Chapter – I
INTRODUCTION

1.1 Polymer Gels

A polymer gel is a solvent-containing network in which adequate amount of crosslinks exist to link all polymer chains to other chains at multiple points. Polymer gels are a novel state of matter, as they have both solid and liquid-like properties. After chemical or physical crosslinking, the individual polymer chains lose their identity and become part of a large three-dimensional interconnected network. The combination of the elastic and fluid properties makes them good candidates for applications in numerous fields ranging from pharmaceuticals, biotechnology, agriculture, food processing and electronics.

Polymer gels can be classified as natural and synthetic gels. Natural polymer gels, such as alginate and collagen, are naturally occurring and are used in tissue engineering applications owing to their biocompatibility. But, they have many disadvantages like batch to batch variations, potential transplant rejection or adverse host response[1]. Synthetic gels on the other hand, are relatively abundant, easy to characterize and reproducible. The majority of synthetic polymer gels are formed by the covalent cross-linking of linear or branched macromolecules using multi-functional cross-linking agents[2]. Such gels are networks with infinite molecular weight and consequently they swell rather than dissolve, when immersed in a solvent. Currently, considerable interest and activity exists in the application of synthetic polymers, particularly hydrogels, for medical and biomedical applications.
1.2 Hydrogels

Researchers, over the years, have defined hydrogels in many different ways. The most common of these is that, hydrogel is a water-swollen, crosslinked polymeric network produced by the simple reaction of one or more monomers or by hydrogen bonds and strong van der Waals interactions between chains [3]. Another definition is that, it is a polymeric material which exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water [4]. Simply put, hydrogels are polymer gels in which the solvent is water [5, 6]. Hydrogels have received considerable attention in the past 30 years, due to their exceptional promise in biomaterial applications. They have a strong resemblance to living soft tissue due to their relatively high water content and soft, rubbery consistency. Hydrogels have existed in nature since the evolution of life. Bacterial biofilms, hydrated living tissues and extracellular matrix components are some examples. A variety of naturally occurring polymers such as collagen, alginate, agarose and gelatin were also explored in early human history. However, the modern history of hydrogels as a class of materials designed for medical use, dates back to the late 1950s. Poly(2-hydroxyethyl methacrylate) commonly known as P-HEMA was the first synthetic hydrogel to be synthesized in 1936 by DuPont scientists[7], but it was not until 1960, that Wichterle and Lim[8] established the importance of P-HEMA hydrogels as excellent candidates for contact lens applications. This innovation led to the contact lens industry and to the modern field of biomedical hydrogels. The commercial success of soft contact lenses generated enormous interest in hydrogels, and eventually led to the development of smart hydrogels, that can change their properties upon application of an external stimulus such as pH, temperature, ionic
strength, salt type, solvent, light or electric field[9-11]. The work of Lim and Sun[12] in 1980 demonstrated the successful use of calcium alginate microcapsules for cell encapsulation. This was followed by Yannas et al.[13], who incorporated natural polymers such as collagen into hydrogels for use in artificial burn dressings. Hydrogels began to be slowly exploited in various research fields such as biomaterials [14, 15], agriculture [16], pharmaceutics [17-19] and biotechnology [20]. More recently, hydrogels have become especially attractive to the field of tissue engineering as matrices for repairing and regenerating a wide variety of tissues and organs.

1.3 Classification of Hydrogels

Hydrogels are mainly classified as natural or synthetic according to their origin. Table-1 lists some of the natural polymers and synthetic monomers from which hydrogels can be prepared. Hydrogels from natural polymers have been widely used for tissue engineering applications, but limitations such as wet physical properties and batch to batch variations, have motivated researchers to modify these polymers as well as to use synthetic polymers to prepare hydrogels, in the past couple of decades.

Hydrogels can also be classified as physical or chemical gels based on their crosslinking. Chemical gels are usually covalently-crosslinked networks produced by crosslinking of water-soluble polymers or by conversion of hydrophobic polymers to hydrophilic polymers to form a network. These gels are permanent or thermoset, meaning the bonds do not break at elevated temperatures and hence do not reform at lower temperatures. The crosslinker used in chemically crosslinked gels is often toxic. This means the crosslinker needs to be removed prior to use in biological systems,
which might alter the gel integrity. As a result, physically crosslinked gels are gaining much attention. Physical gels are held together by molecular entanglements or secondary forces including ionic interactions[21], hydrogen bonds[22-24], crystallization[25], hydrophobic interactions[26] and protein interactions[27]. These gels are thermoreversible and demonstrate a transition from solid to liquid, at a characteristic temperature. There are many other means of classifying hydrogels.

