Graft Copolymerization of Benzyl Methacrylate onto Alginates

Ameer Piro Shakir

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Approval of the Institute of Graduate Studies and Research

Prof. Dr. Elvan Yılmaz
Director

I certify that this thesis satisfies the requirements as a thesis for the degree of Master of Science in Chemistry.

Prof. Dr. Mustafa Halilsoy
Chair, Department of Chemistry

We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Chemistry.

Prof. Dr. Elvan Yılmaz
Supervisor

Examining Committee

1. Prof. Dr. Elvan Yılmaz _____

2. Assoc. Prof. Dr. Mustafa Gazi _____

3. Asst. Prof. Dr. Hatice Nilay Hasipoğlu _____

ABSTRACT

Homopolymerization of benzyl methacrylate has been studied by UV initiation using 25 mg DMPA with 2.5 ml BzMA and 0.5, 2.5 mL hexane for different time intervals. The maximum conversion value 99% has been obtained. Homopolymerization reaction was carried out with and without photo initiator. It was found that without photo initiator polymerization does not occur. DMPA and benzophenone were the two photo initiators tested. DMPA was found to be more effective than benzophenone, in a homopolymerization system of 50 mg DMPA or bezophenone, 2.5 mL BzMA and 0.5 mL hexane irradiated for 15 minutes, conversion resulted 61% and 11.5% respectively. Without photo initiator no polymerization occurred. Alginic acid, sodium alginate and calcium alginate have been grafted with poly(benzyl methacrylate) by the UV-irradiation method. The heterogeneous system was placed in a LZC4 photo-reactor with 15 cm distance from UV lamps (in UVA region, 350 nm) and irradiated for several different intervals of time, at room temperature (25±1◦C) and fixed power (7670 μW/cm2). Effect of irradiation time, monomer concentration and photo initiator concentration on the grafting yield was studied at room temperature. The maximum grafting yield was obtained using 0.52 g sodium alginate with 2.5 mL BzMA and 25 mg DMPA at 15 min. It was found that most vulnerable polymer to benzyl methacrylate grafting among alginic acid, sodium alginate and calcium alginate is sodium alginate with the highest grafting yields under the same conditions with others.

Keywords: Alginate, Benzyl methacrylate, Graft copolymer, Photopolymerization

ÖZ

Benzyl metakrilatın homopolimerizasyonu ve sodyum aljinat, aljinik asit ve kalsium aljinat üzerine aşılanması foto-LZC4 reaktörü içinde 350 nm dalgaboyunda, 7670 $\mu W/cm^2$ sabit güce sahip UV lambaları örnekten 15 cm uzakta konumlanmış şekilde oda sıcaklığında, farklı zaman aralıklarında çalışılmıştır. Işınlama deneyleri ya DMPA ve benzofenon olmak üzere iki farklı foto başlatıcı varlığında ya da foto başlatıcı olmadan yapılmıştır. Foto başlatıcı kullanılmadığı durumda polimerizasyon veya kopolimerizasyonun gerçekleşmediği gözlemlenmiştir. Yirmi dakika ışınlama süresi sonunda 25 mg DMPA, 2.5 mL BzMA ve 0.5 mL hekzan karışımının azami dönüşüm değeri % 99 olarak elde edilmiştir. Benzer koşullarda DMPA varlığında homopolimerizasyon dönüşüm değerinin benzofenona göre daha fazla olduğu bulunmuştur. 50 mg DMPA veya 50 mg benzofenon varlığında homopolimerizasyonun 2.5 mL BzMA ile 0.5 mL hekzan bulunduran homopolimerizasyon sisteminde 15 dakika süre ışınlama süresi sonunda . homopolimerizasyon dönüşüm değerleri sonuçları sırasıyla % 61 ve % 11.5 olarak bulunmuştur. Aljinik asit, sodyum aljinat ve kalsiyum aljinat üzerine gerşekleştirilen aşılama reaksiyonları için ışınlama süresi, monomer konsantrasyonunun ve başlatıcı konsantrasyonunun aşılama yüzdesine etkisi oda sıcaklığında incelenmiştir. En fazla aşılama verimi 39.5% 15 dakikada, 2.5 ml BzMA 25 mg DMPA varlığında 0.52 g sodyum aljinat kullanılarak elde edilmiştir.

Anahtar Kelimeler: Aljinat, Benzil metakrilat, Aşı kopolimer, Fotopolimerleşme

This thesis is dedicated to my Father and Mother and all family who have supported me all the way since the beginning of my studies.

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LIST OF ABBREVIATIONS

AIBN	Azobisisobutyronitrile
BzMA	Benzyl Methacrylate
BPO	Benzoyl Peroxide
CaAlg	Calcium Alginate
CAN	Ceric Ammonium Nitrate
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
IA	Itaconic Acid
NaAlg	Sodium Alginate
PBzMA	Poly Benzyl Methacrylate
PMMA	Polymethyl Methacrylate
PAM	Poly Acrylamide
PVAc	Polyvinyl Acetate
PEG-DA	Polyethylente Glycol Diacrylate
SEM	Scanning Electron Microscope
TGA	Thermal Gravimetric Analaysis
UV	Ultra Violet

Chapter 1

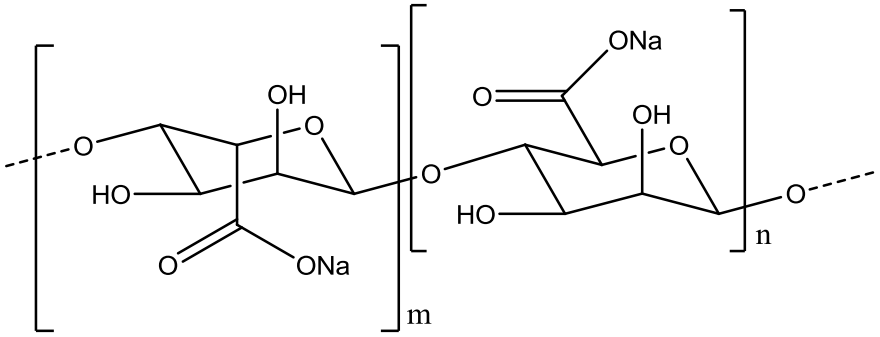
INTRODUCTION

One of the methods that can be used to modify polymers is grafting. Graft copolymerization is a fascinating method which leads to modification. There are ways that are used for graft copolymerization such as grafting via chemical means and irradiation. Monomers are polymerized during grafting and are simultaneously bonded to a polymer substrate via covalent bonds.

Polyacrylates and polymethacrylates are versatile polymers whose synthesis has been studied extensively. Polymers and copolymers of acrylates and methacrylates can be formed by several different mechanisms; free radical, cationic, anionic, atom transfer mechanisms or by radiation initiation. Many different techniques such as bulk, solution, emulsion or suspension polymerization can be applied in acrylate and methacrylate polymerizations. They possess antibacterial properties, optical clarity, adhesivity, and chemical and photo stability. Hence, polymers and copolymers have found uses in various fields extending from biomedicine to industrial applications. Some examples are tissue engineering, eye contact lenses, and dental cements in addition to newer sensor applications. They also have found use in industry as additives and adhesives.

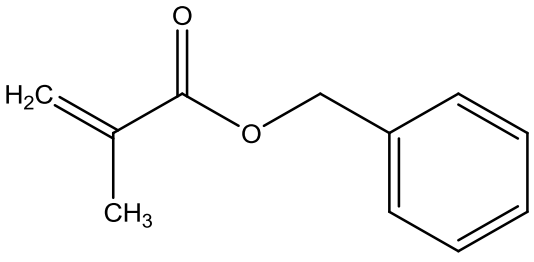
Alginic acid, on the other hand, is a natural polymer obtained from algae. Several derivatives of alginic acid and sodium alginate have been synthesized and characterized.

Alginic acid and its derivatives which can be formed into hydrogels, membranes micro and nanospheres have found potential applications in drug delivery, tissue regeneration, wound dressing, heavy metal ion removal etc. Grafting of methacrylates and acrylamides onto alginates has been employed as one way of modulating hydrophilicity/hydrophobicity, pH sensitivity, pore size and other physicochemical properties.



Scheme1.1. Chemical Structure of Sodium Alginate

Benzyl methacrylate is a photopolymerizable, organosoluble monomer from which a hydrophobic polymer, poly(benzyl methacrylate) is derived upon polymerization. Studies on either homopolymerization or copolymerization of this monomer are scarce in the literature, although it is commercially available as an industrial product.



Scheme1.2. Chemical Structure of Benzyl Methacrylate

Poly(benzyl methacrylate) and its copolymers with alginic acid which are organic derivatives of alginates are anticipated to find biomedical and industrial applications such as pharmaceutical excipients, as polymer blend compatibilizers, stabilizers or as flocculants in wastewater treatment. Synthesis and characterization of these polymers and copolymers free from impurities is a fundamental element of new materials development with possible technological end uses. Therefore, this thesis work explores the optimal conditions of photoinduced grafting of poly(benzyl methacrylate) onto alginates along with photoinduced homopolymerization of benzyl methacrylate. Some physical and chemical features of the products are also examined and compared to those of the parent polymers.

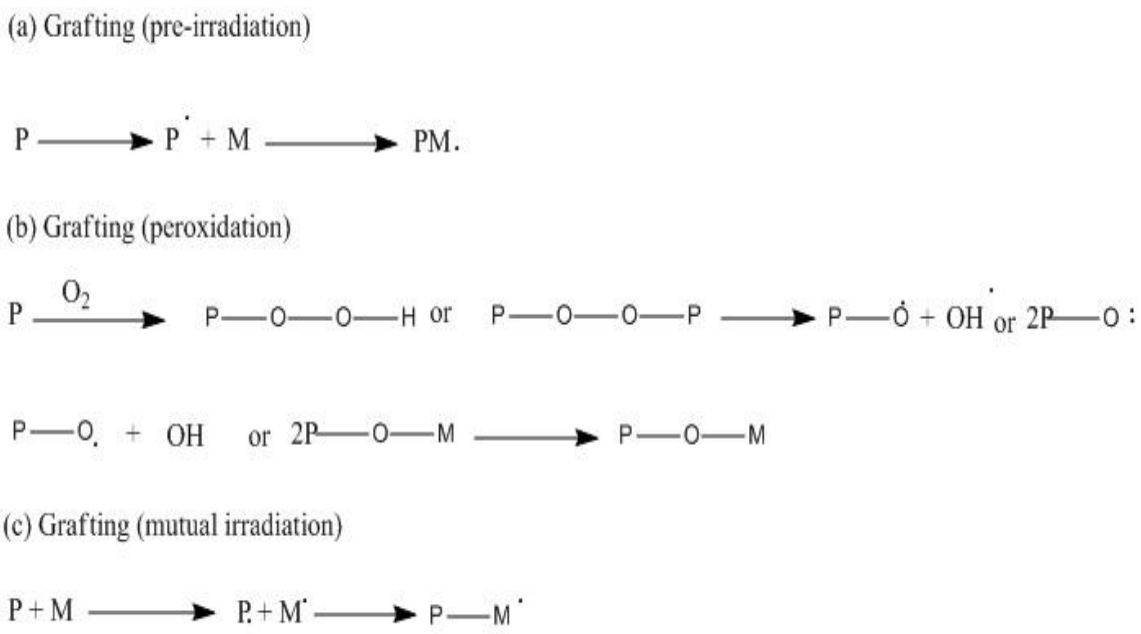
In the following sections of this chapter, a brief literature survey is presented on grafting methods with emphasis on photoinduced (uv-induced) grafting. Alginate modification is illustrated with examples of graft copolymerization studies carried out on this class of polymers. Properties and applications of alginates and polymethacrylates are also introduced. Chapters 2, 3, and 4 describe the methods applied in this research, results and discussion on synthesis and characterization of the products and conclusions respectively.

1.1 Grafting via Irradiation

1.1.1 Free Radicals Grafting

In this method the macromolecule is exposed to radiation like ultra violet or gamma rays which form free radicals on the polymer that lead to reaction. Grafting via radiation can

be done in the presence and absence of initiator depending on medium and substances used. Grafting is carried on by three different means: (1) pre irradiation (2) peroxidation and (3) mutual irradiation. In pre irradiation, first the polymer chain is irradiated in vacuum to produce free radicals. Then irradiated polymer is made to interact with the monomer in an appropriate medium. In peroxidation, the polymer is exposed to high energy radiation in air to produce hydroperoxides or diperoxides depend upon the type of polymer and upon the irradiation condition. These peroxides then interact with the monomer at high temperature whereas peroxides change to radicals that will initiate grafting. The intermediate peroxy that are formed through this technique have the ability to be stored for long times before doing grafting reaction. In mutual irradiation the polymer and monomer are exposed to radiation at the same time to produce free radicals. Then they will react together to produce the grafted copolymer. The advantage of preirradiation is that it is free from homopolymer because the monomer is not irradiated. The disadvantage of preirradiation method is that the main polymer is directly irradiated which result chain scission and can could lead to production of block copolymers. These three techniques are simply described in Scheme 1.3 (Bhattacharya & Misra, 2004).



