ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE, ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF BORON-ACRYLATE/SBA-15 POLYMER COMPOSITES

M.Sc. THESIS

Nargız ALIYEVA

Department of Polymer Science and Technology

Polymer Science and Technology Programme

DECEMBER 2019

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE, ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF BORON- ACRYLATE/SBA-15 POLYMER COMPOSITES

M.Sc. THESIS

Nargız ALIYEVA
(515161033)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. İ. Ersin SERHATLI

DECEMBER 2019

ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BOR-AKRİLAT/SBA-15 POLİMER KOMPOZİTLERİNİN SENTEZ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

Nargız ALIYEVA
(515161033)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. İ. Ersin SERHATLI

ARALIK 2019

Nargız Alıyeva, a M.Sc. student of ITU Graduate School of Science, Engineering and Technology, student ID 515161033, successfully defended the thesis/dissertation entitled "SYNTHESIS AND CHARACTERIZATION OF BORON-ACRYLATE/SBA-15 POLYMER COMPOSITES", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. İ. Ersin SERHATLI** İstanbul Technical University	.....
Jury Members :	**Assoc. Prof. Dr. Tuba ÇAKIR ÇANAK** Istanbul Technical University	.....
	Prof. Dr. Tarık EREN Yildiz Technical University	.....

Date of Submission : 15 November 2019
Date of Defense : 12 December 2019

To my mother,

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.
First of all, I would like to gratefully and sincerely thank my thesis advisor, Prof. Dr. İ. Ersin SERHATLI, for his guidance and offering, knowledge and experience since the day accepting me to his research group.
I would like to thank especially Assoc. Prof. Dr. Tuba ÇAKIR ÇANAK for her all supports and sharing her background knowledge all the time.
In addition, I would like to thank very much to the members of POLMAG especially Büşra Akın and Eda KÜÇÜK, Ozan Gazi DEHMEN, Zeynep BAŞAR, Övgü GÜRER for their supports and the created lovely enviroment.
I also would like to thank Merve GÜÇLÜ who included to my life in master study with her high energy and ambition to work for the motivation, sincere friendship and support in every subject.
I also thank to my best friends, who have always been with me all my life for their love, friendship and patient.
Finally, I would like to express my profound gratitude to my family for their self sacrifices, financial and moral supports during all stages off my life.

December 2019

Nargız ALIYEVA
(Metallurgical and Materials Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

AIBN : Azobisisobutyronitrile

ATRP : Atom transfer radical polymerization

BAc : Boron acrylate

BET : Brunauer-Emmett-Teller method

BJH : Barrett-Joyner-Halenda method

DSC : Differential scanning calorimetry

ex-PB-x : pBAc obtained from the pores

FDU : Fudan University

FRP : Free radical polymerization

FT-IR : Fourier transform infrared spectroscopy

GMA : Glycidylmethylacrylate

HEMA : Hydroxyethylmethylacrylate

HB : Homopolymer of BAc

MAS : Magic angle spinning

MCM : Mobile compositon of matter

meHQ : Methylhydroquinone

MMA : Methyl methacrylate

M-SBA15 : Modified SBA-15

NMR : Nuclear magnetic resosance

pBAc : Boron acrylate polymer

PB : Boron acrylate polymer

PBxS : Boronacrylate/SBA-15 polymer composite

SBA : Santa barbara amorphous

SEM :Scanning electron microscopy

SI : Surface initiated

SS-NMR : Solid s NMR

TEOS : Tetraethyl orthosilicate

Tg : Glass transtion temperature

TGA : Thermal gravimetric analysis

TMSPMA : Trimethoxy sylyl propyl methacrylate

LIST OF TABLES

LIST OF FIGURES

SYNTHESIS AND CHARACTERIZATION OF BORON- ACRYLATE/SBA15 POLYMER COMPOSITES

SUMMARY

Materials with a pore size ranging from 2 nm to 50 nm are called mesoporous materials. Alumina, carbon, metal oxides, such as silicates are the most important of these materials. Since its discovery in the early 1990s, studies with mesoporous silicas have been increasing day by day. These materials have different classifications such as SBA-n, MCM-n, FDU, KIT, have different pore geometries, lattice structures, and pore sizes. SBA-15, which is the abbreviation of Santa Barbara Amorphous, is formed by hexagonal arrangement of large pores from 4.6 nm to 30 nm. SBA-15 is not only large porous but also thermal, mechanical and chemical resistant.

SBA-15 has attractive features including the regular porous structure of silica, high pore volume, high surface area, and avalibility surface modification. Benefiting from these advantages, SBA-15 has been extensively applied in variety of different fields such as catalysis, adsorption, nanoreactors, chromatography, nanotechnology, metal ion extraction, drug delivery systems, and sensors. Nanoreactors are the material structures with internal cavities, which create exclusive confined nanoscale surrounding for chemical reaction. The surface modification of porous silicas allows both the chemical and physical properties of these materials to be modified and thus used in many different fields. Modification of mesoporous silicas is generally achieved by bonding organic functional groups to the surface of the material using organosilanes. During the procedure, mesoporous silicas form functional groups on the outer, inner or both surfaces.

Organic modification of mesoporous silica materials is generally carried out by two basic synthetic strategies. One of them is direct synthesis and the other is grafting method. In the direct synthesis method, silica precursor is added to the synthesis medium while the silica material is synthesized. After calcination, the surface is functionalized. In the grafting method, after the silica material is obtained, the desired modification precursor is added under appropriate conditions. It is important that the mesoporous materials have silanol (Si-OH) groups for the adhesion of organic groups to the surface. After filtration, washing and drying, organically modified mesoporous silica is obtained.

Researchers who was used these ordered mesopores as nanoreactors to adsorb monomers or graft initiator from nanopores surface, following synthesize mesoporous organic-silica composite materials via conventional radical polymerization (CRP) or controlled/living radical polymerization (CLRP), such as reversible addition-fragmentation chain transfer (RAFT), atom transfer radical polymerization (ATRP) , reverse ATRP, surface-initiated (SI) ATRP, activators regenerated by electron transfer (ARGET) for ATRP, etc. CRP which is extensively used to synthesize polymeric materials in industrial scale is simplest method.

In this thesis, monomer named as boron acrylate (BAc) was synthesized by esterification method. The synthesized product was characterized by FT-IR and H-NMR methods.

For the chemically bonded polymer to the SBA-15 surface, the surface needs to be functionalized. For this purpose, the modification is carried out by grafting (post synthesis method) using 3-trimethoxy silylpropyl methacrylate (TMSPMA). HCl was used during synthesis in order to increase the silanol groups on the surface. The resulting product was named M-SBA15.

In the next step, proper conditions were determined for free radical polymerization of boron acrylate polymer. After that, three composites (PBxS) were prepared with M-SBA15 (0.5 g, 1.0 g and 2.0 g) and boron acrylate (10 g). Characterization was performed by using fourier-transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), solid state nuclear magnetic resonance (SS-NMR) (^{13}C), scanning electron microscopy (SEM) and N_2 adsorption/desorption, devices in order to see the successful synthesis process of modification and polymerization and effect of different amounts on the system.

Upon completion of the analyzes, the silica / polymer was etched with HF aqeous solution to remove silica part of material. The obtained polymers (ex-PB) was remained in the SBA-15 pores. Thermal behaviours of these polymers were investigated via differential scanning calorimeter (DSC) and TGA.

At the end of the analyzes, it was seen that hexagonal mesoporous silica (SBA-15) can be modified successfully. Also, pBAc/SBA-15 composite can be successfully synthesized by the free radical polymerization method. Thermal properties of boron acrylate polymer obtained from the mesopores were improved compared to boron acrylate polymer which was synthesized without SBA-15. As a consequence, SBA-15 can be used as nanoreactor for FRP of BAc.

BOR-AKRİLAT/SBA-15 POLİMER KOMPOZİTLERİNİN SENTEZ VE KARAKTERİZASYONU

ÖZET

Gözenek boyutu 2 nm ile 50 nm arasında değişen malzemeler mezogözenekli malzemeler olarak adlandırılmaktadır. Alumina, karbon, metal oksitler gibi çeşitleri olan bu malzemelerin en önemlisi silikatlardır. 1990lı yılların başında keşfedilmesinden itibaren mezogözenekli silikalarla yapılan çalışmalar her geçen gün artmaktadır. SBA-n, MCM-n, FDU, KIT gibi farklı sınıflandırmalara sahip olan bu malzemeler farklı gözenek geometrilerine, kafes yapılarına ve gözenek boyutlarına sahiptirler. SBA-15 4.6 nm'den 30 nm' ye kadar büyük gözeneklerin hekzagonal dizilimiyle oluşan SBA-15 (Santa Barbara Amorphous) adını üretildiği Calirfornia Üniversitesinin bulunduğu bölgeden almıştır. SBA-15 yalnızca büyük gözenekli olmakla kalmayıp aynı zamanda termal, mekanik ve kimyasal olarak da dayanıklıdır.

Mezogözenekli malzeme sentezinin temel yapı taşı; pahalı olmayan, termal kararlılığa sahip, kimyasal olarak inert, zararsız ve yer kabuğunda bolca bulunan silikadır. Isıtılarak kendi kendine birleşen zeolitik malzemelerin aksine mezogözenekli silika, MCM-41 sentezi için katyonik yüzey aktif madde ve SBA-15 sentezi için blok kopolimerler gibi kendi kendini ilişkilendirebilen moleküllerin varlığında oluşmaktadır. Düzenli mezogözenekli silikalar genellikle pH'ı ayarlanmış misel yüzey aktif madde çözeltisine bir silika kaynağının eklenmesiyle sentezlenmektedir. Bu sistem surfaktan-inorganik kompoziti olarak adlandırabilir. Bu kompozitlerin elde edilmesi için, inorganik madde üzerinde etkisi bulunan noniyonik triblok kopolimerler kullanılmaktadır.

SBA-15 sentezinde silika kaynağı olarak yaygın olarak tetraetil ortasilikat (TEOS) kullanılmaktadır. Mezoyapının oluşması için surfaktan-inorganik ara yüzeyinde hidrolize olması gerekmektedir. Triblok kopolimer inorganik malzeme tarafından çevrelenir. Bu haliyle malzemede gözenekten söz edilemez. Mezogözeneklerin oluşturulması için sürfaktanın kimyasal veya termal yöntem kullanılarak sistemden uzaklaştırılması gerekmektedir. Kalsinasyon olarak adladırılan termal yöntem kolay olmasından dolayı tercih edilmektedir. Sıcaklık, pH, konsantrasyon, kurutma yöntemi, kullanılan kopolimerin cinsi gibi parametrelerin değişmesiyle oluşacak mezogözenekli yapının özellikleri değişir.

SBA-15, düzenli gözenekli yapısı, yüksek gözenek hacmi, yüksek yüzey alanı ve kolay fonksiyonlandırılabiliyor olması gibi çekici özelliklere sahiptir. Bu avantajlardan yararlanarak, SBA-15, kataliz, adsorpsiyon, nano-reaktörler, kromatografi, nanoteknoloji, metal iyon çıkarma, ilaç verme sistemleri ve sensörler gibi çeşitli alanlarda yaygın olarak uygulanmıştır. Nanoreaktörler, kimyasal reaksiyon için özel kapalı nano ölçekli yaratan iç boşluklu malzeme yapılardır.

Gözenekli silikaların yüzey modifikasyonu, bu malzemelerin hem fiziksel hem de kimyasal özelliklerinin modifiye edilmesini ve böylece birçok farklı alanda

kullanılmasını sağlar. Mezogözenekli silikaların modifikasyonu, genellikle organik fonksiyonel grupların, organosilanlar kullanılarak malzemenin yüzeyine bağlanmasıyla sağlanır. İşlem sırasında mezogözenekli silikaların dış, iç veya her iki yüzeyinde fonksiyonel gruplar oluşturur.

Mezogözenekli silika malzemelerinin organik modifikasyonu genel olarak iki temel sentetik strateji ile gerçekleşmektedir. Bunlardan bir tanesi doğrudan sentez, bir diğeri ise aşılama yöntemidir. Doğrudan sentez yönteminde silika malzeme sentezlenirken, sentez ortamına modifikasyon öncüsü eklenir. Kalsinasyon işleminden sonra da yüzey fonksiyonlandırılmış olur. Aşılama yönteminde ise silika malzeme elde edildikten sonra uygun koşullarda istenilen modifikasyon öncüsü eklenir. Mezogözenekli malzemelerin silanol (Si-OH) gruplarına sahip olması organik grupların yüzeye tutunması için önemlidir. Filtreleme, yıkama ve kurutma işleminden sonra organik olarak modifiye edilmiş mezogözenekli silika elde edilmiş olur.

Mezogözenekli yapıları nanoreaktör olarak kullanan araştırmacılar, monomerleri veya aşı başlatıcıyı nanoporların yüzeyinden adsorbe etmek için çeşitli polimerizasyon yöntemleri kullanmışlardır. Örnek olarak geleneksel radikal polimerizasyonu (CRP) , kontrollü /yaşayan radikal polimerizasyonu (CLRP), tersinir katılma ayrılma transfer polimerizasyon (RAFT), atom transferi radikal polimerizasyonu (ATRP), ters ATRP, yüzeyden başlatılan ATRP (SI ATRP) gibi yöntemler söylenebilir. Endüstriyel ölçekte polimerik malzemeleri sentezlemek için yaygın olarak kullanılan CRP basit ve önemli bir yöntemdir .

Serbest radikal polimerizasyonu katılma polimerizasyonun en önemli tiplerinden biridir. Genel olarak yüksek molekül ağırlığına sahip polimerler elde etmek için sanayi işlemlerinde kullanılmaktadır. Kullanılan monomer çeşitliliği geniş aralıkta olup, basit deneysel koşullarda polimer veya kopolimer elde edilebilir. Bu tip polimerizasyonda; polimerleşme çiftleşmemiş elektron içiren elektriksel olarak nötral serbest radikallerle başlatılıp doymamış monomerlerin zincir reaksiyonu vermesi ile oluşur. Başlatıcı radikaller genel olarak dışarıdan eklenen termal, elektrokimyasal veya fotokimyasallar yöntemlerle elde edilirken nadir durumlarda monomerlerin kendileri tarafından da üretilebilirler. Serbest radikal polimerizasyonu tipik bir zincir büyüme reaksiyonudur ve bütün zincir büyüme reaksiyonlarında olduğu gibi başlama, ilerleme ve sonlanma olmak üzere üç basamaktan oluşur.

Bu tez çalışmasında öncelikle boron akrilat monomeri (BAc) esterleşme yöntemiyle sentezlenmiştir. Sentezlenen ürün FT-IR ve H-NMR yöntemleriyle karakterize edilmiştir.

Bu tez kapsamında yapılan sentezlerde ticari olarak satın alınan SBA-15 kullanılmıştır. Polimerin SBA-15 yüzeyine kimyasal olarak bağlanması amaçlandığından dolayı yüzeyin fonksiyonlandırılması gerekmektedir. Bu amaçla modifikasyon işlemi 3-trimetoksi sililpropil metakrilat (TMSPMA) kullanılarak aşılama yöntemi ile yapılmışır. Elde edilen ürün M-SBA15 olarak adlandırılmıştır. Yüzey modifikasyon işleminin başarılı olarak gerçekleştirildiğini görmek için FT-IR ve TGA analiz yöntemleri kullanırak karakterizasyon yapılmıştır. Yapılan analizler sonucunda modifikasyon işlemi başarılı bir şekilde gerçekleştirilmiştir.

FT-IR sonucuna bakılarak M-SBA15 örneğinde, SBA-15'de bulunmayan C=O, C=C ve –CH sinyallerinin varlığı açıkca görülmektedir. Bu yeni pikler kullanılan silan ajanından kaynaklanmaktadır. TGA sonucu da bu sentezin başarılı olarak gerçekleştiğini destekler niteliktedir. SBA-15 örneğinde bozunma görünmemesine

karşın M-SBA15'de ise %14 civarında bozunma görünmesinin sebebi sisteme bağlanan organik yapıdır.

Bir sonraki aşamada ise elde edilen modifiye SBA-15 (M-SBA15) malzemesi ile sentezlenen bor akrilat monomeri (BAc) serbest radikalik polimerizasyon metodu kullanılarak sentezlenmiştir. Sabit koşullar belirlendikten sonra, sisteme boron akrilatın ağırlıkça %5, %10 ve %20 olacak şekilde M-SBA15 eklenmiştir. Farklı miktarların sistem üzerindeki etkisini görmek amacıyla FT-IR, TGA, SEM, SS-NMR, azot absorpsiyon/desorpsiyon analizleri yapılmıştır.

FTIR sonucunda karbonil piklerinin şiddetinde artış gözükürken, C=C pik şiddetinin ise azaldığı görülmüştür. Ek olarak M-SBA15 de bulunmayan 1380cm^{-1} dolaylarında görülen yeni pik bize B-O bağının varlığından bahsetmiştir. Dolayısıyla bor akrilatin SBA yüzeyine bağlanarak polimerizasyonun gerçekleştiği sonucuna ulaşılmıştır. Yapılan ^{13}C katı NMR analizinde M-SBA15 ve PB10S örnekleri incelenmiştir. SS-NMR spekturumlarında fonksiyonel organik gruplar tespit edilmiştir. İki sonuç karşılaştırıldığında, PB10S'deki karbonil pikinin şiddeti artarken, C=C bağına ait karbonların pik şiddetlerinde azalma görülmüştür.TGA analizi sonucuna %5'lik M-SBA15 eklenerek hazırlanan kompozit malzemenin (PB5S) en fazla polimer miktarı içerdiği söylenebilir. M-SBA15 miktarı arttıkça polimer miktarı azalmıştır.

