ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THERMALLY CURABLE POLYBUTADIENES BY CLICK REACTION

M. Sc. Thesis by

Sevim M. KUKUT

509061221

Department: Chemistry
Programme: Chemistry

Supervisor: Prof. Dr. Yusuf YAĞCI

JANUARY 2008

ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THERMALLY CURABLE POLYBUTADIENE BY CLICK REACTIONS

M. Sc. Thesis by
Sevim M. KUKUT

509061221

Date of Submission: 24 December 2007
Date of Defence Examination: 29 January 2008

Supervisor (Chairman) : **Prof. Dr. Yusuf YAĞCI**

Members of the Examining Committee: **Prof. Dr. Gürkan HIZAL (I.T.U.)**

Prof. Dr. Hüseyin YILDIRIM (Y.T.U.)

JANUARY 2008

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KLİK KİMYASI İLE ISISAL SERTLEŞTİRİLEBİLEN POLİBUTADİENLER

YÜKSEK LİSANS TEZİ
Sevim M. KUKUT
509061221

Tezin Enstitüye Verildiği Tarih: 24 Aralık 2007
Tezin Savunulduğu Tarih: 29 Ocak 2008

Tez Danışmanı :	**Prof. Dr. Yusuf YAĞCI**
Diğer Jüri Üyeleri	**Prof.Dr. Gürkan HIZAL (İ.T.Ü.)**
	Prof.Dr. Hüseyin YILDIRIM (Y.T.Ü)

Ocak 2008

ACKNOWLEDGEMENTS

With a deep sense of gratitude, I wish to express my sincere thanks to all the people who made this work possible.

I am deeply indebted to my supervisor, Prof. Dr. Yusuf Yağcı, for his kind support and guidance. It was a great pleasure to me to conduct this thesis under his supervision.

I also owe a debt of gratitude to Barış Kışkan for his kind guidance and help during the experiments.

I warmly thank all the members of Yağcı Lab for all their help and interest. Banu Köz, Yasemin Yüksel Durmaz, Binnur Aydoğan, Burçin Gacal, Demet Göen Çolak, M.Atilla Taşdelen, Görkem Yılmaz, Mihrace Ergin, Muhammed Kahveci, Dilek Sureka and Hakan Akat with all of you, it has really been a great pleasure.

I wish to express my special gratitude to Filiz Tezcan for her support, encouragement and patience.

Finally, I would like to thank to my family for their support, encouragement and endless patience.

Ocak 2008 Manolya KUKUT

TABLE of CONTENTS

LIST of ABBREVIATIONS

PB : Polybutadiene
SBS : Styrene-butadiene-styrene triblock copolymer
THF : Tetrahyrofuran
DMF : *N*,*N*-dimethylformamid
GPC : Gel Permeation Chromatography
TGA : Thermal Gravimetric Analysis
NMR : Nuclear Magnetic Resonance Spectroscopy
DSC : Differential Scanning Calorimetry
FRP : Free Radical Transfer Polymerization
Tg : Glass Transition State
Tm : Melting Point
DMSO :Dimethylsulfoxide
FT-IR : Fourier Transform Infrared Spectrophotometer
NaN_3 : Sodium Azide
PP-a : Mono-functional benzoxazine
PB-Benzoxazine : Benzoxazine functionalized polybutadiene
PB-Br : Brominated polybutadiene
Tmax : Maximum Weight Loss Temperature.
Yc : Char yields
Mn : Number Average Molecular Weight
Mw : Molecular Weight
PD : Polydispersity
NaOH : Sodium Hyrdoxide
$MgSO_4$: Magnesium Sulfate

LIST of TABLES

LIST of FIGURES

Page No

LIST of SYMBOLS

$\mathbf{n}$:The number of chain segments per unit volume
$\mathbf{k}$: Boltzmann’s Constant
$\mathbf{T}$: Temperature
∂ : Ideal stress behavior
λ_1 : Distortion in the 1 direction.

THERMALLY CURABLE BUTADIENES BY CLICK REACTIONS

SUMMARY

One of the most significant artificially synthesized materials are polybenzoxazines. Polybenzoxazines are derivatives of phenolic type resins that accomplish deficiencies of the traditional phenolics. Phenolic resins have excellent properties such as good mechanical strength, dimensional stability and flame retardance. In addition to these features polybenzoxazines also show nearly zero shrinkage during, low absorption of water, high char yield and non-toxic by-product upon curing. Benzoxazine monomer can be prepared from the reaction of a starting phenolic compound, formaldehyde and primary amines. Another important synthetic materials are rubbers. Rubbers have several desirable properties that allow them to have wide range of usage. Click chemistry brings another aspect to polymer chemistry and gives the opportunity to combine rubbers with benzoxazines to create a polymer with great features. Click reactions occurs between terminal acetylenes and azide by metal catalyst at room temperature. Click reactions are preferable reactions for modification because of moderate reaction conditions, high yields, short periods of reaction times and high selectivity, tolerance of functional groups, insensitivity of the reaction solvents. There is a wide range of application field of this reaction, which varies with the sort of polymers.

In this study, novel side-chain benzoxazine functional polybutadiene (PB- Benzoxazine) was synthesized by using “Click Chemistry” strategy. First, approximately 10% of double bonds were brominated with Br_2 in CCl_4 then these bromo groups 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, azido functionalized PB 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 PB containing benzoxazine undergoes thermally activated curing in the absence of any catalyst forming PB thermoset with high char yield.

Keywords: thermoset, click reactions, polybutadiene, benzoxazines, polybenzoxazines

KLİK KİMYASI ile ISISAL SERTLEŞTİRİLEBİLEN POLİBUTADİENLER

ÖZET

Önemli sentetik malzemelerden biri olan polibenzoksazinler fenolik reçinelerin bir türevi olup, geleneksel reçinelerin dezavantajlarını ortadan kaldıran polimerlerdirler. Fenolik reçinelerin sahip olduğu mekanik dayanıklılık, yanıcı olamama gibi özelliklerine ek olarak kürleme sırasında geçekleşebilcek hacimce küçülmenin olmaması, düşük su absorpsiyonu, kürleme sırasında toksik yan ürünlerin olmuşmaması ve yüksek verimlilikle char eldesi gibi avantajlara da sahiptirler. Benzoksazin monomerleri fenolik bir bileşik ile başlanarak formaldehit ve primer aminlerin reaksiyonu ile sentezlenebilirler. Sahip olduğu mükemmel özelliklerden dolayı büyük öneme sahip sentetik malzemelerden biri de kaçuklardır. Kullanım alanları oldukça geniş olan kauçukların, polimer kimyasına başka bir bakış açısı getiren klik kimyası ile benzoksazin grupları içeren polimerlerinin sentezleri mümkün olabilir. Klik reaksiyonları terminal asetilenler ve azidler arasında gerçekleşen reaksiyonlardır. Klik reaksiyonlarının tercih edilir olmalarının sebepleri arasında; makul reaksiyon koşullarında gerçekleştirilebilmeleri, yüksek verim alınabilmesi, yüksek seçicilik ile gerçekleşmeleri, fonksiyonel grup çeşitliliğine olanak sağlamaları, kısa reaksiyon sürelerine sahip olmaları ve kullanılan çözücülere karşı hassas olmamaları gösterilebilir. Klik reaksiyonlarının uygulama alanları kullanılacak polimer tiplerine bağlı olarak çeşitlendirilebilir.

Bu çalışmada polibutadienin uygun koşullarda bromlanarak aizdleme reaksiyonuna hazır hale getirilip, polibutadienazid elde edilerek klik kimyası uygulanarak propargilbenzoksazin fonksiyonlarının polybutadiene bağlanarak halka kapanması reaksiyonlarının gerçekleştirilmesi ve böylece yüksek oranlarda ısıya dayanıklı özellikteki polimerlerin elde edilmesi amaçlanmaktadır. Bu yöntemle azidleme ve klik reaksiyonu sonucunda polibutadienin mekanik özelliklerindeki değişimler ve avantajları incelenecektir.Benzoksazin fonksiyonu içeren polybutadienlerin ısısal olarak sertleştirilebilir oldukları gösterilmiştir.Sentezlenen polimerlerin molekül ağırlıkları ile polidisperistelerinin belirlenmesinde GPC kullanılacaktır.

Anahtar Kelimeler: termoset, click reaksiyonları, polibutadien, benzoksazin, polibenzoksazinler

INTRODUCTION

With recent advances in technology, chemistry has accelerated its growing pace in its several branches. Technology is based on polymer science which has shown an incredible boost within past fifty years. As the technology develops, the need for new materials to be synthsized is increasing. One of the most promising material is benzoxazine polymers which have high mechanical properties, expansion or near-zero shrinkage during polymerization. On the contrary with the materials contain hydroxyl groups, benzoxazines provide low absorption of water and also excellent dimensional stability. Phenolic resins have low Tg which is a shortcoming of these type of resins but, polybenzoxazines have high Tg values. Furthermore, flexibility of molecular design, non toxic by-products are some of the advantages of polybenzoxazines. Moreover, polybenzoxazines are very stable when they are heated or exposed to UV light and it is easy to synthesize benzoxaznine monomers. Another important synthetic materials are rubbers. Synthetic rubber is any type of artificially made polymeric material which acts as an elastomer. They have amazing mechanical properties, which can be improved, allow them to recover after applied stress with no deformation. In addition to that, synthetic rubbers can be synthesized by polymerization. Monomer types can vary like 1,3-butadine or isobutylene. There is a wide usage area of rubbers like tires, motor vehicles, pharmaceuticals etc…In conclusion; the world needs new materials with superior properties for advanced technology. Therefore, there is a way of having a polymer by combining benzoxazines with rubbers via click chemistry. This kind of polymer which would have unique features deserves a great attention.

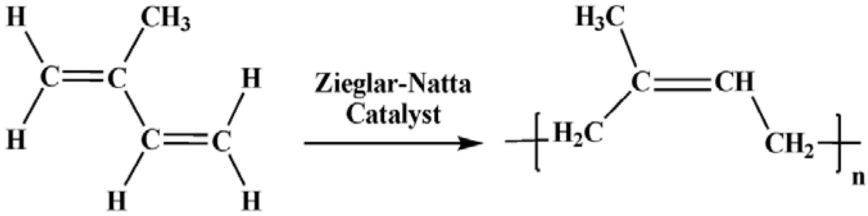
2. THEORETICAL PART

2.1 Rubber

Hydrocarbon polymers which can be found in the cauline of plants are milky colloidal suspensions and they are called rubber [4]. Rubber was first discovered in 1771 by Joseph Prisetly [4, 6]. In its native Central America and South America, rubber was collected for a long time [7]. Rubber has a wide range of usage area begins from household products to tires and tubes. Tires and tubes constitute 56 % total consumption of rubbers [8]. Based on its origin, rubber can be divided into two; natural rubber and synthetic rubber [6].

2.1.1 Natural Rubber

The most famous example of natural rubber is polyisoprene which can be obtained from para rubber tree called Hevea Brasiliensis [9]. Polyisoprene can be synthesized by polymerization of isoprene monomer with Zieglar-Natta catalyst (See Figure 2.1) [1, 2]. Natural rubber can be stretched out and it will return to its original shape upon relaxation. It shows the same mechanical properties with thermoplastics and sometimes even with elastomers [9].Most thermoplastics are high molecular weight polymers and they known as plastics in daily life. A thermoplastic can be melted to liquid by heat and freezes to brittle [34, 35].Also, it can undergo heating and cooling processes over and over [10, 11]. Because of that, it can remould by reheating and that makes it recyclable. Thermoplastic polymer chains can be either linear or branched. These chains stay associated with the effect of London forces, hydrogen bonds and polar interactions. Thermoplastics have amorphous structure, which makes thermoplastic flexible below their Tg values.



(2.1)

Figure 2. 1 Polymerization of isoprene

2.1.2 Synthetic Rubber

The types of polymeric materials, which are artificially made and show elastomer features, are called synthetic rubbers [1-3, 5]. An elastomer remains between the Tm and Tg points. Most of them have amorphous structure. If a stress is applied to an elastomer, it can return to its original shape without permanent deformation by the movements of the backbone [74]. This behavior can be explained in two ways.

Firstly, randomly grew polymer chain has higher entropy than organized polymer chain. As the stress is removed polymer chain prefers its previous size, which has higher entropy [74]. The second reason why a permanent deformation does not occur is coiled-up polymer chains can be inter-linked. These inter-links not only protect the polymer coil from split off and keep attached together but also prevent from permanent deformation [74].

Figure 2.2 shows stressed (B) and unstressed (A) polymer. The dots represent cross-linking points where the polymeric chains linked to each other. After the applied force is removed, polymer returns to the A configuration. This type of presentation is generally accepted as ‘spaghetti and meatball’ structure [74]. There exist many ways to achieve cross-linking between polymer chains. For example, some polymers can be cross-linked by vulcanization process which imparts elastomeric properties to the initial polymer [13, 25].

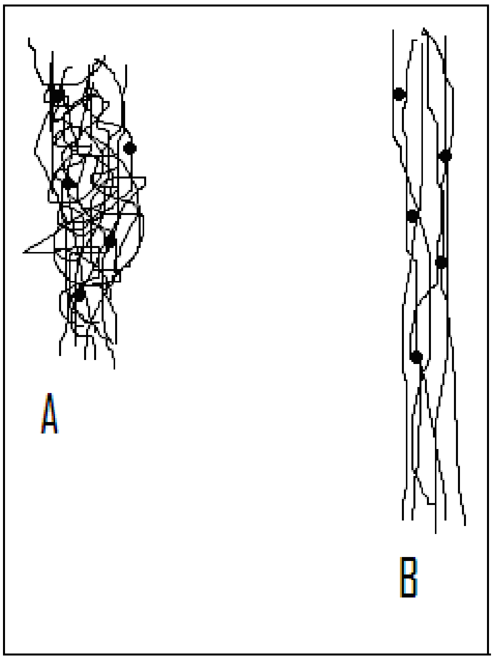


Figure 2.2 Representation of stressed polymer

%1-3 Sulfur is enough to have elastomeric behavior. It should be pointed out that the excess of sulfur cause thermosetting properties [73]. Also we can find the ideal stress behavior by using the laws of thermodynamics;

$$\sigma \ = nkT[\lambda\ _1^2 + \lambda\ _1^{-1}] \tag{2.2}$$

where, *n* is the number of chain segments per unit volume, *k* is Boltzmann’s Constant, *T* is temperature, and λ_1 is distortion in the 1 direction [13].

