ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF BORON CONTAINING POLYMERS

M.Sc. THESIS

Serkan AKPINAR

Department of Polymer Science of Technology

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Thesis Advisor: Prof. Dr. İ.Ersin SERHATLI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

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Serkan AKPINAR
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Polimer Bilimi ve Teknolojisi Bölümü

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Tez Danışmanı: Prof. Dr. İ.Ersin SERHATLI

OCAK 2015

Serkan Akpınar, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 515101041, successfully defended the **thesis** entitled "**SYNTHESIS AND CHARACTERIZATION OF BORON CONTAINING POLYMERS**" which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 15 December 2014
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To my family,

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.

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December 2014 Serkan AKPINAR
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ABBREVIATIONS

^{1}H-NMR : Hydrogen Nuclear Magnetic Resonance
^{13}C-NMR : Carbone Nuclear Magnetic Resonance
^{11}B-NMR : Boron Nuclear Magnetic Resonance
AIBN : 2, 2’ -Azobis-(isobutyronitrile)
BAc : Boron acrylate monomer
p(BAc-co-St) : Boron acrylate-styrene copolymer
p(BAc-co-MMA) : Boron acrylate-methy methacrylate copolymer
pBAc : Boron Acrylate-Homopolymer
pSt : Styrene-Homopolymer
DSC : Differential Scanning Calorimetry
FRP : Free Radical Polymerization
FT-IR : Fourier Transform Infrared Spectroscopy
GPC : Gel Permeation Chromatography
HEMA : 2-Hydroxy ethyl methacrylate
Mn : Molecular weight
MMA : Methyl methacrylate
PDI : Polydispersity index
RP : Radical Polymerization
TGA : Thermogravimetric analysis
THF : Tetrahydrofuran
St : Styrene

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SYNTHESIS AND CHARACTERIZATION OF BORON CONTAINING POLYMERS

SUMMARY

Boron is a Group 13 element that has properties which are borderline between metals and non-metals (semimetallic) which atomic number is 5. Boron compounds have specialized roles in high strength, low weight structural materials. For example, boron is used in glass and ceramic industry for making material resistant to heat. Especially because of its flame retardant properties, usage of boron in polymers is increased in past few years. According to the studies, reactions between boron element and acrylic polymers resulted with acrylic polymers containing boron.

Acrylic polymers can be used in many industries, primarily in dye industry, and also it has many copolymer derivatives. In this study, boron containing acrylic monomers was synthesized and characterized. Afterwards, homopolymers and copolymers were synthesized from the boron containing acrylic monomer. Free radical polymerization is choosen as the polymerization method and finally, polymers are characterized with different methods.

In this thesis, firstly with esterification reaction boron acrylic monomer is synthesized. Boric acid, neopentyl glycol and as for acrylic monomer HEMA (2-hydroxyethyl methacylate) are reacted to obtain boron containing acrylic monomer. Characterization is made by FT-IR, ^{13}C-NMR, ^{1}H-NMR ve ^{11}B-NMR and results of synthesized monomer is compared with HEMA. After the characterization, homopolymer and copolymers with styrene (St) and methyl methacylate (MMA) are synthesized by free radical polymerization. Properties of copolymer synthesized with St is examined detaily. Monomer reactivity ratios for the studied monomer pair were calculated by using extended Kelen-Tudos (EKT) method. Copolymerization composition and reactive ratios show that the copolymerization is occured randomly.

Thermal behaviors of synthesized polymers are studied by TGA and DSC methods. Homopolymer has one glass transition temperature at 72.3 ^{o}C. In addition the styrene homopolymer glass transition temaparature at 74.2 ^{o}C. Depending on the copolymer composition, the glass transition temperatures of boron acrylic-styrene copolymers have between at 62.9 ^{o}C and 97.2 ^{o}C. As a result of TGA analyzes, TGA diagrams of copolymers were determined to be in between TGA diagrams of pBAc and pSt . Based on these results, while St copolymer has one decomposition, BAc homopolymer has two decomposition.

BOR İÇEREN POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Bor, atom numarası 5 olan ve metaller ile non-metaller arasındaki sınır hattını oluşturan özelliklere sahip bir grup 13 yarı metalidir. Doğada toprak, taş veya suyun yapısında kristal veya amorf halinde bulunabilir. Yapısında bulunduğu bileşiklerin ve malzemelerin özelleşmiş rolleri vardır. Örneğin Cam ve seramik endüstrisinde, ilgili malzemelerin ısı şokuna dayanıklı olması için kullanılmaktadır. Buna en yaygın örnek olarak borcam sınıfını gösterebiliriz. Bunun yanında bazı kumaşların yapısına da termal stabiliteyi arttırmak amacıyla katılmaktadır. Doğada sadece 11 elementin erime noktası bor elementinden daha yüksektir. Yanmaya karşı göstermiş olduğu bu yanmazlık arttırıcı termal özelliklerinden dolayı bor elementinin polimerlerde kullanımı 1800'lü yılların başında başlamıştır. Birçok bilim adamı, bu konuda çalışmalar göstermiş ve yeni borlu yapılar geliştirmişlerdir. Fakat bu yıllarda yapılan çalışmalar çokda ileriye dönük devam etmemiştir. 1900'lü yıllarda ise özellikle fosforlu yanmazlık sağlayan ve halojenli alev geciktiricilere alternatif olarak borlu yapıların araştırılmasında artış olmuştur. Borlu alev geciktiriciler, ilk etapta katkı maddesi olarak malzemelerin yapısında yer almıştır fakat bilim adamlarının yoğun çalışmaları ile özellkle polimerik malzemelerin sentezlenmesine yönelik çalışmalar artış göstermiştir. Bu çalışmalar sürecinde borlu polimerlerin sentezi için 2 farklı yöntem geliştirilmiştir. Bunlar ana zincirde bor ihtiva eden polimerik yapılar ve yan grupta bor ihtiva eden polimerik yapılardır. İstenilen malzemenin özelliklerine göre bu yapılara uygun sentez reaksiyonları tespit edilmiştir. Özellikle serbest radikal polimerizasyonu ve kontrollü serbest radikal polimerizasyon yöntemleri, basit mekanizmaları nedeniyle bor içieren polimerlerin sentezinde yaygın olarak kullanılmaktadır. Bunların yanı sıra Ziegler-Natta polimerizasyonu ve halka açılma polimerizasyon metotları da bor içeren polimerlerin sentezi için uygulanan metotlar arasında yer almaktadır. Son yıllarda yapılan çalışmalara göre bor elementinin bazı akrilik yapılar ile reaksiyonu sonucu bor ihtiva eden akrilik bileşikler sentezlenmiştir. Bu bileşiklerin monomer olarak çeşitliliği olmakla beraber polimerizasyonlarına dair örnekler çok fazla yer almamaktadır.

Akrilik polimelerlerin ise başta boya olmak üzere birçok endüstride kullanımı yaygın olmakla birlikte birçok kopolimer türevi mevcuttur. Bu polimerler de kolay mekanizması nedeni ile serbest radikal polimerizasyonu ile kolayca polimerleşebilir. Bu çalışmada ise bor ihtiva eden akrilik monomer sentezlenecek olup ilgili monomerin karakterizasyonu çeşitli test yöntemleri ile yapılacaktır. Daha sonra bu monomerin sebest radikal polimerizasyonu ile homopolimeri ve kopolimerleri sentezlenecektir. Daha sonra da sentezlenen bu polimerlerin çeşitli test yöntemleri ile karakterizasyonu gerçekleştirelecektir. Yapılan çalışmalarda birçok reaksiyon koşulu denenmiş olup reaksiyonlar en uygun şartlarda gerçekleştirilmiştir.

Bu tezde ilk olarak esterifikasyon reaksiyonu ile bor akrilik monomer sentezlenmiştir. Borik asit, neopentyl glycol ve akrilik monomer olan HEMA (2-Hydroxyethyl methacrylate) reaksiyona sokularak bor akrilik monomer elde

edilmiştir. Sentezlenen bu monomerin oluşumunu ve karakteristik yapısını aydınlatmak için, monomer sentezinde kullanılan HEMA (2-Hydroxyethyl methacrylate) bileşiği ile karşılaştırılarak FT-IR testi ile, yapısındaki karbon atomlarının karakteristik özelliği dikkate alınarak ^{13}C-NMR testi ile, yapısında yer alan hidrojen atomlarının karakteristik özelliği dikkate alınarak ^{1}H-NMR testi karakterize edilmiştir. Bunun yanı sıra oluşan monomerin yapısındaki bor varlığı ^{11}B-NMR ile gösterilmiştir. Ayrıca oluşan tüm polimerlerde de bor varlığı ^{11}B-NMR ile gösterilmiştir. Yeni monomerin sentez ve karakterizasyonundan sonra, serbest radikal polimerizasyonu (FRP) kullanılarak homopolimeri, Stiren ve Metil metakrilat monomerleri ile de kopolimerizasyonları gerçekleştirilmiştir. Bor akrilik monomerinin stiren ile oluşturduğu kopolimerinin, yapısında yer alan hidrojen atomlarının karakteristik özelliği dikkate alınarak ^{1}H-NMR testi ile karakterizasyonu gerçekleştirilmiştir. İlgili ^{1}H-NMR verilerinden yararlanılarak yapı ve reaktivite ile sonuçlar arasındaki ilişki hakkında bilgi elde etmek amacı ile her iki monomerin kinetiği de çalışılmıştır. Çalışılan monomer çifti için monomer reaktivite oranları extended Kelen-Tudos (EKT) metodu kullanılarak hesaplanmıştır. Kopolimerlerin bileşimi ve monomer reaktivite oranları kopolimerizasyonun rastgele kopolimerizasyon olduğunu göstermiştir. Ayrıca kopolimer kompozisyonları dikkate alınarak yapıda ilk olarak oluşturulması istenilen ve yapıya oaransal olarak katılan yüzdelerin, oluşan polimerdeki ^{1}H-NMR verileri dikkate alınarak, bor akrilik monomer miktarı arttırıkça stiren miktarının daha baskın ve yüzdece daha fazla olduğu tespit edilmiştir. Bu durum yapılan çalışmalarda bor akrilik miktarının kopolimer içerisinde artması istenmesine rağmen stirenin daha baskın olduğunu vermektedir. Bu çalışmada reaktivite oranlarını belirlemede kullanılan Kelen-Tudos (EKT) yöntemi dışında başka yöntemler de denenibilir.

Yapılan karakterizasyon çalışmalarında; oluşan monomerin sentezini ifade etmek amacı ile öncelikle FT-IR ile karakterizasyon işlemleri gerçekleştirilmiştir. FT-IR cihazı ile yapılan karakterizasyon işlemlerinde spektrumda yer alan HEMA (2-Hydroxyethyl methacrylate) bileşiğinden gelen -OH pikinin oluşan monomerde tamamen kaybolduğu ve yeni yapıda -BO pikinin meydana geldiği gösterilmiştir. Bunun yanı sıra polimerlerin sentezlendiğini göstermek amacı ile ^{1}H-NMR cihazı ile yapılan testte monomerde yer alan C=C protonlarının, oluşan polimerlerin ^{1}H-NMR spektrumları incelendiğinde piklerinin tamamen kaybolduğu tespit edilmiştir. Bunun yanı sıra elde edilen ^{11}B-NMR' ları dikkate alındığında polimerlerin ^{11}B-NMR sonuçlarının kimyasal kayma gösterdiği tespit edilmiştir. Bu kaymanın sebebi ise oluşan polimerlerdeki borlu yan grupların birbirlerini perdelemesidir. Bu durum da bize polimerlerin oluştuğunu gösteren başka bir sonuçtur. Ayrıca sentezlenen polimerlerin termal davranışları incelemek amacıyla TGA ve DSC yöntemleri ile incelenme işlemleri gerçekleştirilmiştir. Yapılan bu çalışmalarda bor akrilik homopolimer, DSC termogramında 72.3 ^{o}C noktasında tek bir camsı geçiş sıcaklığı göstermiştir. Aynı zamanda laboratuvar ortamında diğer polimerlere molekül ağırlığında yakın olarak sentezlenen stiren homopolimerinin camsı geçiş sıcaklığı da DSC termogramında 74.2 ^{o}C olarak bulunmuştur. Bu sonuçlarda bize polimerlerin molekül ağırlıklarının camsı geçiş sıcaklığına etkisini göstermiştir. Sentezlenen bor akrilik ve stiren kopolimerleri, kopolimer bileşimine bağlı olarak DSC termoglarında 62.9 ^{o}C ile 97.2 ^{o}C arasında değişen doğrusal olmayan camsı geçiş sıcaklıkları göstermişlerdir. Bu sonuçlar dikkate alındığında ilgili yapıların camsı geçiş sıcaklık değerlerinin molekül ağırlıklarının düşük olması sebebi ile doğrusal bir sonuç vermemesi ile birlikte sentezlenen kopolimerlerin tek bir camsı geçiş sıcaklık değerli verdiği tespit edilmiştir. Sentezlenen polimerlerin bozunma ve kül miktarlarının

tespiti için yapılan TGA analizleri dikakte alındığında bu kopolimerlerin TGA diagramlarının, kullanınlan bor akrilik ve stiren homopolimerlerinin TGA diagramlarının arasında olduğu tespit edilmiştir. Bu doğrultuda bor akrilik-stiren kopolimeri tek bir bozunma verirken, bor akrilik homopolimeri ise iki bozunma vermiştir. Bunun yanı sıra stiren monomerinden oluşan kopolimerlerin yapısında yer alan bor akrilik segmentelerinin varlığı, oluşan polimerlerlerin kül miktarının stiren homopolimerine oranla daha fazla olduğu tespit edilmiştir. Çalışma içerisinde bor akrilik-metil metakrilat kopolimerinin ise sentezi çeşitli denemeler ile uygun solvent ortamının bulunması ile gerçekleştirlmiş olup molekül ağırlığı GPC ile hesaplanmıştır ve bu yapılan analizin sonuçları çalışmada gösterilmiştir. Son olarak da bu sonuçların yanısıra sentezlene tüm polimerlerlerin çeşitli solventler içerisindeki çözünürlükleri de incelenmiştir. Sentezlenen bor akrilik homopolimerinin THF içerisinde çözünmediği ve sentezlenen tüm polimerlerlerin metanol içerisinde çözündüğü tespit edilmiştir. Ayrıca yapılan çalışmalar ve denemeler sonucunda bor akrilik homopolimerinin en verimli di-etil eterde, bor akrilik-stiren kopolimerlerinin ve bor akrilik-metil metakrilat kopolimerinin en verimli hekzanda çöktükleri tespit edilmiştir. Elde edilen bu çözünürlük bilgileri sayesinde polimerlerin kullanım alanları ve sentezlenme şartları hakkında bilgi sahibi olunmuştur.

1. INTRODUCTION

Boron compounds have specialized roles in high strength, low weight structural materials. For example, boron is used in glass and ceramic industry for making material resistant to heat. In increasing the flame retardancy of polymeric materials the use of borates was probed earlier inthe 20th century. Borates are noticeable flame retardants because impenetrable glass coatings form when they thermally degradate [1]. Boric acid and borate salts have been used as flame retardant additives since early 1800s, but they have been less studied than phosphorous, halogen and other compounds. The use of borates in enhancing the flame retardancy of polymeric materials was reported earlier in the 20th century [1-2]. Borates are effective flame retardants because impenetrable glass coatings form when they thermally degrade. The glass coatings form on the surface, and can contribute to the intumescent effect, because they exclude oxygen and prevent further propagation of combustion. The water of hydration is lost by endothermic decomposition and therefore both dilutes and cools, by absorbing the thermal energy from the flame. The flame retardant action of the boron-containing compounds on polymeric materials is chemical as well as physical. It was found that these inorganic boron compounds promote char formation in the burning [3] process.

Acrylic polymers can be used in many industries, primarily in dye industry, and also it has many copolymer derivatives. Acrylates are a family of polymers, which are a type of vinyl polymer. Acrylate monomers are esters which contain vinyl groups, that is, two carbon atoms double-bonded to each other, directly attached to the carbonyl carbon. Some acrylates have an extra methyl group attached to the alpha carbon, and these are called methacrylates.

In this study, boron containing acrylic monomer was synthesized and characterized. Synthesized monomer was polymerized via free radical polymerization and copolymerization with St and MMA monomers. Emerging monomer and polymers were characterized with FT-IR, ^{13}C-NMR, ^{1}H-NMR and ^{11}B-NMR. The thermal behaviour of these compounds were examined by DSC and TGA analyses.

2. THEORETICAL PART

2.1 Boron

Boron comes from the Arabic word buraq, "white" and baurach in Persian languages. The symbol of Boron element "B", of which atomic number is 5, atomic weight is 10.81 and is located at the top of the 3 Group of the Periodic table. Pure boron made extremely hard yellow monoclinic crystals that are a semiconductor resembling silicon on the other hand ordinary boron is a brown-black amorphous powder. Crystalline boron is an insulator at low temperatures, but it becomes a conductor at high temperatures. Being a semiconductor, it conducts electrical current only slightly; its conductivity increases rapidly increasing temperature The density of crystalline boron is 2.34 g/cc, of amorphous boron, 2.37. It melts at 2300°C and boils at 2550°C (some sources say 2040°C and 4100°C), so it is a very refractory substance. Boron fibers have been used in composite materials because of their great strength [4].

