

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**HYDROXYL CONTAINING MAIN-CHAIN POLYMERIC BENZOXAZINES
AND THEIR MODIFICATIONS**

M.Sc. THESIS

Betül HANBEYOĞLU

Chemistry Department

Chemistry Programme

JUNE 2013

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Thesis Advisor: Prof. Dr. Yusuf YAĞCI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**HİDROKSİL GRUBU İÇEREN ANA ZİNCİR POLİMERİK
BENZOKSAZİNLER VE MODİFİKASYONLARI**

YÜKSEK LİSANS TEZİ

**Betül HANBEYOĞLU
509111046**

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Yusuf YAĞCI

HAZİRAN 2013

Betül Hanbeyoğlu, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 509111046, successfully defended the thesis/dissertation entitled “HYDROXYL CONTAINING MAIN-CHAIN POLYMERIC BENZOXAZINES AND THEIR MODIFICATIONS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Yusuf YAĞCI**
İstanbul Technical University

Jury Members : **Prof. Dr. Oya ATICI**
İstanbul Technical University

Doç. Dr. A. Ekrem MÜFTÜOĞLU.....
Fatih University

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To my family and Ahmet,

FOREWORD

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Betül Hanbeyoğlu
Chemist

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	ix
TABLE OF CONTENTS	xi
ABBREVIATIONS	xiii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
SUMMARY	Hata! Yer işareti tanımlanmamış.
ÖZET	Hata! Yer işareti tanımlanmamış.
1. INTRODUCTION	1
2. THEORETICAL PART	3
2.1 Chemical Approaches for Synthesis of Benzoxazine Monomers	3
2.1.1 Synthesis of mono-functional benzoxazine monomers	4
2.1.2 Synthesis of bifunctional and multi-functional benzoxazine monomers	8
2.2 Synthesis of Benzoxazine Monomers with Different Functional Groups	9
2.3 Combination of Benzoxazines with Other Materials	10
2.3.1 Preparations of blends and composites	10
2.3.2 Preparation of polymers with benzoxazine moieties	10
2.4 Polymeric Benzoxazine Precursors	12
2.4.1 Main-chain precursors	12
2.4.1.1 Condensation of classical diamines with bisphenols	13
2.4.1.2 Amine-terminated siloxanes	15
2.4.1.3 Amine-terminated polyether	15
2.4.1.4 Polymers with mannich condensation of AB-type	16
2.4.2 Side-chain and end-chain precursors	16
2.5 Reaction Mechanism of Ring Opening Polymerization of Benzoxazine	21
2.5.1 Cationic polymerization of benzoxazines	21
2.5.1.1 Acid catalyzed polymerization of benzoxazines	21
2.5.1.2 Photoinitiated polymerization of benzoxazines	23
2.5.2 Thermal polymerization of benzoxazines	24
2.6 Properties of Benzoxazines and Polybenzoxazines	25
2.6.1 Low shrinkage during polymerization	25
2.6.2 Low water absorption	26
2.6.3 High glass transition temperature	26
2.6.4 High char yield	26
2.6.5 Fast physical and mechanical property development	27
2.7 Ring-Opening Polymerization (ROP)	27
2.8 Photopolymerization	29
2.9 Atom Transfer Radical Polymerization (ATRP)	30
3. EXPERIMENTAL PART	33
3.1 Materials	33
3.1.1 Solvents	33

3.1.2 Chemicals	33
3.2 Characterization.....	35
3.2.1 Nuclear magnetic resonance spectroscopy (NMR).....	35
3.2.2 Infrared spectrophotometer (FT-IR)	35
3.2.3 Gel-permeation chromatography (GPC)	35
3.2.4 Differential scanning calorimeter (DSC)	35
3.2.5 Thermal gravimetric analysis (TGA)	35
3.2.6 Differential photocalorimeter	35
3.3 Synthesis.....	36
3.3.1 Synthesis of benzoxazine precursor (MCP).....	36
3.3.2 Synthesis of ϵ -caprolactone functionalized benzoxazine copolymer (MCP- <i>g</i> -PCL)	36
3.3.3 Functionalization of benzoxazine copolymer with methacrylate Group (M-MCP).....	36
3.3.4 Functionalization of benzoxazine copolymer with an initiator for ATRP (MCP-ATRP-I).....	36
3.3.5 Crosslinking investigation by photo-DSC	37
3.3.6 Synthesis of polystyrene grafted benzoxazine with ATRP (MCP- <i>g</i> -PS)	37
4. RESULTS AND DISCUSSION.....	39
5. CONCLUSION.....	57
REFERENCES	59
CURRICULUM VITAE	67

ABBREVIATIONS

¹H-NMR	: Nuclear Magnetic Resonance Spectroscopy
ATRP	: Atom Transfer Radical Polymerization
BAPO	: Phenylbis(2,4,6-trimethylbenzoyl)phosphine Oxide
Bisphenol-A	: 2,2-bis(4-hydroxyphenyl)propane
Da	: Dalton
DMSO	: Dimethyl Sulfoxide
DSC	: Differential Scanning Calorimeter
FTIR	: Fourier Transform Infra Red
GPC	: Gel Permeation Chromatography
HY	: Hydrogen Containing Compound
MA	: Methacrylate
MCBO	: Main-Chain Benzoxazine Oligomer
MCBP	: Main-Chain Benzoxazine Precursor
MCP	: Main-Chain Polymeric Precursor
MCP-ATRP-I	: MCP with an ATRP Initiator Group
MCP-g-PCL	: Poly(ϵ -Caprolactone) Grafted onto MCP
MCP-g-PS	: Polystyrene Grafted onto MCP
Me₆-TREN	: Tris- [2-(dimethylamino)ethyl]amine
M-MCP	: Methacrylate Substituted MCP
PCL	: Poly(ϵ - Caprolactone)
PCl₅	: Phosphorous Pentachloride
PDMS	: Polydimethylsiloxane
PMDETA	: N,N,N',N'',N'''- Pentamethyldiethylenetriamine
PS	: Polystyrene
ROP	: Ring Opening Polymerization
SEC	: Size Exclusion Chromatography
Sn(Oct)₂	: Tin(II) 2-Ethylhexanoate
T_g	: Glass Transition Temperature
TGA	: Thermogravimetric Analyzer

LIST OF TABLES

	<u>Page</u>
Table 2.1 : Benzoxazine monomers with various functionalities.	11
Table 2.2 : Methyl substituted benzoxazine monomers.	23
Table 4.1 : Molecular weight results of the polymers at various stages.	50
Table 4.2 : DSC results of synthesized polymers.....	53
Table 4.3 : Thermal properties of all polymers.	54

LIST OF FIGURES

	<u>Page</u>
Figure 1.1 : Preparing of benzoxazine polymer and its modified structures.	2
Figure 2.1 : Possible benzoxazine ring formation mechanisms.....	4
Figure 2.2 : Synthetic procedure for benzoxazine synthesis.....	4
Figure 2.3 : Mannich bridge formation through ring opening of benzoxazine.....	5
Figure 2.4 : Synthesis of 3,4-dihydro-2H-1,3-benzoxazine [16].	7
Figure 2.5 : Using salicylamines to prepare benzoxazines [17].	7
Figure 2.6 : Synthesis of bifunctional and multi-functional benzoxazine monomers.	8
Figure 2.7 : Synthesis procedure of bifunctional and multi-functional benzoxazines.	9
Figure 2.8 : Benzoxazine functionalized polymers.....	12
Figure 2.9 : AABB-type linear polymer with benzoxazine rings in the main chain.	12
Figure 2.10 : Main applications on main-chain type benzoxazine precursors.....	13
Figure 2.11 : Synthesis procedure for main-chain precursor strategy.	14
Figure 2.12 : MCBP and monomeric dibenzoxazine of same monomer.	14
Figure 2.13 : Block copolymer of PDMS and MCBP (BA-mda-block-PDMS).	15
Figure 2.14 : Jeffamine containing MCBP.	16
Figure 2.15 : AB-type main-chain precursors.....	16
Figure 2.16 : Preparation procedure for side-chain precursors.....	17
Figure 2.17 : Main applications of side-chain benzoxazines.....	18
Figure 2.18 : Macromolecular architectures obtained by the reactions of telechelics.	19
Figure 2.19 : Benzoxazine attached macromonomers.	20
Figure 2.20 : Acid catalyzed ring opening of benzoxazines.....	22
Figure 2.21 : Ring opening of phenoxy-type (Type I) benzoxazine.....	22
Figure 2.22 : Ring opening of phenolic-type (Type II) benzoxazine.	23
Figure 2.23 : Photoinitiated polymerization of benzoxazines.	24
Figure 2.24 : Thermal polymerization of benzoxazines.	25
Figure 2.25 : Typical ring opening of a cyclic ester.	28
Figure 2.26 : Organometallic compounds used as initiator for ROP.....	28
Figure 2.27 : Proposed mechanisms for tin octoate initiated polymerization.....	29
Figure 2.28 : General reaction of Atom Transfer Radical Polymerization.....	30
Figure 2.29 : The reaction mechanism of ATRP.	31
Figure 4.1 : Synthesis of MCPP.....	40
Figure 4.2 : FT-IR spectrum of MCPP.	41
Figure 4.3 : ¹ H-NMR spectrum of MCPP.....	41
Figure 4.4 : Synthesis of MCPP- <i>g</i> -PCL.....	42
Figure 4.5 : FT-IR spectrum of MCPP- <i>g</i> -PCL.	43
Figure 4.6 : ¹ H-NMR spectrum of MCPP- <i>g</i> -PCL.....	44
Figure 4.7 : Synthesis of M-MCPP.....	45
Figure 4.8 : FT-IR spectrum of M-MCPP.	45
Figure 4.9 : ¹ H-NMR spectrum of M-MCPP.....	46

Figure 4.10 : Synthesis of MCPP-ATRP-I.....	47
Figure 4.11 : FT-IR spectrum of MCPP-ATRP-I.	47
Figure 4.12 : ¹ H-NMR spectrum of MCPP-ATRP-I.....	48
Figure 4.13 : Synthesis of MCPP- <i>g</i> -PS by ATRP.	49
Figure 4.14 : FT-IR spectrum of MCPP- <i>g</i> -PS.	49
Figure 4.15 : ¹ H-NMR spectrum of MCPP- <i>g</i> -PS.....	50
Figure 4.16 : DSC thermograms of polymeric benzoxazines.	51
Figure 4.17 : DSC thermogram of MCPP- <i>g</i> -PCL.....	52
Figure 4.18 : DSC thermogram of MCPP- <i>g</i> -PS.....	52
Figure 4.19 : TGA curves of the polymeric benzoxazines.	53
Figure 4.20 : Photoinduced crosslinking of M-MCPP.....	54
Figure 4.21 : Photo-DSC thermogram showing crosslinking of M-MCPP.	55

1. INTRODUCTION

Polybenzoxazines are advantageous materials since they provide the benefits of phenolic resins and have a wide variety of attractive features such as (I) their curing occurs without any need of strong acid catalysts, (II) during curing, they do not or limitedly release any by products, (III) low shrinkage upon curing, (IV) uptaking water hardly any despite having many hydrophilic groups, (V) for some benzoxazines, glass transition temperature is higher than curing temperature and (VI) high char yield [1]. Moreover, they can be easily prepared by commercially available and inexpensive phenols, amines and formaldehyde [2-4]. They can be used for a number of applications due to their adjustable molecular architecture. The polymerization reaction of benzoxazines is a thermally induced self- polymerization without any curative or initiator [2, 5].

The first benzoxazine was synthesized by Holly and Cope [6], however, the potential benefits of polybenzoxazines has gained attention much later, in 1990s starting with Ning and Ishida [2]. Since then, a number of researches have been performed concerning this area [2, 7].

Even though polybenzoxazines have a lot of fascinating features superior to other resin materials, they are not adequately processable because of powdery form of their monomers and fragility of their networks. Therefore, a number of studies involving polymeric precursor developments has been performed. Recently, main-chain, side-chain and telechelic type precursors are in the centre of polybenzoxazine studies. The main aim of these investigations is to improve the processability, solubility and to cast thin films from polybenzoxazines without distorting the favorable properties of polybenzoxazines such as superior mechanical property.

This thesis aims to synthesize linear main-chain benzoxazine polymers in order to improve the properties of these materials. In this respect, we synthesized a main-chain benzoxazine precursor. These polymers were further used to graft poly (ϵ -caprolactone) (PCL) as well as polystyrene (PS) through hydroxyl groups directly or

with their modification using ROP and ATRP, respectively. Additionally, a photochemically polymerizable group, methyl methacrylate was incorporated into the polymer chain, and then this newly obtained polymer was crosslinked by photochemical means.

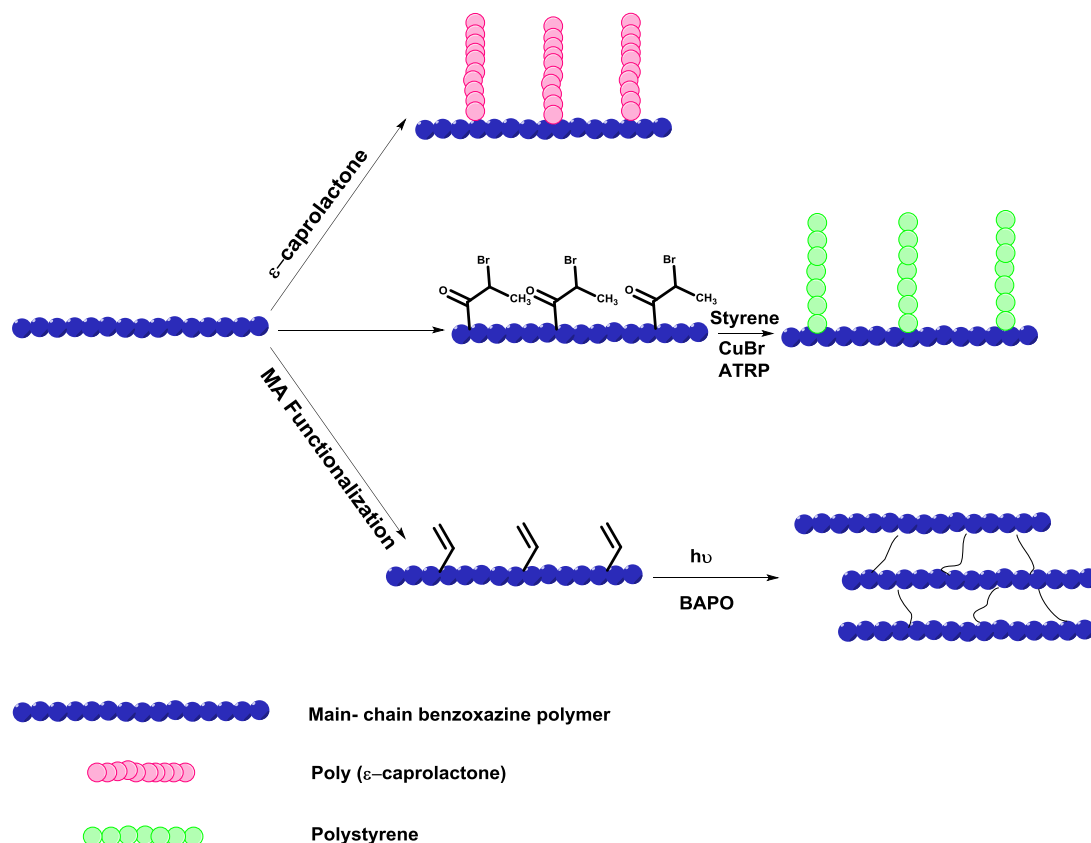
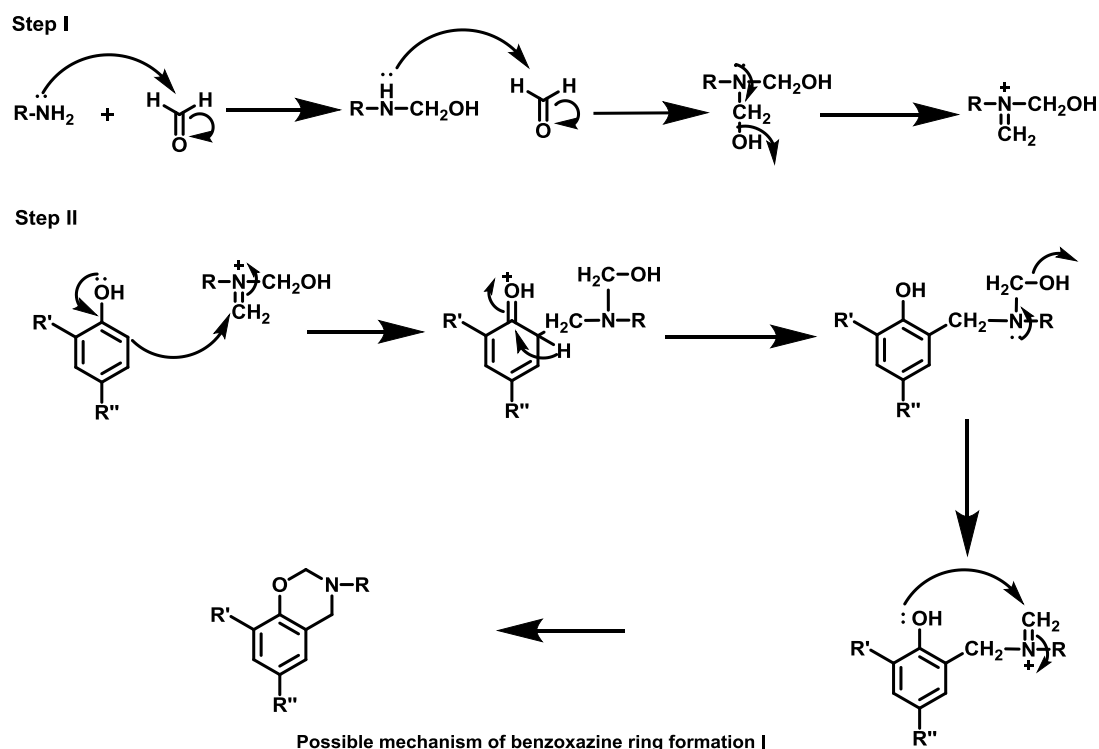


Figure 1.1 : Preparing of benzoxazine polymer and its modified structures.

2. THEORETICAL PART

2.1 Chemical Approaches for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are frequently synthesized using phenol, formaldehyde and aliphatic or aromatic amines in a solvent or by solventless method [8]. Several types of benzoxazine monomers can be obtained by using different phenols and amines. Substitution groups of these phenol and amines may serve additional polymerizable sites which may effect the curing process. Accordingly, polymeric materials with chosen properties can be prepared by using adjusted monomers. In this part of the thesis, synthesis of mono and bifunctional benzoxazine monomers are examined. Possible benzoxazine ring formation mechanisms that are proposed are illustrated in Figure 2.1.



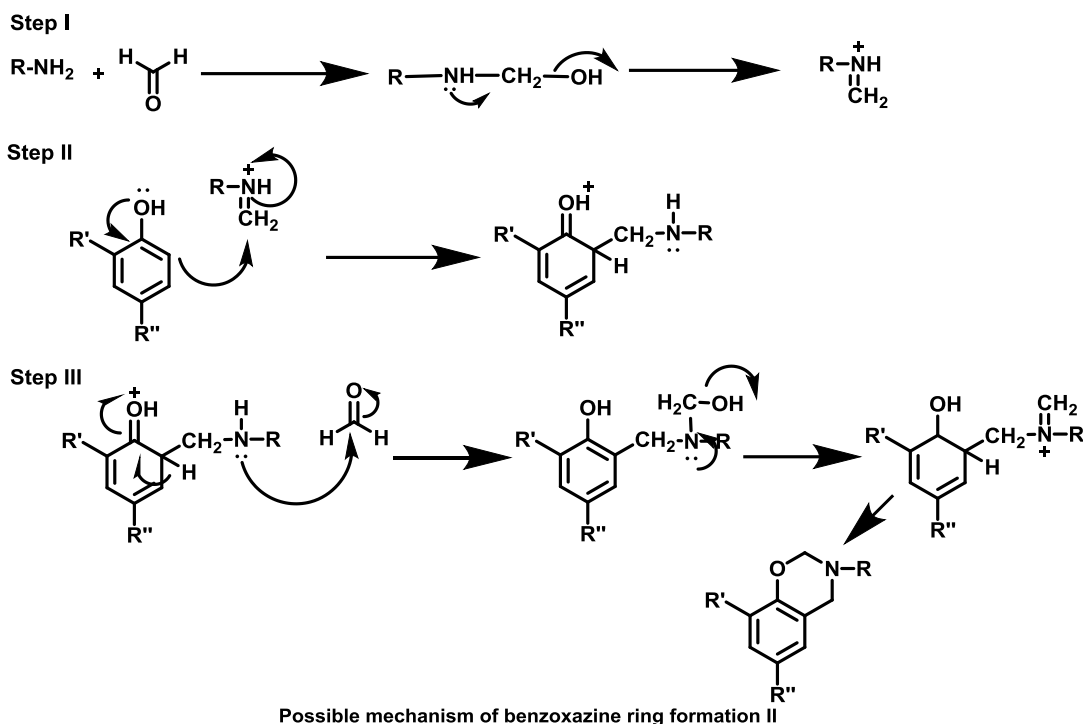


Figure 2.1 : Possible benzoxazine ring formation mechanisms.

2.1.1 Synthesis of mono-functional benzoxazine monomers

Condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers were firstly reported by Holly and Cope [6]. This reaction was performed in a solvent with two steps. Then, they observed that benzoxazine rings react with the free ortho positions of a phenolic compound and forms a Mannich bridge [9]. 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 [10] (Figure 2.2).