Polybutadiene (PB), styrene-butadiene-styrene triblock copolymer (SBS), nitrile rubber etc… are good examples for elastomers.

2.1.2.1 Polybutadiene (PB) Rubber

Polybutadiene (PB) rubber is the second largest volume synthetic rubber produced. Upon low transition temperature, cured PB rubber have low rolling resistance and corrosion resistance [3,36]. Butadiene rubber is usually blended with Styrene-butadiene-styrene (SBS) rubber or natural rubber in order to improve its poor absorption of water (wet traction). A research indicates that, 20.000 tons of high *cis*-PB is used each year in golf ball spheres and also coat of electronic assemlies is butadiene rubber due to its high resistance to electricity [33, 12].

PB is a homopolymer synthesized from the corresponding 1,3-butadiene monomer.

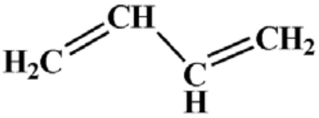


Figure 2. 2 Structure of 1,3 butadiene

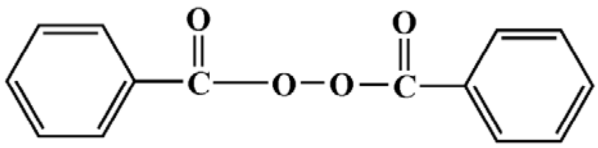
Although 1,3-butadiene undergoes free radical polymerization (FRP) to form PB, the polymerization may lead to some side reaction including cross-linking due to the nature of the monomer [15]. When the polymerization involves between the double bond of C_1-C_2 the polymer contains side chain reactive groups capable of creating cross-linkinking (*vide infra*). However with Zieglar-Natta catalyst it is possible to obtain completly linear polymers [14]. It is the most common and useful reaction to form a polymer from vinyl monomers [72].

FRP has for main steps:

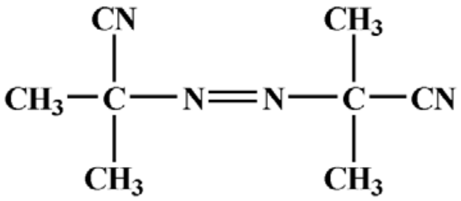
1. Initiation
2. Propagation
3. Transfer Reactions
4. Termination

There are three types of initiators such as organic peroxides, azo compounds and peresters for the initiation step of free radical polymerization (See Figure 2.4) [68, 69] .

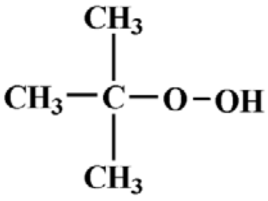
These molecules produces radicals to initiate the polymerization by decomposition (See Figure 2.4).



Benzoyl peroxide



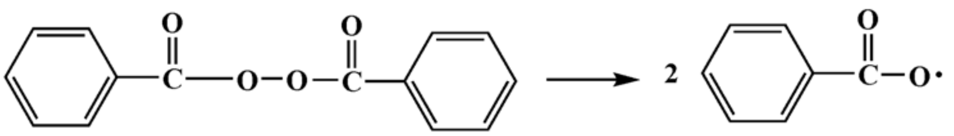
2-2 Azo-bis-isobutyronitrile



Perbenzoate

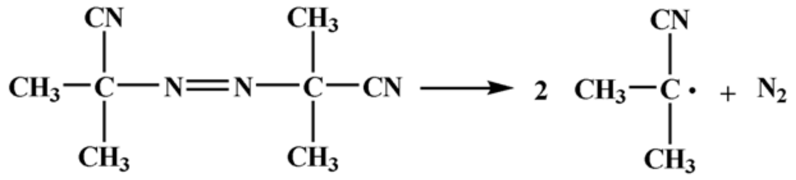
Figure 2. 3 Structures of FRP initiators

The adding of more and more monomer molecules to the growing chains is called propagation [22, 70]. Propagation step occurs very fast in FRP because of that there are always high weight polymers and unreacted monomers in the reaction mixture [71].



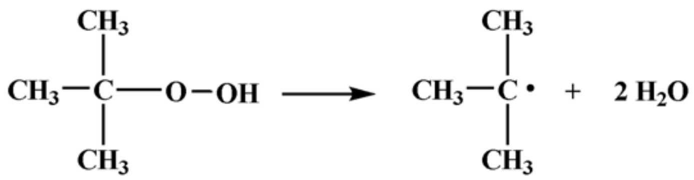
(2.3)

Decomposition of benzoyl peroxide



$$CH_3-\overset{CN}{\underset{CH_3}{C}}-N=N-\overset{CH_3}{\underset{CH_3}{C}}-CN \longrightarrow 2\ CH_3-\overset{CN}{\underset{CH_3}{C}}\cdot + N_2 \qquad (2.4)$$

Decomposition of 2-2'azo-bis-isobutyronitrile



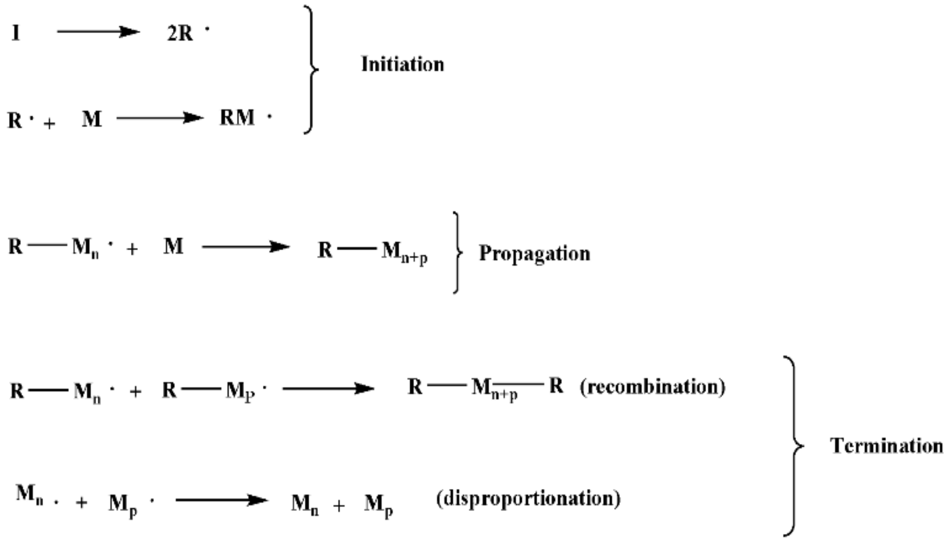
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-OH \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}\cdot + 2\,H_2O \qquad (2.5)$$

Decomposition of perbenzoate

Figure 2. 4 Decompositions of FRP initiators

The third step of FRP is transfer reactions. As the transfer reactions occur, growing side of the polymer which is the chain end will be removed. These reactions can exist between molecule of solvent or initiator or monomer [70].

Termination process usually includes two types of reactions, recombination and disproportionation [70].



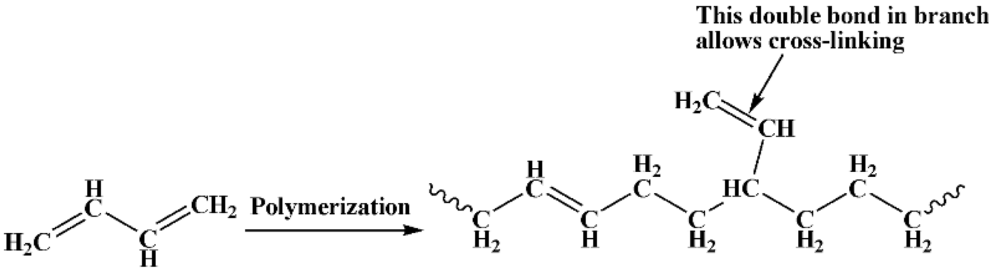
(2.6)

(2.7)

(2.8)

Figure 2. 5 Various steps of FRP

As mentioned before, PB can synthesized by with the presence of Ziegler-Natta catalyst. This catalyst which is a transition metal, helps to generate linear polymers. If the Ziegler-Natta catalyst is used during polymerization of butadiene the final product would be *cis*-PB (See Figure 2.7) [18].But without the catalyst vinyl structures occur on the polymer chain. Vinyl side groups make the polymer avaliable for branching or cross-linking (See Figure 2.8) [16,17].Vinyl tends to increase Tg of the polymer and this is an undesirable condition for rubbers. On the other hand, *cis*-PB has lower Tg and higher cut-growth resistance compared to polymers with vinyl structure after curing[20]. As explained before PB rubbers are mostly used in tires and *cis*-PB rubberss are the most suitable materials for this purpose [19].



(2.9)

Figure 2. 6 Polymerization of butadiene without catalyst

2.1.2.2 SBS Rubber

SBS rubber is a block copolymer consists of butadiene and styrene units. SBS shows plastomer properties [20]. A plastomer is also known as thermoplastic elastomers which behaves like an elastomer without corss-links between the polymer chains [15]. Polystyrene and PB are not suitable polymer types for each other. That means, they do not constitute homogenous mixture [74]. Each polymer prefers to stay seperate phases (See Figure 2.9). Consequently, polystyrene blocks on the copolymer chain, form groups in order to stay together [74]. An outcome of this behavoir of polystyrene, polymer network seems like cross-linked PB by polystyrene groups (See Figure 2.10). When the SBS rubber is heated, polystyrene blocks split off and when it is cooled polystyrene blocks form groups again. This attitude of polymer makes it malleable [74].

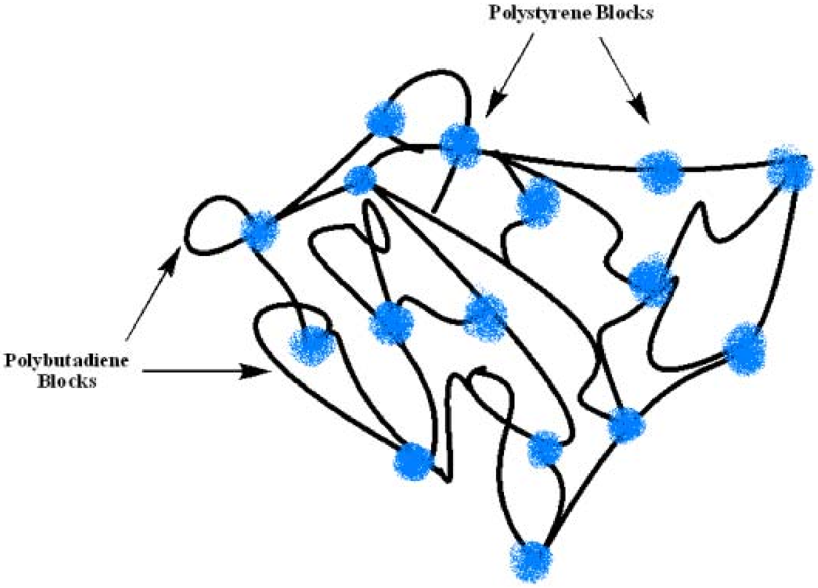


Figure 2.10 Representation of SBS rubber under stress

SBS rubber can be synthesized by living-anionic polymerization. This type of polymerization has only two steps (See Figure 2.11).

1. Initiation
2. Propagation

There would be no termination until all of the monomer has been consumed.

Addition of monomer will let the polymerization continue. This is why it is called living polymerization.

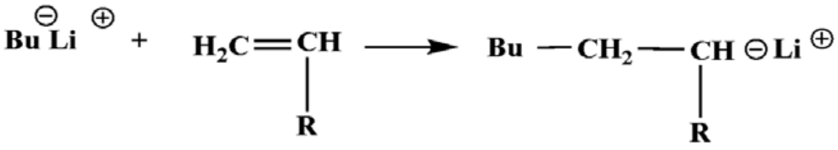
$$I^{\ominus} + M \longrightarrow I{-}M^{\ominus} \quad \Big\} \ \textbf{Initiation} \qquad \textbf{(2.10)}$$

$$I{-}M^{\ominus} + M \longrightarrow I{-}M_{n+1}^{\ominus} \quad \Big\} \ \textbf{Propagation} \qquad \textbf{(2.11)}$$

Figure 2. 7 Various steps of anionic polymerization

There are two types of initiators for living-anionic polymerization.

1. **Metal organic initiators :** Butyl lithium is the simplest example for this type of metal organic initiators. An example is shown below.

