzoxazine based on phenol and methyl amine monomer, Ph-m, pyrolysis mass spectrometry analysis of the monomer applying a heating rate of 10 °C/min from the room temperature to 650 °C and the curing program used for the preparation of the polymer in an oven was applied. After the curing program was completed, the heating was continued further to determine the thermal degradation characteristics of the polymer if generated during the curing under the high vacuum conditions of the mass spectrometer.

### 3.1.1. Curing of benzoxazine monomer based on phenol and methylamine

Pyrolysis of the Benzoxazine based on phenol and methylamine

Pyrolysis of the monomer yielded a total ion current (TIC) curve that is variation of total ion yield as a function of the heating profile, with three shoulders. As discussed in part 2.2.2, presence of more than one peak in the TIC curve indicates presence of either a multi-component sample or units with different thermal stabilities. The relative intensities of intense and/or characteristic peaks present in the mass spectra recorded at the maxima of the peaks present in the TIC curve recorded during the pyrolysis of Ph-m (Figure 3-1) are summarized in Table 3-1.

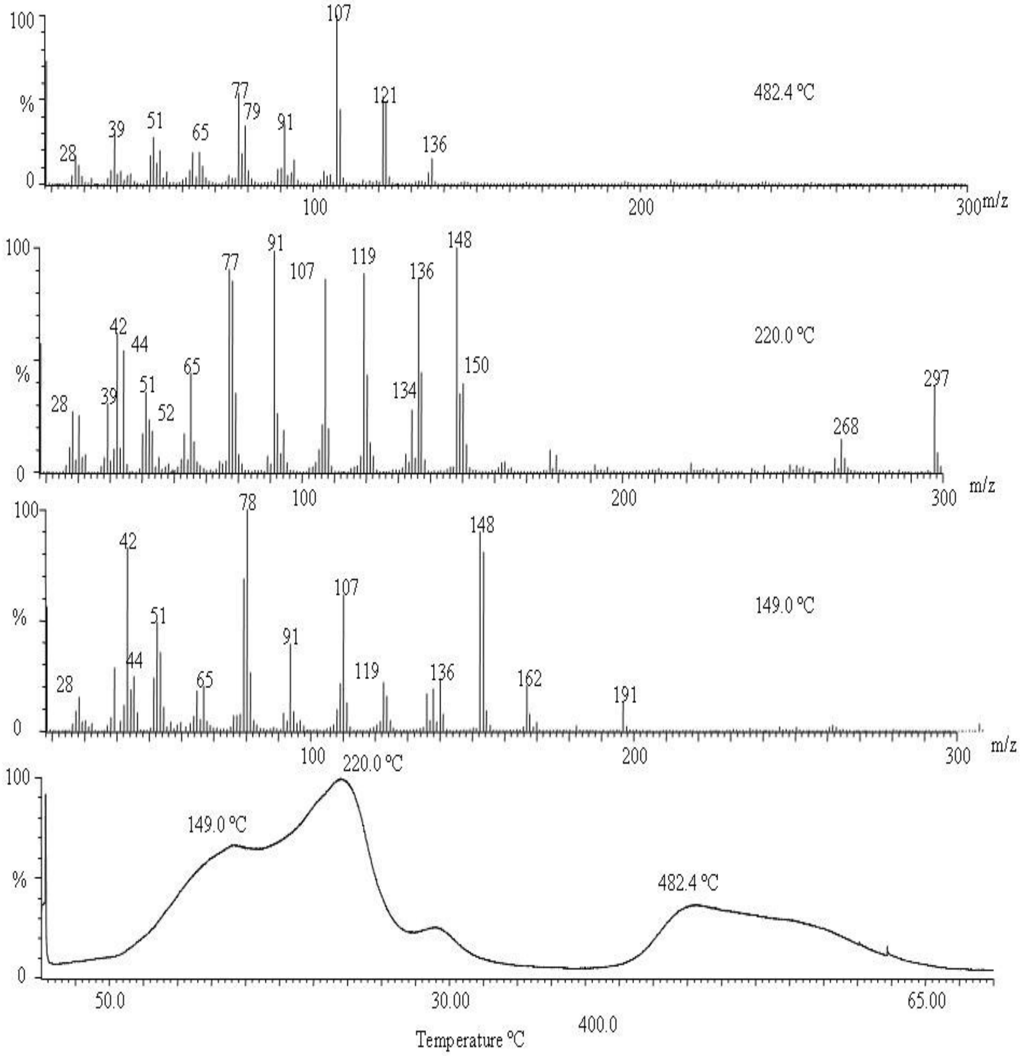


**Figure 3-1 : The TIC curve and the spectra at the three maxima present in the TIC curve of Ph-m monomer.**

**Table 3-1: Mass spectral data recorded during the pyrolysis of Ph-m and the assignments made.**

| m/z | Relative Intensities | | | | Assignment |
|---|---|---|---|---|---|
| | 149ºC | 220ºC | 291ºC | 482ºC | |
| 28 | 151.8 | 13.7 | 997.7 | 115 | $CH_2CH$, $CH_2N$ |
| 30 | 52 | 251.9 | 1000 | 7.6 | $CH_3NH$, $CH_2NH_2$ |
| 31 | 19.4 | 67.7 | 602.3 | 8.1 | $CH_3NH_2$, $CH_3O$ |
| 42 | 840 | 620 | 371.9 | 21.3 | $CH_2$ N $CH_2$, |
| 43 | 187 | 106.8 | 143.9 | 44.5 | $CH_2CH_2NH$ |
| 44 | 262 | 540.8 | 502.1 | 58.8 | $CH_2CH_2NH_2$, $CH_2NHCH_3$ |
| 45 | 78.8 | 36.2 | 260.5 | 11.9 | $CH_2NH_2(CH_3)$ |
| 58 | 35.9 | 37.4 | 125.5 | 2 | $CH_2(CH_3)NHCH_2$, |
| 72 | 8.2 | 4.3 | 26.3 | 1.1 | $CH_2(CH_3)NHCH_2CH_2$ |
| 78 | 1000 | 850.9 | 27.1 | 178.6 | $C_6H_6$ |
| 86 | 14.3 | 7.2 | 2.09 | 14.5 | $CH_2(CH_3)NHCH_2CH_2N$, $C_4N_2H_{10}$ |
| 91 | 401.6 | 984.1 | 45.3 | 348.9 | $C_7H_7$ |
| 107 | 614 | 858.8 | 33.7 | 1000 | $HOC_6H_4CH_2$ |
| 119 | 228.5 | 883.8 | 7 | 22 | $C_6H_4CH_2NHCH_2$, |
| 132 | 159.7 | 79.6 | 4.6 | 22.4 | $C_6H_4CH_2N(CH_3)CH_1$ |
| 136 | 264.9 | 863.5 | 39.7 | 145.4 | $HOC_6H_4CH_2NCH_3$ |
| 148 | 925 | 1000 | 15.2 | 3.9 | $C_6H_4OCH_2N(CH_2)CH_2$ |
| 149 | 780 | 348.9 | 13 | 2.6 | $C_6H_4OCH_2N(CH_3)CH_2$ (Monomer) |
| 150 | 97.5 | 394.6 | 1.8 | 3 | $HOC_6H_4CH_2N(CH_3)CH_2$ |
| 221 | 1.3 | 39.7 | 0.1 | 2.3 | $HOC_6H_4CH{=}CHC_6H_4CH{=}CH$ |
| 238 | 17.6 | 193.6 | 0.3 | 14.7 | $HOC_6H_4CH{=}NCH_2C_6H_4CH{=}NH$ |
| 268 | 2.3 | 148.1 | 0.1 | 0.4 | $HOC_6H_4CH(CH_3)C_6H_4(CH_2NCH_3CH_2CH_2)$ |
| 298 | 31.5 | 86.3 | 0.2 | 0.1 | $(HOC_6H_4CH_2N(CH_3)CH)_{2\,,}$ Dimer) |
| 447 | 0.7 | 155.3 | 0.0 | 0.0 | Trimer |

In order to get a better understanding, single ion evolution profiles, single ion pyrograms, of all products were studied in detail and then the products were grouped taking into account the trends in their evolution profiles. In Figure 3-2, single ion evolution profiles of some monomer based products, namely monomer, M, [M-OH], [M-$C_2H_4N$], $C_6H_6$ and $C_2H_4N$ at m/z=149, 132, 78, and 42 respectively, dimer based products, namely, dimer D, MH, at m/z=298 and 150 and trimer based products, trimer, T, at m/z=497 and [T- $HOC_6H_4CH_2$] at 340 are shown. Both monomer and dimer evolutions were detected in the temperature range 70-260 ºC. However, the monomer evolution was more dominant at around 142 ºC where as that of dimer was more dominant at around 221 ºC. Trimer evolution was detected in a narrower temperature range just above 150 ºC and as the temperature increased, the oligomer yield was also increased. This is an expected behaviour as both the production and the evaporation of dimer should be enhanced with an increase in temperature. On the other hand, evolution of alkyl amines showed significant differences. Evolution profiles of $CH_2NCH_2$ at 42 Da showed identical trends with those of the monomer based products below 260 ºC. However, a third sharp peak with a maximum at 290 C was present in its evolution profiles. A similar trend was observed in the evolution profiles of $(CH_2)_xNH_2$, and $(CH_2)_{x-1}NH(CH_3)$, and $(CH_2)_xN_2$ where x=2, 3, or 4 in the region where no monomer and/or low mass oligomer evolutions were observed. In Figure 2 evolution profiles of $CH_2NH_2$, $CH_2NCH_2$and $C_5H_{10}NH_2$ at m/z=30, 42 and 58 are also included. It is clear that generation of $(CH_2)_xNH_2$ where x=2 or 3 were more significant in this region.

The evolution of dimer and trimer and the observed peaks in accordance with expected classical fragmentation pathways of the monomer pointed out the attack of –$NCH_2$ group to ortho position of the phenol ring as proposed in the literature [4]. On the other hand, the evolution of alkyl amines involving more than three C atoms indicated presence of chains generated by different polymerization routes.

Thus, pyrolysis of the benzoxazine monomer indicated evolution of low mass oligomers and degradation of high mass polymer chains with different structures. It may be thought that all the high mass products may be generated during the pyrolysis process. However, they might have also been produced during the transport and storage.

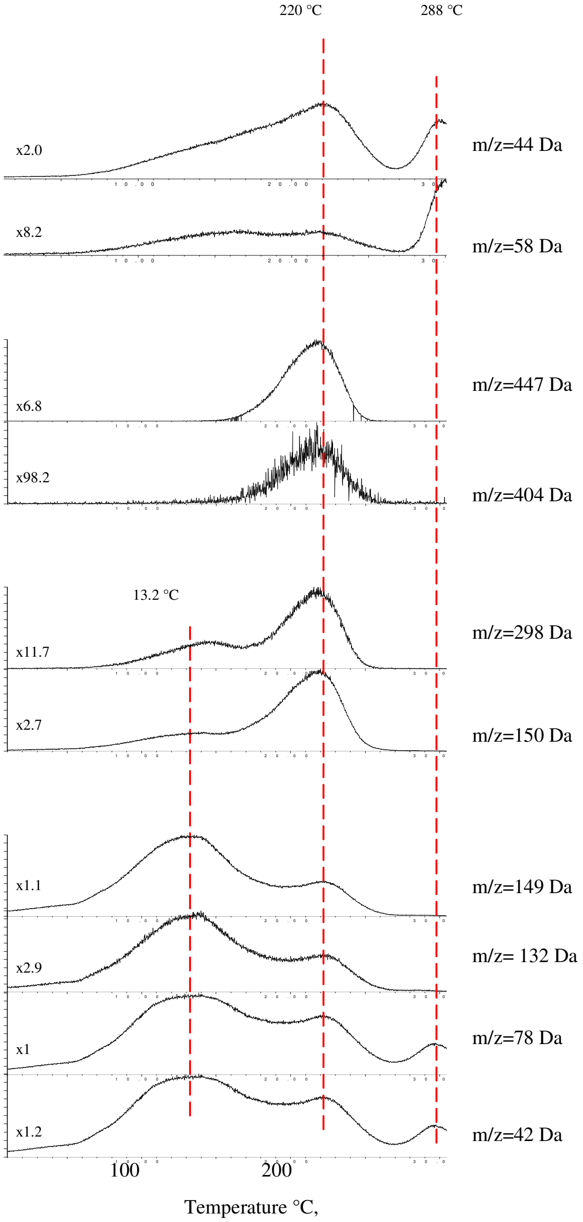
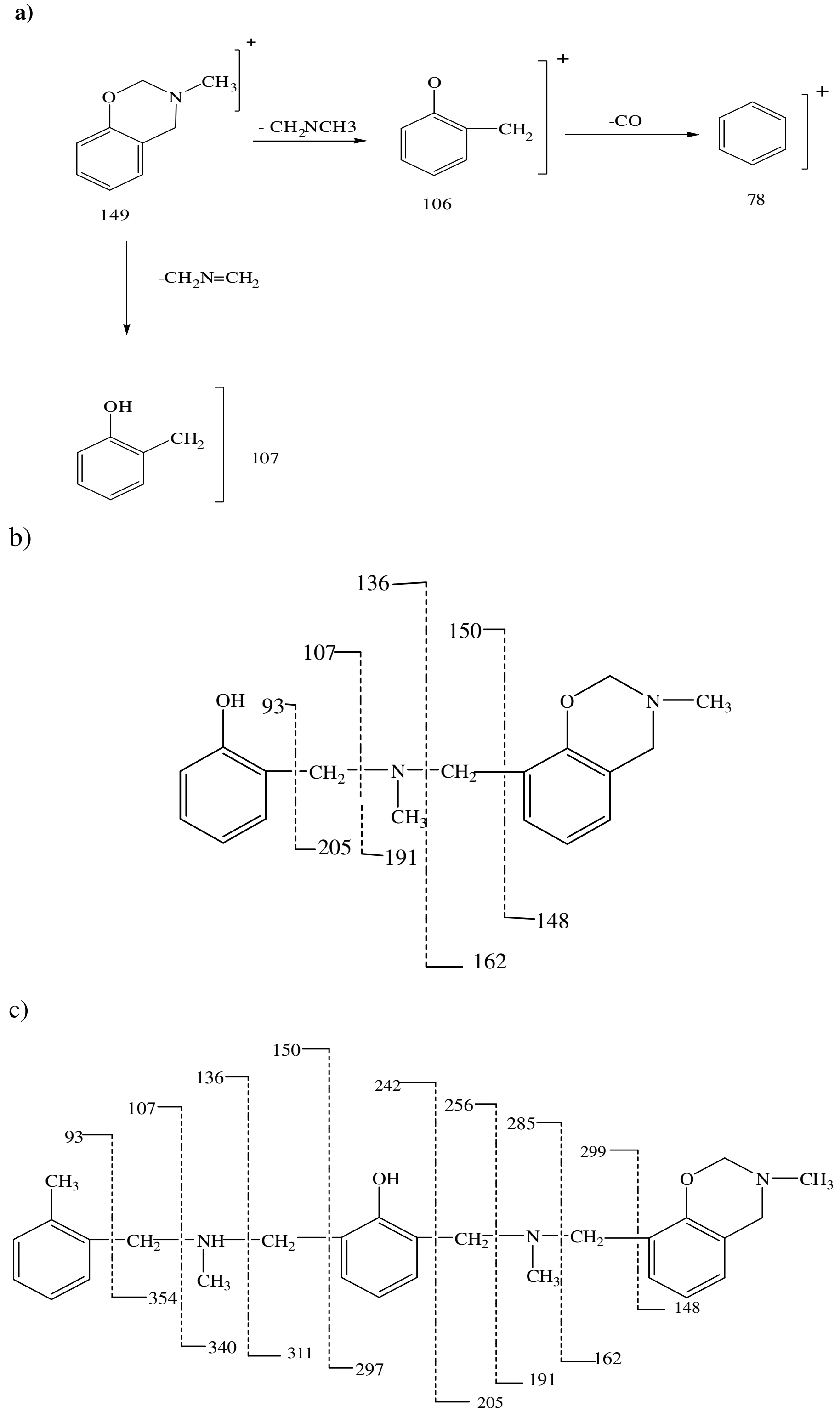


**Figure 3-2: Single ion pyrograms of some selected products of Ph-m monomer.**



**Scheme 3-1: Fragmentation pathways for the dissociative ionization of benzoxazine based on phenyl and methyl amine a) monomer b) dimer c) trimer.**

## Step-wise Curing of Benzoxazine based on phenol and methylamine

During the curing process, polymerization by ring opening of the oxazine ring of the benzoxazine is expected according to the literature results. Decomposition of the monomer and/or low mass oligomers may also take place at least to a certain extent. However, in our case, as the curing process was carried out inside the high vacuum conditions of the mass spectrometer, evaporation of the monomer and low mass oligomers was likely. Thus, the peaks in the mass spectra recorded during the curing process may be due to dissociative ionization of evaporated monomer, low mass oligomers and thermal degradation products during the EI ionization in the mass spectrometer. In general, in case of pyrolysis mass spectrometry analyses of a sample, it is assumed that the ions with identical evolution profiles are generated by dissociative ionization of either a volatile component or a thermal degradation product. Among all the ions having similar evolution profiles the one with the highest m/z value can be assumed to be the parent ion generated by ionization of a component evaporated or degraded from the sample during heating. In general, the similarity between the single ion evolution profiles of the fragment ions with that of the molecular ion confirms evaporation before decomposition. Thus, in order to investigate all the possible processes taking place during curing, single ion evolution profiles of each product detected in the mass spectra were analyzed and compared with each other and with that of the molecular ion.

The total ion current, TIC, curve and the mass spectra recorded at the maximum of the peaks present in the TIC curve recorded during the curing of methyl amine-based benzoxazine, Ph-m, while applying the stepwise curing program are shown in Figure 3-3. Evolution of the monomer under the high vacuum conditions of the mass spectrometer was recorded at initial stages of curing. Evolution of dimer, although not very extensive, was also noted shortly after the temperature was set to 160°C. The yields of monomer and dimer were increased sharply in the first 2 minutes and then decreased almost exponentially. After curing for 4 min, the evaporated monomer yield was only about 1 % of the value at the start. As the curing was proceeded stepwise, a slight increase in the yield of monomer was detected. Evolution of the monomer was totally over after curing at 200 °C.