1.4 Synthesis of Hydrogels

Hydrogels are usually prepared by swelling crosslinked structures in an aqueous medium such as water or alcohols like methanol, ethanol or benzyl alcohol. The crosslinked structures contain either chemical or physical crosslinks. In chemically crosslinked gels, covalent bonds are present between different polymer chains, while physical interactions such as ionic interactions or hydrogen bonding exist between the polymer chains. Table-2 gives a list of a number of ways of classifying hydrogels.
<table>
<thead>
<tr>
<th>Natural Polymers</th>
<th>Synthetic Monomers</th>
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<tbody>
<tr>
<td>Chitosan</td>
<td>Hydroxyethylmethacrylate (HEMA)</td>
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<td></td>
<td>N-(2-Hydroxy propyl) methacrylate (HPMA)</td>
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<tr>
<td>Alginate</td>
<td>N-Vinyl-2-pyrrolidone (NVP)</td>
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<tr>
<td>Fibrin</td>
<td>N-isopropylacrylamide (NIPAMM)</td>
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<td>Collagen</td>
<td>Vinyl acetate (VAc)</td>
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<td>Gelatin</td>
<td>Acryolic acid (AA)</td>
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<td>Hyaluronic acid</td>
<td>Methacrylic acid (MAA)</td>
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<tr>
<td>Dextran</td>
<td>Polyethylene glycol acrylate/methacrylate (PEGA/MA)</td>
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<td></td>
<td>Polyethylene glycol diacrylate/dimethacrylate (PEGDA/DMA)</td>
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<tr>
<td>Classification</td>
<td>Contents</td>
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<td>----------------------------</td>
<td>----------------------------------------------</td>
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<tr>
<td>Source</td>
<td>Natural</td>
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<td>Synthetic</td>
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<tr>
<td>Component</td>
<td>Homopolymer</td>
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<td>Copolymer</td>
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<td>Multipolymer</td>
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<td>Preparation method</td>
<td>Simultaneous polymerization</td>
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<td>Crosslink of polymer</td>
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<td>Electric charge</td>
<td>Nonion</td>
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<td>Anion</td>
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<td></td>
<td>Cation</td>
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<td></td>
<td>Zwitter ion</td>
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<td>Physical structure</td>
<td>Amorphous</td>
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<td>Semicrystalline</td>
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<td></td>
<td>Hydrogen bonded</td>
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<tr>
<td>Crosslink</td>
<td>Covalent bond</td>
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<td></td>
<td>Intermolecular force</td>
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<td>Functions</td>
<td>Biodegradable</td>
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<td>Stimuli responsive</td>
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<td></td>
<td>Superabsorbant</td>
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<tr>
<td>Physical appearance</td>
<td>Matrix</td>
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<td></td>
<td>Film</td>
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<td>Microsphere</td>
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1.4.1 Chemical Crosslinking

Chemical crosslinking can be achieved by radical polymerization, chemical reaction of complementary groups, photo polymerization or by cross linking using enzymes. Radical polymerization involves the cross linking of low molecular weight monomers in the presence of cross linking agents. For example, poly(2-hydroxyethyl methacrylate) or pHEMA is obtained by the polymerization of HEMA in the presence of a suitable crosslinker such as EGD[28]. Other examples include dextran dissolved in water with glycidylacrylate, which has been investigated for the delivery of drugs, proteins and imaging agents[29]. Figure-1 shows chemical crosslinking by copolymerization of a monomer with a crosslinking agent to synthesize a hydrogel.

![Diagram](image)

**Figure 1.** Copolymerization of monomer to form synthetic hydrogel

The solubility properties of water-soluble polymers are due to the presence of functional groups (mainly OH, COOH and NH₂). Covalent linkages between polymer chains can be established by the reaction of such functional groups, if they have complementary reactivity. The crosslinking can be achieved by crosslinking with aldehydes, for example, poly(vinyl alcohol) can be crosslinked using glutaraldehyde[30,31]. However this needs drastic conditions like low pH, high
temperature or adding methanol as a quencher. Crosslinking of gelatin using polyaldehydes by partial oxidation was also reported previously[32] and the resulting hydrogels were used in wound treatment and te delivery of epidermal growth factor. Crosslinking can also be achieved by addition reactions such as reacting bis (or higher) functional crosslinking agents with functional groups of water-soluble polymers. The addition reactions are usually carried out in organic solvents because water can also react with the crosslinking agent.

The crosslinking agents used in these reactions are usually toxic and need to be extracted from the hydrogels, to remove any traces of unreacted crosslinker, before use in biological applications.

