İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THERMALLY CURABLE BENZOXAZINE–SILOXANE COPOLYMERS

M.Sc. Thesis by
Dilek SUREKA

Department : Chemistry

Programme : Chemistry

June 2009

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TERMAL OLARAK KÜRLENEBİLEN BENZOKSAZİN-SİLOKSAN KOPOLİMERLERİ

YÜKSEK LİSANS TEZİ
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FOREWORD

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ABBREVIATIONS

PE : Polyethylene
PP : Polypropylene
PTFE : Polytetrafluroethylene
PS : Polystyrene
PVC : Polyvinylchloride
PMMA : Polymethylmethacrylate
KOH : Possium hydroxide
Bisphenol–A : 4, 4'- isopropylidenediphenol
'H-NMR : Proton Nuclear Magnetic Resonance Spectroscopy
FT–IR : Fourier Transform Infrared Resonance
B–a : 6,6'-propane-2,2-diyl bis 3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine
Oligo-B–a : 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) oligomer
DSC : Differential Scanning Colorimetry
B–m : Benzoxazine monomer
Th : Thiophene
DMA : Dynamic Mechanic analyzer
Tg : Glass Transition Temperature
PBZ : Polybenzoxazine
ROP : Ring Opening Polymerization
RLi : Alkyl -Lityum
B – ala : 6,6' – (propane-2,2'-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3]oxazine
MeOH : Methonol
D_5 : Decamethylpentacyclosiloxan
TMDS : Tetramethyldisiloxane
PBTMDS : : Polybenzoxazinetetramethyldisiloxane
Mn : The number average molecular weight
Pt : Platinium
ppm : parts per million
UV : Ultra-violet

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SUMMARY

Benzoxazines are converted into thermoset polybenzoxazines by the ring opening reaction. Polybenzoxazines are considerable phenolic resin because of the high performance properties that nearly zero-volumetric change upon curing, low water absorption, for some benzoxazine based materials Tg much higher than cure temperature, high char yield, no strong acid catalysts required the curing and release of no products during the curing. But also some short-comings are observed that they are brittle and hard to be film, high glass transition temperature. They are prefered to other phenolic resins but features aren't enough to use them in industry. Because these makes the polymer less available for tailoring the properties of the cured materials for a wide range of applications. In this study, firstly occured the benzoxazine-siloxane oligomer and then reacted with decamethlycyclopentasiloxane to be formed benzoxazine-siloxane copolymer. Thus,the new material have lower Tg that is provided thermally curable and penetrable derivatives of benzoxazine.

Experimantally, cooligomers syntesized by the reaction of allylbenzoxazine with 1,1,3,3-tetramethyldisiloxane in the presence of Pt catalyst. Oligomer is the only product in this condition. This reaction is called as hydrosilation. The way of making the polymer more flexible and have them more molecular weight copolymer is the reaction of the cooligomer with decametyldisiloxane in the presence of tetramethylamoniumhydroxide catalyst by the ring opening reaction of D_5. These polymers are convenient to form film that consist of benzoxazine units which create crosslinked network and impart the polybenzoxazine porperties whereas the siloxane units form the soft segments along the backbone. Thermal crosslinking nature provides the possibility to prepare high performance materials. The enhanced thermal stability was attributed to presence of the siloxane units. These features give an oppotunity to form molecular flexibility, tough and thermal stability of cross-linked polybenzoxazine films**.** The structure of the end product is characterized by H-NMR, GPC, FT-IR, DSC, TGA.

TERMAL OLARAK KÜRLENEBİLEN BENZOKSAZİN-SİLOKSAN KOPOLİMERLERİ

ÖZET

Benzoksazinler ısıtıldıklarında halka açılma tepkimesiyle termoset polibenzoksazinlere dönüşürler. Polibenzoksazin ısıya karşı dayanıklılık, tutuşmazlık, su tutmama gibi özellikleriyle yüksek performanslı tercih edilen bir fenolik reçinedir. Ancak diğer fenolik polimerlere karşı bu üstün özelliklerinin yanı sıra bazı dezavantajlarda gözlenmiştir. Bunlar polibenzoksazinlerin kırılgan yapıda olmaları, film haline getirilmedek zorluklar, yüksek camsı geçiş sıcaklığı (Tg) göstermeleri olarak sayılır. Dolayısıyla bu durum işlenmesi kolay olmayan yapılar olması sonucunu getirir. Diğer fenolik polimerlere göre tercih edilir olmalarına rağmen endüstri kullanımı için yeterli değillerdir. Bu çalışmada, önce benzoksazin siloksan kooligomeri oluşturulmuştur. Daha sonra bu oligomer dekametilsiklopentoksiloksan ile siloksan kopolimer haline dönüştürülmüştür. Böylece düşük Tg ye sahip siloksanların kolay işlenme özelliği gösteren benzoksazin polimer türevi elde edilmiştir.
Deneysel olarak, kooligomerler allilbenzoksazinin Pt(0) katalizör eşliğinde 1,1,3,3-tetrametildisiloksan tepkimesiyle sentezlenmiştir. Bu tepkime koşullarında oligomerler oluşabilecek tek üründür. Bu reaksiyon hidrosilasyon olarak anılır. Elde edilen oligomerlerden daha esnek ve yüksek molekül ağırlıklığına sahip polimerler elde etmek için, polisiloksan-benzoksazin kopolimerleri, tetrametilamonyum hidroksit katalizörü varlığında dekametilsiklopentoksiloksanın halka açılma tepkimesiyle yoluyla reaksiyona sokulur. Elde edilen ürünün siloksan bölümü yapıya esneklik katarken benzoksazinin termal olarak çapraz bağlanabilme özelliği sayesinde termal olarak stabil film yapımını gerçekleştirir. Böylelikle yüksek performanslı metaryaller elde edilmiştir. Benzoksazin-siloksan kopolimerinin siloksan kısmı moleküler esnekliği sağlarken, benzoksazin kısmı termal kararlığı sağlayarak kürlenme ile film oluşturabilmeyi olanak sağlamıştır. Yapı ^{1}H-NMR, FT-IR, GPC, DSC, TGA enstrümantal cihazları ile karakterize edilmiştir.

1. INTRODUCTION

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 wide range of application, as coating, adhesives, engineering and structural materials, for packing and for clothing to name a few. The advances in science and technology made in recent decades owe much to development of polymer science. A key feature of the success and versality of these materials is that it is possible to build in properties by careful design of the organic molecules from which the chains are build up. 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.

One of the existing methods of improving polymer properties is the copolymerization for effecting systematic changes in polymer properties. The incorparation of two different monomers, having diverse physical and chemical properties in the same molecule in varying proportions leads to the formation of materials with great sciencific and commercial importance.

Conventional polymers do not offer the properties associated with thermoset polymers are limited. Thermoset polymers are normally synthesized using step-growth polymerization methods where the chain growth and cross-linking processes arise form the same type of chemical reaction. However, thermoset polymers are not easy processable and their manufacturing is not cost-effective, 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. One of the way to make the linear polymer cured is thermal methods. Thermal methods for the formulation of thermosetting materials usually involve Diels-Alder reactions which may suffer from reversibility.

Polybenzoxazines are class of phenolic polymers formed by thermal ring-opening reaction of 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 for the synthesis of benzoxazine resins. As a result of ring opening polymerization, polybenzoxazines overcome many short-comings associated with tradinational phenolic resins such as releasing condensation by-products and using strong acids as a catalysts, while retaining good thermal properties and flame retardance of phenolics. Benzoxazine resins undergo nearly zero volumetric change and 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.

The other part of the copolymer may have been polysiloxane which is known for their thermal stability and extreme flexibility. The incorparation of siloxane groups into polymer in an alternative way to further improve the properties. The high bond strength demostrated by Si-O bond accounts for the high thermal and oxidative stability of siloxanes and is a result of partial ionic character of the Si-O bond.

The benzoxazine groups act as a thermal cross-linker and while this polymer with the siloxane groups may be accountable for the flexibility of this material. Thus, thermally cross-linked non-brittle polybenzoxazine films can be prepared.

In this study, firstly a novel pathway for preparing oligosiloxanes with benzoxazine moieties in the main chain was studied. This concept relies on Pt-catalyzed hydrosilylation reaction between tetradimethylsiloxane and diallylbisbenzoxazine.Then tetrametylammonium hydroxide is used as a catalyst with the reaction of the oligomers and decametylcyclopentasiloxane. Attaching more siloxane groups with the ring openning reaction of decametylcyclopentasiloxane, the copolymer has high molecular weight and wide range of molecular design flexibility. Transparent flexible thin films were easily obtained by the solvent casting method. As it will also be shown that prepare the thermoplastic elastomers that can be thermally cured in the absence of any catalyst leading to materials with improved properties.

2. THEORICAL PART

2.1 The Methodology for Synthesis of Polymers

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 for high-purity monomers and solvents, reactive initiators and pure conditions have dramatically limited the industrial application of many techniques.[1]

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 polymerizations, are distinguishable.[2]

2.1.1 Step-growth polymerization

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.

2.1.2 Chain-growth polymerization

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 [3] :

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 [4-7] :

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.

2.2 Classification of Polymers

2.2.1 Thermoplastic polymers

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 [8]. 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 ($CH_2=CH_2$) as a monomer (2.1)

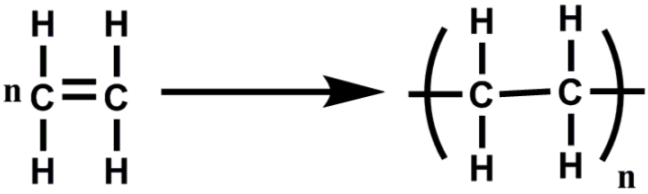


Figure 2. 1 : Polymerization of ethylene

In this case the group $–[–CH_2–CH_2–]–$ is the constitutional unit, n is the number of monomers in the polymer (*degree of polymerization).* 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 R may be hydrogen (as in

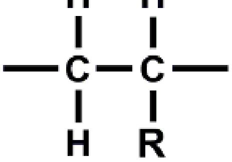


Figure 2. 2 : The repeat unit of polyethylene

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 [9]

Thermoplastic	Composition	Uses
Polyethylene, PE	Partly crystalline	Tubing, Film, Bottles, Cups, Electrical insulation, Packaging
Polypropylene, PP	Partly crystalline	Same uses as PE, but lighter, stiffer, more resistant to sunlight.
Polytetrafluroethylene, PTFE	Partly crystalline	Teflon, Good high-temperature polymer with very low friction and adhesion characteristics. Non-stick saucepans, bearing, seals.
Polystyrene, PS	Amorphous	Cheap mouldeal objects, Toughened with butadiene to make high-impact polystyrene (HIPS). Foamed with CO2 to make common packaging.
Polyvinylchloride, PVC	Amorphous	Architectural uses(window frames, etc.). Gramophone records. Plasticized to make artificial leather, hoses, clothing
Polymethylmethacrylate, PMMA	Amorphous	Perspex, Lucite, transparent sheet and mouldings. Aircraft windows, laminated windscreens.
Nylon 66	Partly crystalline when drawn.	Textiles, rope, mouldings.

