SELF-CROSS LINKABLE SUPERABSORBENT HYDROGELS BASED ON DIFFERENT VINYLALKOXYSILANES AS CROSSLINKER

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ABSTRACT

Novel superabsorbent hydrogels were synthesized through the Free Radical Solution Precipitation polymerization technique. The synthesized materials were characterized by Differential Scanning Calorimetry (DCS), Simultaneous Thermal Analysis (STA), FTIR (Fourier Transmittance Infrared),^{1}H Nuclear Magnetic Resonance Spectroscopy (NMR), ^{29}Si Nuclear Magnetic Resonance Spectroscopy . These characterization methods provide valuable information to understand chemical structure and performance level of water uptake synthesized hydrogels, effect of synthesis parameters; change in cross linker agents, and thermal behavior of polymers.

The effects of synthesis conditions such as monomer feed concentration of acrylamide/ 2-acrylamido-2-methylpropane-1-sulfonic acid (AMc/AMPS) on level of performance of superabsorbent hydrogels were investigated. Highest Equilibrium Swelling ratio (ESR) gravimetrically was obtained for smaller AMc/AMPS ratio when Vinyltrimethoxysilane (VTMS) ratio was kept constant. It was experimentally proved

that increasing molar concentration of cross linking agent in polymerization mixture gave lowest ESR gravimetrically (g/g) in distilled water.

Due to chemical structure and reactivity relationship, when changing the type of cross linking agent in polymerization reactions, while according to the characterization results we studied there was no important change, but different ESR values were obtained for each polymer synthesized with different vinylalkoxysilane. Based on three different chemical structures of vinylalkoxysilane cross linking agents, namely Triethoxyvinylsilane (TEVS), Vinyltrimethoxysilane(VTMS) and Tris(2-methoxyethoxy)vinylsilane (TMEVS), the highest ESR value was obtained for TEVS based samples. This highest ESR value for TEVS based samples is attributed to the higher rate of hydrolysis of alkoxy groups). An increase in electropositive density on Si atom was predicted to be responsible for higher rate of hydrolysis of alkoxy groups of TEVS leading ethanol as leaving group in aqueous medium. For TMEVS, when chemical structure and reactivity can be taken into account, it can be stated that for methoxyethoxy groups on Si atom, there are parallel two inductive powers cancelling each other and providing a weaker electropositive density on silicone atom, hence a slower rate of hydrolysis.

According to thermal analysis, it was observed that the powder samples of superabsorbent hydrogels started to degrade thermally under N_2 around 278 ^{0}C and three different common thermal behaviors were attributed to polymers based on chemical structure.

The Monomer reactivity studies were analyzed according to ^{1}H – NMR results for the synthesized powder samples in the same experimental conditions while excluding any cross linking agents. According to analysis, monomer reactivities of AMc and AMPS were found as 1.32 and 1.25 respectively. Based on monomer reactivity results, it is clear to conclude that for the Free radical solution precipitation polymerization of acrylamide and AMPS occurred randomly.

Experimentally three different polar aprotic solvents were used as solvent medium in reactions,1,4-dioxane,Dimethylacetamide and Dimethylformamide. A significant difference result from using these three polar solvents was the comparable change in

ESR under same conditions. Superabsorbent polymers (SAPs) synthesized in Dimethylformamide provided highest ESR values.

Solution viscosity of prepared standard 6 %(wt/ml) of polymers were measured in Brookfield DV-III Rheometer while keeping torque value 15%. Viscosity of standard solutions of polymer based on three different vinylakoxysilanes were found as lowest for TEVS based polymer and highest for TMEVS based polymer.

Molecular weight of synthesized polymers based on three different vinylalkoxysilanes were calculated according to the results obtained from Dilute Solution Viscometery experiment, while using the constants for polyacrylamide since about 90 % of synthesized polymers are acrylamide. According to dilute solution viscometery calculations, TEVS based polymer was found to have lowest MW, while TMEVS based polymer with highest MW.

^{29}Si NMR analysis were done in order to check the hydrolysis and condensation behaviors of three different vinylalkoxysilanes. Simply, same molar concentration of vinylalkoxysilanes in an aqueous medium in constant temperature yielded different behaviors. According to results, the fastest hydrolysable cross linking agent was found to be TEVS. Two other cross linking agents have different responds in aqueous medium and corresponding hydrolysis products observed on Si^{29} NMR spectrums.

KENDİ KENDİNE ÇAPRAZ BAĞLANABİLEN SÜPERABSORBENT HİDROJELİN FARKLI VİNİLALKOXYSİLAN ÇAPRAZ BAĞLAMA AJANI OLARAK KULLANARAK HAZIRLANMASI

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Anahtar kelimeler: Süperabsorbent, Serbest Radikal Solusyon Çökeltme Polimerizasyonu, Akrilamid, AMPS, Vinilalkoksisilan bağlayıcıları, Denge Su Emme kapasitesi, Çapraz bağlayıcılar

ÖZET

Serbest Radikal solusyon çökeltme polimerizasyon tekniği kullanılarak yeni superabsorbent hidrojeller sentezi gerçekleştirilmiştir. Sentezlenen polimerik malzemeler Diferansiyel Dereceli Kalorimetri (DCS), Simultane Termal Analiz (STA), Forier Transform Infrared (FTIR) and ^{1}H Nükleer Magnetik Resonans Spektroskopisi (NMR), ^{29}Si Nükleer Magnetik Resonans Spectroskopisi karakterize etme teknikleri kullanılarak karakterize edilmiştir. Bu karakterizasyon teknikleri sentezlenen polimerik malzemelerin kimyasal yapıları ve su absorbasyon performansları, sentez parametrelerindeki değişikliklerin etkilerini, çapraz bağlayıcı ajanlarındaki yapısal değişiklerinin ve termal davranışlarını anlamamız hakkında çok önemli bilgilerin anlaşılmasını sağlamıştır.

Sentez reaksiyonları şartlarındaki değişikliklerin etkileri, örneğin monomer (AMc/AMPS) konsantrasyonunlarının birbirine göre değişikliklerin elde edilen polimerik jellerin su çekme kapasiteleri üzerindeki etkileri deneysel olarak ortaya konulmuştur. Maksimum su çekme kapasitesi aynı sentez şartlarında, monomer konsantrasyon (AMPS/AMc) daha düşük olduğu durumda, çapraz bağlayıcı ajanının (VTMS) konsantrasyonu sabit tutulduğunda elde edilmiştir. Monomer konsantrasyon sabit tutularak çapraz bağlayıcı ajanı molar konsantrasyon oranı sistematik olarak artırıldığında, maksimum su çekme kapasitesi (ESR) en düşük çapraz bağlayıcı ajanı konsantrasyonu kullanıldığında elde edilmiştir (g/g) kütlesel olarak.

Kimyasal yapı ve reaktivite arasındaki ilişkiden dolayı, polimerizasyon reaksiyonlarında çapraz bağlayıcı ajanı değiştirildiğinde, karakterizasyon çalışmalarında önemli bir değişiklik gözlenmemesine rağmen, farklı ESR değerleri elde edilmiştir. Polimklılerleşme reaksiyonlarında kullanılan farklı çapraz bağlayıcı ajanı olarak kullanılan vinilalkoksisilanlar, kimyasal yapılarındaki farklılıklardan dolayı, Trietoksivinilsilan(TEVS), Viniltrimetoksisilan (VTMS) ve

Tris(2-metoksietoksi)vinilsilan (TMEVS) için en yüksek ESR değeri TEVS kullanılarak sentezlenen polimerler için elde edilmiştir.

Beyaz toz numune halindeki superabsorbent polimerlerin (SAPs) termal olarak kimyasal degradasyonu 278 ^{0}C civarında başladığı görülmüştür ve üç farklı termal geçiş evresi polimerik malzemenin kimyasal yapısından dolayı termal analiz sonuçları ile örtüştüğü gözlenmiştir.

Polimerleşme reaksiyonlarında kullanılan monomerler, akrilamid (AMc) ve 2-akrilamido-2-metilpropan-1-sulfonik asit (AMPS), monomer reaktivitileri Proton NMR analiz tekniği kullanılarak hesaplanmıştır. Kullanılan polimerleşme şartları sabit tutularak ve sadece çapraz bağlayıcı ajanı kullanılmayarak sentezlenen farklı monomer konsantrasyonlarının Proton NMR sonuçları ile beraber hesaplanmasından elde edilen sonuçlara göre AMc ve AMPS monomerlerine ait monomer reaktiviteleri 1.32 ve 1.25 olarak bulunmuştur.

Deneysel olarak üç farklı polar aprotik çözücü, 1,4-Dioksan, Dimetilasetamit ve Dimetilformamid kullanılmıştır. Üç farklı çözücü sistemi kullanılarak sentezlenen polimerlerden, Dimetilformamid içinde sentezlenen polimerler en yüksek ESR değeri göstermişlerdir.

Hazırlanan standard %6 lık (gr/ml) polimer solusyonlarının viskozite değerleri Brookfield DV-II reometresi tork değeri %15 olacak şekilde sabit tutularak bulunmuştur. Farklı çapraz bağlayıcı ajanlar kullanılarak sentezlenen polimerlerden TEVS vinilalkoksisilanı kullanılarak elde edilen polimer düşük viskozite değerine sahip olduğu saptanmıştır.

Sentezlenen polimerlerin moleküler kütle değerleri Seyretilmiş Solusyon Viskometresi deneyi kullanılarak elde edilen sonuçlara göre hesaplanmıştır. Hesaplamalarda poliakrilamidin su ortamında çözünmesi sonucu elde edilen sabitler kullanılmıştır, çünkü sentezlenen polimerlerin yaklaşık % 90 lık kısmı molar olarak akrilamid monomerinden oluşmuştur. Elde edilen sonuçlara göre, TEVS kullanılarak sentezlenen polimer en düşük moleküler kütleye sahiptir.

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^{29}Si NMR analiz tekniği kullanılarak polimerleşme reaksiyonlarında çapraz bağlayıcı ajanı olarak polimerlere entegre edilen vinilalkoksisilanların hidroliz ve kondezasyon davranışları incelenmeye çalışılmıştır. Vinilalkoksilanların molar konsantrasyon ve reaksiyon sıcaklıkları sabit tutularak sulu ortamda yapılan analizlere göre, farklı vinilalkoksisilanlar, faklı hidroliz ve kondezasyon davranışları göstermişlerdir. Elde edilen sonuçlara göre, TEVS hidroliz reaksiyonuna en hızlı şekilde cevap veren ajan olarak görülmüştür. Diğer iki vinilalkoksilanlar sulu ortamda farklı hidroliz ve kondenzasyon davranışları göstermişlerdir.

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ABBREVIATIONS

AMc : Acrylamide

AMPS : 2-Acrylamido-2-methylpropane sulfonic acid

DMAM : N,N-Dimethylacrylamide

VTMS : Vinyltrimethoxysilane

TEVS : Triethoxyvinylsilane

TMEVS : Tris(2-methoxyethoxy)vinylsilane

DMF : Dimethylformamide

DMAc : N,N-Dimethylacetamide

BPO : Benzoylperoxide

DSC :Differential Scanning Calorimetry

TGA : Thermalgravimetric Analysis

AA : Acetic acid

SAP : Superabsorbent polymer

CHAPTER 1

1. Introduction

The hydrogel can be defined as a crosslinked polymeric network which has the capacity to hold water within its porous structure.

Hydrogels are also regarded as responsive materials that show variations in their volume in response to an outer environmental stimulus such as pH, temperature, electrical field, chemicals and ionic strength. Superabsorbent polymers (SAPs) or hydrogels are loosely crosslinked, three dimensional networks of flexible polymer chains that carry dissociated, ionic functional groups. They are basically the materials that can absorb fluids greater than hundreds of times their own dried weight, either under or without load, such as water, electrolyte solution, synthetic urine, brines, biological fluids such as urine sweat, and blood. They are polymers which are characterized by hydrophilicity containing carboxylic acid, carboxamide, hydroxyl, amine, imide groups so on, insoluble in water, and crosslinked polyelectrolystes. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving by solvation of water molecules via hydrogen bonds, increasing the entropy of the network to make the SAPs swell tremendously [1].

The use of hydrogel for biomedical applications dates back to 1960 when Wichterle and Lim synthesized crosslinked poly (hydroxyethyl methacrylate) (pHEMA) [2]. Since then, the use of hydrogels extended to various applications. Due to their excellent hydrophilic properties, high swelling ratio and biocompatibility, hydrogels have been widely used in agriculture, in biomedicine as antibacterial materials, biosensors and in tissue engineering, in sorbents for the removal of heavy metals, and many other applications . These materials have been also used in the development of the smart drug delivery systems. Hydrogels can control drug release by changing the gel structure in response to environmental stimuli and also can protect the drug from hostile environments [3].

Hydrogels can be classified into two groups depending on the nature of the crosslinking reaction. If the crosslinking reaction involves the formation of covalent bonds, then the hydrogels are termed as a permanent hydrogel. The examples of permanent hydrogels include pMMA(poly(methylmethacrylate)) and pHEMA. If the hydrogels are formed due to physical interactions, such as, molecular entanglement, ionic interaction and hydrogen bonding, among the polymeric chains then the hydrogels are termed physical hydrogels [4]. Examples of physical hydrogels include polyvinyl alcohol-glycine hydrogels, gelatin gels and agar-agar gels.

Hydrogels can also be categorized as conventional and stimuli responsive hydrogels [5]. Conventional hydrogels are the crosslinked polymer chains which absorb water when submerged in an aqueous media and there is no change in the equilibrium swelling with the change in the pH, temperature, or electric field of the surrounding environment while the stimuli responsive hydrogels are the polymeric networks which change their equilibrium swelling with the change of the surrounding environment. PH sensitive hydrogels have been used since long in the pharmaceutical industry as an enteric polymer. The enteric polymers/ hydrogels generally are used to either protect the stomach mucosa from the gastric irritant drugs (e.g. aspirin) or to protect the acid-labile drugs (e.g. penicillin G, erythromycin) from the harsh environment of the stomach [6]. PH sensitive hydrogels have also been used for the development of blood-glucose detection kit and insulin delivery [7]. Temperature sensitive hydrogels are now used in tissue culture. Electric field sensitive hydrogels have been used in artificial muscles and controlled drug delivery systems [8].

There are two commonly used polymerization techniques; free radical or chain polymerization and step or condensation polymerization. Most biomedical hydrogels are synthesized by free radical polymerization. The polymerization reaction can be carried out in bulk, in solution, or in suspension. The monofunctional and multifunctional monomers are mixed together and the polymerization is initiated by addition of a small amount of an initiator. Crosslinks are formed as the multifunctional monomer (crosslinking agent) is incorporated into two or more growing chains. The polymerization reaction can be initiated by free radical generated by thermal, ionization, radiation or by redox means. A wide variety of initiators can be used, such as azo-compounds, peroxide and redox initiators. Gamma-irradiation can be used to initiate the polymerization reaction. The major advantage over chemical initiation is the production of relatively pure, residue-free hydrogels [9].

One of the aims of this work is to synthesize powder hydrogels through a free radical solution precipitation polymerization technique by a simplified method which gives desired product properties such homogeneous size distribution of powders, stability in ambient temperatures and availability of further processes such as gel formation and film casting in an aqueous medium. This simplified method has easy processing steps that ensure applications at larger scales and is cost effective.

In all application areas, hydrogels are generally applicable in gel forms, but for the sake of this work, a precipitated form of hydrogels is desired and precipitated form of hydrogels were obtained above mentioned method. The main purpose behind this idea was to keep alkoxysilane pendant groups nonhydrolyzed prior to gel formation and film casting. When standard aqueous solution of synthesized non-crosslinked polymers is prepared, it is one of the fundamental purposes of this work to cure without any catalysis. Prepared solutions are cured at 80 ^{0}C at vacuum furnace. Alkoxy groups are sensitive to hydrolysis in aqueous mediums; hence a set of polar aprotic solvents was used instead of water as solvent system to dissolve solid monomers in prepolymerization mixture.

Free radical solution precipitation polymerization method provided integration of monomers into polymer in desired properties and easy substitution of same kind of monomers and crosslinking agents. For example, for reactivity and structure relationships, a set of vinylalkoxysilane as crosslinking agents were used.

In this work it is aimed to ensure the controlled synthesis of superabsorbent hydrogels in order to better understand the effects synthesis conditions. To achieve this aim, effects of synthesis parameters such as monomer molar ratio, amount of crosslinking agent, different polar aprotic solvents, reaction temperature and time were investigated. Produced superabsorbent hydrogels and powders were analyzed with DSC, STA, FT-IR and ^{1}H NMR to understand chemical composition, chemical structure and thermal behaviors, effect of synthesis parameters.

CHAPTER 2

2. Literature review on Hydrogels

2.1 Hydrogel

About three decades ago, superabsorbent polymers (SAPs) were introduced into the agriculture and diaper industries, and then their applications were extended to other industries where excellent water holding property was of prime importance [10].

A hydrogel can be defined as a material that exhibits the ability to swell in water and retain a significant fraction of water within its structure. There is a wide variety of natural and synthetic hydrogels. Their ability to absorb water is due to the presence of hydrophilic groups such as –OH, -CONH-, $-CONH_2$, -COOH, and SO_3H [11]. Hydrogels find widespread applications in the biomedicine, bioengineering, pharmaceutical, veterinary medicine, food industry, agriculture and related industries. Hydrogels are used as controlled release systems of drugs and some physiological body fluids, production of artificial organs and contact lenses in biomedicine, as an absorbent in environmental applications for the removal of some undesired agents such as waste water of sanitary, agricultural, and industrial sources [12]. Hydrogels can be neutral or ionic in nature. In neutral hydrogels, the driving force for swelling arises from the water-polymer thermodynamic mixing contribution to the overall free energy which is coupled with an elastic polymer contribution [13]. In ionic hydrogels, the swelling process is due to the previous two contribution as well as interactions between charged polymer and free ions. The ionization of the pendant ionizable groups such as carboxylic acid, sulfonic acid or amine groups renders the polymer more hydrophilic and thus leads to a very high water uptake.

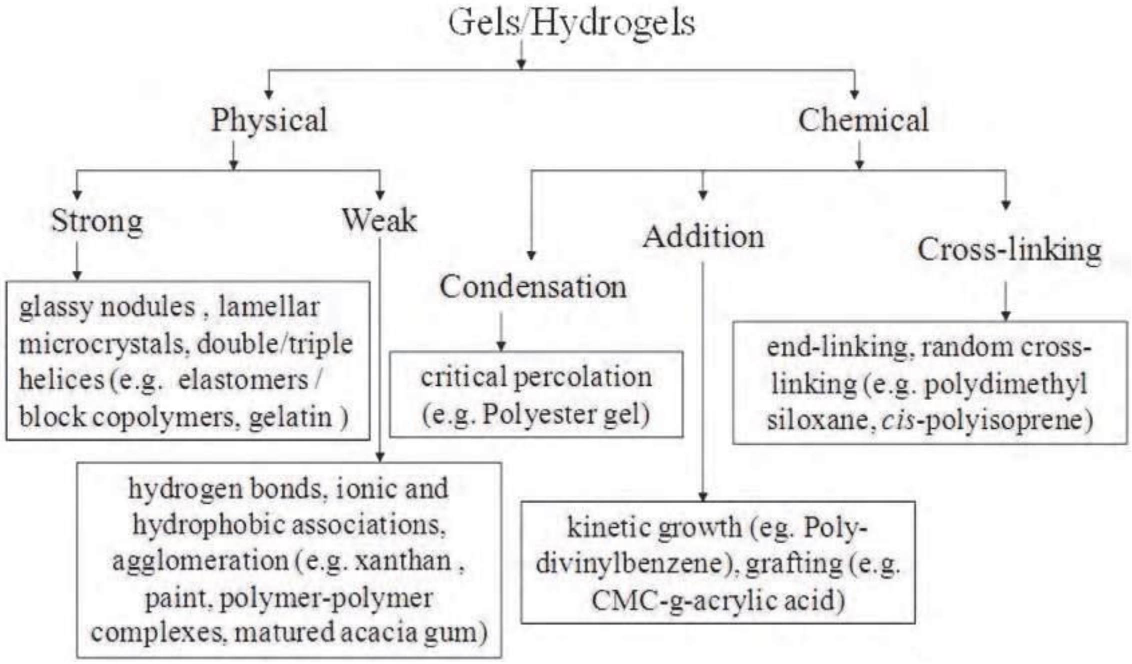


Figure 2.1 Classification of hydrogel based on preparation methods [14].

The swelling properties of hydrogels of ionic hydrogels are unique due to ionization of their pendant functional groups. Many physiological parameters such as pH, ionic strength, temperature, pressure and electromagnetic events can change drastically the equilibrium degree of swelling by several orders of magnitude. The sudden change in the equilibrium degree of swelling occurs near the pK_a of the hydrogel . The range of pH transitions (ΔpH) depends upon polymer morphology as well as the polymer-solvent interaction characteristics. Change in the pH, ionic strength, temperature and electromagnetic radiation can act as inputs; the response of the hydrogels will be a sudden change in the degree of swelling. This principle can be used in the development of various biomedical and pharmaceutical systems ranging from biosensors to artificial muscles, superabsorbent hydrogels or site-specific drug delivery systems [15].

Ionic hydrogels may be used as carriers for swelling-controlled drug delivery devices. The change in pH in the gastrointestinal tract acts as a stimulus for the hydrogel. Anionic hydrogels can be used as drug carriers in oral dosage forms to deliver drugs selectively to the intestine [16]. Ionic hydrogels have been used in the design of glucose-sensitive insulin release system. An insulin reservoir is coated with cationic hydrogel containing amine groups; glucose oxidase converts the latter to gluconic acid and the local pH drops. This leads to protonation of the amine groups, which in turns makes the hydrogel swell and causes insulin release. This is the closed-loop system [17]. Other types of hydrogels utilized in drug delivery are hydrophobic/hydrophilic carriers based on interpenetrating polymer networks [18].

Polyelectrolytes contain ionized macromolecules chains with more than one ionizable group in their backbone. When crosslinked, such polyelectrolytes form three dimensional networks exhibiting high degrees of swellings due to their ionization and ion hydration. In these hydrogels, in addition to the polymer-solvent mixing and polymer elasticity contributions, ionization of fixed charges of the backbone contributes to swelling. The electrostatic repulsion between adjacent fixed charges uncoils the polymer chains. The contribution diffusion inside the gel creates an additional osmotic pressure difference across the gel. This leads to higher water uptake as shown in fig. 2.2.

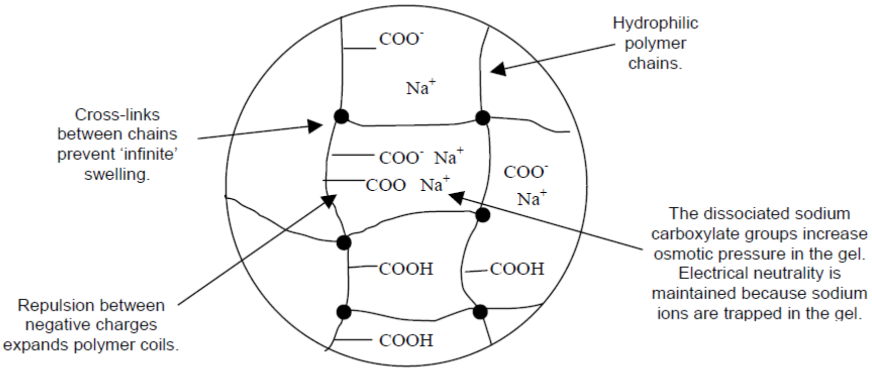


Figure 2.2 Schematic diagram of conformation of a polyelectrolyte chain containing ionizable anionic groups and swelling mechanism [19].