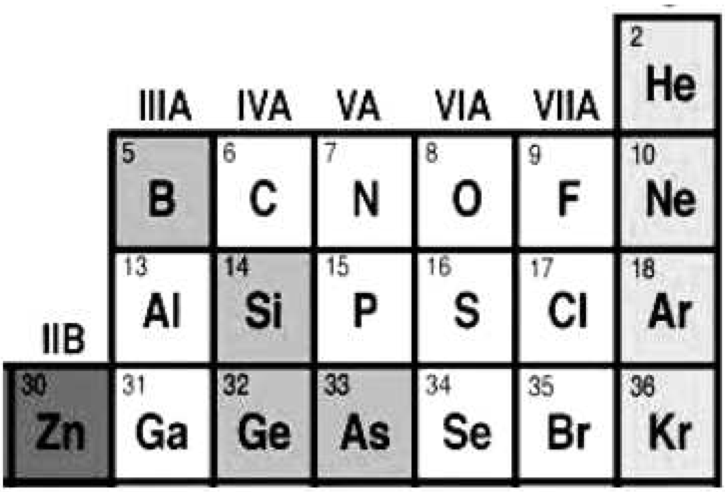


Figure 2.1 : The location of boron on periodic table.

Boron is found on earth in soil, rocks and water that both in crystal and amorphous forms. Boron is a tough element, very hard, and very resistant to heat. In its crystalline form is the second hardest of all the elements on the mohs scale – only carbon (diamond) is harder. Only 11 elements have higher melting points than boron:

these are C, W, Re, Os, Ta, Mo, Nb, Ir, Ru, Hf, and Tc. The crystalline form of Boron is very unreactive but amorphous boron is reactive [5]. The rank of amount of boron on earth is about 10 ppm. The boron that is found in the nature consists of the mixture of two stable isotopes having mass numbers 10 (19.10-20.31%) and 11 (80.90-79.69). Both isotopes may be obtained from commercially and find application in NMR spectroscopy. It is reported that the living organisms evolves in presence of this element.

The boron element was firstly obtained by Gay-Lussac, Louis Jacques Thenard in France in 1808, and independently by Sir Humphrey Davy in England, as the product of the reduction of boric acid with potassium. When boron oxide was heated with potassium. They produced metallic potassium by electrolysis, and then used it to reduce borates to impure boron. In 1892, H.Moissan obtained purer samples by reducing B_2O_3 with magnesium. Amorphous boron of lower purity is obtained by as a brown powder with reaction as below:

$$B_2O_3 + 3\ Mg \rightarrow 2\ B + 3\ MgO$$

Boron behaved excatly as excepted, forming trivalent compounds such as boron trihalides, trialkylboranes, $B(OH)_3$, and borates. William Nunn Lipscomb, fnally crack the mystery of the three-center-bonded polyboranes, proving many of their structures with his ingenious apparatus that enabled the collection of x-ray diffraction data at ultracold temperatures and developing a theoretical foundation based on the concept of the three-center two-electron bond. For these achievements, Lipscomb was awarded the 1976 Nobel Prize in Chemistry [6]. Today, boron is obtained by heating borax ($Na_2B_4O_7 \cdot 10H_2O$) with carbon, although other methods are used if high-purity boron is required [7].

Boron does not occur naturally in elemental form. Even though the element boron takes place on earth at different ratios within more than 230 naturally borate minerals were identified and researchers ensure that many new ones will be found in the future [8]. Boron minerals become ready to be used by related industries following the crushing, sieving, washing and grinding operations after the minerals are taken out of the mine [9]. A lot of reported minerals contain multiple cations, anions, or have changed cation or anion proportions in large families of borates such as borosilicates, rare earths, boracites. On the other hand the number of nonmineral borates produced in the laboratory that is also very large. It s tri- and tetra (negatively charged)-bonded groups with oxygen can combine in a very large number of geometric combinations and polymer types. Also, the borates can combine with any cations, along with double or multiple salts form with many other compounds. Boron minerals contain different amount of B_2O_3 in their structures. Boron minerals that are include B_2O_3 content that can replace each other in use, so it is very important factor for industrial application because of one boron mineral can be trade competitor the other one. For example, the most commercially important traded minerals (salts or borates) are tincal, colemanite, ulexite and kernite [8]. Commonly used boron compounds are orthoboric acid, or simply boric or boracic acid, H_3BO_3, and boron trioxide, B_2O_3, its anhydride. If boron were a normal metal, the hydroxyl ions would separate in water, creating the trivalent boron ion B^{+++}. This, however, does not happen to the smallest degree, and boron does not form ionic bonds. Moreover, boric acid is not gelatinous like aluminum hydroxide, but crystallizes nicely. Boron trifluoride, BF_3 is not an ionic, which has no ions in its crystals. Instead, the hydrogen atoms are lost long before the oxygen atoms.

2.1.1 Borate crystal structure

Borate minerals and synthetic borates crystal structure has been rather thoroughly studied, providing some general rules about their structure. Crystallographers also have systematized the possible automatic arrangements of the borates and helped to explain the very large number of borate compounds. All borates contain combinations of the three-(triangular) or four-bond (tetragonal); negatively charged) B-O structures Figure 2.2 [8]. However, despite these long lists, only a comparative few of the borates are important in commercial deposits. This includes the hydrogen borate sassolite (H_3BO_3); the two sodium borates, borax ($Na_2B_4O_7.10H_2O$) and kernite ($Na_2B_4O_{7.}4H_2$); the calcium borates, colemanite ($Ca_2B_6O_{ll}.5H_2O$), inyoite ($Ca_2B_6O_{11}.13H_2O$), and priceite ($Ca_4B_{10}O_{19}.7H_2O$); the sodium-calcium bo- rates, ulexite ($NaCaB_5O_9.8H_2O$) and probertite ($NaCaB_5O_9$-$5H_2O$); the mag- nesium borates, szaibelyite (ascharite; $Mg_2B_2O_{5.}H_2O$), inderite or kurnakovite ($Mg_2B_6O_{l1}$. $15H_20$; monoclinic or triclinic), and pinnoite ($MgB_2O_4.3H_2O$); the magnesium-calcium borate, hydroboracite ($CaMgB_6O_{11}.6H_2O$); the borosili- cates datolite ($Ca_2B_2Si_2O_9.H_2O$) and ludwigite (Mg_2FeBO_5); and the magne-sium chloride double salt, boracite ($Mg_3B_7O_{13}C1$). Each of these minerals is being, or has been, mined and processed on a commercial scale. A number of other borates that are present in limited quantity (such as danburite, $CaB_2Si_2O_8$), or that result from weathering may be mined with the major minerals. Also, other borates such as howlite ($Ca_4Si_2B_{10}O_2.5H_2O$) are fairly common, but have not yet become commercial minerals. Some of the borates have more than 100 atoms (not counting hydrogen) and very complex polymer structures, implying very long crystallization times [8].

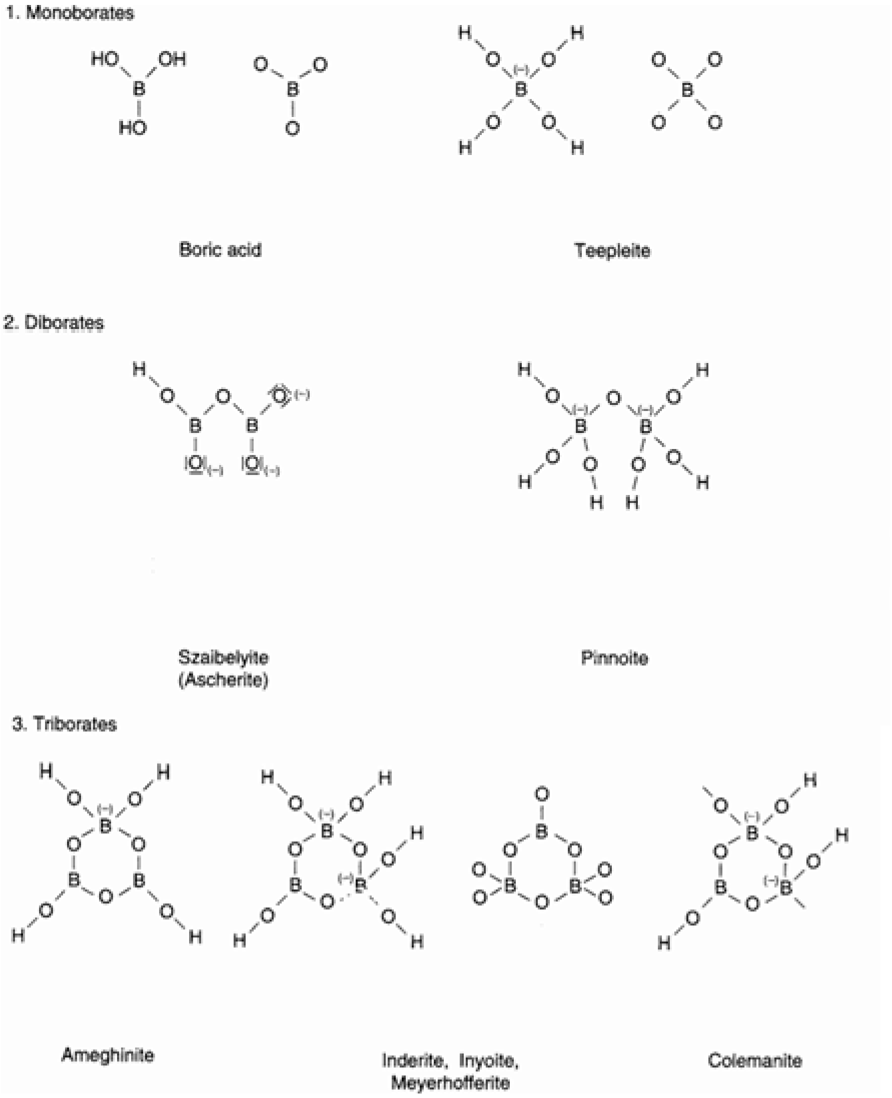


Figure 2.2 : First three groups borates of figures [7].

2.1.2 Boric acid

Boric acid or orthoboric acid (commercially known as Optibor) is a white triclinic crystal that is soluble in water (5.46 wt.%), alcohols, and glycerin. It is a weak acid and has a pH of 4 (saturated solution at room temperature). Upon heating in air to above 75°C, it loses part of its water of hydra- tion to form metaboric acid (HBO) at around 120°C–130°C. The metaboric acid can be further 2 dehydrated to boric oxide at around 260°C–270°C [10].

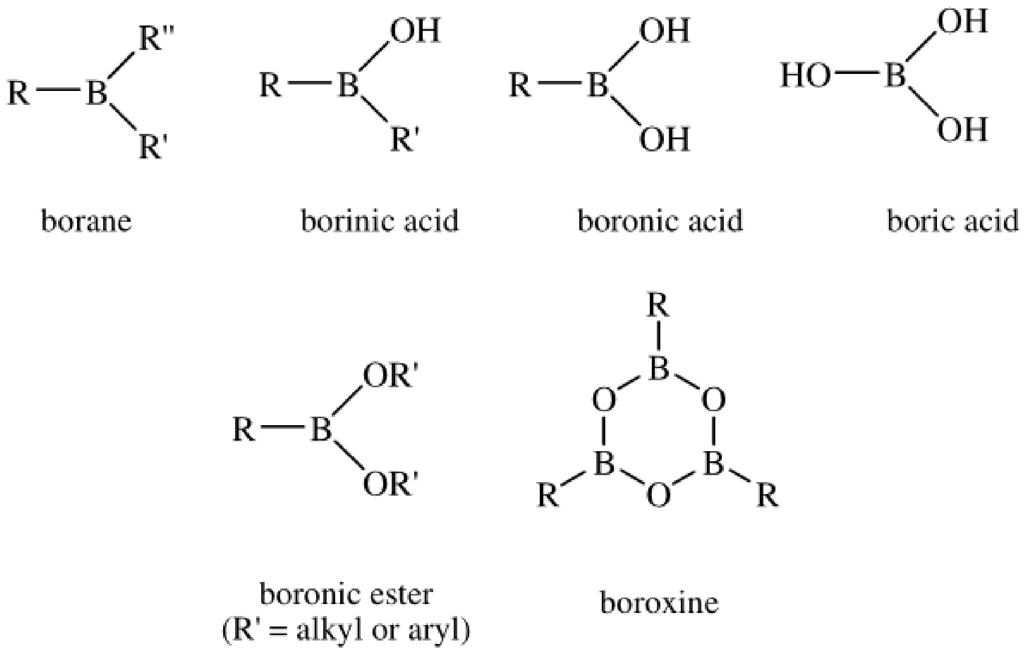
$$2H_3BO_3 \rightarrow HBO_2 + 2H_2O \rightarrow B_2O_3 + H_2O$$

Due to their low dehydration temperatures and water solubilities, boric acid and sodium borates (borax pentahydrate and borax decahydrate) are mostly used as fire retardants in wood/cellulosic products such as timbers, plywood, particle board, wood fiber, paper products, cotton products and polymer matrials. In recent years, boric acid has also been used as fire retardant in epoxy intumescent coating, phenolics, urethane and foam. When necessary, boric acid can be coated with silicone oil such as silicone to alleviate its water solubility in water-based coating.

The best-known and most stable of the organic derivates of boric acid are the trialkyl and triaryl orthoborates, $B(OR)_3$. Unsymmetrical esters, $ROB(OR')_2$, are known but tend to disproportionate to the symmetrical forms. The acid ester derivatives of boric acid, $HOB(OR)_2$ and $ROB(OH)_2$, have never with certainty been isolated, although they have been postulated as intermediates in both the hydrolysis and the dealkylation by hydrogen halides of trialkyl borates. However, chelate compounds of this type are known. Recently, mono-Z-menthyl borate (m.p. 132-135°C.) has been obtained by the controlled hydrolysis of *l*-menthyl metaborate [11].

$$ROBO + H_2O \rightarrow ROB(OH)_2$$

Structurally, boronic acids are trivalent boron-containing organic compounds that possess one alkyl substituent (i.e., a C–B bond) and two hydroxyl groups to fill the remaining valences on the boron atom (Fig.). With only six valence electrons and a 2 consequent deficiency of two electrons, the sp^2 -hybridized boron atom possesses a vacant p orbital. This low-energy orbital is orthogonal to the three substituents, which are oriented in a trigonal planar geometry. Unlike carboxylic acids, their carbon analogues, boronic acids are not found in nature [12].



borane

borinic acid

boronic acid

boric acid

boronic ester
(R' = alkyl or aryl)

boroxine

Figure 2.3 : Compounds of boron [11].

2.1.3 Boron containing polymers

The first reports on the formation of boron polymers came in the early 1900's, when Alfred Stock discovered that boron and its hydrides could form compounds analogous to hydrocarbons, while working on boron hydride chemistry. Following his work, Burg and co-workers discovered that the adduct of diborane with phosphine yielded a trimer which was stable at very high temperatures and also to reduction by sodium in liquid ammonia. They also found that if the same phosphinoborane unit was synthesized in the presence of a slight excess of base, it formed a ring opened compound with as many as 300 repeating units. Because of their high thermal stability and flame retarding properties, polymers that had alternate P and B atoms have been studied extensively since the 1950's. At the same time Heying and Schroeder synthesized a family of carbosiloxane rubbers under the trade name DEXSIL at Olin Laboratories in Connecticut. On similar lines carborane polymers with tin bridges were also synthesized. During the same time Trofimenko and co- workers at DuPont were able to synthesize the first oligomeric boron bridged borate systems [13].

Since the first reports of oligomeric and polymeric boron containing compounds, the polymer chemistry of boron has gained tremendous ground. Boron containing polymers now find applications in a variety of fields like their use as polymeric precursors for high performance materials, supramolecular nanomaterials, polymer supported catalysts for organic transformations, for drug delivery, as optical materials, sensors for nucleophiles etc. These developments have mainly been driven by three fundamental characteristics of boron; its electronic characteristic i.e. its ability to delocalize π-electrons because of the presence of the empty p-orbital, its nuclear characteristic i.e. its neutron capturing ability since it exists naturally in the form of two isotopes, one of which has a large cross-section for neutrons, and its characteristic to react with oxygen at high temperature to form B_2O_3 char or in the case of B-N containing compounds, the formation of boron-nitride ceramic materials [13].

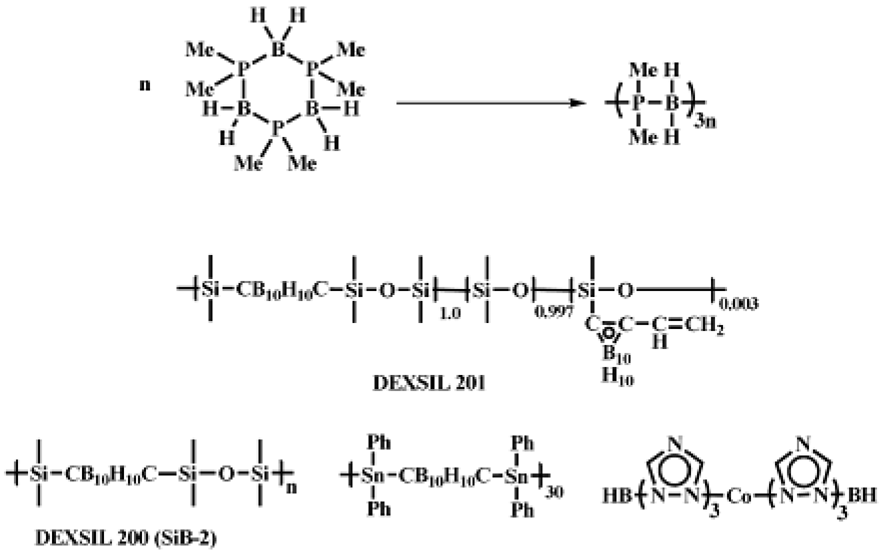


Figure 2.4 : Examples of first boron containing polymer and oligomers.

Boron-containing polymers are an important class of materials in the field of inorganic and organometallic polymers. Of particular interest is the incorporation of organoboranes into the polymers because they can act as Lewis acids due to the empty p-orbital on the boron center. Boron containing polymers can be classified as main-chain and side-chain functionalized compounds. Polymeric compounds present certain advantages over small molecule analogues, such as the possibility of using solution processability (spin casting, roll printing, inkjet printing) for fabrication of devices and in case of sensor materials, the prospect of signal amplification [14].