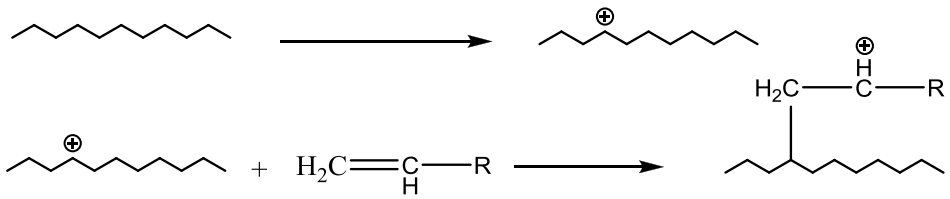
Scheme1.3. Three Irradiation Methods

1.1.2 Ionic Grafting

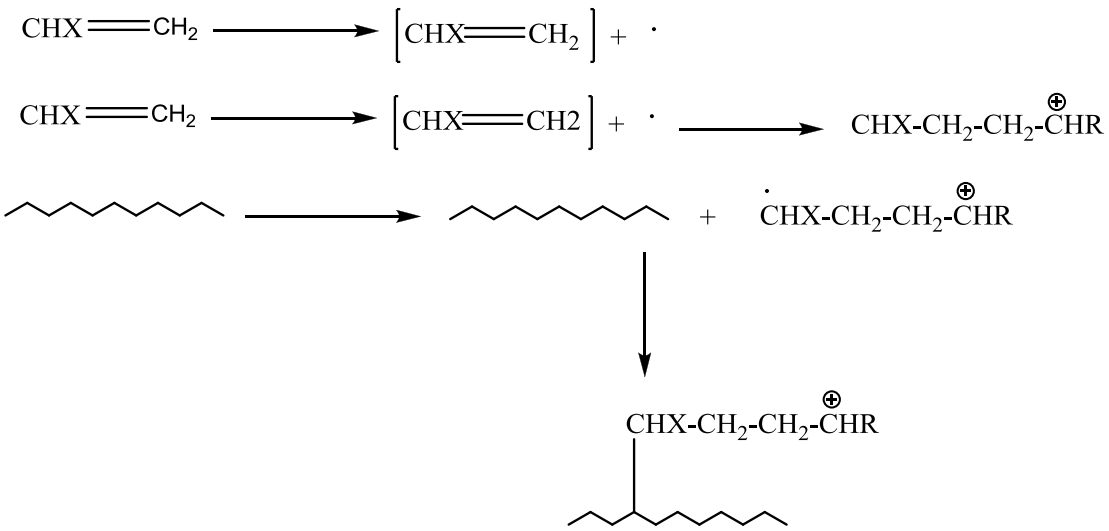
In this method the polymer is exposed to radiation and it will form polymer ion later it will react with monomer to produce grafted copolymer. One prospective advantage of ionic grafting is high reaction rate. Hence grafting reaction could occur with small irradiation.

Ionic grafting has two types: cationic and anionic. In Scheme 1.4 the cationic grafting initiated of polymer backbone or from monomer radical cation is illustrated. The grafting initiated from monomer will produce a dimer then this dimer will undergo charge localization in a way that it will react with polymer radical in which is formed through radiation. In anionic mechanism the initiator in which is an anion will lead to grafting reaction.

Path I



Path II

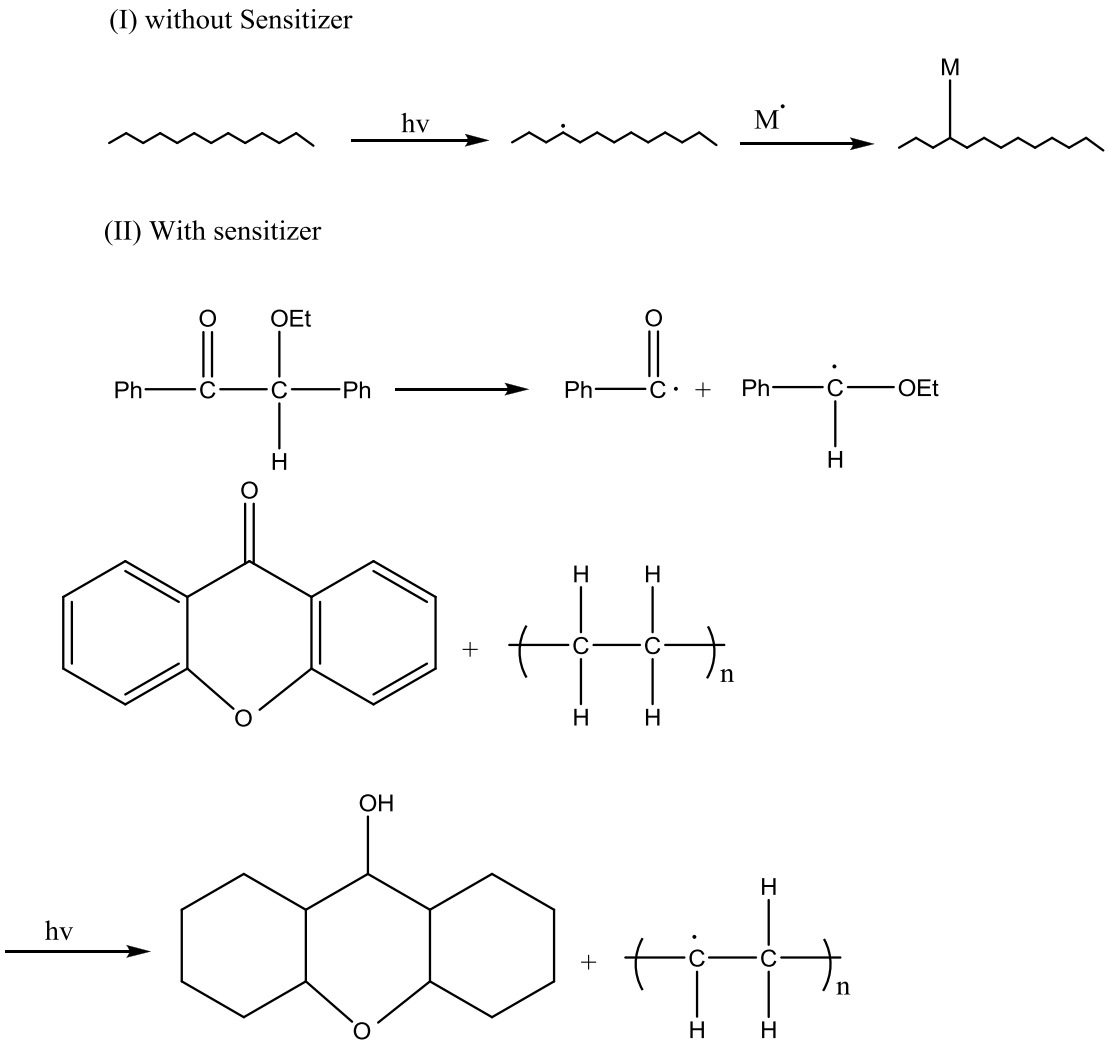


Scheme1.4. PathI. Reaction Mechanism of Cationic Grafting Initiated from Backbone,
Path II. Reaction Mechanism of Cationic Grafting Initiated Through Monomer

1.1.3 Photochemical Grafting

The chromophore on macromolecule will go to excited state by absorbing light and it could dissociate to free radicals when the grafting reaction is initiated. While this absorption do not result production of free radicals by bond rupturing, this operation could be developed by addition of photo initiators (photo sensitizers) like benzoyl peroxide, benzophenone, DMPA or AIBN. So grafting via photochemical method can be carried out with photo initiator and without photo initiator. Without photo initiator free radicals are formed on polymer backbone then will react with monomer to produce the

grafted product. However with photo initiator, the free radicals are formed by photo initiator when it absorbs radiation, so free radical will take hydrogen atom from the main polymer, radical site are formed that needed for grafting process (Bhattacharya & Misra, 2004). (See Scheme 1.5)



Scheme1.5. Mechanism for Photochemical Grafting Method

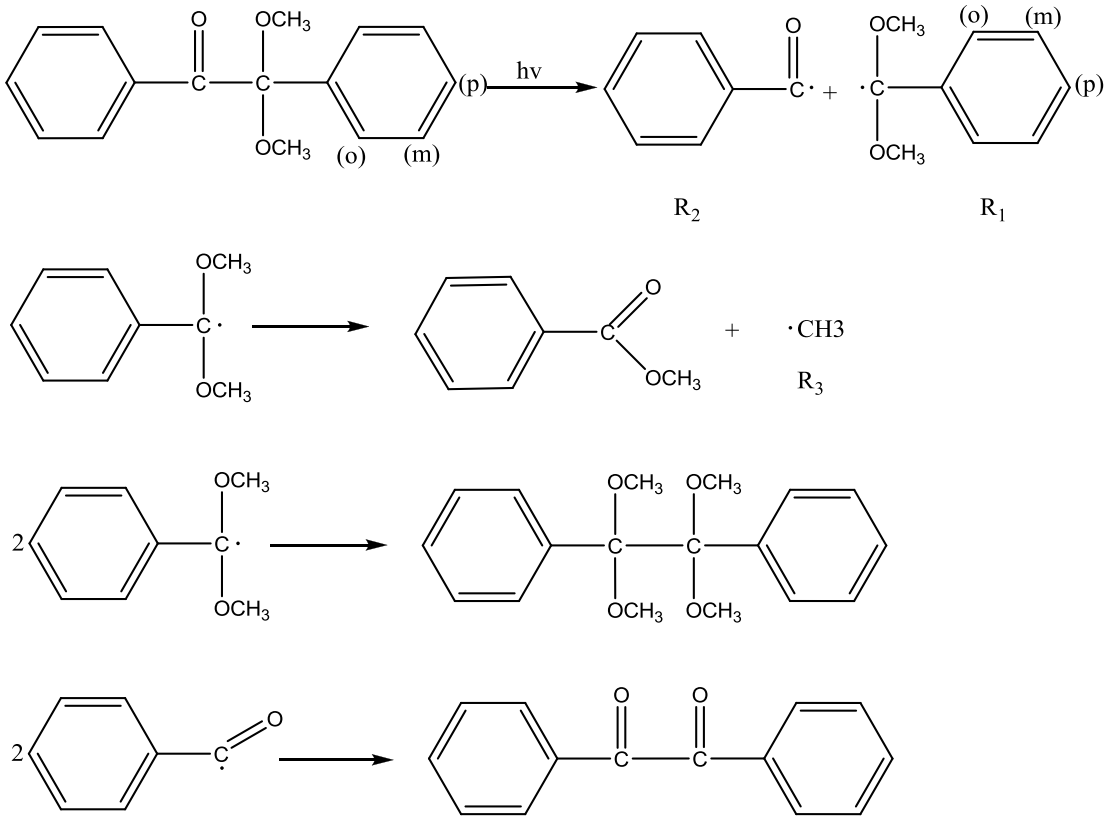
1.1.3.1 UV-Induced Polymerization

Ultra violet radiation can be used to launch chemical reactions such as polymerization. When the monomer is exposed to ultra violet radiation, in the presence of the photo sensitizer (photo initiator) it will lead to formation of large amount of free radicals in the period of time and polymerization will occur. Multifunctional monomers on the other hand will polymerize extensively when exposed to UV light and will form cross-linked polymer networks. UV-induced polymerization has many advantages like solvent free reaction, low level energy is needed, and the reaction can be done at room temperature. The photoinitiator has an important role in controlling the rate of initiation and penetration of the radiation into the sample. The polymerization speed depends upon the reactivity of functional parts, its concentration and the viscosity of the monomer. The monomer's and oligomer's functionality and their structure also play an important role, they will affect the final degree of polymerization and physicochemical properties of the UV obtained polymer (Decker, 2002).

1.1.3.2 DMPA Photoinitiator: 2,2-Dimethoxy-2-phenylacetophenone

DMPA is an affective photo initiator, that is used to initialize radical polymerization e.g. in the preparation of acrylate polymers. DMPA has the ability to absorb UV light from a range 310–390 nm. The mechanism of photolysis of DMPA is shown in Scheme1.6 Mucci and Vallo had studied the efficiency of DMPA in photo polymerization of methacrylate monomers. They found that DMPA is an effective photo initiator for thick sections approximately 2 mm as fast reactions and high conversions occur even when the concentration of DMPA is as low as 0.25 wt %. When the intensity of light increases the rate of photo polymerization also increases. There was an optimum concentration of

photo initiator, the rate of polymerization increases while the concentration of DMPA rose from 0.125 wt % to 0.25 wt %, however it had decreased with additional concentration of DMPA. This decrease is related to screening effect in which is made by excessive amounts of DMPA. When DMPA is irradiated with UV light some photoproducts are formed which absorbed light. These species absorb high part of light on its way towards samples. So light cannot reach deep in the samples. When the intensity of UV light is increased the initiation rate also increases because more primary radicals are produced. DMPA is colorless so this makes it suitable photoinitiator for composites that are used in dentistry (Mucci & Vallo, 2012).