Numunelerin spesifik yüzey alanı, ortalama gözenek genişliği ve toplam gözenek hacim gibi özelliklerinde değişimin gözlenmesi için azot absorpsiyon/desorpsiyon analizi uygulanmıştır. Analiz sonucunda da beklenildiği gibi modifikasyon ve polimerizasyondan sonra SBA-15 değerlerine kıyasla azalma gözlenmiştir. Sonuçlar bize en fazla polimer miktarının PB5S malzemesinin gözeneklerinde olduğunu söylemektedir. Bu da TGA ve FT-IR sonuçlarıyla örtüşmektedir.

Morfolojik analiz için SEM analizi yapılmıştır. SEM sonucunda SBA-15 görüntüleri literatür ile benzerlik göstermektedir. Genel olarak SBA-15, birçok altıgen prizma kısa çubuğun birbirine bağlanarak oluşturduğu uzun çubuk benzeri yapılar sergiler. Modifikasyon ve polimerizasyon işlemlerinden sonra da solucan benzeri bu yapının bozulmadığı sonucuna ulaşılmıştır. Yüzey pürüzlülüğünde de gözle görülür bir farklılığın olmaması, polimerizasyonun mezogözeneklerde gerçekleştiğini destekler niteliktedir.

Analizlerin tamamlanmasının ardından elde edilen silika/polimer kompozit malzemesinden silika HF kullanılarak uzaklaştırılmıştır. İşlem sonucunda SBA-15 gözenekleri içinde kalan polimerler elde edilmiştir. Yapılan FT-IR analizi soncunda Si-O-Si bağına ait pikin yok olduğu ve elde edilen spektranın bor akrilat polimeri ile çakıştığı açıkca görülmektedir. Bu sonuç da bize silikanın ortamdan uzaklaştığını göstermektedir. Camsı geçiş sıcaklığındaki değişim diffarensiyel taramalı kalorimetre (DSC) analizi kullanılarak tayin edilmiştir.Boron akrilat/SBA-15 polimer kompozit malzemesinde Tg değeri belirlenemezken, HF yıkaması sonrasında tekrarlanan analiz ile Tg değerleri 70.76 °C (PB), 70.81 °C (ex-PB-5), 70.97 °C(ex-PB-10) ve 71.34 °C (ex-PB-20) olarak bulunmuştur. Yapılan TGA analizi sonucunda mezogözeneklerde oluşan polimerlerin ısıl kararlılıklarının daha yüksek olduğu görülmüştür.

Yapılan analizler sonucunda TMSPMA ile fonksiyonlendirilen hekzagonal SBA-15'in bor akrilatın serbest radikalik polimerizasyonu için nanoreaktör olarak kullanılabilir olduğu görülmüştür.

1. INTRODUCTION

1.1 Literature Review

Mesoporous materials, which emerged in the early 1990s, have become the focus of interest in an interdisciplinary research [1]. According to IUPAC, porous materials are classified into three main groups based on their pore diameters: microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm) materials [2]. Porous silicates, which are a large family of inorganic materials with open porous frames and large surface area (including internal and external surfaces), are among the materials studied in this field. FDU-n, KIT-n, M41S, MCM-n (Mobile Compositon of Matter), and SBA-n (Santa Barbara Amorphous), which have different structure and pore diameter, can be given as an important examples belonged to porous silicates [3]. Because of the to having a large surface area and uniform and adjustable pore sizes and possibility for surface modification, mesoporous silicates are highly preferred in variety of usage areas such as waste water treatment, indoor air purification, catalysis, bio-catalysis, drug distribution, CO_2 adsorption, bioanalytical sample preparation, membrane development, nanoreactors etc. [4, 5]. Nanoreactors are the material structures with cavities that used as a host at nanoscale for chemical and physical reaction. The cavities of SBA-15 can be used as nanoreactors for incorporating species.

Polymer nanocomposites are also one of the most important fields of study. It has been studied to investigate the effects of various inorganic materials, such as SiO_2, on improving the thermal and mechanical properties of polymers. Yu et al. (2012), the surface of SBA-15 was functionalized with (3-Glycidyloxypropyl) trimethoxysilane (GOTMS) and the material obtained was used in the preparation of SBA-15/PF composite material. The composite material was prepared by in situ condensation polymerization with phenyl, formaldehyde and SBA-15-GOTMS. As a result of the analyzes, it was found that PF and SBA-15-GOTMS were chemically bonded to each other, increasing Tg values and thermal stability of PF with increasing functionalized silicate amount [7]. The effect of SBA-15 on pMMA / SBA-15 was also investigated

by Wei et al. (2013). In this study, composite material was prepared by free radical polymerization method. The increase in the amount of SBA-15 increased the molecular weight and the Tg value of the composite material [8].

The functionalization of mesoporous silicates using organic groups is one of the most important studies in this field [6]. There are many case studies on this subject in the literature. SBA-15s, which are functionalized with various binding agents, are designed for use in different fields. In one of these, Thu, P.T.T et al. (2012) investigated the ability of carbonyl functionalized SBA-15 to adsorb phenol in aqueous solutions. The harmful effects of small amounts of phenol and derivatives on living organisms are known. For this reason, various methods such as adsorption have been developed for cleaning from aqueous solutions. As a result of the measurements, it was found that there is a strong relationship between carbonyl bond and phenol [9].

Researchers was used the mesoporous silicates as a nanoreactor for absorbing the monomers due to their high ordered structure. According to a article that was studied by Chen, M. and friends (2017), MMA could be polymerized in the nanopores of SBA-15 via ARGET ATRP method. Also, it was clearly indicated that silane modified SBA-15 absorbed more MMA monomers than unmodified SBA-15. After HF etching process, the obtained polymers, that was in the pores , was characterized by different methods. As a result, it can be said that glass transition temperatures of PMMA (in pores) was increased compared to common PMMA [10] . In the further study done by same group (2018), SBA-15/polymer composite materials were prepared by surface initiated (SI) ATRP. Brominated SBA-15 surface used as a initiator for the polymerization with glycidyl methacrylate (GMA). Then the prepared materials was used as macroinitiator for MMA polymerization. The grafting of polymers was controlled by time. With the increasing time, more polymers can added to the surface of SBA-15 [11].

Boron compounds have been used in many materials because of their high thermal, mechanical and antibacterial properties. It is a known fact that it is used to increase thermal resistance, especially in the glass and ceramic industry. Boric acid has been used as flame retardant since the 1800s. When borates start to deteriorate under the influence of heat, the surface is covered with glass. As a result, the gas inlet and outlet are prevented and thus the progress of combustion is prevented [12]. There is also evidence in the literature that inorganic borates carbonize during combustion and stop

burning [13]. In the light of this information, various boron compounds have been synthesized and studies in this field are continuing. Boron acrylate is an example of these synthesized materials. Polymerization of said monomer by free radical method was studied and homopolymer and copolymer with styrene were synthesized. Monomer reactivities were also calculated [14].

1.2 Purpose of Thesis

The objective of the present work is showing the posibility of free radical polymerization (FRP) of boron acrylate (BAc) in the mesopores of SBA-15 which was used as nanoreactor. For this purpose, surface of SBA-15 is modified with silane coupling agent for covalent attachment of polymer chains. Investigation of the effects of different amounts of modified SBA-15 particles on FRP of BAc on structural and morphological properties, and the nanocomposites and thermal properties of polymers was the other objective of this study. Also, change on thermal properties of boron acrylate polymer in the pores compared to conventional boron acrylate polymer was examined during this work.

2. THEORICAL PART

2.1 Porous Materials

As a general definition, porous material is a solid body containing hollow spaces in the form of cavities, channels or pores [15]. Porous materials have attracted great interest since sixties result in using in a wide variety of scientific and technological applications. Porous materials include many materials ranging from inorganic compounds (eg alumina silicates) to biological membranes and tissues [1].

Porous materials have been used in many fields of application in the scientific and industrial fields, such as molecular separation, heterogeneous catalysis, adsorption technology or optoelectronic materials, selective absorption, gas storage, sensor and electrode materials due to the properties of narrow distribution of pore size, high surface area, good corrosion resistance, high stability, and tunable pore structure and possibilty of modification [16-22].

The materials can be divided into various classes according to their pore distribution. For example, they may be classified as ordered and irregular porous materials to the pore distribution in the material, while they may also be classified as uniform and non-uniform sized porous materials to the size distribution of the pores[22,23].

But generally, they are classified basen on pore size according to the International Union of Pure and Applied Chemistry (IUPAC) as:

- Microporous having pore diameters of < 2 nm,
- Mesoporous having pore diameters between 2 nm - 50 nm,
- Macroporous having pore diameters of greater > 50 nm.

Mesoporous structures are existing by a broad class of materials including silica, metal oxides and hydroxides, metal salts, carbon, hybrid materials, organic structures and many others. Figure 2.1 [24] shows the examples of different types of porous materials.

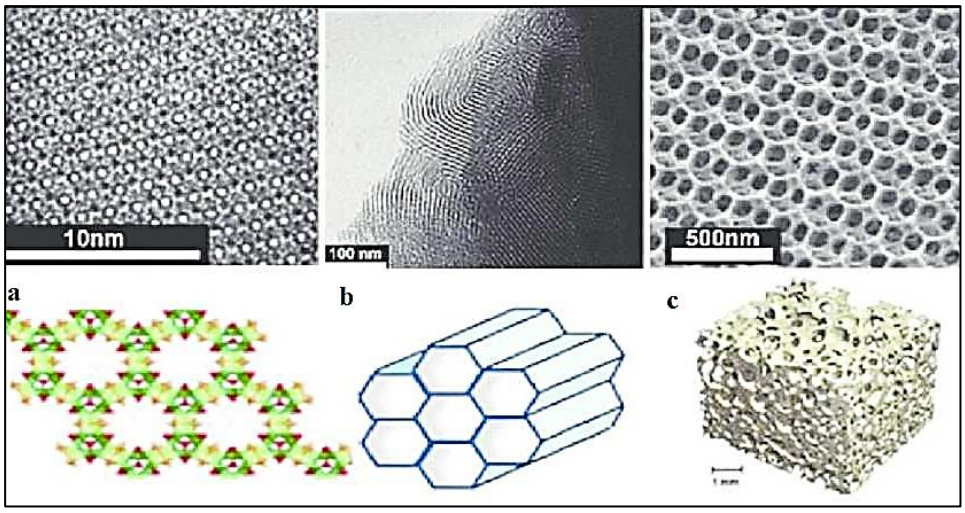

Figure 2.1 : Microporous zeolite (a), Mesoporous silicate (b) and Macroporous ceramic (c).

2.2 Mesoporous Silicates

Porous materials impressed the researchers due to commercial interest in their applications in various field. In literatures, there were a diversity of reports including patents about structurally different porous materials. The desing and modification of porous substances for different application is still arousing interest for the scientist [25]. Zeolitic materials are the best known examples for micropores materials. In despite of advantages of having microporous structure, for bulky reactant molecules, accessing to pore system of some materials as zeolitic materials is inhibited [26].

To overcome this limitations of this type of materials, studies have been focused on the new field of mesoporous molecular sieves, beginning in 1990 by Japan [27]. The pore diameters of these newly developed solids have been changed in 2-50 nm called as mesoporous range. This type of materials also have uniform pore size distribution, that make them suitable for diffusion processes of bulky molecules to internal pores [28].

An advancement began in 1992 with the development by the Mobil Oil Company of the class of ordered mesoporous silica named as the M41S family. This new family of materials has attracted the attention of many researchers for their unique features such as their highly ordered structures, uniform pore sizes, thermal stability and high specific surface areas [29].

After six years old in 1998, the SBA family, a new member of highly ordered mesoporous materials, was produced at the University of California, Santa Barbara. The silica nanoparticles containing pores were arrayed hexagonally.

In addition, scientists from numerous countries (e.g Japan, Korea, China, UK, Canada) have contributed much to the mesoporous families. For example, the KIT series from a Korea scientist, and the FDU series by Prof. Zhao 's group in Fudan University have been extensively investigated [1].

2.2.1 Types of mesoporous silicates

Since microporous materials cannot be used in larger molecular applications, mesoporous materials have attracted considerable attention in researches and practical applications in recent years. The main types of mesoporous materials are M41S, SBA-n, HMS, FSM, FDU and MSU. They all have different pore size or pore structure.

2.2.1.1 M41S family (MCM)

the M41S materials have pore diameters from approximately 2 to 10 nm. This class of material having very large surface areas, ordered pore structure, and well-defined pore size distributions[are the main properties of this classof material [29].

The synthesis of ordered mesoporous silicas (OMS) of the M41S family by sol-gel method based on the use of surfactants was first reported by Kresge and coworkers. [30]. For the formation of M41s family, alkyl ammonium surfactants and TEOS or sodium silicate could be used in basic medium. Self-assembling surfactants have been used as structure directing agents. The diameter of the pores can be controlled by varying the length of the template molecule [31].

The M41S is the generic name for a variety of MCM (Mobile Composition of Matter) types of materials, the numbers after MCM are used to distinguish various types. MCM-41, MCM-48 and MCM-50 are the most known members of M41S family. Schematic representation of different structure belonged to different class is shown in the Figure 2.2 [32].

MCM-41 is the most attractive and studied member of this group, due to its controllable pores between 1.5 and 20 nm, wall thicknesses of 1–1.5 nm, and a surface area of approximately 1200 m^2/g [32].

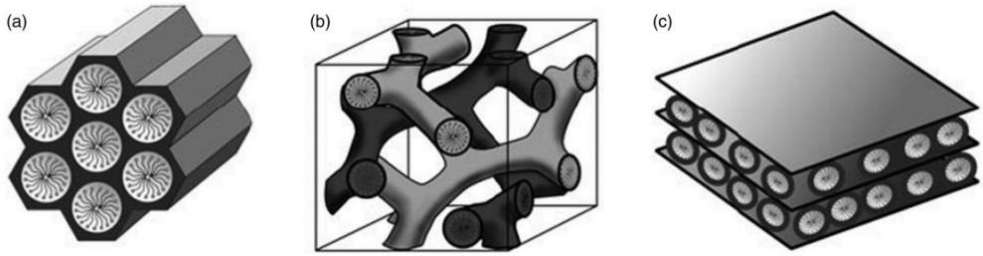

Figure 2.2 : (a) MCM-41 (hexagonal), (b) MCM-48 (cubic), and (c) MCM-50 (lamellar with the presence of surfactant molecules between lamellae).

2.2.1.2 SBA-n family

SBA-n family (Santa Barbara Amorphous) is the other best known and important group of mesoporous silicates. SBA materials have specific pore structure and have been prepared with surfactant in acidic medium [33]. When some members of this family such as SBA-11 (cubic), SBA-12 (hexagonal, 3D), SBA-15 (hexagonal, 2D) and SBA-16(cubic) were synthesized by Zhao and friends in 1998 in acidic medium with using non-ionic surfactants that have polyethylene oxide units, some of them as SBA-1, SBA-2 and SBA-3, were synthesized using cationic surfactants [33-36]

SBA-15 with uniform pore sizes up to ~ 30 nm is the main SBA structure and gained a lot of attention because of its features such as having the highest hydrothermal stability and high specific surface area [37].

The advantage of using nonionic triblock copolymer instead of low molecular weight surfactants gives thicker silica walls with larger pore diameters. The mainly difference between MCM-n and SBA-n materials is coexistence between mesopores and micropores. SBA-n provides this property [38].

2.2.1.3 Others

There are different kinds of mesoporous silica family. Other members of the mesoporous silica family include MSU, HMS, FSM, KIT (Korea Advanced Institute of Sci. & Tech.), FDU (Fudan University) , PMO, CMK, and AMS (anionic surfactant template mesoporous silica) obtained by producing different surfactants under different conditions [39-41].

The pore systems of HMS and MSU materials resemble the worm-like structure, unlike the MCM-41, which has a regular hexagonal structure. However, although they

have the same pore volume and surface area as MCM-41, pore diameter distributions are wider [39]. KIT is a three-dimensional irregular mesoporous material with short worm-like channels of the same width and interconnected completely irregularly [39-41].

Other families of mesoporous silicas are e.g. MSU, KIT, FDU and AMS where the materials are synthesized with variations in e.g. synthesis conditions and surfactants.

2.3 SBA-15

SBA-15, with uniform tubular channels is one of the most widely studied mesoporous silica that is 2D hexagonal and amorphous type . It can be readily prepared over a wide range of uniform pore size from 4.6 up to 30 nm [32]. It consists of micropores and mesopores within its uniformly distributed mesoporous structure as shown in Figure 2.3. The pore walls of these type of materials are thicker that is compared to other type of mesoporous silica (3 – 6 nm). Therefore, these materials show high thermal and hydrothermal stability (up to 850 °C) [18]. The synthesis conditions affect the properties of pores.

While micropores are derived from the PEO (polyethylene oxide) of the surfactant, the mesopores materials are synhesized by using PPO (polypropylene oxide). In addition, the lengths of these two blocks affect the pore wall thickness, amount of the micro-pores and meso-pores. Like pH, temperature or swelling agents parameters could affect the properties of channels. Many researchers are investigating SBA - 15 substances or preparing new materials with SBA-15, because the synthesis is fast and rather inexpensive [46,47].

2.3.1 Synthesis

SBA-15 synthesis is generally carried out in two stages. The first step is the self-regulation process of the silica source and copolymer. The second step is to remove the copolymer from the structure.

In the typical synthesis of SBA-15, triblock copolymer or nonionic triblock copolymer as the structure-controlling template agent, tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate(TEOS) or tetrapropyl orthosilicate (TPOS) as silica source are used [48,49].