2.1.4 Main-chain functionalized organoboron polymers

First main-chain organoboron containing conjugated polymers via hydroboration polymerization (Fig. 2.5), but their characterization was hampered owing to their sensitivity to air and moisture [15-16].

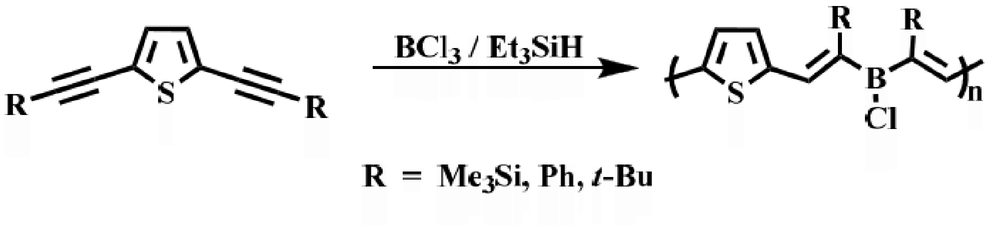


Figure 2.5 : Fisrt examples of boron containing conjugated polymers via hydroboration polymerization.

In the early 1990’s Chujo and co-workers pioneered the hydroboration polymerization methodology and systematically studied the resulting polymers. Chujo et al. have been successful in synthesizing a number of polymers that bear a boron atom in the main-chain. The first stable polymer via hydroboration polymerization was obtained by reaction of mesitylborane with aromatic diynes. They reported molecular weights of ca. M_n = 6500. The n polymers exhibited an intense emission upon irradiation with UV light and showed interesting electronic properties which indicated that the polymers were typical n-type conjugated polymers (Fig. 2.6) [17].

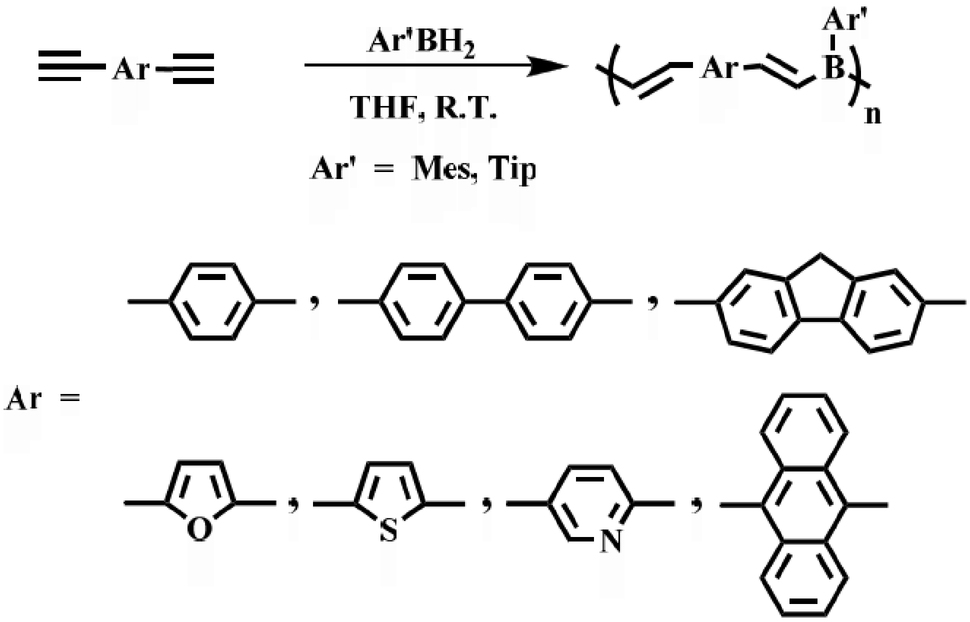


Figure 2.6 : Conjugated boron containing polymers.

Other transition metal containing organoboron polymers are also known. For example, Wagner and co-workers have synthesized a variety of coordination polymers, by the reaction of bis-borylated ferrocene with 4,4’-bipyridine (4,4’-BIPY) (a) and its derivatives, which show interesting charge transfer properties. They have also synthesized related polymers that have pyrazine linkers (b) instead of 4,4’-BIPY which are dark-green in color indicating. The ring-opening polymerization (ROP) of boron bridged ferrocenophanes, a methodology developed by Manners and co-workers, has been utilized for the preparation of ferrocene containing organoboron polymers. Manners et al. also found that silyl-bridged ferrocenophanes could selectively ring open by reaction with boron halides, thus producing functionalized ferrocenylboranes that serve as precursors to boron-containing polymers [18].

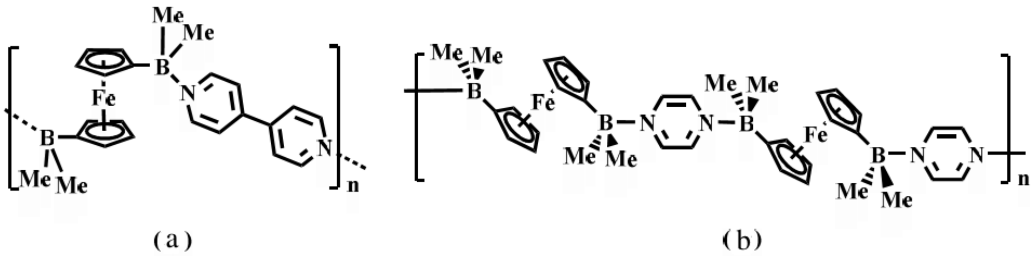


Figure 2.7 : Ferrocene containing organoboron polymers.

2.1.5 Side-chain functionalized conjugated organoboron polymers

While main-chain containing polymers have been extensively studied, comparatively few reports on side-chain functionalized organoboron polymers exist. Side-chain functionalization can offer various advantages like the synthesis of soluble organoboron polymers with controlled architecture, high molecular weights, and varying degree of functionalization possibility of chain extension leading to the synthesis of copolymers with different functionalities and since the boron is attached as a pendant group, two different groups can be attached to the boron center thereby allowing polymers with varying degree of Lewis acidities to be obtained [14].

Main-chain functionalized conjugated organonboron polymers have received a lot of attention, but comparatively few examples of side-chain functionalized conjugated organoboron polymers exist. Electrochemical synthesis of conjugated polymers that feature boronic acid or boronate moieties have been studied by Freund et al. and Fabre et al. Fabre and co-workers reported the synthesis of boronic acid and boronate ester functionalized polypyrrole (c) and its use as a fluoride sensor was studied electrochemically using cyclic voltammetry [19].

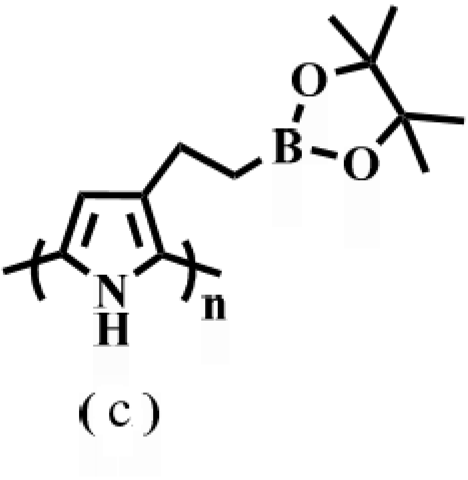


Figure 2.8 : Side-chain functionalized conjugated organoboron polymers.

2.1.6 Polymerization of boron containing monomers

Organoboron polymers can be synthesized either through the polymerization of boron-functionalized monomers or via post-polymer modification reactions. Both these methods have been used for the synthesis of boron containing polymers but polymerization of boron-functionalized monomer has received far more attention than post-polymer modification reactions. While polymerization of the functionalized monomer has been used widely, post-polymer modification reactions allow us to avoid issues, like compatibility of the monomer to polymerization techniques, which one may encounter with direct polymerization methods [14].

A variety of polymerization methods can be used to prepare organoborane polymers from organoboron monomers. Most widely used methods include standard free radical polymerization (d) and controlled free radical polymerization (e, f) due to their simplistic synthetic procedures and reasonable compatibility with B-C bonds [20]. Ziegler-Natta polymerization on the other hand has been employed widely for highly reactive and strongly Lewis acidic monomers which tend to be not very well suited for other polymerization techniques (g, h). Anionic polymerization can not be used for other polymerization techniques (i). such monomers due to their incompatibility with initiators used. ROMP is another methodology that has been employed for the synthesis of boron containing polymers from boron containing monomers (f, g) [21-22].

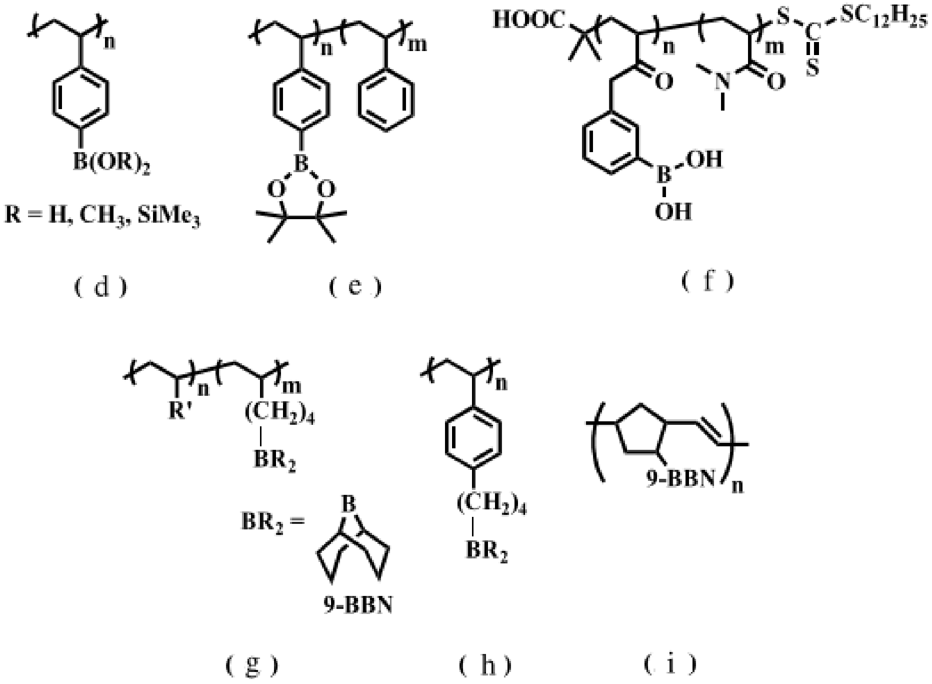


Figure 2.9 : Examples of Boron Functionalized Polymers Synthesized from Boron-Containing Monomers via Free Radical, Controlled Free Radical, Ziegler-Natta and ROMP Techniques.

2.2 Flame Retardancy

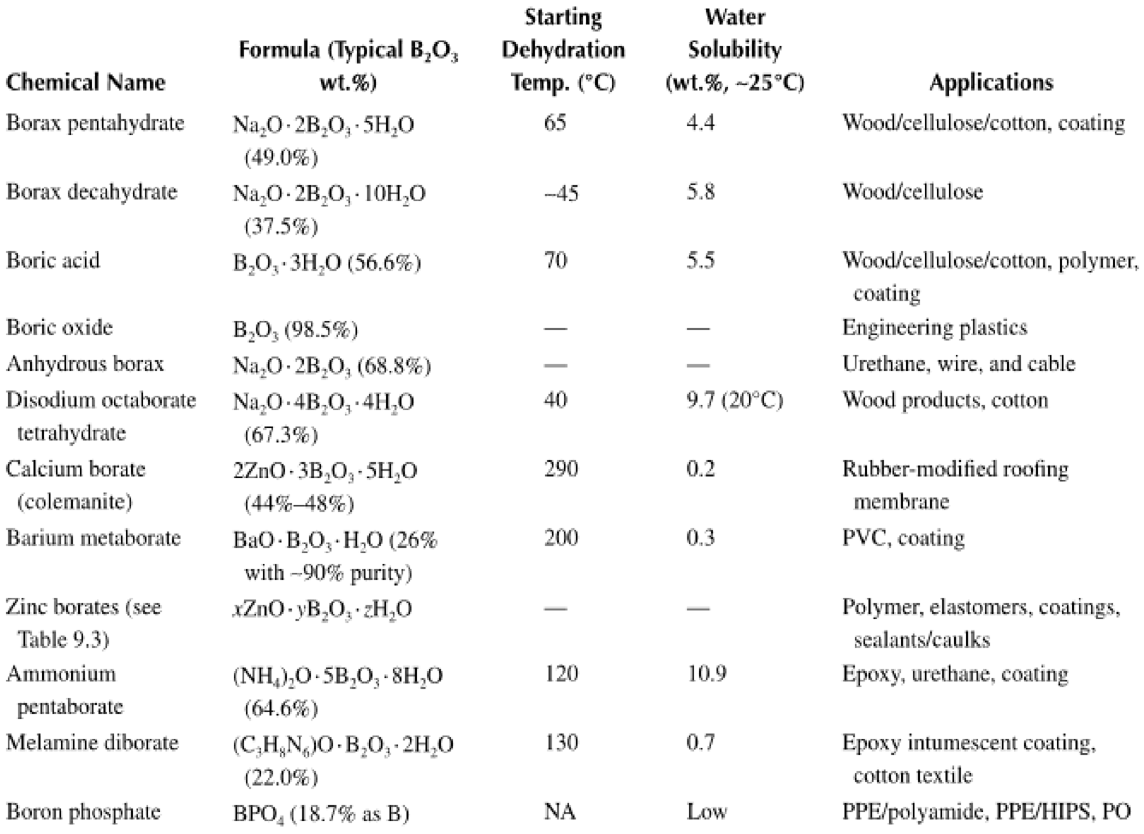
A material is said to have flame retardancy behavior; if it slows down the flame growth and flame propagation when it is subjected to a fire. Similarly, a flame retardant material slows down the growth and propagation of any flames which is caused by the material itself, when it catches fire. A material with flame retardancy property does burn but not easily or rapidly. It can either self-extinguish when the source of flame is removed after ignition, or stay lighted when it is ignited, and it burns relatively slowly [23]. Flame retardants are either additives which makes a polymer burn slowly or polymers which have the ability to retard the flame growth after ignition.

2.2.1 Main ways flame retardants act

Flame retardant materials reveal their flame retardancy property physically, chemically or in both ways.Flame retardants act physically in three distinct ways: cooling, forming a protective layer and dilution. Firstly, flame retardants can cool the sample via endothermic reactions. Secondly, they can prevent heat and O_2 from reaching to the sample and any flammable compound from reaching to vapor phase.

Thirdly, dilution of radicals in flame can be done by release of H_2O and CO_2 [24]. Chemical action of flame retardants can be examined in two ways where the phase of reaction (i.e. gas or solid phase) gains importance. During the reaction in the gas phase, flame retardants prevent formation of radical reactions within the flame. This phenomenon reduces the concentration of radicals which results in extinguishment of flame. By this way, heat releasing processes gradually decay and the system cools down. Unfortunately, these reactions yield release of toxic and irritant semi-burnt products, such as CO. Thus, toxicity of the flame gases may increase. Throughout reaction in the solid phase, fire retardants function as cleaving the polymer; therefore, polymer melts and starts to drop away from the flame. Better solid phase retardants cause formation of carbonaceous char which covers polymer surface as a layer. As a result of char formation, evolution of smoke and semi-burnt products decreases. Synergistic effect of blowing agents results in swelling between polymer and char, which offers better insulation.

2.2.2 Flame retardancy of boron containing polymers



Chemical Name	Formula (Typical B_2O_3 wt.%)	Starting Dehydration Temp. (°C)	Water Solubility (wt.%, ~25°C)	Applications
Borax pentahydrate	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$ (49.0%)	65	4.4	Wood/cellulose/cotton, coating
Borax decahydrate	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$ (37.5%)	~45	5.8	Wood/cellulose
Boric acid	$B_2O_3 \cdot 3H_2O$ (56.6%)	70	5.5	Wood/cellulose/cotton, polymer, coating
Boric oxide	B_2O_3 (98.5%)	—	—	Engineering plastics
Anhydrous borax	$Na_2O \cdot 2B_2O_3$ (68.8%)	—	—	Urethane, wire, and cable
Disodium octaborate tetrahydrate	$Na_2O \cdot 4B_2O_3 \cdot 4H_2O$ (67.3%)	40	9.7 (20°C)	Wood products, cotton
Calcium borate (colemanite)	$2ZnO \cdot 3B_2O_3 \cdot 5H_2O$ (44%–48%)	290	0.2	Rubber-modified roofing membrane
Barium metaborate	$BaO \cdot B_2O_3 \cdot H_2O$ (26% with ~90% purity)	200	0.3	PVC, coating
Zinc borates (see Table 9.3)	$xZnO \cdot yB_2O_3 \cdot zH_2O$	—	—	Polymer, elastomers, coatings, sealants/caulks
Ammonium pentaborate	$(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O$ (64.6%)	120	10.9	Epoxy, urethane, coating
Melamine diborate	$(C_3H_8N_6)O \cdot B_2O_3 \cdot 2H_2O$ (22.0%)	130	0.7	Epoxy intumescent coating, cotton textile
Boron phosphate	BPO_4 (18.7% as B)	NA	Low	PPE/polyamide, PPE/HIPS, PO

Figure 2.10 : Major Boron Based Commercial Flame Retardants [23].