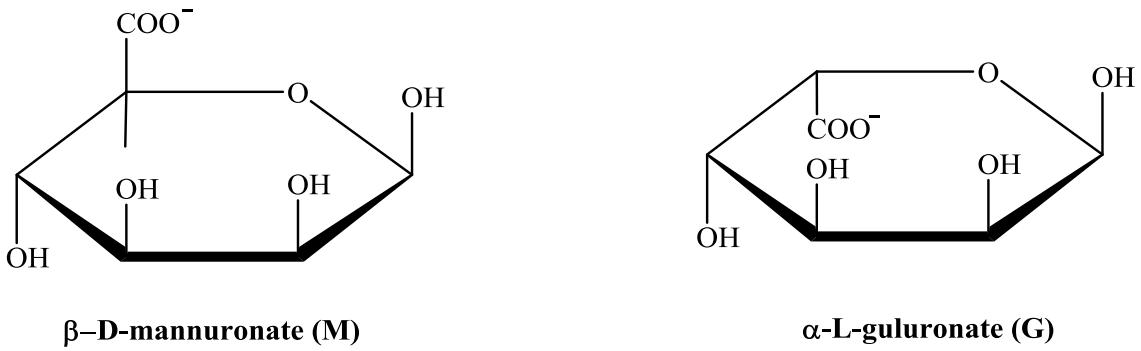
Scheme1.6. Mechanism of Photolysis of DMPA under UV Irradiation

1.2 Alginic Acid

Alginic acid is an anionic polysaccharide that is found in brown algae like Laminara hyperboream, Ascolphyllum nodosum and Macrocytis pyrifera and also some bacteria like azobacter. Alginic acid from different sources may have different compositions due to seasonal and growth conditions. Alginate is a natural polyanionic polymer. It is biocompatible, non-toxic, renewable, bioadhesive and biodegradable (George & Abraham, 2006).

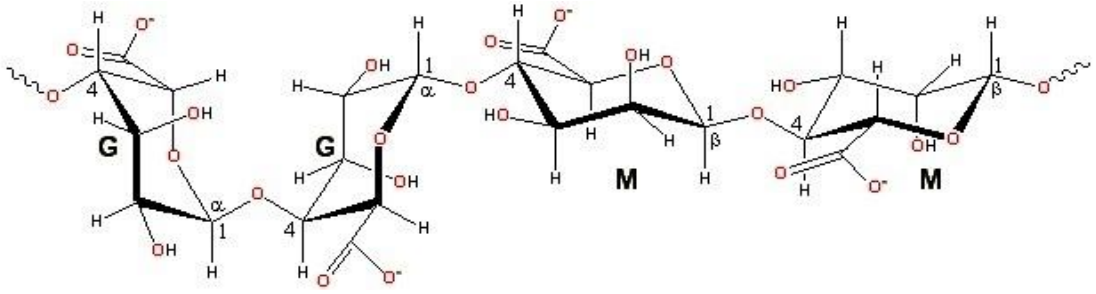
Alginic acid is a linear diblock copolymer consisting of (1→4) linked β-D-mannuronic acid (M blocks) and α-L-guluronic acid (G blocks), it may contain M blocks, G blocks and alternating G-M Blocks (Figure 5)(Draget, SkjakBraek, & Smidsrod, 1997).

a)

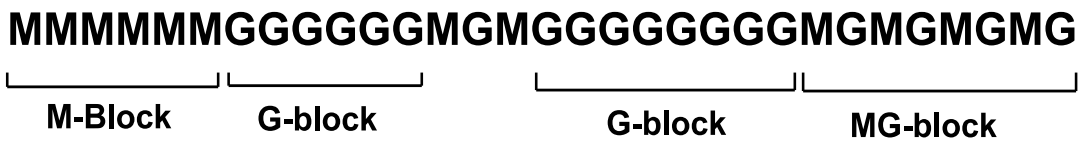


β–D-mannuronate (M) **α-L-guluronate (G)**

b)



c)



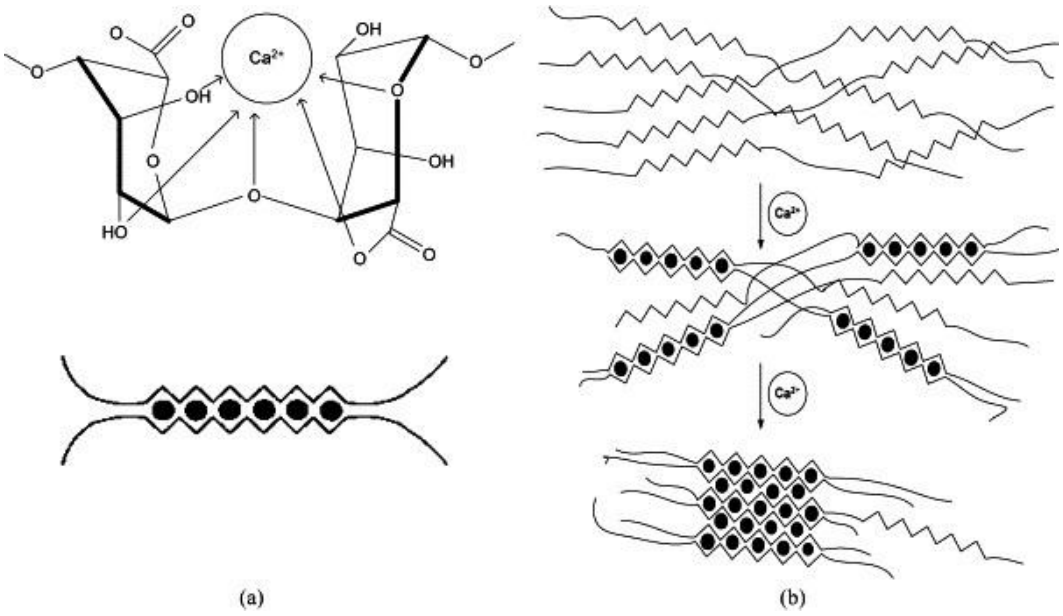
Scheme1.7. Structural Characteristics of Alginates: (a) Alginate Monomers, (b) Chain Conformation, (c) Block Distribution

M blocks are linear, more flexible regions but G-blocks are folded rigid regions so the mechanical properties depend upon the composition.

The great characteristic of alginates is that they are capable of forming gels via reacting with cations like Ca^{2+} in very moderate conditions. Alginate beads are prepared by pouring sodium alginate to calcium chloride solution. This divalent cross linking also

can be done by using Sr^{2+} and Ba^{2+} and it is carried out under a very mild condition. Here the sodium ions on the guluronic acid are replaced by divalent cations and the gelation and cross linking of polymer is attained.

Calcium alginate a salt of alginic acid is not soluble in water and ether, It is slightly soluble in Na_2CO_3, NaOH or Na_3PO_4 and substances that could combine with calcium ions. The gelation of alginate occurs while the calcium ion (Ca^{2+}) interacts with the sodium ion that previously replaced hydrogen in the guluronic acid blocks it will lead to the formation of a three dimensional network that is called “egg-box model”. These crosslinked alginate gels have stable structures and can be used for immobilization of different biological materials for example for removal of some metals from waste water.



Scheme1.8. The ‘‘Egg-box’’ Model for Alginate Gelation with Calcium Ions

1.2.1 Applications

Alginates are biopolymers that have many applications in biomedical science and engineering, in food industry and other areas because of its properties. This biocompatible polymer is used in drug delivery, protein delivery, wound dressing and tissue engineering.

Alginates have a variety of different viscosities that is used to stabilize the foodstuffs for both high and low degree of temperature so it is used widely as a gelling agent. The rate of gelation and the strength of gels can be determined by checking the concentration of calcium ion and hydrogen ion. The strength of alginate gel also can be controlled by checking the number of G block units inside the polyuronate chain. The types of the gels that are formed at low temperatures are specially used in protection of food stuffs such

as meat and fruits which could be damaged and are exposed to oxidation at high temperatures.

Alginate gels are used to deliver the drugs that have low molecular weight; they are so useful while a primary or secondary bond among the drug and alginate is used to manipulate the kinetic of releasing drug. Alginate gels have nanoporous pores which lead to quick diffusion of the small drug molecules via the gels. For example alginate cross linked gels are used for the release of flurbiprofen and it takes 1.5 hours to complete the release of the drug (Lee & Mooney, 2012).

Alginate is an excellent candidate for the transport of protein drugs, because protein can be joined into alginate-based molecule under moderately mild conditions which minimize the alteration of the protein nature and the gels can keep it from degradation till the protein is released. Generally the rate of releasing proteins from alginate gels is very fast because of the natural porousness and hydrophilicity of the alginate gels (Lee & Mooney, 2012).

Alginates are usually used for thickening the different foods such as jams, marmalades ….etc. here a heat reversible interaction occur between alginate and pectin that increase the viscosity. Propylene glycol alginates are commonly used for this purpose. Different type of stable gels of alginate can be prepared at high and low temperatures and also low pH that can be used for stabilizing many foodstuffs in food processing for example in bakery creams. Alginate and hydrocolloids are used to thicken and stabilize ice creams and desserts.

Alginates are used as viscosifier in the industry of textile printing that alginate will affect color yield, brightness and different print levels, Alginate also are used to coat papers to give a uniform surface in welding rods. Ammonium alginate can be used to seal cans because it contain very low ash.

Alginate based wound dressing have many good features in comparison to classical wound dressing. In classical wound dressing for example gauze, it just keeps the wound dry via permitting evaporation of wound exudates where not allowing the pathogen to enter the wound. However the alginate dressing supply a moist wound environment and makes wound curing easier (Lee & Mooney, 2012).

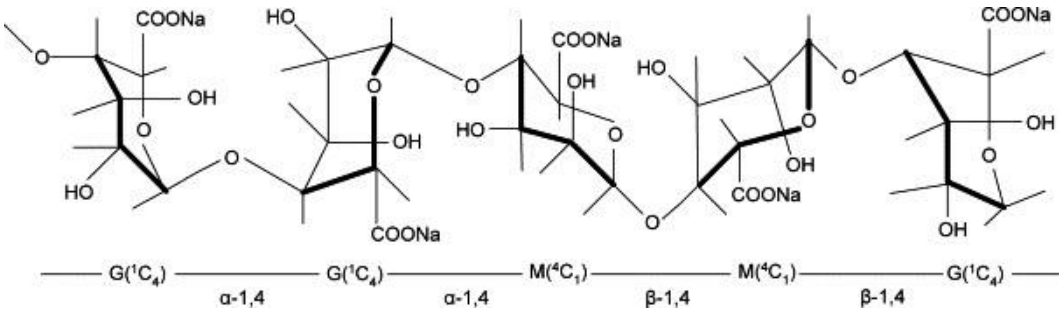
Alginate gels can be used for delivery of protein and cell population in tissue engineering. The different applications of alginate gels are used in the broad range of gelling ways, physical properties, cell adhesion and degradation way of these materials. There are limitations because the pore size of alginate hydrogels is almost 5~ nm so the size of regenerative agent that is going to be released should be considered. Most of the proteins can easily spread out of alginate gels, even if the gel is not degrading, while degradation of the gels can accelerate the release (Lee & Mooney, 2012).

1.2.2 Limitations of Alginates

1.2.2.1 Solubility

Three fundamental factors affect the limited solubility of alginates in water. First factor is pH of the medium, which plays an important role because of the essential of electrostatic charges on the uronic acid blocks. Ionic strength of environment also has an important part and the medium of gelling ions in solvent as well limits solubility of the alginate. Lastly water hardness due to existence of Ca^{2+} ions is seems to be the main problem.

Alginic acid by itself is not soluble in H_2O and organic solvents; it only dissolves in alkaline solution such as Na_2CO_3, NaOH or Na_3PO_4 but slowly. Sodium alginate dissolves in water and forms a sticky solution, it is not soluble in alcohol, hydroalcoholic solution with even more than 30% alcohol and it is also insoluble in chloroform, ether and in acids with a pH less than 3(Shilpa, Agrawal, & Ray, 2003).



Scheme1.9. The Structure of Sodium Alginate

1.2.2.2 Stability

The shell life of the dry powder of pure sodium alginate could be for several months. Sodium alginate can be protected for many years in the freezer with no important reduction in its molecular weight. However dried alginic acid has limited stability at normal temperatures due to intramolecular acid catalyzed degradation could occur. So when using alginates it is significant to consider the parameters that bounds the stability of alginic acid solutions also the chemical reactions that are in charge of degradation. The conditions that cause degradation can seriously lead to reducing viscosity of alginate solution. The glycosidic linkage in alginate is susceptible to acid, alkaline degradation and also susceptible to oxidation via free radicals. It is also susceptible to enzymatic degradation by the action of micro organisms.

1.2.3 Chemical Modification of Alginates

Alginate is a natural anionic polysaccharide that contains many free hydroxyl and carboxyl groups, so it is a brilliant candidate for chemical modification. We can modify these two functional groups and get new derivatives of alginate with altered properties like solubility, hydrophobicity and some other altered physical, chemical and biological properties. Alginates can be modified by oxidation, sulfation, amidation, esterification and copolymerization (Yang, Xie, & He, 2011).

1.2.4 Grafting onto Alginates

Itaconic acid (IA) was grafted onto NaAlg membrane via UV radiation using benzophenone as initiator to improve the hydrophilicity of the membranes. The best reaction conditions to optimize grafting were reached by itaconic acid concentration of 1.0 M, a benzophenone concentration of 0.1 M and a reaction time of 4 h at 25 ˚C,

whereas grafting efficiency was 14%. The grafting efficiency enhances up to 4 h reaction time and then it decreases. When the concentration of (IA) monomer increases the grafting efficiency also increases up to a limiting monomer concentration value. The initiator benzophenone has a similar effect on grafting efficiency. Grafting efficiency increases till the concentration of initiator is 0.1 M then it remains constant. Grafting of itaconic acid onto sodium alginate membrane enhances the hydrophilicity of the membranes (Taskin, Sanli, & Asman, 2011).