2.2 Preparation of Hydrogels

2.2.1. Monomers

Hydrogels are generally synthesized by homopolymerization of ionic monomers or by co-polymerizing ionic monomers with neutral monomers. There are several polymerization techniques commonly employed to synthesize these crosslinked polymers. A first approach is a co-polymerization/crosslinking method which requires reaction of the co-monomers with multifunctional co-monomer acting as a crosslinking agent in the presence of an initiator and a solvent. A second technique involves crosslinking of linear polymers by irradiation or by chemical compounds.

The monomers used in the synthesis of ionic polymer networks contain either an ionizable group, a group that can be hydrolyzed or a group that can undergo a substitution reaction after the polymerization is completed. Table 2.1 lists some of the monomers used in the synthesis of hydrogels. The most commonly used crosslinking agents are ethylene glycol dimethylacrylate , N, N’- methylene bisacrylamide and divinyl benzene.

Table 2.1 Some monomers and their structure used commonly in hydrogel synthesis [20].

Name	Structure
	Anionic monomers
Acrylic acid	**$CH_2CRCOOH$**
p-Styrene sulfonic acid	**$CH_2CHC_6H_4SO_3H$**
Itaconic acid	**$CH_2C(COOH)CH_2COOH$**
Crotonic acid	**$CH_3CHCHCOOH$**
	Cationic monomers
Vinyl pyridine	**$CH_2CHNC_5H_5$**
Aminoethyl methacrylates	**$CH_2C(R)COO[CH_2]_2NR_1(R_2)$**
	Ampholytic monomers
N-Vinyl glycine	**$CH_2C(CH_3)NHCH_2COOH$**
	Neutral monomers
2-Hydroxyethyl methacrylate	**$CH_2CCH_3COOCH_2CH_2OH$**
Vinyl acetate	**$CH_2COOCHCH_2$**
Acrylic monomers	**$CH_2C(R)COOR_1$**
Acrylamide	**$CH_2CHCONH_2$**

2.2.2 Solution co-polymerization/crosslinking

In solution co-polymerization/crosslinking reactions, ionic or neutral monomers are mixed with an appropriate multifunctional crosslinking agent. If the monomers and the cross linking agent are not miscible, then a common solvent is introduced. The polymerization reaction is initiated thermally, by UV-light or by a redox initiator system. This mode of polymerization gives a random polymer and the polymerization is allowed to go completion. The major advantage of solution over bulk polymerization is that the solvent serves a heat sink and thus minimizes temperature control problems. The solvent choice can add greater flexibility in processing and in altering the gel properties. The synthesized network needs to be washed to remove unreacted monomers, oligomers and other impurities and can be swollen to equilibrium to give a gel [21].

If the amount of water present during polymerization is greater than the water content corresponding to the equilibrium degree of swelling, a phase separation occurs during co-polymerization/crosslinking and a heterogeneous polymer network (hydrogel) is formed, consisting of domains of highly crosslinked microgels which are connected by loosely crosslinked chains. This phenomenon is known as ‘microsyneresis’ [22]. For example, during the polymerization of 2-hydroxyethyl methacrylate (HEMA), if the amount of water present in the reaction mixture is more than 43 wt%, a turbid or opaque, heterogeneous pre-swollen PHEMA gel is formed. Its pores formed act as microreservoirs of large-molecular-weight solutes such as proteins or peptides, thus leading to interesting new drug delivery systems. If the amount of water present during polymerization is smaller than the water content corresponding to the equilibrium degree of swelling, the ensuing gel is non-porous. The only solute exclusion is due to the mesh created by the macromolecular chains.

2.2.3 Suspension polymerization

Suspension polymerization is a method to prepare spherical SAP microparticles with size range of 1 μm to 1 mm. In suspension polymerization, the monomer solution is dispersed in the non-solvent forming fine monomer droplets, which are stabilized by the addition of stabilizer. The polymerization is initiated by radicals from thermal decomposition of an initiator. The newly formed microparticles are then washed to remove unreacted monomers, crosslinking agent, and initiator. Some SAPs microparticles of poly(hydroxy ethyl methacrylate) have been prepared by this method. Recently, the inverse suspension technique has been widely used for polyacrylamide-based SAPs because of its easy removal and management of the hazardous, residual acrylamide monomer in the polymer [23].

2.2.4 Polymerization by irradiation

Ionizing high energy radiation, like gamma rays and electron beams, has been used as an initiator to prepare the SAPs of unsaturated compounds. Crosslinking takes place through the reaction between neighboring chains carrying free radicals. Examples of polymers crosslinked by the radiation method are poly(vinyl alcohol), poly(ethylene glycol) and poly(acrylic acid). The major advantage of the radiation initiation over the chemical initiation is the production of relatively pure and initiator-free SAPs. The other method is by using a bifunctional crosslinking agent which can react with the pendant functional groups of the polymer. The reaction is carried out in solution and crosslinking is achieved rapidly [24].

2.2.5 Crosslinking in superabsorbent hydrogels

There are two main types of crosslinking, bulk and surface crosslinking in most advanced SAPs. Network formation is caused by post-polymerization crosslinking or curing in the case of using a UV source. A bi-functional or multifunctional monomer is first mixed with the pre-formed polymer chains and a coupling reaction between the crosslinker and the functional groups on the preformed polymer is triggered by low temperature mixing, followed by heating. Ionic crosslinking and covalent crosslinking are the two different types of postpolymerization crosslinking.

a) *Bulk crosslinking*: Such a crosslinking of the polymer normally takes place during the polymerization stage of the monomer to form a network in which a crosslinking agent is actually a co-monomer with a higher functionality (generally bifunctional) than the main monomer. The reactivity ratio of the crosslinker and the monomer is very important. If the reactivity ratio of the crosslinker is higher than that of the monomer, it will react at low monomer conversion. On the other hand, if the reactivity ratio of the crosslinker is lower than that of the monomer, it will react at a high monomer conversion. Extractable product contains low molecular weight polymer chains that are not incorporated in the polymer network and can be readily extracted in excess liquid.

b) *Surface crosslinking:* This type of surface crosslinking is a new process that improves the absorbtion against the pressure profile of the polymer gel, such as for femini napkins. For the surface crosslinking reaction, surface treatmen is necessary. Because high swelling capacity is obtained, but poor absorbtion against pressure occurs due to low elastic gel strenght, caused by the low bulk crosslinking level.

Hydrogels can be prepared by other methods. For example, physical crosslinks including entanglements, charged complexes, junctions due to hydrophobic or specific interactions, or crystallites can lead to formation of hydrogels. Certain polymers such as poly(vinyl alcohol) can form crystallites. These crystallites act as physical crosslinks and prevent the gel from dissolving.

Linear polymers can form complexes due to hydrogen bonding or ionic interactions. For example, hydrogen bonding complexes are formed between the carboxylic acid groups of poly(acrylic acid) and the hydroxyl groups of polyethylene glycol. The resulting gel can act as a physical crosslinked network. Ionic interactions/bonding between the carboxylic acid groups of poly(acrylic acid) and poly(vinyl pyrrolidone) can lead to the formation of physical crosslinks. These crosslinks are temporary in nature and can be weakened or broken by changing the pH and/or ionic strength of the external swelling medium [25].

Interpenetrating polymer networks (IPN) are produced by first synthesizing a linear polymer, swelling it in a monomer and polymerizing the latter to form a mesh of two different polymers. The hydrophilicity /hydrophobicity of these IPNs can be controlled by a proper selection of the two polymers and by varying their composition. A classical example of IPN is a poly(acrylic acid)-polyethylene glycol system. IPNs can also be prepared by synthesizing simultaneously two polymers by different polymerization techniques such as condensation and free radical polymerization [26]. Semi-IPNs are synthesized by treating the polymer surface with a monomer or prepolymer and then forming a polymer or a crosslinked system on the surface. The major application of these systems is when a change of the surface characteristics of the polymers surface is required: e.g., when making the polymer surface biocompatible with an antithrombogenic character.

Various polymerization reactions can be used to control the properties of hydrogels networks. The hydrophilic/hydrophobic balance can be manipulated by choosing a proper combination of two monomers. The degree of crosslinking as well as the morphology of the polymer network can be altered or fixed by an appropriate reaction method. Other important characteristics can be controlled such as tacticity, i.e. the arrangement of ionizable and pendant groups as these are strong functions of the solvent, concentration and temperature.

2.3 Factors affecting the swelling of hydrogels

Hydrogels could be imbibe water via a combination of many mechanisms, physical entrapment of water via capillary forces in their macro-porous structure, hydration of functional groups and essentially dissolution and thermodynamically favored expansion of the macromolecular chains, which is limited by the crosslinkages [27].

When a dry hydrogel is brought into contact with a physiological fluid, the solution diffuses into the network and volume phase transition occurs, resulting in the expansion of the hydrogel. Diffusion involves the migration of the fluid into pre-existing or dynamically formed spaces between the hydrogel chains. Swelling of the hydrogels involves large segmental motion resulting, ultimately, in the increased separation of the hydrogel chains. The swelling behavior is followed by the degree of swelling, until thermodynamic equilibrium is reached. The swelling equilibrium occurs when the values of the osmotic

force driving the solvent into the network and of the of the elastic force of the stretched sub-chains become equal [28].
It is noted that important that important physical characteristics of hydrogels are linked to changes in specific environmental parameters such as temperature, pH, electric field, solvent quality, light intensity and wavelength, pressure, ionic strength, nature of ions in the swelling medium, and specific chemical triggers like glucose and biological fluids.

Salt concentration and charge valence significantly affect the swelling behavior of hydrogels. The presence of salts in the swelling medium is very important in biomedical applications. The great effect of salt on swelling behavior is a result of changes in the mechanical properties and matrix of the gel, which are responsible for different diffusion coefficients of drug release. A possible consequence of salt ions in the swelling medium is a change in osmotic pressure as a result the difference between the ionic concentration of the interior of the macroporous SAP and the external solution.

The effect of the concentration of sodium chloride solution on the swelling behavior of AMc–NMA superabsorbent hydrogels was investigated [29]. According to results, it was stated that the swelling ratio of hydrogel decreased in salt solution as the ionic concentration of the salt solution increased. This is attributed to the decrease in the expansion of the gel network because of repulsive forces of counter-ions acting as the polymeric chain shielded by the bound ionic charges. Therefore, the difference in the osmotic pressure between the gel network and the external solution decreased with increase in the ionic strength of the saline concentration.

Halide ions of any salt have a significant effect on the swelling ratio of hydrogels in terms of their sizes. An ion with a greater size in solution medium prevents diffusion into the interior of the gel and results in a decrease in ionic concentration, which in turn results generally in a higher swelling ratio than that of the other ions in the medium.

Cations that have ability of forming complexes with carboxylate groups in hydrogels leads to deswelling or contraction. For example according to experimental results of Mohan, Murthy and Raju Ca^{+2} and Fe^{+3} can form complexes hence had lower swelling ratios than did K^+ ionic medium. Because K^+ is not able to form comlexes hence normal swelling capacity.

SAPs/hydrogels that are pH responsive have found enormous applications in the drug delivery systems. The principle involved in drug delivery is the pH-controlled swelling of gel, which normally result in the relaxation rate of network chains of the gel by changing the pH of the medium. For example, an increase in swelling behavior of macroporous SAPs in pH 2-7 can be explained by the increase in the ionization of the carboxylic groups of ionizable functional groups on polymer backbone as the pH of the medium increased. The resulting anionic charged species in the hydrogels network repel each other, leading to relaxation of the hydrogel networks, responsible for easy penetration of water molecules into the hydrogel three-dimensional networks. As the alkaline medium increased beyond pH=7, the swelling behavior decreases because of the greater charge density in the hydrogel networks, which in turn prevents the entrance of water molecules.

2.4 Thermodynamics of polymer hydrogels

Thermodynamics may describe the swelling or collapse phenomenon observed when a polymer network is brought into contact with a swelling agent. The underlying idea is the interpenetration of the swelling equilibrium as equilibrium of the osmotic pressures inside and outside the gel. In the case of non-ionic gels, the swelling behavior is described in the form of two opposing free-energy contributions. The first is due to the polymer-solvent interactions which promotes swelling. The second contribution is due to elasticity of the network and opposes swelling. During swelling of ionic network electrostatic interactions play an additional important role.

2.5 Crosslinked structure of hydrogels and mechanical behavior

Effect of main-chain structure; The presence of flexible groups such as an ether link makes the main chain more flexible and reduces the glass transition temperature (Tg), whereas the introduction of an inflexible group, e.g. a terephthalate residue, increases Tg.

Influence of side groups; It is generally true that bulky, inflexible side groups increase Tg. In a similar way, increasing the length of the flexible side groups reduces the temperature of the main transition.

Effect of main-chain polarity; Tg increases with an increase in the main chain polarity. Presumably this is due to the increase in the intermolecular forces.

Effect of crosslinking; Increase in the degree of crosslinking increases Tg. For very highly crosslinked polymers there is no glass transition because they degrade before attaining glass transition temperature.

Effect of plasticizers; The major effect of a plasticizer (such as water) is to lower the Tg; essentially plasticizers make it easier for changes in molecular conformation to occur. Plasticizers also broaden the loss peak, and the degree of broadening depends on the nature of the interaction between the polymer and the plasticizer [30].

Increasing the water content weakens the mechanical strength of the hydrogel and may reduce its transparency as a result of macroscopic phase separation between water and polymer. To achieve high molecular strength and transparency while maintaining a high water content in a hydrogel, a composite structure at the molecular level is required. It consists of a hydrophobic component which contributes to the mechanical strength and a hydrophilic component which absorbs a large amount of water. Interpenetrating polymeric networks of N-vinyl-2-pyrrolidone, MMA, and cellulose acetate were synthesized and it was observed that these hydrogels had similar tensile strength but better water permeability than PHEMA. As the hydrophobic component in the IPN increased, the tensile strength of the IPN also increased, provided the degree of crosslinking remained the same. Therefore, by changing the IPN composition, they were able to synthesize a network with proper swelling characteristics and mechanical characteristics.

2.6 Application areas

The hydrogels have been used extensively in various biomedical applications, such as drug delivery, cell carriers and/or entrapment, wound management and tissue engineering.

2.6.1 Application of hydrogels in drug delivery

Hydrogels have been used for the development of controlled delivery systems for a long time. When the drug bearing hydrogel comes in contact with aqueous medium, water penetrates into the system and dissolves the drug. Diffusion is the main phenomena by which the dissolved drug diffuses out of the delivery systems to the surrounding aqueous medium. Hydrogels are 3-dimensionally crosslinked polymer networks and hence act as a permeable membrane for the drug thereby governing the release rate of the drug. The diffusion of the drug through the hydrogels may be affected by the property (such as pH sensitivity, light sensitivity, pressure sensitivity) of the hydrogel depending on the chemistry of the hydrogels and has been used successfully to design delivery systems which may release drug at a suitable environment.

Scientists are working on new strategies to develop delivery systems which can deliver the drug in a controlled manner. For the purpose, hydrogels suggest them a large variety of properties, such as, bio-adhesive and environment sensitive nature, to achieve the goal.

Hydrogels have already been successfully used to develop oral, rectal, ocular, transdermal and implantable drug delivery.

Neutralized poly(Methyl acrylic acid-co-methyl methacrylate) have been successfully employed for the delivery of liposome into the oral cavity [31].

2.6.2 Application of hydrogels in wound healing

As mentioned before, hydrogel is a crosslinked polymer matrix which has the ability to absorb and hold water in its network structure. Hydrogels act as a moist wound dressing material and have the ability to absorb and retain the wound exudates along with the foreign bodies, such as bacteria, within its network structure.

Additionally, hydrogels have been found to promote fibroblast proliferation by reducing the fluid loss from the wound surface and protect the wound from external noxae necessary for rapid wound healing. Fibroblast proliferation is necessary for complete epithelialisation of the wound, which starts from the edge of the wound. Since hydrogels help to keep the wound moist, keratinocytes can migrate on the surface. Hydrogels may be transparent, depending on the nature of the polymers, and provide cushioning and cooling effects to the wound surface. The main advantage of the transparent hydrogels includes monitoring of the wound healing without removing the wound dressing. PVA (poly vinyl alcohol) - clay nanocomposite hydrogels were employed in wound dressing [32].

2.6.3 Application of hydrogels in tissue engineering

Tissue engineering (TE) is a multidisciplinary area and involves the expertise of materials science, medical science and biological science for the development of biological substitutes (tissue/ organ). The principles of TE have been used extensively to restore the function of a malfunctioning tissues or organs. In practice, the patient’s cells are generally combined with a scaffold for generating new tissue. A scaffold can be made up of either ceramic or polymer, which can be either permanent or resorbable. The scaffolds made up of polymers are generally hydrogels. Every year thousands of people are victims of tissue loss and organ failure caused either due to disease or trauma.

In recent years use of resorbable hydrogels in TE has gained much importance because (a) it is easy to process the polymers; (b) the properties of the hydrogels can be tailored very easily; and (c) resorbable polymers like polylactic acid (PLA), polyglycolic acid (PGA), and their co-polymers (PLA-co-PGA; PLGA) are being used for biomedical application since long time. Poly (lactic-co-glycolic acid) (PLGA) polymer foams are seeded with preadipocytes for the epithelial cell culture of the breast [33].

2.6.4 Application of hydrogels in gene deliver

Gene delivery is defined as the incorporation of foreign DNA particles into the host cells and can be mediated by viral and non-viral methods. The delivery of gene into the host cells by utilizing a virus uses the capability of a virus to incorporate its DNA into the host cells. For the purpose retroviruses and adenoviruses have been used. These viral vectors are used as they can provide efficient transduction and high gene expression. At the same time, the use of viral vectors is quite limited as they can produce immunogenic reactions or mutagenesis of transfected cells. Hence, scientists are tuning their interest towards the available non-viral techniques, which produces less complexity.

Recently researchers have begun the use of polymers, for example poly-L-lysine (PLL), polyamidoamine dendrimer (PAMAM), polyethylenimmine (PEI), PGA, PLA and PLGA, for gene delivery. Though PAMAM and PEI can provide high transfection efficiency, their use is limited due to their poor degradability. This is why the use of biodegradable polymers, such as PLA, PLGA and PGA, has gained importance.

2.6.5 Application of hydrogels in agriculture

Drought is a great problem in agricultural production as it restricts normal plant growth, brings about enormous economic loss and deteriorates ecological environment. There is an increasing tendency in research to promote water-saving agriculture by means of integrated systems, such as water – saving technologies and appropriate agriculture managements. In recent years, some chemicals are being applied in agriculture as additives to improve water retention. Super-absorbent polymers (SAPs)/hydrogels are one type of developed chemical water-saving agents.

There are mainly two types of SAP, polyacrylamide and polyacrylate polymers, being widely used in agriculture and forestry industry. Water absorbing polymer gels work by absorbing high quantities of water, in addition to beneficial nutrients, and then slowly releasing the water through osmosis. When mixed into the soil, the gel polymers come in direct contact with the roots of the garden plants and grass, thus making the water easily available to the plants. This translates to extremely efficient use of water in the landscaping or with the potted plants. In addition to storing water and reducing water use in the agriculture uses, water absorbing polymers have other benefits. Because they expand and take up space in the soil, they can help with soil aeration and soil porosity. If the agricultural areas have clay soils, gel polymers can help increase soil porosity and the amount of oxygen in the soil. Gel polymers are not affected by extreme weather conditions or soil compaction

2.7 Synthesis of superabsorbent hydrogels

2.7.1 Free radical polymerization

In practice, polymerization of simple alkenes is more often initiated by a free radical than it is by a proton. Regardless of the initiator, the basic chain reaction mechanism applies.
Fig. 2.3 reviews the process which most often begins with the homolytic cleavage of the O-O bond of organic peroxide.

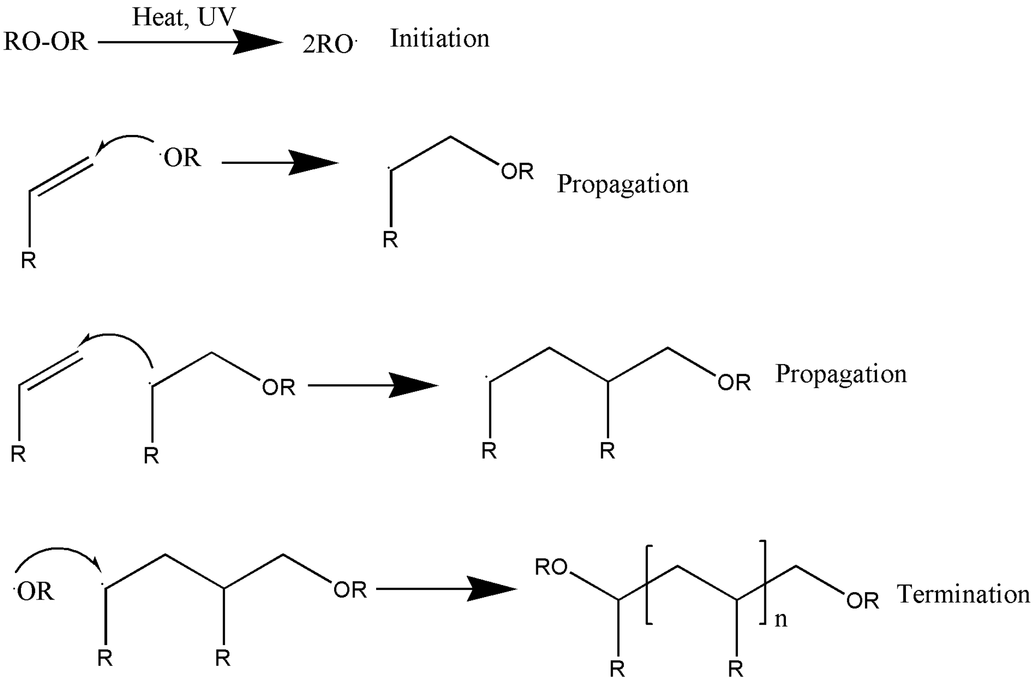
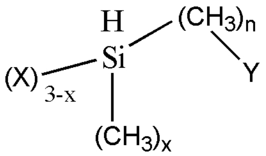


Figure 2.3 Proposed mechanism for free radical polymerization.

2.8 Chemistry of Organofunctional alkoxysilanes

The general formula of an alkoxy silane shows two classes of moieties attached to the silicon atom:



X= MeO-,EtO-,iPrO-,Cl-,-OAc,...
x=0,1,2
Y=-NH2,-NHCH2CH2NH2, epoxy,-SH,
-NCO,methacryloxy
n=1,3,4....

Figure 2.4 General formula of an organofunctional silane.

Organofunctional silanes, characterized by both organic functional groups and an inorganic reactive prone to hydrolysis, are commercially used since the 1950's and demand is growing steadily. Major applications fields of organofunctional silanes are filler/material treatmen and utilization as adhesion promoters or crosslinkers, respectively. This large range of applications relies on the biofunctionality of the organofunctional silanes, giving rise to the possibility to form chemical bonds to the both inorganic and organic substrates and also between two organofunctional silane molecules [34].

Alkyl and aryl silanes are utilized to improve gloss, hiding power, mixing time, and other properties related to improved pigment dispersion. Alkyl and aryl silanes are also utilized to provide hydrophobic surfaces in applications such as water repellents. The X represents alkoxy moieties, most typically methoxy or ethoxy, which react with the various forms of hydroxyl groups and liberate methanol or ethanol. These groups can provide the linkage with inorganic substrates, pigment, or filler to improve coating integrity and adhesion. The methoxy groups are also capable of reacting with hydroxy functional polymers.