Another technique that is commonly used for chemically crosslinking gels is high energy irradiation or photopolymerization. Photopolymerization is the use of visible or ultraviolet (UV) light to interact with light-sensitive compounds called photo-initiators to create free radicals that can initiate polymerization to form crosslinked hydrogels[33]. Photopolymerization has several advantages like fast curing rates, spatial and temporal control over polymerization, and minimal heat production[34]. The most important advantage however is the ability to create hydrogels in situ from aqueous precursors in a minimally invasive manner. Examples of hydrogels prepared by photopolymerization include PEG acrylate derivatives[35], PEG methacrylate derivatives[36], polyvinyl alcohol (PVA) derivatives and modified polysaccharides such as hyaluronic acid[37] and dextran methacrylate[38]. Photopolymerized gels have been used as barriers following tissue injury to improve healing response, as scaffolds for cartilage regeneration, for cell encapsulation, and for localized drug delivery.
Covalent crosslinking of hydrogels is also achieved using high energy radiation like gamma irradiation[39] or electron irradiation[40-42]. Unlike photopolymerized hydrogels, irradiated hydrogels do not need a photoinitiator whose toxicity may be of issue in clinical applications. The high energy radiation directly creates free radicals which form intramolecular linkages as shown in Figure-2. Some examples of polymers that readily crosslink when irradiated include polyethylene, polypropylene, polystyrene, polyacrylates, PEG, PVA and polyamides. Hydrogels prepared using this technique have been previously used as drug delivery systems and for wound dressings[43-45].

![Figure 2. Intra-molecular crosslinking in hydrogels by irradiation](image)

Another interesting technique, first pioneered by Sperinde et al.[46], is the use of enzymes to synthesize PEG-based hydrogels. In their work, a tetrahydroxy PEG was functionalized with glutaminy1 groups (PEG-Q₈) and PEG networks were formed by adding transglutaminase to aqueous solutions of PEG-Q₈ and poly(lysine-co-phenylalanine). The advantage of this method is that, the gel usually forms between 5 to 30 min under mild conditions, and since the gelation kinetics can be well controlled, these systems are very suitable as *in situ* gelling systems.
1.4.2 Physical Crosslinking

Chemical crosslinking uses crosslinking agents which are usually toxic and can affect the integrity of cells or proteins that need to be entrapped by the hydrogels. This has led to a great interest in physically crosslinked gels over the past few years. Physical crosslinking can be achieved by ionic reactions, crystallization, protein interactions or through hydrogen bonds. Hydrogels involving ionic reactions are synthesized by forming ionic bridges between polymeric chains. Itonically crosslinked hydrogels can be classified into two groups based on the type of polymer, either anionic or cationic. Cationic polymers such as chitosan are positively charged and need to be reacted with negatively charged components (ions or molecules) for gelation to occur. The presence of the ionic bonds can be demonstrated by IR spectra, turbidimetric titration or viscometry. The advantage of ionic crosslinking is that it can be performed at both the room temperature as well as at the physiological temperature. Thus alginate gels which form by ionic reactions are used as matrix for encapsulation of living cells[47] and for the release of proteins[48]. Crystallization is another physical crosslinking mechanism through which a hydrogel can be synthesized. The hydrogel is usually formed due to the formation of crystallites which act as physical crosslinking sites in the network. Crystallization can occur in homopolymer systems such as PVA[49] and Dextran 6000 or by stereocomplex formation such as PLLA and PDLA[50].

Protein engineering is a very recent field in materials chemistry and has been used to synthesize new biomaterials for use in biological applications. The major advantage of employing proteins in hydrogels is that the physical and chemical properties of the gel can be precisely controlled by the proper design of the genetic
code in synthetic DNA sequences and synthetic amino acids. Cappello et al.[51,27] prepared sequential block copolymers which are associated in the form of beta strands and sheets and undergo irreversible sol-to-gel transition with time under physiological conditions. Natural proteins can also be used to prepare hydrogels. Kopecek and coworkers[52,53] investigated natural and engineered proteins which showed coiled-coil interactions and used them as crosslinkers for poly(N-(2-hydroxypropyl) methacrylamide) commonly known as PHPMA.

1.5 Properties of Hydrogels

For any material, the physical, chemical and mechanical properties play an important role in determining if it is suitable for a given application. However, for hydrogels, these properties are highly dependant on the environmental conditions as well. Thus, while determining the properties of a hydrogel, mimicking the in situ conditions becomes imperative. Hydrogels have a variety of properties including their absorption capacity, swelling behavior, permeability, surface properties, optical properties and mechanical properties which make them promising materials for a wide variety of applications. The characteristics of the polymer chains and the crosslinking structures in these aqueous solutions play an important role in the outcome of the properties of the hydrogel.

1.5.1 Swelling and Absorption Capacity

The polymer chains in a hydrogel interact with the solvent molecule (usually water) and tend to expand to the fully solvated state, while the crosslinked structure applies a retractive force to pull the chains inside. Equilibrium is achieved when these expanding and retracting forces counterbalance each other. Swelling ratio or water
content, given by Eq. 1 and Eq. 2, are generally used to describe the swelling behavior of hydrogels.

\[
\text{water content} = \frac{\text{weight of water}}{\text{weight of water} + \text{weight of gel}} \times 100 \quad \ldots (1)
\]

\[
\text{swelling ratio} = \frac{\text{weight of swollen gel}}{\text{weight of dry gel}} \quad \ldots (2)
\]

The swelling characteristics are crucial to the use of hydrogels in biomedical and pharmaceutical applications since the equilibrium swelling ratio influences the solute diffusion coefficient, surface wettability and mobility and the optical and mechanical properties of the hydrogel. The swelling properties are determined by many factors, including the type and composition of monomers, crosslinking density and other environmental factors such as temperature, pH and ionic strength.

