İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

BENZOXAZINE CONTAINING POLYESTER THERMOSETS WITH IMPROVED ADHESION AND FLEXIBILITY

M. Sc. Thesis by
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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BENZOKSAZİN İÇEREN POLİESTER TERMOSETLERİNİN YAPIŞKANLIK VE ESNEKLİK ÖZELLİKLERİNİN GELİŞTİRİLMESİ

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HAZİRAN 2010

FOREWORD

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June 2010 Alev TÜZÜN

Chemist

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ABBREVIATIONS

PVA : Poly(vinyl alcohol)
UP : Unsaturated polyester
PET : Poly(ethylene terephthalate)
PBT : Poly(butylenes terephthalate)
PTT : Poly(trimethylene terephthalate)
DMT : Dimethyl terephthalate
EG : Ethylene glycol
B-a : Bisbenzoxazine
P-a : *N*-Phenyl-3,4-dihydro-2*H*-1,3-benzoxazine
B-m : 6, 6’ - (propane-2,2-diyl)bis(3-methyl-3,4-dihydro-2H-benzo[e][1,3] oxazine)
B-a : 6 , 6’- (propane-2,2-diyl) bis (3-methyl-dihydro-2H-benzo[e][1,3] oxazine)
BBD : 5, 5'-(6,6'-(propane-2,2-diyl)bis(2H-benzo[e][1,3]oxazine-6,3(4H)-diyl))dipentan-1-ol
BBA : 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid
PBCT : Poly(benzoxazine-carboxyterephthalate)
PBCHP : Poly(benzoxazine-carboxyhexafluro isoproplylidene phthalate)
ABTS : 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)
M_n : Number Average Molecular Weight
M_w : Molecular Weight
^{1}H-NMR : Nuclear Magnetic Resonance Spectroscopy
FT-IR : Fourier Transform Infrared Spectrophotometer
ASTM : American society for testing and materials
DIN : German patent
DSC : Differential scanning calorimetry
TGA : Thermal gravimetric analysis
DMA : Dynamic mechanical analysis
GPC : Gel-permation chromotography

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M_n : The number average molecular weight
M_w : The weight average molecular weight
M_w/M_n : The molecular weight distribution

BENZOXAZINE CONTAINING POLYESTER THERMOSETS WITH IMPROVED ADHESION AND FLEXIBILITY

SUMMARY

High molecular weight polyesters containing thermally curable benzoxazine units in the main chain have been synthesized. For this purpose, first the diol functional monomer is synthesized through the Mannich and subsequent ring closure reactions of bisphenol-A, paraformaldehyde, and 5-amino-1-pentanol. Polycondensation of the resulting benzoxazine and pyromellitic dianhydride or 4-4'-(hexafluroisoproplylidene) diphatalic anhydride with or without dibutyltin laurate yielded the corresponding polyesters with the molecular weights between 5800 and 7000 Da. The structures of the precursor diol monomer and the resulting polyesters are confirmed by Fourier transform infrared spectroscopy and proton nuclear magnetic resonance spectroscopy analysis. Curing behavior of both the monomer and polymers has also been studied by differential scanning calorimetry. Flexible films of the polyesters are obtained by solvent casting on tin plates and they further cross-linked. The films exhibited high flexibility and adhesion on the tin plates, which are determined by ASTM and DIN tests. Thermal properties of the cured polymers are also investigated by thermogravimetric analysis.

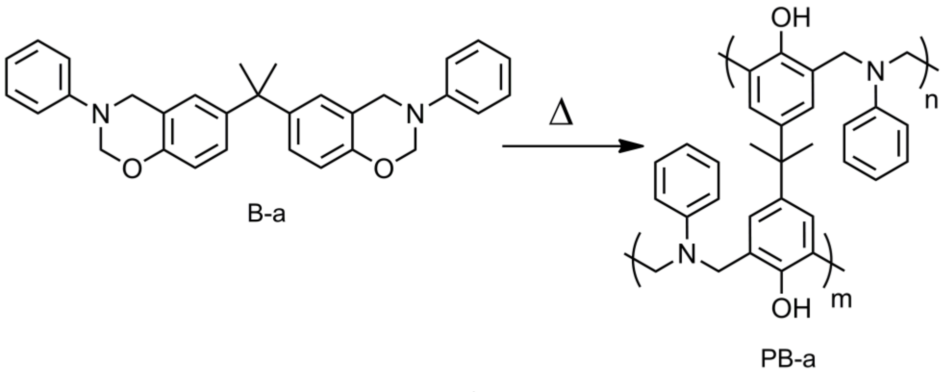
BENZOKSAZİN İÇEREN POLİESTER TERMOSETLERİNİN YAPIŞKANLIK VE ESNEKLİL ÖZELLİKLERİNİN GELİŞTİRİLMESİ

ÖZET

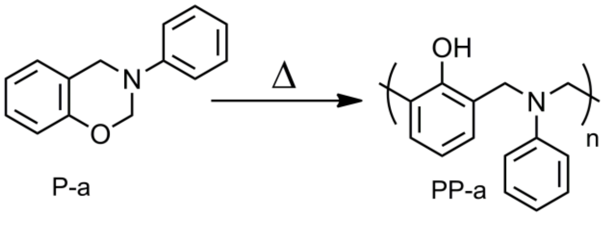
Ana zincirinde termal olarak kürlenebilen benzoksazin ünitesi içeren, yüksek molekül ağırlığına sahip poliesterlerin sentezi gerçekleştirildi. Bu amaçla ilk olarak, diol fonksiyonalitesine sahip monomer; bisfenol-A, paraformaldehit ve 5-amino-1 pentanolün Mannich ve halka kapanması reaksiyonları ile sentezlendi. İkinci aşamada elde edilen benzoksazin ve piromelitic dianhidrit veya 4-4'-(heksafloropropiliden) diftalik anhidritin katalizörlü ve katalizörsüz polikondenzasyon reaksiyonu yapıldı. Bu polimerizasyon sonucunda 5800 ve 7000 Da arasında molekül ağırlığına sahip polimerler elde edildi. Diol-momomerinin ve poliesterlerin yapıları FT-IR ve ^{1}H-NMR spektrokometreleri ile belirlendi. Monomer ve poliesterlerin termal davranışları DSC ve TGA ile çalışıldı. Poliesterlerin metal üzerindeki esnekliği çözücü içerisinde çözünüp hazırlanan filmlerin kürlendirilerek ASTM ve DIN göre testlerine yapışkanlık ve esneklik özellikleri test edildi. Poliester filmler metal üzerinde yüksek yapışkanlık ve esneklik özellikleri gösterdiler.

1. INTRODUCTION

Polybenzoxazines are relatively new class of materials, which are alternative to phenol formaldehyde resins. They have a good combination of attractive properties such as (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) high T_g, in some cases higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, and (vi) release of no by-product during curing [1]. The cured materials also possess thermal and flame retarding properties of phenolics along with better mechanical performance. The striking feature is connected with dimensional stability during the conversion from monomer to polymer due to the ring opening nature of the polymerization. In fact, the polymerization occurs through thermal activation of the corresponding benzoxazines without any catalyst and without generating any by-products (Equatian 1.1 and 1.2) [2-3].



(1.1)



(1.2)

Moreover, benzoxazine monomers can be prepared simply from inexpensive and commercially available phenols, primary amines, and formaldehyde [4,5-6].

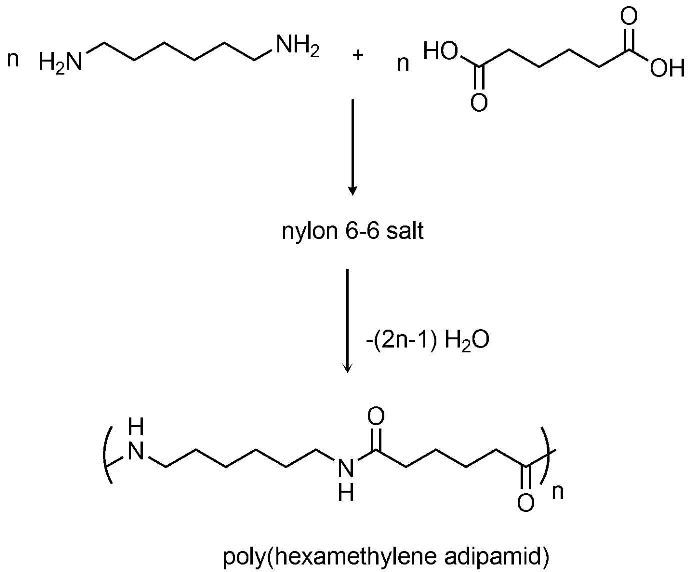
Therefore, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using appropriate starting materials and polybenzoxazine properties can be tailored. Polybenzoxazines prepared from the monomer precursors form some limitations on their use in practical applications. The monomers are usually powder and processing into thin films is rather difficult. Additionally, the formed polymers are brittle as a consequence of the short molecular weight of the network structure. To overcome these limitations various approaches were proposed. These include (i) synthesis of specially designed novel monomers [7-8], (ii) blending with polymers or fillers and fibers [9-10], or (iii) synthesis of end-chain, side chain or main-chain polybenzoxazines [11-12]. In spite of the significant improvements on some properties, the desired flexibility and adhesion could still not be achieved. Aiming at expanding their industrial applicability it seemed appropriate to prepare a family of highly flexible benzoxazine polycondensates tailored to meet different requirements, depending on the specific application. The concept of this study is based on creating polymeric backbones integrating segments that induce molecular flexibility and adhesion on metals on one hand, and that comprise thermally curable benzoxazine moieties on the other hand. This study describes synthesis, characterization and thermal curing of polyesters containing benzoxazine moieties in the main chain from diacid anhydrides and diol containing bisbenzoxazines. The obtained polymers exhibit an enhanced adhesion and flexibility even after thermal curing.

2. THEORETICAL PART

2.1 Condensation (Step-Growth) Polymerization

Step-growth polymers, also called **condensation polymers**, are made by combining two molecules while, in most cases, removing a small molecule, generally water or an alcohol. The reacting molecules have reactive functional groups at each end. Functionality of monomers is important in these reactions. These monomers; dicarboxylic acids, diols or their derivates, etc., are active on both of their sides where they give reactions and a multifunctional polymer is obtained.

Carothers, at Du Pont company, obtained nylon 6,6 ,the first commercial polymer, from condensation (step-growth) of adipic acid and hexamethylenediamine [13] (Equation 2.1).



(2.1)

Nylon found wide use in textiles, carpets and many other applications. The extended applications of nylon precipitated a search for new ‘super fibers’ with super strength and super heat resistance. Nylons have extremely good abrasion resistance. But the largest plastics applications of nylons have been in mechanical engineering [14].

Polyesters, polyamides, polycarbonate and polyurethanes are known types of condensation polymers. Examples of polymers are shown as respectively (see Figure 2.1):

Polyester

Polycarbonate

Polyamide

Polyurethane

Figure 2.1 : Examples of step-growth polymers.