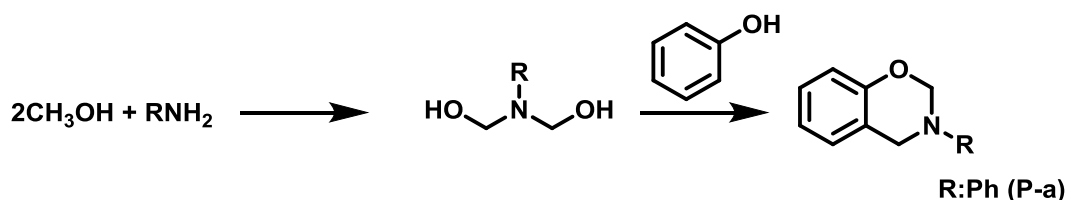


Figure 2.2 : Synthetic procedure for benzoxazine synthesis.

For some benzoxazines, the ring opening was found to take place in existence of active hydrogen containing compounds (HY) like carbazole, imides, naphthol, indoles and aliphatic nitro compounds even phenol (which is also one of the starting materials for the synthesis), and small oligomeric structures form as by products [11]. Figure 2.3 shows the Mannich bridge formation through the ring opening of benzoxazine in acidic medium.

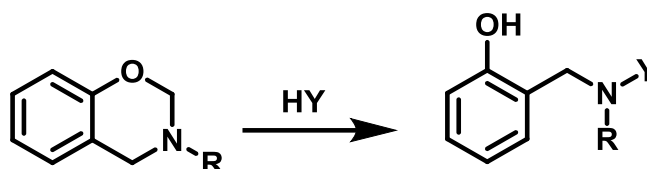


Figure 2.3 : Mannich bridge formation through ring opening of benzoxazine.

Benzoxazine ring stability is strongly affected from the substituents on the ring. When there is more than one reactive ortho position in the starting product, it may lead to another aminoalkylation reaction [12]. Ortho substituent having phenols provide higher yields in produced benzoxazines.

This solution procedure has many disadvantages such as slow reaction rate, requirement of large amount of solvent, poor solubility of the precursors in some cases, increasing cost of products and environmental problems due to using large amounts of organic solvent and solvent residue in precursor which cause problems during processing of benzoxazine resins. *Solventless synthesis* in the melt state was developed by Ishida et al. to overcome these limitations [13]. Liu proposed the reaction mechanism and kinetics for this method [14]. The reactants, i.e, aldehyde, amine and phenolic precursors are mixed together physically, heated to their melting temperature and then reaction is carried on at a temperature sufficient to generate desired benzoxazine product. Formaldehyde is not used in this synthesis, because it evaporates easily and loses stoichiometry very fast. Instead, paraformaldehyde is used for this procedure. Solventless synthetic method provides improved reaction times compared with the traditional synthetic method and fewer unwanted intermediates and by products are formed.

Synthesis of benzoxazine monomers are done with high boiling point nonpolar solvents as a novel solution method, recently [15]. The basis of this technique depends on two different reasons: first reason is that phenol as a starting material

dissolves poorly in common organic solvents used in traditional benzoxazine synthesis, and the second reason is the reaction of diamines with formaldehyde afforded a stable triaza gel structure, which was difficult to be broken by phenols. All of these slow down the wanted monomer formation. Using xylene or dichlorobenzene which are high boiling point nonpolar solvents at higher reaction temperature (130°C) is developed as a new approach to overcome this shortcomings. These nonpolar solvents increase the solubility of phenols and speed up the breakage of triaza gel by phenols. It results monomer formation properly without producing any side reactions because the solvents are nonpolar. All monomers obtained with this method are easily soluble in general polar and nonpolar solvents like dimethylsulfoxide, dimethylformamide, dioxane, ethyl acetate, chloroform and tetrahydrofuran.

Benzoxazines can be synthesized through different methods besides traditional phenol, formaldehyde and primary amines using concept. For example, Aversa et al. [16] prepared 3,4-dihydro-2H-1,3-benzoxazine by synthesizing N-(2-hydroxy-3,5-dimethylbenzyl)-aminopropanoic acid firstly via the Mannich reaction between 2,4-dimethylphenol, aqueous formaldehyde, and 3 aminopropanoic acid in ethanol. This amino acid was allowed to react in 96% sulfuric acid at room temperature. After neutralization, 3-(2-hydroxy-3,5-dimethyl)benzyl-3,4-dihydro-6, 8-dimethyl-2H-1,3-benzoxazine was obtained. Reaction steps are depicted in Figure 2.4.

Benzoxazines can also be prepared by heating the mixture of 2,4-xylenol and hexamethylenetetramine (3:4:1 mole) at 135°C for 2 h in air. The reaction of 1 mole of 2-hydroxybenzylamine with 2 moles of formaldehyde produces bis-(3,4-dihydro-2H-1,3-benzoxazine-3-yl)-methylene.

Using salicylamines(o-hydroxybenzylamine) with glyoxal or -diketones in methanol at a temperature lower than 20 °C is also a way (Figure 2.5) to prepare benzoxazines [17].

One more synthesizing method is directed ortho metallation technique. This offers a predictable and widely applicable synthetic strategy for the regiospecific construction of heterocyclic compounds [18].

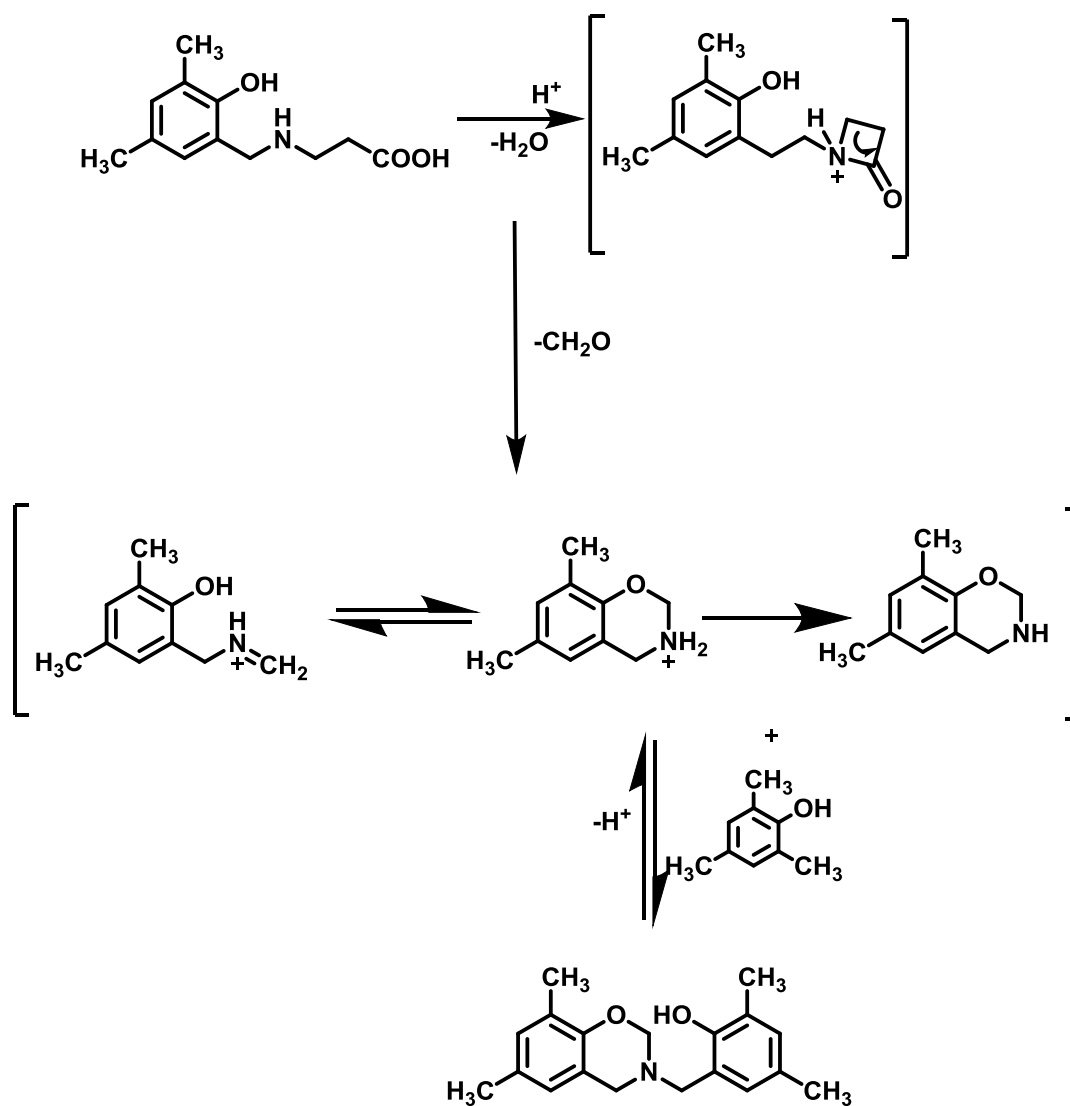


Figure 2.4 : Synthesis of 3,4-dihydro-2H-1,3-benzoxazine [16].

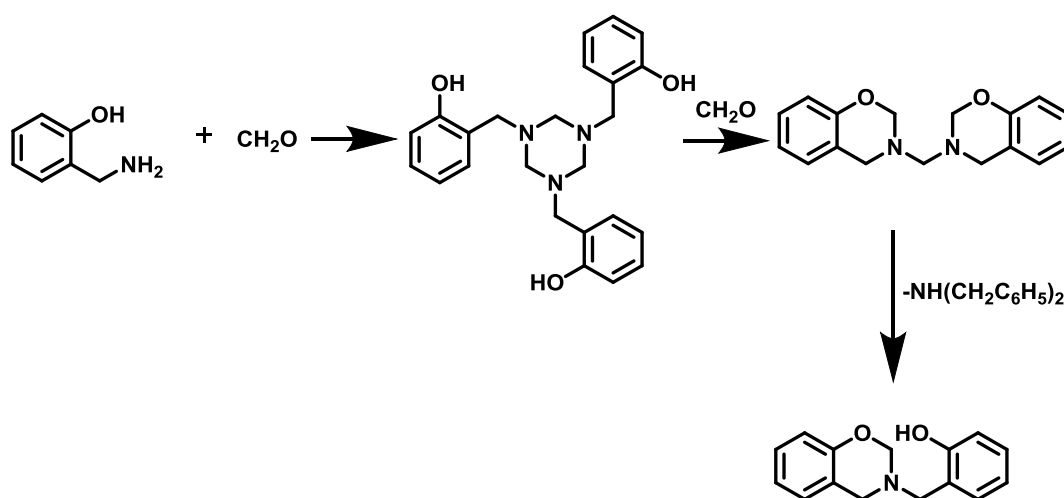


Figure 2.5 : Using salicylamines to prepare benzoxazines [17].

2.1.2 Synthesis of bifunctional and multi-functional benzoxazine monomers

Only oligomeric structures with molecular weight around 1000 Da are formed as a result of curing mono-functional benzoxazines with phenol. In this case, thermal dissociation energy competes with chain propagation energy so that any material cannot be prepared using this strategy [19]. Ishida and coworkers [2, 20, 21] developed a new strategy to overcome this problem and obtain high molecular weight polymers. This strategy involved synthesizing difunctional or multi-functional benzoxazine monomers and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The obtained monomers that were prepared by using bisphenol A, formaldehyde and methylamine had benzoxazine rings at two sides of bisphenol A and named as B-m (Figure 2.6a) (referred to bisphenol A and methylamine). The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by NMR, FTIR and SEC. Product composition is found to depend on the polarity of the solvent. Wide design adjustability can be achieved with this method and it has few simple steps.

Using aniline instead of methylamine, a similar benzoxazine monomer was synthesized [5, 22, 23] and it was named as B-a (Figure 2.6b) (bisphenol A and aniline) and oligomers were oligo B-a. Preparation procedure is illustrated in (Figure 2.7).

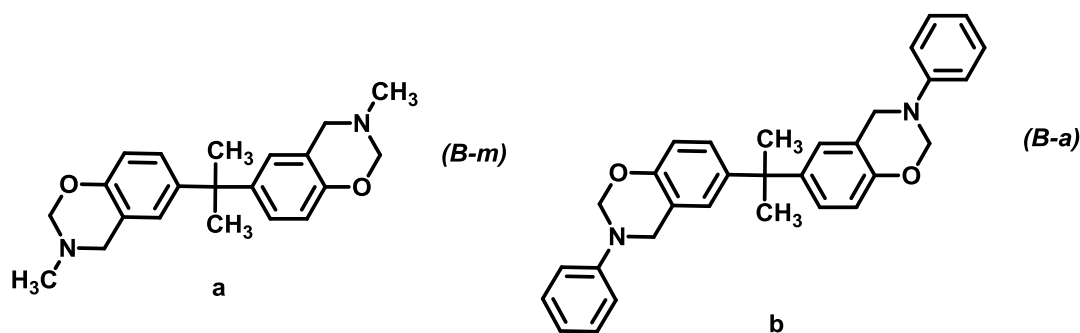


Figure 2.6 : Synthesis of bifunctional and multi-functional benzoxazine monomers.

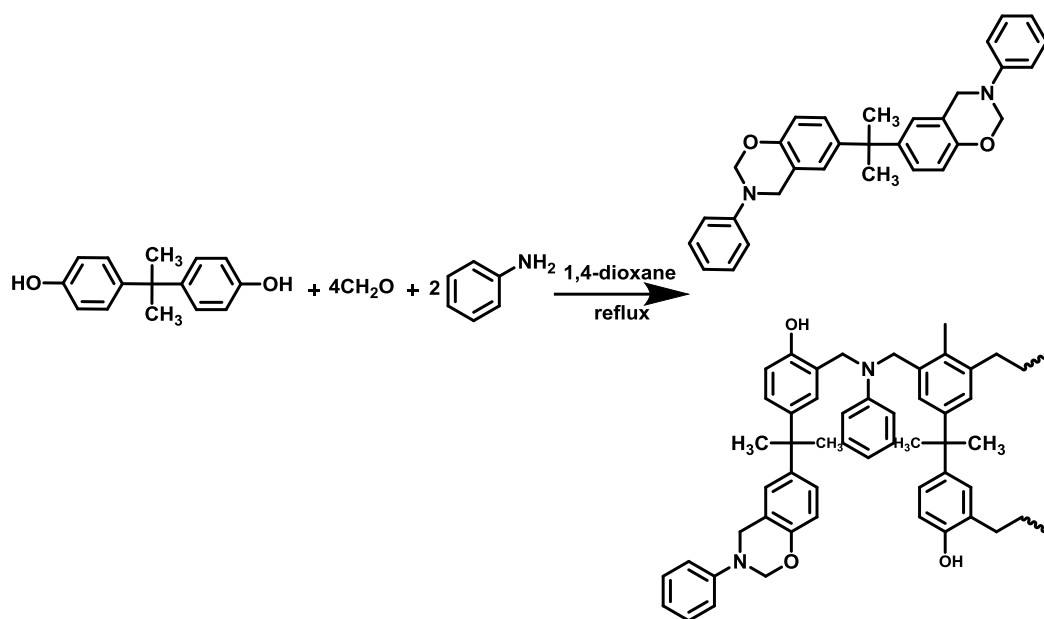


Figure 2.7 : Synthesis procedure of bifunctional and multi-functional benzoxazines.

This material was investigated in terms of cure kinetics with DSC. These measurements indicated that the curing of benzoxazine precursors is an auto-catalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process afterwards [24].

Solventless method was successfully employed for synthesis of a series of difunctional monomers [13, 25-28].

2.2 Synthesis of Benzoxazine Monomers with Different Functional Groups

Typical benzoxazines show some disadvantages such as their brittleness and the high cure temperature needed for the ring opening polymerization. In order to overcome these disadvantages, some strategies have been developed. (a) Synthesizing specially designed monomers, (b) combining benzoxazines with other polymeric materials and (c) preparing linear benzoxazines are the major approaches used for this purpose.

Benzoxazine chemistry shows a wide range of molecular design flexibility just by choosing suitable materials for synthesizing. For specific application fields, the structure of benzoxazines can be adapted and this is done by simply using a large number of different starting compounds [1, 8, 19, 29-31]. Allyl, acetylene, propargyl ether, nitrile, maleimide, norbornane, coumarin, epoxy groups containing benzoxazine monomers were prepared by different researchers. (See Table 2.1)

2.3 Combination of Benzoxazines with Other Materials

2.3.1 Preparations of blends and composites

As stated previously, several approaches to overcome some of the shortcomings of polybenzoxazines, such as mechanical properties, high curing temperature and low process ability, have been proposed which include monomer modification, preparing benzoxazine blends and synthesizing linear benzoxazine polymers. The first methodology which concerns modifying monomers has been considered in the previous section. This part will discuss combination of polybenzoxazines with other polymeric materials or inorganic compounds.

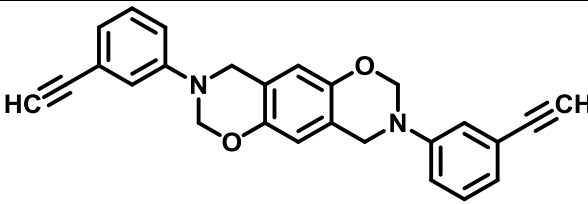
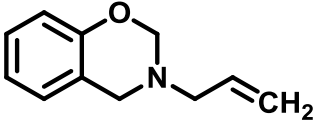
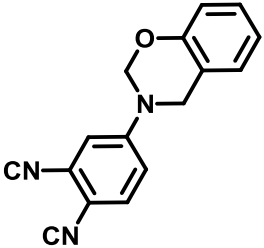
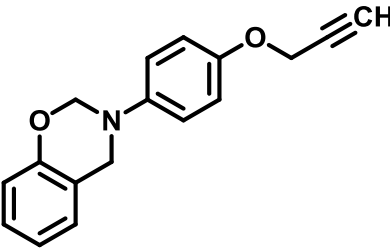
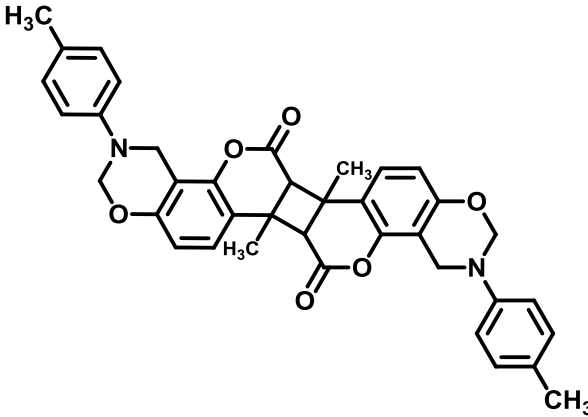
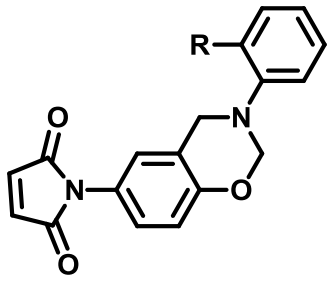
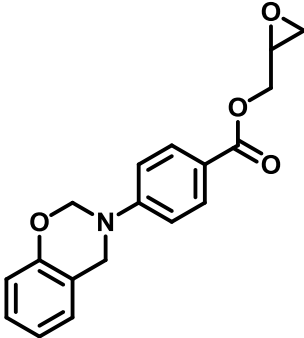
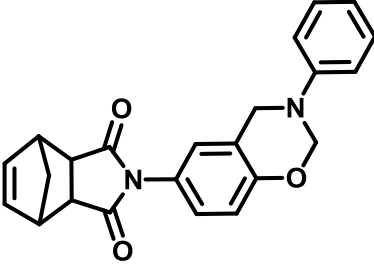
Polybenzoxazines were successfully blended with a large number of different materials like rubber [32-35], polycarbonate [36, 37], poly (ϵ -caprolactone) [38-41], polyurethane [42-44], epoxy resins [45-47], phosphorous containing compounds [30, 48, 49] and clay [50-52].

2.3.2 Preparation of polymers with benzoxazine moieties

Blending polybenzoxazines is a strategy to improve their properties so that benzoxazines can be used in a large number of areas. Another method is preparing polymers containing benzoxazine moieties in their chains. A macromonomer technique was applied for chemical linking of polybenzoxazines with other conventional polymers. 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.

Benzoxazine functionalized polystyrene (Figure 2.8a) [53], poly (ϵ -caprolactone) (Figure 2.8b) [54] and poly (methyl methacrylate) (Figure 2.8c) [55] were illustrated.

Table 2.1 : Benzoxazine monomers with various functionalities.

Benzoxazine Monomers	
 Acetylene-containing benzoxazine [56]	 Allyl-containing benzoxazine [57]
 Nitrile-containing benzoxazine [58]	 Propargyl-ether-containing benzoxazine [59]
 Coumarin-containing benzoxazine [60]	 Maleimide-containing benzoxazine [61]
 Epoxy-containing benzoxazine [62]	 Norbornane-containing benzoxazine [61]

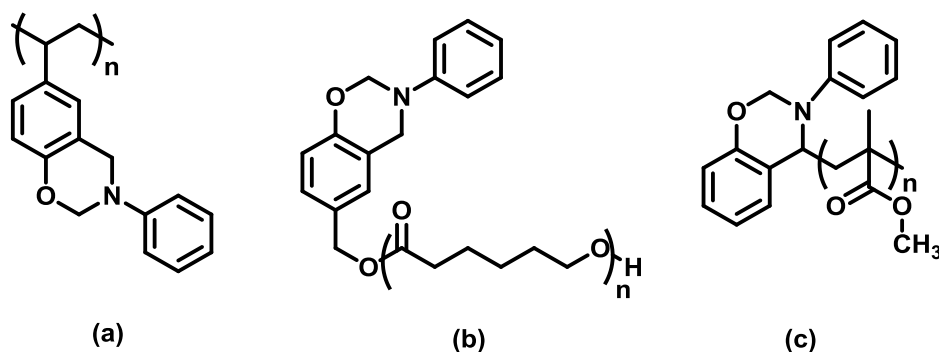


Figure 2.8 : Benzoxazine functionalized polymers.