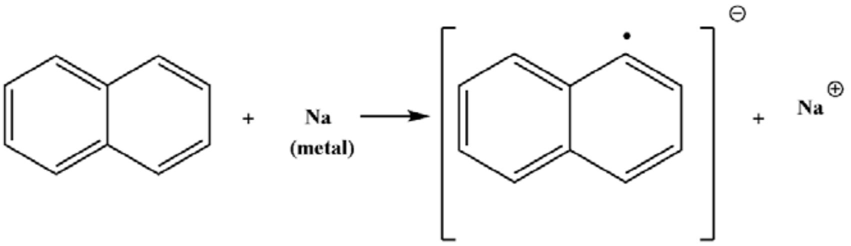


$$\overset{\ominus}{Bu}\,\overset{\oplus}{Li} + H_2C{=}CH(R) \longrightarrow Bu{-}CH_2{-}CH(R)^{\ominus}Li^{\oplus}$$

(2.12)

Figure 2. 8 An example of metal organic initiators

2. **Radical-Ionic initiators :** Biphenyl and napthalene are the best initiators as radical-ionic initiator. (See Figure 2.13)



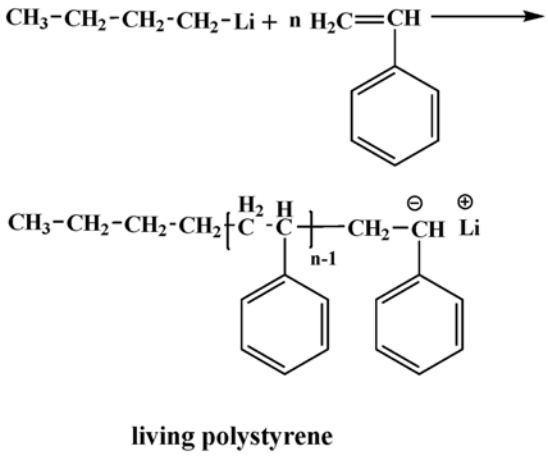
(2.13)

Figure 2. 9 An example of radical-ionic initiators

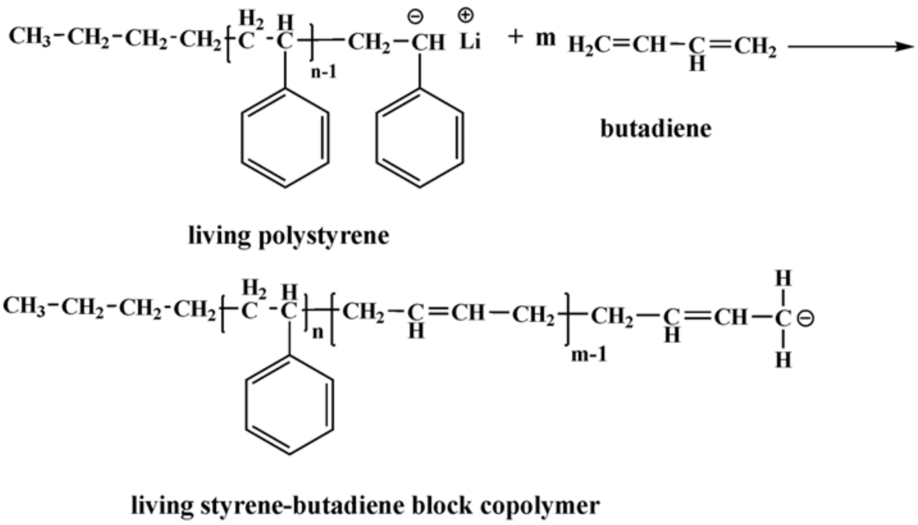
Interaction between Na metal and chosen aromatic hydrocarbon results in electron source species. And this specie will transfer the additional electron back to the any compound which has higher electron affinity than itself.

After the initiation (the electron transfer) species undergo dimerization to yield dianions and polymerization proceeds from these two ends.

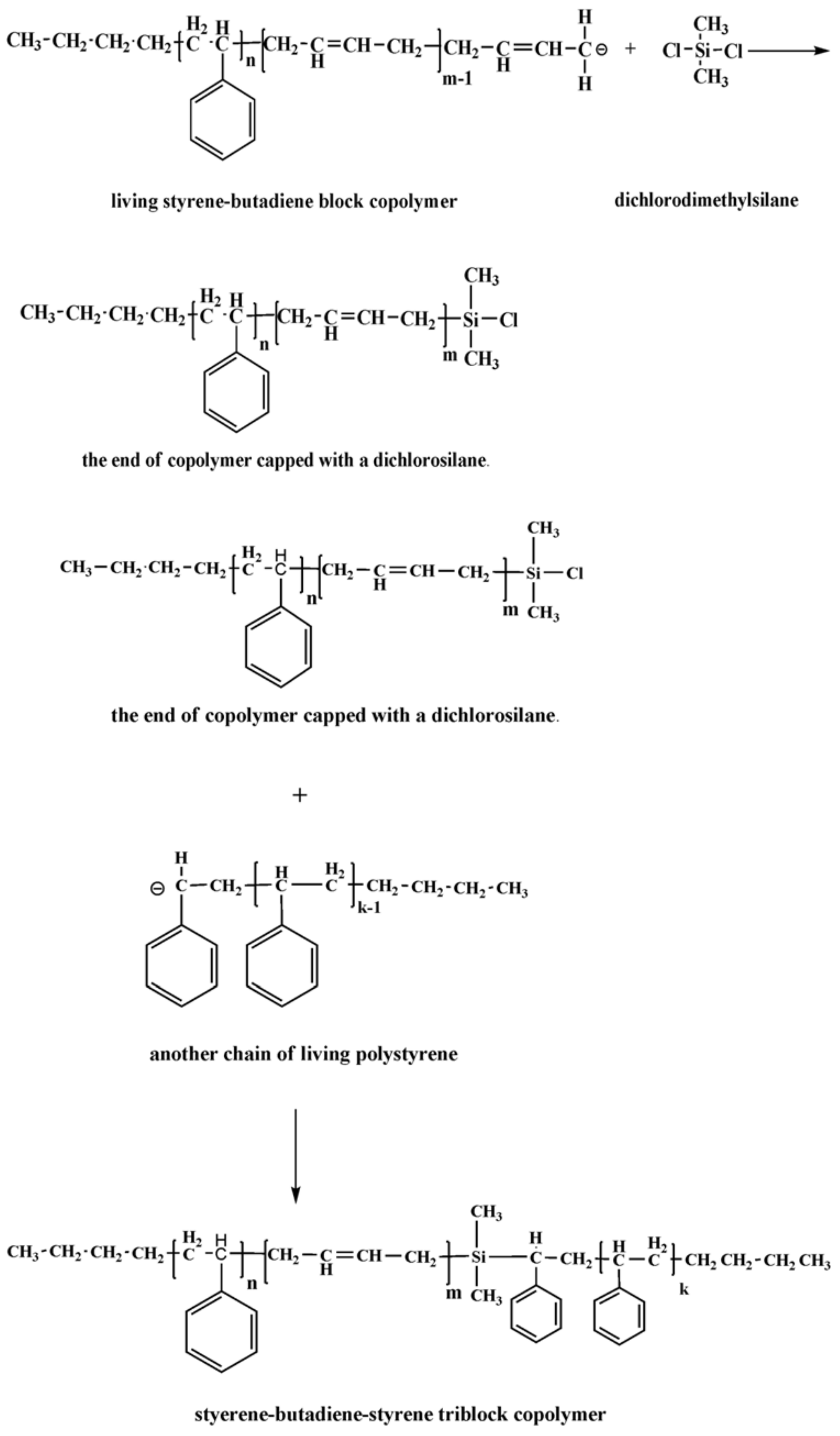
Synthesis of SBS rubber by living-anionic polymerization is shown in Figure 2.14.



(2.14)



(2.15)



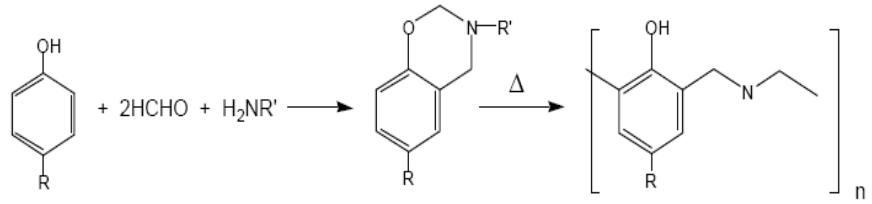
(2.16)

(2.17)

Figure 2. 10 Synthesis of SBS rubber

2.2 Benzoxazines

One of the most significant artificially synthesized materials are polybenzoxazines. Thus, their popularity in scientific society results the researcher to incline on them every each day. This material can be described as a phenolic resin derivative, obtained from the reaction of a starting phenolic compound, formaldehyde and primary amines [28.29]. These polymers can be produced thermally. The proceeding reactions can be performed either in the presence or absence of initiators and catalysts. Basic reaction scheme can be demonstrated as follows [30]:



(2.18)

Figure 2. 11 Basic reaction Scheme for monomer synthesis and polybenzoxazine formation

2.2.1 Features of Benzoxazines

Thermally produced polymers have attracted more attention due to their typical characteristics [28, 29].As Ishida asserts; benzoxazine resins offer several very unusual properties few polymers are known to exhibit. First, they have expansion or near-zero shrinkage upon polymerization [75, 76]. Moreover, they provide low absorption of water and excellent dimensional stability because of a low shrinkage upon curing, which cannot be found in the traditional phenolic resins. Secondly, these materials possess very high char yield in spite of higher aliphatic content than traditional phenolic resins, much higher hydrophobicity than epoxies and phenolics in spite of high concentration of hydrophilic groups in the polymer chain structure [75, 76].As indicated above, polybenzoxazines' heat resistance character is as a result of char formation and this formation can clearly be seen in the following chart (See Figure 2.16) [30]:

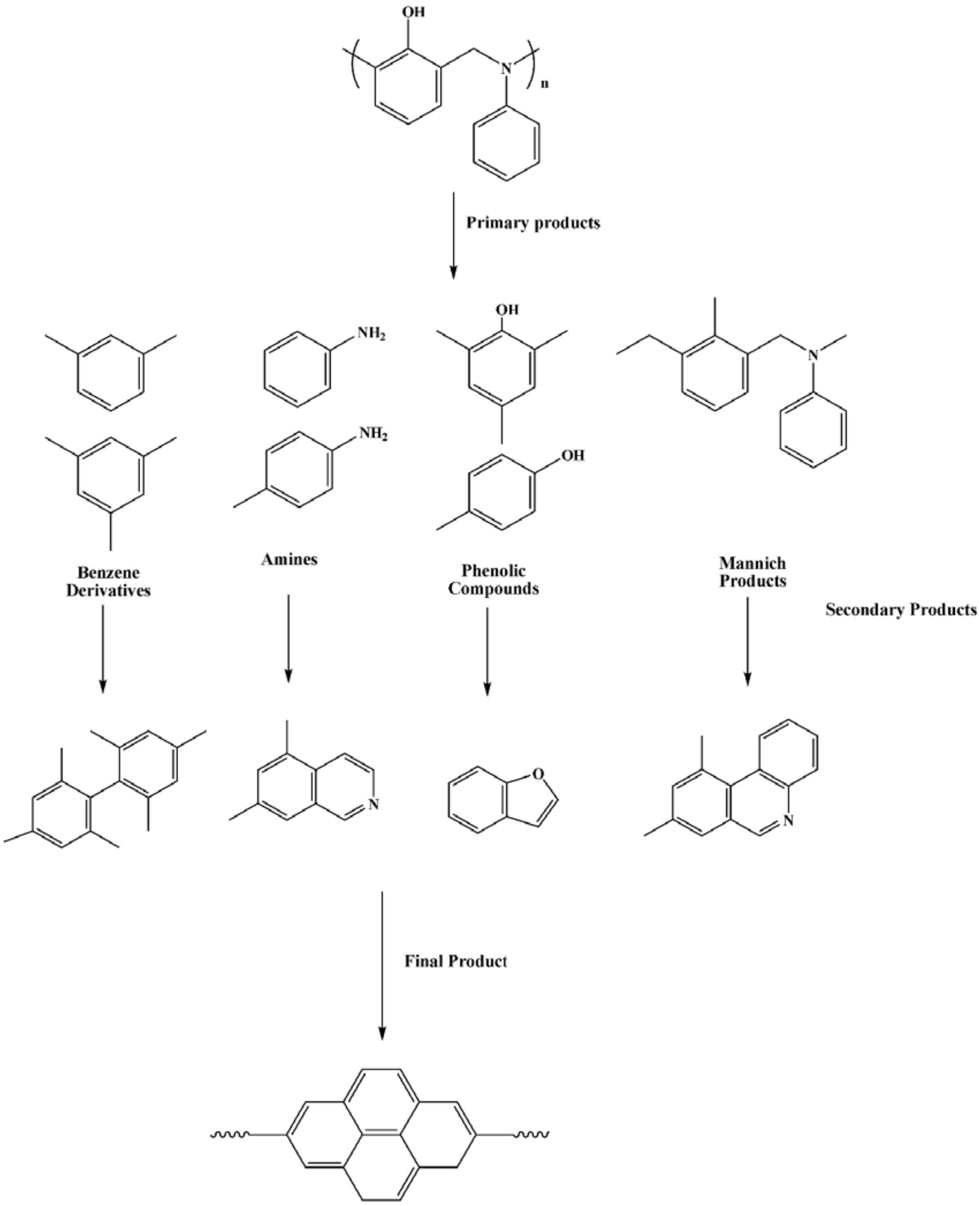


Figure 2. 12 Char Formation

Moreover, their good anti-flammability characteristics can be clearly seen from the below illustration:

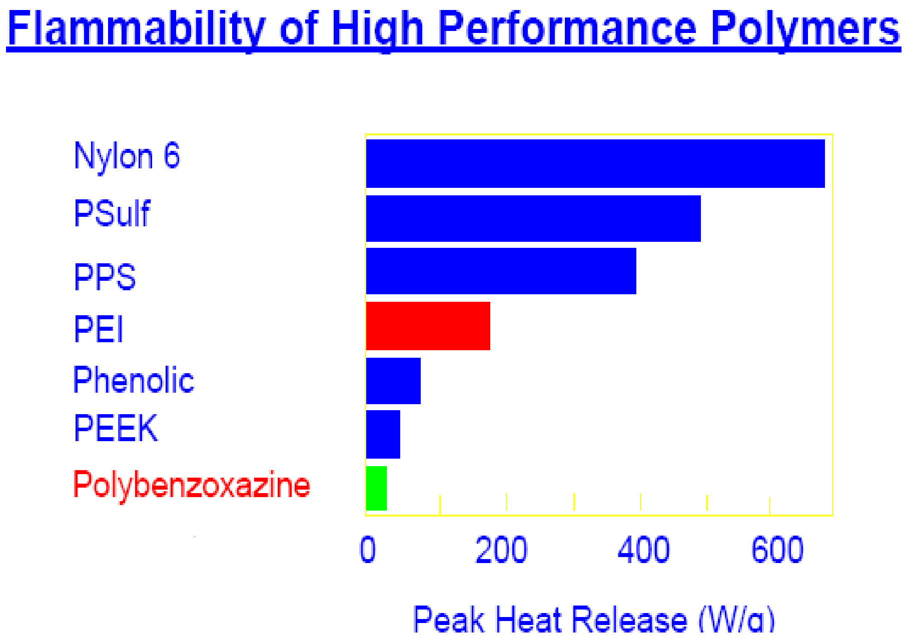


Figure 2.13 Flammability of high performance polymers

Thirdly, development of materials with high mechanical and physical properties at low conversion can be achieved by extremely rich molecular design flexibility.