1.5.2 Permeability of Hydrogels

Permeability is the ability of a hydrogel to transmit another substance such as fluids, cells or proteins. Developing hydrogel membranes and coatings of appropriate permeability characteristics is key to the success of a number of bioartificial organ transplantations. The permeability of a hydrogel to water and solutes can be adjusted over a wide range by varying the crosslinker concentration at synthesis or copolymerizing with more hydrophilic or hydrophobic monomers[54]. Some of the real life situations where permeability of hydrogels is critical are oxygen permeation for contact lens applications, nutrient and immunological biosubstance transport for immunoisolation and release of drugs and proteins for drug delivery systems.
1.5.3 Surface Properties of Hydrogels

Biocompatibility is the ability of a hydrogel to reside in the body without inducing significant immune response or toxicity. The important question in biocompatibility is how the hydrogel transduces its structural makeup to direct or influence the response of proteins, cells and organisms. This transduction occurs through the surface properties of the hydrogel, i.e. the body reads the surface structure and responds to it. The surface of a hydrogel can be rough, smooth or stepped; it can be composed of different chemistries or could be highly crystalline, disordered and inhomogeneous. Studies have been performed on the importance of roughness, wettability, surface mobility, chemical composition, crystallinity and heterogeneity, however significant research has not yet been performed on determining which parameters are of utmost importance in understanding biological responses to surfaces. Some of the techniques used for determining the surface property include electron spectroscopy[55-57], secondary ion mass spectrometry[58], scanning electron microscopy, Fourier transform infrared spectroscopy[59], scanning tunneling microscopy and atomic force microscopy. The information obtained using these methods can be used to monitor contamination, ensure surface reproducibility and explore the interaction of the hydrogels with living systems.

1.5.4 Mechanical Properties of Hydrogels

The mechanical properties of hydrogels depend on their composition and structure. Because of the high water content of fully swollen hydrogels, they normally have weak mechanical strengths. The mechanical properties of the hydrogel are affected by the comonomer composition, crosslinking density, polymerization
conditions and degree of swelling. The mechanical strength of the hydrogel is often
derived entirely from the crosslinks in the system, particularly in the swollen state
where physical entanglements are almost nonexistent. The dependence of mechanical
properties on crosslink density has been studied intensively by many researchers.
However it should be noted that when the crosslinking density is altered, changes to
properties other than strength also occur. For example, increasing the crosslinker
concentration would make the polymer chains to come closer, thus reducing the
diffusivity, release and swelling rates including the maximum degree of swelling. This
would mean that these properties will need to be re-measured every time additional
crosslinks are added.

The mechanical behavior of hydrogels is best understood by theories of
elasticity and viscoelasticity. These theories are based on the time-independent and
time-dependent recovery of the chain orientation and structure respectively. Elasticity
theory assumes that when a stress is applied to the hydrogel the strain response is
instantaneous. However for many biomaterials, including hydrogels and tissues, this
is not a valid assumption. For example, if a weight is suspended from a specimen of
ligament, the ligament continues to extend even though load is constant. Similarly, if
the ligament is elongated to a fixed length, the load drops continuously with time.
This is due to creep and stress relaxation respectively and these are the result of
viscous flow in the material. Despite this liquid- like behavior, hydrogels are
functionally solids and are thus assumed to be perfectly elastic.
1.6 Theory of Elasticity

Elasticity is the physical property of a material by virtue of which it returns to its original shape after the force under which it deforms is removed. The applied force is usually referred to as stress, which is the force acting per unit cross-sectional area of the material, while the relative deformation is called as strain. The elastic regime is characterized by a linear relationship between stress and strain. The ratio of stress to strain is constant for a given material and is the defining mechanical property of the material. Based on whether the force applied is perpendicular or parallel to the area supporting it, the stresses and strains can be axial or shear. The proportionality constant obtained for the ratio of the axial stress to the axial strain is called as Young’s modulus (represented by $E$) while the ratio of the shear stress to shear strain is referred to as shear modulus (represented by $G$). For a linearly, isotropic and homogenous material $E$ and $G$ are sufficient to completely characterize the mechanical properties of the material. However, most polymeric materials and tissue samples are anisotropic, meaning they have different properties in different directions. For example, bone, ligament and sutures are stiffer in the longitudinal direction as compared to the transverse direction. For such materials, on a macroscopic scale, more than two elastic constants are required to relate the stress and the strain properties. However, on a microscopic scale, polymers are comparatively isotropic and the elastic and shear modulus are adequate to fully characterize their local mechanical properties. In the next chapter, construction of a microscope based four magnet device will be presented. This device can be non-intrusively utilized to fully characterize the local mechanical properties of hydrogels.
1.7 Review of literature

