

**THERMALLY CURABLE POLYSTYRENE VIA
CLICK CHEMISTRY**

M. Sc. Thesis by

Mihrace ERGİN

Department: Polymer Science and Technology

Programme: Polymer Science and Technology

Supervisor: Prof. Dr. Yusuf YAĞCI

JANUARY 2008

**THERMALLY CURABLE POLYSTRENE VIA CLICK
CHEMISTRY**

**M. Sc. Thesis by
Mihrace ERGİN**

515051032

Date of Submission: 24 December 2007

Date of Defence Examination: 28 January 2008

| | |
|--|--|
| Supervisor (Chairman) : | Prof. Dr. Yusuf YAĞCI |
| Members of the Examining Committee: | Prof. Dr. Gürkan HIZAL (I.T.U.) |
| | Prof.Dr. A. Tunçer ERCİYES (I.T.U.) |

JANUARY 2008

**“CLİCK” KİMYASI İLE TERMAL OLARAK
KÜRLENEBİLEN POLİSTİREN**

**YÜKSEK LİSANS TEZİ
Mihrace ERGİN
515051032**

**Tezin Enstitüye Verildiği Tarih : 24 Aralık 2007
Tezin Savunulduğu Tarih : 28 Ocak 2008**

**Tez Danışmanı : Prof. Dr. Yusuf YAĞCI
Diğer Jüri Üyeleri Prof.Dr. Gürkan HIZAL (İ.T.Ü.)
Prof.Dr. A. Tunçer ERCİYES (İ.T.Ü.)**

OCAK 2008

ACKNOWLEDGEMENTS

I would like to thank all the people who made this work possible. It is a pleasant aspect that I have now the opportunity to express my gratitude to all of them.

First of all, I am deeply indebted to my supervisor, Prof. Dr. Yusuf Yağcı, for his kind support and guidance.

I would also like to thank Res. Asst. Barış Kışkan for his valuable contribution during all stages of the experimental work.

I wish to express my special thanks to my Laboratory colleagues; M. Atilla Taşdelen, Res. Asst. Burçin Gacal, Res. Asst. Demet Çolak, Res. Asst. Hakan Durmaz, , Güniz Demiray, Yasemin Durmaz, Binnur Aydoğan, Muhammed Ü. Kahveci, Manolya Kukut, Mirnur Aşan, Görkem Yılmaz, Orhan Destanoğlu, Gülben Sayılan, Banu Köz, Dilek Surekan, Elif Şahkulubey for all their help, kindness and support in all possible ways during my laboratory work.

Finally, I'm grateful to my mother Güler Ergin, father Galip Ergin, brother M. Fatih Ergin and Ayfer Ergin for their encouragement, understanding, patience and support all through my education.

Thank you all...

January 2008

Mihrace ERGİN

TABLE of CONTENTS

| | |
|---|-------------|
| LIST of ABBREVIATIONS | v |
| LIST of TABLES | vii |
| LIST of FIGURES | viii |
| SUMMARY | x |
| ÖZET | xi |
| | |
| 1. INTRODUCTION | 1 |
| | |
| 2. THEORETICAL PART | 3 |
| 2.1 Linear and Thermoset Polymers..... | 3 |
| 2.1.1 Thermoplastics..... | 5 |
| 2.1.2 Thermosets | 7 |
| 2.1.3 Elastomers..... | 9 |
| 2.2 Controlled Free Radical Polymerization | 10 |
| 2.2.1 Nitroxide Mediated Radical Polymerization..... | 10 |
| 2.3 Polystyrene..... | 12 |
| 2.3.1 History of Polystyrene | 12 |
| 2.3.2 Preparation of Polystyrene | 13 |
| 2.3.2.1 Dehydrogenation..... | 13 |
| 2.3.3 Polymerization of Polystyrene | 14 |
| 2.3.4 Properties and Structure of Polystyrene..... | 15 |
| 2.3.5 Applications of Polystyrene | 16 |
| 2.4 Polybenzoxazines..... | 17 |
| 2.4.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers | 19 |
| 2.4.1.1 Mono-functional Benzoxazine Monomers | 19 |
| 2.4.1.2 Di-functional and Multifunctional Benzoxazine Monomers | 22 |
| 2.4.2 Preparation of Polymers with Benzoxazine Moieties | 24 |
| 2.4.2.1 Benzoxazine functionalized polystyrene | 24 |
| 2.4.3 Polymeric Benzoxazine Precursors | 25 |
| 2.4.3.1 Main-chain precursors | 25 |

| | |
|--|-----------|
| 2.4.3.2 Side-chain precursor | 26 |
| 2.4.4 Reaction Mechanism of Ring Opening Polymerization of Benzoxazine | 27 |
| 2.4.4.1 Thermal Polymerization of Benzoxazines | 28 |
| 2.4.5 Benzoxazine with propargyl ether functional group..... | 31 |
| 2.4.6 Properties and Application Polybenzoxazines..... | 32 |
| 2.5 Click Chemistry..... | 34 |
| 2.5.1 Click Reactions on linear polymers..... | 37 |
| 3. EXPERIMENTAL WORK..... | 38 |
| 3.1 Materials and Chemicals..... | 38 |
| 3.2 Equipments..... | 38 |
| 3.2.1 FT-IR..... | 38 |
| 3.2.2 NMR..... | 38 |
| 3.2.3 DSC..... | 38 |
| 3.2.4 TGA..... | 38 |
| 3.2.5 GPC..... | 39 |
| 3.3 Preparation Methods..... | 39 |
| 3.3.1 Preparation of N-(4-hydroxyphenyl)acetamide..... | 39 |
| 3.3.2 Preparation of N-(4-(prop-2-ynyloxy)phenyl)acetamide... | 39 |
| 3.3.3 Preparation of p-propargyloxy aniline..... | 39 |
| 3.3.4 Preparation of 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine..... | 40 |
| 3.3.5 Synthesis of PS- <i>co</i> -PCMS copolymer..... | 40 |
| 3.3.6 Synthesis of (PS- <i>co</i> -PMS-N ₃) copolymer..... | 40 |
| 3.3.7 Synthesis of (P(S- <i>co</i> -BS)) copolymer..... | 40 |
| 4. RESULTS and DISCUSSION..... | 42 |
| 4.1 Synthesis of Benzoxazine Functionalized Polystyrenes..... | 42 |
| 4.2 Characterization of the Polymers..... | 44 |
| 4.2.1 Thermally Activated Cruring of Benzoxazine Functional Polystyrene..... | 47 |
| 4.2.2 Thermal Properties of Cured Polystyrene..... | 48 |
| 4.3 Conclusion..... | 49 |
| REFERENCES..... | 51 |
| AUTOBIOGRAPHY..... | 59 |

LIST of ABBREVIATIONS

| | |
|----------------------|--|
| PE | : Polyethylene |
| PP | : Polypropylene |
| PTFE | : Polytetrafluoroethylene |
| PS | : Polystyrene |
| HIPS | : High-Impact Polystyrene |
| PVC | : Polyvinylchloride |
| PMMA | : Polymethylmethacrylate |
| PBZ | : Polybenzoxazine |
| NMP | : Nitroxide Mediated Radical Polymerization |
| SFRP | : Stable Free Radical Polymerization |
| ROMP | : Ring-opening Metathesis Polymerization |
| ATRP | : Atom-transfer Radical Polymerization |
| RAFT | : Radical Addition- Fragmentation Transfer |
| TEMPO | : 2,2,6,6-tetramethyl-1-piperidinyloxy |
| BPO | : Benzoyl Peroxide |
| AIBN | : Azobisisobutyronitrile |
| PRE | : Persistent Radical Effect |
| GR-S | : Government Rubber-Styrene |
| IUPAC | : International Union of Pure and Applied Chemistry |
| T_g | : Glass Transition Temperature |
| KOH | : Potassium Hydroxide |
| HY | : Active Hydrogen |
| NMR | : Nuclear Magnetic Resonance Spectroscopy |
| FTIR | : Fourier Transform Infra-red |
| TGA | : Thermal Gravimetry Analysis |
| DSC | : Differential Scanning Calorimetry |
| GPC | : Gel-permeation Chromatography |
| B-a | : 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine). |
| B-pt | : 6,6'-(propane-2,2-diyl)bis(3-p-tolyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) |
| B-mt | : 6,6'-(propane-2,2-diyl)bis(3-m-tolyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) |
| B-ot | : 6,6'-(propane-2,2-diyl)bis(3-o-tolyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) |
| B-35m | : 6,6'-(propane-2,2-diyl)bis(3-(3,5-dimethylphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine) |
| B-m | : 6,6'-(propane-2,2-diyl)bis(3-methyl-3,4-dihydro-2H-benzo[e][1,3]oxazine). |
| 22P-a | : 8,8'-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine). |
| 440-a | : 6,6'-bis(2,3-dihydro-3-phenyl-4H-1,3-benzoxazinyl) |
| PVP | : Poly <i>p</i> -vinylphenol |

| | |
|-------------------------|---|
| Th | : Thiophene |
| CuAAC | : Copper-Catalyzed Azide–Alkyne Cycloaddition |
| BPO | : Benzoyl Peroxide |
| AIBN | : Azoisobutyronitrile |
| PRE | : Persistent Radical |
| CMS | : Chloromethylstyrene |
| PS-<i>co</i>-CMS | : Polystyrene- <i>co</i> -chloromethylstyrene |
| DMF | : N,N-dimethylformide |

LIST OF FIGURES

| | <u>Page No</u> |
|--|----------------|
| Figure 2.1 : Synthesis of 3,4-dihydro-2H-1,3-benzoxazines | 19 |
| Figure 2.2 : Ring opening of benzoxazine in acidic medium | 20 |
| Figure 2.3 : Formation of 1,3-oxazine ring from 2-hydroxybenzylamine | 21 |
| Figure 2.4 : Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.. | 23 |
| Figure 2.5 : Synthesis of poly(<i>p</i> -vinylphenol) based benzoxazine | 24 |
| Figure 2.6 : Synthesis of benzoxazine functional polystyrene macromonomer.... | 25 |
| Figure 2.7 : Synthesis of polybenzoxazine precursors | 26 |
| Figure 2.8 : Synthesis of semi-conductive side-chain polybenzoxazine precursor | 27 |
| Figure 2.9 : Curing of monofunctional and difunctional benzoxazines | 28 |
| Figure 2.10 : Initiation of ring-opening polymerization of benzoxazines | 30 |
| Figure 2.11 : Thermal polymerization of B-a through cationic mechanism | 30 |
| Figure 2.12 : Electrophilic substitution reaction of aniline moiety | 31 |
| Figure 2.13 : Synthesis of propargyl ether containing benzoxazine monomers. | 32 |
| Figure 4.1 : Synthesis of Propargyl Functional Benzoxazine | 43 |
| Figure 4.2 : Benzoxazine Functional Polystyrene | 43 |
| Figure 4.3 : ¹ H-NMR spectrum of polystyrene- <i>co</i> -chloromethyl styrene (P(S- <i>co</i> -CMS)) | 44 |
| Figure 4.4 : ¹ H-NMR spectrum of <i>p</i> -propargyloxy aniline | 45 |
| Figure 4.5 : ¹ H-NMR spectrum of 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine | 45 |

| | | |
|-------------------|--|----|
| Figure 4.6 | ^1H -NMR spectrum of PS- <i>co</i> -PMS-N ₃ (a) and PS- <i>co</i> -PMS-benzoxazine (b) | 46 |
| Figure 4.7 | FT-IR spectrum of PS- <i>co</i> -PMS-N ₃ (a) and PS- <i>co</i> -PMS-benzoxazine (b) | 47 |
| Figure 4.8 | The DSC thermogram of the click product | 48 |
| Figure 4.9 | : The TGA curves of the click product | 49 |

LIST of TABLES

| | <u>Page No</u> |
|--|-----------------------|
| Table 2.1. Composition and use of thermoplastics | 6 |
| Table 2.2. Composition and application of some thermosets | 8 |
| Table 2.3. Composition and use of elastomers | 9 |
| Table 2.4. Difunctional Benzoxazine Monomers | 23 |
| Table 4.1. TGA analysis of cured benzoxazine-Pst | 49 |

THERMALLY CURABLE POLYSTYRENE VIA CLICK CHEMISTRY

SUMMARY

Recently, high performance polymeric materials have received considerable studies for their wide application in electronics, biomaterials, and other industrials. Among the developed materials, polybenzoxazines possess outstanding properties of small shrinkage in curing, low water absorption, good thermal stability, and high glass transition temperatures. These advantages of benzoxazines receive considerable increase on the studies of benzoxazines and their corresponding polymers.

At the present there is considerable interest not only in synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization for effecting systematic changes in polymer properties. The incorporation of two different monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance.

In this study novel side-chain benzoxazine functional polystyrene was synthesized by using “Click” chemistry strategy. First, a random copolymer of styrene (S) and chloromethyl styrene (CMS) with 39.8 mol% CMS content was prepared by Nitroxide Mediated Radical Polymerization (NMP) process. Then, the chloromethyl groups were converted to azido groups by using NaN_3 in DMF. Propargyl benzoxazine was prepared independently by a ring closure reaction between *p*-propargyloxy aniline, paraformaldehyde and phenol. Finally, azidofunctionalized polystyrene was coupled to propargyl benzoxazine with high efficiency by click chemistry. The spectral and thermal analysis confirmed the presence of benzoxazine functionality in the resulting polymer. It is shown that polystyrene containing benzoxazine undergoes thermal curing in the absence of any catalyst forming polystyrene thermoset with high thermal stability.

Keywords: thermal curing, “click” chemistry, benzoxazine, polystyrene, thermal stability

“CLICK” KİMYASI İLE TERMAL OLARAK KÜRLENEBİLEN POLİSTİREN

ÖZET

Son zamanlarda yüksek performanslı polimerik malzemeler; elektronik, biyomalzeme ve diğer endüstriyel alanlardaki geniş kullanım yelpazelerinden dolayı bir çok önemli çalışmalara konu olmuştur. Benzoksazin polimerler, reçineleşme sırasındaki ufak hacim değişiklikleri (büzüşme), düşük miktarda su absorplamaları, ısıl dayanımları ve yüksek camı geçiş sıcaklıkları gibi göze çarpan üstün özelliklere sahiptirler. Bu özellikler benzoksazin ve benzoksazin polimerleri hakkında yapılan çalışmaların önemli bir şekilde artmasına sebep olmuştur.

Günümüzde, sadece yeni tür plastik malzemelerin sentezlenmesi değil, aynı zamanda yeni uygulamaların getirdiği gereklilikleri karşılamak için varolan polimerlerin modifiye edilmesi ayrı bir önem kazanmaktadır. Kopolimerizasyon polimer özelliklerini geliştirme metodlarından bir tanesidir. Çeşitli fiziksel ve /veya kimyasal özelliklere sahip iki farklı monomerin değişen oranlarda aynı polimer molekülüne dahil edilmesi bilimsel ve ticari öneme sahip yeni malzemelerin oluşumuna yol açmaktadır.

Bu çalışmada benzoksazin fonksiyonlu polistiren “Click” kimyası stratejisi kullanılarak sentezlenmiştir. İlk olarak stirenin (S), % 39,8 oranında klorometil stiren (CMS) içeren rastgele kopolimeri kararlı serbest radikal polimerizasyonu (NMP) kullanılarak hazırlanmıştır. Daha sonra bu kopolimerin klor grupları NaN_3 ile dimetil formamid (DMF) varlığında azid gruplarına çevrilmiştir. Ayrı bir yerde propargil benzoksazin yapısı p-propargil anilin, p-formaldehit ve fenol arasındaki halka kapanma reaksiyonuyla sentezlenmiştir. Son olarak azid fonksiyonlu polistiren gruplarıyla propargil benzoksazin grupları “click” kimyası kullanılarak yüksek verimle birleştirilmiştir. Oluşturulan polimerdeki benzoksazin fonksiyonel grubunun varlığı spektral ve termal analizlerle tespit edilmiştir. Benzoksazin içeren polistirenin termal olarak kürlenebildiği ve yüksek termal kararlılığa sahip olduğu gösterilmiştir.

Anahtar Kelimeler: termal kürlenme, “Click” kimyası, benzoksazin, polistiren, termal kararlılık

1. INTRODUCTION

At the present there is considerable interest not only in synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization for effecting systematic changes in polymer properties. The incorporation of two different monomers, having diverse physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance.