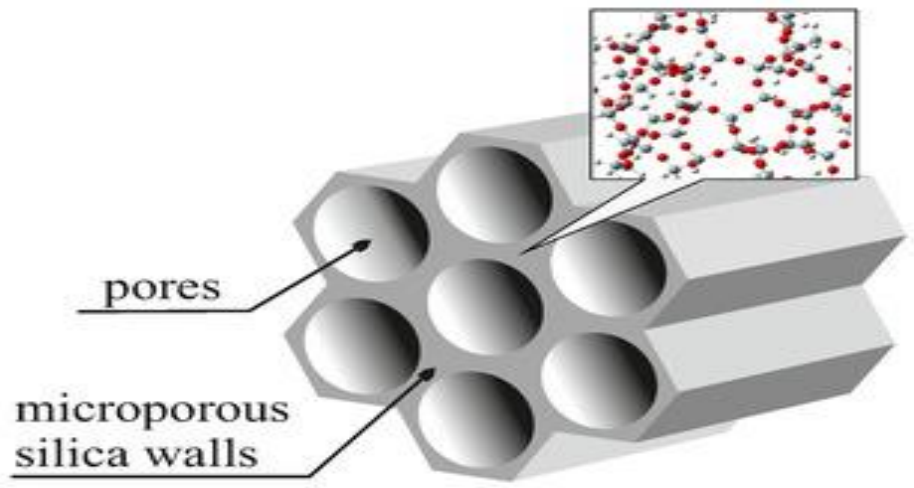

Figure 2.3 : Structural representation of SBA-15 material.

Zhao et al. (2000), regular hexagonal structure and 30 nm pore size SBA-15 in a strongly acidic environment (pH~1) synthesized using amphiphilic triblock copolymer. They observed that when the pH value is greater than isoelectric of silica (pH 2-6), gel formation does not occur as silica precipitation [48]. They observed that irregular or amorphous silica is formed at neutral pH (pH=7). Nevertheless, Cui et al. (2005) developed SBA-15 synthesis in the range of 2-5, which is above the isoelectric point of silica. Cui et al. Suggested that pre-hydrolysed TEOS would interact with the template agent when pH <3 to form a mesophase under acidic conditions [50].

The removal of the template, which is the second step in the synthesis of SBA-15, is very important for obtaining the desired porous structure. Calcination is a conventional method for removing the template from the structure. In order to investigate the properties of the porous structure formed after calcination, some researchers focused on the calcination behavior during the de-stenciling process. Kleitz et al. (2003), the SBA-type silica materials by calcination process of the removal of the template and the change in the structure with calcination examined the various analysis methods [51]. The overall synthesis method of SBA-15 are given in the Figure2.4 [29].

2.3.2 Surface modification

When organic and inorganic blocks are combined, the new material should have functional diversity of organic group at the same time it can gain the some important properties (e.g. hermal stability) from inorganic ones. Beacause of this kind of possibilities, this subject is more attractive for scientist.

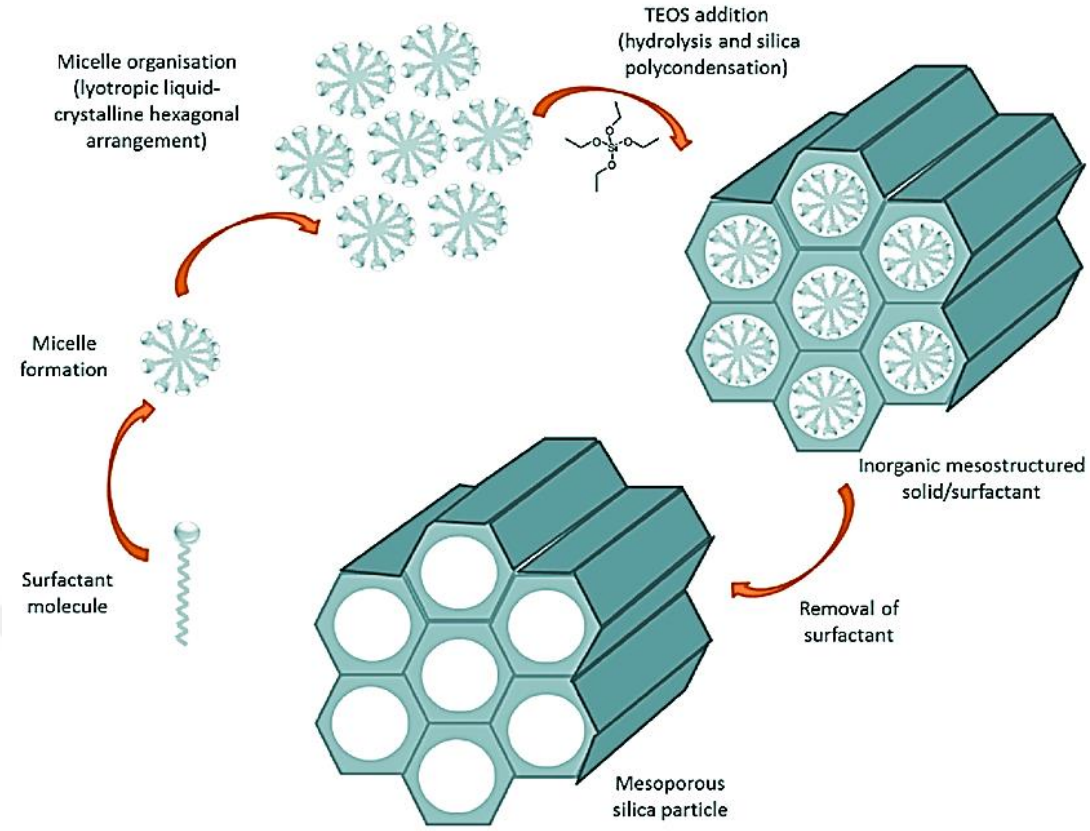

Figure 2.4 : Formation of SBA-15 by structure-directing agent.

Funcitionalizaton of the pore surfaces of an inorganic matrix by the addition of organic chemicals extends considerably the range of materials that can be used.

There are two general methods for chemical surface modification of mesoporous silica via covalent bonding of organic molecules. The first method is called as post-synthesis procedure which grafts organic groups onto the surface of mesoporous silica. The other method is co-condensation procedures which introduce organic groups onto the surface of mesoporous silica when mesoporous silica frame is formed from silica sources [52,29] .

2.3.2.1 Co-condensation method

Process of direct functionalizaton, which is the other name of co-condensation, uses the organotrialkoxysilane (R'-Si(OR)$_3$) as silica sources. Depending on the desired type of the mesoporous material, synthesis process could be accomplished neutral, acidic or alkaline medium. The two reason of using organosilane are contributing to the silica network and being substitution of the silanol groups on the backbone with the functional groups of the organosilane. To obtain porous solid, removing of

surfactant template is neccesary. Calcination or chemical extraction are the two ways to remove the template. The criteria for choosing the method depends on the nature of the organic groups, surfactant and the process being followed [53, 54]. The shematic represantaion of co-condensation method is given in the Figure 2.5 [29].

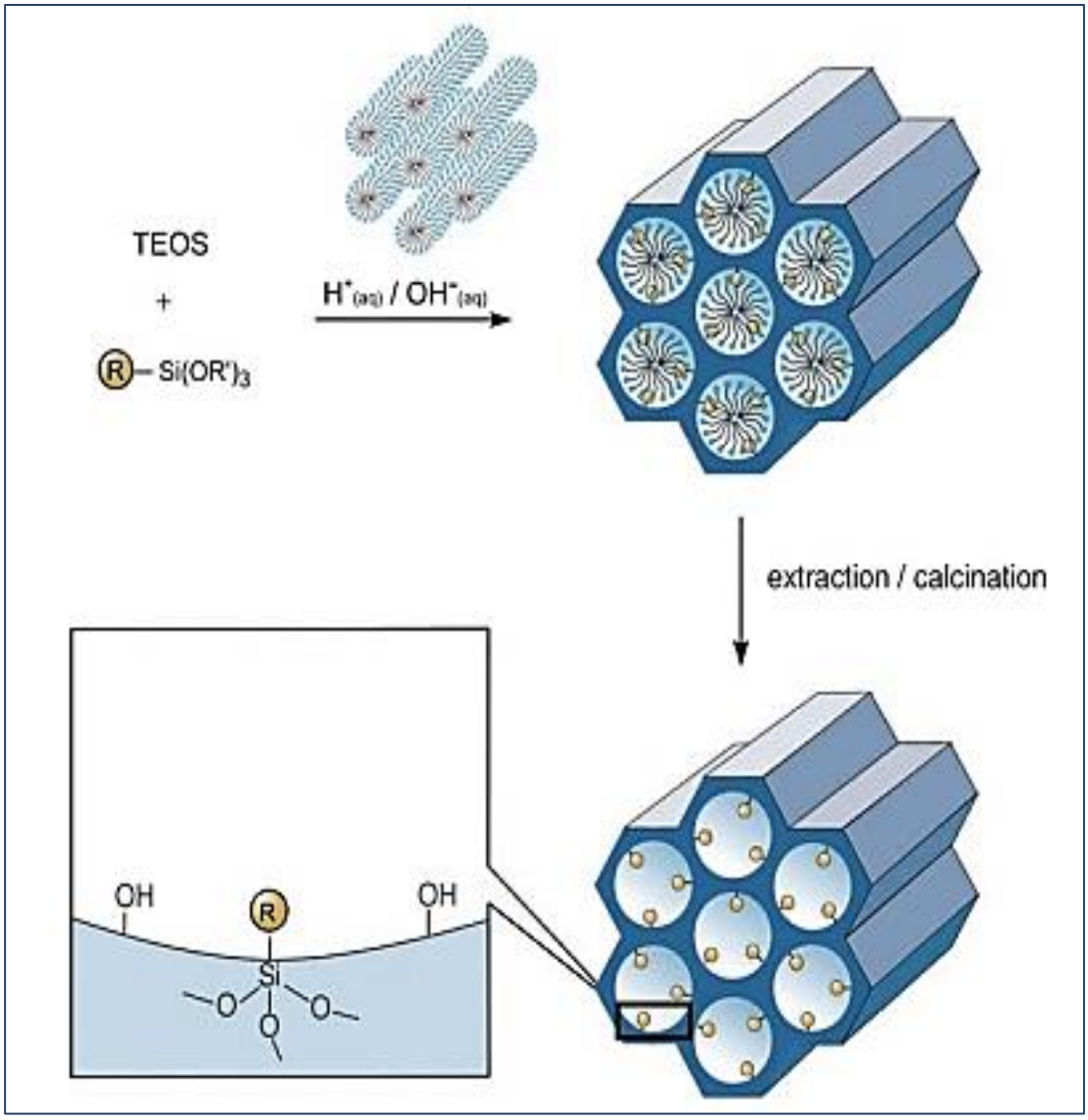

Figure 2.5 : Surface modification by direct synthesis method.

2.3.2.2 Grafting method

Grafting is another method used to modify mesoporous materials. It is also known as the " two - step " synthesis method. This process is achieved by grafting of the functional organic groups on the surface and pore wall of a silica material [29].

This method, usually after removal of the surfactant, mesopore surfaces by binding to the functional molecules of the previously prepared mesoporous structure means post-

synthesis modification (Figure 2.6) [29]. Mesoporous silicas have surface silanol (Si-OH) groups present at high concentrations and act as suitable attachment points for organic functionalization, as in amorphous silica [55, 56]. Surface modification takes place by silylation reaction of $(R'O)_3SiR$ (orgonosilane) , or less frequently $cClSiR_3$ (chlorosilane) or $HN(SiR_3)_3$ (silazanes) with silanol groups. [57, 58]. Silylation is typically carried out by one of the following reactions shown in eq. 2.1, eq. 2.2 and eq. 2.3 [59]:

$$\equiv Si - OH + Cl - SiR_3 \longrightarrow \equiv Si - OSiR_3 + HCl \quad (2.1)$$

$$\equiv Si - OH + R' - SiR_3 \longrightarrow \equiv Si - OSiR_3 + HOR' \quad (2.2)$$

$$\equiv Si - OH + HN(SiR_3)_2 \longrightarrow \equiv Si - OSiR_3 + NH_3 \quad (2.3)$$

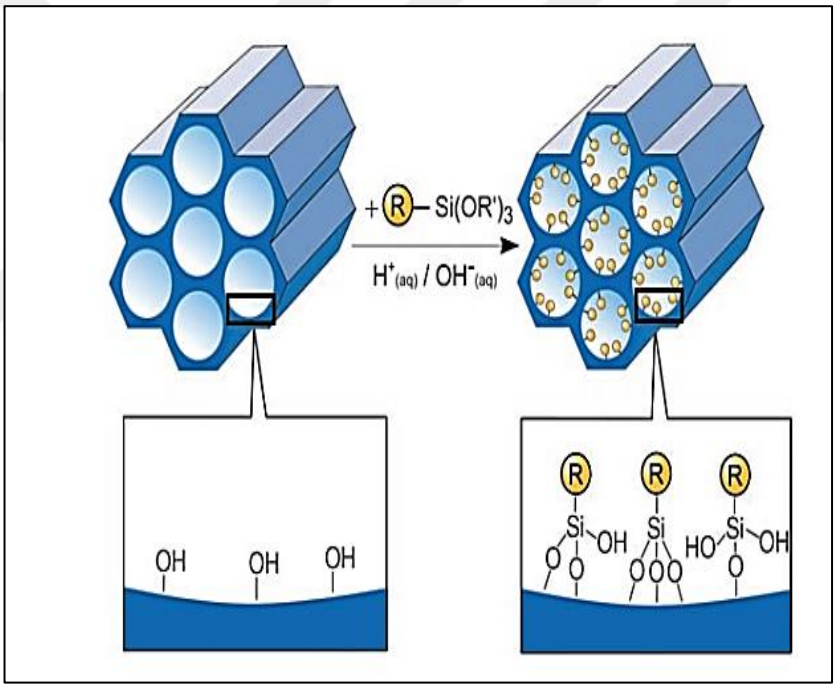

Figure 2.6 : Surface modification by post-synthesis method.

Grafting method have some advantages comparing wtih the co-condensation method. First of all it has the very easy procedure. The vacuum oven for drying mesoporous materials is a device that can be found in almost any laboratory. The solvent used in the second step is a conventional organic solvent such as benzene, toluene, xylene, cyclohexane. If polar solvents such as THF, dichromethane, chloroform which donot react with orgonasilane, they can also be used. The temperature of grafting can be made at room temperature or solvent reflux temperature, depending on the precursor [60].

Selecting the appropriate precursor simplifies the grafting reaction. The choice of graft precursor can be varied to include an active group capable of reacting with silanol groups such as silane coupling agents, phosphorous esters, alkyl halides or metal halides[1,18,60-62].

The structure and arrangement of the mesoporous material can be maintained even after grafting. The control of the pore size and structure is relatively simple because the reaction takes place on the surface of the mesoporous silica prepared previously. Therefore, it is a suitable method for studies in which the pore size and structure are known and only the effect of the modification is investigated. In addition, the amount of grafted organic groups can be achieved by controlling the amount of free silanol groups on the surface [1, 18, 60-62].

2.4 Free Radical Polymerization

Free radical polymerization is one of the most important types of addition polymerization. In general, it is widely used in industrial processes to obtain polymers of high molecular weight.

Most of polymers can be obtained under simple experimental conditions. In this type of polymerization; polymerization occurs when free radicals containing unpaired electrons are initiated and the unsaturated monomers give chain reactions. To initiate the radical generally thermal, electrochemical or photochemical methods can be used.

Free radical polymerization is consists of three steps: initiation, propogation and termination.

2.4.1 Initiation

The initiator; are compounds which undergo homolytic degradation as a result of various methods and yield radicals with higher activity than monomers. Radicals must react with saturated monomers and break the double bond present in the monomer to form a new radical active center and remain stable for long enough to form an active radicalic center [64].

Although there are variety of chemical, thermal, redox, and photochemical methods using to decompose two radicals from initiator. Azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) are the most known and used chemical initiator that are used

in free radical polymerization (FRP). The chemical structure and decomposition of two main initiators are shown in the Figure 2.7 (AIBN) and Figure 2.8 (BPO) . Two radicals and N_2 gas are formed in the result of decomposition of AIBN. During decepomsiton of BPO two different types of radicals can be formed: benzoic acid and benzene radicals. When benzoic acid radical is exposed to further decomposition, CO_2 gas can be produced beside benzene radicals [65].

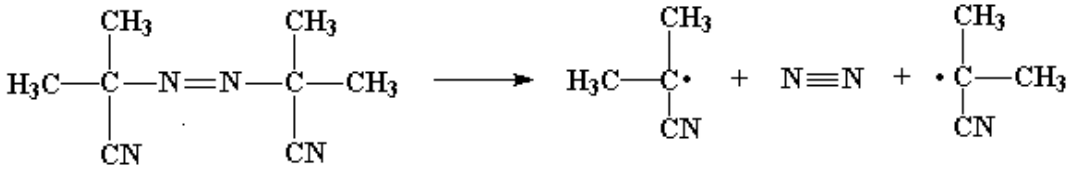

Figure 2.7 : Chemical structure and decomposition of AIBN.

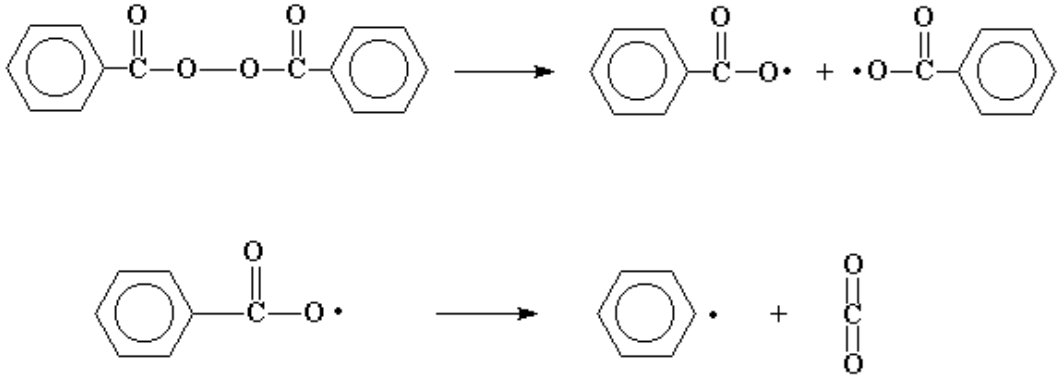

Figure 2.8 : Chemical structure and decomposition of BPO.

