SYNTHESIS AND CHARACTERIZATION OF A POLYBENZOXAZINE FROM A DIFUNCTIONAL AMINE AND A TRIFUNCTIONAL PHENOL

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF A POLYBENZOXAZINE FROM A DIFUNCTIONAL AMINE AND A TRIFUNCTIONAL PHENOL

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Synthesis of a polymer with benzoxazine units in the main chain backbone by a trifunctional phenol, a difunctional amine, and paraformaldehyde was achieved. Thermal, mechanical and spectroscopic characterization and the viscosity properties of the synthesized polymer were studied. In the first step of this study, a fast and feasible method for the synthesis of the benzoxazine precursors was developed since some methods mentioned in the literature about the synthesis of the benzoxazine derivatives last long time. The second step was to polymerize the benzoxazine precursors thermally. The curing of benzoxazine precursors was done via ring opening polymerization at 150 ^{o}C and a final polymerization was observed at about 250 ^{o}C.

^{1}H NMR, ^{13}C NMR and FT-IR spectroscopies revealed the characteristic peaks for the formation of benzoxazine ring. Among them, ^{13}C NMR gave important clue on the formation of the benzoxazine.

The thermal characterization of the benzoxazine precursors and the polymers indicated that the ring opening polymerization of these precursors started at around 110 ^{o}C and a final polymerization was about at 230 ^{o}C. Differential Scanning

Calorimetry thermograms of the polybenzoxazine indicated a secondary transition at around 270 ^{o}C. An onset decomposition of the benzoxazine oligomers started around 100 ^{o}C in Thermal Gravimetric Analysis thermograms performed under N_2 atmosphere and two major maximum weight losses were observed at 273 ^{o}C and 439 ^{o}C. However, polybenzoxazine showed a starting degradation at about 260 ^{o}C and the maximum weight loss temperatures were seen at 296 ^{o}C and 465 ^{o}C.

Viscosity variation of the reaction mixture was studied by Ubbelohde Viscometer at 30 ^{o}C. Viscosity results indicated that the increase in the intrinsic viscosity of the reaction mixture till 50th minute and followed by a decrease due to possible branching and the intra-crosslinking of the benzoxazine oligomers. Mechanical properties of the polymer films, prepared by compression molding at 180 ^{0}C, were investigated. Test results showed that low tensile strength whereas comparatively high elongation.

Keywords: Oxazine Ring, Ring Opening Polymerization, Polybenzoxazine, Characterization.

ÖZ

ÇİFT FONKSİYONLU AMİN VE ÜÇ FONKSİYONLU FENOLDEN BENZOKSAZİN SENTEZİ VE KARAKTERİZASYONU

Kaya,Şafak

Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü

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Bu çalışmada, ana zincirinde benzoksazin birimi içeren bir polimerin, üç fonksiyonlu fenol, çift fonksiyonlu amin ve paraformaldehit ile sentezi ve üretilen bu polimerin ısıl, mekanik, spektroskopik karakterizasyonu ile vizkozite özellikleri araştırılmıştır. Çalışmanın ilk aşamasında, benzoksazin monomerlerinin sentezi için hızlı ve uygulanabilir bir yöntem geliştirilmiştir ki bilindiği gibi literatürde bahsedilen bazı yöntemlerin uzun süre alması ve aynı zamanda sentez aşamasında bazı karışıklıklar içermesindendir. İkinci aşamada ise, sentezlenen benzoksazin monomerlerinin ısıl pişirme yolu ile polimerizasyonu gerçekleştirilmiştir. Pişirme aşamasında, benzoksazin monomerlerinin yaklaşık 150 ^{o}C' de halka açılım polimerizasyonu ile polimerleştikleri ve 250 ^{o}C' den sonra da bir kez daha polimerizasyona uğradıkları gözlenmiştir.

^{1}H NMR, ^{13}C NMR ve FT-IR spektroskopisi analizleri sonucu benzoksazin halkasına ait olan karakteristik sinyaller gözlenmiştir. Bununla birlikte FT-IR analizi sonunda elde edilen spektrumlarda da bu iki olgunun varlığı görülmüştür.

Benzoksazin oligomerlerinin ve bu oligomerlerden sentezlenen polimerlerin ısıl karakterizasyonları halka açılım polimerizasyonunun 110 ^{o}C den sonra başladığını ve

ayrıca 230 ^{o}C' de son bir polimerizasyon gerçekleştiğini göstermiştir ve polibenzoksazinin ısıl karakterizasyonu 270 ^{o}C civarında ikincil bir değişimi göstermiştir. Azot atmosferi altında benzoksazin oligomerlerinin 100 ^{o}C civarında bozulmaya başladıkları tespit edilmiştir ve ayrıca iki farklı ana azami ağırlık kaybı ilki 273 ^{o}C' de ikincisi 439 ^{o}C olmak üzere gözlenmiştir. Bununla birlikte polimerin bozunumunun 260 ^{o}C civarında başladığı ve azami ağırlık kayıplarının 296 ^{o}C ve 465 ^{o}C de olduğu gözlenmiştir.

Benzoksazin oligomerlerinin sentezi esnasında, reaksiyon ortamının vizkozite değişimi 30 ^{o}C de Ubbelohde Vizkometresi ile incelenmiştir. Vizkozite sonuçları reaksiyon karışımının intrinsik vizkozitesinin 50. dakikaya kadar arttığını fakat 50. dakikadan sonra muhtemel dallanma ve çapraz bağlanmadan dolayı azaldığını göstermiştir. Aynı zamanda sıkıştırma döküm ile hazırlanan polibenzoksazin filmlerinin uzamaya göre gerilme özellikleri araştırılmıştır. Test sonuçları polimer filmlerin uzamasının yeteri kadar iyi olmasına rağmen gerilme kuvvetinin oldukça az olduğunu göstermiştir.

Anahtar Kelimeler: Oksazin Halkası, Halka Açılım Polimerizasyonu, Polibenzoksazin, Karakterizasyon.

To my family…

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ABBREVIATIONS

THPE	1, 1, 1-Tris (4-hydroxy-phenyl) ethane
HDA	Hexamethylenediamine
PF	Paraformaldehyde
DSC	Differential Scanning Calorimetry
TGA	Thermal Gravimetric Analysis
NMR	Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared Resonance

CHAPTER 1

INTRODUCTION

1.1 Phenolic Resins

High performance polymeric materials have been used in so many industrial applications such as electronics, aerospace technology, biomaterials, etc. Eventually, the interest on these materials has increased reasonably. [1,2]

One of these high performance materials is phenol formaldehyde resin which is the earliest commercial synthetic resin with the commercial name of Bakelite and formation is done from an elimination reaction of phenol with formaldehyde. Crosslinking of hydroxymethyl phenols is achieved by heating it around 120 ^{o}C in order to form methylene and methyl ether bridges. At this point the resin starts to form the highly extended three dimensional web of covalent bonds that is one of the typical properties of polymerized phenolic resins. It is highly crosslinked nature of phenolics, which gives them hardness and good thermal stability and which makes them impenetrable to most chemical attack and solvation and it is also the reason why they are called as thermosets.[3]

In the thermosetting resins, the polymer chains are cross-linked by intermolecular bonding.[4] The curing of thermosets may be achieved by using chemicals, heat (generally above 200 ^{o}C), or radiation such as electron beam processing.[4,5] Thermoset materials are usually liquid or malleable prior to curing and designed in order to be molded into their final form or used as adhesives; others are solids like that of the molding compound used in the semiconductors and integrated circuits. [4]

The cross-linking process forms a molecule with a larger molecular weight, resulting in a material with a higher melting point. During the reaction, the molecular weight has increased to a point so that the melting point is higher than the surrounding ambient temperature and the material forms into a solid material. [4,5] Uncontrolled reheating of the material results in reaching the decomposition temperature before the melting point is obtained. Therefore, a thermoset material cannot be melted and re-shaped after it is cured. This implies that thermosets cannot be recycled, except as filler material. [5]

Materials that are electrically conductive, resistive, insulating, or suitable for high voltage applications are commonly available as a thermosetting resin. Flame retardant materials reduce the spread of flames or resist ignition when exposed to high temperatures. Thermal compounds form a thermally conductive layer on a substrate, either between components or within a finished electronic product. Purging compounds are used to clean molding machines between runs of different colors or compositions. Gap filling or underfill compounds are used to fill in gaps or spaces between two surfaces to be bonded or sealed. [6]

Many types of thermosets and thermoset materials are available. Important thermosets include phenolics, ureas, melamines, epoxies, polyesters, silicones, rubbers, and polyurethanes. [4,5]

The usage of the phenolic resins started in the early stages of the twentieth century and they are considered as the first fully synthetic polymers to achieve the commercial success.[7] The phenolic resins possess extreme characteristics such as dimensional stability, good electrical and chemical resistance, flame retardant, heat resistance, good mechanical strength, low water absorption and low cost, as a result of these properties they are widely used in various industrial applications such as aerospace industry, construction materials, electronics, molded parts, insulating varnishes, laminated sheets, industrial coatings, and wood bonding, berbonding, and plywood adhesives. [8,9] However, the traditional phenolic resins also have some disadvantages like brittleness, poor shelf life, and large volumetric shrinkage after

cure and utilization of acid or base type catalyst during the synthesis of the resin may corrode the processing environment also the formation of some by-products such as water and ammonia may affect the characteristics of the resin by forming micro voids after the cure. [8] These deficiencies come from the synthetic method through the condensation reaction of phenolic methylols. [10]

Prior to the usage of the phenolic resins in the industrial applications, they must be first treated with a base material such as paper, glass, or cotton. The base material is dependent upon the designed application of the finished product. Paper phenolics are used in the manufacturing of electrical components such as punch-through boards and households laminates. [11]

Polybenzoxazines have been recently developed as a class of a thermosetting phenolic type polymeric material to create an alternative more fascinating solution for epoxy and phenolic resins to eliminate their shortcomings. [1,2] These high performance phenolic resins can be easily synthesized by means of a Mannich Condensation Reaction of a phenolic derivative, an amine and formaldehyde as starting materials either by solution or solventless method (melt-state reaction). [2,8]

1.2 Historical Development of Polybenzoxazine

Studies conducted in the area of phenols and formaldehydes started with Adolf von Bayer [12] in 1872 and Losekam [13] in 1889. Laccain was the first commercial phenolic resin and it was introduced by Blumer [13] in 1902 as a substitute for shellac. However; the usage of the phenolic resins was popularized by the heat and pressure patents of Dr. Leo H. Baekeland [14-17] who is known as the father of phenolic resins in 1907. In the present day; some of the most popular phenolic resins posses the trade name of the Bakelite in reference to the company that Dr. Leo H. Baekeland formed in 1910. [14]

Although polybenzoxazine has been developed recently [18] as a novel type of high performance phenolic resin, it was synthesized first by Holy and Cope [19] in 1940s. According to their reported procedure; the synthesis of well-defined benzoxazine

monomers was performed by a condensation reaction of primary amines with formaldehydes and substituted phenols and the experiment was conducted in a solution environment in two steps [19]. After the report of Holy and Cope [19]; Burke and coworkers [20-21] improved number of variations on the procedure for the synthesis of benzoxazine monomer. In addition; Burke [22] figured out that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich Bridge and dimeric structures as seen in Figure 1. After that Schreiber [23-24] proposed the potential of the benzoxazines for the preparation of phenolic materials with improved properties furthermore; Reiss and coworkers [25] have done some research on the usage of the benzoxazines as precursors for the phenolic resins and they also proposed thermally initiated and phenol catalyzed systems can lead to polymerization of monocyclic benzoxazine to oligomeric species. [25]

Figure 1: Formation of Mannich Bridge and benzoxazine ring.[22]

1.3 General Properties of Polybenzoxazine

Because of the variation in the molecular structure of the polybenzoxazine, it has a very good flexibility which allows the polymer to be processed more easily than other general phenolic resins. The properties which separate the polybenzoxazine form other phenolic resins are; [8]

1) After the cure, the volumetric change is almost zero
2) Water absorption is very low
3) High char yield

4) During curing the polybenzoxazine, a strong acid catalysts is not needed
5) During curing, there is not any by-product formed
6) Glass transition temperatures of some polybenzoxazine may be higher than the cure temperature

1.4 Synthesis of Polybenzoxazine

1.4.1 Reaction Mechanism of the Synthesis of Benzoxazine Precursors

The suggested mechanism for the synthesis of oxazine ring is that amine reacts first with the formaldehyde to form an intermediate which is called as aminomethylol group and by the time; this aminomethylol intermediate reacts with phenol and formaldehyde to generate the oxazine ring. The suggested mechanism for the formation of benzoxazine ring and the general structure of oxazine ring are shown in Figure 2 and in Figure 3, respectively.

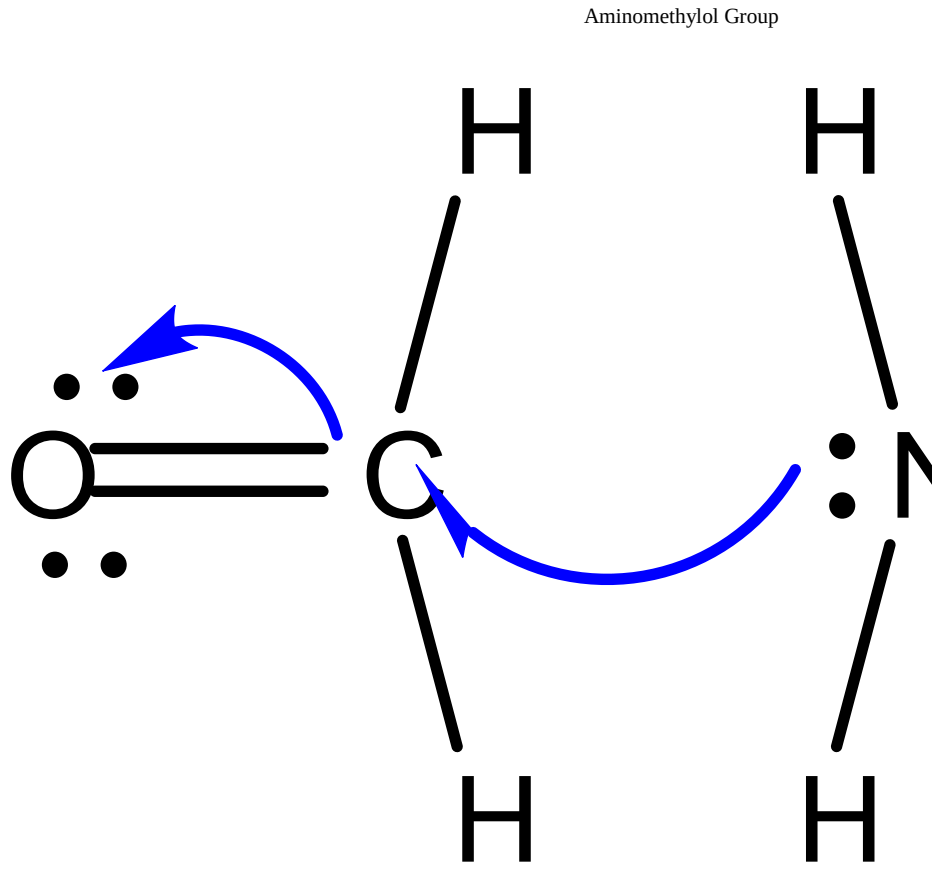


Figure 2: General reaction mechanism of a monofunctional benzoxazine synthesis.

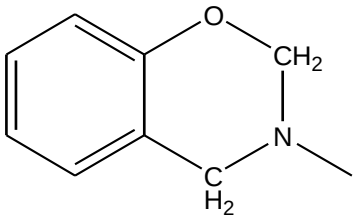


Figure 3: General structure of benzoxazine ring

1.4.2 Ring Opening Polymerization

The ring opening polymerization of benzoxazine is as if the reverse of Mannich Reaction. The polymerization begins with the approach of the phenol to the benzoxazine by the means of intermolecular hydrogen bonding. The first step leads to the formation of a complex intermediate that provides a floor for the movement of the electrons from the nitrogen atoms to the hydroxyl group. When the ring opening polymerization of multifunctional monomers is activated thermally, the resulting thermosetting polymers have high modulus and excellent thermal, mechanical, and electrical properties. [2]

The presence of compounds with active hydrogen atom such as naphthols, indoles, carbazole, imides, and aliphatic nitro compounds even phenol derivatives may cause the ring-opening polymerization of some benzoxazine monomers and small oligomer formation can be observed. The formation of Mannich bridge structure due to the ring-opening polymerization in acidic medium is shown in Figure 4. [8]

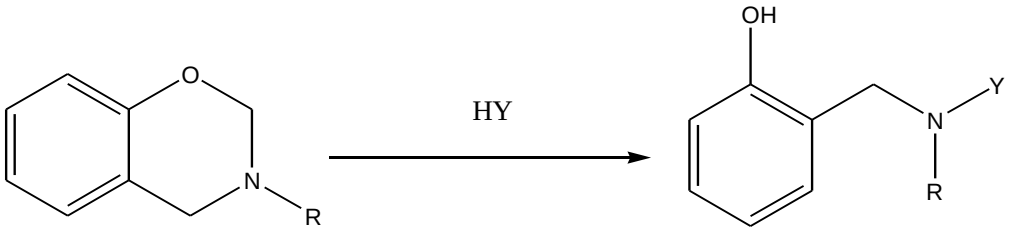


Figure 4: Ring opening of benzoxazine (HY: naphthols, indoles, carbazole, imides, and aliphatic nitro compounds even phenol derivatives)

If a strongly basic amines and a less acidic phenol are used in the formation of benzoxazine, a more stable benzoxazine is formed to hot alcohols. In addition, if there is more than one substitution on the ortho position, the initial product may lead to another amino alkylation reaction. [8]

1.4.3 Some Other Approaches Related to Synthesis of Polybenzoxazine

Another approach is saying that the synthesis of the polybenzoxazine starts with a Mannich Condensation Reaction of phenol, amine and formaldehyde and then it continues with a ring-opening polymerization without any catalyst. The mechanism of the ring-opening polymerization of benzoxazine has been investigated and a formation of an iminium ion as an intermediate has been suggested for this mechanism as a probable method. Another method proposed for the ring opening polymerization of the benzoxazine monomer is an ionic ring opening mechanism that is coupled with a chain transfer growth and after that there has been done some investigation about the conversion and the rate of the ring-opening polymerization of the purified monomer and also these were compared with the conversion and the rate of the polymerization of as-synthesized precursors under isothermal conditions. [26, 27] The suggested mechanism for the formation of iminium ion and carbocation is shown in Figure 5.