From the thermal history of this compound suggests that, the polymerization of benzoxazine monomers occurs through heterocyclic ring opening at high temperatures in the absence of a catalyst and without generating any by-products [76]. DCS analysis of benzoxazine which shows the exotherm of ring opening reactions is shown in Figure 2.18 [37]. Consequently, benzoxazine monomers are able to polymerize by ring –opening mechanisms due to heat, presence of catalysts or when exposed to UV light [76].

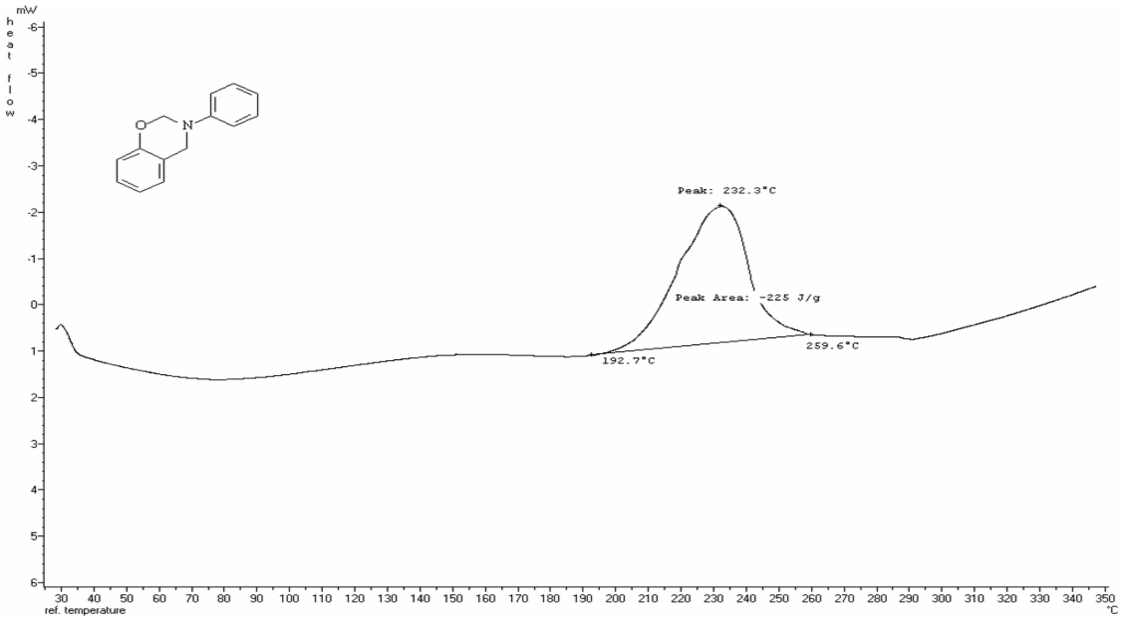


Figure 2. 14 DCS analysis of benzoxazine

2.2.2 Significance of Benzoxazines

Polybenzoxazines can construct these superior properties, in various applications where a high – performance material is needed. Furthermore, it can be said that their significance increases due to their ease in preparation [76].It can therefore be generalized that benzoxazine-based polymeric systems possess distinguishable superiorities, which can be categorized as follows: monomer synthesis, polymerizability, structural variations offered by the polymerization method, and high performance properties of the resulting polymers [32]. Besides this, it is suggested that their high - performance properties as thermosetting resins can further be improved by tightening their network structure [32]. Moreover additional properties for specific applications such as processability, flame retardancy, and mechanical strength can be introduced in several ways. For example, the thermal and mechanical properties of polybenzoxazines can be improved by blending with a polymer or clay [76].Maleimide-based benzoxazine polymers exhibit better thermal stability and high char yield which gives good flame retardancy [76-78].Similarly, chemical modification of novolac resins with benzoxazine rings, or the grafting of various phosphorous compounds to benzoxazine-modified resins, gives rise to non-flammable coatings. And also, benzoxazine monomers with additional polymerizable acetylene functional groups form highly thermally stable cross-linked networks [76]. In another example ortho-, meta-, and para-phenylnitrile-functionalized benzoxazines have been polymerized at different compositions with phthalonitrile functionalized monomers yielding copolymers with high thermal stability and easy processability.

2.2.3 Necessities for Modification of Benzoxazines

Monobenzoxazine and polybenzoxazines compounds have significant application as high-performance materials in semiconductor fabrication industry. As indicated previously, this is due to their high heat resistance, superior electrical properties, low penetration of water, no gas evaporation, low dielectric constant and lastly no shrinkage on cure. On the other hand, these materials' processability is limited because of high viscosity and their tendency to be brittle [75].Consequently, lack of flexibility leads them to not to be used in electronic devices where elasticity is required. In order to create new molecular designs, which are appropriate for electronic devices usages, curable compositions containing at least one monobenzoxazine or polybenzoxazine are needed [77].

2.2.4 Suitable Benzoxazine Compounds for Modification

The previous work suggests that the suitable benzoxazine compounds include those of formula [75-78] (See Figure 2.19, 2.20). Notice that R^1 may be aliphatic and aromatic or both and may contain heteroatoms like, oxygen, nitrogen, sulfur, phosphorous, or halogen.

Moreover, according to the same research, in addition to the below presented compounds, benzoxazines in the polymeric form may be synthesized [75-77]. The curable composition that contains the benzoxazine function has the w/w ratio within the range of 1 % or more to 99 %. We have previously reported on several synthetic strategies to combine benzoxazine structures with conventional polymers, namely polystyrene, poly (ε-caprolactone), poly (methyl methacrylate) and poly (propylene oxide).

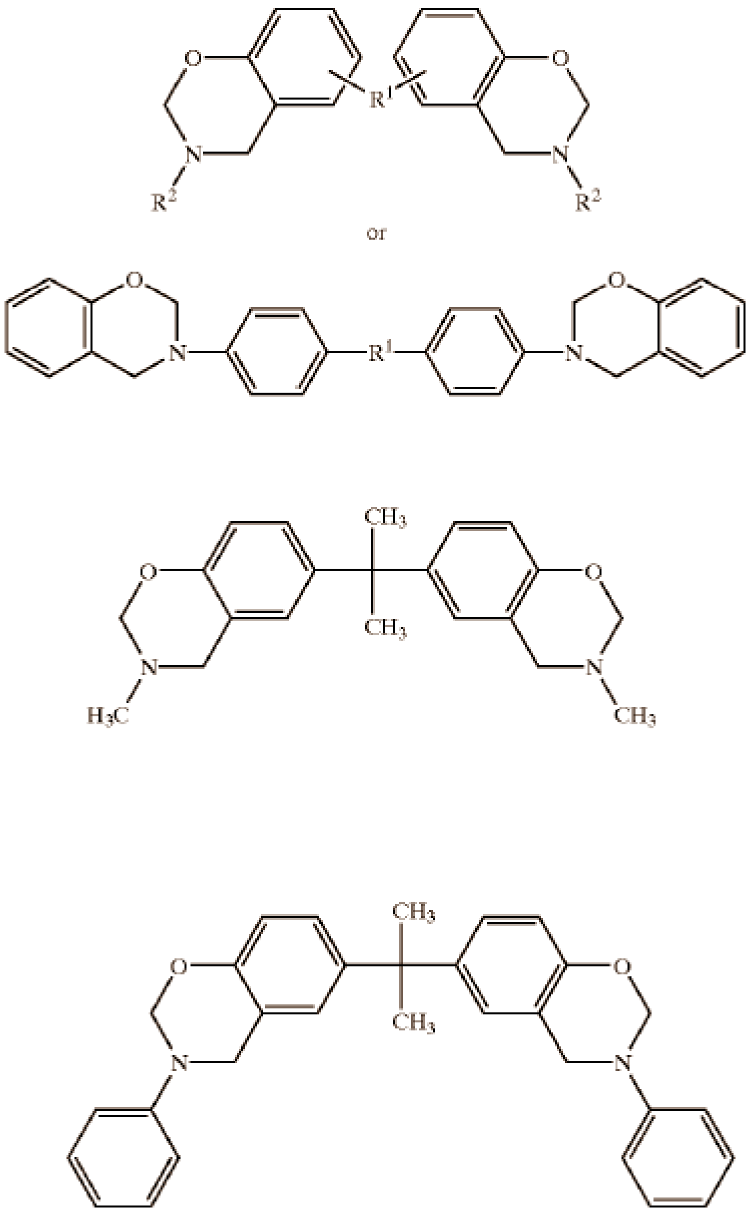


Figure 2. 15 Suitable benzoxazine compounds for modification

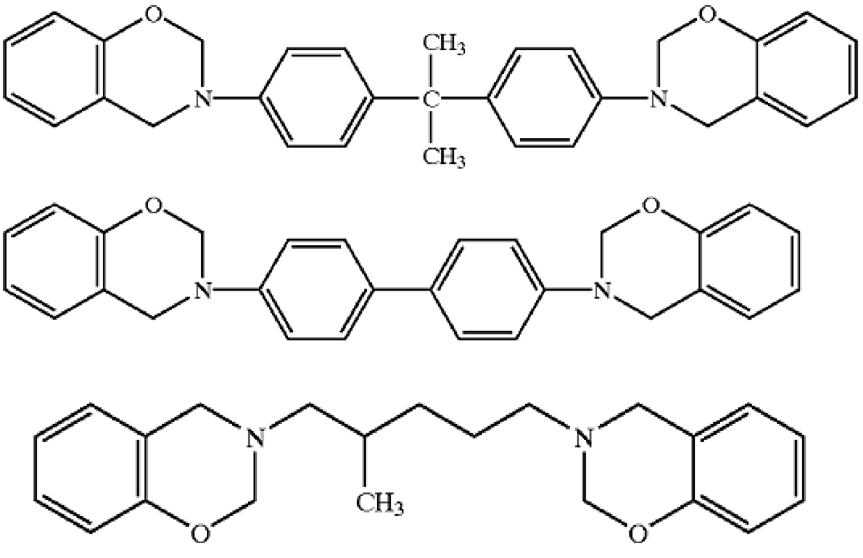


Figure 2. 16 Benzoxazine compounds for modification

The polymers contained one or two benzoxazine functionalities per chain and thermal ring-opening copolymerization of these macromonomers with low molar mass benzoxazines yielded cross-linked polybenzoxazines [76]. In these cases, the polymers are linked to the network structure as dangling chains. However, the incorporation benzoxazines as a thermally reactive group into the backbone or side-chains of conventional polymers has scarcely been investigated.

2.2.5 Formation of Curable Resins

The benzoxazines are preferably blended by the curable resins which have vinyl ethers, vinyl silanes, resins containing vinyl or allyl functionality, thiol–enes, or resins including cinnamyl or styrenic functionality, fumurates, maleates, acrylates maleimides, and cyanat esters [75] (See Figure 2.21, 2.22).

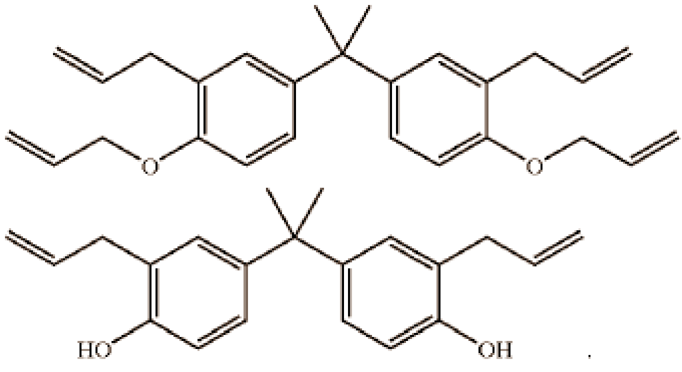


Figure 2. 17 Hybride Resins Including Both Epoxy and Cinnamyl or Styrenic Functionality

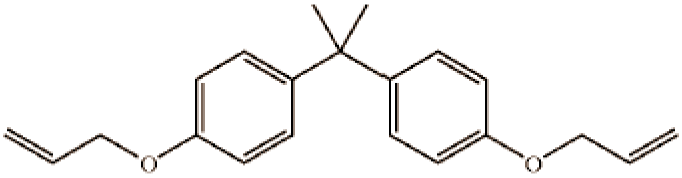


Figure 2. 18 Hybride Resins Including Both Epoxy and Cinnamyl or Styrenic Functionality

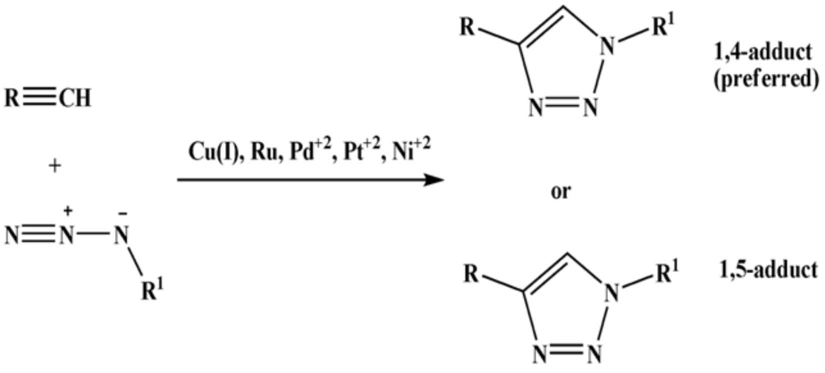
2.2.6 Rubber Modified Benzoxazines

Main problem of thermosets is being brittle. Modifying thermosets with rubber is a way of managing the problem [76, 79, 80]. Cavitations of rubber species may be a reason for rigit structure but it is not the only reason for it [81, 82]. Reasons for brittleness differ from particle size, particle size distribution to matrix-to-particle adhesion [76, 86-84] .The effect of cavitations of rubber is not only a reason for strict structure, but also it has an impact on plastic deformation of the network [76]. The mechanism of the deformation by rubber species can be divided into two; (i) shear yielding of matrix between the neighboring rubber particles and (ii) plastic void growth of the matrix surrounding the particle [83, 85]. According to properties of liquid rubbers like low viscosity and polarity, which is mostly preferred for modification of epoxy, resins can be used to soften the benzoxazine structure [81, 82, 84].