Reaction of these silanes involves four steps (see Figure 2.5). Initially, hydrolysis of the alkoxy (X) groups occurs. It is after the first and second alkoxy groups are hydrolyzed that condensation to oligomers follows. Compared to the hydrogen of a carbinol moiety, the silanol hydrogen is more electrophilic and much more reactive. This is due to the larger, more electropositive, atomic structure of silicon which results in a high dipole moment for the silanol group and greater hydrogen bonding. The tendency toward self condensation can be controlled by using fresh solutions, alcoholic solvents, dilution, and by careful selection of pH ranges.

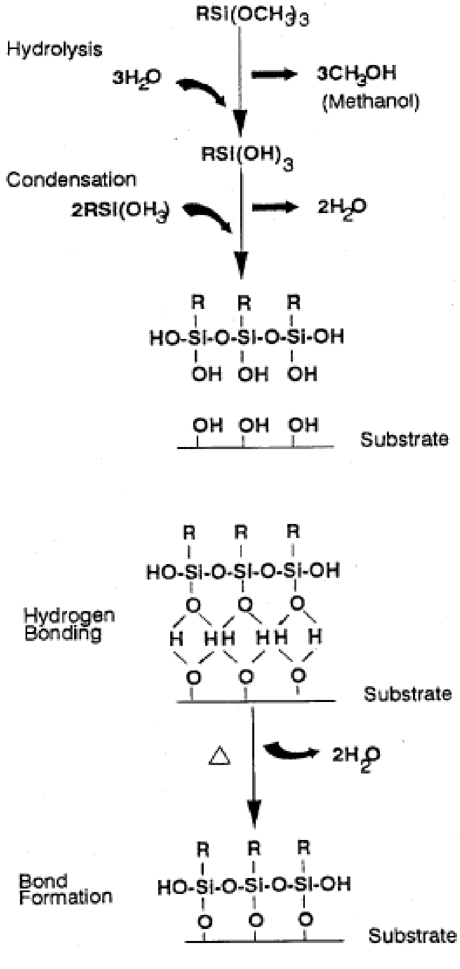


Figure 2.5 Reaction Process of alkoxysilanes.

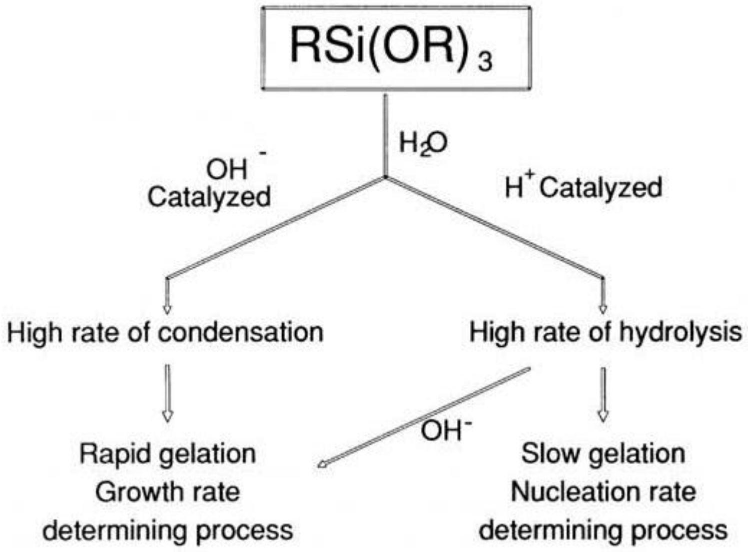


Figure 2.6 Effect of pH on alkoxysilane hydrolysis [36].

Effect of pH on alkoxysilane hydrolysis is shown schematically in fig. 2.5. Commercially important reactions at the organosilicon moeity can be divided into two categories , namely hydrolysis and condensation which are displayed in fig. 2.7. These reactions are both reversible, many of them being equlibria with the substantial concentration of both products and reactants present under typical conditions unless by-products liberated are removed from the equilibrium or the products separate from the reaction medium, such as precipitation. In addition , the reaction scheme is complicated by the fact that both hydrolysis and condensation can occur at the same time w,th comparable reaction rates.

The rate with which the respective equilibrium is reached strongly depends on various parameters, such as Ph, temperature. In genral, the following simplfied statements can be made, with exceptions depending on the specific structures of the silane;

- In neutral medium, the hydrolysis rate of alkoxysilanes show a minimum.
- Under basic conditions below pH 10, hydrolysis of the first alkoxy grouıps is the rate determining step and a S_N2 mechanism is possible at –Si moeity.
- In acidic medium, hydrolysis of the first alkoxy group is fast compared to the hydrolysis of further alkoxy groups present in the molecule. The hydrolysis rate

strongly depends on the kind of the leaving group with hydrolysis rate decreasing in the order MeO→EtO→$MeOCH_2CH_2O$-

- The rate of condensation of silanols strongly depends on the substution pattern at silicon: Trisilanols show a condensation rate minimum at about pH 4, whereas disilanols are most stable at about pH 6.Finally, monosilanols show a rate minimum at about pH 6.5-7.
- Under acidic conditions, hydrolysis in most cases is faster than condensation. In contrast, in basic medium condensation of partially hydrolyzed alkoxysilanes may occur prior to complete hydrolysis.

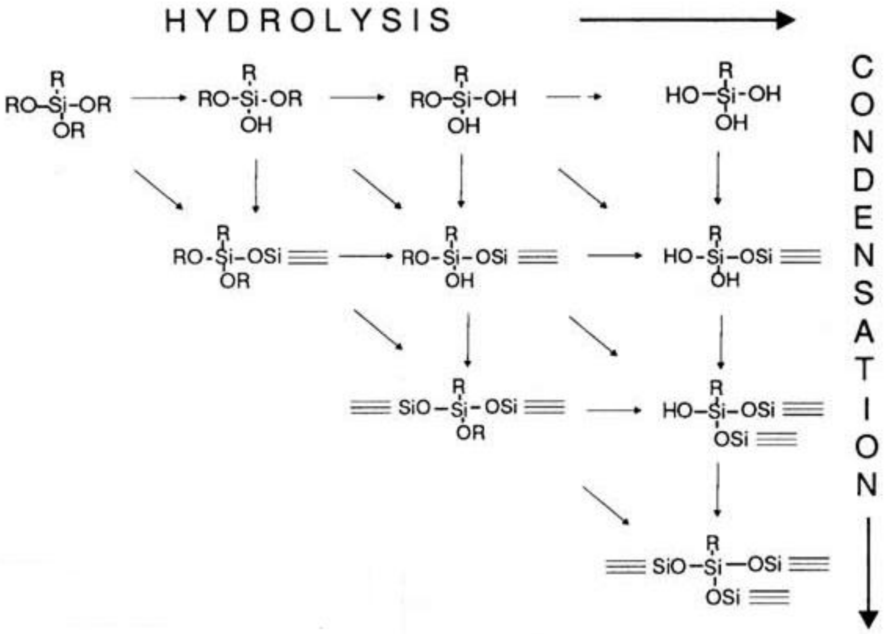


Figure 2.7 Possible hydrolysis and condensation pathways of tetrafunctional alkoxysilanes.

The possible hydrolysis and condensation pathways of a tetrafunctional alkoxysilane are displayed in fig. 2.12. The overall pathway for the hydrolysis and full condensation of an alkoxysilane is complicated. There are possible six hydrolysis paths and 21 possible water producing condensations and 36 possible alcohol producing reactions [35].

CHAPTER 3

3. Experimental

This chapter contains experimental processes used in this thesis work. This part covers the Free Radical Solution Precipitation polymerization of superabsorbent hydrogels based on different vinylalkoxysilanes as crosslinker and characterization with Differential Scanning Calorimetry, Simultaneous Thermal Analysis, ^{1}H NMR spectroscopy, ^{29}Si-NMR spectroscopy. Additionally, functional groups determination of synthesized polymers with FTIR, Elemental Analysis, Molecular Weight determination with Dilute Solution Viscometry and Linear viscosity values from Brookfield Viscometry were covered in this section.

3.1 Materials

For the synthesis of superabsorbent hydrogels, the specific chemicals and structures properties required are listed and tabulated below.

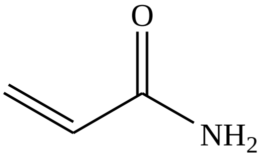
Compound	**Physical State at RT**	**Property**	**Molar mass (g/mol)**	**Tm (^{0}C)**	**Tb (^{0}C)**	**Density (g/cm^3)**
Acrylamide (AMc)	White powder crystals	monomer	71.08	Poly.	-	1.13
2-Acrylamido-2- methylpropane-1-sulfonic acid (AMPS)	White powder crystals	comonomer	207.25	195	-	1.1
Benzoylperoxide (BPO)	White powder crystals under 10 ^{0}C	Free radical initiator	242.23	103	-	1.334
Dimethylacetamide (DMAc)	Colorles liquid	Solvent^A	87.12	-	165	0.937
Dimethylformamide (DMF)	Colorles liquid	Solvent ^{B}	73.09	-	152	0.948
Vinyltrimethoxysilane (VTMS)	Colorles liquid with aromatic odor	Crosslinking agent^1	148.23	-	123	0.968
Triethoxyvinylsilane (TEVS)	Colorles liquid with aromatic odor	Crosslinking agent^2	190.31	-	161	0.903
Tris(2-methoxyethoxy)vinylsilane (TMEVS)	Colorles liquid with aromatic odor	Crosslinking agent^3	280.39	-	136	1.034
Acetic acid (AcOH)	Colorles liquid with vinegar odor	Acid catalyzing agent	60.05	16	118	1.049

Table 3.1 Monomers and chemical agents used in polymerization procedures.

Tm: Melting point, Tb: Boiling point under normal conditions.

A, B; Polar aprotic solvents 1, 2, 3; Three different vinylalkoxysilane crosslinker

- **Monomers**


acrylamide

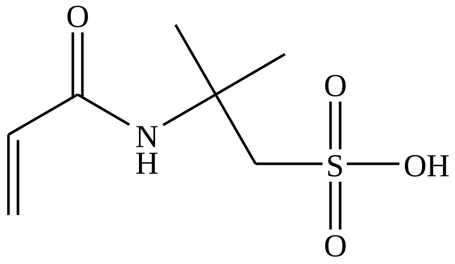

2-acrylamido-2-methylpropane-1- sulfonic acid

Table 3.2 The chemical structures of the monomers used in polymerization. Acrylamide (≥99% HPLC) and AMPS (≥99%) were purchased from Sigma Aldrich and used without any further purification.

- **Free Radical Initiator**

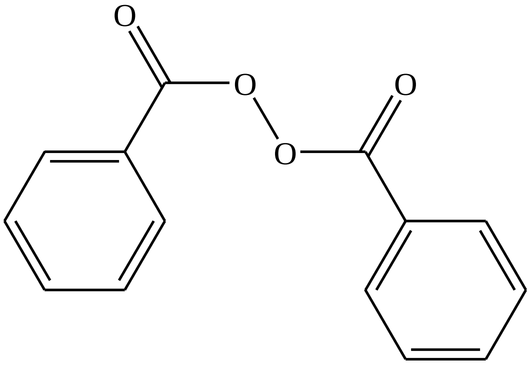
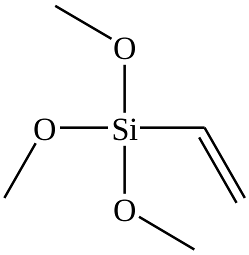
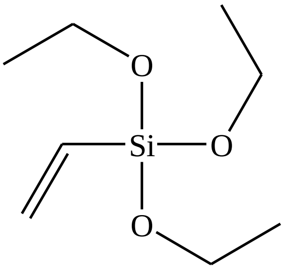

Benzoylperoxide

Table 3.3 The chemical structure of a thermally decomposable free radical initiator. Benzoylperoxide (≥97% moistened with water) was purchased from Sigma Aldrich and used without any further purification.

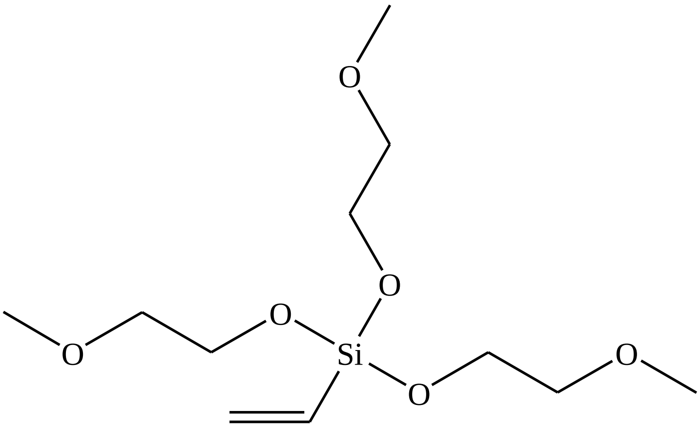
- **Crosslinking agents**



Vinyltrimethoxysilane



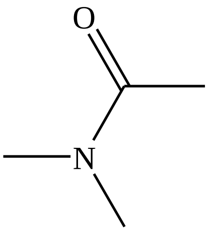
Triethoxyvinylsilane



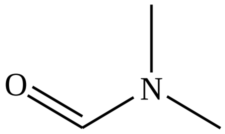
Tris(2-methoxyethoxy)vinylsilane

Table 3.4 The chemical structures of different vinylalkoxysilane crosslinking agents. Crosslinking agents, Vinyltrimethoxysilane (VTMS) (98%), Triethoxyvinylsilane (TEVS) (97%) and Tris(2-methoxyethoxy)vinylsilane (TMEVS) (98 %) were purchased from Sigma Aldrich and used without further purification.

- **Solvents**



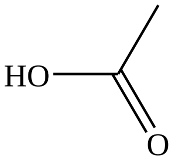
Dimethylacetamide



Dimethylformamide

Table 3.5 The chemical structures of polar aprotic solvents used in polymerization reactions. Dimethylformamide (DMF) and Dimethylacetamide(DMAc) were purchased from Merck Millipore and used without further purification.

- **Organic acid**



Acetic acid

Table 3.6 The chemical structure of acid hydrolyzing catalyzing organic acid. Acetic acid was purchased from Merck Millipore and used without further purification. Chemicals were used as received without any further purification.

3.2 The Synthesis of Superabsorbent Hydrogels

Predetermined amounts of acrylamide (AMc) and 2-acrylamido-2-propanemethyl-1-sulfonic acid (AMPS) monomers are dissolved in approximately 20 ml of Dimethylacetamide (DMAc) in a 50 ml beaker supplied with a magnetic fish and let to dissolve completely on a magnetic stirrer for 20 minutes. After all monomers are dissolved and clear transparent solution is obtained, 0.2 ml (0.194 g) of Vinyltrimethoxysilane (VTMS) is added by using a micropipette. After addition of crosslinker, VTMS, the whole solution must be well mixed prior to the N_2(g) purge. The colorless transparent solution is then transferred into a three necked 100 ml round bottom flask (rbf) and connected to condenser apparatus which is in a connection with water supply.

The reaction bottle is purged for 15 minutes with a highly pure nitrogen in order to provide a oxygen and air free environment while stirring. After thoroughly purging the reaction flask, about 0.0525 g of Benzoylperoxide (BPO) weighted, dissolved in 5 ml of DMAc and injected into reaction mixture after the reaction mixture has been already set down in a silicon oil bath.

Finally, after all constituents are added and nitrogen has been purged, reaction flask which is connected to water condenser apparatus, begins polymerization while refluxing, at 80 ^{0}C for 3 hours. While the reaction is undergoing, about 30 minutes later, a clear transparent monomer mixture is turned to white cloudy heterogeneous solution, indicating the successful completion of the polymerization reaction. While polymer chains are formed, they are insoluble in DMAc, and hence precipitating out as white fine powder, after about one hour. Although the polymerization reaction is about to finish, it is necessary to run the reaction for a full 3 hours while refluxing in order to increase the polymerization yield and complete the reaction properly.

After the reaction flask is removed, there is a wet white precipitated product in the solvent. Since monomers are soluble in DMAc, but synthesized polymer is insoluble in any solvent except water, it is required to remove the unreacted monomers from the product. In order to obtain a highly pure product, wet precipitated product is first filtered through an ordinary suction filtration, and then the solvent free product is washed thoroughly with DMAc two times well and for each washing out procedure, polymer - solvent mixture is filtered and washed with solvent again.

Monomer and any impurity free, wet polymer is next subjected to an evaporation procedure in order to remove all residual solvent. The temperature is kept constant at 100 ^{0}C, over one night in vacuum furnace and one night under a constant temperature 100 ^{0}C. Hence as a result of this careful drying-out process, white powder samples were obtained.

3.4 Equilibrium Swelling Ratio (ESR) Measurements

To measure the equilibrium swelling ratio (ESR) of the obtained polymer, it is necessary to form thin homogenously crosslinked films. In order to form films, it is necessary to dissolve the already purified powder polymer in distilled water in weight percentage in which, 0.12 g of fine powder product is to 2 ml of water, hence obtaining 6% (wt/ ml) in a 50 ml beaker.

When adding distilled water in weighted polymer, initially a sudden gelation takes place, because of the highly hydrophilic nature of the polymer chains adsorbed most of the water molecules and as a result a gely-like substance has been formed. In order to expand the long polymeric chains, a mechanical force is needed, so vigorous stirring with a magnetic stirrer supplied with magnetic fish, enables a slightly viscous clear colorless solution be prepared.

A prepared 6% (wt/ml) solution is casted in 3×5 mm×mm Teflon plates and left overnight at 80 ^{0}C to crosslink the long polymer chains through hydrolysis and condensation reactions of alkoxysilanes groups, respectively or conqueratly. Because the formed films do not adhere to Teflon, removal is much easier with films or plastic plates.

The swelling ratio measurements of hydrogels can be done through various methods, for our work a gravimetric one is applied. Casted film samples are broken into small pieces and initially the weight of the dry sample is measured via a electronic balance, and the weighted sample is then dipped into distilled water For the sample to reach its equilibrium swelling capacity 24 hours must pass. After this period, the swollen sample is collected through simple steel sieve and a few seconds later, any remaining traces of unabsorbed water are removed from the hydrogel for accurate weighing.

Equilibrium swelling ratio can be calculated according to following formula;

ESR= $\frac{Ws-Wd}{Wd}$ where Ws stands for the weight of the swollen sample and Wd stands for the weight of the dry sample at 23 ^{0}C.

We use the gravimetric method in which time-dependent records are taken at every hour, so as to observe the degree of swelling of the hydrogel sample.

This procedure is applied in its entirety to polymer synthesis and work-up except for changing the crosslinker and crosslinker ratio for the already synthesized terpolymer, Poly-1, Poly-2, Poly-3,Poly-4, Poly-5 and Poly-6 and their derivatives.

In this work, three control parameters were studied. These are;

1) Different polar aprotic solvent effect
2) Different vinylalkoxysilanes as cross linker
3) Effect of acid catalysis

3.5 Flowchart for Polymer synthesis and Work-up

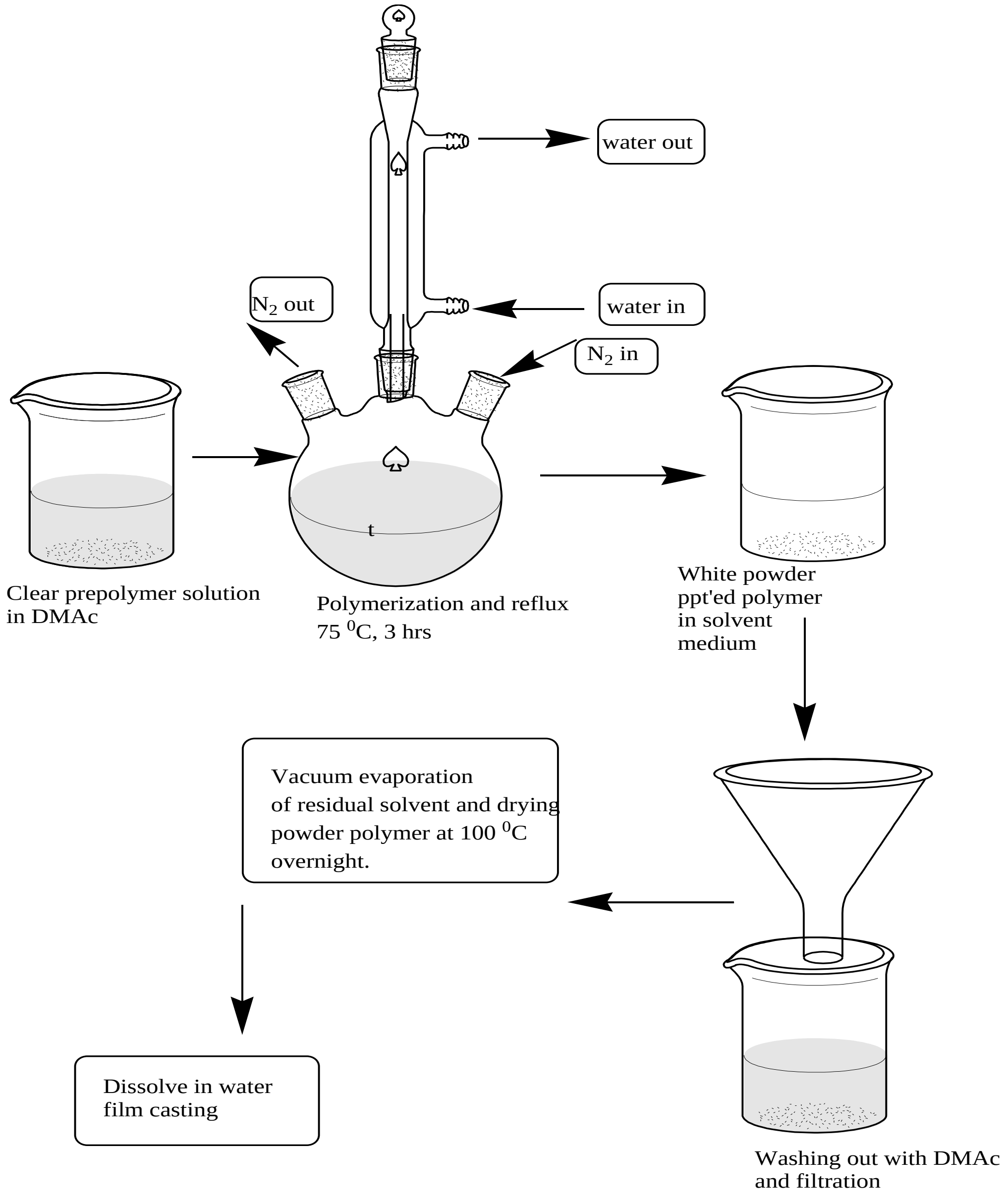


Table 3.7 The effect of use different crosslinker agents in DMAc medium.

Polymer	AMc (g)	AMPS (g)	VTMS (ml)	TEVS (ml)	TMEVS (ml)	BPO (g)	T (^{0}C)	Time (hrs)
Poly-1	4.0124	1.0213	0.200	-	-	0.0565	75	3
Poly-2	4.0023	1.0312	-	0.275	-	0.0554	75	3
Poly-3	4.0201	1.0241	-	-	0.352	0.0536	75	3

Table 3.8 The effect of different crosslinker agents in DMF medium.