Borate and boric acid have been well known to function as flame retardants, particularly in a synergistic fashion with halogenated polymers and halogen additive polymeric system [25]. However, the use of boron compounds such as zinc borate, ammonium pent- aborate (APB), melamine borate, boric oxide, boron phosphate, and other metal borates in polymers has become prominent only since early 1980s. The flame retardancy of boron compounds is known to have its origin in the ability of the compounds to form a surface layer of an intumescent protective char, which acts as a barrier to oxygen, and consequently to the oxidation of carbon. According to this special thermal stability properties that many scientis improved the new boron containing polymer structures. This polymers were synthesized with different methods.

2.3 Free Radical Polymerization

Free-radical reactions are of importance in a wide variety of commercial applications in industry; because generation of a radical is easy, many polymers can be polymerized and radical polymerizations are tolerant to the impurities (moisture, protic solvents), that normally would terminate an ionic polymerization. The first papers in this area were published in the 1940s and 1950s. However, even before that, in the 1930s, the applicability of this technique rapidly propelled this method to the commercial scale for the manufacture of diverse polymers starting from oil derivatives. Nowadays, FRP is the solid foundation of many industrial processes and a source of a number of polymeric materials. Materials such as polyethylene, polystyrene, polyvinylalcohol, polyvinylacetate, polybutadienes, and other well-known commodities have significantly improved day-to-day life. However, the considerable growth of this petro-chemical segment over seven decades is now in danger because of environmental issues and high oil prices. Hence, to improve profit margins and avoid reputation losses, the industry has been moving toward bioresourced polymers during the last two decades. In addition, during the mid-1990s, FRP was revitalized with the introduction of the reversible deactivation techniques -commonly known as controlled/living RP-opening the possibility to form very diverse block copolymers or more complex structures, which could not be synthesized earlier by FRP techniques [26].

2.3.1 Basic mechanism

The most conventional kinetic scheme of FRP includes initiation, propagation, and bimolecular termination reaction steps. Additional reactions such as chain transfer are introduced to improve the process description. Free radicals are highly reactive chemical species produced by the homolytic dissociation of covalent bonds. Such species are produced through physical (thermoexcitation, radiation) or chemical methods (oxidation–reduction, addition, etc.). Generally, their survival time is less than a second, except for those radicals highly stabilized by specific chemical groups; the hybridization state is sp^2. Free radicals react in six different manners as illustrated or in Figure 2.11 [27-28].

In an FRP, all these reactions are susceptible to occur, but in a concentrated monomer environment, the dominating reactions are the addition (propagation) and termination by disproportionation or coupling. The fragmentation, abstraction, and transmutation reactions are detrimental for the chain formation; however, sometimes they can be induced to regulate the degree of polymerization.

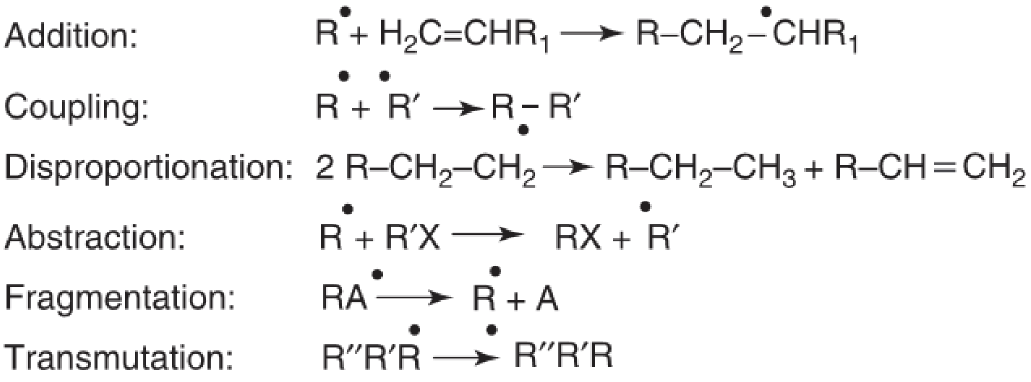


Figure 2.11 : Free radical reactions

The central mechanism of chain formation involves the generation of free radicals, the initiation, propagation and termination. The radical generation and the first monomer addition to an initiating radical constitute the initiation step, whereas the successive monomer additions over a new free radical and the termination of chain growth by disproportionation and/or coupling actually constitute the formation of chains as represented in **Figure 2.12**.

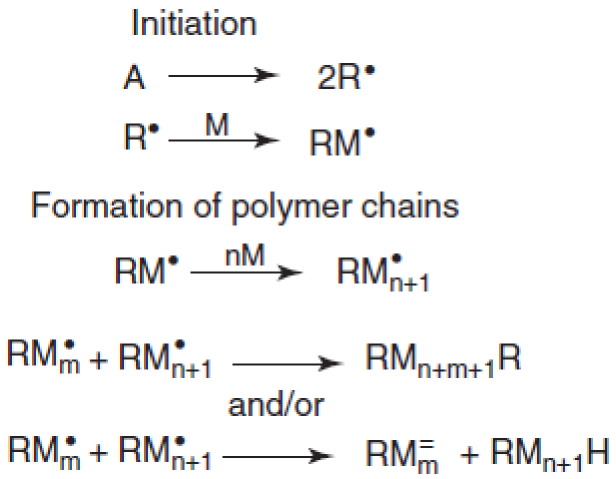


Figure 2.12 : Reaction induced by an initiating radical generated from the initiator A

If we show the FRP main steps basically in **Figure 2.13**; initiation, propagation, and termination. I represents the initiator, R● represents a radical generated by either thermal or photo decomposition of I, M represents a monomer unit, M● represents a monomer radical, and Pn ● represents a polymer radical after the subsequent n monomer additions. Free radicals are generated through the initiation step, which usually involves the photo- or thermal decomposition of an initiator into a pair of radicals [29]. Common free-radical initiators include benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN). 2,3 Monomers then subsequently add to these radicals during the propagation step. Finally, the polymer chains stop growing via termination. Two possible termination pathways are possible, combination and disproportionation. Both of these processes involve the presence of two polymer radicals. During combination, two polymer radicals couple together, resulting in a polymer chain whose length is a sum of the two coupled polymers. Disproportionation results when the hydrogen that is on the carbon next to one of the radical centers transfers to another radical center. This process results in one of the polymer chains with a saturated chain end and the other with an unsaturated chain end (i.e., a double bond). Disproportionation is by far the more common termination pathway. Two key aspects of conventional free-radical polymerization affect the molecular weight distribution of the resulting polymers. First, the rate of initiation is typically much slower than the rate of propagation [29]. Additionally, the rate of termination is comparable to the rate of initiation throughout most of the polymerization [30]. As such, polymer chains are initiated and terminated throughout the polymerization. Assuming that termination occurs via disproportionation, polymers generated from conventional free-radical polymerizations thus have molecular weights characterized by the most probable distribution. The polydispersities (PDIs) of these polymers are given by the following equation [29].

$$PDI = \frac{M_w}{M_n} = 1 + p \tag{2.1}$$

where *Mw* is the weight-average molecular weight of the polymer, *Mn* is its numberaverage molecular weight, and *p* is the fraction of monomer units reacted. The PDIs of polymers synthesized by conventional free-radical polymerizations thus approach 2 at high conversions. Consequently, the main limitation to conventional free-radical polymerization is the formation of polymers with PDIs approaching 2. The major limitation of RP is poor control over some of the key structural elements that allow the preparation of well defined macromolecular architectures such as molecular weight (MW), polydispersity, end functionality, chain architecture and composition.

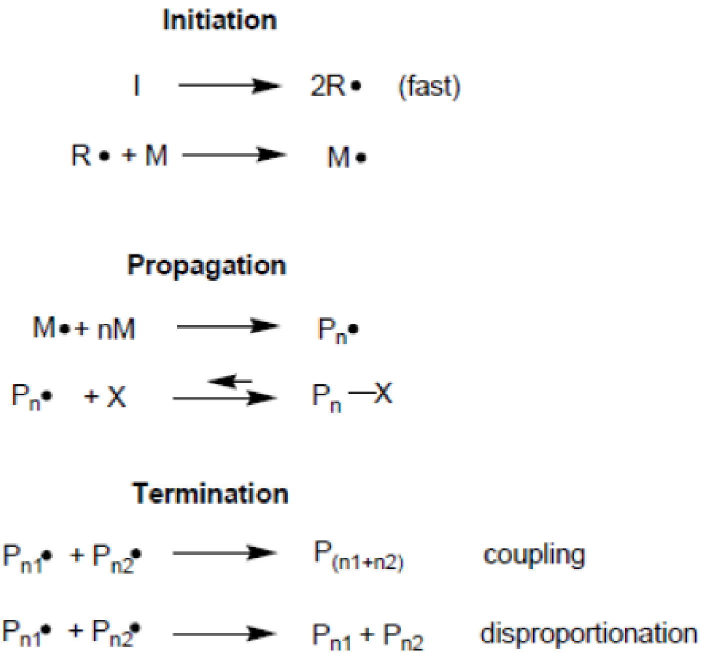


Figure 2.13 : The reaction steps associated with free-radical polymerization.

2.3.2 Free radical copolymerization

The mechanism of free radical copolymerization, similar to any radical polymerization [31]. Some observations are relevant to the consideration of copolymerization kinetics are;

- The number of reactions involved in copolymerization of two or more monomers increases geometrically with the number of monomers. Consequently, the propagation step in the copolymerization of two monomers involves four reactions.
- The number of radicals to be considered equals the number of monomers. The terminal monomer unit in a growing chain determines almost exclusively the reaction characteristics; the nature of the preceding monomers has no significant influence on the reaction path.
- There are two radicals in the copolymerization of two monomers. Consequently, three termination steps need to be considered.
- The composition and structure of the resulting copolymer are determined by the relative rates of the different chain propagation reactions.

By designating the two monomers as M_1 and M_2 and their corresponding chain radicals as $M_1\cdot$ and $M_2\cdot$, the four propagation reactions and the associated rate equations in the copolymerization of two monomers may be written as follows [31].

Reaction	Rate equation
$M_1\cdot + M_1 \rightarrow M_1\cdot$	$k_{11}\,[M_1\cdot][M_1]$
$M_1\cdot + M_2 \rightarrow M_2\cdot$	$k_{12}\,[M_1\cdot][M_2]$
$M_2\cdot + M_1 \rightarrow M_1\cdot$	$k_{21}\,[M_2\cdot][M_1]$
$M_2\cdot + M_2 \rightarrow M_2\cdot$	$k_{22}\,[M_2\cdot][M_2]$

(2.2)

Here the first subscript in the rate constant refers to the reacting radical, while the second subscript designates the monomer. Now, it is reasonable to assume that at steady state, the concentrations of $M_1\cdot$ and $M_2\cdot$ remain constant. This implies that the rates of generation and consumption of these radicals are equal. It follows therefore that the rate of conversion of $M_1\cdot$ to $M_2\cdot$ necessarily equals that of conversion of $M_2\cdot$ to $M_1\cdot$. Thus from equation 2.2 [31];

$$k_{21}[M_2\cdot][M_1]=k_{12}[M_1\cdot][M_2] \tag{2.3}$$

The rates of disappearance of monomers M_1 and M_2 are given by

$$\frac{-d[M_1]}{dt}=k_{11}[M_1\cdot][M_1]+k_{21}[M_2\cdot][M_1] \tag{2.4}$$

$$\frac{-d[M_2]}{dt}=k_{12}[M_1\cdot][M_2]+k_{22}[M_2\cdot][M_1] \tag{2.5}$$

By using equation 2.3, one of the radicals can be eliminated. By dividing equation 2.4 by equation 2.5 we obtain:

$$\frac{d[M_1]}{d[M_2]}=\frac{[M_1]}{[M_2]}\,\frac{r_1\,[M_2]+[M_2]}{[M_1]+r_2\,[M_2]} \tag{2.6}$$

where r_1 and r_2 are monomer reactivity ratios defined by

$$\begin{gathered} r_1=k_{11}/k_{12} \\ r_2=k_{22}/k_{21} \end{gathered} \tag{2.7}$$

Equation 2.6 is the copolymer equation. Let F_1 and F_2 represent the mole fractions of monomers M_1 and M_2 in the increment of polymer formed at any instant during the polymerization process, then

$$f_1 = 1 - f_2 = d[M_1]/d([M_1]+[M_2]) \tag{2.8}$$

Similarly, representing the mole functions of unreacted M_1 and M_2 in the monomer feed by f_1 and f_2, then

$$F_1 = 1 - F_2 = \frac{[M_1]}{[M_1]+[M_2]} \tag{2.9}$$

Substitution of Equations 2.8 and 2.9 in Equation 2.6 yields:

$$f_1 = \frac{r_1 F_1^2 + F_1 F_2}{r_1 F_1^2 + 2 F_1 F_2 + r_2 F_2^2} \tag{2.10}$$

2.3.3 Types of copolymerization

Different types of copolymerization behavior are observed depending on the values of the monomer reactivity ratios. Copolymerizations can be classified into three types based on whether the product of the two monomer reactivity ratios r_1r_2 is unity, less than unity, or greater than unity.

By definition, r_1 and r_2 represent the relative preference of a given radical that is adding its own monomer to the other monomer. The physical significance of Equation 2.10 can be illustrated by considering the product of the reactivity ratios.

$$r_1 r_2 = \frac{k_{11} k_{22}}{k_{12} k_{21}} \tag{2.11}$$

2.3.3.1 Ideal copolymerization (r_1r_2=1)

Ideal copolymerization occurs when the two types of propagating species M1· and M2· show the same preference for adding one or the other of the two monomers. Under these conditions

$$\begin{aligned} &r_1 r_2 = 1, \quad \text{then} \\ &r_1 = 1/r_2 \quad \text{or} \quad k_{11}/k_{12} = k_{21}/k_{22} \end{aligned} \tag{2.12}$$

and the relative rates of incorporation of the two monomers into the copolymer are independent of the identity of the unit at the end of the propagating species. For an ideal copolymerization Equation 2.12 is combined with Equation 2.6 or 2.10 to yield the copolymerization equation as

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]} \tag{2.13}$$

$$f_1 = \frac{r_1 F_1}{F_1(r_1 - 1) + 1} = \frac{r_1 F_1}{r_1 F_1 + F_2} \tag{2.14}$$

It is evident that for ideal copolymerization, each radical displays the same preference for adding one monomer over the other. Also, the end group on the growing chain does not influence the rate of addition. For the ideal copolymer, the probability of the occurrence of an M_1 unit immediately following an M_2 unit is the same as locating an M_1 unit after another M_1 unit. Therefore, the sequence of monomer units in an ideal copolymer is necessarily random. The relative amounts of the monomer units in the chain are determined by the reactivities of the monomer and the feed composition. To illustrate this, we note that the requirement that $r_1r_2 = 1$ can be satisfied under two conditions:

$r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$. In this case, one of the monomers is more reactive than the other toward the propagating species. Consequently, the copolymer will contain a greater proportion of the more reactive monomer in the random sequence of monomer units. An important practical consequence of ideal copolymerization is that increasing difficulty is experienced in the production of copolymers with significant quantities of both monomers as the difference in reactivities of the two monomers increases.

$r_1 = r_2 = 1$. Under these conditions, the growing radicals cannot distinguish between the two monomers. The composition of the copolymer is the same as that of the feed and as we said above, the monomers are arranged randomly along the chain. The copolymer equation becomes:

$$f_1 = \frac{F_1 F_2}{F_1 + F_2} = F_1 \tag{2.15}$$

2.3.3.2 Alternating copolymerization (r_1=r_2=0)

Alternating copolymerization is characterized by r_1r_2= 0 (or r_1= r_2= 0), where neither r_1 nor r_2 is greater than one. Consequently, the monomer units are arranged alternately along the chain irrespective of the feed composition. In this case the copolymer reduces to:

$$\frac{d[M_1]}{d[M_2]} = 1 \tag{2.16}$$

or F_1= 0.5.

Perfect alternation occurs when both r_1 and r_2 are zero. As the quantity r_1r_2 approaches zero, there is an increasing tendency toward alternation. This has practical significance because it enhances the possibility of producing polymers with appreciable amounts of both monomers from a wider range of feed compositions.

2.3.3.3 Block copolymerization (r_1 > 1, r_2 > 1)

If both r_1 and r_2 are greater than unity (and therefore, also r_1r_2 > 1) there is a tendency to form a block copolymer in which there are blocks of both monomers in the chain. That means each radical would prefer adding its own monomer. The addition of the same type of monomer would continue successively until there is a chance addition of the other type of monomer and the sequence of this monomer is added repeatedly. Thus the resulting polymer is a block copolymer. In the extreme case of this type of polymerization (r_1= r_2= ∞) both monomers undergo simultaneous and independent homopolymerization; however, there are no known cases of this type of polymerization. Even though cases exist where r_1r_2 approaches 1 (r_1r_2= 1), there are no established cases where r_1r_2 > 1. Indeed, the product r_1r_2 is almost always less than unity. This type of behavior is rarely encountered.

3. EXPERIMENTAL PART

3.1 Chemicals

3.1.1 Monomers

Styrene (St, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use and distilled in vacuo over CaH2 just before use.

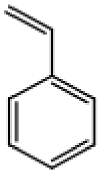


Figure 3.1 : Styrene

Methyl methacrylate (MMA, 98% , Fluka):

It was passed through a basic alumina column to remove the inhibitor before use and distilled in vacuo over CaH2 just before use.

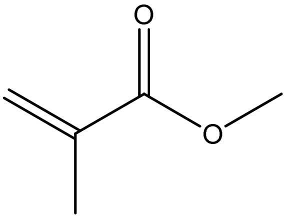


Figure 3.2 : Methyl methacrylate

3.1.2 Solvents

Hexane (≥99%, Sigma):

It was used as received.

Toluene (≥99%, Sigma):

It was dried and distilled.

Tetrahydrofuran (THF, 99.8%, J.T. Baker):

It was dried and distilled over benzophenone-Na.