2.4 Polymeric Benzoxazine Precursors

Although the concept of main-chain type polybenzoxazines where oxazine rings are incorporated in the main chain of a polymer was reported in early days of polybenzoxazine studies, only in the recent several years have detailed studies on the benefits of the main-chain type been reported.

2.4.1 Main-chain precursors

As stated previously, mono-functional benzoxazines lead to small oligomers upon polymerization and do not produce structurally strong, cross-linked polymers, unless they are combined with groups that polymerize in non-benzoxazine chemistry. These precursors also brittle as a consequence of the low molecular weight of the network structure, and casting films from them is difficult because of being powdery for most of them. In order to overcome these problems, main-chain benzoxazine precursors strategy, which leads to more ductile cross-linked polybenzoxazines and enhanced thermal properties, was developed. Liu et al. [63] were the first to prepare main-chain type benzoxazine precursors using 4,4'-methylenebis(2,6-dimethylaniline), bisphenol-A, and formaldehyde, later Takeichi et al. [64] and Chernykh et al. [65] published detailed studies of the synthesis of high molecular weight MCBP through the polycondensation of diamines and bisphenols to produce an AABB-type linear polymer with benzoxazine rings in the main chain (Figure 2.9).

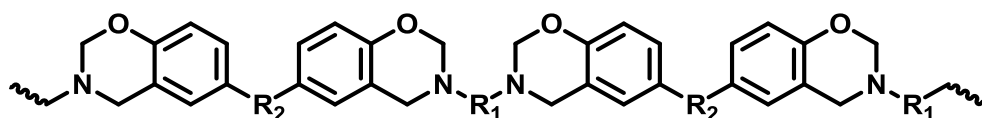


Figure 2.9 : AABBB-type linear polymer with benzoxazine rings in the main chain.

MCBPs can be easily processed as thermoplastics in melt processing equipment, as a result of their higher molecular weights in comparison to benzoxazine monomers. Figure 2.10 shows applications of main- chain benzoxazine precursors.

2.4.1.1 Condensation of classical diamines with bisphenols

Synthesizing an AABB type linear polymer by the reaction of diamines and bisphenols is the first approach to be developed for main-chain benzoxazine precursor strategy. Typically, bisphenol, diamine and formaldehyde (Figure 2.11) are used in a 1:1:4 molar ratio and this generate polymers with high oligomeric sizes ($1000 < M_n < 10000$).

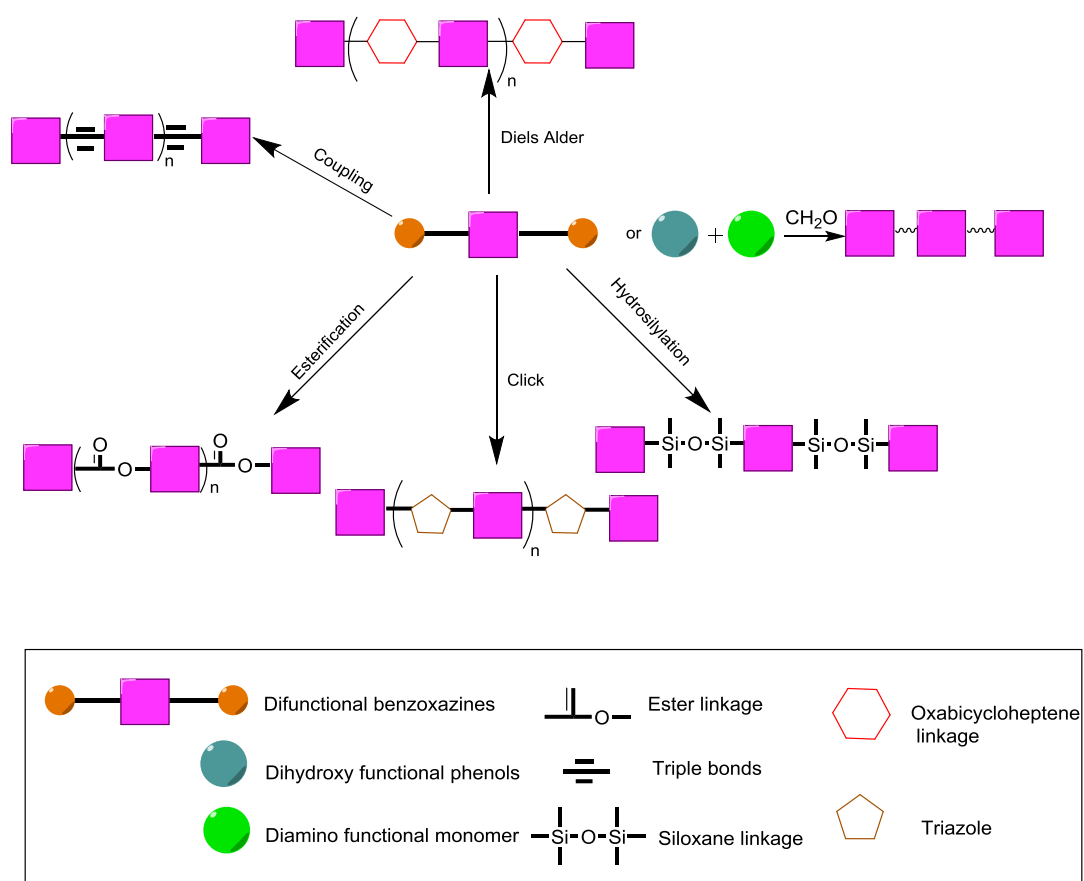


Figure 2.10 : Main applications on main-chain type benzoxazine precursors.

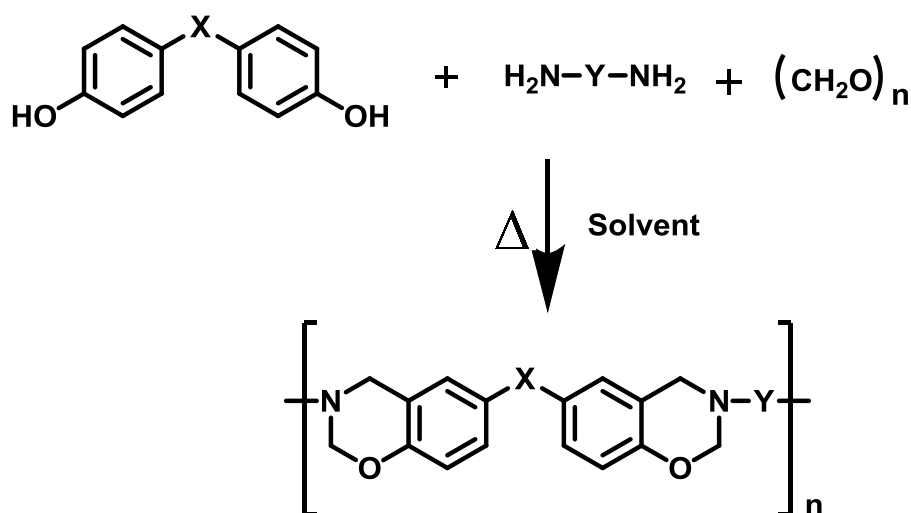


Figure 2.11 : Synthesis procedure for main-chain precursor strategy.

This reaction is usually performed in nonpolar solvents such as chloroform, because the main product water that occurs from the benzoxazine reaction, accelerates the formation of benzoxazine ring. On the other hand, the parameters of the reaction (e.g., time and temperature) should be empirically determined and they change for different reactants [64, 66]. Ring opening of benzoxazine and side reactions may occur when the reaction is not terminated at the right time. This is due to the nature of step polymerization itself, where the probability of side reactions and oligomer cyclization is high [67]. Furthermore, in order to avoid any premature branching and crosslinking of the formed benzoxazine, equilibrium between the ring opening and formation reactions must be pushed toward the latter [64].

MCBPs obtained from this Mannich condensation route have better properties when compared to the monomeric type dibenzoxazines, for example, using the same phenolic compound as bisphenol A, MCBPs (BA-mda) glass transition temperature is lower than the monomeric benzoxazine (BA-a) after polymerization (Figure 2.12).

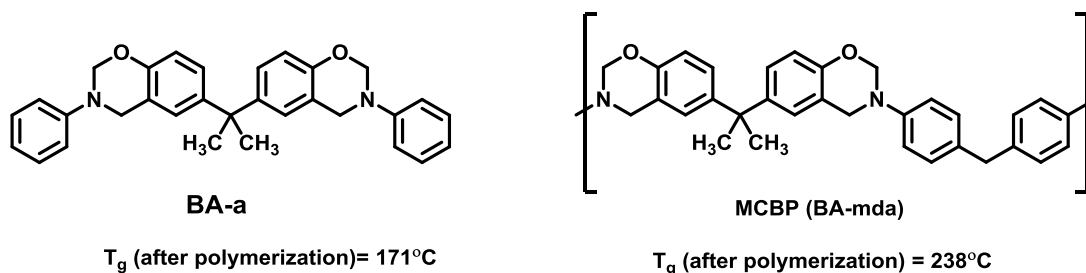


Figure 2.12 : MCBP and monomeric dibenzoxazine of same monomer.

With regard to mechanical properties, MCBPs have superiorities to the benzoxazine polymers obtained from monomeric benzoxazines. The polymers that prepared by MCBPs have increased tensile strength and elongation at break because of precursors high molecular weights and linearity. The modulus is not affected from the molecular weight of precursor except the one that has longer aliphatic chain in the diamine.

2.4.1.2 Amine-terminated siloxanes

These linear polymers can be used in an alternative way to hybridize MCBPs with other polymers, polycondensation reaction with phenol-capped MCBP. Wang et al. [68] reported an example for his method in which an amine-terminated siloxane was reacted with MCBP having phenolic end groups that can undergo polycondensation to produce block copolymers of both benzoxazine and siloxane. First, bisphenol-A and methylenedianiline was reacted to prepare MCBP(BA-mda) with excess bisphenols to cap the linear polymer with phenol functional groups. Later, diamine-terminated polydimethylsiloxane (PDMS) was used to perform second polycondensation and block copolymers of MCBP (BA-mda-block-PDMS) were obtained (Figure 2.13) [68]. The first reaction was performed in chloroform, the second reaction was carried out at 85°C for 12 h.

Dimethylsiloxane chains are flexible and hydrophobic, so that adding these groups at the chain ends of MCBPs increase the hydrophobicity of the cross-linked benzoxazine slightly.

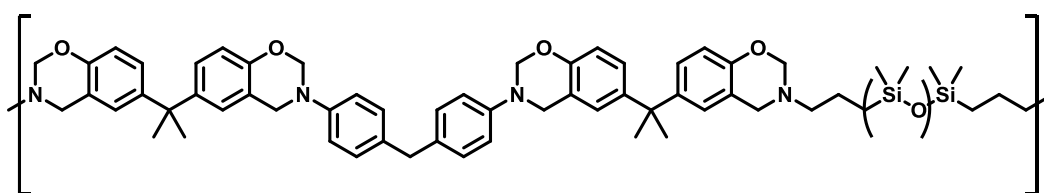


Figure 2.13 : Block copolymer of PDMS and MCBP (BA-mda-block-PDMS).

Takeichi et al. [69] prepared new MCBPs containing PDMS units from the reaction of α,ω -bis(aminopropyl)polydimethylsiloxane of various molecular weights (248, 850, and 1622) and bisphenol-A.

2.4.1.3 Amine-terminated polyether

A novel class of MCBPs using Jeffamines by classical Mannich base polycondensation was reported by Agag et al. [70]. They used Jeffamines of different

molecular weights in toluene as solvent under reflux at 90 °C for 8 h (Figure 2.14). This newly developed MCBP class has a major advantage because they have low viscosity at moderate temperatures, and this property make their processability easier also expand their applications.

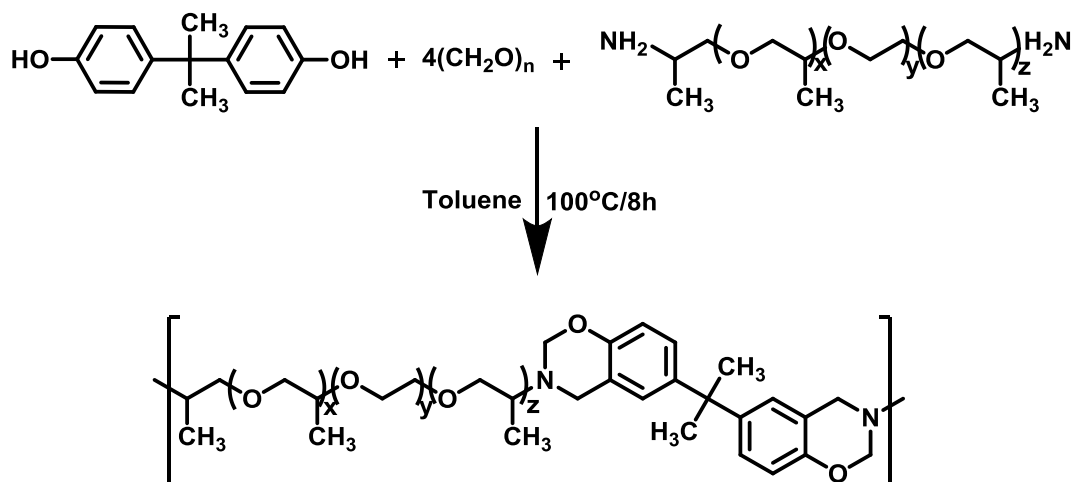


Figure 2.14 : Jeffamine containing MCBP.

2.4.1.4 Polymers with mannich condensation of AB-type

Agag and Takeichi developed a new series of MCBP using aminophenols and A-B type starting materials, instead of the classical A-A-B-B type MCBPs [71]. These MCBPs are able to self condensate in the existence of formaldehyde and can form linear polymers with benzoxazine rings in the chain (Figure 2.15). The reaction is performed in chloroform or chloroform/dioxane solution under reflux for 6 hours. Because of the limited availability of aminophenols, only one study has been reported so far with this procedure. The advantages of this AB-type MCBPs are higher T_g and higher char yield compared with the polymers obtained from classical precursors.

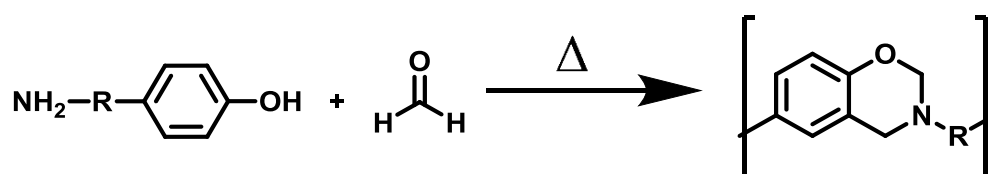


Figure 2.15 : AB-type main-chain precursors.

2.4.2 Side-chain and end-chain precursors

Kimura et al. [25] were first to synthesize side-chain type benzoxazine precursors from poly(vinylphenol), aniline, and formaldehyde (Figure 2.16). they blended this

polymer with epoxy resins and examined the thermal behavior and curing characteristics of this system.

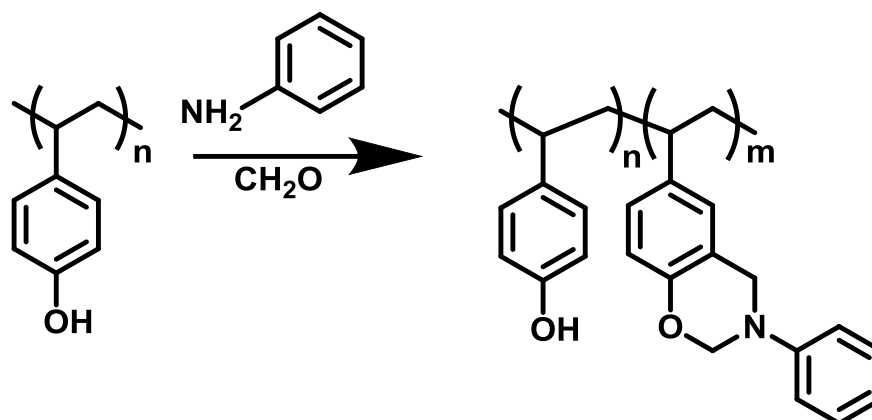


Figure 2.16 : Preparation procedure for side-chain precursors.

Methacrylate[72] and maleimide [73] containing benzoxazine monomers are the other examples for side-chain polymers.

Oxidative polymerization was used as another method for side-chain polymeric benzoxazine precursor (polyP-a) [74].

Side chain precursors can also be prepared by Click Chemistry processes. poly(vinyl chloride) PVC [75], polystyrene [76], and polybutadiene [77] are examples for these processes. Main applications of side- chain benzoxazines are illustrated in Figure 2.17.

The term “telechelic” can be defined as reactive end-groups containing macromolecules, which have the ability to react selectively with another molecule. They can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Additionally, with coupling reactions of difunctional or multifunctional telechelic polymers, star, dendritic or hyper-branched polymers may be synthesized [78]. Various macromolecular architectures obtained by the reactions of telechelics are represented in Figure 2.18.

Due to their brittleness, benzoxazine resins cannot be easily processed for applications. Telechelic approach provide connecting benzoxazine moieties onto thermoplastic chains so that processing gets easier.

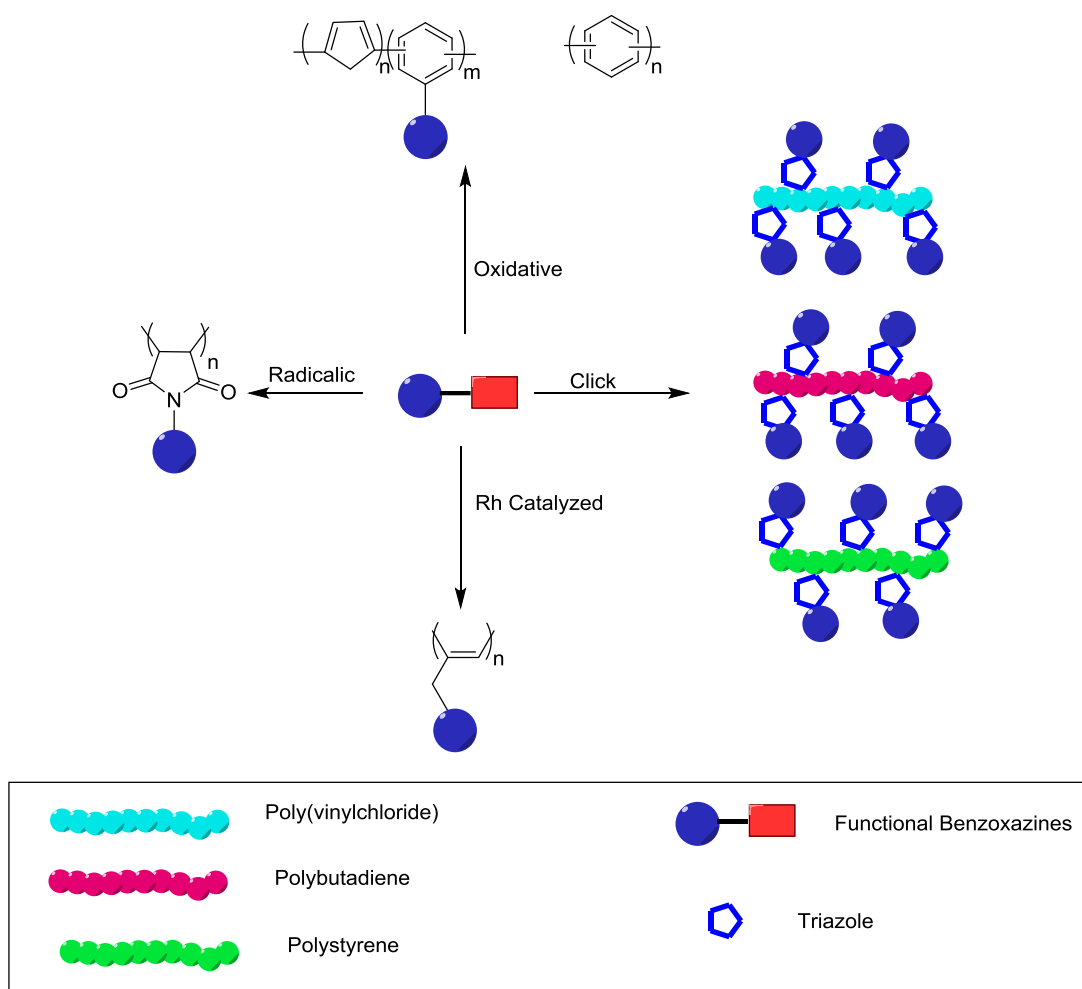


Figure 2.17 : Main applications of side-chain benzoxazines.

Kışkan et al. [53] reported synthesis of a benzoxazine attached PSt macromonomer (PSt-B macromer) (Figure 2.19a). Benzoxazine [38, 39] and naphthoxazine containing PCL macromonomers [79] (Figure 2.19b), naphthoxazine-functionalized poly(propylene oxide)s [80] (Figure 2.19c) and benzoxazine containing poly(arylether)s [81] (Figure 2.19d) were also synthesized.