Polymer	AMc (g)	AMPS (g)	VTMS (ml)	TEVS (ml)	TMEVS (ml)	BPO (g)	T (^{0}C)	Time (hrs)
Poly-4	4.0084	1.0012	0.2	-	-	0.0527	75	3
Poly-5	4.0041	1.0231	-	0.275	-	0.0557	75	3
Poly-6	4.0078	1.0057	-	-	0.352	0.0536	75	3

Table 3.9 Control experiments for polymerization work in DMF medium.

Polymer	AMc (g)	AMPS (g)	VTMS (ml)	TEVS (ml)	TMEVS (ml)	BPO (g)	T (^{0}C)	Time (hrs)
Poly-7	4.0011	-	0.2	-	-	0.0525	75	3
Poly-9	4.0034	-	-	-	-	0.0527	75	3
Poly-11	4.0000	1.0051	-	-	-	0.0556	75	3

Table 3.10 Hydrogel synthesis with DMAM in DMAc.

Polymer	DMAM (g)	AMPS (g)	VTMS (ml)	TEVS (ml)	TMEVS (ml)	BPO (g)	T (^{0}C)	Time (hrs)
Poly-12	5.5708	1.0125	0.2	-	-	0.0528	70	3
Poly-13	5.5786	1.0413	-	0.275	-	0.0539	70	3
Poly-14	5.5723	1.0602	—	-	0.352	0.0581	70	3

Table 3.11 Effect of crosslinker agent on swelling under constant monomer concentration.

Crosslinker ratio	Moles %	Weight %	Moles	Weight(g)
1	2.080	3.730	1.300	0.194
2	4.090	7.200	2.610	0.388
3	6.020	10.42	3.920	0.582
4	7.890	13.43	5.235	0.776
5	9.670	16.24	6.540	0.970

3.6 Characterization

Various characterization techniques were implemented to examine the superabsorbent hydrogels based on different vinylalkoxysilane as crosslinker. Amongst these 3 vinylalkoxysilanes, the only variant occurs in the existence of alkoxy groups. These groups possess different chain lengths which constitute the subject of enquiry of this research. Each chain length provides us information regarding different hydrolysis and condensation properties. Such properties determine the rate of the hydrolysis and condensation and consequently the application of such vinylalkoxysilanes. Thus, various thermal and molecular characterization techniques were applied to understand these behaviors.

Simultaneous Thermal Analysis was then chosen to determine the thermal behavior of superabsorbent hydrogels in white powder state. Measurements were performed on a Netzsch STA 449 C Jupiter differential thermogravimetric analyzer (precision of temperature measurement ±2^{o}C, microbalance sensitivity <5 μg) under N_2 atmosphere with a flow rate 50 ml/min, at a linear heating rate of 10^{o}C/min.

The infrared spectrum of superabsorbent polymers in powder state was obtained using a Thermo scientific Nicolet IS10 FTIR spectroscopy to observe the surface functional groups of the samples. The ATR mode was used with Smart ITR diamond ATR and samples were scanned between wavenumbers (cm^{-1}) 4000 and 600.

VISTA PRO-CCD Simultaneous ICP OES was chosen for Carbon and Nitrogen elemental analysis. Temperature was kept at 1000 K during analyses; this technique affords the recording of results in the weight percentage.

Structural properties of polymeric samples were studied with ^{1}H NMR and Si^{29} an Inova 500 MHz NMR Varian spectrophotometer.

A heat-flux-type Differential Scanning Calorimetry (TA Instruments Q2000) examined the main thermal transitions and properties of powdered polymeric samples. Measurements were performed on TA Instruments Q2000 DSC 204 C differential scanning Calorimetry (precision of temperature measurement ±1^{o}C, microbalance sensitivity of between 6 and 12 mg under N_2 atmosphere with flow rate 50 ml/ min, at a linear heating rate of 10^{o}C/min.

To study the linear viscosity values of prepared standard solutions of superabsorbent polymeric samples, Brookfield Viscometery DV–III model was used. The precision of model used was between 0.5 and 2 ml, torque accuracy up to 15% of the full scale range.

The molecular weight values of synthesized polymeric samples were calculated based on the principles of a Dilute Solution Viscometry experiment and Ubbolehte (Capillary Viscometry) technique employed.

CHAPTER 4

4. Results and Discussion

4.1. Superabsorbent (SAPs) polymer synthesis

Properties and feasible application routes of superabsorbent hydrogels as a common material for different types of applications have great importance for performance of the material. Because of this importance, many studies were done as in the literature to characterize produced SAPs and to achieve well controlled synthesis procedures. SAPs and powder samples were analyzed with DSC, STA, FTIR and ^{1}H NMR, ^{29}Si NMR, Elemental analysis. These characterization methods provide valuable information to understand chemical and macro scale structure, effect of synthesis parameters, thermal behavior and possible application potentials.

4.1.1 Chemical structures of synthesized SAPs

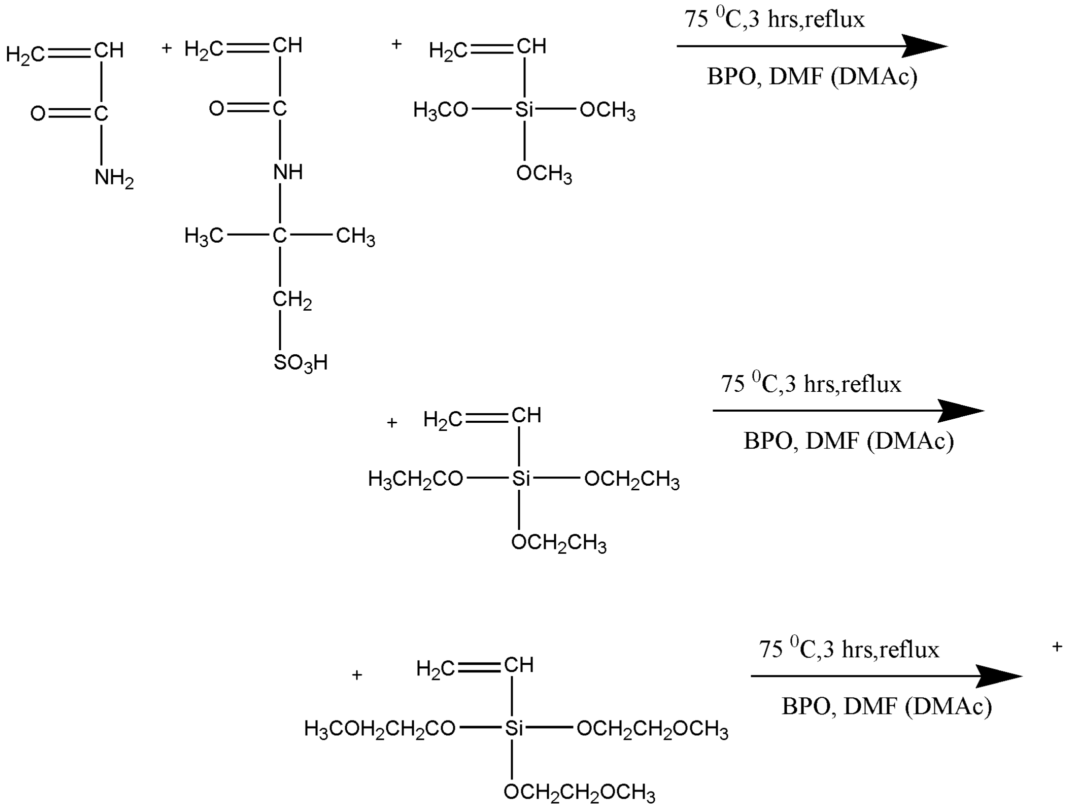
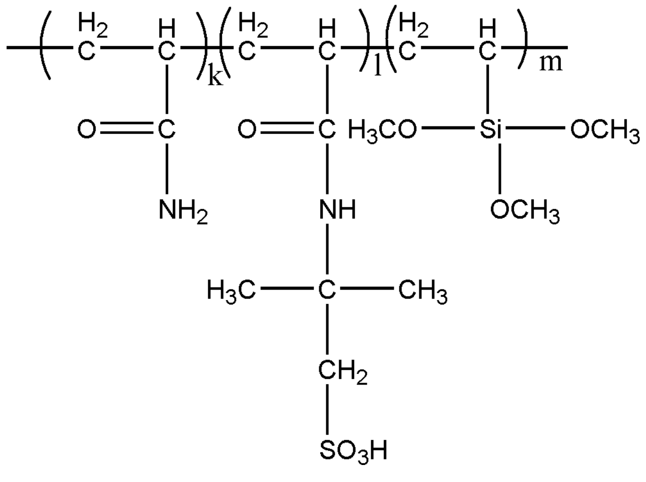


Figure 4.1 The Proposed scheme for the monomer mixture and reaction conditions used for powder SAPs samples.



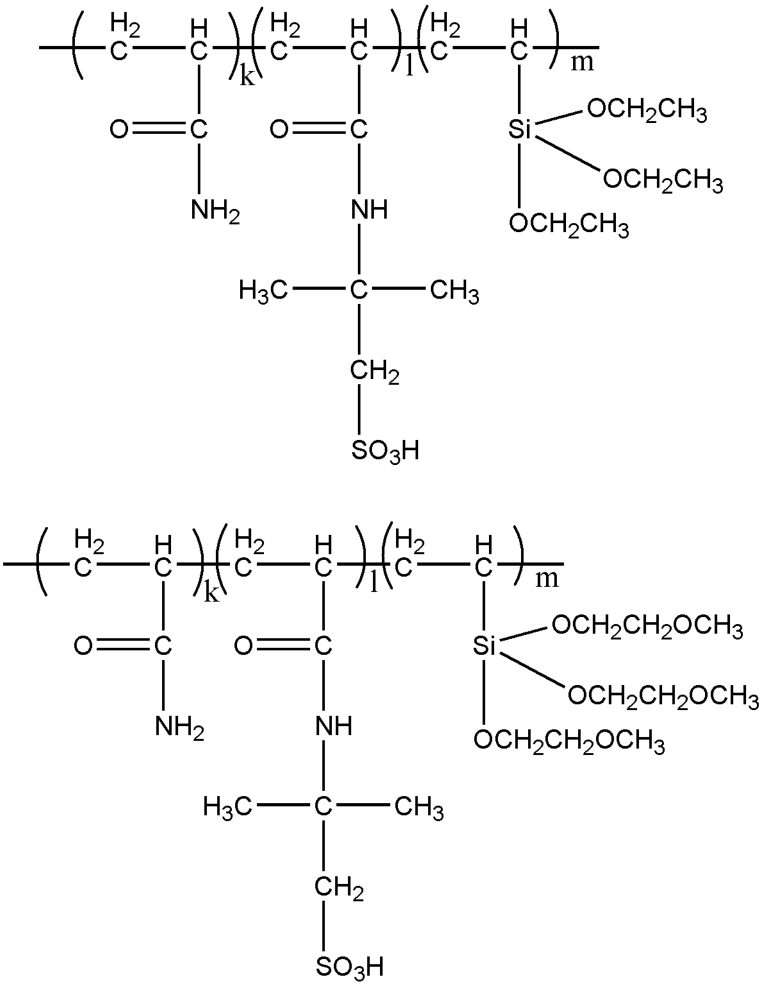


Figure 4.2 The Chemical structures for synthesized non hydrolyzed powder samples based on different vinylalkoxysilanes.

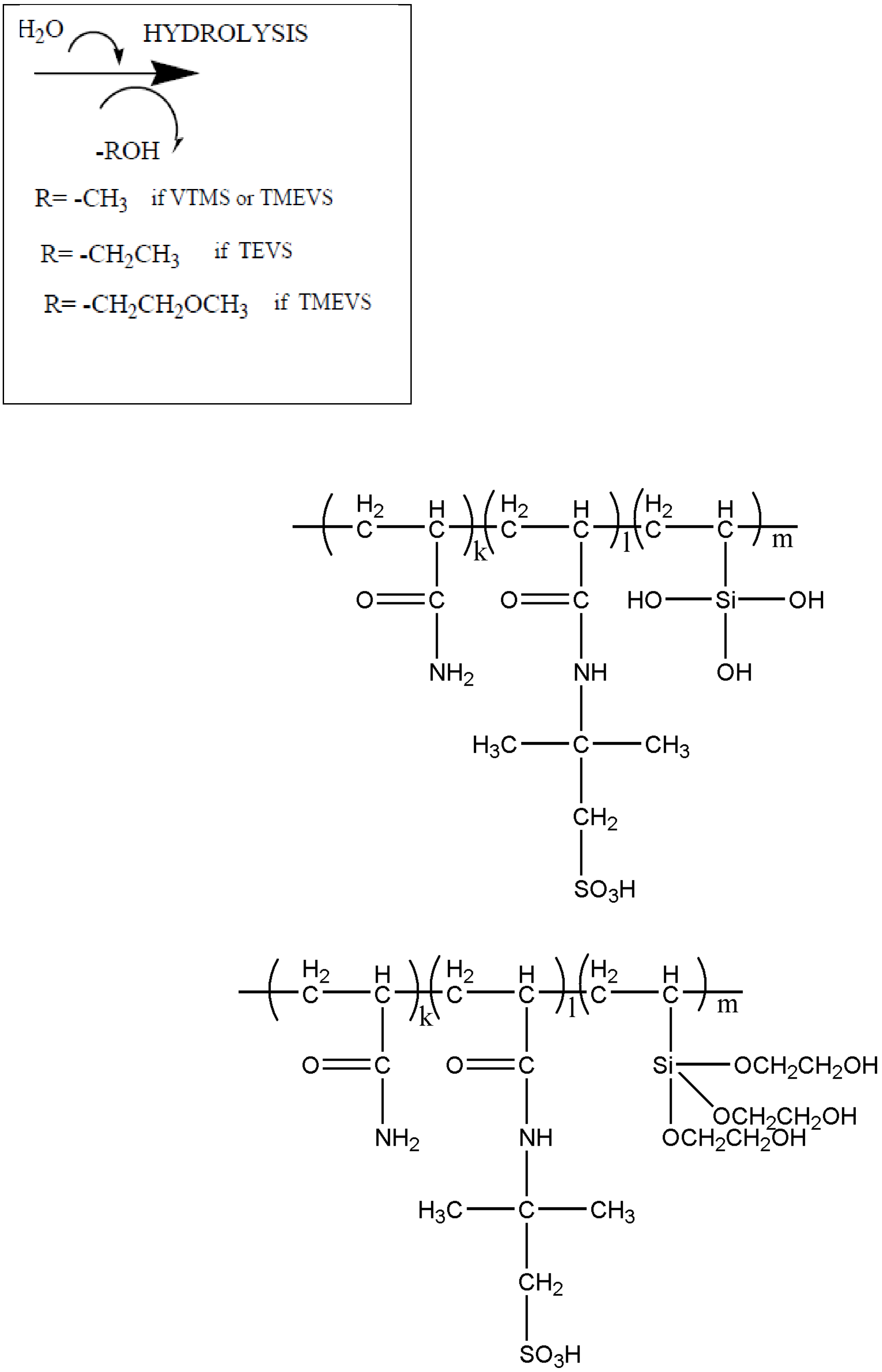


Figure 4.3 Chemical structures for hydrolyzed SAPs in an aqueous medium.

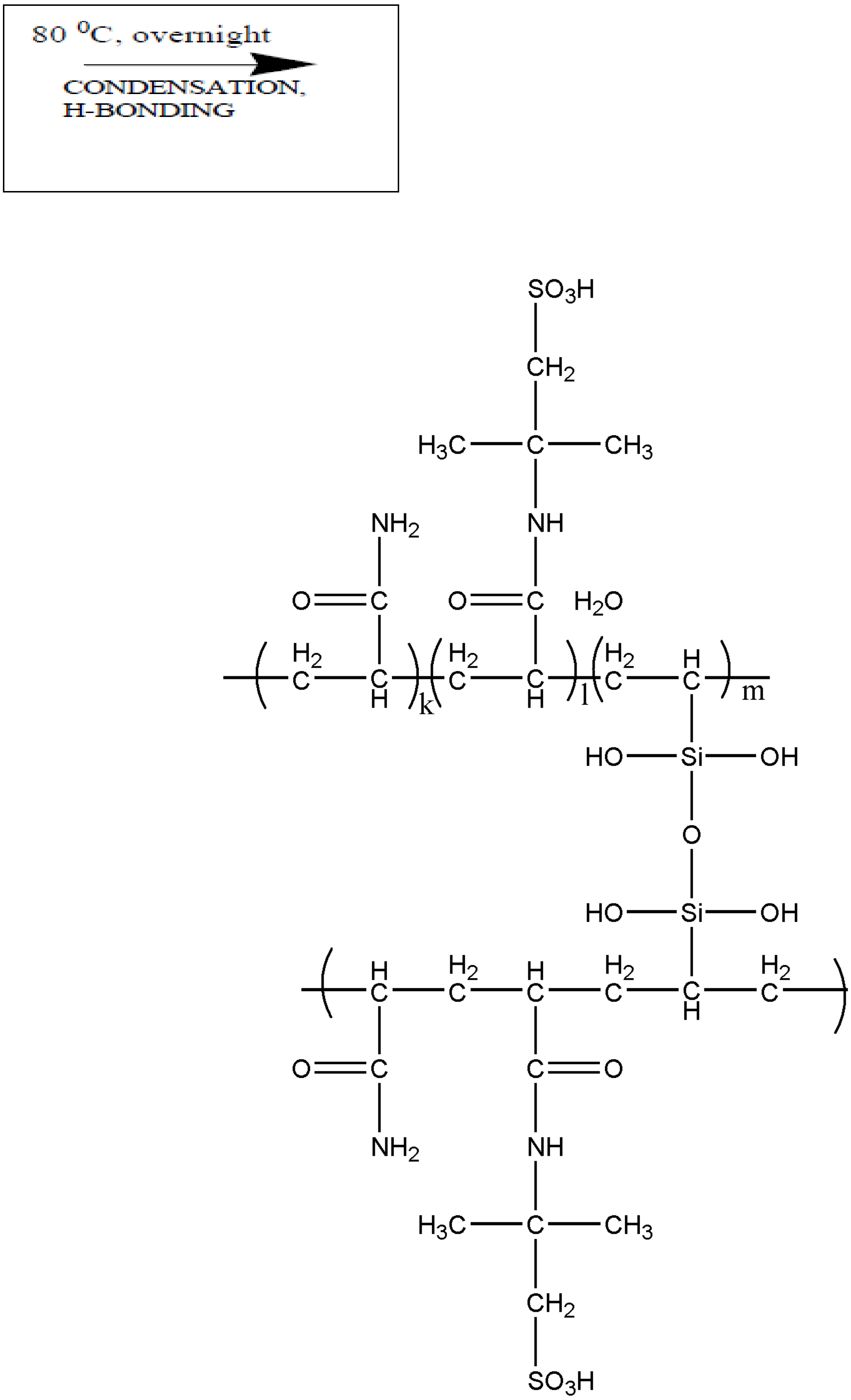


Figure 4.4 The Proposed chemical structures of crosslinked superabsorbent polymers in casted films.

4.2 Advantages of Applied Experimental Method

We have applied the free radical solution polymerization technique which is generally used for the synthesis of superabsorbent hydrogels. However, instead of water, we have employed an organic solvent have made use of organic (polar aprotic) solvent, because the non-crosslinked polymer chains precipitate out of such solvents. The end of the work up processes enables us to obtain powder samples which to be processed further. The rationale for such a choice lies in the ability of any polar solvent with hydrolyzing power to immediately to hydrolyze the alkoxy groups of vinylalkoxysilane used as crosslinkers. Without such an approach, we would have early cross-linked gel-like polymers which are insoluble in water and any organic solvent. Instead of water or any hydrolyzing solvent, we have, instead, used a polar aprotic solvent as a solvent system. In a polar aprotic solvent, monomers used are readily dissolvable and as a result a colorless clear monomer mixture can be obtained. During the polymerization, as polymerization takes place, formed polymers start to precipitate out as white fine powders.

After work-up processes which were described above, white powder samples can be processed.

4.3 Characterization of synthesized SAPs

By described procedures in the previous chapters, synthesized SAPs were characterized through characterization techniques. DSC, STA, FTIR and ^{1}H NMR, ^{29}Si NMR characterization were applied to SAPs in non crosslinked powder form, as well crosslinked film samples of the corresponding polymers were also characterized.

4.3.1 FTIR (FOURIER TRANSFORM INFRARED) analysis

FTIR characterization was applied in order to observe the presence of common functional groups in polymeric chains. FTIR analysis for both non crosslinked powder samples and crosslinked film samples monitored any change in functionality of the groups present in polymer chains.

In figure 5.2.1 we can see the main functional groups present on the linear polymeric chains. Peaks at 3327.60 and 3191.61 cm^{-1} are attributed to the stretching of –NH groups due to acrylamide unit; and additionally, the possible presence of –OH on sulfonic acid end group of the AMPS unit and –NH overlap might be also observed around this range. The peak observed around 2934.88 cm^{-1} is due to –CH stretching of on the main polymer backbone. Stretching modes for –CH around this range relatively are weak which is attributed to hindered stretching (motion) of polymer backbone and the capability of weak stretching on the pendant groups for any other –CH groups.

Peak observed at approximately 1650.88 cm^{-1} is a characteristic one due to –C=O (carbonyl) peak of polyacrylamide. Moreover, the carbonyl peak on the pendant AMPS units on polymer backbone overlapped with this peak. Characteristic peaks for –C-N groups on acrylamide are observed at around 1447 cm^{-1}. Peak around 1411 cm^{-1} is due to –NH_2 groups on acrylamide unit. Sulfonate end groups on AMPS produces peaks around 1037.67 cm^{-1} and this peak is a characteristic one for sulfonate groups. In the range of finger print it is possible to see –C-C- vibrations around 619.07 cm^{-1}.

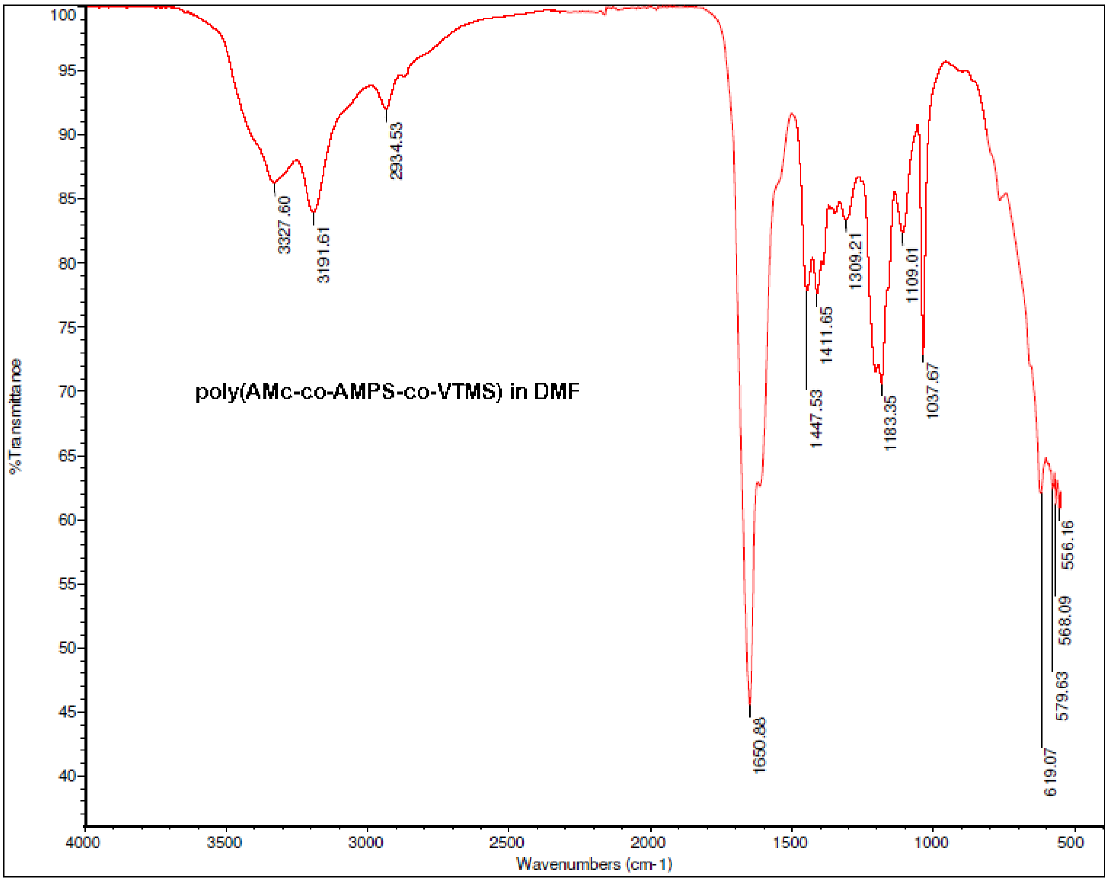


Figure 4.5 FTIR spectrum of poly(AMc-co-AMPS-co-VTMS) synthesized in DMF medium.