2.2.2 Thermoset polymers

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 polymerization, reacting two components (a resin and a hardener) either at room temperature or on heating. In this case different kinds of molecules are joined by a chemical reaction that releases a by-product, a small molecule such as water [10]. 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 materialsin fibre reinforced polymer composites.

Table 2. 2 : Composition and application of some thermosets [9]

Thermoset	Composition	Uses
Epoxy	Amorphous	Fiberglass, Adhesives. Expensive.
Polyester	Amorphous	Fiberglass, Laminates. Cheaper than epoxy.
Phenol-formaldehyde	Amorphous	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).

2.2.3 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 [4].

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 of the rubber makes it 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 [9]

Elastomer	Composition	Uses
polyisoprene	Amorphous except at high strains	Natural rubber
polybutadiene	Amorphous except at high strains	Synthetic rubber, cartyres
polychloroprene	Amorphous except at high strains	Neoprene. An oil-resistant rubber, used for seals.

2.3 Polybenzoxazines

Polybenzoxazine is a recently advanced addition polymerized phenolic system, containing a wide range of interesting qualites and has the capability to overcome various deficiencies of conventional novalac and resole type phenolic resins. These materials exhibit (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazines Tg 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 [11].

Phenolic resins are greatly used for 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 [12], the potential of polybenzoxazines has been recognized only recently [13].

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.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.[14]

2.3.1 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 monomers 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 [11].

2.3.1.1 Mono-functional benzoxazine monomers

Holly and Cope [12] 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 [15]. 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 [14] (Figure 2.3).

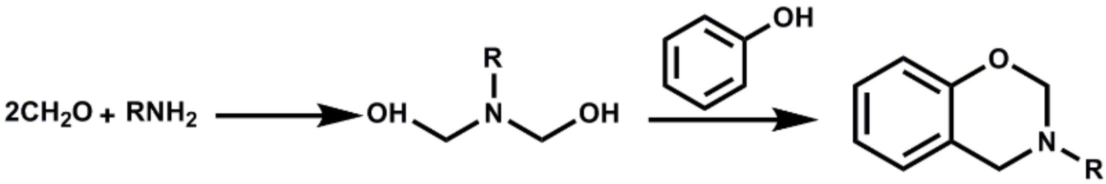


Figure 2. 3 : Synthesis of 3, 4 – dihydro – 2H – 1, 3 - benzoxazine

As an example, to prepare 3,4-dihydro-3-cyclohexyl-6-*t*-butyl-1,3,2H-benzoxazine, Burke [15] employed two procedures:

(i) Cyclohexylamine was mixed with 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 [16-18].

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) [19] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [14] is shown below in Figure 2.4.

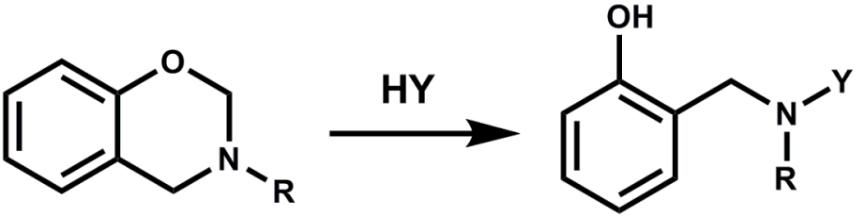


Figure 2. 4 : Ring opening of benzoxazine in acidic medium

The benzoxazines derived from a strongly basic amine and a less acidic phenol was found to be more stable in the hot alcohols [20]. 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 [21]. 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 [22].The reaction mechanism and kinetics of this solventless synthesis were proposed by Liu [23]. In a typical synthesis, the reactants, i.e., aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and there after 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 [11].

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 [12]. 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 [15]. This benzoxazine can further react with phenol to form 3,4-dihydro-3-(2-hydroxy)benzyl-2H-1,3-benzoxazine [13] (Figure 2.5; Figure 2.6).

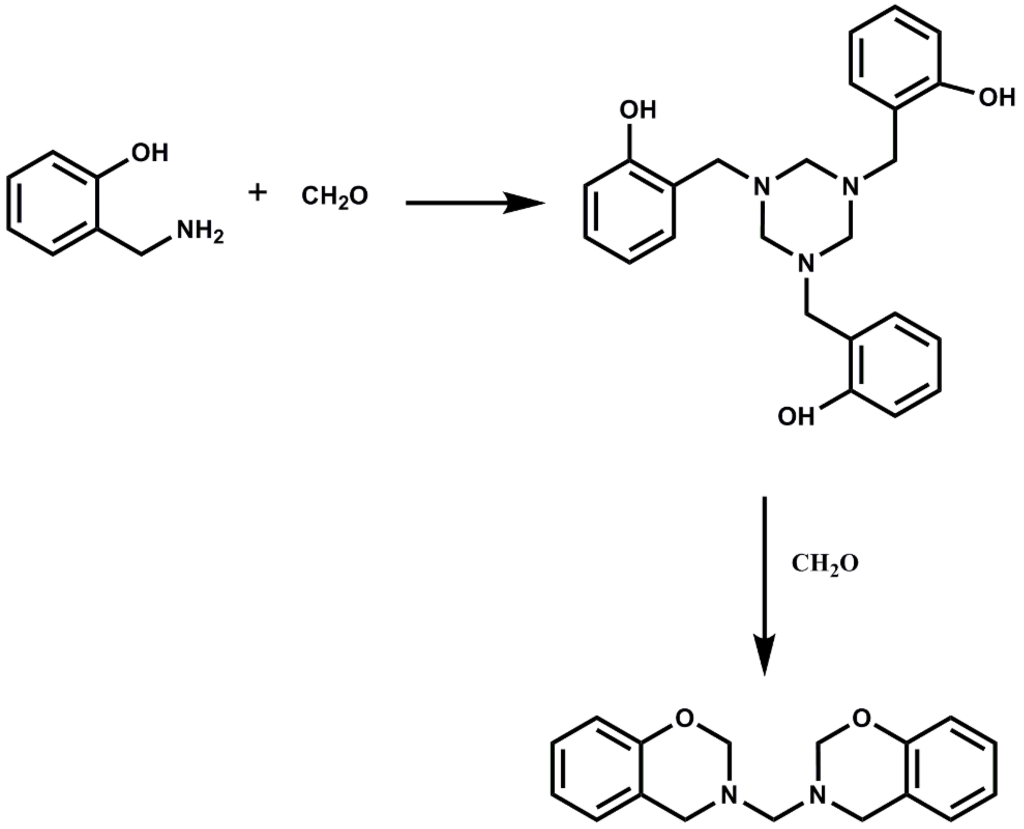


Figure 2. 5 : Formation of di(2H –benzo[e] [1,3] oxazine – 3(4H)-yl)methane

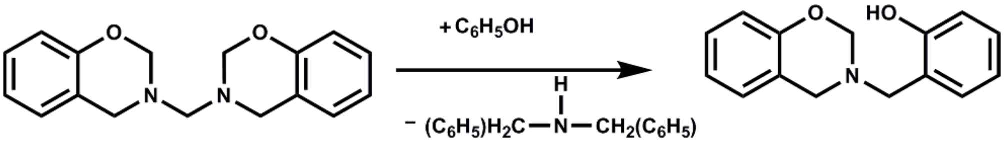


Figure 2. 6 : Formation of 1, 3 –oxazine ring from 2 – hydroxylbenzylamine

2.3.1.2 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 [24]. 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 [25]. To overcome this limitation, Ishida and coworkers [18, 26] 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 [27, 28] 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 2.7 [27]. 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 [28].

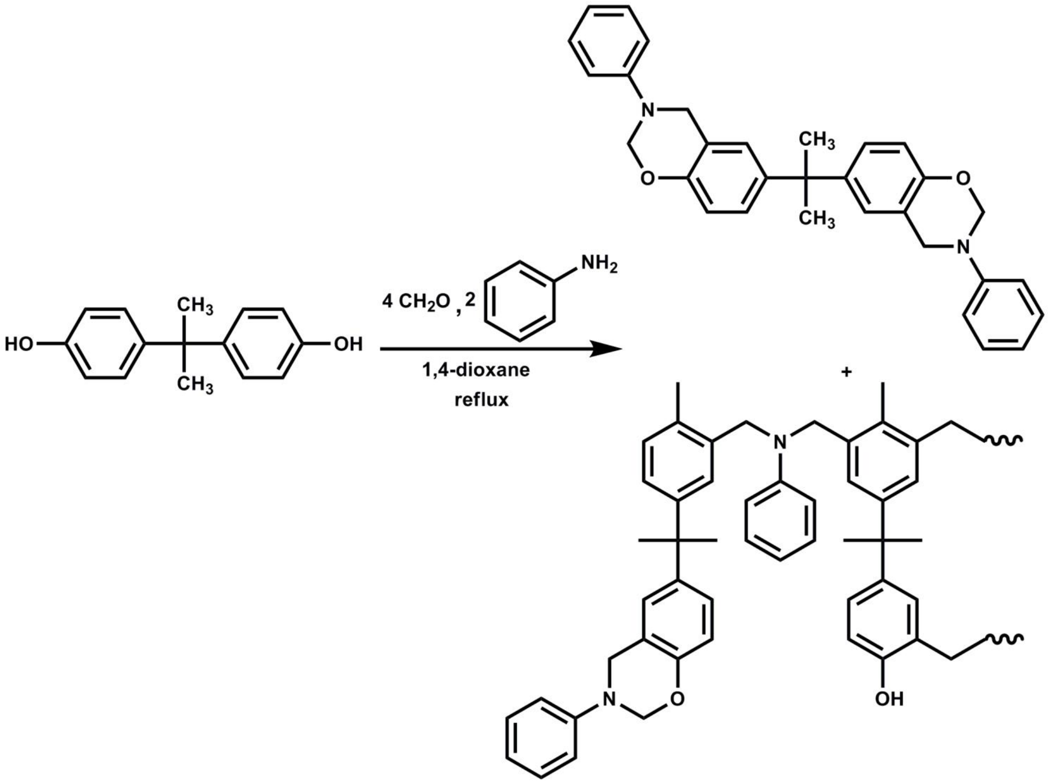
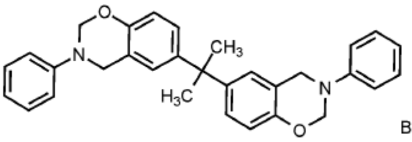
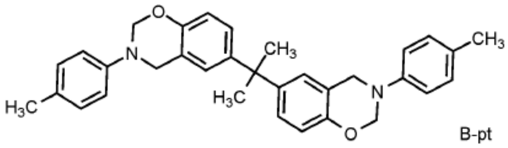
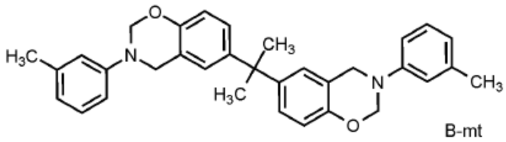
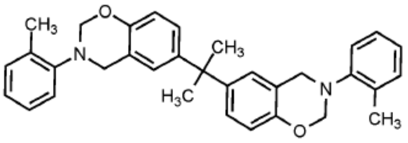
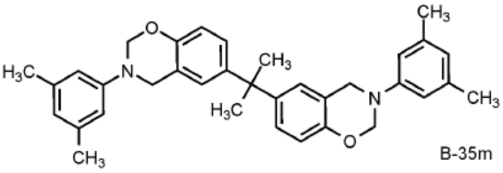
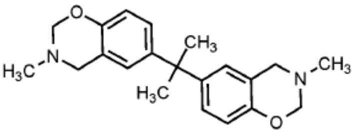
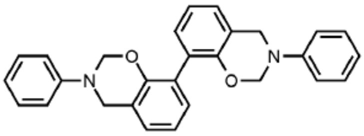
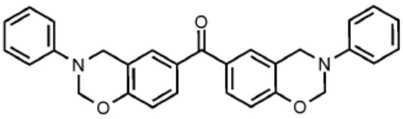