Diethyl ether (Carlo Erba) :

It was used as received.

Methanol (99.9%, Merck) :

It was used as received.

Dimethylformamide (DMF) (≥99.5%, Merck) :

It is used as received.

1,4-Dioxane (99,5%, Labkim)

It is used as received.

3.1.3 Other chemicals

2,2-Dimethyl-1,3-propanediol (Neopentyl glycol) (99%, abcr) :

It is used as received.

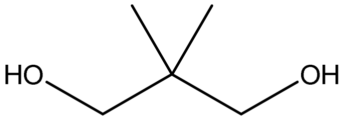


Figure 3.3 : Neopentyl glycol

2-Hydroxyethylmethacrylate (HEMA) (BDH Chemicals) :

Stabilized with 0,02% w/v 4-methoxyphenol. It is used as received.

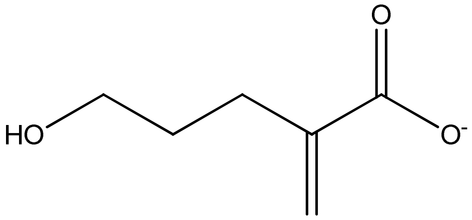


Figure 3.4 : HEMA

Hypophosphorus acid, 50% w/w aqueous solution (abcr) :

It is used as received.

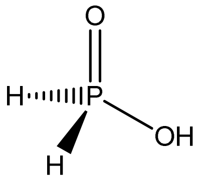


Figure 3.5 : Hypophosphorus acid

Boric acid (99,5-100,5%, Merck) :

It is used as received.

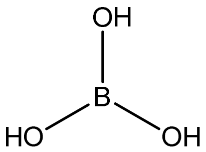


Figure 3.6 : Boric acid

2-Methylhydroquinone (99%, abcr) :

It is used as received.

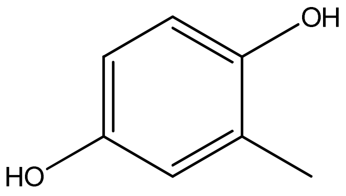


Figure 3.7 : 2-Methylhydroquinone

2,2'-Azobis(2-methyl-propionitrile) (AIBN) (98%, Acros Organics) :

It is used as received.

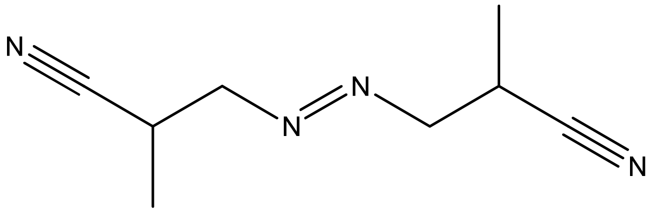


Figure 3.8 : AIBN

3.2 Equipments

3.2.1 Fourier transform infrared spectroscopy (FT-IR)

Analyses were performed with Thermo Scientific Nicolet IS FT-IR Spectrometer. Resolution mode is 4 cm^{-1}. Sixteen scans were averaged for each sample in the range 4000-400 cm^{-1}.

3.2.2 Nuclear magnetic resonance (NMR)

^{1}H-NMR, ^{13}C-NMR, ^{11}B-NMR analyses were performed with Agilent VNMRS spectrometer at 500 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) and deurterated chloroform ($CDCl_3$) were used as solvent.

3.2.3 Gel permeation chromatography (GPC)

sea Analyses were performed with a set up consist of Agilent pump and refractive index detector and three Agilent Zorbax PSM 1000S, 300S, 60S columns (6.2 x 250 mm, 5 micron) measuring in the range of 10^4-10^6, $3x10^3$-$3x10^5$,$5x10^2$-10^4 respectively. THF was used as the eluent at a flow rate of 0.5 ml/min at 30°C. M_ws were calculated with the aid of pSt and pMMA standards.

3.2.4 Viscometer

Viscosities of polymer solutions were measured with DMF as a solvent at 25 °C by using Ubbelohde glass viscometer. The driving pressure in this viscometer was determined by measuring the distance from the level of the liquid in the bulb to the level, which is the bottom of the capillary.

3.2.5 Differential scanning calorimetry (DSC)

Analyses were performed with TA DSC Q10 instrument in a flowing nitrogen atmosphere from 30°C at scanning rate of 10°C/min.

3.2.6 Thermogravimetric analyser (TGA)

Analyses were permormed with TA Q50 instrument under the nitrogen atmosphere at a heating rate of 20°C/min rising rom room temperature to 800°C. The weights of samples are between 6-10 mg. Calibration was achieved with indium as reference material.

3.3 Synthesis

3.3.1 Synthesis of boron acrylate monomer (BAc)

The monomer was synthesized with two step by esterification reaction. In first step 17 mL toluene was added to a 100 mL two-necked round flask that equipped with a Dean-Stark apparatus and a Friedrich condenser. The flask equipped with a stopper and needle for air pump. Additionaly the flask equipped with drying tube. The heater was opened and set to 60 °C. Than 5 g boric acid, 0,056 mL Hyphophosphorous acid, Neopentyl glycol was added to system and the heat was set to 125 °C for dissolving. The system was stirred and exposured to air during all reaction. 2 eq water was removed by azeotropic distillation with Dean-Stark apparatus. In second step 0,0556 g Methylhydroquinone, 9,8 mL HEMA was added to flask and 1 eq water removed. At the end of reaction the solvent was removed to system with vacuum distillation. Product was synthesized transparent and liquid. The yield was 78% and it was caculated by water content.

3.3.2 Synthesis of boron acrylate homopolymer (BAc Homopolymer)

The polymerizations were performed in a dry Schlenk tube which was charged with determined amount of monomer BAc, 5 ml of methanol and AIBN (2.5 mol % of total monomer). Oxygen was removed by three freze-pump-thaw cycles by applying vacuum and backfilling with nitrogen. The tube with the polymerization mixture was immersed into a silicon oil o bath, preheated to 70 °C. After the desired time, the tube was removed from the bath and cooled rapidly down to ambient temperature, and the reaction mixture was diluted with methanol. The polymers were precipitated into diethyl ether and dried under vacuum.

3.3.3 Synthesis of boron acrylate-styrene copolymer (p(BAc-*co*-St))

The polymerizations were performed in a dry Schlenk tube which was charged with determined amount of monomers (BAc and St), 2 ml of toluene and AIBN (2.5 mol % of total monomer). Oxygen was removed by three freze-pump-thaw cycles by applying vacuum and backfilling with nitrogen. The tube with the polymerization mixture was immersed into a silicon oil o bath, preheated to 80 °C. After the desired time, the tube was removed from the bath and cooled rapidly down to ambient temperature, and the reaction mixture was diluted with THF. The polymers were precipitated into hexane and dried under vacuum.

3.3.4 Synthesis of boron acrylate-methylmethacrylate copolymer (p(BAc-*co*-MMA))

The polymerizations were performed in a dry Schlenk tube which was charged with determined amount of monomers (BAc and MMA), 2 ml of 1,4 Dioxane and AIBN (2.5 mol % of total monomer). Oxygen was removed by three freze-pump-thaw cycles by applying vacuum and backfilling with nitrogen. The tube with the polymerization mixture was immersed into a silicon oil o bath, preheated to 70 °C. After the desired time, the tube was removed from the bath and cooled rapidly down to ambient temperature, and the reaction mixture was diluted with methanol. The polymers were precipitated into hexane and dried under vacuum.

4. RESULTS AND DISCUSSION

In this thesis, Boron acrylate monomer was sythesized that was used for polymerization for BAc homopolymer, BAc-*co*-St and BAc-*co*-MMA copolymers. Synthesized materials characterizated by NMR, FT-IR, GPC, DSC, TGA, Ubbelohde viscometer. In addition reactive ratios of BAc-*co*-St copolymers determined by Kelen-Tüdos method.

4.1 Boron Acrylate Monomer (BAc Monomer)

Boron Acrylate monomer is classified as a saturated cyclic borate ester which was synthesized from 2,2-dimethyl-1,3-propanediol(neopentyl glycol) and boric acid by esterefication reaction (**Figure 4.1**). This reaction was performed in two-steps. 2 eq H_2O collected on first step with dean-stark aparatus, then 1 eq H_2O collected on second step. Toluene was to be a carrier phase in this reaction.

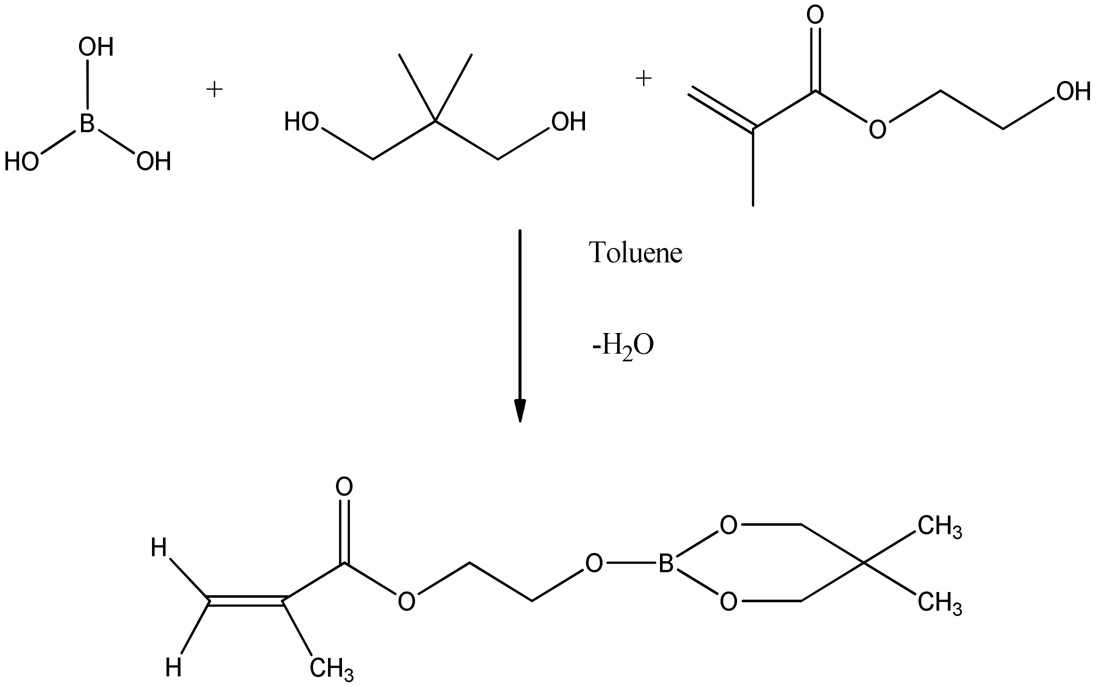


Figure 4.1 : Synthesis of BAc.

The structure of BAc monomer was confirmed by spectroscopic investigations. The FT-IR spectrum showed at 2960 cm^{-1} -CH band, the characteristic C=O ester band at 1717 cm^{-1} and C=C band at 1637 cm^{-1} and B-O group at 1417 cm^{-1} at **Figure 4.2**.

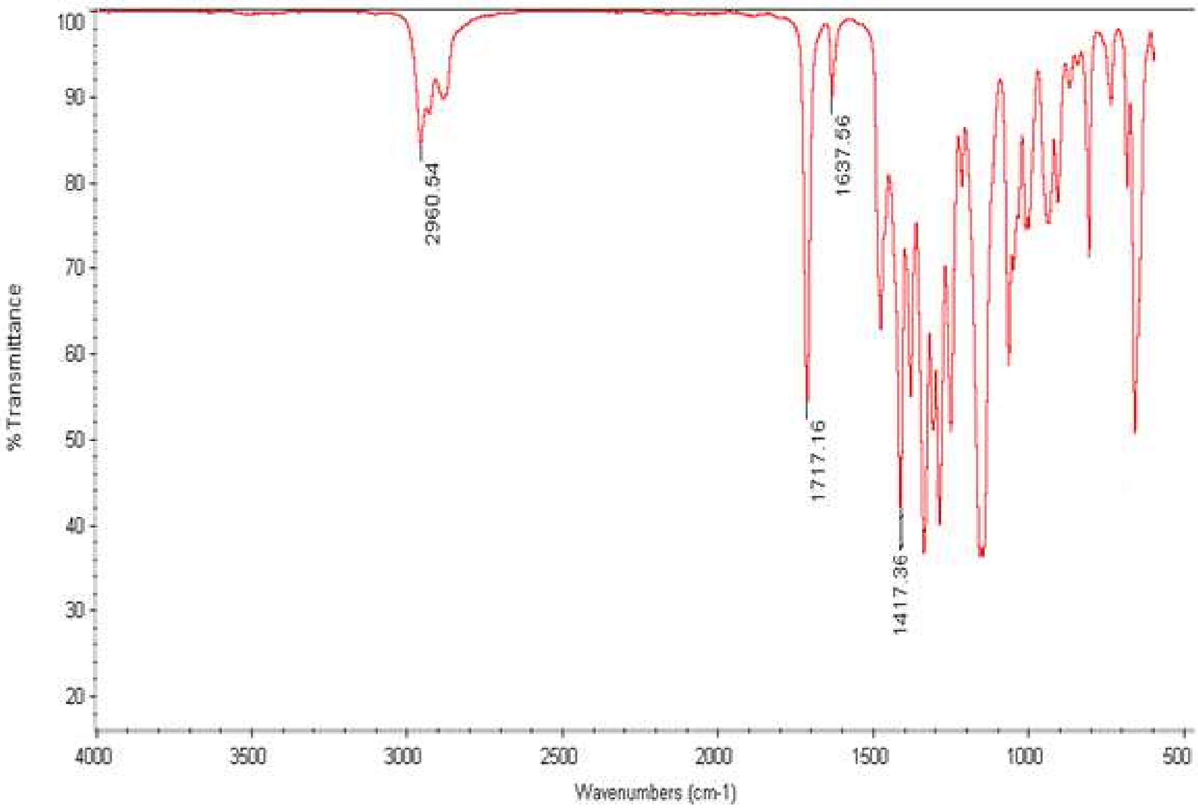


Figure 4.2 : FT-IR Spectrum of BAc.

The FT-IR spectra of HEMA and BAc given in **Figure 4.3.** Differences between these two spectra are the dissappearance of characteristic peak of -OH group around 3420 cm^{-1} and new B-O band ensued at 1417 cm^{-1}.

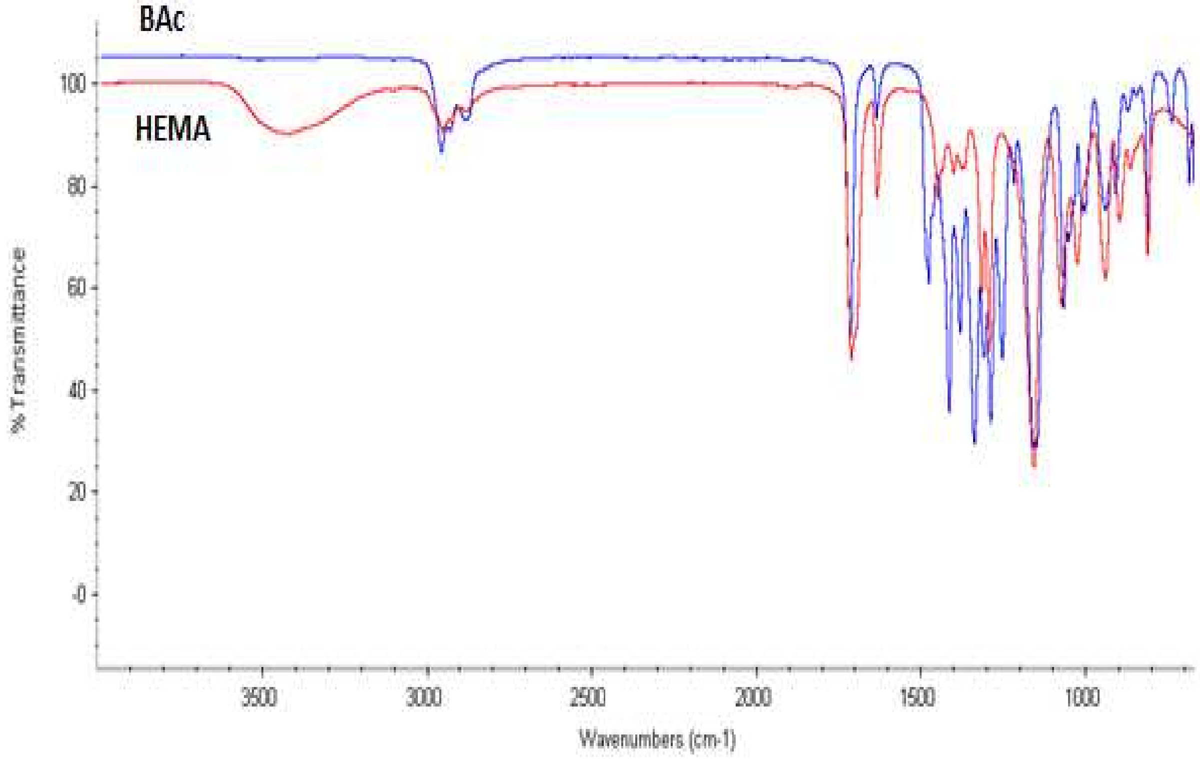


Figure 4.3 : FT-IR spectra of BAc and HEMA.

Figure 4.4 was representated the ^{1}H-NMR spectrum of BAc which were recorded in $CDCl_3$. The peak observed between 5.5 ppm and 6.1 ppm corresponded to C=C-H protons. Spectrum indicated two different $-OCH_2$ protons. One of them observed between 3.8 ppm and 4.2 ppm, the other peaks observed one signal around 3.5 ppm. $-CH_3$ protons signal were recorded at 1.8 ppm and 0.8 ppm. We showed that the BAc monomer form to compared ^{1}H-NMR spectrum of HEMA and ^{1}H-NMR spectrum of BAc in **Figure 4.4** and **Figure 4.5**. While -OH peak of HEMA disappeared, new C=C-H peaks and - CH_3 peak formed in these reaction. **Figure 4.6** was representated the ^{13}C-NMR Spectrum of BAc.

