

SYNTHESIS AND CHARACTERIZATION OF POLYBENZOXAZINE

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**SYNTHESIS AND CHARACTERIZATION OF POLYBENZOXAZINE**

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## ABSTRACT

### SYNTHESIS AND CHARACTERIZATION OF POLYBENZOXAZINE

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A new method for polybenzoxazine synthesis was developed and carried out throughout this work. Bisphenol-A, hexamethylenediamine, and paraformaldehyde were reacted through Mannich condensation reaction forming polybenzoxazine precursors. The reaction was followed by Gel Permeation Chromatography (GPC) as a molecular weight determination method in order to decide the end of reaction. The synthesized product, polybenzoxazine precursors, was polymerized thermally. Polybenzoxazine precursors were also characterized by using spectroscopic methods,  $^1\text{H-NMR}$  and FTIR, giving an approximation to structural determinations.

Thermal characterization of precursors and polybenzoxazine showed that the materials had two exotherms at around  $220^\circ\text{C}$  and  $260^\circ\text{C}$ . The first exothermic peak was an indication of polymerization and preliminary crosslinking reactions while the second peak was due to the final polymerization of polybenzoxazine precursors. These precursors showed no significant structural change in isothermal period of 20 minutes at 200, 220, 225,  $235^\circ\text{C}$ . Mechanical tests were performed on the polybenzoxazine films. The films cured at  $180^\circ\text{C}$  possessed a tensile strength at break  $21.04 (\pm 3.56)$  MPa and an average elongation of  $2.7 (\pm 0.93)$  %. Young's modulus was calculated as  $0.93 (\pm 0.05)$  GPa for polybenzoxazine films.

Keywords: Mannich condensation reaction, polybenzoxazine synthesis, characterization

## ÖZ

### POLİBENZOKSAZİN SENTEZİ VE KARAKTERİZASYONU

Efe, Tuğba

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Polibenzoksazin sentezi için yeni bir yöntem geliştirilmiş ve çalışma boyunca kullanılmıştır. Polibenzoksazin oligomerleri, Bisfenol-A, heksametilendiamin ve paraformaldehidin Mannich yoğunlaşma reaksiyonu sonucu elde edilmiştir. Reaksiyonu sonlandırmaya karar vermek için reaksiyonun takibi moleküler ağırlık tayini yöntemiyle, büyüklükçe ayırma kromatografisi, yapılmıştır. Sentezlenen ürünler polibenzoksazin oligomerleridir ve bu ürünler ısıl uygulamayla polimerleştirilmiştir. Polibenzoksazin oligomerleri spektroskopik yöntemlerle karakterize edilmiş, yapı belirlenmesinde <sup>1</sup>H-NMR ve FTIR kullanılmıştır.

Polibenzoksazin ve oligomerlerinin ısıl karakterizasyonları yaklaşık 220°C ve 260°C'lerde iki ekzoterm göstermektedir. İlk ekzotermik tepe noktası, polimerizasyon ve ön çapraz bağlanma reaksiyonlarının bir göstergesidir. İkinci tepe noktası ise polibenzoksazin oligomerlerinin nihai polimerizasyonu ile ilgilidir. 200, 220, 225, 235°C'lerdeki 20 dakikalık izotermal süreçlerde bu oligomerlerde önemli bir yapısal bozunma olmadığı gözlenmiştir. Mekanik özellikler polibenzoksazin filmlerde incelenmiştir. 180°C'de ısıl işlem ile elde edilen filmler kırılma noktasında ortalama 21.04 (±3.56) MPa direç ve ortalama 2.7 (±0.93) % uzama göstermişlerdir. Young'ın modülüsü ortalama 0.93 (±0.05) GPa olarak bulunmuştur.

Anahtar kelimeler: Mannich yoğunlaşma reaksiyonu, polibenzoksazin sentezi, karakterizasyon

To my family and  
to the memory of my father

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## LIST OF ABBREVIATIONS

BA	: Bisphenol-A
hda	: Hexamethylenediamine
PF	: Paraformaldehyde
DSC	: Differential Scanning Calorimetry
NMR	: Nuclear Magnetic Spectroscopy
<sup>1</sup> H-NMR	: Hydrogen NMR
FTIR	: Fourier Transform Infrared Resonance Spectroscopy
GPC	: Gel Permeation Chromatography
TGA	: Thermal Gravimetric Analysis
MW	: Molecular Weight
M <sub>n</sub>	: Number Average Molecular Weight
M <sub>w</sub>	: Weight Average Molecular Weight

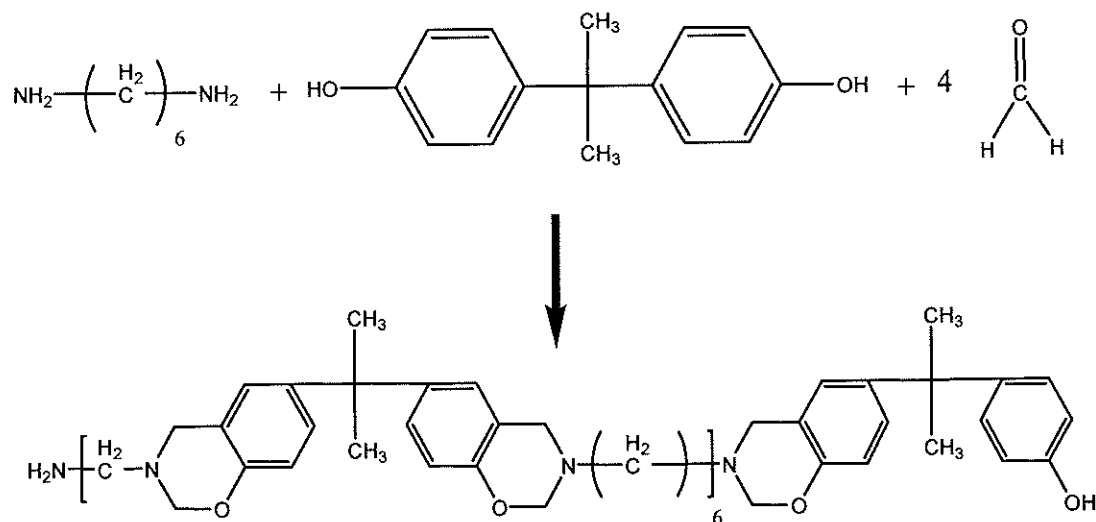
## CHAPTER 1

### INTRODUCTION

Phenolic resins serve as high performance materials in many areas due to their excellent properties [1]. These properties include mechanical strength, dimensional stability, flame retardance, high heat resistance, electrical and chemical resistance, low water absorption, and low cost [1-3]. Besides these desired characteristics, phenolic resins possess a number of shortcomings such as brittleness, poor shelf life, requirement of strong acid catalysts for polymerization, void formation due to volatile products, and formation of hazardous condensation by-products [1-4]. In order to overcome these shortcomings, scientists have concentrated on developing polybenzoxazines which are a novel type of phenolic resins [2, 4].

Polybenzoxazines are produced by the ring-opening polymerization of benzoxazine monomers. The monomers are easily obtained by Mannich reaction of phenols, amines, and formaldehyde [2]. The general reaction of the polybenzoxazines synthesis can be seen in Figure 1 [3].

Recently, polybenzoxazine chemistry has attracted great attention and grew very rapidly. The literature in this field has had a large number of publications in a short period. Cope and Holy [5] first synthesized benzoxazines in 1940s as a result of Mannich reaction, in which phenols, primary amines, and formaldehyde react. After then, this work is patented in 1953 [6]. Moreover, during curing of novolac resins, nuclear magnetic resonance (NMR) spectroscopy showed that benzoxazine structures arise as intermediates [7]. Schreiber conducted another study about heating this kind of resins into a hard, brittle mass excluding investigations of structure and other characteristic properties was patented in 1973 [4, 8, 9].



**Figure 1** Synthesis of polybenzoxazines

Monofunctional benzoxazine reactions in bulk by using phenol as the initiator were examined by Riess et al. with NMR and size exclusion chromatography (SEC) [4]. Further studies about polybenzoxazines include the improvement of resins using various kinds of mono- and difunctional phenols and/or amine groups in the synthesis [4, 10-12]. Developments in polybenzoxazine chemistry continued with finding alternative ways to synthesize and polymerize benzoxazine monomers. Furthermore, performance improvement of polybenzoxazines including insertion of functional groups, composite and blend preparation in addition to investigation of their properties has been performed [1, 13, 14]. Thermal degradation of this novel polymer has been explored [15-17]. Further studies in polybenzoxazines chemistry include enhancement of polymerization conditions, consideration of mechanisms of other degradation types, improvement of this high performance polymers with special design, and blending polybenzoxazines with other high performance polymers, fillers, or fibers [16].

Polybenzoxazines are still developing in the laboratories, as a result of this they have not been applied in industry. These polymers which are the products of polyfunctional benzoxazines and reactive polyamines could be used for coating and encapsulating [4, 18]. They possess high performance polymer properties and are

superior to phenolic resins so they might replace with phenolic resins, or such kind of other high performance polymers used in many areas. Gaea et al. reported that they will find use as protection coatings for circuits in TV studios, computer chips, and airplane bodies [19-20]. They can be employed to produce materials for airplane interiors, as well as curing agents for other synthetic resins, and varnishes which form water/alkali/solvent-resistant films [19-21].

## **1.1 Synthesis of Polybenzoxazines**

Benzoxazine monomers are synthesized by condensation of various kinds of amines with formaldehyde and substituted phenols. The condensation reaction takes place by applying either solution or solventless methods [1, 22]. Use of different kinds of amines such as aliphatic, aromatic, or multifunctional; and alternating the phenol group by substitution gives polybenzoxazines more available polymerization sides leading to design flexibility [1]. Polymerization of benzoxazine monomers is achieved by ring-opening polymerization of aromatic oxazines [17].

### **1.1.1 Synthesis Methods**

Benzoxazine monomers are synthesized by several methods including solution, solventless, and other methods.

For the solution method, the reactive species, i.e. a phenolic derivative, an amine, and an aldehyde, are dissolved in an appropriate organic solvent such as dioxane, toluene, and alcohol and refluxed. As mentioned in British Patent No. 694,489, evaporating the solvent, or precipitating the product with a suitable non-solvent, the benzoxazine monomer is obtained from solution [15].

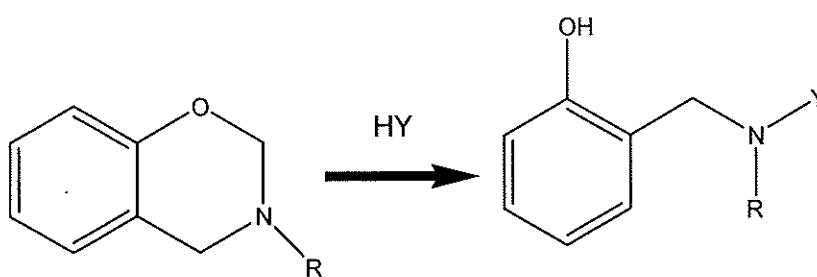
In literature, while hexamethylenetetramine decomposes at elevated temperatures in the presence of phenol, benzoxazines are met as stable side products in solid state [22, 25].

Bishop et al. proposes that 1,3,5-tribenzylhexahydro-1,3,5-triazine is condensed with phenol and the product obtained is only 2-phenylaminomethylphenol [22, 24]. On the



other hand, another survey claims that benzoxazine synthesis in solution can be achieved by the use of benzylamine which is produced from 1,3,5-tribenzylhexahydro-*s*-triazine [22, 26].

Polymerization of monomers is achieved by ring-opening polymerization. The active hydrogen present in compounds, for example, naphthol, indole, imides, and even phenol (as starting material) propagates the ring opening reaction which is shown below in Figure 2 [1, 27]. This reaction favors the oligomer formation at lower temperatures together with polybenzoxazine structures.



**Figure 2** Ring opening polymerization of monofunctional benzoxazine

When mono-functional benzoxazines are cured with phenols, average molecular weight of the oligomers is not more than 1000Da. Thermal dissociation of monomer and chain propagation opposes so that higher molecular weight linear polymers cannot be obtained [1,28].

Hydrogen bonding in benzoxazine resins should be overcome since it prevents reactivity below a temperature where Mannich reaction reverses back [15]. Difunctional or multifunctional benzoxazine synthesis and applying ring opening reactions to form phenolic materials starting with dimers and higher oligomers are other solutions to avoid this restriction [10]. An example for this kind of a reaction involves the reaction of Bisphenol-A, formaldehyde, and methylamine to produce a difunctional benzoxazine monomer which contains two oxazine ring structures at

both end of Bisphenol-A [1]. Functionality of benzoxazine monomer can be altered by varying amine used in the synthesis [29, 30].

Synthesis of high molecular weight polybenzoxazine precursors is accomplished by the reaction of aromatic or aliphatic diamine and Bisphenol-A with paraformaldehyde. Oxazine ring in the main chain results in low molecular weight precursors and crosslinking in the structure because of the Mannich reaction between multifunctional groups. Inhibiting the side reactions, Mannich polymerization yields more ring-closed structures compared to ring-opened structures. This work makes this material to be used as polybenzoxazine precursor [1]. Precursor solution is then thermally cured at 240°C after it is casted on a glass-plate as transparent film.

Benzoxazine monomers are polymerized typically at elevated temperatures in the absence of catalysts [30]. For improvement, monomers are cured with catalyst; the results show that initiation of curing time is reduced in addition to speeding up the rate of reaction [31]. However, maximum exotherm temperature was not so high that polymerization is not noteworthy below 100°C.

The heterocyclic benzoxazine ring with its N and O atoms provides polymerization via ring-opening mechanism under certain reaction conditions. Lewis definition of basicity for these atoms makes the molecule available for ring opening with cationic mechanism [32].

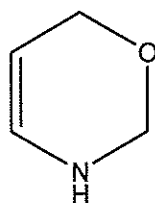
There have been several attempts for progression in the polymerization procedures. Some kind of initiators like  $\text{PCl}_5$ ,  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{AlCl}_3$ , and  $\text{MeOTf}$  were reported to be the helpful for polymerization of benzoxazines with high  $T_g$  and high char yield [10]. Moreover, photoinitiated polymerization with certain initiators, radical sources, and photosensitizers was also studied [33] as well as acid catalysed and thermal polymerization.

### **1.1.2 Reaction Mechanism**

Holly and Cope reported that benzoxazine monomers can be obtained with the condensation reaction of primary amines with formaldehyde and substituted phenols

in solution [5]. Mannich reaction takes place when free ortho positions of a phenolic compound are attacked by the benzoxazine rings and form a Mannich bridge [23].