Figure 2. 7: Synthesis of bisphenol – A and aniline based benzoxazine (B-a) monomer

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 [29].

Solventless method was successfully employed for synthesis of a series of difunctional monomers listed in table 2.4. [22, 27, 29-32].

Table 2. 4 : Series of difunctional benzoxazine monomers

 B-a	 B-pt
 B-mt	 B-ot
 B-35m	 B-m
 22P-a	 44O-a

2.3.1.3 Allyl-containing monomers

The main advantage of the allyl group [33,34] is not only that it provides additional crosslinkable sites, but that it can easily be cured at a temperature lower than that needed for acetylene groups. Allyl-containing monomers have attracted much attention because they are used as reactive diluents of bismaleimides to improve the toughness of the cured resin [35,36]. Ishida also reported [22] the preparation of an allyl containing benzoxazine monomer, 3-phenyl-3,4-dihydro-8-allyl- 2H-1,3-benzoxazine, from allylphenol, aniline, and paraformaldehyde. A similar benzoxazine monomer based on allylphenol was reported for silylation of the allyl group to enhance the interface between the matrix and glass or carbon fiber in fiber reinforced polybenzoxazine [37] Also, Pei et al. reported similar bifunctional allylphenol-derived polybenzoxazine [38]. Because of the absence of activated ortho position to the phenolic hydroxyl group, these allylphenol-based benzoxazine monomers, however, are considered to be difficult to polymerize through ring-opening and are not good candidates for preparing high performance polybenzoxazines. The synthetic approaches adopted by Agag and Takeichi [39] for the preparation of two novel benzoxazine monomers modified with allyl groups:

(i) 3-allyl-3, 4-dihydro 1,3-benzoxazine and (ii) bis(3-allyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane are shown in Figure 2.8 . It was reported that benzoxazines containing allyl group can polymerize at temperatures below 150 °C. However, this polymerization occurring at low temperature was not from the benzoxazine ring-opening reaction, but from the allyl group and a high temperature above 250 °C was needed to complete the polymerization of benzoxazine rings.

Synthesis of a series of allyl group containing mono-functional benzoxazine monomers, where the allyl group is attached with nitrogen and derived from cresol and allyl amine by a solventless method has been reported and the effect of these allyl groups on polymerization reaction and the performance enhancement of the cured polymers at high temperature has been reported by Takeichi et al. [40].

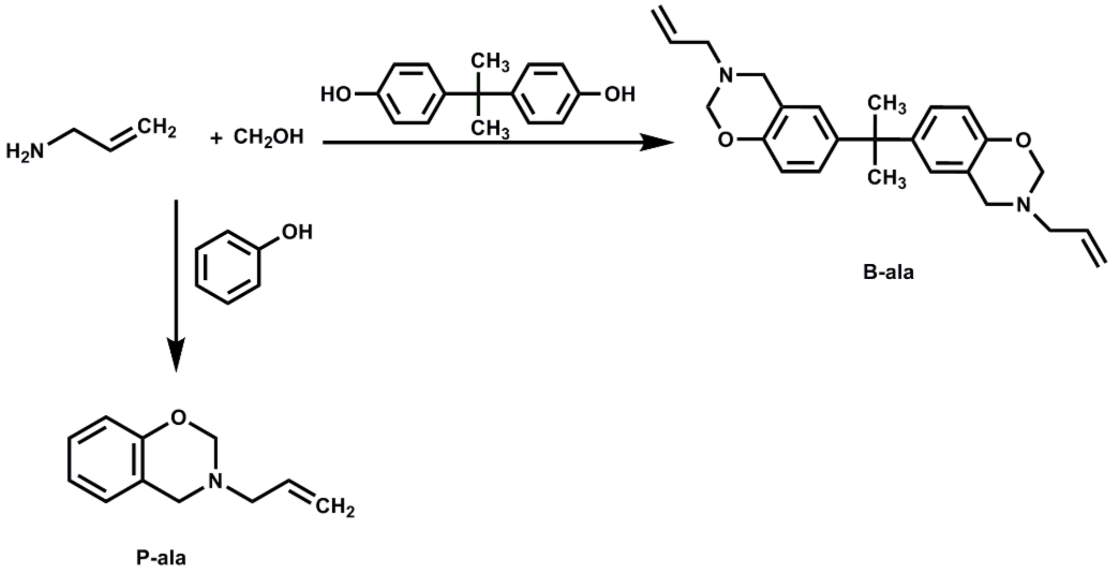


Figure 2. 8 : Synthesis of allyl containing benzoxazine monomers

2.3.2 Polymeric benzoxazine precursors

2.3.2.1 Main-chain precursors

High molecular weight polybenzoxazine precursors can be synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (Figure 2. 9).

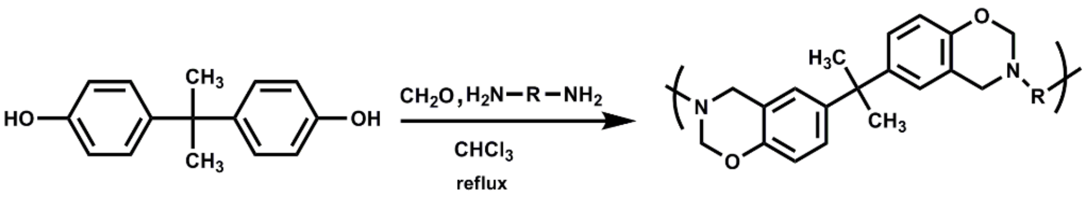


Figure 2. 9 : Synthesis of polybenzoxazine precursor

The possibility of the preparation of polymers containing oxazine ring in the main chain was first discussed by Liu *et.al* [13]. Later, more detailed work on the effect of water, solvents, catalyst, ratio of reactants and temperature was reported by the same research group [23]. 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 ^{o}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 ^{o}C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability [41,42].

2.3.2.2 Side-chain precursors

The only reported side-chain polymeric benzoxazine precursor is based on polyphenylene structure. Soluble and thermally curable conducting high molecular weight polybenzoxazine precursors were prepared by oxidative polymerization

3-phenyl-3,4-dihydro-2H-benzo[e][1,3] oxazine (P-a) alone and in the presence of thiophene (Th) with ceric ammonium nitrate in acetonitrile (Figure 2.10; Figure 2.11). 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 [43].

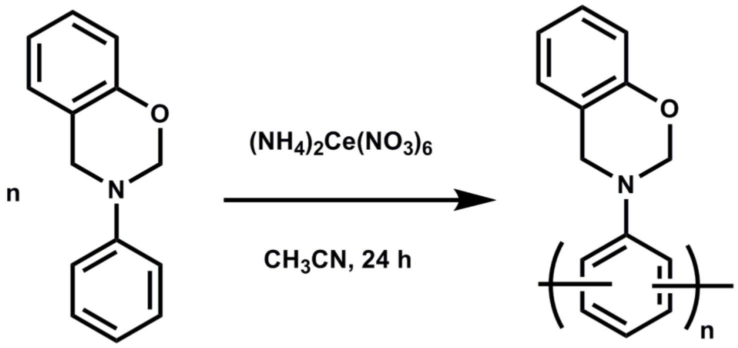


Figure 2. 10 : Synthesis of semi-conductive side chain polybenzoxazine precursor

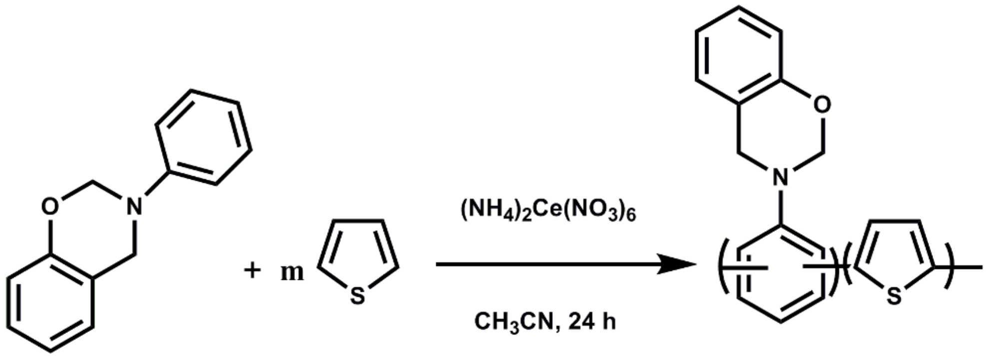


Figure 2. 11 : Synthesis of semi-conductive side chain polybenzoxazine precursor by reacted with thiophene

2.3.3 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 [44, 45]**.** 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*. [14]. 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* preferency 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 [24]. The typical method of polymerization of benzoxazine monomers is thermal curing without using any catalyst [17, 28, 31, 46, 47,48]. It should be emphasized that the polymerization mechanism of benzoxazine resins is still not well established.