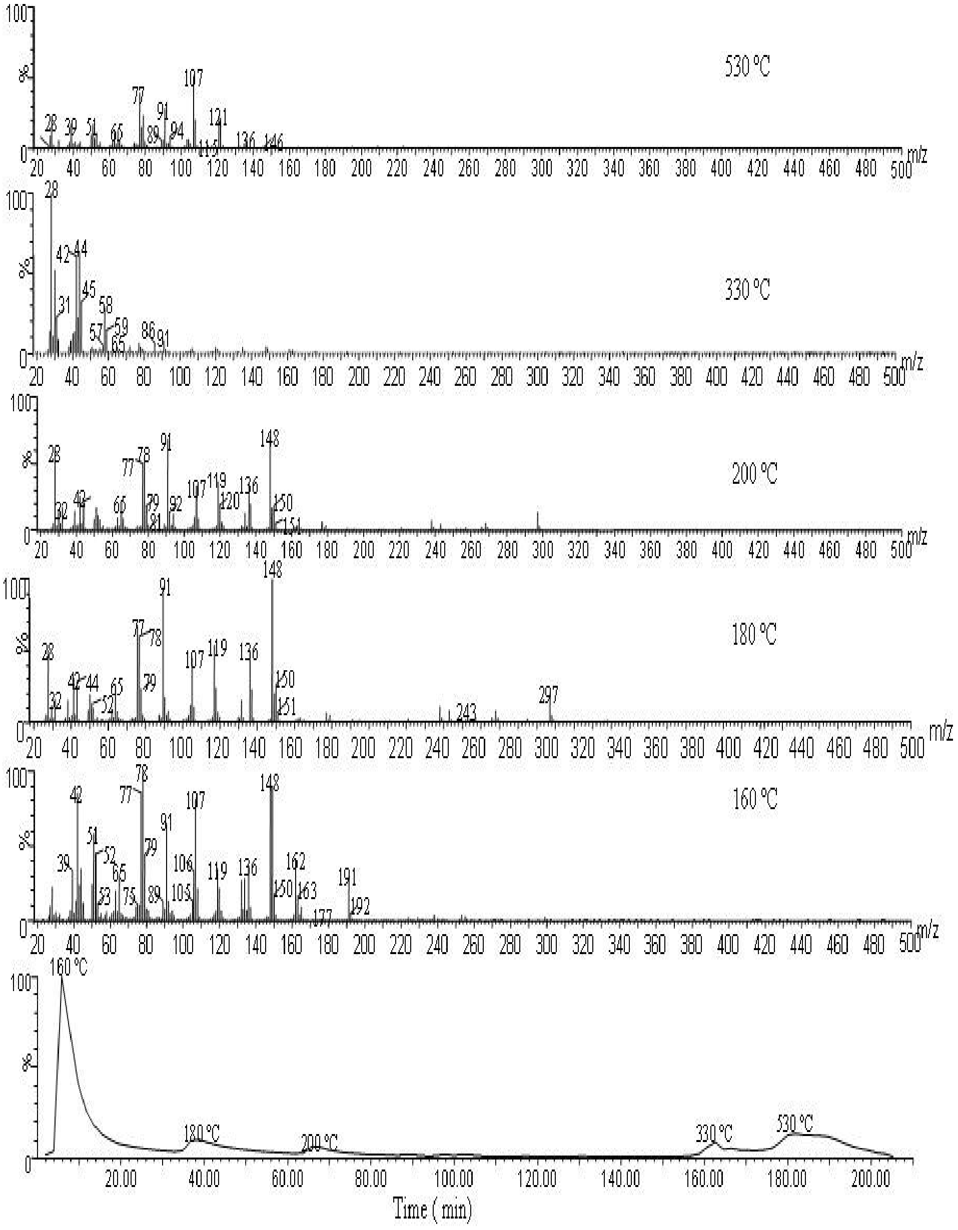


**Figure 3-3: The TIC curve and the spectra recorded at the maxima present in the TIC curve recorded during the curing and pyrolysis of Ph-m.**

The mass spectra were dominated with peaks that can directly be associated with $C_6H_4CH_2N(CH_3)CH_2$, $C_6H_4CH_2NCH_3$, $HOC_6H_4CH_2$, and $OC_6H_4CH_2$ with m/z values 132, 119, 107 and 106 due to loss of OH, $CH_2$=O $CH_2$=$NCH_2$, and $CH_2$=$NCH_3$ respectively, $C_6H_6$ (m/z=78) due to loss of CO from $OC_6H_4CH_2$ (O-$C_7H_6$) and alkyl amines indicating dissociative ionization parallel to the proposed fragmentation pattern of the monomer (Scheme 3-1).

A careful study of the mass spectra and the single ion pyrograms of each fragment ion pointed out evaporation of the monomer, and some dimer and trimer before decomposition until the last step of curing at 210 °C. In Figure 3-4, single ion evolution profiles of monomer, M, (m/z=149), dimer (m/z=298) and trimer (m/z=447) and some characteristic fragments such as $HOC_6H_4CH_2$ (m/z=107 Da), $C_6H_6$ (m/z=78 Da) and $CH_2$=$NCH_2$ (m/z=42 Da) are shown.

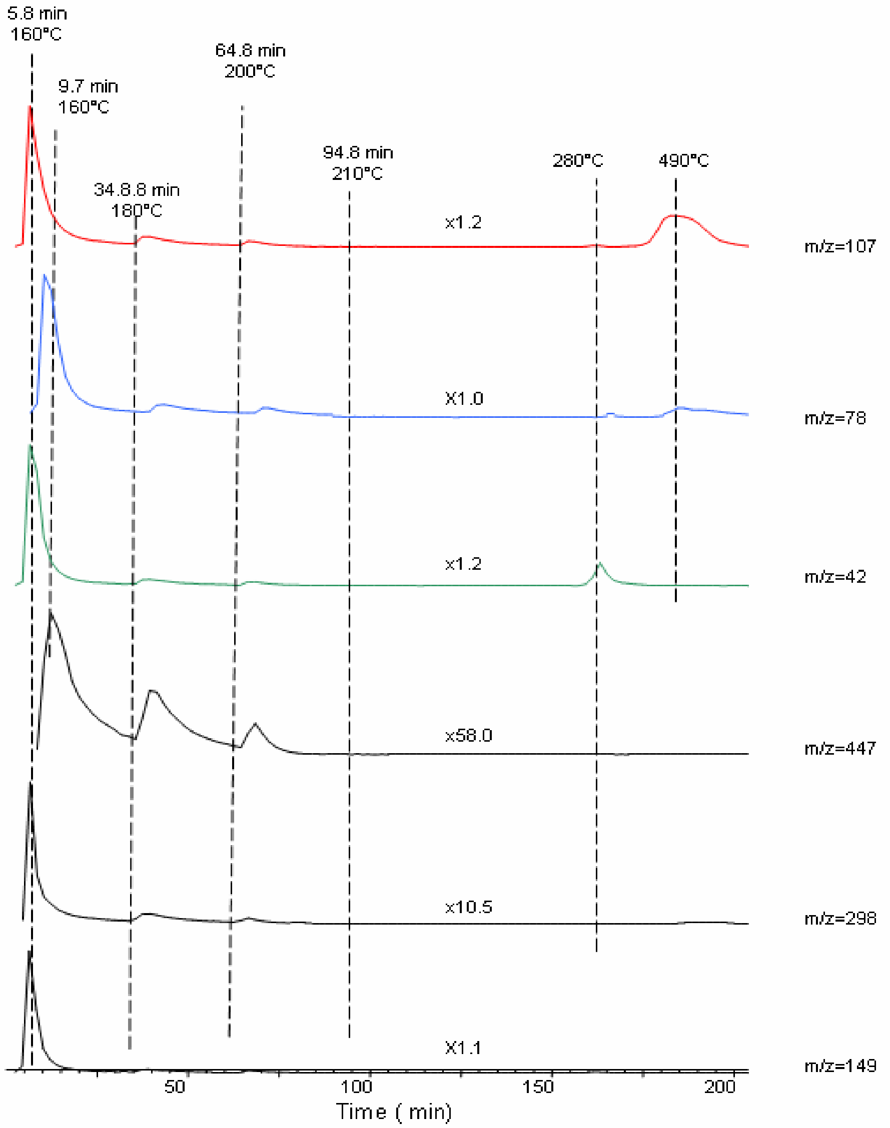


**Figure 3-4: Single ion evolution profiles of selected products detected during the curing of Ph-m monomer.**

The monomer cured inside the mass spectrometer was further heated at a rate of 10° C up to 650 °C. Evolution of thermal degradation products were detected above 250°C. The TIC curve recorded through out the process and the pyrolysis mass spectra at the maximum of the peaks present in the TIC curve are shown in Figure 3-3. Above 250 °C the appearance of the TIC curve and the pyrolysis mass spectra were identical to those recorded during the pyrolysis of the polymer (Section 3.1.2). The evolution profiles of the products also showed similar trends. Thus, it can be concluded that polymerization proceed almost through to same reaction pathways even under high vacuum conditions of the mass spectrometer. Almost an identical trend was observed when the heating rate for stepwise curing was decreased. The peaks present in the pyrolysis mass spectra recorded during the curing process were almost similar to the corresponding ones recorded during the application of the first heating program.

In order to be sure whether oligomer and polymer formation took place during the pyrolysis and curing of the monomer inside the mass spectrometer or during the transport and storage, experiments to purify the monomer were carried out. The pyrolysis mass spectrometry analysis of the monomer recrystallized in methanol yielded almost identical results. Monomer evolution at initial stages of pyrolysis was recorded. Again, upon further heating to 650 °C after the curing program was completed, evolution of products that can readily be attributed to decomposition of a polymeric structure was detected. On the other hand, the relative intensities of dimer and trimer peaks present in the mass spectra during the curing process decreased significantly. Thus, it can be concluded that only low mass oligomers were generated during the transport and storage and evolution of products at elevated temperatures were due to the thermal decomposition of the polybenzoxazine generated during the curing process inside the mass spectrometer.

### 3.1.2. Thermal degradation of polybenzoxazine based on phenol and methylamine

The TIC curve and the mass spectra recorded during the pyrolysis of the polymer prepared according to the step-wise curing program in an oven were almost identical (Figure 3-5) to the corresponding ones detected for the polymer produced inside the mass spectrometer during curing process. The TIC curve was quite similar to TGA curve (Figure 2-1.a) showing to maxima at 278 and 493 °C. The two step weight losses were detected at 268 and 503°C during the TGA analyses. Presence of more than one peak in the TIC curve of a polymeric substance indicates either a multi step thermal degradation and/or presence of different units. Evolutions of alkyl amines and fragments that can be attributed to diamines were detected at around 270 °C. Products involving phenyl ring evolved at relatively high and broad temperature range, 430 to 600 °C. The relative intensities of the characteristic and/or intense peaks present in these spectra and the assignments made are summarized in Table 3-2.

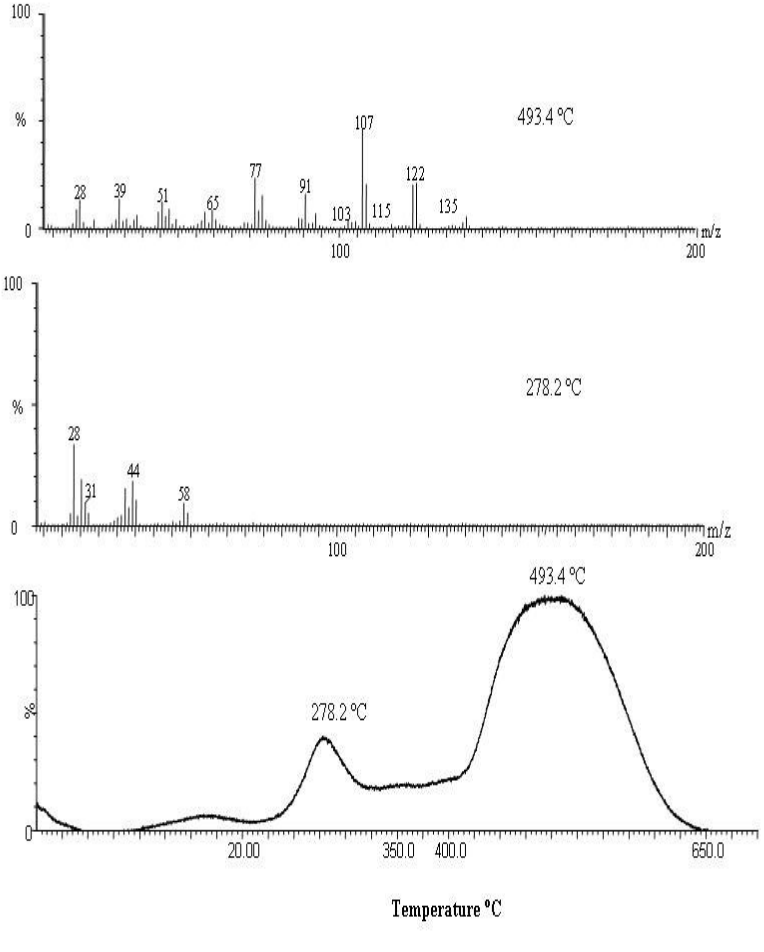


**Figure 3-5: The TIC curve and the spectra at the two maxima present in the TIC curve of PPh-m.**

**Table 3-2: Relative intensities of intense and/or characteristic peaks detected in the pyrolysis mass spectra of polybenzoxazine, PPh-m.**

| m/ | 285° | 474° | 548° | 570° | Assignments |
|---|---|---|---|---|---|
| 30 | 175 | 9 | 8 | 6 | $CH_3NH$ |
| 42 | 175 | 32 | 32 | 21 | $CH_2CH_2N$ |
| 43 | 87 | 81 | 93 | 56 | $CH_2NCH_3$ |
| 58 | 99 | 7 | 6 | 3 | $CH_2(CH_3)NHCH_2$, |
| 77 | 10 | 458 | 103 | 292 | $C_6H_5$ |
| 86 | 4 | 10 | 14 | 10 | $CH_2(CH_3)NHCH_2CH_2N$, $C_4N_2H_{10}$ |
| 91 | 8 | 340 | 329 | 297 | $C_7H_7$ |
| 94 | 4 | 103 | 165 | 226 | $C_6H_5OH$ |
| 10 | 5 | 65 | 77 | 90 | $C_6H_5CH_2NH$ |
| 10 | 3 | 20 | 18 | 57 | $HOC_7H_6$ |
| 10 | 7 | 822 | 1000 | 527 | $HOC_6H_4CH_2$ |
| 12 | 5 | 460 | 388 | 102 | $HOC_6H_4CH_2N$ |
| 12 | 2 | 412 | 424 | 147 | $HOC_6H_4CH_2NH$ |
| 13 | 6 | 65 | 37 | 8 | $HOC_6H_4CH_2NCH_2$ |
| 13 | 1 | 137 | 90 | 16 | $HOC_6H_4CH_2NCH_3$ |
| 14 | 6 | 4 | 3 | 2 | [M-H] |
| 16 | 1 | 12 | 16 | 19 | $HOC_6H_4CH_2NHCH_2CH_2NH$ |
| 17 |  | 4 | 6 | 18 | $HOC_6H_4CH_2NHCH_2CH_2NCH_2$, |
| 19 |  | 2 | 3 | 15 | $C_6H_4CH{=}CHC_6H_4CH_2$ |
| 19 | 2 | 7 | 8 | 7 | $C_6H_4CH_2NCH_2C_6H_4$, $HOC_6H_3CH{=}CHC_6H_4$ |
| 20 |  | 2 | 4 | 15 | $C_6H_4CH{=}CHC_6H_4CH_2N$, |
| 20 |  | 24 | 35 | 22 | $C_6H_4CH_2NHCH_2C_6H_4CH_{2,}$ |
| 21 |  | 1 | 18 | 14 | $HOC_6H_4CH{=}NCH_2C_6H_4$ |
| 22 | 1 | 19 | 29 | 15 | $HOC_6H_4CH{=}CHC_6H_4CH_2N$ |

Actually, the pyrolysis mass spectra of the polymers are usually very complex as thermal degradation products further dissociate in the mass spectrometer during ionization. Furthermore, all the fragments with the same mass to charge ratio have contributions to the intensity of the same peak in the mass spectrum. Thus, in pyrolysis MS analysis, not only the detection of a peak but the changes in its intensity (single ion pyrograms, evolution profiles) as a function of temperature has significant importance. Presence of more than one peak in the single ion evolution profile indicates either generation of the same product from different polymeric chains through different degradation mechanism or evolution of fragments with the same m/z value but different structures. The trends observed in the single ion evolution profiles of the products were quite different; product yields were maximized at about four different temperatures, at 285, 474, 548 and 570 °C. The evolution profiles of some diagnostic products, $CH_2NCH_2$ (m/z=42), $CH_2NCH_3$ (m/z=43), $C_6H_4CH_2NCH_3$ (m/z=121), $HOC_6H_4CH_2NCH_2$ (m/z=136), $HOC_6H_4CH_2$ (m/z=107), $C_6H_5CH_2NH$ (m/z=105), $HOC_6H_5$ (m/z=94), $C_7H_7$ (m/z=91) AND $HOC_6H_4CH$ (m/z=106), are given in Figure 3-6. The evolution profiles of products that can be attributed to units involving amines and/or diamines with more than three carbons ($C_5H_{14}N$ or $C_4H_{12}N_2$ with m/z=86) and to units involving unsaturation ($HOC_6H_4CH{=}CHC_6H_4CH_2N$, $C_6H_4CH{=}CHC_6H_4CH_2N$ and $C_6H_4CH{=}CHC_6H_4CH_2$ with m/z=223, 206 and 192 Da respectively) are also included in Figure 3-6.

Ring opening polymerization of benzoxazines, cleavage of O-$CH_2$ bond of oxazine ring followed by attack of –$NCH_2$ group to the phenol ring was proposed in several studies in the literature [4]. Thermal degradation of such a polymer (PPh1-m) should yield fragments due to cleavages at β carbon to the phenyl ring or to N atom as in the case of the dissociative ionization of benzoxazine monomer, dimer and trimer (Scheme 3-1). Presence of peaks at 136, 107 and 77 that can directly be attributed to $HOC_6H_4CH_2NCH_3$, $HOC_6H_4CH_2$ and $C_6H_5$ respectively supports this proposal. However, unlike what was observed for the monomer in the temperature range up to 210°C, the trends in the evolution profiles of alkyl amines and phenyl involving fragments showed significant differences. Evolutions of alkyl amines and/or diamines involving more than three C atoms were mainly detected at around 285 °C. In this region, the relative intensities of the peaks that can be attributed to fragments involving aromatic ring were quite weak.