The Mannich reaction has been used for the introduction of substituted aminomethyl groups into organic compounds as well as transaminomethylation with Mannich bases. For benzoxazine synthesis in solution, the reaction proceeds through adding amine to formaldehyde at lower temperatures and form N,N-dihydroxymethylamine,  $-N(-CH_2OH)_2$ . At elevated temperatures, oxazine ring is produced by reaction of this product preferentially with the ortho position of the phenol and labile hydrogen of the hydroxyl group [24]. An oxazine ring structure is shown in Figure 3.



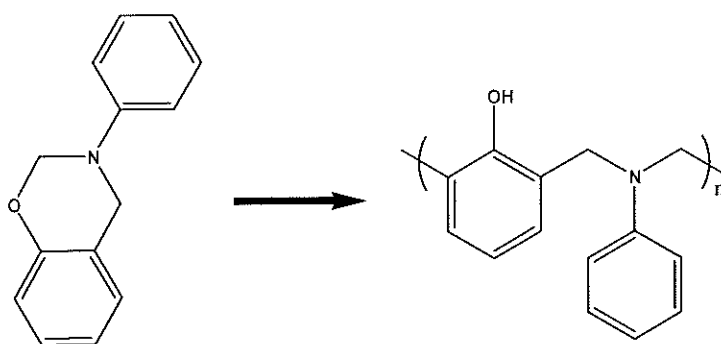
**Figure 3** Structure of an oxazine ring

The oxazine ring is formed during benzoxazine synthesis. It is assumed to be in a distorted semi-chair conformation in order to achieve minimum energy [32]. This ring strain enables polymerization by ring-opening. In addition, ring opening polymerization is favored by Lewis basicity of nitrogen and oxygen atoms by means of cationic mechanism [10]. Indeed, oxygen is believed to be the polymerizable site because its negative charge distribution is higher than nitrogen [1].

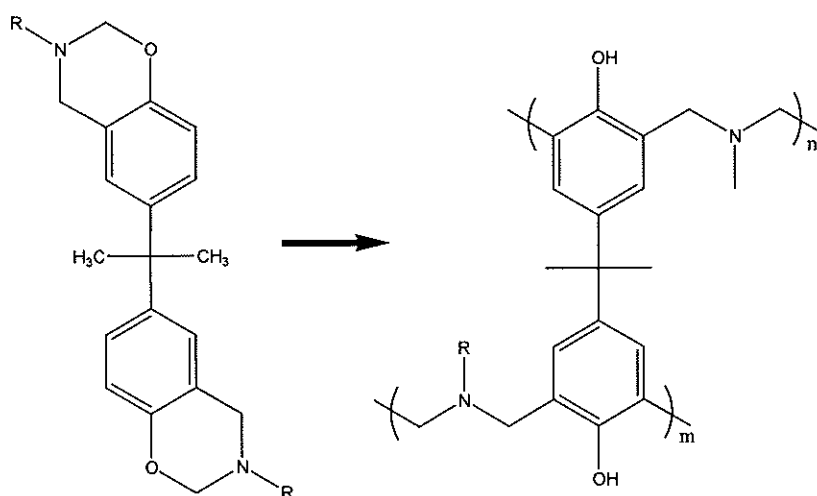
During the benzoxazine monomer synthesis, besides benzoxazines as the major products, dimers and small oligomers are also formed. These structures with free hydroxyl groups activate the monomer to be self-initiated towards polymerization and crosslinking reactions [4].

Polymerization of mono- or multifunctional benzoxazines results in structures similar to phenolic polymers except their Mannich bridges. A general polymerization reaction of polybenzoxazines can be seen in Figure 4 [21].

Thermal polymerization of the benzoxazines by ring-opening mechanism is supposed to proceed by means of the formation of a carbocation and an iminium ion. These molecules are assumed to exist in equilibrium as illustrated in Figure 5 [34]. The carbocation attacks to the benzene ring by electrophilic substitution and polymerization continues with this substitution of available ortho or para position of phenolic group [34].



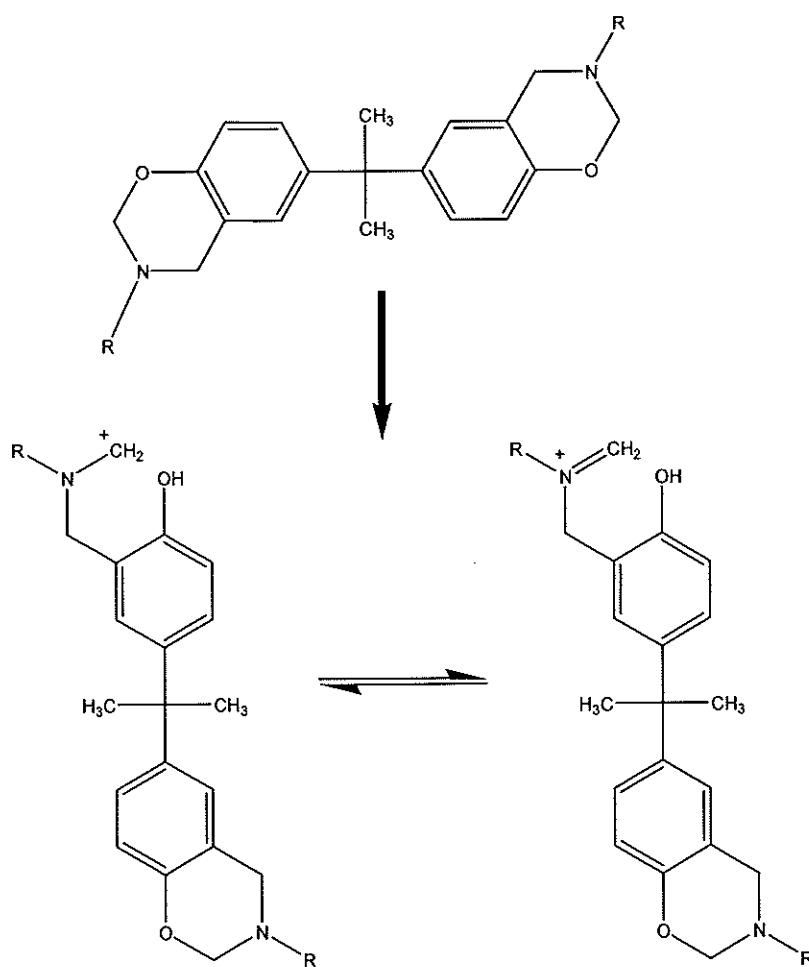
(a)



(b)

**Figure 4** Polymerization of (a) monofunctional and (b) difunctional benzoxazine monomers

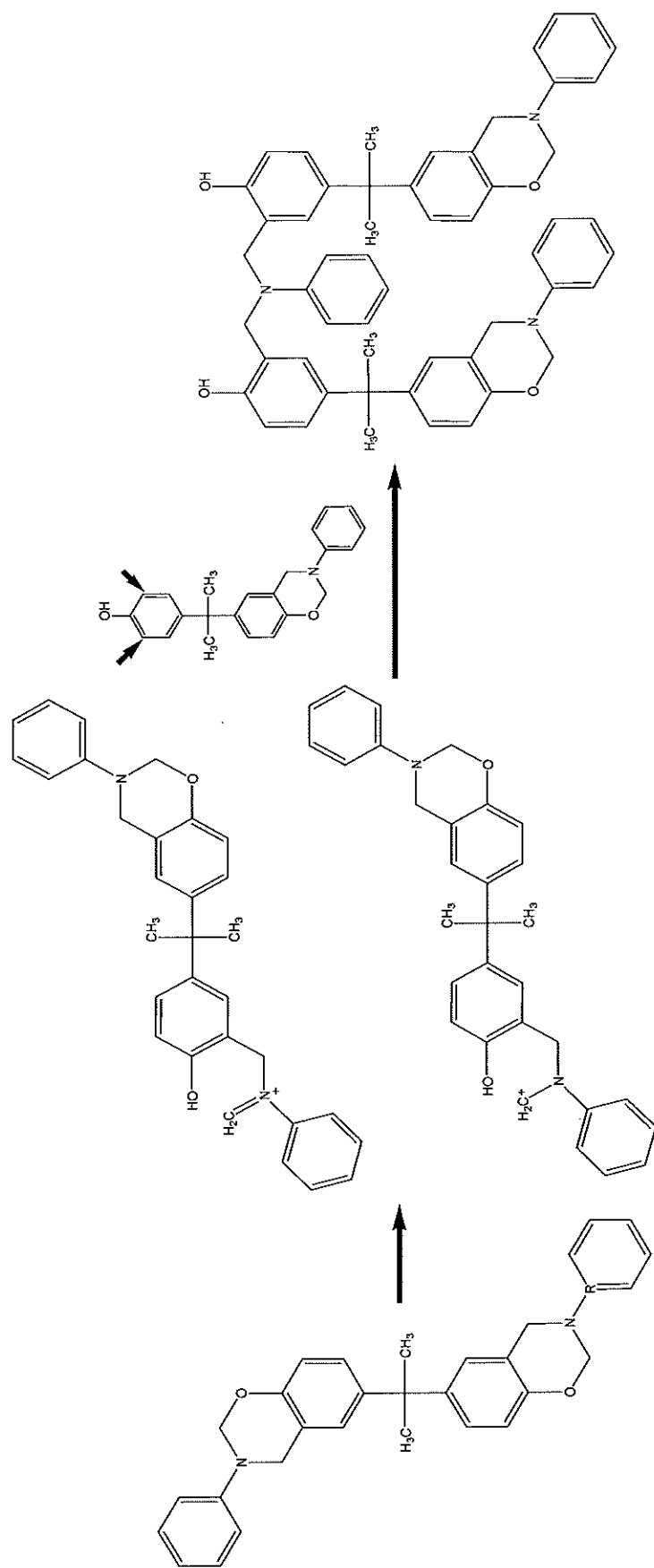
The stability of these intermediate molecules affects polymerization. First of all, the carbocation propagates the polymerization reaction so the iminium ion should be stabilized for higher polymerization yields. Moreover, the basicity of the amine group plays an important role on the reactivity of the equilibrium ion pair. Amine group with more electron density around nitrogen atom provide stabilization of more positive charge of iminium ion. Further, temperature is another parameter for the propagation reaction. Propagation reaction involves the chain transfer to benzene ring so early stages in the reaction are temperature independent, however; later in the reaction, temperature affects propagation rate. Propagation continues with vitrification at high cure temperatures. In this case, viscosity increases and the curing kinetics are affected as an indirect result of temperature [34, 35].



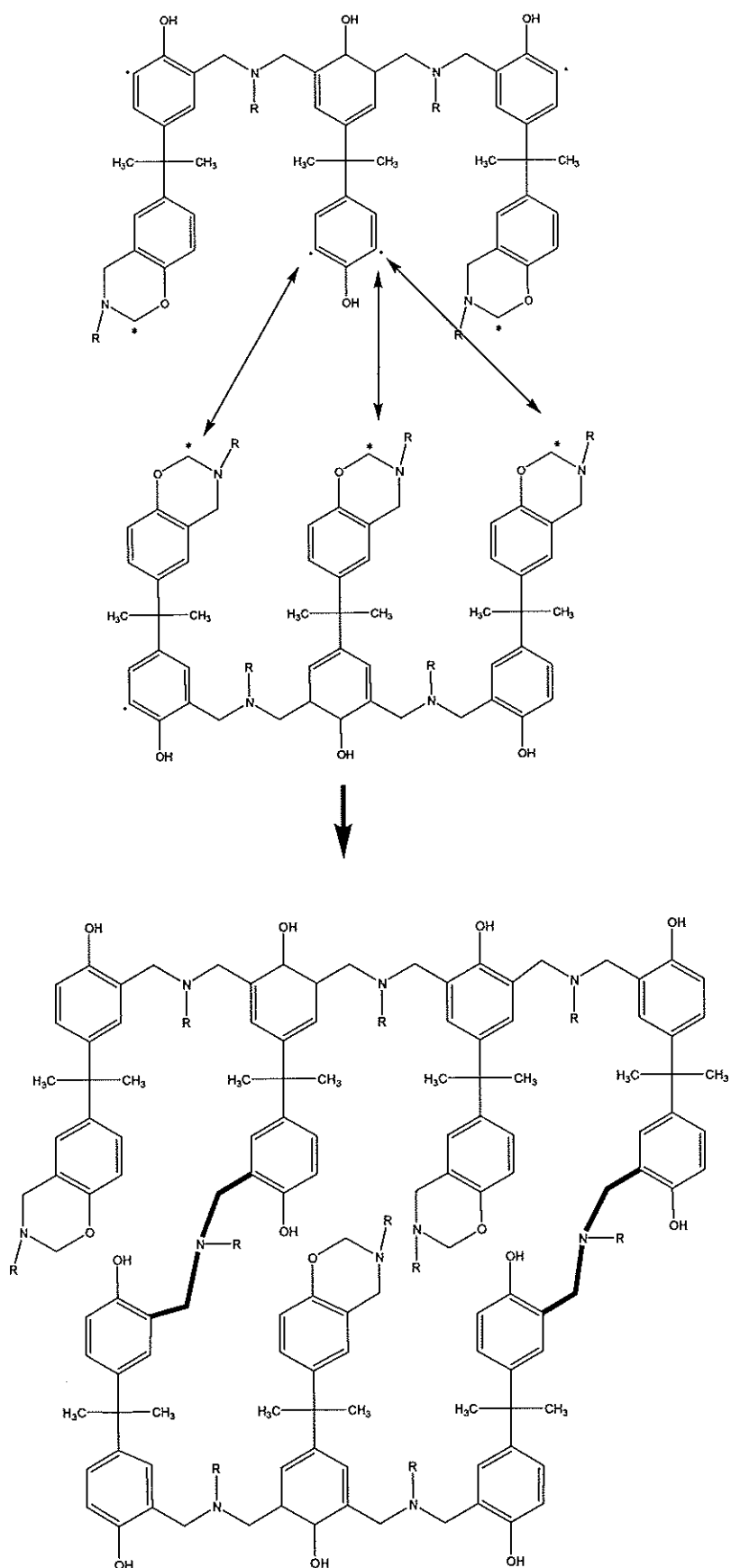
**Figure 5** Formation of carbocation and iminium ion

Polymerization of a difunctional benzoxazine, Bisphenol-A based, monomer is shown in Figure 6 where polymerization proceeds through cationic mechanism thermally [34].

The crosslinking reactions are possible during polymerization of benzoxazine monomers. During thermal polymerization of difunctional or multifunctional benzoxazines which are derived from diamines, crosslinking between side chains occur. A presumed structure for a crosslinked polybenzoxazine by showing the available reactive points is given in Figure 7 [34, 35].