We expected to see –Si-O- peak around 1100 cm^{-1}, but when the spectrum was checked, we concluded that this peak is under the peak sulfonate group peaks. A further explanation for this conclusion is that, the possibility of a strong interaction between silane groups from alkoxysilane units and sulfonate groups prevents the formation of this characteristic peak, hence it is not possible to observe this characteristic peak. Finally, it is concluded that we observed the presence of all characteristic peaks of the common functional groups on the polymer backbone. Moreover, absence of any characteristic vinyl groups around 1600 cm^{-1} confirms the full integration of monomeric units into polymeric chains.

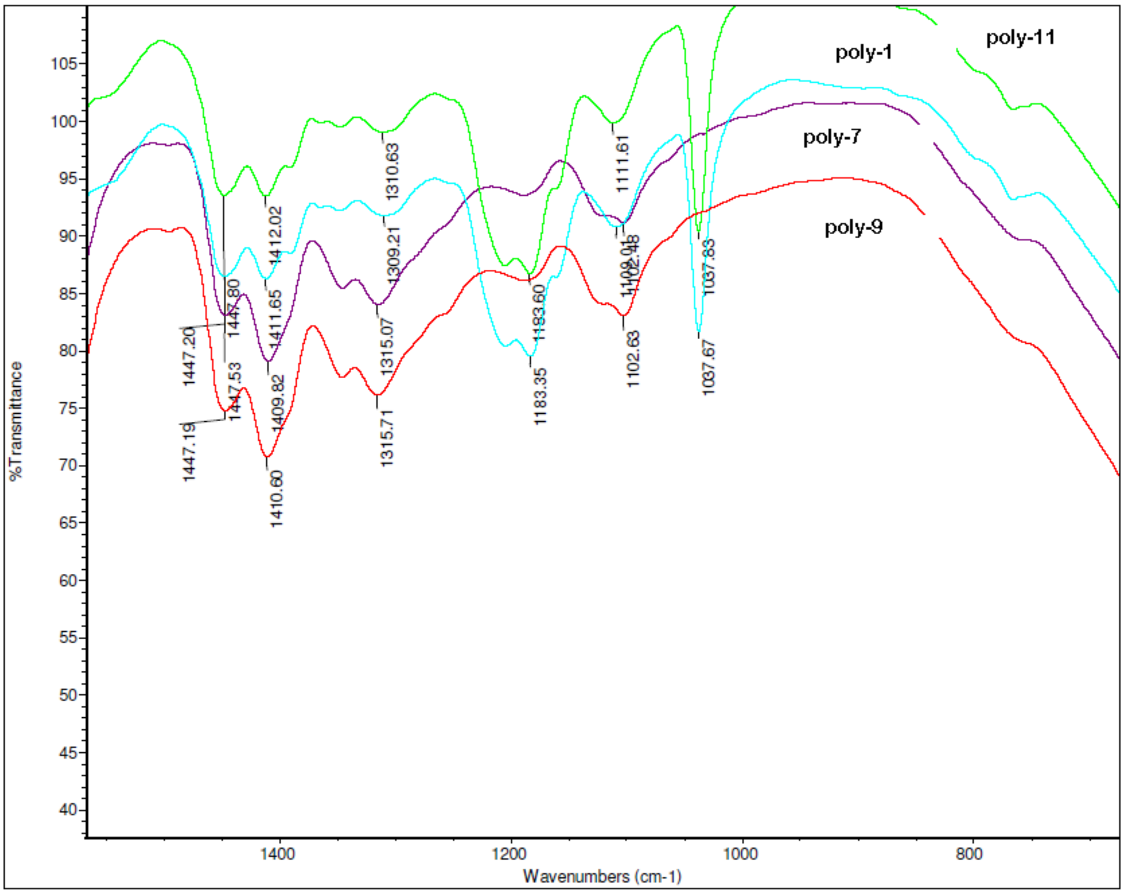


Figure 4.6 FTIR spectrums prepared polymers poly-11, poly-1, poly-7 and poly-9.

Poly-1 →poly(AMc-co-AMPS-co-VTMS)

Poly- 7→poly(AMc-co-VTMS)

Poly- 9→poly(AMc)

Poly-11→poly(AMc-co-AMPS)

Table 4.1 Abbreviations for polymers on the figure 4.7.

Figure 4.2 was prepared from the overlapping of polymers, poly-1, poly-11, poly-7 and poly-9 on the same spectrum in order to observe the main changes with respect to changing one of the component in the polymerization reaction while keeping the polymerization conditions same.

First of all, it is possible to observe the characteristic peaks sulfonate groups on the poly-1 and poly-11 around 1037 cm^{-1}. It is also reasonable to conclude that, peaks for silane groups coming from alkoxysilane units are overlap under the peak around 1100 cm^{-1} for those of polymers containing alkoxysilane crosslinking agents, poly-1 and poly-7. Fundamental peaks for all polymers depicted on the FTIR spectrum are same as discussed earlier. As a result it is reasonable to state that we could control our components in polymerization procedure and their integration into polymers.

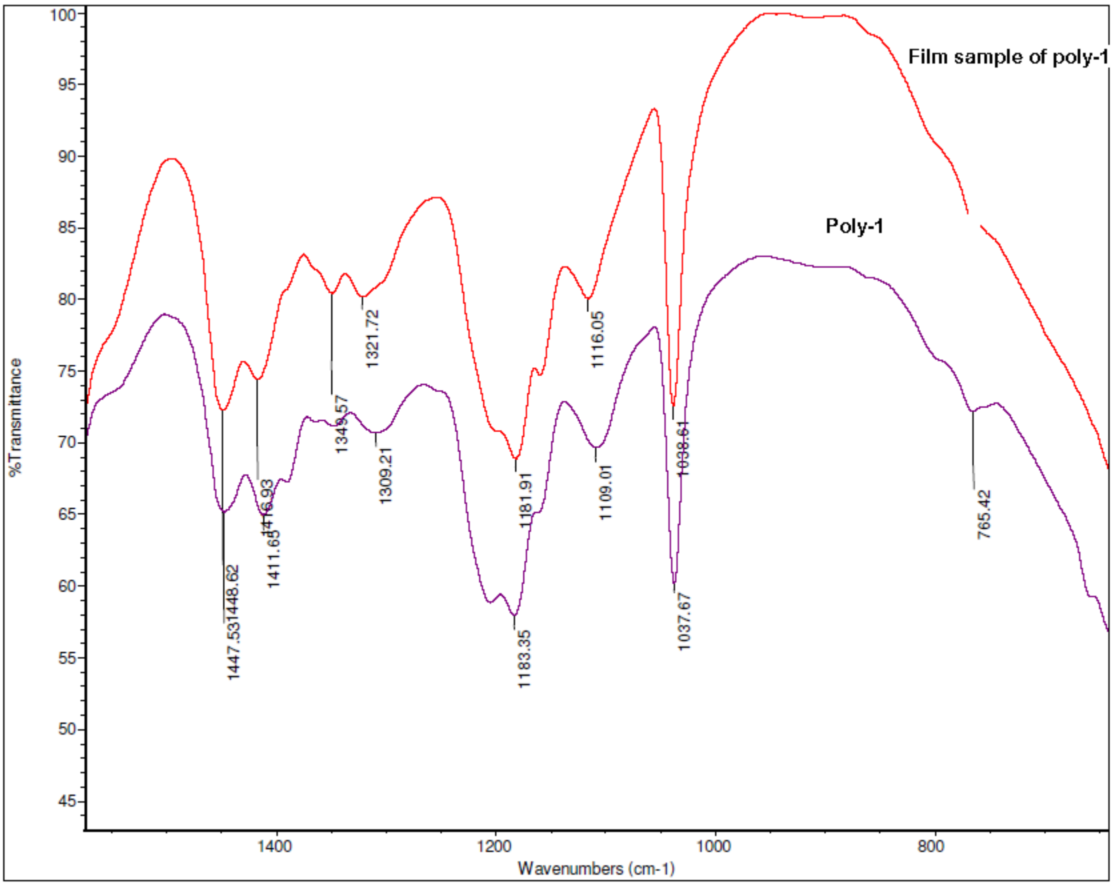


Figure 4.7 FTIR spectrum of overlaid spectrums of film sample of Poly-1 and powder form of poly-1.

The purpose of overlapping two spectrums of poly-1 in casted film and powder sample which is the non crosslinked polymeric sample, was to determine whether there is any fundamental change occurs during crosslinking. From these spectrums, we can conclude that there is no important change in functional groups during crosslinking which is attributed to the following two possible conditions; firstly two spectrums have almost the same functional groups presence and no fundamental change, hence polymer in powder sample is also slightly crosslinked, by film casting in aqueous medium the crosslinking density on the polymeric chains is enhanced, secondly, the presence of alkoxysilane groups on the polymeric backbone is not detectable in both casted film sample and non crosslinked powder sample.

4.3.2 Nuclear Magnetic Resonance Analysis

4.3.2.1 Monomer Reactivity ratios

In order to examine interaction of two monomers in copolymerization, a Proton NMR based analysis was done for the copolymerization of acrylamide(AMc) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and their reactivity ratios were then determined. Table 4.2 shows the two polymers with two different AMPS monomer feed under the same polymerization conditions. Corresponding Proton NMR spectrums of these prepared powder polymer dissolved in d-H_2O are depicted in figures 4.9 and 4.10, respectively.

The reactivity of monomers was determined by using the characteristic methylene peak due to pendant groups of AMPS which is observed around 2.70 ppm. The integral value of this peak to the overlapped peak due to polymerization observed around 2.00 ppm; a value which is corresponds to amount of AMPS units in the polymer chain. According to table 4.2 we already know the feed concentration of AMPS and AMc in prepolymer mixture; hence a reactivity ratio formula for nonideal polymerization gave the monomer reactivity ratios.

According to calculations, it was determined that monomer reactivity of AMc and AMPS are 1.32 and 1.25 respectively. It can be stated that both monomers have a higher tendency of reacting each other rather reacting with its kinds. For these free radical solution precipitation reactions, it is expected to observe random polymerization.

Table 4.2 Change in AMPS content with respect to AMc in polymerization.

Polymer	AMc (g)	AMPS (g)	BPO (g)	DMF (ml)	Time (hrs)	Temperature (^{0}C)
Poly(AMc-co-AMPS)-1	4.0013	1.2531	0.0536	25	3	75
Poly(AMc-co-AMPS)-2	4.0010	1.5015	0.0541	25	3	75

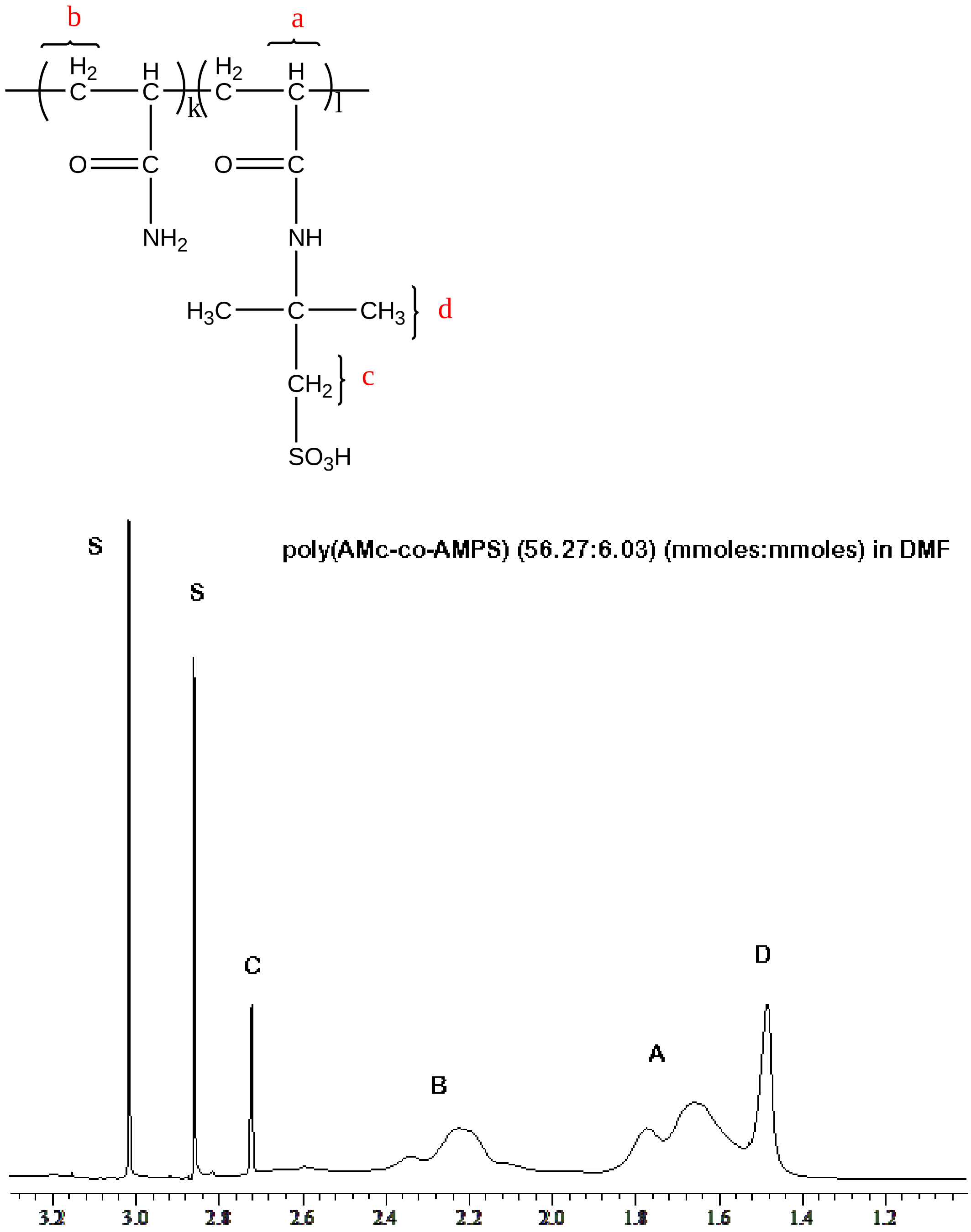
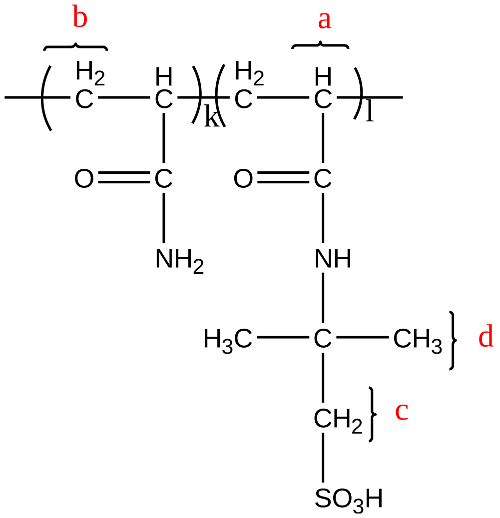


Figure 4.8 Proton NMR spectrum of poly(AMc-co-AMPS) (56.27:6.03) (mmoles:mmoles) synthesized in DMF medium, dissolved in d-H_2O.



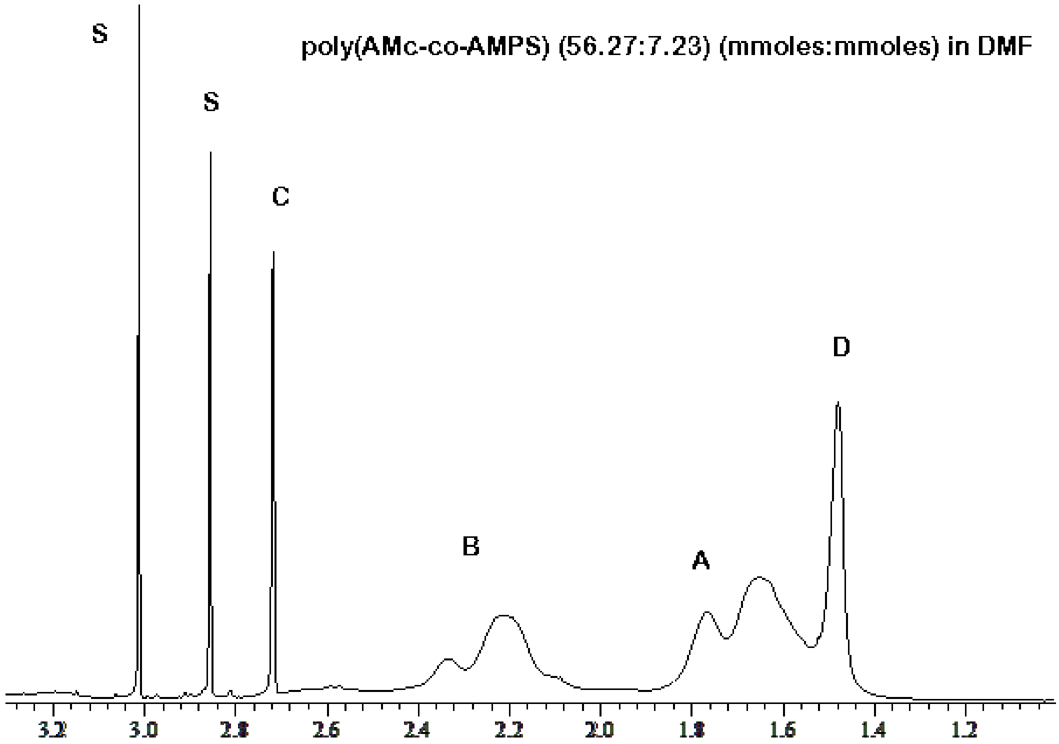
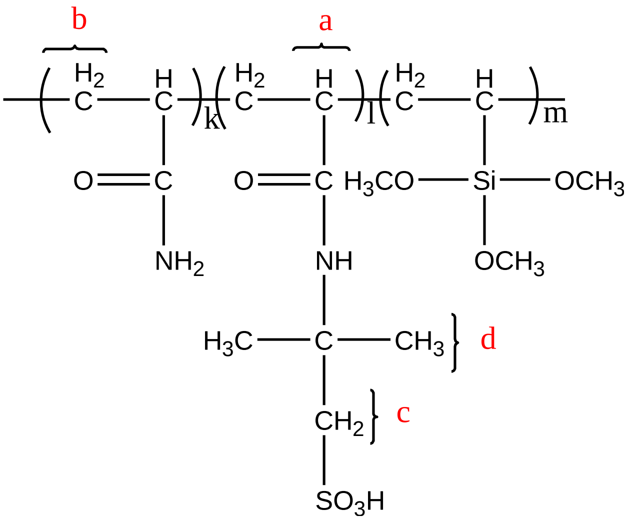


Figure 4.9 Proton NMR spectrum of poly(AMc-co-AMPS) (56.27:7.23) (mmoles:mmoles) synthesized in DMF medium, dissolved in d-H_2O.

4.3.2.2 Proton NMR Spectroscopy



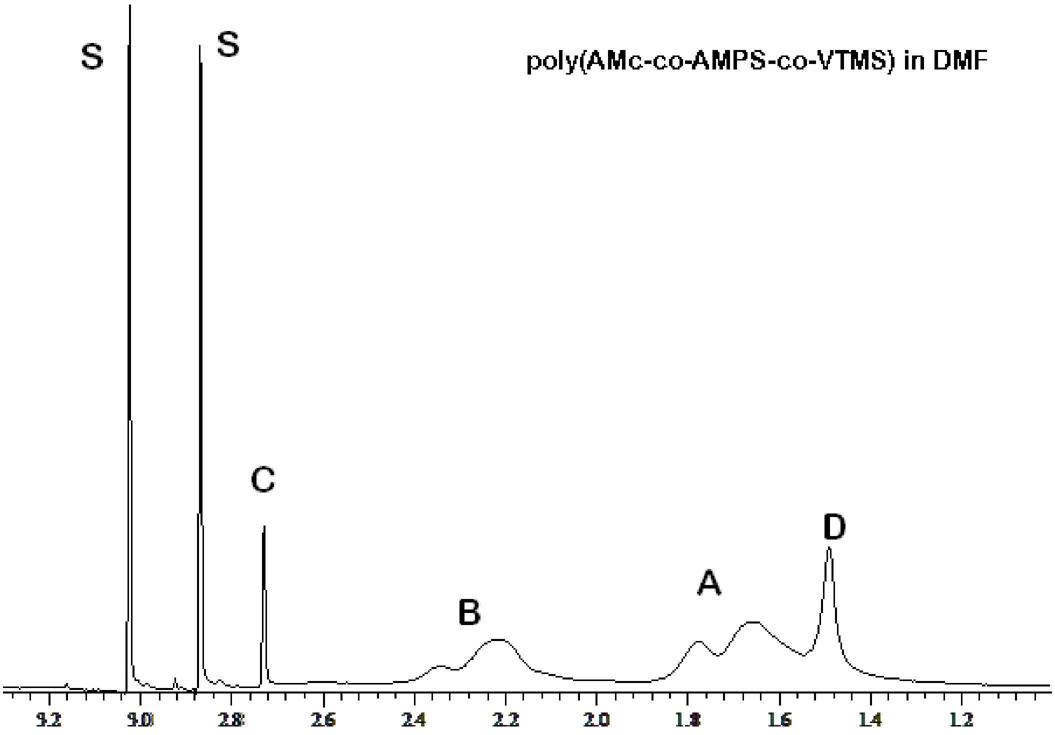


Figure 4.10 Proton NMR spectrum of poly-1 synthesized in DMF medium, dissolved in d-H_2O.

The proton NMR analysis technique was applied to synthesized powder sample of superabsorbent hydrogels in order to confirm the chemical composition and presence of functional groups on polymer backbone. Firstly a solubility test for powder samples was run in order to identify out the best solvent for polymer to run a solution ^{1}H NMR analysis. In terms of results, it was confirmed that the best dispersing medium for powder samples is water, hence deuterium water was used employed in NMR analysis. About 5 mg of powder non crosslinked polymer samples was dissolved in 800 µl d-H_2O and 600 µl of this solution transferred into NMR test tubes and analysis were conducted at RT (Room Temperature).