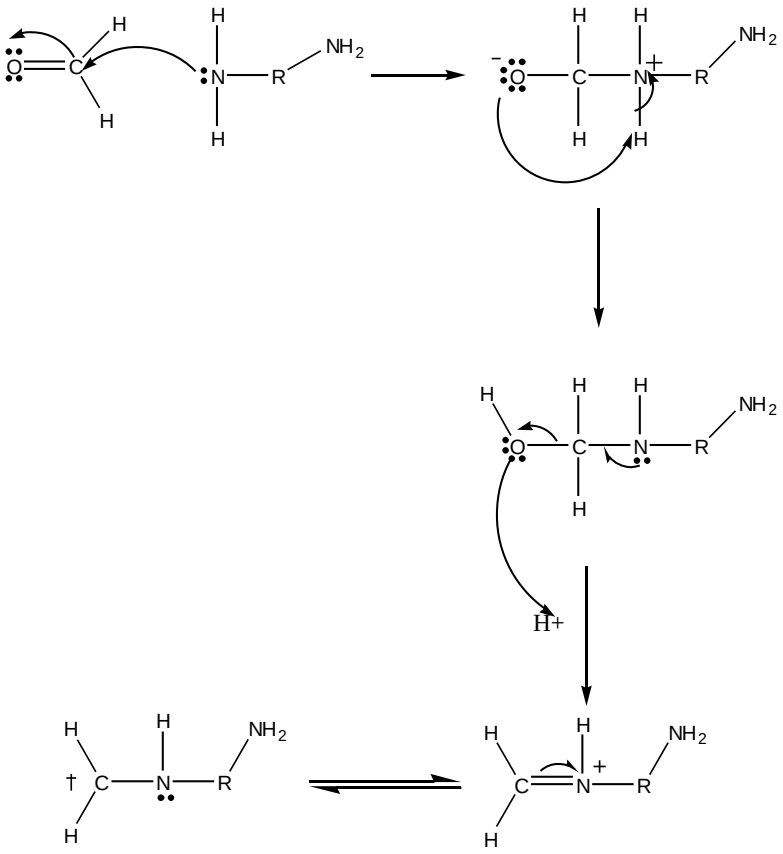


Figure 5: General mechanism for the formation of the iminium ion and carbocation

1.4.4 Development of Solventless Method

During the synthesis of polybenzoxazine done by a reaction mixture of the starting materials in a solution; some difficulties may be faced. For example; it may take several hours to fulfill a desired reaction and to separate the reaction products from the solvent will also take an extra time. In addition, another additional time will be required if a purification step is needed and unfortunately it is necessary for all synthesis of polybenzoxazine in solution method. Also, using a solvent in the reaction and getting a clear solvent after the reaction will increase the cost of the synthesis of polybenzoxazine. Furthermore, low solubility of starting materials and difficulty of processing into thin films from the typical monomers can be another

problem. [28] In order to overcome these drawbacks, Ishida et al. [28] developed a solventless method of the synthesis of polybenzoxazines. Liu [29] was the first to suggest the reaction mechanism and the kinetics of this solventless system that is; the starting materials which are phenol, amine and aldehyde are mixed physically and then the mixture is heated to their melting point. After that in order to complete the total interaction of the reactants for producing the desired benzoxazine polymer a sufficient temperature is kept constant. [8] However, it should be noticed that formaldehyde evaporates more easily and loses the stoichiometry of the reaction more quickly than the other reactants therefore the formaldehyde is not typically used in the synthesis. During the production of polybenzoxazines; selecting type of phenol and amine reactants will help to design the monomer structure for tailoring desired properties of the resulting benzoxazine polymer. Solventless method has superior advantages than the solution method. The most important of them are that the reaction time quite less than the traditional synthetic route and the formation of unwanted intermediates and by-products are lessened by solventless method. [8]

1.4.5 Curing of Benzoxazine Precursors

Ishida and Wang [30] conducted a research on the curing of polybenzoxazine. Two different types of polymerization mechanism result in two types of polybenzoxazine. These are the phenoxy type and the phenolic type benzoxazines. If there is a substituent such as a methyl group in the ortho or meta position of benzoxazine ring; the ring opening polymerization is hindered and the resulting polymer is a phenoxy type polybenzoxazine with a low molecular weight. If there is no substituent in the benzoxazine ring, a phenolic type polybenzoxazine with a high molecular weight can be obtained. Ishida [30] reported that during the curing of allyl containing polybenzoxazine which is synthesized from an allyl-phenol, aniline and paraformaldehyde, the ring opening polymerization that is necessary to form a phenolic bridge is hindered by the ally group of the phenol. However, there is no such hindrance is observed when the polybenzoxazine is synthesized from the reaction of allyl-amine, paraformaldehyde and phenol. That is why the glass

transition temperature of the polybenzoxazine synthesized from allyl-phenol is much lower than that of polybenzoxazine synthesized from allyl-amine. [31]

1.5 Structure-Property Relationship of Polybenzoxazine

The benzoxazine monomer has a six membered heterocyclic ring with constitutive nitrogen and oxygen atoms. In addition, the molecular modeling results indicate that in a benzoxazine molecule, the oxazine ring adopts a distorted semi chair structure to obtain the minimum energy and this structure results in a strain in the ring that enables for benzoxazine molecule to go through a ring-opening polymerization under certain reaction conditions. Furthermore, the basic property of oxygen and nitrogen atoms (according to Lewis acid-base definition) provides the oxazine ring to be opened most probably by means of a cationic mechanism. [32]

Analyzing the oligomeric model compounds of the complex, high molecular weight polymeric systems can provide a theory about the characterization of these polymeric systems. Polybenzoxazines possess [-Ph (OH)-CH_2-NR-CH_2-] repeating unit and a Mannich Bridge in the structure provides the polybenzoxazines be more flexible than any traditional phenolic resins. Model of phenol – formaldehyde oligomers indicated the existence of intramolecular and intermolecular hydrogen bonding between the hydroxyl groups which affect the properties of oligomers and their conformations. In addition, oligomers of polybenzoxazines showed the same hydrogen bonding. Hydroxyl groups in the polybenzoxazines are also capable of hydrogen bonding to near hydroxyl groups and the lone pair of nitrogen atom in the Mannich Bridge. In addition, phenol – formaldehyde oligomers can chelate with metal cations as well as the polybenzoxazine oligomers do since the hydroxyl groups with the help of their acidic moiety can ionize during the stabilization by the intramolecular hydrogen bonds. [33]

Although monofunctional benzoxazine molecules can form linear polymers, they generally do not form large molecular weight polymers. Because of the hydrogen bond formation at the growth front, termination of the benzoxazine chain occurs at the dimer length and the solution of this problem comes by the usage of many

difunctional benzoxazines to obtain cross-linked polymers with useful properties. Initial studies show that while the molecular connectivity of the polymer is improved, interference with the chain growth by hydrogen bond formation does not change. As a conclusion, there may be some nanoscale aggregates that are loosely connected even for a homopolymer. However, if a polymer has a benzoxazine ring in the main chain, the molecular connectivity among these nanoscale aggregates may be dramatically improved. As a result, the polymer will have better mechanical and physical properties. [34]

In some applications, polymeric precursors are preferred more than monomeric precursors for further polymerization. In addition, polybenzoxazines have a rich molecular design flexibility. By the help of this adjusting polybenzoxazine structure will give us an opportunity to enhance the characteristics of them further over the monomeric benzoxazine resins. For example, polymeric precursors offer the ability to prepare a varnish with low solid content that forms good quality films and in the synthesis of polybenzoxazines. If a diamine with both ortho positions occupied is used, it will be possible to minimize the formation of branches**.** [35]

Ishida and Allen reported [2] that the interactions of polymer chains because of the strong hydrogen bonding support the network structure of the polybenzoxazine as well as the chemical crosslinking. In order to interpret the structure-property relationship in the polybenzoxazine, the strong hydrogen bonding can play critical role while taking into account the low crosslinking density in polybenzoxazines. [36]

Hydrogen bonds also exhibit a very important effect on the properties of the polybenzoxazines. In the structure of the polybenzoxazines; O—H---O intramolecular and intermolecular hydrogen bonding and O—H---N intramolecular hydrogen bonding were observed. In addition to these hydrogen bonding; when the aromatic amines are used in the synthesis of the polybenzoxazines, OH--π hydrogen bonding is observed. These hydrogen bonds contribute to the high glass transition temperatures of polybenzoxazines, as the cross-linking densities of polybenzoxazines were relatively low for being compared with other typical thermosets. In the

development of the performance characteristics of the polybenzoxazines, some studies have been conducted. One of them is related to the incorporation of the furan groups to the benzoxazine monomers. The reasons for the incorporation of furan groups are [37]

1) To simplify polymerization reactions
2) To enhance the thermal stability and the glass transition temperatures of the polybenzoxazine by the formation of linkages between Mannich Bridge and aromatic furan groups
3) To promote the formation of the OH--π hydrogen bonding and O—H---N hydrogen bonding
4) To enrich the formation of the char

1.6 Effect of Functionality in the Synthesis of Polybenzoxazine

In order to form an infinite network structure after the polymerization the polyfuncionality should be achieved. Derivation of the polyfuncionality can be provided by using a bifunctional phenolic molecule with a monoamine, a difunctional amine with a monophenol, or a difunctional amine with a bi functional phenol. [7] Most of the published researches for benzoxazine so far have focused on the multifunctionality provided by the phenol derivatives like bisphenol to be able to acquire an infinite network structure. However, that kind of way only causes the polybenzoxazine to have a rigid-aromatic backbone of a crosslinked network. As a result; polybenzoxazine will have the same disadvantages of brittleness like phenolic resins and the other conventional thermosets. In another approach, aliphatic diamines and the monofunctional phenols are used for the synthesis of polybenzoxazine. The resulting polymers posses excellent mechanical characteristics such as flexural modulus, strength etc. [7]

The monomers of benzoxazine can be prepared easily from phenols, primary amines and formaldehyde. Wide variations in the usage of the phenols and amines during the synthesis of the polybenzoxazine provide good molecular-design flexibility for the

cyclic monomers. Process continues with a ring-opening polymerization of the monomers by heat treatment without any catalysts or without generating by-products that lets the polymer be possessed of excellent dimensional stability. [38]

1.7 Modification of Polybenzoxazine

Although polybenzoxazine has superior properties than all phenolic resins it also shares a deficiency that is brittleness. This brittle characteristic of polybenzoxazine comes from the rigid phenol backbone and the low molecular weight of the network structure. This characteristic also restricts the polybenzoxazine in their application areas. For example, processing into thin film from monomers is difficult since most of the monomers of benzoxazine have powdered moiety. [2] Recently, in order to improve the performance of polybenzoxazine, some investigation has been done related to rubber and thermoplastic polymer modification of polybenzoxazine. Reactive blending which introduce chemically a flexible chain such as polycaprolactone, poly(vinylphenol), epoxy, polyurethane into the polybenzoxazine matrix can be another development way of the brittleness of the polybenzoxazine. [2, 39-41] Another approach is the modification of the monomer by introduction of other cross-linkable functional units that are very effective to enhance the thermal properties. Hybridization with inorganic materials such as layered clay and nanoparticles of metal oxides is another investigation which improves the properties of the polybenzoxazine. All of these approaches involve the addition of a foreign component into the polymer matrix. [2, 38-42]

There have been some approaches applied to improve the high performance characteristics of polybenzoxazines especially by designing the benzoxazine monomers specially. First approach was related to the incorporation of the naphthalene, biphenyl, and benzophenone groups to benzoxazines. However they have high melting points, high polymerization temperatures, and poor solubility in organic solvents; therefore, the processability was very poor. [42] Other approach was the introduction of another polymerizable group to the benzoxazine monomers. The possible polymerizable groups were ethynyl, phenyl ethynyl, nitrile, propargyl, and

maleimide groups. [1,43-45] In order to increase the crosslinking density of the polymer, the polymerizable groups and the benzoxazine rings were *in situ* polymerized under heat. The resulting polymers have high glass transition temperatures and good thermal stability. However, this approach has a disadvantage when the polymerization of the benzoxazine ring and the polymerizable groups take place at different temperatures. Complicated polymerization reactions and/or high curing temperatures were encountered with accompanied with the benzoxazine monomers. Furthermore; the first polymerization (due to the polymerizable groups or benzoxazine rings) may create cross-linked structure that can hinder the achievement of the full polymerization, or reduces the total conversion of polymerization reactions, or increases the polymerization temperatures. In order to overcome this problem; a third approach is related to the modification of benzoxazine monomers with nonpolymerizable groups such as cyclic alkyl substituent including adamante and terpephenyl groups. [46] The resulting polymers have high thermal stability, water resistance, and high glass transition temperatures. In the presence of the β-cyclodextrin, the adamante groups could intend to form rotaxane complexes which causes the polymer having higher temperatures of glass transition and decomposition. [46]

Development of the properties of the polymers by the modification plays an increasingly critical role as the polymer applications have been increased in variety. For example, in order to prepare solvent free compounds for the applications of coating, adhesive or composite, a diluting agent has been used in several polymers. The usage of the organic solvents to obtain the low resin viscosity has been also applied extensively formerly; however, the usage of these volatile organic compounds has become increasingly restrictive due to the environmental regulations. [35]

There are two types of diluting agent which are reactive diluents and nonreactive diluents. A reactive diluent is actually one of the components of the reaction mixture; in other words, it undergoes a reaction with the resin and becomes a part of the polymer. On the other hand, although a nonreactive diluent lowers the viscosity of

the resin, it does not become a part of the polymer. Benzoxazine resins provide self polymerizable crosslinking systems with high thermal and mechanical properties. In addition, one of the most useful properties of benzoxazine resins is the low a-stage viscosity that provides the resin to have an ability in order to accommodate the large quantity of filler while still maintaining their good processability when compared with the traditional phenolic resins. [35] According to the report of Ishida and Rimdusit [47], the thermal conductivity of the composite can be improved by the usage of benzoxazine resins which possess the low melt viscosity with the boron nitride ceramics. Furthermore, the wood-flour-filler improves the thermal and the mechanical properties of the wood composites when it is incorporated in the polybenzoxazine matrix. [35]

Some of the bifunctional benzoxazine resins are solid at room temperature and in order to lower the liquefying temperature and to reduce the melt viscosity of the benzoxazine resins, some reactive diluting agents have been used. In the report of Ishida and Allen [2], addition of a liquid epoxy to a benzoxazine matrix improved the crosslinking density of the polybenzoxazine and also affects the mechanical properties of the polymer and lowers the liquefying temperature of the resin. Furthermore, Rimdusit et al. [47] figured out that because of an addition of more flexible molecular segments to the polybenzoxazine matrix, the toughness of the rigid polybenzoxazine was improved as the amount of the epoxy was increased. On the other hand, addition of a small fraction of phenolic novalac resin into the benzoxazine-epoxy matrix was reported to help to lower the curing temperatures. [35]

In addition, a liquid monofunctional benzoxazine was used as a reactive diluent for solid bifunctional benzoxazine resins to lower the melt viscosity of the polymer. Yet the usage of the monofunctional benzoxazine as a reactive diluent for a solid benzoxazine also caused to lower the crosslinking density of the polymer and decreased the temperature of the thermal degradation char yield of the polybenzoxazine. Furthermore, Ishida and Wang's [48] work on monofunctional phenol-aniline type benzoxazine showed superior processability in their aryl-amine based resins as well as the thermal stability in their phenol-toluidine type and the

phenol-xylidine type resins. Moreover, degradation temperature and the char yields of the phenol aniline type benzoxazines indicated higher values than the bisphenol-A-aniline type benzoxazines. [35]

1.8 Aim of the Study

The first aim of the study was to synthesize a polymeric material which contains benzoxazine units in the main chain backbone from a difunctional amine and a trifunctional phenol and the second is to characterize them thermally and with spectroscopy and to investigate the mechanical and viscosity properties of the polymer. Some works in the literature criticized vastly because of the reproducibility and caused some confusion in experimental process; therefore, we tried to develop a new method in order to have better, faster and feasible ways.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

99 % pure 1,1,1-Tris(4-hydroxy-phenyl)ethane (THPE) was purchased from Aldrich Chemicals. 95 % pure paraformaldehyde (PF) was obtained from Merck and 97 % pure hexamethylenediamine (HDA) was supplied from Fluka AG. 99 % pure pyridine was used as solvent in our study and supplied from Merck. The reason why pyridine was used as solvent is that THPE is not soluble enough in any general solvents a like; therefore, we needed a strong solvent like pyridine was needed for the study and we did not need any further purification for our reactants.

2.2 Synthesis of Benzoxazine Precursors

5.22 g of HDA was firstly dissolved completely in 100 ml of pyridine in a three-neck round-bottom flask. 4.59 g of THPE was dissolved with 50 ml of pyridine in another flask and then the solution of THPE was taken into a separatory funnel and connected to three-neck round-bottom flask which contained the HDA solution.