Condensation poylmers, have generally low molecular weight and is requried heat for synthesis. The end group of chain is active, so that group of short chain react with longer chains in the late state of polymerization. Because of that, polymer is obtained at the end of the polymerization. Most of condensation polymers involves polar groups at their side chain and thereby this affects chain-chain attractions, and there is also strong intermolecular interaction between the polymer backbone. If these involve hydrogen bonds, crystallinity and tensile strength enhance. So step-growth polymers such as polyesters and polyamides possess more robust mechanical properties, including toughness, stiffness, and higher temperature resistance.

Polyesters are important cormmercial materials.

2.2 Polyesters

Among the polycondensation polymers, the most important and widely used today is polyesters. Polyesters are defined as polymers containing at least one ester linking group per repeating unit. They can be obtained by a wide range of reactions, the most important being polyesterifications between dibasic acids and diols or their derivatives (see Figure 2.2) [15].

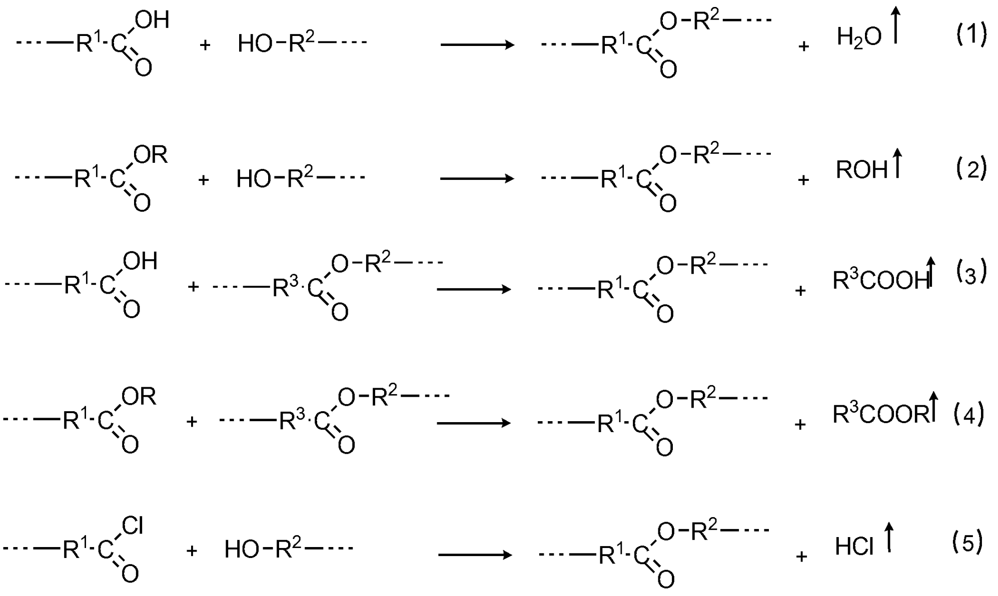


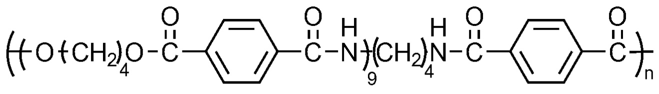
Figure 2.2 : Polyesterification of dibasic acids and diols or their derivates.

Many other reactions for the synthesis of polyesters, such as reactions between:

- dicarboxylic acid salts and dialkyl halides,
- chlorocarbonyloxy-terminated monomers and diacids,
- bisketenes and diols.

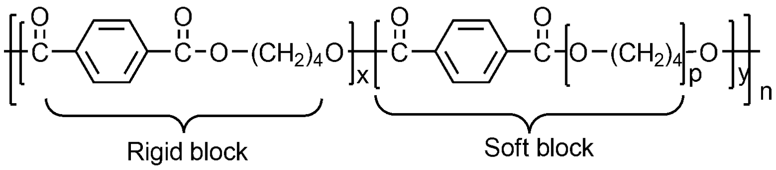
These reactions are not available for obtaining high-molar-mass polyesters economically since limited to very specific laboratory-scale syntheses. However, there is two notable exception rections which are the ring-openning polymerization of lactones and lactides, to produce degradable polyesters and biosynthesis of aliphatic polyesters by bacteria [16].

Depending on the nature of monomers (Figure 2.2), polyesters exhibit an enormous variety of structures, properties, and applications: (i) aliphatic polyesters which consist of low-molar-mass macromonomers ending with hyroxy groups made use of synthesis of polyurethanes, (ii) aliphatic-aromatic polyesters such as poly(ethylene terephthalate) (PET) and poly(buthylene terephthalate) (PBT) are commercial materials in use films, fibers and engineering termoplastics, (iii) wholly aromatic copolyesters have (a) high mechanical properties, (b) heat resisitance and (c) flexural strenght, (iv) unsaturated polyesters and alkyd resins are considerably used in coating and composite industiries and (v) the other polyester members are polyester thermoplastic elastomers, such as PBT and poly(oxytetramethylene) (PTMO) block copolymer, have commercial applications and present the typical mechanical properties of rubber. Many other ester-containing polymers could be added to polyester family for instance polycarbonates (see Figure 2.1) polyesteramides, or block copolyesters(see Figure 2.3(a) and 2.3(b)).



(a)

Polyesteramide



(b)

Block copolymer

Figure 2.3 : Examples for polyesteramide and block coppolymer

Polyesters are now one of the economically most important classes of polymers. Production of polyesters is increasing annually and is expected to continue to do so during the next years. This production is driven by packaging applications, due to a very favorable image of environmentally friendly and recyclable polymers and by textile applications, due to a strong demand in the far-east area to satisfy the needs of an increasing population. In figure 2.4 the dispersion of chemical fibers on the world [17]. So we could see the importance of polyester on the world.

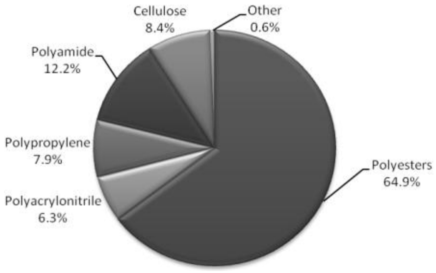


Figure 2.4 : Share of different types of chemical fibres on the world market.

The historical development of polyesters from past to these days is showen in table 2.1

Table 2.1 : The historical development of polyesters from past to these days

Years	Prominent developments	Applications and properties
1910-1920s	The General Electric Company researched on the chemistry of phtalic anhydride-glycerol reaction and developed the technology of alkyd resins.	These resins are soluble in aromatic and aliphatic hydrocarbons and using coatings, varnishes and paints.
1930s	This year is the beginning of modern polyester chemistry. Carothers [18-19] proved the macromolecular theory of Staudinger from experimental studies on reactions between aliphatic dibasic acids and diols and established the relationships between degree of polymerization, conversion, functionality, and gel point, that is, the base relationships of step-growth polymerization. And also nylon was discovered by carothers at DuPont Company. At the end of the 1930s, Carothers and Flory obtained a new thermosetting resin [20], based on unsaturated polyesters. Unsaturated polyesters are synthesized by reacting mixtures of saturated and unsaturated dibasic acids or anhydrides with aliphatic 1,2-diols.	Have low melting points, were sensitive to hydrolysis and not suitable for commercial applications. Nylon’s high tenacity fibers are used for seatbelts Excellent abrasion resistance. High resistance to insects, fungi, animals, as well as molds, mildew, rot and many chemicals. Unsaturated polyester (UP) resins found their first applications in combination with glass fibers for protective radar domes during World War II [54], UPs are now one of the most important matrix resin for glass-fiber-reinforced composite materials.

1940s	Whinfield synthesized high-melting-point fiberforming polyesters from terephthalic acid and aliphatic diols [21-22].	Major commercial polymers. PET is now one of the most produced polymers, primarily for textile and packaging applications. PBT finds uses as solid-state molding resin.
1950s	Technology is available for using UP.	The first commercial applications of aliphatic polyesters appeared only in the late 1950s and the 1960s, with the development of polyurethane foams and elastomers.
1970s	A number of polyester block copolymers were reported in the literature, but only one found commercial success: the polyesterether block copolymers marketed by DuPont under the tradename Hytrel [23].	Hytrel exhibiting the characteristics of thermoplastic elastomers [23].
1980s	Attention was focused on wholly aromatic polyesters.	These polymers have commercially applications in high-technology markets.
1990s	The importance of environment began to be popular. The versatility of the ester linkage, able to undergo hydrolysis, alcoholysis, and acidolysis in some conditions, makes polyesters the polymers of choice to fulfill the increasing	PET production is also strongly driven by the demand of recyclable polymers. The markets of poly(lactones), poly(lactides) and copolyester containing aliphatic moieties were improved.

2.2.1 The Relationsips Between Structure and Properties

The nature—aliphatic or aromatic—of the $-R^1-$ and $-R^2-$ in polyester chains (see Figure 2.2) exerts a profound influence on the properties of polyesters and define four main classes of linear polyesters [24]:

1. Aliphatic polyesters are low-melting (40–80^{o}C) semicrystalline polymers or viscous fluids and present inferior mechanical properties. Notable exceptions are poly(α-hydroxy acid)s and poly(β-hydroxy acid)s. Due to low hydrolytic and chemical resistance and to low melting point, aliphatic polyesters have long been considered to be limited to applications such as plasticizers or macromonomers for the preparation of polyurethane foams, coatings, or elastomer.

2. Aromatic–aliphatic polyesters, are generally high-melting (150–270^{o}C) semicrystalline materials such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) that find applications as engineering thermoplastics, films, or fibers and for some other applications with amorphous engineering plastics such as polycarbonate.

3. Wholly aromatic polyesters, are either high-T_g amorphous polymers or very high melting semicrystalline polymers that often exhibit liquid crystalline properties. Amorphous polyarylates are light-amber transparent materials which exhibit mechanical properties comparable to that of unfilled PET in terms of tensile or flexural strength and modulus.

4. Polyester thermoplastic elastomers, which are obtained by replacing a part of the R^2 diol by dihydroxy polyether macromonomer, present biphasic morphology and rubberlike properties.

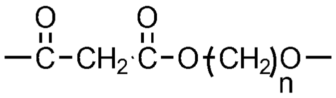
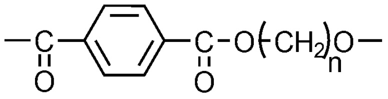
2.2.2 Thermal Properties of Polyesters

There are close correlations between melting temperature and a number of important polymer properties: high-melting polymers generally present high tensile strength and modulus, high deflection temperature under load, high thermal resistance, low elongation at break, and low solubility in common solvents.

Melting is a thermodynamic equlibrium so melting temperature effect the entropy (ΔS) ana enthalpy (ΔH). So T_m can be obtained information about polymer properties like chain flexibilty since it is am measure of intermolecular interaction. Therefore

T_m is considerably sensitive to form of R^1 and R^2 (see Figure 2.1). In aliphatic polyesters when chain length grow, melting point increas. But at equivalent ester group contetnt, T_m of aromatic polyesters is higher than T_m of aliphatic polyesters (Table 2.2). Aromatic– aliphatic polyesters with even numbers of methylene groups melt at higher temperature Aromatic polyesters that do not contain any flexible structural units are often nonmeltable or extremely high melting polymers that cannot be processed.