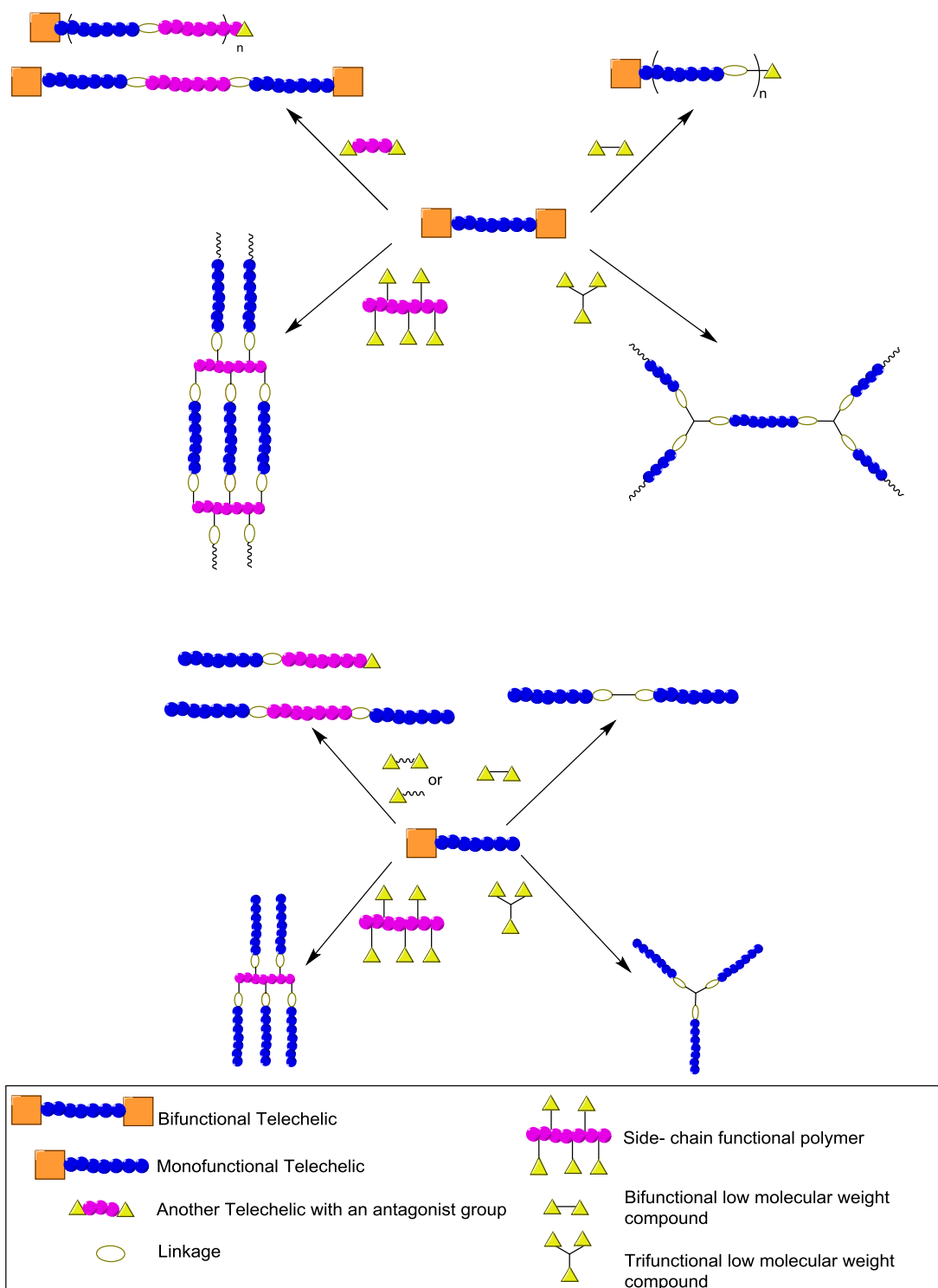


Figure 2.18 : Macromolecular architectures obtained by the reactions of telechelics.

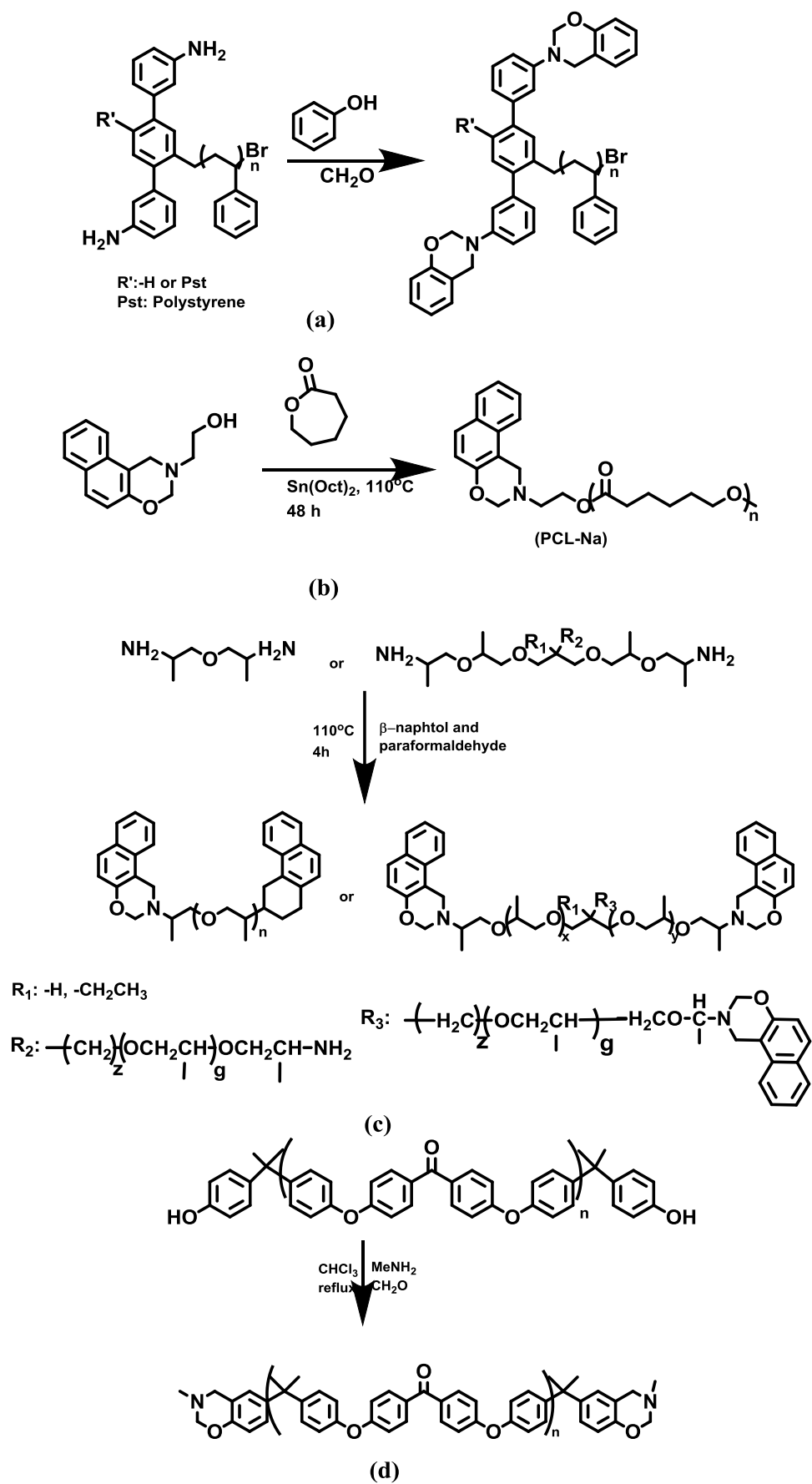


Figure 2.19 : Benzoxazine attached macromonomers.

2.5 Reaction Mechanism of Ring Opening Polymerization of Benzoxazine

Mono-oxazine ring containing benzoxazine has a distorted semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. This six membered ring can easily undergo ring opening reaction at specific conditions as a consequence of this conformation. Additionally, both the oxygen and nitrogen atoms are strongly basic and they can act as potential cationic polymerization initiation sites so that the benzoxazine ring becomes very likely to open by a cationic mechanism [82, 83]. It is estimated that the oxygen might be the preferred polymerization site due to its high negative charge distribution (O, -0.311; N, -0.270).

The typical method of polymerization of benzoxazine monomers is thermal curing without using any catalyst [23]. It should be emphasized that the polymerization mechanism of benzoxazine resins is still not well established.

2.5.1 Cationic polymerization of benzoxazines

2.5.1.1 Acid catalyzed polymerization of benzoxazines

It has been proposed that the ring opening polymerization of the benzoxazine proceeds through a cationic mechanism [84, 85]. McDonagh and Smith [12] reported that 3,4-dihydro-2H-1,3-benzoxazine exhibits ring/chain tautomerism with protonation, by migration of the proton from the nitrogen to the oxygen atom, and thereby produce iminium ions in the chain form. It was proposed that an electrophilic substitution reaction follows this ring opening (Figure 2.20) [86].

This mechanism does not consider the pKa of the acid catalyst, but the pKa controls the structure of the reaction intermediate. In the presence of strong acid catalyst, benzoxazine monomer converts to polybenzoxazine immediately at low temperatures after ring opening. The intermediate was proposed to be an iminium ion. Though, when weak acid catalyst is used, the polymerization reaction is slow in the beginning of the reaction. Using weak carboxylic acids as catalyst generate aminomethyl ester species as intermediates and the reactions are considered to be auto-accelerated reactions.

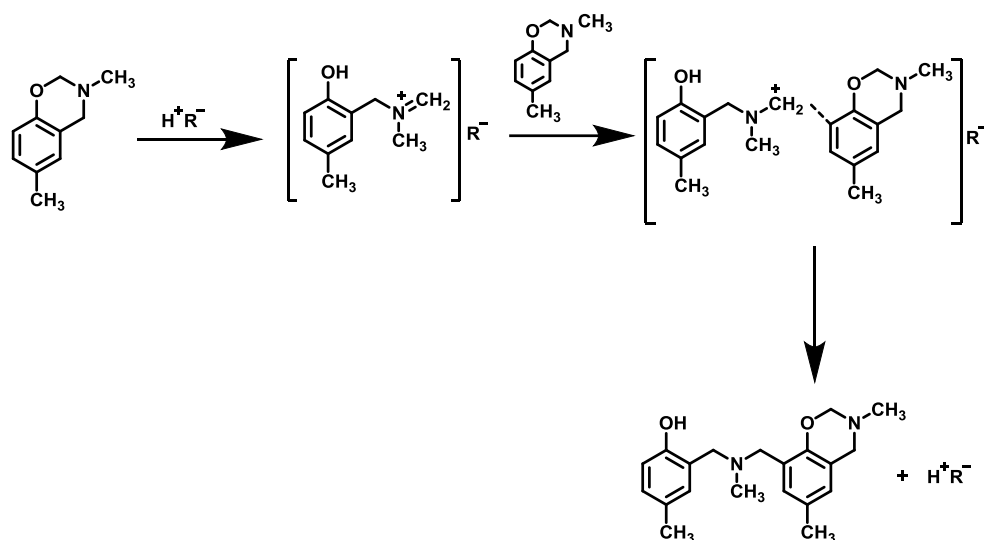


Figure 2.20 : Acid catalyzed ring opening of benzoxazines.

Wang and Ishida [83] examined PCl_5 initiated polymerization of substituted 3,4-dihydro-2H-1,3-benzoxazines that have different mono-oxazine ring. They discovered that benzoxazines have two types of Mannich base structure; phenoxy type (Type I) and phenolic type (Type II) and these two architectures polymerize with different mechanisms, the mixture of phenoxy and phenolic type benzoxazines polymerize with the Type I as the major constituent. The mechanisms are demonstrated in (Figure 2.21) and (Figure 2.22). Phenoxy Type (Type I) and phenolic type (Type II) Mannich base having benzoxazines are listed in **Table 2.2**.

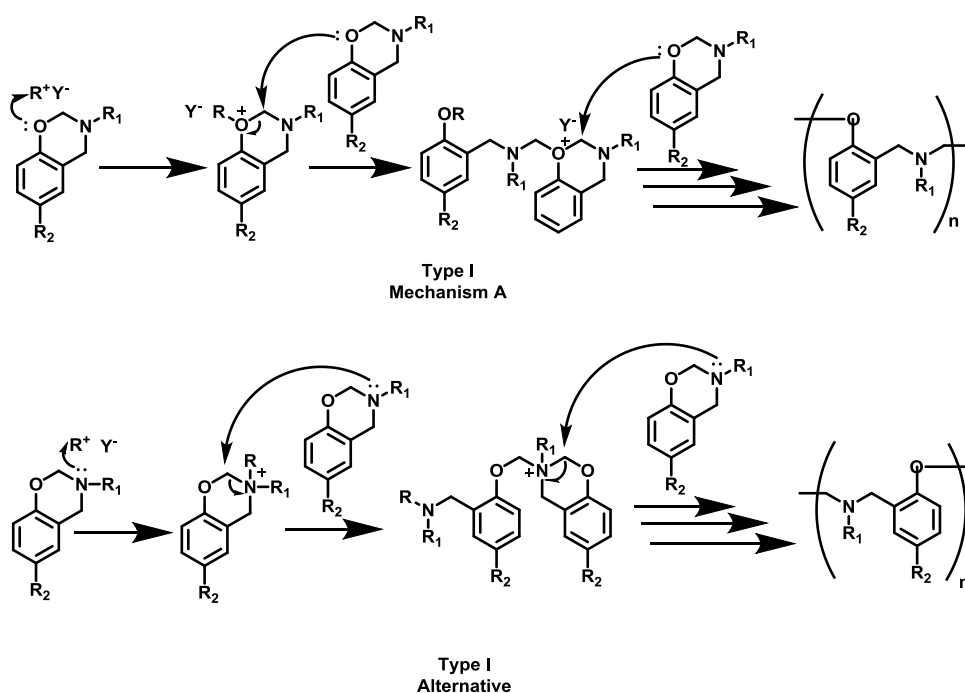


Figure 2.21 : Ring opening of phenoxy-type (Type I) benzoxazine.

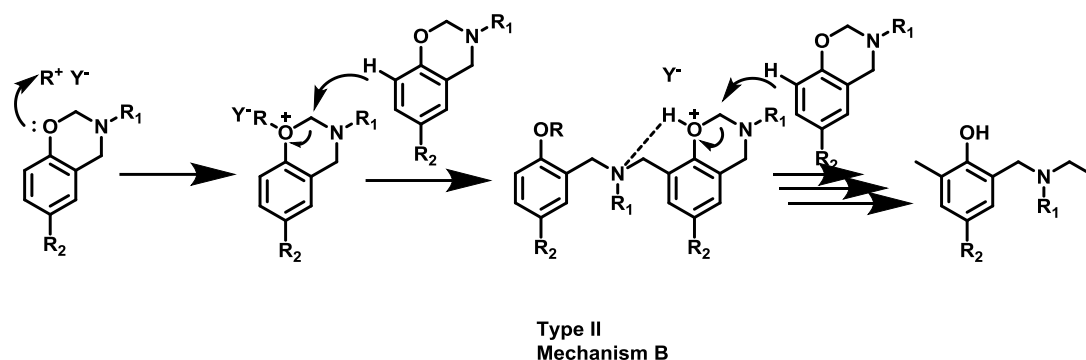


Figure 2.22 : Ring opening of phenolic-type (Type II) benzoxazine.

Table 2.2 : Methyl substituted benzoxazine monomers.

pC-m	24DMP-m
235TMP-m	345TMP-m

2.5.1.2 Photoinitiated polymerization of benzoxazines

A mono- functional benzoxazine, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (P-a), was examined in terms of its photoinitiated ring-opening cationic polymerization with diphenyliodonium hexafluorophosphate and triphenylsulfonium hexafluorophosphate as initiators by Kasapoglu et al. [87]. This study discovered that the obtained polymer structure is related to the ring opening of the protonated monomer either at the oxygen or nitrogen atoms. The phenolic mechanism also contributed, but its influence decreased with decreasing monomer concentration. Free radical assisted cationic polymerization of benzoxazines was also investigated in this work. Polymerization can be achieved at much higher wavelengths and carbon centered radicals were oxidized to form carbocations (Figure 2.23). Different probable routes were proposed for the next step of the polymerization.

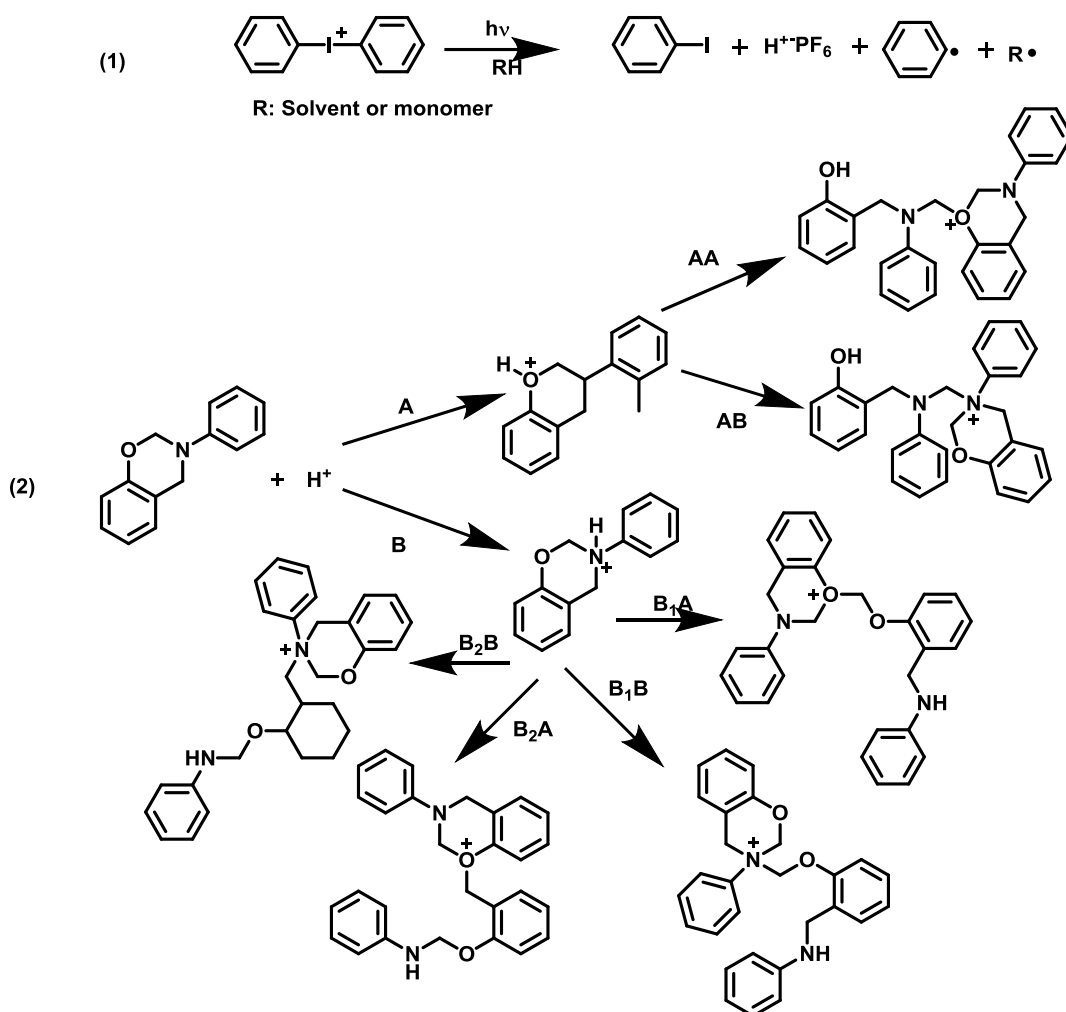


Figure 2.23 : Photoinitiated polymerization of benzoxazines.

2.5.2 Thermal polymerization of benzoxazines

The ring- opening of benzoxazine is recommended to produce a carbocation and an iminium ion which exist in equilibrium. This carbocation attacks to the benzene ring as an electrophile, preferring the free ortho and para positions of the phenol ring, to continue polymerization. Propagation rate immensely depends on the stability of the iminium ion since carbocation is responsible for the propagation. Different mechanisms are proposed for thermal polymerization of benzoxazines (Figure 2.24).

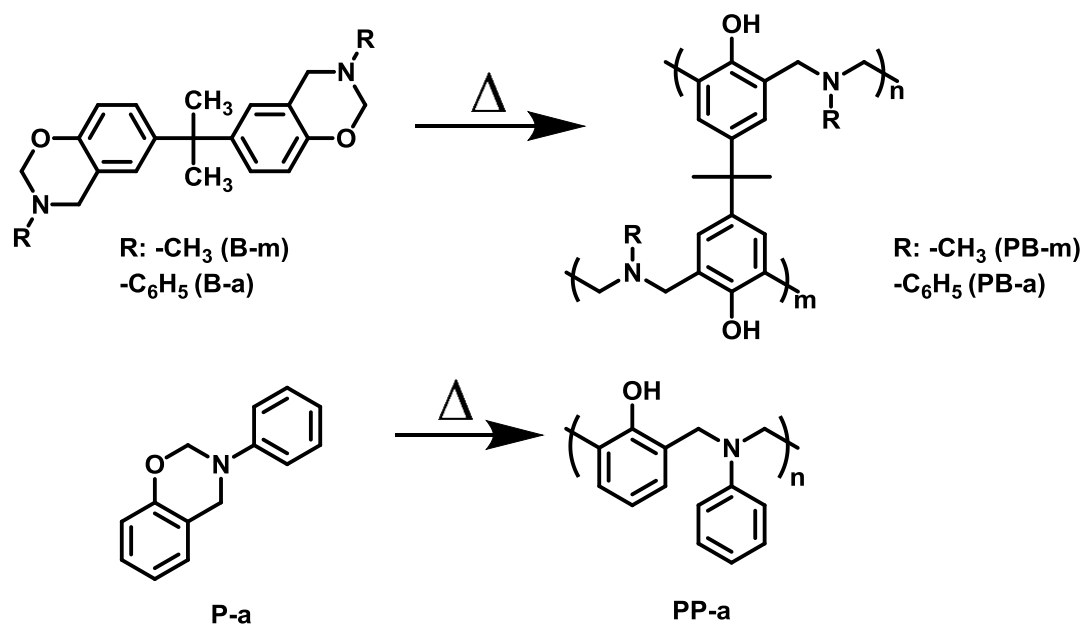


Figure 2.24 : Thermal polymerization of benzoxazines.

2.6 Properties of Benzoxazines and Polybenzoxazines

Benzoxazine precursors and their cross-linked polymers show a series of unique properties as detailed below in this section.