2.3.3.1 Thermal polymerization of benzoxazines

A cross-linked network structured polybenzoxazines, with higher Tg 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 2.12 [39]. Obviously, difunctional benzoxazines derived from diamines are expected to undergo similar cross-linking [49, 50].

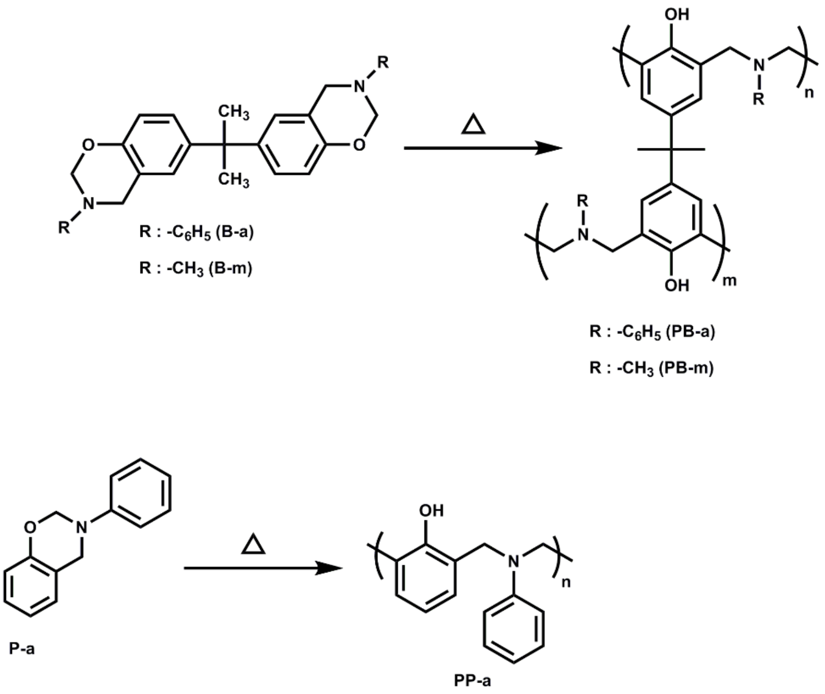


Figure 2. 12 : Curing of monofunctional and difunctional benzoxazines

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 °C and 230 °C 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. 223 °C and maximum at 249 °C corresponding to the ring-opening polymerization of benzoxazine. The amount of exotherm for B-a was 79 cal/g [39].

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 [18].

Attempts have been taken to understand the cure mechanism and kinetics of the thermal curing of mono and difunctional benzoxazines utilizing DSC, FTIR, DMA, 13 C and 15 N solid sate NMR spectroscopic measurements [42, 51-57].

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 [51] (Figure 2.13). 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.

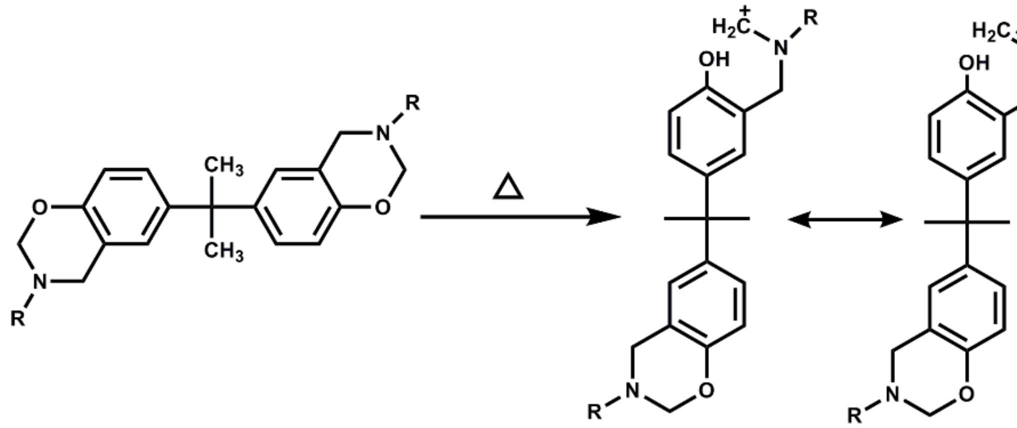


Figure 2. 13 : Initiation of ring-opening polymerization of benzoxazine

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 Tg 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 Tg. 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 [51]. Figure 2.14 illustrates the thermal polymerization of B-a through cationic mechanism.

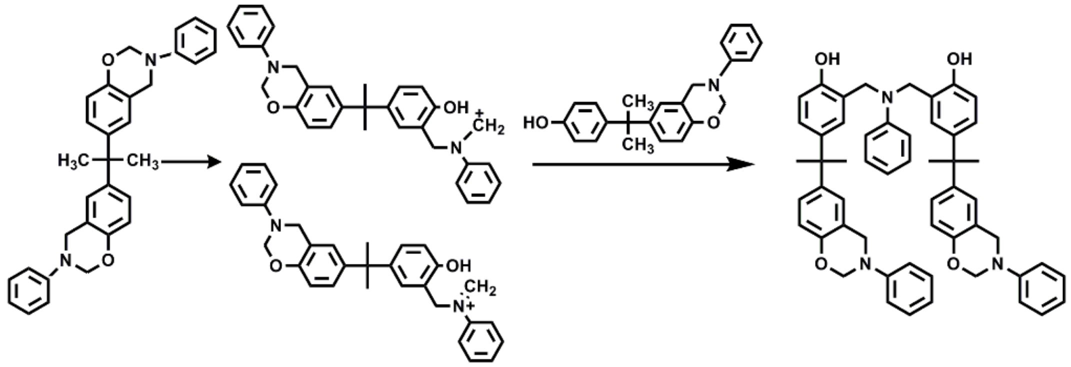


Figure 2. 14 : Thermal polymerization of B-a through cationic mechanism

Solid State 15N-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 2.15 [52].

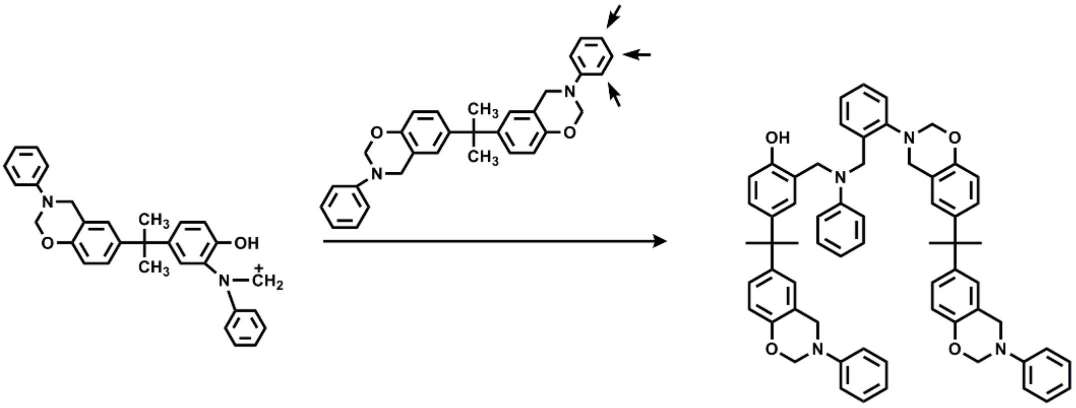


Figure 2. 15 : Electrophilic subtitution reaction of aniline moiety

2.3.4 Properties and applications of polybenzoxazines

PBZ materials are widely used all around the world in recent years for their advantegeous 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 [58,59].

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 Tg 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 [60,61].

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 [62-64]. 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 [65].

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 [66, 67].

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.

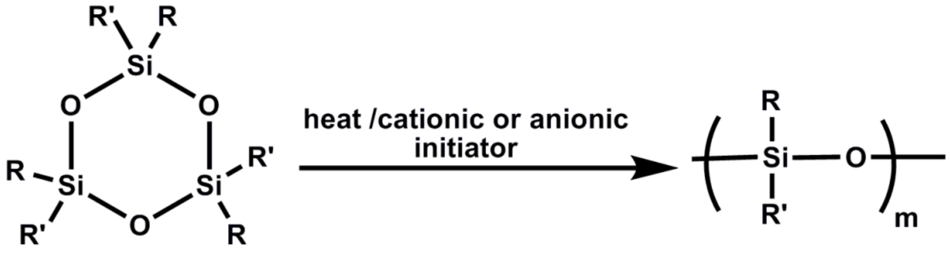
Thermosetting benzoxazine resin compositions can bind a substrate to a metallic surface [68-69]

Incorporation of benzoxazine moiety with the polymer chain provides better processibility and improved mechanical properties. The PBZ resin has advantages such as [11,73]:

- 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

2.4 Polysiloxane

Polysiloxanes first developed in the 1930's and 1940's, represent a billion dollar global industry [74,75]. Indeed, these are the only class of inorganic polymers which can be considered as commodity materials. The exceptional properties of polysiloxanes are a direct result of their inorganic backbone of silicon and oxygen atoms and have resulted in their widespread use as high-performance elostomers and fluids,surface modifiers,adhensives, biomedical materials and materials for the soft contact lenses and artificial skin [76,78]. The polysiloxane backbone contains long Si-O bonds (1.64 A° compared with 1.54 A° for a C-C bond) and lacks subtituents on every other skeletal atom (oxygen). The wide bond angle at oxygen (Si-O-Si 143° compared with C-C-C 109°) imparts unique dynamic flexibility and therefore these materials retain elasticity at very low temperatures (Tg= -123 °C for polydimetylsiloxane) the strong Si-O bonds (bond energies: Si-O ca. 450 and C-C ca. 348 kJ/mol) bring oxidative, thermooxidative and UV radiation stability to polysiloxanes [79].



R: Vinyl, Me, H
R': Vinyl, Me

Figure 2. 16 : Ring opening reaction of hexamethylcyclotrisiloxane

2.5 Methodology of Synthesis Polymer Containing Siloxane Moities

2.5.1 Ring opening polymerization

The main methods of synthesis involve polycondensation and anionic or cationic ring opening polymerization routes (Figure 2.16). Cross linking for elastomer applications can be achieved by a variety of techniques including heating with peroxides or transition metal-catalyzed hydrosilylations for Si-vinyl and Si-H functionalized polymers.