2.7 g of solid PF was put in to a 100 ml-flask and this flask was connected to three-neck round-bottom flask with an isolated glass bridge. Finally, a condenser was connected to the head of three-neck round-bottom flask and the experimental set up was finished. Beside that the three-neck round-bottom flask, the flask of paraformaldehyde and the glass bridge are isolated with aluminum foil and cotton for the precautions of any explosion. The experimental set-up of the study is shown in Figure 6. According to the Mannich Reaction mechanism, THPE should react with

the outcome of the reaction between PF and HDA; therefore, in order to lower the possibility of any side reaction between THPE and HDA to increase the purity of the synthesized benzoxazine precursors we separate three reagents.

Figure 6: The experimental set up for the synthesis of the polybenzoxazine precursors.

The reaction started with heating up the PF flask and wait until the gas formaldehyde bubbled in the solution of HDA and then we turned on the valve of the separatory funnel to let the solution of THPE drop by driblets into the main solution. The use of controlled flow of gaseous formaldehyde into the reaction vessel is to reduce the reaction time and increase the reaction rate. The reaction mixture was mixed and refluxed continuously, and the temperature was kept at 35-40 ^{o}C. The reaction continued until the all of the paraformaldehyde is consumed completely and transferred to the main flask in the form of formaldehyde. Then, the solvent pyridine

from the reaction mixture was removed by Rotary Evaporator RE100 and Lindberg/Blue V09140 vacuum pump and the resulting product was used as precursors for further polymerization.

2.3 Purification of the Benzoxazine Precursors

After the removal of the pyridine by rotary evaporator, the yellowish precursors were taken to the vacuum oven, in order to remove the last remains of pyridine we apply an extra purification step on our precursors at 80 ^{o}C for approximately 5 hours in vacuum oven. During this process, because of the ring opening polymerization which starts at around 100 ^{o}C we cannot exceed 100 ^{o}C even though the boiling point of pyridine is 115 ^{o}C that is why the purification took 5 hours. Finally, we obtained yellow brittle material which was characterized as benzoxazine precursors.

2.4 Curing

The cure characteristics of thermoset materials is essential for their applications, therefore, cure studies for polybenzoxazine are necessary in the determination of their practical usage. There are several methods in order to follow the cure process For example, d.c. conductivity, infra-red absorption, and differential scanning calorimetry (DSC).

DSC has been widely used in the cure studies of the thermosetting resins. In addition, the results obtained from isothermal method would be the most consistent and reliable technique. Therefore, the isothermal technique of DSC was employed in this study to investigate the cure characteristics of polybenzoxazine.

Before the curing process the precursors were washed with chloroform to get rid of the last impurities and after that the precursors were filtered and heated up to 150 ^{o}C for 1 hour for both discarding the remaining of solvent pyridine and curing in vacuum oven.

2.5 Spectroscopic Analysis

2.5.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

The product resulted from the reaction of HDA, THPE, and PF was examined with H-NMR and the measurement was done on Bruker NMR operating at 400 MHz for liquid samples and chloroform was used as solvent in the analysis.

2.5.2 Fourier Transform Infrared Resonance (FTIR) Spectroscopy

For further information in the characterization of the polybenzoxazine precursors and the cured polybenzoxazine, Perkin Elmer Spectrum-One FTIR Spectrometer was used to inspect the IR- spectra of benzoxazine to clarify the structural information of benzoxazine.

2.6 Thermal Analysis

2.6.1 Differential Scanning Calorimetry (DSC) Analysis

Scinco DSC N-650 instrument was used to investigate the thermal behavior of the benzoxazine precursors. The analysis was performed in the temperature range of 25-300 ^{o}C by a heating rate of 10 ^{o}C / min and under N_2 atmosphere.

2.6.2 Thermogravimetric Analysis (TGA)

In order to obtain complete qualitative and quantitative characterization of a thermal decomposition process of benzoxazine precursors and cured polybenzoxazine, Schimadzu–DTG60H TGA instrument was used for the observation of the thermal degradation of both benzoxazine precursors and polymerized benzoxazine with time. The temperature range of our analysis was 25 ^{o}C - 500 ^{o}C by a heating rate of 10 ^{o}C / min under N_2 atmosphere.

2.6.3 Thermogravimetry and FTIR Spectrometry (TGA+FTIR)

Perkin Elmer Pyris 1 TGA & Spectrum 1 FTIR Spectrometer system was used in order to understand decomposition process of the benzoxazine oligomers and the polymers synthesized from these oligomers. The analysis was conducted in air and

under N_2 atmosphere to see the effect of O_2 in the decomposition of the samples and the temperature range of the analyis was 25 ^oC - 300 ^oC by a heating rate of 10 ^oC / min. FTIR spectrometry indicated a way of decomposition of the samples at different temperatures.

2.7 Viscosity Measurements

The viscosity variation of the reaction mixture at 30 ^oC was determined by Ubbelohde Viscometer. Throughout the experiment 10 ml samples were collected from the reaction vessel with a time interval of 10 minute throughout one hour. First the flow time of the pure solvent pyridine through a capillary tube in Ubbelohde Viscometer was recorded and then the analysis continued with recording the flow time of the samples taken from reaction vessel but during this procedure 5 ml of solvent pyridine was added to the 10 min-samples and the flow time of these solutions were recorded this procedure has been repeated two more times until added amount of pyridine became 15 ml in the solution. This procedure has been repeated for all the samples taken from the reaction vessel. By using these recorded times we could estimate the relative viscosity of these solutions for each 10 min-sample by the formula of;

$$\eta_{rel}= \qquad (2.1)$$

From the relative viscosity (η_{rel}) information the specific viscosities (η_{sp}) and reduced viscosities (η_{red}) of these solutions were calculated for each 10-min-sample with the formulas of;

$$\eta_{sp}=1-\eta_{rel} \qquad (2.2)$$

$$\eta_{red}= \eta_{sp}/c \qquad (2.3)$$

'c' in the reduced viscosity calculation represents the concentration of the solution which was based on the calculation of the total dissolved amount of monomers

(12,51 g total weight in 150 ml of pyridine. The composition was 4.59 g of THPE + 5.22 g of HDA + 2.7 g of PF); therefore, the initial concentration of the solution was assumed to be 8.34 g/dl, when 10 ml samples have been taken from these solution and added 5, 10 15 ml portions of pyridine, then the concentrations of these solutions became 5.56 g/dl, 4.17 g/dl, 3.34g/dl, respectively. Therefore, all viscosity calculation is based on the monomer concentration. After the calculation of reduced viscosities of these solutions the intrinsic viscosities of each 10 minute-sample were calculated with linear regression from the formula of;

$$\eta_{red} = [\eta] + kc \qquad (2.4)$$

2.8 Mechanical Testing

The tensile properties of the transparent films which were prepared by using compressing molding were determined by the Instron TM1102 instrument. We obtained our films at 180 ^{o}C. The films were cut about 4.0 cm in length, and 1.0 cm in width. The average thickness of samples was about 0.1 cm and rate of tensile testing was 0.1 mm / min.

CHAPTER 3

RESULT AND DISCUSSION

3.1 Spectroscopic Analysis

The characterization of general molecular structure of the benzoxazine precursors was determined by using the method of ^{1}H MNR, ^{13}C NMR and FTIR spectroscopies. The reactants used in the synthesis of benzoxazine precursors are shown in Figure 7. In addition, general structure of polybenzoxazine after thermal cure was given in Figure 8.

3.1.1 Nuclear Magnetic Resonance Spectroscopy

Information related to the general molecular formula, structure and the structural arrangement of the benzoxazine precursors was attained by using Bruker NMR spectroscopy. The spectra are shown in Figure 9, Figure 10 and Figure 11 and the detailed shifts of the molecules are indicated in Table 1.

In the spectrum shown in Figure 9, a peak appears at 4.8 ppm due to formation of the oxazine ring when a -(CH_2)- group attached to both nitrogen and oxygen atoms on the oxazine ring. Other peak at about 3.8 ppm belongs to the CH_2 group between benzene ring and nitrogen atom in the oxazine ring. These two peaks are the evidence for formation of the oxazine ring. Besides that, the peak at about 2.2 ppm belongs to the CH_3 group which is connected to the CH_2 group among three benzene rings. Normally it comes at about 1 ppm; however, because of the β affect of three benzene rings the peaks of CH_3 group shifts to 2.2 ppm. Another peak appears at about 1.3 ppm belongs to the 3^{rd}, 4^{th} and 5^{th} CH_2 groups in the hexyl chain between

nitrogen atoms and the peak at 1.5 ppm belongs to CH_2 group which is on the 2^{nd} position in the alkyl chain between nitrogen atoms. These peaks can be seen in detail in Figure 10 or Figure 11. In addition, the peak of CH_2 group connected to the nitrogen atom of the oxazine ring comes by 2.3 ppm and the peak of CH_2 connected to the other nitrogen atom appears at about 2.6 ppm and the peak of the aromatic rings comes between 6.7 to 7.0 ppm.

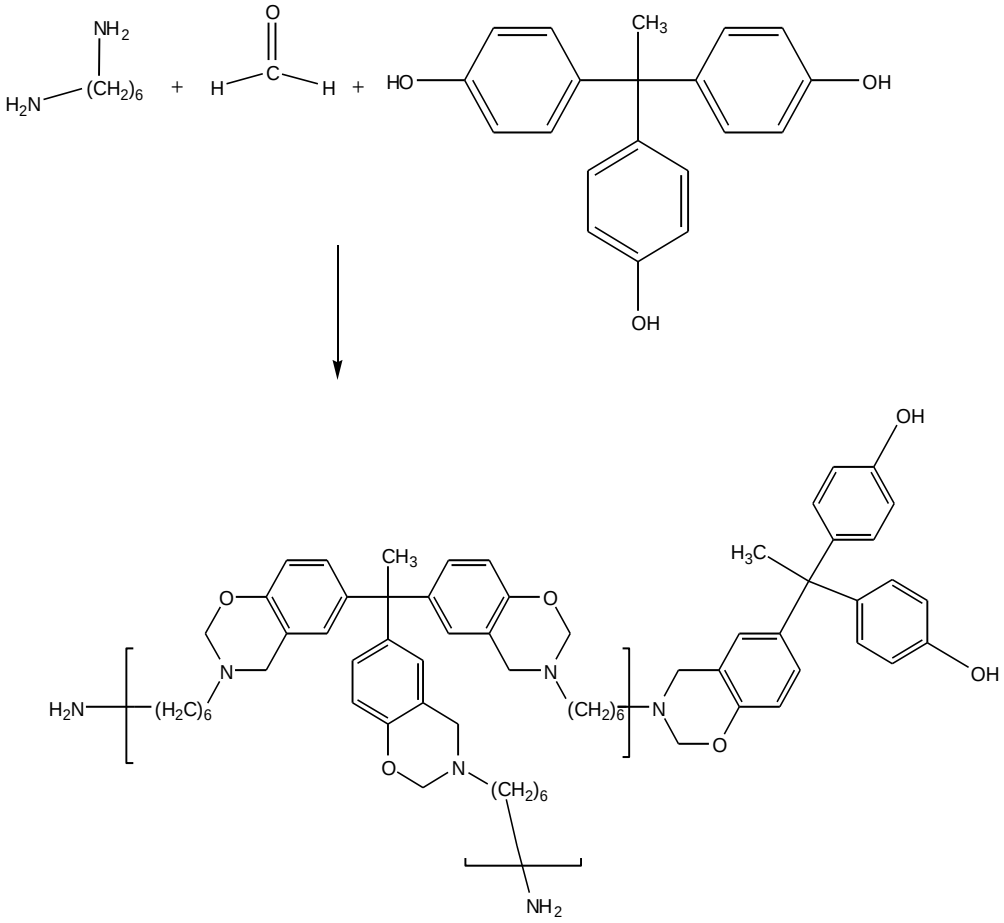
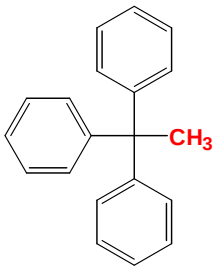
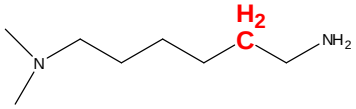
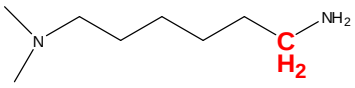
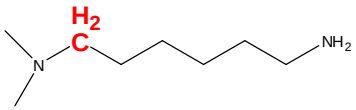


Figure 7: General synthesis scheme of polybenzoxazine.

Figure 8: General structure for polybenzoxazine after thermal cure.

Table 1: ^{1}H NMR results of our precursors before thermal cure. The related H atoms were shown on the structure.

Chemical Shift in the H NMR	Structure
4.8 ppm	
3.8 ppm	
2.1 ppm	
1.3 ppm	
1.4 ppm	
2.3 ppm	
2.7 ppm	
6.7-7.0 ppm	Aromatic Rings

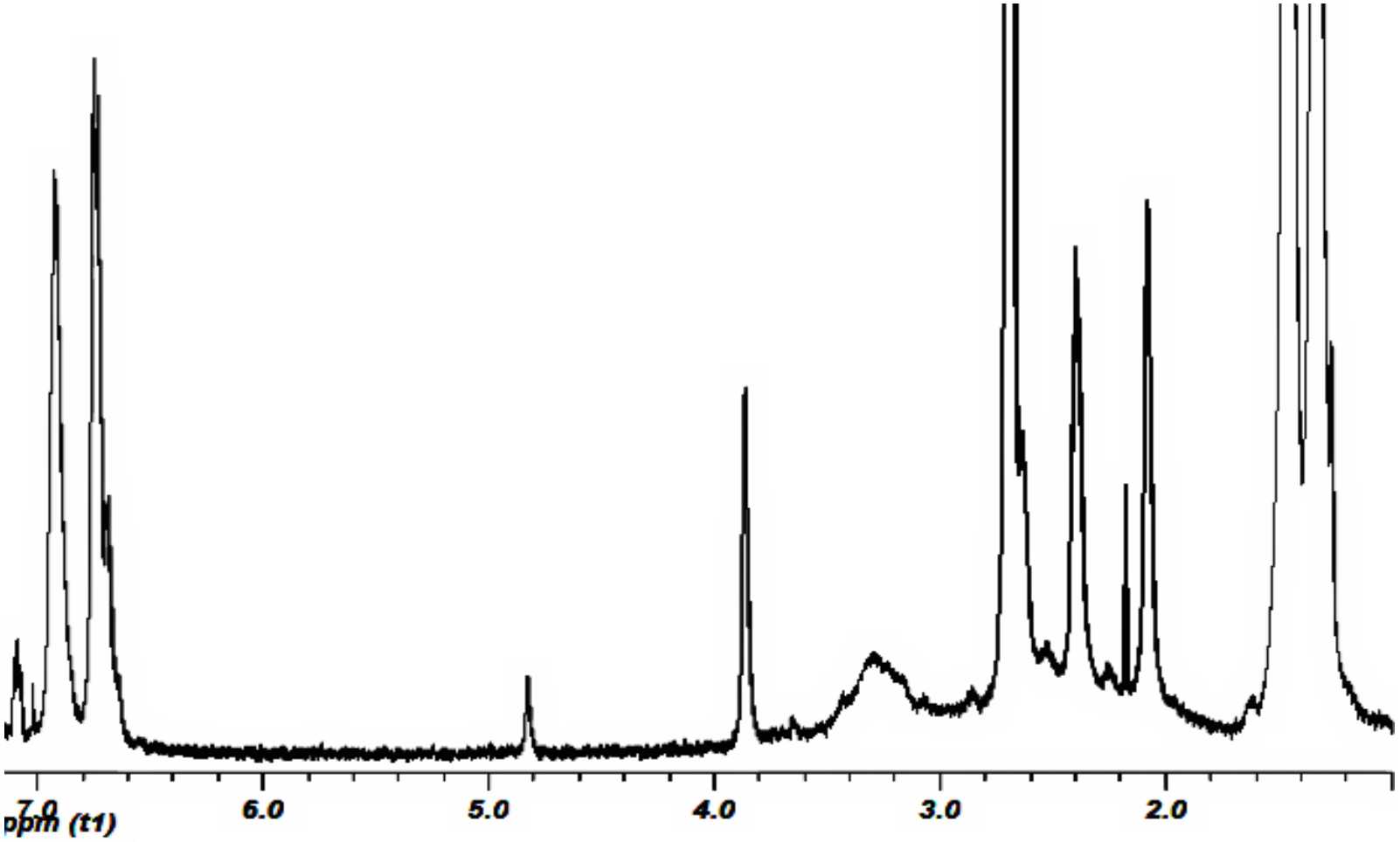


Figure 9: ^{1}H-NMR of polybenzoxazine precursors before thermal cure.

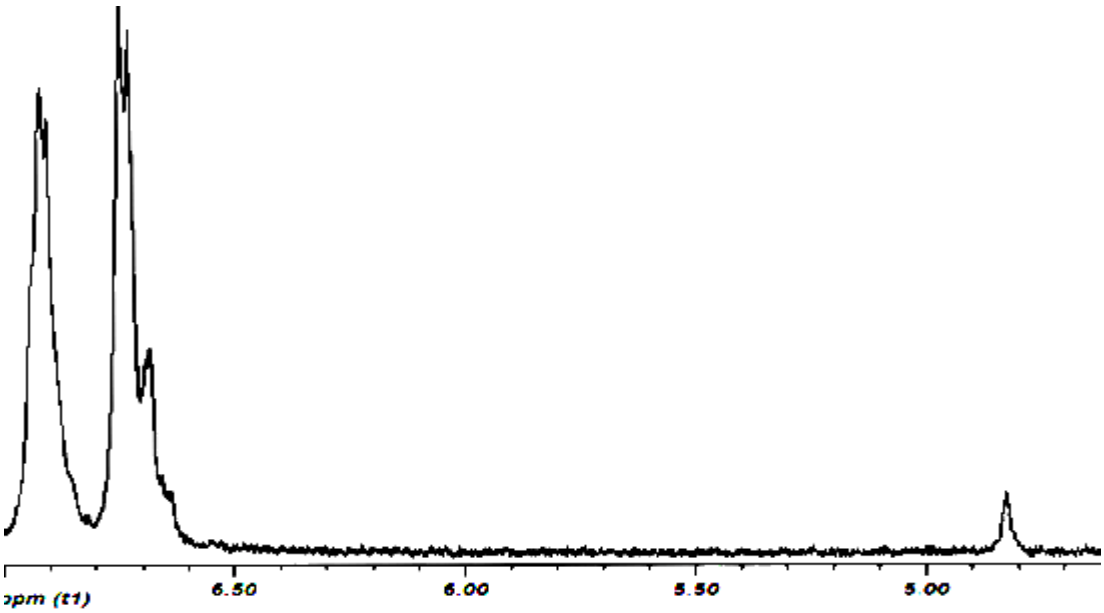


Figure 10: The detail of ^{1}H-NMR of polybenzoxazine precursors before thermal cure.