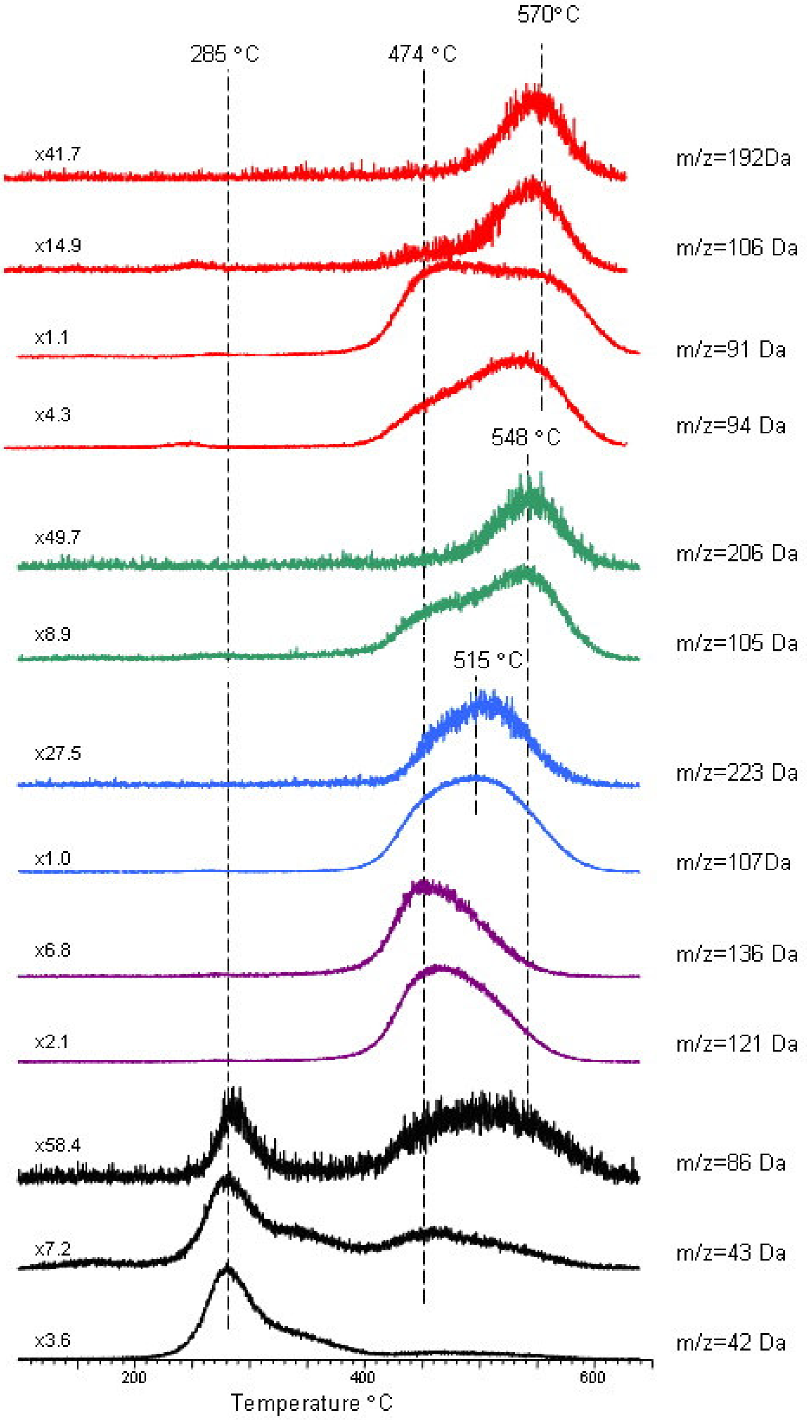
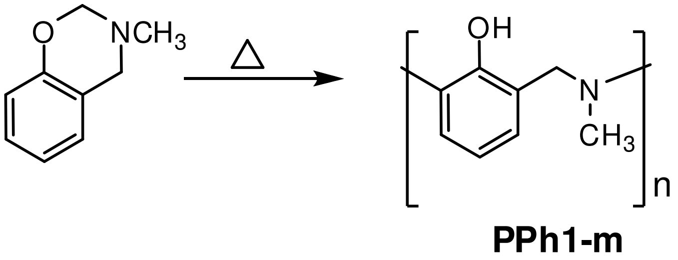


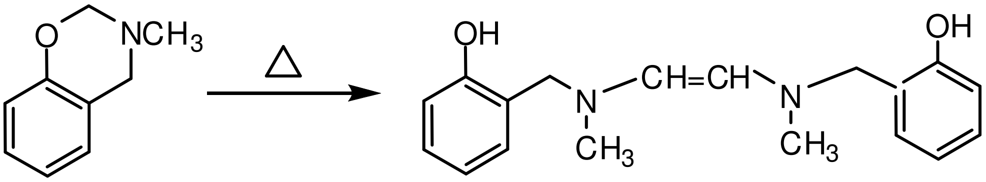
**Figure 3-6: Evolution profiles of some diagnostic products detected during the pyrolysis of PPh-m.**

On the other hand, the evolution of species bearing phenyl ring were detected above 450°C and followed different trends pointing out presence of units with different structures due to polymerization through different pathways in addition to the proposed route given in the literature [4].



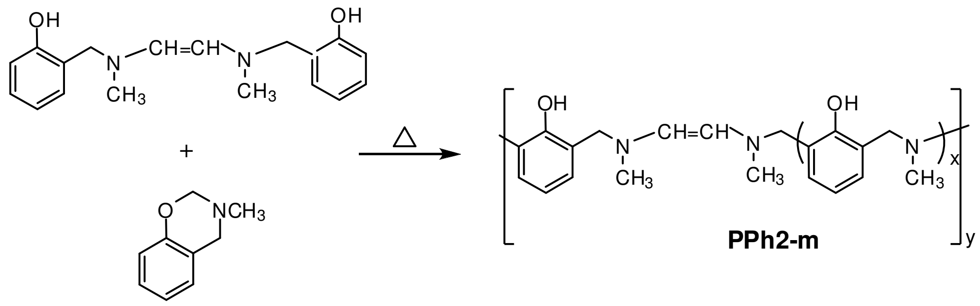
**Scheme 3-2: Ring opening polymerization of benzoxazine proposed in the literature.**

The evolution of alkyl amine or diamines involving more than three C atoms, (i.e. $C_4H_{10}N_2$ or $C_5H_{12}N$ and $C_3H_8N_2$ or $C_4H_{10}N$ fragments with m/z values 86 and 72) at early stages of pyrolysis revealed presence of chains generated by coupling of -$NCH_2$ groups as shown in Scheme 3-3 at least to a certain extent. Consecutive reactions (Scheme 3-2 and/or 3-3) would yield a polymer (PPh2-m) involving phenol units connected by both mono and diamine alkyl chains (Scheme 3-4.a). Another possibility is the polymerization of the dimer generated by coupling of -$NCH_2$ groups, through the ethylene units yielding a vinyl polymer (PPh3-m) with phenolic side chains (Scheme 3-4.b).

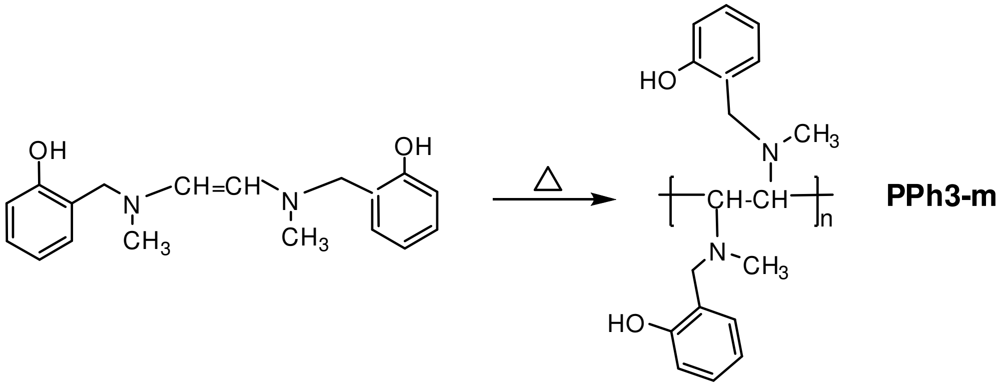


**Scheme 3-3: Generation of dimer by coupling of -NCH2 groups via ring opening of oxazine ring.**

### 3.4.a. Polymerization via ring opening

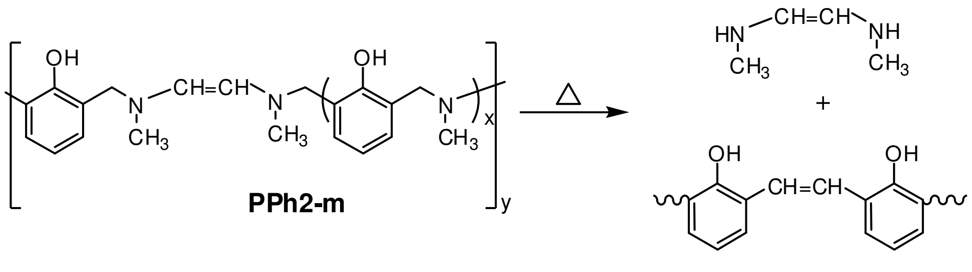


### 3.4.b. Polymerization through vinyl linkages



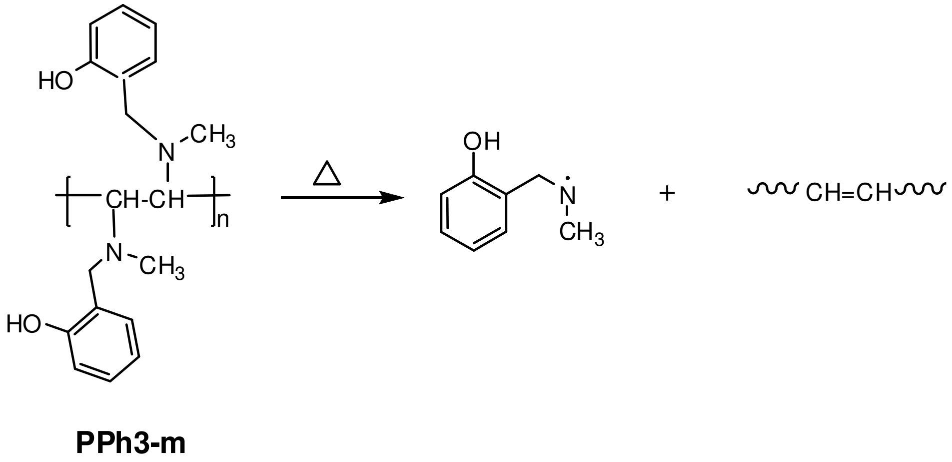
**Scheme 3-4: Polymerization of benzoxazine dimer involving diamine linkage.**

Thermal degradation of both PPh2-m and PPh3-m can be expected to occur in two steps. Loss of relatively labile diamine chains from PPh2 at early stages of pyrolysis would yield benzyl radicals that can couple and generate more stable units, –CH=CH- or -$CH_2$-$CH_2$-, that would degrade at relatively high temperatures as shown in Scheme 3-5.



**Scheme 3-5: Thermal degradation of PPh2-m.**

On the other hand, thermal degradation of the vinyl polymer PPh3-m should again occur in two steps, the first being the loss of side chains and the second being the decomposition of the unsaturated polymer backbone (Scheme 3-6). The crosslinking processes that would increase the char yield should also be considered for the polymer backbone generated by the loss of side chains of PPh3-m (Scheme 3-6).



**Scheme 3-6: Thermal degradation of PPh3-m.**

Considering the proposed polymer structures it may be thought that the thermal degradation was started by loss of relatively labile diamine units of PPh2-m at around 285°C. The fragments with m/z values 91, 94, 105, 121 and 136 that can directly be attributed to $C_7H_7$, $C_6H_5OH$, $C_6H_6CH_2NH$, $HOC_6H_5CH_2N$ and $HOC_6H_5CH_2NCH_3$ showing either a maximum or a shoulder at around 465°C in their evolution profiles may be associated with the degradation of PPh1 and $HOC_6H_4CH_2NHCH_3$ units of PPh2-m. On the other hand, the evolution of products maximizing at around 500°C may be attributed to the decomposition of PPh2 polymer backbone generated by the loss of diamines at around 280 °C involving –CH=CH linkages. On the other hand, the ones reaching maximum yield at around 570 °C may be associated with the degradation of the unsaturated polymer backbone generated by loss of phenolic side chains from PPh3-m.

## 3.2. Polymerization and thermal degradation of benzoxazine based on phenol and aniline

In order to investigate the effect of aniline group on the fragmentation pathways of phenol and aniline based benzoxazine monomer (Ph-a) and polymer (PPh-a) pyrolysis mass spectrometry analysis were performed. Mass spectra were recorded during the curing of the monomer by applying the two curing programs, and pyrolysis of the monomer and polymer. Experiments were also repeated for the recrystallized monomer. However, only the results obtained from the mass spectrometry analysis of curing of the virgin monomer and pyrolysis of the polymer prepared using the same curing program in an oven are discussed, as no extra information was obtained from the data on curing and pyrolysis of the monomer.

### 3.2.1. Curing of benzoxazine monomer based on phenol and aniline

Heating of the aromatic amine, aniline-based benzoxazine applying the program used for the curing process, yielded a total ion current (TIC) curve with several peaks and shoulders. The TIC curve and the pyrolysis mass spectra recorded at the maxima of the peaks present in the TIC curve are shown in Figure 3-7. Both molecular ion peak of the monomer and $CH_2=NC_6H_5$ fragment ion peaks were significantly intense as expected for aromatic structures. On the other hand the molecular ion peak for dimer was quite weak due to the high molecular mass. Yet, the presence of peaks such as those at 316 and 224 that can directly be attributed to fragments generated by lose of $C_6H_5$ and CO, and $HOC_6H_4CH_2NC_6H_5$ from the dimer during dissociative ionization in the mass spectrometer. The relative intensities of the characteristic and/or intense peaks present in these spectra and the assignments made are summarized in Table 3-4. Thus, fragmentation pattern of Ph-a monomer and dimer were proposed considering the peaks detected in the mass spectra and classical fragmentation patterns of organic molecules as shown in Scheme 3-7, indicating evolution of monomer, and dimer at initial stages of curing.

Inspection of single ion evolution profiles indicated increase in the extent of evolution of monomer slightly before the evolution of dimer. In Figure 3-8 single ion pyrograms of some intense and/or characteristic products namely monomer (m/z=211), dimer (m/z=422), $C_6H_6$, (m/z=78), $C_6H_5NCH_2$ (m/z=93) and $C_6H_5OCH_2$ (m/z=107) are shown. The appearance of intense peaks in the high temperature ranges pointed out polymerization of the sample even under the high vacuum conditions of the mass spectrometer. The fragmentation patterns for the monomer and dimer proposed in the light of mass spectral findings and the knowledge of classical fragmentation patterns of organic molecules are shown in Scheme 3-7.

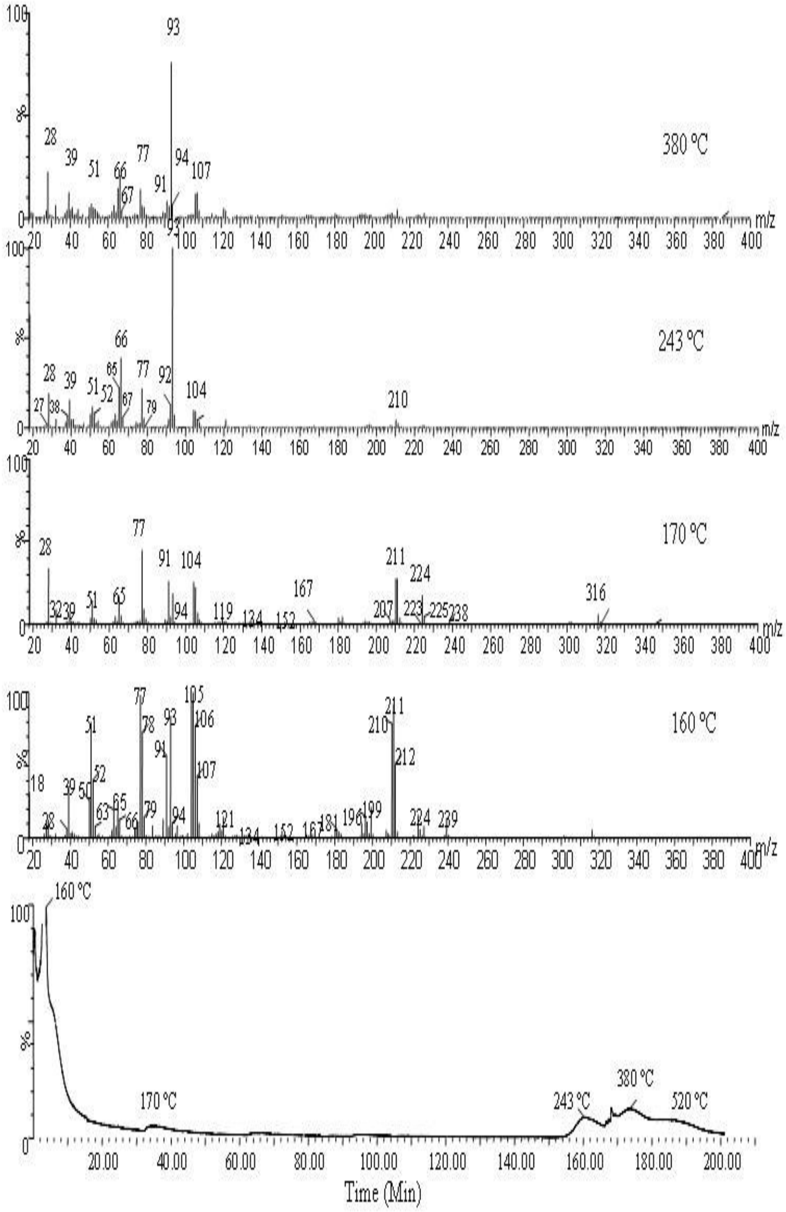


**Figure 3-7: The TIC curve and the spectra recorded at the maxima present in the TIC curve recorded during the curing and pyrolysis of Ph-a.**

**Table 3-3: Relative intensities and/or characteristic of intense peaks detected in the mass spectrum at 160 °C during the curing of Ph-a monomer.**

| m/z | RI | Assignment |
|---|---|---|
| 77 | 1000 | $C_6H_5$ |
| 78 | 673 | $C_6H_4OCH_2$ |
| 91 | 535 | $C_7H_7$ |
| 93 | 775 | $C_6H_5OH$ |
| 94 | 70 | $C_6H_5OH$ |
| 105 | 507 | $C_6H_5NCH_2$ |
| 106 | 761 | $C_6H_4OCH_2$ |
| 107 | 341 | $C\ _6H_4(OH)CH2$ |
| 134 | 12 | $C_6H_4O\ CH_2NCH_2$ |
| 182 | 19 | $C_6H_5CHN\ CH_2\ (C_6H_5)$ |
| 195 | 14 | $C_6H_5CH_2NH\ CH_2\ (C_6H_5)$ |
| 198 | 16 | $C_6H_5(OH)CH2N(C_6H_5)$ |
| 210 | 644 | $C_6H_5CH_2NH\ CH_2\ (C_6H_5)$ |
| 211 | 896 | $CH_3OC_6H_4CHNC_6H_5$, $C_6H_4O\ CH_2N(\ C_6H_5)\ CH_2$ |
| 212 | 357 | $C_6H_4(OH)CH2N(\ C_6H_5)\ CH2$ |
| 224 | 12 | $CH_2C_6H_4CH_2N(C_6H_5)CH_2O$ |
| 225 | 14 | $CH_2C_6H_3(OH)CH_2N(C_6H_5)CH_2$ |
| 316 | 2 | $C_6H_5OHCH_2N(C_6H_5)CH_2C_6H_4ON(C_6H_5)CH_2$ |
| 344 | 0 | $C_6H_5OHCHNCH_2C_6H_4ON(C_6H_5)CH_2$ |
| 345 | 0 | $C_6H_4(OH)CH_2N(C_6H_5)CH_2C_6H_4O\ CH_2NCH_2$ |
| 422 | 0 | $C_6H_4(OH)CH_2N(C_6H_5)CH_2C_6H_4O\ CH_2N(C_6H_5)CH_2$ |