Table 2.2 : Melting Point, T_m (°C), and Glass Transition Temperature, T_g (°C), of Poly(alkylene adipate)s and Poly(alkylene terephthalate)s.

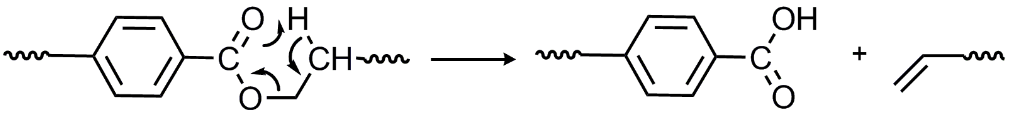
Repeating – Unit Formula	 $-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O\left(CH_2\right)_nO-$			
n	T_g[a]	T_m[b]	T_g[c]	T_m[c]
1	-	-	101	269
2	-63	50	69[a]	265[b]
3	-59	45	35	233
4	-74[d]	55,8[d]	17[a]	232[b]
5	-	61[e]	10	134
6	73[e]	-	-9	154
7	-	-	-	85

[a] [25] [b] [26] [c] [27] [d] [28] [e] [29]

Glass transition temperature (T_g) reflects the segmental mobility in the amorphous phase and follows similar trend as that observed for T_m, increasing chain rigidity leading to increasing T_m and T_g. Amorphous aliphatic polyesters are usually low-T_g viscous oils while amorphous aromatic polyesters are high-T_g polymers, some of which find applications as engineering thermoplastics.

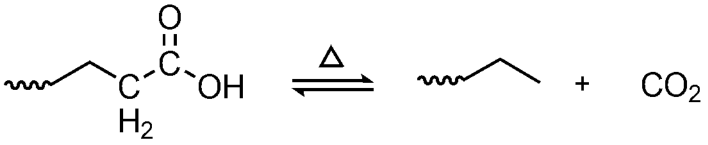
2.2.3 Thermal and Thermo-Oxidative Degradation

The thermal resistance of polyesters increases with the aromatic group content: Aliphatic polyesters are stable up to 220°C, while aromatic–aliphatics begin to undergo thermal degradation above 280°C only. The primary degradation process involves random ester scission through a six-center concerted mechanism with a *β*-CH hydrogen transfer. It results in the formation of carboxyl and vinyl endgroups [30-31] (Equation 2.2).



(2.2)

Wholly aromatic liquid crystalline polyesters have been reported to degrade at 450–550°C through the homolytic scission of ester linkages releasing CO, CO_2, phenol, and other aromatics [32]. The decarboxylation of carboxy end groups taking place during high temperature syntheses is another important polyester degradation reaction (Equation 2.3). Decarboxylation takes place at significantly lower temperature for polyesters deriving from aliphatic acids than from aromatic ones. This temperature is particularly low for polyesters of oxalic and malonic acids, which, therefore, cannot be synthesized by the conventional diacid–diol bulk reaction [33].



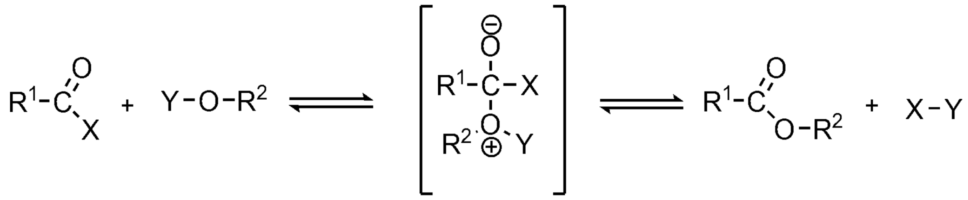
(2.3)

2.3 Synthetic Methods for Polyesters

2.3.1 General Considerations

The main polyesterification reactions are assumed to proceed through a substitution reaction at the carbonyl carbon with the formation of a tetrahedral intermediate, according to the $A_{AC}2$ addition–elimination mechanism of Ingold's classification [34] (Equation 2.4). This scheme applies to (i) hydroxy–carboxy direct esterification ($X = -OH$, $Y = -H$), (ii) hydroxy–ester interchange (alcoholysis, $X = -OR^3$, $Y = -H$), (iii) carboxy–ester interchange (acidolysis, $X = -OH$, $Y = R^4CO-$), (iv) ester–

ester interchange (transesterification, X = $-OR^3$, Y = R^4CO-), (v) acid chloride–hydroxy reaction (X = $-Cl$, Y = $-H$), and (vi) anhydride–hydroxy reaction (X = R^3COO-, Y= $-H$), where R^1 to R^4 represent either monomer or growing-chain ends.


(2.4)

According to Equation 2.4, when X is a good leaving group and $-OY$ a strong nucleophile, the reaction proceeds at high rate in mild conditions. On the other hand, reactions involving poor leaving groups and weak nucleophiles must be carried out at high temperature during a long reaction time. Increasing the electron-withdrawing character of R and/or X decreases the electron density on the carbonyl carbon atom and favors the formation of reaction intermediate, thus increasing the reaction rate.

2.3.2 Direct Polyesterification

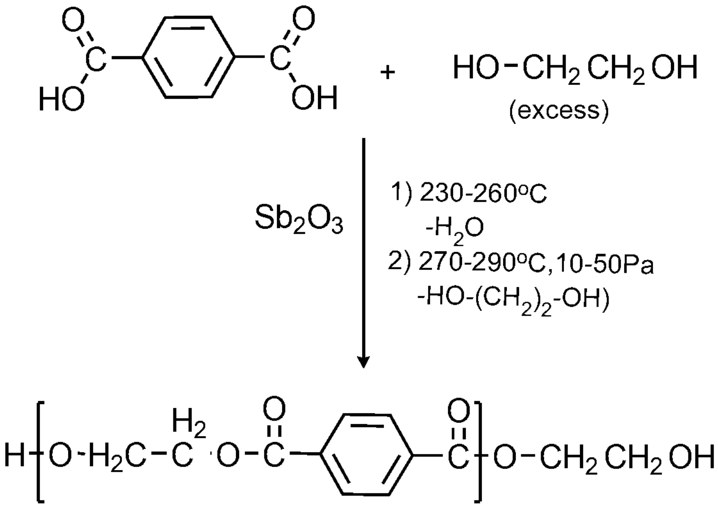
The carboxy–hydroxy reaction (direct esterification) is the most straightforward method of polyester synthesis. polyesters from diacids and diols (Equation 2.5) or from hydroxy acids [35-36] (Equation 2.6). Direct polyesterification is rather slow at room temperature and must be carried out at high temperature (150–290°C depending on monomers) and high endgroup concentration, preferably in the bulk. Vacuum is generally applied during the last steps of reaction to distill off reaction water and to continuously shift the reaction toward the formation of high-molar-mass polyester.

$$n\mathrm{HOOC{-}R^1{-}COOH} + n\mathrm{HO{-}R^2{-}OH} \xrightarrow[\text{Bulk}]{160\text{-}290^{\circ}\mathrm{C}} \mathrm{H}\left(\mathrm{OOC{-}R^1{-}COO{-}R^2}\right)_n\mathrm{OH} + (2n-1)\,\mathrm{H_2O}\uparrow \quad \textbf{(2.5)}$$

$$n\mathrm{HO{-}R{-}COOH} \xrightarrow[\text{Bulk}]{160\text{-}290^{\mathrm{O}}\mathrm{C}} \mathrm{HO}\left(\mathrm{R{-}COO}\right)_n\mathrm{H} + (n-1)\,\mathrm{H_2O}\uparrow \quad \textbf{(2.6)}$$

Direct polyesterification is particularly well suited to the syntheses of aliphatic polyesters, unsaturated polyesters, and aromatic–aliphatic polyesters such as PET

[37] (Equation 2.7) and PTT, which involve reactions between aliphatic or aromatic carboxylic acids and primary or secondary aliphatic alcohols.



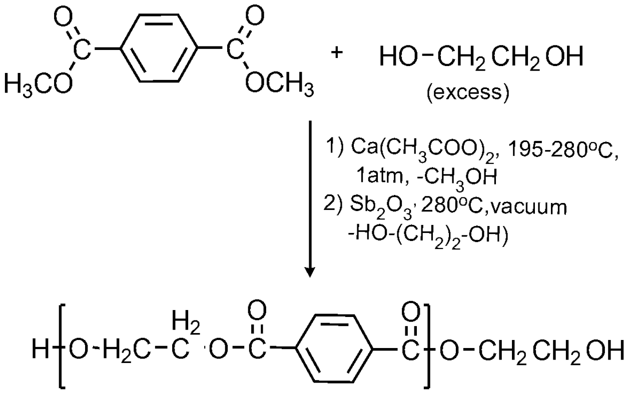
(2.7)

2.3.3 Transesterification Polymerizations

Transesterifications, also termed ester exchange or ester interchange reactions, include hydroxy–ester, carboxy–ester, and ester–ester reactions.

Hydroxy–ester reaction is the most important one and is used for many aromatic–aliphatic and wholly aromatic polyester syntheses. Hydroxy–ester interchange (alcoholysis) reactions play a predominant role in most industrial preparations of aliphatic and aromatic–aliphatic polyesters.

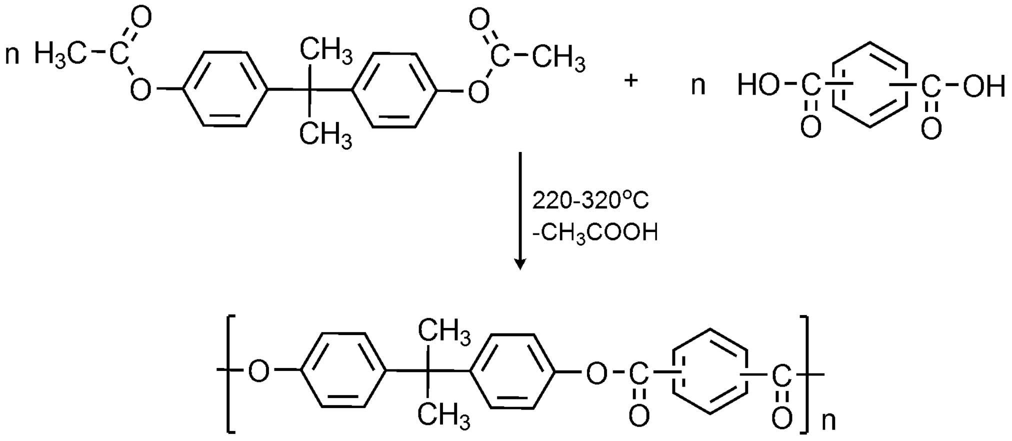
The original industrial synthesis of PET [38] is based on the reaction between dimethyl terephthalate (DMT) and excess EG (Equation 2.8). The reaction is carried out in two stages. During the first stage, methanol is distilled off and a low-molar-mass hydroxyethyl terephthalate– terminated oligomer is produced.