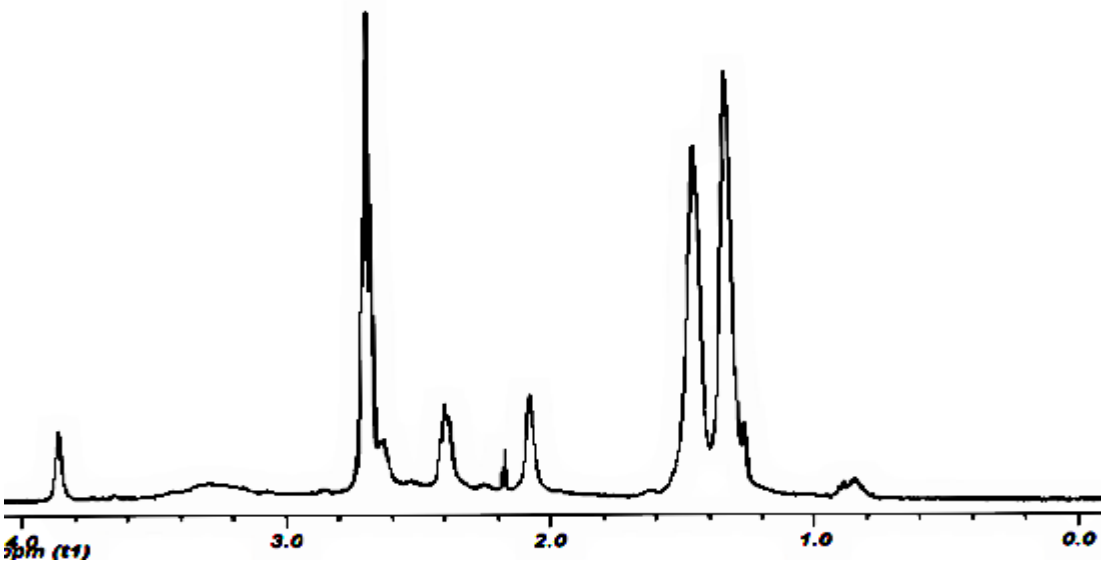
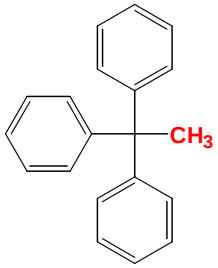
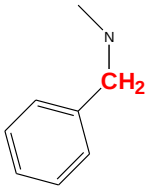
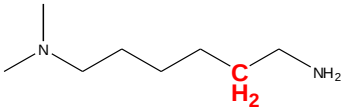
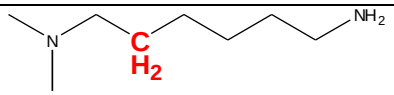
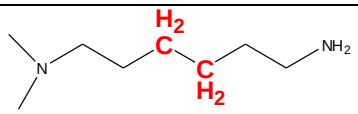
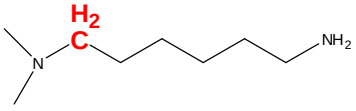
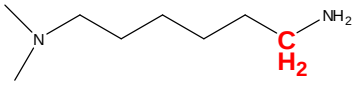


Figure 11: The detail of ^{1}H-NMR of polybenzoxazine precursors before thermal cure.

Another information was obtained from ^{13}C NMR spectroscopy in order to clarify the characterization of benzoxazine precursors. The instrument used for this analysis was Bruker ^{13}C NMR operating at 400 MHz. In the Figure 12 which was obtained before the thermal cure a peak is seen at approximately 75 ppm which shows the presence of -(CH_2)- group between the nitrogen and oxygen atoms. Beside that, the peak appears around 20 ppm belongs to CH_2 groups which are on the position of 3rd and 4th in the alkyl chain between the nitrogen atoms and the peak of CH_2 groups which is bonded to nitrogen atoms appear around 45 ppm. In addition, the peaks appear after 100 ppm belongs to the aromatic groups in the precursors and some other shifts are listed in the Table 2.

These ^{13}C NMR and ^{1}H NMR spectra are the proof for the formation of benzoxazine ring.

Table 2: ^{13}C NMR of benzoxazine precursors before thermal cure.

Chemical Shift in C-NMR	Structure
75 ppm	
32 ppm	
52 ppm	
35 ppm	
30 ppm	
27 ppm	
50 ppm	
42ppm	
Above 100 ppm	Aromatic Rings

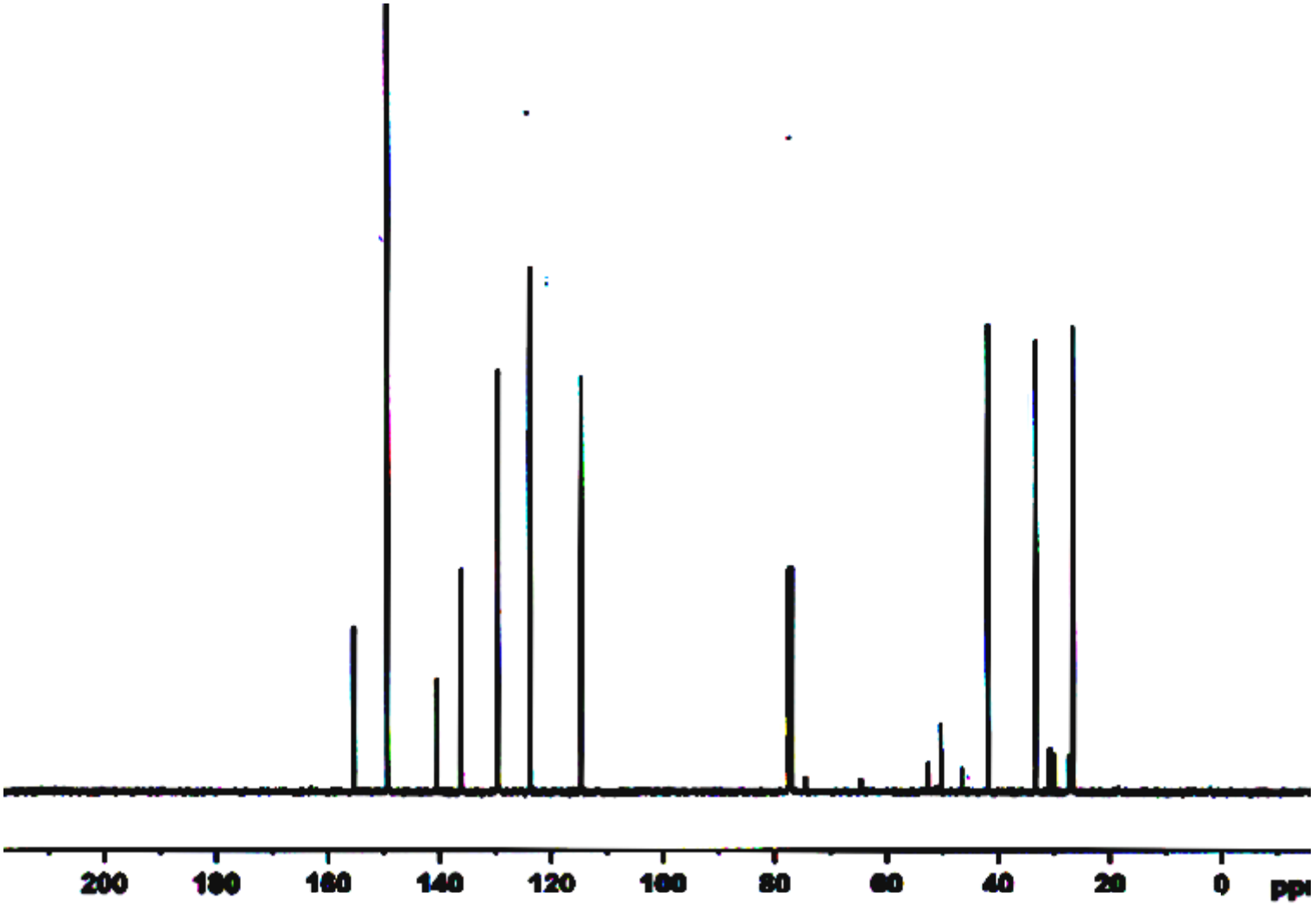


Figure 12 : Solution C-NMR of polybenzoxazine precursors before thermal cure

3.1.2 Fourier Transform Infrared Resonance Spectroscopy

FTIR spectra of the benzoxazine before and after the thermal cure are given in Figure 13 and Figure 14, respectively.

In Figure 14 a very weak broad band is seen between 3000 and 3300 $cm^{-1.}$ This feature is consistent with the low concentration of symmetrical and anti-symmetrical stretching of NH_2 group. Also, because of the wagging of NH_2 group, a band was also seen at approximately 830 cm^{-1}. In addition, due to the anti-symmetrical and symmetrical stretching of the CH_2 group in hexyl chain a sharp band between 2800 and 2950 cm^{-1} was observed. Strong and sharp band was observed due to the ring stretching of the aromatic rings of polybenzoxazine precursors at between 1450 and 1600 cm^{-1}. Due to the out of plane bending and rocking of the tri-substituted aromatic rings, a sharp band occurred between 700 and 750 cm^{-1}. The stretching of the O-C-(N)-C is the reason of the appearance of the strong bands at between 1100 and 1250 cm^{-1}. Furthermore, anti-symmetrical coupled stretching of the C-O to C-C was observed as a weak band at approximately 1010 cm^{-1}. The symmetric bending of CH_3 group caused a weak sharp band at about 1370 cm^{-1} and a sharp band was observed at approximately 575cm^{-1} due to the wagging of the OH group. All these assigned bands are consistent with the proposed structure of the benzoxazine ring in the main chain. We also obtained the FTIR spectrum of the cured polybenzoxazine which is given in Figure 14.

Table 3: Interpretation of FTIR spectrum of benzoxazine oligomers.

Wavelength (cm^{-1})	Vibration type of the groups
3300-3000 cm^{-1}	Symmetrical, anti-symmetrical stretching of NH_2
830 cm^{-1}	Wagging of NH_2
2950-2800 cm^{-1}	Symmetrical, anti-symmetrical stretching of CH_2 in the alkyl chain between nitrogen atoms
1600-1450 cm^{-1}	Ring stretching of the aromatic rings
750-700 cm^{-1}	Out of plane bending , rocking of tri-substituted aromatic ring
1250-1100 cm^{-1}	Stretching of O-C-(N)-C-
1010 cm^{-1}	Anti-symmetrical coupled stretching of C-O to C-C
1370 cm^{-1}	Symmetric bending of CH_3
575 cm^{-1}	Wagging of OH

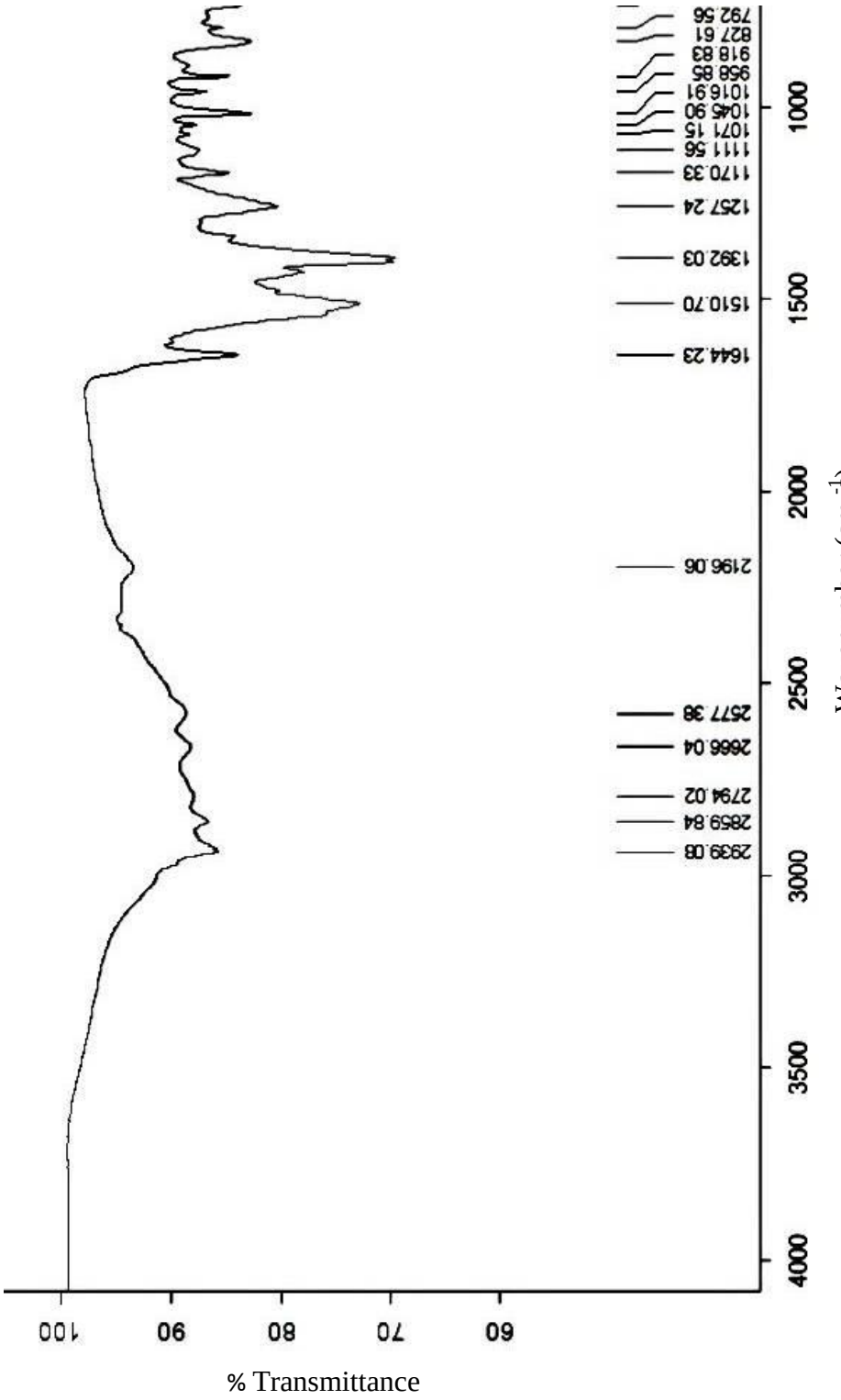


Figure 13: FTIR spectrum of benzoxazine precursors.

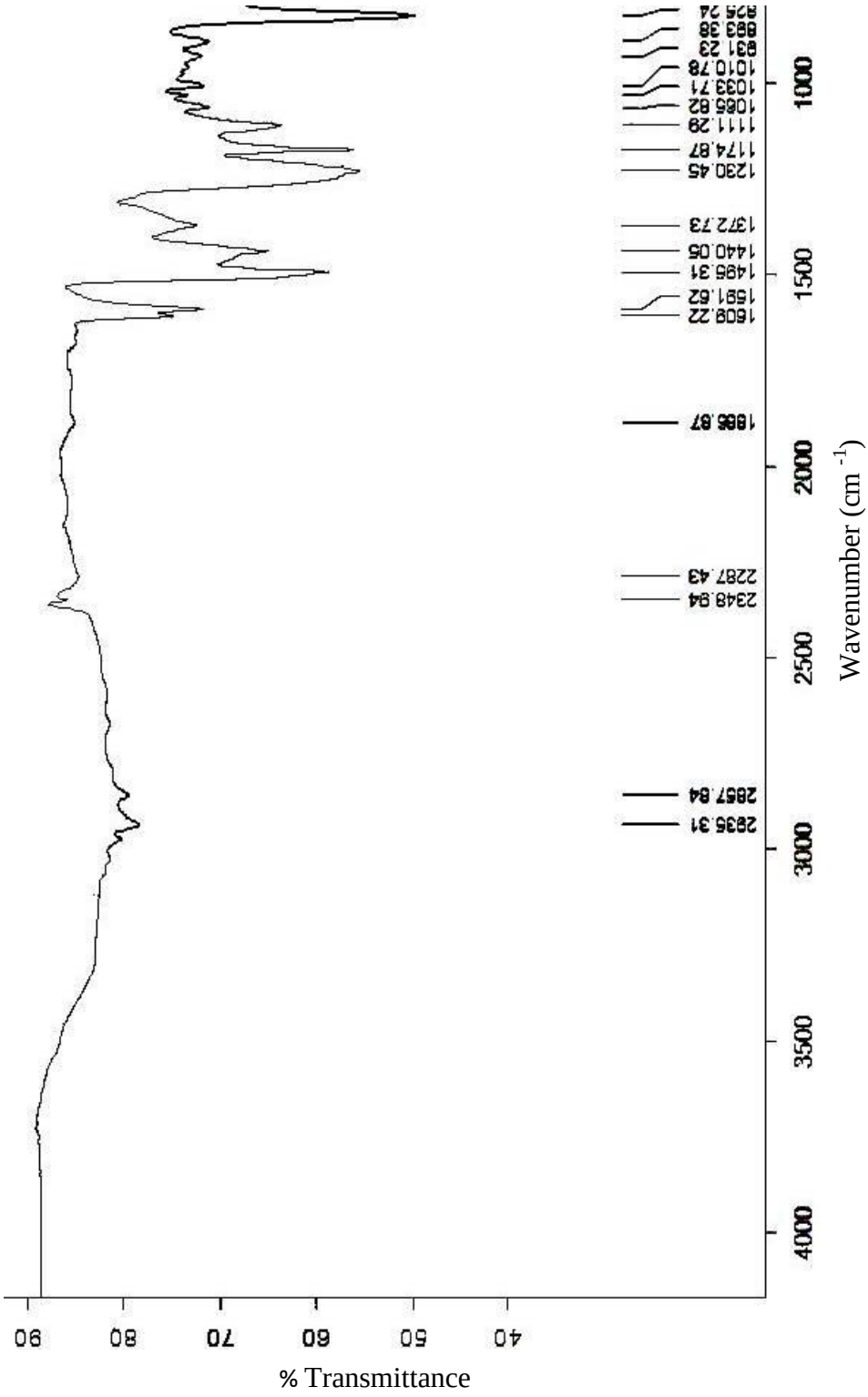


Figure 14: FTIR spectrum of polybenzoxazine after thermal cure.