**Figure 6** Thermal polymerization of a Bisphenol-A based monomer through cationic mechanism

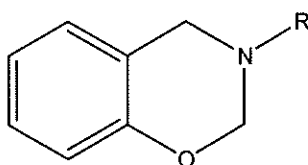


**Figure 7** Possible crosslinking reactions during polymerization



## 1.2 Polybenzoxazine Structure

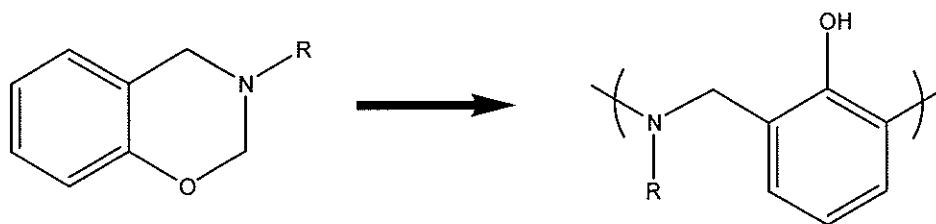
Benzoxazine is composed of a benzene ring next to a six-membered heterocyclic ring which constitutes nitrogen and oxygen elements. As it can be seen from Figure 8, this part of the molecule is named as oxazine ring and it is supposed to be in the shape of a chair conformation in order to provide minimum energy [10]. The consequence of this conformation facilitate the molecule polymerize by opening this ring strain.



**Figure 8** Benzoxazine structure

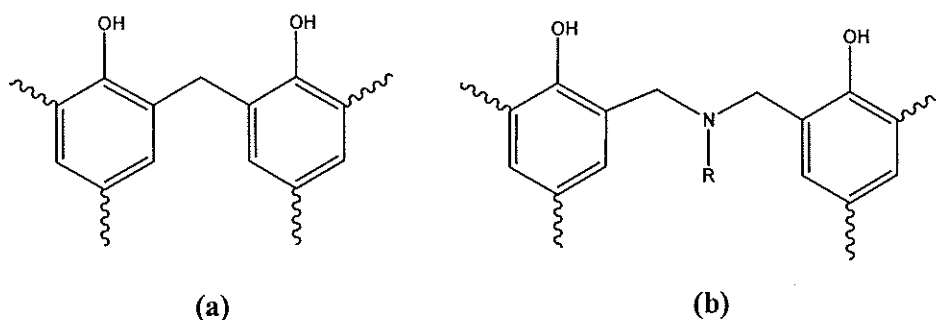
Polybenzoxazine is a kind of derivative of phenolic resins in which methylene bridges connect phenolic groups. Phenolic moieties are attached by Mannich bridges, i.e. C-N-C links, in polybenzoxazines [36, 37].

Polybenzoxazines are obtained by ring opening polymerization of benzoxazine monomers and have the following form:



**Figure 9** Polymerization of benzoxazine monomer by ring opening

Polybenzoxazines differ from traditional phenolic resins in that Mannich bridges in polybenzoxazines cause more flexibility in the molecule and dimensional variations as shown in Figure 10 [38]. These bridges also promote inter and intra hydrogen bonding with hydroxyl groups as in the case of phenol-formaldehyde oligomers [37, 38]. Hydroxyl groups may form hydrogen bond to either nearby hydroxyl group or the lone pair of nitrogen in the Mannich bridge [38, 39]. A study about these interactions conducted by Kim et al. proposes that in the oligomers with longer chains, helical structures may be formed [40]. As for phenol-formaldehyde resins, acidity of hydroxyl groups in polybenzoxazines makes these groups chelate to metal cations once their ionization is stabilized by intramolecular hydrogen bonding [41].



**Figure 10** Structures of (a) phenolic resin and (b) polybenzoxazine

In Figure 10, R group indicates aliphatic or aromatic group that are connected to the molecule by reaction of mono or multifunctional amine reactant. If the amine used for the synthesis is not a monofunctional amine, the end group contains another amine group. Phenolic reactant may also vary the composition in such a way that multifunctional phenolic molecules undergo polymerization through all functional groups. These functionalities affect the structure of the polybenzoxazines, and design variations occur by this way.

A thermal decomposition study of polybenzoxazines by Laobuthee et al. revealed that the side functional groups, R, of the Mannich bridge, as shown in Figure 10b, were the weakest points in the crosslinked network structures [16]. The outcome was

confirmed by the fact that decomposition proceeded through the scission of amine fragments. In order to stabilize this phenomenon, end-capping of functional groups of amine by introducing different polymerizable groups is suggested.

### **1.3 Properties of Polybenzoxazines**

Polybenzoxazines show similar properties to phenolics since they are assumed to be their derivatives. They maintain many of the characteristics of phenolic resins while improving some of the shortcomings associated with them [5].

The common properties of phenolic resins and polybenzoxazines include good heat resistance, good electrical properties and flame retardance. In addition to these properties, polybenzoxazines possess such unique characteristics like low water absorption, dimensional stability, near-zero volumetric shrinkage or expansion upon curing, high char yield [10, 42]. Moreover, various kinds of the reactants result design flexibility for molecular architecture so that polymers with advanced properties can be generated [3]. They demonstrate high mechanical properties besides easy processing which is a result of low melt viscosity [16, 43]. Polybenzoxazines do not require strong acids or catalysts for polymerization as well as they do not release condensation by-products which cause problems for traditional phenolic resins [16].

These properties mentioned above offers polybenzoxazines replace with other high performance resins. Though there are some disadvantages of polybenzoxazines as well. Typically, polybenzoxazines are brittle and ring opening polymerization requires high temperatures [22]. Several attempts for the performance improvement are divided into two groups. Structure modification of benzoxazine monomers such as preparing novel high-performance polybenzoxazines with high glass transition temperature ( $T_g$ ) and high decomposition temperature is the one way [22]. By this way, benzoxazine monomers are modified with other polymerizable groups similar to ethynyl, nitrile, or propargyl groups [13a,b, 44]. Second way is a very attractive method, in which copolymers, alloys, fiber reinforced composites, clay nanocomposites are prepared [45]. Toughening by liquid rubber or other high

performance thermoplastics like poly(imide-siloxane) is also classified in this method [13e, 46].

#### **1.4 Aim of the Study**

In this work, we tried to develop a new method for the synthesis of polybenzoxazine by using a difunctional amine and a difunctional phenol to overcome some shortcomings of previous works. Most of the traditional methods for polybenzoxazine synthesis resulted in some conflicts in the literature. The results obtained in the analysis using the traditional methods generated very low yields. These methods offered the reaction to proceed at room temperature; however, the materials did not dissolve at room temperature. Therefore, a new and different method has been searched in this work. The reaction temperature was increased to 50°C in this method, and paraformaldehyde was added to the reaction mixture in the form of formaldehyde vapor. At the end of the reaction, polybenzoxazine precursors were obtained. Polymerization of the precursors was carried out by heating them at higher temperatures. The resulting polymer was examined for its thermal and mechanic properties.

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 Materials

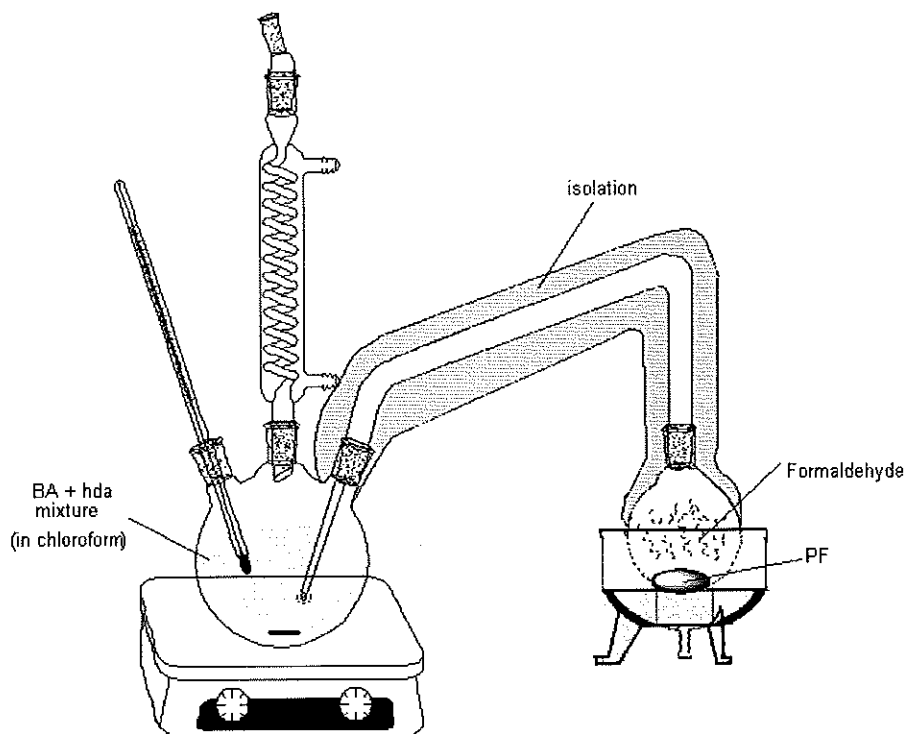
Bisphenol-A with 99+ % purity was supplied from Aldrich chemicals. Hexamethylenediamine was used as the amine supplier and brought from Fluka AG. Paraformaldehyde is supplied from Merck Chemicals. Chloroform was used as the solvent and it was extra pure Merck grade. All chemicals were used without further purification.

#### 2.2 Synthesis Method

##### 2.2.1 Preparation of Benzoxazine monomers and precursors

Initially, 9.15 g of Bisphenol-A (BA) and 4.65 g of hexamethylenediamine (hda) were dissolved with a magnetic stirrer in 150 mL of chloroform in a three-necked glass balloon equipped with a condenser and thermometer at 50°C. Into another balloon, 6 g of paraformaldehyde (PF) was taken and this balloon was connected to the three-necked balloon with glass tubing. After 15 minutes, when BA and hda were totally dissolved, a milky solution was formed. Then, PF was heated until all PF evaporated and decomposed into formaldehyde. The gaseous formaldehyde, with the effect of heating, flowed into the main reaction balloon. The solution became yellowish transparent liquid in 30-40 minutes indicating the reaction was completed.

Chloroform was removed from this solution consisting of benzoxazine monomers and oligomers by using Bibby Rotary Evaporator RE100. The resulting gel was further dried with a vacuum pump, and then it was used as the precursor for polymerization. The experimental set-up was shown in Figure 11.



**Figure 11** Glassware used for the synthesis of polybenzoxazine precursors

### 2.2.2 Curing of Precursors

#### a) Solvent Casting Curing

The precursor material was dissolved in chloroform at a weight ratio of (2 : 12) (precursor/chloroform). This solution was put into a petri dish, and then the solvent was removed in an oven at 25 °C for 30 minutes. After chloroform was removed, the remaining part was a colorless gel. At 180 °C, the gel was cured for 2 hours in the oven. A yellow-orange film was obtained.

#### b) Compression Molding Curing

In this method, the precursor material was placed between steel plates equipped with a steel mold. The Rucker PHI 8PW-2200-A compression press was heated until 180°C. The material was pressed with a pressure of 10 tons for 15 minutes. The resulting material formed a thin film with a thickness of 0.05 cm.

## **2.3 Thermal Analysis**

### **2.3.1 Differential Scanning Calorimetry (DSC) Analysis**

DSC method was used in order to investigate the behavior of precursors. The thermograms were recorded on a Dupont Thermal Analyst 2000 DSC 910S and Scinco N-650 DSC Instrument. The analysis of samples was performed under N<sub>2</sub> atmosphere in the temperature range of 25-300°C with a heating rate of 10°C/min. These thermograms demonstrated the curing temperature of the monomers. In addition, the material was heated isothermally at 200, 210, 225, and 235°C for the investigation of their behavior against heat.

## **2.4 Spectroscopic Analysis**

### **2.4.1 Nuclear Magnetic Resonance (NMR) Spectroscopy**

The material obtained as a result of the chemical reaction between BA, hda, and PF was characterized by <sup>1</sup>H-NMR. The spectra obtained with Bruker 400 MHz solid-liquid NMR gave an idea about the structural information of benzoxazines. The peak assignments indicated the characteristics of formations.

### **2.4.2 Fourier Transform Infrared Resonance (FTIR) Spectroscopy**

Structural investigation of benzoxazine precursors was also inspected with Vertex 70 FTIR/ATR Spectrometer. FTIR spectra clarified the structure of the precursor, as confirmed by NMR measurements.

## **2.5 Gel Permeation Chromatography (GPC)**

Number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity index values for the synthesized material were analyzed with Polymer Laboratories PL-GPC 220 instrument in Central Laboratory at METU. GPC method was applied by THF as the eluent solvent at 45°C, and Universal Polystyrene (PS) calibration technique was used. GPC was standardized by anionically synthesized PS

with a narrow molecular weight distribution. The calibration was done by using PS with MW of 1290, 4920, 9920, 30300, 60450, 170800, 299400.

## **2.6 Viscosity Measurements**

The change in molecular weight was investigated by using an Ubbelohde viscometer. The viscosity measurements were done by using Chloroform as the eluent solvent at 45°C. This temperature was just 5°C below the reaction temperature. Therefore, we do not expect any other side effects either precipitation or phase separation.

## **2.7 X-Ray Analysis**

Crystallinity in the structure of polybenzoxazine precursors was considered with Rigaku Miniflex Diffractometer, Cu K $\alpha$  30kV, 10 mA,  $\lambda=1.5405$  Å with a speed of 1°/min and 0,05° step.

## **2.8 Thermal Gravimetric Analysis (TGA)**

Weight-loss of samples by applying high temperatures was monitored for precursors and polybenzoxazine films. The analysis was performed by Shimadzu-DTG60H in a temperature range of 25-400°C with a heating rate of 20°C/min.

## **2.9 Mechanical Tests**

The tensile properties of the transparent films were determined by the use of Instron TM1102 instrument. The films were cut 3 cm in length, and 0.5 cm in width. The thickness of samples was about 0.05 cm. The results were presented as the average of 5 samples.



## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Synthesis Method

The synthesis of polybenzoxazine oligomers was carried out by using a traditional Ishida method [3]. In this method, the three reactants; paraformaldehyde (PF), Bisphenol-A (BA), and hexamethylenediamine (hda) were continuously stirred and refluxed for 20 hours at room temperature. PF was chosen as the aldehyde component of the reaction due to its superiority compared to formaldehyde which decomposes and evaporates easily and loses its stoichiometry quickly [1].

Application of this method showed some conflicts as Agag et al. mentioned in their work [2]. The details of preparation and characterization of polybenzoxazine was not given by Ishida [18]. The material synthesized by this method in our laboratory was characterized by  $^1\text{H-NMR}$  and the results showed that the product yield was very low. The integration of characteristic peaks for oligomeric polybenzoxazine was very low compared to reactants.

The other method suggested by Agag et al [2] took 5 hours to complete the reaction. The results of the analysis showed that the product yield was not as low as that obtained by Ishida's method but they were not very satisfactory. This situation made us develop a new method for the polybenzoxazine synthesis.