2.3 Click Reactions

The reaction that gives opportunity to attach ligands onto polymers for modification is called click reaction and it is also known as Sharpless ‘click’ reaction [26, 27]. This modification process provides; a) often quantitative yields, b) a high tolerance of functional groups c) an insensitivity of the reaction to solvents and d) reaction at various types of interfaces such as solid/liquid, liquid/liquid, or even solid/solid interfaces [27,73]. Click reactions are preferable reactions for modification because of moderate reaction conditions, high yields, short periods of reaction times and high selectivity [50, 63, 62]. There is a wide range of application field of this reaction, which varies with the sort of polymers [64]. Click reactions enabled the C-C bond formation in a quantitative yield without side reactions and requirement for additional purification steps. Click reactions are particularly important in preparative methods, in which high conversion of functional groups is desirable [51-53]. Numerous applications of click chemistry in polymer science as well as molecular biology and nanoelectronics have recently been reviewed [27, 26, 50].

Click reactions are derivatives of Huisgen 1, 3 dipolar cyloaddition reactions and occurs between terminal acetylenes and azides by metal catalyst at room temperature (See Figure 2.23) [26, 44, 45].Ru, Ni, Pt, Pd and especially Cu (I) species can be used as catalyst for click reactions [61-63]. As stated by several authors, these metals speed up the reactions [62, 63].



(2.19)

Figure 2. 19 Azide/alkyne-type click reactions

2.3.1 Suitable Compounds for Click Reactions

Exceptions of self-reactive reagents and materials that can produce stable complexes with Cu (I), all functional groups are suitable for click reactions [58-60]. The figure shows the compounds, which are not suitable for, azide/alkyne-type click reactions because of the Huisgen 1, 3 dipolar cyloaddition side reactions [55-57].

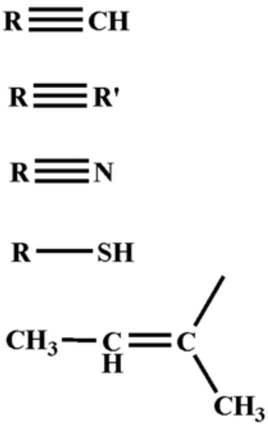


Figure 2. 20 Unsuitable compounds for azide/alkyne type click reaction

2.3.2 Mechanism of Click Reactions

As it mentioned before click reactions occurs between terminal acetylenes and azide by metal catalyst. The mechanism of click reactions first explained by Meldal and co-workers and Sharpless and co-workers [38, 58, 59]. Multifarious catalytic systems are present to affect the 1, 3-dipolar cycloaddition process. Cu (I) salts can be directly used or Cu (I) species can be obtained from the reduction of Cu (II) by sodium ascorbarte or metallic copper in catalytic systems [12, 58, 59].The mechanism of click reactions, shown below, depends on the Cu-acetylide formation [58, 59].

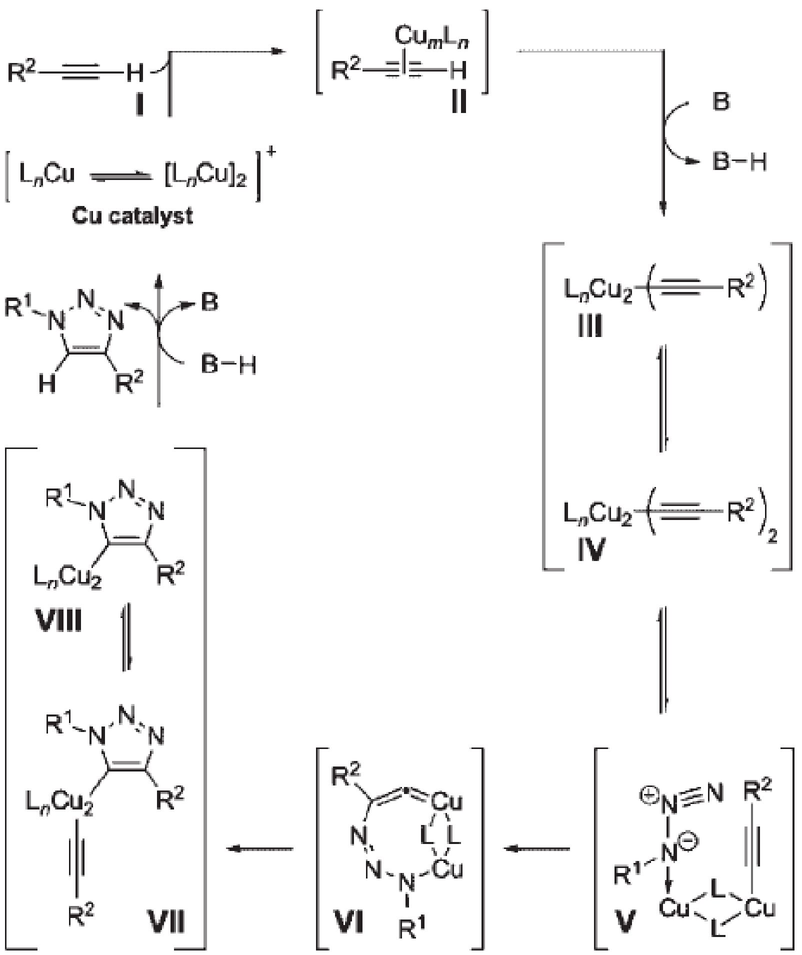


Figure 2. 21 Mechanism of click reaction

Terminal alkynes and Cu (I) particles produce a π-complex (Cu-acetylide) to lower pKa value of the terminal alkynes that allow attack onto C-H bond [63-65].In addition, 1-5 equivalents of base have positive influences on the formation of the copper (I)-acetylide. THF, diethyl ether, DMF, DMSO or halogenated solvents are applicable for click reactions. And also, water/alcohol or water/toluene systems can give excellent results [65-67].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Polymers

Polybutadiene (PB)

PB is kindly provided by Dr. Jergio Corona Galvan. It was used as recieved.

3.1.2 Solvents

Methanol (Technical)

Methanol was used for the precipitation of polymers without further purification.

Chloroform (Sigma)

Chloroform was used without further purification.

Tetrahydrofuran (THF) (J.T.Baker)

Predried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately before use.

***N,N*-dimethylformamid (DMF) (Merck)**

Predried over magnesium sulfate followed by sodium wire.

Carbon tetrachloride (J.T.Baker)

Carbon tetrachloride was used as solvent for PBR and SBS without further purification.

Ethanol (Aldrich)

Ethanol was used as recieved.

1,4-Dioxane (Sigma-Aldrich)

1,4 dioxane was used as recieved.

Diethylether (Sigma-Aldrich)

Diethylether was used as recieved.

3.1.3 Other Chemicals and Reagents

Sodium Azide (Carlo-erba)

It was used as received.

Acetic anhydride (Sigma-Aldrich)

Acetic anhydride was used as recieved.

HCl (Sigma-Aldrich)

HCl was used as recieved.

Sodium hydroxide (Sigma-Aldrich)

Sodium hydroxide was used as recieved.

Anhydrous magnesium sulfate (Sigma-Aldrich)

Anhydrous magnesium sulfate was used as received.

Phenol (Sigma-Aldrich)

Phenol was used as received.

Paraformaldehyde (Sigma-Aldrich)

Paraformaldehyde was used as received.

***p*-Aminophenol (Acros Organics)**

p-Aminophenol was used as received.

Propargyl bromide (Fluka)

Propargyl bromide was used as received.

Brom (Merck)

It was used as received.

2,2-Bipyridine (bpy) (Aldrich)

It was used as received.

Copper (I) Bromide (CuBr) (Aldrich)

It was used as received.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.2 Infrared Spectrophotometer (IR)

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

3.2.3 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed with a set up consisting of a Waters 410 Differential Refractometer, a Waters 515 HPLC Pump and an apparatus equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular weights were calculated on the basis of a calibration curve recorded with monodisperse polystyrene standards.

3.2.4. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) was performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 ºC min under nitrogen flow.

3.2.5 Differential Scanning Calorimetry (DSC)

Differential scanning Calorimetry (DSC) was performed on Perkin–Elmer Diamond DSC with a heating rate of 10 °C min under nitrogen flow.

3.3 Preparation Methods

3.3.1 Preparation of N-(4-hydroxphenyl) 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 ^{o}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 ºC)

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

In a 250 mL flask, of *N*-(4-hydroxphenyl)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 ^{o}C for 3 h. After neutralizing with aqueous sodium hydroxide, the solution was extracted with chloroform, and the organic layer was dried over anhydrous $MgSO_4$. 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 Preperation 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 Polybutadiene Bromine (PB-Br)

In a 100 mL flask, polybutadiene dissolved in 20 mL of carbontetrachloride was cooled by ice bath. To this solution, 5-6 drop of brom (Br2) was added. After about 2-3 hours, the precipitation was filtered. The product (See Figure 3.1) was dissolved in chloroform and precipitated into methanol (400mL), filtered and dried under vacuum.

3.3.6 Synthesis of PB-N3 Coploymer

Polybutadienebromine was dissolved in *N*,*N*-dimethylformamid (DMF), NaN3 (2 times excess to the mole of bromine of polybutadiene) was added. The resulting solutuion was allowed to stir at 25°C overnight and precipitated into methanol/water mixture (1/1 by volume).

3.3.7 Synthesis of Polybutadiene Containing Benzoxazine Side Groups (PB-Benzoxazine)

In a flask, PB-N3 (0.30 g), 3-(4-(prop-2-ynyloxy)phenyl)-3,4-dihydro-2H-benzo[e][1,3]oxzaine (0,4 g 1.5 mmol), copper(I)bromide (0,5, 3mmol), 2,2-bipyridine (0,9g, 7mmol), and dry THF (10mL) was 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 (200mL), filtered and dried under vacuum.

4. RESULTS and DISCUSSION

In this study, we tried to incorporate benzoxazine moieties into PB rubber by using "Click reaction". The synthetic strategy followed involves several steps. First benzoxazine monomer with suitable click functionality was synthesized. The other click component was formed on the rubber molecule. The final click step yields the desired rubber with curable benzoxazine functionalities**.** The various steps of the procedure will be described below.

4.1 Synthesis and Characterization of Propargylbenzoxazine

In this study, propargylbenzoxazine was selected as thermally reactive click component, which was prepared according to the modified procedure described by Agag and Takeichi [41]. The chemical structure of propargylbenzoxazine was confirmed by both FT-IR and ^{1}H-NMR.

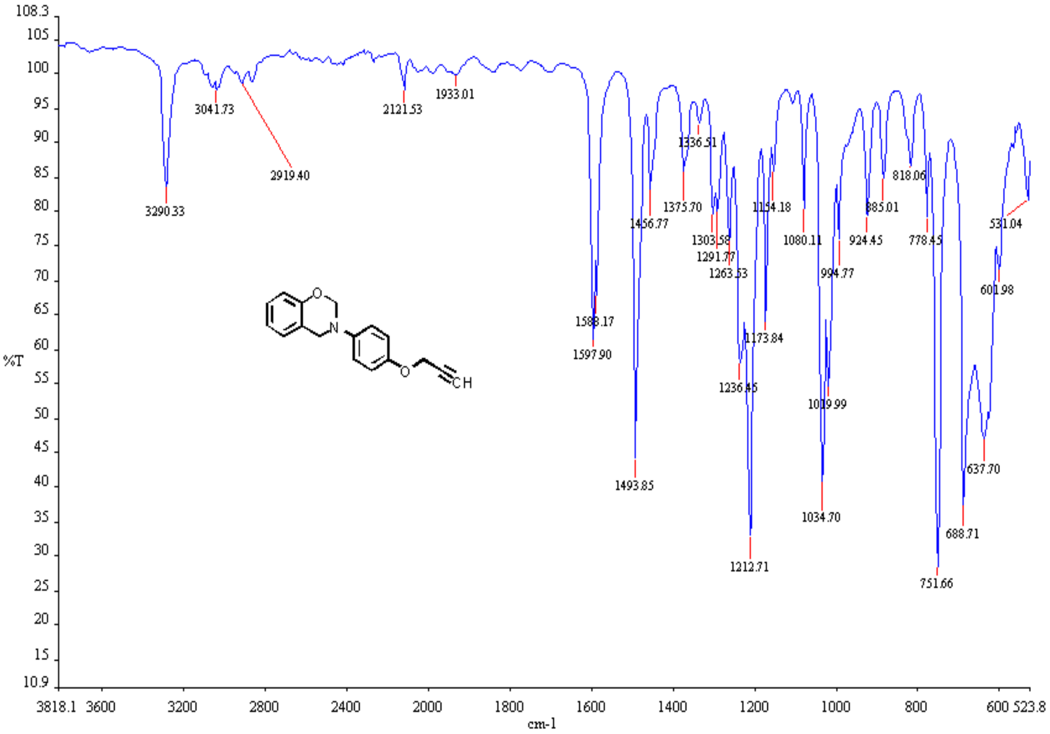


Figure 4. 1 FT-IR spectrum of propargylbenzoxazine

The characteristic absorptions of benzoxazine structure appeared at 1236 cm^{-1} (asymmetric stretching of C-O-C), 924 and 1493 cm^{-1} (trisubstituted benzene ring). The Click functionality, propargyl group was evidenced by characteristic bands of H-C≡ and -C≡C- appeared at 3290 and 2121 cm^{-1}, respectively (See Figure 4.1). The ^{1}H-NMR spectrum of propargylbenzoxazine showed a triplet at 2.5 ppm and a doublet at 4.5 ppm which are assigned to H-C≡ and CH_2 (See Figure 4.2). Also, N-CH_2-O and N-CH_2-Ar protons of oxazine ring are detectable at 5.3 and 4.6 ppms.