3.2 Thermal Analysis

DSC and TGA analysis were used to understand the thermal behavior of the benzoxazine precursors and the polybenzoxazine. Also a simple method was tried as keeping the sample polymer in an oven for a certain time to see the weight loss of the polymer after certain temperatures.

3.2.1 Differential Scanning Calorimetry

The thermograms were recorded in the temperature range of 25- 300 ^{o}C by a heating rate of 10 ^{o}C / min under N_2 atmosphere in DSC. These thermograms are given in Figure 15 and Figure 16.

Figure 15 represents the thermogram of the polybenzoxazine precursors before the thermal cure. Because of the ring opening polymerization and crosslinking of the precursors an exothermic peak was seen at about 175 ^{o}C. The second peak at about 230 ^{o}C indicates the further polymerization of the benzoxazine precursors that was stated by Ishida [33] and Takeichi [38]. These exothermic peaks show that for the formation of the ring opening polymerization energy is needed. However, a strong endothermic peak around 250-260 ^{o}C may be due to some other secondary transition which is observed also in polybenzoxazine in the following Figure 16. The increase in the thermal line afterwards indicates a fast decomposition. Indeed, this matches with TGA measurements (see page 41,42).

Figure 16 represents the DSC thermogram of the polybenzoxazine cured at 150 ^{o}C. In the DSC thermogram, a distinctive endothermic peak was seen at about 270 ^{o}C and this peak is related to a secondary transition. The synthesized polymer was not a crystalline and it is a low molecular weight polymer.

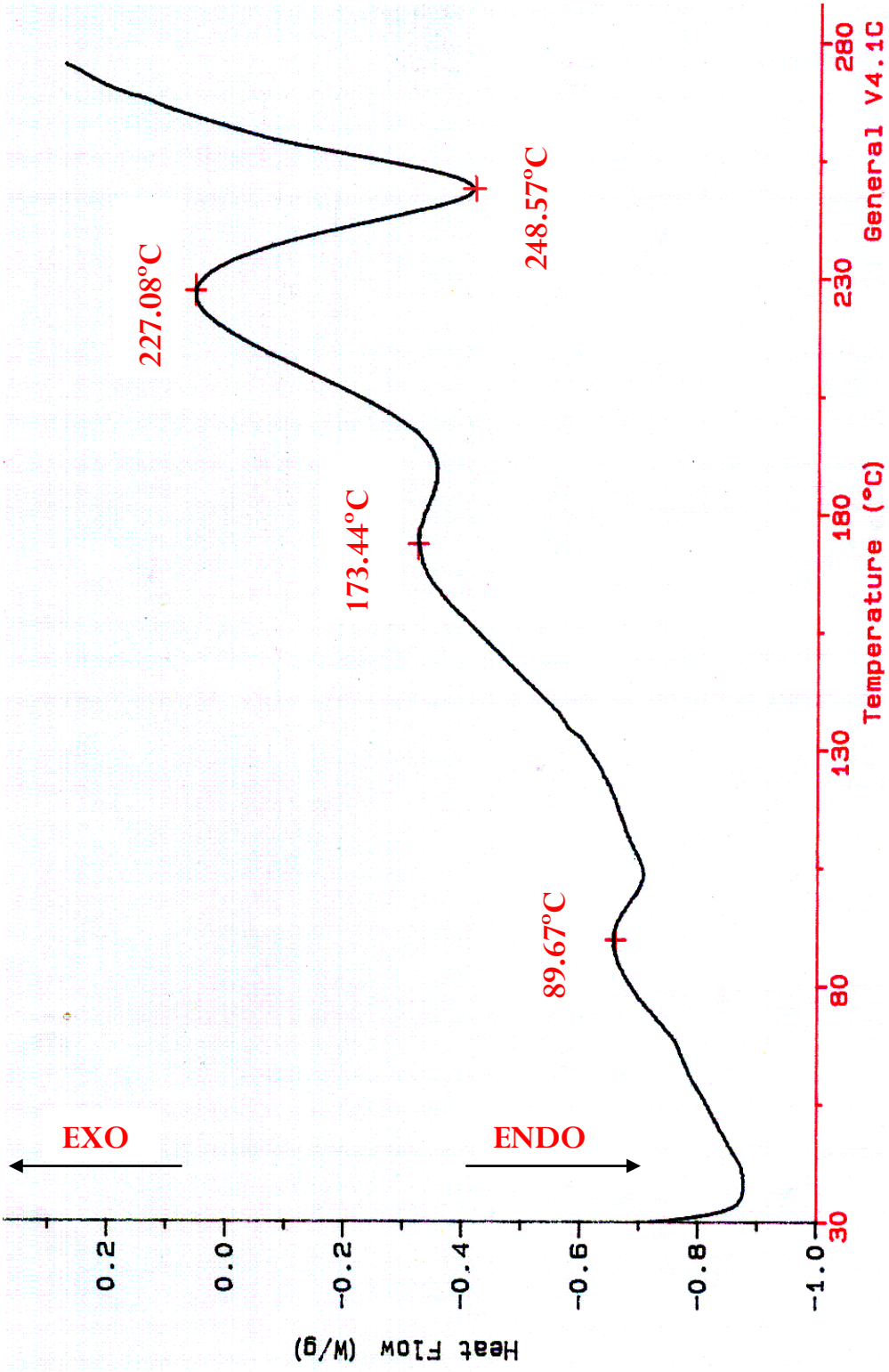


Figure 15: DSC thermogram of the benzoxazine precursors before thermal cure.

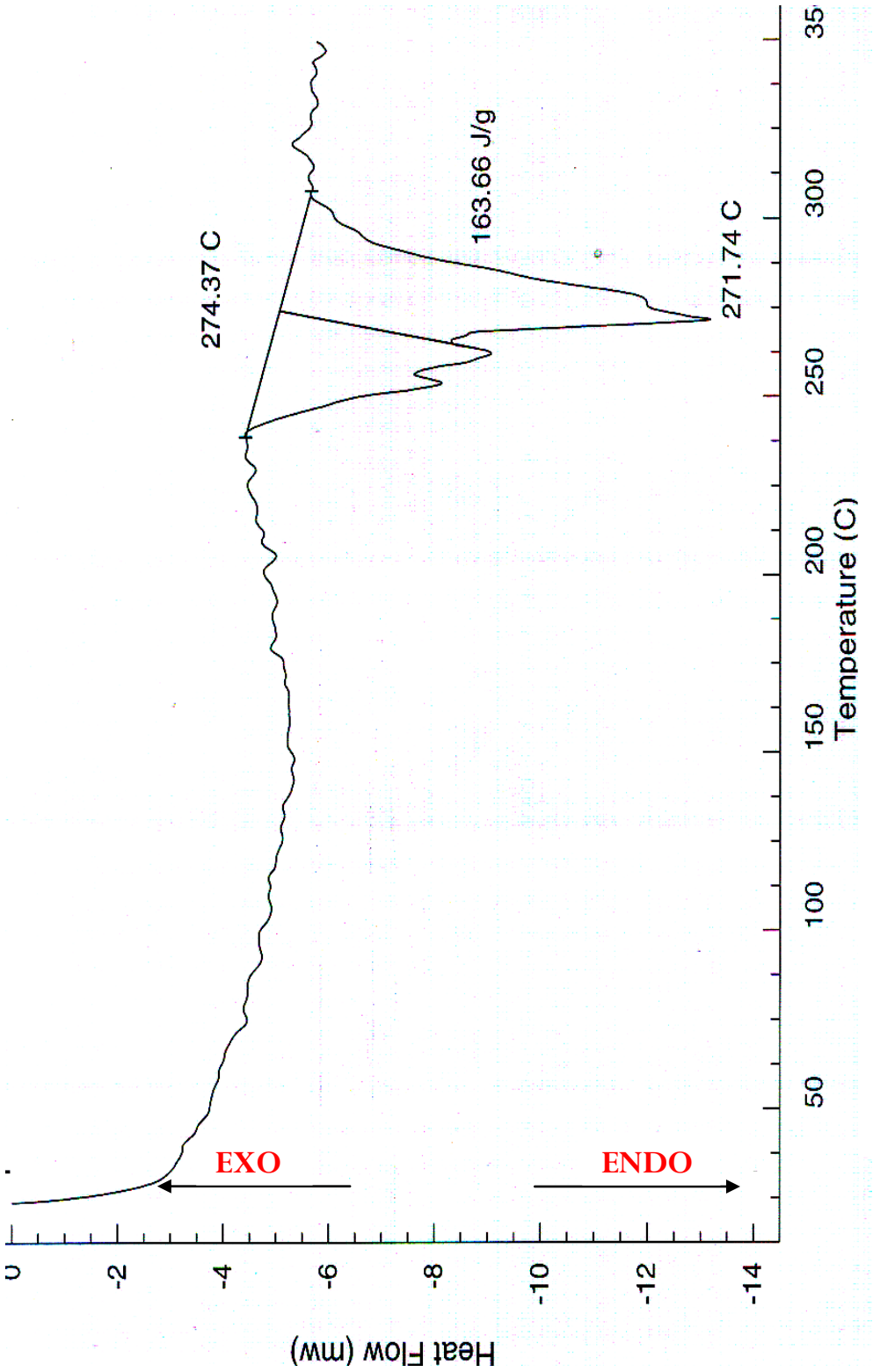


Figure 16: DSC Thermogram of the cured polybenzoxazine.

3.2.2 Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The thermograms obtained from TGA analysis were given in Figure 17 and Figure 18.

Figure 17 represents the TGA thermogram of benzoxazine precursors before the thermal cure. The thermogram and the derivative weight-loss curve showed that the decomposition of the benzoxazine oligomers starts as early as 100 ^{o}C and degraded rapidly to the maximum weight loss at 273 ^{o}C. Note that there is also a major weight loss at 230 ^{o}C. This weight loss may be due to the degradation of the low molecular weight oligomers or other side chain reactions. Furthermore, in this experiment the temperature increased rapidly but the benzoxazine precursors could find enough time to yield polymer to a certain extent which was indicated by the maximum weight loss at 273 ^{o}C.

The decomposition of the benzoxazine precursors continued with another rapid weight loss at 439 ^{o}C because of the degradation of the higher molecular weight benzoxazine formed during heating. The char yield of the benzoxazine precursors is 18.3 %. The char yield defined in this paper as the residual weight to the total weight used in this analysis at 500 ^{o}C under N_2 atmosphere.

Figure 18 represents the TGA thermogram of the polybenzoxazine. The thermogram and the derivative weight-loss curve indicate onset degradation at approximately 260 ^{o}C. From the derivative weight-loss curve the first weight loss has its maximum at 296 ^{o}C and the second weight loss is centered around 465 ^{o}C. The char yield of polymerized benzoxazine is 32.4%. In the polymer the molecular weight loss shifts to higher temperatures, and more char yield, nearly twice compared to precursors, was obtained.

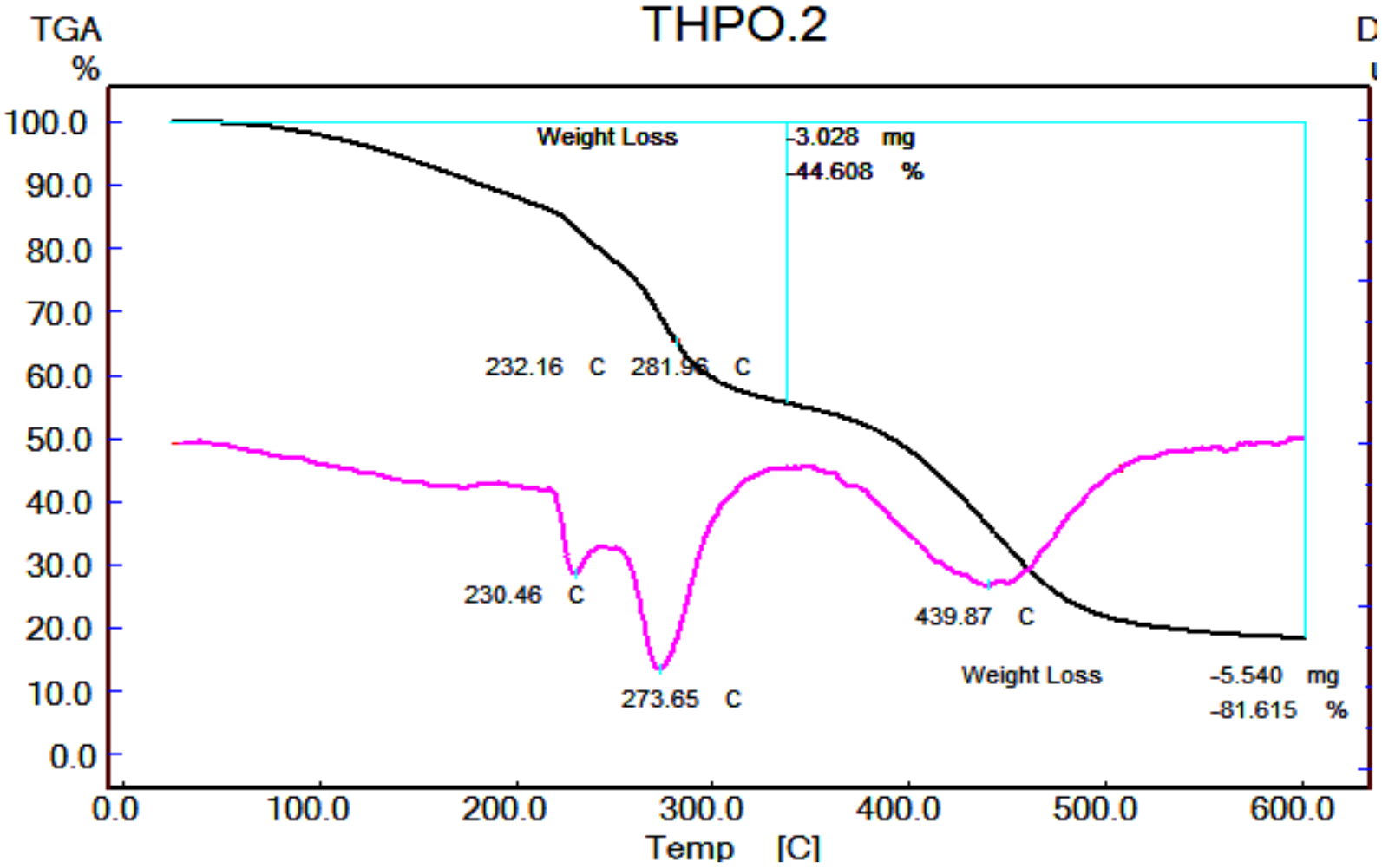


Figure 17: The TGA thermogram of benzoxazine precursors before thermal cure under N_2 atmosphere.