Synthesis of high performance polymers and their high-tech applications have attracted significant attention in recent years. Conventional polymers do not offer the properties associated with thermoset polymers and hence their applications as high performance polymers are limited. Thermoset polymers are normally synthesized using step-growth methods where chain growth and cross-linking processes arise from the same type of chemical reaction. However, thermoset polymers are not easily processable and their manufacturing are not cost-effective, and thus remain prohibitively expensive for these applications. Cross-linking of linear polymers is one approach to improve the properties and consequently to access the demanding regimes of high-tech applications. Cross-linking of conventional polymers is readily achieved by the incorporation of a multifunctional monomer during the polymerization process. High energy radiation or photochemical irradiation have been used but, in addition to the cross-linking, both methods may also involve chain scission that can result in polymer degradation or the introduction of unwanted impurities. Therefore, particularly in photochemical cross-linking, the incorporation of chromophoric groups into polymers absorbing selectively at irradiation wavelengths, where the polymer is transparent, is a crucial prerequisite. Alternative thermal methods for the formulation of thermosetting materials usually involve Diels-Alder reactions which may suffer from the reversibility. Thermally induced

irreversible dimerization reaction of benzocyclobutene was proposed as a versatile route to form cross-linked high-performance polymers.

Polybenzoxazines are class of phenolic polymers formed by thermal ring-opening of the corresponding benzoxazines without any catalyst.

In recent years the development of the benzoxazine-based family of phenolic resins has attracted significant attention. Various phenols and primary amines have been used synthesize benzoxazine resins. As a result of the ring-opening polymerization, polybenzoxazines overcome many shortcomings associated with traditional phenolic resins such as releasing condensation by-products and using strong acids as catalysts, while retaining good thermal properties and flame retardance of phenolics. Also, like epoxide based polymers and polyimide, polybenzoxazines have excellent mechanical properties and molecular design flexibility. Benzoxazine resins undergo near-zero volumetric changes or expansion upon polymerization. By using particular types of amine and phenol, polybenzoxazines with char yield as high 80% have recently been obtained. These advantages of benzoxazines receive considerable increase on the studies of benzoxazines and their corresponding polymers.

This study describes the functionalization of polystyrene with benzoxazine groups using Click reaction of propargyl benzoxazine with azido containing polystyrene. In addition, thermal behavior of the resulting polymers were examined. As it will also be shown, these polymers undergo thermal cross-linking by ring opening polymerization of benzoxazine groups without any catalysts.

2. THEORETICAL PART

2.1 Linear and Thermoset Polymers

Polymers are widely used in all walks of human life and play a vital role in shaping modern man's activities to be as important and comfortable as they are today. The advances in science and technology made in recent decades owe much to development of polymer science. The synthesis and design of new polymeric materials to achieve specific physical properties and specialized applications, and attempt to find interesting applications involving advanced structures and architectures, are in continuous development in the period of the polymer science.

Basically, a polymerization process is based on a repetitive reaction in which a monomer is converted into polymer segment. To achieve such a goal, polymer chemists have a variety of synthetic processes to choose from reactions with very high selectivity when planning a particular synthesis. However, each method has its strengths and its weaknesses, and often requires high-purity reagents and special conditions. Indeed, the need high-purity monomers and solvents, reactive initiators and pure conditions have dramatically limited the industrial application of many techniques.

A comprehensive classification of both linear and crosslinked polymers may be based on the mechanism of the polymerization process. From the point of view of the polymer growth mechanism, two entirely different processes, step and chain polymerization, are distinguishable [1].

Step-growth polymerization proceeds via a step-by-step succession of elementary reactions between reactive sites, which are usually functional groups such as alcohol, acid, isocyanate, etc. Each independent step causes the disappearance of two coreacting sites and creates a new linking unit between a pair of molecules. To obtain polymers, the reactants must be at least difunctional; monofunctional reactants interrupt the polymer growth.

In chain-growth polymerization, propagation is caused by the direct reaction of a species bearing a suitably generated active center with a monomer molecule. The active center (a free radical, an anion, a cation, etc.) is generated chainwise by each act of growth; the monomer itself constitutes the feed (reactive solvent) and is progressively converted into the polymer.

For both mechanisms of polymer growth, if one of the reactants has functionality higher than 2, branched molecules and an infinite structure can be formed. To summarize both mechanisms it may be stated that [2]:

1. A step-growth polymerization (with or without elimination of low-molar-mass products) involves a series of monomer + monomer, monomer + oligomer, monomer or oligomer + macromolecule, and macromolecule + macromolecule reactions.

The molar mass of the product grows gradually and the molar mass distribution becomes continuously wider. Functionalities of monomers and the molar ratio between coreactive sites are the main parameters for controlling the polymer structure.

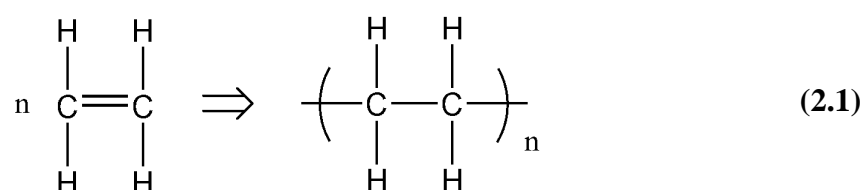
2. A chainwise polymerization proceeds exclusively by monomer + macromolecule reactions. When the propagation step is fast compared to the initiation step, long chains are already formed at the beginning of the reaction. The main parameters controlling the polymer structure are the functionalities of the monomers and the ratios between the initiation and propagation rates and between initiator and monomer concentrations.

The polymers are usually classified into three groups [3-6]:

1. Thermoplastics such as polyethylene which can be repeatedly softened by an increase in temperature and hardened by a decrease in temperature;
2. Thermosets or thermosetting polymers such as epoxy resin which harden when two components are mixed together and can not be melted without decomposition;
3. Elastomers or rubbers which can be stretched repeatedly to at least twice their original length and will return to their approximate original length upon immediate release of stress.

2.1.1 Thermoplastics

The thermoplastics are build-up of long chains. Strong covalent bonds exist along the chains (primary bonds) but the interatomic forces between the chains (secondary bonds) are weak. They are often described as linear polymers. The long molecules may be packed together in a great variety of configurations including amorphous (e.g. polystyrene), crystalline or more frequently partly crystalline or semicrystalline (e.g. polyethylene) structures. The thermoplastics are stable in melting; they can be melted and solidified repeatedly [7]. The melting temperature depends on length of chains and in practical cases is not so sharp as that in metals. The linear polymers are usually made by additional polymerization, meaning that one kind of unsaturated molecules is joined together by covalent bonding. Typical example is the formation of polyethylene from ethylene ($\text{CH}_2=\text{CH}_2$) as a monomer (2.1).



In this case the group $-\text{[CH}_2\text{-CH}_2\text{-]}-$ is the constitutional unit, n is the number of monomers in the polymer (*degree of polymerisation*). In polyethylene, n can be as large as 50,000 to 500,000. Many commercially important thermoplastics (*the polyvinyls*) may be simply derived from the atomic group



where the radical \mathbf{R} may be hydrogen (as in polyethylene), Cl in polyvinyl chloride or CH_3 in polystyrene (2.2). Many linear polymers have more complex constitutional units e.g. nylon 66. In Table 2.1, the composition and use of several thermoplastics are listed.

Table 2.1 : Composition and use of thermoplastics [8].

| Thermoplastic | Composition | Uses |
|-------------------------------|---|---|
| Polyethylene, PE | $\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right)_n$ <p>Partly crystalline</p> | Tubing, Film, Bottles, Cups, Electrical insulation, Packaging |
| Polypropylene, PP | $\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \right)_n$ <p>Partly crystalline</p> | Same uses as PE, but lighter, stiffer, more resistant to sunlight. |
| Polytetrafluoroethylene, PTFE | $\left(\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right)_n$ <p>Partly crystalline</p> | Teflon, Good high-temperature polymer with very low friction and adhesion characteristics. Non-stick saucepans, bearing, seals. |
| Polystyrene, PS | $\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} \right)_n$ <p>Amorphous</p> | Cheap moulded objects, Toughened with butadiene to make high-impact polystyrene (HIPS). Foamed with CO ₂ to make common packaging. |

| | | |
|------------------------------|--|--|
| Polyvinylchloride, PVC | $\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right)_n$ | Architectural uses(window frames, etc.). Gramophone records. Plasticized to make artificial leather, hoses, clothing |
| Polymethylmethacrylate, PMMA | $\left(\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{COOCH}_3 \end{array} \right)_n$ | Perspex, Lucite, transparent sheet and mouldings. Aircraft windows, laminated windscreens. |
| Nylon 66 | $\left(\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{---C---}(\text{CH}_2)_4\text{---C---NH---}(\text{CH}_2)_6\text{---NH---} \end{array} \right)_n$ | Textiles, rope, mouldings. |
| | Partly crystalline when drawn. | |

2.1.2 Thermosets

In thermosets or resins, cross-linking agents rigidly bond the chains together by covalent bonds. The three dimensional network structure results in improved strength. However, these polymers can not be melted without degradation. The thermosets are prepared usually by condensation polymerisation, reacting two components (a resin and a hardener) either at room temperature or on heating. In this case different kind of molecules is joined by a chemical reaction that releases a by-product, a small molecule such as water [9]. The thermosets have generally amorphous structure. The prototype of network polymers has been the phenol-formaldehyde, one of the first synthetic polymers. It is well known under its trade name Bakelite. Other important thermosets are epoxy resins and polyesters (Table 2.2). They are widely used among others as matrix materials in fibre reinforced polymer composites.

Table 2.2 : Composition and application of some thermosets [8].

| Thermoset | Composition | Uses |
|---------------------|--|---|
| Epoxy | $\left(\text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\overset{\text{OH}}{\text{CH}}-\text{CH}_2 \right)_n$ <p style="text-align: center;">Amorphous</p> | Fiberglass, Adhesives. Expensive. |
| Polyester | $\left(\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_m-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{CH}_2\text{OH}}{\underset{\text{CH}_2\text{OH}}{\text{C}}} \right)_n$ <p style="text-align: center;">Amorphous</p> | Fiberglass, Laminates. Cheaper than epoxy. |
| Phenol-formaldehyde | $\left(\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}_6\text{H}_2}}-\text{CH}_2 \right)_n$ <p style="text-align: center;">Amorphous</p> | Bakelite, Tufnol, Formica. Rather brittle. |

Thermosetting polymers may be formed in two ways:

1. By polymerizing (step or chain mechanisms) monomers where at least one of them has a functionality higher than 2.
2. By chemically creating crosslinks between previously formed linear or branched macromolecules (crosslinking of primary chains, as vulcanization does for natural rubber).

2.1.3 Elastomers

The elastomers or rubbers are either natural or synthetic linear polymers. Their structures are somewhere between the linear and network polymers. They consist of linear chains but the chains are cross-linked in several places e.g. in rubber, sulphur atoms join the elastomer chains together [3].

The elasticity of rubber is determined by the number of cross-links. Low sulphur additions leave the rubber soft and flexible. Increasing the sulphur content the rubber becomes more rigid. To provide the optimal elasticity up to 30 – 40% sulphur is usually added. Typical examples of elastomers are listed in Table 2.3

Table 2.3 : Composition and use of elastomers [8].

| Elastomer | Composition | Uses |
|-----------------|---|---|
| polyisoprene | $\left(\begin{array}{cccc} \text{H} & & & \text{H} \\ & & & \\ \text{---C---} & \text{C}=\text{C} & \text{---} & \text{C---} \\ & & & \\ \text{H} & \text{H} & \text{CH}_3 & \text{H} \end{array} \right)_n$ | Natural rubber |
| | Amorphous except at high strains | |
| polybutadiene | $\left(\begin{array}{cccc} \text{H} & & & \text{H} \\ & & & \\ \text{---C---} & \text{C}=\text{C} & \text{---} & \text{C---} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array} \right)_n$ | Synthetic rubber, cartyres |
| | Amorphous except at high strains | |
| polychloroprene | $\left(\begin{array}{cccc} \text{H} & & & \text{H} \\ & & & \\ \text{---C---} & \text{C}=\text{C} & \text{---} & \text{C---} \\ & & & \\ \text{H} & \text{H} & \text{Cl} & \text{H} \end{array} \right)_n$ | Neoprene. An oil- resistant rubber, used for seals. |
| | Amorphous except at high strains | |

2.2 Controlled Free Radical Polymerization

Many vinyl monomers can be polymerized by a conventional free radical polymerization. However, conventional free radical polymerization does not allow to prepare polymers with well-defined structures. Previously, only ionic methods were used to synthesize such controlled macromolecular structures. However, recent breakthrough in controlled free radical polymerization made it possible to obtain polymers with low-polydispersity and controlled structures. Today, there exist several controlled polymerization methods. In the present study we have utilized Nitroxide Mediated Radical Polymerization (NMP) as the controlled polymerization as it is particularly useful for styrene based monomers. The details of this polymerization will be given below.

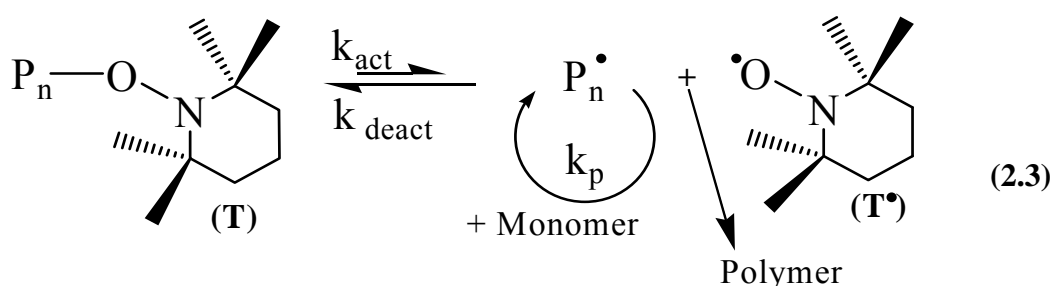
2.2.1 Nitroxide Mediated Radical Polymerization

Nitroxide Mediated Radical Polymerization (NMP), also referred as Stable free radical polymerization (SFRP), is one of the versatile methods of the controlled/"living" polymerizations. NMP is generally based on the use of nitroxyl radicals (nitroxides) or alkoxyamines. Rizzardo and Solomon first used alkoxyamines for the polymerization of various vinyl monomers [10-12]. However, only low molecular weight polymers were obtained. Later Georges et al. showed that high molecular weight polystyrene ($M_n < 50,000$) with low polydispersity (< 1.5) could be prepared using benzoyl peroxide (BPO) and a nitroxyl radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [13]

Two initiation systems have been generally employed in the NMP. First is a bimolecular system consisting of conventional radical initiator such as BPO or azoisobutyronitrile (AIBN), and a nitroxide (i.e. TEMPO). The conventional radical initiator is decomposed at an appropriate temperature in order to initiate free radical polymerization. The initiator-monomer adduct is trapped by the nitroxide leading to formation of the alkoxyamine *in situ*. Second is the unimolecular system utilizing the alkoxyamine that is decomposed into a nitroxide and an initiating radical. This radical can consequently initiate the free radical polymerization (reaction 2.3). By using the unimolecular initiator, the molecular weight can be properly controlled, since the number of initiating sites per polymeric chain is determined. Also

functionalized unimolecular initiators can afford the fully functional groups at the ends of the polymer chain.

The key kinetic aspect of the living radical polymerization systems, including NMP is described through the persistent radical effect (PRE) [14]. In the initial stages of the polymerization, a small fraction of the initiating radicals formed from decomposition of the initiator (alkoxyamine) undergo biradical termination. This results in the removal of two initiating radicals from the system and necessitates a small increase in the concentration of mediating radical (persistent radical) relative to the initiating radical/propagating radical.



However, mediating radical does not undergo coupling or does not initiate polymerization. This increased concentration of mediating radical is self-limiting since a higher concentration leads to more efficient formation of polymer with dormant chain end and a decrease in the amount of radical coupling reaction, leading to the PRE and to the ultimate control over the polymerization process [15].

Styrenic type monomers have been the most widely studied using NMP in the presence of TEMPO or its derivatives as mediating radical. This is mainly because the controlled polymerization of acrylates by SFRP is restricted. It was apparent that the structural changes in the nitroxide as a mediating radical were required. On this basis, alicyclic nitroxides were synthesized. These compounds have a hydrogen atom on one of the α -carbons adjacent to nitrogen atom. Alkyl methacrylates can also be polymerized via NMP strategy using NO/NO₂ mixtures [16].

Numerous studies were performed to elucidate the mechanism and the polymerization kinetics of NMP. Because of the space limitations, we will not cover all these detailed studies, but compile the existing literature data on all nitroxide radicals as mediating radicals and their use in NMP.