(2.8)

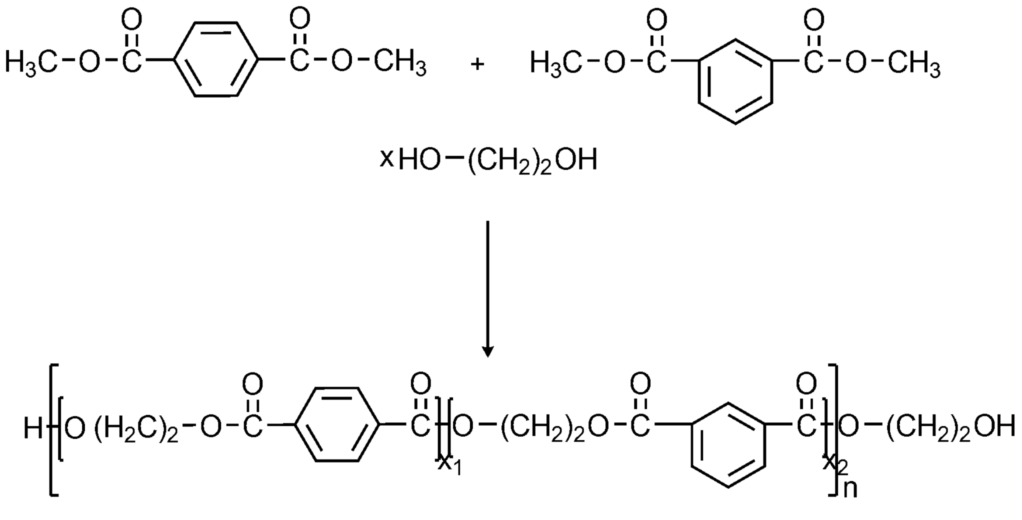
The second stage involves intermolecular reactions between hydroxy and ester endgroups with elimination of EG. Vacuum is applied at the end of the reaction until high-molar-mass PET is obtained. This stage is similar to the second stage of the direct esterification method.

Carboxy–ester interchange is restricted to the synthesis of wholly aromatic polyesters while the ester–ester route is rarely used for polyester preparation due to slow kinetics. High-temperature melt reactions between bisphenol diacetates and aromatic dicarboxylic acids (Equation 2.9) or between bisphenols and aromatic dicarboxylic acid diphenyl esters are the preferred routes for the synthesis of wholly aromatic polyesters.



(2.9)

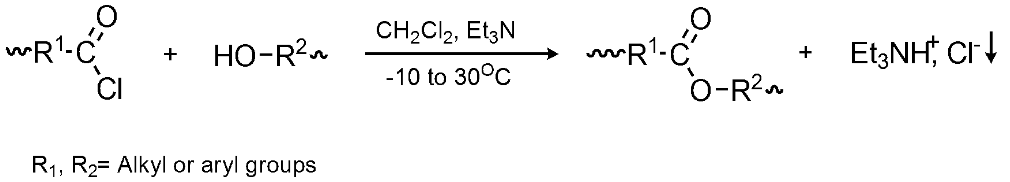
Ester-ester interchange reaction is much slower than hydroxy-ester and carboxy-ester intercahnge reactions and is seldom applied to polymer synthesis. Ester-ester interchange reactions are used wholly aromatic polyesters [39] (Equation 2.10).



(2.10)

2.3.4 Acid Chloride-Alcohol Reaction

The reaction between acid chlorides and aliphatic alcohols or phenolic compounds commonly takes place at low to moderate temperature (-10^{o}C to 100^{o}C) in solution or by interfacial or dispersion polymerization techniques. It has been widely applied to polyester synthesis [40-41] (Equation 2.11).



(2.11)

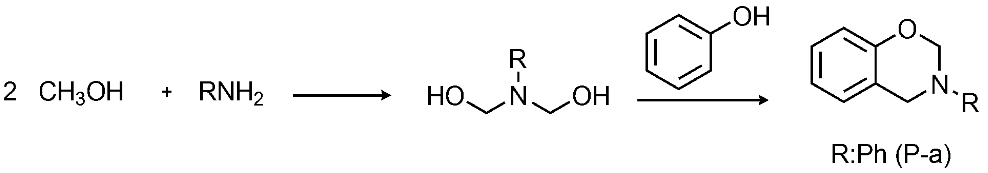
2.4 Polybenzoxazines

2.4.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution method or solventless method. Using various types of phenols and amines, having different substitution groups attached, various types of benzoxazine monomer can be synthesized. These substituting groups can provide additional polymerizable sites and also affect the curing process. In order to obtain polymeric materials, with desired properties, by tailoring the benzoxazine monomer with different functionality and a wide variety of monomers can be synthesized by using appropriate chosen phenol and amine. In this section synthesis of mono and di-functional benzoxazine monomers have been discussed.

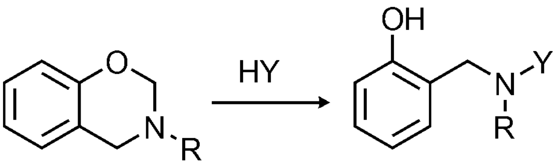
2.4.1.1 Mono-Functional Benzoxazine Monomers

Condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers was reported. According to the reported procedure, this reaction was performed in a solvent in two-steps. It was found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and forms a Mannich bridge [42]. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an *N,N*dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and *ortho* position of the phenol at the elevated temperature to form the oxazine ring [43] (Equation 2.12).



(2.12)

It has been observed that for some benzoxazines, the ring opening occurs in the presence of compounds with active hydrogen (HY), such as naphthol, indoles, carbazole, imides, and aliphatic nitro compounds even phenol (which is also one of the starting compound for synthesis) [44] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [45] is shown below in equation 2.13.



(2.13)

The benzoxazines derived from a strongly basic amine and a less acidic phenol found to be more stable in the hot alcohols [46]. Substituent on the benzoxazine ring affects the stability of the ring. The presence of more than one reactive *ortho* position in the initial product may lead to another aminoalkylation reaction [47]. A significantly higher yield obtained when the benzoxazine derived from phenol having an *ortho* substituent.

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, solventless synthesis in the melt state was developed [48].

The reaction mechanism and kinetics of this solventless synthesis were proposed [49]. In a typical synthesis, the reactants, *i.e.*, aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. In this connection, it should be pointed out that formaldehyde is not typically used as it evaporates easily and lose stoichiometry quickly. Instead, paraformaldehyde is used. The choice for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and byproducts.

2.5.1.2 Di-Functional and Multi-Functional Benzoxazine Monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high molecular weight linear structures were unobtainable [50]. Actually, there is no convincing evidence reported for the thermal dissociation theory, though it was mentioned in the literature. Moreover, it was reported that the reduction of reactivity is due to the hydrogen bonding formation. Such phenomenon was observed in the temperature range below where reverse Mannich reaction occurs in benzoxazine chemistry [51]. To overcome this limitation, a new class of difunctional or multifunctional benzoxazine monomers [52] have been developed, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized using bisphenol-A, formaldehyde and methyl amine in different solvents and referred as B-m, (see Figure 2.5(a)) as a reference to two of its original ingredients: bisphenol-A and methylamine. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by $^{-1}$H-NMR, FT-IR and DSC. It was observed that, the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.

Similar type of difunctional benzoxazine was prepared using aniline instead of methyl amine [53-54] and the pure monomer was referred as B-a and oligomers were as oligo-B-a (see Figure 2.5(b)).

Solventless method was successfully employed for synthesis of a series of difunctional monomers [54-55].

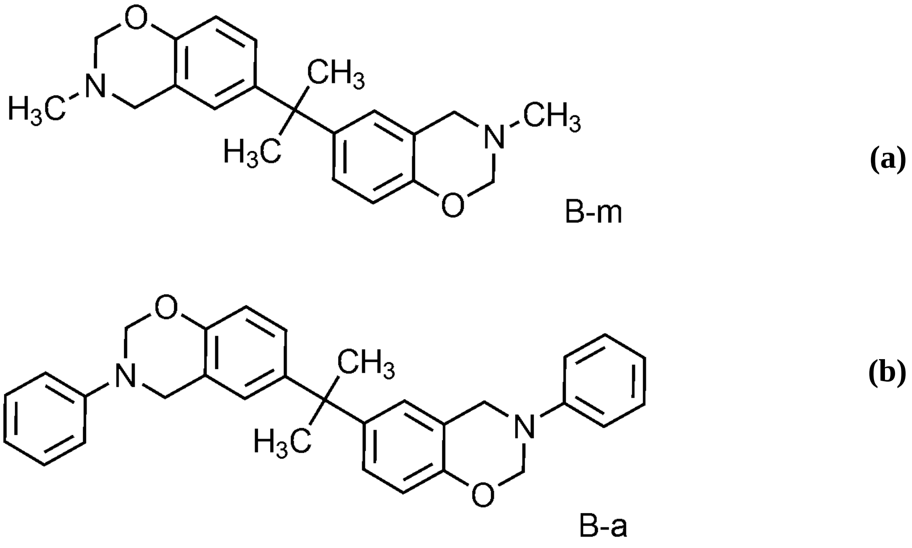


Figure 2.5 : Difunctional benzoxazine B-m and B-a

2.4.2 Preparation of Polymers with Benzoxazine Moieties

To improve the mechanical properties and processibility several strategies have been reported, one of them is blending of benzoxazines with polymers. Regarding chemical linking of polybenzoxazines with the other conventional polymers the macromonomer technique was followed. The benzoxazine groups are introduced by initiation of a selected polymerization or synthesizing benzoxazines from amino or phenol functional prepolymers. In the former case, the propagating species should be unreactive towards the benzoxazine ring and N and O hetero atoms.

Here some examples for polymers with benzoxazine moities can see in figure 2.6. Figure 2.6 (a) is benzoxazine functional polystyrene [56] ; figure 2.6 (b) is benzoxazine functional poly(ε-caprolactone) [57] and figure 2.6 (c) is benzoxazine functional poly(methyl methacrylate) [58].