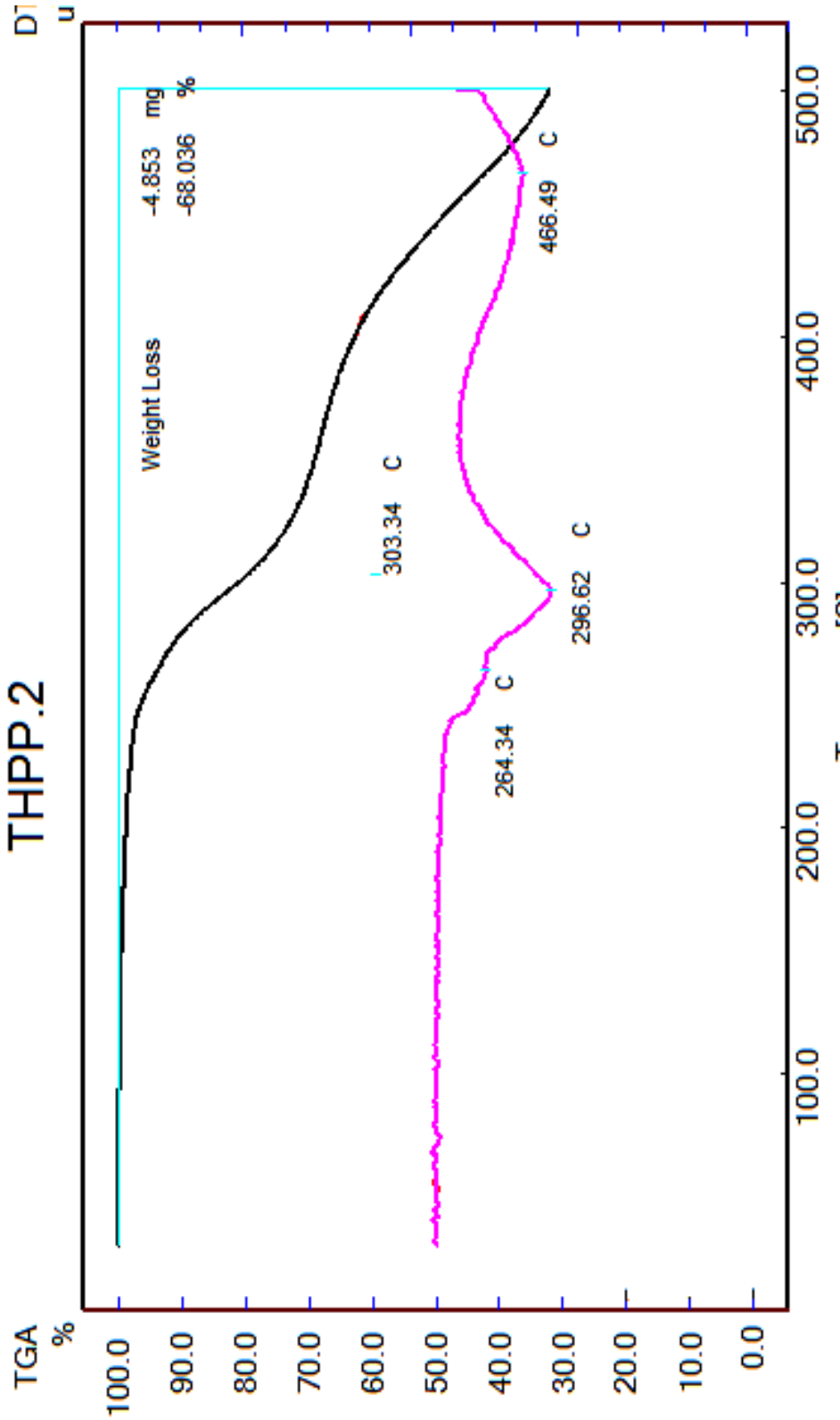


Figure 18: The TGA thermogram of the cured polybenzoxazine under N_2 atmosphere.

3.2.3 Thermogravimetry and FTIR Spectrometry

3.2.3.1 TGA+FTIR System for Benzoxazine Oligomers in Air

The qualitative and quantitative properties of thermal decomposition processes of the synthesized benzoxazine oligomers and their polymers was followed by TGA + FTIR system in a temperature range of 25 ^{o}C-300 ^{o}C by a heating rate of 10 ^{o}C / min both in air and under N_2 atmosphere. FTIR spectra obtained during TGA analysis were recorded at the time of the maximum weight loss events and at the beginning of the analysis.

Figure 19 represents the TGA thermogram of the benzoxazine oligomers. Thermogram shows that decomposition of benzoxazine oligomers starts at around 110 ^{o}C. There are two maximum weight loss observed in the derivative weight loss curve the first maximum weight loss is at 175 ^{o}C and the second is at around 288 ^{o}C.

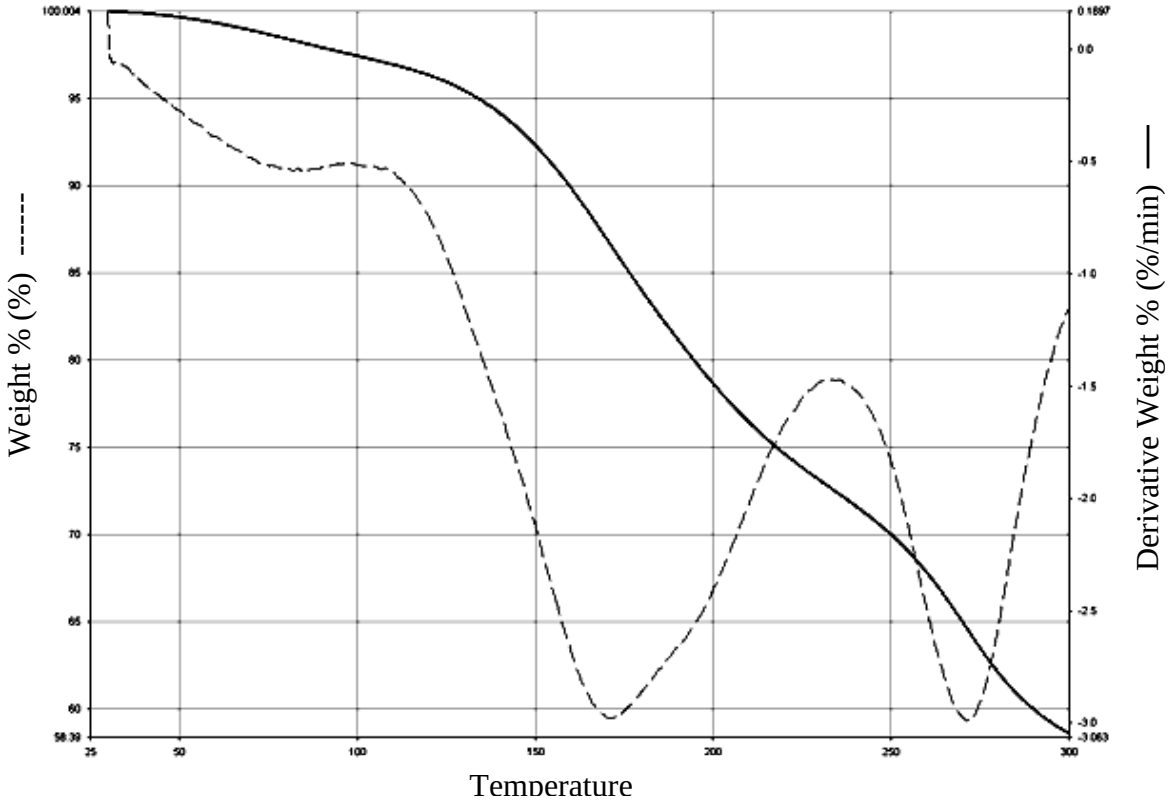


Figure 19: TGA thermogram of benzoxazine oligomers in air.

Figure 20 represents the FTIR spectrum of the possible decomposition products of the benzoxazine oligomers obtained at the beginning of the TGA in air at 51 ^{o}C (corresponds to nearly 160 seconds in TGA heating). There was no distinguishable decomposition gas product at this stage in FTIR therefore there is no definable band.

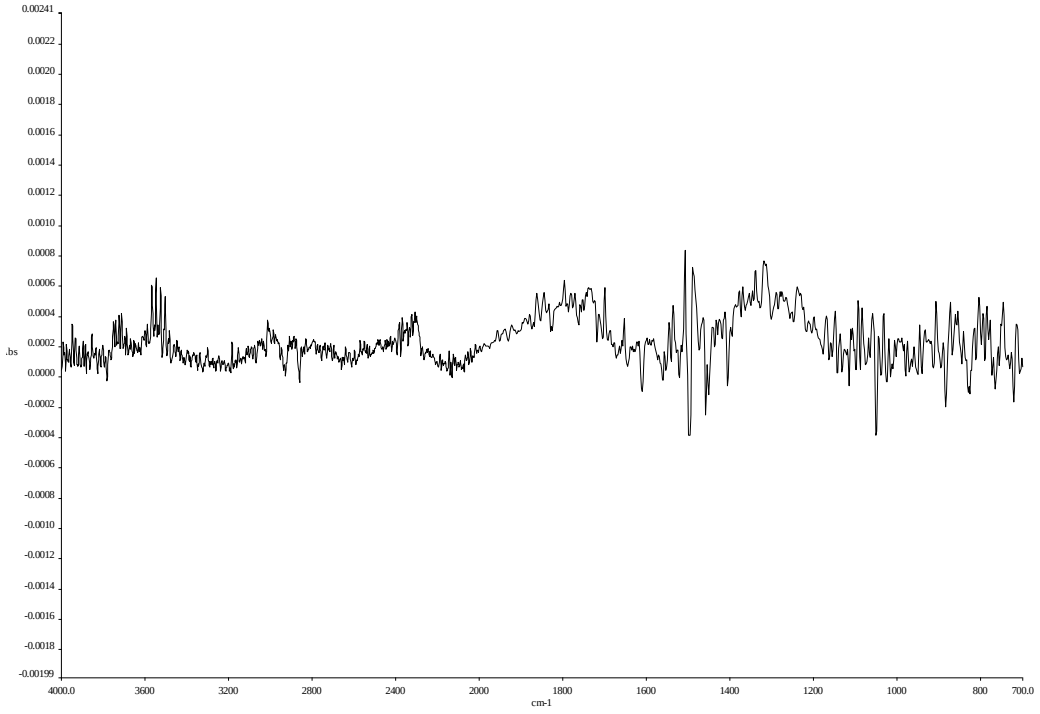


Figure 20: FTIR spectrum of benzoxazine oligomers at the beginning of the TGA

However, at 150 ^{o}C (corresponds to 900 seconds in TGA heating) FTIR spectrum of the gaseous decomposition products of the benzoxazine oligomers provided distinguishable bands at the first major maximum weight loss. The detailed information related to the interpretation of the bands in the FTIR spectrum is given in Table 4. The most intense bands appeared at 3600 cm^{-1}, 3010-2890 cm^{-1}, 1830 cm^{-1}, 1720 cm^{-1}, 1410 cm^{-1}, 1230-1340 cm^{-1}, 1040-1120 cm^{-1} and 950-1050 cm^{-1}. For a possible decomposition mechanism, further information was needed such as Mass Spectrometry; however in this study no MS study has been done.

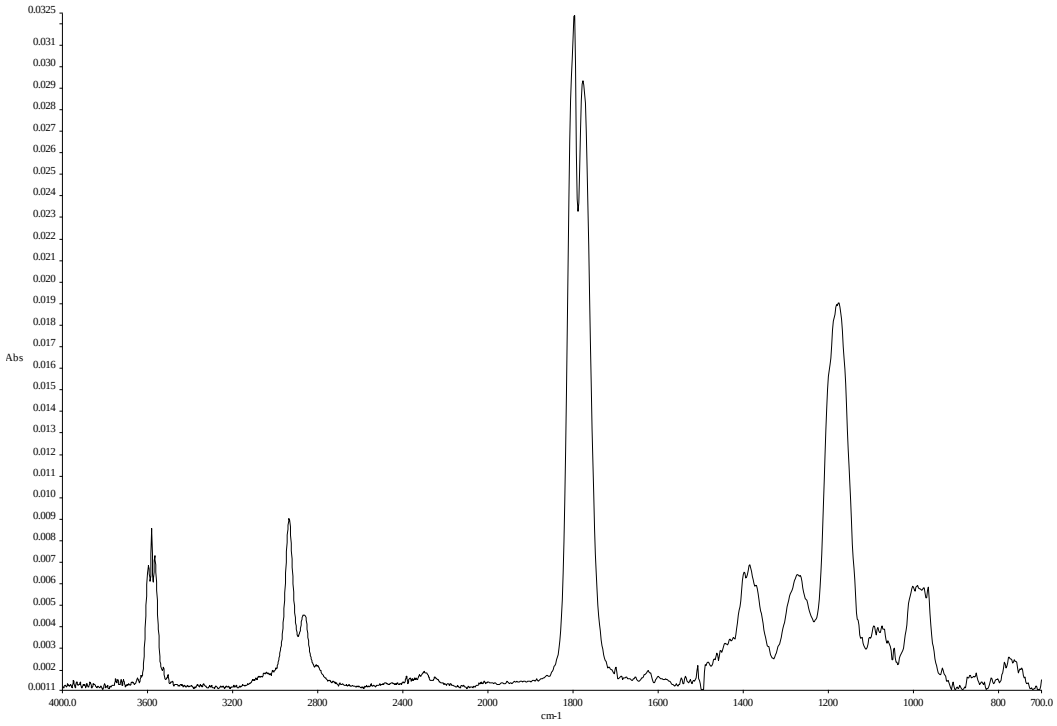


Figure 21: FTIR spectrum of benzoxazine oligomers obtained at the first maximum weight loss.

Table 4: Interpretation of FTIR spectrum of benzoxazine oligomers obtained at the first maximum weight loss event during TGA analysis.

Wavelength (cm^{-1})	Vibration type of the groups
3550-3620 cm^{-1}	Stretching of OH molecule in phenol, or Anti-symmetrical stretching of NH_2 molecule
2890-3010 cm^{-1}	Symmetric and Anti-symmetric stretching of C-H in CH_3 molecule
2750-2890 cm^{-1}	Stretching of C-H on N-CH_2
2180-2350 cm^{-1}	Stretching of C-O-C-N
1720-1830 cm^{-1}	Symmetrical and Anti-symmetrical stretching of anhydride (open chain acid anhydride)
1340-1410 cm^{-1}	Bending of OH molecule in phenol
1230-1340 cm^{-1}	Stretching of -C-N-
1040-1120 cm^{-1}	1^{o}anti-symmetrical coupled stretching of C-O to C-C
950-1040 cm^{-1}	3 ^{o}anti-symmetrical coupled stretching of C-O to C-C
830-880 cm^{-1}	1,4- Disubstitution (para) in aromatic ring
700-800 cm^{-1}	Out of plane bending of aromatic C-H

Figure 22 represent the FTIR spectrum of oligomers at the second major maximum weight loss at 288 ^{o}C (corresponds nearly to 27 minutes in TGA heating). Increasing and decreasing of the intensity of some bands in the FTIR spectra obtained during the first and the second maximum weight loss events is because of the decomposition of the different groups at different temperatures.

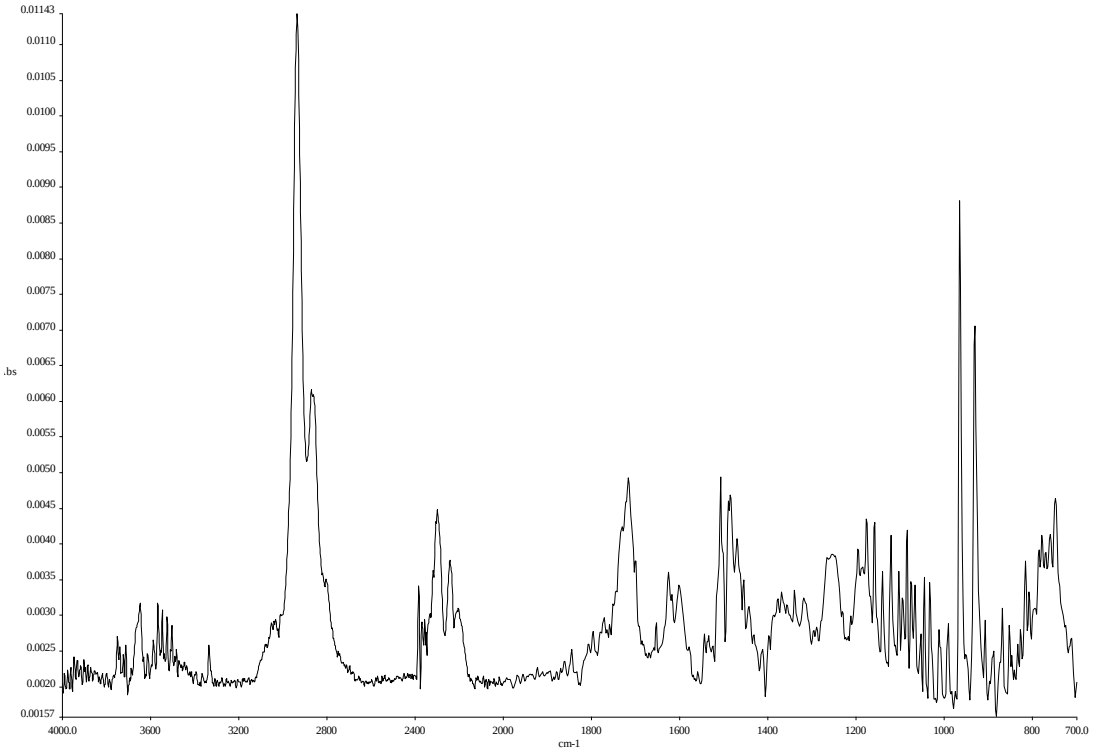


Figure 22: FTIR spectrum of benzoxazine oligomers obtained at 288 ^{0}C.

3.2.3.2 TGA+FTIR System for Benzoxazine Oligomers under N_2 Atmosphere

The TGA thermogram shows that decomposition of the benzoxazine oligomers starts at around 115 ^oC under N_2 atmosphere. 5 ^oC shift was observed under N_2 atmosphere due to the absence of O_2. The maximum weight loss events occur at 176 ^oC and 290 ^oC. There exist almost no differences between the maximum weight loss temperatures in air and in N_2 atmosphere at these high temperatures because the oligomers are, at the same time, polymerized with increasing temperature. Appearance of the decomposition of low molecular weight benzoxazine oligomers was observed as first maximum weight loss in the derivative weight loss curve and the second maximum weight loss were related to the decomposition of the higher molecular weight benzoxazine oligomers.