Figure 4.11 displays the Proton NMR spectrum obtained for poly(AMc-co-AMPS-co-VTMS) synthesized in DMF. From this spectrum it can be seen that the overlapped region attributed to –CH_2 units (A) on the polymer backbone around 1.5 and 1.8 ppm. The characteristic peaks corresponding to –CH units (B) are observed around 2.0 to 2.4 ppm. A single sharp peak observed around 2.70 ppm (C) is due to -CH_2 units on the pendant AMPS group on the polymer chain. The germinal dimethyl groups on AMPS are observed around 1.4 ppm. These characteristic groups are what can be expected from such polymeric sample. VTMS groups have trimethoxy groups which have characteristic peaks around 3.5 ppm on the Proton NMR spectrum. However on the Proton NMR spectrum of terpolymer composed of Acrylamide (AMc), 2-Acrylamido-2-methylpropane-1-sulfonic acid (AMPS) and Vinyltrimethoxysilane (VTMS) in which the monomer feed concentration is 90.19 %, 7.72 % and 2.08 % respectively , it is difficult to see these characteristic peaks due to methoxy groups because of the very low concentration of VTMS in overall polymer concentration. This results can be also supported by FTIR spectrum discussed above of both casted film samples and nonhydrolyzed powder samples of poly-1 in which it was stated that there is no common difference on the spectrums for detecting alkoxysilanes and crosslinked units. This further explains that there are slightly crosslinked regions on powder samples or alkoxy groups already hydrolyzed and have -OH units which can be labile and not easily detectable.

If the chemical composition of integrated monomeric units in terpolymer is considered, the integral values for each peaks on the spectrum can be taken into consideration. The integral value of methylene group on AMPS to all –CH integral value (on the polymer backbone) ratio gives the percentage of AMPS unit in terpolymer which is about 5.57 % . On the basis of this integration and their respective ratio value, it is easy to find out the integral value for germinal dimethyl groups on AMPS unit which is somehow overlapped with the region –CH_2 s on the polymer backbone. Based on this principle the integral value for geminal dimethyl groups is about 9.18 in overall polymer. If the integral values of -CH_2 on the polymer backbone to integral value of -CH on the polymer background after subtracting the integral value of germinal dimethyl groups were considered the ratio was found as 1.85 which is close the molar concentration of -CH_2 on the polymer backbone to the -CH on the polymer backbone. On the AMPS unit in the polymer sample, the –OH groups on the sulfonic acid end groups is not detectable on Proton NMR when the solvent medium is water, because of the labile nature of proton on hydroxyl group. Moreover, proton atom attached to amine groups on both AMc and AMPS groups were not detected. Hence, there is no characteristic peak due to this chemical structure. As a results based on this Proton NMR analysis, it can stated that monomeric unit were well integrated into terpolymer in terms of molar concentration and integral value calculation and characteristic peaks observed on the spectrum.

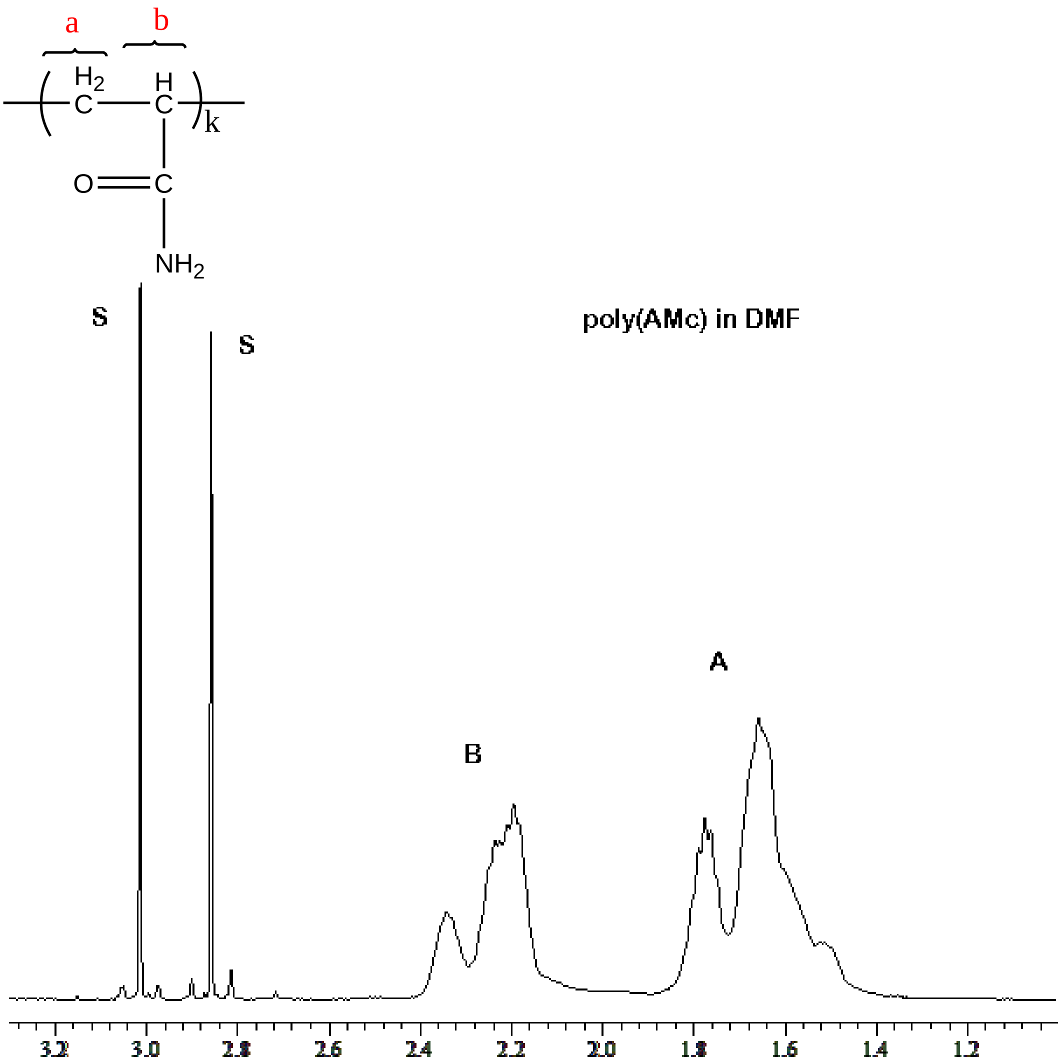


Figure 4.11 Proton NMR spectrum of poly-9 synthesized in DMF medium, dissolved in d-H_2O.

Figure 4.12 shows the Proton NMR spectrum obtained from the synthesized poly-9 under the same condition with terpolymer. The purpose to characterize this homopolymer was to check the any changes in functional groups on the polymer backbone. Hence, on the spectrum it can be easily observed that characteristic peaks (A) around 1.5 to 1.8 ppm are due to -CH_2 , peaks (B) around 2.0 to 2.4 ppm are due to -CHs on the polymer backbone. Since it is difficult to detect any peaks due to amine groups on acrylamide unit, it is reasonable to say that this polymer is purely the homopolymer of acrylamide. Both on this spectrum and other Proton NMR spectrum there are two sharp peaks (C) and (D) around 3.0 to 3.2 ppm are due to the solvent used, Dimethylformamide in the polymerization reaction as solvent medium. Also the integral value ratio (area under the corresponding peaks) of $–CH_2$ to $-CH$ on the polymer backbone is about 2.0 which is a correction for full integration of acrylamide units purely to homopolymer.

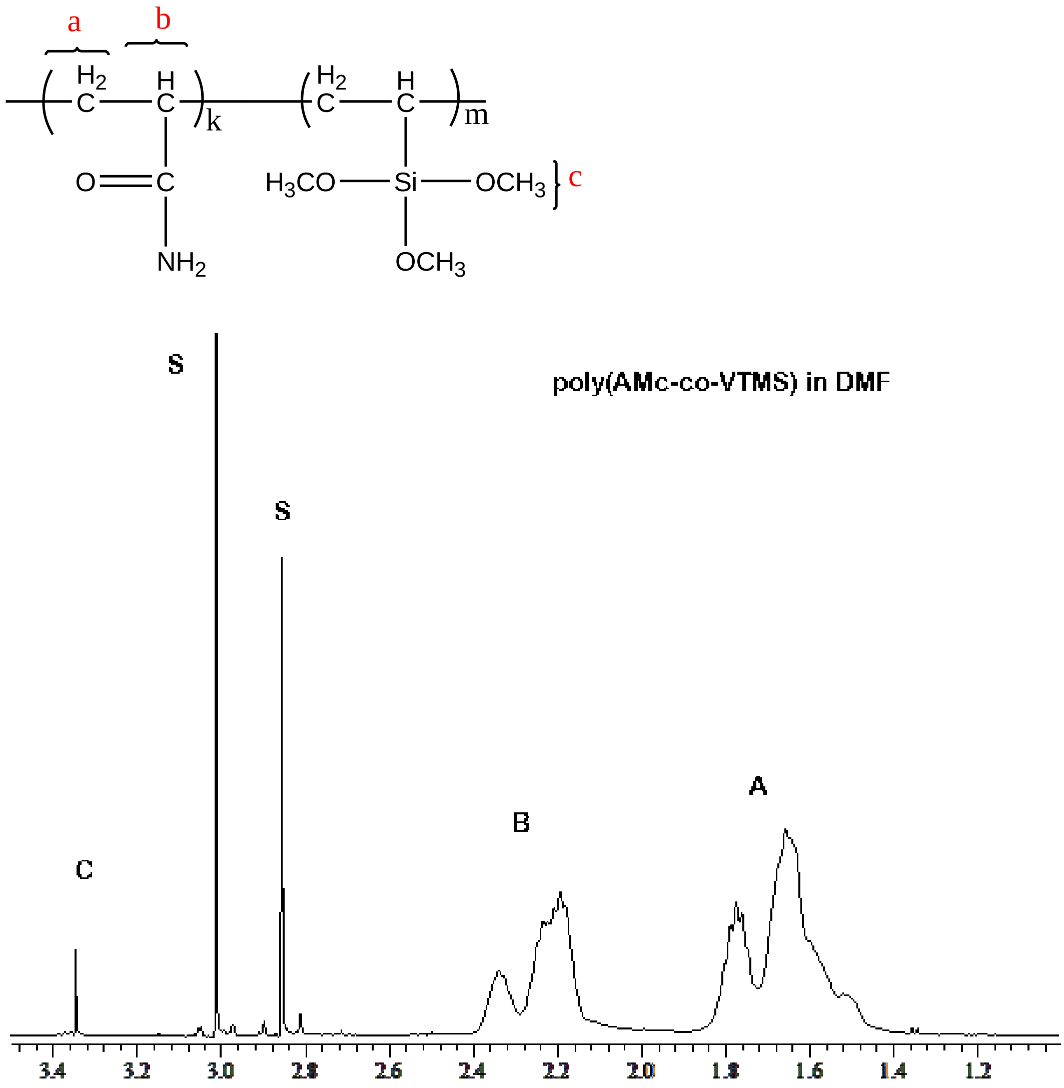


Figure 4.12 Proton NMR spectrum of poly-7 synthesized in DMF medium, dissolved in d-H_2O.

Figure 4.13 shows the Proton NMR spectrum of poly(AMc-co-VTMS) synthesized under the same conditions of production terpolymer in Dimethylformamide. On this spectrum, the characteristic peak due to methoxy groups on VTMS units is observed around 3.4 ppm. Also peaks due to functional groups on the polymer backbones can be seen around 1.4 to 1.8 ppm and around 2.0 to 2.4 ppm.

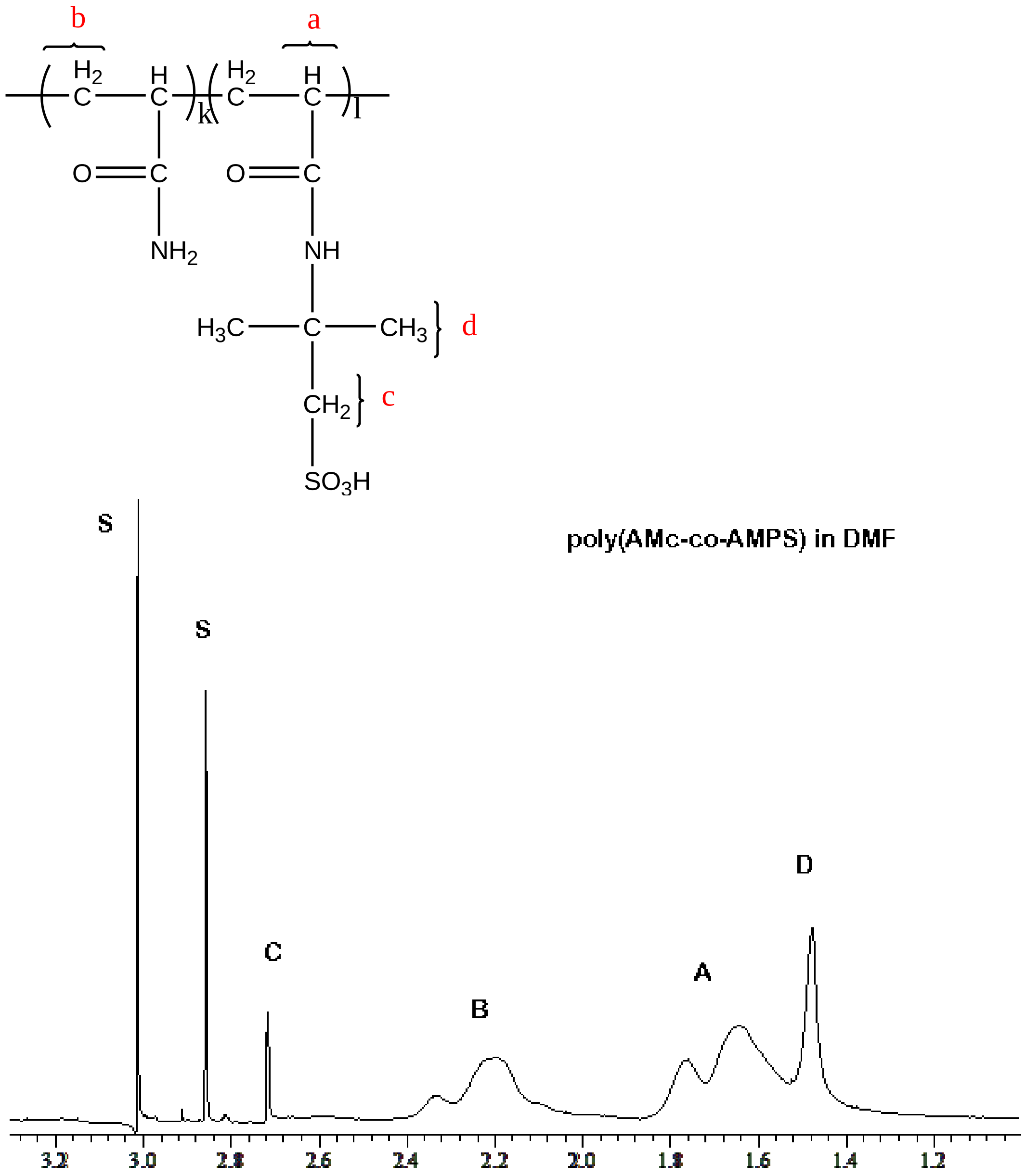


Figure 4.13 Proton NMR spectrum of poly-11 synthesized in DMF medium, dissolved in d-H_2O.

Figure 4.14 shows the spectrum of poly(AMc-co-AMPS) synthesized under the same conditions of terpolymer polymerization in DMF. This spectrum shows the characteristic peaks for the functional groups on the copolymer. Peaks (C) around 2.70

ppm is due to methylene groups on AMPS units. Peak (A) around 2.0 to 2.4 ppm is due to –CH and peak (A) around 1.4 to 1.8 is due to -CH_2 on the polymer backbone and (D) is due to germinal dimethyl groups on AMPS again.

Through the results and discussion about Proton NMR spectrums to characterize the synthesized polymers, it can be easily stated that there is a well integration of monomeric units into terpolymer and corresponding homopolymer and copolymers based on chemical structure analysis and chemical composition of monomeric units on the polymer backbone.

4.3.3 ^{29}Si NMR Spectroscopy analysis

In order to study the hydrolysis and condensation behaviors of crosslinking agents, vinylalkoxysilanes in aqueous medium, a silicone NMR technique was applied. For the purpose, an aqueous solution of 1.30 mmoles of each vinylalkoxysilanes (VTMS, TEVS and TMEVS) and 0.0016 M of Chromium (III) acetyacetonato in 15 ml distilled water was prepared and at room temperature silicone NMR spectrums were taken. In order to observe the step by step change on spectrum, at each 10 minute interval an analysis was recorded. Hydrolysis and condensation behaviors of used crosslinking agents in terpolymerization are important in terms of rate of crosslinking during post treatments. After the hydrolysis process, alkoxy groups of trialkoxysilanes are hydrolyzed to form silanol-containing species. The silanol containing species are highly reactive intermediates which are responsible for bond formation with substrate. Silanols usually self-condense or with alkoxysilanes to form siloxanes. The obtained spectrums of silicone NMR provided results about the hydrolysis behaviors of alkoxysilane. On the figures, which can be easily observed that TEVS has highest rate of hydrolysis compared to other two crosslinking agents TEVS has longer alkoxy groups(ethoxy) compared to VTMS (methoxy). An increase in electropositive density on Si atom was predicted to be responsible for higher rate of hydrolysis of alkoxy groups of TEVS leading ethanol as leaving group in aqueous medium. For TMEVS, when chemical structure and reactivity can be taken into account, it can be stated that for methoxyethoxy groups on Si atom, there are parallel two inductive powers cancelling each other and providing a weaker electropositive density on silicone atom, hence a slower rate of hydrolysis. As a result, it can be stated that applying silicone NMR technique provides information about hydrolysis and condensation behaviors of crosslinking agents.

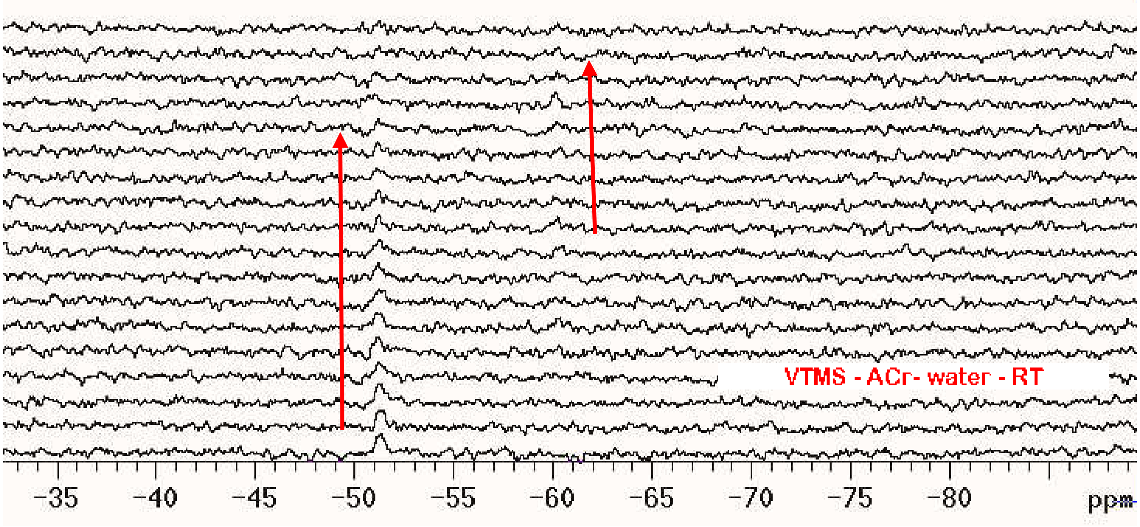


Figure 4.14 ^{29}Si NMR Spectroscopy of VTMS-ACr-water solution at RT.

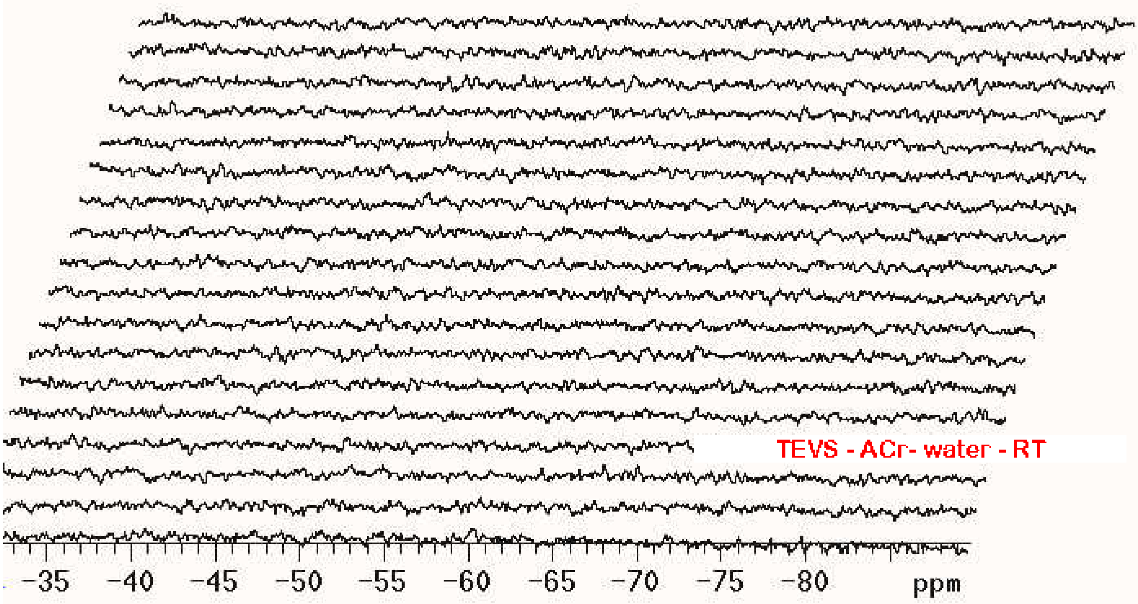


Figure 4.15 ^{29}Si NMR Spectroscopy of TEVS-ACr-water solution at RT.

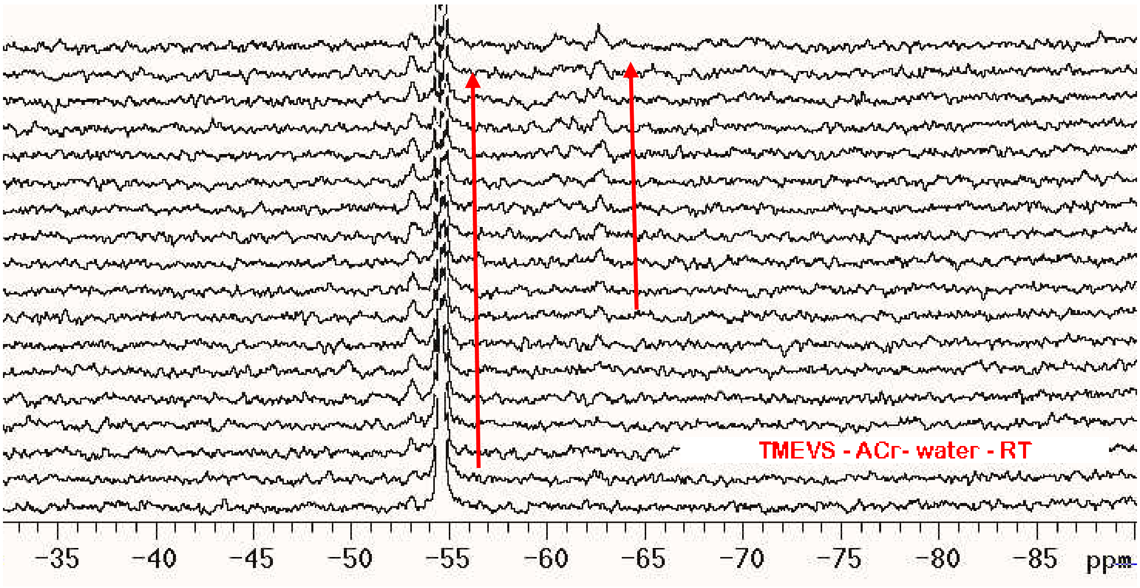


Figure 4.16 ^{29}Si NMR Spectroscopy of TMEVS-ACr-water solution at RT.