Acrylonitrile (AN) and acrylic acid (AA) monomers were directly grafted onto chitosan using ammonium persulfate (APS) as an initiator and methylenebisacrylamide (MBA) as a crosslinking agent under an inert atmosphere was studied by Mohammed Sadeghi by thermogravimetric analysis (TGA). The effect of grafting variables, that is, AA/AN weight ratio and concentration of MBA and APS, was systematically optimized to achieve a hydrogel with swelling capacity as high as possible. The water absorbency increased with increasing the AA amount in the monomer feed due to formation of polyelectrolyte. The swelling of the hydrogel samples in saline solution (0.15 mol/l NaCl, CaCl₂ and AlCl₃) was examined. The results indicate that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. This behavior can be attributed to charge screening effect for monovalent cations, as well as ionic crosslinking for multivalent cations [60].

E. Karada et al., studied the equilibrium swelling and sorption properties of chemically crosslinked copolymeric hydrogels as biopotential sorbent consisting of acrylamide gravimetrically. The hydrogels showed enormous swelling in aqueous urea/water medium and displayed swelling characteristics that were highly depended on the chemical composition of the hydrogels. FTIR spectroscopy was used to identify the presence of different repeating units in the semi IPNs. Some swelling and diffusion characteristics were calculated for different semi IPNs and hydrogels prepared under various formulations. For sorption of cationic dye, Lauths violet into the hydrogels was studied by batch sorption technique at 25°C. Dye removal capacity, adsorption percentage and partition coefficient of the hydrogels was investigated.
Swelling and dye sorption properties of AAm/AMPS hydrogels and AAm/AMPS/PEG semi IPNs were investigated as a function of chemical composition of the hydrogels[61].

Terpolymers based on N-isopropylacrylamide, sodium 2-acrylamido-2-methylpropanesulfonate, and N-tert-butylacrylamide were synthesized by free-radical copolymerization with 2,2'-azobisisobutyronitrile as an initiator. The lower critical solution temperatures (LCSTs) of the linear polymer aqueous solutions were determined by the measurement of the transmittance on UV at different temperatures. The influence of the polymer concentration, polymer composition, and ionic strength on the LCSTs of the linear polymers was investigated. The LCST decreased with increases in the hydrophobic monomer N-tert-butylacrylamide, polymer concentration, and ionic strength. The phase transition became sharp when the polymer concentration and ionic strength increased. Meanwhile, the crosslinked hydrogels were prepared with the same recipe used for the linear terpolymers, but a crosslinker was added to the reaction system. The swelling ratios of the hydrogels at various temperatures and salt solutions were determined. The hydrogels possessed both high swelling ratios and thermosensitivity[62].

Polymer-clay hydrogel composite was prepared on the basis of polyacrylamide (PAAm) gel containing the clay mineral sepiolite. The properties of swelling and dye adsorption of poly(acrylamide-sepiolite) (AAm/Sep) composite hydrogel were investigated. The parameters of swelling and diffusion in water and dye solutions were calculated for the AAm and AAm/Sep hydrogels. It was found that the equilibrium swelling degree of obtained composite higher than that of AAm gel.[63]
Temperature-sensitive ionic hydrogels based on N-t-butylacrylamide (TBA), acrylamide (AAm), 2-acrylamido-2- methylpropane sulfonic acid sodium salt (AMPS) and N,N0-methylenebis(acrylamide) (BAAm) monomers were prepared by M.M.Ozmen. The molar ratio of TBA to the monomers AAm and AMPS was fixed at 60/40, while the AMPS content of the hydrogels was varied. The elastic modulus of the hydrogels was in the range of 347–447 Pa, much lower than the modulus of PAAm or poly(N-isopropylacrylamide) hydrogels due to the reduced crosslinking efficiency of BAAm in TBA/AAm copolymerization. The hydrogels exhibited swelling–deswelling transition in water depending on the temperature. Increasing ionic group (AMPS) content resulted in shifting of the transition temperature interval in which the deswelling takes place. The higher the ionic group content, the broader the temperature interval at the phase transition[64].