Methyl acrylate was grafted to sodium alginate using potassium diperiodatocuprate (iii) as initiator. (redox system). When the ratio of two monomers, temperature and pH was kept constant, Percent of grafting increases with increasing initiator concentration and with methyl acrylate/sodium alginate ratio when all other factors kept constant. According to TGA results the grafted product shows better thermal stability because of the addition of polymethyl acrylate to the parent polymer backbone in which could widen the application of sodium alginate (Liu, Li, Yang, Liu, & Bai, 2005).

Alginate-g-polyethylene glycol acrylate has been synthesized, alginate is a bioadhesive polymer due to its anionic property, it is capable of making hydrogen bonds with mucin-type glycoproteins via carboxyl group-hydroxyl group interaction moreover it has many pharmaceutical applications. Polyethylene glycol is also mucoadhesive, non-toxic, non-immunogenic and have high solubility in water. Alginate-polyethylene glycol acrylate is prepared in two steps, first alginate-thiol is prepared then PEG-DA is conjugated to alginate backbone. This new polymer has no cytotoxicity and could adhere to the mucus

surface and can be used for controlled drug release due to its novel mucoadhesive property (Davidovich-Pinhas & Bianco-Peled, 2011).

Polymethyl methacrylate-g-sodium alginate has been prepared using micro wave assisted redox initiator using CAN as the initiator and used as flocculant. During synthesis process no homopolymer was produced. Different levels of grafting product would be achieved by altering the methyl methacrylate and cerium ammonium nitrate concentration. Highest grafting percent is 87% when 1 g of sodium alginate, 7.5 g methyl methacrylate, o.4 g initiator CAN for 50 seconds irradiation and it shows highest intrinsic viscosity whereas the power of microwave was kept at 800 W. All grafted copolymer of SAG-g-PMMA exhibits greater intrinsic viscosity of sodium alginate because of addition of polymethyl methacrylate to the main chain of the polymer so the grafted copolymer can be used as an excellent vicosifier. The product shows good flocculation property and it can be used in waste water treatment or coal washery effluents (Rani, Mishra, & Sen, 2013).

N-vinyl-2-pyrrolidone was grafted onto alginate using potassium peroxymonosulphate/glycolic acid as initiator. N-vinyl-2-pyrrolidone is hydrophilic and not toxic in nature is usually used as a reactive diluents in ultra violet and electron beam curable polymers which are applied like inks, coatings and adhesives. Experimental results exhibit that maximum grafting percent is 413%. The grafted copolymer has better thermal stability than pure chitosan. The grafted product has better metal ion sorption and flocculation properties in compare to alginate (Sand, Yadav, Mishra, & Behari, 2010).

Grafting of 2-acrylamidoglycolic acid onto alginate has been carried out via radical polymerization by potassium peroxydiphosphate/silver nitrate redox system in the presence of nitrogen gas. 2-acrylamidoglycolic acid is type of acrylamides that contain hydroxyl and carboxyl groups that are excellent candidate for removal of apatite from siliceous gangue. Grafting of 2-acrylamidoglycolic acid onto alginate will improve alginate drawbacks such as biodegradability. It also enhances flocculation and swelling ability of alginate. The grafted copolymer could be applied as absorbent and in coating material because it shows high thermal stability and flocculent to take off impurities from waste water in coal mines. The maximum grafting percent was 463.7% (Yadav, Mishra, Sand, & Behari, 2011).

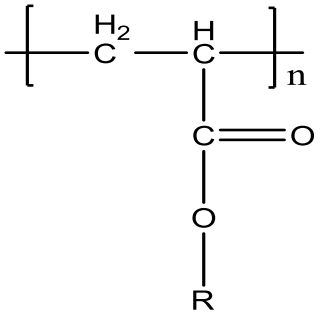
Graft copolymer of sodium alginate-g-poly(acrylic acid)/sodium humate was prepared by grafting of sodium alginate, acrylic acid and sodium humate in aqueous solution, using ammonium persulfate as initiator and the crosslinker which used was N,N'-methylenebisacrylamide. Sodium alginate-g-poly(acrylic acid) was cross linked with sodium humate in which increase the water absorption and the superabsorbent. This superabsorbent copolymer is multifunctional it is biodegradable and can be used for the slow release of fertilizers. Adding sodium humate to sodium alginate-g-poly(acrylic acid) will improve its thermal stability (Hua & Wang, 2009).

Acrylamide was grafted to sodium alginate via solution polymerization and the initiator ceric ammonium nitrare. Polyacrylamide (PAM) has good flocculation properties and it is for water treatment, however using polyacrylamide is limited because it is harmful to human nerve by its monomer. Sodium alginate as a flocculant is nontoxic and

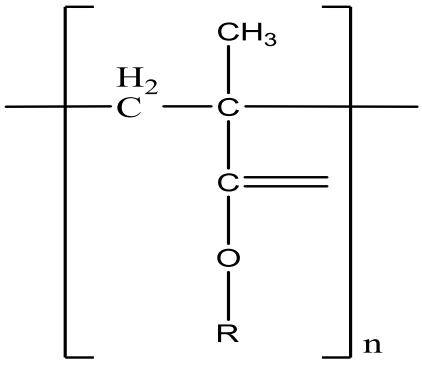
biodegradable, therefore it will not lead to any secondary pollution, and however its flocculation property is not good. Sodium alginate shows good flocculation for dyeing wastewater treatment. The flocculability of sodium alginate is associated to conversion of acrylamide. As the percent of conversion increases the longer branch of polyacrylamide is grafted to its backbone and this long grafted branches prefer forming of adsorption-bridge.

1.3 Methacrylates

Methacrylates are compounds in which derived from methacrylic acid $CH_2=C(CH_3)COOH$, that is the methyl derivative of acrylic acid the most simple unsaturated aliphatic acid. The methacrylates are reactive monomers that are principally used to produce polymeric materials. There is a big group of monomers are available that gives opportunity to design a variety of products with different chemical and physical properties that offers various applications. In spite of their different composition and physical shape the methacrylate polymers have many mutual qualities such as film charity, excellent resistance to a lot of chemical agents, atmospheric attack and degradability via light. General formula of polyacrylate and polymethacrylate is shown in Scheme 1.10 and Scheme 1.11.



Scheme1.10. General Formula of Polyacrylate, R= Alkyl Group



Scheme1.11. The Chemical Structure of Polymethacrylate Repeat Unit, R= Alkyl Group

1.3.1 Properties of Polymethacrylates

Acrylates and methacrylates polymers have properties like brightness, optical lucidity, high transparency, good mechanical and adhesive properties. Acrylic and methacrylic polymers generally have very high photo-stability. The carbonyl ester group will not be straightly photo-chemically active in these polymer units, but other impurities in polymer could initiate degradation through the radiation. The reactivity of acrylates is higher than that of methacrylates for oxidation. The photo-chemical oxidations of acrylic and methacrylic polymers will not occur autocatalytically. The polymethacrylates decomposition through radiation is inversely proportional to the ester group's length of methacrylate monomers.

Despite the fact that polyacrylates and polymethacrylates are resistant to hydrolysis, there is a doubt in the valuation of the function of water throughout natural ageing of these polymers; oxidation could happen before hydrolysis, or it would be occur on the hydrolysis products. Acrylic acid thin films established paints could be obtained by aqueous dispersions that are coordinated to improve cross-linking and yellowing even after retained in the darkness (Chiantore, Trossarelli, & Lazzari, 2000).

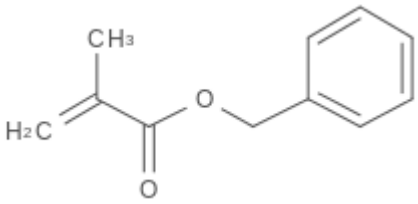
The acrylates and methacrylates polymers, physical characteristics like solubility, density, and softening point to a great extent, rely on the length and branching of the residues of alcohols. These ester polymers are sizeable and they are soluble in solvents like aromatic hydrocarbons, esters, ketones, and halohydrocarbons. The polymers that contain bigger alcohol residues are also soluble in alkanes. Polyacrylates have lower softening points than methacrylates. Polyacrylates and polymethacrylates have also

some other worthful properties such as clarity, transparency and they also have important stability toward light.

1.3.2 Benzyl Methacrylate

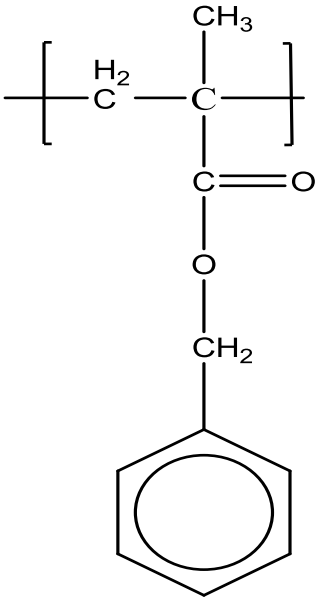
Benzyl methacrylate BzMA is a methacrylate monomer that is characterized by bulky benzyl side chain. Its other names are methacrylic acid benzyl ester, Benzyl 2-methyl-2-propenoate and phenylmethyl ester. It is an organo soluble monomer with limited solubility in aqueous media (insoluble in water). This methacrylate monomer can undergo photo polymerization. Benzyl methacrylate is base product for adhesives.

The polymer derived from benzyl methacrylate, poly(benzyl methacrylate) is of hydrophobic nature.



Scheme1.12. Benzyl Methacrylate Chemical Structure

Polybenzyl methacrylate (PBzMA) is usually used as curing agent in polymer chemistry. The *T*g value of it is intermediate 60 °C between those of polyvinyl acetate (PVAc) 30 °C and PMMA 105 °C so it has been chosen for modifying thermosets (Arribas et al., 2006). The general formula for PBzMA is given in Scheme 1.13.



Scheme1.13. The General Formula for PBzMA

Benzyl methacrylate was used as a monomer to synthesize a nanoimprint by using a top-down/bottom-up approach (Tsai & Wang, 2006). Polymer brushes form on the pattern network by controlled-radical polymerization, using this method is possible to obtain different nanoscopic structures with different sizes and functional groups. The advantage of this method is that the reaction takes place at ambient temperature. This is the advantage of benzyl methacrylate in this study and that's why benzyl methacrylate is chosen for surface-initiated polymerization.

Copolymer of BzMA with MMA is also a valuable end product especially in pharmaceutical industry. Ishikawa and co-workers have obtained controlled-release tablet by oxygen plasma irradiation (Ishikawa, Noguchi, Niwa, & Kuzuta, 1995)**.** Since PBzMA has dual intramolecular functions, a plasma degradable main chain and a plasma-cross-linkable benzyl group in the side chain as an effect of plasma irradiation copolymer of MMA and BzMA was used as a single wall material. In this work it was

shown that the dissolution profiles can be varied so as to cause release of drug at different rates, depending on the set of conditions chosen for tablet manufacture and for plasma operation which is mainly depended on the degradation of copolymer.

In s study carried by Tsukada et al in 1997, benzyl methacrylate was grafted on wool fibers using initiator ammonium peroxydisulphate. Grafted sample with a range 7% to 180% were prepared by altering monomer concentration. The grafted wool fibers exhibited better thermal stability according to TGA and DSC results. Grafting caused some phyico-mechanical and structural change in wool fibers that did not damage the intrinsic property of it (Tsukada, Shiozaki, Freddi, & Crighton, 1997).

Chapter 2

EXPERIMENTAL

2.1 Methods

2.1.1 Materials

All chemicals given in Table 2.1 are commercially available. They are used as received.

Table 2.1. Materials and Manufacturers

Material	Manufacturer
Sodium Carbonate	Merck-Germany
Alginic Acid	Alfa Aesar- Germany
Calcium Chloride	Merck- Germany
Ethanol	Merck- Germany
Tetrahydrofuran	Analar-England
Chloroform	Merck- Germany
Hexane	Merck- Germany
Dichloro Ethane	Merck- Germany
Dimethylacetamide	Merck- Germany
Benzyl Methacylate	Aldrich-USA
2,2-Dimethoxy-2-phenylacetophenone	Aldrich-UK
Sodium Alginate	Sigma-Aldrich-USA
Potassium Bromide	Merck-Germany
Benzoyl Peroxide	Sigma-USA
DMF	Analar-England

2.1.2 Synthesis

2.1.2.1 UV Induced BzMA Homopolymerization

DMPA, the photo initiator was dissolved in hexane, and then mixed with benzyl methacrylate. The procedure was carried out for predetermined time intervals in 10 mL quartz tubes. The amount of DMPA used was 25 mg while 2.5 mL of BzMA was used in each experiment. Hexane was taken as 2.5 mL in one set of experiments (2.95 mol/L BzMA) and 0.5 mL (4.92 mol/L BzMA) in the second set as summarized in Table 2.2.

2.1.2.2 Preparation of Calcium Alginate

Sodium alginate solution was prepared by adding 2.000 g alginic acid into sodium carbonate solution (1.5% w/v) and stirring vigorously for 2 hours at 55˚C. Then, sodium alginate solution was added to 0.5 M of calcium chloride solution drop wise. Calcium alginate that precipitated was kept in solution for 24 hours and dried at room temperature for 48 hours.

2.1.2.3 UV Induced Copolymerization of BzMA onto Alginates

DMPA was dissolved in hexane, and then mixed with benzyl methacrylate. The mixture was then poured onto alginic acid, sodium alginate or calcium alginate. The amount of DMPA used was 25 mg while 2.5 mL of BzMA and 0.5 mL hexane was used in each experiment as summarized in Table 2.3. The procedure was carried out for predetermined time intervals in 10 mL quartz tubes. LZC4 photoreactor with equipped with UV lamps of 350nm wavelength and 7670 uW/cm2 power was used in all UV initiated reactions. The samples are placed at 15 cm distance from the lamps. The product was washed two times with 50 ml THF for removal of homopolymer.