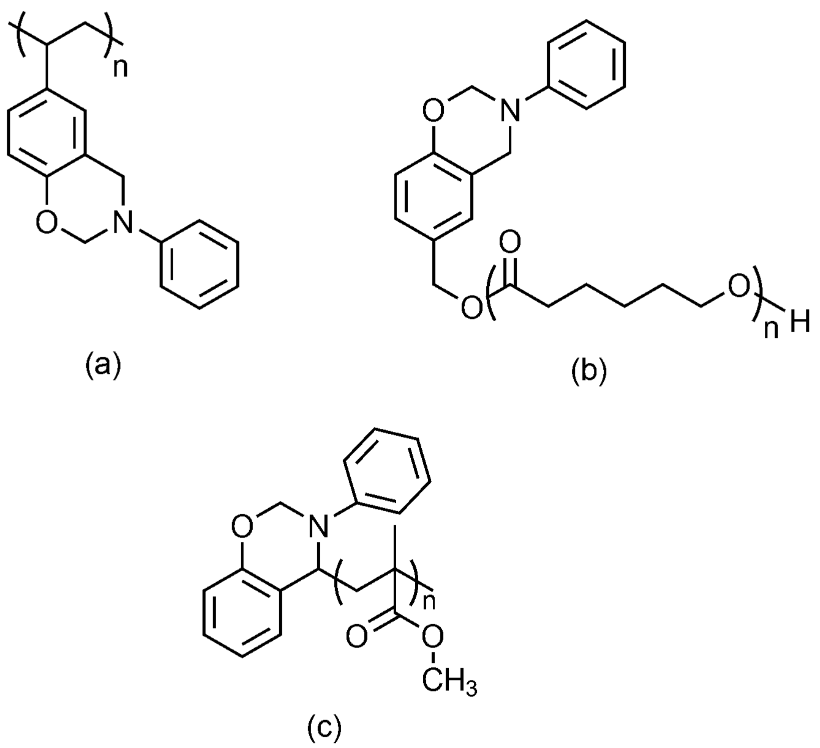
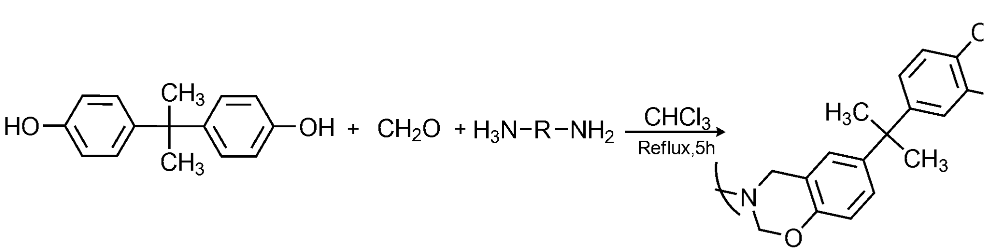


Figure 2.6: Examples of polymers with benzoxazine moiteis.

2.4.3 Polymeric Benzoxazine Precursors

2.4.3.1 Main-Chain Precursors

High molecular weight polybenzoxazine precursors can be synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (Equation 2.14).



(2.14)

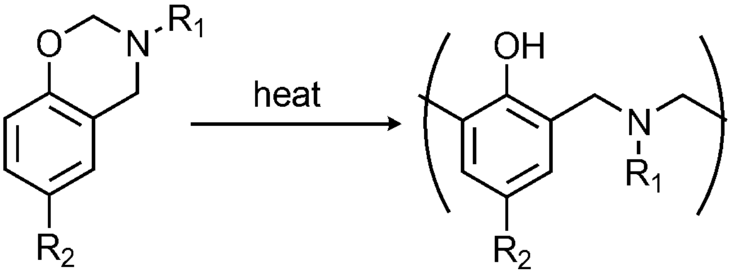
The major problems associated with the preparation of such main-chain benzoxazine precursor polymers are low molecular weight and crosslinking arising from the Mannich reactions of multiple functional groups. The choice of the right conditions for a Mannich reaction is critical for achieving high yields with the minimum of side reactions. In this type of Mannich polymerization, partially ringopened structures were also observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as polybenzoxazine precursors. The precursor solution was cast on glass plate, giving transparent and self-standing precursor films, which was thermally cured up to 240°C to give brown transparent polybenzoxazine films. The toughness of the cross-linked polybenzoxazine films from the high molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass transition temperature of the polybenzoxazines derived from the high molecular weight precursors were as high as 238-260°C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability [59-60].

2.4.3.2 Side-Chain Precursors

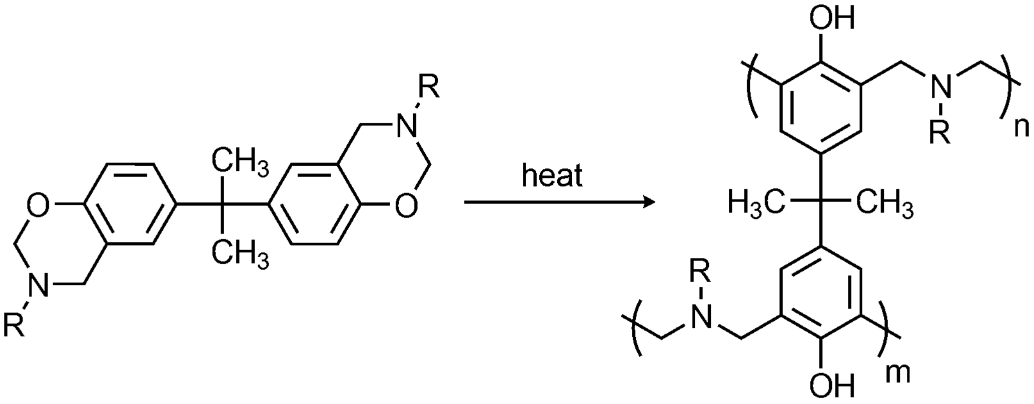
The only reported side-chain polymeric benzoxazine precursor is based on polyphenylene structure. Soluble and thermally curable conducting high molecular weight polybenzoxazine precursors were prepared by oxidative polymerization 3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3] oxazine (P-a) alone and in the presence of thiophene (Th) with ceric ammonium nitrate in acetonitrile. The resulting polymers exhibit conductivities around 10^{-2} S cm^{-1} and undergo thermal curing at various temperatures. The partially ring-opened structure which was formed during the oxidative polymerization affects the thermal curing behavior of the polymers. The cured products exhibited high thermal stability but lower conductivity, than those of the precursors [61].

2.4.4 Reaction Mechanism of Ring Opening Polymerization of Benzoxazine

Mono-oxazine ring containing benzoxazine is a distorted structure, with the nitrogen and carbon, between oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six-membered ring to undergo ring-opening reaction under specific conditions. In addition, due to their high basicity (by Lewis definition) both oxygen and nitrogen of the oxazine ring can act as potential cationic polymerization initiation site and makes the ring very likely to open via a cationic mechanism [62-53].



(2.15)



(2.16)

Several mechanisms have been proposed to explain the curing of benzoxazines that the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which in equilibrium.[63] Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and para position of the phenol group. The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Though, several authors have proposed different mechanism of thermal curing of benzoxazine, however, the mechanism is not well established.

2.4.5 Properties of Polybenzoxazines and Their Blends and Composites

2.4.5.1 Properties of Polybenzoxazines

A typical polybenzoxazine, prepared from mono-functional 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a), exhibit Tg at 146 and 161°C, obtained from maximum of loss modulus and the maximum of tan δ respectively of DMA results. The storage modulus decreases sharply at about 110°C. From TGA profile it was observed that, its 5 and 10% weight loss temperatures were 342 and 369°C, respectively and char yield was 44% [64].

A comparative investigation on several physical properties of polybenzoxazines (PBa and PB-m), prepared by thermal curing of difunctional B-a and B-m monomers, has been reported [65]. They exhibit high T_g and significantly higher tensile moduli. than both phenolics and epoxies at the same time maintain adequate tensile strength and impact resistance.

The PB-a has a higher storage modulus in the glassy region than the PB-m, as observed from their respective room-temperature values of 2.2 and 1.8 GPa. The glass transition temperature of the PB-m (180°C), however, is significantly higher than that of the cured PB-a material (150°C), as determined from the maxima of the loss spectrum. As the presence of high free volumes responsible for lowering of T_g, it was postulated that the PB-a might contain a greater free volume than the PB-m.

For these polybenzoxazines the concentration of network chains is significantly lower than is typically seen in cross-linked epoxides. Though the polybenzoxazines posses low cross-linking density, they exhibit higher T_gs. The intra and intermolecular hydrogen bonding in the network of the polybenzoxazines and the cured materials are responsible for low crosslink density [66-67]. According to many authors for epoxy resins, the crosslink density has little or no influence on stiffness or rigidity in the glassy state [68-69]. Generally, intermolecular packing, free volume, molecular architecture, and molecular weight between cross-links influence the large-strain glassy state properties, namely tensile strength and elongation at break. Higher free volume tends to enhance the mobility of network segments under load to increase ultimate elongation.

Hydrogen bonding should decrease the flexibility of a cross-linked network as it hinders rotational isomeric configurational changes and other segmental motion of chain.

When thermogravimetric analysis was employed to determine the thermal stability of these materials three major events were observed. Ishida and coworkers analyzed the evolved gases to determine the nature of these weight loss events and also proposed degradation mechanism [59]. The first event near 310 °C was due to the breakage of Mannich bridge in the phenolic Mannich bridge network which produced free aniline via a deamination reaction, along with some *N*-methyl anilines by deaminomethylation. During second event at about 400°C, the breakup of the isopropylidene linkage of the bisphenol A occurred. The primary weight loss products were aniline and various phenolic species. Finally the last weight loss, centered near 460 °C, was attributed to the degradation of char, with release of traces of phenolic and significant amount of substituted benzene compounds [70].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Solvents

Methanol (Technical) : Methanol was used for the precipitation of polymers without further purification.

Chloroform (Riedel-de Haën, 99.4%) : Chloroform was used without further purification.

N,N-dimethylformamid (DMF) (Merck, 99.8%) : Predried over magnesium sulfate followed by sodium wire.

Diethylether (Sigma-Aldrich) : It was used as recieved.

Dimethyl sulfoxide (DMSO) (J.T.Baker) : It was used as recieved.

1-4 Dioxane (Riedel-de Haën 99.5%) : It was used as recieved.

Dichloromethane (≥99%, J.T. Baker) : It was used as recieved.

Ethanol (≥99.5%, Aldrich) : It was used as recieved.

3.1.2 Other Chemicals and Reagents

Paraformaldehyde (powder, J.T.Baker, 95%) : It was used as received.

Phenol (loose crystals, ≥99.0%, Sigma-Aldrich): It was used as received.

Sodium hydroxide (Carlo Erba, 97%) : It was used as received.

4,4'-Isopropylidenediphenol (Acros, 97%): It was used as received.

5-amino-1-pentanol (Aldrich, 97.0%): It was used as received.

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

Pyromellitic dianhydride (Merck, 97%): It was used as received.

Dibutyltin laurate (Aldrich, 95.0%): It was used as received.

4-4'-(hexafluroisoproplylidene)diphatalic anhydride (Aldrich, 99.0%): It was used as received.

Phenol (loose crystals, ≥99.0%, Sigma-Aldrich) : It was used as received.

4-aminobenzoic acid (99%, Across): It was used as received.

*Aniline (≥99.5%, Sigma-Aldrich):*It was used as recieved.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded in $CDCL_3$ and Dimethylsulfoxide with D6 with $Si(CH_3)$ as internal standart, using a Bruker 250 MHz NMR Spectrometer.

3.2.2 Fourier Transform Infrared Spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.3 Gel-Permation Chromotography (GPC)

a). Gel permeation chromatography instrument equipped with a Waters 1515 pump and Waters styragel column (HT4) utilizing DMF containing 5mM NH_4PF_6 at a flow rate of 0.5 ml/min and the column oven set to 50°C.