An organic-inorganic block copolymer,was first prepared in the early 1970’s by the researhers at Dow Corning via anionic polymerization [80]. Living polystyrenylithium was prepared and used to initiate the ROP of hexamethylcyclosiloxane (Figure 2.17). Propagation of the siloxane segment required addition of promoters such as tetrahydrofuran or diglyme. Delibarate termination using acetic acid or chlorodimethylvinylsilane was conducted. Selected metarials from this series were also found to undergo solid-state self assembly in thin films [79].

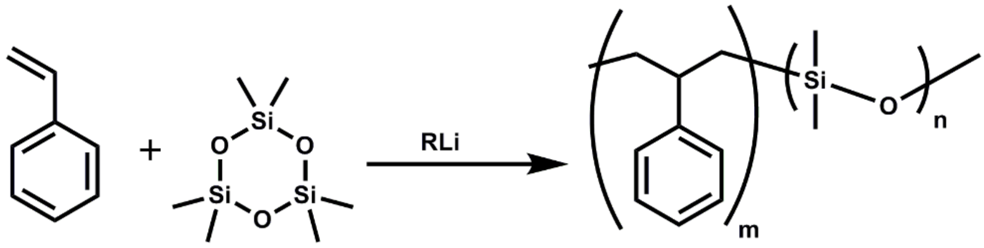


Figure 2. 17 : The anionic polymerization of sytrene with hexamethylcyclotrisiloxane

2.5.2 Hydrosilylation

It is well-documated that certain hydrosilanes undergo addition across the carbon-carbon multiple bonds under catalysis by transition metal complexes and the reaction is referred to as the hydrosilylation [81;84]. In corporation of chiral ligands into metal catalyst can in principle make the hydrosilylation result in the formation of optically active alkylsilanes. Since an efficient oxidative cleavage of a carbon-silicon bond to furnish a carbon oxygen bond was found by Tamao [85,86] in 1978,enantioselective hydrosilylation has been recognized to be a variant of the enantioselective hydrotion of olefin in general. Thus,optically active alkylsilanes are converted to the correspondig optically active alcohols by oxidation, which proceeds with retention of configuration at the stereogenic carbon center to give the alcohols without loss of their enantiomeric purity.

A transition metal complex, ML_n (L=ligand), especially an electron-rich complex of a late transition metal such as Co(I), Rh(I), Ni(I), Pd(0), Pt(0) as a precatalyst,activates both hydrosilanes,$HSiR_3$, and a variety of substrates, typically alkenes. A catalytic cycle is considered to involve further two steps as depicted in Scheme 1. The conventional hydrosilylation of alkenes catalyzed by $H_2PtCl_6.6H_2O$/iPrOH (called the Speier catalyst [87]) is generally assumed to proceed by Chalk-Harrod mechanism [88,89]. Oxidative addition of a hydrosilane gives a hydro-silyl complex which is coordinated with the substrate alkene. The complex undergoes migratory insertion of alkene into the M-H bond (hydrometallation) to give the alkyl-silyl species. Reductive elimination of alkyl and silyl ligands from II forms the hydrosilylation product. Althoug the Chalk-Harrod mechanism accounts for an alkene isomerization, an H-D exchange between deuteriosilanes and alkenes,as well as the observed regioselectivity always associated with the catalytic hydrosilylation, an alternative mechanism has been proposed which involves preferentially an alkene insertion into the M-Si bond by using Rh(I) or Co(III) catalyst precursor to form the B-silylalkyl-hydrido intermediate, followed by the reductive elimination to complete the hydrosilylation [90,91]. It is worthy of note that hydrosilanes exhibit a wide spectrum of reactivities in the oxidative addition depending on the substituents on the silicon atom and the nature of the metal catalyst. Thus, Pt complexes tolerate any hydrosilane,such as $HSiCl_nMe_{3-n}$ (n=1-3),$HSi(OR)_3$, or H_nSiR_{4-n} (n=1-3; R=alkyl or Ph) in the hydrosilylation, while, Pt complexes are applicable mostly to $HSiCl_nR_{3-n}$ (n=2,3) and Rh complex to preferably $HSiR_3$ [84]. (Figure 2.18)

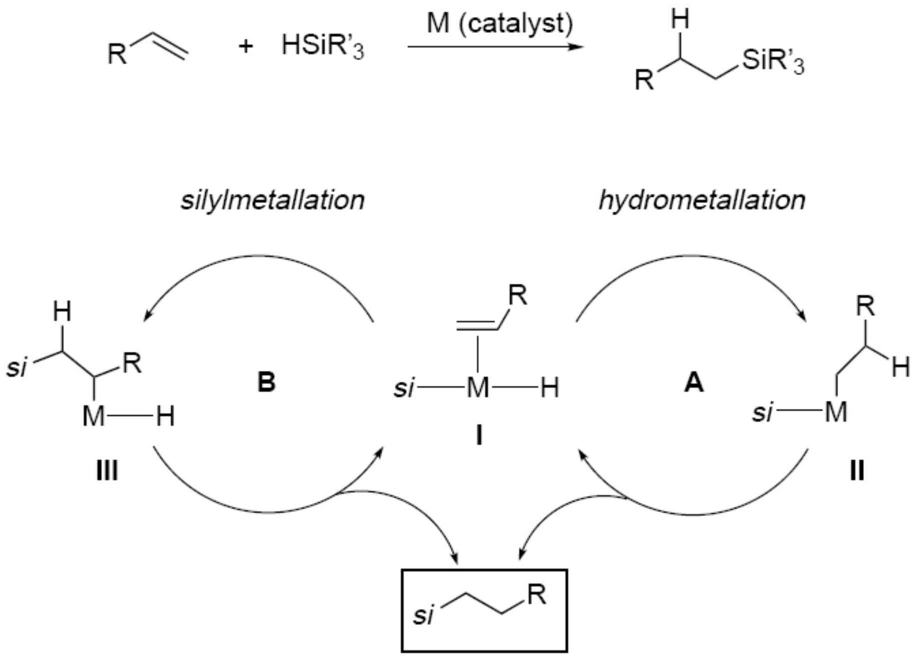


Figure 2. 18 : Mechanism of hydrosilylation

3. EXPERIMENTAL PART

3.1 Metarials and Chemicals

4,4'-Isopropylidenediphenol (Aldrich, 97 %), paraformaldehyde (Acros, 96 %), sodium hydroxide (Acros, 97 %), methanol (Aldrich, ≥99 %), 1,1,3,3-tetramethyldisiloxane (Aldrich, 97 %), platinium (0)- 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (approximately 2%Pt) (Aldrich) diethylether, 1, 4 – dioxane (Aldrich, ≥ 99%), toluene (Aldrich, 99%) sodium sulfate (Across 99%), and chloroform (Across, 99+%),tetramethylammonium hydroxide, 25 wt.% in solution methonol (Aldrich) decamethylpentacyclosilaxan (D_5) (Merck) were used as received.

3.2 Equipments

The ^{1}H NMR (250 MHz) spectra were recorded on a Bruker NMR Spectrometer in $CDCl_3$. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One-B spectrometer. Differential scanning Calorimetry (DSC) was performed on Perkin–Elmer Diamond DSC with a heating rate of 20°C min under nitrogen flow. Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10ºC min under nitrogen flow. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}), a Viscotek UV detector and Viscotek a differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software.

3.3 Preparation Methods

3.3.1 Preparation of allyl benzoxazine

Synthesis of 6, 6′-(propane-2, 2′-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3] oxazine) (B-ala)

In a 250 ml flask, allylamine (0.54 mol, 30.8 g) was dissolved in 200 ml 1, 4-dioxane in ice bath because of its toxic behavoir. Bisphenol A (0.27 mol,61.6 g) was added to solution after followed by adding paraformaldehyde (1.08 mol,32.5 g) portion-wise with stirring for 10 min in an ice bath. The temperature was raised and refluxed for 24 h.

After removing 1,4-dioxane under vacuum, the resulting crude product was purified by dissolving in 200 mL of diethyl ether and washing various times with 0.1 N sodium hydroxide, and finally two times with distilled water. After drying with $NaSO_4$, filtering and evaporating diethyl ether. Pale yellowish oil was obtained. The oil was dissolved in 20 ml of MeOH; water was added to this solution until it became turbid and then refrigerated. The precipitated sticky mass was obtained after decantation and subsequently washing with water. The mass was dried under vacuum at 60 °C for 24 h to afford solid. (reaction temperature: 110 °C ; yield: %62)

3.3.2 Preparation of benzoxazine-siloxane oligomer

A 100 ml, round-bottomed, three-necked flask equipped with a magnetic stir bar, condenser, and gas inlet adapter was charged with B-ala (0.50 g, 1.28 mmol), 25 ml of toluene, and six drops of platinium(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (~2 % Pt). The mixture was stirred at room temperature (r.t.) for about 15 min. After stirring, an equimolar amount of 1,1,3,3-tetramethyldisiloxane (0.17 g, 1.28 mmol) was added and the reaction flask was placed into 90 °C oil bath. After ca. 2 min, the mixture began to reflux and it was heated for a given time in the 90 °C oil bath. After the heating period, most of the volatiles were removed using rotary evaporator. The flask was then kept at 50 °C under vacuum for ca. 3 h. The crude product was purified by dissolution in a minimum amount of toluene, and then adding the solution drop-wise to a large excess of rapidly stirred methanol that was cooled in an ice bath. After ca. 15 min, the product had conglomerated as a sticky, light brown mass on the bottom of the flask. The methanol was slowly decanted and the sticky product was dried by exposure to high vacuum for 3 h at 50 °C.

3.3.3 Preparation of polybenzoxazine-siloxane copolymer

In a 100 ml,round bottomed,three-necked flask with a magnetic stir bar,condenser and gas inlet adapter charged with oligomers (1 gr) and D_5 (3 gr; 13,4 mmol) ,15 ml of toluene,with tetrabutylammonium hyroxide (0,5 gr; 5,5 mmol) as a catalyst. Before using catalyst, methanol should have been evapotared.The mixture was stirred at room temperature for 15 min.after stiring,decamethylpentacyclosilaxan added slowly to the reaction flask. It was heated for 5 hours in the 80 °C oil bath in the inert atmosphere. After the heating period,most of the volutiles were removed using rotary evaporator. The crude product was purified by dissolution in a minumum amount of toluene,and then adding the drop-wise to a large excess of rapidly stirred methonol that was cooled in a ice bath.For accelated precipition used salt-water solution.The methonol was slowly decanted and the sticky light yellow product was dried by exposure to high vacuum for 8 h at 50 ° C.