Figure 2.9 shows the initiation step for FRP. In the figure, "I" represents the chemical intiator, "M" represent the monomer unit, "R·" is used to represent the free initiator radicals while "M·" represent the monomer radicals. After generation of radicals , the second the addition of a monomer to the primary radical "R·" to yield the chain radical.

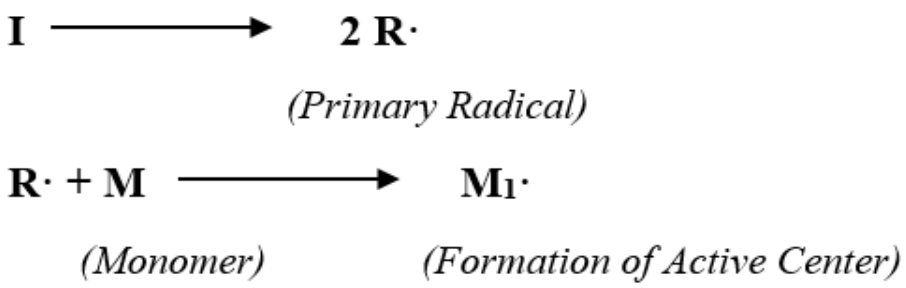

Figure 2.9 : Initation step of FRP.

2.4.2 Propogation

It is the step in which a growing polymer chain is formed by the rapid addition of monomers to the active center formed by the reaction of the free radical with a monomer (Figure 2.10).

During polymerization, most of polymerization time is spent to increase the chain length, or as other name propagation [66].

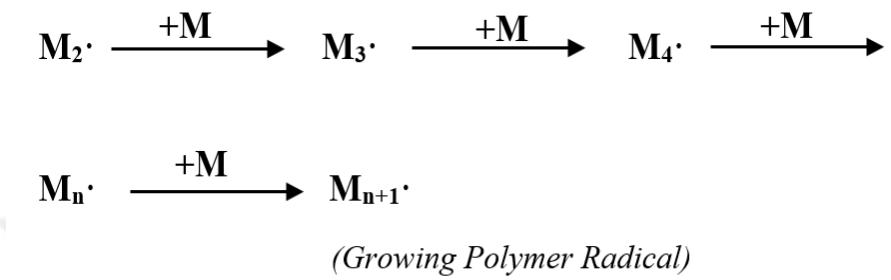

Figure 2.10 : Propogation step of FRP.

2.4.3 Termination

In the termination step, the bimolecular reaction of two radicals occurs to give a dead polymer, meaning that propagation of active chains ceases. Typically two mechanisms dominate the termination step (Figure 2.11): coupling and disproportionation. Coupling is the process by which two growing chains combine to give a polymer with the initiator fragment at the ends of the polymer.

Another process is disproportionation. In disproportionation mechanism, a hydrogen atom on the beta carbon of one growing chain is abstracted by another growing chain. This process results in a polymer with an unsaturated end group at one end plus a polymer with a saturated end [67].

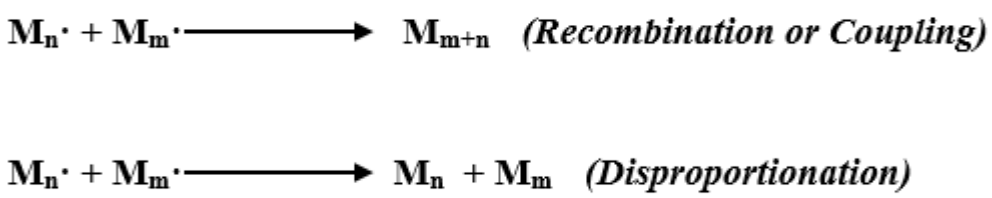

Figure 2.11 : Termination step of FRP.

3. EXPERIMENTAL PART

In this thesis, commercial SBA-15 was modified with 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA). Modified silica was used for the free radical polymerization (FRP) with synthesized boron acrylate monomer. Synthesized materials characterized by FT-IR, TGA, SEM and N_2 absorption/desorption. After characterization, to observe thermal behaviours of grafted polymer , silica part of copolymer was etched with HF. Obtained polymers was characterized with FT-IR, TGA and DSC.

3.1 Materials

SBA-15 (99%, Sigma Aldrich), anhydrous toluene (≥99%, Merck), 3-(trimethoxyslyl)propyl methacrylate (TMSPMA) (98%, Sigma Aldrich), hydrochloric acid (HCl) (37%, Merck), acetone, distilled water, diethyl ether (Carlo Erba), ethanol (≥99%, Merck), acetone (≥99%, VWR Chemicals), hydrofluoric acid (HF) (48%, Merck) , boric acid (99%, Merck), dimethyl-1,3-propanediol (neopentyl glycol) (99%, Abcr), 2-hydroxyethylmethacrylate (HEMA) (Organik Kimya), hypophosphorus acid (50% w/w aqueous solution, Abcr), 2 methylhydroquinone (MeHQ) (99%, Abcr), and 2,2'-Azobis(2-methyl-propionitrile) (AIBN) (98%, Acros Organics), hydrofluoric acid (HF) (48%, Merck)

3.2 Synhthesis of Samples

3.2.1 Synthesis of boronacrylate monomer (BAc)

BAc monomer was synthesized as described previously [63] by esterification reaction. In first step, unhydrous toluene, aquous hypophosphorous acid, neopentyl glycol and boric acid were added into two-necked round bottom flask equipped with Dean-Stark apparatus and condenser at room temperature. Reaction mixture was stirred and, temperature was increased to 125 °C. After removing two equivalents of water by azeotropic distillation, liquid mixture was cooled down room temperature. Beginning of the second step, MeHQ and HEMA were added into flask. Temperature was increased again to 130 °C. Reaction was continued until to obtain one equivalent of

water. To get the colorless liquid product, vacuum distillation process was carried to remove solvent. The whole reaction route was represented in Figure 3.1. Monomer was charactezied by H-NMR and FT-IR.

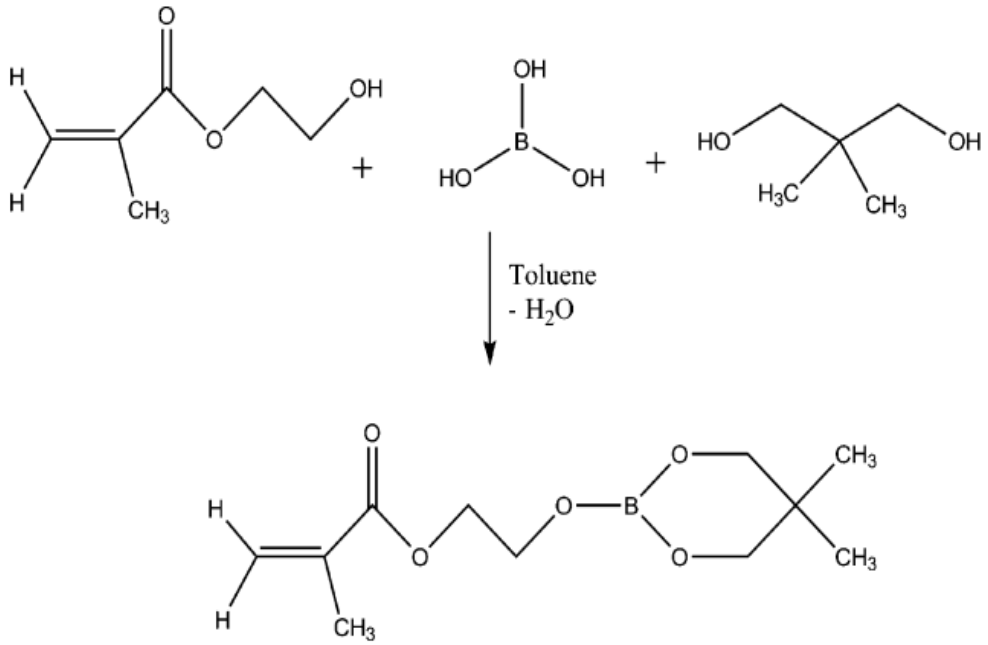

Figure 3.1 : Synthesis of boron acryalte monomer (BAc).

3.2.2 Modification of SBA-15 surface

The surface of SBA-15 particles were functionalized using TMSPMA. 1g of dried SBA-15 dispersed in 11ml HCl (2M) was treated in ultrasonic for 10 min in 250 ml two-necked round bottom flask. 80 ml of unhydrous toluene was added into flask and stirred for 30 min. Then, solution was allowed to refluxe at 120 °C for 4 hour under nitrogen atmosphere. The pre-mixed solution of 1.25 ml of TMSPMA and 10 ml toluene was added into flask drop by drop when mixture cooled down 40 °C. After 1 h of stirring at 40 °C, solution was refluxed again for 16 h at 120 °C under continuous N_2.

The solid was isolated by filtration and washed with toluene, acetone and water, respectively to remove the unreacted TMSPMA. The product was dried in vacuum oven at 70 °C for 24 h. The obtained white powder samples was denoted as M-SBA15. Schematic illustration of modification of SBA-15 was shown in Figure 3.2. When the red dots refer to -OH, green dots refer to bonded silane agent.

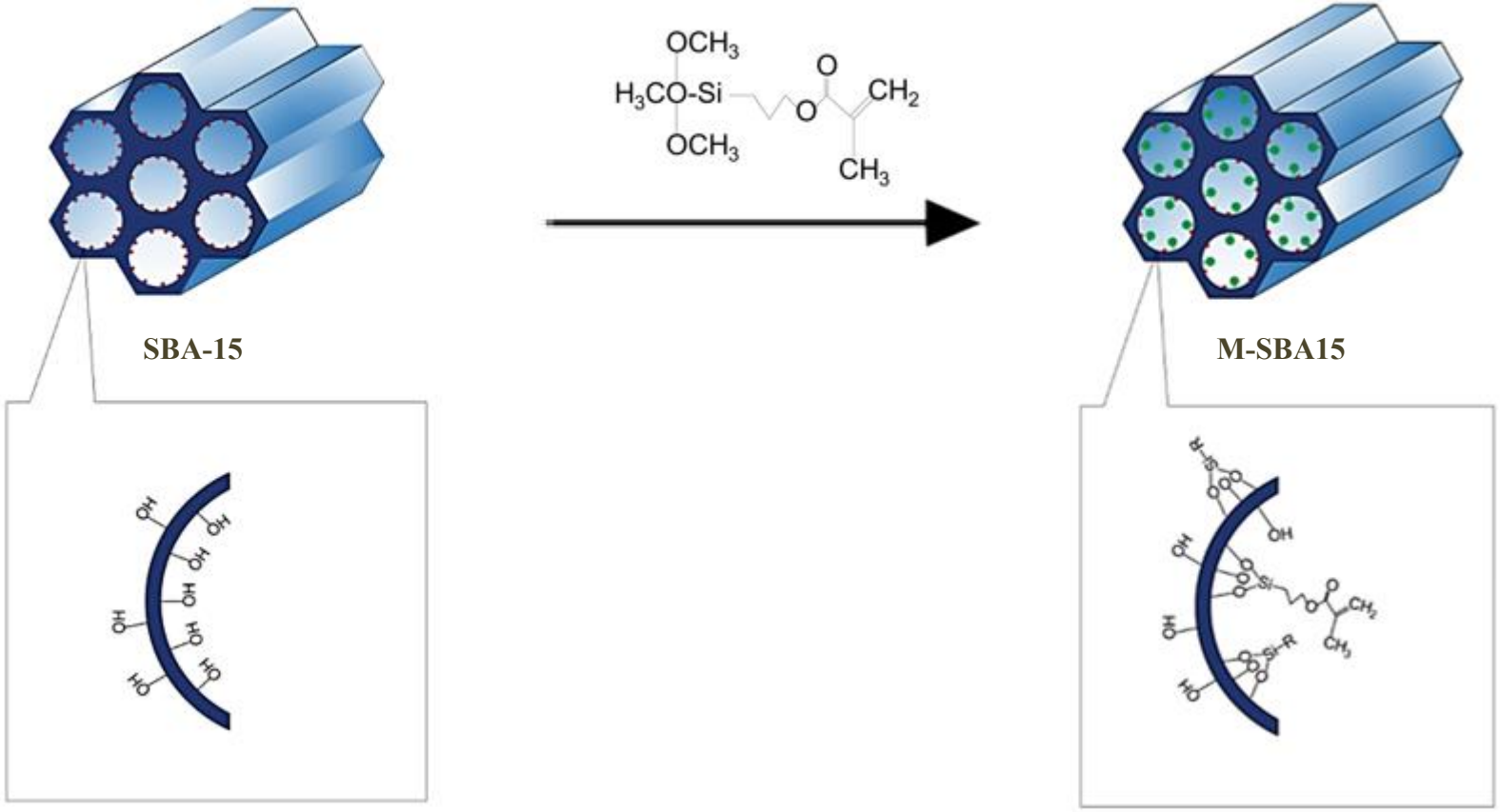

Figure 3.2 : Surface modification of SBA-15.

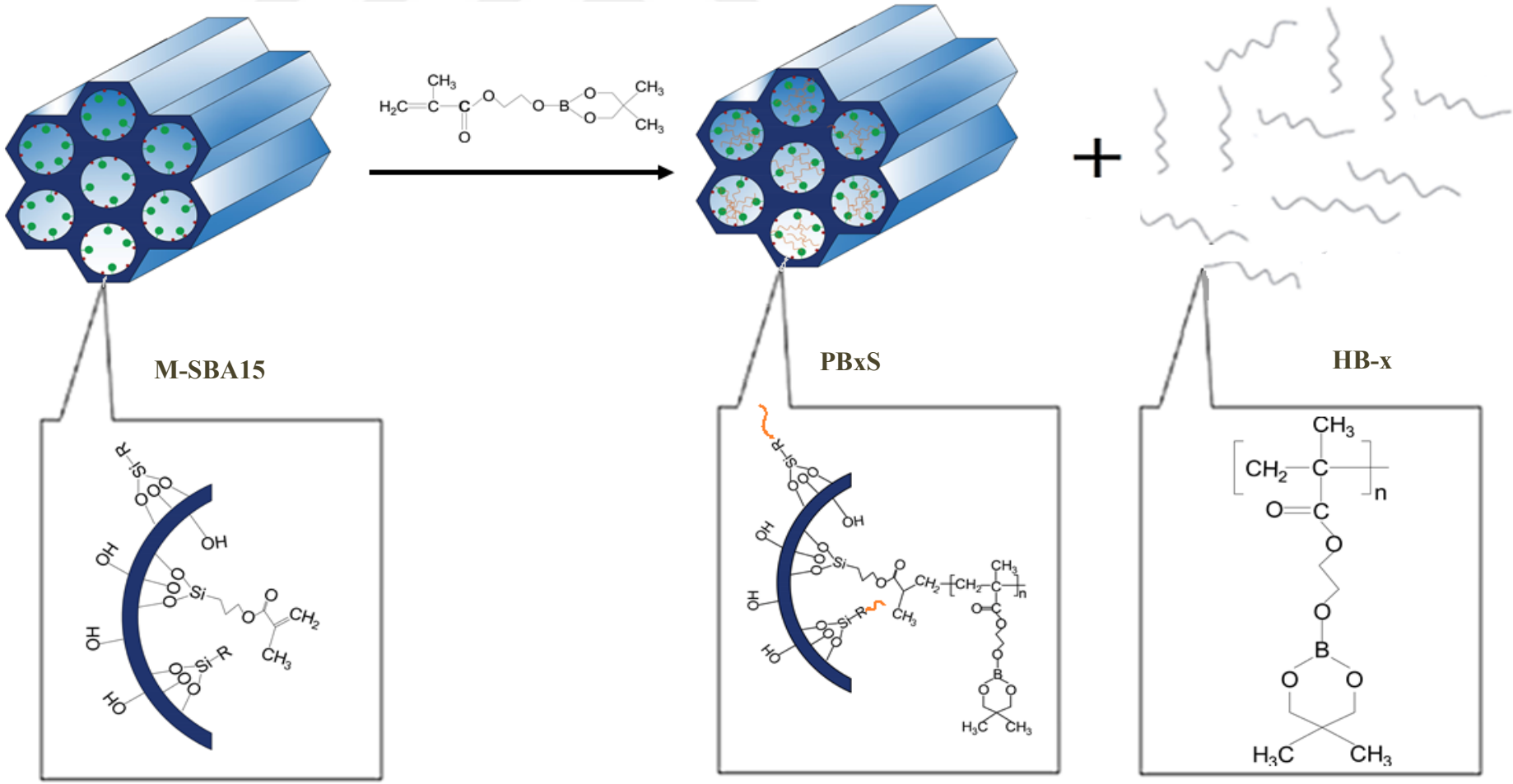

Figure 3.3 : Polymerization of boron acrylate with M-SBA15.

3.2.3 Polymerization of Modified SBA-15 with Boron Acrylate (BAc)

First of all, to obtain suitable polymerization conditions and for comparison boron acrylate polymer was synthesized. For polymerization 100 ml schlenk tube was used. Nitrogen-vacuum cycle was applied for 3 times. AIBN was added into well-mixed toluene and BAc. For polymerization, sealed tube was immersed in 70 °C silicon oil bath for 6h. After 6 h, the tube was cooled rapidly down to ambient temperature, and the reaction mixture was diluted with methanol. The polymers were precipitated into cold diethyl ether. Precipitated polymer was dried under vacuum at 40 °C.