3.2.4 Diffrential Scanning Calorimeter (DSC)

Differential scanning calorimeter was performed on a Perkin Elmer Diamond DSC with a heating rate of 10°C min-1 under nitrogen flow.

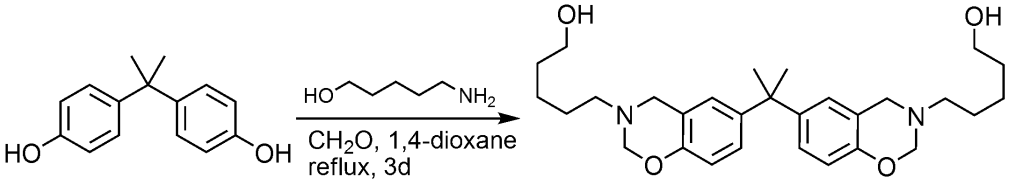
3.2.5. Thermal Gravimetric Analysis (TGA)

TGA was carried out on Perkin Elmer Diamond TA/TGA with a heating rate of 0°C min-1 under nitrogen flow.

3.3 Preparation Methods

3.3.1 Synthesis of Diol Containing Bisbenzoxazine (BBD)

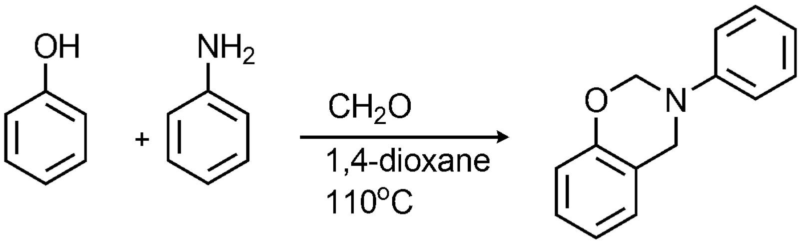
Synthesis of diol functional bisbenzoxazine (Equation 3.1) was performed as followed. To 150 mL of 1,4-dioxane, paraformaldehyde (176 mmol, 5.3g), 5-amino-1-pentanol (88 mmol, 9.08g), 4,4'-isopropylidenediphenol (44 mmol, 10g) were added and refluxed for 3 days. Then 1,4-dioxane was evaporated under vacuum. Oily raw product was dissolved in chloroform and washed five times with 25 mL 0.2 N NaOH aqueous solution and distilled water, respectively. The chloroform solution was dried with anhydrous magnesium sulfate, filtered and evaporated under vacuum to afford orange-yellow oil. (Yield: 62%)



(3.1)

3.3.2 Synthesis of 3-phenyl-3,4-dihydro-1,3-benzoxazine (P-a monomer)

The general procedure is as follows; 18.6 g (0.2 mol) aniline is added slowly to the flask containing 12.0 g (0.4 mol) paraformaldehyde, keeping the temperature below 10°C in ice bath. The mixture is stirred for 10 min, 18.8 g (0.2 mol) phenol is added to the mixture. Then the flask heated up to 110°C for one and half an hour. The content of the flask is dissolved in ethyl ether. The ether solution was washed several times with 1N sodium hydroxide solution and de-ionized water, respectively. Organic layer was dried with anhydrous sodium sulfate and diethyl ether was evaporated to yield light yellow viscous liquid. Solid product was formed after applying vacuum at 50°C in 24 h. (Yield: 65%) Synthesis reaction of P-a monomer is shown in Eq. 3.2 ^{1}H-NMR ($CDCl_3$): δ=4.49 (s, 2H, N-CH_2-Ar), 5.37 (s, 2H, N-CH_2-O), 6.79-7.30 (m, 9H, aromatics) Characterization of this monomer is published [43].

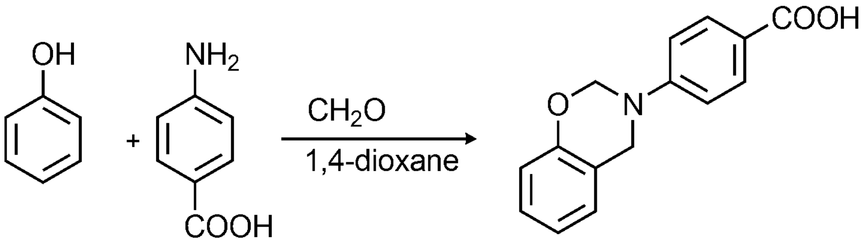


(3.2)

3.3.3 Synthesis of 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid (BDA)

A mixture of phenol (5.0 g, 53 mmol), 4-aminobenzoic acid (7.0 g, 51 mmol), and paraformaldehyde (3.2 g, 105 mmol) was placed in a 500-mL round-bottom flask and 200 ml of 1,4-dioxane was added to this mixture. The mixture was refluxed, and the reaction was monitored with thin layer chromatography (20:1 dichloromethane/ethanol) until the initial product disappeared (5 days).After cooling to room temperature, the mixture was filtered and concentrated by evaporating 4/5 of 1,4-dioxane at rotary evaporator. Ethyl ether (150 mL) was added to the mixture with magnetic stirring, and a yellow precipitate was obtained. The yellow solid was filtered and dried under reduced pressure (Yield: 50%) [71]. Synthesis reaction of 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid (BDA**)** is shown in Equation 3.3

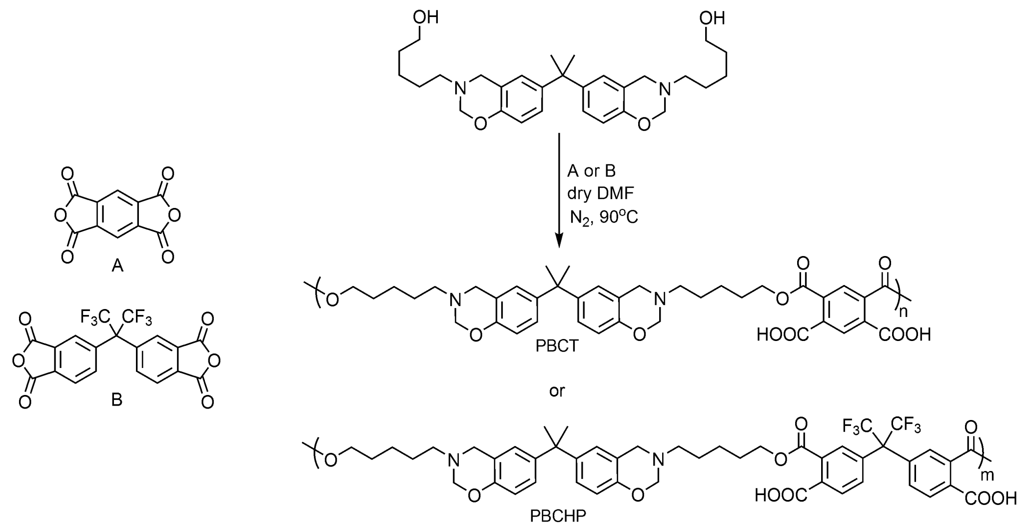
^{1}H-NMR ($CDCl_3$): δ=4.81 (s, 2H, N-CH_2-Ar), 5.57 (s, 2H, N-CH_2-O), 6.78-7.84 (m, 8H, aromatics), 12.45 (broad s, 1H, COO*H*)



(3.3)

3.3.4 Synthesis of Benzoxazine Containing Polyesters (PBCT and PBCHP)

Typical procedure: To 45 mL of dried N,N dimethylformamide, 4,4’-isopropylidenediphenol (3.9 mmol, 1.89 g) and 1,2,4,5-benzene-tetracarboxylic-1,2:4,5-dianhydride (3.9 mmol, 0.85 g) were added and refluxed under N_2(g), at 90 °C for 24 hours. The polymer was precipitated in 500 mL of water and washed with methanol. Then, the polymer was dried under vacuum over two nights. Same procedure was applied for catalytic reactions. In that case, two drops of dibuthyltinlaurate were added to reaction mixture. Synthesis reaction of polymers is shown in equation 3.4.



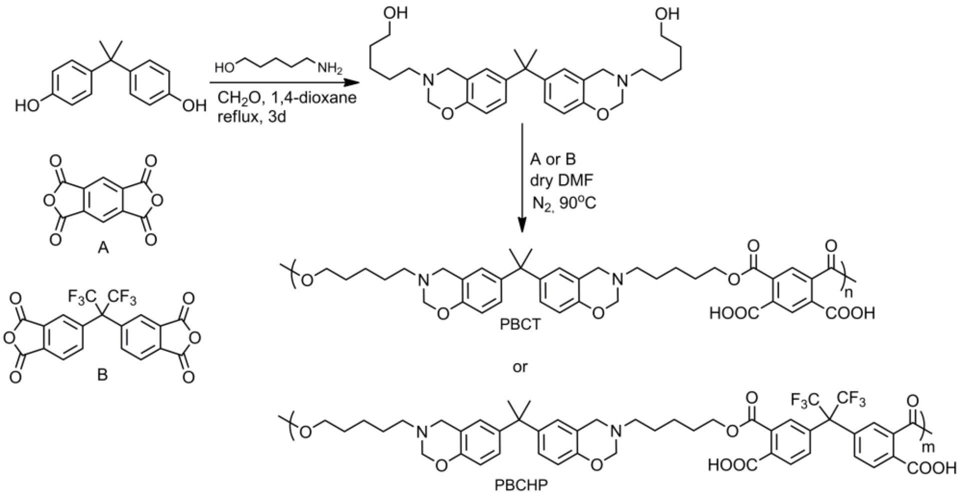
(3.4)

3.3.5 Determination of Adhesion and Flexibility Properties of Films

The samples were dissolved in DMF in 1:1 (w/w) solid to solvent ratio. The resulting viscous solutions were applied on tin plates by using an automatic film applicator to obtain 40 μm films. These films were cured at 160 °C for 1 h (mono functional benzoxazine P-a and 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid) and at 170 °C for 2 h (benzoxazine containing polyesters). The adhesion [72] and flexibility [73] properties of films thus obtained were determined according to the related standards.

4. RESULTS AND DISCUSSION

Polyesters are one of the most important and widely used polycondensates. Depending on the nature of monomers, polyesters exhibit an enormous variety of structures, properties, and, therefore, applications. Thus, the polyester properties are governed by the design and synthesis of suitable monomers. In our work, we selected aminoalcohol group as the primary amine component in the benzoxazine ring forming reaction to introduce hydroxyl groups in the final benzoxazine. Hence, diol containing benzoxazine was synthesized as the monomer for the subsequent polyesterification process by reacting bisphenol-A, 5-amino-1-pentanol, and paraformaldehyde as depicted in Equatian 4.1.



(4.1)

The structure of monomer (BBD) and polyesters were confirmed by spectral and thermal analysis. As can be seen from Figure 4.1 (c) the ^{1}H-NMR spectrum of the monomer exhibits not only the specific signals of the benzoxazine ring, but also chemical shifts that belong to the alkyl chain and hydroxyl groups.