E.Karada investigated the equilibrium swelling and sorption properties of chemically crosslinked copolymeric hydrogels as biopotentail sorbent consisting of acrylamide (AAm) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). Semi-interpenetrating polymer network (semi IPNs) hydrogel, composed of AAm with AMPS as co-monomer, with poly (ethylene glycol) (PEG) and a multifunctional crosslinker such as trimethylolpropane triacrylate (TMPTA) was prepared. AAm/AMPS hydrogels and AAm/AMPS/PEG semi IPNs were synthesized by free radical solution polymerization by using ammonium persulphate (APS)/N,N,N'N'-tetramethylethylene diamine (TEMED) as redox initiating pair. Swelling experiments were performed in water, 0.01 M and 0.03 M aqueous urea solutions at 25oC, gravimetrically.
The hydrogels showed enormous swelling in aqueous urea/water medium and displayed swelling characteristics that were highly depended on the chemical composition of the hydrogels[65].

Superporous hydrogels (SPHs), based on poly(2-hydroxyethyl methacrylate) (PHEMA), were prepared by adding minute amounts of an ion-complexable hydrophilic acrylic acid. PHEMA SPHs are generally strong, but their swelling is minimal. To improve the swelling, different poly(HEMA-co-acrylic acid) hydrogels were polymerized and crosslinked, then physically treated with divalent calcium and trivalent aluminum cations. The incorporation of acrylic acid copolymer into the SPH, followed by crosslinking of the copolymer with calcium or aluminum ions produced SPHs with improved swelling and strength. Cells in the presence of hydrogel showed high viability indicating the absence of cytotoxicity and stimulatory effect[66]. Swelling superabsorbent was synthesized with biodegradable N-maleyl chitosan as cross-linker, acrylic acid (AA) and acrylamide (AM) as the monomers, ammonium peroxodisulfate–sodium bisulfite (NaHSO3) as redox initiation system, by means of aqueous solution polymerization. The best reaction condition was based on the orthogonal experiment design. The optimal conditions on distilled water absorbency and on 0.9 wt% NaCl solution absorbency were monomer concentration 20 wt%, mole ratio of AA to (AA/AM) 60%, the neutralization degree of AA 40%, cross-linker concentration 2% and monomer concentration 25 wt%, mole ratio of AA to (AA / AM) 60%, neutralization degree of AA 50% and cross-linker concentration 1%, respectively. Factors influencing the water absorbency of superabsorbent also were investigated, by single factor experiment method. The absorbency of superabsorbents in distilled water and 0.9 wt% NaCl solution increased and then decreased with the
increasing of monomer concentration, mole ratio of AA to (AA / AM) and degree of neutralization of AA. With the increasing of cross-linker concentration, the absorbency in distilled water increased and then decreased, but it decreased all the time in 0.9 wt% NaCl solution. In enzymatic degradation tests, the weight loss of superabsorbent was related to the content of cross-linker[67].

R.Akkaye et al. investigated the preparation and characterization of the composites formed from Bentonite (B) and Zeolite (Z) minerals, and polyacrylamide-co-maleic acid (PAA-MA) hydrogel polymers. The procedures used in obtaining the polymers were also applied in preparation of the composites by direct polymerization of the monomers of interests dissolved in the suspension of B or Z. The prepared PAA-MA and the composites were characterized with the data and analysis results obtained from FT-IR, TGA, SEM, BET-porosity and Zero Point of Surface Charge (PZC). The results of FT-IR, TGA, SEM, BET-porosity and PZC analysis presented certain evidences for the formation of composites, it was impressed that the composites were the mixtures composed of two phases composing of organic (PAA-MA) and inorganic (B or Z) phases rather than the formation of polymer/mineral hybrid[68].

Thermosensitive hydrogels consist of elastic networks whose interstitial space can take up as much as 90% (w/w) water. These hydrogels undergo reversible sol-gel transitions upon exposure to physiological temperature and possess mechanical properties that resemble those of living tissues. The ideal hydrogel for successful tissue regeneration should display the following characteristics: (1) an extensive three-dimensional network that allows cell migration and attachment, and diffusion of physiological fluids; (2) biocompatibility, providing an environment suitable for cell
proliferation and differentiation, and lacking residual chemical reagent contamination; and (3) appropriate mechanical properties and a capacity for biodegradation that is compatible with the target tissue. Thermosensitive hydrogels that meet these criteria could act as delivery vehicles for therapeutic agents and serve as cell culture scaffolds, guaranteeing the successful regeneration of tissue[69].

Copolymer hydrogels of acrylic acid (AA) with N,N-dimethylacrylamide (NNDMAAm) were synthesized by solution free radical polymerization at different feed mol monomer ratios. The monomer reactivity ratios were determined by Kelen-Tüdös method. According to that, the monomer reactivity ratios for poly(AA-co-NNDMAAm) were $r_1 = 0.650$ (M$_1$=AA) and $r_2= 1.160$ (M$_2$=NNDMAAm), $(r_1 \times r_2= 0.753)$. The effect of reaction parameters including; the concentration of cross-linking reagent, monomer concentration, pH, temperature, salt solutions, and solvent polarity on the water absorption have been studied. The hydrogels achieved water-absorption values of 544 g water/g xerogel for the copolymer poly(AA-co-NNDMAAm) 3:1 at pH 5. Low critical solution temperature (LCST) values of hydrogels, showed an increase when the hydrophilic AA moiety content increased in the copolymers[70].