Firstly, according to the procedure patented by Ishida [18], reaction takes place at room temperature but BA does not completely dissolve in chloroform at room temperature. So as a first step, we increased the temperature of the medium from room temperature to 50°C in order to have a complete dissolution of BA. Moreover, instead of mixing three reactants as expressed in Ishida's method, the third reactant, formaldehyde, was added into reaction vessel after dissolving BA and hda in chloroform at 50°C in our method. Taking into account that hda and PF would

previously react according to Mannich reaction mechanism, and then BA would react with them; the condensation reaction started with the addition of PF into the reaction medium. Addition of PF was performed by bubbling gaseous formaldehyde obtained from decomposition of PF at around 270°C into this mixture. This solution was stirred and refluxed at 50°C up to 40 minutes while all stoichiometric formaldehyde was transferred into the three-necked balloon. Therefore, the completion of the reaction became less than an hour.

The results of the characterization of polybenzoxazine synthesized with our method agreed well with the polymers synthesized by Ishida's method [3]. However, due to uncertain points in the procedure of Ishida's synthesis method, we faced with some problems in synthesis part. As mentioned previously in the thesis, this situation has already been mentioned by Takeichi et al in most of their works that the synthesis method was not given in details by Ishida but those results of their characterization were in agreement with Ishida's [2, 14, 16, 17].

### 3.2 GPC Analysis

During the synthesis of benzoxazine precursors, 10 mL portions were taken from the reaction vessel at certain times. The solvent, chloroform, was removed and the dried precursor was kept for molecular weight (MW) analysis. Figure 12 shows GPC output of these samples with MW distribution for 10<sup>th</sup>, 40<sup>th</sup>, 50<sup>th</sup> and 60<sup>th</sup> minute of reaction. Numerical values obtained for number average MW ( $M_n$ ) and weight average MW ( $M_w$ ) are given on the graph,  $M_w$  in box in the figure. MW results of the samples gave an approximate approach to the exact MW since they were given relative to polystyrene. When MW of precursors is considered, both  $M_n$  and  $M_w$  increased in time during reaction.

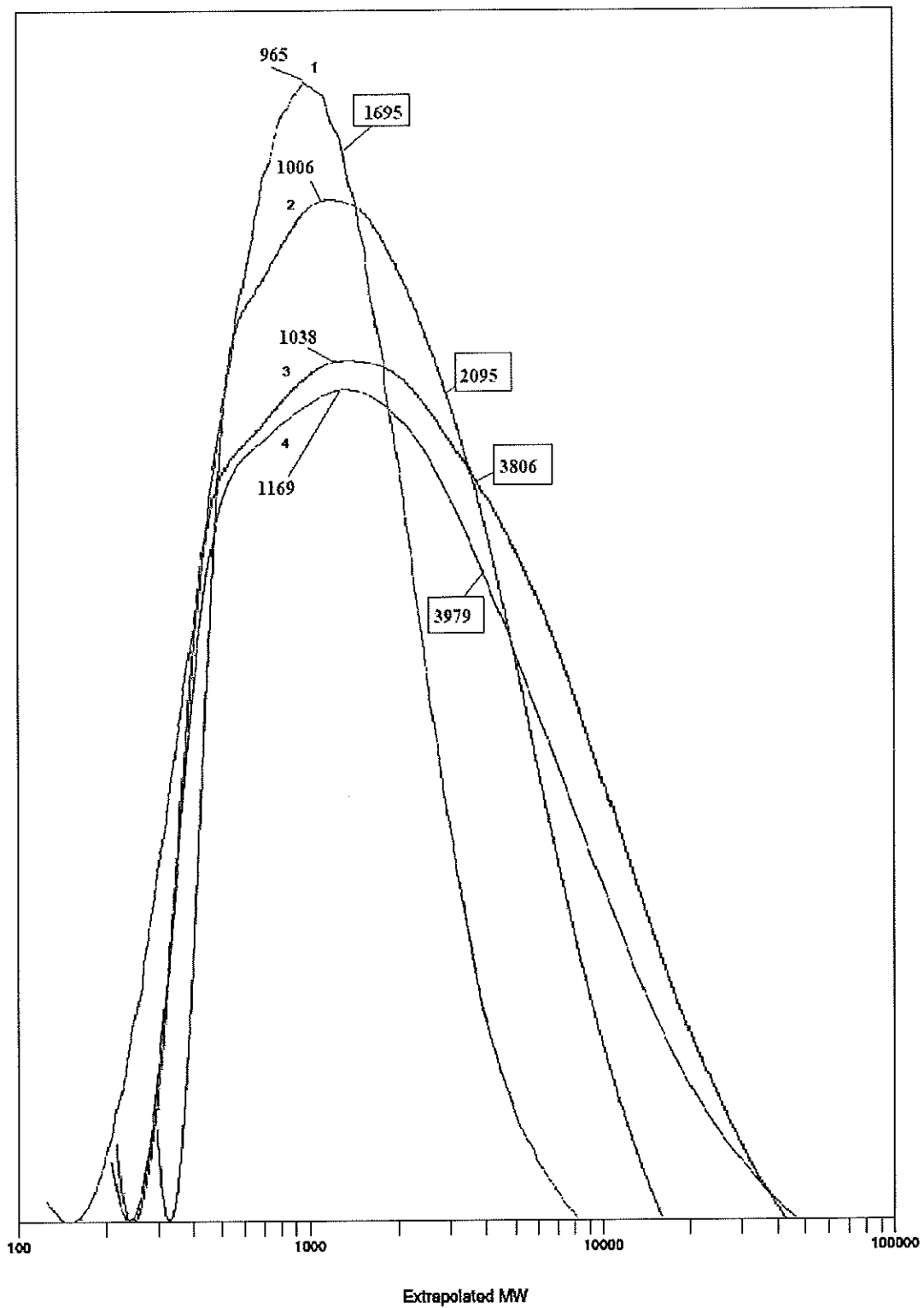
The variation of  $M_n$  and  $M_w$  with time is given in Figure 13. The MW increased with time of the reaction, and reached a plateau after formaldehyde transfer was finished in the reaction medium. The sudden rise in MW in Figure 13 in about 10 minutes was a result of possible crosslinking reactions. This was proved by solvation process of samples which were used in viscosity analysis. The aliquots taken from the reaction vessel at 50<sup>th</sup> and 60<sup>th</sup> minutes did not dissolve completely after they were

dried. Therefore, we can conclude that 40 minutes was enough for a complete reaction, as given in Figure 13.  $M_w$  was found as 2095 when all formaldehyde was used up at 40 minutes.  $M_n$  was found to be 1006. The MW values were given by Takeichi 8858 for  $M_w$ , and 2358 for  $M_n$  [2].  $M_w$  value came across to five (5.34 as determined) repeating units for a chain in the precursor form. The polydispersity index (PDI) value was found as 2.08 based on GPC results of these samples. For condensation polymers, the best distribution was obtained when PDI is about 2 [3]. However, this large range contributed some distinctions during MW determinations in our experiment because GPC displays the optimum results for polymers with PDI of one.

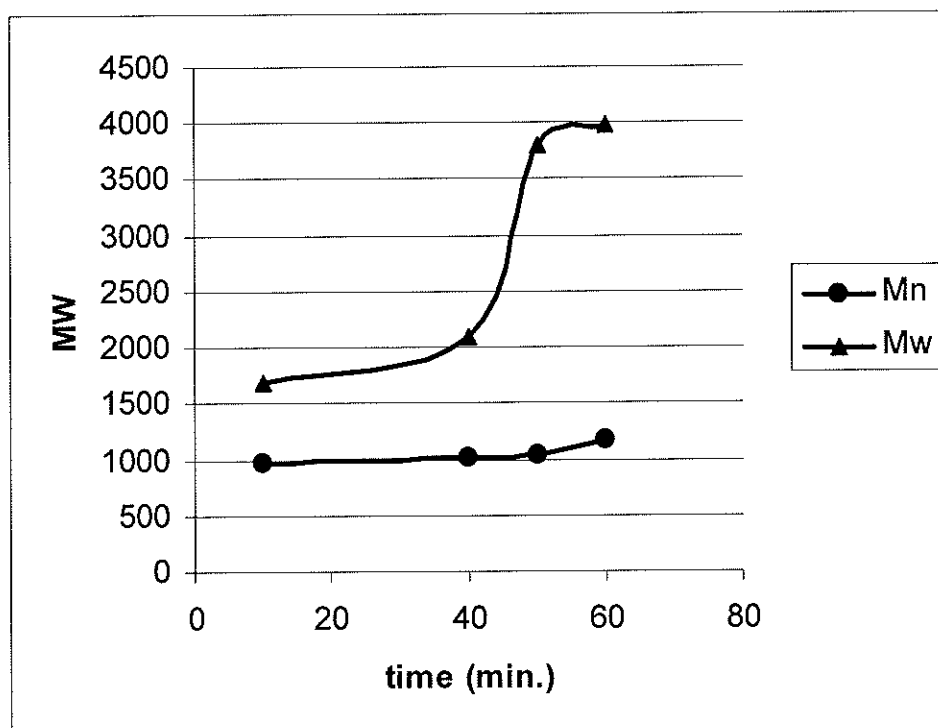
According to the MW results, relative Mark-Houwink constants were calculated. Mark-Houwink formula relate viscosity with molecular weight according to the formula, (1),

$$[\eta] = K \times M^\alpha \quad (1)$$

In the formula  $[\eta]$  is used for intrinsic viscosity,  $K$  and  $\alpha$  are constants the values of which depend on the nature of the polymer and solvent as well as on temperature and  $M$  is usually one of the relative molecular weight averages [47]. These constants were found as  $\alpha=0.523$  and  $K=282.25$  in our GPC analysis.



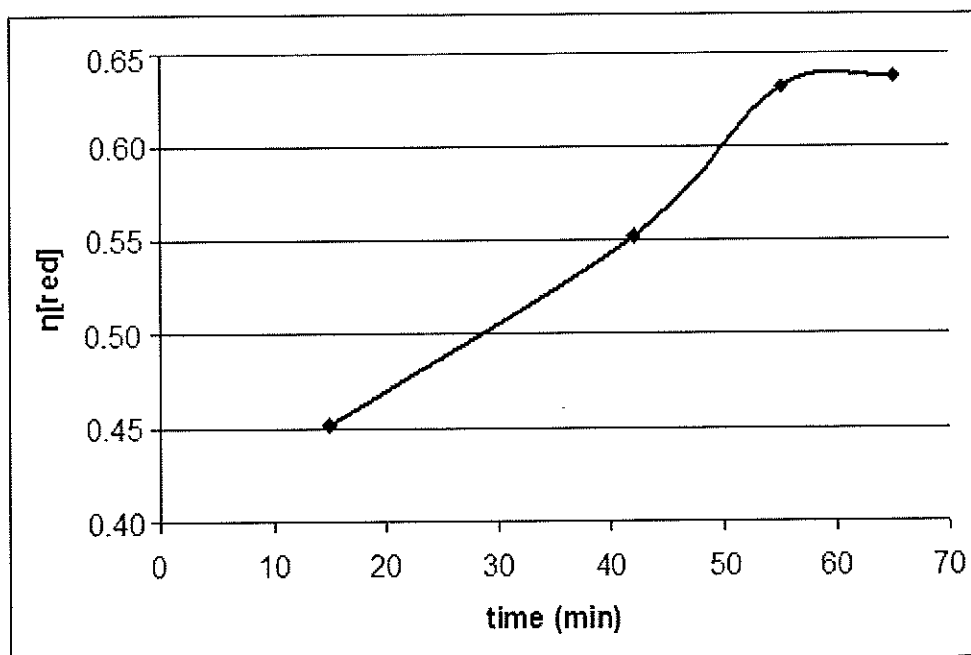
**Figure 12** Change in molecular weight of precursors during reaction:  
 (1) 10<sup>th</sup> minute, (2) 40<sup>th</sup> minute, (3) 50<sup>th</sup> minute, (4) 60<sup>th</sup> minute



**Figure 13** Change in Mn and Mw during reaction

### 3.3 Solution Viscosity

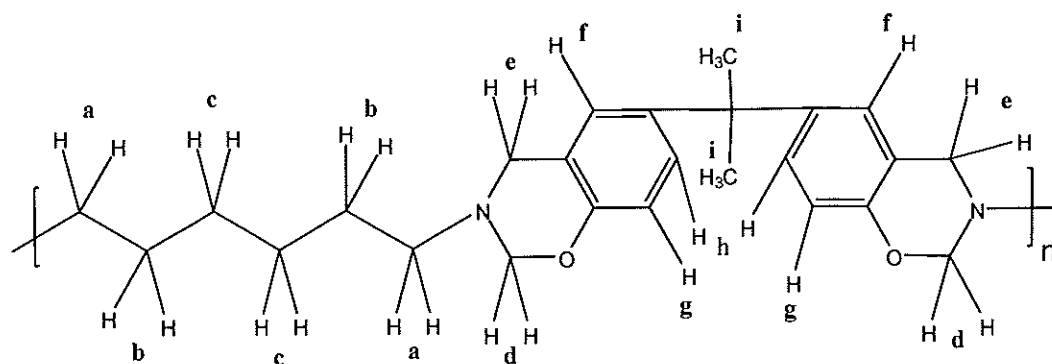
The solution viscosity measurements were performed for the same volume of aliquots taken from the reaction medium. When the reaction was completed, small oligomers were produced by opening of the oxazine ring. Since the concentrations of polybenzoxazine precursors were not known in these samples, we were able to follow only the change in the viscosity in these aliquots. Therefore, the viscosity plots were drawn as if the concentrations were correctly obtained. The viscosity plots, reduced viscosity,  $\eta_{red}$ , versus time emphasize the increasing molecular mass of polybenzoxazine with time as given in Figure 14. The results revealed that the increase of Mw slows down after all formaldehyde was reacted with the reactants in the medium. Viscosity measurements verified the results obtained by GPC analysis.