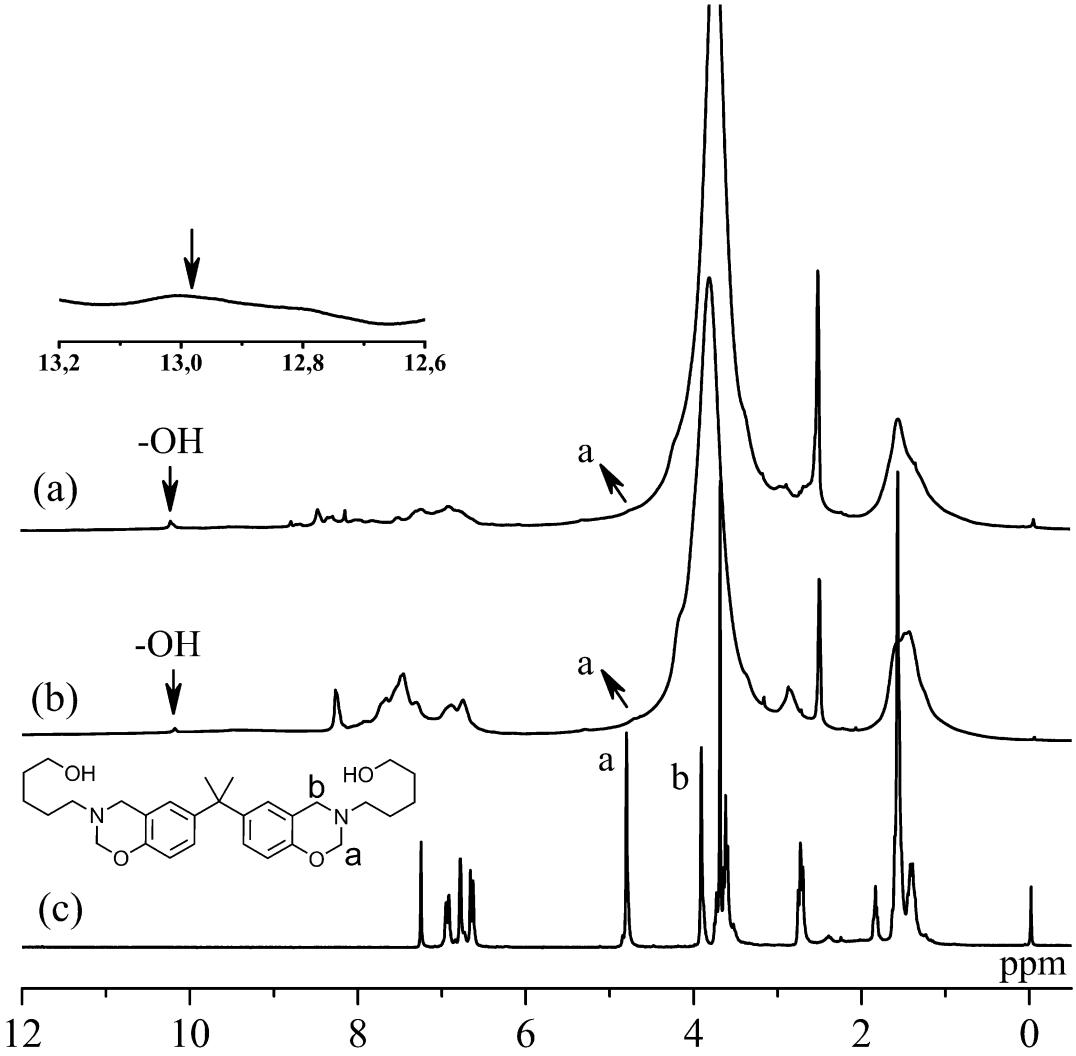


Figure 4.1: ^{1}H-NMR spectra of PBCT (a), PBCHP (b) and BBD (c).

The ^{1}H-NMR spectra for polyesters were evaluated to confirm the structures. The ^{1}H-NMR spectrum of the polyesters, namely poly(benzoxazine-carboxyterephthalate) (PBCT) and poly(benzoxazine-carboxyhexafluro isoproplylidene phthalate) (PBCHP), derived from pyromellitic dianhydride and 4-4'-(hexafluroisoproplylidene) diphatalic anhydride, are shown in Figure 1a and 1b, respectively. The spectra reveal the characteristic peaks assigned to methylene protons (O-C$\boldsymbol{H}_2$-N) of the oxazine ring at 4.76 ppm for both polymers with low intensity, which indicates the ring opening of oxazine during polymerization. Same issue is also evidenced by the peaks of phenolic O$\boldsymbol{H}$ protons at 10.2 ppm. Moreover, COO$\boldsymbol{H}$ protons of polyesters appeared at 12.9 ppm and the methylene protons of Ar-C$\boldsymbol{H}_2$-N could not be detected due to the overlapping with -O-CH_2 protons of ester and broad water peak of D$_6$-DMSO.

Moreover, the FT-IR spectrum of the diol monomer further indicates the structure. As can be seen from Figure 4.2 (c), addition to the band corresponding to the C-O-C oxazine ring mode at 1382 cm^{-1} and broad aromatic C-H stretching vibration around 3010 cm^{-1}, the O-H and C-O (primary alcohol) stretching bands at 3391 cm^{-1} and 1054 cm^{-1}, respectively, were observed. Furthermore, the band at 932 cm^{-1} is the mode that arises from the benzene ring to which oxazine ring is attached [74].

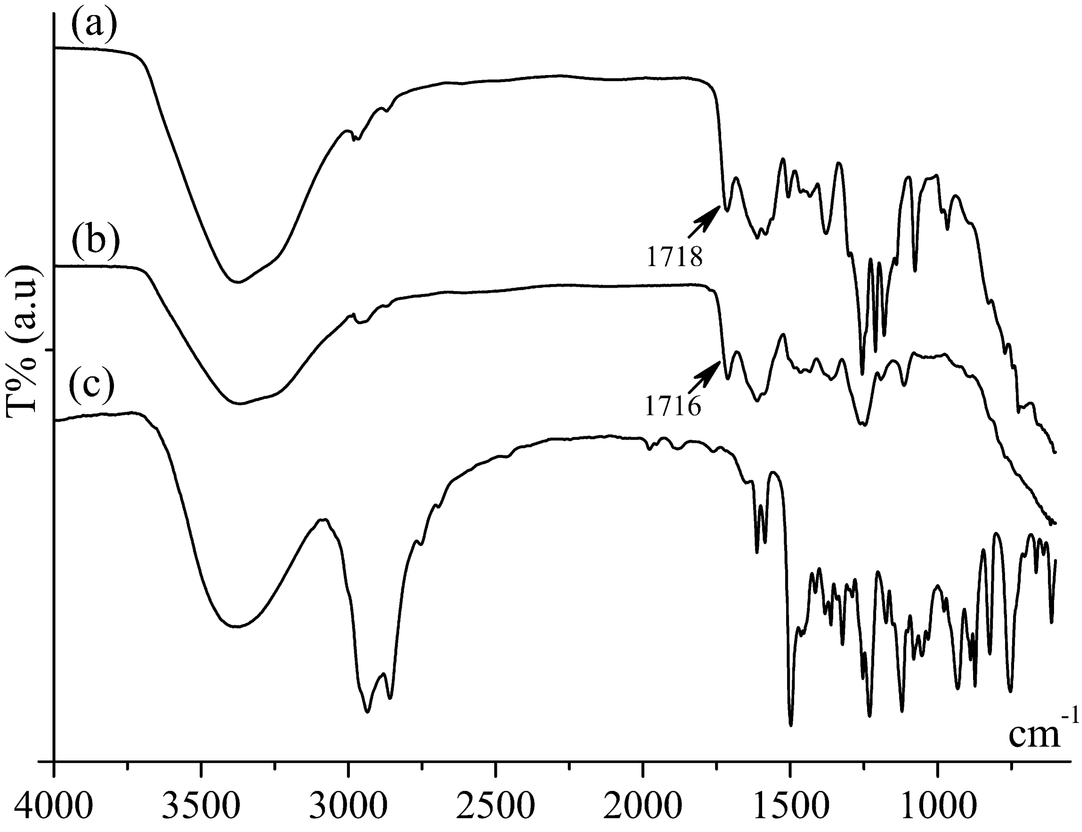


Figure 4.2 : FT-IR spectra of PBCT (a), PBCHP (b) and BBD (c).

The structure of the both polyesters was also confirmed by FT-IR. Figure 4.2 (a) and 2 (b) shows the IR spectra of the polyesters. The characteristic carbonyl stretching vibrations were observed at 1718 and 1716 cm^{-1} for PBCT and PBCHP, respectively. In addition, the respective CO***OH*** stretching vibrations of the polyesters at 3367 and 3373 cm^{-1} are emerged as broad bands. Also, C=O stretching vibration modes of carboxylic acid are detectable at 1613 and 1612 cm^{-1}, respectively.

The results of the polymerizations are given in Table 4.1. In our experiments, the amount of dibutyltin laurate, a Lewis acid catalyst, was deliberately kept low so as to prevent ring opening reaction of benzoxazine.

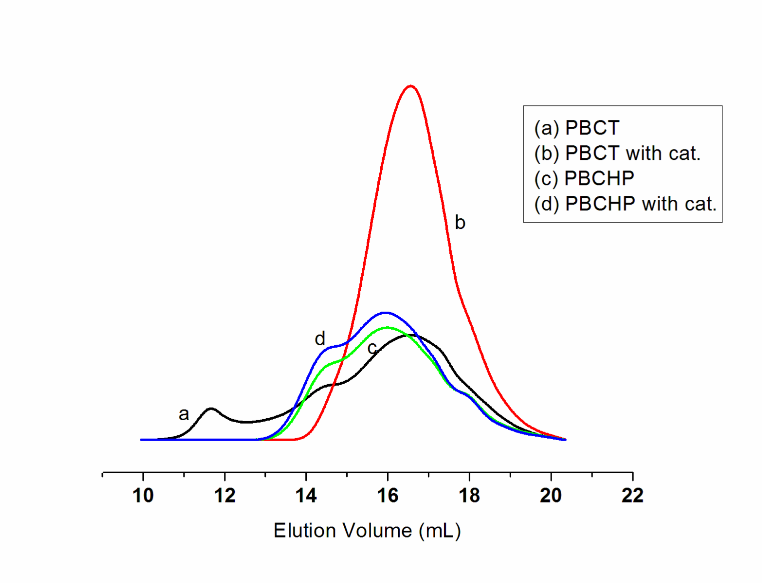


Figure 4.3: GPC thraces of polyethers.

Tabel 4.1 : Polycondensation of BBD[a] with anhydrides in DMF at 90 °C.