2.6.1 Low shrinkage during polymerization

Thermoplastic and thermosetting resins lose their volume during polymerization process. Even low shrinkage materials exhibit a change about 2-10% [88, 89]. This shrinkage is a disadvantage when adapting them as high performance materials like adhesives, coatings and sealants. Warping of composites and optical distortion is defeated by low shrinking materials.

Benzoxazines and polybenzoxazines exhibit near-zero shrinkage with high mechanical unity [85, 89, 90]. Generally during curing, the monomers lose their dimension by $\pm 1\%$. During isothermal curing at elevated temperature, shrinkage occurs slightly. Though, at room temperature, when before and after polymerization volumes are compared, the densities and volume changes have found to be little. In order to demold and minimize the residual stress, combining the properties of small volume difference during isothermal curing and near-zero shrinkage at room temperature is beneficial.

2.6.2 Low water absorption

Polyester, vinylester, phenolic, epoxy, bismaleimide, and polyimide resins have a problem of uptaking water greatly at saturation, they absorb water by 3-20 % [91, 92]. The polar groups existing in the resin structure is the reason of this absorption, benzoxazine resins also have polar groups such as phenolic OH and Mannich base in each repeating unit, but adversely they absorb much less water than these resins, their water uptake is around 1%. When using more hydrophobic radicals having phenols or amines, this uptake can be reduced. Lower water absorption is an advantage if the dielectric constant of the polymer is desired to be low, because the dielectric constant changes with increasing water content. Also, the difference between the dry T_g and wet T_g is small in the case of low water uptaking materials.

2.6.3 High glass transition temperature

Glass transition temperature is an important feature to be considered within thermal properties of thermosetting resins. Thermal stability of thermosettings with high T_g is better than low T_g having thermosettings. Increasing cross-linking density leads to high T_g s and brittleness on polymer resins. Adding more polymerizable sites to resins raise the glass transition temperature to higher temperatures, for instance.

Crosslinked polybenzoxazines exhibit unexpectedly high glass transition temperatures between 160 and 400°C. Furthermore, polybenzoxazine structure can be tailored in order to achieve sub-zero T_g s. This increase may depend on two reasons. One is that benzoxazine resins are formed with the chain polymerization rather than condensation polymerization, and the other is, after polymerization temperature, polymer chains keep giving further reactions and structural realignment.

Polymerization temperature and glass transition temperature are exceedingly different in thermosetting resins, this property provides advantages in many applications [7].

2.6.4 High char yield

Flammability control of materials is an important area of research because legislations get harder and new technologies are developed. Burning of a material starts with thermal initiation followed by thermo-oxidative degradation of the flammable particles. Designing inherently high char forming materials is an approach

to reduce burning. Char also reduces the diffusion rate of decomposed, flammable gases toward the flame front. Consequently, flame-resistant material applications require high char yield polymers. Under nitrogen at 800°C, many polymers have char yields insufficient for industrial applications. Increment of benzene group content increases char yield usually, but there is not a correlation between them.

Heat release capacity calculating is a considerable property to compare flammability characteristics in theory [93]. Polybenzoxazines are intrinsically flame retardant materials because their hydroxyl groups, tertiary amine and benzene groups are abundant in molarity. Degredation starts with amine group vaporization, so that addition of a group to this amine end will reduce vaporization and expand char formation. Acetylene, allyl, nitrile, maleimide and phtalonitrile groups bring very high char yield to polybenzoxazine thermosets [56-58, 94-98]. Phenolic component of benzoxazine also effects the char yield and rate of weight loss [99].

2.6.5 Fast physical and mechanical property development

Condensation polymers develop physical and mechanical properties slowly at low degrees of polymerization and require a high degree of conversion to achieve good properties. Hence, the difference in degree of conversion by a few percent near the end of polymerization displays much more important changes in mechanical properties than 10-20% increment in conversion around 50% degree of conversion. This is in contrary to addition polymerization where rapid development of molecular weight at an early degree of polymerization is detected. Glass transition temperature and other mechanical properties of polybenzoxazines expand immediately as the polymerization makes a start. For bisphenol-A type epoxy resin, almost 25% of the ultimate T_g would be developed at the same conversion. This means that even at a relatively low conversion, the green strength of the polybenzoxazine product will be excellent, and may reduce cycle time [100-102].

2.7 Ring-Opening Polymerization (ROP)

Ring-opening polymerization is one of the two routes to obtain polylactones and polylactides besides polycondensation. Polycondensation technique is less expensive when compared to ring-opening, however, is difficult to synthesize high molecular weight polymers, to prepare well-defined copolyesters, and to achieve specific end

groups. Ring-opening polymerizations are carried out under similar conditions, and frequently with similar initiators to those used for ionic polymerizations of unsaturated monomers; they are likewise sensitive to impurities. In some cases one succeeds in the ring-opening polymerization of cyclic olefins with formation of straight chain unsaturated polymers [103].

High molecular weight polylactones and polylactides are obtained by the ROP of the corresponding cyclic monomers. ROP of a cyclic ester is shown in (Figure 2.25).

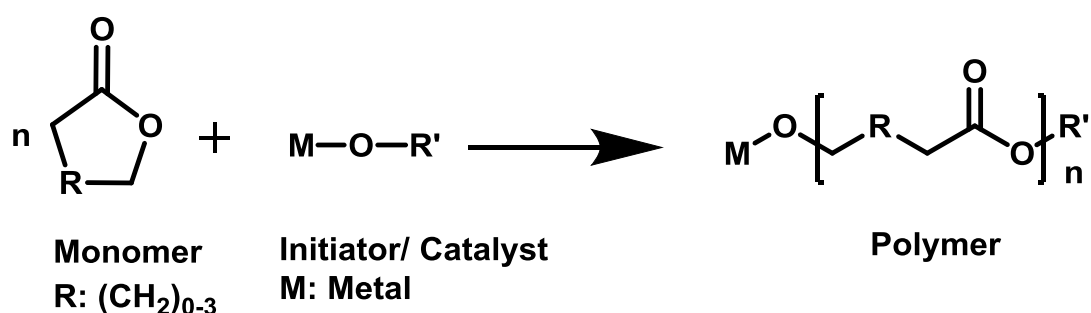


Figure 2.25 : Typical ring opening of a cyclic ester.

The ring- opening reaction can be carried out either as a bulk polymerization, or in solution, emulsion or dispersion. Polymerization needs a catalyst or initiator to start. In short periods of time, high molecular weight polymers with low polydispersity can be obtained. ROP eliminates the shortcomings associated with the polycondensation route like the need for exact stoichiometry, high reaction temperatures and the removal of the low molecular weight by products.

Ring-opening proceeds with three different mechanisms, depending on the initiator : cationic, anionic and coordination-insertion [104, 105].

Various organometallic compounds are used as initiator for ROP reactions. Stannous octoate and aluminium isopropoxide are illustrated in (Figure 2.26).

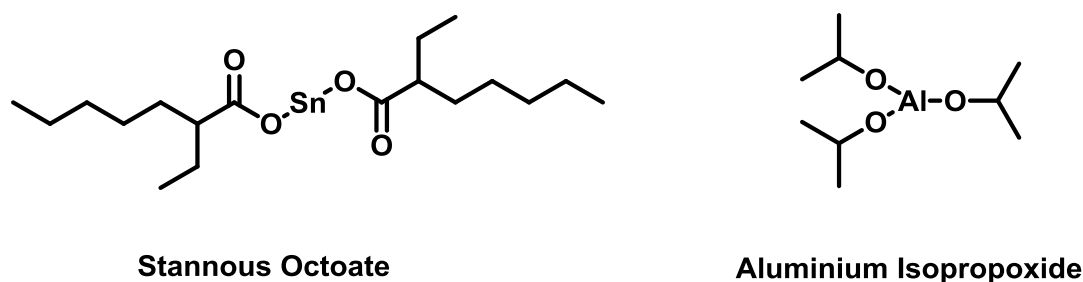


Figure 2.26 : Organometallic compounds used as initiator for ROP.

Tin (II) 2-ethylhexanoate, commonly referred to as Stannous octoate $[\text{Sn}(\text{Oct})_2]$, is widely used in ROP reactions. It is not thought to be the actual initiator, because the molecular weight of the obtained polymer does not depend on the $\text{Sn}(\text{Oct})_2$ -monomer ratio. Two different proposed mechanisms for stannous octoate initiating polymerization are demonstrated in (Figure 2.27).

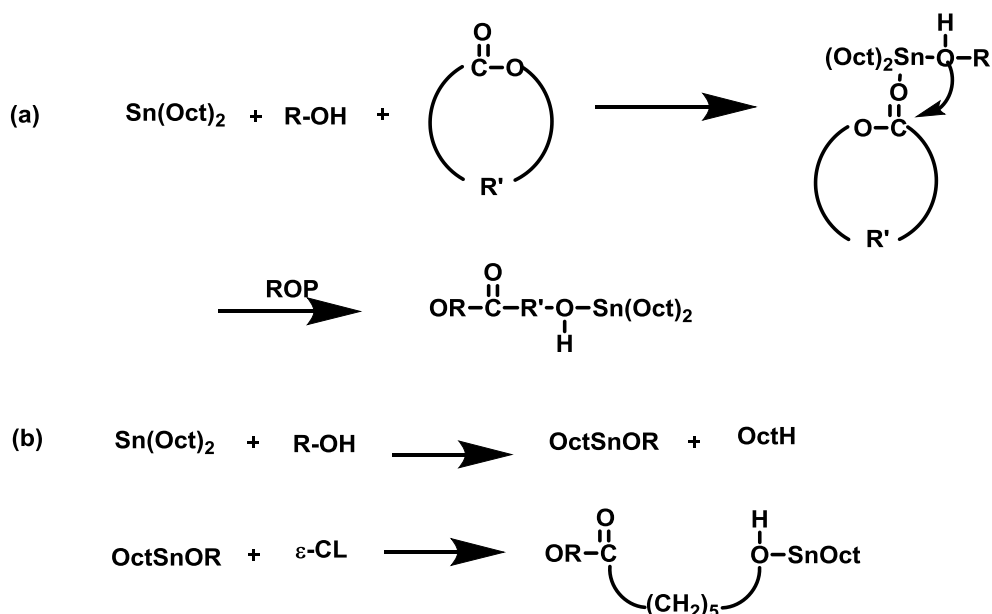


Figure 2.27 : Proposed mechanisms for tin octoate initiated polymerization.

2.8 Photopolymerization

Photochemical or photoinitiated polymerizations occur when radicals are produced by ultraviolet and visible light irradiation of a reaction system. In general, light absorption results in radical production by either of two pathways:

- Some compound in the system undergoes excitation by energy absorption and subsequent decomposition into radicals.
- Some compound undergoes excitation and the excited species interacts with a second compound (by either energy transfer or redox reaction) to form radicals derived from the latter and/or former compound(s).

The term photosensitizer was originally used to refer to the second pathway, especially when it involved energy transfer, but that distinction has become blurred. The mechanism for photoinitiation in a reaction system is not always clear-cut and may involve both pathways. Photosensitizer is now used to refer to any substance

that either increases the rate of photoinitiated polymerization or shifts the wavelength at which polymerization occurs.

Photoinitiation offers several advantages. Polymerization can be spatially directed (i.e., confined to specific regions) and turned on and off by turning the light source off and on. The initiation rates can be very fast and are controlled by a combination of the source of radicals, light intensity, and temperature. Industrial photopolymerizations typically use solvent-free systems, which offer advantages for both economic and/or environmental considerations. The significant limitation of photopolymerization is that penetration of light energy through a thickness of material is low. However, photopolymerization is well suited for surface and other thin-layer applications in the printing and coatings industries. Photopolymerization can be used with heat-sensitive substrates, since polymerization is rapid even at ambient temperatures [67].

2.9 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is a controlled/living polymerization method. Controlled polymerization can be described as the method which provides synthesis of polymers with predetermined molecular weights, low polydispersities and controlled functionalities. Transfer and termination reactions are reduced as possible by appropriate reaction conditions.

An ATRP system contains an initiator, a copper (I) halide complexed with some ligands and monomer. Repetition of addition of monomer to a growing radicals produced from inert alkyl halides by a reversible redox process by transition metal compounds complexed by amine ligand. General ATRP reaction is shown in (Figure 2.28). the mechanism is demonstrated in (Figure 2.29).

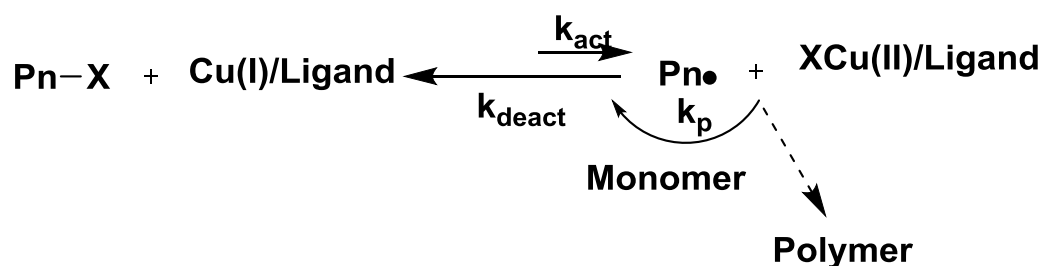
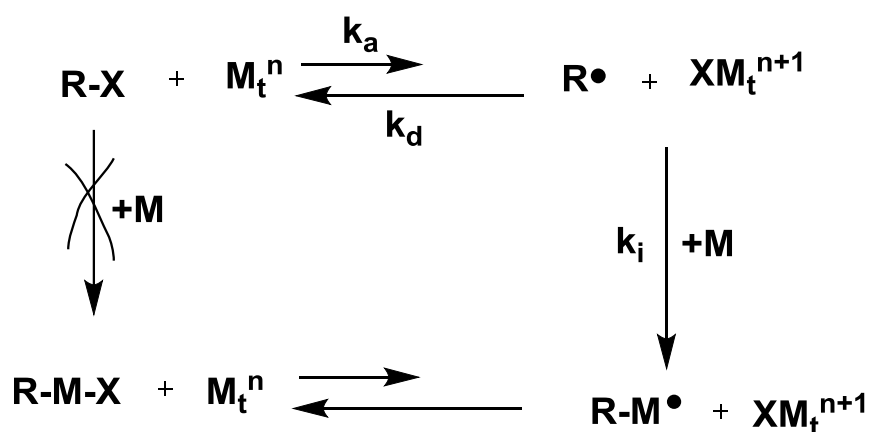


Figure 2.28 : General reaction of Atom Transfer Radical Polymerization.

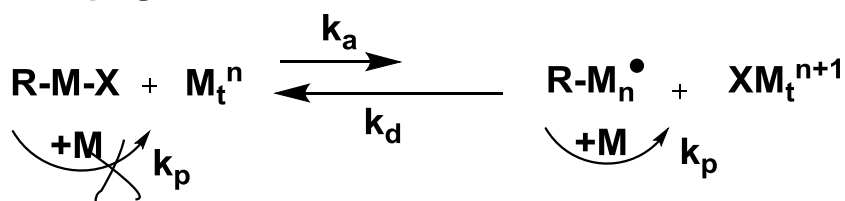
Initiators (organic halides) should have a structure similar to the corresponding polymer end group.

Transition metals used in ATRP should be highly selective towards atom transfer reactions have the ability of resulting $X-M_{t+1}$ species. The ligand should not be a participant of the atom transfer reactions, but should attend to an one- electron process that would result in oxidative addition/reductive elimination. Also, it should be highly compatible with the atom/group X , but not to the hydrogens and alkyl radicals. The most important catalysts used in ATRP are $Cu(I)Cl$, $Cu(I)Br$, $Ni(II)$, $Ru(II)/Al(OR)_3$ and $Fe(II)/3(PR)_3$ [95, 96].

Initiation



Propagation



Termination



Figure 2.29 : The reaction mechanism of ATRP.

The ligands have three important roles at ATRP. First is the effect on the redox chemistry, second is selectivity control by steric and electronic effects and for the last, they increase the solubility of catalytic systems. 2,2-bipyridine derivatives are

the most efficient ligands used in ATRP e.g. substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), and tris-[2-(dimethylamino) ethyl]amine (Me₆-TREN).

A large amount of vinyl monomers can successfully be polymerized with atom transfer radical polymerization route (styrenes, (meth)acrylates, (meth)-acrylamides, dienes, and acrylonitrile).

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3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Solvents

Chloroform (CHCl₃, VWR, 99,2%)

It was used as received.

Ethanol (Aldrich)

It was used as received.

Toluene (Merck, 99,9%)

It was used as received.

Diethyl ether (J.T. Baker)

It was used as received.

Methanol (Merck, 99,9%)

It was used as received.

1,4 dioxane (Riedel-deHaen, 99,5%)

It was used as received.

Dimethylformamide (DMF, Aldrich)

It was used as received.

3.1.2 Chemicals

Triethylamine (J.T. Baker, 98%)

It was dried with NaOH before using.

Benzyl alcohol (Aldrich, 98%)

It was used as received.

2-Bromopropionyl chloride (Aldrich)

It was used as received.

1,3-Diamino 2-Propanol (Fluka, 98,0 %)

It was used as received.

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, Acros, 97 %)

It was used as received.

Paraformaldehyde (Aldrich, 95,0- 100,5 %)

It was used as received.

1,6-Hexanediamine (Acros, 99,5%)

It was used as received.

ϵ - Caprolactone (Aldrich)

It was used as received.

Stannous octoate (Aldrich, 95%.)

It was used as received.

Methacryloyl chloride (Fluka, 97%)

It was used as received.

Bisphenolachylphosphin / Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide / BAPO (Ciba)

It was used as received.

PMDETA / N,N,N',N'',N''-Pentamethyldiethylenetriamine

It was distilled before use.

Copper (I) bromide (CuBr, 98%, Acros)

It was used as received.

Styrene (Aldrich,99%)

It was filtered through basic aluminium oxide.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^1H NMR measurements were recorded using an Agilent VNMRs 500 MHz instrument in methanol as internal standard for homopolymer, d-DMSO as internal standard for copolymer and CDCl_3 with $\text{Si}(\text{CH}_3)_4$ as internal standard for other polymers.

3.2.2 Infrared spectrophotometer (FT-IR)

The FTIR spectra are recorded at Perkin Elmer Spectrum One with an ATR accessory (ZnSe, Pick Miracle Accessory) and cadmium telluride (MCT) detector. Resolution was 4°cm^{-1} and 12 scans with 0.2°cm/s scan speed.

3.2.3 Gel-permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three Viscogel GPC columns (G2000HHR, G3000HHR and G4000HHR), (7.8 mm internal diameter, 300 mm length) were used in series. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C . Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.2.4 Differential scanning calorimeter (DSC)

Differential Scanning Calorimeter was observed on a Perkin Elmer Diamond DSC with a heating rate of 15°Cmin^{-1} under nitrogen flow 20.0 (mL/min) .

3.2.5 Thermal gravimetric analysis (TGA)

Thermal Gravimetric Analysis was done on Perkin Elmer Diamond TG/DTA with a heating rate of 5°Cmin^{-1} under nitrogen flow 20.0 (mL/min)

3.2.6 Differential photocalorimeter

This experiment was performed with a Perkin Elmer DSC 400.

3.3 Synthesis

3.3.1 Synthesis of benzoxazine precursor (MCP)P

In a 250 mL round bottom flask, 1,46 g hexanediamine (12,5 mmol), 1,1 g 1,3-diamino 2- propanol (12,2 mmol), 5,55 g bisphenol A (24,3 mmol) and 2, 92 g paraformaldehyde (97 mmol) was blended in a solution of 50 mL toluene and 25 mL ethanol, the reaction was stirred at 120°C for 24 hours. Solvents was evaporated under vacuum and the product was precipitated in cold methanol. The residues were dried under vacuum for two days. Result was yellow powder. Yield was 64,8%.

3.3.2 Synthesis of ϵ -caprolactone functionalized benzoxazine copolymer (MCP-g-PCL)

100 mg benzoxazine precursor and 0,7 mL ϵ -caprolactone (6,32 mmol) were placed in a Schlenk tube under nitrogen. Polymerization was catalyzed by stannous octoate for 96 hours in 5 mL of toluene as solvent. The mixture was precipitated in cold methanol and dried under vacuum, resulted as light yellow powder. Yield was 27,5%.

3.3.3 Functionalization of benzoxazine copolymer with methacrylate Group (M-MCP)

0,5 g benzoxazine precursor was dissolved in 10 mL of anhydrous triethylamine and 100 mL of anhydrous chloroform in a 500 mL round bottom flask. The mixture was cooled to 0°C and 1,5 mL of methacryloyl chloride solution in 10 mL chloroform was added at a period of 30 minutes under nitrogen. Reaction medium was stirred for overnight at room temperature, then refluxed for 2 hours. The mixture was washed three times with 0,1 N Na_2CO_3 solution and dried with Na_2SO_4 . The dessicant was filtered and chloroform was evaporated under vacuum. Product was precipitated in cold methanol,dried under vacuum, which obtained yellow powder. Yield was 8%.

3.3.4 Functionalization of benzoxazine copolymer with an initiator for ATRP (MCP-ATRP-I)

It was done as (M-MCP), using 0,5 g benzoxazine precursor, 1,5 mL 2-bromopropionylbromide and solution system of 10 mL triethylamine, 100 mL

chloroform. Solvent was evaporated under vacuum, product was precipitated in diethyl ether and dried under vacuum. Yield was 15,48%.

3.3.5 Crosslinking investigation by photo-DSC

5 mg (M-MCPP), 0,3 mL dimethylformamide, 2 mg bisphenolachylphosphin was mixed and a gelly solution prepared. This solution is put in a pan for photo-DSC, and cured for 30 minutes.

3.3.6 Synthesis of polystyrene grafted benzoxazine with ATRP (MCPP-*g*-PS)

1 mL of styrene and 5 mg copper (I) bromide was dissolved in 1 mL of dimethylformamide in a Schlenk tube. 8,3 μ L of PMDETA was added to this solution. Finally, 25 mg (MCPP-ATRP-I) was added and solved completely. The air in the tube was drained with a pump in liquid nitrogen, melted and dried again. Reaction mixture was stirred at 90°C for 4 hours. It was filtered from neutral silica gel twice, precipitated in methanol and dried under vacuum. Yield was 5,5 %.