**Figure 14** Change in viscosity with time

### 3.4 NMR Spectroscopy

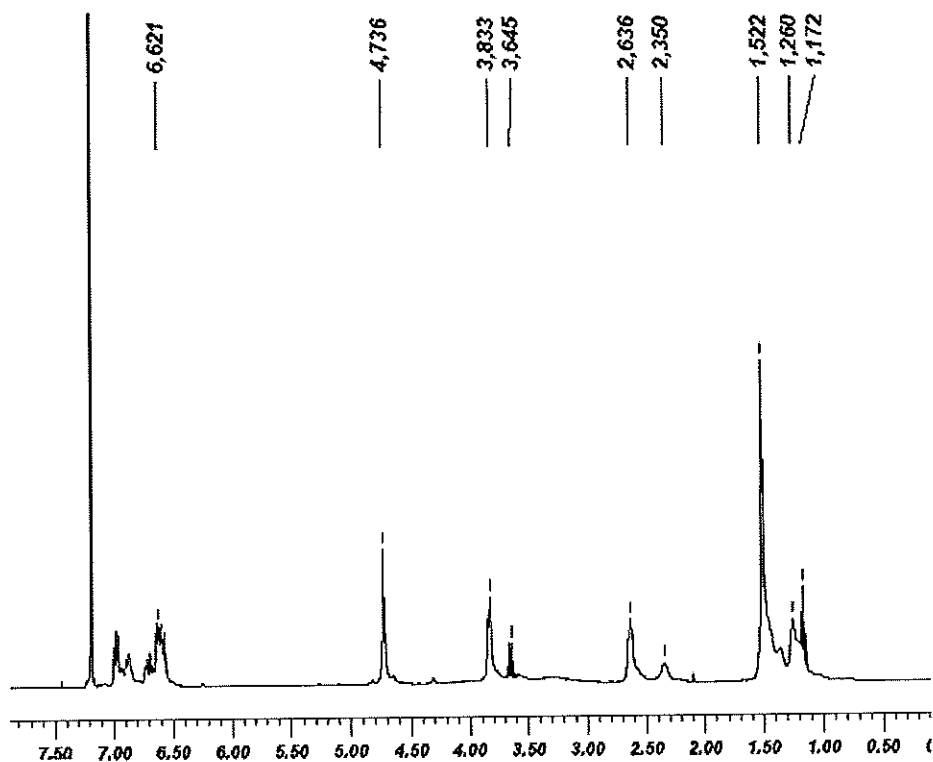
The synthesized product including the oligomers of benzoxazine was investigated for its structure by  $^1\text{H}$ -NMR spectroscopy. General structure of a polybenzoxazine can be seen in Figure 15. The  $^1\text{H}$ -NMR spectrum of polybenzoxazine oligomers is given in Figure 16. Chemical shifts of a characteristic polybenzoxazine precursor placed at 3.83 and 4.73 ppm. These peaks belong to the protons of oxazine ring carbons (e, d). Except for these peaks, resonance for the protons of methylene groups of BA were observed at 1.5 ppm, and other resonances of protons related to the amine group are shown in Table 1.



**Figure 15** General structure of polybenzoxazine precursor

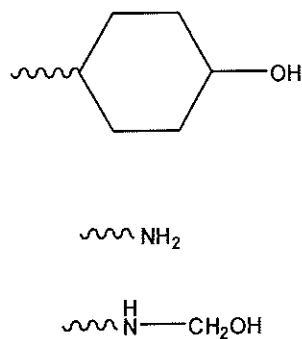
**Table 1** Resonances of protons of polybenzoxazine oligomer

Chemical shift (ppm)	Related group	marking
1.17- 1.53	CH <sub>2</sub> of hda	b,c
1.53	CH <sub>3</sub> of BA	i
2.35-2.63	CH <sub>2</sub> of hda	a
3.83	CH <sub>2</sub> of oxazine ring (Ar-CH <sub>2</sub> N)	e
4.74	CH <sub>2</sub> of oxazine ring (O-CH <sub>2</sub> -N)	d
6.62, 6.95	CH of phenolic ring	f, g, h
7.07	Phenolic end group	-



**Figure 16**  $^1\text{H}$  NMR Spectrum of polybenzoxazine precursors

Doublet peaks around 7.07 ppm point out the free phenolic groups at the chain ends, and they are due to the meta protons of BA. Possible chain-end groups are given in Figure 17. At the chain-ends of polybenzoxazine phenolic groups due to BA and primary amines could be found in addition to the methylol groups bonded to the amine group. Besides, the amine related peaks at the ends of the chains can be assigned for the chemical shifts at around 3.65 ppm which is also related to the methylol groups as mentioned in the work by Ishida [22].



**Figure 17** Possible chain-end groups of polybenzoxazine



### 3.5 FTIR Spectroscopy

In the FTIR spectrum of the precursors, the vibrations of groups are shown in Table 2. The structure of the synthesized oligomers was confirmed with this analysis. In Figure 18, the band at  $822\text{ cm}^{-1}$  belongs to the C-H of 3-substituted benzene ring; this group also gives a peak at  $1500\text{ cm}^{-1}$ . The characteristic oxazine ring vibrations are seen at  $927\text{ cm}^{-1}$  and  $1362\text{ cm}^{-1}$  indicating the attachment of benzene to oxazine ring and wagging of  $\text{CH}_2$  group of oxazine, respectively. As it can be seen in Figure 18, the OH group of methylol and phenolic OH bonded to N of amino methylol show peaks at  $3410\text{ cm}^{-1}$  with very low concentration and at  $2900\text{ cm}^{-1}$ . In Figure 19, most of the peaks appear at the same frequencies with precursors, however; some of the peaks disappeared in the spectrum obtained for the polybenzoxazine. The removal of these bands with the wavenumbers  $927$  and  $1362\text{ cm}^{-1}$  explained the ring-opening of oxazine and polymerization of the precursors.

For the peaks around  $1174\text{ cm}^{-1}$ , Ishida [3] mentions about the C-N-C asymmetric stretching, however; the nitrogen related peaks cannot be easily detected by FTIR spectroscopy. This peak in the spectrum was probably due to the C-O-C stretching of aromatic ether group.

**Table 2** FTIR peaks observed for polybenzoxazine oligomers

IR absorption frequency( $\text{cm}^{-1}$ )	Related part
822	CH of 3-substituted benzene ring (bending vibration)
927	Benzene attached to oxazine (bending vibration)
1174	C-N-C asymmetric stretching
1225,1250	Aromatic ether (C-O-C) stretching
1362	$\text{CH}_2$ wagging of oxazine
1500	CH of 3-substituted benzene ring
2930	$\text{CH}_2$ bands of hexane group
3350, 2900	OH group of methylol and phenolic OH bonded to N of amino methylol
3410	Primary amine

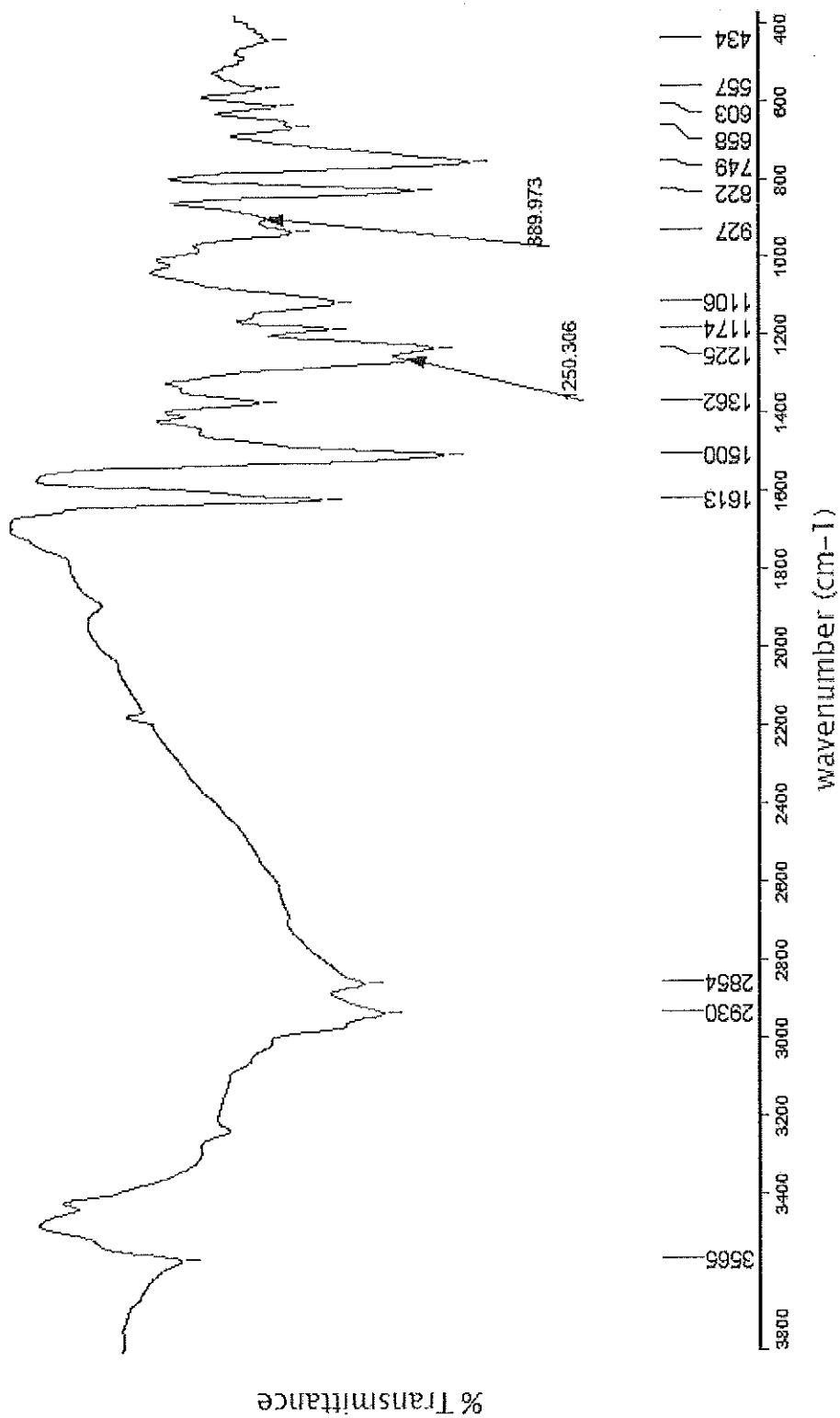


Figure 18 FTIR spectra for polybenzoxazine oligomers

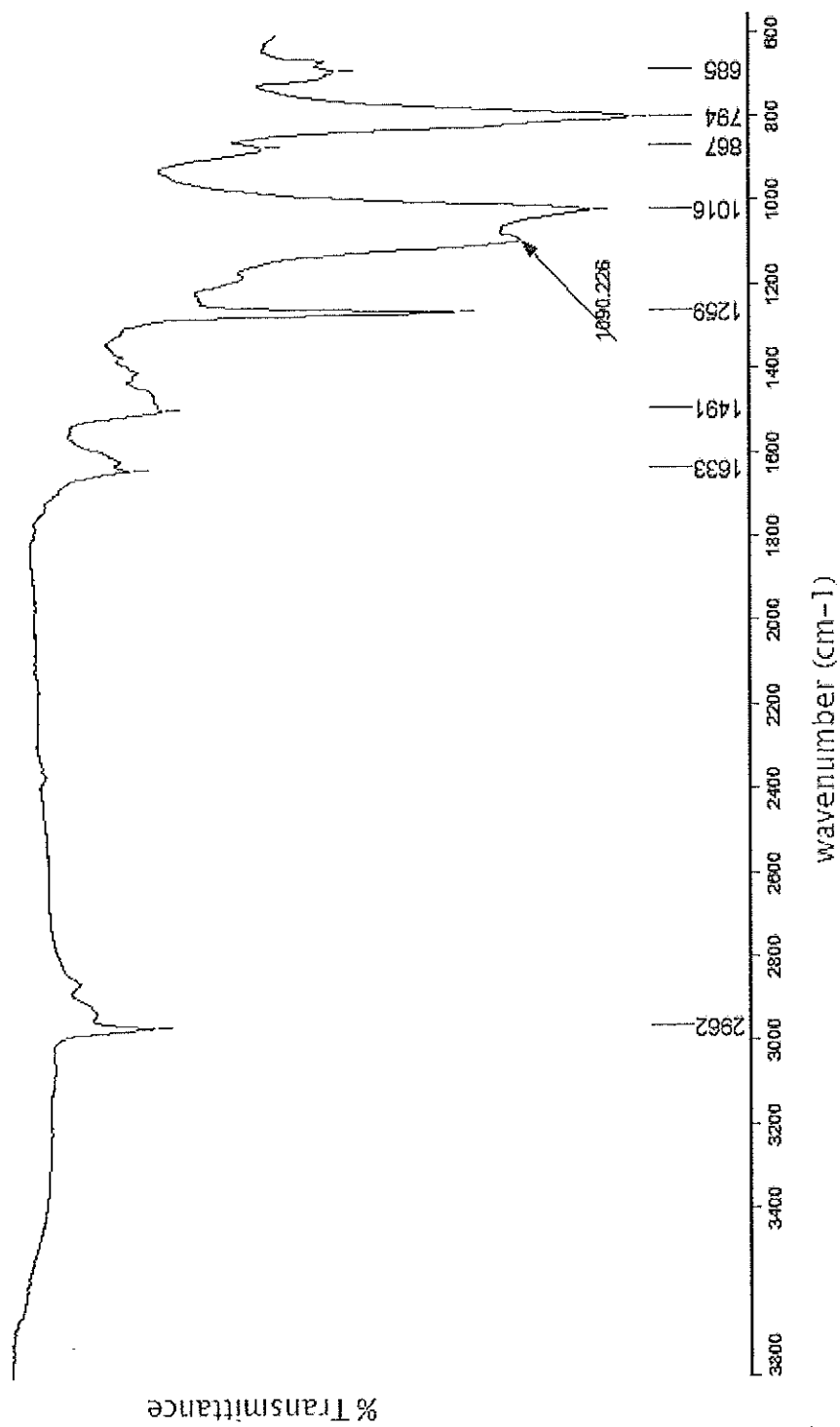


Figure 19 FTIR spectra for polybenzoxazine polymer

### 3.6 DSC Analysis

Polybenzoxazine oligomers show two exothermic peaks in the DSC thermograms. As it can be seen from Figure 20, first peak is centered around 218°C which indicates the polymerization and preliminary crosslinking of the precursors. The next peak is seen at 261°C. This peak is supposed to be the final polymerization as stated by Ishida [3] and Takeichi [2] implies the polymerization reaction at this temperature.