4.3.4 Thermal analysis

The simultaneous Differential Scanning Calorimetry (DSC) curves of synthesized polymers, poly-1 in DMF and poly-7 in DMF are indicated in figure 4.18. Prior to analysis, it can be stated that copolymers, poly(AMc-co-AMPS-co-VTMS) and poly(AMc-co-VTMS) were prepared to check the presence of energy curves related to functionalities on polymer backbone. The DSC peaks show that there two clear energy curves correspond to the possible degradations on polymer backbone and one glass transition peak. The broad endothermic peak in the range of 55-110 ^{0}C is attributed to loss of adsorbed water. The second endothermic peak around 230-290 ^{0}C is attributed to the amide group degradation and cleavage of weak crosslinks. The third shoulder endothermic peak around 300 ^{0}C is attributed to degradation of sulfonic groups. Moreover, an endothermic baseline shift corresponding to a Tg on the order of 160 ^{0}C is observed for poly(AMc-co-AMPS-co-VTMS). Further degradation is related to polymer backbone.

Dried powder polymer samples consist different forms of water in both inter and intra molecular structure. The different forms of water that exist in superabsorbent samples were shown on figure 4.19 On DSC curve, it is clearly demonstrates the free water freezing at 0 ^{0}C, free bulk water crystallization around 37 ^{0}C and evaporation of adsorbed water around 100 ^{0}C. Different forms of water exist on inter and inter molecular structure of highly hydrophilic polymers.

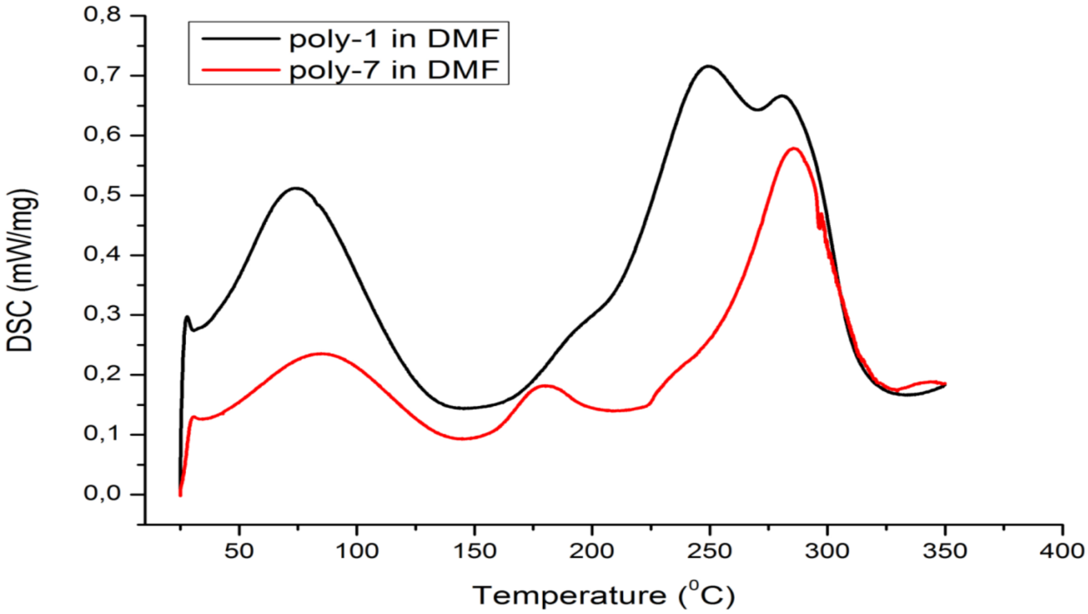


Figure 4.17 DSC curves of synthesized dry powder samples of poly-1 in DMF and poly-9 in DMF.

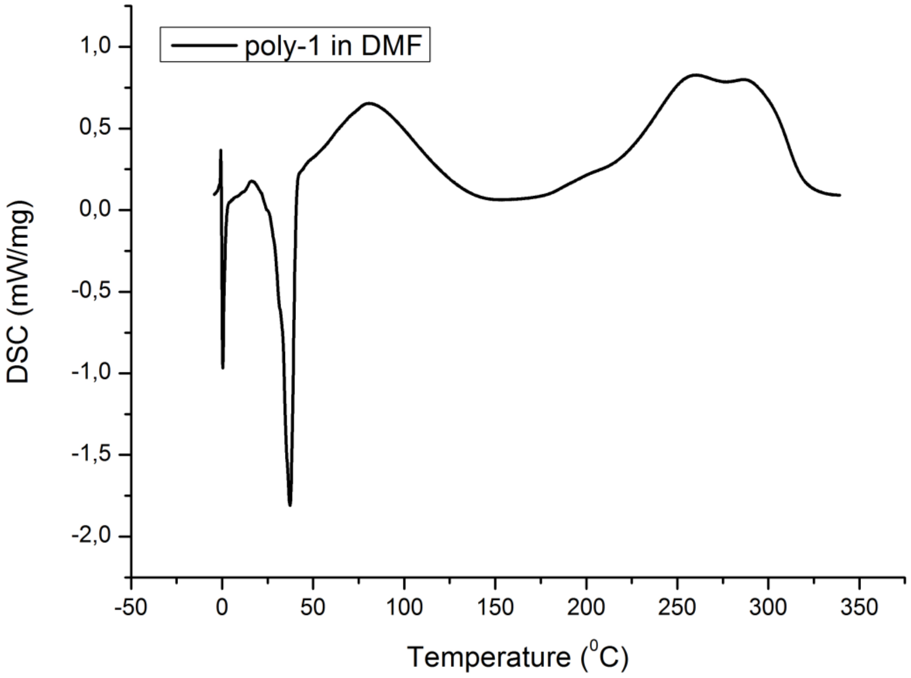


Figure 4.18 DSC curves of synthesized dry powder samples of poly-1 in DMF.

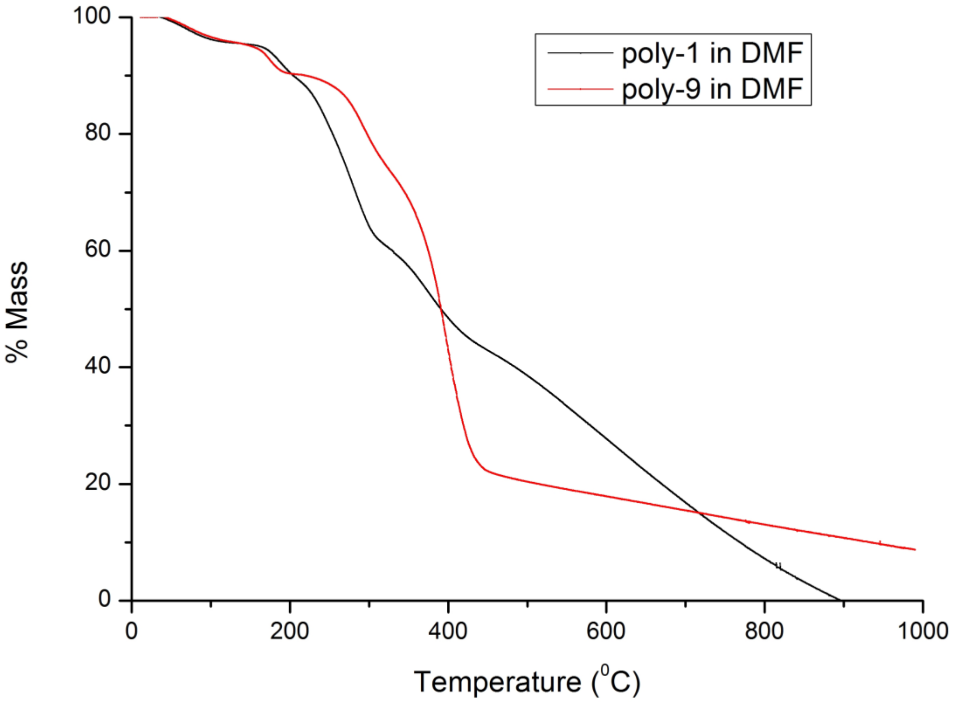


Figure 4.20 % Mass loss curve of synthesized dry powder samples of poly-1 and poly-9 in DMF.

Mass lost of poly-1 is shown in figure 4.20 in percentage increments. The mass lost curve of polymer sample shows four stages of weight loss. The first weight loss is found to be about 14% from 70 to 230 ^{0}C. This weight loss is due to removal of adsorbed water in the sample. The second stage of weight loss is about 10-14% from 230-277 ^{0}C.

At this stage irreversible chemical changes may occur due to thermal degradations. Specifically, around this stage the degradation of amide groups on polymer backbone is expected. During the third stage of decomposition of polymer sample, which is in the range of 280 to 340 ^{0}C and a mass loss of 14 % is attributed to degradation sulfonic groups on polymer backbone. A fourth stage of degradation for poly-1 is breakdown of polymer backbone starting from about 340 ^{0}C to 570 ^{0}C and loss percentage is about 30%. Step by step thermal degradation polymer sample may occur when the chemical functional groups on the polymer backbone are considered. On the chemical structure of polymer sample there are one primary amide group attached to acrylamide units and one secondary amide groups attached to the AMPS units on the polymer backbone. However, secondary amide groups on AMPS units are hindered to a further amide hydrolysis and degradation by germinal dimethyl groups. Hence, thermal degradation of secondary amide groups is considered within degradation pathway of polymer backbone.

Chemical composition of poly-1 is explained both in terms of thermogravimetric analysis and Proton NMR analysis on the figure 4.11. Proton NMR spectra gives chemical contribution of AMPS units to terpolymer of poly(AMc-co-AMPS-co-VTMS). According to Proton analysis, it is concluded that weight fraction of AMPS in polymer sample is about 8-11% which is also closely related to molar feed of monomer. According to % Mass loss curve, a fraction of loss is found to be about 10 to 14 % with some uncertainty quantities. As a result, both ^{1}H-NMR analysis and thermogravimetric results are found to be supportive each other.

4.3.5 Elemental Analysis

VISTA PRO-CCD Simultaneous ICP OES was used for Carbon and Nitrogen elemental analysis. Temperature was kept at 1000 K during temperatures and results can be taken at % wt with this technique.

Table 4.3 Carbon and Nitrogen elemental analysis results.

Polymer	N %(wt)	C %(wt)
Poly-1 in DMF	15.587	42.799
Poly-2 in DMF	16.515	45.095
Poly-3 in DMF	16.767	45.919

According to Carbon and Nitrogen elemental analysis, a clear increase in carbon percentages occurs when poly-3 and also poly-2 compared to poly-1. The reason for this increase is attributed to the chemical groups substitution of alkoxysilane crosslinking agents, which are an methoxy groups for poly-1 and ethoxy and methoxyethoxy groups for poly-2 a-nd poly-3 respectively. The percentage of Nitrogen in polymer backbone is higher than calculated values. The possible reason for these higher values can be a result of trapped solvent molecules in polymer sample. This hypothesis can be verified with help of Proton NMR results. According to NMR results we observed sticky and not easily removable solvent peaks coming from DMF.

4.3.6 Molecular Weight determination, Viscosity and % polymerization yield

Table 4.4 Viscosity values of synthesized poly-1,poly-2 and poly-3 in aqueous medium, concentration of 6 %(wt/ml).

Polymer	Poly-1 in DMF	Poly-2 in DMF	Poly-3 in DMF
Viscosity (cP)	115	31	213

Table 4.4 shows the solution viscosity values of synthesized poly-1, poly-2 and poly-3 in c P. For 6% (wt/ml) concentration of each polymer solution, there is no correlation with the polymer backbone structure and resulting viscosity values. The highest viscosity value for different polymer solution is obtained for TMEVS based polymers because of bulky methoxyethoxy pendant groups. An important role of hydrolysis and condensation behavior of pendant alkoxysilane groups on polymer backbone may also responsible for lowest viscosity value of TEVS based polymer. Because the fast rate of hydrolysis of the alkoxysilane groups may decrease the bulkiness of polymer chains and more linear and lighter polymer.

Table 4.5 Calculated molecular weight values of synthesized polymers based on different alkoxysilanes as crosslinker.

Polymer	Poly-1 in DMF	Poly-2 in DMF	Poly-3 in DMF
MW(g/mol)	167,000	129,000	280,000

Table 4.5 shows the molecular weight values of synthesized polymers based on different alkoxysilanes as crosslinkers. Since the weight percentages of acrylamide units in prepolymer mixture is about 77, and molar percentage of acrylamide also is about 90, the constant values of polyacrylamide were used to calculate the molecular weight of synthesized polymer through the Dillute Solution viscometery experiment. The constants for polyacrylamide at 25 ^{0}C are a=0,8, K=6,31*10^{-3} in distilled water. The dilute solutions of prepared standard solutions were 0.25, 0.50, 0.75 and 1% (wt/ml). The experiments were conducted in constant temperature of 23 ^{0}C, using 1C capillary viscometry tube. According to results the highest molecular weight value was calculated for TMEVS based superabsorbent hydrogel and the lowest value for TEVS based superabsorbent hydrogel.

Table 4.6 % yield calculated gravimetrically for synthesized polymers in DMF medium.

Polymer	Poly-1	Poly-2	Poly-3	Poly-7	Poly-9
Yield %	94.14	88.10	87.64	88.40	97.25

Table 4.6 shows the % yield of calculated gravimetrically for synthesized polymers in DMF medium. As can be seen from the Table, the highest conversion value from monomeric units into polymer structure was obtained for poly-9 which is polyacrylamide homopolymer. The high value of conversion can be attributed to the high reactivity of acrylamide monomer with its same kind monomer in homopolymerization. Free radical solution precipitation polymerization of acrylic based and sulfonic acid based acrylamido vinyl monomers in a polar aprotic medium has certain level of yield percentage for copolymerization, homopolymerization and terpolymerization. The average conversion value is above 88 %.

4.3.7 Drop Shape Analysis

Contact angle measurement, using the sessile drop technique, is widely used for investigation of the surface characteristics of various materials. On the other hand, the surface free energies of polymers control their adhesion, adsorption, lubrication, steric stabilization, wettability, and similar surface-related properties. Drop shape analysis were done for synthesized polymers in order to understand the polymer surface characteristics. Synthesized powder polymers were dissolved in distilled water in 1%(wt/ml) and dip coated on mica surfaces and a sessile drop technique was used to determine the average contact angle of water and hexane on polymer surfaces. For each polymer surfaces on mica samples, 6 drops and their contact angles were taken and hence averaged contact angle values. Then contact angles were employed to calculate surfaces energies for corresponding polymers. Taken contact angles for each polymers and calculated surface energies according to theory were tabulated below in table 4.7.

When contact angle results were taken into consideration, there is no significant difference between average contact angle values of terpolymers, namely poly(AMc-co-AMPS-co-VTMS), poly(AMc-co-AMPS-co-TEVS), and poly(AMc-co-AMPS-co-TMEVS). However, contact angle values for poly(AMc-co-AMPS) and poly(AMc) are much smaller than average contact angle values for terpolymers most probably due to rigid crosslinked polymer structure of terpolymers compared to homopolymer and coppolymer. Moreover contact angle results for terpolymer are in the range of 28 to 32 θ which is an important indication of superhydrophilicity nature of synthesized superabsorbent capability of polymers. Calculated corresponding surface energies for polymers are reason wettability of thin film of synthesized polymers through diffusion and other water uptake mechanisms of biological fluids into polymer networks.

Table 4.7 Average contact angles in water and hexane of synthesized and dip coated 1%(wt/ml) polymer solutions and calculated surface energies according to Fowke's theory.

Polymer	**Ave.Contact angle in H_2O (θ)**	**Ave.Contact angle in Hexane(θ)**	**Surface energy calculated for polymers**
Poly(AMc)	14.40	83.5	81.27
Poly(AMc-co-AMPS)	14.9	84.1	81.29
Poly(AMc-co-AMPS-co-VTMS)	32.13	126.34	84.60
Poly(AMc-co-AMPS-co-TEVS	28.42	115.3	84.04
Poly(AMc-co-AMPS-TMEVS)	28.64	87.60	87.40

4.4 Equilibrium Swelling Ratio studies

4.4.1 Equilibrium Swelling Ratio studies for polymers synthesized in 1,4-Dioxane

Synthesis and characterization studies of superabsorbent hydrogels for this thesis were initially carried out in 1,4-dioxane solvent medium. Predetermination of the content of comonomers in prepolymerization was tabulated in table 3.9 in experimental part. Predetermination of monomer content in prepolymer mixture were done in order to select the composition which yields the highest ESR value in time-dependent records, while crosslinking agent ratio was kept constant. For a desired level of water uptake of crosslinked polymer material, the degree of crosslinking as well as the chemical composition of monomeric units is important. Hydrophilic nonionic monomer acrylamide and AMPS, in order to increase the ionic hydrophilicity in polymer structure, was chosen as monomer and highly dissociable comonomer respectively. According to initial work, the highest ESR value was found for 14:1 mole ratio of AMc: AMPS which was about 518.5 g/g in distilled water. With constant crosslinking degree of superabsorbent hydrogels, there is a balance between crosslinking and ionic character of polymer structure.

While keeping comonomer concentration constant in polymerization, a preliminary work was done in order to determine the composition of crosslinking which yield best results. The tabulated work is shown in table 3.10. While keeping commoner concentration constant, the highest ESR was measured for the lowest concentration of alkoxysilane based crosslinking agent.

Based on these predeterminations, the best composition of polymer AMc: AMPS: VTMS is 56.27:4.82:1.30 (mmols) in 1,4-dioxane medium. The further modification and studies were based on this composition. However, since 1,4-dioxane is a cylic ether and there is a possible formation of peroxide on the alpha carbon next to the ether linkage. After polymerization, there were a great explosion of reaction vessel, and spread out of both cancerogenic solvent and polymer product and unreacted monomer. This consequences were observed for about 90 % of set reactions and hence the polymer synthesis in 1,4-dioxane medium were given up. Details of initial studies both experimentally and result based discussions are described in Appendix A part.

4.4.2 Equilibrium Swelling Ratio studies for polymers synthesized in DMAc

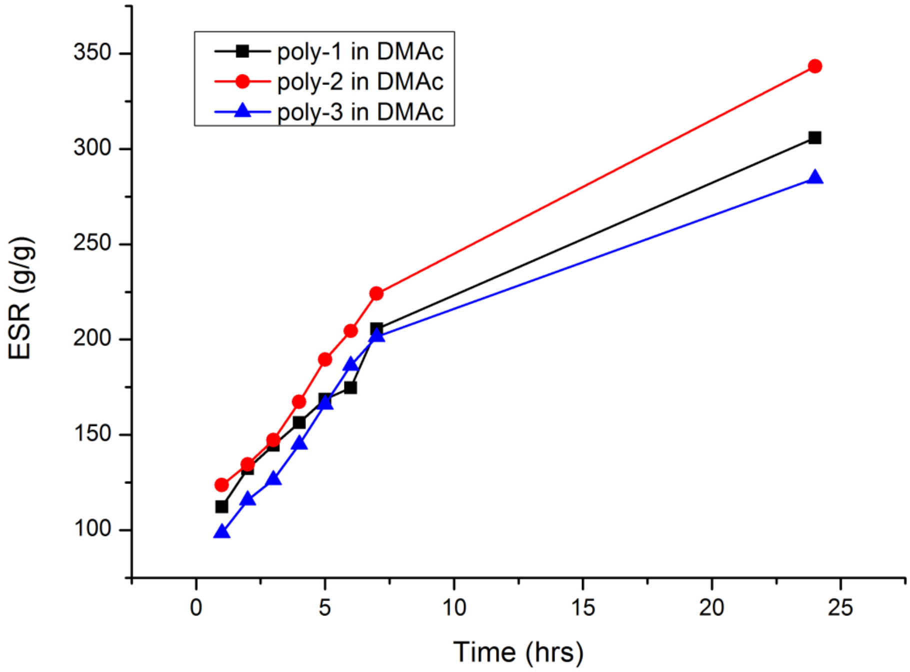


Figure 4.19 ESR (g/g) values of poly-1 in DMAc, poly-2 in DMAc and poly-3 in DMAc vs. time plot.

Equilibrium swelling ratio values of prepared hydrogel film samples (6% wt/ml) with three different crosslinking agents were plotted vs. time and shown on figure 4.21. According to swelling results in distilled water, the highest ESR (g/g) value was obtained from TEVS based polymer. The ESR (g/g) value for this sample was 343 g/g in 24 hrs. The lowest swelling results obtained for TMEVS based polymer, which was about 284 g/g of its dry weight.

4.4.3 Equilibrium Swelling Ratio studies for polymers synthesized in DMF

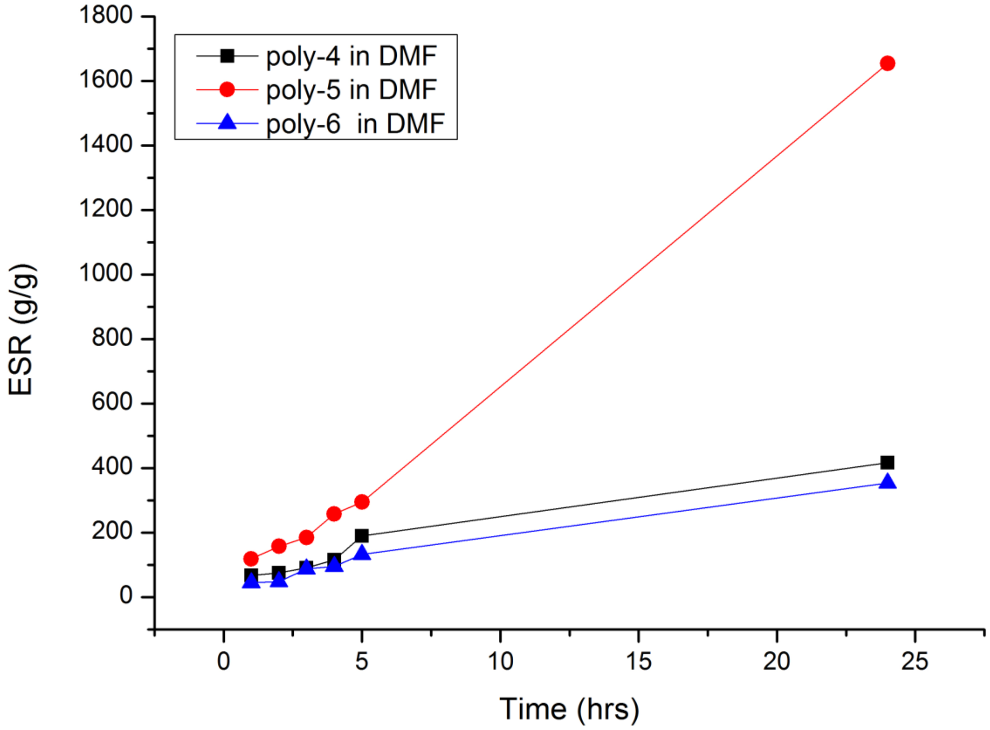


Figure 4.20 ESR(g/g) values of poly-4 in DMF, poly-5 in DMF and poly-6 in DMF vs. time plot.