4. RESULTS AND DISCUSSION

Although benzoxazines have many superiorities over phenolic resins in the matter of thermal and mechanical properties, these properties should still be enhanced in order to broaden the application fields of benzoxazines because benzoxazines have some disadvantages such as high curing temperature, poor processability and ductility. The molecular structure is favorable to adapt them for many applications and they can easily be prepared from cheap starting materials so that it is possible to expand synthetic methods. This can be done by either combining with some other materials, or modifying benzoxazine monomers or precursors. The monomers are generally powder and casting film is challenging. By adding elastomeric materials, fragility problem can be solved as a well known pathway. Nevertheless, this way might deteriorate the thermosetting properties of benzoxazines. In order to improve the properties and keep the thermosetting nature, benzoxazine precursors strategy has been developed. This precursor can either be main-chain, side-chain or telechelic types. The crosslinked structure obtained from these types of precursors are assumed to have increased mechanical property with keeping advantageous properties of benzoxazines.

This study aims to prepare a benzoxazine precursor from two diamines one of which contain a hydroxyl group in its structure and the other has a longer aliphatic chain. Precursor was obtained from bisphenol and diamines. The hydroxyl groups present in the precursor facilitate grafting process through two different polymerization methods, namely ring opening polymerization and atom transfer radical polymerization. The obtained new polymers were characterized by ^1H -NMR, FT-IR and Gel Permeation Chromatography (GPC) devices. Using Differential Scanning Calorimeter (DSC) and Thermogravimetric Analyzer (TGA), their thermal properties were investigated.

The preparation of benzoxazine precursor was carried out by condensation of bisphenol A, two diamines one of which having hydroxyl functionality and formaldehyde using the monomer synthesis strategy. The structure of the obtained polymer, Main-Chain Benzoxazine Precursor (MCP) was confirmed by ^1H NMR

and FTIR spectroscopies. The synthesis pathway of the precursor is demonstrated in Figure 4.1.

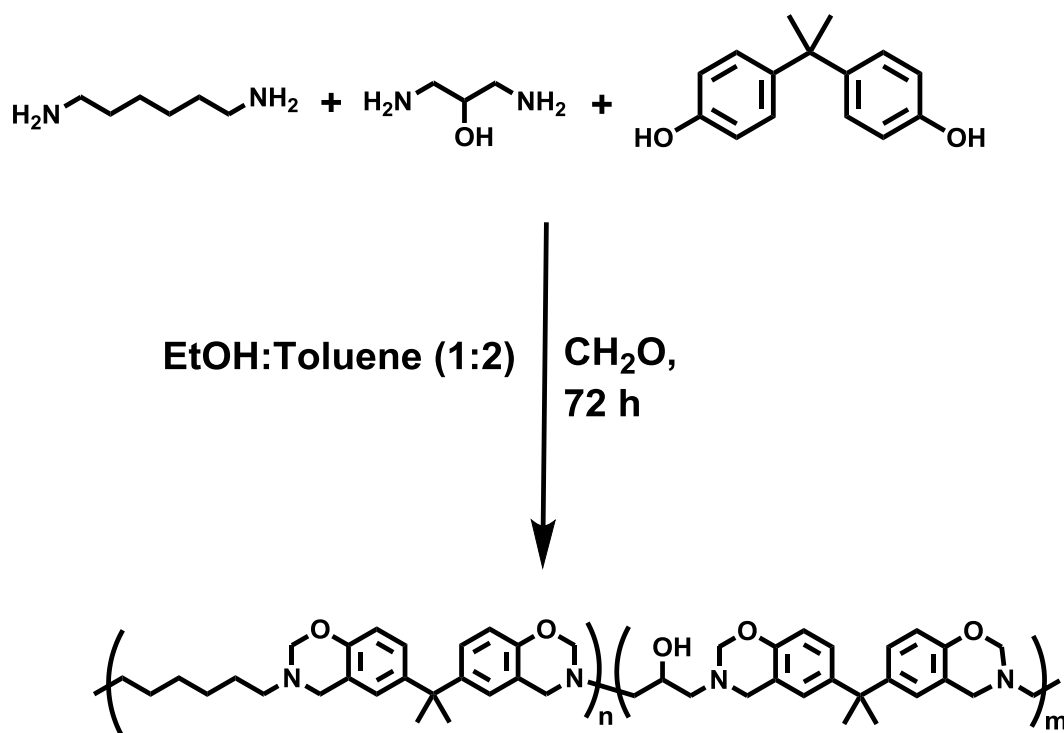


Figure 4.1 : Synthesis of MCP.

FTIR spectra all polymers shows a sharp peak around 1500 cm^{-1} , indicating that there is C-O and C-N bonds corresponding to oxazine ring structure. MCP also exhibits a broad band near 3393 cm^{-1} , where the O-H bond is placed. Aromatic C-C stretching band appears at 1613 and 1464 cm^{-1} in the spectra of all polymers. The peaks at 2850 and 2925 cm^{-1} demonstrates the C-H stretches of the aliphatic group in the precursor and C-N bond in aliphatic amine group occurs at 1230 cm^{-1} , (Figure 4.2).

^1H NMR spectrum of MCP exhibits O-CH₂-N protons of oxazine ring at 4.68 ppm, while the aliphatic protons are located at between 1,04-1,2 ppm. The proton in -OH group which is the distinguishing point in the precursor appears near the oxazine ring at 4,8 ppm (Figure 4.3).

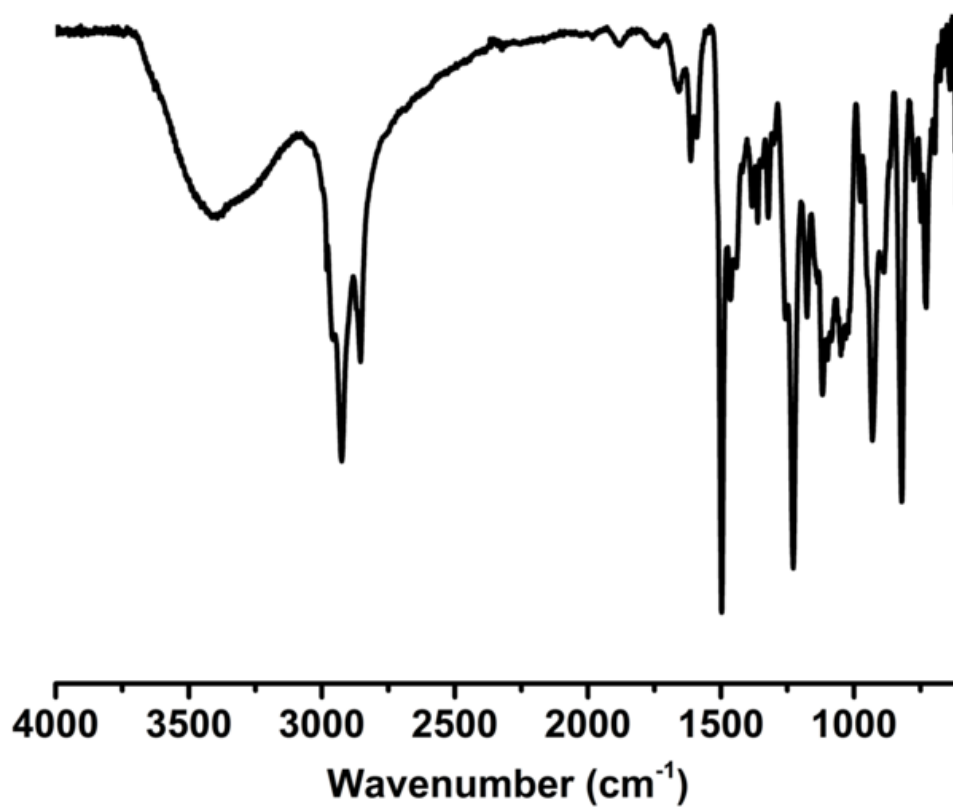


Figure 4.2 : FT-IR spectrum of MCPP.

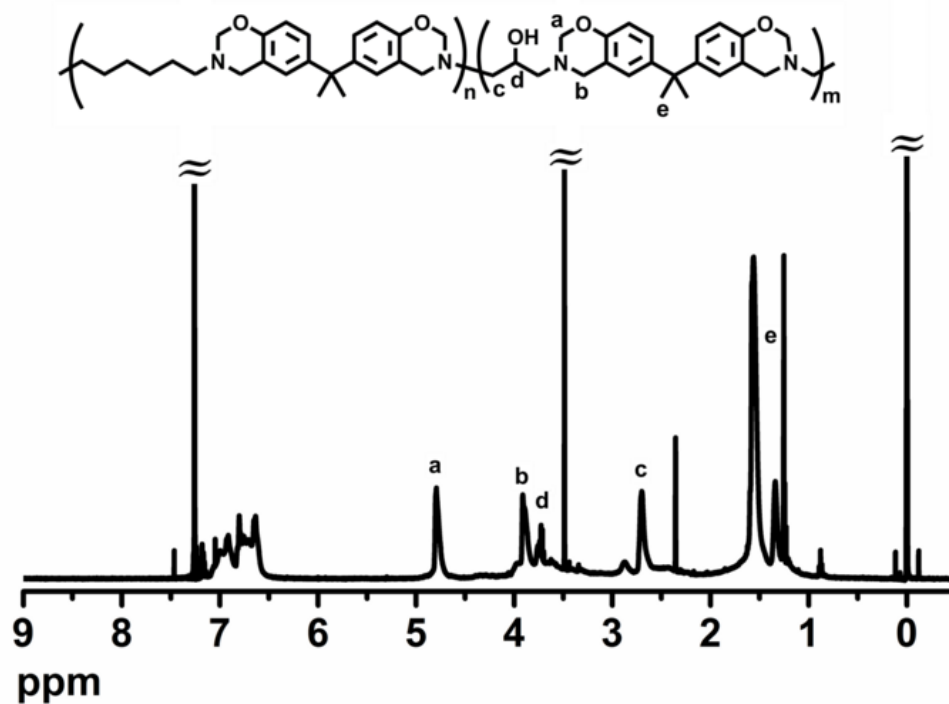


Figure 4.3 : ¹H-NMR spectrum of MCPP.

The precursor was then used in various modification and polymerization processes. Tin(II) 2-ethylhexanoate, commonly known as Tin octoate (in short Sn(Oct)₂) is the most widely used initiator to prepare designed polymers based on PCL. In particular when used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, linear and star-shaped block copolymers or networks can be obtained via corresponding alkyl octoate formation. In the light of previous studies that reporting the role of hydroxyl groups as ring opening polymerization initiators, in this thesis, hydroxyl functionalized benzoxazine prepolymer was used as initiator and PCL was expected to be successfully grafted onto the benzoxazine chain .

The synthesis of Poly (ϵ -caprolactone) Grafted Main-Chain Benzoxazine Precursor, MCPP-*g*-PCL, involved the reaction of MCPP with ϵ -caprolactone in the presence of tin octoate as catalyst. Synthesis scheme is depicted in Figure 4.4.

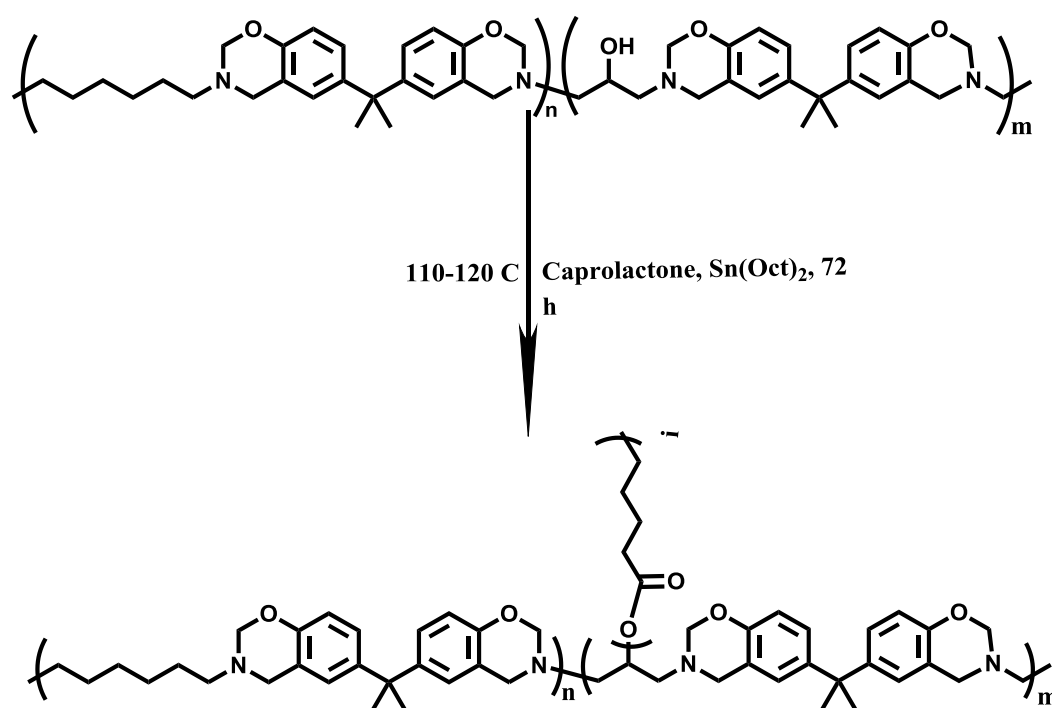


Figure 4.4 : Synthesis of MCPP-*g*-PCL.

The incorporation of Poly (ϵ -caprolactone), (PCL) segment was confirmed by spectral investigations. As shown in Figure 4.5 where the IR spectrum of MCPP-*g*-PCL is presented, the presence of stretches in MCPP, except O-H bond are noted. Expectedly, the strong peak at 1720 cm⁻¹ attributed to the aliphatic ester carbonyl, proves successful grafting of ϵ -caprolactone repeating units.

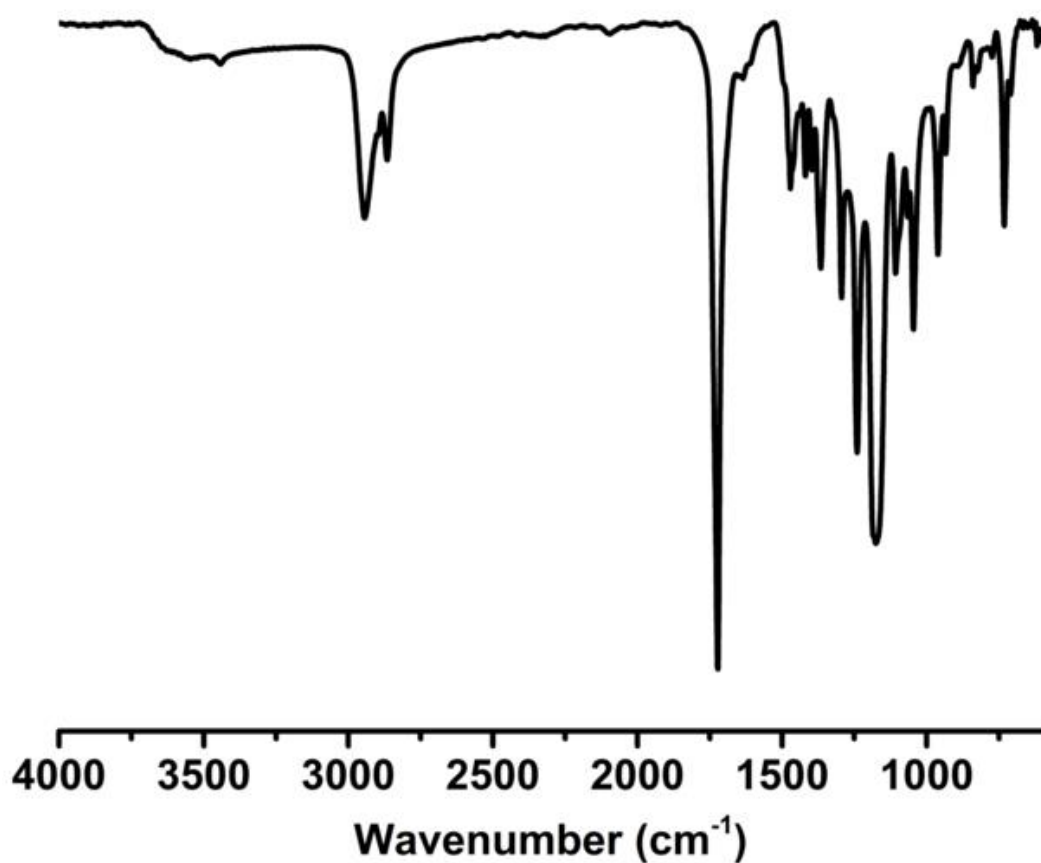


Figure 4.5 : FT-IR spectrum of MCPP-*g*-PCL.

However, ^1H NMR spectrum showed no specific peak for the oxazine ring structure. This could be due to the dilution of the benzoxazine groups by the incorporation of PCL segment. It is also possible that under experimental conditions, the ring opening process did not proceed through the hydroxyl groups. This point needs further investigation.

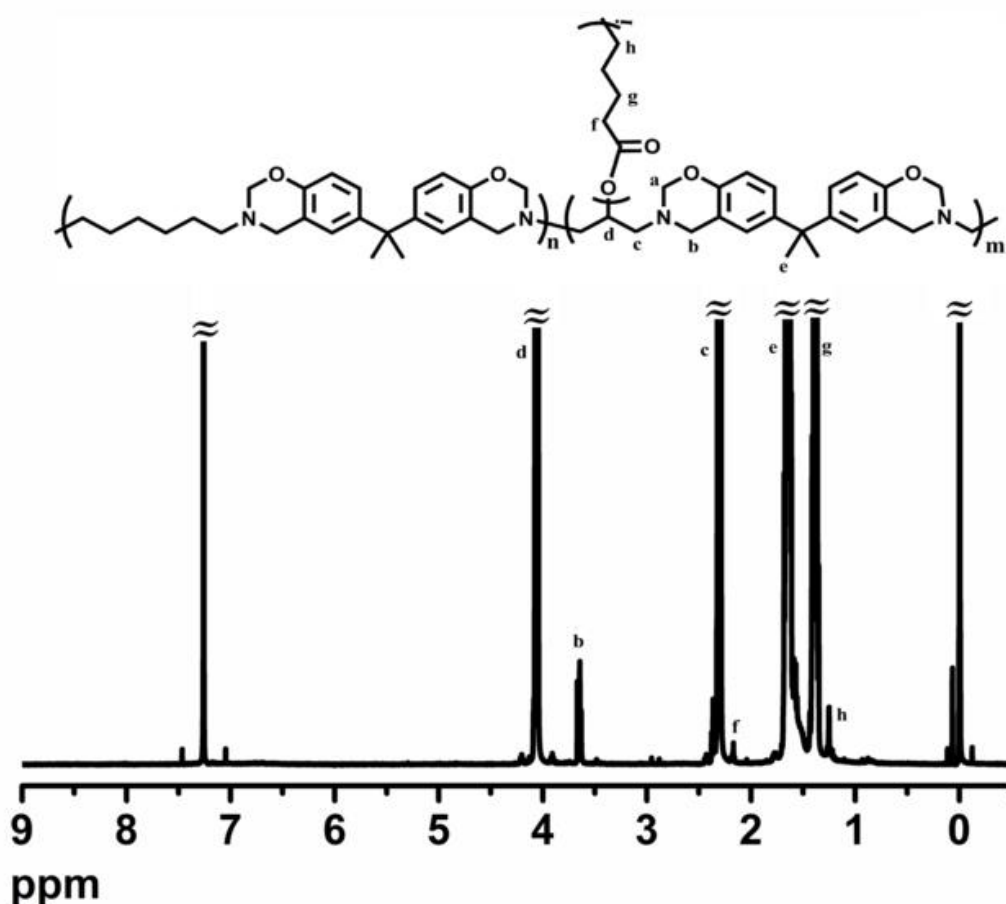


Figure 4.6 : ^1H -NMR spectrum of MCPP-*g*-PCL.

Photopolymerization is an appropriate method in synthetic polymer chemistry because it gathers up a number of ecological and economic predictions. The photopolymerization reactions are environmentally friendly because they are usually carried out without usage of solvents. Additionally, these reactions are controllable as means of time and space, and can be achieved at room temperatures and below, contrarily to thermal polymerizations. Certain further benefits might be attempted when cooperated with thermally activated benzoxazine polymerization, for instance, incorporating photochemically polymerizable groups such as methacrylates into the benzoxazine chain, sequential photochemical and thermal activation would lead to the formation of network with higher cross-linked density. Preparation of Methacrylate Functional Main-Chain Benzoxazine Precursor, M-MCPP, is outlined at Figure 4.7.