Table 2.2. Synthesis of Poly(Benzyl methacrylate) Homopolymer

Sample ID	BzMA (mol/L)	Hexane (mL)	Irradiation time (min)	DMPA (mg)
B1HP5	2.95	2.5	5	25
B1HP7.5	2.95	2.5	7.5	25
B1HP10	2.95	2.5	10	25
B1HP12.5	2.95	2.5	12.5	25
B1HP15	2.95	2.5	15	25
B1HP20	2.95	2.5	20	25
B5HP5	4.92	0.5	5	25
B5HP7.5	4.92	0.5	7.5	25
B5HP10	4.92	0.5	10	25
B5HP12.5	4.92	0.5	12.5	25
B5HP15	4.92	0.5	15	25
B5HP20	4.92	0.5	20	25
B5HP15	4.92	0.5	15	12.5
B5HP15	4.92	0.5	15	50

Table 2.3. Preparation of Poly(Benzyl methacrylate) Grafted Alginates

Sample ID	BzMA (mol/L)	Hexane (mL)	Irradiation time (min)	Alginic acid (g)	NaAlg (g)	CaAlg (g)
B5ACP5	4.92	0.5	5	0.52	-	-
B5ACP10	4.92	0.5	10	0.52	-	-
B5ACP15	4.92	0.5	15	0.52	-	-
B5ACP20	4.92	0.5	20	0.52	-	-
B5ACP25	4.92	0.5	25	0.52	-	-
B5NaACP5	4.92	0.5	5	-	0.52	-
B5NaACP10	4.92	0.5	10	-	0.52	-
B5NaACP15	4.92	0.5	15	-	0.52	-
B5NaACP20	4.92	0.5	20	-	0.52	-
B5NaACP25	4.92	0.5	25	-	0.52	-
B5NaACP5	4.92	0.5	5	-	-	0.52
B5CaACP10	4.92	0.5	10	-	-	0.52
B5CaACP15	4.92	0.5	15	-	-	0.52
B5CaACP10	4.92	0.5	20	-	-	0.52
B5CaACP25	4.92	0.5	25	-	-	0.52

2.1.3 Solubility Characteristics of Products

Solubility of the monomer, homopolymer, alginic acid, sodium alginate, calcium alginate, and sodium alginate copolymer was tested in double distilled water, sodium hydroxide, tetrahydrofurane, dimethylacetamide, toluene, dimethylformamide and ethanol. 20 mg sample was tested in 10 ml solvent.

2.2 FTIR Analysis

FTIR characterization was done using Perkin Elmer Spectrum-65 FT-IR spectrometer. KBr pellets of the samples were used in FTIR analysis.

2.3 SEM Analysis

SEM pictures were taken in TUBITAK MAM using JEOL JSM-6510 scanning electron microscope.

Chapter 3

RESULTS AND DISCUSSION

3.1 UV Induced BzMA Homopolymerization

The polymerization of benzyl methacrylate via UV irradiation was investigated. The results are shown in Table 3.1. The maximum conversion percent was 99%. The effect of time, monomer concentration and initiator concentration on polymer conversion was studied.

Table 3.1. Gravimetric Data for Homopolymer Formation

Sample ID	Conversion (%)
B1HP5	4.0
B1HP7.5	13
B1HP10	21
B1HP12.5	33
B1HP15	43
B1HP20	58
B5HP5	16
B5HP7.5	28
B5HP10	48
B5HP12.5	57
B5HP15	86
B5HP20	99

Optical pictures of the homopolymer sample obtained using 2.95 mol/L BzMA alter 5, 10, 15 min irradiation are shown in Figure 3.1 (a), (b), (c) respectively. It can be observed that increasing reaction time results in higher amount of product. The polymer obtained is a sticky substance.

a) b) c)

Figure 3.1. Optical Pictures of Homopolymers Obtained After a) 5min b) 10min c) 15min Irradiation Using 2.95 mol/L BzMA

3.2 FTIR of BzMA and PBzMA

FT-IR spectrum of PBMA Figure 3.3 shows a strong band at 1729 cm^{-1}, this was attributed to the stretching vibration of the ester carbonyl group. Both bands at 1143 and 1238 cm^{-}were assigned to symmetric and asymmetric stretching of the –C(=CO)–O–C group, respectively.

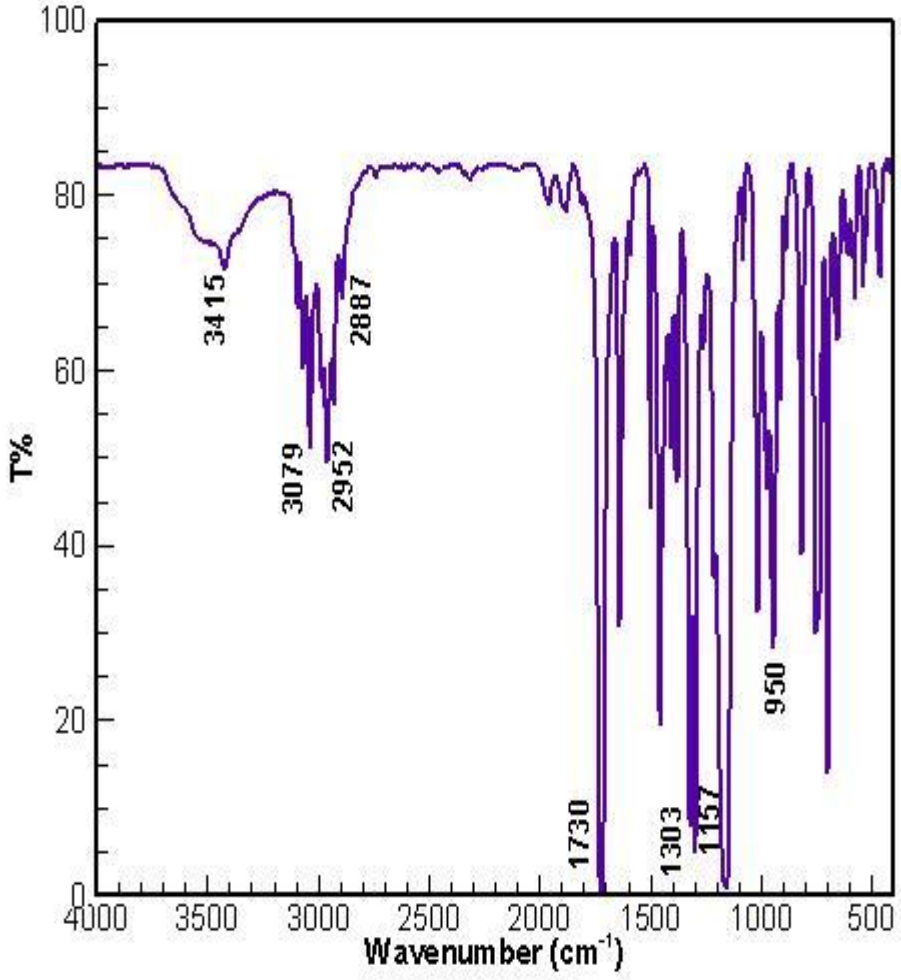


Figure 3.2. FTIR Spectrum of BzMA

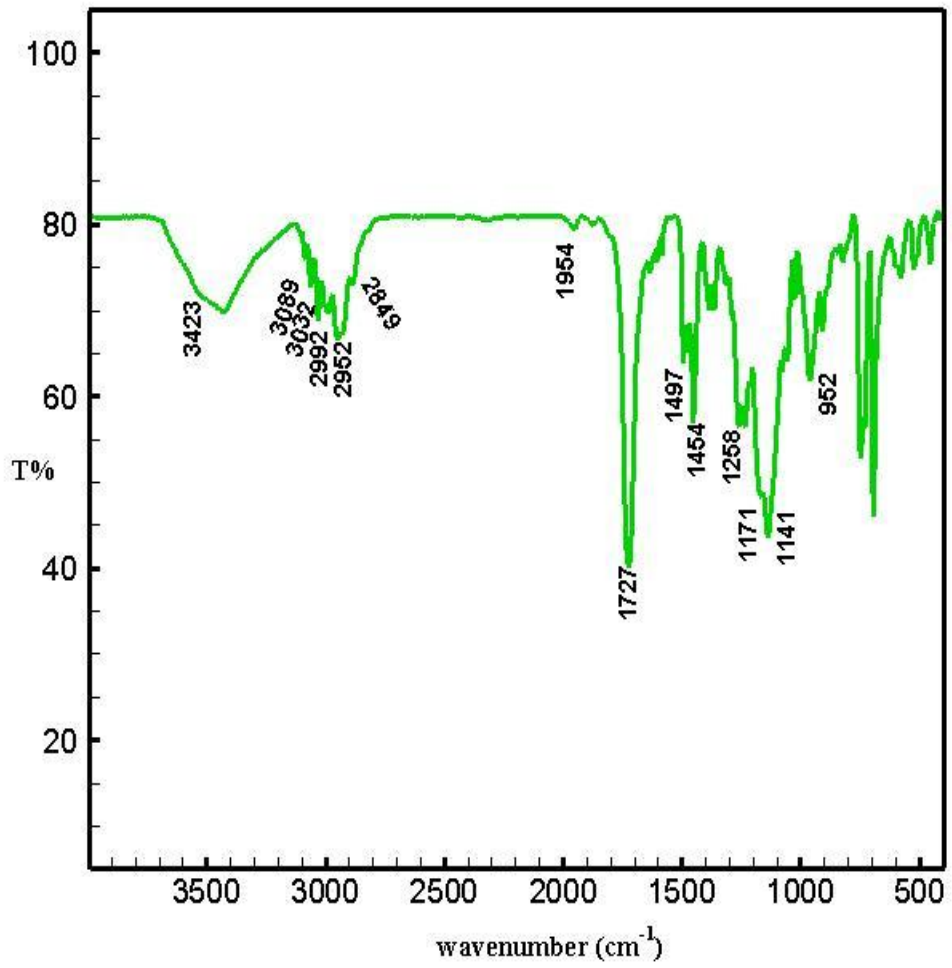


Figure 3.3. FTIR Spectrum of PBzMA

3.3 Optimization of Homopolymerization Conditions

3.3.1 Effect of Reaction Time on Homopolymer

When monomer BzMA is exposed to UV radiation, in the presence of a photoinitiator DMPA, the photoinitiator absorbs the incident light and generates large amounts of reactive free radicals. Polymerization of BzMA proceeds under this high initiation rate

conditions. As irradiation time increases the polymerization rate increases, so percent conversion increases, since in time more DMPA free radicals attack the monomer and more polymerization occurs.

The highest conversion percent is 99% that occur within 20 minutes. Alarifia and Aouaka had studied homopolymerization of benzyl methacrylate (BzMA) using the Ni(acethylacetonate)$_2$ -MAO catalytic system, the highest conversion percent was 90% for a reaction time 5 hours at 50˚C. Therefore it can be stated that homopolymerization of BzMA can be achieved under ambient conditions, namely at room temperature and in air in a reasonly short period of time. Hence, photoinitiated polymerization is an environment friendly alternative method for the synthesis of poly(BzMA).

3.3.2 Effect of Monomer Concentration on Homopolymer

In the first set of experiments where the monomer concentration was 2.95 mol/L the maximum percent of conversion was 58%, but in the second set with the monomer concentration 4.92 mol/L, the maximum conversion percent was 99%, hence almost all of the monomer is converted to polymer within 20 minutes. We can conclude that as the concentration of monomer increases the conversion also increases as shown in Figure 3.4. Homopolymer conversion% increases with time up to 20 min, and then exhibits a tendency to reach a plateau. At a high monomer concentration, the polymerization medium is more viscous. The growing chains have a high probability of encounters. Hence the probability of termination reaction is less. The small monomer molecules having a higher mobility find a higher chance of reacting growing chains and hence rate of propagation increases leading to higher conversion values.