4. RESULTS AND DISCUSSION

Thermally curable and penetrable benzoxazine-siloxane copolymer is synthesized by the hydrosilylation reaction after followed by ring-opening reaction in the presence of base catalyst. First 6,6′-(propane-2,2′-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3] oxazine) (B-ala) synthesized as a monomer. Secondly the benzoxazine-siloxane oligomer is formed by the hydrosilylation reaction. Finally the reaction with D_5 in the presence of tetrabutylammonıum hydroxide that enhance the high molecular weight of polymer by increasing the siloxane groups in the main chain and yield the desired thermally curable and flexible product. The details of procedure will be given below.

4.1 Sythesis of Allylbenzoxazine

Benzoxazine monomers are typically synthesized through the Mannich condensation of phenol, formaldehyde, amine either by employing solvent or by solventless method [92]. Various types of benzoxazine monomer can be obtained by having different substitution groups attacted different types of phenols and amines. Allyl amine groups have been employed and their main advantage is proving additional crosslinkable sites and cured at a lower temperature. A similar benzoxazine monomer based on allylphenol was reported for silylation of the allyl group to enhance the interface between the matrix and glass or carbon fiber in fiber-reinforced polybenzoxazine.[11] Also, Pei et al. Reported similar bifunctional allylphenol-derived polybenzoxazine. Because of the absence of activated ortho position to the phenolic hydroxyl group, these allylphenol-based benzoxazine monomers, however, are considered to be difficult to polymerize through ring-opening and are not good candidates for preparing high performance polybenzoxazines. For this purpose, as it is outlined in Figure 4.1, 6,6′-(propane-2,2′-diyl)bis(3-allyl-3,4-dihydro-2H-benzo[e][1,3] oxazine) (B-ala) was obtained in one-pot reaction and used to synthesize allylbenzoxazine as a readily available monomer for hydrosilylation reactions [93].

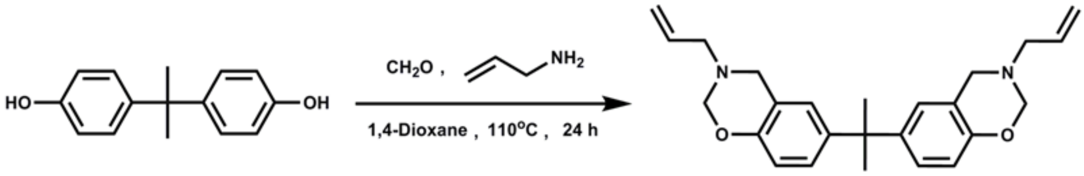


Figure 4. 1 : Synthesis of allyl benzoxazine (B-ala)

4.2 Characterization of Allyl Benzoxazine

The chemical structure of allyl benzoxazine was confirmed by both FT-IR and ^{1}H-NMR spectroscopy. FT-IR spectrum presented in Figure 4.2 (a) shows characteristic absorptions of benzoxazine structure at 1226 cm^{-1} (asymmetric stretching of C-O-C), 1321 cm^{-1} (CH_2 wagging), and 921 and 1496 cm^{-1} (trisubstituted benzene ring). Absorption bands of allyl group are typically located at 3076 cm^{-1} (stretching of =C-H) and at 1642 cm^{-1} (stretching of C=C). Additionally, the out of plane bending vibrations of olefinic C-H were observed at 820-858 and 987 cm^{-1}.

The ^{1}H-NMR spectrum shown in Figure 4.6 (a) also establishes the structure of B-ala. The two multiples at 5.2-5.3 and 5.9-5.6 ppm are typical for the protons of $=CH_2$ and =CH- in allyl group, respectively. The protons of $-CH_2-$ of allyl group showed a doublet at 3.4 ppm. The characteristic protons of oxazine ring appeared at 4.0 and 4.8 ppm assigned to $-Ar-CH_2-N-$ and $-O-CH_2-N-$, respectively. The aromatic protons appeared as multiplet at 6.7-7.0 ppm.

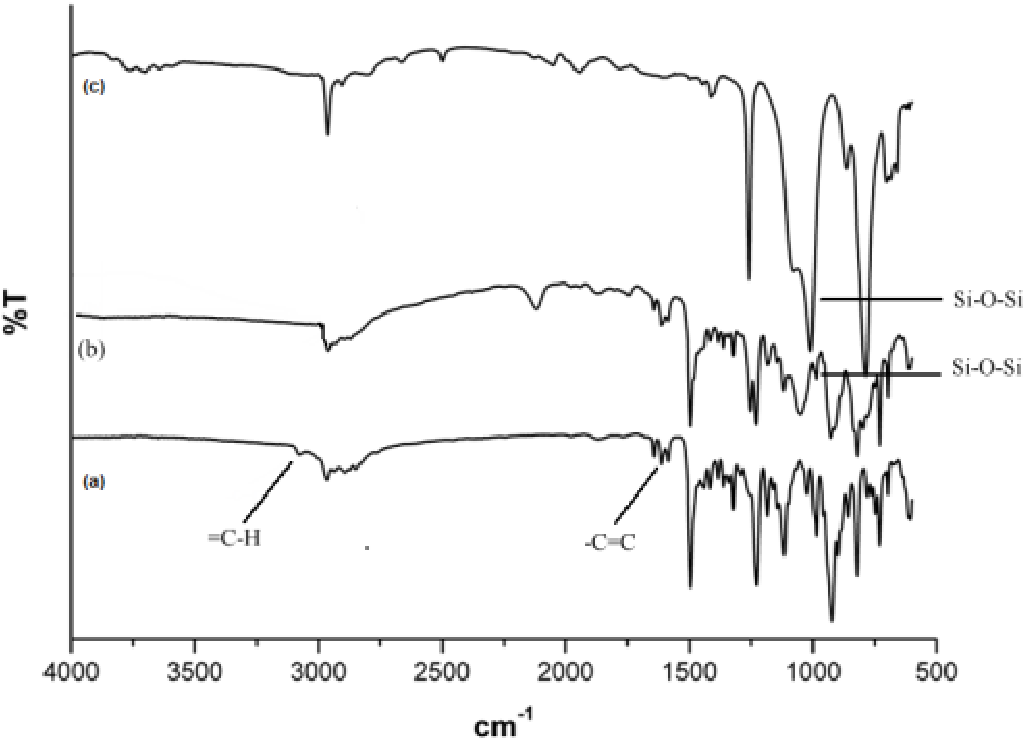


Figure 4. 2 : FT-IR specturm of B-ala (a);PBTMDS oligomer (b); PBTMDS copolymer (c)

4.3 Synthesis of Polybenzoxazine-Tetramethyldisiloxane Oligomer

The Si-H bond is polar, long, weak, and therefore, very reactive. Its addition across a double bond (hydrosilylation) is an important reaction not only in orgonosilicon chemistry but also organic synthesis and dendrimer and polymer chemistry. Therefore, B-ala contains terminal allyl groups in the structure and it is expected to yield polymer upon hydrosilylation with 1,1,3,3-tetramethyldisiloxane**.** It is a catalytic reaction for which a large variety of catalysts is available. Most of these catalysts operate according to the well-established Chalk-Harrod [94] mechanism which including oxidative addition Si – H, olefin insertion into the [M] – H bond, reductive elimination of resulting product, and regeneration of the reaction catalyst [95]. This mechanism can be presented as follows: (Figure 4.3).

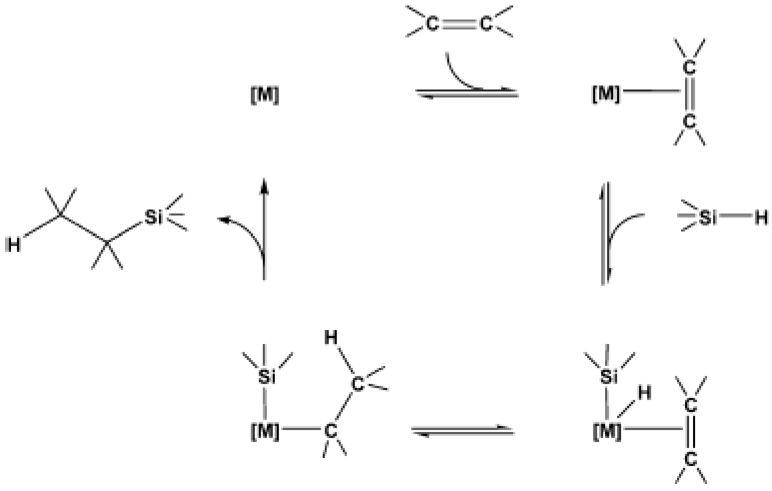


Figure 4. 3 : Classical Chalk-Harrod mechanism for the hydrosilylation of olefins

Hydrosilylation is usually catalyzed by transition metal, typically platinium, complexes, among which one of the most often used is the soluble Pt(0)-1,3–divinyltetramethyldisiloxane complex, also known as Karstedt's catalyst. The figure of Pt –DVTMDS chelated species in Figure 4.4 .

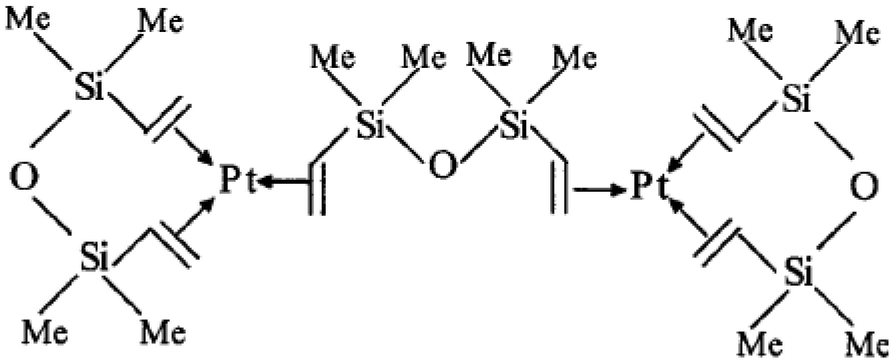


Figure 4. 4 : Proposed structure of Karstedt's catalyst

Although platinium complexes have been widely used for many reactions, it has shortage of reliable information and disaggrement among the published data. The mechanism is effected by the nature of double bond, solvent, the concentration of the reactant is known [96].