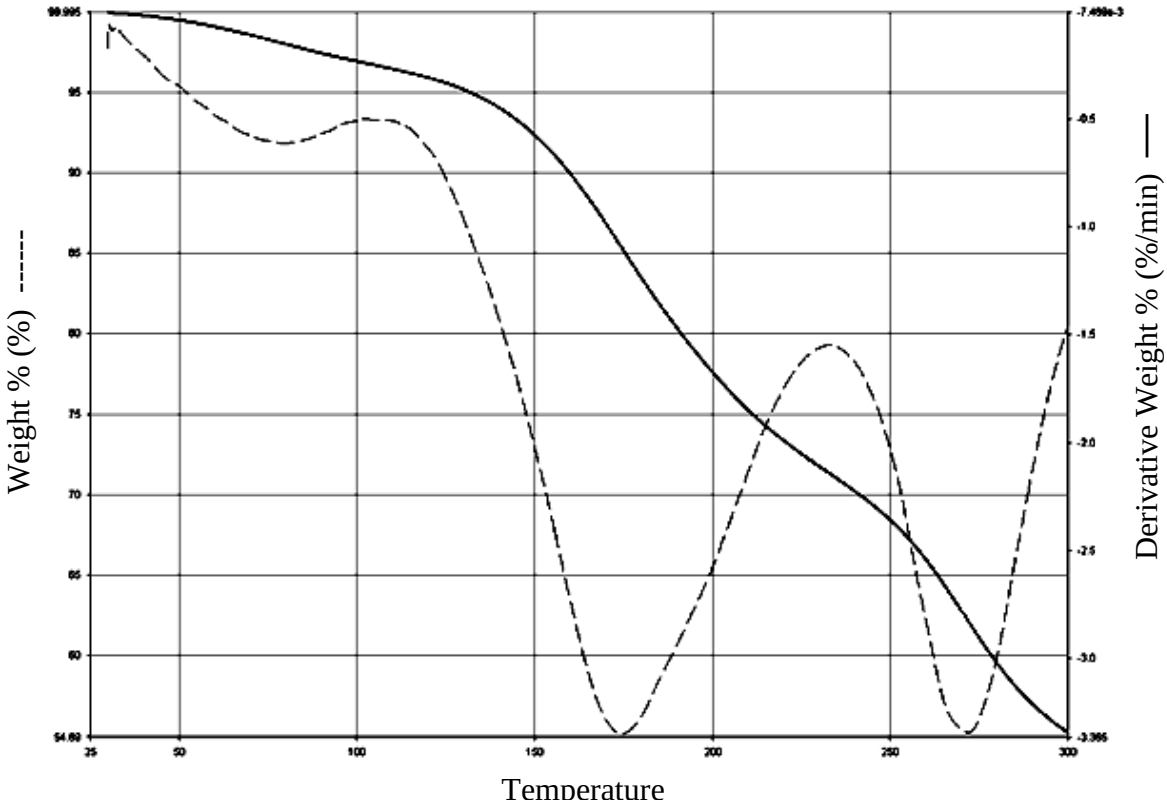


Figure 23: TGA thermogram of the benzoxazine oligomers in N_2 atmosphere.

The FTIR spectrum of the benzoxazine oligomers obtained on the first major maximum weight loss at 176 ^{o}C (corresponds to about 900 seconds in TGA heating) under N_2 atmosphere are shown in Figure 24. The detailed information of the bands in the spectrum is given in Table 4, too. However, there is a difference between the spectra obtained in air and under N_2 atmosphere. The broad band which appears at around 2350 cm $^{-1}$ in the FTIR spectrum obtained in air is not seen in the FTIR spectrum obtained under N_2 atmosphere because of the absence of the O_2.

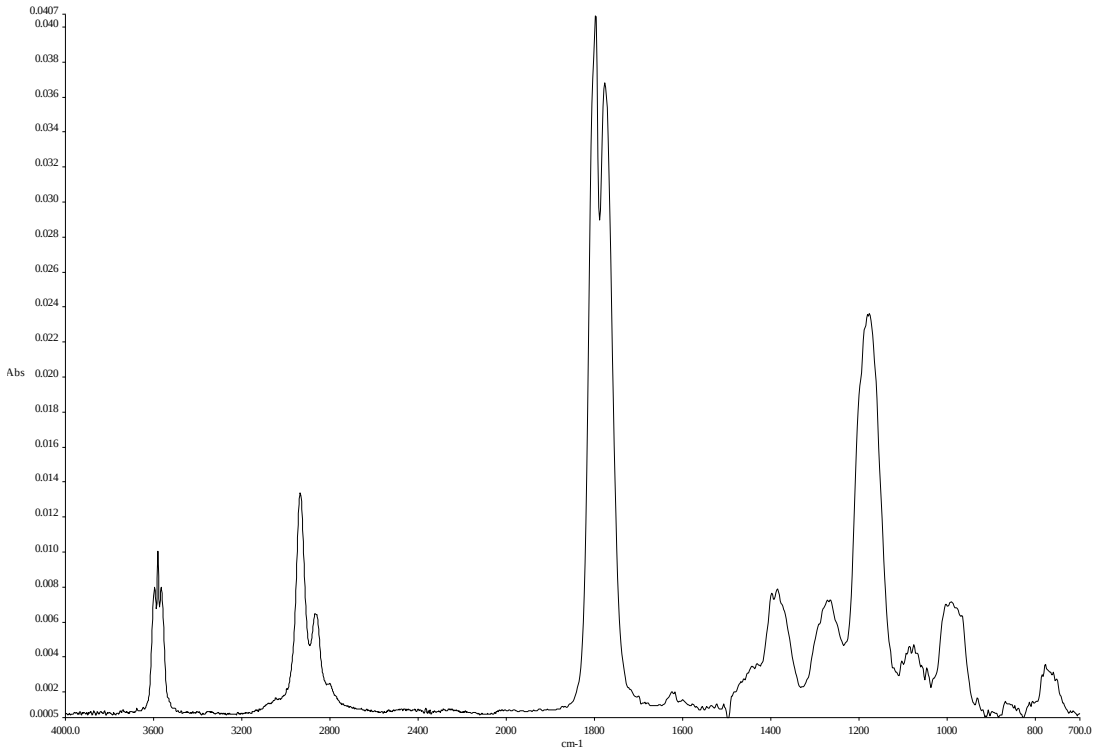


Figure 24: FTIR spectrum of the benzoxazine oligomers

Figure 25 represents the FTIR spectrum of the benzoxazine oligomers at 290 ^{o}C (corresponds nearly to 27 minutes in TGA heating) obtained on the second major maximum weight loss under N_2 atmosphere. Difference in the intensity of some bands in FTIR spectra obtained during the first and the second maximum weight loss is due to the decomposition of the different groups at different temperatures.

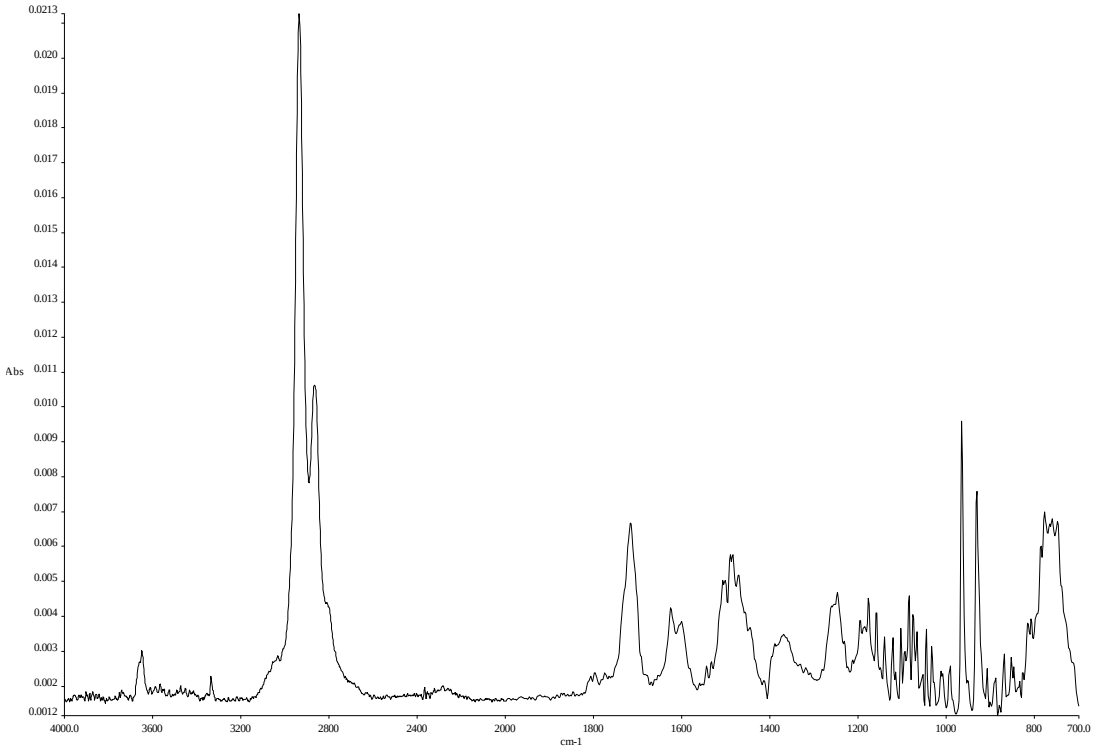


Figure 25: FTIR spectrum of the benzoxazine oligomers

3.2.3.3 TGA+FTIR System for Polybenzoxazine in Air

Figure 26 represents the TGA thermogram of the polybenzoxazine cured at 150 ^{o}C. Thermogram shows that the decomposition of the cured polybenzoxazine starts at around 105 ^{o}C and a weight loss is observed at about 150 ^{o}C. The major maximum weight loss was seen around 260 ^{o}C. The first weight loss appear in the derivative weight loss curve is because of the decomposition of the lower molecular weight polymers and the maximum weight loss curve represents decomposition of the higher molecular weight polybenzoxazine.

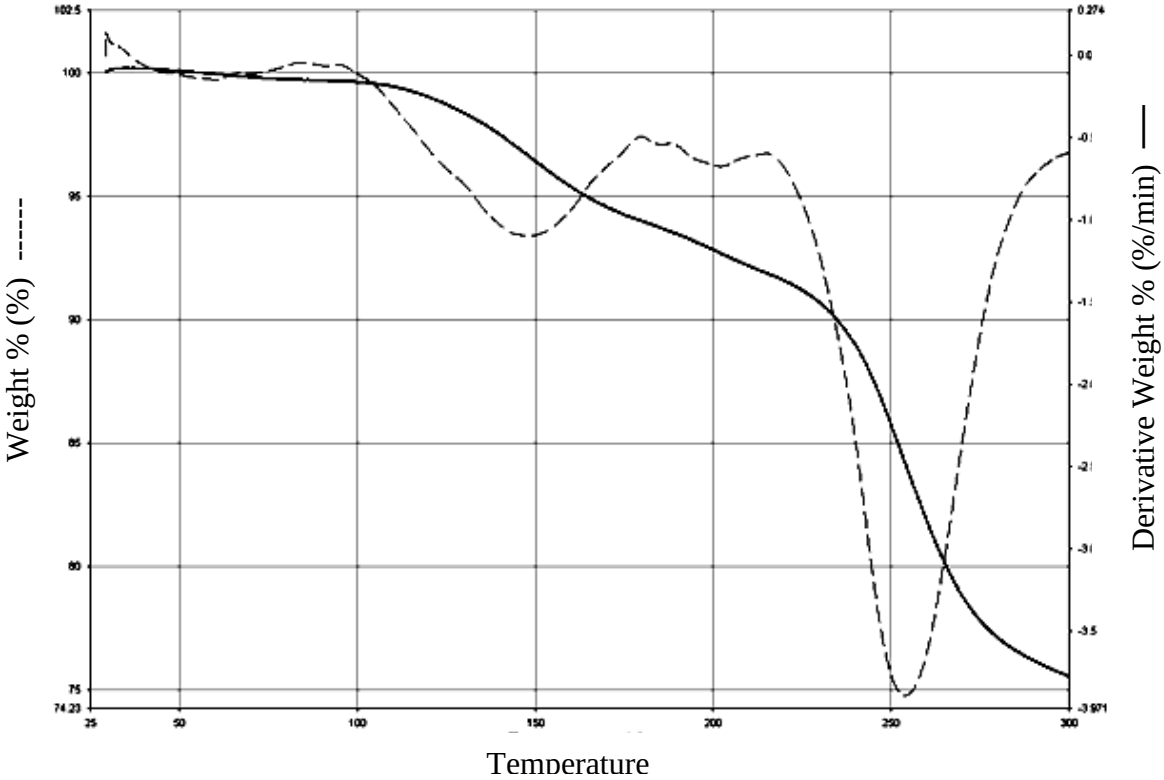


Figure 26: TGA thermogram of the polybenzoxazine obtained in air.

The spectrum shown in Figure 27 obtained at 51.5 ^{0}C (corresponds to 160 seconds) and TGA thermogram does not show any decomposition process at this temperature; therefore, any band cannot be defined in this spectrum.

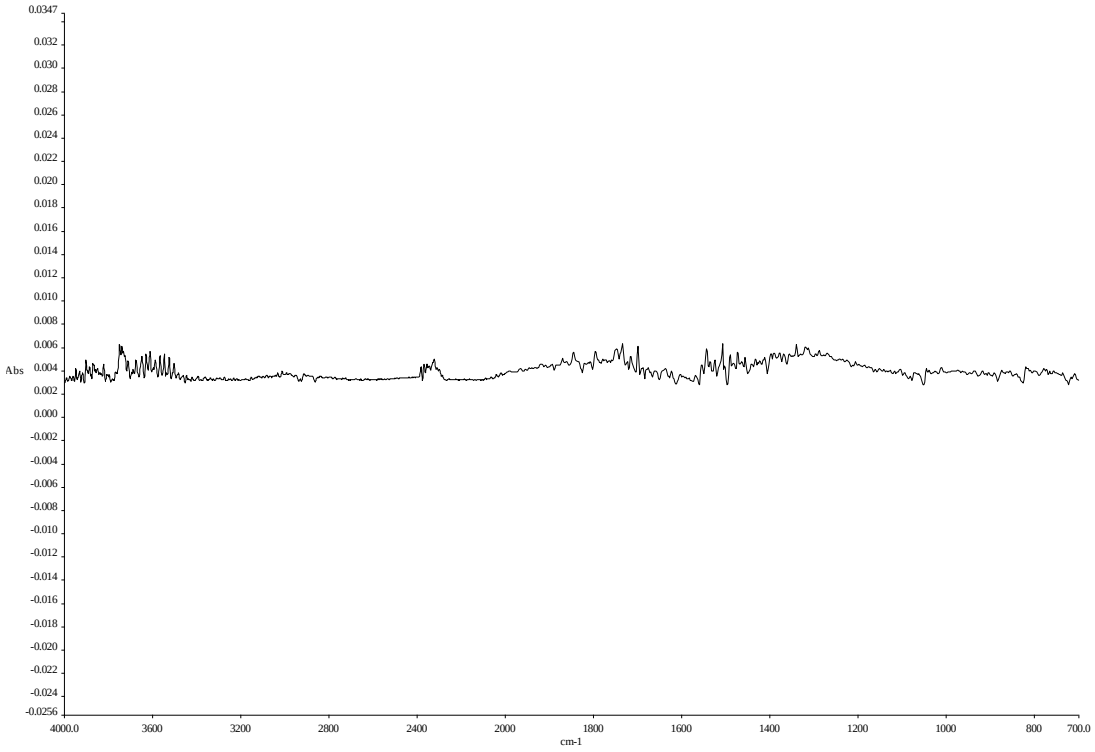


Figure 27: FTIR spectrum of the polybenzoxazine

Figure 28 represents the FTIR spectrum of the cured polybenzoxazine obtained at 260 ^{0}C (corresponds nearly to 1400 seconds in TGA heating) on the maximum weight loss. The detailed information related to the interpretation of the bands shown in the FTIR spectrum is given in Table 5, but the spectrum is apparently more complex compared to the spectrum of the benzoxazine precursors.

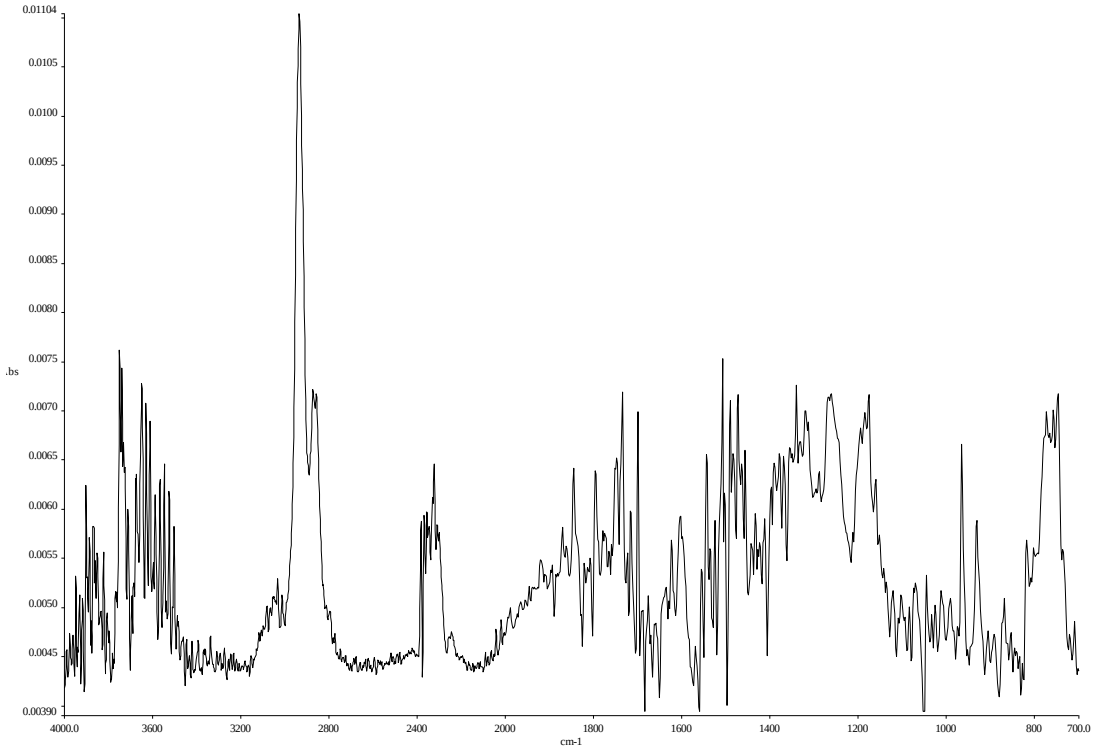


Figure 28: FTIR Spectrum of the polybenzoxazine at 260 ^{0}C

Table 5: Interpretation of FTIR spectrum of polybenzoxazine obtained at the maximum weight loss event during TGA analysis.