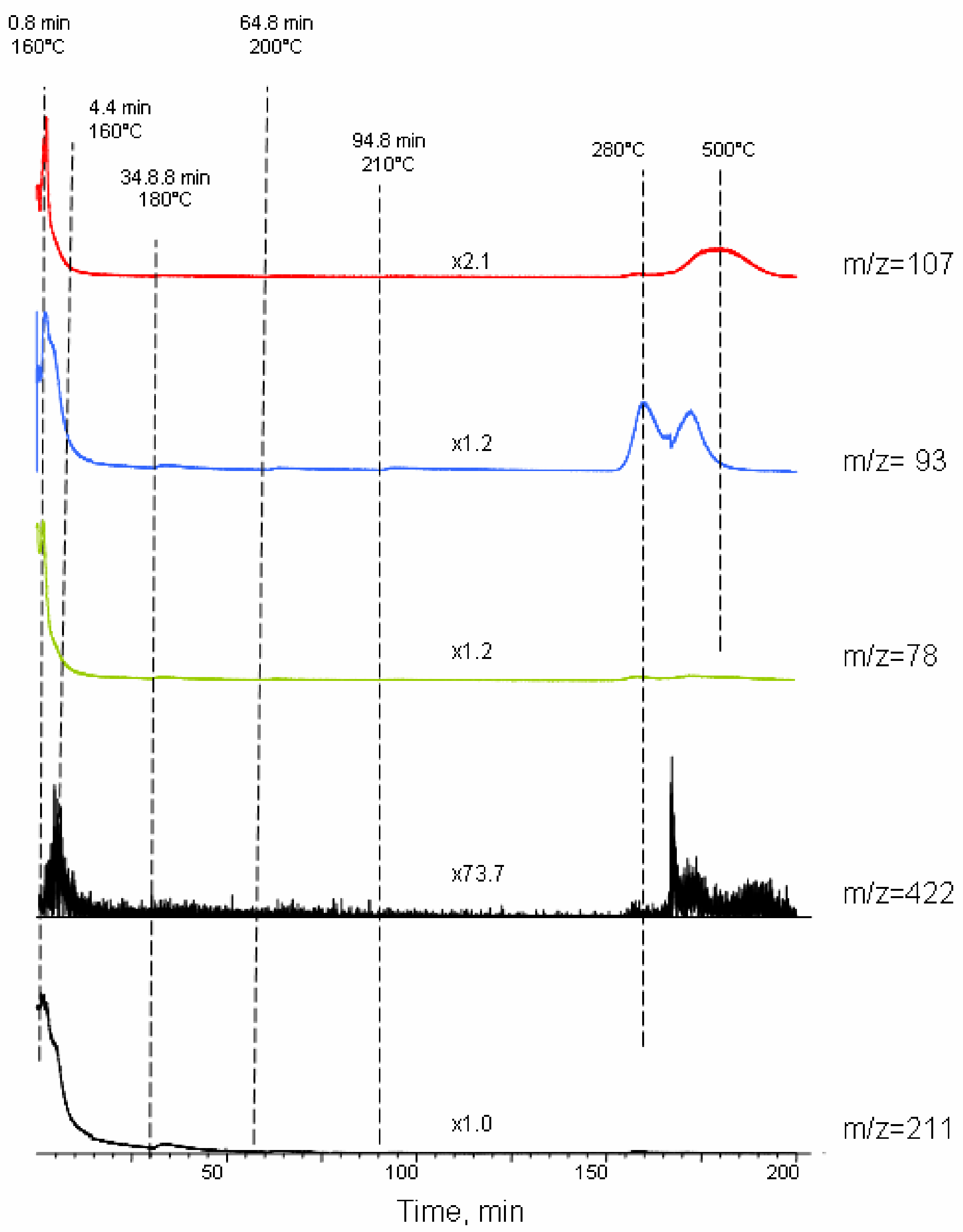
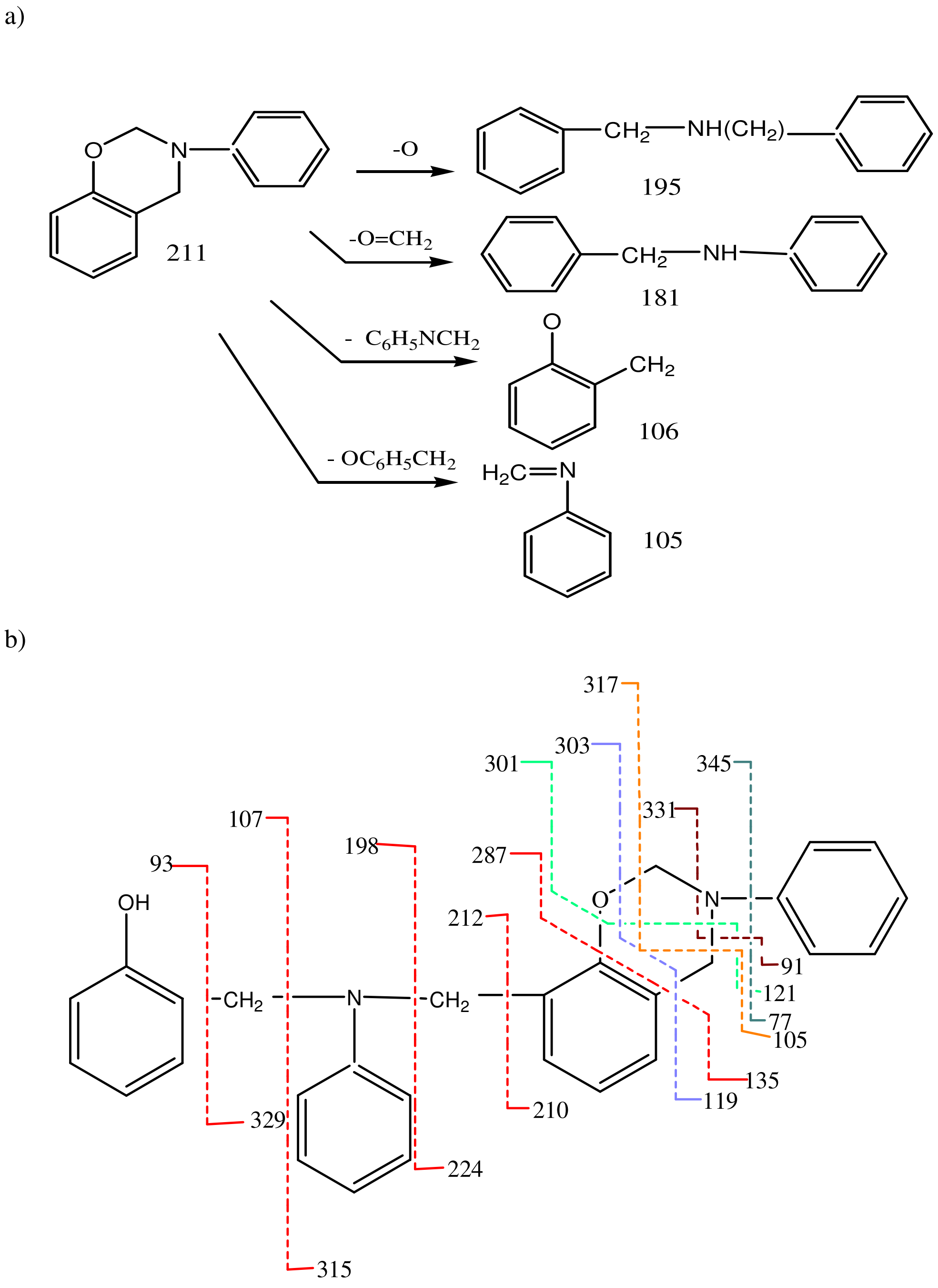


**Figure 3-8: Evolution profiles of some diagnostic products detected during the pyrolysis of Ph-a monomer.**



**Scheme 3-7: Fragmentation pathways during ionization of a) Ph-a monomer b) Ph-a dimmer.**

### 3.2.2. Thermal degradation of polybenzoxazine based on phenol and aniline

The TIC curve and the pyrolysis mass spectra at the peak maxima recorded during the pyrolysis of phenol and aniline based polybenzoxazine, PPh-a, are shown in Figure 3-8. Unlike PPh-m three peaks with maxima at 275, 430 and 520 °C were present in the TIC curve as in case of TGA. Yet, the mass spectra recorded around 275 and 430 °C were almost identical especially in the mass range below 200. The main decomposition product was aniline (m/z= 93 Da) upto 450°C. Above this temperature, the base peak was at m/z= 107 due to $HOC_6H_4CH_2$. The relative intensities of the characteristic and/or intense peaks present in these spectra and the assignments made are summarized in Table 3-4.

Similar fragment peaks were present in the pyrolysis mass spectra of PPh-m and PPh-a, yet, their relative intensities were significantly different. The yield of products generated by degradation of Mannich base was more intense for PPh-a. Furthermore, the relative yields of peaks attributed to $HOC_6H_4CHNH$ and $HOC_6H_4CH_2NH$ decreased drastically in accordance with the general expectations. Cleavage of N-phenyl bond is energetically unfavourable.

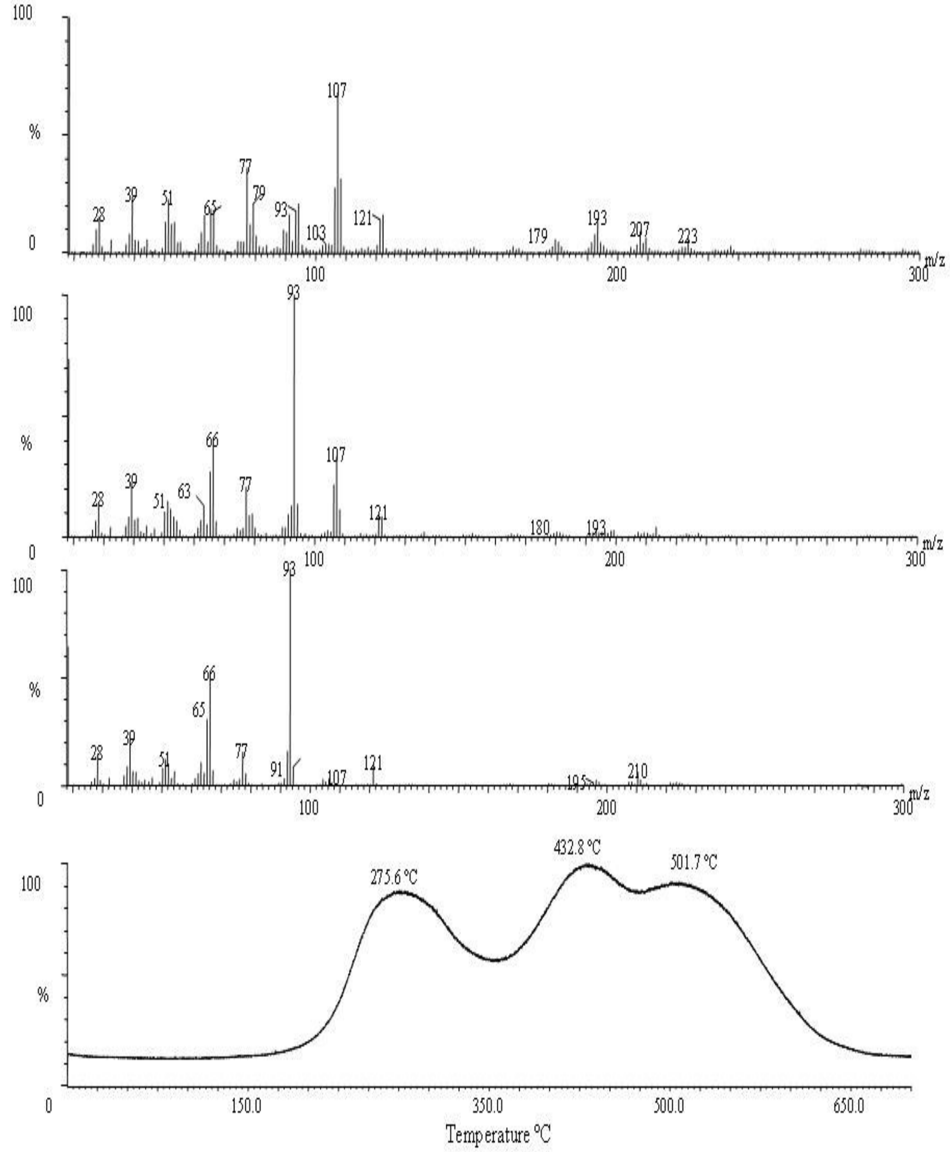


**Figure 3-9: The TIC curve and the spectra at the three maxima recorded during the pyrolysis of PPh-a.**

**Table 3-4: Relative intensities of intense and/or characteristic peaks detected in the pyrolysis mass spectra of polybenzoxazine, PPh-a.**

| m/z | Relative intensity | | | | Assignments |
|---|---|---|---|---|---|
| | 275 | 432 | 500 | 530 | |
| 86 | 2 | 6 | 15 | 14 | $C_4N_2H_{10}$ |
| 91 | 1 | 7 | 107 | 114 | $C_7H_7$ |
| 93 | 871 | 1000 | 157 | 77 | $C_6H_5NH_2$ |
| 94 | 3 | 103 | 100 | 162 | $C_6H_5OH$ |
| 105 | 15 | 16 | 22 | 26 | $C_6H_4CH_2NH$, $CH_2NC_6H_5$ |
| 106 | 27 | 138 | 190 | 133 | $C_6H_5NHCH_2$, $HOC_7H_6$ |
| 107 | 11 | 170 | 440 | 361 | $HOC_6H_4CH_2$, $C_6H_5NH_2CH_2$ |
| 115 | 4 | 14 | 17 | 20 | $CH_2C_6H_3CH{=}CH$, |
| 121 | 74 | 49 | 88 | 64 | $HOC_6H_4CH_2N$, $NHCH_2C_6H_4NH_2$ |
| 122 | 9 | 39 | 100 | 81 | $HOC_6H_4CH_2NH$, $NH_2CH_2C_6H_4NH_2$ |
| 165 | 2 | 2 | 19 | 18 | $HOC_6H_4CH_2NHCH_2CH_2NH$ |
| 178 | 2 | 1 | 24 | 27 | $HOC_6H_4CH_2NHCH_2CH_2NCH_2$, $C_6H_4CH{=}CHC_6H_4$ |
| 182 | | 4 | 9 | 4 | $C_6H_5NCH_2C_6H_5$ |
| 193 | 4 | 22 | 114 | 123 | $C_6H_4CHNC_6H_4CH_2$ |
| 194 | 6 | 17 | 37 | 34 | $C_6H_4CH_2NC_6H_4CH_2$, $HOC_6H_3CH{=}CHC_6H_4$, $C_6H_5NCHC_6H_4CH_2$ |
| 199 | 9 | 33 | 5 | 4 | $HOC_6H_4CH_2NHC_6H_5$ |
| 207 | 15 | 10 | 79 | 90 | $C_6H_4CH{=}CHC_6H_4CH_2NH$, $C_6H_4CH_2N(C_6H_5)CH{=}CH$ |
| 209 | 5 | 12 | 46 | 49 | $HOC_6H_4CH{=}CHC_6H_4CH_2$, $C_6H_5NCH_2C_6H_4NCH_2$ |
| 210 | 1 | 15 | 13 | 14 | [M-H], $C_6H_5NHCH_2C_6H_4N{=}CH_2$, $HOC_6H_4CH{=}NCH_2C_6H_4$ $C_6H_5NHCH{=}CHNHC_6H_5$ |
| 213 | 10 | 50 | 6 | 3 | $HOC_6H_4CH_2NH(C_6H_5)CH_2$ |
| 221 | 10 | 3 | 24 | 27 | $HOC_6H_4CH{=}CHC_6H_4CH{=}CH$ |
| 223 | 5 | 8 | 48 | 49 | $HOC_6H_4CHN(C_6H_4CH{=}N)$, $CH_2NC_6H_4CH_2N(C_6H_5)CH_2$ |
| 227 | 4 | 21 | 3 | 1 | $HOC_6H_4CH{=}NCH_2C_6H_4OH$ |
| 237 | 1 | 3 | 20 | 19 | $HOC_6H_4CH{=}CHC_6H_4CH_2NCH_2$, $HOC_6H_4CHCHC_6H_3(OH)CHCH$ $CH_2NC_6H_4CH_2NC_6H_5CH_2NH$ |
| 294 | | 2 | 15 | 13 | $C_6H_4CH{=}CHC_6H_4CH{=}CHC_6H_4CH_2$ |
| 308 | | 1 | 7 | 9 | $C_6H_4CH{=}CHC_6H_4CH{=}CHC_6H_4CHNH$ |

Studies on single ion evolution profiles again indicated presence of units with different thermal stabilities and structures. Some examples, grouped taking into account the similarities in the evolution profiles, $C_6H_5NH_2$ (m/z=93), $HOC_6H_4CH_2NHC_6H_5$ (m/z=199), $HOC_6H_4CH_2NH(C_6H_5)CH_2$ (m/z=213), $HOC_6H_4CH{=}NCH_2C_6H_4OH$ (m/z=227), $C_7H_7$ (m/z=91), $HOC_6H_5$ (m/z=94), $HOC_6H_4CH_2NHCH_2CH_2NH$ (m/z=165), $C_6H_4CH_2NC_6H_4CH_2$ and/or $HOC_6H_3CH{=}CHC_6H_4$ and/or $C_6H_5NCHC_6H_4CH_2$ (m/z=194), $HOC_6H_4CH_2$ and/or $C_6H_5NH_2CH_2$ (m/z=107), $HOC_6H_4CH_2NH$ and/or $NH_2CH_2C_6H_4NH_2$ (m/z=122), $HOC_6H_4CH$ and/or $C_6H_5NHCH_2$ (m/z=106), $C_6H_4CH_2N(C_6H_5)CH_2$ (m/z=193), $C_6H_4CH{=}CHC_6H_4CH_2NH$ and/or $C_6H_4CH_2NC_6H_5CH{=}CH$ (m/z=207), $HOC_6H_4CH_2N(C_6H_5)CH_2$ and/or $HOC_6H_4CH{=}CHC_6H_4CH_2N$ and/or $HOC_6H_4CHN(C_6H_4CH{=}N)$ (m/z=223) and $C_6H_4CH{=}CHC_6H_4CH{=}CHC_6H_4CH_2$ (m/z=294) are shown in Figure 3-10.

Again, as in the case of PPh-m, degradation of Mannich base was detected at initial stages of pyrolysis. Evolution of aniline, the major degradation product, at around 270 °C where the yield of the products that can be attributed to substituted phenols were quite weak, indicated presence of a polymeric structure quite different than the monomer. Thus, besides the expected ring opening polymerization of benzoxazines given in the literature (PPh1-a), similar polymerization mechanisms, coupling of $N(C_6H_5)CH_2$- groups, yielding a dimer that can further polymerize by ring opening polymerization of Ph-a monomer can be proposed as in case of PPh2-m (Scheme 3-8) yielding PPh2-a.