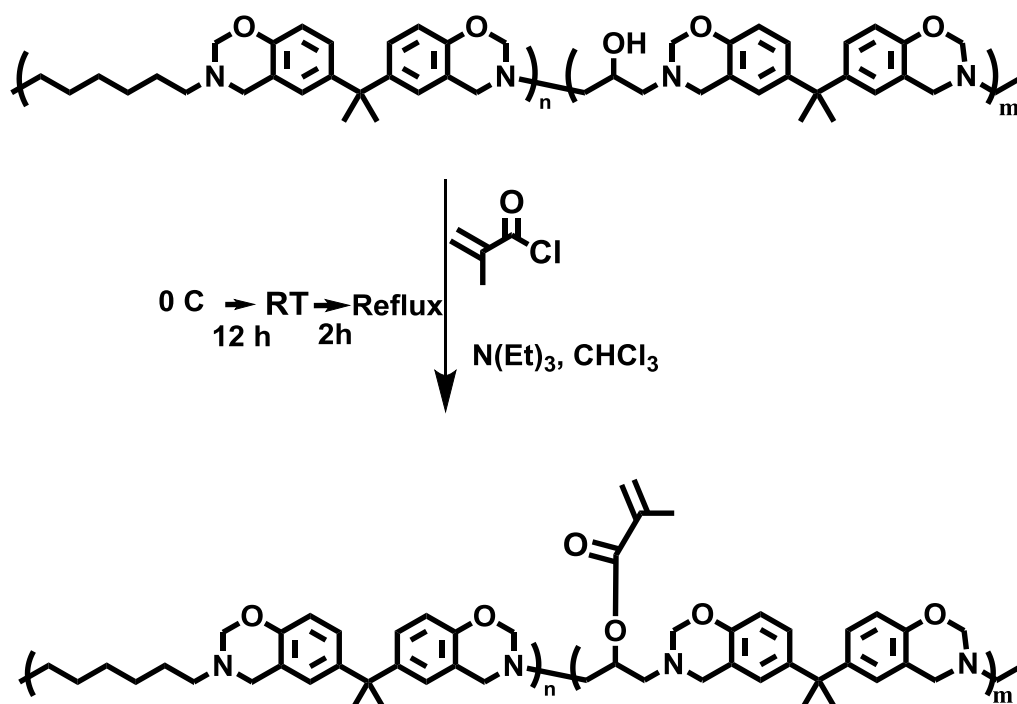


Figure 4.7 : Synthesis of M-MCPP.

Figure 4.8 illustrates the spectrum of M-MCPP, showing the incorporation of methyl methacrylate into the polymer chain. The peak at 1735 cm^{-1} corresponds to carbonyl group while C-O stretch appears at 1100 cm^{-1} .

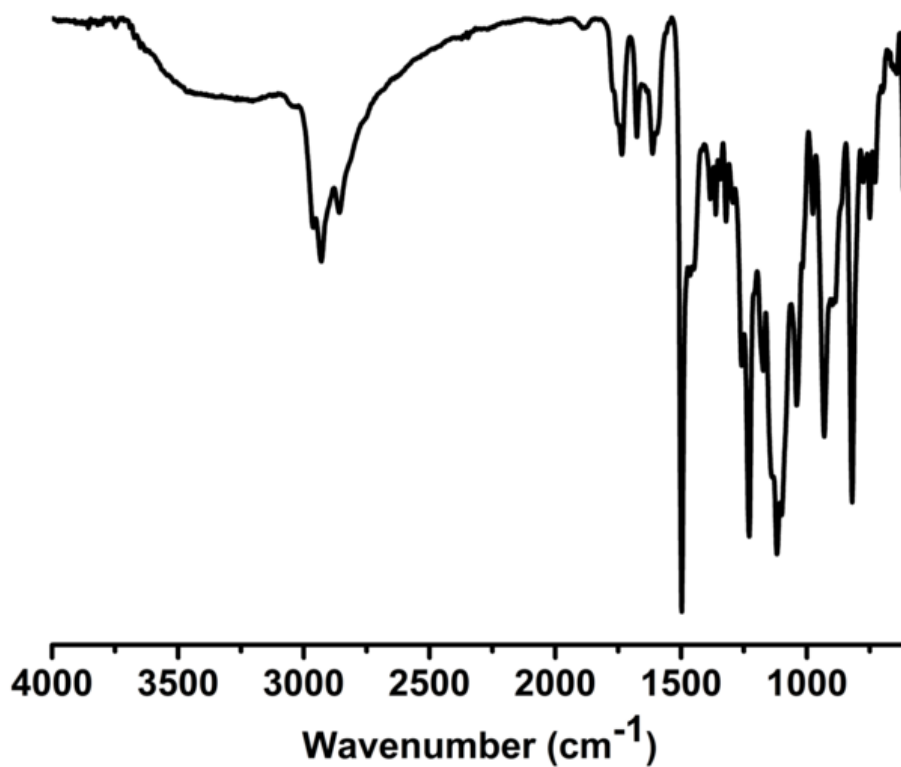


Figure 4.8 : FT-IR spectrum of M-MCPP.

The ^1H -NMR spectrum of the modified polymer is shown in Figure 4.9. Individual peak at 6.64 ppm indicates that methyl methacrylate was successfully incorporated to the benzoxazine precursor (Figure 4.9). CH_3 protons of methacrylate group are also located between 2.17- 2.71 ppm. O- CH_2 -N stretch of oxazine ring appears at 4.90 ppm.

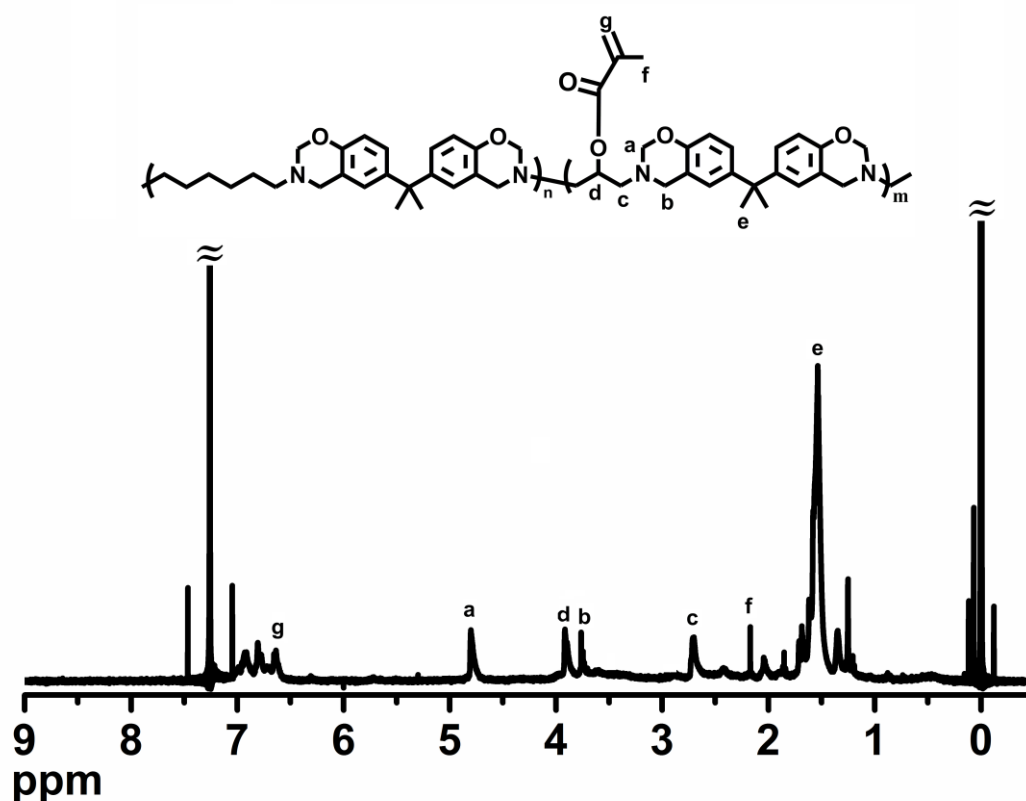


Figure 4.9 : ^1H -NMR spectrum of M-MCPP.

It has been shown that $\text{CuBr}/\text{PMDETA}$ complex is very effective for Atom Transfer Radical Polymerization together with alkyl halides. In our work we also aimed to design an initiator, on the benzoxazine precursor. The ATRP initiator was obtained by the reaction of MCPP and a bromo-functionalized propionyl compound in the presence of triethylamine to prevent the propionyl compound from polymerizing on its own. Reaction is demonstrated at Figure 4.10.

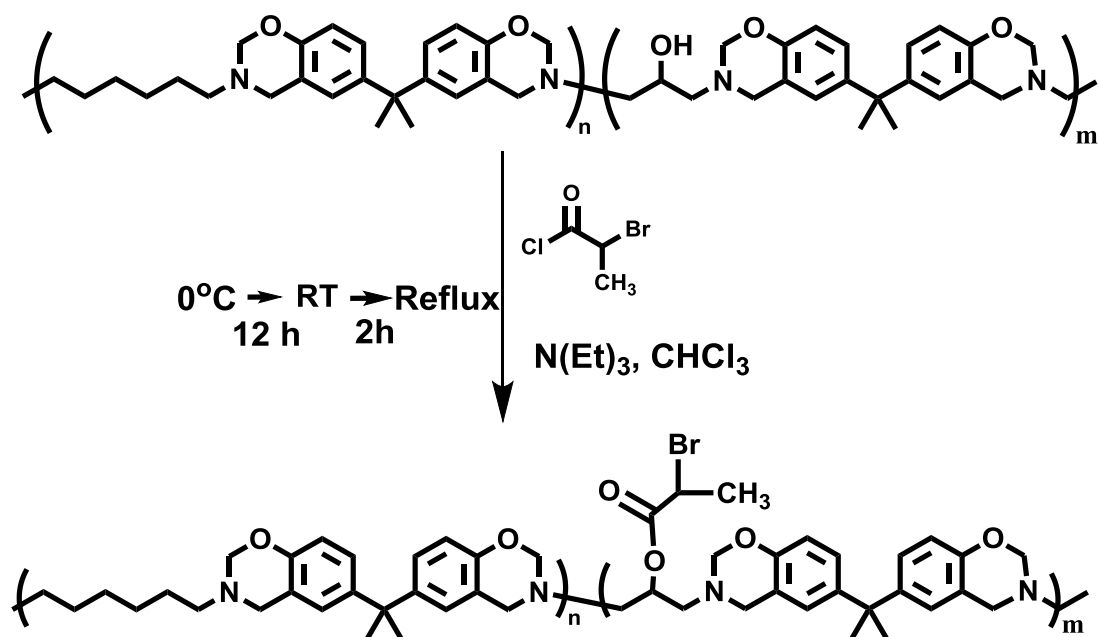


Figure 4.10 : Synthesis of MCPP-ATRP-I.

As is seen in FTIR spectrum, bromo function of Main-Chain Benzoxazine Precursor with an ATRP Initiator Group, MCPP-ATRP-I, was evidenced by the presence of a medium peak at 665 cm^{-1} (Figure 4.11).

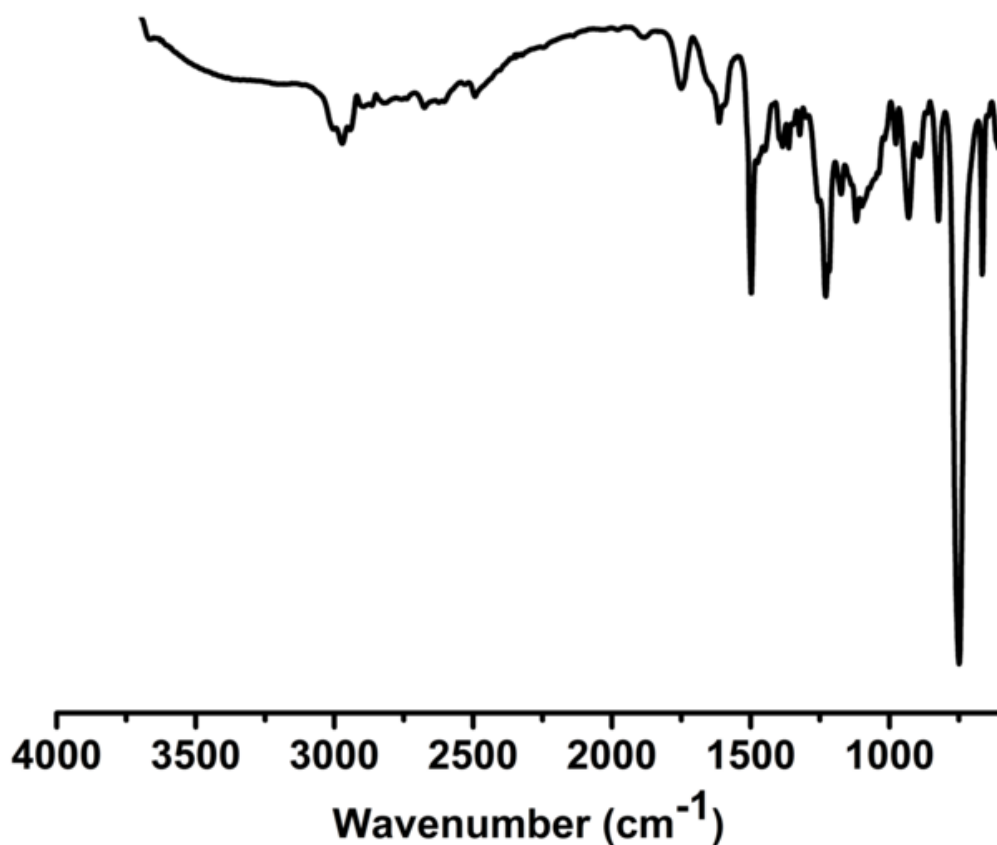


Figure 4.11 : FT-IR spectrum of MCPP-ATRP-I.

The structure of the ATRP initiator, MCPP-ATRP-I was also confirmed by ^1H -NMR analysis (Figure 4.12). The methyl protons of the bromo functional substituent resonate at 1.62 ppm, while CHBr proton appears at 3.91 ppm. The $\text{O-CH}_2\text{-N}$ protons in the oxazine ring stands at 4.79 ppm.

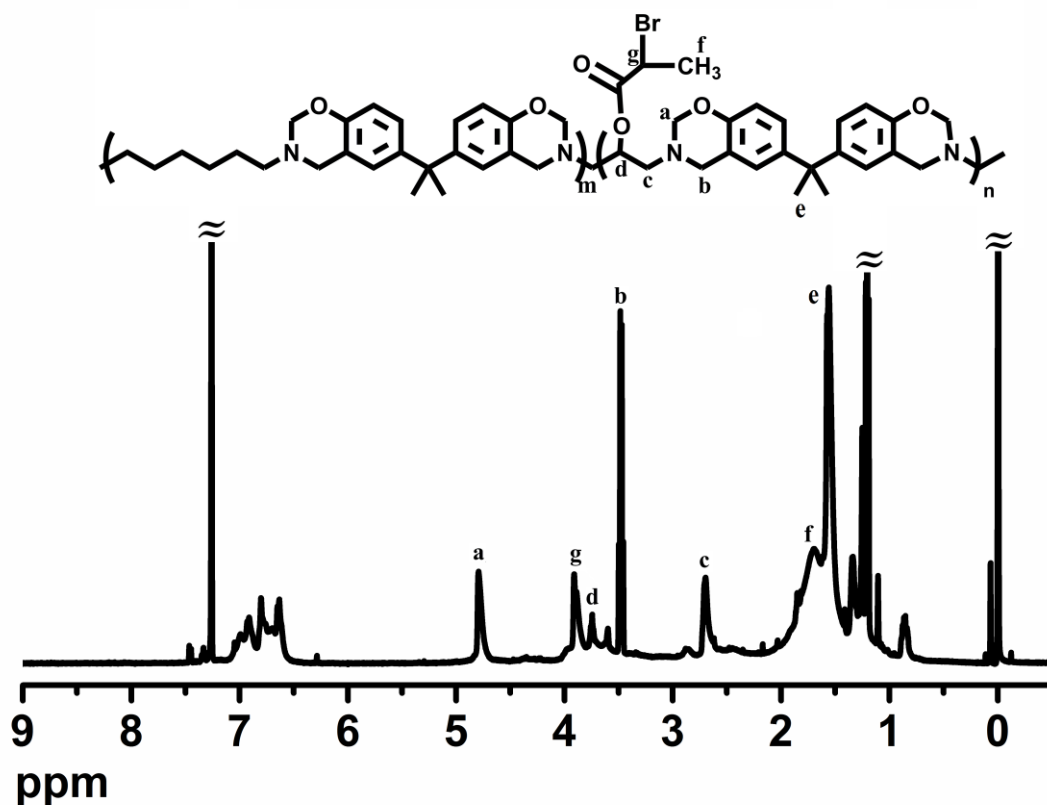


Figure 4.12 : ^1H -NMR spectrum of MCPP-ATRP-I.

Subsequent ATRP of styrene in dimethylformamide at 90 °C by means of the polymeric initiator obtained in conjunction with a Cu(I)Br/PMDETA yielded polystyrene grafted benzoxazine (MCPP-*g*-PS) (Figure 4.13).

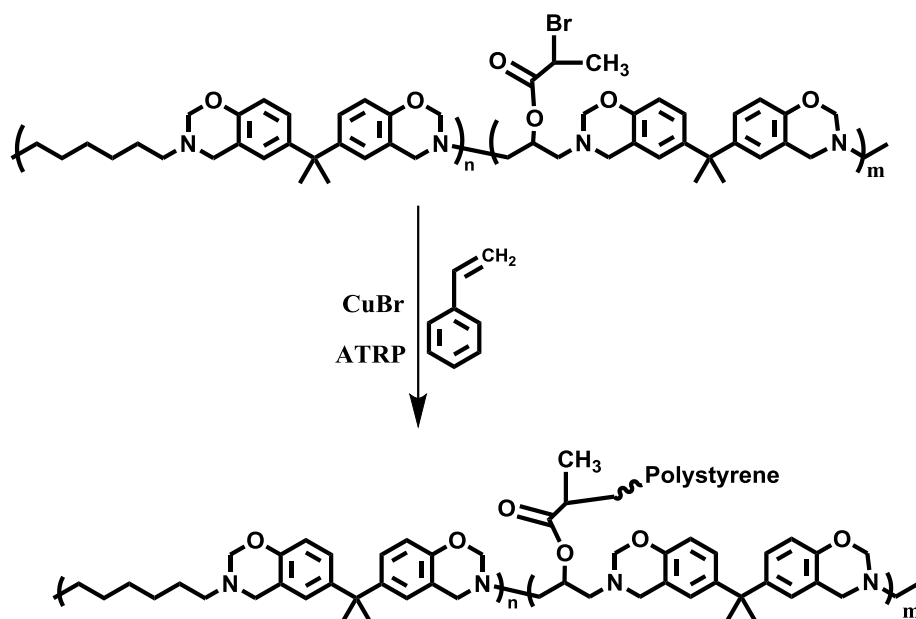


Figure 4.13 : Synthesis of MCPP-*g*-PS by ATRP.

The structure of the graft copolymer is confirmed by spectral analyses. In the ^1H NMR spectrum, the intensity of the aromatic protons increased due to the polystyrenes additional contribution. Similar increase in the aliphatic protons around 0.8- 1.2 ppm was also noted. Also, the aromatic C-C stretch appears at 1103 cm^{-1} with a strong peak that indicates the polystyrene incorporation (Figures 4.14 and 4.15).

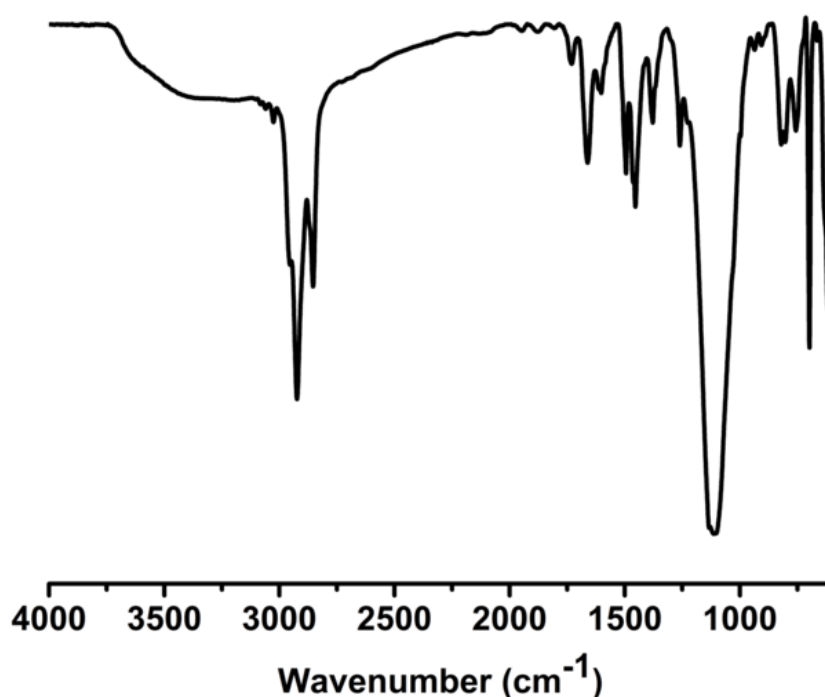


Figure 4.14 : FT-IR spectrum of MCPP-*g*-PS.

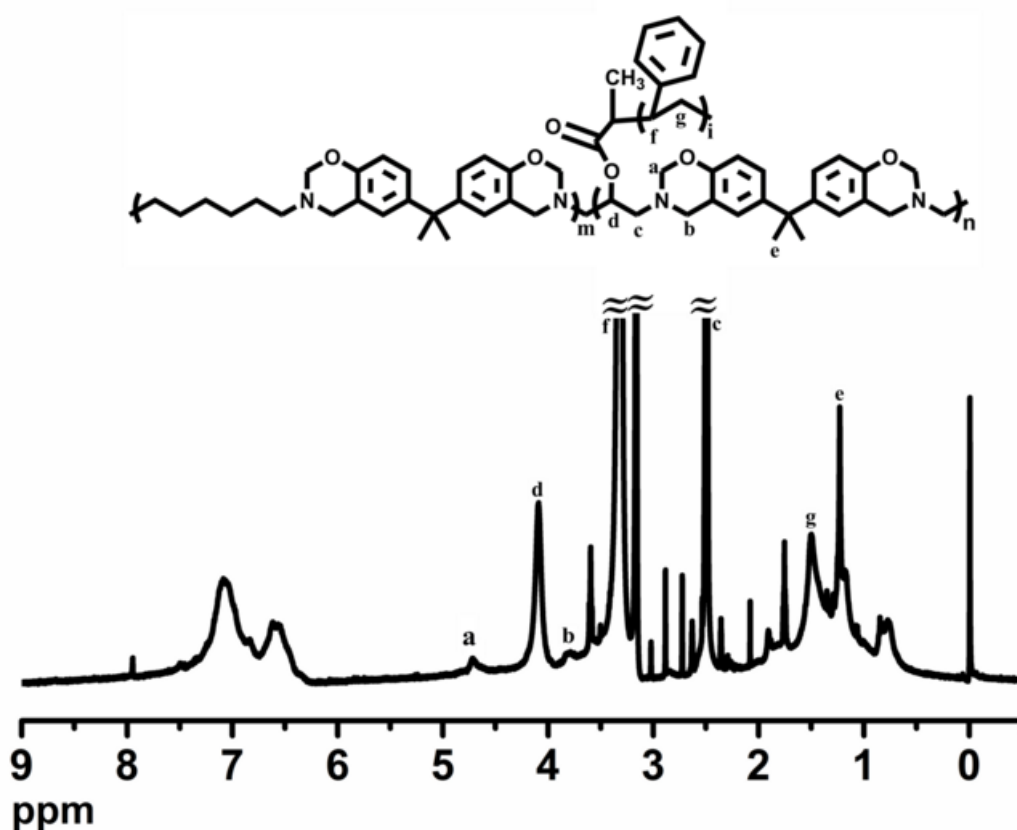


Figure 4.15 : ^1H -NMR spectrum of MCPP-*g*-PS.