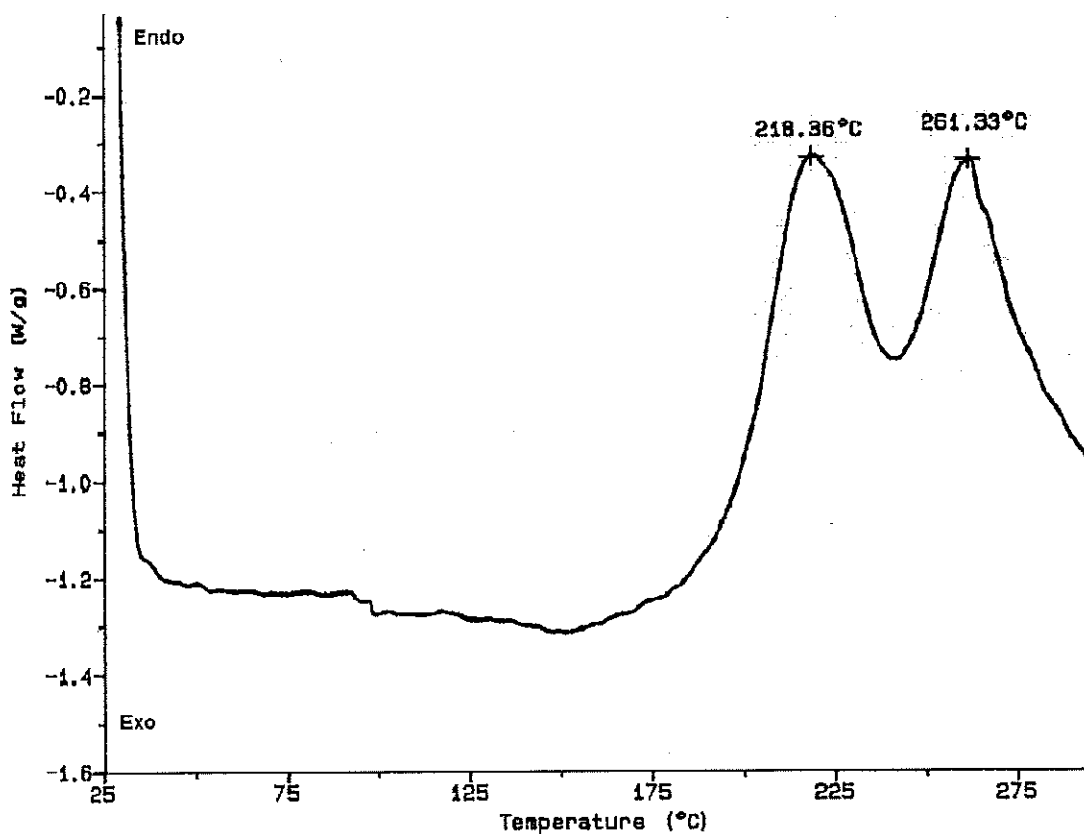


Figure 20 DSC Thermogram of polybenzoxazine oligomers

Behaviors of the materials showed some changes upon curing at higher temperatures. Polybenzoxazine cured at 180°C showed two exothermic peaks at around 212°C and 237°C in Figure 21. (During our work, DSC was replaced by a new one, and the figures after Figure 21 were the measurements of the new instrument.)

First peak in Figure 21 became smaller and then disappeared when the oligomers were cured at 200°C, 215°C, and 245 °C. Figure 22 shows the thermogram obtained for polybenzoxazine which was cured at 200°C. The peak placed at around 212°C in Figure 21 disappeared when the curing temperature increased to 200°C. This showed that this peak is related to curing of the polybenzoxazine oligomers.

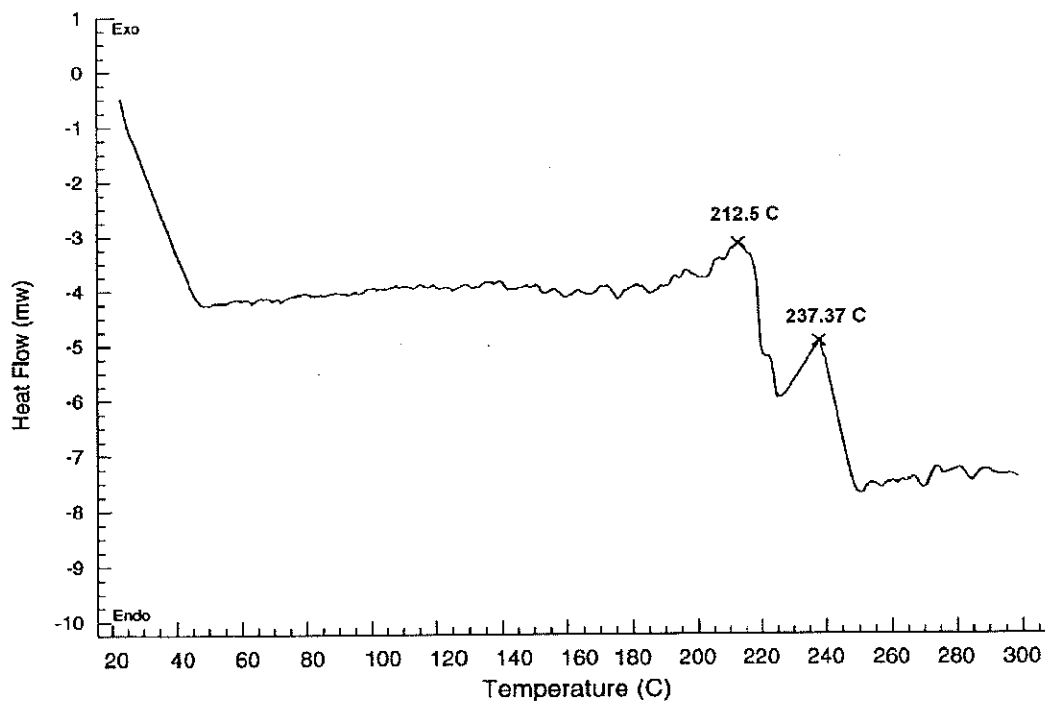
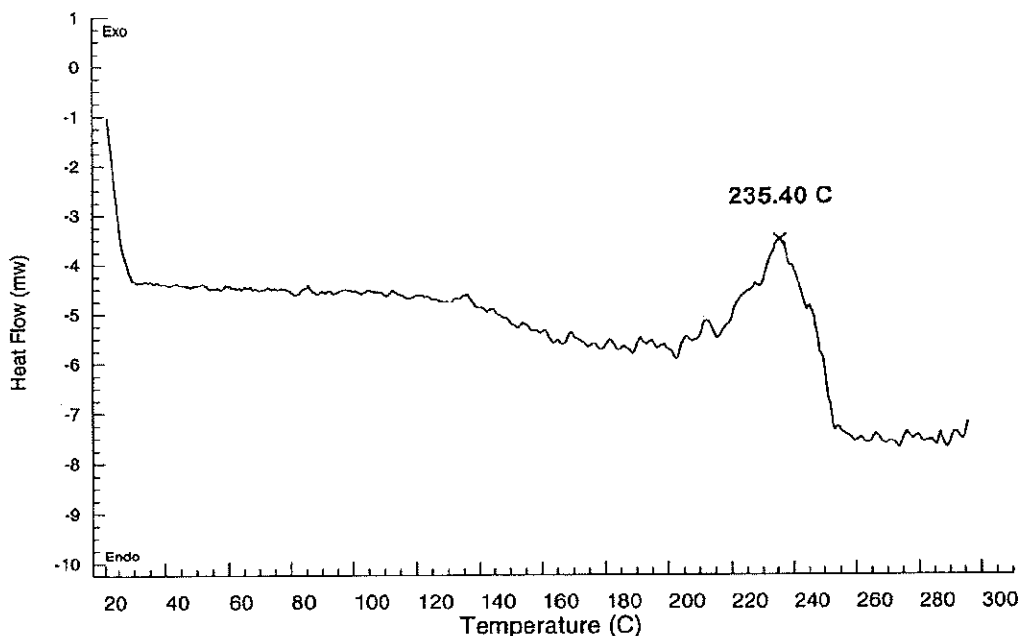
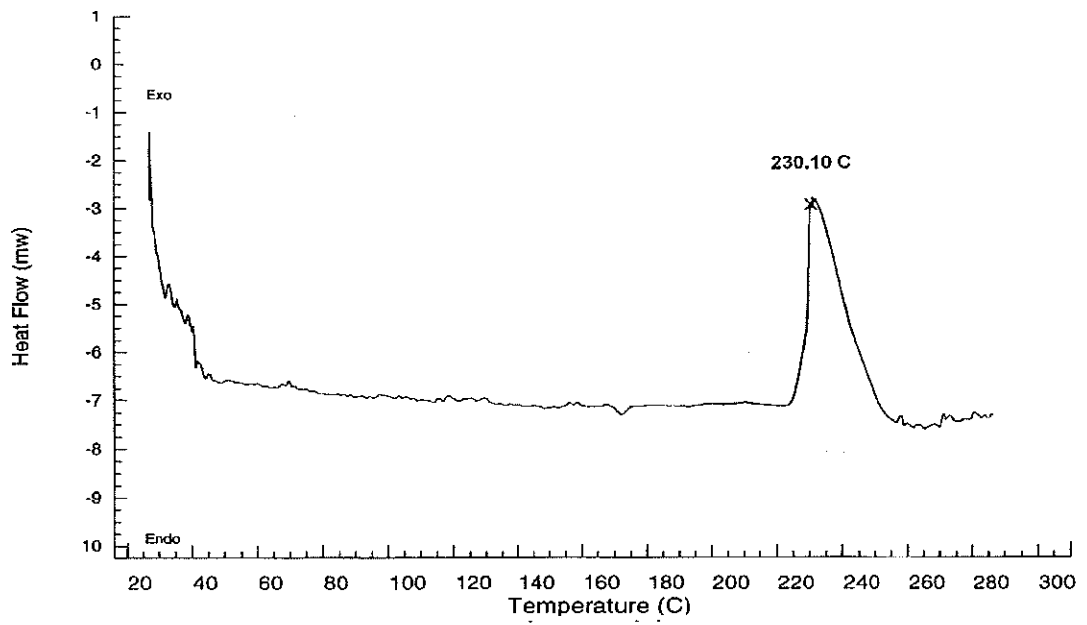


Figure 21 DSC thermogram of polybenzoxazine cured at 180 °C

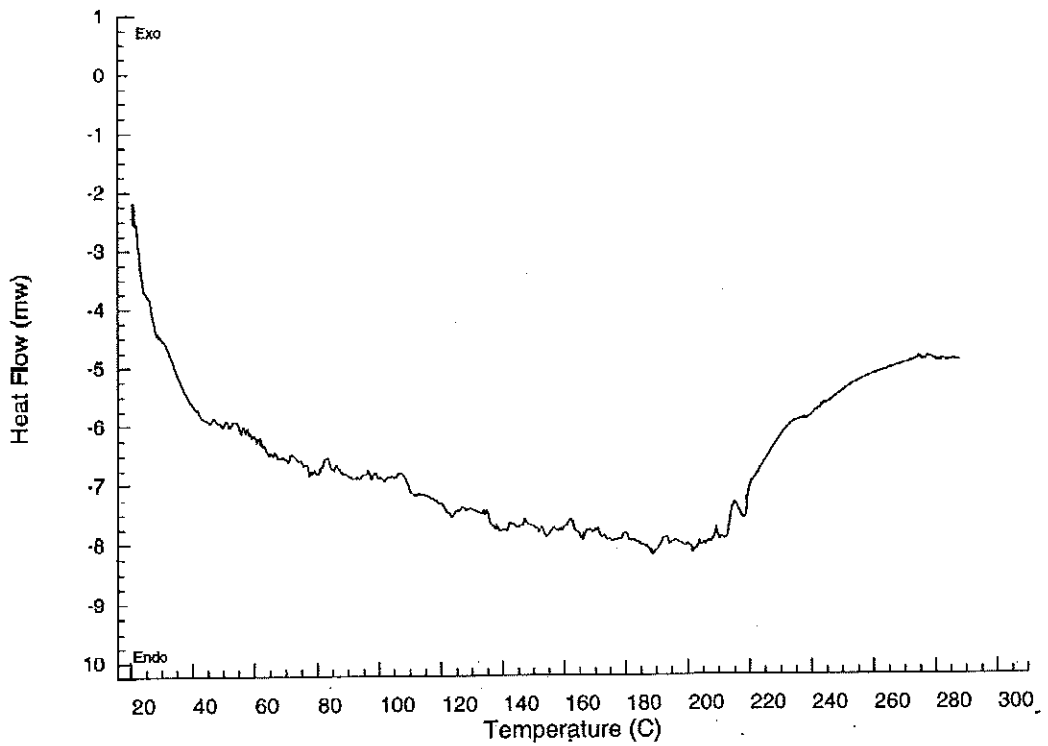


**Figure 22** DSC Thermogram of polybenzoxazine cured at 200 °C

When curing temperature was increased to 215°C, second peak in the thermogram got smaller. In Figure 23, the peak at 230°C lost its intensity when it was compared to the exothermic peak in Figure 22. Raising the curing temperature above 215°C resulted in the complete disappearance of this peak. The thermogram of polybenzoxazine which was cured at 245°C displayed no exothermic peaks in Figure 24. Elevation of curing temperature above 215°C brought about no more polymerization for the polymer.