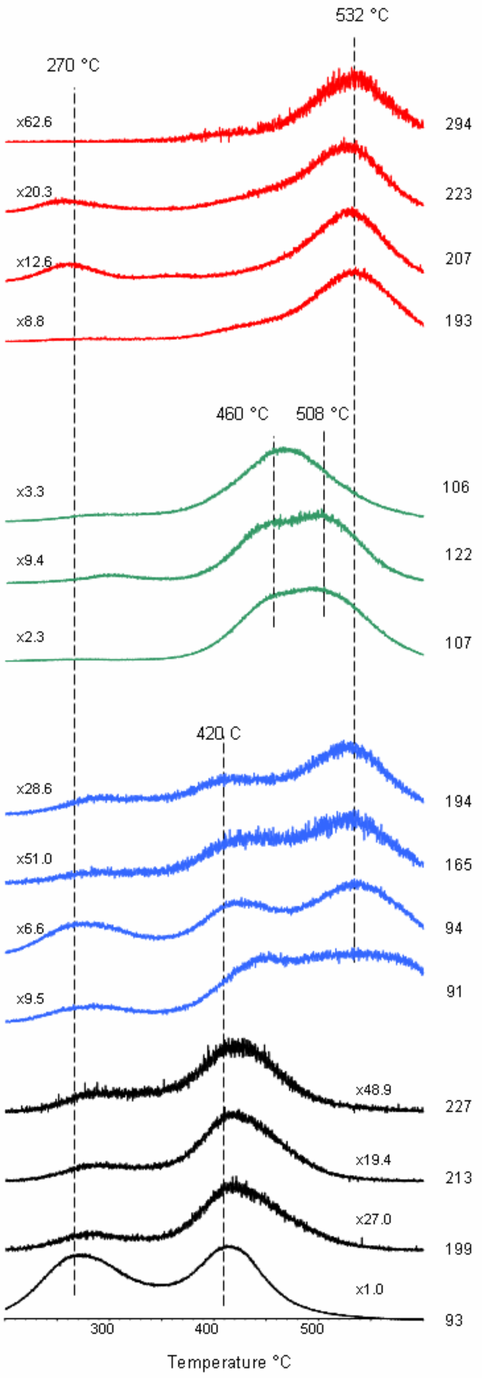
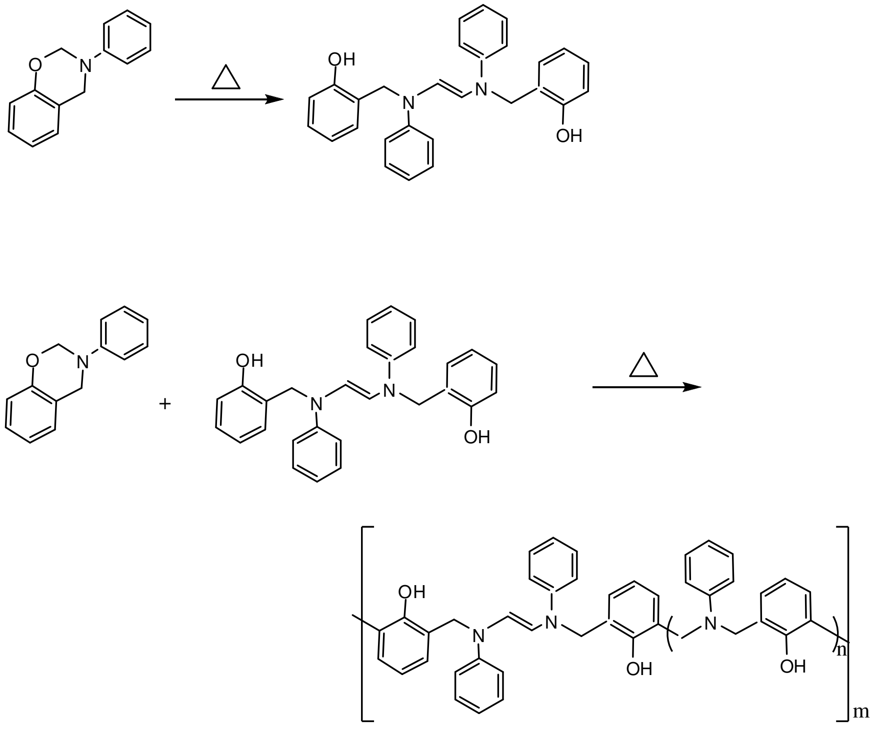


**Figure 3-10: Evolution profiles of some diagnostic products detected during the pyrolysis of PPh-a.**

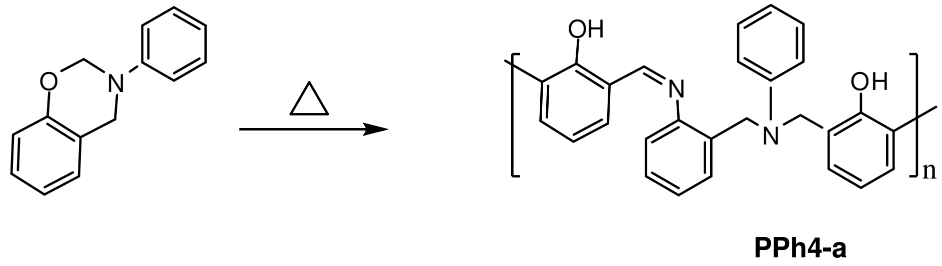


**PPh2-a**

**Scheme 3-8: Polymerization of Ph-a via coupling of N(C6H5)CH2- groups.**

However, for Ph-a polymerization of the dimer through the CH=CH bond should be less likely due to the presence of bulky phenyl groups. During the pyrolysis of PPh-a, no product above 550 °C was detected, contrary to what was observed for PPh-m. The fragments evolved at elevated temperatures during the pyrolysis of PPh-m were associated with unsaturated and/or crosslinked units generated by loss of side chains of the vinyl polymer, PPh3-m. Thus, the lack of high temperature evolutions confirmed that the polymerization of the dimer through the vinyl units was not one of the major polymerization pathways during the curing of PPh-a.

On the other hand, the para and ortho positions of the benzene ring in aniline are also potentially reactive though to a lower extent compared to the benzene ring of the phenols. In a recent GC-MS study on thermal and thermo-oxidative degradation of aromatic amine-based polybenzoxazines, besides the major degradation product, aniline, generation of p-aminotoluene was detected [15]. Detection of ortho (or para) substituted anilines confirmed that the polymerization took place by attack of –$NCH_2$ radicals to the benzene ring attached to the nitrogen. A similar mechanism was proposed for aromatic amine based naphtoxazine monomer in our previous studies [24]. The trends in the evolution profiles of fragments that can also be associated with ortho (or para) substituted anilines such as those with m/z value 121, 122 and 207 confirmed that the polymerization PBA-m also took place by attack of –$NCH_2$ radicals to the benzene ring attached to the nitrogen yielding polymer PPh4-a (Scheme 3-9) .



**Scheme 3-9: Polymerization by attack of N-CH2 groups to aniline ring.**

Taking into consideration all possible polymeric structures, the low temperature evolution of aniline around 290°C can be attributed to loss of units generated by coupling of -$(C_6H_5)NCH_2$ groups of PPh2-a. On the other hand, the decomposition products, those reaching maximum yield at around 420°C, may be associated with degradation of chains generated by ring opening polymerization of oxazine ring and attack of -$(C_6H_5)NCH_2$ to phenol ring (PPh1-a) as proposed in the literature. Thermal degradation of PPh1-a would occur by random cleavages at β carbon to phenol or N atom yielding fragments such as $HOC_6H_4CH_2NHC_6H_5$ (m/z=199) and $HOC_6H_4CH_2NH(C_6H_5)CH_2$ (m/z=213) [4]. The products showing two maxima in their single ion evolution profiles such as products $C_6H_5NHCH_2$ (m/z=106), $NHCH_2C_6H_4NH_2$ (m/z=121) and $NH_2CH_2C_6H_4NH_2$ (m/z=122) may be related to decomposition of units generated by attack of -$(C_6H_5)NCH_2$ groups to aniline ring (PPh4-a). Presence of two maxima in the evolution profiles of these products may be attributed to variations in the stability of these linkages as a result of polymerization through both phenyl and methylene groups.

It may be thought that the decomposition of the polymer, PPh2-a, backbone generated by coupling of radicals formed by loss of aniline from PPh2-a at initial stages of pyrolysis, occurred at around 530 °C yielding fragments such as $HOC_6H_4CH{=}CHC_6H_4CH_2N$ (m/z=223) and $C_6H_4CH{=}CHC_6H_4CH{=}CHC_6H_4CH_2$ (m/z=294).

Thus, DP-MS results supported polymerization of phenol and aniline based benzoxazine by opposing reactions following the cleavage of $O\text{-}CH_2$ bond of oxazine ring; attack of $-C_6H_5NCH_2$ radicals to phenol, (PPh1-a) and/or aniline ring, (PPh2-a) and coupling reactions of $C_6H_5NCH_2$, (PPh4-a).

## 3.3. Polymerization and thermal degradation of benzoxazine based on bisphenol-A and methylamine

In order to investigate the effect of structure of phenol group on curing and thermal characteristics, all mass spectrometry analyses were repeated using bisphenol-A and methyl amine based benzoxazine monomer (BA-m) and the corresponding polymer (PBA-m). Again, only the results obtained from the mass spectrometry analysis of curing of the virgin monomer and pyrolysis of the polymer prepared using the same curing program in an oven are discussed, as no extra information was observed from the other curing and pyrolysis data of the monomer.

### 3.3.1. Curing of benzoxazine monomer based on bisphenol-A and methylamine

During the curing process, under the high vacuum conditions of the mass spectrometer, dissociative ionization of the monomer has occurred. The TIC curve and the pyrolysis mass spectra recorded at the maxima of the peaks present in the TIC curve are shown in Figure 3-11. The peak obtained in low temperature was due to the low temperature evolution of the monomer during the curing process. The high temperature peak at around 450°C was associated with the thermal degradation of the polymer generated during the curing of the monomer. Molecular ion peak, m/z=338 was significantly intense due to the presence of the aromatic group. Because of the high molecular weight of the bisphenol and methyl amine based monomer, the probability of production of dimer and/or trimer was quite low. The relative intensities of the characteristic and/or intense peaks present in the mass spectra and the assignments made are summarized in Table 3-5.

The fragmentation pattern of BA-m monomer proposed considering distributions of the peaks detected in the mass spectra and the classical fragmentation pathways known for organic molecules is shown in Scheme 3-10.

The single ion evolution profiles of monomer and some characteristic fragments generated during the dissociative ionization processes are shown in Figure 3-12. The trends in the evolution profiles detected during curing were totally different than those detected during the pyrolysis of the polymer generated inside the mass spectrometer during curing. This behaviour may be attributed to structural differences between the monomer and polymer.

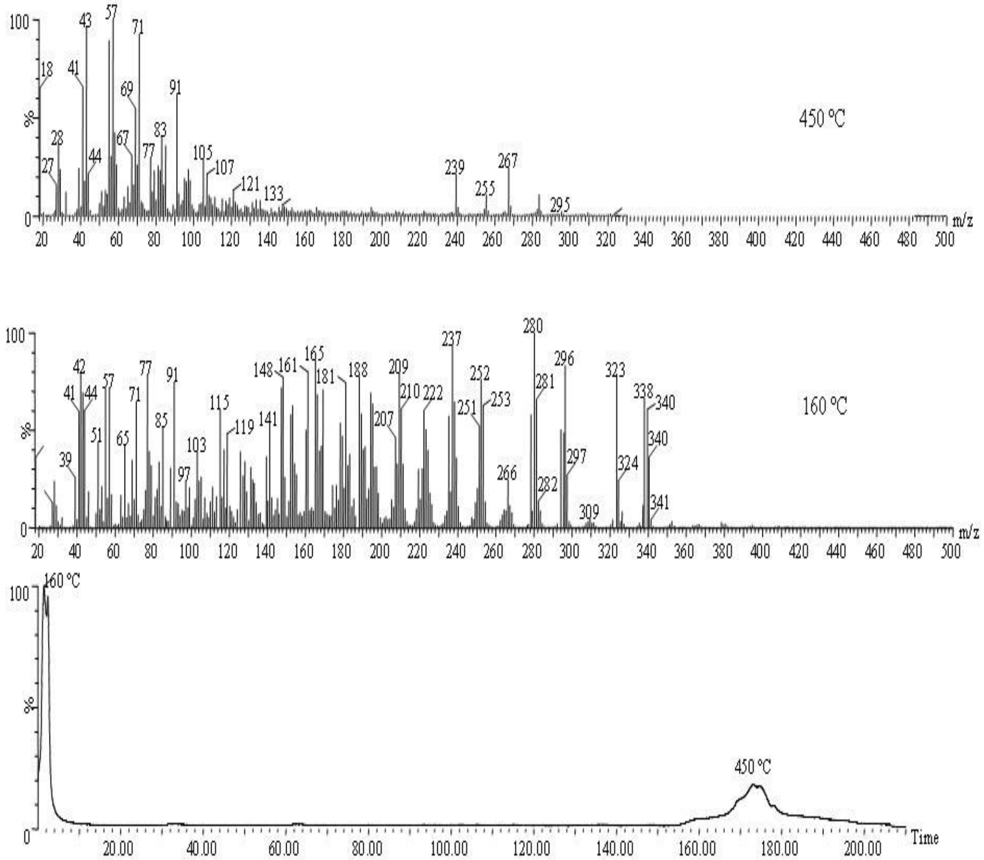
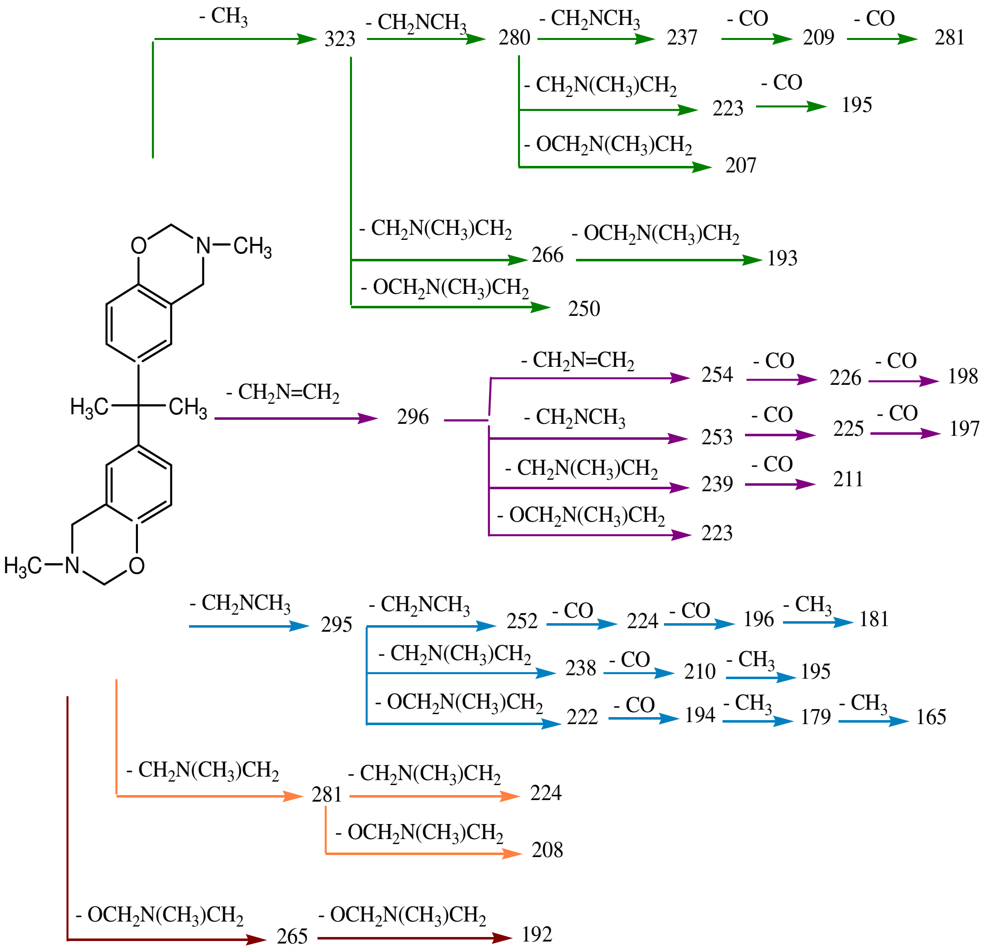


**Figure 3-11: TIC curve and the mass spectra recorded during the curing and pyrolysis of BA-m.**

**Table 3-5: Relative intensities of intense and/or characteristic peaks detected in the mass spectrum at 160°C during the curing of benzoxazine, BA-m.**

| m/z | RI | Assignment |
|---|---|---|
| 43 | 11 | $CH_2NCH_3$ |
| 77 | 768 | $C_6H_5$ |
| 78 | 396 | $C_6H_4OCH_2$ |
| 91 | 752 | $C_7H_7$ |
| 103 | 410 | $C_6H_3CHNH$ |
| 104 | 233 | $CH_3CC_6H_5$ |
| 117 | 360 | $CHC(CH_3)\ C_6H_5$ |
| 119 | 488 | $C(CH_3)_2C_6H_5$ |
| 132 | 248 | $CH_3CC_6H_3OCH_2$ |
| 147 | 735 | $C(CH_3)_2C_6H_3OCH_2$ |
| 148 | 784 | $CH_3NCH_2C_6H_4OCH_2$ |
| 175 | 98 | $CH_3CC_6H_3OCH_2N(CH_3)CH_2$ |
| 181 | 756 | $(CH_3)_2C(C_6H_5)\ (C_6H_5)$ |
| 190 | 396 | $C(CH_3)_2C_6H_3OCH_2N(CH_3)CH_2$ |
| 193 | 204 | $(CH_3)\ C(C_6H_3)\ (C_6H_3O)$ |
| 209 | 801 | $(CH_3)_2C(C_6H_3OCH_2)\ (C_6H_5)$ |
| 237 | 954 | $(CH3)_2C(C_6H_3OCH_2)\ (C_6H_3OCH_2)$ |
| 250 | 199 | $(CH_3)\ C(CH_3NCH_2C_6H_3OCH_2)\ (C_6H_3)$ |
| 266 | 135 | $(CH_3)\ C(CH_3NCH_2C_6H_3OCH_2)\ (C_6H_3O)$ |
| 280 | 1000 | $(CH3)_2C(CH_3NCH_2C_6H_3OCH_2)\ (C_6H_3OCH_2)$ |
| 323 | 780 | $(CH_3)\ C(CH_3NCH_2C_6H_3OCH_2)_2$ |
| 338 | 1 | $(CH_3)_2C(CH_3NCH_2C_6H_3OCH_2)_2$ |