In order to show molecular changes of the polymers at various stages, the weight characteristics were tabulated in Table 4.1. As can be seen that the value for the precursor is comparable with the literature data as Mannich polymerizations yield polymers with low molecular weights. Moreover, the related increases by each modification are noted.

Table 4.1 : Molecular weight results of all prepared polymers.

Polymer	M_n	M_w	M_z	M_p	M_w/M_n (PDI)
MCPP	1811	3022	4741	2648	1,668
MCPP- <i>g</i> -PCL	3135	4385	6621	3695	1,399
M-MCPP	2095	3343	4742	3288	1,596
MCPP-ATRP-I	2609	3550	4637	3522	1,361
MCPP- <i>g</i> -PS	3452	4279	5492	2317	1,240

Molecular weights of polymers were measured by GPC.

It is well known that thermally activated ROP of 1,3- benzoxazines is an exothermic process, which have maximums at around 200-250°C depending on the functionalities of the benzoxazines. We have investigated the thermally activated

ring opening process of the initial precursor and modified structures derived therefrom by DSC. Figure 4.16 demonstrates the DSC thermograms of polymeric benzoxazines.

DSC thermogram of MCPP exhibits an exotherm with an onset at 163,88°C, maximum at 237,72°C and completion at 279,47°C. The precursor extended an energy of 258,55 J/g. MCPP-*g*-PCL has no significant peak of oxazine ring- opening, but only a small exotherm around 239°C. It also has a sharp peak around 50°C, indicating the glass transition temperature of PCL. The cumulative DSC thermogram also does not clearly represent the benzoxazine ring opening of MCPP-*g*-PS. For better presentation, the thermograms of the grafted structures, MCPP-*g*-PCL and MCPP-*g*-PS were presented individually in Figures 4.17 and 4.18.

All results of DSC thermograms are listed in Table 4.2.

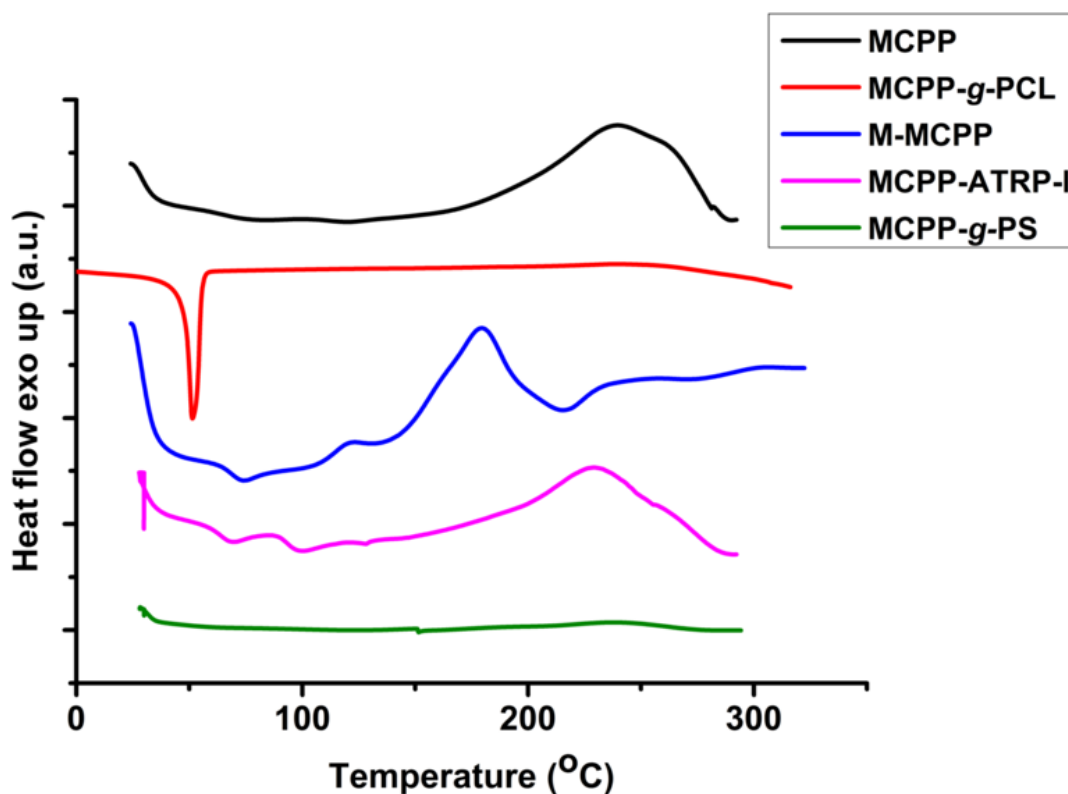


Figure 4.16 : DSC thermograms of polymeric benzoxazines.

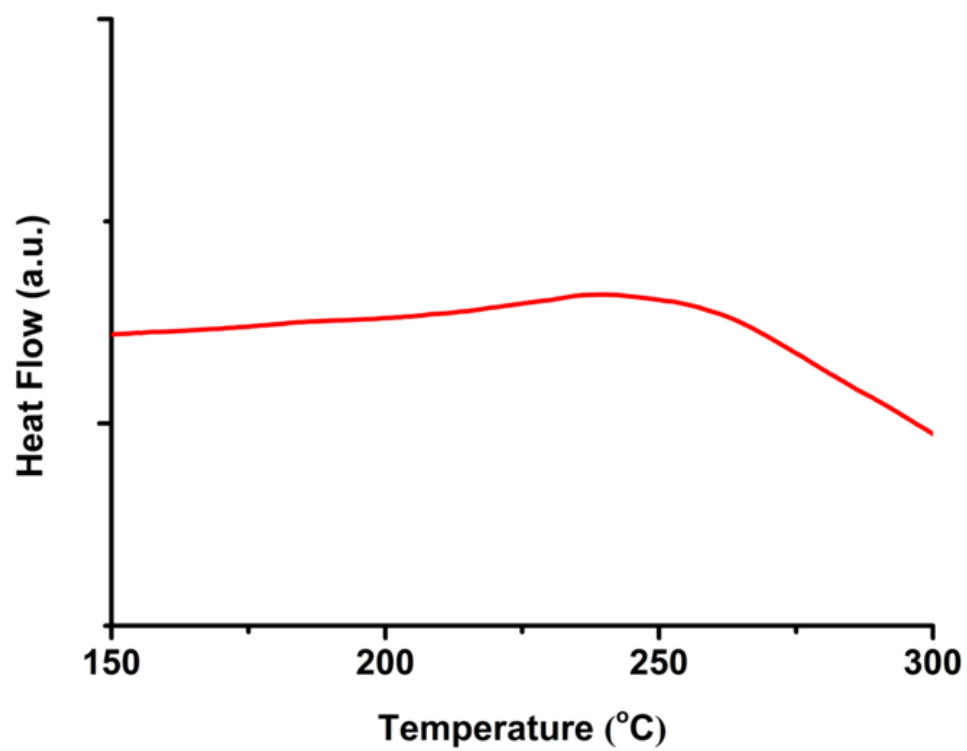


Figure 4.17 : DSC thermogram of MCPP-*g*-PCL.

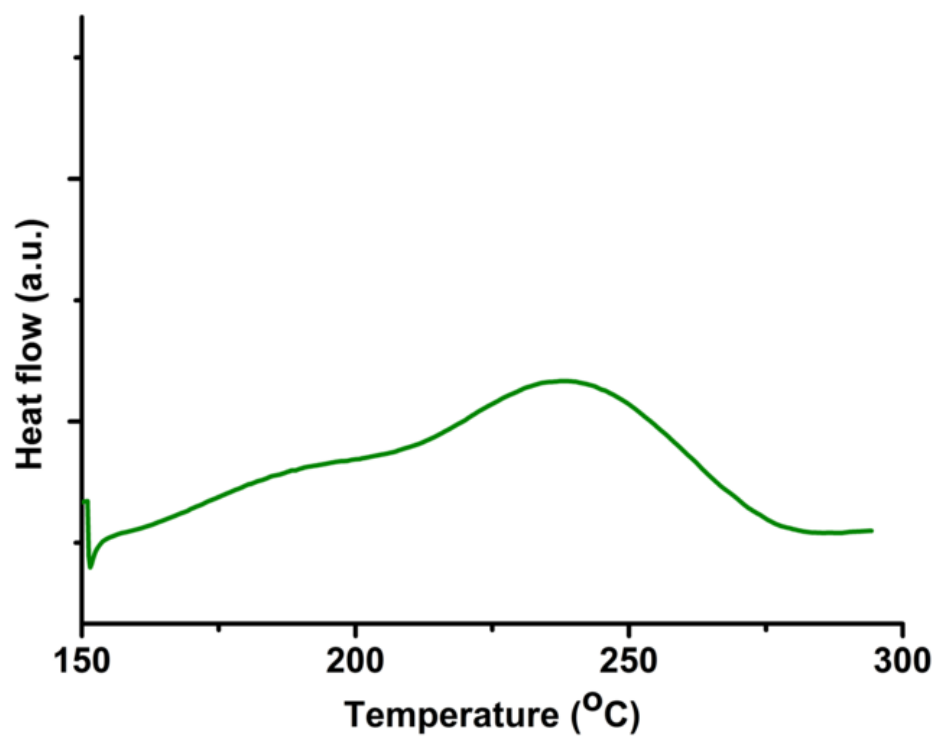


Figure 4.18 : DSC thermogram of MCPP-*g*-PS.

Table 4.2 : DSC results of synthesized polymers.

Polymer	T _g (°C)	ΔH(J/g)	Onset(°C)	Maximum(°C)	Endset(°C)
MCPP	83,60	-258,55	163,88	237,72	279,47
MCPP- <i>g</i> -PCL	51,51	-393,887	252,97	239,3	310,81
M-MCPP	74,17	-63,624	179,66	215,25	273,27
MCPP-ATRP-I	68,93	-44,536	180,69	219,97	252,32
MCPP- <i>g</i> -PS	151,52	-13,279	209,71	240,28	272,08

Thermal stabilities of the polymers were investigated by TGA under nitrogen atmosphere. The comparative thermograms of MCPP, MCPP-*g*-PCL, M-MCPP and MCPP-ATRP-I are shown in Figure 4.11. The results are also summarized in Table 4.2. The 5 % weight loss temperatures are at 282,9, 299,8, 236,9 and 250,5 °C for MCPP, MCPP-*g*-PCL, M-MCPP and MCPP-ATRP-I, respectively. The differences in char yields are obviously seen for the cured and non-cured benzoxazines. TGA analyses of MCPP and MCPP-*g*-PCL were done after a thermal curing, the others were done without curing. It is obvious that the bare precursor has a better thermal stability compare to the modified structures. This is expected since all the incorporated structures namely, PS, PCL segments and MA moiety decomposes much earlier.

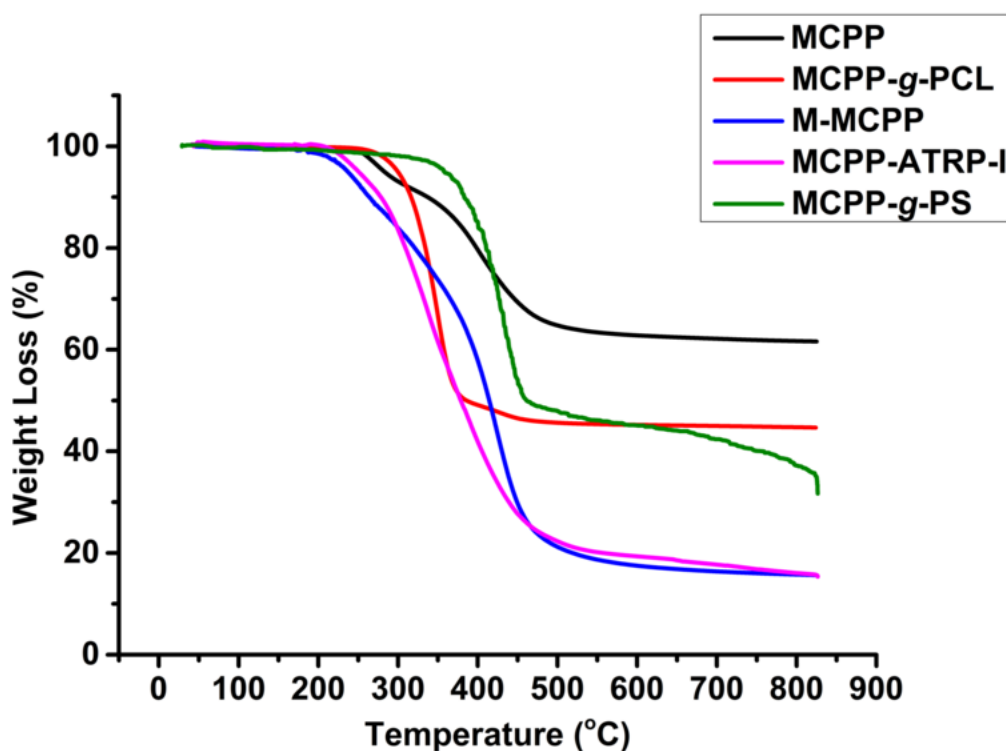
**Figure 4.19** : TGA curves of the polymeric benzoxazines.

Table 4.3 : Thermal properties of all polymers.

Polymer	T _{5%} (°C)	T _{10%} (°C)	T _{max} (°C)	Char % at 800 °C
M CPP	282,9	337,2	825	61,69
M CPP- <i>g</i> -PCL	299,8	316,4	823,9	44,72
M-MCPP	236,9	264,1	825,6	15,75
M CPP-ATRP-I	250,5	278,4	826,5	16,05
M CPP- <i>g</i> -PS	358,21	383,1	826,44	37,17

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

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

Char %: Char yields at 800°C under nitrogen atmosphere.

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

Methacrylate groups are photochemically crosslinkable sites. We have, therefore, tested the possibility of photocuring of methacrylate modified precursor. The photocuring behavior was investigated by Photo-DSC of the solution containing M-MCPP in the presence of BAPO. As presented in Figure 4.18, upon irradiation the double bonds of the methacrylate function undergo crosslinking.

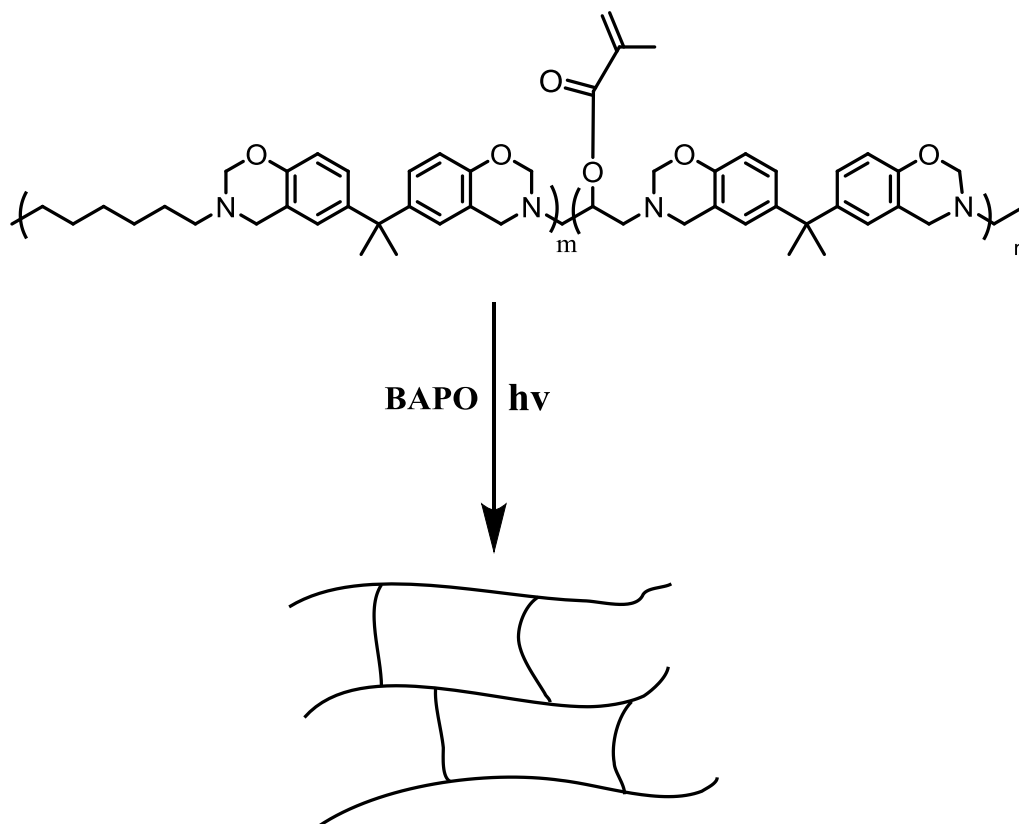


Figure 4.20 : Photoinduced crosslinking of M-MCPP.

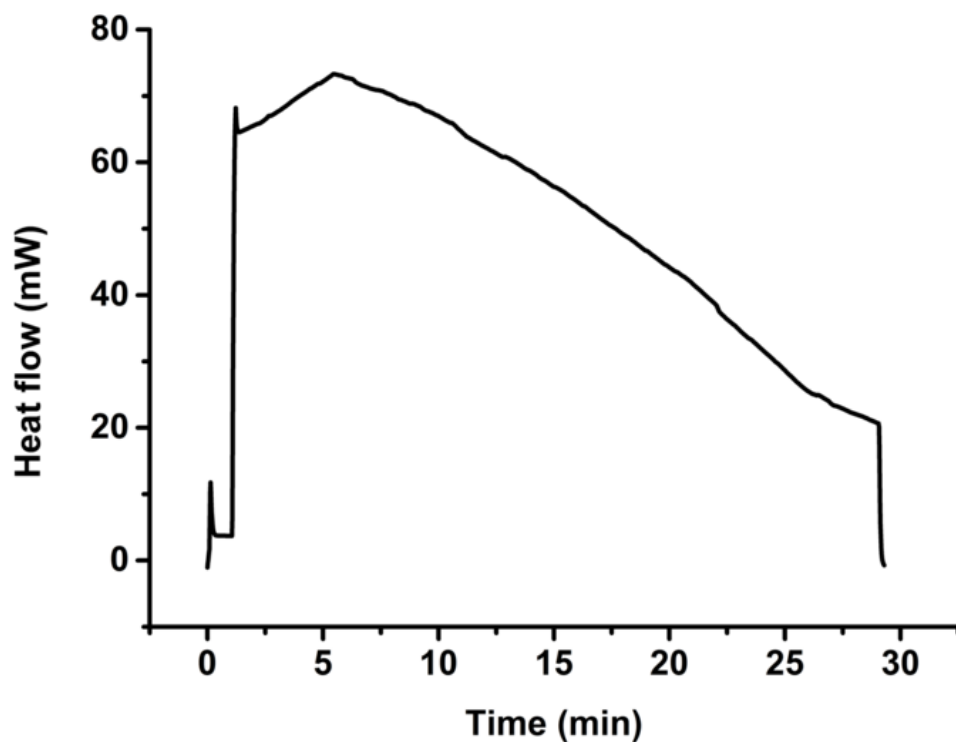


Figure 4.21 : Photo-DSC thermogram showing crosslinking of M-MCPP.

The conversion diagram for this photochemically crosslinked polymer could not be drawn because the end group quantity can not be accurately calculated. This point will be further investigated.

5. CONCLUSION

To sum up, we synthesized a novel linear main-chain type polymeric benzoxazine and modify it with different techniques. Desired polymeric structure was obtained by using bisphenol A and two different diamines, one of which contains hydroxyl group. The reactivity of this hydroxyl group provide possibility to incorporate many organic species, especially polymers such as polylactones and vinyl polymers as well as crosslinkable sites. The structural and molecular weight characterization of the precursor and resulting modified structures were carried out by spectral analysis and GPC measurements. The thermal curing behavior and thermal stability were investigated by DSC and TGA analysis, respectively.

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CURRICULUM VITAE



Name Surname: Betül HANBEYOĞLU
Place and Date of Birth: Istanbul, 11/05/1989
E-Mail: betulhamamci@yahoo.com
B.Sc.: Kocaeli University Chemistry Department
High School: Üsküdar Çağrıbey Anadolu Lisesi

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Hamamcı B.**, Kışkan B, Yağcı Y., 2013, Synthesis and Characterization of Modified Benzoxazine Precursors, *International Congress- Advances In Applied Physics & Materials Science Congress*, April 24- 28 ,2013, Antalya, Turkey
- **Hanbeyoğlu, B.**, Kışkan, B., Yağcı, Y., 2013, Hydroxyl Functional Polybenzoxazine Precursor for Post-Polymer Modification via Atom Transfer Radical Polymerization (ATRP) (to be submitted)