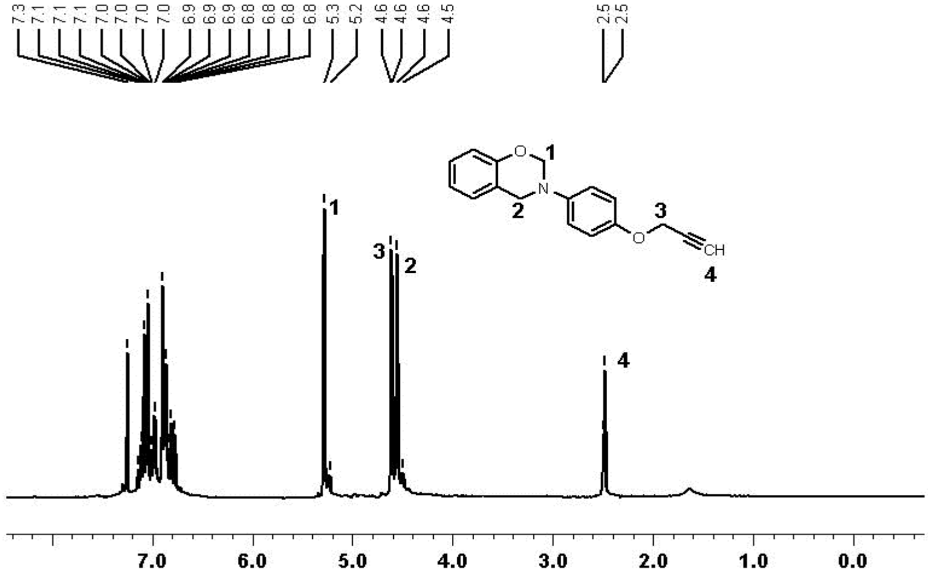
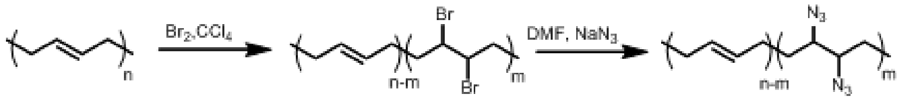


Figure 4. 2 ^{1}H-NMR spectrum of propargylbenzoxazine

4.2 Synthesis and Characterization of Azide Functional PB

For the synthesis of parent azide functionalized PB (PB-N_3), approximately 10% of double bonds were brominated with Br_2 in carbontetrachloride then bromo groups converted to azido groups by using NaN_3(Sodium Azide) in DMF (See Figure 4.3). Functionalization was kept deliberately at low level so as to preserve PB properties.



(4.1)

Figure 4. 3 Bromination and azidation steps of PB

The structure of PB-N_3 was further supported by the observation of the azide stretching band at 2094 cm^{-1} in the FT-IR spectrum of PB-N_3 presented in Figure 4.4b.

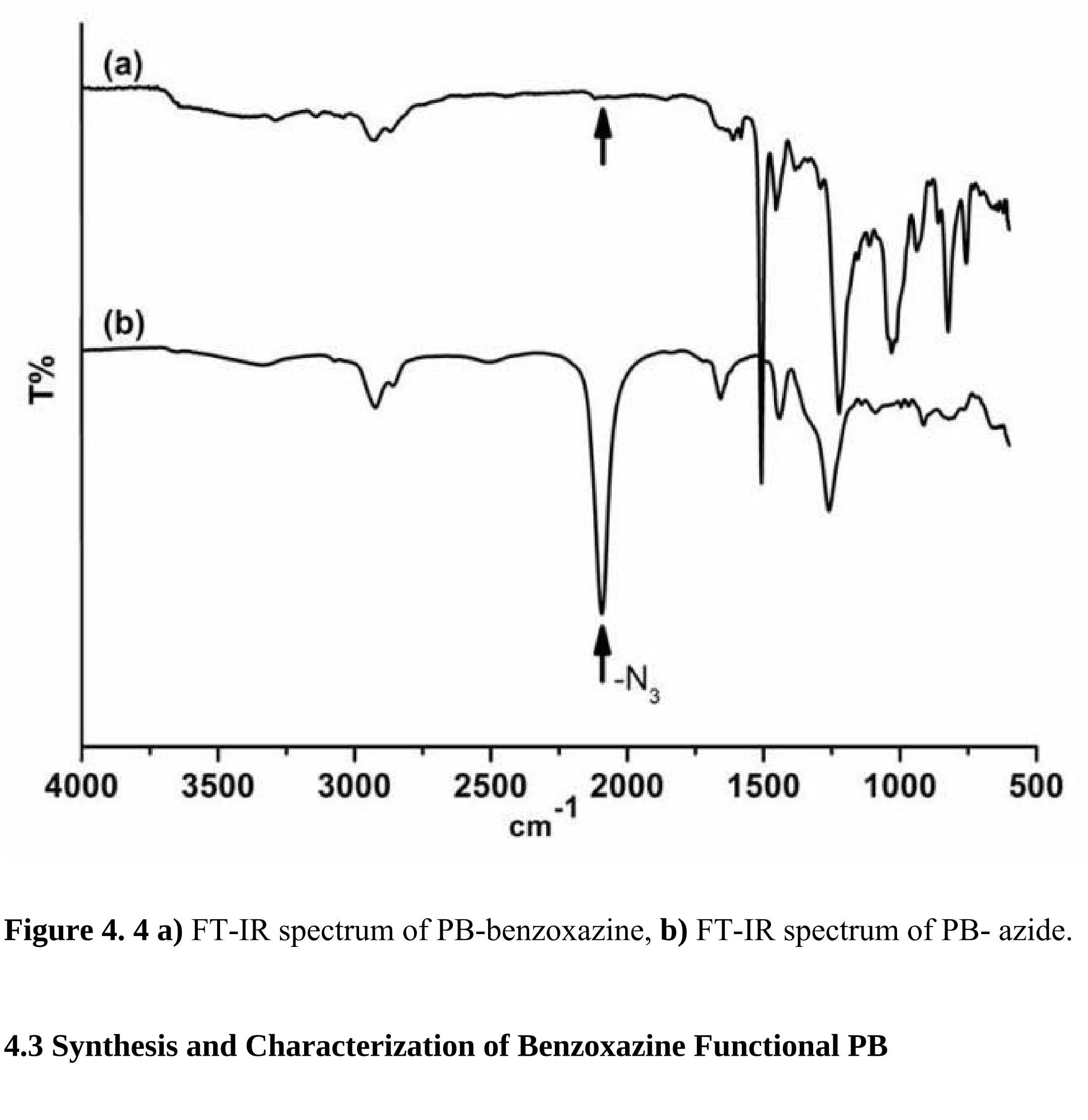
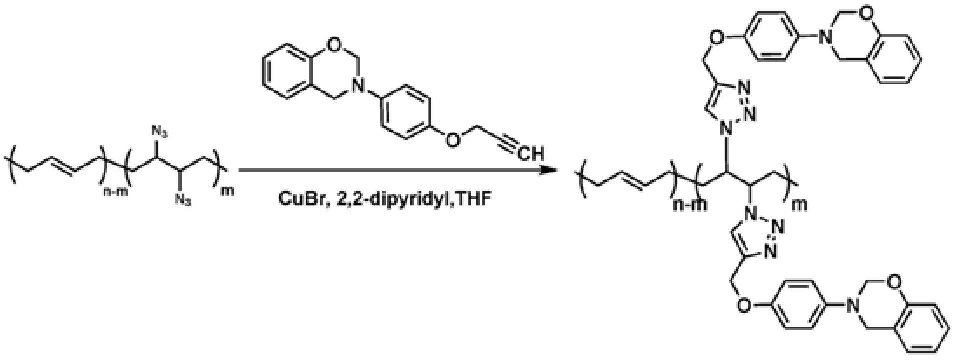


Figure 4. 4 a) FT-IR spectrum of PB-benzoxazine, **b)** FT-IR spectrum of PB- azide.

4.3 Synthesis and Characterization of Benzoxazine Functional PB

For the click reaction, the PB-N_3 was dissolved in THF and reacted with propargyl benzoxazine in the presence of CuBr/bipyridine ligand at room temperature (See Figure 4.5). After removing the catalyst by filtration, the polymer was precipitated and dried under vacuum. As far as the ultimate use of the resulting polymer (PB-

Benzoxazine) in thermal curing is concerned, two points were important; the extent of conversion of the side azido moieties to triazoles and the effect of click reaction on the stability of benzoxazine ring.



(4.2)

Figure 4. 5 Synthesis of PB-benzoxazine

The fist issue was monitored by ^{1}H NMR spectroscopy by observing the appearance of the new methylene protons adjacent to the triazole ring at 5.1 ppm (triazole-C$\boldsymbol{H}_2$-OPh) and the triazole proton (N-C$\boldsymbol{H}$=C-) at 7.6 ppm (Figure 4.6). Moreover, the band corresponding to -N_3 group at 2094 cm^{-1} completely disappeared (Figure 4.4a). Thus, the side group click reaction was efficient, as evidenced by near-quantitative functionalization. Besides, the presence of signals at 5.3 and 4.5 ppm in ^{1}H-NMR spectra corresponding to N-C$\boldsymbol{H}_2$-O and N-C$\boldsymbol{H}_2$-Ar clearly indicate the retention of the benzoxazine ring during the click reaction.

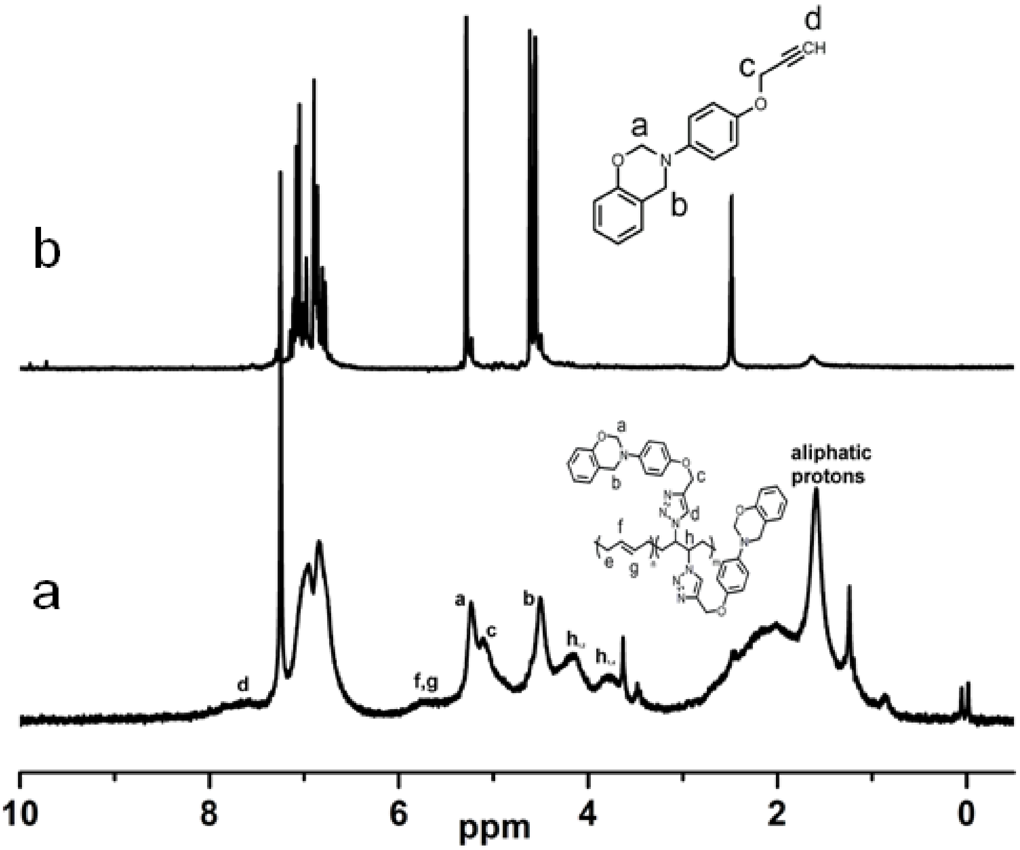
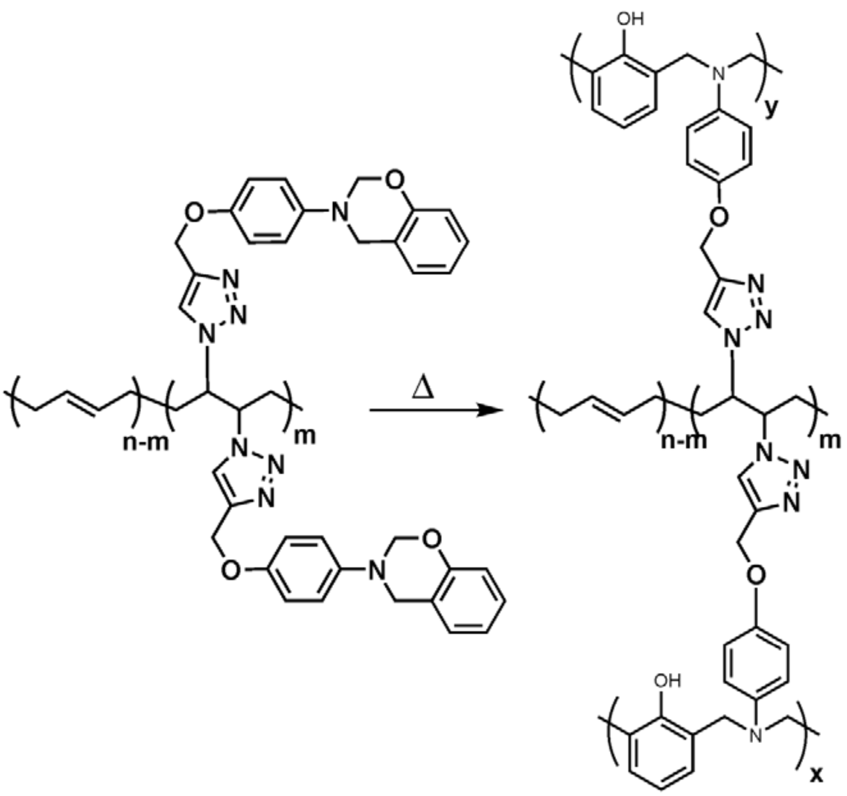


Figure 4. 6 a) ^{1}H-NMR spectra of propargylbenzoxazine and **b)** ^{1}H-NMR spectra of PB-benzoxazine

4.3.1 Thermally Activated Curing of PB-Benzoxazine

The thermally activated curing behavior of resulting polymer was examined by DSC. Figure 4.8 shows the DSC profile for benzoxazine containing PB. The side-chain benzoxazine groups are expected to undergo thermally activated intramolecular ring opening reaction to yield insoluble PB network as depicted in Figure 4.7.