Advantages of SFRP over other controlled/"living" radical polymerization systems are that any metal catalyst is not necessary and no further purification after polymerization is required. However, major drawbacks of SFRP are the long polymerization time, the limit of the range of the monomers, and the higher temperatures (>125 °C). The synthesis of the new nitroxides leads to a wider range of monomers to be polymerized by SFRP at lower temperatures in shorter polymerization time.

2.3. Polystyrene

2.3.1 History of Polystyrene

It may well be argued that the history of polystyrene is more closely bound up with the history of the 20th century than is the case with any other plastics material.

In the US semi-plant-scale work at the Dow Chemical Company showed promise of commercial success in 1934. As a consequence there became available shortly before World War II a material of particular interest because of its good electrical insulation characteristics.

In 1942 the US Government initiated a crash programme for the installation of plants for the manufacture of a rubber from butadiene and styrene. This product, then known as GR-S (Government Rubber-Styrene), provided at that time an inferior substitute for natural rubber but, with a renewed availability of natural rubber at the end of the war, the demand for GR-S slumped considerably [17].

After the war, however, there was a large surplus capacity of plant for the manufacture of styrene and polystyrene together with a great deal of knowledge and experience that had been collected over the war years. It was therefore found possible to produce polystyrene, not as an expensive electrical insulator, but as a cheap general purpose thermoplastic.

In the late 1990s a crystalline form of polystyrene, *syndiotactic polystyrene* became commercially available but unless otherwise stated references to polystyrene in this chapter will refer to the traditional amorphous polymer. The rarely used systematic IUPAC name for polystyrene is poly-(1 -phenylethylene).

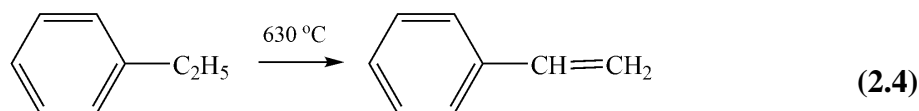
2.3.2 Preparation of Polystyrene

Production of PS is based on polymerization of styrene. This polymer has an enormous industrial importance.

In 1869 Berthflot reported the production of styrene by dehydrogenation of ethylbenzene. This method is the basis of present day commercial methods. Over the year many other methods were developed, such as the decarboxylation of acids, dehydration of alcohols, pyrolysis of acetylene, pyrolysis of hydrocarbons and the chlorination and dehydrogenation of ethylbenzene [17].

2.3.2.1 Dehydrogenation

Styrene is produced from the ethylbenzene by a process of dehydrogenation (reaction 2.4)

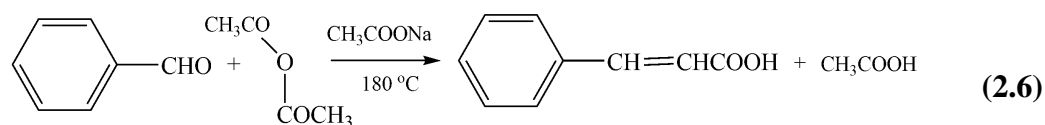
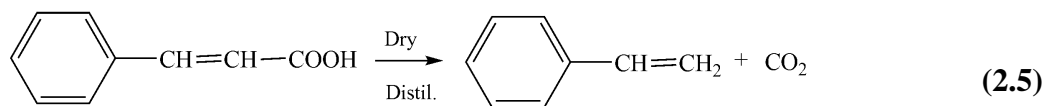


This is an endothermic reaction in which a volume increase accompanies dehydrogenation. The reaction is therefore favoured by operation at reduced pressure. In practice steam is passed through with the ethylbenzene in order to reduce the partial pressure of the latter rather than carrying out a hightemperature reaction under partial vacuum. By the use of selected catalysts such as magnesium oxide and iron oxide a conversion of 35-40% per pass with ultimate yields of 90-92% may be obtained [18]

There are today two methods of interest, (a) the laboratory preparation, and (b) commercial preparation.

a) Laboratory Preparation

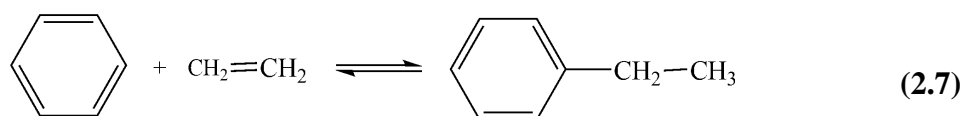
The principal constituent of storax is cinnamic acid and for laboratory purposes styrene is still most easily obtained in high purity but dry distillation of cinnamic acid and its salts under atmospheric pressure (reaction 2.5)



The cinnamic acid is readily prepared by heating benzaldehyde with acetic anhydride and sodium acetate.(reaction 2.6)

b) Commercial Preparation

The bulk of commercial styrene is prepared by the Dow process or some similar system. The method involves the reaction of benzene and ethylene to ethylbenzene, its dehydrogenation to styrene and a final finishing stage. It is therefore useful to consider this process in each of the three stages. Ethylbenzene is prepared by reaction of ethylene and benzene in the presence of a Friedel-Crafts catalyst such as aluminium chloride at about 95°C (reaction 2.7)



To improve the catalyst efficiency some ethyl chloride is added which produces hydrochloric acid at the reaction temperatures.

2.3.3 Polymerization of Polystyrene

Polystyrene was first made by E. Simon in 1839 who at the time believed he had produced an oxidation product, which he called styrol oxide. Since that time the polymerization of styrene has been extensively studied. In fact a great deal of the work which now enables us to understand the fundamentals of polymerization was carried out on styrene.

Styrene can be polymerized by ionic, free-radical or coordination polymerization. Ionic polymerization is used mostly for manufacture-specialty polymers. In industrial manner, free-radical polymerization is preferred more than other types because the yield of the reaction is nearly the same with other methods' yields and during this

reaction, impurity affects the yield less. The rate of free-radical polymerization can be controlled by the choice of initiator and by changing the reaction conditions [17].

Polymerization methods of styrene are mainly; mass (bulk), solution, suspension and emulsion. An industrially important method of production is emulsion polymerization [18]. The key feature of polystyrene is its insolubility in its monomer. Instead of solution, it is negligently swollen by styrene. Also, this is another differing point of polystyrene, neither well swollen nor poorly swollen by its monomer, so its emulsion polymerization is not a regular heterogeneous process [18].

2.3.4 Properties and Structure of Polystyrene

Polystyrene has the simple repeating structure shown in reaction 2.8 and as might be expected from such a substantially linear polymer it is thermoplastic. As with polypropylene, PVC and other vinyl compounds there is the possibility of various stereo-regular forms. Because of its amorphous nature the commercial polymer has for long been regarded as atactic. As with poly(methyl methacrylate) subsequent work has, however, indicated that the syndiotactic segments are more frequent than atactic segments and it appears that this may be a common feature of most free-radical initiated vinyl polymers. The specific position of the benzene ring is, however, sufficiently random to inhibit crystallization [17].



Because of the chain-stiffening effect of the benzene ring the *T_g* of commercial materials are in the range 90-100°C and isotactic polymers have similar values (approx. 100°C). A consequence of this *T_g* value plus the amorphous nature of the polymer is that we have a material that is hard and transparent at room temperature. Isotactic polystyrenes have been known since 1955 but have not been of commercial importance. Syndiotactic polystyrene using metallocene catalysis has recently

become of commercial interest. Both stereoregular polymers are crystalline with T_g values of 230°C and 270°C for the isotactic and syndiotactic materials respectively.

They are also somewhat brittle. Being a hydrocarbon with a solubility parameter of 18.6MPa^{1/2} it is dissolved by a number of hydrocarbons with similar solubility parameters, such as benzene and toluene. The presence of a benzene ring results in polystyrene having greater reactivity than polyethylene. Characteristic reactions of a phenyl group such as chlorination, hydrogenation, nitration and sulphonation can all be performed with polystyrene. Chain rupture and discolouration are frequently additional effects of such reactions. The pure hydrocarbon nature of polystyrene gives it excellent electrical insulation characteristics, as a result of both the fundamentally good characteristics of the material and to the low water absorption of such a hydrocarbon polymer. The insulation characteristics are therefore well maintained in humid conditions [18].

Polystyrene is a hard, rigid transparent thermoplastic which emits a characteristic metallic ring when dropped. It is free from odour and taste, burns with a sooty flame and has a low specific gravity of 1.054. Because of its low cost, good mouldability, low moisture absorption, good dimensional stability, good electric insulation properties, colourability and reasonable chemical resistance it is widely used as an injection moulding and vacuum forming material. Additionally the low thermal conductivity has been made use of in polystyrene foam used for thermal insulation. The principal limitations of the polymer are its brittleness, inability to withstand the temperature of boiling water and its mediocre oil resistance [19].

2.3.5 Applications of Polystyrene

For many applications polystyrene might be considered to be too brittle a polymer. Because of this, polystyrene manufacturers have made a number of attempts to modify their products [17].

The methods of approaching this problem include:

- (1) Use of higher molecular weight polymers.
- (2) Use of plasticisers.
- (3) Incorporation of fillers such as glass fibre, wood flour, etc.

(4) Deliberate orientation of the polymer molecules.

(5) Copolymerisation

(6) The use of rubbery additives.

Of these methods the first gives only marginal improvements whilst the second approach has far too severe an effect on the softening point to be of any commercial value.

Very many copolymers with styrene as the principal constituent have been prepared and a number have been marketed. In some instances there is an appreciable increase in toughness but usually in such cases the softening point of the copolymer is much lower than that of the homopolymer.

As mentioned earlier, unmodified polystyrene first found application where rigidity and low cost were important prerequisites. Other useful properties were the transparency and high refractive index, freedom from taste, odour and toxicity, good electrical insulation characteristics, low water absorption and comparatively easy processability. Carefully designed and well-made articles from polystyrene were often found to be perfectly suitable for the end-use intended. On the other hand the extensive use of the polymers in badly designed and badly made products which broke only too easily caused a reaction away from the homopolymer. This resulted, first of all, in the development of the highimpact polystyrene and today this is more important than the unmodified polymer [19]

In recent years general purpose polystyrene and high-impact polystyrenes have had to face intensive competition from other materials, particularly polypropylene, which has been available in recent years at what may best be described as an abnormally low price. Whilst polystyrene has lost some of its markets it has generally enjoyed increasing consumption and the more pessimistic predictions of a decline have as yet failed to materialise.

2.4 Polybenzoxazines

Polybenzoxazine is a recently advanced addition polymerized phenolic system, containing a wide range of interesting qualities and has the capability to overcome various deficiencies of conventional novolac and resole type phenolic resins. These

materials exhibit (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazines T_g much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, (vi) release of no toxic by-product during curing. Enormous design flexibility which permits tailoring the properties of the cured materials are offered by the molecular structure of polybenzoxazines for wide range of applications.[20]

Phenolic resins are greatly used to high technology aerospace in industry and commercial market in various applications, from commodity and construction materials. Though several desirable properties, such as good mechanical strength, dimensional stability, resistance against various solvents, flame retardance, are characteristics of the phenolic resins, a number of short-comings are also associated with these materials. For example, they are brittle, have poor shelf life, acid or base catalysts are often used for the preparation of resin, which corrode the processing equipments, and they release by-products (such as water, ammonia compounds during curing) which sometimes affect the properties of cured resins by forming micro voids. To overcome these problems recently a new type of addition-cure phenolic system, polybenzoxazines, has been recently developed. They have gained immense interest in the field of polymer research because they have the capability to exhibit such properties which are the combination of thermal and flame retardance properties of phenolics along with mechanical performance and molecular design flexibility. Although the benzoxazines were first synthesized by Cope and Holy in 1940s [21], the potential of polybenzoxazines has been recognized only recently [23].

The molecular structure of polybenzoxazines offers enormous design flexibility which allows the properties of the cured materials to be tailored for wide range of applications. These newly developed resins possess unique features, namely (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazine based materials T_g much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, (vi) release of no by-products (even non-toxic) during curing [25]. Though several researchers have reported different synthetic methodologies of many benzoxazine containing monomers, blends, composites, and their cure reactions and properties, no extensive and critical review is available solely devoted to these materials. A special section

has been dedicated to describe the recent trend to incorporate benzoxazine groups into macromolecular chains.

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 different benzoxazine monomers have been discussed [20].

2.4.1.1 Mono-functional Benzoxazine Monomers

Holly and Cope [21] first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later, Burke found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and forms a Mannich bridge [24]. 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 [25] (Figure 2.1).

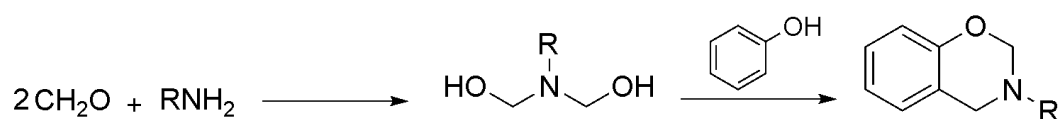


Figure 2. 1 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines

As an example, to prepare 3,4-dihydro-3-cyclohexyl-6-*t*-butyl-1,3,2H-benzoxazine, Burke [24] employed two procedures:

- (i) Cyclohexylamine was mixed formaldehyde in dioxane. After addition of *p*-butyl phenol the mixture was refluxed for 2 h. Upon cooling to room temperature, a crystalline product was obtained, which was then recrystallized from 95 % ethanol and the yield was 78 %.
- (ii) Paraformaldehyde was dissolved in warm methanolic KOH solution. The solution was cooled during the portion-wise addition of cyclohexylamine. After the addition of 4-*t*-butylphenol, the resulting solution was cooled to room temperature and the product was recrystallized from 95 % ethanol and the yield was 92 %. Synthesis of a *p*-cresol based benzoxazine by using aniline, formaldehyde and *p*-cresol as starting materials in dioxane has been reported [26-28].

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) [29] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [22] is shown below in Figure 2.2.

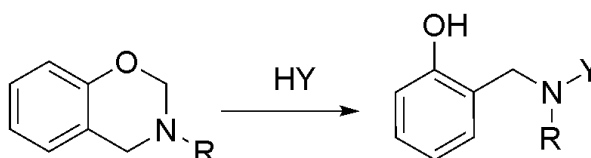


Figure 2. 2 Ring opening of benzoxazine in acidic medium

The benzoxazines derived from a strongly basic amine and a less acidic phenol was found to be more stable in the hot alcohols [30]. 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 [31]. A significantly higher yield was found when the benzoxazine was 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, Ishida *et al* developed a solventless synthesis in the melt state [32]. The reaction mechanism and kinetics of this solventless synthesis were proposed by Liu [33]. 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 by-products [20].

In this method, the alkylating agent arises from acid-induced deamination of the phenolic Mannich base. Thus, the variety of substituent on the N-3 position of the benzoxazine ring is limited. Benzoxazine can also be obtained by heating the mixture of 2,4-xylenol and hexamethylenetetramine (3:4:1 mole) at 135 °C for 2 h in air [21]. 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 [24]. This benzoxazine can further react with phenol to form 3,4-dihydro-3-(2-hydroxy)benzyl-2H-1,3-benzoxazine [22] (Figure 2.3).

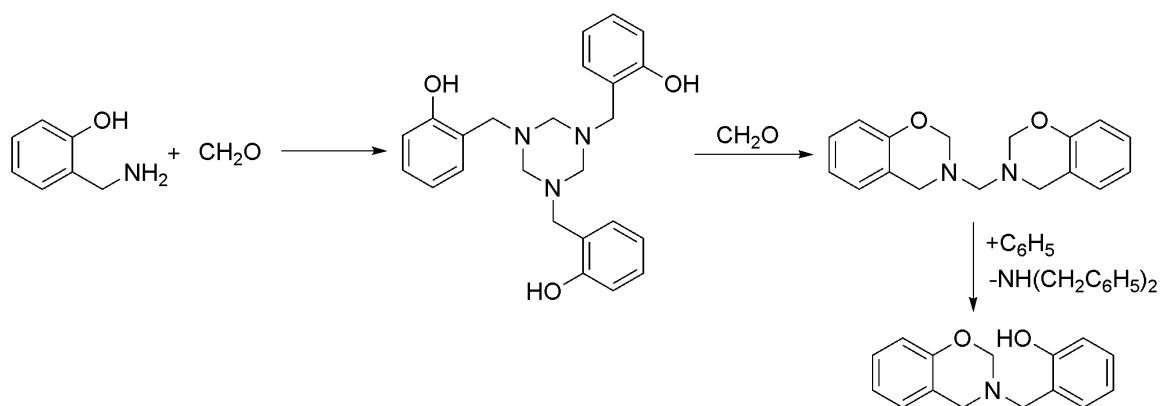


Figure 2. 3 Formation of 1,3-oxazine ring from 2-hydroxybenzylamine

2.4.1.2 Di-functional and Multifunctional 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 [34]. Hemvichian K. *et al.* have 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 [35]. To overcome this limitation, Ishida and coworkers [28, 36] have developed a new class of difunctional or multifunctional 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 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 NMR, FTIR and SEC. 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 [37, 38] and the pure monomer was referred as **B-a** and oligomers were as **oligo-B-a**. The structures of oligo-B-a and B-a were analyzed by ¹H-NMR measurements. The overall synthetic procedure is shown in Figure 2.4 [37]. To achieve successful processing, cure kinetics of this material was investigated by using DSC, which 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 [38].