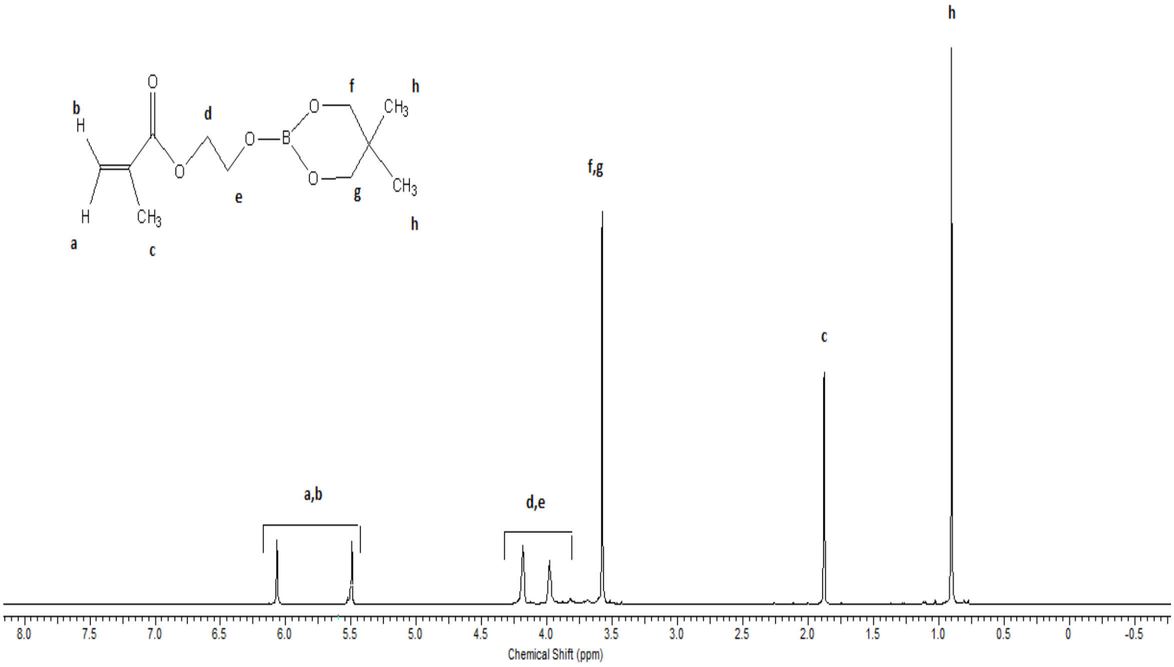


Figure 4.4 : ^{1}H-NMR Spectrum of BAc.

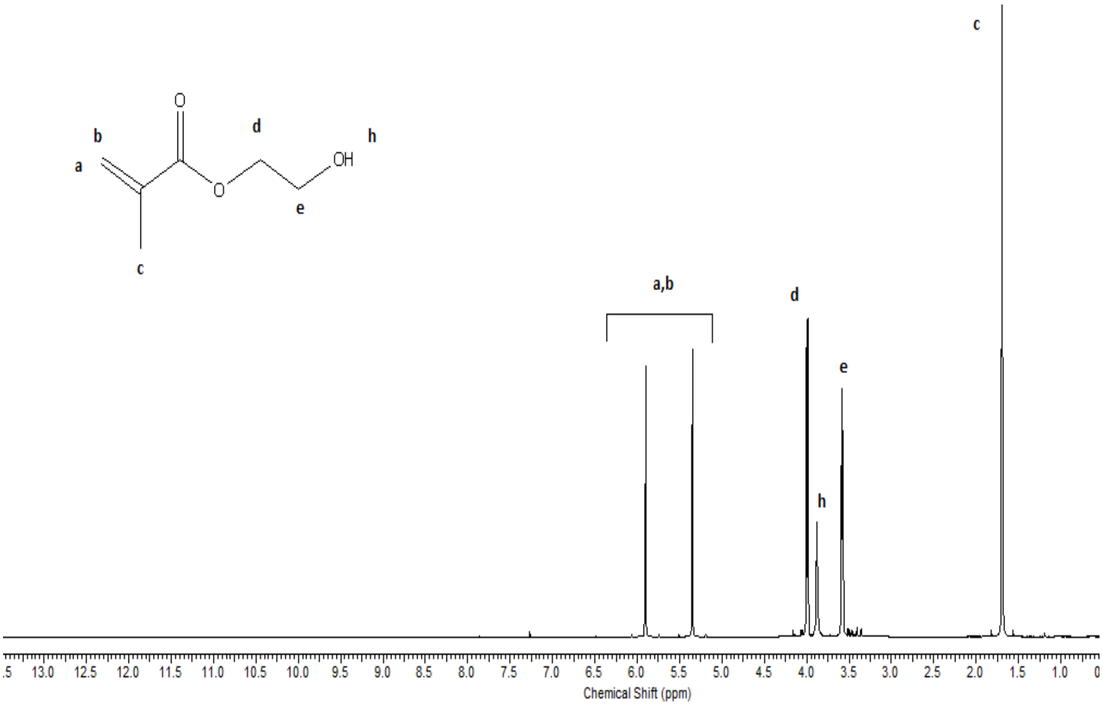


Figure 4.5 : ^{1}H-NMR Spectrum of HEMA.

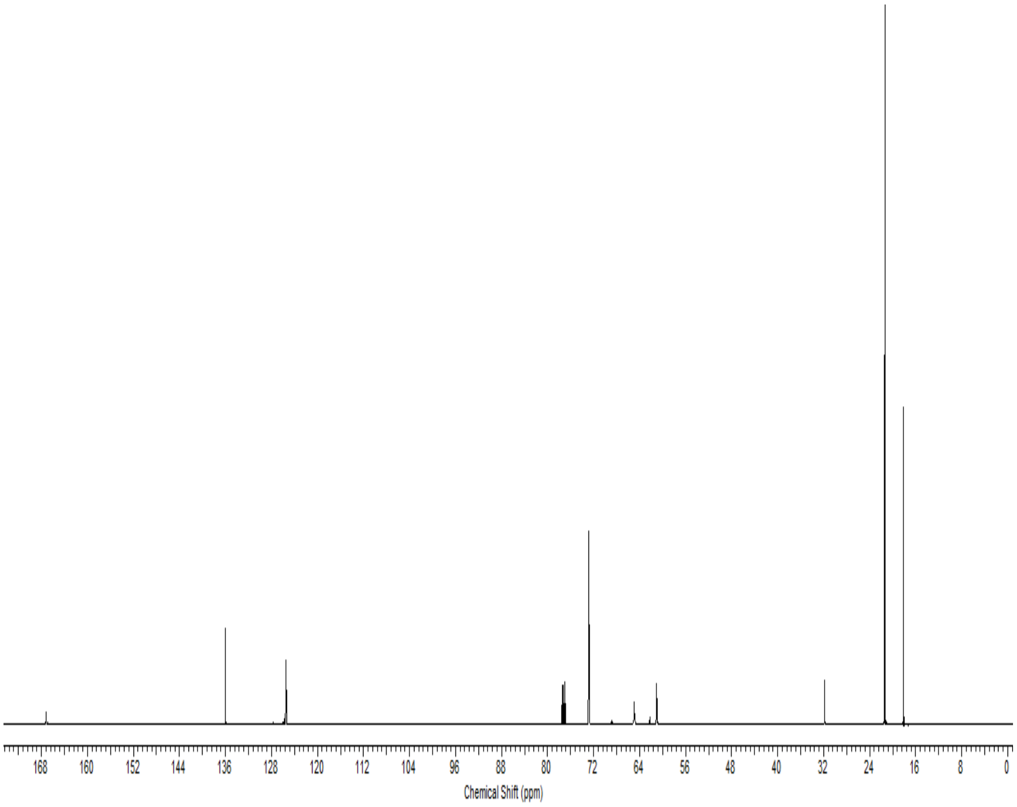


Figure 4.6 : ^{13}C-NMR Spectrum of BAc.

4.2 Boron Acrylate Homopolymer (BAc Homopolymer)

In this study, Boron acrylate homopolymer were synthesized via free radical polymerization with AIBN in methanol at 70 °C for 1 hour (**Figure 4.7**). The polymer precipitated in diethyl ether. The polymer were characterizated with ^{1}H-NMR and ^{11}B-NMR.

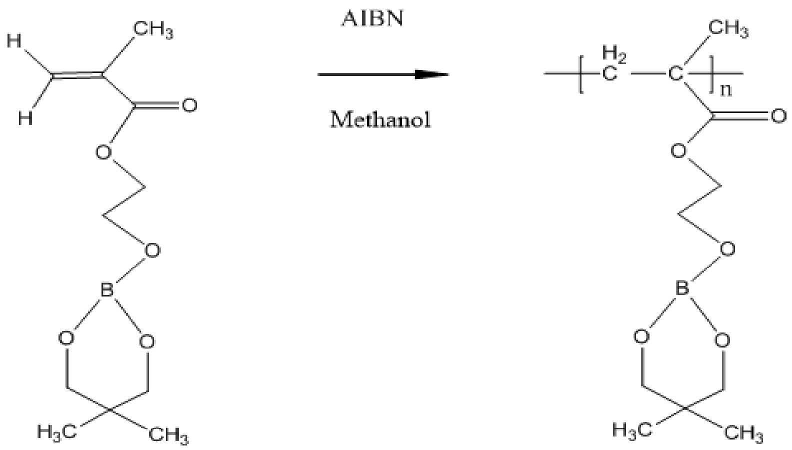


Figure 4.7 : Synthesized of BAc homopolymer

The different between ^{1}H-NMR spectra of BAc monomer and BAc homopolymer is disappearance of the peak between 5.5 ppm and 6.1 ppm corresponded to C=C-H protons in **Figure 4.8** because of the polymerization. The spectrum of BAc homopolymer indicated two different -OCH$_2$ protons like BAc monomer. One of them observed between 3.9 ppm and 4.8 ppm, the other peaks observed one signal between 3.6 ppm. -CH$_3$ and -CH$_2$ signals were observed between 1.9 ppm and 0.8 ppm.

In ^{11}B-NMR of BAc monomer, there is a sharp peak between -20 ppm and 20 ppm. After polymerization the peak remains the same range but it gets broader (**Figure 4.9**)

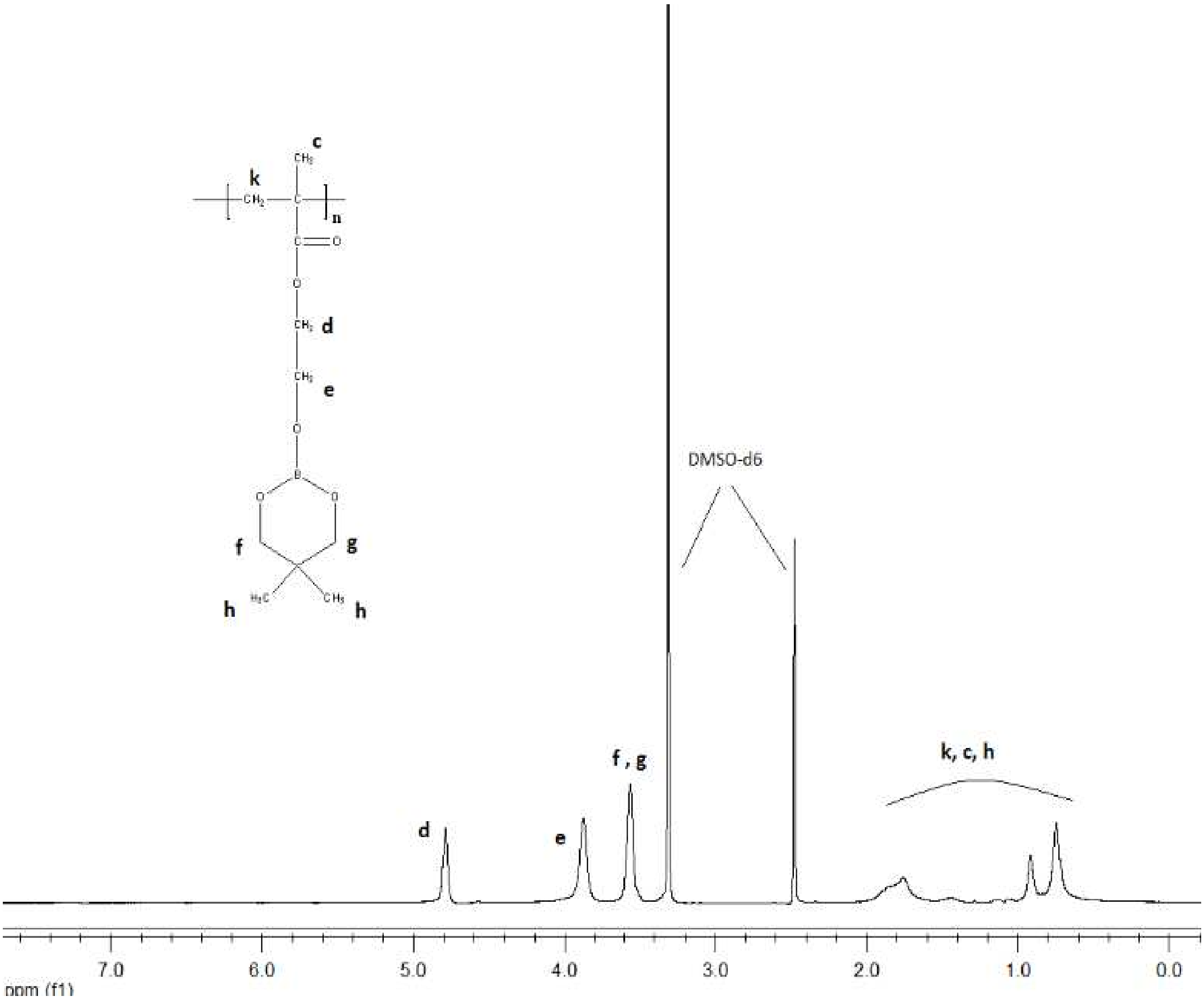


Figure 4.8 : ^{1}H-NMR Spectrum of BAc homopolymer

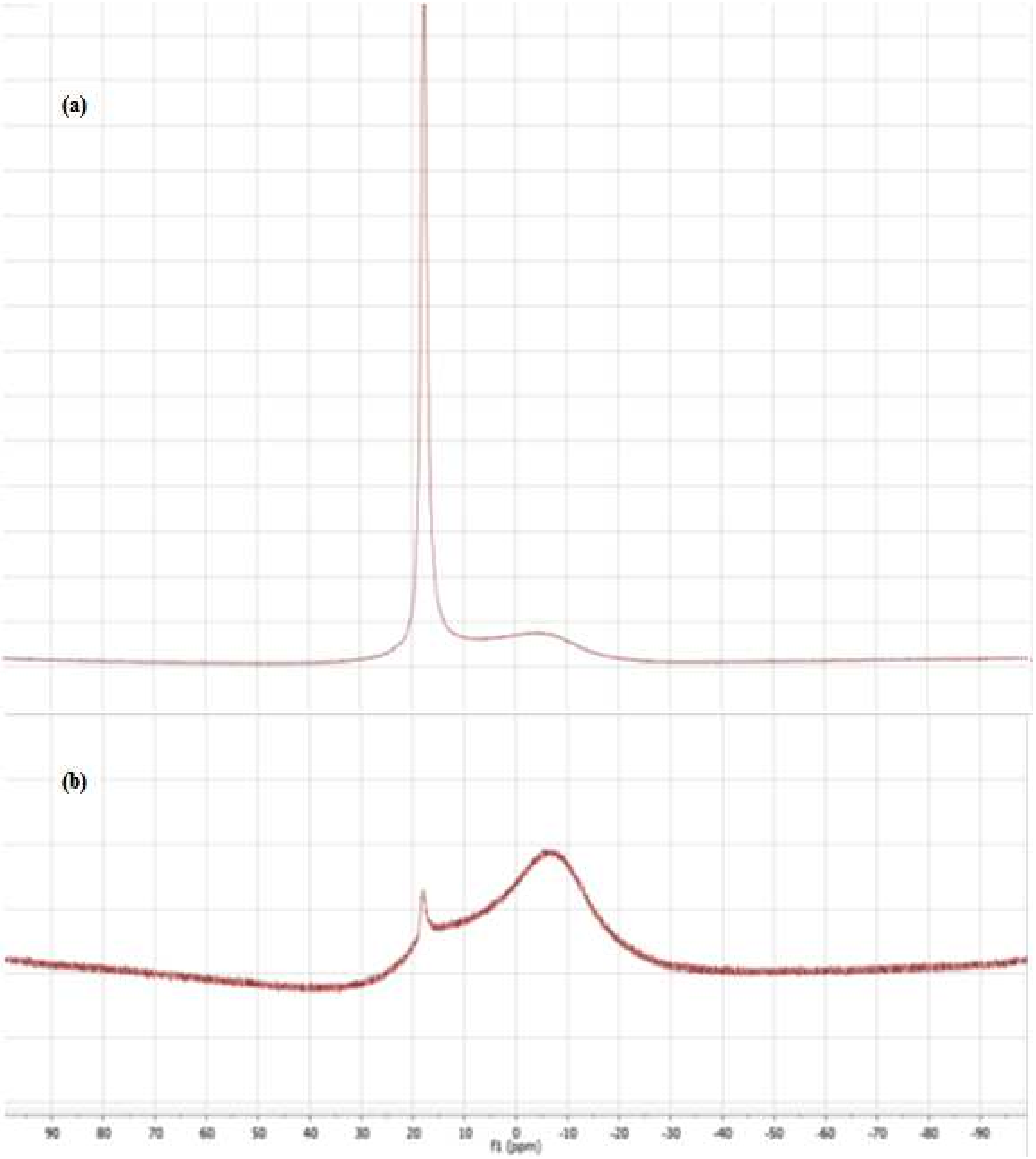


Figure 4.9 : (a) ^{11}B-NMR spectrum of BAc monomer (b)^{11}B-NMR spectrum of BAc homopolymer.