A series of interpenetrating polymer network (IPN) hydrogels having higher swelling ratio (SR) and thermosensitivity were synthesized from sodium acrylate (SA) and N-isopropyl acrylamide (NIPAAm) by a two-step method. A series of the porous poly(sodium acrylate -co-1-vinyl-2-pyrrolidone) [poly(SA-co-VP)], (SV), hydrogels were prepared from acrylic acid having 90% degree of neutralization and VP monomer in the first step. The second step is to immerse the SV dried gels into the NIPAAm solution containing initiator, accelerator, and crosslinker to absorb NIPAAm solution and then polymerized to form the poly(SA-co-VP)/poly(NIPAAm) IPN
hydrogels (SVN). The effect of the different molar ratios of SA/VP and the content of NIPAAm on the swelling behavior and physical properties of the SVN hydrogels was investigated. Results showed that the SVN hydrogels displayed an obviously thermoreversible behavior when the temperature turns across the critical gel transition temperature (CGTT) of poly(NIPAAm) hydrogel. The pore diameter distributions inside the hydrogel also indicated that the pore sizes inside the SVN hydrogels were smaller than those inside the SV hydrogels. At the same time, the more proportion of SA was added into the hydrogel, the larger pore diameter of the SV hydrogel was formed. The results also showed that the SR decreased with an increase of the VP content in the SV hydrogel and more obviously decreased in the SVN hydrogels. The SVN networks also showed stronger shear moduli than SV hydrogels[71].

The predictions of the Flory-Rehner theory of swelling equilibrium including the ideal Donnan equilibria were compared with the experimental swelling data obtained from poly(acrylamide-co-sodium acrylate) hydrogels swollen in water and in aqueous salt (NaCl) solutions. For this comparison, the fraction of counter ions which are effective in the gel swelling was taken into account. The ionic hydrogels were prepared from acrylamide and sodium acrylate (NaAc) monomers with 0 to 5 mol% NaAc and using N,N'-methylenebis(acrylamide) as the crosslinker. As expected, at a fixed crosslinker ratio, the volume swelling ratio of hydrogels in water increases sharply when the mole fraction of NaAc increases or the NaCl concentration in the external solution decreases. Taking into account the wasted counterions within the hydrogels, the theory correctly predicts the swelling behavior of hydrogels in water and in aqueous salt solutions. Not predicted by the theory is the increased swelling
ratio of hydrogels with less than 4 mol% NaAc content with increasing salt concentration from $10^{-1}$ to $10^0$ M[72].

The rheology of a superabsorbent hydrogel based on starch and polyacrylonitrile was investigated by F. Soleimani. The physical mixture of starch and polyacrylonitrile was hydrolyzed by NaOH solution to yield starch-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR spectroscopy[73].

Temperature-sensitive hydrogels based on N-t-butylacrylamide (TBA), acrylamide (AAm), and sodium alginate were prepared by free radical polymerization method. Methylenebisacrylamide (MBA) and ammonium persulfate (APS) were applied as water soluble crosslinker and initiator, respectively. The chemical structure of the hydrogels was confirmed by FT-IR spectroscopy and thermogravimetric analysis (TGA) methods. Morphology of the samples was examined by scanning electron microscopy (SEM). By changing the initial TBA/AAm mole ratios, hydrogels with different swelling properties were obtained. The rate parameters were found to be 2.0, 2.4, and 3.5 min for the superabsorbents with AAm/TBA weight ratio of 1.0, 1.3 and 2.0 respectively. The swelling behavior in distilled water and different pH solutions was investigated. A preliminary swelling kinetics and the absorbency under load (AUL) were also studied. At the applied pressure (2.07 kPa), maximum swelling was found to be 17, 19, and 21 (g/g) for the superabsorbent hydrogels with AAm/TBA weight ratios of 1.0, 1.5 and 2.0, respectively[74].
Temperature-sensitive ionic hydrogels based on N-t-butylacrylamide (TBA), acrylamide (AAm), 2-acrylamido-2- methylpropane sulfonic acid sodium salt (AMPS) and N,N'- methylenebis(acrylamide) (BAAm) monomers were prepared by M.M.Ozmen. The molar ratio of TBA to the monomers AAm and AMPS was fixed at 60/40, while the AMPS content of the hydrogels was varied. The elastic modulus of the hydrogels was in the range of 347–447 Pa, much lower than the modulus of PAAm or poly(N-isopropylacrylamide) hydrogels due to the reduced crosslinking efficiency of BAAm in TBA/AAm copolymerization. The hydrogels exhibited swelling–deswelling transition in water depending on the temperature. Increasing ionic group (AMPS) content resulted in shifting of the transition temperature interval in which the deswelling takes place. The higher the ionic group content, the broader the temperature interval at the phase transition. Ionic hydrogels exhibited first-order reentrant conformational transitions in ethanol–water and in dimethylsulfoxide (DMSO)–water mixtures. The higher the ionic group content of the hydrogels the narrower the ethanol (or DMSO) range in which the reentrant phenomena occur. By taking into account the difference of the solvent mixture composition inside and outside the gel, the equilibrium swelling theory provided a satisfactory agreement to the experimental swelling data of the hydrogels immersed in the solvent mixtures[75].