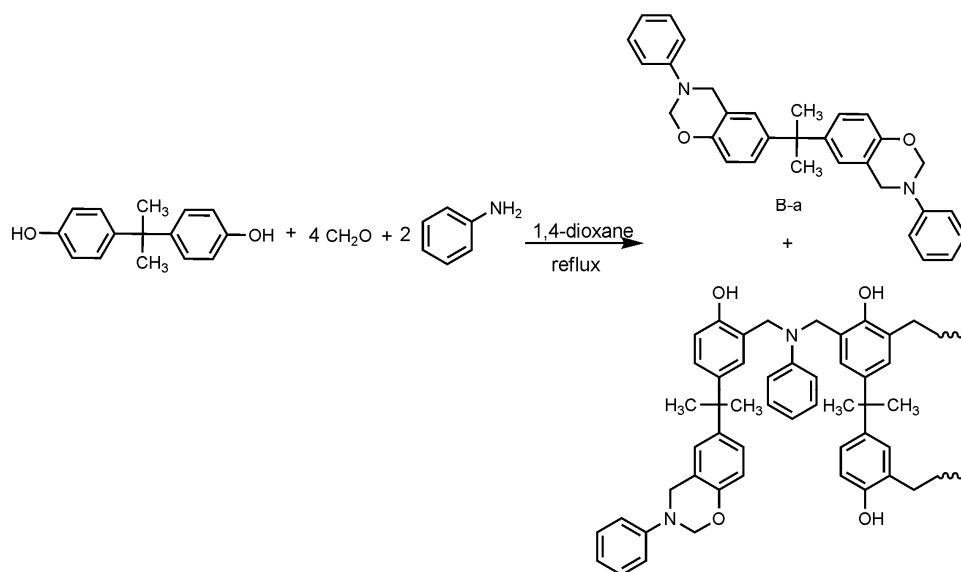


Figure 2. 4 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer. The synthesis of 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) (B-a) in high yield by the solventless reaction process using 1,3,5 triphenyl(alkyl) hexahydro-1,3,5 triazine, paraformaldehyde and bisphenol A has been reported [39].

Solventless method was successfully employed for synthesis of a series of difunctional monomers listed in table 2.4. [32, 37, 39-42].

Table 2.4. Difunctional Benzoxazine Monomers.

| | |
|--|--|
| | |
| | |
| | |
| | |

2.4.2 Preparation of Polymers with Benzoxazine Moieties

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 [20].

2.4.2.1 Benzoxazine Functionalized Polystyrene

Poly(*p*-vinylphenol) (Poly(VP)) based benzoxazine was prepared from Poly(VP), formaline, and aniline (Figure 2.5). The curing behavior of the benzoxazine with the epoxy resin [42] and the properties of the cured resin were investigated.

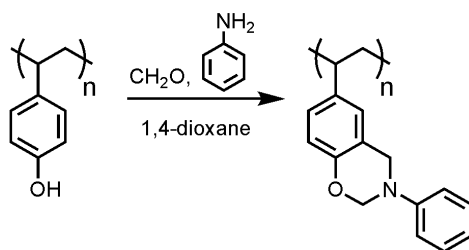


Figure 2. 5 Synthesis of poly(*p*-vinylphenol) based benzoxazine.

Consequently, the curing reaction did not proceed at low temperatures, but it proceeded rapidly at higher temperatures without a curing accelerator. The reaction induction time or cure time of the molten mixture from Poly(VP) based benzoxazine and epoxy resin was found to decrease, compared with those from conventional bisphenol A based benzoxazine and epoxy resin. The curing reaction rate of Poly(VP) based benzoxazine and epoxy resin increased more than that of conventional bisphenol A based benzoxazine and epoxy resin. The properties of the cured resin from neat resins and from reinforced resins with fused silica were evaluated. The cured resins from Poly(VP) based benzoxazine and epoxy resin showed good heat resistance, mechanical properties, electrical insulation, and water resistance compared to the cured resin from VP and epoxy resin using imidazole as the catalyst [43].

A unique synthetic route was reported by Kiskan *et al* [44] for the synthesis of a macromonomer where benzoxazine ring was anchored to the polystyrene polymer. Dibromophenyl terminated polystyrene was synthesized using Atom Transfer Radical Polymerization (ATRP), which was then followed by Suzuki coupling reaction to prepare amino functional polymers. These amino functional polymers when reacted with phenol and paraformaldehyde at 110°C for 2 h produced benzoxazine functionalized polystyrene macromonomer. The synthetic strategy is illustrated in Figure 2.6.

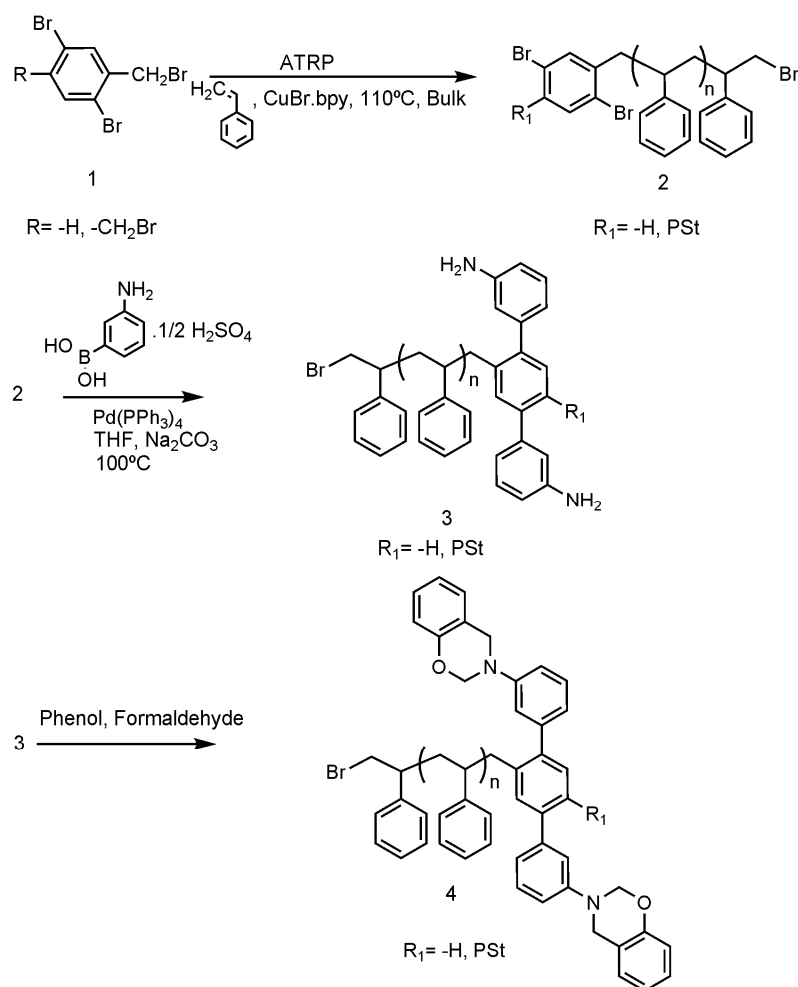


Figure 2. 6 Synthesis of benzoxazine functional polystyrene macromonomer.

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 (Figure 2. 7).

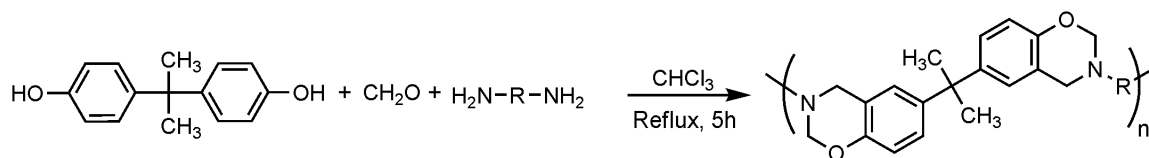


Figure 2. 7 Synthesis of polybenzoxazine precursors.

The possibility of the preparation of polymers containing oxazine ring in the main chain was first discussed by Liu *et.al* [22]. Later, more detailed work on the effect of water, solvents, catalyst, ratio of reactants and temperature was reported by the same research group [33]. The major problems associated with the preparation of such main-chain benzoxazine precursor polymers were low molecular weight and cross-linking 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 ring-opened 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 [46, 47].

2.4.3.2 Side-chain Precursor

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-2H-benzo[e][1,3] oxazine (P-a) alone and in the presence of thiophene (Th) with ceric ammonium nitrate in acetonitrile (Figure 2. 8). 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 [48].

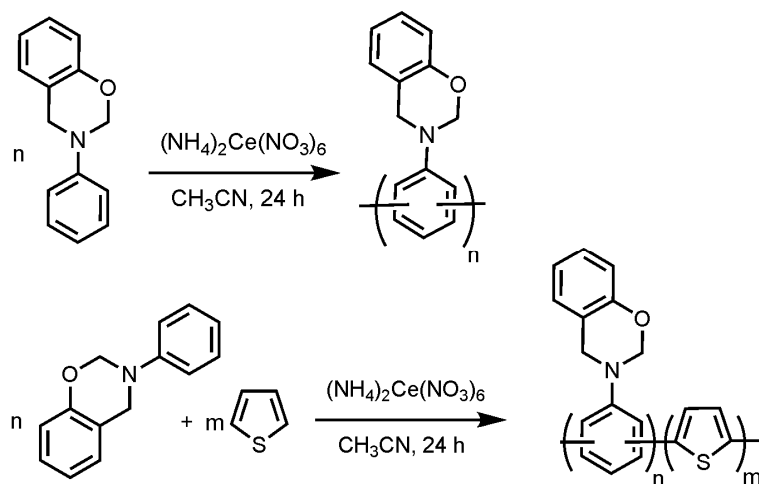


Figure 2. 8 Synthesis of semi-conductive side-chain polybenzoxazine precursor.

2.4.4 Reaction Mechanism of Ring Opening Polymerization of Benzoxazine

To understand the polymerization reaction mechanism of benzoxazines, understanding of the chemical structure of its oxazine ring is very important. A single crystal X-ray crystallographic study revealed that the preferential conformation of a mono-oxazine ring containing benzoxazine is a distorted semi-chair 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. 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 the oxygen and the 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 [49, 50]. The electron charge calculation after energy minimization predicts that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270).

The ring opening reaction of the benzoxazine was first reported by Burke *et al.* [25]. In the reaction of 1,3- dihydrobenzoxazine with a phenol, having both *ortho* and *para* position free, it was found that aminoalkylation occurred preferentially at the free *ortho* position to form a Mannich base bridge structure, along with small amount reaction at *para* position. To explain this *ortho* preference formation of a intermolecular hydrogen-bonded intermediate species was proposed. Riese *et al.* also observed the high reactivity of the *ortho* position when following the kinetics of mono-functional benzoxazines with 2,4-di-*tert*-butylphenol catalyst [34]. The typical method of polymerization of benzoxazine monomers is thermal curing without using any catalyst [27, 38, 41, 45, 51, 52]. It should be emphasized that the polymerization mechanism of benzoxazine resins is still not well established.

2.4.4.1 Thermal Polymerization of Benzoxazines

A cross-linked network structured polybenzoxazines, with higher T_g and degradation temperature, can be obtained when difunctional or multifunctional benzoxazines undergo polymerization. The polymeric structures form due to curing of mono-functional and difunctional benzoxazines are shown below in Figure 2.9 [53]. Obviously, difunctional benzoxazines derived from diamines are expected to undergo similar cross-linking [54, 55].

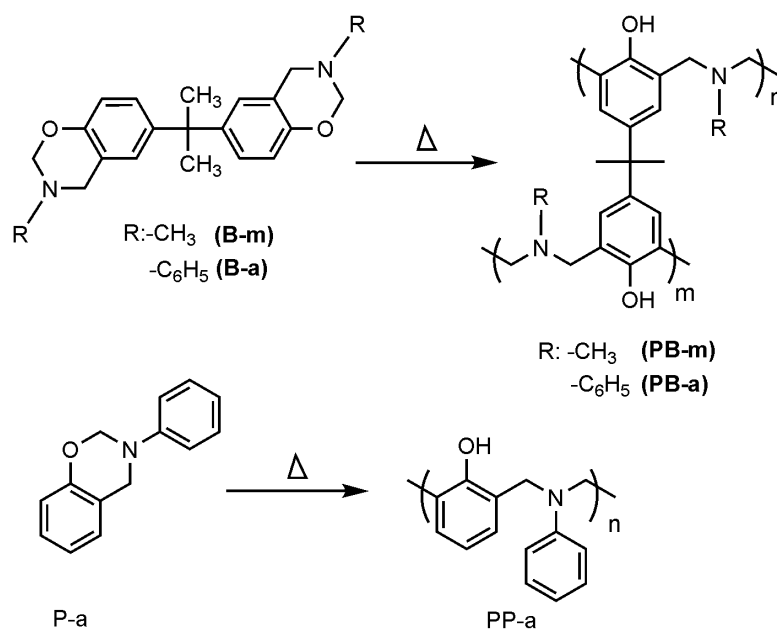


Figure 2. 9 Curing of monofunctional and difunctional benzoxazines.

In the DSC thermogram of a mono-functional benzoxazine, P-a, a sharp exotherm was observed with onset and maximum temperatures of the exotherm at 202 and 230⁰C respectively, corresponding to the ring-opening polymerization. The amount of exotherm for P-a was 62 cal/g. In case of difunctional benzoxazine, B-a, DSC showed an exotherm on with onset at ca. 223⁰C and maximum at 249⁰C corresponding to the ring-opening polymerization of benzoxazine. The amount of exotherm for B-a was 79 cal/g [53].

It has been observed that during synthesis of a difunctional benzoxazine (from bisphenol A, formaldehyde and methyl amine) not only bisphenol-A based benzoxazine (B-m) monomer forms as major product but also dimers and small oligomers form by the subsequent reactions between the rings and *ortho* position of bisphenol A hydroxyl groups. These free phenolic hydroxy structure containing dimers and oligomers trigger the monomer to be self-initiated towards polymerization and cross-linking reactions [28].

Attempts have been taken to understand the cure mechanism and kinetics of the thermal curing of mono and difunctional benzoxazines utilizing DSC, FTIR, DMA, ¹³C and ¹⁵N solid state NMR spectroscopic measurements [47, 56-62].

It has been proposed that, the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which exist in equilibrium [56] (Figure 2.10). 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. Further, the reactivity of the equilibrium pair depends on the basicity of the amine group. The more basic the amine, with more the free electron density of the nitrogen, has the capability to stabilize more the positive charge of the iminium ion. If the iminium ion is more stable, the equilibrium shifts toward it, causing lowering in propagation rate. If the iminium ion is unstable, the equilibrium will be shifted toward the carbocation, resulting in a higher propagation rate.

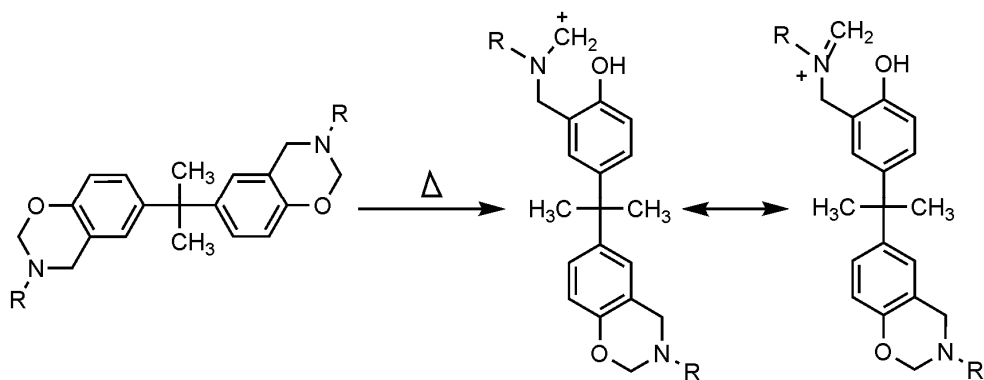


Figure 2. 10 Initiation of ring-opening polymerization of benzoxazines.