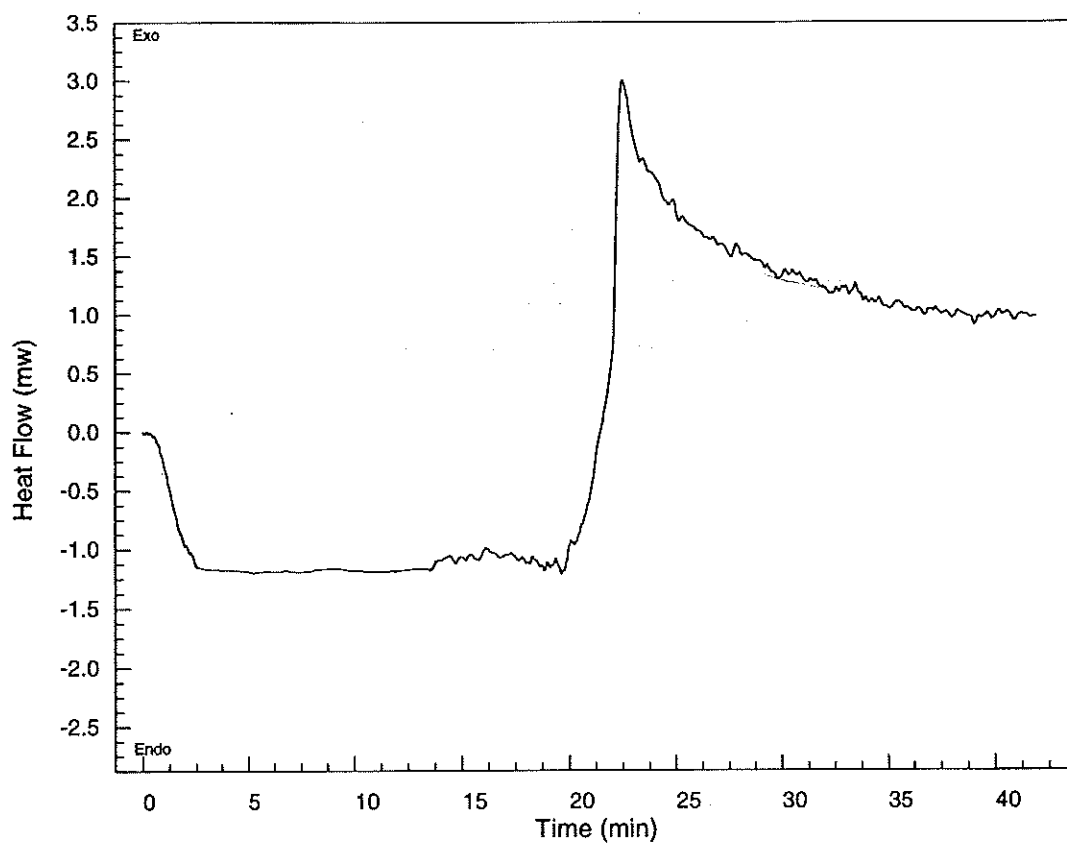


**Figure 23** DSC Thermogram of polybenzoxazine cured at 215 °C



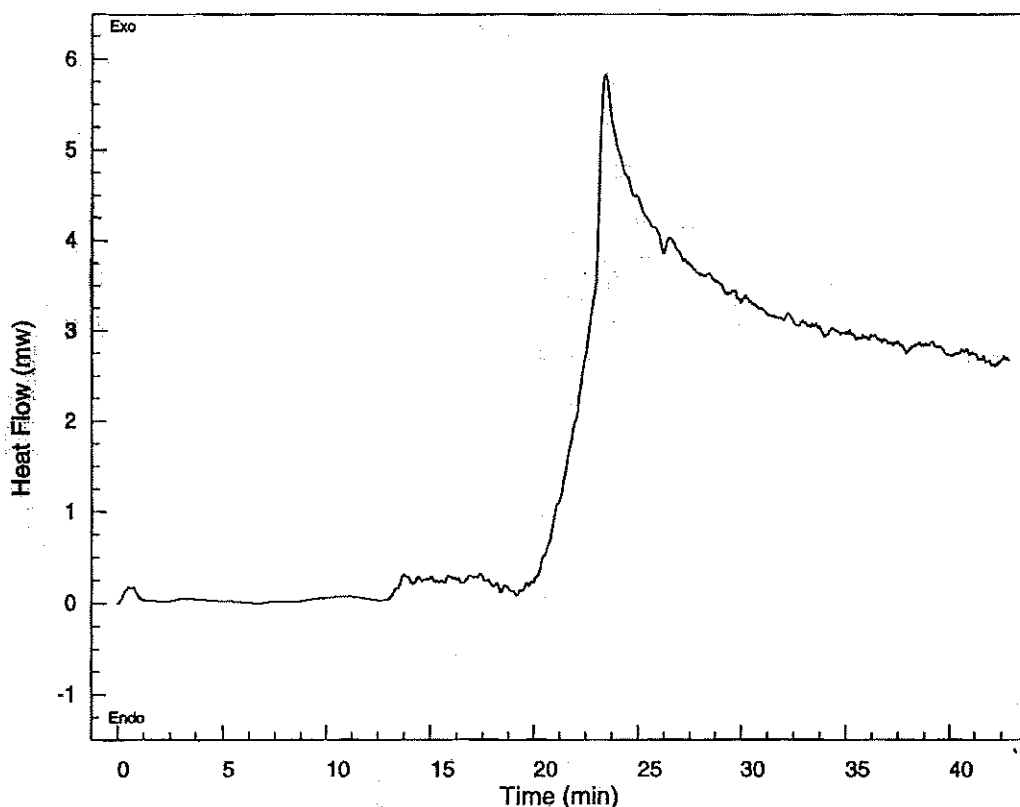
**Figure 24** DSC Thermogram of polybenzoxazine cured at 245 °C

Polybenzoxazine precursors were investigated for their isothermal heating behavior. They were heated to higher temperatures and isothermal heating lasted for 20 minutes at these temperatures. The change in their behavior was examined according to the change of heat flow in isothermal duration at 200, 220, 225, 235°C. The thermograms in Figure 25 and 26 obtained for the precursor polybenzoxazines exhibited a continuous linear line in isothermal period at each temperature. The linear line figured out that precursors did not decompose or degrade when they were exposed to heat at these temperatures for at least 20 minutes.



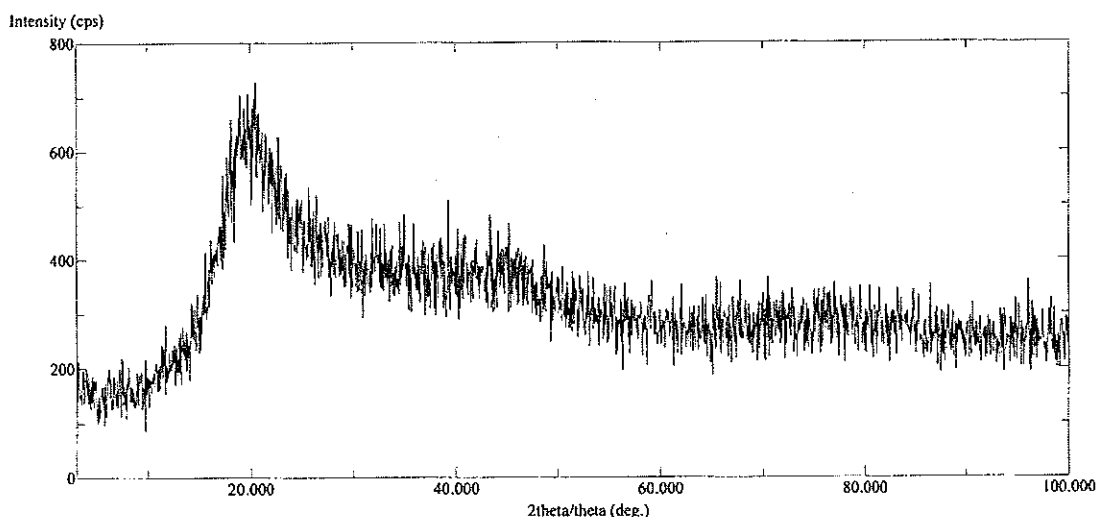
**Figure 25** DSC thermogram of polybenzoxazine precursors isothermally heated at 225 °C





**Figure 26** DSC thermogram of polybenzoxazine precursors isothermally heated at 235°C

DSC Thermograms of polybenzoxazine oligomers and polymers indicated that no melting took place. Since melting takes place for crystalline polymers, the crystallinity of polybenzoxazine was investigated by X-ray analysis. In Figure 27, X-Ray diffraction pattern of polybenzoxazine precursors can be seen where note that the very low intensity indicates that there was no significant crystallization so polybenzoxazine structure was determined to be amorphous.



**Figure 27** X-Ray diffraction pattern of polybenzoxazine precursors

### 3.7 TGA Study

Thermograms for gravimetric analysis gave approximation to polybenzoxazine decomposition. The TGA thermogram of freshly synthesized polybenzoxazine oligomers is given in Figure 28. In this figure, two step weight-losses were observed at 100 and 279°C, respectively. Weight loss began around 100°C indicating the removal of small oligomers and monomers. This thermogram belonged to freshly synthesized oligomers. In the next figure, Figure 29, a TGA thermogram of 2-week-aged sample of polybenzoxazine oligomers can be seen. The thermogram in Figure 29 represented a two-step weight-loss at around 113 and 276°C as in Figure 28; however, the amount of weight losses differed. For the fresh oligomers, the first weight loss was about 19% whereas 14% of the total amount was lost in the aged sample. The second weight loss percentages were 57 and 39 for the fresh and aged oligomers, respectively. Self-polymerization or formation of small oligomers and addition of oligomers may lead to about 8°C shift of the peaks. For thermal gravimetric manner of polybenzoxazine precursors, we can conclude that except for the volatilization and removal of small groups at 100°C, the significant weight loss was observed at 276°C for both fresh and aged polybenzoxazine oligomers.

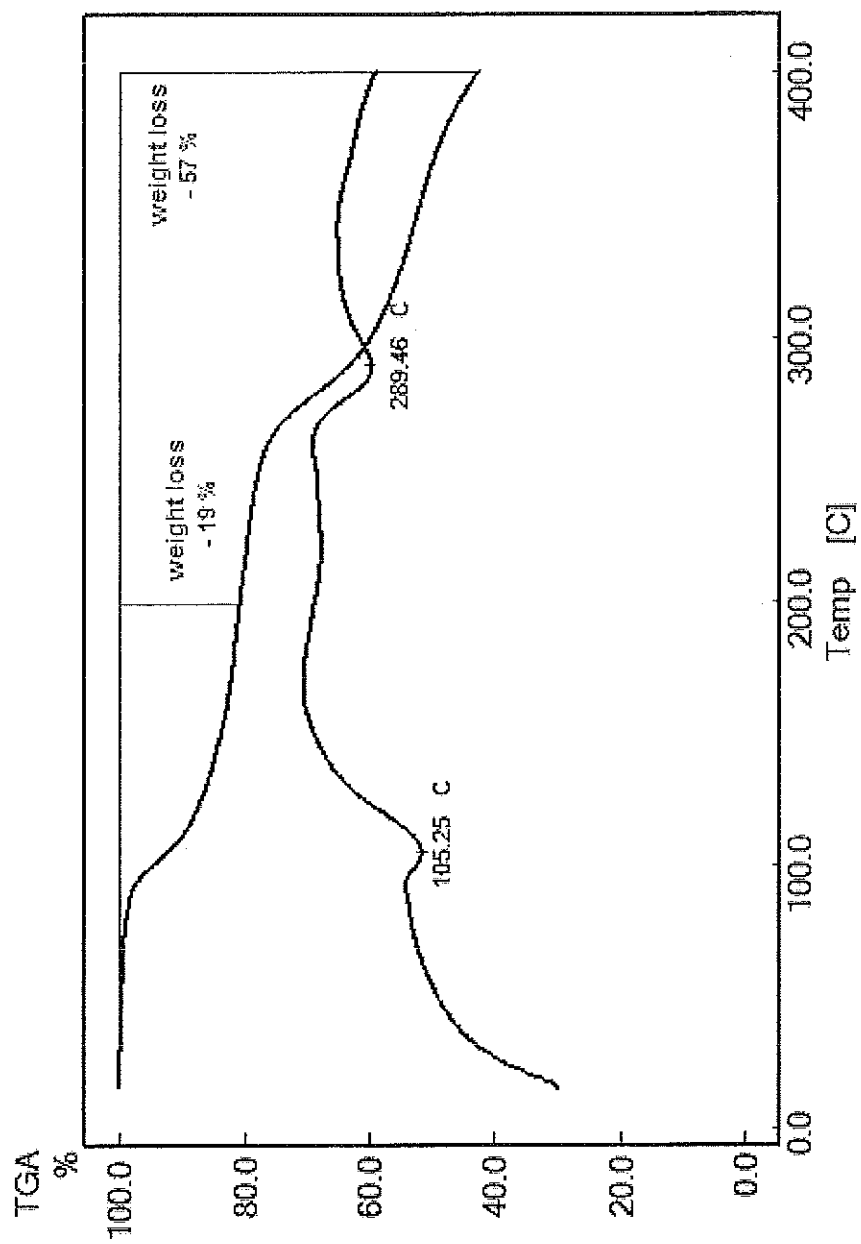


Figure 28 TGA thermogram of freshly synthesized polybenzoxazine oligomers  
(The plot below in the graph shows the derivative of weight loss)