In the seacond step,modified silica particles were first degassed under vacuum at to remove moisture within the pores for one night. Desired amount of M-SBA15 dispersed in unhydrous toluene were added into well-dried tube. They were stirred for 45 min on magnetic stirrer under N_2 atmosphere. Then, BAc monomer was mixed into tube and followed with ultrasonic treatment for 1 h for guarantee that the mixed reaction reagents were well-adsorbed into the nanopores of M-SBA-15. After adding AIBN, the system was sealed up and placed in 70 °C oil bath for 6h.

At the end of the reaction, solution was diluted methanol. The product was successively washed with methanol (x3 times), ethanol (x2 times) and water (x1 times). For washing process, mixture was sonicated for 5 min and this process was followed by the centrifugation for 10 min. The decanted methanol solution was used to get the homo-boronacrylate polymers (HB) which was polymerized each other instead of polymerized with M-SBA15 in the medium. After evaporation of solvent, homo-polymers was precipitated in cold diethyl ether. The insoluble part of polymers was denoted as PBxS, and soluble part denoted as HB.

The used amounts of materials for reactions was given in detailed in Table 1. Also given Fig 3.,and Fig. 4 belongs to schematic illusturaiton of polymerization of pBAc sand PBxS, respectively. In the Figure 3, orange wavy lines refers to bonded polymer chain and grey wavy lines refer to homo boron acrylate polymer (HB).

3.2.4 Cleavage of grafted polymer from the mesopores

The grafted pBAc polymer was separated from the silica particles using hydrofluoric acid (HF) according to the procedure described in Ref [10]. The pBAc in the nanopores of the M-SBA15 was treated by chemical etching with a 5% HF aqueous solution for 48 h, and then the suspended particles of pBAc were centrifuged, washed

for three times and dried. For the three etching process, 0.5 g of samples (PB5S, PB10S and PB20S) were used. The obtained products pBAC in PB5S, PB10S and PB20S are marked as ex-PB-5, ex-PB-10 and ex-PB-20, respectively.

Table 2.1 : Synthesized samples.

Sample	M-SBA15	BAc (ml)	Toluene (ml)	AIBN (g)	Insoluble product	Soluble product
PB	-	9.62	48.10	0.17	-	6.10 g
PB5S	0.5	9.62	48.10	0.17	0.53 g	4.57 g
PB10S	1.0	9.62	48.10	0.17	4.30 g	4.31 g
PB20S	2.0	9.62	48.10	0.17	2.09 g	2.91 g

3.3 Test and Analysis

3.3.1 Fouirer transform infrared spectreophrometer (FT-IR)

To obtain FT - IR spectrums Nicolet FT-IR iS10 spectrometer was used. Resolution mode was 4 cm^{-1} . Sixteen scans were averaged for each sample in the range of 4000-400 cm-1 at room temperature.

3.3.2 Thermal gravimetric analysis (TGA)

Analyses were performed with TA Q50 instrument. Nitrogen gas and air were used during analysis at the heating rate of 20°C/min rising from room temperature to 800°C. The weights of samples are between 6-15 mg.

3.3.3 Scanning electron microscopy (SEM)

The surface morphology of materials were investigated using a Fei Quanta FEG 200 scanning electron microscope, at an accelerate voltage of 30 kV.

3.3.4 Nuclear magnetic resonance (NMR)

1H-NMR, analys was performed with Agilent VNMRS spectrometer at 500 MHz. Deuterated chloroform ($CDCl_3$) was used as solvent.

3.3.5 Solid state nuclear magnetic resonance (SS-NMR)

Solid state nuclear magnetic resonance C13 (SSNMR C13) was performed with Varian Unity Inova 500 MHz by applying 8 KHz magic angle spinning (MAS).

3.3.6 Nitrogen absorption/desorption

Nitrogen adsorption measurements were obtained using a Micrometrics Gemini VII Version 3.03. Samples were degassed at 100 °C for 6 h before adsorption measurements. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method in the relative pressure range P/P_0 0.05-0.3. The total pore volume was calculated from the amount adsorbed at a relative pressure of 0.9. The pore size and total pore volume were calculated using the Barrett-Joyner-Halenda (BJH) method. For calculation of total pore volume, relative pressure was 0.99.

3.3.7 Differential scanning calorimeter (DSC)

Differential scanning calorimetry analysis was conducted with a Perkin Elmer Diamond DSC. Analysis procedure is that heating from 50 °C to 170 °C under nitrogen atmosphere with heating rate 10 °C/min.

4. RESULTS AND DISCUSSION

This section of the thesis includes the results and discussion of characterization.

4.1 Synthesis of Boron Acrylate Monomer (BAc)

The structure of BAc monomer was determined by FT-IR and ^{1}H-NMR analysis. The FT-IR spectrum given in the Figure 4.1. The characteristic peaks of 2960 cm^{-1}, 1718 cm^{-1}, 1636 cm^{-1} and 1386 cm^{-1} correspond to the band of –CH, C=O, C=C and B-O respectively.

^{1}H-NMR spectrum of BAc in $CDCl_3$ is represented in the Figure 4.2. The observed peak at 7.27 ppm is the characteristic peak of $CDCl_3$. The peaks between 6.14 and 5.57 ppm corresponded to C=C-H protons. It proves the existence of acrylic group in the monomer. The two different CH_2 protons are detected at the peak between 4.26 and 4.02 ppm. One signal of CH_3 peak is observed at 1.95 ppm. The other signal of CH_3 protons attached to cycling ring was recorded at 0.97 ppm. The both FT-IR and H-NMR results are matched up with the results in reference [63]. So, it can be said that BAc was synthesized successfully.

4.2 Characterization of Modifed SBA-15 and pBAc/SBA15 Composites

4.2.1 Structural Analysis

For the structural analysis of synthesized materials two test methods were used: FT-IR and SS-NMR (^{13}C). Figure 4.3 shows FTIR spectras of the SBA-15, TMSPMA and modified SBA-15 (M-SBA15) with silane. SBA-15 M-SBA15 have the intense broad signal at 1044 cm^{-1} and 804 cm^{-1} corresponded to the stretching and bending vibration of Si-O-Si. Also The peaks at 3422 and 1636 cm^{-1} corresponded to the stretching vibration of O–H as mentioned in reference [11,69,70]. After modification, new peaks are appeared in the spectra of M-SBA15. The existence of the peaks at 1718 cm^{-1} corresponding to the C=O (carbonyl group). Also, increasing intensity at 1636 cm^{-1} corresponded to the C=C stretching vibrations which was resulted from the

grafted structure (TMSPMA). The new peaks suggest the accomplished modification of silane agent (TMSPMA).

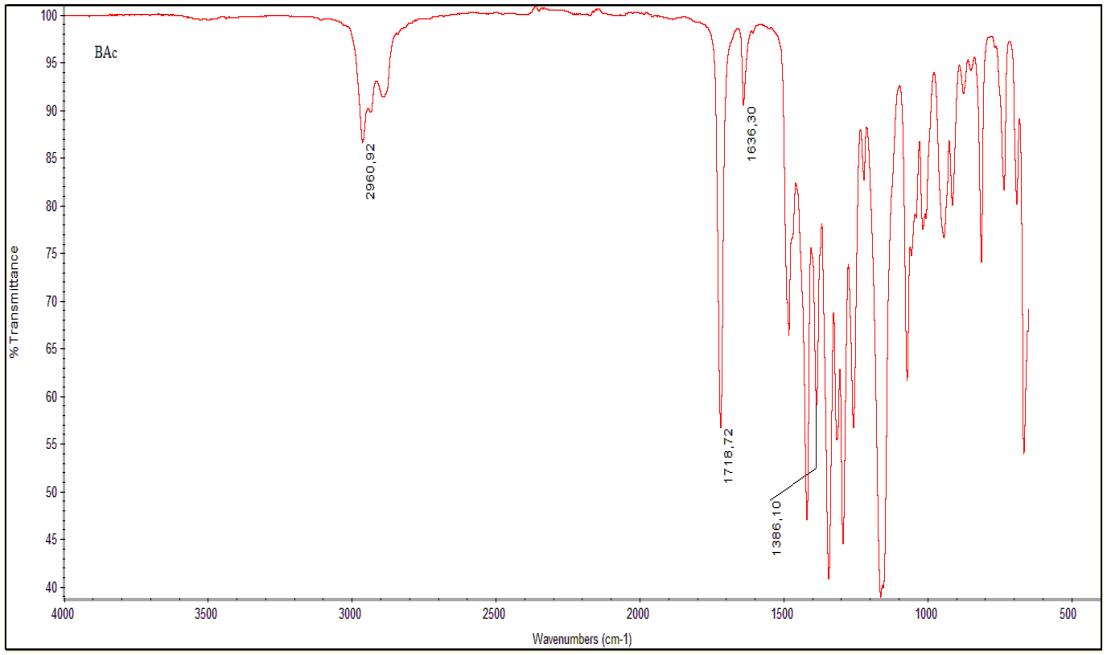

Figure 4.1 : FT-IR spectra of BAc.

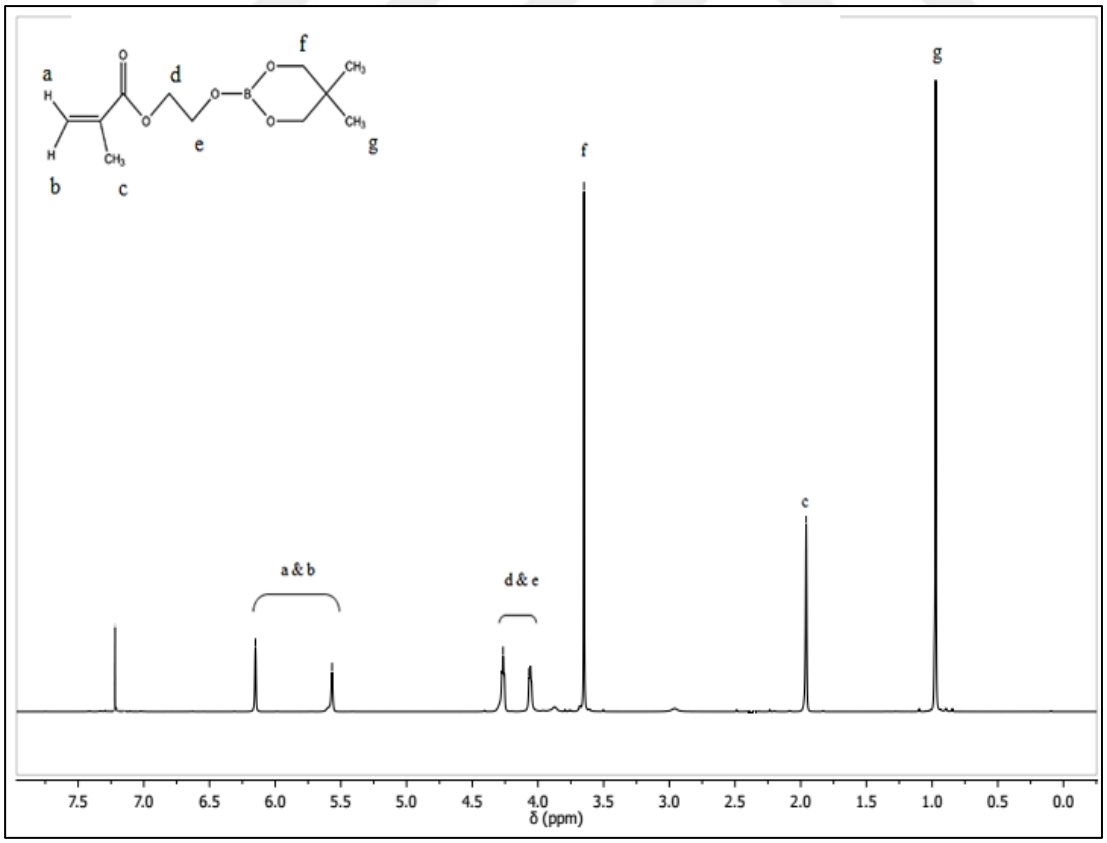

Figure 4.2 : H-NMR spectra of BAc

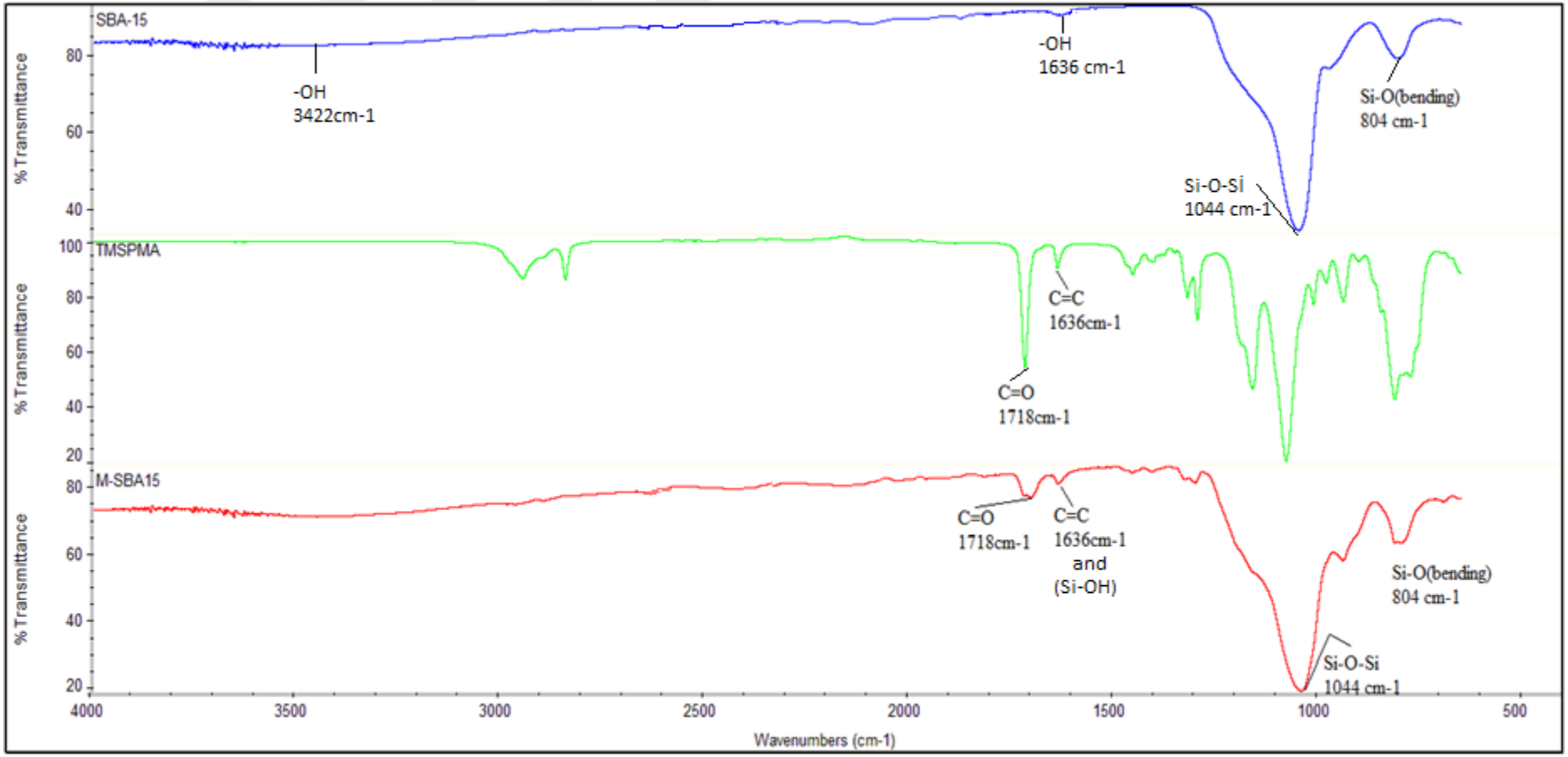

Figure 4.3 : FT-IR Spectras SBA-15, TMSPMA and M-SBA15

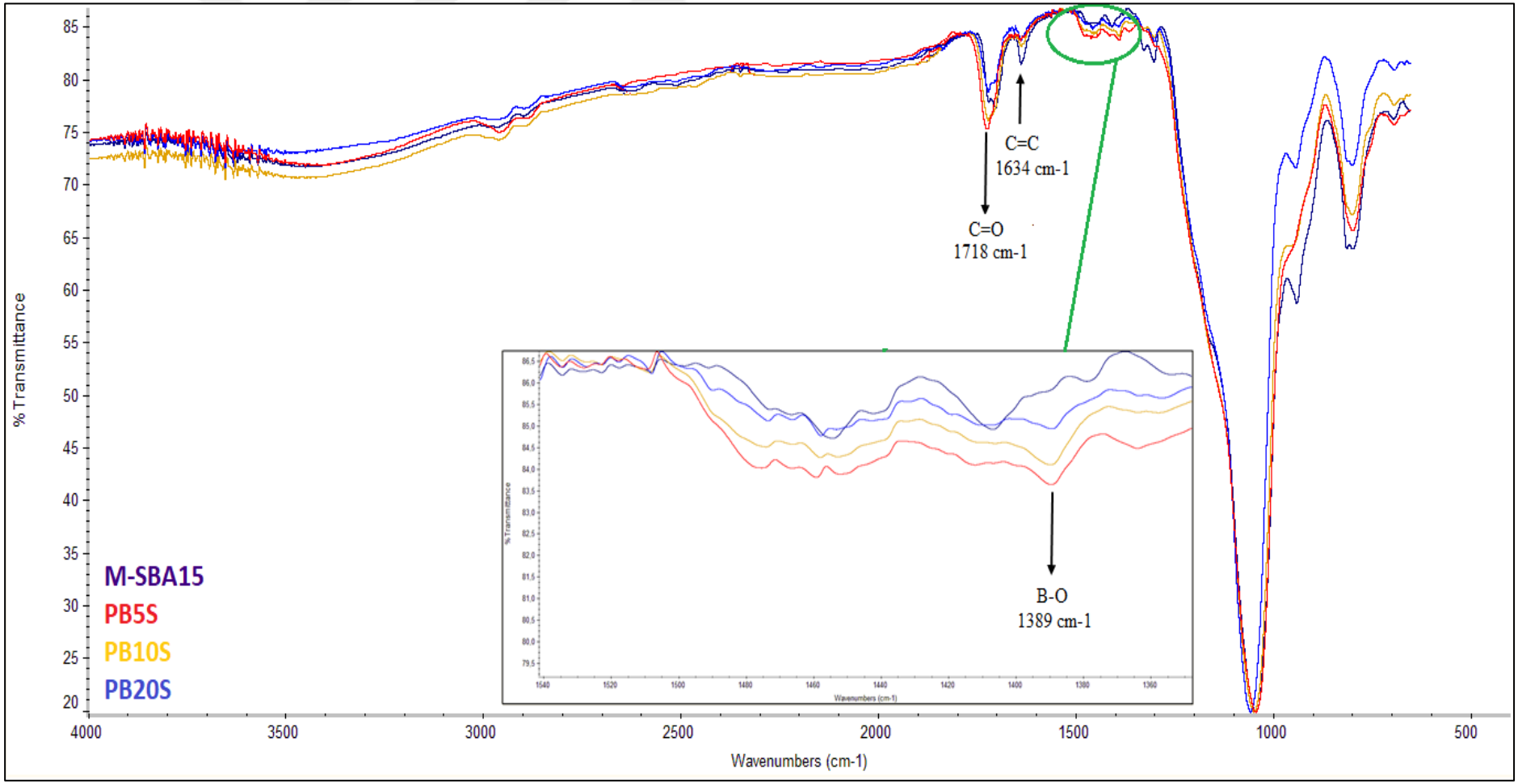

Figure 4.4 : FTIR spectra of M-SBA15, PB5S, PB10S and PB20S

For the following FT-IR analysis of M-SBA15, PB5S, PB10S and PB20S is given in the Figure 4.4. As shown in Figure 4.4, after polymerization with BAc, when intensity of carbonyl peak of M-SBA15 was increased, the intensity of double bond was decreased. Also, all composite materials (PB5S, PB10S and PB20S) have a signal at 1389 cm^{-1} corresponded to B-O bond. All these are the prove that boron-acrylate/SBA-15 polymer composites obtained succesfully. Also, it can be said that PB5S sample contained the maxiumum amount of boron acrylate polymer compared to PB10S and PB20S.