**Scheme 3-10: Fragmentation pattern of BA-m.**

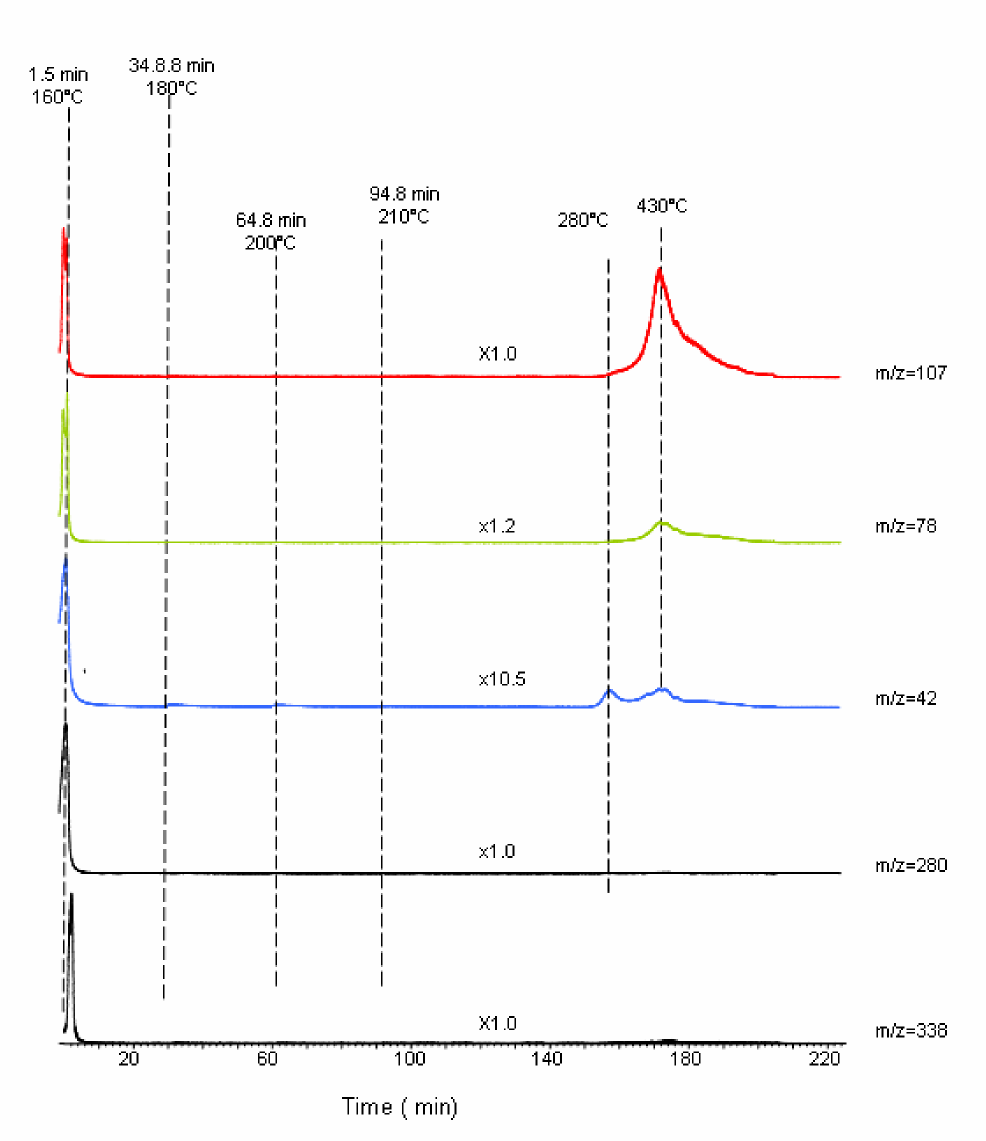


**Figure 3-12: Evolution profiles of some diagnostic products detected during the pyrolysis of BA-m.**

### 3.3.2. Thermal degradation of polybenzoxazine based on bisphenol-A and methylamine

The TIC curve recorded during the pyrolysis of bisphenol-A and methyl amine based polybenzoxazine, PBA-m, and the pyrolysis mass spectra recorded at the peak maxima are shown in Figure 3-13. Again the trends observed in the TIC curve were very similar to what were observed in TGA analysis. The pyrolysis mass spectra of PBA-m were dominated with almost the same peaks recorded in those of PPh-m. Furthermore, as in case of PPh-m, evolution of alkyl amines was detected at initial stages of pyrolysis at around 270 °C, and the yield of the fragments involving phenyl ring were maximized at moderately high temperatures at around 425°C. However, significant changes in the relative intensities were detected. The relative intensities of the characteristic and/or intense peaks present in these spectra and the assignments made are summarized in Table 3-6. The drastic increases in the relative intensities of the peaks attributed to alkyl amines and some of the peaks related to fragments involving phenyl ring were detected. Actually, the bisphenol-A based monomer is basically two phenol based benzoxazine monomers connected by $C(CH_3)_2$ group. Thus, similar polymerization and degradation mechanisms and almost similar pyrolysis mass spectra can be expected. Increase in the relative intensities of some of the fragments involving phenyl ring(s) such as those with m/z values 121, 135, 165, 223 and 237 may be expected due to the contributions of the fragments involving $C_6H_3C(CH_3)_2$ units (see Table 3-6). Furthermore, it may be thought that the relative intensity of the base peak at m/z= 107 due to $HOC_6H_4CH_2$ should slightly be decreased as it would not be generated directly by the cleavage at β- C to the aromatic ring as in case of PPh-m. However, the significant increase in the relative intensities of some N containing fragments can not be associated only with the change in the structure of the monomer.

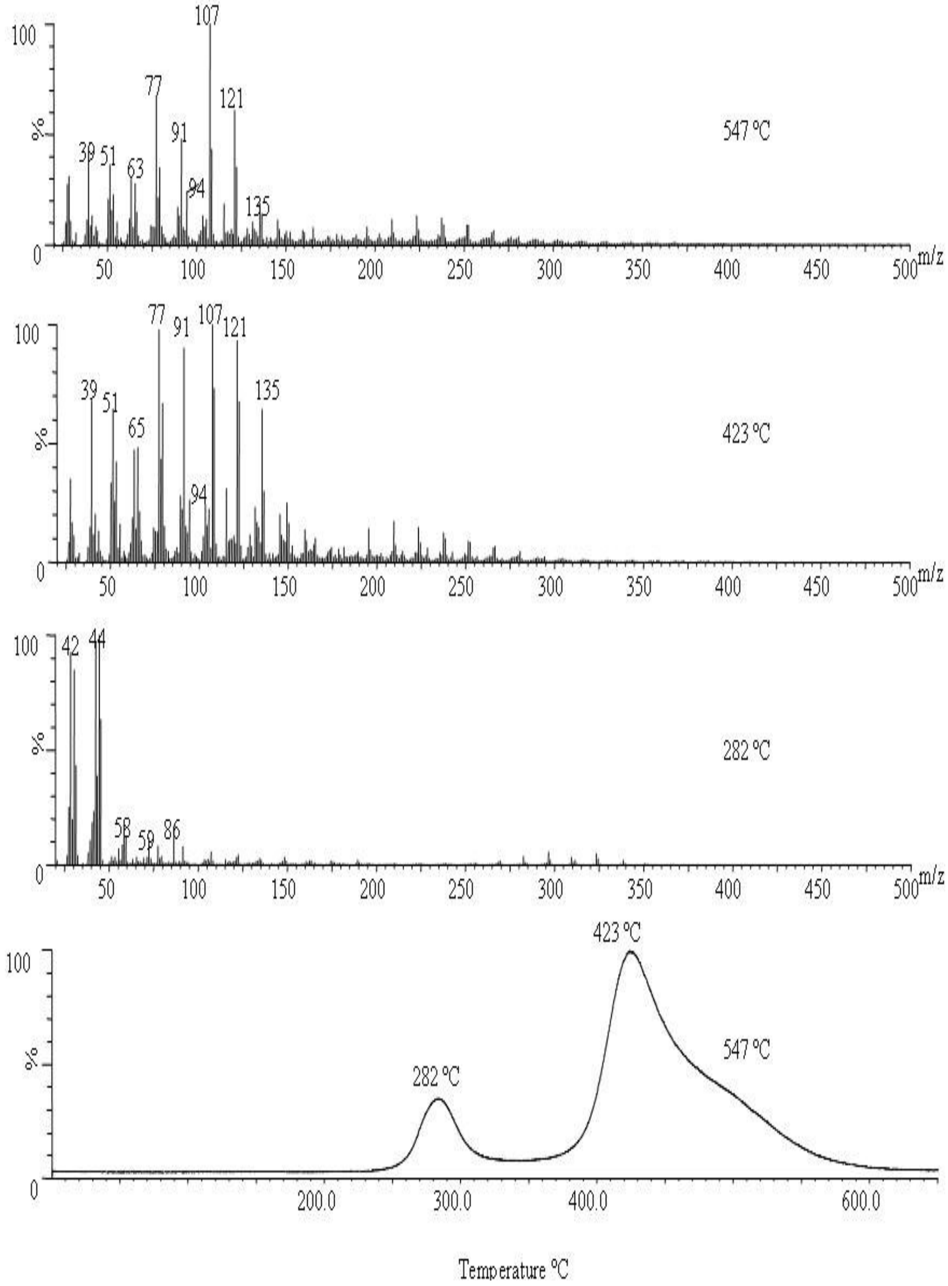
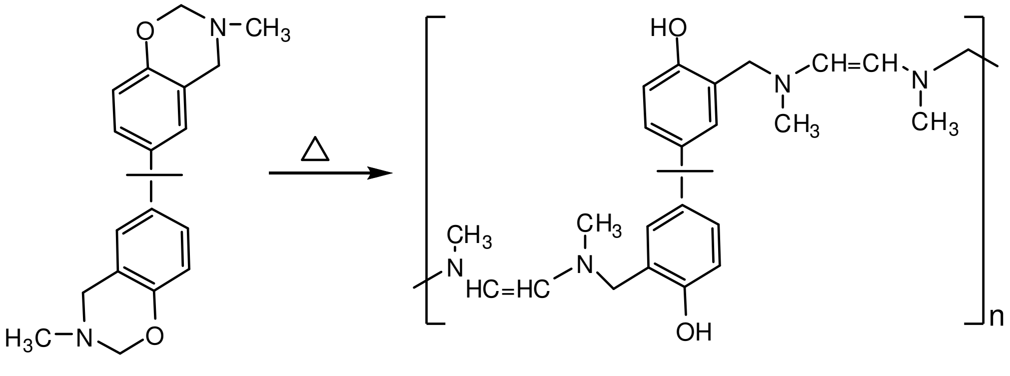


**Figure 3-13: TIC curve and the spectra at the three maxima present in the TIC curve recorded during pyrolysis of PBA-m.**

**Table 3-6: Relative intensities of intense and/or characteristic peaks detected in the pyrolysis mass spectra of polybenzoxazine, PBA-m.**

| m/z | 282°C | 423°C | 547°C | Assignments |
|---|---|---|---|---|
| 30 | 733 | 21 | 12 | $CH_3NH$ |
| 42 | 853 | 44 | 25 | $CH_2CH_2N$ |
| 43 | 361 | 127 | 44 | $CH_2NCH_3$ |
| 58 | 159 | 14 | 14 | $CH_2(CH_3)NHCH_2$, |
| 77 | 57 | 956 | 365 | $C_6H_6$ |
| 86 | 135 | 43 | 16 | $CH_2(CH_3)NHCH_2CH_2N$, $C_4N_2H_{10}$ |
| 91 | 64 | 925 | 262 | $C_7H_7$ |
| 94 | 10 | 262 | 124 | $C_6H_5OH$ |
| 105 | 19 | 228 | 66 | $C_6H_5CH_2NH$ |
| 106 | 10 | 58 | 22 | $HOC_7H_6$ |
| 107 | 51 | 1000 | 506 | $HOC_6H_4CH_2$ |
| 121 | 25 | 945 | 325 | $HOC_6H_4CH{=}NH$, $C_6H_5CH_2NHCH_3$, |
| 122 | 32 | 681 | 186 | $HOC_6H_4CH_2NH$, $HOC_6H_4CH_2CH_3$ |
| 135 | 15 | 671 | 100 | $HOC_6H_4CH_2NCH_2$, $HOC_6H_4C(CH_3)_2$ |
| 136 | 6 | 294 | 77 | $HOC_6H_4CH_2NCH_3$ |
| 148 | 27 | 85 | 2 | $HOC_6H_2CH_2N(CH_3)CH_2$ |
| 165 | 13 | 105 | 40 | $HOC_6H_4CH_2NHCH_2CH_2NH$, |
| 178 | 4 | 53 | 27 | $HOC_6H_4CH_2NHCH_2CH_2NCH_2$, |
| 192 | 3 | 13 | 6 | $C_6H_4CH{=}CHC_6H_4CH_2$ |
| 194 | 4 | 30 | 4 | $C_6H_4CH_2NCH_2C_6H_4$, $HOC_6H_3CH{=}CHC_6H_4$ |
| 206 | 3 | 14 | 6 | $C_6H_4CH{=}CHC_6H_4CH_2N$, |
| 209 | 5 | 181 | 59 | $C_6H_4CH_2NHCH_2C_6H_4CH_2$, |
| 210 | 4 | 71 | 7 | $HOC_6H_4CHNCH_2C_6H_4$, |
| 223 | 4 | 147 | 64 | $HOC_6H_4CH{=}CHC_6H_4CH_2N$, |
| 237 |  | 129 | 60 | $HOC_6H_3C(CH_3)C_6H_4CH_2NCH_2$ |
| 296 | 49 | 4 | 1 | $HOC_6H_3C(CH_3)_2(CH_2NCH_2)C_6H_3(OH)CH_2N$ |

The single ion evolution profiles of the products discussed for PPh-m detected during the pyrolysis of PBA-m are given Figure 3-14. Again noticeable differences between the evolution profiles of the products involving alkyl amines and phenyl ring were detected. Evolution of alkyl amines and/or diamines involving more than three C atoms was again attributed to coupling of –$NCH_2$ groups during the curing process as in the cases of PPh2 –m and PPh2-a at least to a certain extent (Scheme 3-4.a). However, in this region the relative intensities of most of the fragments involving phenyl ring were quite weak. Thus, it can be concluded that coupling of radicals generated by loss of alkyl amines and diamines took place generating a more stable structure, PBA2-m as shown in Scheme 3-11.



**PBA2-m**

**Scheme 3-11: Coupling of –NCH2 groups during curing of BA-m.**

The relative yields of alkyl amines and diamines were significantly higher than the corresponding ones recorded for PPh-m, and the expected values considering the structural effects. This behavior indicated that the coupling of –$NCH_2$ groups was more efficient for PBA-m. Actually, in case of phenol-based benzoxazine, coupling of –$NCH_2$ groups can only generate a dimer. The polymerization of this dimer by successive reactions as shown in Scheme 3-4.a would yield PPh2-m involving alternating amine and diamine linkages. Generation of diamines during the degradation of PPh1-m and PPh3-m is not likely. Thus, the yield of diamines depends on the number of diamine involving dimer along the PPh2-m chain. However, unlike phenol based benzoxazines, bisphenol-based benzoxazine can polymerize by coupling of -$NCH_2$ groups of both oxazine rings as shown in Scheme 3-11 yielding PBA2-m. Thus, the significant increase in the relative intensities of diamine peaks was in accordance with this proposal.

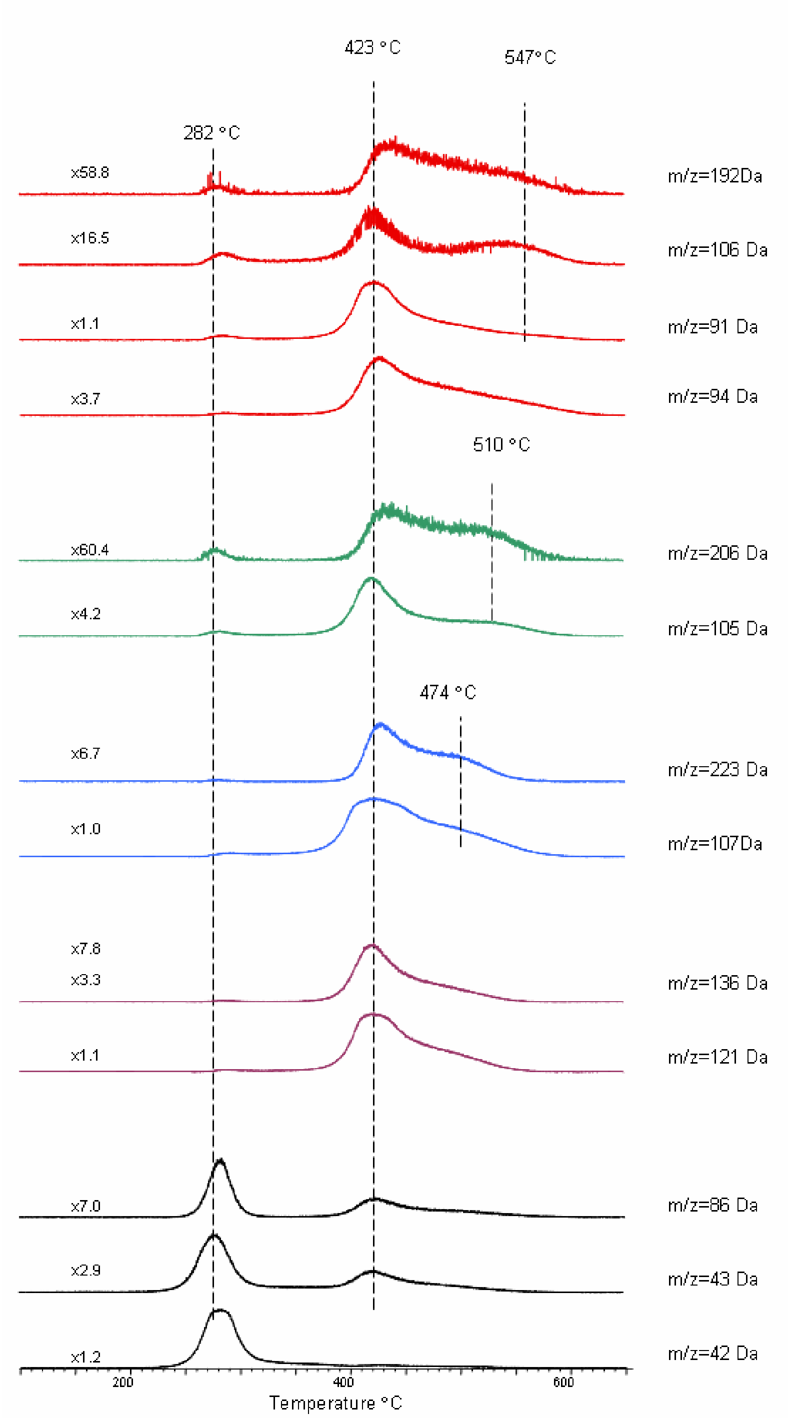


**Figure 3-14: Evolution profiles of some diagnostic products detected during the pyrolysis of PBA-m.**

On the other hand, a slight decrease in the relative intensity of fragments involving unsaturated linkages was detected. These fragments were associated with degradation of unsaturated polymer backbone generated by loss of phenolic side chains from PPh3-m. It may be thought that for PBA2-m, the vinyl dimer involving diamine units containing bulky groups would inhibit the vinyl polymerization. Furthermore, if polymerization by coupling of $NCH_2$ groups, as shown in Scheme 3-11, was achieved then the probability of vinyl polymerization that can yield an unsaturated and/or crosslinked structure during thermal degradation by loss of the side chains should further decrease. Thus it may be concluded that crosslinking did not take place for PBA2-m during curing. The TGA results in the literature indicating lower char yield for both PPh-a and PBA-m compared to PPh-m and the present DP-MS findings are in accordance with these proposals.