It should be noted that since the propagation reaction involves chain transfer to a benzene ring temperature should have a great impact on the rate of propagation. Kinetic study indicated that in the early stages of polymerization, the reaction may be relatively independent of the cure temperature. As the reaction proceeds, the temperature effect on propagation becomes more evident in the reaction kinetics.

Curing reactions at two different temperatures, below and above T_g temperature, demonstrate that the kinetics are significantly different for the two cure temperatures. Vitrification occurs sooner at higher cure temperature than the lower cure temperature, especially below the T_g . As vitrification causes a large increase in the viscosity of the system, at the reaction becomes largely diffusion-controlled, and greatly affect the curing kinetics [56]. Figure 2. 11 illustrates the thermal polymerization of B-a through cationic mechanism.

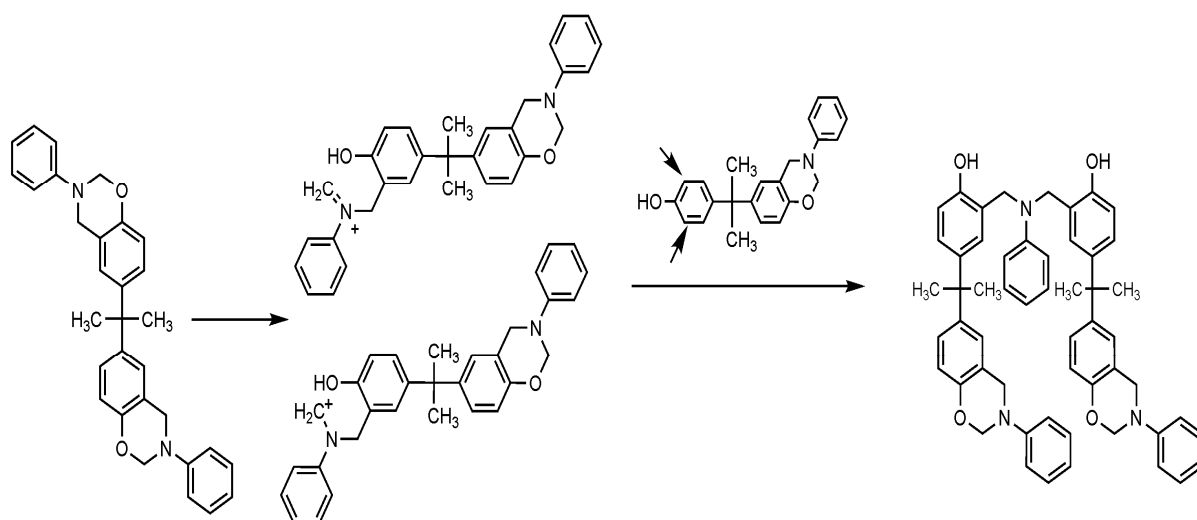


Figure 2. 11 Thermal polymerization of B-a through cationic mechanism

Solid State ^{15}N -NMR study identified the formation of a structure generated possibly due to the electrophilic substitution reaction between *ortho* position of the aniline and carbocation. Similar to phenol, the electron donating nature of nitrogen of the aniline makes its *ortho* and *para* position as possible sites for electrophilic substitution with the carbocation. The formation of this structure is shown in Figure 2.12 [57].

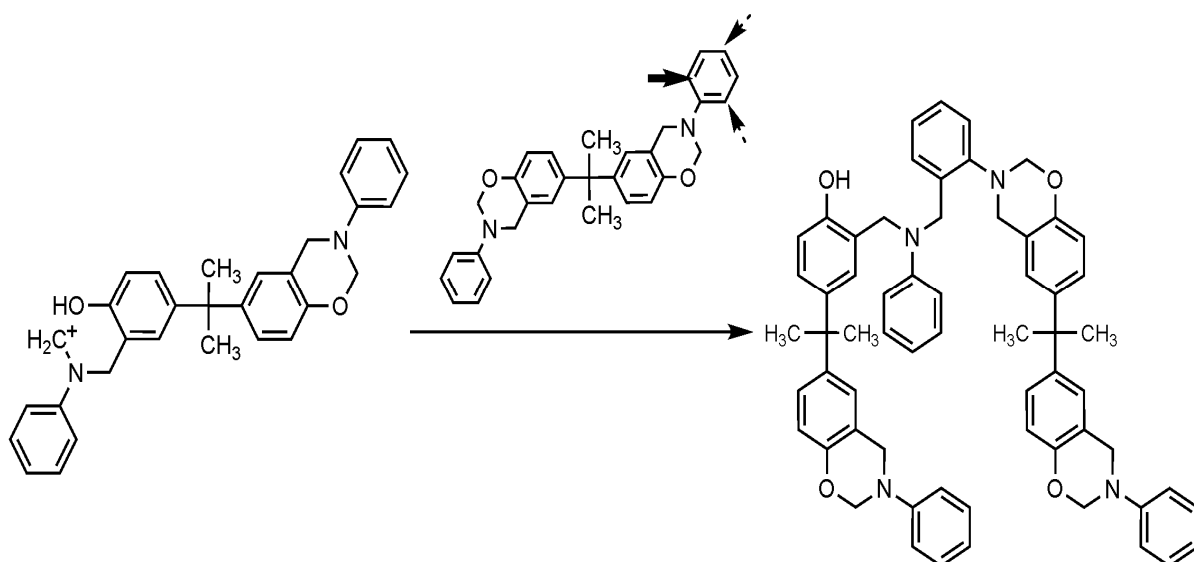


Figure 2. 12 Electrophilic substitution reaction of aniline moiety

2.4.5 Benzoxazine with Propargyl Ether Functional Group

Propargyl ether group, as a thermally reactive end capping agent, has attracted much attention because these monomers can be synthesized in high yield with low cost, in contrast to ethynyl-containing monomers which the preparation procedure is in low yield and high price [63]. Agag and Takeichi have prepared novel benzoxazine monomers containing a propargyl ether group as the cross-linkable functional group according to Figure 2.13 and obtained novel polybenzoxazines with attractive thermal properties [64]. The ring-opening polymerization of oxazine ring and cross-linking of propargyl ether group occurred at almost the same temperature range, at 230°C for mono-functional and 249°C for bifunctional monomer. Polybenzoxazines derived from these monomers exhibited significantly improved thermal properties than the typical polybenzoxazines.

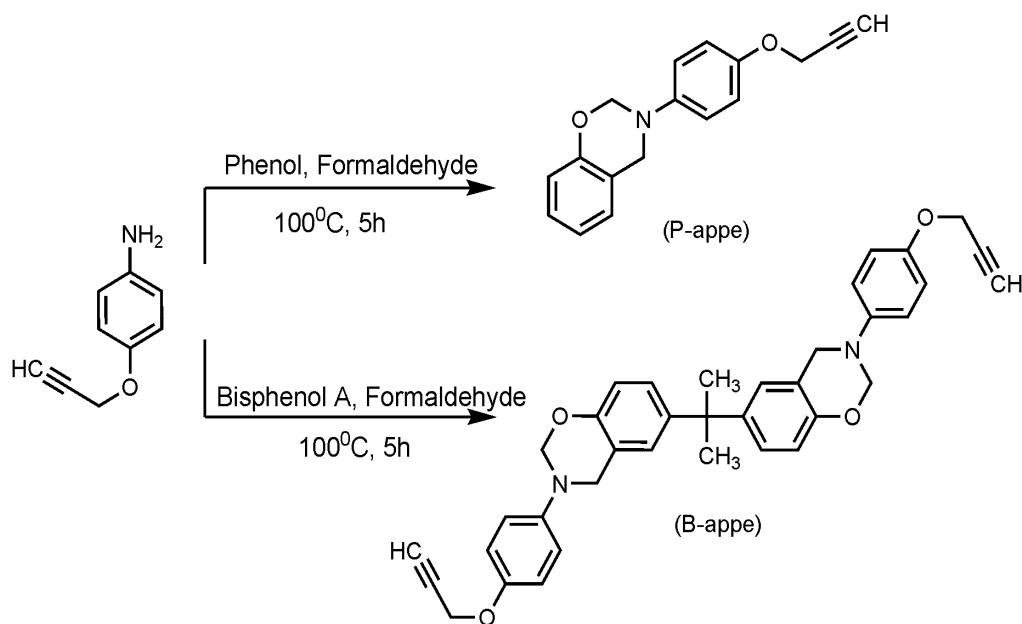


Figure 2.13 Synthesis of propargyl ether containing benzoxazine monomers.

2.4.6 Properties and Applications of Polybenzoxazines

PBZ materials are widely used all around the world in recent years for their advantageous nature of functionalizing, non-flammable structure and thermally stable character.

PBZ resins are more preferable than resole type phenolic and novalac resins. Phenol and formaldehyde are precursors of PBZ, they enhance design flexibility and polymer property tailoring [65,66].

The main advantage of PBZ material is its curable character supported by ease of design. In industrial manner, cured materials which serve for specific purposes can be produced. PBZ materials show (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazines T_g much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, (vi) release of no toxic by-product during curing [67,68].

Benzoxazine ring can undergo ring-opening reaction under specific conditions. Oxygen and nitrogen cause basicity of the oxazine ring, by Lewis definition. Therefore, oxazine ring becomes the cationic polymerization initiation site and the ring-opening can follow cationic mechanism [69-71]. During thermal curing process, it also follows the cationic mechanism but impurities in the reaction media act as

initiator. By using substituted amines, phenols and pendant groups, additional polymerizable sites can be formed and they can affect cross-linking of the polymer chains [72].

Phenolic resins are important due to their good mechanical strength, dimensional stability, resistance against various solvents, and flame. But on the other side, they are brittle, they have poor shelf life and during the preparation of the resin, acid or base catalysts that corrode the equipments are used. To overcome these problems, PBZ is developed. PBZ is the replacement of highly flammable epoxy and/or polyurethane adhesive for interior usage and also the replacement of epoxy or phenolic resins with its higher insulating capability [73, 74].

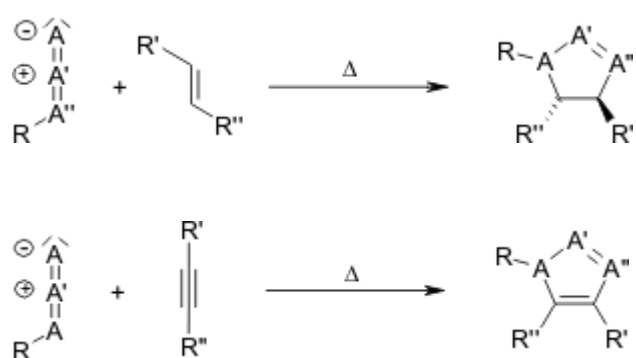
Benzoxazine based compositions are curable and they comprise a benzoxazine compound or resin with at least one more additional curable structure. Invention compositions are especially useful for increasing adhesion at interfaces. Optionally, the composition can also include a curing agent and/or filler. These compositions are mainly used as adhesives, encapsulants and coatings. Within the semiconductor fabrication industry, materials such as die attach adhesives, films, underfill materials and lead free solders are developed. PBZ compositions have near-zero volume change after post cure and this enables the usage of them as coating material. Heat curable composition of benzoxazine is useful in aerospace industry applications. Thermosetting benzoxazine resin compositions can bind a substrate to a metallic surface [75-76]

Incorporation of benzoxazine moiety with the polymer chain provides better processibility and improved mechanical properties. The PBZ resin has advantages such as [20, 79]:

- Near zero volumetric change upon polymerization
- Low water absorption
- Tg much higher than cure temperature
- Fast mechanical property build-up as a function of degree of polymerization
- High char-yield
- Low coefficient of thermal expansion
- Low viscosity
- Excellent electrical properties

2.5 Click Chemistry

A new approach in organic synthesis that involves the successful achievement of a polymerization process represents an important task in macromolecular science. Cycloaddition reactions, among them the metal catalyzed azide/alkyne 'click' reaction which is a variation of the Huisgen 1,3-dipolar cycloaddition reaction between terminal acetylenes and azides were shown to be the most effective and versatile and thus became the prime example of click chemistry (see reaction 2. 9).



(2.9)

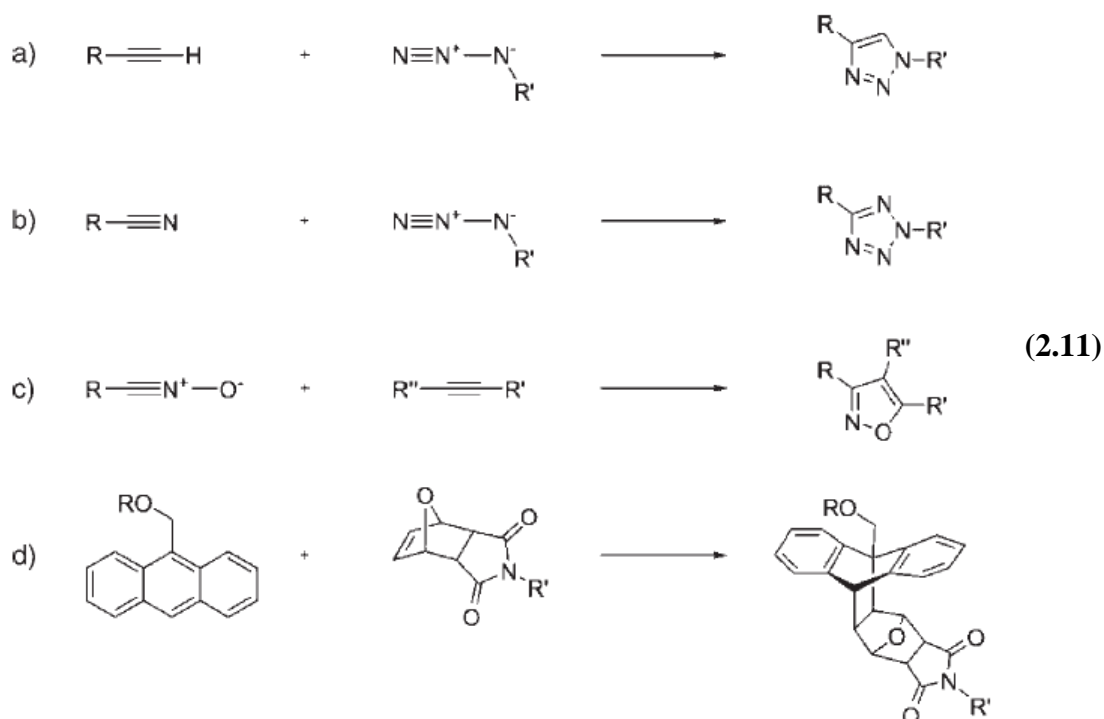
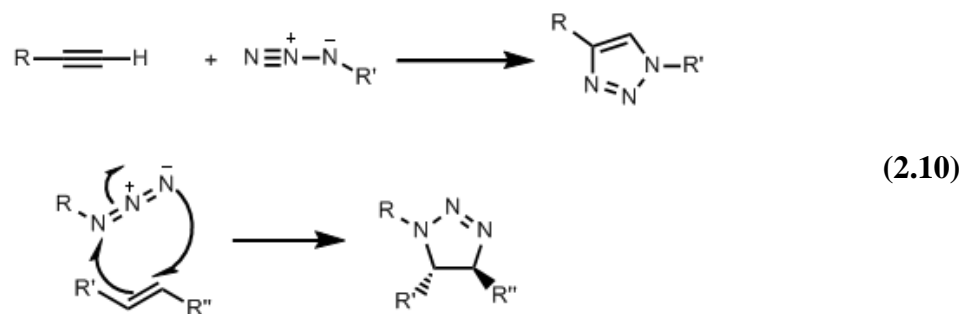
The Huisgen Cycloaddition is the reaction of a dipolarophile with a 1,3-dipolar compound that leads to 5-membered (hetero)cycles. Examples of dipolarophiles are alkenes and alkynes and molecules that possess related heteroatom functional groups (such as carbonyls and nitriles). 1,3-Dipolar compounds contain one or more heteroatoms and can be described as having at least one mesomeric structure that represents a charged dipole [80]. The reaction yield is above 95% with a high tolerance of functional groups and solvents, as well as moderate reaction temperatures between 25°C-70°C. Click reactions have gained popularity in materials science in recent years [81, 82].

The major scientific challenge of nanomaterial development is the requirement of high degree of structural order and defined properties. To meet this demand, the design of novel organic or inorganic molecules using sophisticated multistep experimental procedures is necessary. As a result, the discovery and selection of simpler and universal synthetic methods is essential.