The solid state ^{13}C MAS NMR spectrums shown in Figure 4.5 (M-SBA15) and Figure 4.6 (PB10S) provide information about the presence of organic functional groups within the mesopores. In the Figure 4.6 resonance of the carbonyl group at ~ 170 ppm and resonance of –CO at ~ 70 ppm are observed. The peak is around 135-145 ppm that are responsible from double bond carbon atoms. Other carbon atoms located around 20-30 ppm.

SS-NMR spectrum of PB10S illustrated in Figure 4.6, broadness of the peaks between 10-90 ppm is observed clearly. Although the exact chemical shifts were not determined, it was obviously related with carbon bonds with boron acrylate polymer which was appeared after polymerization of M-SBA15. Also, while carbonyl peak (~ 160-175 ppm) was broading, the peak of C=C (145 ppm) double bond was disappeared.

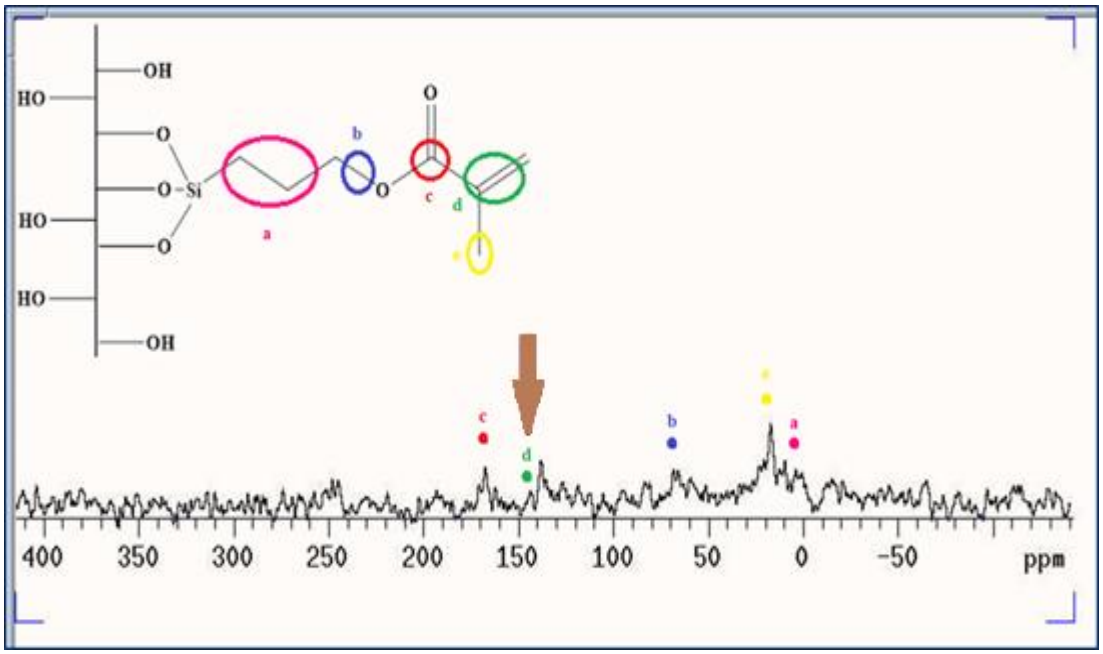

Figure 4.5 : ^{13}C SS-NMR spectra of the M-SBA

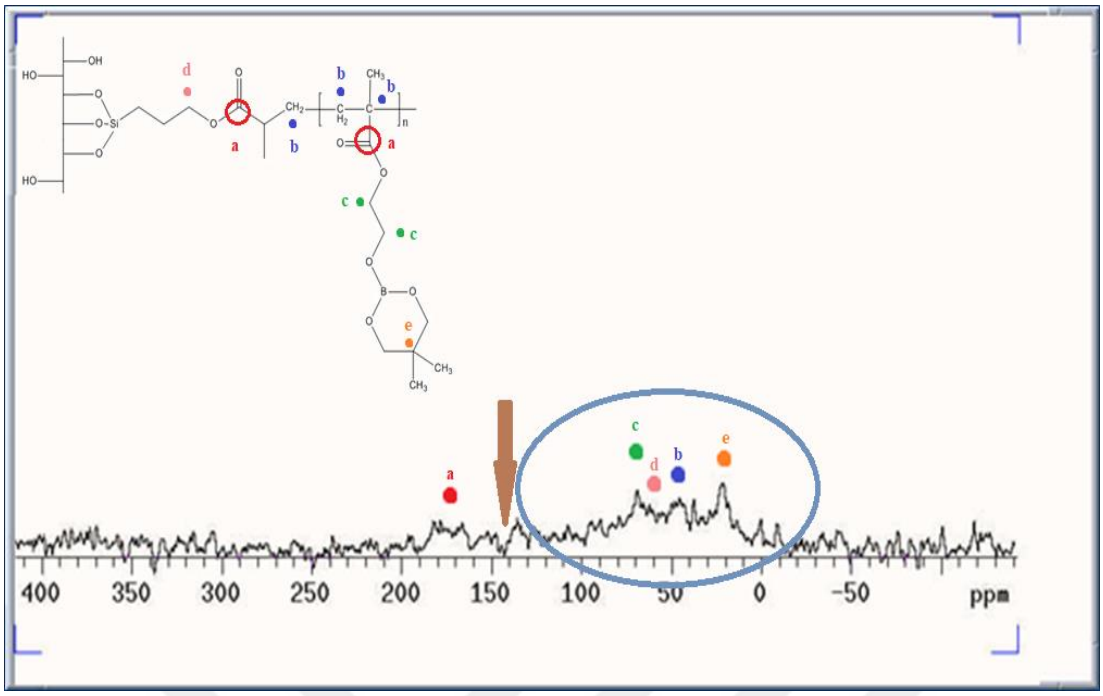

Figure 4.6 : ^{13}C SS-NMR spectra of the PB10S.

Also, FT-IR analysis was utilized for the homopolymers. All homopolymers (HB-20, HB-10 and HB-5) had the same spectra as PB as (Figure 4.7). It shows the polymerization was took place correctly in the presence of SBA-15.

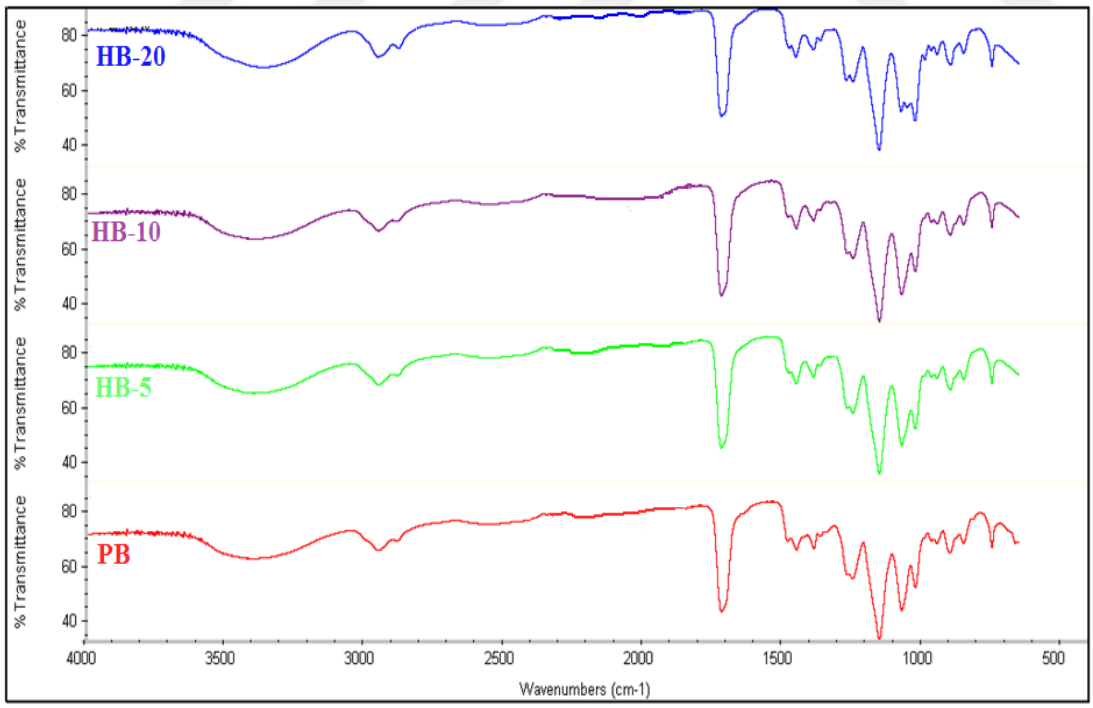

Figure 4.7 : FT-IR of homopolymers.

4.2.2 Thermal properties of samples

Thermal behaviour of synthesized M-SBA15 and boron acrylate/SBA-15 polymer composites (PBxS) was examined via TGA under nitrogen and air atmosphere. The Figure 4.8 displays the TGA curves of samples which was analyzed under N_2 atmosphere. Also, amount of residues at different temperatures is given Table 4.1. As seen Figure 4.8, SBA-15 had the one decomposition stage below 100 °C due to the absorbed humidity. After modification, the water loss of M-SBA15 decreased providing the change of surface characteristics. Also, the residue about 66% at 800 °C was the corroborating evidence for successful grafting of organic group to the SBA-15 surface. As seen the curves of PB5S, PB10S and PB20S, the weight loss of sample between 300-450 °C increased, corresponding to the decomposition of polymer backbones. When the amount of M-SBA15 in the polymerization system was 0.5 g (5%), 1.0 g (10%) and 2.0 g (5%), the loading amount of the polymer was the 11.73, 11.49 and 3.22 %, respectively. To increase the polymerization rate in the pore, amount of adding M-SBA15 should be determined as 5%. In addition, it can be said that thermal stability of M-SBA15 under nitrogen atmosphere were decreased with the bonding of pBAc. To obverse the thermal stabilites of samples under air atmosphere another thermal gravimetric analysis was carried out. The thermogram was given in the Figure 4.9. In this figure it was clearly seen that thermal stability of M-SBA15 was rised with increasng amount of grafted boron acrylate polymer when decompostion took place under the air atmosphere. PB5S, which was contained high amount of boron acrylate polymers in pores, showed higher oxidation resistance compared to other samples. The reason of this rise should be the composed boron-oxide layers during decomposition.

Table 4.1 : Residue (%) of sample at different temperatures under N_2 atmposhere.

Sample	250 °C	300 °C	350 °C	400 °C	450 °C	800 °C
SBA15	89.08	87.94	86.74	85.7	84.71	80.84
M-SBA	93.85	92.68	85.27	77.91	73.5	66.33
PB	60.97	43.75	18.79	5.12	4.86	2.34
PB5S	89.67	78.95	68.80	61.83	58.59	53.37
PB10S	91.72	85.66	74.58	66.65	63.19	57.32
PB20S	93.29	88.15	80.32	73.11	69.14	63.11

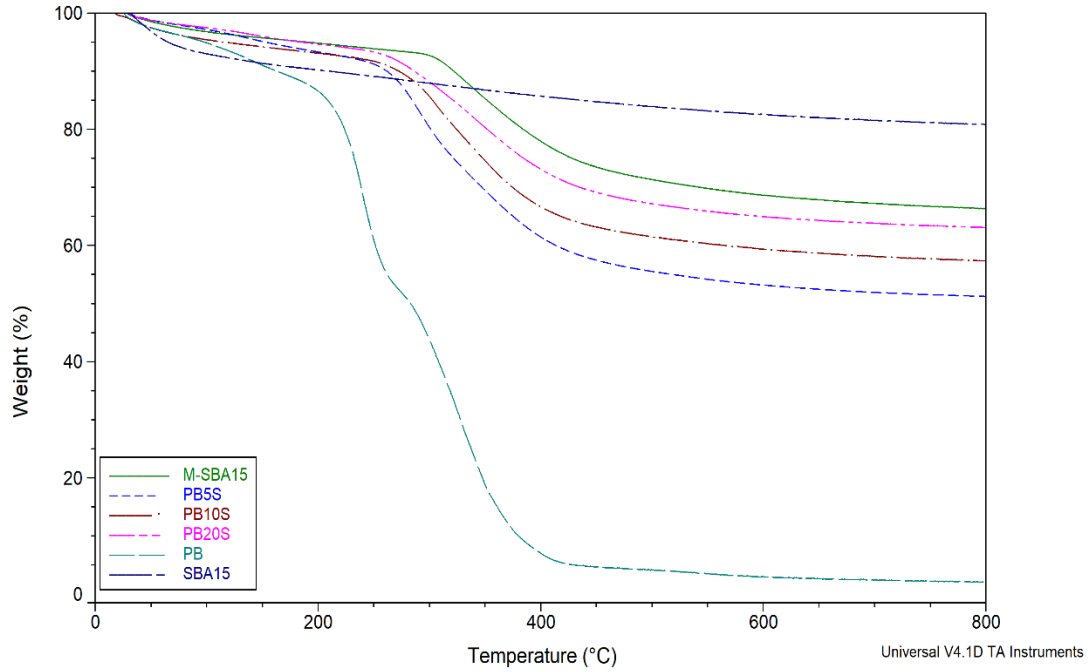

Figure 4.8 : Thermogram of SBA-15, M-SBA15, PB5S, PB10S, PB20S and PB under nitrogen atmosphere.

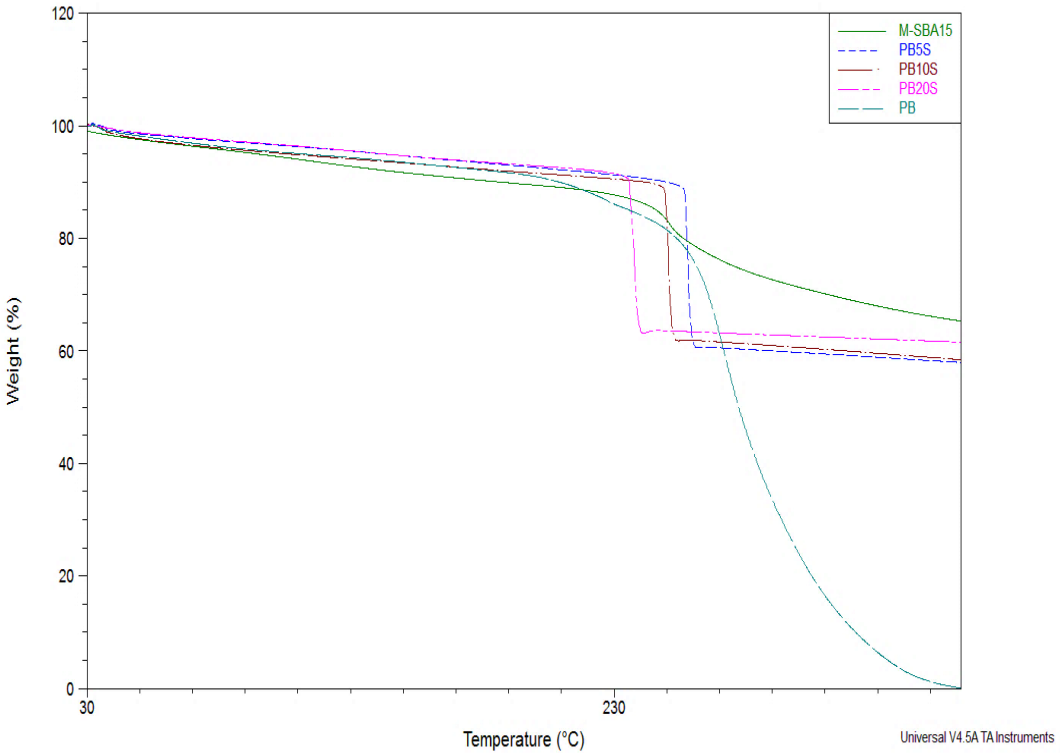

Figure 4.9 : Thermogram of SBA-15, M-SBA15, PB5S, PB10S, PB20S and PB under air atmosphere.