The low temperature peak at around 280 °C was attributed to loss of diamines during the degradation of PBA2-m chains, whereas, the evolutions around 547 °C were associated with the decomposition of the unsaturated polymer chains generated by coupling of the radicals formed by loss of diamine linkages. Considering the degradation processes for PPh-m and PPh-a, decomposition of PBA1-m was proposed to take place at around 420-470°C indicating a significant decrease in thermal stability for PBA-1, that should be generated through the similar polymerization routes with PPh1-m and PPh1-a. This behaviour may be attributed to presence of relatively labile $–C(CH_3)_2$ linkages connecting the phenol units.

## 3.4. Polymerization and thermal degradation of benzoxazine based on bisphenol-A and aniline

In order to investigate the polymerization and thermal degradation mechanisms of benzoxazine based on bisphenol-A and aniline, BA-a, in the first step, mass spectrometry analysis of the monomer, the curing program used for the preparation of the polymer, PBA-a, in an oven was applied. After the curing program was completed, the heating process was continued further to determine the thermal degradation characteristics of the polymer if generated during the curing under the high vacuum conditions of the mass spectrometer. Mass spectrometric analyses were repeated also at a slower rate and using recrystallized monomer. Pyrolysis of the monomer and the polymer prepared in the oven was also performed. However, only the results obtained from the mass spectrometry analysis of curing of the virgin monomer at a flash rate and pyrolysis of the polymer prepared using the same curing program in an oven are discussed, as no extra information was observed from other data.

### 3.4.1. Curing of benzoxazine monomer based on bisphenol-A and aniline

Heating the aromatic amine, aniline-based benzoxazine, while applying the curing program used for the polymerization process yielded a total ion current, (TIC), curve with several peaks and shoulders. The TIC curve and the mass spectra recorded at the maxima of the peaks present in the TIC curve are shown in Figure 3-15. The mass spectra recorded were less crowded than those of BA-m. Both molecular ion peak of the monomer (m/z=462) and $CH_2=NC_6H_5$ fragment ion peak were significantly intense as expected for aromatic structures. On the other hand, the molecular ion peak of the dimer and any peak with an m/z value greater than that of the monomer were not present in the mass spectra recorded during curing process. The relative intensities of the characteristic and/or intense peaks present in the spectrum recorded at 180 °C and the assignments made are summarized in Table 3-7. Thus, fragmentation pattern of BA-a monomer was proposed considering the distribution of the peaks in the mass spectra and the classical fragmentation pathways of organic molecules as shown in Scheme 3-12, indicating evolution of monomer at initial stages of curing.

On the other hand, analyses of the single ion evolution profiles pointed out the degradation of the monomer as the curing program proceeded at least to a certain extent. In Figure 3-16 single ion pyrograms of some intense and/or characteristic products namely monomer (m/z=462), [M-$C_6H_5NCH_2$] (m/z=357), $C_6H_6$, (m/z=78), $C_6H_5NCH_2$ (m/z=93) and $C_6H_5OCH_2$ (m/z=107) are shown. The appearance of intense peaks in the high temperature ranges, at around 400 °C confirmed polymerization of the sample even under the high vacuum conditions of the mass spectrometer.

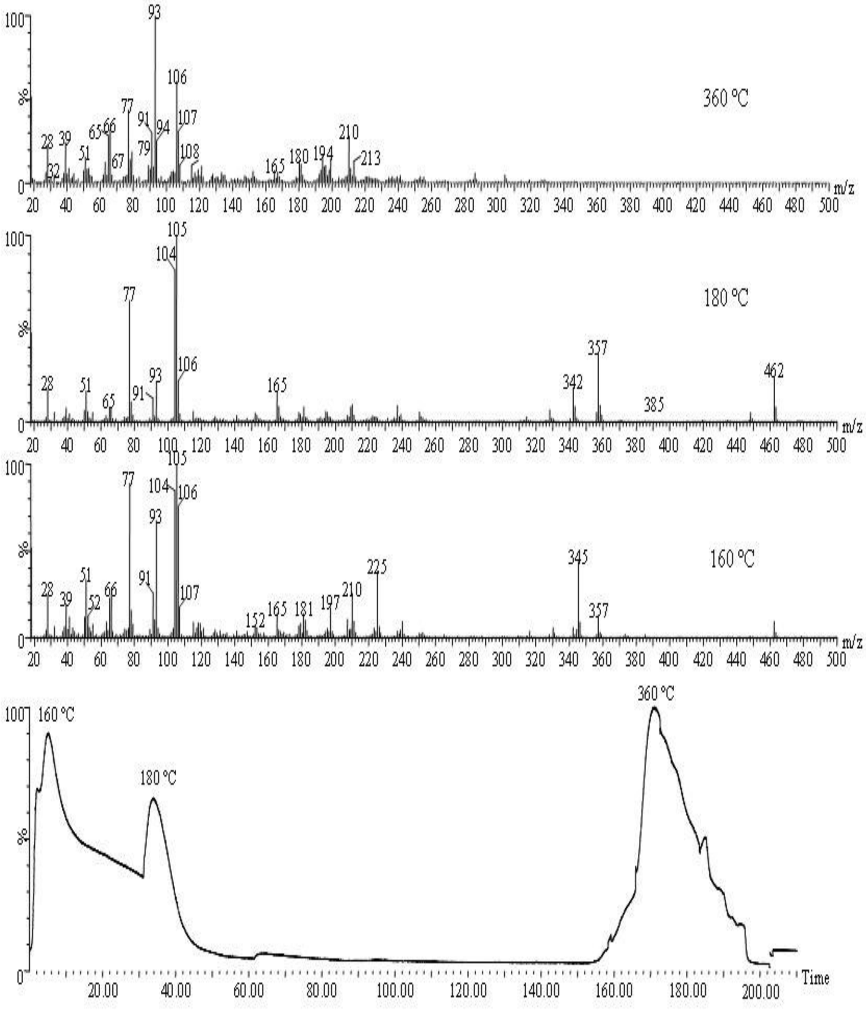


**Figure 3-15: The TIC curve and the spectra recorded during curing of BA-a monomer.**

**Table 3-7: Relative intensities of intense and/or characteristic peaks detected in the pyrolysis mass spectra of benzoxazine, BA-a.**

| m/z | RI at 180 ºC | Assignment |
|---|---|---|
| 77 | 905 | $C_6H_5$ |
| 78 | 168 | $C_6H_4OCH_2$ |
| 91 | 264 | $C_7H_7$ |
| 93 | 703 | $C_6H_5OH$ |
| 94 | 58 | $C_6H_5OH$ |
| 104 | 875 | $CH2OC6H5CH2(CH_3)$ |
| 105 | 1000 | $C_6H_3OCH2$ |
| 106 | 748 | $C_6H_4OCH_2$ |
| 107 | 179 | $C\ _6H_4(OH)CH2$ |
| 119 | 82 | $C_6H_5C\ (CH_3)_2$ |
| 134 | 15 | $C_6H_4O\ CH_2NCH_2$ |
| 147 | 42 | $CH_2OC_6H_3C\ (CH_3)_2$ |
| 175 | 1 | $NCH_2CH_2OC_6H_3C\ (CH_3)_2$ |
| 181 | 144 | $CH_2OC_6H_5CH_2(CH_3)\ C_6H_3O\ CH_2$ |
| 198 | 35 | $C_6H_5(OH)CH2N(C_6H_5)$ |
| 209 | 48 | $CH_2OC_6H_5CH_2(CH_3)\ C_6H_3O\ CH_2O$ |
| 210 | 251 | $C_6H_3O\ CH_2NCH_2(\ C_6H_5)\ CH_2$ |
| 211 | 94 | $CH_3OC_6H_4CHNC_6H_5$, $C_6H_4O\ CH_2N(\ C_6H_5)\ CH_2$ |
| 222 | 20 | $(C_6H_5)NCH_2CH_2OC_6H_3C\ (CH_3)_1$ |
| 224 | 31 | $CH_2OC_6H_3C\ (CH_3)_2\ C_6H_5$ |
| 237 | 34 | $(C_6H_5)NCH_2CH_2OC_6H_3C\ (CH_3)_1$ |
| 238 | 23 | $C_6H_3C\ (CH_3)_2\ C_6H_3O\ CH_2$ |
| 252 | 30 | $(C_6H_5)NCH_2CH_2OC_6H_3C\ (CH_3)_2$ |
| 314 | 3 | $CH_2OC_6H_5CH_2(CH_3)\ C_6H_3O\ CH_2N(C_6H_5)CH_2O$ |
| 342 | 51 | $CH_2OC_6H_3CH_2(CH_3)\ C_6H_3O\ CH_2N(C_6H_5)CH_2O$ |
| 343 | 17 | $C_6H_3C\ (CH_3)_2\ C_6H_3O\ CH_2N(C_6H_5)CH_2$ |
| 357 | 117 | $(C_6H_5)NCH_2CH_2OC_6H_3C\ (CH_3)_2\ C_6H_3O\ CH_2$ |
| 447 | 3 | $(C_6H_5)NCH_2CH_2OC_6H_3CH_2(CH_3)\ C_6H_3O\ CH_2N(C_6H_5)CH_2O$ |
| 462 | 88 | $(C_6H_5)NCH_2CH_2OC_6H_3C\ (CH_3)_2\ C_6H_3O\ CH_2N(C_6H_5)CH_2$ |

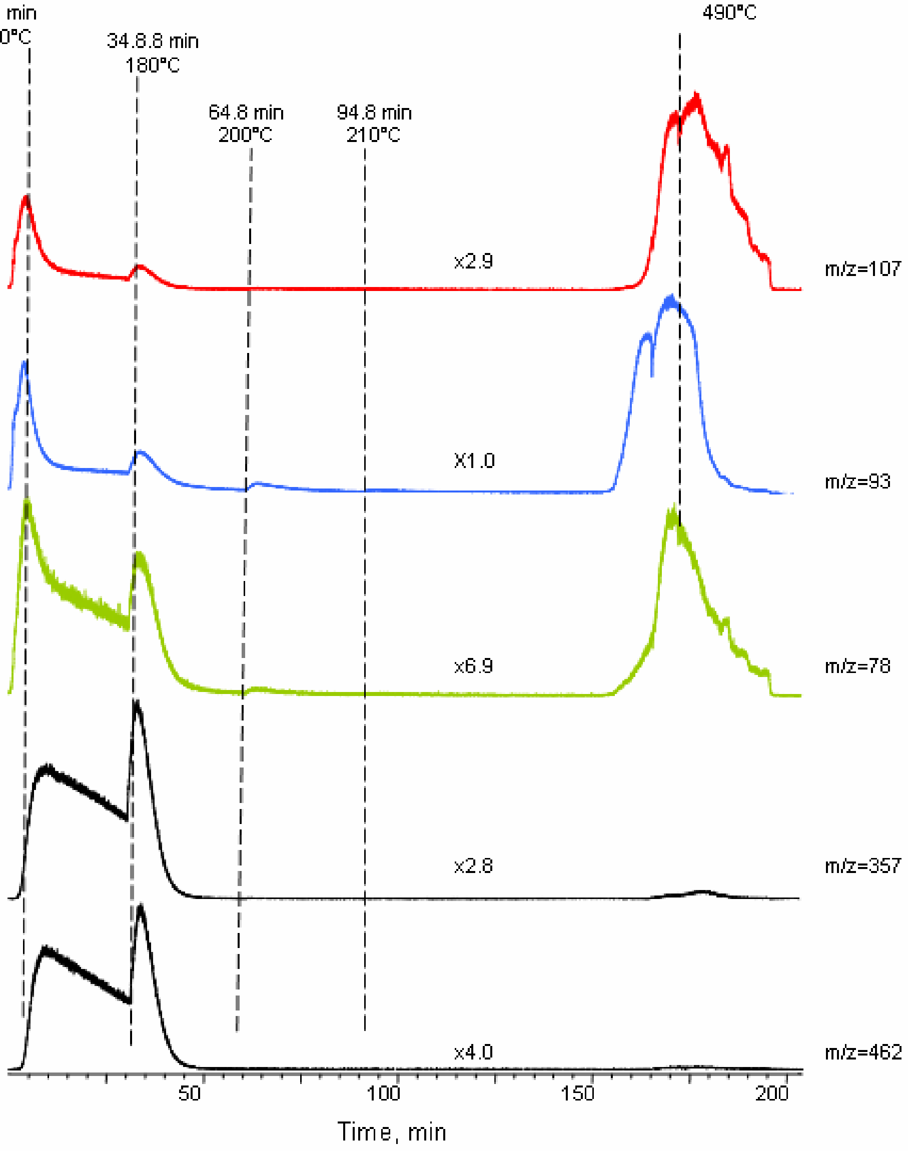
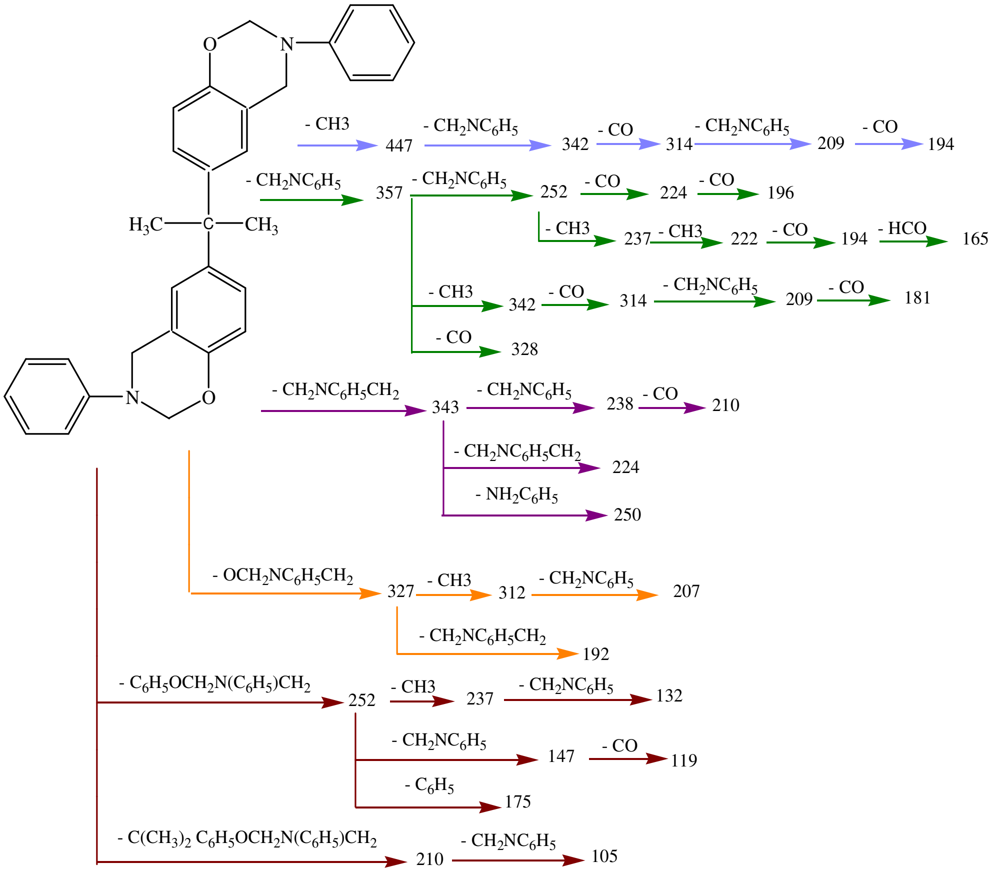


Figure 3-16: Evolution profiles of some diagnostic products detected during the curing and pyrolysis of BA-a monomer.



**Scheme 3-12: Fragmentation of BA-a monomer.**

## 3.4.2. Thermal degradation of polybenzoxazine based on bisphenol-A and aniline

The TIC curve and the pyrolysis mass spectra at the maximum (406° C) and at the shoulder (490° C) of the peak present in the TIC curve recorded during the pyrolysis of bisphenol-A and aniline based polybenzoxazine, PBA-a, are shown in Figure 3-17. Again as in case of PPh-a, the main decomposition product was aniline (m/z= 93). The peak at m/z= 107 due to $HOC_6H_4CH_2$ was the base peak above 450°C. The relative intensities of the characteristic and/or intense peaks present in these spectra and the assignments made are summarized in Table 3-8.

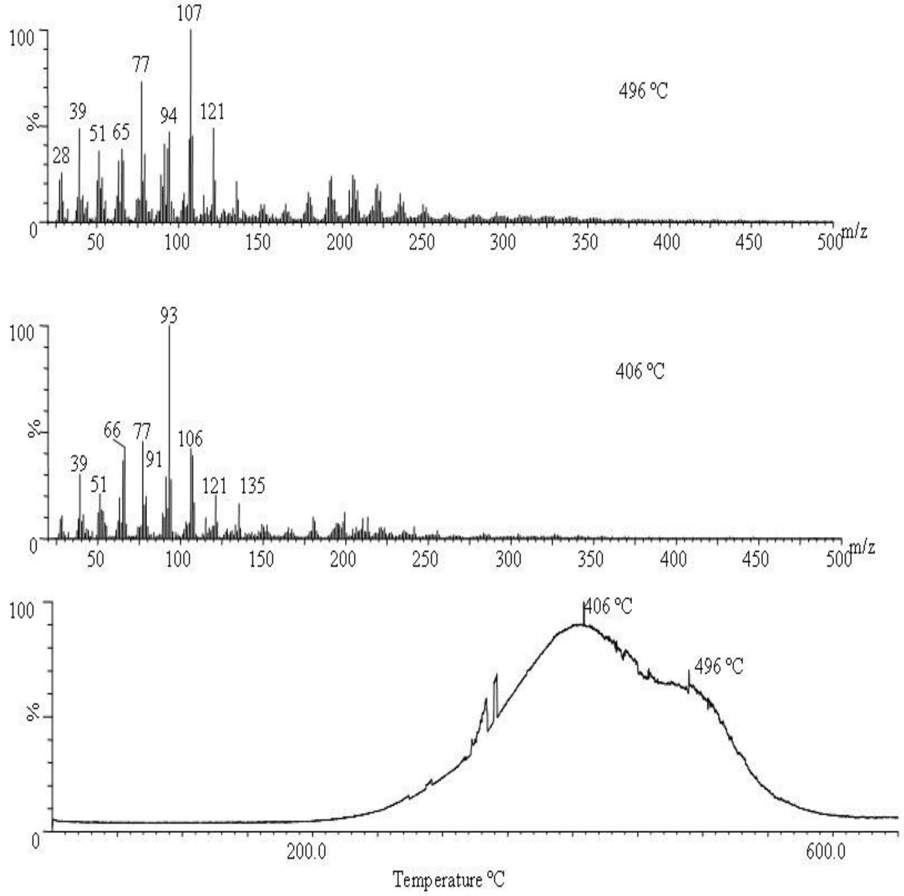


**Figure 3-17: curve and the spectra recorded during the pyrolysis of PBA-a.**

The results indicated a higher thermal stability for PBA-a, compared to all of the polybenzoxazines under investigation. This behaviour was also noted during TGA analyses. The first maximum in the TIC curve was at 380°C, almost 100°C higher than the value detected for all other polybenzoxazines. Furthermore, evolution of the decomposition products being over just above 500 °C, indicated a narrower thermal degradation range. These observations may be associated with generation of a thermally more stable and homogeneous polymer.