(4.3)

Figure 4. 7 Cross-linking of PB-benzoxazine

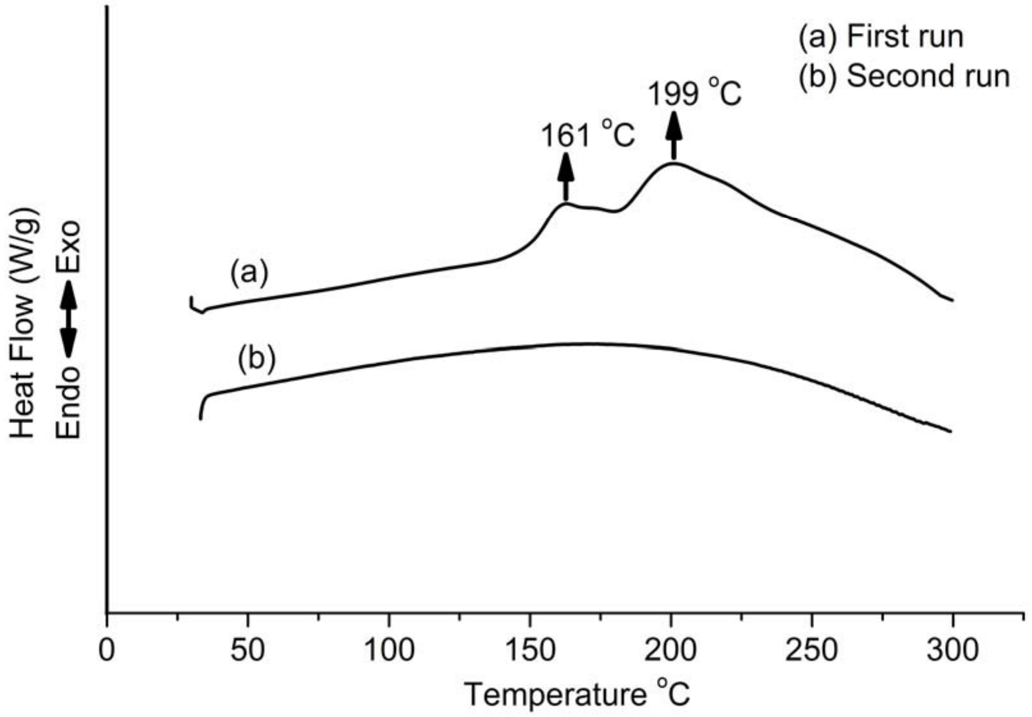
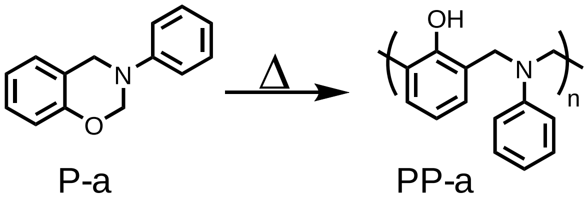


Figure 4. 8 DSC thermogram of PB-benzoxazine

The thermogram, shown in Figure 4.8 revealed two exotherms with maximums around 161 and 199°C at the fist run. According to literature, depending on the substituents, the benzoxazine ring opens at the temperature range between 200-250 ^{o}C. Hence, the exotherm at 199 °C corresponds to the ring opening polymerization of benzoxazine moiety and cross-linking of the polymer. The second exotherm at 161°C may be due to a transformation of 1, 2, 3-triazole ring. In fact, there is limited information in the literature about the thermal stability of the 1, 2, 3-triazole ring, formed via click chemistry, at elevated temperatures. Interestingly, DSC thermograms of several model compounds possessing triazole ring including those prepared from polystyrene have also exhibited similar exotherm. The possibility of the decomposition of the triazole ring by the evolution of nitrogen was disregarded as it would have exhibited an endotherm. Also, there is no meaningful weight loss observed around 161 ^{o}C due to the nitrogen evolution in thermal gravimetric analysis (TGA) of the polymer. The second DSC run did not show any exotherm indicating highly densed network formation and completion of ring opening. Furthermore, it should be noted that thermally treated polymer was not soluble in all common solvents.

Thermal stability of the thermally cured PB was investigated by TGA and compared with commercial PB and cured mono-functional benzoxazine (PP-a, See Figure 4.9). The TGA curves are presented in Figure 4.7 and weight loss behaviors of the species are tabulated at Table 4.1.



(4.4)

Figure 4. 9 Polymerization of mono-funtional benzoxazine

Table 4.1 TGA analysis of cured PB-benzoxazine with PP-a and PB

Polymer	$T_{5\%}$[a] (ºC)	$T_{10\%}$[b] (ºC)	$T_{max.}$[c] (ºC)	Y_c[d] at 500°C (%)
PB	363	411	449	0
PB-benzoxazine (cured)	234	267	309	43
PP-a	297	347	452	50

[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] $T_{max.}$: Maximum weight loss temperature.
[d] Y_c: Char yields

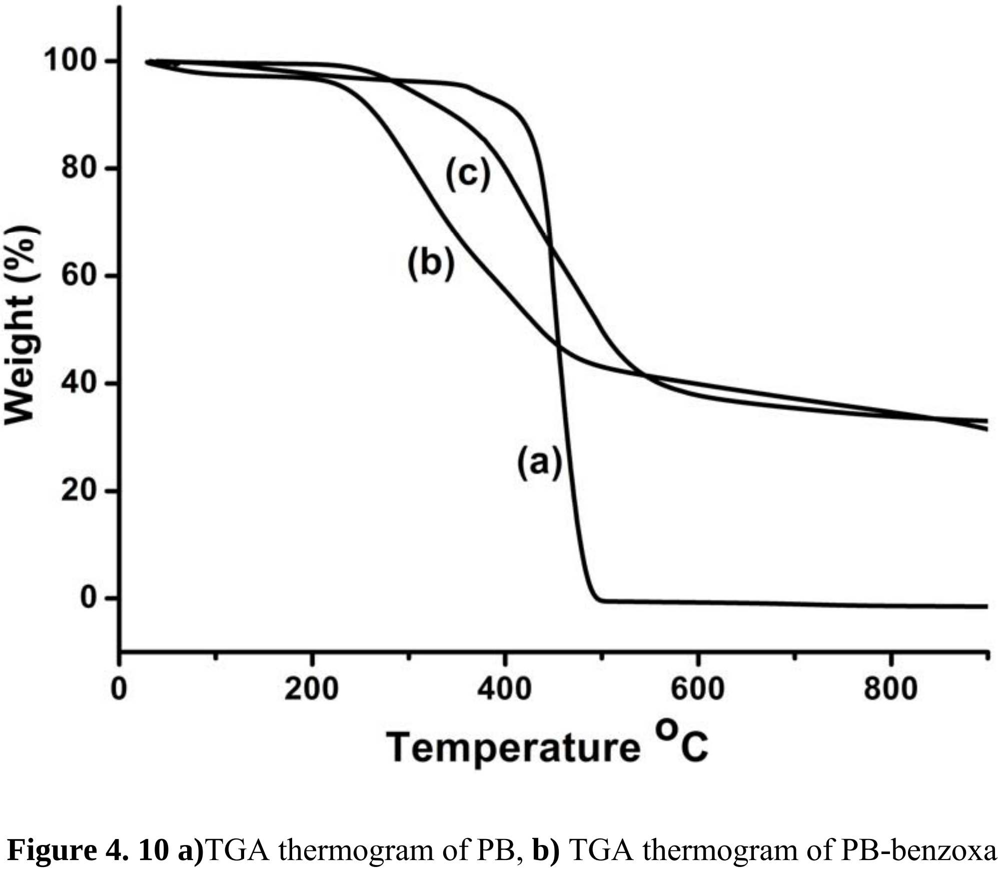


Figure 4. 10 a)TGA thermogram of PB, **b)** TGA thermogram of PB-benzoxazine **c)** TGA thermogram of PP-a

According to data obtained from TGA studies. It clear that the char yield of the thermally cured PB is enhanced far too much compared to commercial PB. Another noticeable feature is that the degradation of the thermally cured PB is not similar to the degradation profile of PP-a.

Molecular weight averages of PB, PB-Br, PB- N_3 and PB-benzoxazine are shown below (See Table 4.2).

Table 4.2 TGA analysis of cured PB-benzoxazine with PP-a and PB

Polymer	Mn	Mw	PD
PB	9251	10980	1,186
PB-Br	17551	19039	1,085
PB- N_3	15468	15594	1,008
PB-Benzoxazine	15622	18169	1,163

Mn: Number of Average Molecular Weight
Mw: Molecular Weight
PD: Polydispersity

In summary, a simple click reaction route to side-chain benzoxazine functional PB is described. This route has the unique feature of being quantitative and at the same time preserving the benzoxazine ring structure. The benzoxazine groups have been shown to readily undergo thermal ring-opening reaction in the absence of added catalyst to form cross-linked polymer networks. The polymers cured in this way, has much more char yield than commercial PB. It is anticipated that this new family of thermally curable polymers can be used as intermediates for the design of more complex macromolecular systems such as interpenetrating networks, nano-particles via intramolecular chain collapse, and high performance thermo-set polymers when used in conjunction with low molar mass benzoxazines. Further studies in this line are now in progress.

REFERENCES

[1] **Treloar, L.R.G.,** 1975. The Physics of Rubber Elasticity, Oxford University, England.

[2] **Meyers, K. and Chawla, H.,** 1999. Mechanical Behaviors of Materials, Prentice Hall, Inc.

[3] **Sun, H.P. and Wristers, J.P.**, 1992. Butadiene, *Encyclopedia of Chemical Technology, 4th Ed,* vol. 4, pp. 663–690, John Wiley & Sons. , NewYork.

[4] **Midgley, T., Henne A.L and Renoll M.W,** 1932. Natural and Synthetic Rubber, XI. Constituents of The Milled Rubber Hydrocarbon, *J. Am. Chem. Soc.,* **54,** 3381-3383.

[5] **Gent, A. N. and Campion, R. P**, 1992. Division of Rubber Engineering With Rubber: *How to Design Rubber Components*, American Chemical Society, Hanser Publishers, Munich.

[6] **Gent, Hanser**, 1992. Engineering with Rubber, Prentice Hall, Inc., England.

[7] **Midgley, T. and Henne A.L,** 1937. Natural and Synthetic Rubber. XVII. The Separation of Sol Rubber and Gel Rubber, *J. Am. Chem. Soc.,* **59,** 706-707.

[8] **Mastral, A. M., Murillo, R.; Perez-Surio, M. J.and Callen, M**., 1996. Coal Hydrocoprocessing with Tires and Tire Components, *Energy & Fuels,* **10,** 941-947.

[9] **Bowers, J.E,** 1990. Natural Rubber-Producing Plants for the United States, pp.13-15, National Agricultural Library, Beltsville.

[10] **Gower, M. and Gower, I.A,** 1995. Handbook of Plastic and Rubber Additives, *J. Am. Chem. Soc,* **119,** 7416-7583.

[11] **Dossin, L. M., Graessley, W.W.,** 1979. Rubber Elasticity of Well-Characterized Polybutadiene Networks, *Macromolecules,* **12**, 123-130.

[12] **Lutz, J.F,** 2007. 1, 3-Dipolar Cycloadditions of Azides and Alkynes: A Universal Ligation Tool in Polymer and Materials Science, *Angew. Chem. Int.*., **46**, 1018 – 1025.

[13] **Payne, A. R**, 1962. The Dynamic Properties of Carbon Black-Loaded Natural Rubber Vulcanizates, *J. Appl. Polym. Sci.* **19**, 57–53.

[14] **IUPAC**, 1996. Glossary of Basic Terms in Polymer Science, *Pure Appl. Chem*., **68**, 2287-2311.

[15] **Painter, P and Coleman, M**, 1997. Fundamentals of Polymer Science, pp.96-100, Wiley-Interscience, New York.

[16] **Brandrup, J., Immergut, E.H. and Grulke, E.A**, 1999. Polymer Handbook 4th Ed, Wiley-Interscience, New York.

[17] **IUPAC**, 1976. Nomenclature of Regular Single-Strand Organic Polymers, *Pure Appl. Chem.*, **48**, 373-385.

[18] **Ashby, M. and Jones, D.**, 1996. Engineering Materials, pp. 191-195. Oxford: Butterworth-Heinermann.

[19] **Armstrong, H.E. and Miller, A.K**., 1886. The decomposition and genesis of hydrocarbons at high temperatures. I. The products of the manufacture of gas from petroleum, *Journal of the Chemical Society* , **49**, 80-83.

[20] **Budinski, Kenneth G., Budinski, Michael K.**, 2002. Engineering Materials: Properties and Selection 7th Ed.

[21] **Yadav, J.S, Reddy, B.V , Reddy G. and Chary, D.N,** 2007**.** Three component, regioselective, one-pot synthesis of b-hydroxytriazoles from epoxides via 'click reactions', *Tetrahedron Letters*, **48,** 8773-8776.

[22] **Zhu, J., Zhu, X., Kang E.T. and Neoh, K.G.,** 2007**.** Design and synthesis of star polymers with hetero-arms by the combination of controlled radical polymerizations and click chemistry, *Polymer Communication*, **48**, 6992-6999.

[23] **Yan, Z.Y., Niu, Y.N., Wei, H.L.,Wu, L.Y., Zhao Y.B. and Lianga, Y.M.,**2006**.** Combining proline and 'click chemistry': a class of

versatile organocatalysts for the highly diastereo- and enantioselective Michael addition in water, *Tetrahedron: Asymmetry*, **17**, 3288–3293.

[24] **Meudtner R.,M.,Ostermeier, M.,Goddard R., Limberg C. and Hecht, S., 2007.** Multifunctional "Clickates" as Versatile Extended Heteroaromatic Building Blocks: Efficient Synthesis via Click Chemistry, Conformational Preferences, and Metal Coordination, *Chem. Eur. J.,* **13,** 9834-9838.

[25] **Fletcher, W. P. and Gent, A. N**., 1953. Non-Linearity in the Dynamic Properties of Vulcanised Rubber Compounds, pp. 266–280.

[26] **Binder, W.H. and Sachsenhofer, R.**, 2007. 'Click' Chemistry in Polymer and Materials Science, *Macromol. Rapid Commun*., **28**, 15-54.