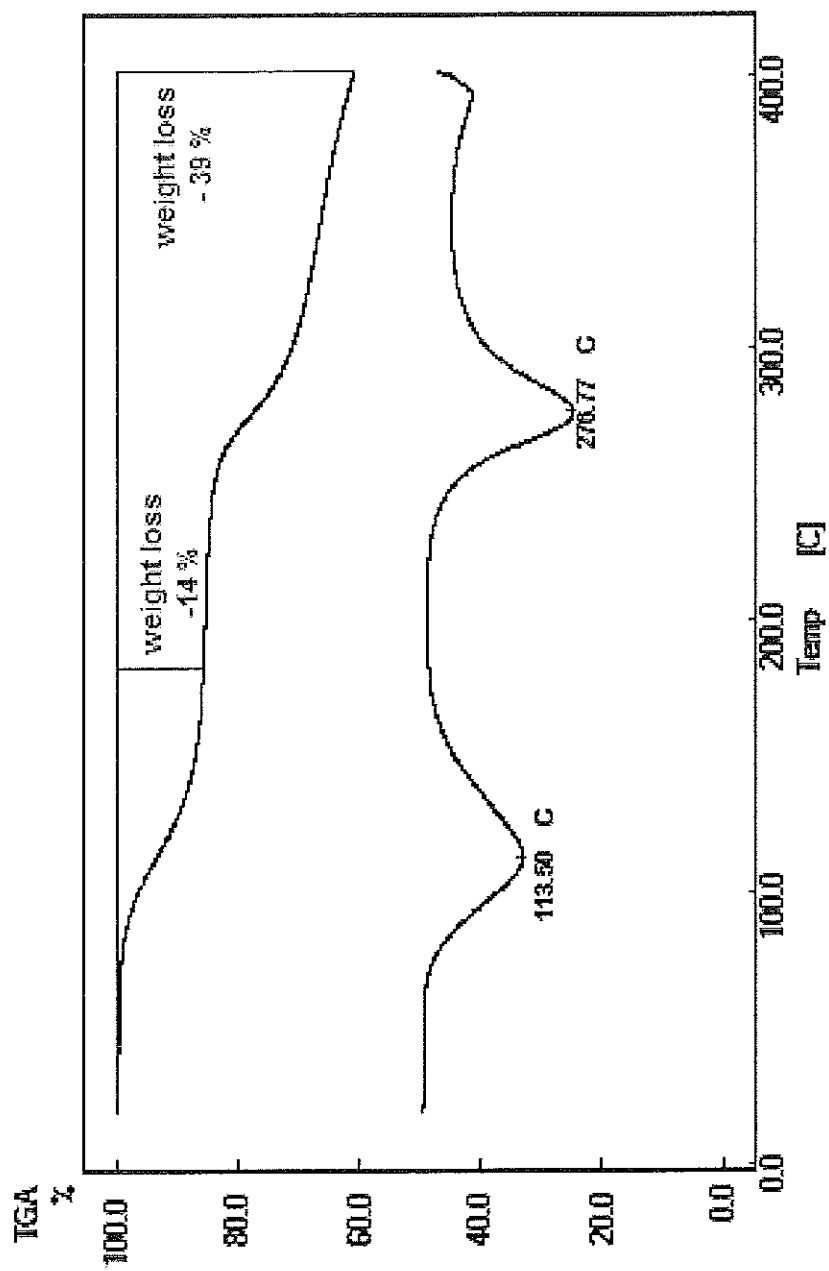


Figure 29 TGA thermogram of 2-week-aged polybenzoxazine oligomers

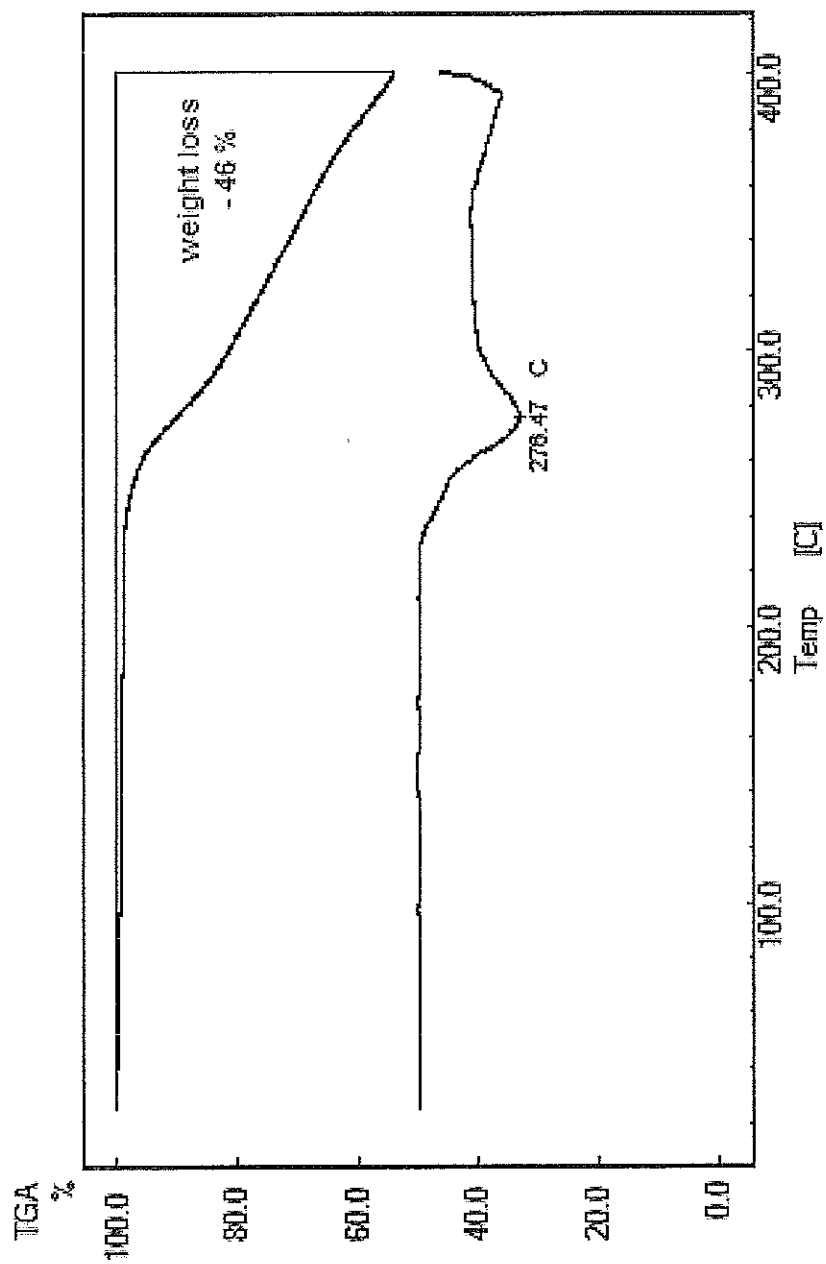


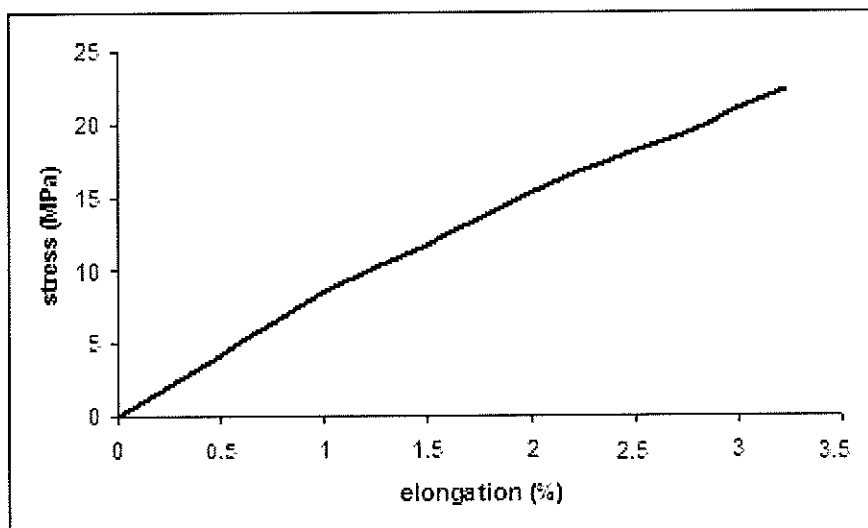
Figure 30 TGA thermogram for polybenzoxazine

Polybenzoxazine cured at 180°C exhibited a one-step weight-loss as seen in Figure 30. In this graph, the first peak around 100°C observed in oligomers was not present at all. Polymerization of oligomers resulted in the removal of this peak and the decomposition was then observed at 276°C which was also obtained for oligomers. The weight-loss peak was observed with a 46% weight reduction of polybenzoxazine.

### **3.8 Mechanical Tests**

The mechanical properties of the polybenzoxazine films which were cured at 180 °C were investigated for their strength. Tensile stress with respect to elongation of polybenzoxazine films were examined as shown in Figure 31. Young's modulus was found to be 0.93 ( $\pm 0.05$ ) GPa at average. Among the polybenzoxazine samples, highest elongation was observed as 3.6%. For the percentage strain, the average value was 2.7 ( $\pm 0.93$ ). Polybenzoxazine films possessed 21.04 ( $\pm 3.56$ ) MPa stress at break. Stress at break was found as 65 MPa with a 2 GPa tensile modulus and the elongation was 4.1% in the study by Takeichi [2]. The difference was due to the MW obtained during our study since the value of MW of precursors was one forth of their result.

The polymer films were mostly broken from the points that they were hold to the instrument. Thus, the values obtained for the analysis were taken for the polybenzoxazine films which were broken around the midpoint of the gauge.



**Figure 31** Stress vs. elongation of a polybenzoxazine sample

## CHAPTER 4

### CONCLUSIONS

A new method was applied in the synthesis of polybenzoxazine precursors. The synthesis of polybenzoxazine oligomers achieved the reaction of PF, hda, and BA through Mannich reaction mechanism was achieved. The time of the reaction was reduced to about 40 minutes from 5 to 20 hour-reflux for completion of the polybenzoxazine oligomer synthesis.

Molecular weight determinations with GPC and viscosity analysis enabled us to understand the end of reaction time. The highest molecular weight could be obtained at around 40 minutes of reaction time before crosslinking reactions of precursors began.

Spectroscopic analysis namely,  $^1\text{H-NMR}$  and FTIR, for the structural determinations supported the formation of polybenzoxazine oligomers. The oligomers obtained with this procedure showed more intense characteristic peaks for both  $^1\text{H-NMR}$  and FTIR spectra.

Thermal analysis of polybenzoxazine precursors and polybenzoxazine samples showed two exothermic peaks for DSC analysis. First peak was related to the curing of precursors in addition to the preliminary crosslinking reactions. This peak disappeared for polybenzoxazines cured above  $180^\circ\text{C}$ . Second peak stood for higher polymerization of polybenzoxazine precursors, and it is not observed in the thermograms of polybenzoxazines which were cured at temperatures above  $215^\circ\text{C}$ .

Polybenzoxazines were also tested for their reaction against heat so they were heated isothermally. The isothermal heating lasted for 20 minutes and the results showed that there had been no significant change in the behavior of samples during this period. Polybenzoxazine precursors were determined to be heat resistant materials according to this analysis.



TGA results of polybenzoxazine precursors displayed two-step weight-loss. First weight-loss was related to the removal of monomers and small oligomers at around 100°C whereas the second weight-loss was observed around 276°C. There had been a decrease from 19% to 14% and 57% to 39% in the weight-loss amount for freshly synthesized and aged oligomers, respectively. Volatilization of small oligomers and monomers in time lead to this reduction in weight-loss amounts. For the polybenzoxazine case, 45% weight-loss was observed with a one step at around 276°C since the oligomers transformed into polymeric forms.

Polybenzoxazine films exhibited an average stress at break of 21.04 ( $\pm 3.56$ ) MPa. The average elongation was found to be 2.7 ( $\pm 0.93$ ) %. Young's modulus for the polybenzoxazine films was calculated as 0.93 ( $\pm 0.05$ ) GPa at average.

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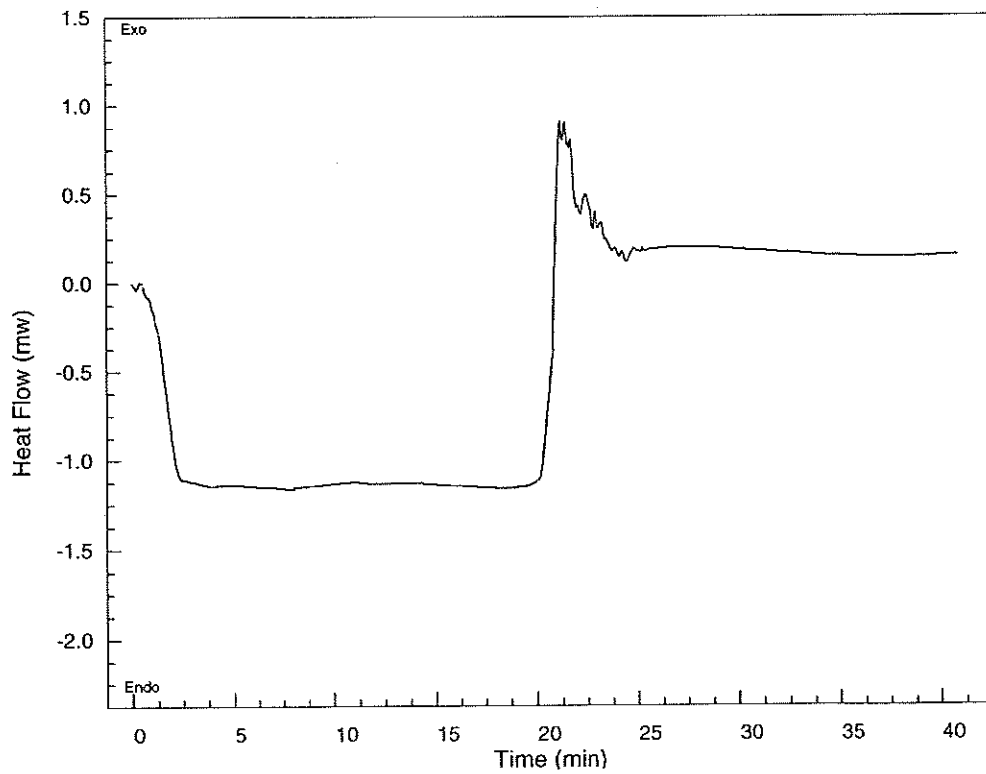
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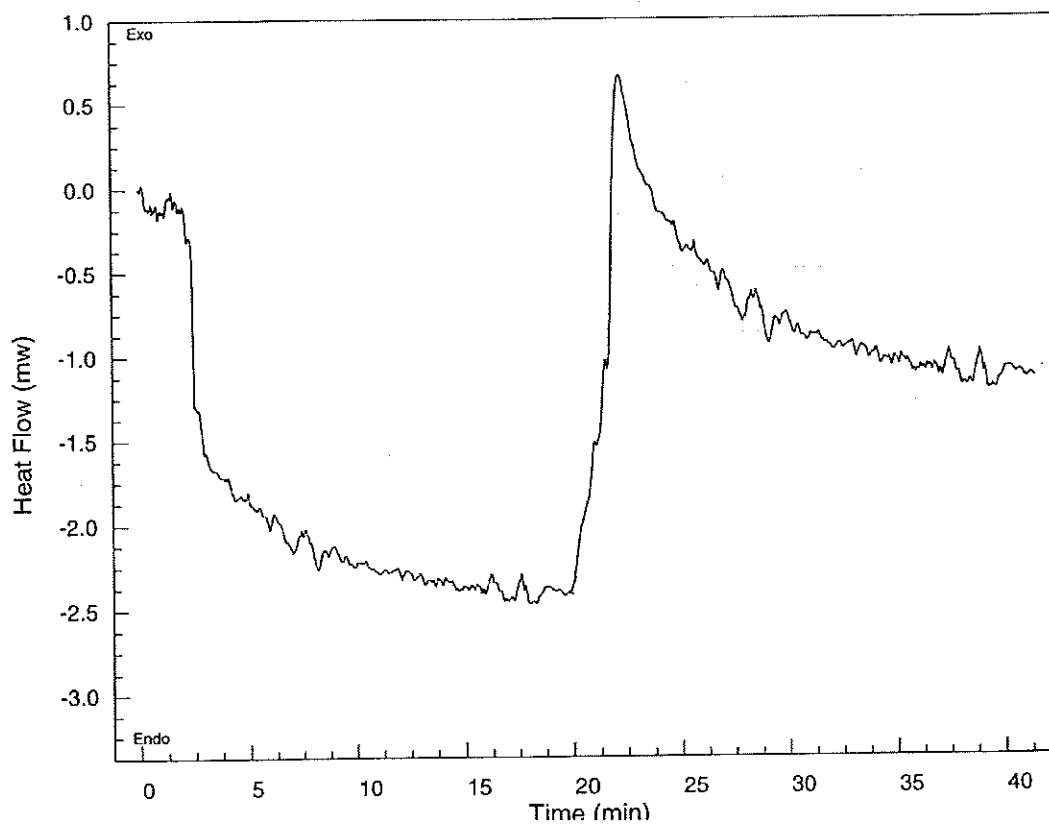
## APPENDIX A

### DSC THERMOGRAMS OF POLYBENZOXAZINES FOR ISOTHERMAL RUNS



**Figure A. 2** DSC thermogram of polybenzoxazine precursors isothermally heated at 200°C





**Figure A. 3** DSC thermogram of polybenoxazine precursors isothermally heated at 220°C

## APPENDIX B

### TENSILE PROPERTIES DATA

**Table B. 1** Stress at break for polybenzoxazine samples cured at 180°C

Sample no.	$\sigma$ (MPa)	$\varepsilon$ (GPa)	Elongation (%)
1	24.4	0.83	3.6
2	23.7	0.94	3.2
3	17	0.74	2.7
4	19	0.97	2.4
*5	12	0.88	1.5
<b>Av.</b>	21.04 ( $\pm 3.56$ )	0.93 ( $\pm 0.05$ )	2.7 ( $\pm 0.93$ )

\* Excluded data