The azide/alkyne 'click' reaction which is an appealing concept proposed by Sharpless and co-workers is not a scientific discipline but rather a synthetic

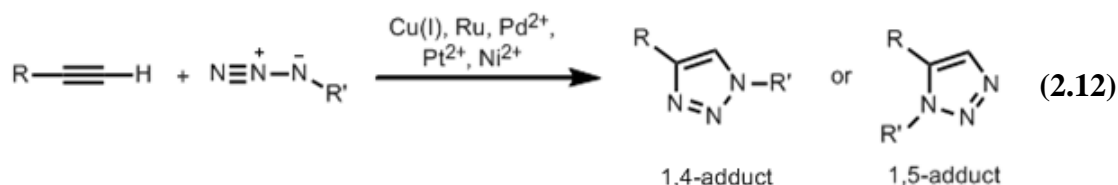
philosophy inspired by the simplicity and efficiency of the chemistry that takes place in nature. The objective of click chemistry is to establish an ideal set of straightforward and highly selective reactions [81-84]. Click reaction of azide/alkyne is a recent re-discovery of a reaction fulfilling many requirements for the affixation of ligands onto polymers by post-modification processes, which include often quantitative yields, a high tolerance of functional groups, an insensitivity of the reaction to solvents, irrespective of their protic/aprotic or polar/non-polar character, and reactions at various types of interfaces, such as solid/liquid, liquid/liquid, or even solid/solid interfaces [81].

The basic reaction are defined reactions between C-C triple (2.10), C-N triple bonds, and alkyl-/aryl-/sulfonyl azides (2.11).



The relevant outcomes of this reaction are tetrazoles, 1,2,3-triazoles, or 1,2-oxazoles (Scheme 1a–c, respectively). Besides the 1,3-dipolar cycloaddition reaction, classical Diels-Alder-type reactions (Scheme 1d) have been used greatly for the functionalization of polymeric materials and surfaces.[85] These reactions are located within a series of reactions named click reactions, thus leading to reactions characterized by high yields, high purity, simple reaction conditions, fast reaction times, and high selectivity. The 1,3-dipolar cycloaddition process has revealed among many reactions tested, as the method of selection to effect the requirements of ligating two molecules in a general, fast, and efficient process.

The central, purely thermal Huisgen process can be extremely accelerated by the addition of various metal species (Ru, Ni, Pt, Pd), but mostly by CuI species, within the reaction system. Click chemistry is widely recognized with copper-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes [86-89]. This reaction is usually quite slow in the absence of an appropriate catalyst for alkynes are poor 1,3-dipole acceptors but in the presence of copper(I), which can bind to terminal alkynes, cycloaddition reactions are quite accelerated and regioselective (see 2.12).



Among many reactions tested, the 1,3-dipolar cycloaddition process has emerged as the method of choice to effect the requirements of ligating two molecules in a general, fast, and efficient process [81, 82]. The gain of thermodynamic enthalpy of at least 20 kcal/mol [84], thus leading to reactions characterized by high yields (more than 95%), simple reaction conditions, fast reaction times, and high selectivity. Moreover, the copper-catalyzed azide–alkyne cycloaddition (CuAAC) can be performed in various solvents including water and in the presence of numerous other functional groups [88, 89].

Sharpless and co-workers published a paper in 2002, where the formation of 1,2,3-triazoles by the CuI-catalyzed Huisgen reaction between non-activated alkynes and alkyl/aryl azides was described [82].

A catalytic cycle based on a concerted mechanism via a Cu acetylide intermediate was proposed, which has been recently revised to include a binuclear reaction mechanism on the basis of several observations [88]. Acetylide ion has a strong nucleophilic character and the critical ‘invention’ of this process is the transformation of a purely thermal 1,3-dipolar cycloaddition process to a 1,3- dipolar cycloaddition process catalyzed by metal salts which are mostly CuI salts, but recently also Ru, Ni, Pd, and Pt salts. As a result, the reaction runs at ambient temperature, is nearly solvent insensitive, and with an extremely high tolerance of functional groups [81].

Click chemistry is not a strategy only for organic synthesis, today it has an enormous potential in materials science, polymer chemistry, biological applications comprising drug discovery and biolabeling [81, 84, 87-89].

2.5.1 Click Reactions on Linear Polymers

Since many known polymerization reactions in macromolecular chemistry require the absence of specific functional groups, there is considerable interest in the fixation of ligands onto polymers after a successful polymerization reaction has been conducted. This is most important when living polymerization mechanisms are used, since especially the highly sophisticated chemical mechanism and equilibria of (quasi-) living polymerization reactions are often highly substrate specific and, therefore, strongly affected by even small amounts of functional groups or the respective coupling agents required for affixation [86]. Another issue concerns the binding of large numbers of ligands onto polymers (i.e., sidechain-modified polymers) or dendrimers, which require highly efficient coupling reactions to this purpose as well. Further interest is directed towards the heterogeneous functionalization of polymers in solvent mixtures. Because of the limited solubility of many polymers, reactants for post-functionalization reactions cannot always be applied in homogeneous solution with the derivatized polymer. In these cases, highly efficient reactions acting in heterogeneous reaction media are desired. Thus it is not surprising that the Sharpless click reaction has been brought into the limelight recently because of its high efficiency, often reaching yields of >99% irrespective of the ligand structure, even in inhomogeneous reaction systems. The nature of the initial polymerization reaction (if known) as well as the structure of the initial,

starting polymers are given. Many of the controlled polymerization reactions derive from atom-transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), and quasi-living cationic polymerization, some are from nitroxide-mediated polymerization (NMP), radical addition- fragmentation transfer (RAFT), or polycondensation reactions. Only a few examples of living anionic polymerization and free radical polymerization reactions have been described up to now in junction with the click reaction. The catalytic systems used for the click-type reaction are also given, the vast majority with a focus on the copper-catalyzed azide/alkyne click reaction. In general it can be stated that only relatively lowmolecular- weight polymers ($M_n < 30\,000 \text{ g mol}^{-1}$) are used, where a good characterization of the final polymer (in relation to the initial functionalization) is possible. High molecular weights are obtained in only a few cases, where the click reactions are used to build-up polymers with the triazole moiety within the main chain [89].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

Ethanol ($\geq 99.5\%$, Aldrich), HCl (37%, Sigma-Aldrich), 1,4-dioxane ($\geq 99.0\%$, Sigma-Aldrich), chloroform ($\geq 99\%$, Sigma), acetic anhydride ($\geq 99\%$, Sigma-Aldrich), sodium hydroxide, ($\geq 97.0\%$, Sigma-Aldrich), 2,2'-bipyridyl ($\geq 99\%$, Aldrich), anhydrous magnesium sulfate (99%, Sigma-Aldrich), phenol ($\sim 99\%$, Sigma-Aldrich), paraformaldehyde (95%, Sigma-Aldrich), diethylether ($\geq 98\%$, Sigma-Aldrich), copper(I)bromide ($\geq 97.0\%$, Riedel-de Haën), methanol ($\sim 99\%$, Acros Organics), *p*-aminophenol (99%, Acros Organics), propargyl bromide (~ 80 volume % in toluene, Fluka,) were used as received.

3.2 Equipments

3.2.1 Fourier transform infra-red (FT-IR)

FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer..

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR spectra were recorded in DMSO- d_6 with $\text{Si}(\text{CH}_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

3.2.3 Differential Scanning Calorimetry (DSC)

Differential scanning Calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC with a heating rate of $10\text{ }^\circ\text{C min}$ under nitrogen flow.

3.2.4. Thermal Gravimetry Analysis (TGA)

Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of $10\text{ }^\circ\text{C min}$ under nitrogen flow.

3.2.5. Gel-permeation Chromatography (GPC)

Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters styragel column (HR series 2, 3, 5E) with THF as the eluant at a flow rate of 0,3 ml/min and a Waters 410 Differential Refractometer detector.

3.3 Preparation Methods

3.3.1 Preparation of *N*-(4-hydroxyphenyl)acetamide

A suspension of *p*-aminophenol (15.3 g, 140 mmol,) in water (50 ml) was taken into a 250 mL flask. Acetic anhydride (14.2 ml, 150 mmol,) was added to this solution. The mixture was heated at 60 °C with vigorous stirring until formation of clear solution. After about 20 minutes, the solution cooled to ambient temperature and the crude product was filtered and washed with deionized water. Crude solid was recrystallized from water to yield white crystals. (Yield: 80 %, mp: 169 °C)

3.3.2 Preparation of *N*-(4-(prop-2-ynyloxy)phenyl)acetamide

In a 250 mL flask, of *N*-(4-hydroxyphenyl)acetamide (8.1 g, 50 mmol) was dissolved in 100 mL of 0.4 N NaOH. The mixture was heated at 70 °C until a clear solution was formed. To this solution, tetrabutylammonium bromide (1.6 g, 5 mmol,) was added as a phase transfer catalyst. A solution of propargyl bromide (6.5 g 55, mmol) in 50 mL of toluene was added portion wise to the solution. The mixture was kept stirring at 70 °C for 24 h. Then it was cooled to afford solid. In addition, the toluene layer was separated and washed repeatedly with water. Evaporating toluene afforded extra solid. The crude product was dissolved in 1,4-dioxane and precipitated in water (ca. 200 mL) , then filtered, and washed repeatedly with copious amount of water. (Yield: 94 %)

3.3.3 Preparation of *p*-propargyloxy aniline

In a 250 ml flask, *N*-(4-(prop-2-ynyloxy)phenyl)acetamide (8,5 g, 45 mmol) was dissolved in ethyl alcohol (70 ml) and HCl (36%, 70 ml) was added. The mixture was stirred at 90 °C for 3 h. After neutralizing with aqueous sodium hydroxide, the solution was extracted with chloroform, and the organic layer was dried over anhydrous MgSO₄. Evaporation of chloroform gave a yellowish brown viscous

product. The crude product was purified by distillation under reduced pressure (bp: 95 °C, 10 mmHg) to afford a colorless and highly viscous liquid, which crystallized into yellowish white crystals after a while in the flask (Yield: 75 %, mp: 49-50 °C).

3.3.4 Preparation of 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine

In a 250 mL flask, paraformaldehyde (1.9 g, 63 mmol) in 100 mL of dioxane was cooled by ice bath. To this solution, *p*-propargyloxy aniline (34 mmol, 5 g) in 25 mL of dioxane was added portion-wise. The solution was kept stirring for 15 min below 5 °C. Thereafter, a solution of phenol (3.3 g, 35 mmol,) in 25 mL of dioxane was added. The solution was refluxed at 110 °C for 6 h. Removal of the solvent in a rotary evaporator gave a viscous residue that was dissolved in 100 mL of diethylether and washed several times with 1 N sodium hydroxide solution and finally with distilled water. Then, the ether solution was dried with anhydrous sodium sulfate, followed by evaporation of ether under vacuum to afford pale yellow viscous fluid. (Yield: 60 %)

3.3.5 Synthesis of Polystyrene-*co*-chloromethyl styrene PS-*co*-PCMS copolymers

P(S-*co*-CMS) containing 39.8 mol % chloromethyl groups was prepared via nitroxide-mediated radical polymerization (NMP) of styrene and chloromethylstyrene at 125 °C.

3.3.6 Synthesis of (PS-*co*-PMS-N₃) copolymer

PS-*co*-PCMS copolymers dissolved in N,N-dimethylformamid (DMF), NaN₃ (2 times excess to the mole of chloro group of each copolymers) was added. The resulting solution was allowed to stir at 25 °C overnight and precipitated into methanol/ water mixture (1/1 by volume).

3.3.7. Synthesis of polystyrene containing benzoxazine side groups (P(S-*co*-BS))

In a flask, PS-N₃ (0,32 g), 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine (**4**) (0.4 g 1.5 mmol), copper(I)bromide (0,5g, 3 mmol), 2,2'-bipyridine (0.9 g, 7 mmol), and dry THF (10 mL) were added. The flask was capped with a septum and purged with dry nitrogen for 10 minutes. The mixture was stirred overnight at ambient temperature. Copper salts were filtered and

functionalized polymer was precipitated in methanol (200 ml), filtered and dried under vacuum.

4. RESULTS and DISCUSSION

Thermally curable polystyrene was synthesized by using “Click Reaction” concept. This procedure involves the preparation of polymer and benzoxazine possessed with the appropriate click components. First, benzoxazine with acetylene terminal groups was synthesized. The other component, namely azide group functional polystyrene was synthesized independently. The two click reactive molecules were then combined to yield the desired polymers. The details of the procedure will be given below.

4.1 Synthesis of Benzoxazine Functionalized Polystyrene

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution method or by solventless method (ref). Using different types of phenols and amines, having different substitution groups attached, various types of benzoxazine monomer can be synthesized. Propargyl ether group, as a thermally reactive end-capping agent, to obtain novel propargyl containing benzoxazines. Polybenzoxazines derived from these monomers exhibited significantly improved thermal properties than the typical polybenzoxazines. Another aspect for this monomer is the suitability for click reactions due to its terminal acetylene group. Therefore, click-type synthetic procedures can easily be applied to incorporate benzoxazines to any azide containing polymer to yield thermoset with further thermal treatment. For this purpose, as it is outlined in Figure 4.1, *p*-propargyloxy aniline was obtained after three stages, and used to synthesize propargyl benzoxazine as a readily available monomer for click type reactions.

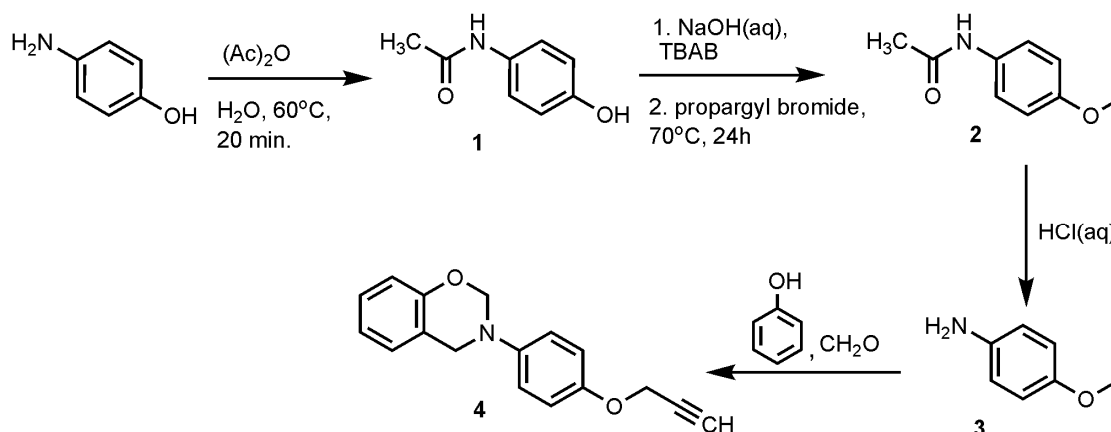


Figure 4.1 Synthesis of Propargyl Functional Benzoxazine

Benzoxazine functionalized polystyrenes were synthesized previously by two approaches. In the first method poly(*p*-vinylphenol) (VP) based benzoxazine was prepared from VP, formaline, and aniline. In this fashion, addition to the high cost of the VP, functionalization of all the phenolic parts of the VP was impossible. Because oxazine ring formation is a kind Mannich reaction with a subsequent ring closure and such reactions give approximately 60% yield which is low compared to click type reactions. In the second approach, a unique synthetic route was reported by Kiskan *et al.* for the synthesis of a macromonomer that benzoxazine ring was anchored to the polystyrene polymer. Atom Transfer Radical Polymerization (ATRP) and Suzuki coupling reactions were used to prepare amino functional polymers. These amino functional polymers then reacted with phenol and paraformaldehyde at 110⁰C for 2 h to produce benzoxazine functionalized polystyrene macromonomer.

Addition to the above mentioned approaches, benzoxazine functional polystyrene was synthesized with click chemistry (see Figure 4.2), which is modular, wide in scope and also it gives very high yields.

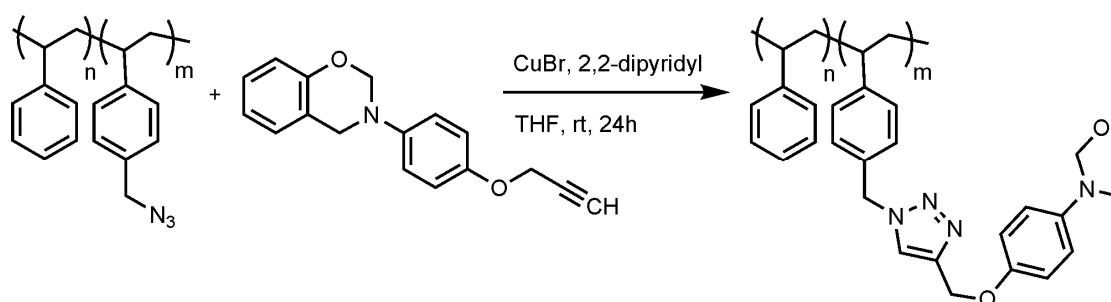


Figure 4.2 Benzoxazine Functional Polystyrene

4.2. Characterization of the Polymers

The structure of the benzoxazine functionalized polystyrene was analyzed by ^1H NMR and IR spectroscopies. It is important to recognize that click reactions achieve their required characteristics by having a high thermodynamic driving force usually it is greater than $20 \text{ kcal}\cdot\text{mol}^{-1}$. Such processes proceed rapidly to completion and also tend to be highly selective for a single product. As expected from the described above, the reaction of propargyl benzoxazine with azide containing polystyrene (PS-*co*-PMS- N_3) yielded approx. 100% transformation of azides to 1,2,3-triazoles.