Equilibrium swelling ratio values of prepared hydrogel film samples (6% wt/ml) with three different crosslinking agents were plotted vrs time and shown on figure 4.22. According to swelling results in distilled water, the highest ESR (g/g) value was obtained from TEVS based polymer. The ESR (g/g) value for this sample was about 1600 g/g in 24 hrs of its dry weight. The lowest swelling results obtained for TMEVS based polymer, which was about 343 g/g of its dry weight.

4.4.4 Equilibrium Swelling Ratio studies for polymers synthesized in DMF with addition of Acetic acid

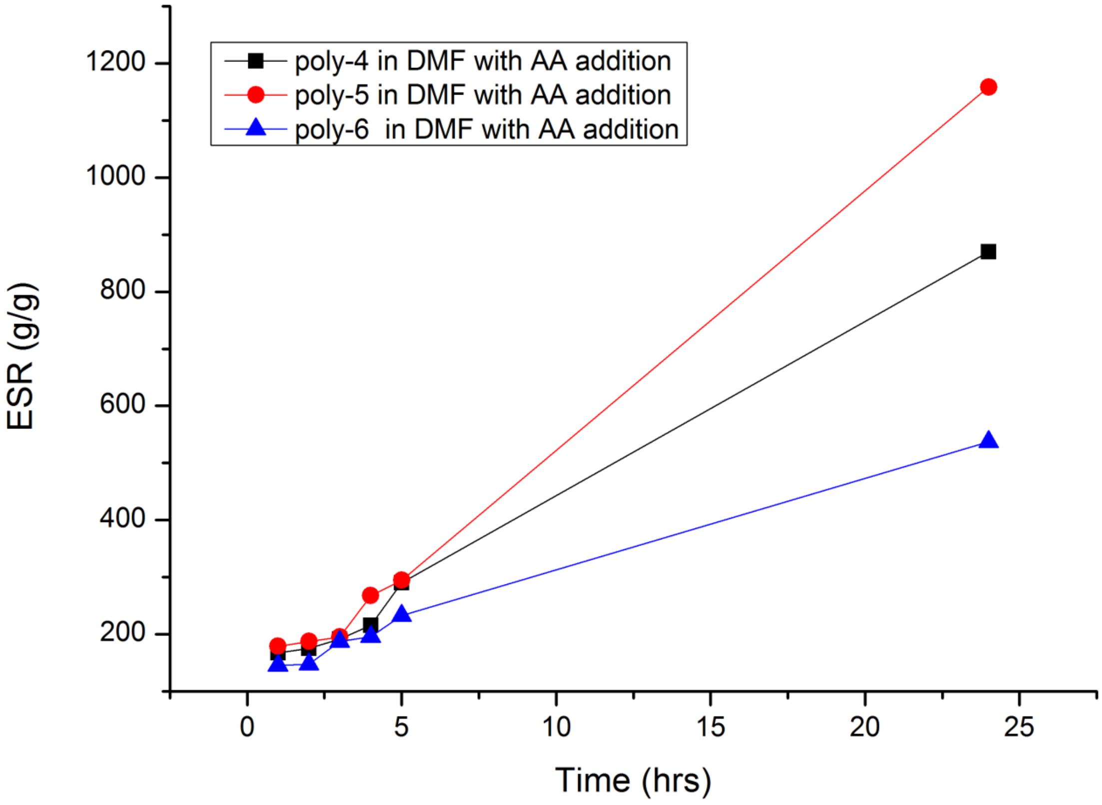


Figure 4.21 ESR(g/g) values of poly-4 in DMF, poly-5 in DMF and poly-6 in DMF with addition of AA vs. time plot.

Equilibrium swelling ratio values of prepared hydrogel in DMF with addition of AA film samples (6% wt/ml) with three different crosslinking agents were plotted vrs time and shown on figure 4.23. According to swelling results in distilled water, the highest ESR (g/g) value was obtained from TEVS based polymer. The ESR (g/g) value for this sample was about 1200 g/g in 24 hrs of its dry weight. The lowest swelling results obtained for TMEVS based polymer, which was about 540 g/g of its dry weight. As it is plotted on graph the ESR values for poly-4 in DMF and poly-6 in DMF with addition of AA enhanced to higher values compared to same polymer with same concentration of polymer solution for polymer preparation without AA addition. However, ESR value for poly-5 in DMF decreased to lower value compared to one without any addition of AA. The swelling behaviour of film samples prepared with addition of AA can be explained in terms of crosslinking density. It can be stated that with addition of AA, there is an increase in crosslinking degree for poly-5 and heavily crosslinks on polymer backbone. Because TEVS based poly-5 has higher rate of hydrolysis and formation of reactive silanol pendant groups. Addition of acid enhances the crosslinking degree and diffusion of water into polymer networks are limited to some extent. However, there is also an enhancement in crosslinking degree of poly-4 and poly-6 in DMF because of acid hydrolysis and condensation, hence higher ESR values compared to uncatalysed polymer solutions.

4.4.5 Equilibrium Swelling Ratio studies with change in X-linker ratio

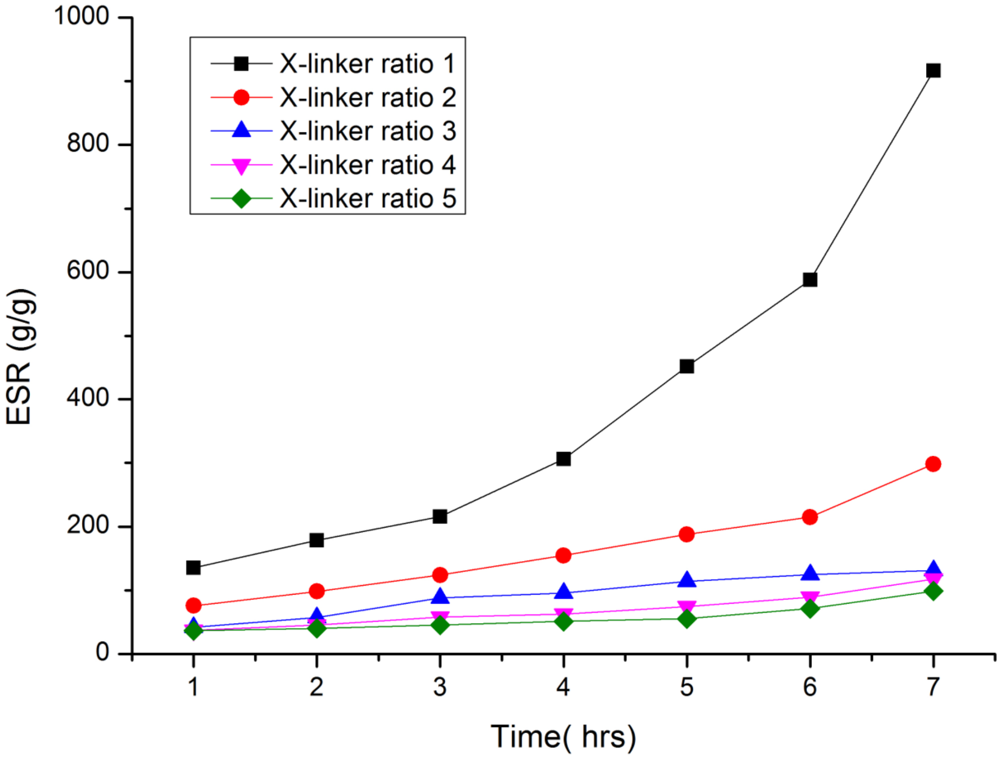


Figure 4.22 ESR (g/g) vs. time graph obtained for series of hydrogels prepared with different amount of X-linker feed.

Effect of crosslinker agent on ESR vs. time graph is shown on fig. 4.24. In order to understand effect of increase in amount of crosslinker feed in prepolymer mixture, a gradual increase in amount of VTMS in polymer mixture was studied under constant monomer mixture. It is clearly noticed that with increase in amount of crosslinker, we observed a decrease in ESR drastically. This is likely to be due to the increase in the crosslinking density that will then restrict the movement of the copolymer chains and limit the swelling capability of the SAPs.

4.4.6 Equilibrium Swelling Ratio studies for polymer with DMAM synthesized in DMAc

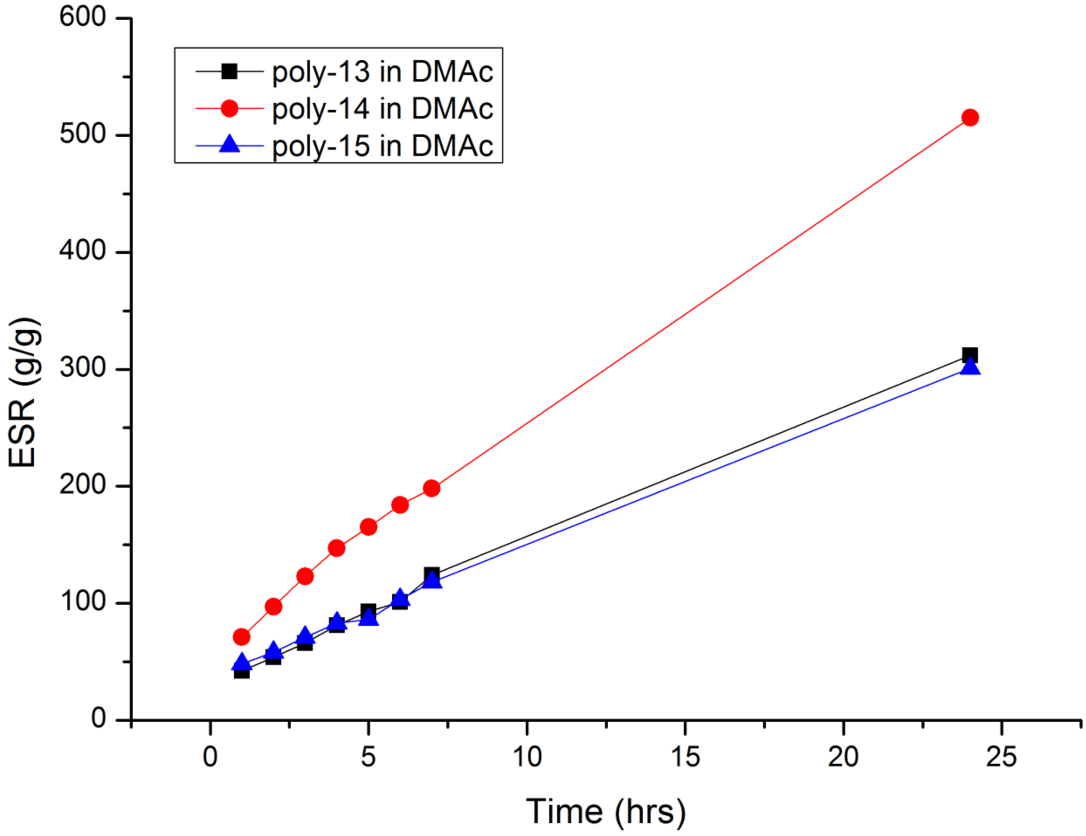


Figure 4.23 ESR (g/g) values of poly-13 in DMF, poly-14 in DMF and poly-15 in DMAc vs. time plot.

Equilibrium swelling ratio values of synthesized hydrogel in DMAc film samples prepared (6% wt/ml) with three different crosslinking agents were plotted vs. time and shown on figure 4.25. According to swelling results in distilled water, the highest ESR (g/g) value was obtained from TEVS based polymer. The ESR (g/g) value for this sample was about 512 g/g in 24 hrs of its dry weight. The lowest swelling results obtained for TMEVS based polymer, which was about 301 g/g of its dry weight.

CHAPTER 5

5. Conclusions

✓ The main aim of this study is to synthesize and characterize novel self-crosslinkable superabsorbent hydrogel based on three different vinylalkoxysilanes as cross linking agents and also a third monomer in terpolymer system. This aim was achieved by the Free Radical Solution precipitation polymerization technique in three different polar aprotic solvent systems. The effect of different solvent system, different nonionic hydrophilic monomers and ionic nature comonomer and also different vinylalkoxysilanes were all investigated through both experimental works and characterization studies on Equilibrium Swelling Ratios (ESR). Thermal and molecular characterization of powder polymer samples showed that, there is a robust integration of monomeric units in polymer networks. Useful characterization instruments, FT-IR, NMR, DSC and STA indicated chemical functionalities on polymer backbone, chemical compositions and identities on polymer backbone, and main thermal behaviors respectively.

✓ The applied experimental method was very successful, simple, and easy to apply larger scales and effective in obtaining precipitated and stable powder polymers. Hence, there was no need to precipitate out further the formed polymers in solvent system. As a result powder polymers were easily processed further. Unreacted monomers and initiators were washed with polar aprotic solvents used in polymerization system. The applied experimental method provided a shorter time of polymerization.

✓ Three different polar aprotic solvent systems were used in polymerization work in order to obtain precipitated powder samples with non hydrolyzed alkoxysilane pendant groups on polymer backbone, hence prone to further work ups. Firstly 1,4-dioxane as polar aprotic cyclic solvent was used in polymerization work, but cyclic ether solvents are generally are capable of forming explosive peroxide and at elevated temperatures and in the presence of trace amount of oxygen easily explodes. In our system, we observed explosions of reaction vessel just after exothermic free radical polymerization and for the safety of work, 1, 4-dioxane were substituted with another polar aprotic solvent

Dimethylacetamide (DMAc). With the use of DMAc, we obtained a precipitated polymer in reaction vessel and polymers were processed further and required analysis could be done. Superabsorbent hydrogels synthesized in DMAc showed certain level of swelling in distilled water. The third solvent system used in polymerization of nonhydrolyzed superabsorbent powder samples was Dimethylformamide (DMF). Polymers synthesized in DMF showed the highest degree of swelling compared to other two polar aprotic solvents.

✓ Due to chemical structure and reactivity in terms of hydrolysis and condensation behaviors of different vinylalkoxysilanes used as crosslinking agents and also third monomer in terpolymer system, three different vinylalkoxysilanes were selected as crosslinking agents. The selected compounds were Vinyltrimethoxysilane (VTMS), Triethoxyvinylsilane (TEVS) and Tris (2-methoxyethoxy)vinylsilane (TMEVS). Although, in terms of molecular and thermal characterizations, there was no important change while using these three crosslinking agents, standard solutions of each polymer synthesized showed different viscosity, Molecular weight values and ESR. The highest molecular weight value with use of Dilute solution experiment was obtained for TMEVS based polymer and lowest molecular weight was obtained for TEVS based polymer. This trend was also observed for viscosity measurements with standard polymer solutions. The highest viscosity value obtained for TMEVS based polymer is a result of capability of forming higher degree of hydrogen bonding and bulky groups present of polymer backbone. However, there is no correlation between molecular weight and viscosity trend and ESR. This results showed that the polymer which has the highest molecular weight does not give the highest ESR value in a recorded time. For example, TEVS based polymers synthesized in all three different polar aprotic solvents showed the highest degree of swelling in distilled water at room temperature. This highest degree of swelling of prepared film samples based TEVS is a result of chemical structure and reactivity crosslinking agent. It is stated that a possible rate of hydrolysis and condensation results in more homogeneous crosslinking in polymers and higher degree of diffusion and hydration of polymer networks.

✓ Selected comonomer, AMPS shows a higher degree of dissociation in whole pH range, hence Equilibrium Swelling Ratio of film samples are independent of pH in aqueous solutions. Synthesized polymer shows self-crosslinking behavior at both ambient temperatures and higher curing temperatures. Self crosslinking of film samples required no addition of any acid or base catalysis and this self crosslinking somehow might be achieved with highly acidic sulfonic acid groups present on AMPS monomer. In order to check the control addition of acid in standard polymer solution prepared for temperature curing, we added dropwise Acetic Acid (AA). Thin film samples prepared with addition of AA showed an increase in ESR value for VTMS and TMEVS based polymers and unfortunately decrease in TEVS polymer. This behavior are attributed to degree of crosslinking on polymer chains, that is degree of crosslinking was further increased with addition of acid for TEVS based polymer leading a diffusion of water molecules with difficulties. However, an enhancement in crosslinking network in polymer chains based VTMS and TMEVS and homogeneity of crosslinking increased and higher degree of swelling compared thin film samples without any addition of acid.

✓ As a final conclusion, with our present work, we studied synthesis and characterization of novel self-crosslinking superabsorbent hydrogels based on three different vinylalkoxysilanes as crosslinking agents. Use of different vinylalkoxysilanes as both comonomer and crosslinking agents seems to be novel in superabsorbent technology. The applied experimental method is novel synthesis path in synthesis of superabsorbent polymers.

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APPENDIX A

SELF-CROSSLINKABLE SUPERABSORBENT HYDROGEL BASED VINYLALKOXYSILANES AS CROSSLINKER

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ABSTRACT

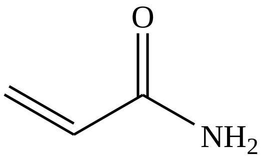
In the present research, aim is to synthesize novel self-crosslinkable superabsorbent hydrogels based on a vinylalkoxysilane crosslinking agent, Vinyltrimethoxysilane (VTMS). The experimental work starts with determination of the content of monomers with constant crosslinker agent amount in terms of highest Equilibrium Swelling Ratio (ESR) (g/g). The highest ESR (g/g) was obtained for with smaller AMPS/AMc with constant VTMS feed composition. The experimental work done with varying VTMS feed in prepolymer mixture, there is balance with monomer composition and crosslinking agent with but increasing crosslinking agent amount in constant monomer composition, there is drastically decrease in ESR value of prepared thin film samples. The highest ESR values of 518.5 g/g in distilled water, was obtained for polymer composition of AMc: AMPS with (57.49: 4.89)

(mmoles: mmoles) and mmoles ratio 14.

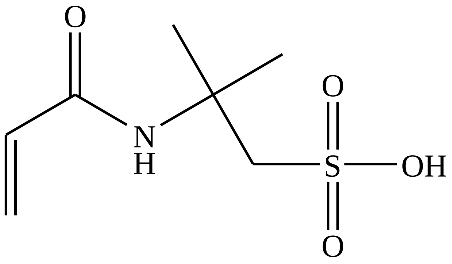
EXPERIMENTAL PROCEDURE AND MATERIALS:

Materials:

- **Monomers**

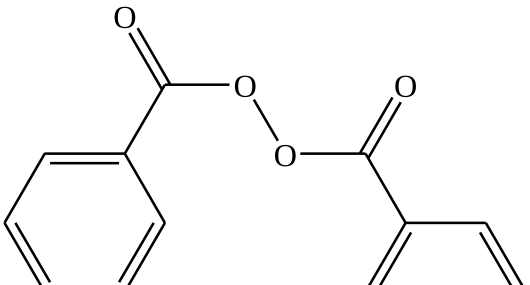


acrylamide



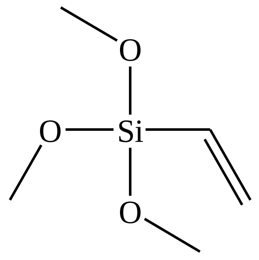
2-acrylamido-2-methylpropane-1- sulfonic acid

- **Free Radical Initiator**



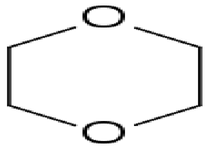
Benzoylperoxide

- **Crosslinking agent**



Vinyltrimethoxysilane

- **Solvent**



1, 4-Dioxane

Synthesis:

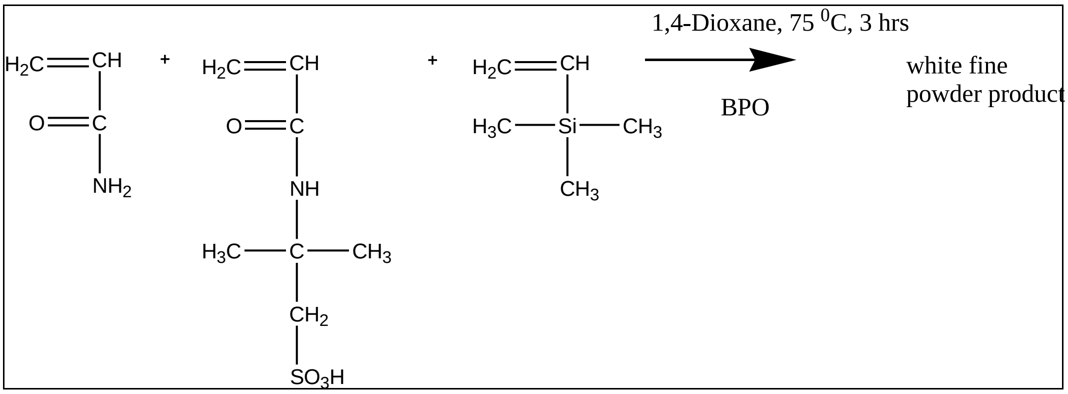


Table 1 AMPS monomer content in polymerization.

Polymer	AMc (g)	AMPS (g)	VTMS (ml)	BPO (g)	1,4-dioxane (ml)	T (^{0}C)	Time (hrs)
S-1	4.0864	0.5101	0.2	0.0525	25	78	1.20
S-2	4.0245	1.0138	0.2	0.0549	25	78	1.20
S-3	4.0551	1.5186	0.2	0.0526	25	78	1.20

Table 2 Predetermination of amount of crosslinker in polymerization.

Polymer	AMc (g)	AMPS (g)	VTMS (ml)	BPO (g)	1,4-dioxane (ml)	T (^{0}C)	Time (hrs)
S-4	4.0270	1.5196	0.1	0.0588	30	60	2.5
S-5	4.0561	1.5150	0.15	0.0588	30	60	2.5
S-6	4.0551	1.5125	0.2	0.0572	25	60	2.5

RESULTS AND DISCUSSION

Equilibrium Swelling Ratio (ESR) Measurements

Synthesis and characterization studies of superabsorbent hydrogels for this thesis were initially carried out in 1,4-dioxane solvent medium. Predetermination of the content of comonomers in prepolymerization was tabulated in table 1 in experimental part. Predetermination of monomer content in prepolymer mixture were done in order to select the composition which yields the highest ESR value in time-dependent records, while crosslinking agent ratio was kept constant. For a desired level of water uptake of crosslinked polymer material, the degree of crosslinking as well as the chemical composition of monomeric units is important. Hydrophilic nonionic monomer acrylamide and AMPS, in order to increase the ionic hydrophilicity in polymer structure, was chosen as monomer and highly dissociable comonomer respectively. According to initial work, the highest ESR value was found for 14:1 mole ratio of AMc: AMPS which was about 518.5 g/g in distilled water. With constant crosslinking degree of superabsorbent hydrogels, there is a balance between crosslinking and ionic character of polymer structure.

While keeping comonomer concentration constant in polymerization, a preliminary work was done in order to determine the composition of crosslinking which yield best results. The tabulated work is shown in table 2. While keeping commoner concentration constant, the highest ESR was measured for the lowest concentration of alkoxysilane based crosslinking agent.

Based on these predeterminations, the best composition of polymer AMc:AMPS:VTMS is 56.27:4.82:1.30 (mmols) in 1,4-dioxane medium. The further modification and studies were based on this composition. However, since 1,4-dioxane is a cylic ether and there is a possible formation of peroxide on the alpha carbon next to the ether linkage. After polymerization, there were a great explosion of reaction vessel, and spread out of both cancerogenic solvent and polymer product and unreacted monomer. This consequences were observed for about 90 % of set reactions and hence the polymer synthesis in 1,4-dioxane medium were given up.

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