4.3 Boron Acrylate-Styrene Copolymer (p(BAc-*co*-St))

p(BAc-*co*-St) synthesized via free radical copolymerization with AIBN in Toluene at 80 °C for 0,5 hour and precipitated in Hexane (**Figure 4.10**). The polymer were characterizated with ^{1}H-NMR.

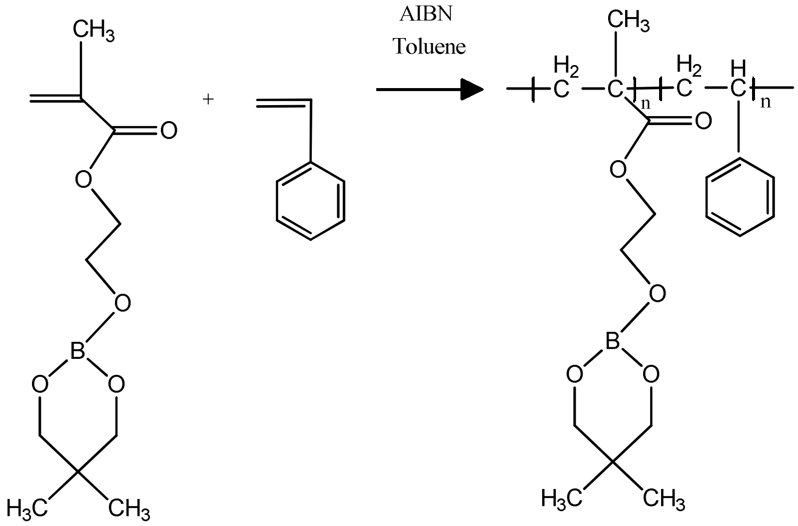


Figure 4.10 : Synthesized of p(BAc-*co*-St) copolymer.

In the ^{1}H-NMR spectrum of p(BAc-*co*-St) (**Figure.4.11**) , peaks appearing at around 6.5-7.5 ppm were assigned to the aromatic protons and peaks apperaing at around 3.4-3.6 ppm were assigned to –OCH_2 protons. The other –OCH_2 protons appeared between 3.8 ppm and 4.1 ppm. All other remaining peaks observed between 0.8 ppm and 2.0 ppm.

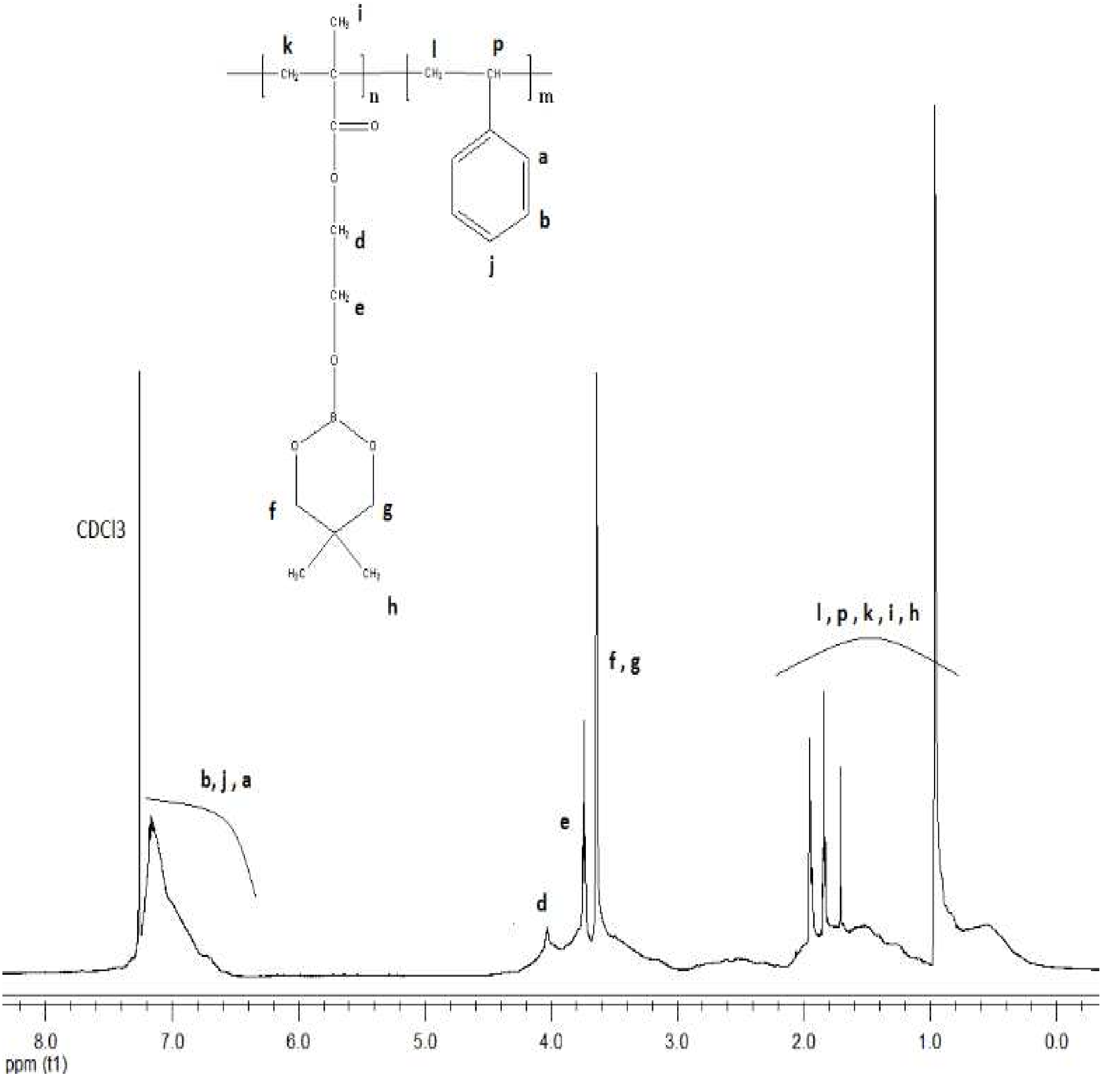


Figure 4.11 : ^{1}H-NMR Spectrum of p(BAc-*co*-St) copolymer.

Table 4.1 lists the polymer characteristics of the prepared samples. The following notation will be used for the different copolymers. p(BAc) and p(St) are the homopolymers of BAc and St. p(BAc-*co*-St)-50/50 represents a random copolymer of 50 mol % BAc and 50 mol % St in the monomer feed. Thus, p(BAc-*co*-St)-10/90 is a random copolymer of 10 mol % BAc and 90 mol % St in the monomer feed. The copolymer compositions of the p(Bac-*co*-St) copolymers were determined by ^{1}H-NMR. The experimental fraction of BAc monomers was slightly lower than the corresponding fraction in monomer feed, as shown in **Table 4.1.**

Table 4.1 : Free radical copolymerization of BAc(M_1) and St (M_2) at 80°C.[a]

	Monomer Feed (mol %)		Copolymer Composition [b] (mol %)				
	F_1	F_2	f_1	f_2	Conv. %	M_n [c]	M_w/M_n [c]
p(BAc-*co*-St)-10/90	10	90	9	91	7	5830	1,81
p(BAc-*co*-St)-20/80	20	80	17	83	31	6358	1,81
p(BAc-*co*-St)-30/70	30	70	28	72	12	8563	1,90
p(BAc-*co*-St)-40/60	40	60	32	68	30	6692	1,76
p(BAc-*co*-St)-50/50	50	50	35	65	27	10650	2,30
p(BAc-*co*-St)-60/40	60	40	41	59	46	6838	2,8
p(BAc)	100	-	100	-	44	14669[d]	-
p(St)	-	100			29	6624	1,4

a Initiator: AIBN (8.5x10^{-3} M), [BAc]+[St] = 0.034 M, time: 0,5 hour
b Determined ^{1}H-NMR data.
c Determined by GPC measurement.
d Determined by Ubbelohde viscometer. K=8.9x10^{-3}, a=0.73 in DMF at 25°C [32].

Figure 4.11 shows the ^{1}H-NMR spectrums of p(BAc-co-St) copolymers. In the spectrums peaks appearing at around 6.5-7.5 ppm were assigned to the aromatic protons from p(St) polymer fraction, at around 3.4-3.6 ppm were assigned to $–OCH_2$ protons from p(BAc) polymer fraction. The compositions of the copolymers in **Table 4.1** were calculated on the basis of the ^{1}H-NMR results, comparing the values of the integrals of the peaks appearing at around 3.4-3.6 ppm, which is characteristic for $–OCH_2$ protons in the BAc monomer and the peaks appear in the range of 6.5-7.5 ppm which are for aromatic protons of St monomer.

Copolymerization of newly synthesized Boron acrylic monomer (BAc) with St was evaluated by free radical polymerization with different monomer feeds to calculate the reactivity ratio of the monomers. For this purpose, during the copolymerizations, total momomer composition and time were maintained constant as well as temperature within ± 0.1 ^{0}C. All runs were carried out by employing the initiator 2.5 mol % of the total momomer amount. Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed in the batch, semi-batch or continuos reactors and to understand the kinetic and mechanistic aspects of copolymerization. The change in the reaction medium with conversion affects the monomer reactivity ratio values. Among several procedures available to determine monomer reactivity ratio, the methods of Mayo - Lewis (ML) [33], Finemann - Ross (FR) [34], inverted Finemann - Ross (IFR), Kelen - Tüdos (KT) [35], extended Kelen - Tüdos (EKT) [35-36], Tidwell - Mortimer (TM) [37], Mao-Huglin (MH) [38], are appropriate for the determination of monomer reactivity ratios at low conversions. Extended Kelen-Tüdos and Mao-Huglin methods consider the drift of comonomer and copolymer composition with conversion. Therefore they are suitable for the manipulation of high conversion data. For our system the monomer reactivity ratios of BAc and St for their free radical copolymerization were calculated by the well known extended Kelen-Tüdos method from the composition of the monomer feed and that of the instantaneously formed copolymer (**Table 4.2**).

Table 4.2 : EKT Parameters for monomer BAc and St using ^{1}H-NMR

Run	Parameters of EKT Equation			
	H	***G***	ξ	η
p(BAc-*co*-St)-10/90	0.13	-1.02	0.11	-0.88
p(BAc-*co*-St)-20/80	0.33	-1.01	0.24	-0.74
p(BAc-*co*-St)-30/70	0.48	-0.68	0.32	-0.45
p(BAc-*co*-St)-40/60	1.09	-0.81	0.51	-0.38
p(BAc-*co*-St)-50/50	2.39	-0.97	0.70	-0.28
p(BAc-*co*-St)-60/40	8.13	-1.04	0.89	-0.11

This method essentially uses the equation

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \qquad \textbf{(4.1)}$$

where η and ξ are functions of both feed and copolymer compositions defined as,

$$\eta = G/(H + \alpha) \text{ and } \xi = H/(H + \alpha) \qquad \textbf{(4.2)}$$

H and *G* are defined using a conversion-dependent constant Z, which is expressed as,

$$Z = \log(1 - \xi_1) / \log(1 - \xi_2) \qquad \textbf{(4.3)}$$

ξ_1 and ξ_2 are respectively, the partial molar conversions in monomers M_1 and M_2 and are given as,

$$\xi_1 = \xi_2(Y/X) \text{ and } \xi_2 = [\omega(\mu + X)]/(\mu + Y) \qquad \textbf{(4.4)}$$

where,

$$Y = f_1/f_2 \ , \quad X = F_1/F_2 \ , \quad \mu = \mu_2/\mu_1 \qquad \textbf{(4.5)}$$

μ_1 and μ_2 represent the molecular weights of monomer 1 and 2, respectively, and ω is the total fractional conversion. Thus, the *H* and *G* values are defined,

$$H = Y/Z^2 \text{ and } G = (Y - 1)/Z \qquad \textbf{(4.6)}$$

and α is an arbitrary parameter, usually taken as,

$$\alpha = (H_{max} . H_{min})^{1/2} \qquad \textbf{(4.7)}$$

Monomer reactivity ratios (r_1 and r_2) were calculated using experimental data, presented in **Table 4.3**, treated by EKT method [39].

Table 4.3 : Monomer Reactivity Ratios (r_1, r_2)

M_1	M_2	$r_1=k_{11}/k_{12}$	$r_2=k_{22}/k_{21}$	$r_1.r_2$	$1/r_1=k_{12}/k_{11}$	$1/r_2=k_{21}/k_{22}$
BAc	St	0.08	0.95	0.07	12.50	1.05

The linear plot according to equation (4.1) gives $r_1 + r_2/\alpha$ as slope and $-r_2/\alpha$ as intercept (**Figure 4.12**).

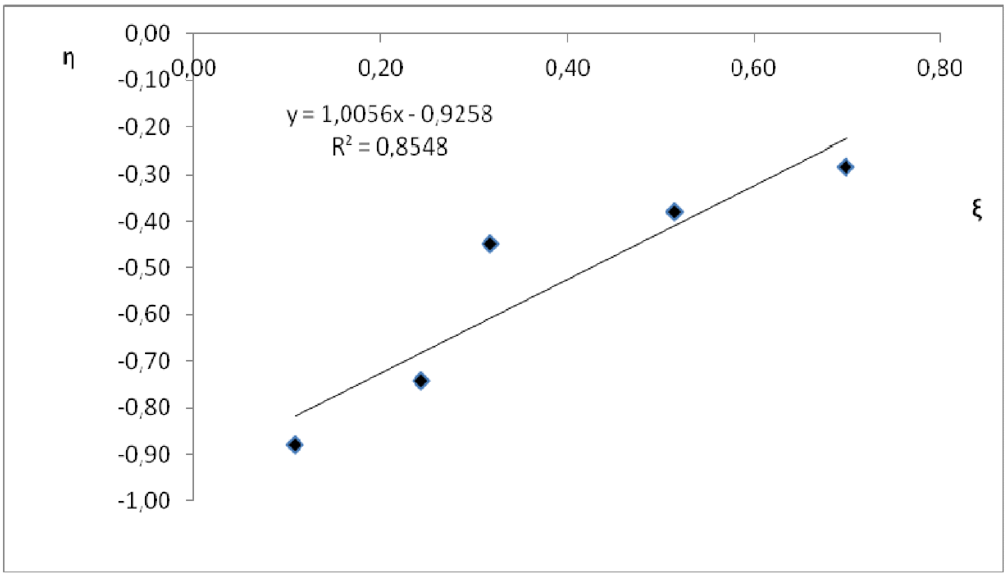


Figure 4.12 : EKT plots of ξ versus η for the free radical copolymerization of BAc (*M1*) with St (*M2*). (α = 1.03)

The reactivity ratios which were found to be $r_1 = 0.08$, $r_2 = 0.95$ and $r_1.r_2 < 1$ for the pair BAc-St show that this system undergoes random copolymerization. The value of r_1 is less than 1 which means that boron acrylic monomer (BAc) terminated propagating chain prefers to add St than another BAc monomer that is involved in the reaction. According to the obtained results it can be concluded that there occurs some composition drift that the produced copolymer contains more St than expected. The value of r_2 nearly than unity implies the copolymerization initially is dominated by this species which is the more reactive monomer (**Table 4.3**)

4.4 Synthesis of Boron Acrylate-Methylmethacrylate Copolymer (p(BAc-*co*-MMA))

p(BAc-*co*-MMA) synthesized via free radical copolymerization with AIBN in Dioxane 1,4 at 70 °C for 6 hour and precipitated in hexane (**Figure 4.13**). In this experiment, we determined moleculer weight of p(BAc-*co*-MMA) in these conditions by GPC measurement (**Tabele 4.4**).

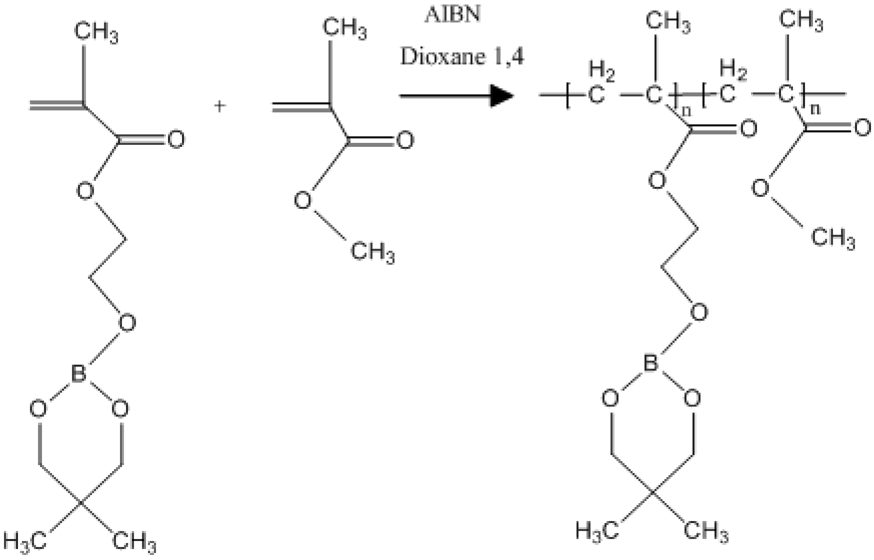


Figure 4.13 : Synthesized of p(BAc-*co*-MMA) copolymer.