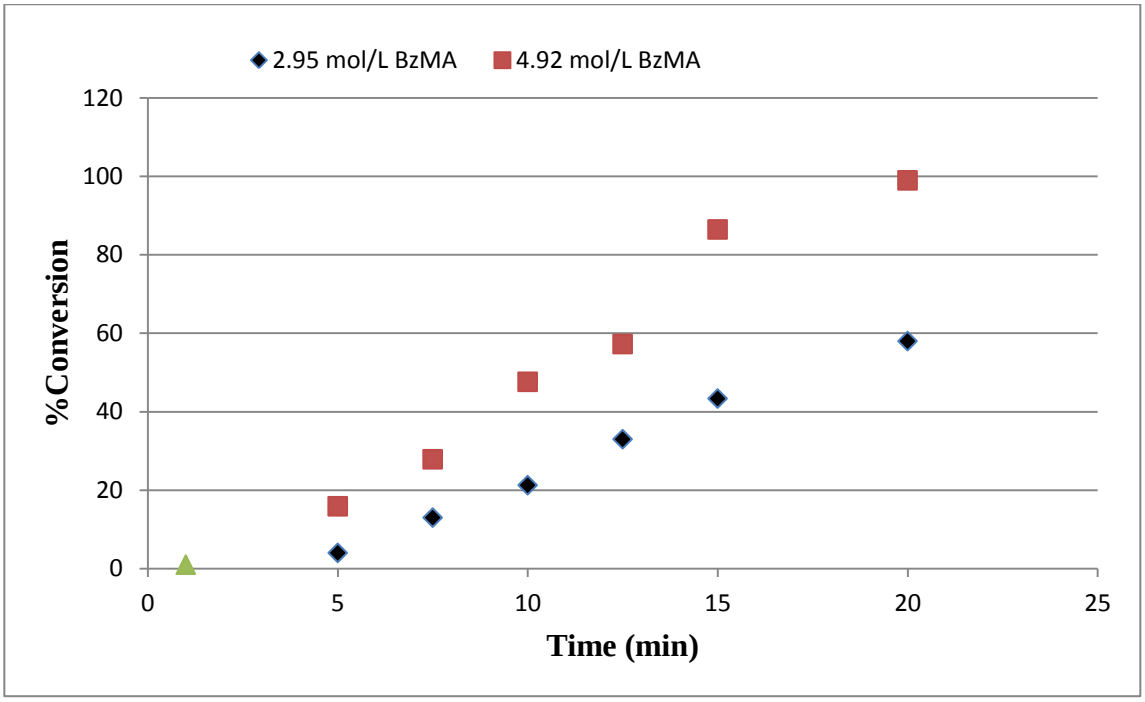


Figure 3.4. Homopolymerization of BzMA by UV Irradiation

3.3.3 Effect of Photoinitiator on Hopolymerization

DMPA 2,2-Dimethoxy-2-phenylacetophenone was used as photo initiator. The UV induced polymerization of BzMA was carried both in the presence of photo initiator DMPA and in the absence of photo initiator. In the absence of photo initiator no polymerization was observed even for 24 hours. In the presence of photo initiator the optimum amount of photo initiator is 25 mg which leads to 99% conversion. When the amount of DMPA decreases to 12.5 mg the conversion decreases to 73% and when it is increased to 50 mg also conversion percent decreases to 61% as shown in Figure 3.5. A similar result is reported by Mucci and Vallo when they studied the efficiency of DMPA

in thick sections (2~ mm) (Mucci & Vallo, 2012). As explained by Mucci and Vallo, when the amount of DMPA is exceeds an optimum amount, some photo products formed may absorb the UV light decreasing the intensity of light reaching the sample.

Benzophenone was also tested as photoinitiator. At same reaction conditions with 4.92 mol/L BzMA, 0.5 mL hexane and irradiation time 15 min 50 mg of benzophenone and 50 mg DMPA gave 11.5% and 61% conversion respectively. Hence benzophenone is not a suitable photoinitiator for the homopolymerization of BzMA under the condition tested.

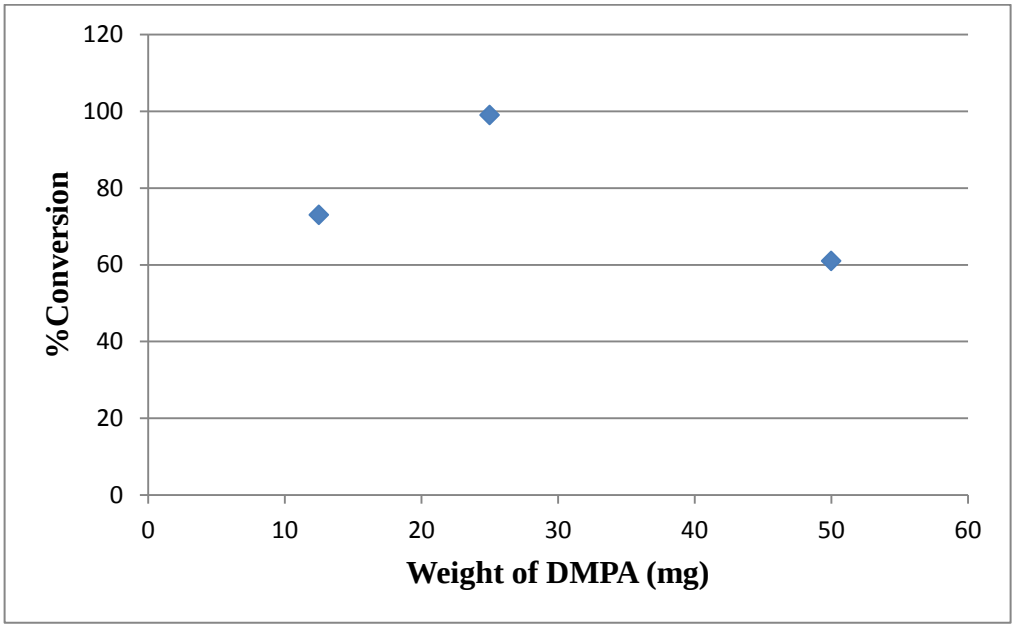


Figure 3.5. Effect of DMPA on Conversion

3.4 UV Induced Graft Copolymerization

Graft copolymerization of benzyl methacrylate onto alginates via UV irradiation was investigated. The results are shown in Table 3.3. When a mixture of 4.92 mol/L BzMA 0.5 mL hexane, 25 mg DMPA and 0.52 g alginate was exposed to irradiation for 15 min.

The maximum grafting percent obtained was 39.4% for sodium alginate, 27% for alginic acid and 16.5% for calcium alginate respectively. Characterization of products was carried out by FTIR spectrometry and SEM.

Table 3.2 Grafting% of Copolymers

Sample ID	Grafting%
B5ACP5	4
B5ACP10	9.4
B5ACP15	27
B5ACP20	17
B5ACP25	14
B5NaACP5	8
B5NaACP10	25
B5NaACP15	39
B5NaACP20	19
B5NaACP25	16
B5NaACP5	0.00
B5CaACP10	0.00
B5CaACP15	16.5
B5CaACP10	2.30
B5CaACP25	1.90

3.5 Optimization of UV Induced Alginate Derivatives with BzMA Conditions

3.5.1Effect of Reaction Time on Copolymerization

In order to evaluate the effect of irradiation time on the extent of grafting, a set of predetermined reaction conditions in homopolymerization and copolymerization such as

BzMA concentration, solvent concentration, type and amount of photoinitiator based on preliminary tests were kept constant, but the time of irradiation was changed from 5 min to 25 min. The optical pictures of calcium alginate grafted benzyl methacrylate are shown in Figure 3.6. There is an initial increase in the grafting percentage when the time of irradiation is increased up to 15 minutes for alginic acid, sodium alginate and calcium alginate. The result can be observed in Figure 3.7, 3.8, 3.9 respectively. Grafting yield decreases after 15 minutes reaction time in all cases.

A maximum grafting of 39.4% for sodium alginate, 27% for alginic acid and 16.5% for calcium alginate were obtained. Any further increase in the irradiation time results in decreases in the G% value. This behaviour is related to the free radical density in the medium. At initial stages of the reaction, an increase in the radical density in time produces new active sites susceptible to grafting, thus increasing the grafting yield and grafting efficiency. But, beyond a given irradiation time, when there is no available sites of alginate, the amount of homopolymer increases. So, a decrease in the number of available sites for the photografting monomer onto alginate will cause a decrease in grafting percentage. The fact calcium alginate allows least amount of grafting should be related to its high crystallinity and egg-box model of gel structure which inhibits diffusion of monomer in the structure. This proposal needs to be tested by XRD analysis.

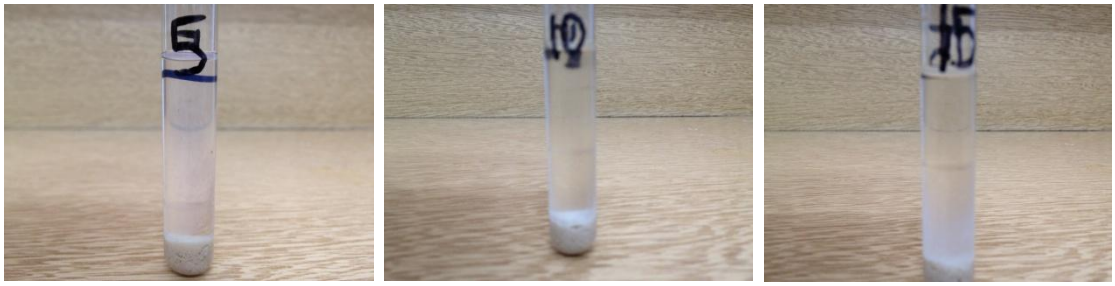


Figure 3.6. Effect of Reaction Time of Copolymerization of Calcium Alginate With BzMA