**Table 3-8: Relative intensities of intense and/or characteristic peaks detected in the pyrolysis mass spectra of polybenzoxazine, PBA-a.**

| m/z | 380 | 406 | 444 | 496 | Assignments |
|---|---|---|---|---|---|
| 91 | 262 | 310 | 216 | 156 | $C_7H_7$ |
| 93 | 1000 | 1000 | 487 | 126 | $C_6H_5NH_2$ |
| 94 | 268 | 277 | 199 | 194 | $C_6H_5OH$ |
| 107 | 318 | 433 | 453 | 404 | $HOC_6H_4CH_2$ |
| 121 | 166 | 220 | 212 | 183 | $HOC_6H_4CH{=}NH$, $HOC_6H_4CHCH_3$, $NHCH_2C_6H_4NH_2$ |
| 122 | 52 | 87 | 92 | 83 | $HOC_6H_4CH_2NH$, $NH_2CH_2C_6H_4NH_2$ |
| 165 | 55 | 55 | 39 | 40 | $HOC_6H_4CH_2NHCH_2CH_2NH$, $HOC_6H_3CH(CH_3)_2(CH_2NH_2)$ |
| 178 | 28 | 33 | 7 | 43 | $HOC_6H_4CH_2NHCH_2CH_2NCH_2$, $C_6H_4CH{=}CHC_6H_4$ |
| 180 | 114 | 101 | 25 | 52 | $C_6H_4CHNC_6H_5$ |
| 182 | 41 | 36 | 19 | 13 | $C_6H_4CH_2NHC_6H_5$ |
| 192 | 43 | 44 | 63 | 97 | $C_6H_4CH{=}CHC_6H_4CH_2$ |
| 194 | 84 | 64 | 46 | 50 | $C_6H_4CH_2N(C_6H_4CH_2)$, $HOC_6H_3CH{=}CHC_6H_4$ |
| 199 | 142 | 111 | 33 | 12 | $HOC_6H_4CH_2NHC_6H_5$ |
| 206 | 45 | 63 | 85 | 90 | $C_6H_4CH{=}CHC_6H_4CH_2N$, $CH_2C_6H_4CH{=}CHC_6H_4CH_2$ |
| 207 | 28 | 36 | 61 | 100 | $C_6H_4CH{=}CHC_6H_4CH_2NH$, $C_6H_4CH_2NC_6H_5CH{=}CH$ |
| 210 | 140 | 77 | 25 | 22 | $HOC_6H_4CHNCH_2C_6H_4$, $HOC_6H_3C(CH_3)_2C_6H_4$ |
| 221 | 43 | 54 | 72 | 77 | $HOC_6H_3(C{=}CH_2)C_6H_4CHN$,$CH_2NC_6H_4CHNC_6H_4CH_2$, $HOC_6H_4CH{=}CHC_6H_4CHCH$ |
| 223 | 39 | 50 | 63 | 68 | $HOC_6H_4CH{=}CHC_6H_4CH_2N$, $HOC_6H_3C(CH_3)C_6H_4CH_2N$, $CH_2NC_6H_4CH_2N(C_6H_5)CH_2$ |
| 237 | 23 | 29 | 41 | 45 | $HOC_6H_3C(CH_3)C_6H_4CH_2NCH_2$, $HOC_6H_3C(CH_3)_2C_6H_4CHN$ $HOC_6H_3C(CH_3)CH_2NC_6H_4CH_2$ |
| 294 | 7 | 10 | 8 | 18 | $C_6H_4CH{=}CHC_6H_4CH{=}CHC_6H_4CH_2$ |
| 298 | 9 | 12 | 19 | 10 | $HOC_6H_3(CH_2NC_6H_5)C{=}CH_2C_6H_3$ |
| 315 | 7 | 10 | 20 | 10 | $HOC_6H_3(CH_2NC_6H_5)C{=}CH_2C_6H_3OH$, $HOC_6H_4(CHNC_6H_4CH_2N(C_6H_5)CH_2$ |
| 326 | 17 | 24 | 24 | 7 | $HOC_6H_3(CH_2NC_6H_5)C{=}CH_2C_6H_3CH_2N$, $HOC_6H_3(CH_2NC_6H_5CH_2)C{=}CH_2C_6H_3CH_2$ |
| 340 | 10 | 17 | 22 | 7 | $HOC_6H_3(CH_2NC_6H_5)C{=}CH_2C_6H_3CH_2NCH_2$ |
| 357 | 5 | 7 | 14 | 5 | $HOC_6H_3(CH_2N(C_6H_5)CH_2)C{=}CH_2C_6H_3(OH)CH_2N$ |

In order to get a better understanding, again the single ion evolution profiles of all products were studied in detail. In Figure 3.18 evolution profiles of $C_6H_5NH_2$ (m/z=93), $HOC_6H_4CH_2NHC_6H_5$ (m/z=199), $C_6H_5OH$ (m/z=94), $HOC_6H_4CH_2NHCH_2CH_2NH$ and/or $HOC_6H_3CH(CH_3)_2(CH_2NH_2)$ (m/z=165), $C_7H_7$ (m/z=91), $HOC_6H_3(CH_2NC_6H_5)C{=}CH_2C_6H_3CH_2N$ and/or $HOC_6H_3(CH_2NC_6H_5CH_2)C{=}CH_2C_6H_3CH_2$ (m/z=326), $HOC_6H_3(CH_2NC_6H_5)C{=}CH_2C_6H_3OH$ and/or $HOC_6H_4(CHNC_6H_4CH_2N(C_6H_5)CH_2$ (m/z=315), $HOC_6H_4CH_2$ (m/z=107), $HOC_6H_4CH{=}NH$, and/or $HOC_6H_4CHCH_3$ and/or $NHCH_2C_6H_4NH_2$ (m/z=121), $HOC_6H_3(C{=}CH_2)C_6H_4CHN$ and/or $CH_2NC_6H_4CHNC_6H_4CH_2$, $HOC_6H_4CH{=}CHC_6H_4CH{=}CH$ (m/z=221) and $C_6H_4CH{=}CHC_6H_4CH{=}CHC_6H_4CH_2$ (m/z=294) are shown. Although, the thermal decomposition of PBA-a was completed over a narrow temperature range, the evolution profiles of products showed different trends pointing out presence of various polymeric structures for the polybenzoxazine based on bisphenol-A and aniline also.

Evolution of the monomer and the characteristic dissociation products of monomer such as $C_6H_4CH_2NHC_6H_5$ (m/z=180), $HOC_6H_3(CH_2NC_6H_5CH_2)C(CH_2)_3C_6H_3OH(CH_2NHC_6H_5)$ (m/z=451) and $HOC_6H_3(CH_2NC_6H_5CH_2)C(CH_2)_3C_6H_3OH(CH_2NHC_6H_5)$, although not very extensive, confirmed polymerization of BA-a through ring opening polymerization of oxazine ring followed by the attack of $(C_6H_5)NCH_2$ groups to phenol rings as proposed in the literature yielding PBA1-a [4]. However, presence of two peaks at 385 and 500°C in the evolution profiles of these products pointed out presence of two different linkages connecting the monomer units.

The low temperature evolution of aniline may again associated with presence of polymer chains, PBA2-a generated by coupling of $(C_6H_5)NCH_2$ groups. As in case of PBA-m the growth of the polymer by coupling reactions following the cleavage of both oxazine rings can be expected. This polymerization pathway should be favourable compared to the polymerization of the diamine dimer through the vinyl bond due to the steric effects of the bulky group substituted on the vinyl carbons. The decomposition of the polymer generated by coupling of the radicals, PBA2-a formed by loss of aniline at early stages of pyrolysis occurred around 500 °C yielding fragments such as $HOC_6H_4CH=CHC_6H_4CHCH$ (m/z=221) and $C_6H_4CH=CHC_6H_4CH=CHC_6H_4CH_2$ (m/z=294).

Finally, the products such as products $NH_2C_6H_4CH_2NH$ (m/z=121) and $NH_2CH_2C_6H_4NH_2$ (m/z=122) may again be related to decomposition of units generated by attack of -$(C_6H_5)NCH_2$ groups to aniline ring. As in case of PPh-a, the broad evolution profiles of these products with two maxima at 415 and 500°C may be attributed to variations in the stability of these linkages as a result of polymerization through both phenyl and methylene groups.

Thus, it can be concluded that polymerization of the benzoxazine monomer, PBA-a, after the cleavage of O-$CH_2$ bond of the oxazine ring again proceeded through opposing reactions; attack of $C_6H_5NCH_2$- to groups to ortho position of phenol (PBA1-a) or aniline ring (PBA4-a) and coupling of $C_6H_5NCH_2$ groups yielding diamine linkages (PBA2-a). The increase in the thermal stability may be attributed to growth of polymer chains through both oxazine rings and presence of an aromatic amine.

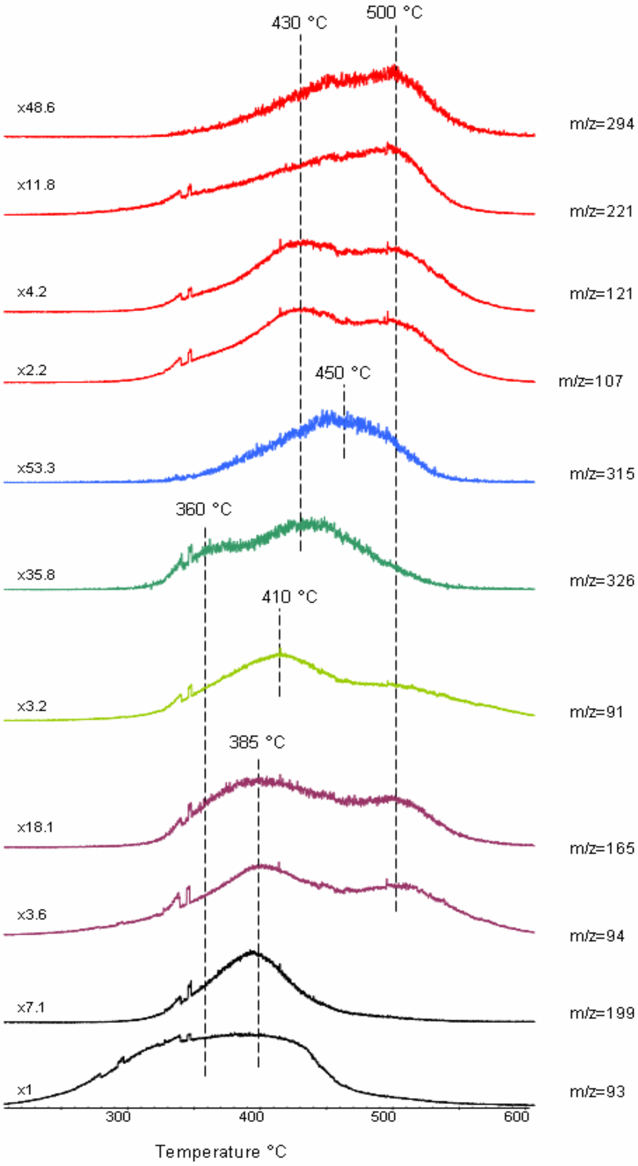


**Figure 3-18: Evolution profiles of some diagnostic products detected during the pyrolysis of PBA-a.**

# CHAPTER 4

# CONCLUSION

The direct pyrolysis mass spectrometry analyses of benzoxazines based on phenol and methyl amine (PPh-m) or aniline (PPh-a) and bisphenol-A and methyl amine (PBA-m) or aniline (PBA-a) were performed to investigate polymerization and thermal degradation mechanisms. With the light of experimental findings the following conclusions were made.

At initial stages of the stepwise curing processes carried out inside the mass spectrometer, evaporation of the monomers was recorded. During the continuous heating following the curing process, evolution of various fragments in the temperature range 250 to 600°C was observed pointing out that polymerization of the monomers were achieved even under the high vacuum conditions of the mass spectrometer, although evaporation of the monomer also took place to a certain extent. Thermal degradation behavior of the corresponding polybenzoxazines prepared by applying the same curing programs in an oven, were almost identical.

Thermal degradation of all polybenzoxazines started just above 250°C except polybenzoxazine based on bisphenol-A and aniline. The higher thermal stability of polybenzoxazine based on bisphenol-A and aniline can be attributed to both possibility of polymerization through both oxazine rings and increased thermal stability of amine linkages as a result of phenyl substitution to N.

The total ion current curves detected during the pyrolysis of all polybenzoxazines showed more than one peak indicating presence of multi-step degradation mechanism and/or presence of chains with different structures. Evolution of products due to cleavages at β carbon to phenol ring and to N atom pointed out ring opening polymerization of benzoxazines (PPh1 and PBA1) as proposed in the literature.

However, for all benzoxazine monomers, strong evidences to confirm coupling of $(CH_3)NCH_2$ or $(C_6H_5)NCH_2$ groups yielding dimers involving diamine linkages that further polymerize by reactions with the corresponding monomer were also detected. As a result, polymer chains (PPh2 and PBA2) with random labile diamine units were generated. For polybenzoxazines based on bisphenol-A, clues indicating polymerization of the dimer by coupling of both of the oxazine rings were detected. Thermal decomposition of the chains involving diamine linkages took place in two steps. The first step was attributed to the decomposition of the chains involving diamine linkages, low temperature evolution of alkyl amines and diamines during the pyrolysis of polybenzoxazines based on methyl amine and evolution of aniline during the pyrolysis of polybenzoxazines based on aniline. The second step was associated with the degradation of the polymer backbone generated by coupling of the benzophenols produced in the first step.

On the other hand, for the benzoxazine monomer based on phenol and methyl amine thermal degradation products pointing out polymerization of the dimer through the ethylene units (vinyl polymerization) was also recorded (PPh3). A two step decomposition mechanism, loss of side chains generating an unsaturated and/or crosslinked polymer backbone that degrades at elevated temperatures was proposed for this vinyl polymer. Absence of fragments supporting polymerization of the dimer through the ethylene units for the benzoxazines based on aniline and/or bisphenol was attributed to steric effects. The highest char yield detected in TGA studies for the polybenzoxazine based on phenol and methyl amine was in accordance with this proposal.

For polybenzoxazines based on aniline another polymerization pathway involved attack of radicals generated by cleavage of the oxazine ring to aniline ring (PPh4 and PBA4).

# REFERENCES

[1] Stuart, B. H.; Polymer analysis, (2002), page 17

[2] H. Y. Low, H. Ishida, Mechanistic Study on the Thermal Decomposition of Polybenzoxazines, Journal of Polymer Science: Part B: Polymer Physics, Vol. 36, 1935–1946 (1998)

[3] Fried, J.R.; polymer science and technology, 1995, pages 331-333

[4] N.N. Ghosh1, B. Kiskan, Y. Yagci, Polybenzoxazines—New high performance thermosetting resins, Science direct, volume 32 (2007) 1344–1391

[5] A. Yildirim, B. Kiskan, A. L. Demirel and Y. Yagci, Synthesis, characterization and properties of naphthoxazine-functional poly(propyleneoxide)s, European polymer journal, Volume 42, Issue 11, November 2006, Pages 3006-3014

[6] S. B. Shen, H. Ishida, Synthesis and characterization of polyfunctional naphthoxazines and related polymers, Journal of Applied Polymer Science, volume 61 issue 9, pages 1595-1605

[7] T. Takeichi, Y. Saito, T. Agag, H. Muto, T. Kawauchi, High-performance polymer alloys of polybenzoxazine and bismaleimide, Science direct, Polymer 49 (2008), pages 1173-1179

[8] K. Hemvichian and H. Ishida, Thermal decomposition processes in aromatic amine-based polybenzoxazines investigated by TGA and GC–MS, Science direct, Polymer Volume 43, Issue 16, July 2002, Pages 4391-4402.

[9] Y. L. Liu, C. I. Chou, High performance benzoxazine monomers and polymers containing furan groups, Journal of Polymer Science Part A: Polymer Chemistry, Volume 43 Issue 21, Pages 5267 - 5282

[10] E. Calò, A. Maffezzoli, G. Mele, F. Martina, S. E. Mazzetto, A. Tarzia and C. Stifani, Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites, *Green Chemistry.*, 2007, 9, Pages 754 – 759.

[11] B.Kiskan, B. Gacal, M. A. Tasedelen, D. Kolak, Y. Yagci, Design and Synthesis of Thermally Curable Polymers With Benzoxazine Functionalities, Willy Inter Science Volume 245-246 Issue 1, Pagse 27-33

[12] Z. , R. Lyon, H. Ishid, Thermal properties of phthalonitrile functional Polybenzoxazines Zdenka, Journal of applied polymer science, 1999 volume 73, Pages 2937-2949

[13] H. Y. Low, H. Ishida, Structural effects of phenols on the thermal and thermo-oxidative degradation of polybenzoxazines, Elesevier, Polymer 40 (1999), Pages 4365–4376

[14] S. W. Choi, S. Ohba, Z. Brunovska, K. Hemvichian, H. Ishida, Synthesis, characterization and thermal degradation of functional benzoxazine monomers and polymers containing phenylphosphine oxide, Polymer Degradation and Stability 91 (2006), Pages 1166-1178

[15] K. Hemvichian, H. Ishida, Thermal decomposition processes in aromatic amine-based polybenzoxazines investigated by TGA and GC–MS, Polymer Degradation and Stability 43 (2002), Pages 4391–4402

[16] Thermal and oxidative Degradation of polymers, http://nvl.nist.gov/pub/nistpubs/sp958-lide/344-346.pdf , last visited on 10 september 2008,

[17] Hajaloglu, J., ‘‘ Pyrolys Mass Spectrometry For Molecular Ionization Methods’’, The Encylopedia Of Mass Spectrpmetry: Ionization Methods, Vol. 6, Edited by Gross, M. L., et al., Elsevier Science Ltd, (2007), pages 925-938

[18] Montaudo, G.; Puglisi, C.; Samperi, ‘‘Chemical Reactions Occurring in the Thermal Treatment of PC/PMMA Blends, Jornal of polymerr science, part A: Polymer chemistry, Volume 36, Issue 11 (pages 1873-1884)

[19] M.M. Fares, J. Hacaloglu, S. Suzer , "Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry," *European Polymer Journal*, vol. 30, pages 845-850 (1994)

[20] M. C. Gupta and S. G. Viswanath, Role of Metal Oxides in the Thermal Degradation of Poly(vinyl chloride), American Chemical Society, Ind. Eng. Chem. Res., 1998, 37 (7), pp 2707–2712

[21] Wim M. Groenewoud, Characterisation of Polymers by Thermal Analysis, 2001, Pages 195-196

[22] Vincent B. F. Mathot, Calorimetry an Thermal Analysis of Polymers, 1994, Pages 327-330

[23] General Scheme of a Mass Spectrometer, http://www.biologie.uni-regensburg.de/Biochemie/Deutzmann/Praktika/MS_Ionenerzeugung.pdf, last visited on 14 September 2008,

[24] T. Uyar, Z. Koyuncu, H. Ishida, J. Hacaloglu, Polymerization and Degradation Processes in Aromatic Amine-based naphtoxazine, Polymer Deg Stability 93, 2096-2113, 2008)

[25] The University of Arizona, Introduction to mass spectrometry, http://www.chem.arizona.edu/massspec/inter_html/inter.html, last visited on 15 september 2008,