The composition of copolymer was determined using ^1H NMR spectroscopy. (see Figure 4.3) The mole fractions of CMS and S were calculated from the ratio of the peak areas around 4.5 ppm, corresponding to two methylene protons of in the side chain of CMS to the total area between 6.3 and 7.4 ppm, which was attributed to the total aromatic protons. (PS-*co*-CMS) with $M_{n(\text{GPC})} = 11.290$ and 39.8 mol % chloromethyl groups was then quantitatively converted into polystyrene-azide (PS- N_3) in the presence of NaN_3/DMF at room temperature.

From the ^1H NMR spectrum of PS- N_3 shown in Figure 4.4.a, it was observed that while the signal at 4.5 ppm corresponding to $\text{CH}_2\text{-Cl}$ protons of the precursor (PS-*co*-CMS) completely disappeared, and a new signal appeared at 4.25 ppm due to CH_2 linked to azide groups.

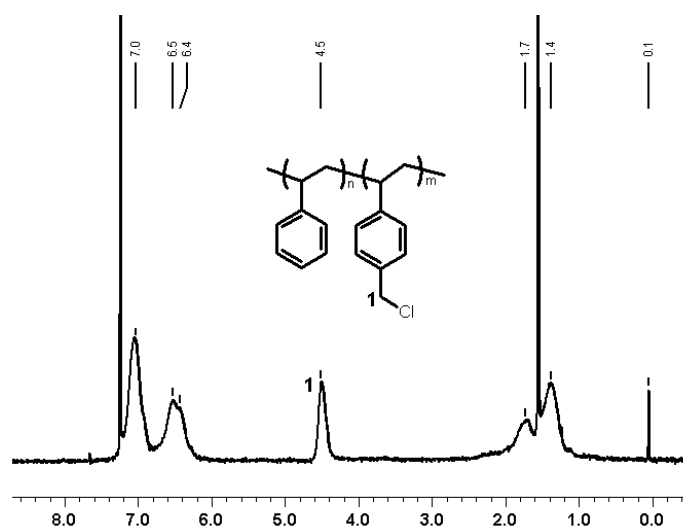


Figure 4. 3 ^1H -NMR spectrum of polystyrene-*co*-chloromethyl styrene (P(S-*co*-CMS))

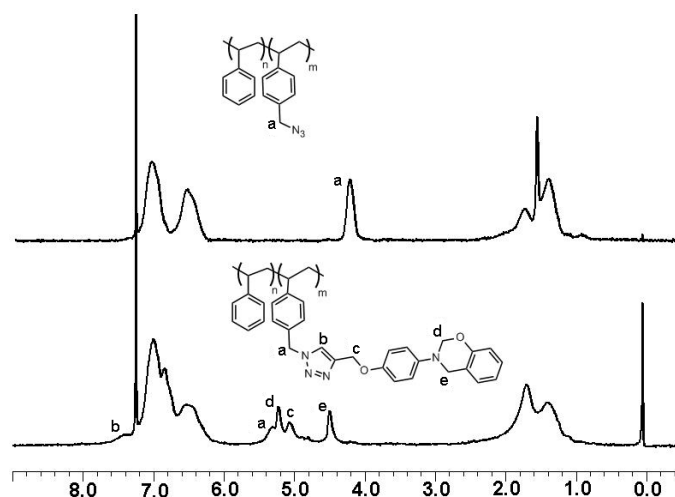


Figure 4.6. ^1H -NMR spectrum of PS-*co*-PMS- N_3 (a) and PS-*co*-PMS-benzoxazine (b)

At figure 4.6., this high yield transformation can be seen when compared the ^1H -NMR spectra of the PS-*co*-PMS- N_3 and the click reaction product. $-\text{CH}_2-\text{N}_3$ protons (a) of the PS-*co*-PMS- N_3 at 4.2 ppm at the spectrum (A) completely shifted to 7.4 ppm at the spectrum (B). Moreover, Ar-O- CH_2 -N (c) protons at 5.1 ppm coming from the ether part, N- $\text{CH}=\text{C}$ - (b) aromatic proton of triazole at 7.4 ppm appeared. Also, N- CH_2 -O (d) and N- CH_2 -Ar (e) protons of the oxazine ring can clearly be detected from the spectrum B, which shows the incorporation of benzoxazine to the polymer without having any ring opening of oxazine during click reaction.

The side group click reaction was efficient, as evidenced by near-quantitative functionalization. Moreover, general agreement between the molecular weight of the clicked polymer ($M_n = 13\,500$) and that of the precursor azido-polymer ($M_n = 7480$) obtained by GPC also confirms efficient coupling. The observed increase in the molecular weight is due to the additional benzoxazine moiety incorporated, It was also of interest that whether benzoxazine ring would be preserved during the click reaction.

FT-IR spectrums of PS-*co*-PMS- N_3 (a) and PS-*co*-PMS-benzoxazine (b) at figure 4.7. also indicate the consumption of $-\text{N}_3$ group of PS-*co*-PMS- N_3 with a quantitative yield.

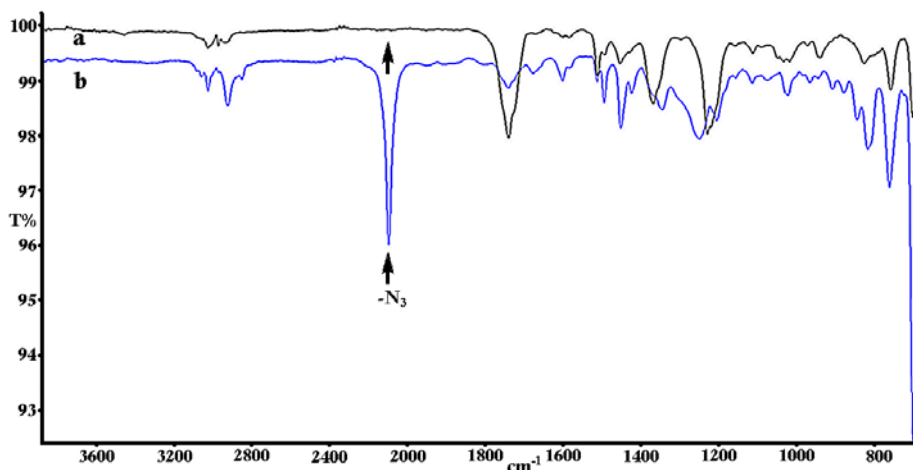


Figure 4.7. FT-IR spectrums of PS-co-PMS-N₃ (a) and PS-co-PMS-benzoxazine (b)

4.2.1 Thermally Activated Curing of Benzoxazine Functional Polystyrene

It is known that, benzoxazines undergo thermal ring opening polymerization at around 200-250°C with the release of heat and this exothermic reaction can be monitored by differential scanning calorimeter (DSC) (ref). In figure 4.8., the DSC thermogram of the click product exhibits two exotherms around 150 and 250°C and a T_g of the polystyrene segment at ca. 111°C at the first run. The exotherm at 250 °C belongs to the ring opening reaction of benzoxazine as usual, and the second exotherm at 150°C should belong to a transformation of 1,2,3-triazole, which is seen at the DSC thermograms of the model 1,2,3-triazoles. This transformation did not yield cleavage of the polystyrene segment from the polybenzoxazine matrix, because the resulting thermoset did not release any soluble product. Additionally, the second run did not show any T_g or exotherm as the result of the formation of thermoset and completion of ring opening reaction.

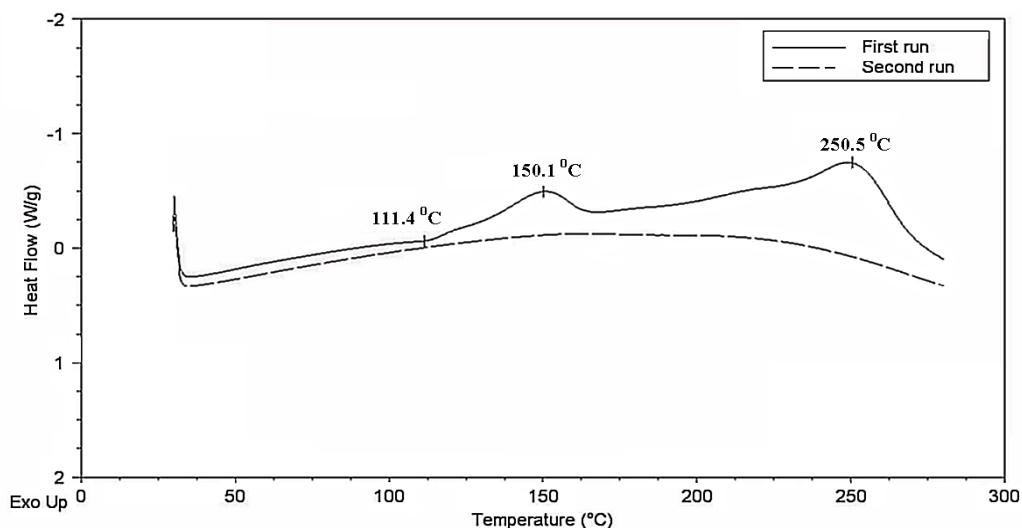


Figure 4.8. The DSC thermogram of the click product

4.2.2 Thermal Properties of Cured Polystyrene

As a high performance thermoset, polybenzoxazines have thermal stability with high char yield. In our case, incorporation of benzoxazines should provide this desired property. In figure 4.9, TGA curve and the derivative of this curve can be seen. Those data portray an initial weight loss around 220°C which is less than 5% may be ascribed to initial degradation of polystyrene segment and a main weight loss around 400°C which is assigned overall polystyrene degradation together with the amine evaporation that is the consequence of the Mannich base cleavage of the polybenzoxazine. Weight losses after 400°C can be attributed to the phenol decomposition and following thermal aromatization and crosslinking during degradation which finally leads to char formation (ref). From table 1, it is evident that cured click product exhibit better thermal properties than polystyrene itself. Besides, it exhibits comparable char yield and 5%, 10% weight losses to many polybenzoxazines. For example, a polybenzoxazine which is coded as PB-a (polybenzoxazine derived from the monomer synthesized from bisphenol-A, aniline and formaldehyde) have 5, 10% weight losses at around 310 and 327°C with a 32% char yield at 800°C (ref).

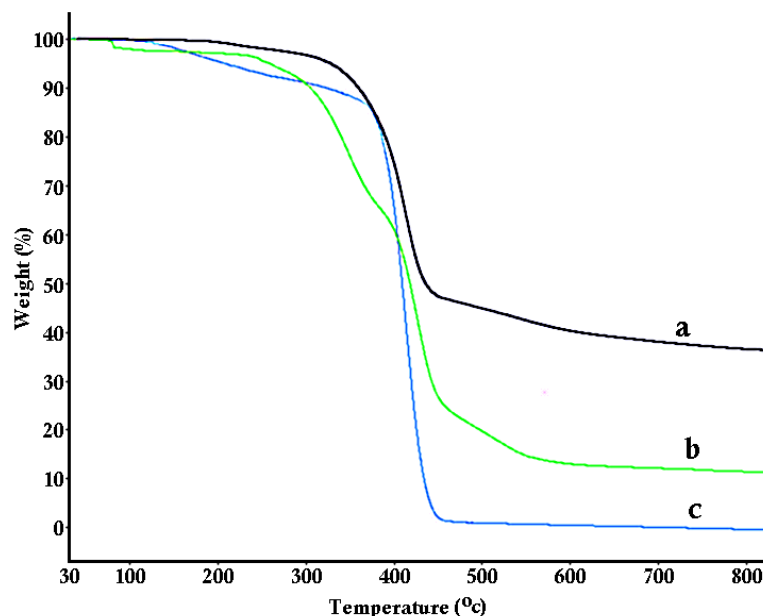


Figure 4.9. The TGA curves of the click product

Table 4.1 TGA analysis of cured benzoxazine-Pst

| | $T_{5\%}^a$ (°C) | $T_{10\%}^b$ (°C) | T_{\max}^c (°C) | Y_c^d at 800°C (%) |
|-----------------|---------------------|----------------------|----------------------|-------------------------|
| benzoxazine-Pst | 326.6 | 357.7 | 413.8 | 36.5 |

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

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

^c T_{\max} : The temperature for which the weight loss is maximum

^d Y_c : Char yields

4.3. Conclusion

In conclusion, we report the usage of click reaction to obtain side chain benzoxazine containing polystyrene as curable polymer with superior thermal properties than polystyrene itself and the previous benzoxazine containing polystyrenes. The procedure itself is simple. The curability of a well-known and commercial polymer makes this concept particularly useful for practical applications and opens a new pathway for the other commodity polymers. The curing process requires no additives and polymers are simply heated to give cross-linked networks. In addition to the curability, the benzoxazine functionality also brings an enhanced thermal stability.

In conclusion, we report the usage of click reaction to obtain side chain benzoxazine containing polystyrene as curable polymer with superior thermal properties than polystyrene itself and the previous benzoxazine containing polystyrenes. Further studies are now in progress to use 1,3-dipolar cycloaddition reaction for benzoxazine chemistry.

REFERENCES

- [1] **Pascault, J. P.; Sautereau, H.; Verdu, J.; Williams, R. J. J.** 1976. Thermosetting Polymers, Clemson, South Carolina, *Chapter 2*
- [2] **Bikales, N. M.**, 1982. Basic concepts and definitions, *Polymers*, pp. 3730-3732.
- [3] **Kaufman, H. S.**, 1982. Classification by use and properties, *Polymers*, pp. 3739-3743.
- [4] **Hall, C.**, 1989. Polymer Materials: An Introduction for Technologists and Scientists, 2nd ed., Wiley, New York,
- [5] **Seymour, R. B. Carraher, C. E.**, 1988. Polymer Chemistry, 2nd ed., Marcel Dekker, New York,
- [6] **Thomas, E. L. (ed.)**, 1989. Structure and Properties of Polymers, vol. 12 in [1.12]
- [7] **Meckel, W., Goyert, W., Wieder, W., Legge, N. R.; Holden, G. and Schroeder, H. E.**, 1987. Thermoplastic Elastomers, *New York: Carl Hanser Verlag*. Ch. 2.
- [8] **McGraw-Hill** 1994. Modern Plastics Encyclopedia *Handbook*;: New York,
- [9] **Dusek, K. F.L, Lunak, S., Mach, M., Dukova, D. In C. K. Riew and J. K. Gillham, Eds.**,1984.Rubber-Modified Thermoset Resins, *Washington, DC: ACS*
- [10] **Solomon, D.H.**,. et al.,1986. *US Pat* 4,.
- [11] **Solomon, D.H.**, et al. 1985. Polymerization Processes, *Eur Patent Appl* 135.
- [12] **Moad, G. and Rizzardo, E.**, 1995. Alkoxyamine-initiated living radical polymerization: Factors affecting alkoxyamine homolysis rates, *Macromolecules*, **28**, 8722
- [13] **Georges, M.K.**, et al. 1993. Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process, *Macromolecules*, **26**, 2987,
- [14] **Fischer, H.**, 1997.The persistent radical effect in "living" radical polymerization, *Macromolecules*, **30**, 5666,

- [15] **Hawker, C.J.**, et al. 2001. New polymer synthesis by nitroxide mediated living radical polymerizations, *Chem Rev*, **101**, 3661,
- [16] **Detrembleur, C.**, et al. 2003. Controlled radical polymerization of alkyl methacrylates in the presence of NO/NO₂ mixtures, *Acs Sym Ser*, **854**, 496.
- [17] **Brydson, J.A.**, 1999. *Plastics Materials*, Butterworth heinemann, oxford
- [18] **Davenport, N. E., Hunbbard, L. W., and Pettit, M. R.**, 1959. *Brit Plastics*, **32**, 549
- [19] **Skinner, S. J., Baxter, S., and Grey, P. J.**, 1964. *Trans. Plastics Inst.*, **32**, 180
- [20] **Ghosh, N.N., Kiskan, B. and Yagci, Y.**, 2007., Polybenzoxazines-New high performance thermosetting resins:Synthesis and properties, *Prog. Polym. Sci.*, **10**, 1016
- [21] **Holly, F.W. and Cope, A.C.**, 1944. Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine. *J. Am. Chem. Soc.***66**,1875-1879.
- [22] **Liu, J. Ishida, H. and Salamone, J.C.**, (Ed) 1996. A New Class of Phenolic Resins with Ring-Opening Polymerization. *The Polymeric Materials Encyclopedia. Florida: CRC Press*, 484-494.
- [23] **Nair, C.P.R.**, 2004. Advances in addition-cure phenolic resins. *Prog. Polym. Sci.* **29**, 401-498.
- [24] **Burke W.J.**, 1949, 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of p-Substituted Phenols with N,N-Dimethylolamines. *J. Am. Chem. Soc.*, **71**, 609-612.
- [25] **Burke, W.J., Bishop, J.L., Glennie, E.L.M., Bauer, W.N.**, 1965. A New Aminoalkylation Reaction. Condensation of Phenols with Dihydro-1,3-aroazines. *J. Org. Chem.*,**30**, 3423-3427.
- [26] **Kimura, H., Matsumoto, A., Hasegawa, K., Ohtsuka, K., Fukuda, A.**, 1998. Epoxy resin cured by bisphenol A based benzoxazine. *J. Appl. Polym. Sci.*, **68**, 1903-1910.