Table 4.4 : Moleculer weight values of p(BAc-*co*-MMA).

	Conv. %	M_n [a]	M_w/M_n [a]
p(BAc-*co*-MMA)	20	6703	1,9

[a] Determined by GPC measurement.

4.5 Thermal Behaviour of Boron Containing Polymers

Thermal behaviours of synthesized polymers were analysed with DSC and TGA methods. DSC measurements were conducted with a heating rate of 20 °C/min. The thermal stability measurements were evaluated by TGA under nitrogen at a heating rate of 20 °C/min. The results of thermal analysis are summarized in **Table 4.5**.

Table 4.5 : DSC and TGA results of synthesized polymers

	T*g* (°C)	**Residue at 200°C (%)**	**Residue at 500 °C (%)**	**$T_{\%5}$°C**	**$T_{\%50}$°C**
pBAc	74.2	97,93	2,16	215	356
pSt	72.3	99,21	1,35	348	424
p(BAc-*co*-St)-10/90	97.2	98,16	1,72	307	417
p(BAc-*co*-St)-20/80	62.9	99,35	1,17	314	410
p(BAc-*co*-St)-30/70	74.3	98,43	5,12	278	410
p(BAc-*co*-St)-40/60	68.4	99,06	1,74	291	406
p(BAc-*co*-St)-50/50	77.1	98,65	1,53	285	404

The T_g value of pBAc was 74.2 ^{o}C (**Figure 4.15**) and the T_g value of pSt was 72.3 ^{o}C (**Figure 4.16**). Normally, standart pSt T_g values is above 100 ^{o}C in many refereneces. But the T_g of pSt change to the molecular weight which shown in **Figure 4.14** [40]. Depending on the copolymer composition, St copolymers glass transition temperatures have between at 62.9 ^{o}C and 97.2 ^{o}C (**Figure 4.17**).

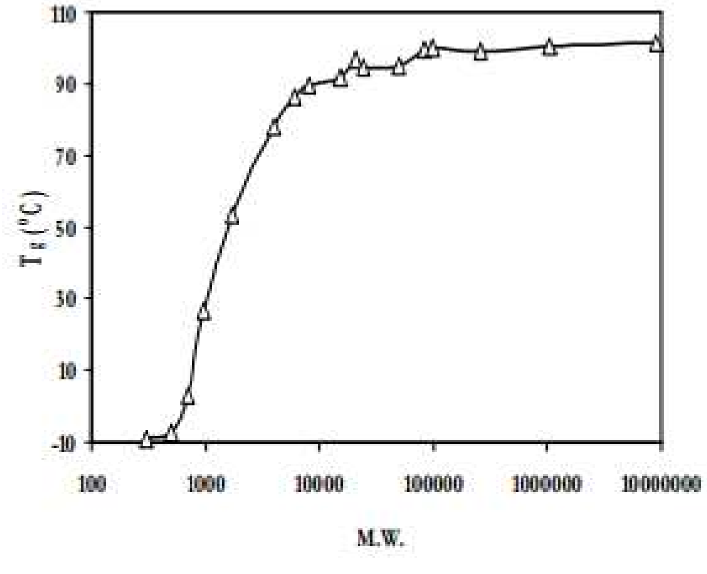


Figure 4.14 : T*g* of polystyrene as function of molecular weight.

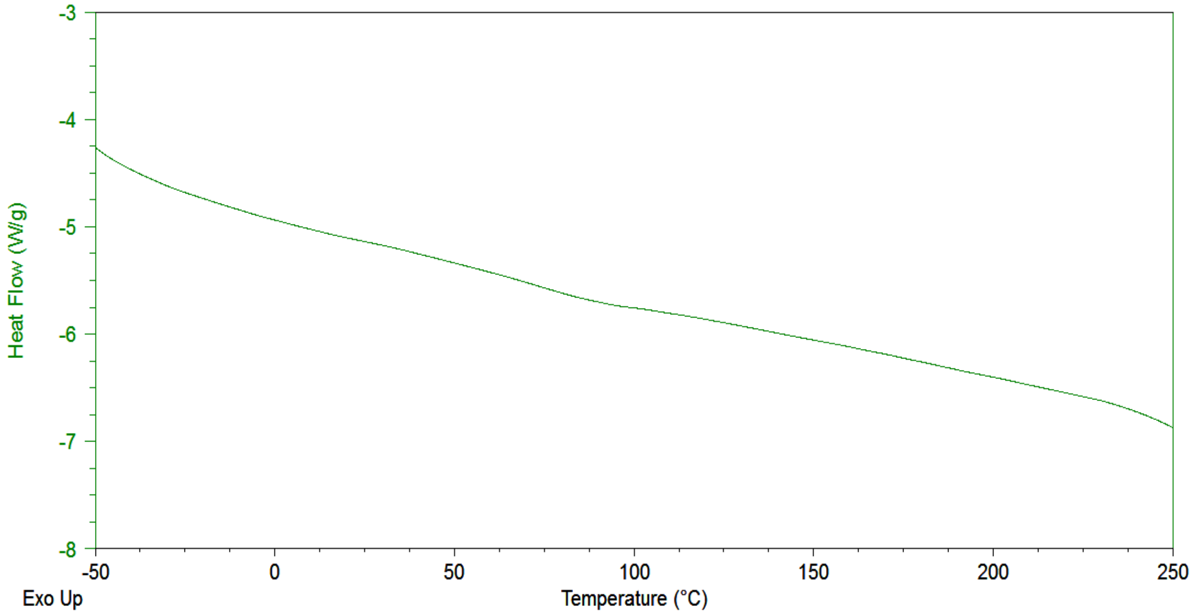


Figure 4.15 : DSC thermogram of BAc-homopolymer.

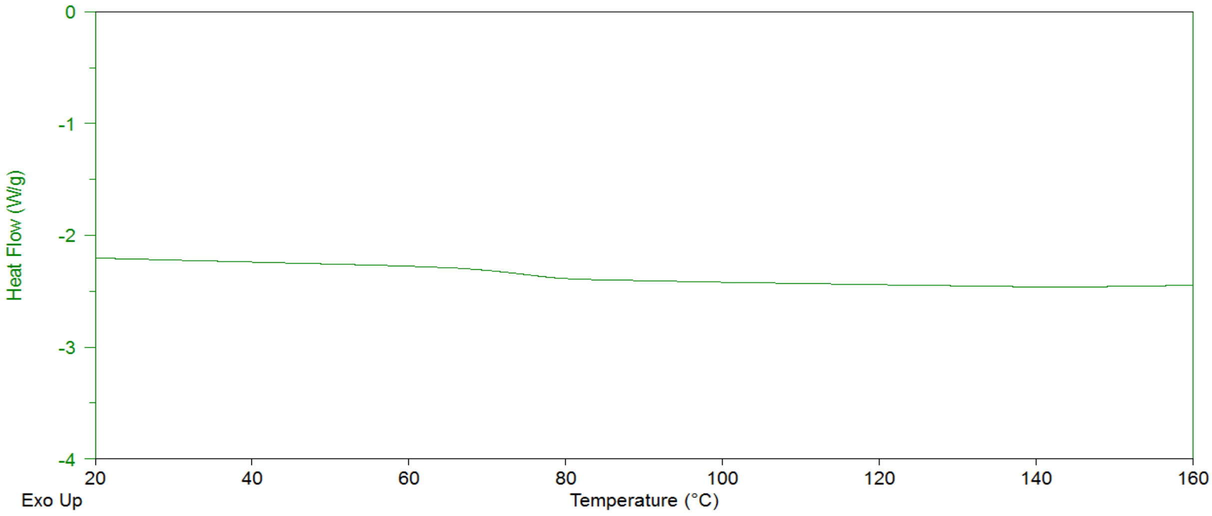


Figure 4.16 : DSC thermogram of St-homopolymer

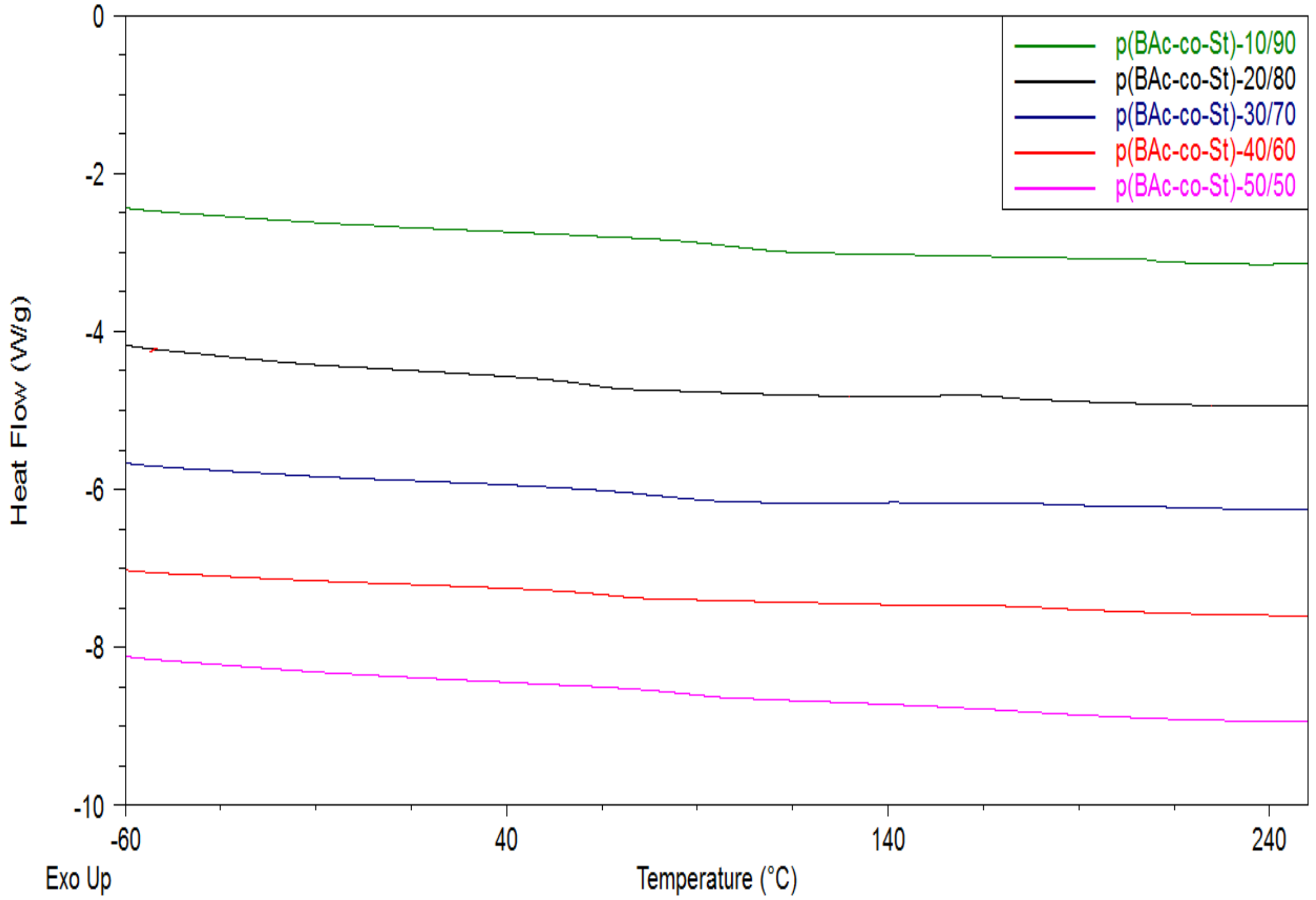


Figure 4.17 : DSC thermogram of p(BAc-*co*-St) copolymers

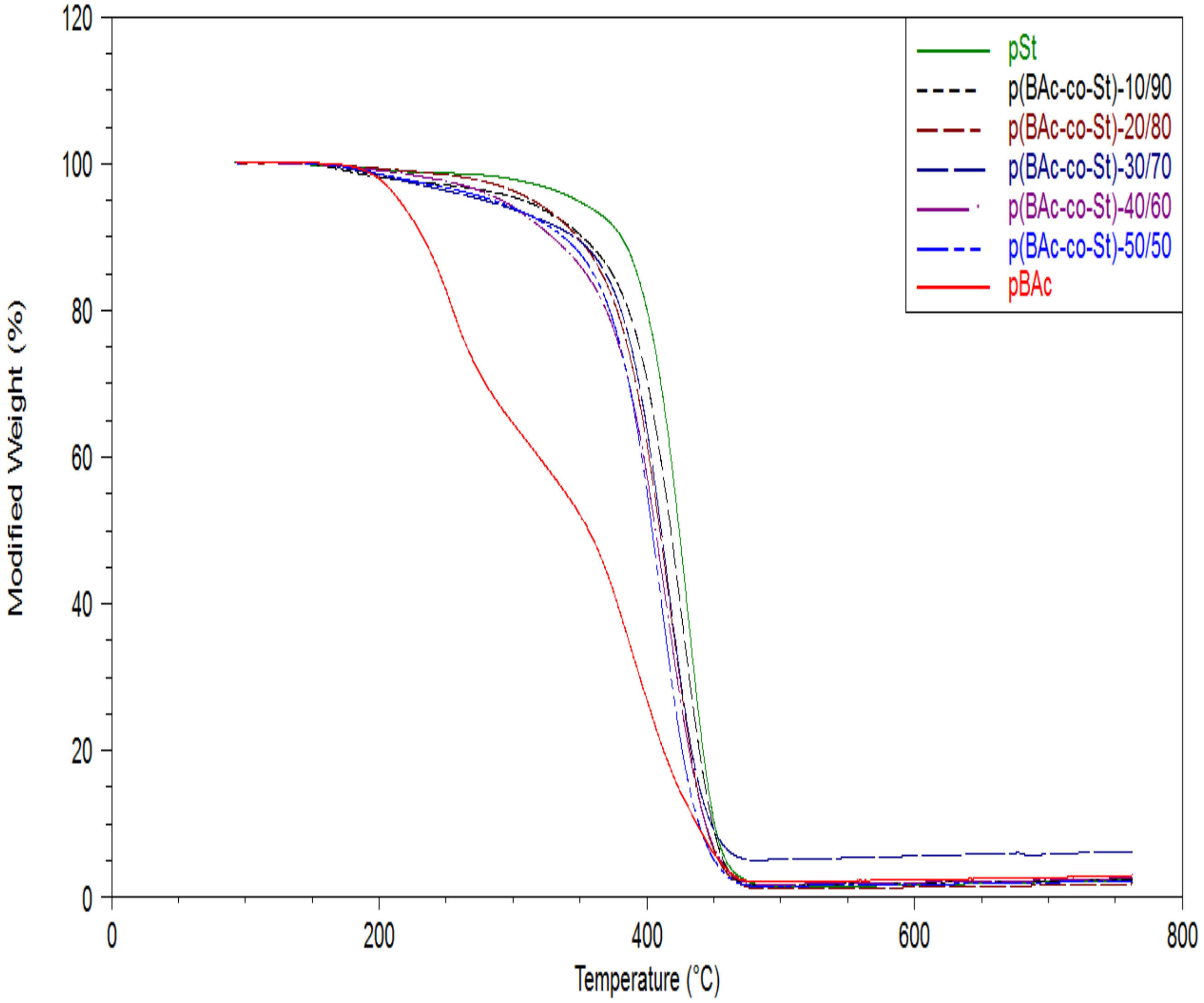


Figure 4.18 : TGA thermograms of synthesized polymers.

Figure 4.18 shows us TGA diagrams of copolymers were determined to be in between TGA diagrams of pBAc and pSt. Based on these results, while St homopolymer and copolymers have one decomposition, BAc homopolymer has two decomposition. In these results, char yields were increased by pBAc content in pSt copolymers.

4.6 Solubility of Synthesized Polymers

In this study, solubility of synthesized polymers were tested in different solvents. Results can be seen in **Table 4.6**.

As a result, BAc homopolymer was dissolved only in DMSO and DMF. On the other hand p(BAc-co-St) copolymer was dissolved in DMSO, THF, DMF, ethylacetate, diethyl ether, methanol. p(BAc-co-MMA) almost showed behaviour as p(BAc-co-St) except ethylacetate. While p(BAc-co-St) was dissolved in ethylacetate, p(BAc-co-MMA) was not dissolved in ethylacetate.

Table 4.6 : Solubility of synthesized polymers in different solvents

	BAc	p(BAc-*co*-St)	p(BAc-*co*-MMA)
DMSO	+	+	+
THF	-	+	+
DMF	+	+	+
Acetonitrile	-	-	-
Ethylacetate	-	+	-
Diethyl ether	-	-	-
Chloroform	-	+	+
DCM	-	+	+
Methanol	+	+	+

5. CONCLUSION

The aim of this study is to synthesize novel boron containing monomer and polymers. In this study, BAc monomer initiators was synthesized and used to perform free radical polymerization of its homopolymer and copolymer with St and MMA. The structures of the monomer and polymers were characterized and confirmed using NMR and FT-IR spectroscopy. Monomer reactivity ratios for the studied monomer pair were calculated by using extended Kelen-Tudos (EKT) method. Copolymerization composition and reactive ratios show that the copolymerization is occured randomly. The T_g value of pBAc was 74.2 ^oC and the T_g value of pSt was 72.3 ^oC. Depending on the copolymer composition, St copolymers glass transition temperatures have between at 62.9 ^oC and 97.2 ^oC. TGA diagrams of copolymers were determined to be in between TGA diagrams of pBAc and pSt. Based on these results, while St homopolymer and copolymers have one decomposition, BAc homopolymer has two decomposition. In these results, char yields were increased by pBAc content in pSt copolymers. Also solubility of homopolymers and copolymers were examined with different solvents.

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