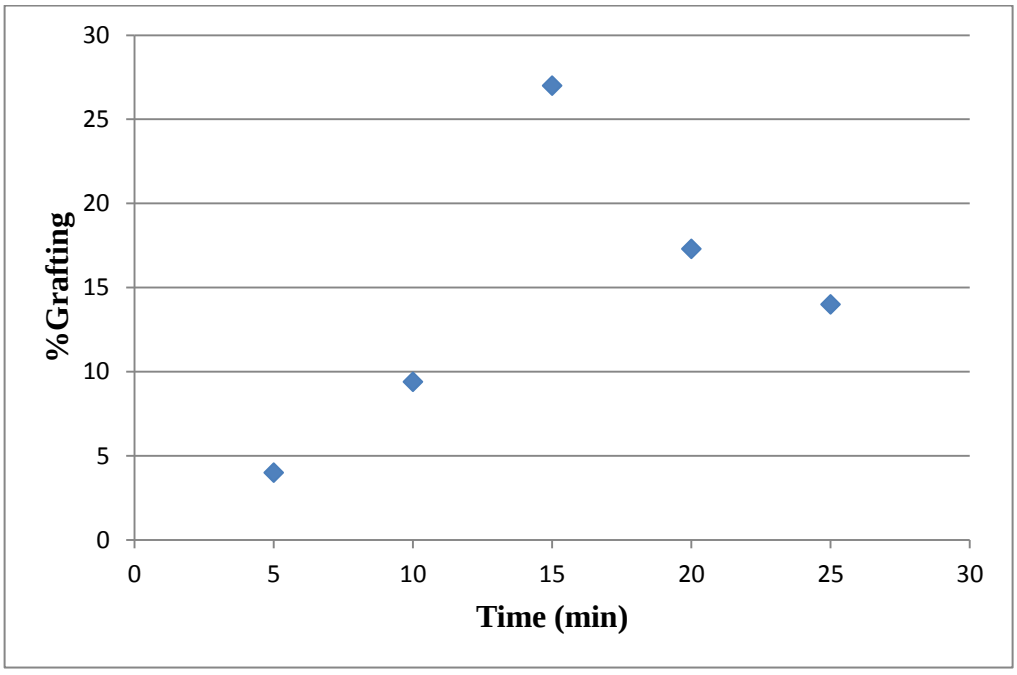


Figure 3.7. Effect of Time on Grafting Percentage of Alginic Acid-g-PBzMA

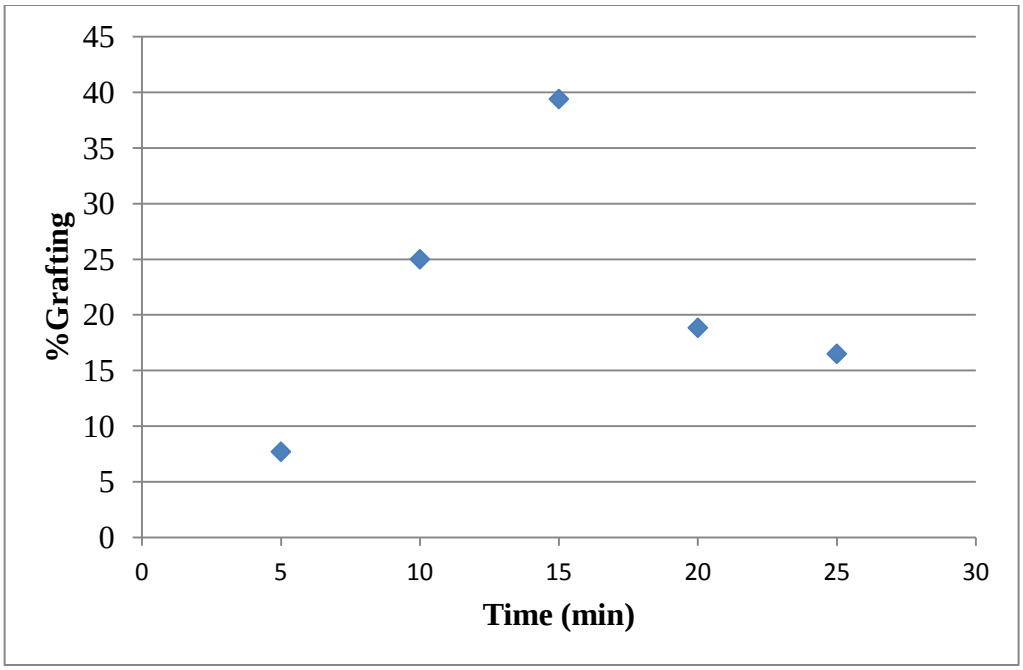


Figure 3.8. Effect of Time on Grafting Percentage of Sodium Alginate-g-PBzMA

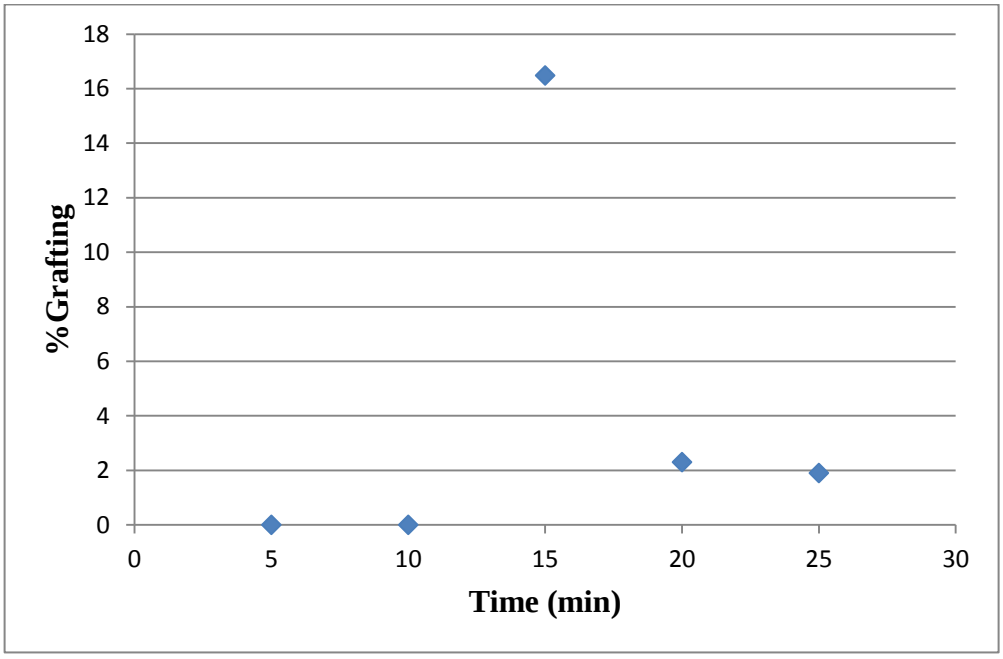


Figure 3.9. Effect of Time on Grafting Percentage of Calcium Alginate-g-PBzMA

3.5.2 Effect of Photoinitiator on Copolymer Formation

The effect of the amount of initiator on the grafting yield was studied for sodium alginate/BzMA. Similar to the behaviour observed in homopolymerization, the optimum amount of photoinitiator, DMPA, was found to be 25 mg. When the initiator amount is decreased to 12.5 mg the grafting percent also decreases and when it is doubled grafting percent decreases as well as shown in Figure 3.10. The results can be explained in the same way as discussed for the homopolymerization in section 3.3.3.

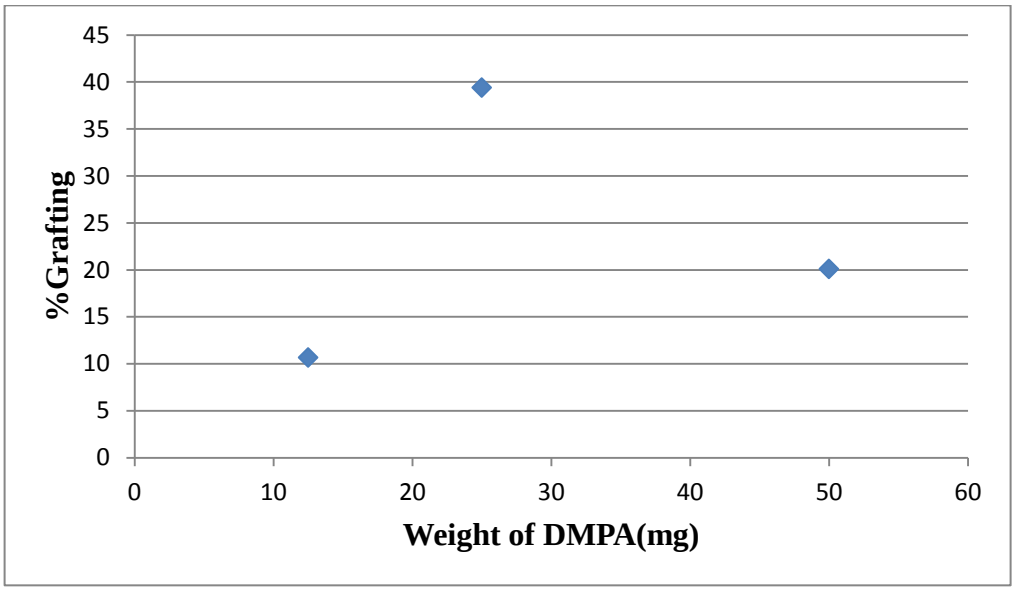


Figure 3.10. Effect of Initiator on Grafting%

3.6 FTIR Spectroscopy

3.6.1 FTIR Analysis for Calcium Alginate-g-Benzyl methacrylate

In figure 3.11 (a), (b), (c), the FTIR spectrum of calcium alginate, poly(benzyl methacrylate) are shown respectively. In the spectrum of calcium alginate the characteristic absorption bonds of carboxylate are observed at 1630 cm^{-1} and 1430 cm^{-1} which are attributed to asymmetric of COO^{-} and asymmetric stretching of the 'C=O' group respectively. In the spectrum of poly(benzyl methacrylate) the characteristic bonds interpreted in section 3.2 are available. In the calcium alginate-graft-PBzMA given in figure 3.11 (c) beside characteristic bonds of calcium alginate, an additional bond appears at 1725 cm^{-1} which is attributed to the carbonyl stretching of BzMA. The peak carbonyl stretch at 1914 cm^{-1} also exhibits itself as a small peak in spectrum of the grafted product. It is interesting to site that the carboxylate stretching at 1630 cm^{-1} shifts to 1610 cm^{-1} indicating reduced interactions between the carboxylate and calcium ions in the egg-box structure. This should be due to the screening effect of the grafted PBzMA chains. One possibility for the structure of the grafted product is given in Scheme 3.1. It can also be observed that 'C=C' stretching vibration bonds of benzyl methacrylate and 'C=O' stretching of the alginate overlap to form a strong absorption at 1447 cm^{-1} .

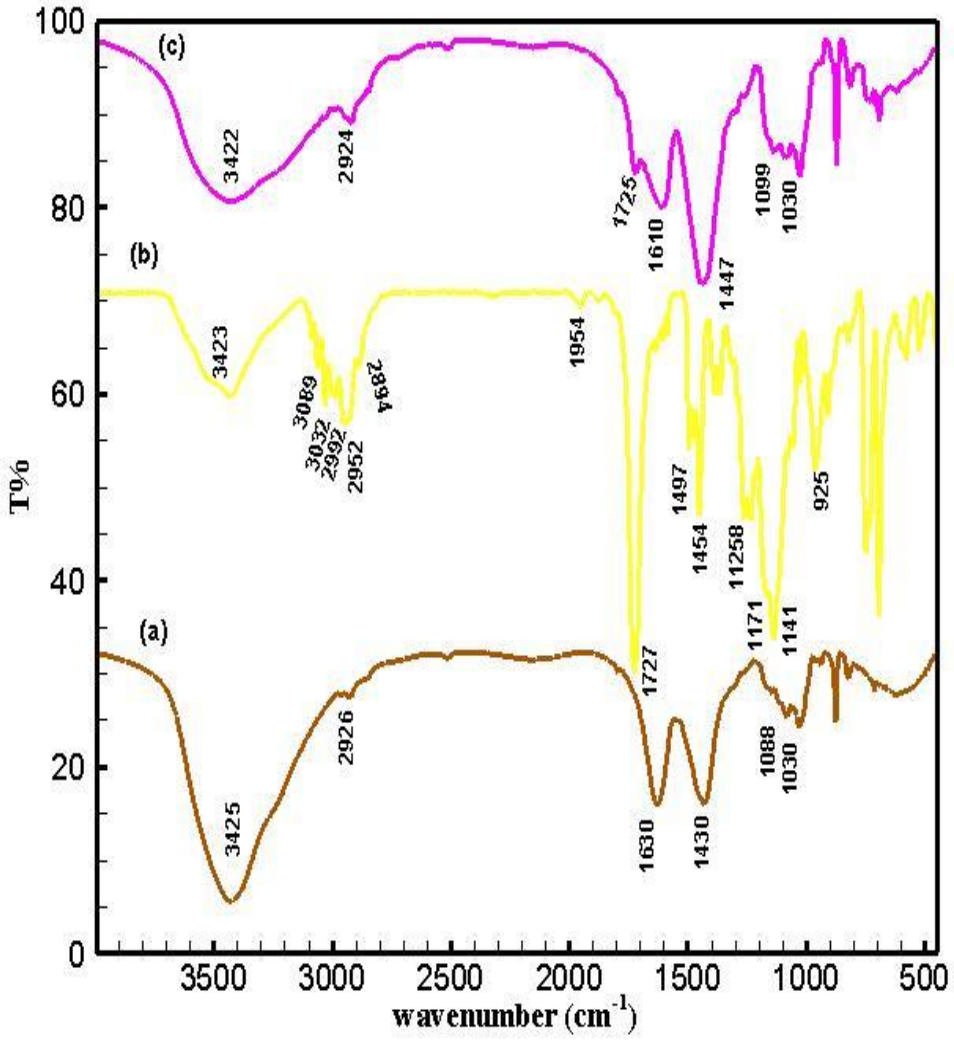
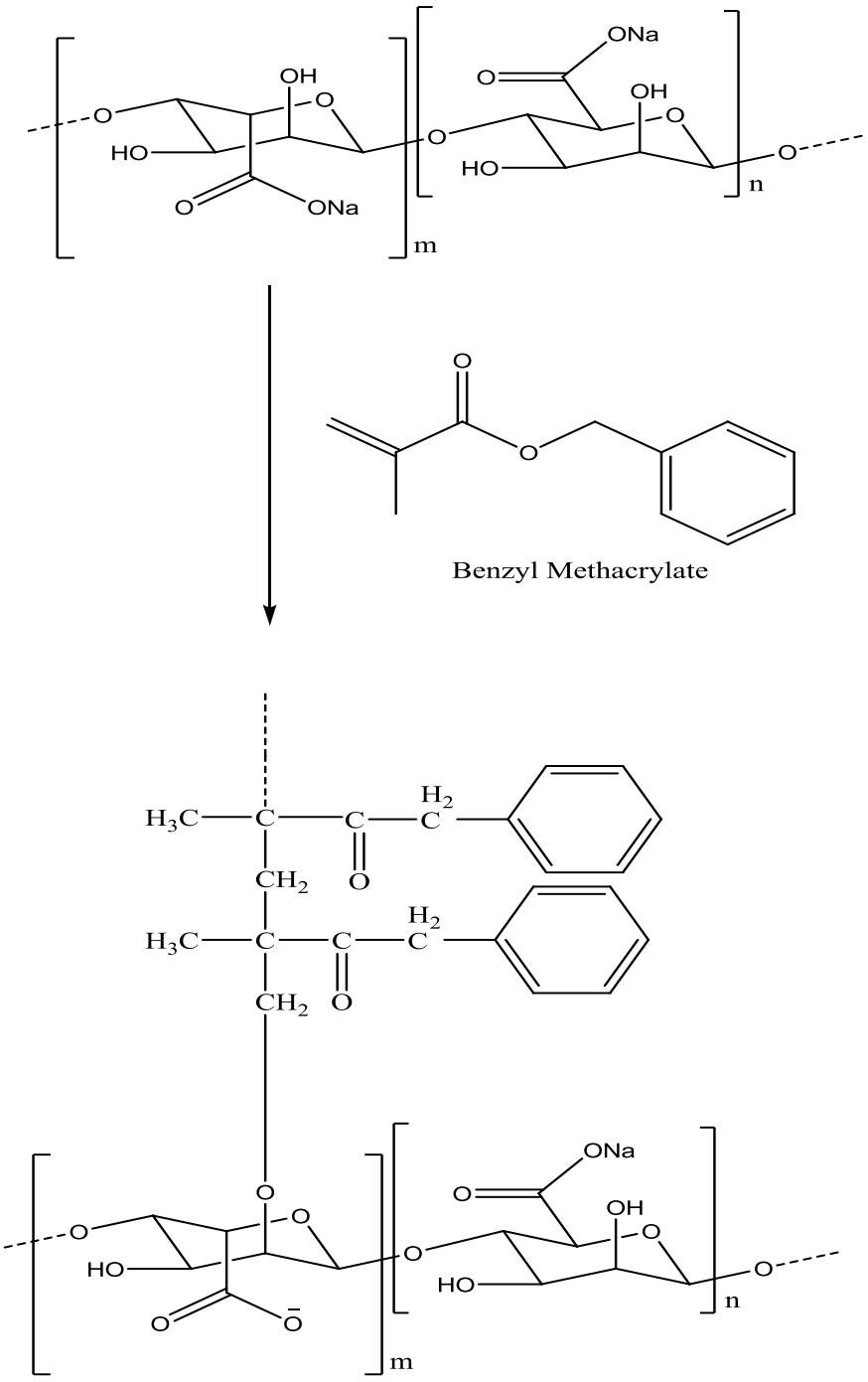


Figure 3.11. FTIR Spectra of (a) Calcium Alginate (b) PBzMA (c) Calcium Alginate-g-PBzMA



Scheme 3.1. One Possible Chemical Structure of Graft Copolymer

3.6.2 FTIR Analysis for Sodium Alginate-g-Benzyl methacrylate

As evident from Figure 3.12 (a), sodium alginate has a O-H stretching peak at 3423cm^{-1}, C-H stretching peak at 2925 cm^{-1} and C- O- C stretching peak at 1606 cm^{-1}.Two COO^- symmetric stretching peaks are evident at 1415 and 1154 cm^{-1} respectively. From Figure 3.12 (c) it is clear that in addition to the above peaks, NaAlg-g-BzMA have an additional peak at 1710 cm^{-1}, which is attributed to the stretching vibration of 'C=O' bonds of the grafted PBzMA chains. The existence of this peak indicates grafting of PBzMA chains onto the backbone of sodium alginate. The carboxylate stretching shift to 1632 cm^{-1} . This shift to higher wave numbers (lower frequencies) may be explained by increased interaction between the chains as a result of PBzMA chains affecting chain conformations. One possible chemical structure is shown in Scheme 3.1.