- [27] **Ning, X. and Ishida, H. S.**, 1994. Phenolic materials via ring-opening polymerization of benzoxazines – effect of molecular-structure on mechanical and dynamic-mechanical properties, *J. Polym. Sci., Part B: Polym. Phys.*, **32**, 921-927.
- [28] **Ning, X. and Ishida, H.** 1994. Phenolic materials via ring-opening polymerization synthesis and characterization of bisphenol A based benzoxazines and their polymers, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 1121-1129.
- [29] **Burke, W.J., Kolbezen, M.J., Stephens, C.W.**, 1952. Condensation of Naphthols with Formaldehyde and Primary Amines. *J. Am. Chem. Soc.* **74**, 3601-3605.
- [30] **Burke, W.J., Glennie, E.L.M. and Weatherbee, C.**, 1964. Condensation of Halophenols with Formaldehyde and Primary Amines. *J. Org. Chem.*, **29**, 909-912.
- [31] **McDonagh, A.F., Smith, H.E.**, 1968. Ring-chain tautomerism of derivatives of o-hydroxybenzylamine with aldehydes and ketones. *J. Org. Chem.* **33** 1-8.
- [32] **Ishida, H.** US Patent 5, 543, 516, assigned to Edison Polymer Innovation Corporation
- [33] **Liu, J.**, 1995., Characterization, Reaction Mechanism and Kinetics of 3,4-dihydro-2H-1,3-benzoxazine and Its Polymers. Thesis, Case *Ph. D. Thesis* Western Reserve University, Cleveland OH. May
- [34] **Riess, G., Schwob, M., Guth, G., Roche, M., Lande, B., In: Culbertson, B.M. and McGrath (eds)** 1985 *Advances in Polymer Synthesis*, New York: Plenum,.
- [35] **Hemvichian, K., Laobuthee, A., Chirachanchai, S., Ishida, H.** 2002. Thermal decomposition processes in polybenzoxazine model dimers investigated by TGA-FTIR and GC-MS. *Polym. Degrad. Stab.*, **76**, 1-15.
- [36] **Wang, Y.X. and Ishida, H.** 2002. Development of low-viscosity benzoxazine resins and their polymers. *J. Appl. Polym. Sci.*, **86**, 2953-2966.

- [37] **Kimura, H., Taguchi, S. and Matsumoto, A.**, 2001. Studies on new type of phenolic resin (IX) curing reaction of bisphenol A-based benzoxazine with bisoxazoline and the properties of the cured resin. II. Cure reactivity of benzoxazine. *J. Appl. Polym. Sci.*, **79**, 2331-2339.
- [38] **Ishida, H. and Rodriguez, Y.**, 1995., Curing Kinetics of A New Benzoxazine-Based Phenolic Resin By Differential Scanning Calorimetry, *Polymer*, **36**, 3151–3158.
- [39] **Brunovska, Z., Liu, J.P., Ishida, H.**, 1999. 1,3,5-triphenylhexahydro-1,3,5-triazine - active intermediate and precursor in the novel synthesis of benzoxazine monomers and oligomers. *Macromol. Chem. Phys.*, **200**, 1745-1752.
- [40] **Wirasate, S., Dhumrongvaraporn, S., Allen, D.J. and Ishida, H.**, 1998. Molecular origin of unusual physical and mechanical properties in novel phenolic materials based on benzoxazine chemistry. *J. Appl. Polym. Sci.*, **70**, 1299-1306.
- [41] **Shen, S.B. and Ishida, H.**, 1999. Dynamic mechanical and thermal characterization of high-performance polybenzoxazines. *J. Polym. Sci., Part B: Polym. Phys.*, **37**, 3257-3268.
- [42] **Ishida, H. and Sanders, D.P.**, 2000. Improved thermal and mechanical properties of polybenzoxazines based on alkyl-substituted aromatic amines. *J. Polym. Sci., Part B: Polym. Phys.*, **38**, 3289-3301.
- [43] **Kimura, H., Matsumoto, A., Sugito, H., Hasegawa, K., Ohtsuka, K. and Fukuda, A.** 2001. New thermosetting resin from poly(p-vinylphenol) based benzoxazine and epoxy resin., *J. Appl. Polym. Sci.*, **79**, 555-565.
- [44] **Kiskan, B., Colak, D., Muftuoglu, A. E., Cianga, I. and Yagci, Y.**, 2005. Synthesis and characterization of thermally curable benzoxazine-functionalized polystyrene macromonomers., *Macromol. Rapid Commun.*, **26**, 819-824.
- [45] **Ergin, M., Kiskan, B., Gacal, B. and Yagci, Y.**, 2007. Thermally Curable Polystyrene via Click Chemistry. *Macromolecules*, **40**, 4724-4727

- [46] **Chernykh, A., Liu, J.P. and Ishida, H.**, 2006. Synthesis and properties of a new crosslinkable polymer containing benzoxazine moiety in the main chain., *Polymer*, **47**, 7664-7669.
- [47] **Takeichi, T., Kano, T. and Agag, T.**, 2005. Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets. *Polymer*, **46**, 12172-12180.
- [48] **Kiskan, B., Yagci, Y. and Sahmetlioglu, E. L. T.**, 2007. Preparation of Conductive Polybenzoxazines by Oxidative Polymerization. *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 999-1006.
- [49] **Wang, Y. X. and Ishida, H.**, 1999. Cationic ring-opening polymerization of benzoxazines, *Polymer*, **40**, 4563-4570.
- [50] **Wang, Y.X., Ishida, H.**, 2000. Synthesis and properties of new thermoplastic polymers from substituted 3,4-dihydro-2H-1,3-benzoxazines. *Macromolecules*, **33**, 2839-2847.
- [51] **Schreiber, H.**, German Patent 2 255 504.
- [52] **Ishida, H. and Allen, D.J.**, 1995. Rheological Characterization during Cure of near-Zero Shrinkage Polybenzoxazines. *Abstracts of Papers of the American Chemical Society*, **210**, 272-PMSE.
- [53] **Agag, T. and Takeichi, T.** 2003. Synthesis and characterization of novel benzoxazine monomers containing allyl groups and their high performance thermosets. *Macromolecules*, **36**, 6010-6017.
- [54] **Xiang, H., Ling, H., Wang, J., Song, L. and Gu, Y.**, 2005. A novel high performance RTM resin based on benzoxazine., *Polym. Compos.*, **26**, 563-571.
- [55] **Lee, Y.H., Allen, D.J. and Ishida, H.**, 2006. Effect of rubber reactivity on the morphology of polybenzoxazine blends investigated by atomic force microscopy and dynamic mechanical analysis. *J. Appl. Polym. Sci.*, **100**, 2443-2454.
- [56] **Russell, V.M., Koenig, J.L., Low, H.Y. and Ishida, H.**, 1998. Study of the characterization and curing of benzoxazines using C-13 solid-state nuclear magnetic resonance. *J. Appl. Polym. Sci.* **70**, 1413-1425.
- [57] **Russell, V.M., Koenig, J.L., Low, H.Y. and Ishida, H.**, 1998. Study of the characterization and curing of a phenyl benzoxazine using N-15 solid-

- state nuclear magnetic resonance spectroscopy. *J. Appl. Polym. Sci.*, **70**, 1401-1411.
- [58] **Su, Y.C., Yei, D.R. and Chang, F.C.**, 2005. The kinetics of B-a and P-a type copolybenzoxazine via the ring opening process. *J. Appl. Polym. Sci.*, **95**, 730-737.
- [59] **Yu, D.S., Chen, H., Shi, Z.X. and Xu, R.W.**, 2002. Curing kinetics of benzoxazine resin by torsional braid analysis, *Polymer* **43**, 3163-3168.
- [60] **Ishida, H. and Allen, D.J.**, 2001. Gelation behavior of near-zero shrinkage polybenzoxazines, *J. Appl. Polym. Sci.*, **79**, 406-417.
- [61] **Zhang, X.Q., Potter, A.C. and Solomon, D.H.**, 1998. The chemistry of novolac resins .5. Reactions of benzoxazine intermediates, *Polymer*, **39**, 399-404.
- [62] **Zhang, X.Q. and Solomon, D.H.**, 1998, The chemistry of novolac resins .6. Reactions between benzoxazine intermediates and model phenols., *Polymer*, **39**, 405-412.
- [63] **Douglas, W.E. and Overend, A.S.**, 1991. Curing Reactions in Acetylene Terminated Resins .1. Uncatalyzed Cure of Arylpropargyl Ether Terminated Monomers, *Eur. Polym. J.*, **27**, 1279-1287.
- [64] **Agag, T. and Takeichi, T.**, 2001. Novel benzoxazine monomers containing p-phenyl propargyl ether: Polymerization of monomers and properties of polybenzoxazines, *Macromolecules*, **34**, 7257-7263.
- [65] **Ishida, H. and Rodriguez, Y.**, 1995. *J Polym Sci Polym Chem Ed.*, **58**, 1751.
- [66] **Ishida, H.**, 1998. Versatile Phenolic stands up to the heat, in *Modern Plastics International*, **6**, pp. 87-90., (Kaplan WA, Compiler).
- [67] **Ishida, H. and Allen, D.**, 1996., Physical and mechanical characterization of near-zero shrinkage polybenzoxazines, *J. Polym. Sci-B*, **34**, 1019-30.
- [68] **Shen, S. B., and Ishida, H.**, 1996., Development and characterization of high-performance polybenzoxazine composites *Polym. Comp.*, **17**, 710-719.
- [69] **Ishida, H. and Low, H. Y.**, 1997., A Study on the Volumetric Expansion of Benzoxazine-Based Phenolic Resin, *Macromolecules*, **30**, 1099-106.

- [70] **Cid, J. A., Wang, Y. X. and Ishida, H.** 1999. Cationic polymerization of benzoxazine monomers by boron trifluoride complex, *Polym. Polym. Compos.*, **7**, 409-420.
- [71] **Espinosa, M. A., Cadiz, V. and Galia, M.** 2004. Development of novel flame-retardant thermosets based on benzoxazine-phenolic resins and a glycidyl phosphinate, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 279-289.
- [72] **Rimdusit, S. Ishida, H.,** 2000. Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins, *Polymer*, **41**, 7941-7949.
- [73] **Rimdusit, S. Ishida, H.,** 2000. Synergism and multiple mechanical relaxations observed in ternary systems based on benzoxazine, epoxy, and phenolic resins, *J. Polym. Sci. Part B: Polym. Phys.*, **38**, 1687-1698.
- [74] **Morel, E., Bellenger, V., Bocquet, M. and Verdu, J.,** 1989. Structure-properties relationships for densely cross-linked epoxide amine systems based on epoxide or amine mixtures.3. elastic properties, *J. Mater. Sci.*, **24**, 69-75.
- [75] **Archibald, T. G., Malik, A. A. and Baum, K.,** 1991. Thermally stable acetylenic adamantane polymers, *Macromolecules*, **24**, 5261-5265.
- [76] **Bellenger, V., Verdu, J. and Morel, E.,**1989. Structure-properties relationships for densely cross-linked epoxide amine systems based on epoxide or amine mixtures.2. water-absorption and diffusion, *J. Mater. Sci.*, **24**, 63-68.
- [77] **Kirchhoff, R. A., Bruza, K., Carriere, C. and Rondan, N.,** 1992. Benzocyclobutenes in polymer synthesis, *Makromol. Chem., Macromol. Symp.*, **54-5**, 531-534.
- [78] **Allen, N. S., Marin, M. C., Edge, M., Davies, D. W., Garrett, J. and Jones, F.** 2001. Photoinduced chemical crosslinking activity and photo-oxidative stability of amine acrylates: photochemical and spectroscopic study, *Polym. Degrad. Stab.*, **73**, 119-139.

- [79] **Harth, E., Horn, B. V., Lee, V. Y., Germack, D. S., Gonzales, C. P., Miller,**
A facile approach to architecturally defined nanoparticles via intramolecular chain collapse., *J. Am. Chem. Soc.*, **124**, 8653-8660.
- [80] **Demko, Z. P. and Sharpless, K. B.** 2002. A click chemistry approach to tetrazoles by Huisgen 1,3-dipolar cycloaddition: Synthesis of 5-sulfonyl tetrazoles from azides and sulfonyl cyanides., *Angew. Chem., Int. Ed.*, **41**, 2110-2113.
- [81] **Kolb, H. C., Finn, M. G. and Sharpless, K. B.,** 2001. Click chemistry: Diverse chemical function from a few good reactions., *Angew. Chem., Int. Ed.*, **40**, 2004-2021.
- [82] **Rodionov, V., Fokin, V. and Finn, M. G.,** 2005. Mechanism of the ligand-free Cu-I-catalyzed azide-alkyne cycloaddition reaction., *Angew. Chem., Int. Ed.*, **44**, 2210 -2215.
- [83] **Helms, B., Mynar, J. L., Hawker, C. J. and Frechet, J. M. J. J.,** 2004. Dendronized linear polymers via "click chemistry"., *Am.Chem. Soc.*, **126**, 15020-15021.
- [84] **Johnson, J. A., Lewis, D. R., Diaz, D. D., Finn, M. G., Koberstein, J. T. and Turro, N. J.** 2006. Synthesis of degradable model networks via ATRP and click chemistry., *J. Am. Chem. Soc.*, **128**, 6564-6565.
- [85] **Parrish, B., Breitenkamp, R. B. and Emrick, T.,** 2005. PEG- and peptide-grafted aliphatic polyesters by click chemistry., *J. Am. Chem. Soc.*, **127**, 7404-7410.
- [86] **Binder, W. H. and Sachsenhofer, R.,** 2007. 'Click' chemistry in polymer and materials science, *Macromol. Rapid Commun.*, **28**, 15-54.
- [87] **Lutz, J.-F.,** 2007. 1,3-dipolar cycloadditions of azides and alkynes: A universal ligation tool in polymer and materials science., *Angew. Chem., Int. Ed.*, **46**, 1018-1025.
- [88] **Molengraft, A.,** 2005 'Click' chemistry a new approach to familiar reactions
- [89] **Kolb H.C., Finn, M. G. And Sharpless K.B.,** 2001. Click chemistry diverse chemical function from a few good reactions, *Angew. Chem. Int. Ed.*, **40**, 2004-2021

AUTOBIOGRAPHY

Mihrace Ergin was born in Malatya on December 11, 1983. She was graduated from Bahçelievler High School. She was admitted to Trakya University, Department of Chemistry in 2001. She was registered as M.Sc. student to the Polymer Science and Technology Program at Istanbul Technical University leading to a degree of Master of Science under the guidance of Professor. Dr. Yusuf Yagci, in 2006.

Publications

Thermally Curable Polystyrene via Click Chemistry.

Ergin, M., Kiskan, B., Gacal, B. and Yagci, Y., 2007. *Macromolecules*, 40, 4724-4727

Proceedings

[1] Thermally Curable Polystyrene via Click Chemistry

Ergin, M., Kiskan, B., Gacal, B. and Yagci, Y.,(Poster), The 21th National Chemistry Symposia İnönü University, Malatya, Turkey, (2007)

[2] Thermally Curable Polystyrene via Click Chemistry

Ergin, M., Kiskan, B., Gacal, B. and Yagci, Y.,(Poster), The 7th International Conference on Advanced Polymers via Macromolecular Engineering, Miami Beach, USA, (2007)