Polyester	Anhydride (mol L^{-1})	Tin laurate (mol L^{-1})	Conversion[b] (%)	M_n[c]	M_w/M_n
PBCT	8.6×10^{-2}	-	64	5800	1.54
PBCT	8.6×10^{-2}	8.4×10^{-4}	68	4700	1.62
PBCHP	8.6×10^{-2}	-	66	5900	2.45
PBCHP	8.6×10^{-2}	8.4×10^{-4}	69	6500	2.46

[a] 8.6×10^{-2} mol L^{-1}
[b] Determined gravimetrically based on anhydrides
[c] Determined by GPC according to the polystyrene standards

4.1 Thermal Analysis

Polyesters can be synthesized by various routes. Conventionally, under appropriate conditions diols can react either with diacid chlorides, diacids or dianhydrides to form polyesters. For our convenience, pyromellitic dianhydride and 4-4'-(hexafluroisoproplylidene) diphatalic anhydride were used as the dianhydride components to obtain desired carboxylic acid containing polyesters (Equation 3.4). The polymerization reactions were performed without or with catalyst (dibutyltin laurate) at 90 °C. Due to the nature of the reaction, in every repeating unit there occurred two molecules of carboxylic acid adjacent to benzoxazine units. This is an important restriction for the preservation of the benzoxazine rings as acids readily undergo ring opening reaction with benzoxazines. In fact, this issue could be monitored spectrally and also by thermal characterization using DSC.

It is well known that 1,3-benzoxazines polymerizes with thermal induction around 200–250 °C and exhibit exotherm, which can be monitored by DSC. DSC was used for characterizing the curing behavior of the polyesters (Figure 4.4). The thermogram in Figure 4.4 (a) reveals a ring opening exotherm with an onset at 182 °C and a maximum at 210 °C, and 31 J/g as the exothermic energy. Notably, a degradation process begins after 249 °C.

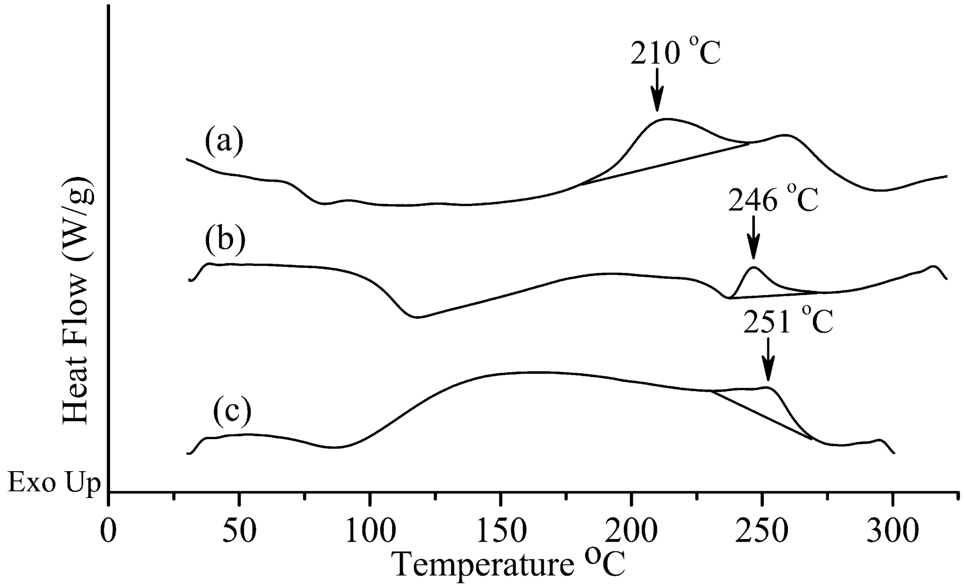


Figure 4.4 : DSC traces of BBD (a), PBCHP (b) and PBCT (c).

As stated previously, benzoxazine groups are expected to undergo ring opening polymerization. This exothermic event was detected for both polymers. PBCT exhibited an onset at 231 °C and a maximum at 251 °C with 15 J/g of exotherm energy. Similarly, for poly(benzoxazine-*co*-carboxy hexafluroisoproplylidene phthalate), the onset of the exotherm started at about 236 °C with a maximum at 246 °C, and 10 J/g as the heat of polymerization. Expectedly, both polymers resembled almost the same thermal properties as they are structurally similar and every repeating unit contains one benzoxazine unit. The slight difference observed for the amount of exotherm is probably due to aliphatic and aromatic nature of the components.

The thermal stabilities of the both polyesters are similar. The comparative TGA curves are illustrated in Figure 4.5 and the results are summarized in Table 4.2.

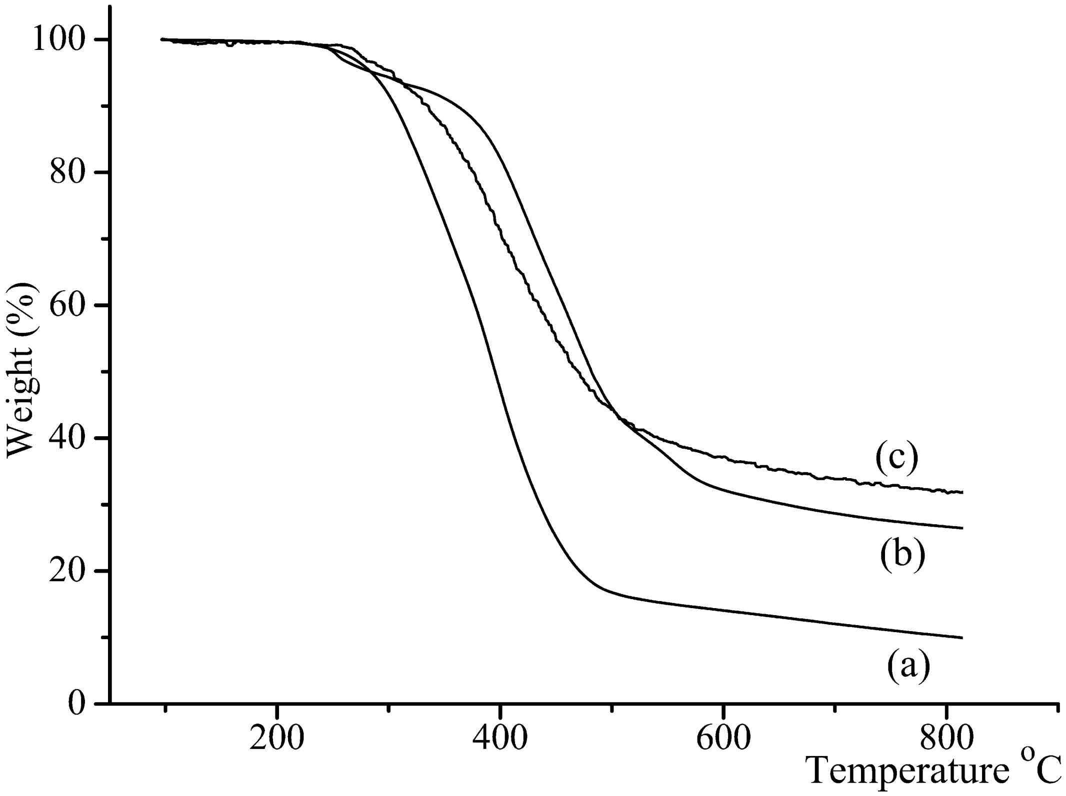


Figure 4.5 : TGA thermograms of cured BBD (a), cured PBCT (b) and PBCHP (c).

Tabel 4.2 : Thermal properties of the cured bisbenzoxazine-diol and the polyesters.

Cured Polymer[a]	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Y_c (%)
BBD	285	305	394	10
PBCT	301	334	419	32
PBCHP	285	361	426	27

[a] Cured in TGA at 220 °C for 15 min. under N_2 stream (20 mL/min.)

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

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

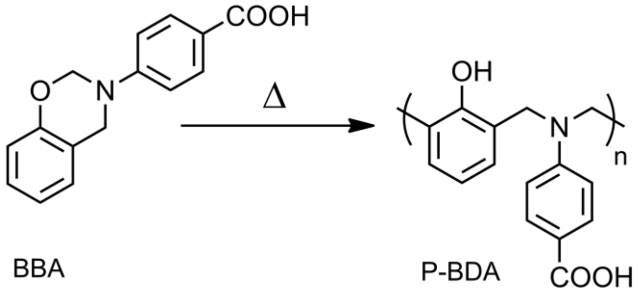
Y_c: Char yields at 800 °C under nitrogen atmosphere

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

Cured PBCT exhibited slightly higher char yield due the rigid aromatic group in the structure imparted by terephthalate group. Interestingly, the thermal degradation of this polymer occurs faster in 315-515 °C temperature range than cured PBCHP. Although they possess COOH groups in the structure which may undergo decarboxylation, the char yields of cured polyesters are higher than that of cured diol monomer. In fact, this value is even comparable to that of PP-a, which has a 34 % char at 800 °C. The observed enhancement in the thermal stability can again be attributed to the aromatic groups and increased cross-link density through additional hydrogen bonding.

4.2 Adhesion and Flexibilty Properties

The film forming property of the polyesters were also investigated. The adhesion and flexibility of the cured films were measured by ASTM and DIN tests [48-49] and compared with that of the cured conventional monofunctional benzoxazine (Pa) and carboxylic acid containing benzoxazines, 4-(2H-1,3-benzoxazin-3(4H)-yl)benzoic acid (BBA) (see Equatian 4.1, 4.2 and 4.3, respectively for the structures). In each case, the films from the corresponding compounds were prepared on tin plates and thermally cured at 170 ^{o}C for 2h. In the case of cured P-a and BBA, the films were very brittle and adhesion were very poor. Cracks were formed even by bending over the cylinder having 20 mm diameter and the adhesions were found to be low. The poor flexibility and adhesion is due to the lacking of film forming property and rigid structure of the network.



(4.3)

In contrast, the polyester samples showed good flexibility and adhesion. The films showed no crack even upon bending over the cylinder having 2 mm diameter and the adhesion were found to be 5B for both polyester samples. The linear chain segments having pentyl and ester groups provide the flexibility in the network. Also, hydroxyl and carboxylic acid groups promote the adhesion of molecules to metals. In Table 4.3, adhesion values of the low molar mass structurally related model benzoxazines and polyesters were tabulated.

Tabel 4.3 : Adhesion of various thermally cured[a] benzoxazines.

Benzoxazine	Adhesion
P-a	2B
P-BBA	2B
PBCT[b]	5B
PBCHB[b]	5B

[a] Cured at 170 °C for 2h.

[b] Polymers obtained by with or without catalyst

5.CONCLUSION

In conclusion, novel polyesters containing benzoxazine moieties in the main chain were synthesized and characterized. Two kinds of polyesters with the molecular weights between 5800-7000 Da were readily obtained by polycondensation of bisbenzoxazine-diol with pyromellitic dianhydride and 4-4’-(hexafluroisoproplylidene)diphatalic anhydride. Flexible thin films were formed by solvent casting on tin plates and further cross-linked by thermally activated ring opening reaction of the benzoxazine groups present in the main chain. The cured polyesters exhibited comparable thermal stability with respect to low molar mass analogous. They also showed high flexibility induced by the soft pentyl and esters groups. Moreover, these cured films showed striking adhesion on tin plates due to the phenolic hydroxyls and carboxylic acid groups. The synthetic strategy presented may open new pathway to prepare other thermoplastic elastomers that can thermally be cured in the absence of any catalyst leading to materials with improved properties.

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