4.2.3 Morphological Properties

Scanning electron microscope (SEM) was used for examination of the morphology of SBA-15 during grafting polymer. As a result of SEM, SBA-15 images shown in Figure 4.10 carries the similar structure as mentioned in the literature. In general, the SBA-15 exhibits long rod-like structures formed by the connection of several hexagonal prism of short rods. After the modification and polymerization, its worm-like structure did not deteriorate and preserved orginal structure. The absence of a noticeable difference in surface roughness suggests that polymerization was took place in mesopores.

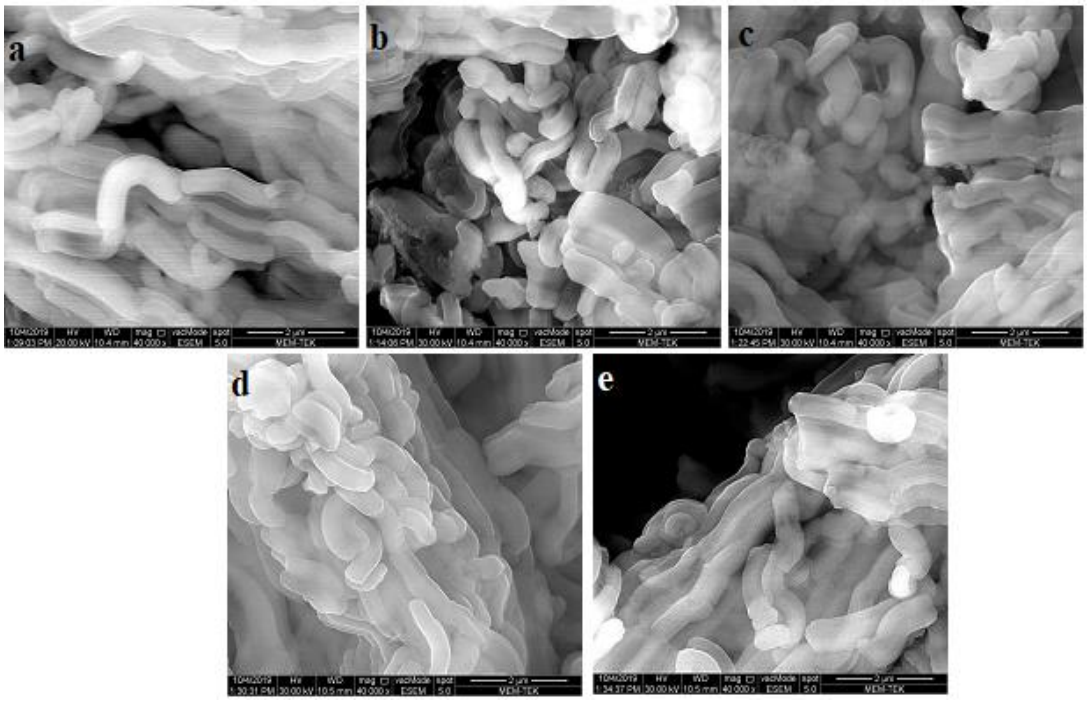

Figure 4.10 : SEM images of SBA-15 (a), M-SBA15 (b), PB5S (c), PB10S (d) and PB20S (e).

4.2.4 N_2 absorption/desorption analysis

N_2 absorption/desorption analysis was applied for the determination of specific surface area, average pore width and total pore volume. Decrease in quantity of adsorbed N_2 after grafting organic substance means the filling of the pores. According to result of analysis, specific surface areas, total pore volumes and pore width of the samples are illustrated in Table 4.2.

Silane-modified SBA-15 exhibit smaller specific surface areas, pore volumes, and avarage pore width than unmodified SBA-15. These results to successful modification

of SBA-15 with TMSPMA. After polymerization, it is expected decreasing in all properties. M-SBA15 has the higher specific surface area, avarage pore with and total pore volume than PB5S, PB10S and PB20S.

The most decline on the specific surface area, total pore volumes and avarage pore widthis seen for PB5S. It means the most polymer chain was grafted to the surface of mesopores of SBA-15. Also, there is not big difference between PB10S and PB20S. This result is in good agreement with the both TGA and FTIR analysis.

After BAc polymerization in the pores of the SBA-15, the pore structural parameters of the composites decreased compared to SBA-15 and M-SBA15. It is suggested the absorption of monomer into the nanopores of the M-SBA-15 and polymerization successfully. The most decline on the specific surface area, total pore volumes and most pore size is seen for PB5S. It means more polymer chain was grafted to the surface of mesopores of SBA-15. This result is in good agreement with the both TGA and FTIR analysis.

Table 4.2 : Textural properties for samples.

Sample	Specific Surface Area[a] (m^2/g)	Avarage pore width[b] (nm)	Total Pore volume[b] (cm^3/g)
SBA-15	713.30	2.19	0.47
M-SBA15	484.92	2.18	0.13
PB5S	194.15	2.10	0.07
PB10S	251.50	2.15	0.10
PB20S	266.21	2.16	0.12

[a] Determined by BET method. [b] Determined by BJH method.

4.3 Cleavage of Grafted Polymer

The amount of pBAc's, which were obtained from the mesopores in PBxS, is listed in the Table 4.3. For the highest amount of PB was collected from the PB5S. In the given Figure 4.11, it was clearly seen that ex-PB's possess the same characteristic peaks with PB (boron acrylate polymer), and the characteristic peaks of Si-O-Si at 1044 cm^{-1} disappeared, suggesting that the silica support had been removed succesfully.

Table 4.3 : The amounts of pBAc in the pores of PBxS.

Sample	Soluble product
ex-PB-5	0.12 g
ex-PB-10	0.08 g
ex-PB-20	0.04 g

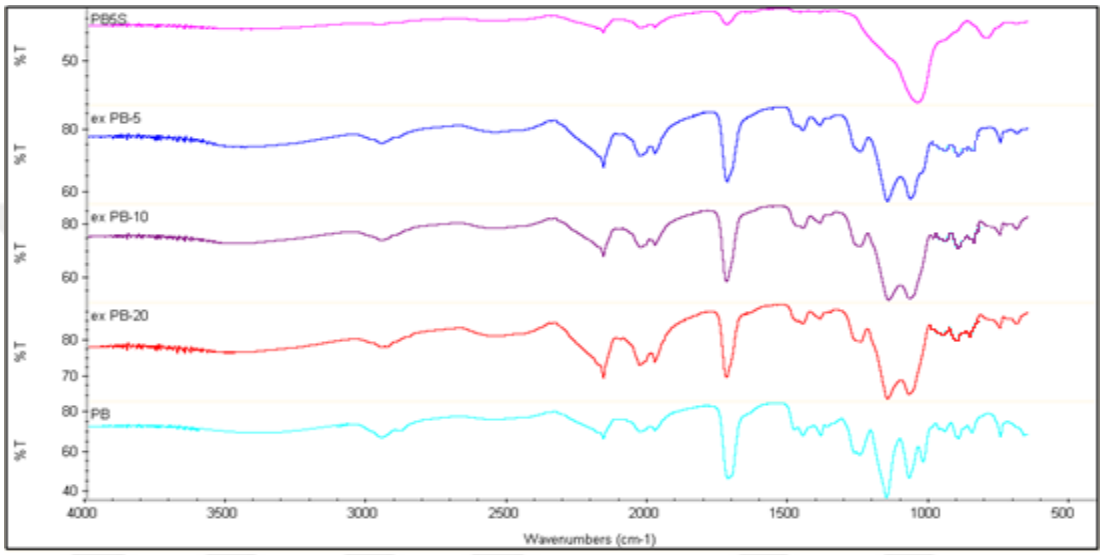

Figure 4.11 : FT-IR spectra of PB, ex-PB-5, ex-PB-10 and ex-PB-20.

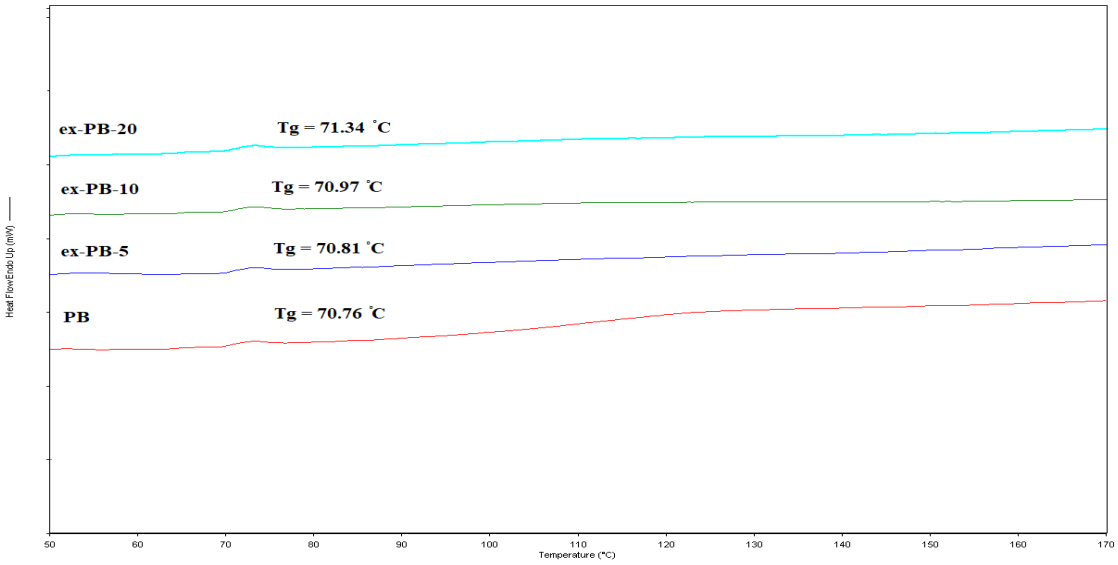

Figure 4.12 : DSC curves for ex-PBs and PB.

DSC and TGA analysis were also utilized for the investigation of the thermal properties of obtained boron acrylate polymer in the pores. Figure 4.12 compares the DSC curves of PB, ex-PB-5, ex-PB-10 and ex-PB-20. Glass transtion temperatures were calculated as 70.76 °C, 70.81°C, 70.97 °C and 71.34 °C for PB, ex-PB-5, ex-PB-10 and ex-PB-20, respectively. These calcuated Tg values showed similar values with previously synthesized boron acrylate polymer in the reference [68]. The results showed that there were minor differences between glass transtion temperatures. So, it can be said that of confined polymerization didnot affect the glass transition temperatures.

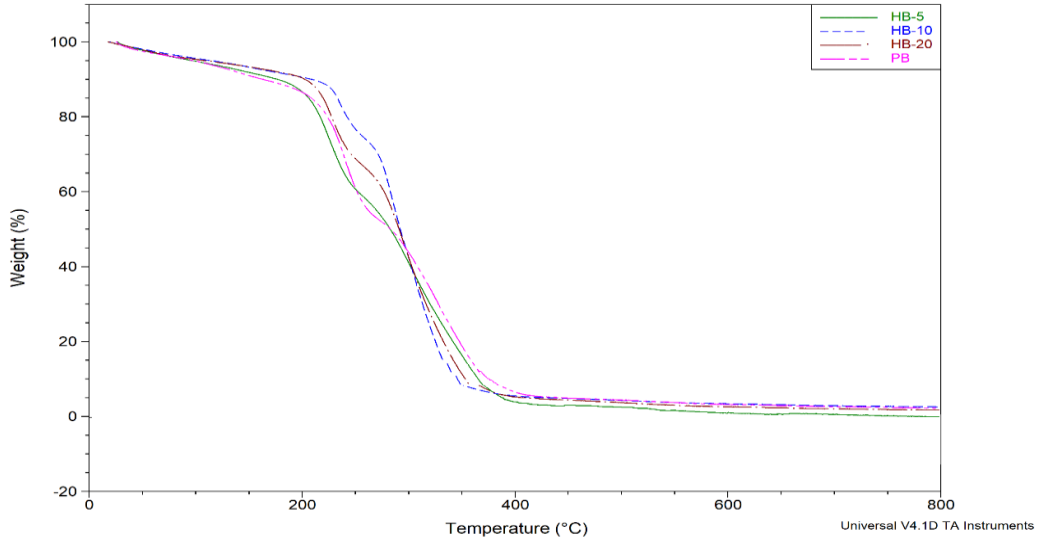

Figure 4.13 : TGA curves of PB, HB-5, HB-10 and HB-20.

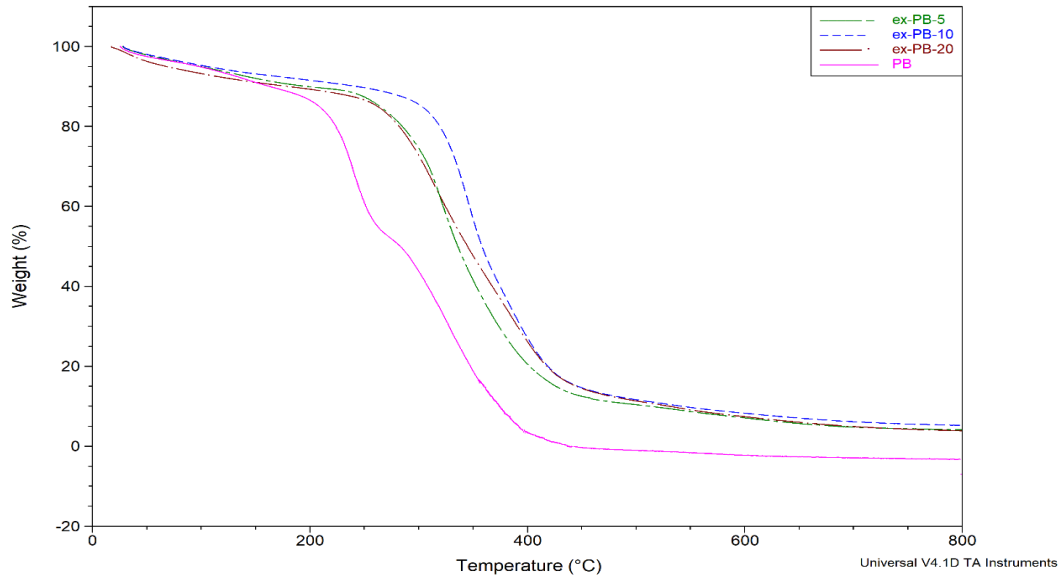

Figure 4.14 : TGA thermograms of the PB and ex-PBs under N_2 atmposhere.

Figure 4.13 shows the TGA curves of the PB and homopolymers which were not react with the surface of SBA-15 for polymerization All samples have two decompositon step. When first degradation step around 210-270 °C was resulted from weak head to head linkages, the second step between 260- 410 °C represented of random chain scission of the main chain of polymer.

Figure 4.14 is the representation of TGA curves of the PB and ex-PBs obtained from mesopores. It can be observed clearly that the thermostability of ex-PBs were improved significantly in comparison with PB. When thermal degradation of both ex-PB-5 and ex-PB-20 started around 265 °C, decomposition of ex-PB-10 got start at 300 °C. Also ex-PBs had the only one decompositon step between 260 – 460 °C as a comparison to HBs. This might indicated that the nanoconfinement effect playedan active role in the polymerization proccess that reduced the chain termination. According to these results, the mesopores of SBA-15 had significantly confinement effects on BAc polymerization.

5. CONCLUSION

The aim of this study is to polymerize the boron containing monomer in the mesopores of SBA-15. In this study, BAc monomer was synthesized and used to polymerize by free radical polymerization in the mesopores by grafting to method. It was the first study that used BAc for the synthesis polymer/SBA-15 composite. For the covalently attachment of BAc polymer chains to the surface of SBA-15, modification by post synthesis method was utilized with TMSPMA. To get the furher information about the pBAc in the pores, silica frame of SBA-15 was removed with usage of HF aqeous solution.

The structures of the monomer was characterized and confirmed with NMR and FT-IR spectras. After polymerization with BAc, FT-IR and SS-NMR (^{13}C) characterization method was utilized for the structural analysis of all samples (SBA-15, M-SBA15, PB5S, PB10S and PB20S). Both generation and growth of the carbonyl peak and reduction of C=C peak in the FT-IR spectrum were resulted from the succesful synthesis processes. Rise on the decomposition rate was observed with increase of organic substance in pores on the TGA thermogram. When the TGA analysis repeated under air atmosphere, thermal stablities of composite was increased with increasing boron acrylate polymers in pores. The presence of the chemicals shifts of organic subtances on the ^{13}C SS-NMR spectrums also confirmed the both modification and polymerization process was accompolished. Distinct difference between SBA-15 and PBxS was not seen on SEM images. It was indicated that most polymerization took place in the pores. Textural properties as spesific surface area, total pore volume and average pore width were determined via N_2 absorption/desorption analysis. It can be seen textural properties of M-SBA15 and PBxS showed decrease compared to SBA-15 as expected. These decline resulted from the filling of the mesopores.

By the FT-IR analysis it was seen that silica frame was succesfully removed from the composite. For the investigation of thermal properties, boron acrylate polymer in the pores were characterized via DSC and TGA. There was not found the big difference

between T_g values of ex-PBs which were obtained from pores and BAc polymer (PB). Thermostability of ex-PBs were improved significantly in comparison with PB.