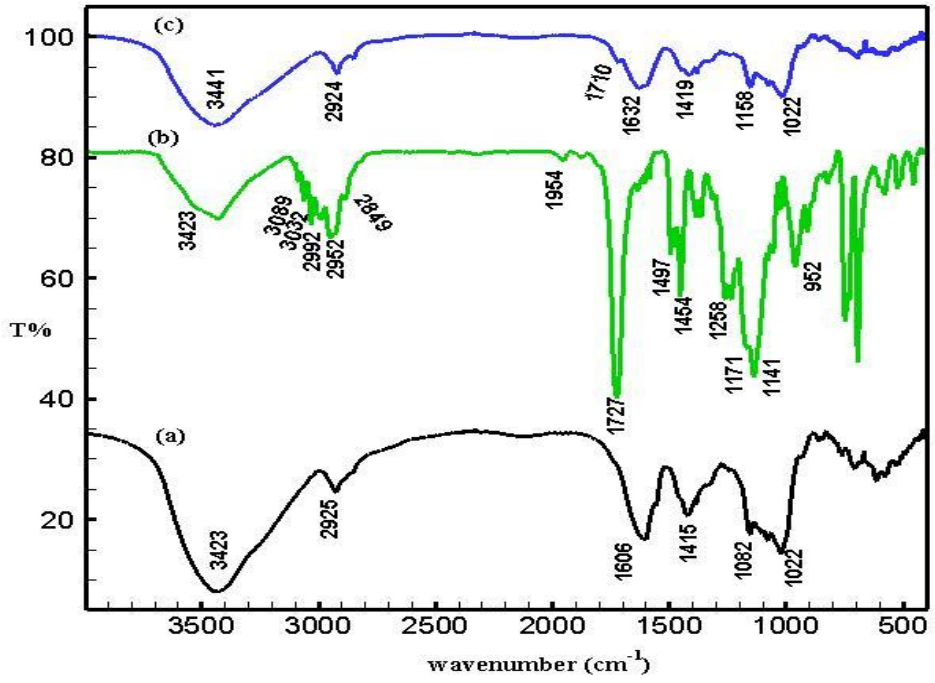


Figure 3.12. FTIR Spectra of (a) Sodium Alginate (b) PBzMA (c) Sodium Alginate-g-PBzMA

3.6.3 FTIR Analysis for Alginic Acid-g-Benzyl methacrylate

The FTIR spectra of alginic acid is shown in figure 3.13, as it shown the strong band at 1745 and 1635 cm^{-1} could be indicative of anti symmetric and symmetric COO^- stretching vibration. The band in 3448 and 2925 cm^{-1} is attributed to O-H stretch and C-H stretching vibrations respectively. The intense peak at 1420 cm^{-1} was derived from the existence of the C=O stretching band. As shown in Figure 3.13 the intensity of the peak at 1738 cm^{-1} for carboxylic groups in the FTIR spectrum decreased for graft copolymer compared with that of alginic acid, but increased a little in 1631 cm^{-1}. It is probable that some active centres are formed on the carboxylic acid groups resulting in new ester bond formation due to the grafting reaction. One possible chemical structure for the grafted product is shown in Scheme 3.1.

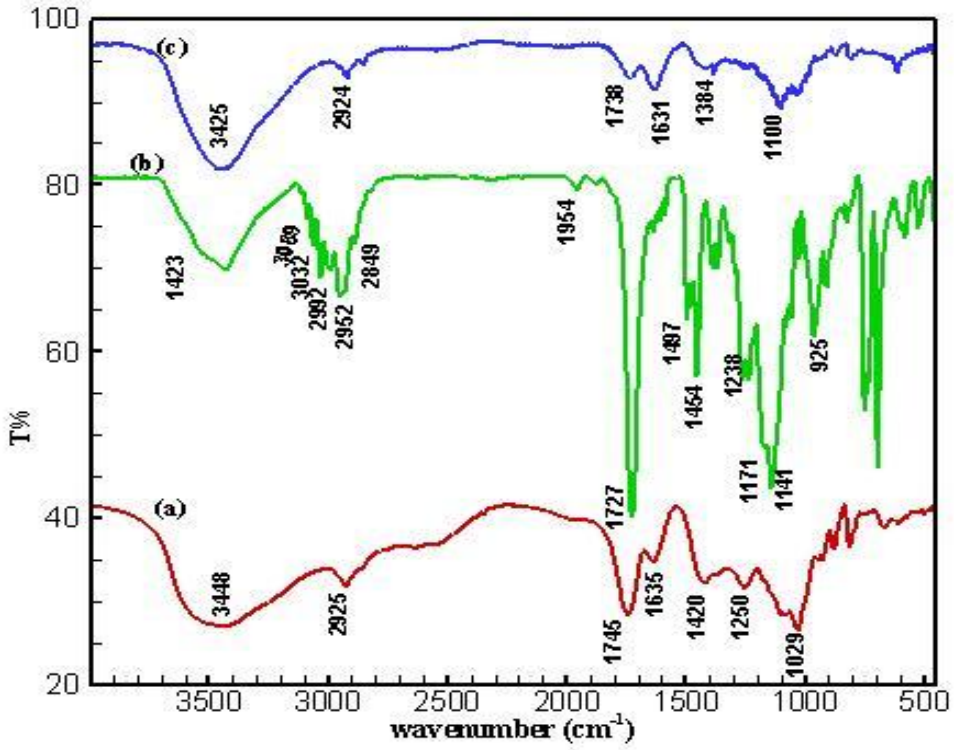


Figure 3.13. FTIR spectra of (a) alginic acid (b) PBzMA (c) alginic acid-g-PBzMA

3.7 SEM Analysis

Figure 3.14 (a) shows that the sodium alginate sample used in this study has a size distribution of 10-100 μm. When SEM picture of sodium alginate grafted with poly BzMA shown in Figure 3.14 (e) is compared to that of pure sodium alginate Figure 3.14 (a) it can be observed that the average particle size becomes bigger since the particles are grafted by poly benzyl methacrylate on the surface. Furthermore, some grafted particles have agglomerated forming particles of bigger size.

In Figure 3.14 (b) and (f) the pure sodium alginate and grafted sample are shown with x500 magnification respectively. Similar observation can be made by examining the pictures with higher magnification than Figure 3.14(a) and (e).

Sodium alginate grafted with PBzMA shown in Figure 3.14 (g) has more homogenous surface when compared to that of sodium alginate Figure 3.14(c). This observation leads to conclusion that the surface of sodium alginate particles are covered by the poly benzyl methacrylate chains grafted onto the surface.

In Figure 3.14 (d) the microfibrillar structure of sodium alginate is observable whereas this microstructure is lost upon grafting as shown in Figure 3.14 (h).

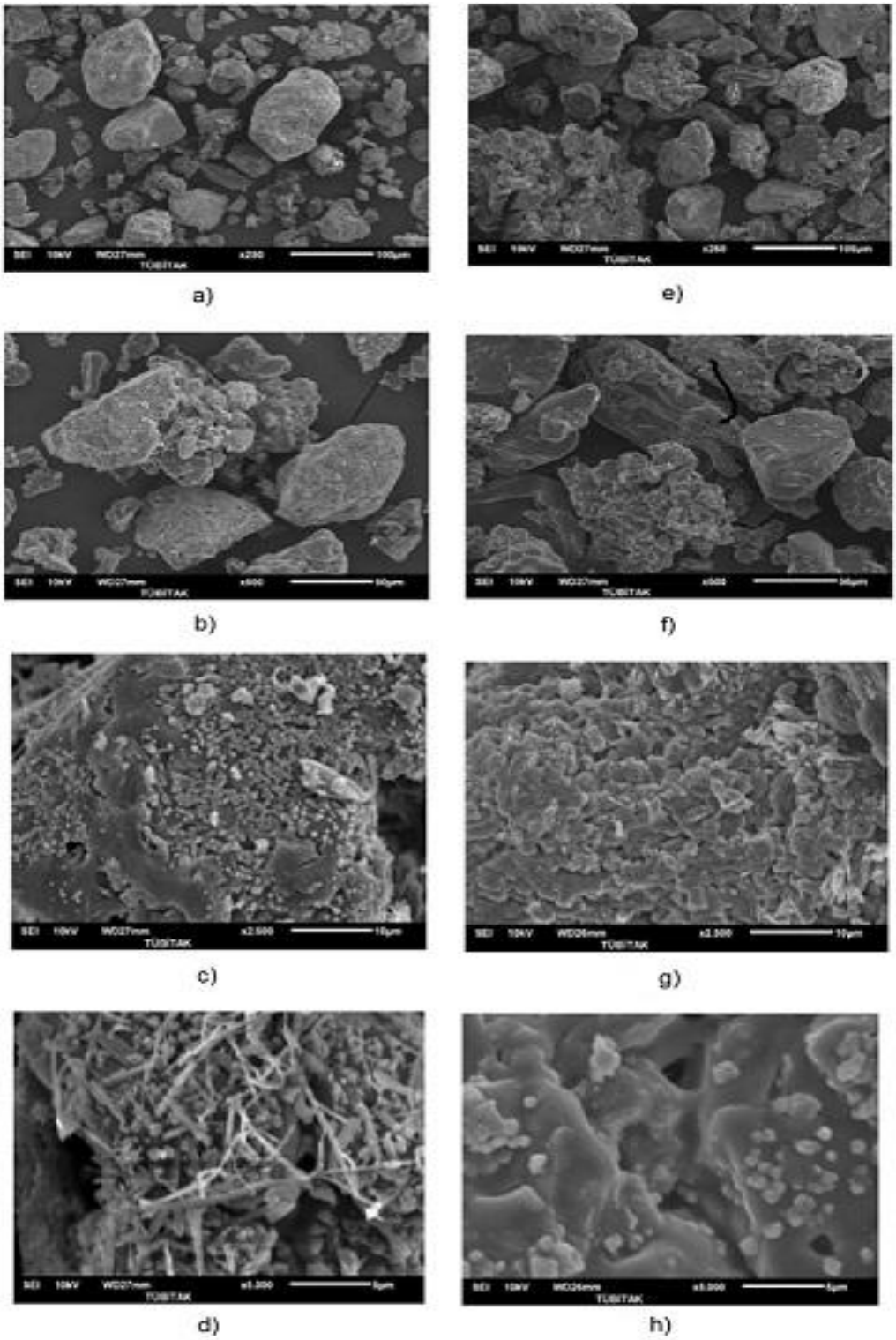


Figure 3.14. SEM Micrographs of sodium alginate (a) x200 (b) x500 (c) x2500 (d) x5000 and sodium alginate-g-PBzMA (e) x200 (f) x500 (g) x2500 (h) x5000

3.8 Solubility Characteristics of the Products

Before the polymerization was carried out, solubility of samples to be used in the experiment were tested and following result given in Table 3.3 were obtained.

Table 3.3. Solubility Test

Sample ID	**ethanol**	**$CHCl_3$**	**hexane**	**DCA**	**H_2O**	**THF**	**DMAc**
Alginic acid	-	-	-	-	-	-	-
BzMA	+	+	+	+	+/-		
Sodium alginate	-	-	-	-	+	-	-
PBzMA	-	+	-	-	-	+	+

+: soluble/miscible - : insoluble/immiscible +/-: partly soluble/partly miscible

Table 3.4. Solubility Test of Grafted Copolymer

Sample ID	**H_2O**	**NaOH**	**THF**	**DMAc**	**toluene**	**DMF**	**ethanol**
Na-Alg grafted	-	-	-	-	-	-	-

- : insoluble

Chapter 4

CONCLUSIONS

Poly(benzyl methacrylate) was synthesized by using UV-initiation method, using UV source with a wavelength 350 nm and fixed power (7670 μW/cm2) under mild and easily affordable conditions not reported before. The homopolymer of PBzMA is synthesized in a short period of time, 20 minutes with 99% conversion at room temperature using 25 mg DMPA in 0.5 mL hexane at a monomer concentration of 4.92 mol/L.

Benzyl methacrylate was grafted onto alginates by UV-induced copolymerization and using DMPA as photoinitiator, the maximum grafting yield were obtained to be 39.5% for sodium alginate, 27% for alginic acid and 16.5% for calcium alginate at monomer concentration of 4.92 mol/L, 25 mg DMPA and 0.5 ml hexane within 15 minutes. SEM pictures displayed that the surface of sodium alginate grafted PBzMA copolymer was more homogenous that of sodium alginate providing evidence for surface grafting of PBzMA onto the alginate. Both homopolymer and graft copolymer obtained have a potential to be used as additives and adhesives in dental cements due to their sticky and UV-curable nature.

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