[27] **Kolb, C.H.,Finn, M.G. and Sharpless, K.B.**, 2001. Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angew. Chem. Int.,* **40**, 2004 – 2021.

[28] **Ergin, M., Kiskan, B., Gacal, B. and Yagci ,Y.,** 2007**.** Thermally Curable Polystyrene via Click Chemistry**,** *Macromolecules***,** ***40***, 4724-4727.

[29] **Ghosh, N.N, Kiskan, B. and Yagci, Y.,** 2007. Polybenzoxazines - New High Performance Thermosetting Resins: Synthesis and Properties, *Progress in Polymer Science*,**32**,1344-1391.

[30] **Kiskan, B., Colak, D.,Muftuoglu, A., Cianga, I. and Yagci, Y.,** 2005. Synthesis and Characterization of Thermally Curable Benzoxazine Functionalized Polystyrene Macromonomers, *Macromol. Rapid Commun.* , **26**, 819-822.

[31] **Gacal, B., Durmaz, H., Tasdelen, M.A, Hizal, G.,Tunca, U. and Yagci, Y.,** 2006**.** Anthracene-Maleimide Based Diels-Alder "Click Chemistry" as a Novel Route to Graft Copolymers, *Macromolecules*, **39**, 5330-5334.

[32] **Kiskan, B., Gacal, B., Tasdelen, M.A., Colak, D. And Yagci, Y.,** 2006. Design and Synthesis of Thermally Curable Polymers with Benzoxazine Fuctionalities, *Macromol. Symp*., **245**, 27-33.

[33] **Ndoni, S., Vorup, A. and Kramer, O.,** 1998**.** Random Polybutadiene Rubber Networks with Unattached Chains, *Macromolecules***,** **31**, 3353-3360.

[34] **Saito, T., Yamamoto, Y. and Kawahara, S.,** 2007. Effect of LiBr Concentration on Carbonation of Natural Rubber with Supercritical Carbon Dioxide, *American Chemical Society,* **129,**

[35] **Toki, S. and Hsiao, B.S.,** 2003. Nature of Strain-Induced Structures in Natural and Synthetic Rubbers under Stretching, *Macromolecules***,** **36**, 5915-5917.

[36] **Khongtong, S. and Ferguson, G.S.,** 2001**.** Integration of Bulk and Interfacial Properties in a Polymeric System: Rubber Elasticity at a Polybutadiene/Water Interface, *J. Am. Chem. Soc.***,** **123**, 3588-3594.

[37] **Garea, S.A., Iovu, H., Nicolescu, A. and Deleanu, C.,** 2007**.** Thermal Polymerization of Benzoxazine Monomers Followed by GPC, FTIR and DETA, *Polymer Testing,* **26**, 162-171.

[38] **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.

[39] **Dirlikov, S. K. H.** , 1990. Propargyl-terminated Resins,*High Perform. Polym.*, **2**, 67-77.

[40] **Douglas, W. E.and Overend, A**. , 1991. Curing reactions in acetylene terminated resins-I. Uncatalyzed cure of arylpropargyl ether terminated monomers, *Eur. Polym. J.*, **27**,1279-1287

[41] **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.

[42] **Cid, J. A., Wang, Y. X. and Ishida, H.,** 1999**.** Development and characterization of high-performance polybenzoxazine composites*Polym. Polym. Compos.* , **7**,409-420.

[43] **Kasapoglu, F., Cianga, I., Yagci, Y. and Takeichi**, 2003. Photoinitiated cationic polymerization of monofunctional benzoxazine, T. *J. Polym Sci.,Part A: Polym. Chem.*, **41**, 3320-3328.

[44] **Fleischmann, S., Komber, H., Appelhans, D. and Voit, I.B**., 2007. Synhesis of Functionalized NMP Initiators for Click Chemistry: A Versatile Method for the Preparation of Functionalized Polymers and Block Copolymers, *Macromolecular Chemistry and Physics*, **208**, 1050-1060.

[45**] Huisgen, R. ,Szeimies, G., Mobius L.,** 1967. General Review,*Chem. Ber*. ,**100**, 2494-2501.

[46] **Gothelf, K.V. and Jorgensen, K.A,** 1998. Asymmetric 1, 3-Dipolar Cycloaddition Reactions, *Chem. Rev*., **98**, 863-910.

[47] **Tornoe, C.W.,Christensen, C. and Meldal, M.**, 2002. Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides *J. Org. Chem.,***67,** 3057- 3064.

[48] **Rostovtsev, V.V., Green, L.G, Fokin, V. And Sharpless K.B.,** 2002**.** A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes**,** *Angew. Chem. Int. Ed*., **41**, 2596-2599.

[49] **Bock, V.D., Heimstra, H. and Maarseveen, S.H., 2006.** CuI-Catalyzed Alkyne-Azide " Click " Cycloadditions from a Mechanistic and Synthetic Perspective, *Eur. J. Org. Chem*., **1**, 51-68.

[50] **Kolb, H.C. and Sharpless, K.B.,** 2003. The growing impact of click chemistry on drug discovery, *Drug Discovery Today*, **8**,1128-1137.

[51] **Binder, W.H. and Kluger, C.,**, 2006. Azide/Alkyne-"Click Reactions": Applications in Material Science and Organic Synthesis, *Curr. Org. Chem*., **10**, 1791-1815.

[52] **Wang, Q., Chittaboina, S. and Barnhill, H.N**, 2005. Advances in 1,3-Dipolar Cycloaddition Reaction of Azides and Alkynes – A Prototype of "Click" Chemistry *Lett. Org., Chem*., **2**, 293-301.

[53] **Köhn, M. And Breinbauer, R.,** 2004. Die Staudinger-Ligation- ein Geschenk für die Chemische Biologie, *Angew. Chem*., **116**, 3168-3178.

[54] **Langenhan, J.M. and Thorson, J.C**,2005. Recent Carbohydrate-Based Chemoselective Ligation Applications**,** *Curr. Org. Synth*., **2**,59-81.

[55] **Huisgen, R**.,1989. Kinetics and reaction mechanisms: selected examples from the experience of forty years, *Pure Appl. Chem*., **61**, 613.

[56] **Lwoski, W**., 1984. 1,3-Dipolar Cycloaddition Chemistry, Wiley, Vol. I, Chapter 5, New York

[57] **Huisgen**,**R**., 1988. Advances in Cycloaddition, Vol. I, pp. 1–31.Eds., D. P. Curran, D. Regnat, E. Peters, K. Peters, H. G. von Schnering., JAI Press, London.

[58] **Molteni, G., Bianchi, C.L,Marinoni, G.,Santo, N. and Ponti, A**.,2006.Cu/Cu-oxide nanoparticles as catalyst int the “click” azide-alkyne cycloaddition *New.J. Chem.,***30**, 1137.

[59] **Pachon, L.D, Maarseveen, J.H. and Rothenberg, G.,**2005**.** Click Chemistry: Copper Clusters Catalyse the Cycloaddition of Azides with Terminal Alkynes *Adv.Synth. Catal.*, **347**, 811.

[60] **Chan, T.R, Hilgraf, R., Sharpless, K.B. and Fokin, V.V**,2004. Polytriazoles as Copper(I)-Stabilizing Ligands in Catalysis,*Org.Lett*., **6**, 2853-2855.

[61] **Lewis, W., Magallon, F.G., Fokin, V.V. and Finn, M.G,** 2004. Discovery andCharacterization of Catalysts for Azide-Alkyne Cycloaddition by Fluorescence Quenching *J. Am. Chem. Soc.*, **126**, 9152- 9153.

[62] **Himo, F., Lovell, T., Hilgraf, R., Rostovtsev V., Noodleman, L., Sharpless, K.B. and Fokin, V.V**,2005. Copper(I)-Catalyzed Synthesis of Azoles. DFT Study Predicts Unprecedented Reactivity and Intermediates *J. Am. Chem. Soc*., **127,** 210-216.

[63] **Himo, F., Demko, Z.P., Noodleman, L. and Sharpless, K.B**,2002. Mechanisms of Tetrazole Formation by Addition of Azide to Nitriles *J. Am.Chem. Soc.*, **124**, 12210-12216.

[64] **Demko, Z. P. and Sharpless, K. B.** , 2002. A Click Chemistry Approach to Tetrazoles by Huisgen 1,3-Dipolar Cycloaddition: Synthesis of 5-

Acyltetrazoles from Azides and Acyl Cyanides, *Chem. Int. Ed.*, **41,** 2113-2116.

[65] **Schnabel, W, Levchik, G.F, Wilkie, C.A, Jiang, D.D. and Levchik, S.V.,**. 1999. Thermal degradation of polystyrene, poly (1, 4-butadiene) and copolymers of styrene and 1,4-butadiene irradiated under air or argon with ^{60}Co-γ-rays, *Polym Degrad Stab,* **63**, 365-375.

[66] **Jiang, D.D., Levchik, GF, Levchik, S.V and Wilkie, C.A.,** 1999._Cross-linking of polystyrene by Friedel–Crafts chemistry to improve thermal stability, *Polym Degrad Stab.* , **65**, 387-395.

[67] **Decker, C., Nguyen, T. and Viet T**., 1999. Photocrosslinking of functionalized rubbers, 8. The thiol-polybutadiene system, *Macromol. Chem. Phys*., **200**, 1965–1974.

[68] **Barner, C., Kowollik, P.V, and Davis, T.P.**, 2002. The Kinetics of Handbook of Radical Polymerization, Edited by Krzysztof M. And Thomas P. Davis.John Wiley & Sons, Inc.

[69] **Flory, P. J.,** 1953. *Principles of Polymer Chemistry*, Cornell University Press, Ithaca.

[70] **Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, P. F.,** 1958. *The Kinetics of Vinyl Polymerization by Radical Mechanisms*, Butterworths, London.

[71] **Yagci, Y. and Mishra, M. K.,** 1998. Handbook of radical vinyl polymerization Marcel Dekker, Inc., New York, pp. 149-203.

[72] **Crivello, J. V.,** 1978. *Curing: Science and Technology, pp. 23-77*, Ed. Pappas, S.P., Technology Marketing Corp., Norwalk, CT.

[73] **Malkoch, M., Thibault, R.J., Drockenmuller, E., Messerschmidt, M., Voit, B., Russell, T.P, and Craig J. Hawker,** 2005. Orthogonal Approaches to the Simultaneous and Cascade Functionalization of Macromolecules Using Click Chemistry, *J. Am. Chem. Soc,* **127,** 14942-14949.

[74] **Sacak M.,** 2002. Polimer Kimyası, pp.33-81, Gazi Kitapevi, Ankara.

[75] **Reghunadhan C. P**., 2004. Nair CPR. Advances in addition-cure phenolic resins. *Prog. Polym. Sci.*, **29,** 401-498.

[76] **Ghosh, N.N, Kiskan, B. and Yagci, Y.,** 2007. Polybenzoxazines—New high performance thermosetting resins:Synthesis and properties, *Prog.Polym. Sci* , **32**, 1344-1391

[77] **Liu, Y.L., Yu, J.M. and Chou, C.I.,** 2004. Preparation and properties of novel benzoxazine and polybenzoxazine with maleimide groups, *J.Polym. Sci., Part A: Polym. Chem.*, **42**, 5954-5963.

[78] **Liu YL and Yu JM.**, 2006. Cocuring behaviors of benzoxazine and maleimide derivatives and the thermal properties of the cured products, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 1890-1899.

[79] **Kinloch, A.J.**, 1989.Rubber-Toughened Plastics; Riew, Ed. Riew, C.K., DC: ACS, p. 67, Washington

[80] **Lee, Y.H. and Ishida, H**., 2005. Probing the properties of particle-matri interphase in reactive rubber-grafted polybenzoxazine resins byatomic force microscopy, *Compos.Interfaces*,**12**, 481-499.

[81] **Pearson, R.A. and Yee, A.F.,** 1986. Toughening Mechanisms in Elastomer-Modified Epoxies. 2.Microscopy Studies, *J. Mater. Sci.*, **21**, 2475-2488.

[82] **Kinloch, A.J., Shaw, S.J. and Tod, D.A.,** 1983. Hunston DL. Deformation and Fracture-Behavior of a Rubber-Toughened Epoxy Microstructure and Fracture Studies, *Polymer*; **24**, 1341-1354.

[83] **Kang, B.U., Jho, J.Y., Kim, J., Lee, S.S., Park, M., Rim, S., Choe andC.R.,** 2001. Effect of the phase separation on fracture behavior of rubber-modified epoxy adhesives., *J. Mater. Sci.Lett.*, **20**, 375-379.

[84] **Bussi, P., and Ishida, H.,**1994. Composition of the Continuous-Phase in Partially Miscible Blendsof Epoxy-Resin and Epoxidized Rubber by Dynamic-Mechanical Analysis, *Polymer*; **35**, 956-966.

[85] **Jang, J. and Seo, D.,**1998. Performance improvement of rubber-modified polybenzoxazine. *J.Appl. Polym. Sci*, **67**, 1-10.

[86] **Shaffer, O.L., Bagheri, R., Qian, J.Y., Dimonie, V., Pearson, R.A. and Elaasser, M.S**.1995.Characterization of the Particle-Matrix Interface in Rubber-Modified Epoxy by Atomic-Force Microscopy, *J. Appl. Polym. Sci.,***58**, 465-484.

[87] **Mathur, D. and Nauman, E.B.,**1999.Impact strength of bulk PS/PB blends: Compatibilization and fracture studies, *J. Appl. Polym. Sci.,***72**, 1151-1164.

[88] **Chen, T.H., Bai, Y.W. and Sun, R.H**., 1998. Study on relationship between mechanical properties and particle size distribution for polyhexamethylene carbonate diol toughened epoxy resin, *J. Appl. Polym. Sci.*, **67**, 569-575.

[89] **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.

AUTOBIOGRAPHY

Sevim M. KUKUT was born in Istanbul in 1983. She was graduated from Ata College School in 2001. She was admitted Istanbul Technical University (ITU) to Department of Chemistry in 2001.She was graduated as a chemist in 2006.

She was registered as M.Sc. student to the Chemistry Program of the Institute of Science and Technology of Istanbul Technical University in 2006.