As a consequence , it was found that utilizing of SBA-15 as a nanoreactor for the BAc polymerization in the mesopores was possible. The most amount of polymer chain was grafted to SBA in PB5S sample. Using the less amount (%5 w/w of BAc) of modified SBA-15 had favourable effect on raise of amount of the boron acrylate polymers in the pores. For the futher studies different paramaters or polymerization method will be studied to increase the polymerization rate. Also, the effect of boron-acrylate/SBA-15 polymer composite in epoxy acylate on thermal properties should be investigated.

.

REFERENCES

[1] **Zhao, D., Wan, Y., & Zhou, W**. (2013). Ordered mesoporous materials. Weinheim: Wiley-VCH.

[2] **Solano-Umaña, V. and Vega-Baudrit, J.R**. (2015) Micro, Meso and Macro Porous Materials on Medi-cine. *Journal of Biomaterials and Nanobiotechnology*, **6**, 247-256 doi:10.4236/jbnb.2015.6423

[3] **Yang, P., Gai, S. & Lin, J.** (2012) Functionalized mesoporous silica materials for controlled drug delivery. Chemical Society Reviews 41: 3679-3698

[4] **Akti, F**. (2018). Düşük Sicaklik Co2 Adsorpsiyonu Için Pani/sba-15 Sorbentlerin Sentezi Ve Yapisal Özelliklere Sentez Parametrelerinin Etkisi. *Uludağ University Journal of The Faculty of Engineering*, *23*(3), 261–272. doi: 10.17482/uumfd.454638

[5**] Hanrahan, J.P, O'Mahony, T.F, Tobin, J.M & Hogan, J.J.** (n.d.) Mesoporous silica and their applications, Retrieved on March 1, 2019 from https://www.sigmaaldrich.com/technicaldocuments/articles/materialsscience/renewble-alternative-energy/mesoporous-silica.html

[6] **Mehmood, A., Ghafar, H., Yaqoob, S., Gohar U.F. & Ahmad, B.** (2017) Mesoporous silica nanoparticles: A review. J. Develop Drugs 6: 174. doi:10.4172/2329-6631.1000174

[7] **Yu, C.B., Wei, C., Lv, J., Liu H.X. & Meng, L.T.** (2012) Preperation and thermal properties of mesoporous silica/phenolic resin nanocomposites via in situ polymerization. Express Polymer Letters: 6(10), 789-793 doi: 10.3144/expresspolymlett.2012.84

[8] **Wei, Z.B, Bai, R., Zhang F.A. & Zhou, L**. (2013) Effects of SBA-15 and its content on MMA solution polymerization and PMMA composites. Iran Polym J, 22: 571-578 DOI 10.1007/s13726-013-0156-0

[9] **Thu, P.T.T., Dieu, H.T., Phi, H.N., Viet, N.N.T., Kim, S.J. & Vo, V**. (2012) Synthesis, characterization and phenol adsorption of carbonyl-functionalized mesoporous silicas. J Porous Mater. 19: 295-300 DOI 10.1007/s10934-011-9475-8

[10] **Chen, M., Zhou, H., Zhou, L., & Zhang, F.** (2017). Confined polymerization: ARGET ATRP of MMA in the nanopores of modified SBA-15. *Polymer, 114*, 180–188. doi: 10.1016/j.polymer.2017.02.031

[11] **Chen, M., Qin, L., Liu, Y., & Zhang, F**. (2018). Controllable preparation of polymer brushes from mesoporous silica SBA-15 via surface-initiated ARGET ATRP. *Microporous and Mesoporous Materials, 263,* 158–164. doi: 10.1016/j.micromeso.2017.12.019

[12] **Çanak, T.Ç., Kaya, K. & Serhatli, İ.E**. (2014) Boron containing UV-curable epoxy acrylate coatings *Progress in Organic Coatings* 77: 1911–1918

[13] **Martín, C., Ronda, J.C. & Cádiz, J.** (2006) Boron-containing novolac resins as flame retardant materials, *Polym. Degrad. Stab.* 91 (4) 747–754

[14] **Çanak, T.Ç, Akpınar, S. & Serhatlı, İ.E**. (2017) Homopolymerization and synthesis of a new methacrylate monomer bearing a boron side group: characterization and determination of monomer reactivity ratios with styrene. *Turkish Journal of Chemistry* 41: 209 – 220

[15] **Polarz, S.** (2004). Ordered Mesoporous Materials. In H. S. Zalwa (Ed.) *Encyclopedia of Nanoscience and Nanotechnology*. (Vol. 8, pp.239–258) ISBN: 1-58883-064-0/$35.00

[16] **Meynen, V., Cool, P., & Vansant, E.F**. (2009) "Verified syntheses of mesoporous materials". *Microporous and Mesoporous Materials,* 125:170–223

[17] **Li, W., Liu, J., & Zhao, D.** (2016). Mesoporous materials for energy conversion and storage devices. *Nature Reviews Materials*, 1(6). doi: 10.1038/natrevmats.2016.23

[18] **Sevimli, F.** (2011). *Surface functionalization of SBA-15 particles for amoxicillin delivery*. (Master thesis). Middle East Technical University, Department of Chemistry, ANKARA

[19] **Antonelli,,D.M. and Ying, J.Y.** (1996) Mesoporous materials. *Current Opinion in Colloid & Interface Science*, 1(4): pp.523-529.

[20] **Hartmann, M.** (2005). Ordered mesoporous materials for bioadsorption and biocatalysis. *Chemistry of Materials*, 17(18): pp. 4577-4593

[21] **Wan, Y. and Zhao, D.Y.** (2007) On the controllable soft-templating approach to mesoporous silicates. *Chemical Reviews*, 107(7): pp. 2821-2860.

[22] **Hasanzadeh, M., Shadjou, N., Eskandani, M. ve Guardia, M**., (2012). Mesoporous silica based materials for use in electrochemical enzyme nanobiosensors. *Trends in Analytical Chemistry*, 40:106-11

[23] **Arruebo, M.** (2011). Drug delivery from structured porous inorganic materials. *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology*, 4(1): 16-30.

[24] **Smith, S.** (2019). Nanoporous Materials Market Growth Factors, Applications, Regional Analysis, Key Players And Demand By 2022. *Over Blog*. Retrieved October 23, 2019 from http://psmarketresearch-reports.over-blog.com/2019/01/nanoporous-materials-market-growth-factors-applications-regional-analysis-key-players-and-demand-by-2022.html

[25] **Lu,Y., Tonigold, M., Bredenkötter, B., Volkmer, D., Hitzbleck J.,Langstein, G.,** (2008) A Cobalt(II)-containing metal-Organic framework showing catalytic activity in oxidation Reactions *Z. Anorg. Allg. Chem*., (634): 2411-2417.

[26] **Berube, F., Kleitz, F. & Kaliaguine, S**. (2009) J Mater Sci., 44 (24) 6727-6735.

[27] **Yanagisawa, T., Shimizu, T. & Kuroda, K**. (1990). The preparation of alkyltriinethylaininonium-kaneinite complexes and their conversion to microporous materials. *Bull. Chem. Soc. Jpn*., 63: 988-992

[28] **Ambili, V.K.** (2011) *Studies on catalysis by ordered mesoporous SBA-15 materials modified by transition metals*. (Doctorial thesis). Cochin University of Science and Technology, Kerala/INDIA

[29] **Hoffmann, F., Cornelius, M., Morell, J., & Froeba, M. (**2006). Silica-Based Mesoporous Organic—Inorganic Hybrid Materials. *Chem Inform*, 37(34). doi:10.1002/chin.200634291

[30] **Kresge, C. T., Leonowicz M. E, Roth W. J., Vartuli J. C. and Beck J. S**. (1992). Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359 :710-712.

[31] **Tang F, Li L and Chen D.** (2012). Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery. *Adv Mater* , 24: 1504–1534.

[32] **Schwanke, A. J., Balzer, R., & Pergher, S.** (2017). Microporous and mesoporous materials from natural and inexpensive sources. *Handbook of Ecomaterials*, 3379–3399. doi: 10.1007/978-3-319-68255-6_43

[33] **Sayari, A. and Hamoudi, S.** (2001). Periodic mesoporous silicabased organicinorganic nanocomposite materials. *Chem Mater*, 13: 3151–3168.

[34] **Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G.H., Chmelka B.F.&Stucky, G.D.** (1998). Triblock copolymer syntheses of

mesoporous silica with periodic 50 to 300 angstrom pores. *Science* 279, 548–552. doi:10.1126/science.279.5350.548

[35] **Chen, F.** (2004). Microporosity of SBA-3 mesoporous molecular sieves. *Micropor. Mesopor. Mater.* 75: 231–235. doi:10.1016/j.micromeso.2004.07.028

[36] **Anunziata, O.A., Beltramone, A.R., Martínez,M.L., Belon, L.L**. (2007). Synthesis and characterization of SBA-3, SBA-15, and SBA-1 nanostructured catalytic materials. *J. Colloid Interface Sci.* 315: 184–190. doi:10.1016/j.jcis.2007.06.033

[37] **Li, H., Li, J., Ni, H., & Song, D.** (2006). Studies on cobalt catalyst supported on silica with different pore size for Fischer–Tropsch synthesis. *Catalysis Letters*, *110*(1-2), 71–76. doi: 10.1007/s10562-006-0086-y

[38] **Ryoo, R., Ko, C. H., Kruk, M., Antochshuk, V., & Jaroniec, M**. (2000). Block-Copolymer-Templated Ordered Mesoporous Silica: Array of Uniform Mesopores or Mesopore−Micropore Network? *The Journal of Physical Chemistry B*, *104*(48), 11465–11471. doi: 10.1021/jp002597a

[39] **Rahmat, N., Abdullah, A.Z. ve Mohamed, A.R**. (2010). Review: mesoporous santa barbara amorphous-15, types, synthesis and its applications towards biorefinery production. *American Journal of Applied Sciences*, 7 (12): 1579- 1586

[40] **Melde, B.J., Holland, B.T., Blanford, C.F. and Stein, A**. (1999). Mesoporous sieves with unified hybrid inorganic/organic frameworks. *Chemistry of Materials*, 11:3302-3308

[41] **Nakahira, A., Takimura, M. and Yamasaki, Y.** (2007). Synthesis of bulky mesoporous silica (FSM) by hydrothermal hot-pressing method. *Journal of Non-Crystalline Solids* 353:4203–4207.

[42] **Ryoo, R., Kim, J.M., Ko, C.H. and Shin, C.H.** (1996). Disordered molecular sieve with branched mesoporous channel network. *Journal of Physical Chemistry*, 100:17718-17721.

[43] **Yu, C., Yu, Y., Miao, L. and Zhao, D**. (2001).Hhighly ordered mesoporous silica structures templated by poly(butylene oxide) segment di- and tri-block copolymers. *Microporous and Mesoporous Materials*, 44–45: 65–72.

[44] **Xi, J., & Tang, X**. (2005). Novel composite polymer electrolyte comprising poly(ethylene oxide) and triblock copolymer/mesostructured silica hybrid used for lithium polymer battery. *Electrochimica Acta*, 50(27), 5293–5304. doi: 10.1016/j.electacta.2005.02.025

[45] **Garcia, N., Benito, E., Guzman, J., Tiemblo, P., Morales, V., & Garcia, R. A.** (2007). Functionalization of SBA-15 by an acid-catalyzed approach: A

surface characterization study. *Microporous and Mesoporous Materials,* 106 , 129 - 139.

[46] **Meynen, V., Cool, P., & Vansant, E. F**. (2009). Verified synthesis of mesoporous materials. *Microporous and Mesoporous Materials, 125*, 170 - 223.

[47] **Zhao, D., Huo, Q., Feng, J., Chmelka, B.F. & Stucky, G.D**. (1998). Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered hydrotermally stable mesoporous silica structures. *Journal of the American Chemical Society*, *120*:6024–6036.

[48] **Zhao, D., Sun, J., Li, Q. & Stucky, G.D.** (2000). Morphological control of highly ordered mesoporous silica SBA-15. *Chemistry of Materials*, 12: 275-279

[49] **Cui, X., Zin, W.C., Cho, W.J. & Ha, C.S.** (2005). Nonionic triblock copolymer synthesis of SBA-15 above the isoelectric point of silica (pH = 2-5). *Materials Letters,* 59:2257-2261.

[50] **Kleitz, K., Schmidt, F. & Schüth, F.** (2003). Calcination behavior of different surfactant-templated mesostructured silica materials. *Microporous and Mesoporous Materials*, 65:1-29.

[51] **Giraldo, L.F., López, B.L., Pérez, L., Urrego, S., Sierra, L. & Mesa, M. (**2007)Mesoporous silica applications. *Macromol. Symp*. 258: 129-141

[52] **Liu,Y.** (2009). *Mesoporous silica/polymer nanocomposite* (Doctorate thesis). Georgia Institute of Technology, Textile Engineering GEORGIA

[53] **Garcia, N., Benito, E., Guzman, J., Tiemblo, P., Morales, V., & Garcia, R. A**. (2007). Functionalization of SBA-15 by an acid-catalyzed approach: A surface characterization study. *Microporous and Mesoporous Materials, 106,* 129 - 139.

[54] **Lebeau, B., Gaslain, F., Fernandez - Martin, C., & Babonneau, F**. (2009). *In Ordered Porous Solids* (p. 286). Elsevier B. V.

[55] **Stein, A., Melde, B.J. and Schroden, R.C.** (2000). Hybrid Inorganic-Organic Mesoporous Silicates-Nanoscopic Reactors Coming of Age, *Advanced Materials, 12:*1403-1419.

[56] **Price, P.M., Clark, J.H. and Macquarrie, D.J.** (2000). Modified Silicas for Clean Technology, *Journal of the Chemical Society, Dalton Transactions,* 101-110.

[57] **Ishikawa, T., Matsuda, M., Yasukawa, A., Kandori, K., Inagaki, S., Fukushima, T. ve Kondo, S.** (1996). Surface Silanol Groups of Mesoporous Silica FSM-16, *Journal Of The Chemical Society-Faraday Transactions*, 92:1985-1989.

[58] **Kimura, T., Kuroda, K., Sugahara, Y. And Kuroda K.** (1998). Esterification of the Silanol Groups in the Mesoporous Silica Derived from Kanemite, *Journal of Porous Materials*, 5:127-132.

[59] **Zhao, X.S. and Lu, G.Q.** (1998). Modification of MCM-41 by Surface Silylation with Trimethylchlorosilane and Adsorption Study. *Journal of Physical Chemistry*, *102*:1556-1561.

[60] **YITMEZ GOK, B**. (2018*). Synthesis of mesoporous silica nanoparticles mcm-41 and sba-15,surface modification studies with aminoorganoalkoxy silane and boralkoxides and comparison of drug delivery and release parameters (*Master thesis). Akdeniz University, Antalya/TURKEY

[61] **Rosenholm, J. M., & Lindén, M**. (2008). Towards establishing structure - activity
relationships for mesoporous silica in drug delivery applications. *Journal of Controlled Release*,*128*, 157 – 164

[62] **Lebeau, B. G.** (2009). In *Ordered Porous Solids* (pp. 287 - 288). Elsevier B. V.

[63] **Çanak, T. Ç., Kaya, K., & Serhatlı, I.** (2014). Boron containing UV-curable epoxy acrylate coatings. *Progress in Organic Coatings*, *77*(11), 1911–1918. doi: 10.1016/j.porgcoat.2014.06.021

[64] **Celik, O**. (2016). *Synthesis and characterization of triazole side group containing proton conductive styrenic copolymers via stable radical polymerization and "click" chemistry technics.* (Master thesis). Gebze Technical University, Kocaeli/TURKEY

[65] **Caneba, G.** (2010). *Free radical retrograde precipitation polymerization (Frrpp): novel concept, processes, materials, and energy aspects*. Berlin: Springer.

[66] **Guerrero-Santos, R., Saldívar-Guerra, E., & Bonilla-Cruz, J.** (2013). Free Radical Polymerization. In E. Sald´ıvar-Guerra & E. Vivaldo-Lima (Eds.),*Handbook of Polymer Synthesis, Characterization, and Processing* (pp. 65-83). Hoboken, New Jersey: John Wiley & Sons, Inc

[67] **Akin, B**. (2019). *Synthesis of Acrylic Modified Hexagonal Boron Nitride Polymers by ATRP* (Master thesis). Istanbul Technical University, Istanbul/TURKEY

[68] **Çanak, T. Ç., Akpinar, S., & Serhatli, I. E.** (2017). Homopolymerization and synthesis of a new methacrylate monomer bearing a boron side group: characterization and determination of monomer reactivity ratios with styrene. *Turkish Journal Of Chemistry*, *41*, 209–220. doi: 10.3906/kim-1603-106

[69] **Goscianska, J., Olejnik, A., & Nowak, I.** (2017). APTES-functionalized mesoporous silica as a vehicle for antipyrine – adsorption and release studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *533*, 187–196. doi: 10.1016/j.colsurfa.2017.07.043

[70] **Vo, V., Kim, H.-J., Kim, H.-Y., Kim, Y., & Kim, S. J.** (2013). Synthesis of Poly(methacrylic acid)-functionalized SBA-15 and its Adsorption of Phenol in Aqueous Media. *Bulletin of the Korean Chemical Society*, *34*(12), 3570–3576. doi: 10.5012/bkcs.2013.34.12.3570

CURRICULUM VITAE

Name Surname **:** Nargız Alıyeva

Place and Date of Birth **:** Azerbaijan, 21.11.1991

E-Mail **:** naliyeva91@gmail.com

EDUCATION **:**

- **B.Sc.** **:** 2017, Istanbul Technical University, Faculty of Chemical and Metallurgical , Metallurgical and Materials Engineering

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2016, Referans Metal (*Sales Engineer*)
- 2015, ITU Dept. of Metallurgical and Materials (*LAB Intern*)
- 2014, Ferro Döküm (*Production Intern*)
- 2013, Takımsaş Kesici Takım Makine **(***Manufacturing Intern*)