The Pt-catalyzed hydrosilylation reaction in toluene proceed smoothly in 90 °C and gave the expected poly(B-ala-tetramethyldisiloxane) as aclear,light brown,viscous liquid after precipitation. (Figure 4.5) [93]

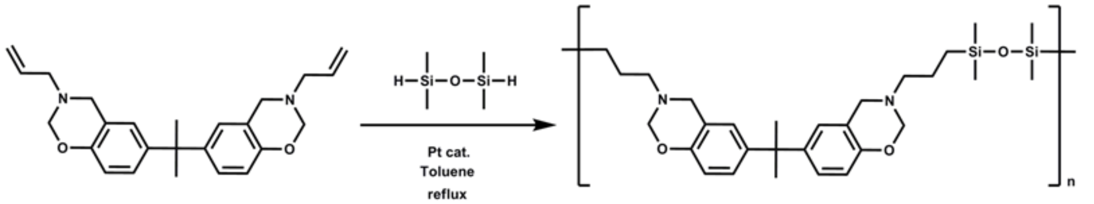


Figure 4. 5 : Synthesis of Benzoxazine containing siloxane oligomer

4.4 Characterization of Polybenzoxazine-Tetramethyldisiloxane Oligomer

B-ala contains terminal allyl groups in the structure and it is expected to yield polymers upon hydrosilylation with 1, 1, 3, 3-tetramethyldisiloxane (TMDS) (Figure 4.5). The Pt-catalyzed hydrosilylation reaction in toluene proceeded smoothly at 90°C and gave the expected poly (B-ala-tetramethyl disiloxane) s (PBTMDS) as a clear, light brown, viscous liquid in various yields after precipitation. In this reaction, platinum (0) divinyltetramethyldisiloxane complex, known as Karstedt's catalyst, was deliberately selected as the polymerization catalyst due to its widespread use in related polymerizations in the silicone industry.

The chemical structures of the PBTMDSs obtained were confirmed by both FT-IR and ^{1}H-NMR spectroscopy. In the FT-IR spectrum , the disappearance of the allylic =C-H and C=C stretching vibrations at 3076 cm^{-1} at 1642 cm^{-1}, respectively, was clearly noted. Additionally, the observation of Si-O-Si stretching vibration bands in the range of 1019-1035 cm^{-1} indicates the incorporation of siloxane groups into oligomers. The remaining bands of the benzoxazine group, such as aromatic C=C stretching vibrations, aromatic overtones and C-O-C symmetric and asymmetric vibrations etc. are another spectral evidences detected from the FT-IR. (Figure 4.2 (b)).

Further analysis of PBTMDS via ^{1}H-NMR showed the strong characteristic peak for Si-C$\boldsymbol{H_3}$ at 0.0-0.1 ppm. Additionally, -Si-C$\boldsymbol{H_2}$-CH$_2$,-Si-CH$_2$-C$\boldsymbol{H_2}$, -N-C$\boldsymbol{H_2}$-protons at 0.5, 1.0 and 2.7 ppm, respectively and the aromatic protons at 6.6-7.0 ppm indicate successful chemical linking between B-ala and TMDS monomers. As far as the subsequent use of the resulting polymer (PBTMDS) in thermal curing is concerned, the effect of hydrosillylation reaction on the stability of benzoxazine ring was an important issue. Thus, O-C$\boldsymbol{H_2}$-N and Ar-C$\boldsymbol{H_2}$-N protons of the oxazine structure appearing at 4.8 and 3.9 ppm, respectively, clearly indicates the retention of the benzoxazine ring during the hydrosilylation reaction. The allylic end groups were also detected as -CH=C$\boldsymbol{H_2}$ and C**H**=CH$_2$ protons at 5.2-5.3 and 5.8-5.9 ppm, respectively and used for molecular weight calculations by ^{1}H-NMR.

(Figure 4.6 (b)). The molecular weight were measured by GPC and were found to be in the range of Mn =1.400 with the polydispersity index of the oligomer was ~ 1.0. The general agreement for the result of average molecular weight (M_n) obtained by GPC also confirms efficient polymerization through hydrosilylation. (Table 4.1).

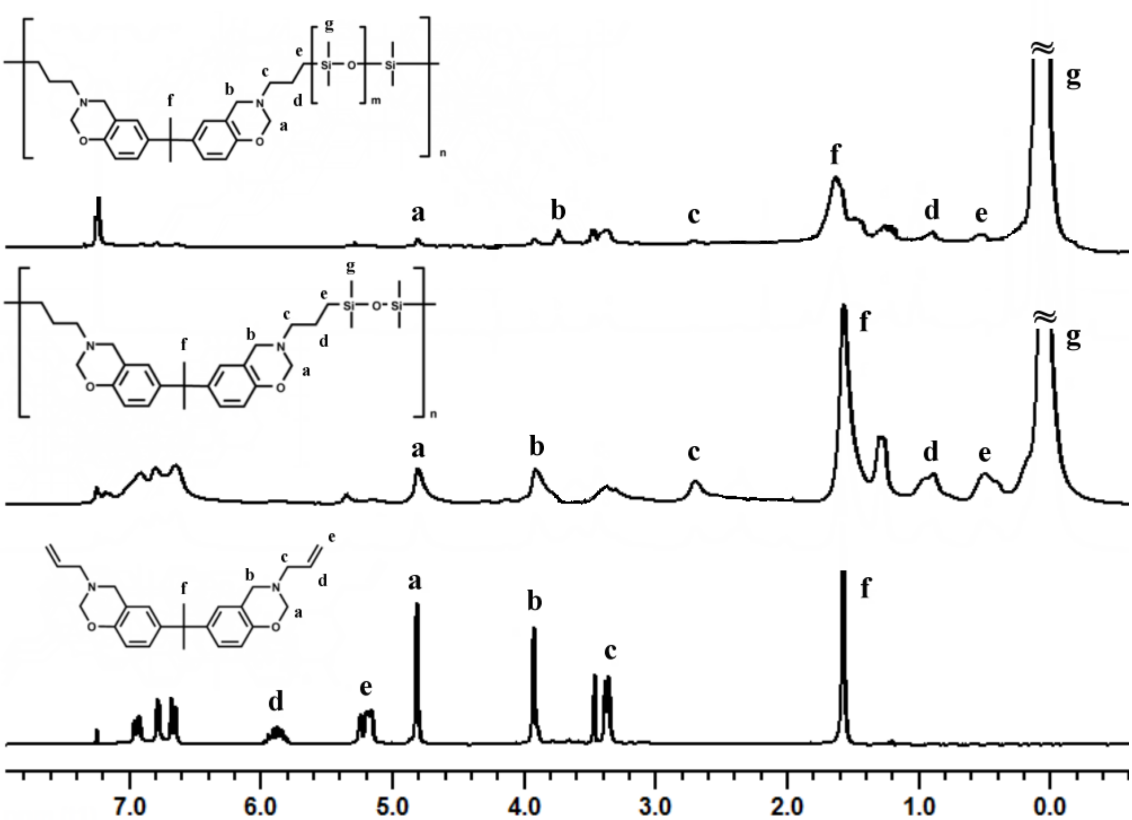


Figure 4. 6 : H-NMR spectrum of B-ala (a);B-ala-PMDS oligomer (b); B-ala-PMDS polymer (c)

4.5 Sythesis of Benzoxazine - Siloxane Copolymer

As can be seen, in all cases, although reasonable yields were attained, only siloxanes with 4-8 repeating units were formed with hydrosilation reaction. Limited chain growth is probably due to the poisoning of Pt catalyst. For enhancing the siloxane groups in the benzoxazine-siloxane copolymer the novel method has been recently found. The method rely on a base-catalyzed ring-opening reaction of cyclic siloxane named as decamethylpentacyclosilaxan employing tetramethlammonium hydroxide as a catalyst [97] to yield high molecular weight polysiloxane containing benzoxazine moieties in the main chain. (Figure 4.7)

The polymerization mechanism of cyclosiloxanes (such as D_4 and D_3)under base catalysts is a typical anionic ring opening polymerization, which is a very important reaction in the synthesis of linear polysiloxanes and extensively used in both industry and research laboratories.

The catalyst initiates D_4 to yield the base-catalyzed (or anonic) active species. The chain propagation is believed to proceed first with the nucleophilic attachment of the anionic species on the silicon atom of siloxane linkage and subsequently the redistribution of electron cloud density, and then the siloxane linkage is dissociated upon heating to yield new anionic active centers,which continue to react and stepwise propagate.

Catalysts such as tetramethylammonium hydroxide have special advantages since their reactivity can be destroyed upon vigorous heating after the polymerization is completed.

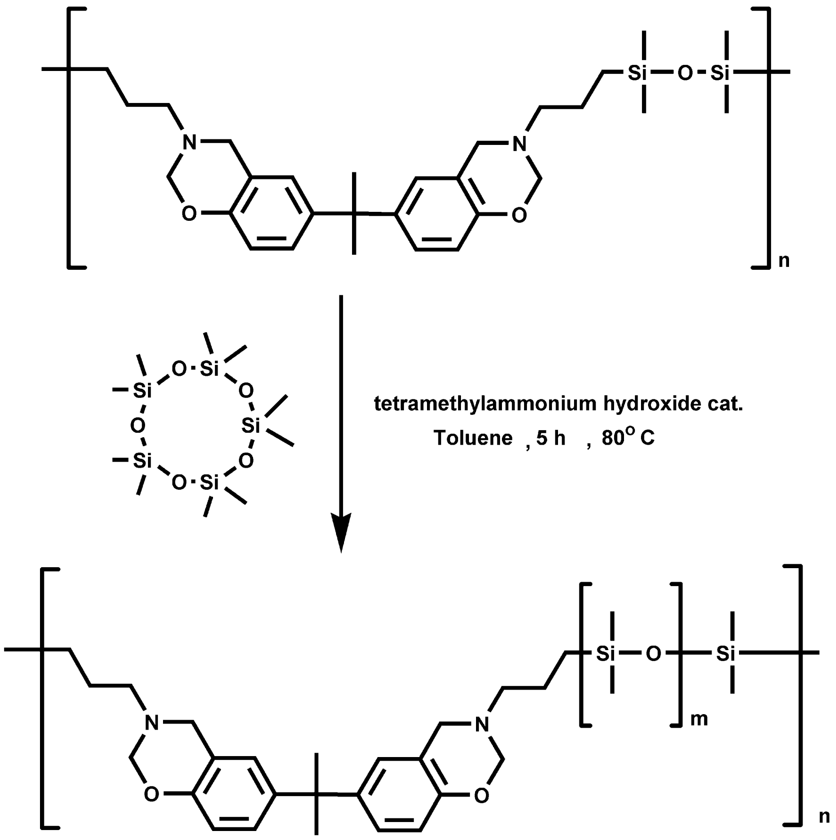


Figure 4. 7 : Synthesis of polysiloxane containing benzoxazine moieties.