Wavelength (cm^{-1})	Vibration type of the groups
3550-3620 cm^{-1}	Stretching of OH molecule in phenol, or Anti-symmetrical stretching of NH_2 molecule
2890-3010 cm^{-1}	Symmetric and Anti-symmetric stretching of C-H in CH_3 molecule
2750-2890 cm^{-1}	Stretching of C-H on N-CH_2
1230-1340 cm^{-1}	Stretching of -C-N-
700-800 cm^{-1}	Out of plane bending of aromatic C-H

3.2.3.4 TGA+FTIR System for Polybenzoxazine under N_2 Atmosphere

Thermogram of the cured polybenzoxazine indicates that the decomposition of the polymer starts at around 105 ^{o}C. Decomposition of the low molecular weight polybenzoxazine is the reason for the appearance of a weight loss in the derivative weight loss curve; however, this is not a maximum weight loss which appears at about 260 ^{0}C because of the decomposition of the higher molecular weight polybenzoxazine. The derivative weight loss curve also indicates that the amounts of the low molecular weight polybenzoxazine is less than that of the higher molecular weight polybenzoxazine and which means that during the curing process polymerization was achieved well and the high molecular polymeric material was obtained more.

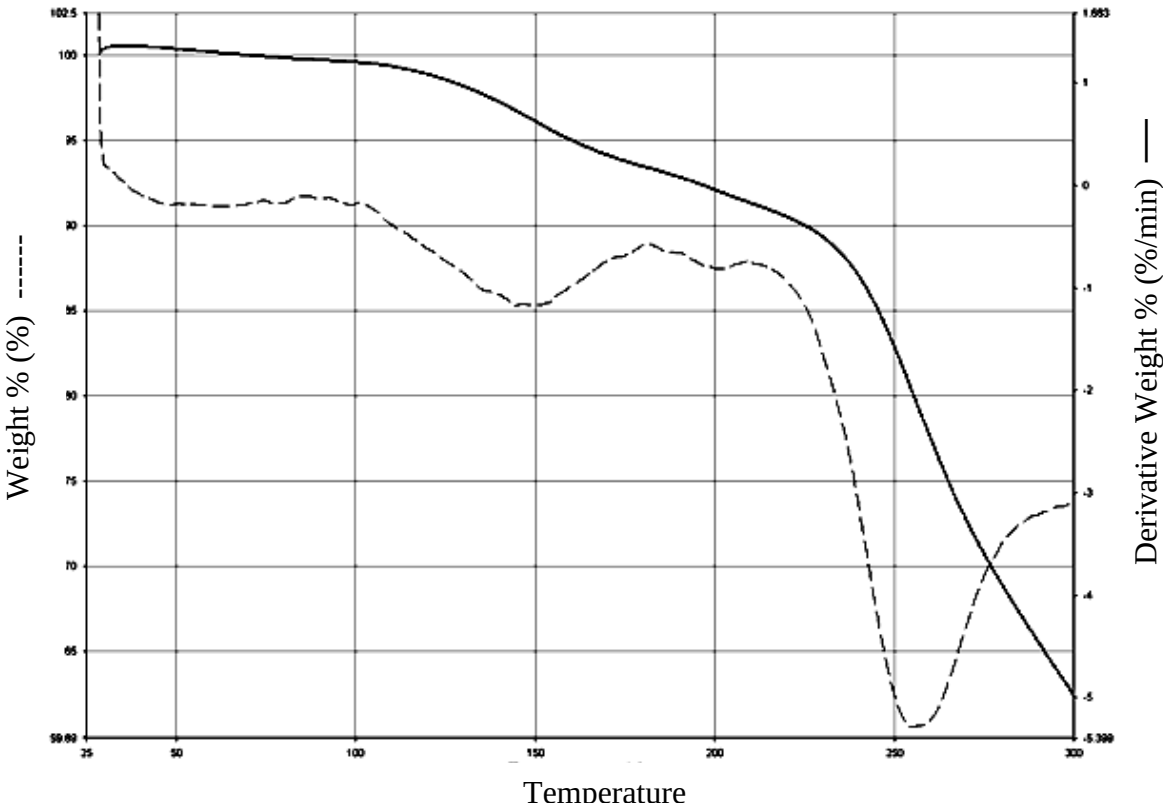


Figure 29: TGA thermogram of polybenzoxazine obtained in N_2 atmosphere.

This spectrum represents the FTIR spectrum of the cured polybenzoxazine obtained on the maximum weight loss event at 260 ^{0}C (corresponds to nearly 1400 second in TGA heating). Information related to the interpretation of the band in this spectrum is given in Table 5.

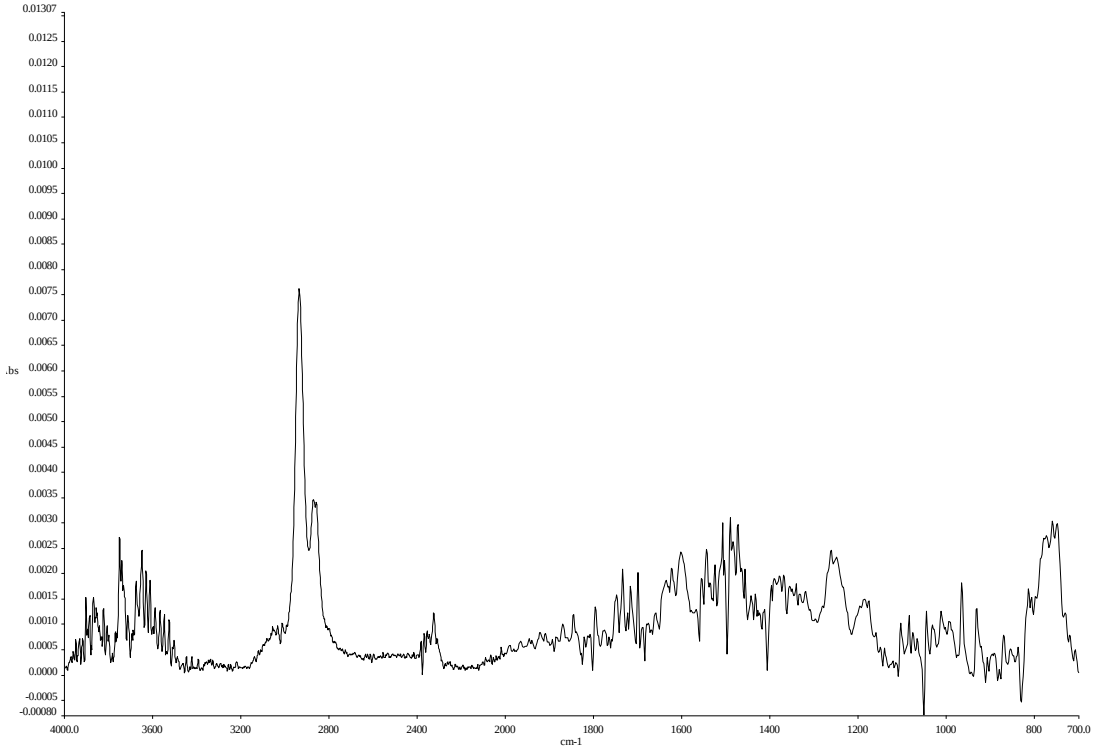


Figure 30: FTIR spectrum of the polybenzoxazine obtained in N_2 atmosphere at 260^{0}C.

3.3 Viscosity Measurement

The variation of the intrinsic viscosity in the reaction mixture during the synthesis of benzoxazine precursors was investigated by using Ubbelohde Viscometer at 30 ^{0}C and shown in Figure 31.

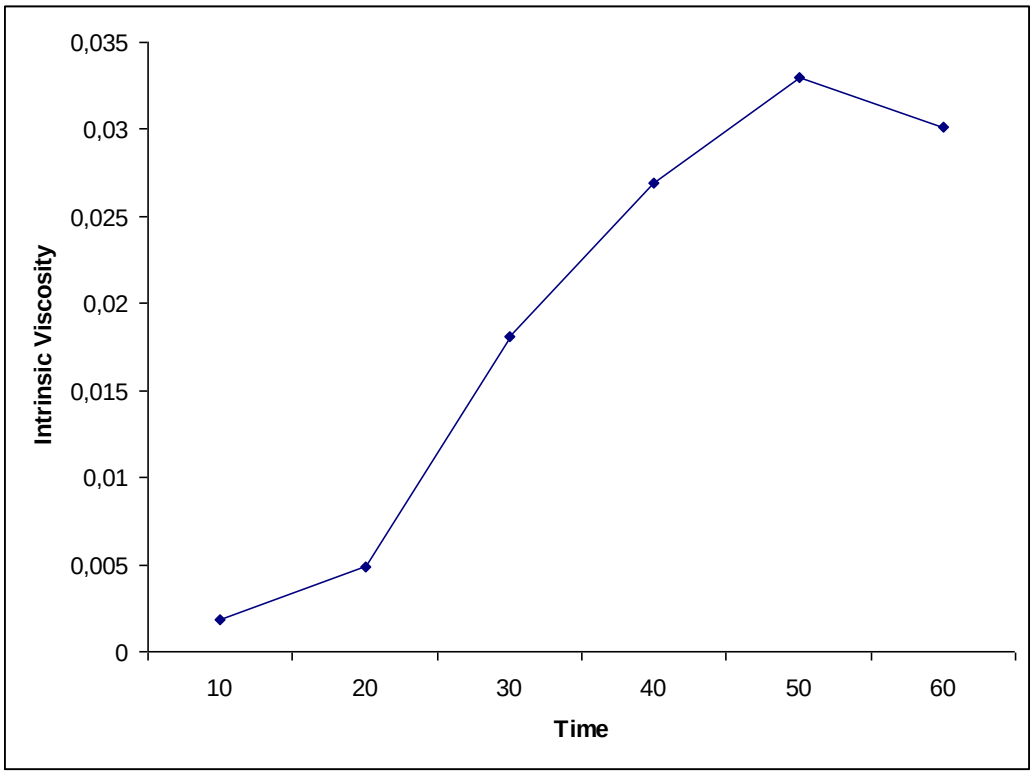


Figure 31: Intrinsic viscosity variation in the reaction medium during the synthesis of the benzoxazine precursors.

In conclusion, increasing of intrinsic viscosity in the reaction mixture indicates the increasing of the molecular weight. However, after 50th minute the measured intrinsic viscosity decreased slightly. There can be two different reasons for this decrease. The first reason can be the decomposition of the oligomers during the reaction, but this possibility is very low because there is not any condition which can cause degradation during the reaction. The second and the most probable reason is branching and intra cross-linking of the oligomers during the reaction.

3.4 Mechanical Analysis

The mechanical tests were done on thin films of polybenzoxazine prepared in compressing molding at 180 ^{0}C. The stress-strain curve of polybenzoxazine was shown in Figure 32.

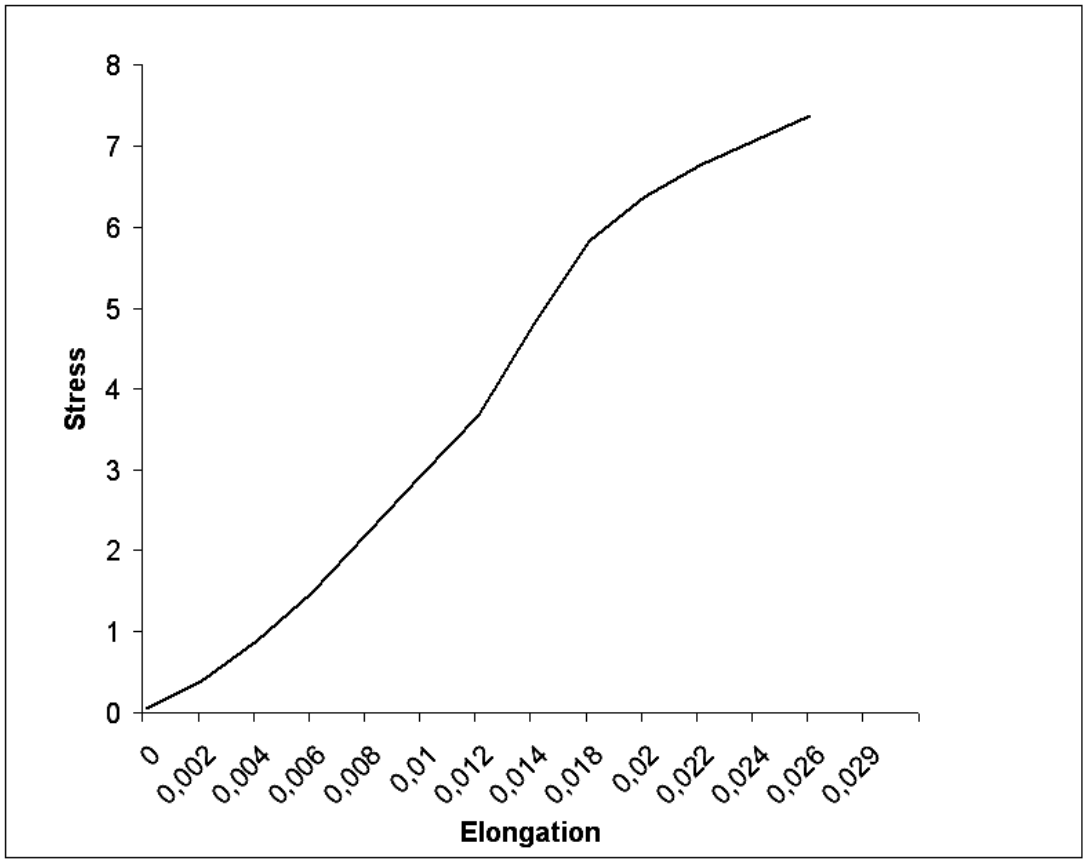


Figure 32: Stress-elongation curve of polybenzoxazine films cured at 180^{0}C

The average tensile strength of the polybenzoxazine films at break was found as 5.42 ± 1.0 MPa. Owing to the results of the mechanic tests we could understand that there was not enough entanglement or crosslinking in the polymer for a sufficient transfer of the stress. In other words, the low molecular weight poylmers were formed. Therefore the mechanical properties of the material was not goood enough. Recorded highest elongation of the polybenzoxazine films was 3.3 % that was a sufficiently good elongation for the polymer films. In addition, the average value of the percentage strain and the average value of the Young's Modulus were calculated as 2.39 ± 0.5 and 2.27 ± 0.5 GPa, respectively. Another reason is that the polymer has insufficient mechanical properties could be the plasticization effect of the solvent pyridine which could not be removed from the polymeric material completely.

CHAPTER 4

CONCLUSION

The commonly used starting materials for the synthesis of polybenzoxazine precursors are phenols, amines and formaldehyde. By means of using substituted amines and phenols additional polymerizable sites can be integrated to the precursors. This advantage helps us to design a wide range of monomers and after cure polymeric materials with desired properties. In this study, a polymer with benzoxazine units in the main chain has been successfully synthesized by using a trifunctional phenol and difunctional amine and paraformaldehyde. The structure of the benzoxazine precursors and cured polybenzoxazine has been verified by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopies. The qualitative analysis and thermal behavior of the benzoxazine oligomers and cured polybenzoxazine were achieved by DSC, TGA, and DMA.

From the spectroscopic analysis of the samples, it was found that the formation of the benzoxazine ring was achieved successfully during the reaction. ^{1}H NMR and ^{13}C NMR which was taken after the thermal cure of benzoxazine precursors provided that the ring opening polymerization took place successfully during the thermal cure.

The peaks appeared at 4.8 ppm and 3.8 ppm in ^{1}H NMR which was recorded before the thermal curing showed the formation of the benzoxazine ring in ^{1}H NMR. ^{13}C NMR also supports that information by the appearance of the peak at around 75 ppm which shows a successful benzoxazine ring formation. FTIR study of the benzoxazine precursors also indicates the formation of benzoxazine ring with the appearance of the strong band at about 1250 cm $^{-1}$.

The DSC thermograms of the benzoxazine precursors indicate that the ring opening polymerization of the precursors take place at about 175 ^{o}C and at that temperature also some crosslinking reactions occurs between the precursors beside that further polymerization of benzoxazine precursors was observed at about 230 ^{o}C in the DSC thermograms of benzoxazine precursors. On the other hand, the DSC thermograms of the thermally cured polybenzoxazine showed an endothermic peak at about 270 ^{o}C due to a secondary transition. Another thermal analysis conducted in this study was TGA. TGA thermogram of the benzoxazine oligomers showed an onset decomposition at about 100 ^{o}C. The derivative weight loss curve showed that the weight losses took place at 230 ^{o}C, 273 ^{o}C and 439 ^{o}C. The TGA thermogram and derivative weight-loss curve of the polybenzoxazine indicated that a thermal degradation started at approximately 260 ^{o}C. The weight lost event had its maximum at 296 ^{0}C and the second weight lost event was centered on 465 ^{0}C with higher char yield.

Viscosity analysis indicated that the intrinsic viscosity of the reaction mixture increased with time in the synthesis of benzoxazine oligomers. A decrease in the intrinsic viscosity was observed at the end of the reaction with the time of 50 minutes, which may be due to the branching and intra crosslinking of oligomers.

Results of the mechanical test indicated that the synthesized polymer has a low tensile strength, moderately good elongation and acceptable Young's Modulus, this may be due to, as mentioned, branching and possible intra crosslinking because of three functional monomer; therefore, the tensile strength of the polymer films were very low even though the elongation of them was sufficiently good.

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