4.6 Characterization of Polysiloxane-Benzoxazine Copolymer

The ring strain of oxazine allows benzoxazines to undergo ring-opening polymerization under thermally activated reaction conditions. Because of the multifunctional nature; oligosiloxanebenzoxazines were expected to form cross-linked networks upon heating. The chemical structure of benzoxazine-siloxane copolymers obtained were composed by FT-IR and ^{1}H NMR spectroscopy. As it is clearly shown in Figure 4.2 (c) the broadening of Si-O-Si stretching vibration bands in the range of 1019-1035 cm^{-1} indicates the incorporation of siloxane groups into oligomers.

Analysis of benzoxazine-siloxane copolymers via ^{1}H-NMR showed the strong characteristic peak for Si-C$\boldsymbol{H_3}$ at 0.0-0.1 ppm. Additionally, -Si-C$\boldsymbol{H_2}$-CH$_2$,-Si-CH$_2$-C$\boldsymbol{H_2}$, -N-C$\boldsymbol{H_2}$-protons at 0.5, 1.0 and 2.7 ppm, respectively and the aromatic protons at 6.6-7.0 ppm indicate successful chemical linking between B-ala and TMDS monomers. O-C$\boldsymbol{H_2}$-N and Ar-C$\boldsymbol{H_2}$-N protons of the oxazine structure appearing at

4.8 and 3.9 ppm, respectively, clearly indicates the retention of the benzoxazine ring. The allylic end groups were also detected as -CH=C$\boldsymbol{H_2}$ and C$\boldsymbol{H}$=CH$_2$ protons at 5.2-5.3 and 5.8-5.9 ppm, respectively and used for molecular weight calculations by ^{1}H NMR. (Figure 4.6 (c)). The peak area differences between oligomer and copolymer show that the high molecular weight copolymer were obtained. Mn was measured by GPC and were found to be in the range of Mn = 29.400 with the polydipersity index of the copolymer was 1.9 (Table 4.1)

Table 4. 1 : Result of GPC:PBTMDS-oligomer; PBTMDS-copolymer

Polymer	Mn	Mw	Mn/Mw
PBTMDS-oligomer	1400	1450	1.0
PBTMDS-copolymer	29400	55500	1.9

The thermally activated cure behavior of B-ala-PMDS polymer was studied by differential scanning calorimetry (DSC). The exhoterm at around 218 ^{o}C corresponds to the polymerization of allylic group and benzoxazine ring opens at a lower temperature of 250^{o}C. This behavior is also in accordance with the reported curing temperatures of allylic resins observed at higher temperatures up to 320 ^{o}C [96,97].

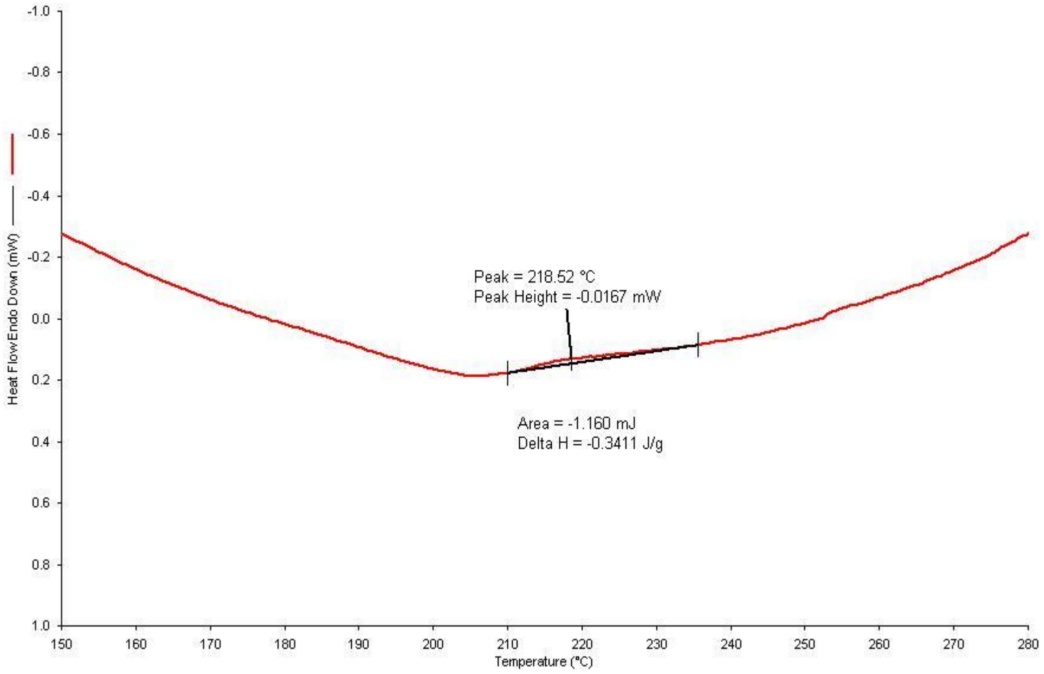


Figure 4. 8 : DSC data of PBTMDS copolymer

4.7 The Result for Cross-linking of The Copolymer

Thermal stability of the novel polybenzoxazines was investigated by TGA under nitrogen exposure. The TGA profiles of B-ala, PBTMDS oligomer and B-ala-PMDS polymer are shown in Figure 4.9. It can be seen that although the thermal stability of the cured B-ala is significantly improved in PBTMDS by incorporating siloxane units, it is decreasing in B-ala-PMDS polymer. It is known that polyhedral oligomeric silsesquioxane (POSS) and polybenzoxazine composites exhibit better thermal stability than polybenzoxazines themselves.

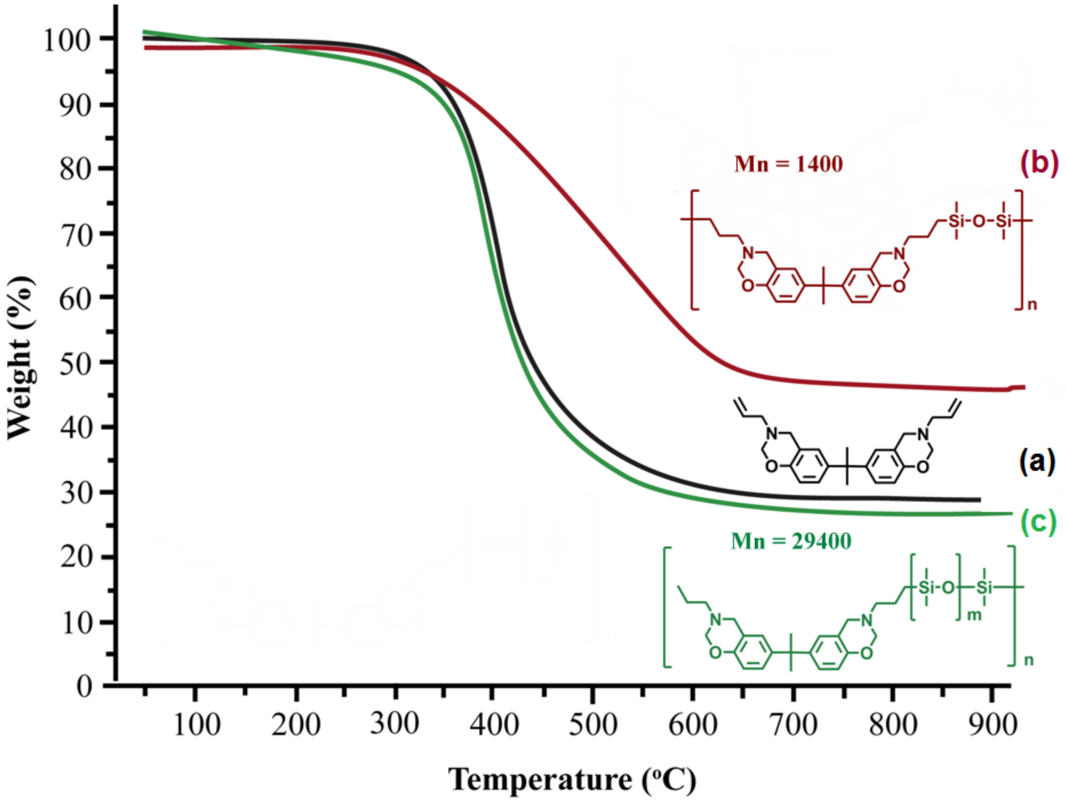


Figure 4. 9 : The results of B-ala (a); PBTMDS oligomer (b); PBTMDS copolymer(c)

The film forming properties and flexibility of benzoxazine-siloxane were also demonstrated. For this purpose, free standing films were prepared by the method of solvent casting of the polymers on Teflon plates. As can be seen from Figure 4.10, the copolymer completely bendable without any problem. After heat treatment a cured film retained its size and shape.

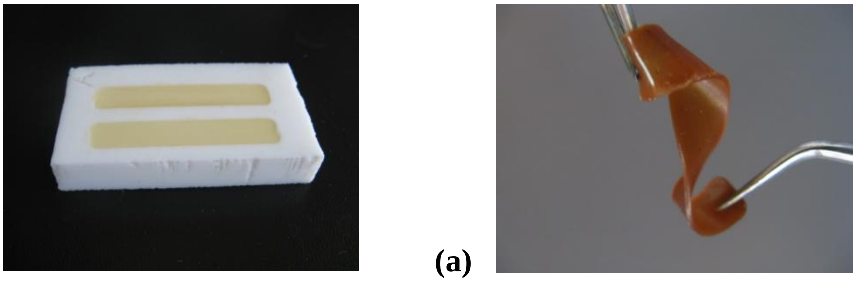

(a) (b)

Figure 4. 10 : The picture of PBTMDS copolymer before curing (a); after curing (b)

5. CONCLUSION

In conclusion, we have synthesized high molecular weight polysiloxane containing benzoxazine moities. Thermally activated ring opening reaction in the absence of added catalyst to form cross-linked polymer network. Thermal crosslinking nature provides the possibility to prepare high performance materials. The enhanced thermal stability was attributed to presence of the siloxane units. These features give an oppotunity to form molecular flexibility, tough and thermal stability of cross-linked polybenzoxazine films**.**

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