NTBA hydrogels were prepared by free radical polymerization in water–dioxane mixture with fixed molar ratio (25 mol%) of N-isopropylacrylamide (NIPAM) and varying remaining molar concentrations of N-tert-butylacrylamide (NTBA) and acrylamide (AAm). The structure of the resultant hydrogels was studied by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) techniques. The thermal properties of the hydrogels were analyzed by
thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods. DSC thermograms were used for the quantitative determination of free, interfacial and bound water contents. The result showed that the free and interfacial water contents increased with increase in the hydrophilic AAm content, and the bound water content increased with hydrophobic NTBA content in the hydrogels. Swelling behavior of the hydrogels was evaluated at different temperatures. The percentage swelling and diffusion kinetic parameters (network structure constant, type of diffusion and diffusion constant) were calculated for all samples. The diffusion was found to be Fickian type for copolymer having equimolar concentrations of NTBA and AAm and non-Fickian type for others. Diffusion coefficients of the hydrogels were found to be increased with increasing temperature. In addition, poly(NIPAM-co-NTBA-co-AAm) hydrogels were used in concentration separation process for BSA solution. The result showed that the copolymer with equimolar NTBA and AAm contents has high separation efficiency with good thermo-responsive behavior among all copolymers[76].

A series of ionic poly(N-t-butylacrylamide-co-acrylamide) [P(NTBA-co-AAm)] hydrogels were synthesized by free-radical crosslinking copolymerization of N-t-butylacrylamide (NTBA) and acrylamide (AAm) monomers in fixed amount, but changing amount of maleic acid (MA) comonomer in methanol using N,N-methylene-bis-acrylamide (BAAm) as the crosslinker, ammonium persulfate (APS) as the initiator, and N,N,N',N'-tetramethylethlenediamine (TEMED) as the activator. The swelling behavior of these hydrogels was analyzed in buffer solutions at various pHs. The prepared hydrogels also were investigated swelling-deswelling transition in water depending on the temperature. For the bovine serum albumin (BSA) adsorption,
the effect of pH, temperature, initial protein concentration and adsorption rate were
investigated. Maximum BSA adsorption was observed at pH 5.0 which is close to the
isoelectric pH of BSA (pH 4.8). The highest adsorption rate was achieved in about
12 h. and also, maximum BSA adsorption was found at +5°C[77].

Superadsorbent cellulose-graft-acrylic acid (C-g-AA) hydrogels were
successfully prepared via free radical polymerization in phosphoric acid solution.
Phosphoric acid solution provides a homogeneous reaction system. The C-g-AA
hydrogels have a porous network inner structure with cellulose as the backbone. The
introduced carboxyl groups enable the C-g-AA hydrogels with good swelling property
(swelling ratio 7327%) and excellent MB adsorption capacity (equilibrium adsorption
amount 2197 mg g⁻¹). The dynamic swelling behaviors of the hydrogels were tested,
water intake of hydrogels followed a non-Fickian type diffusion[78].

Thermo-sensitive hydrogels of chitosan (CS) networks sandwiched by poly
(N-isopropylacrylamide) (PNIPAAm) and poly(acrylamide) (PAAm) were prepared.
The formation of chitosan networks inside the gel was done by immersing the PAAm-
co-PNIPAAm/CS mixture in a 1.5% glutaraldehyde aqueous solution. The water
uptake (WU) and water absorption mechanism of PAAm-co-PNIPAAm/CS were
studied in following conditions: 25 and 37 degrees C, swelling pHs of 3.80 and 7.01,
and cross-linking times of CS in glutaraldehyde of 2 and 40 min. The characterization
of the PAAm-co-PNIPAAm/CS was done by scanning electron microscopy (SEM),
infrared analysis (FT-IR), and thermogravimetric analysis (TGA). Pore size was
larger at pH 25 degrees C than at pH 37 degrees C. Increase in CS content,
crosslinking time, temperature, and swelling pH lead to a decrease in the sensitivity of
the hydrogel to water. The chitosan networks improved the mechanical properties of
the hydrogel. On the other hand, the hydrophilic/hydrophobic groups present in PNIPAAm are responsible for a low thermostensitivity observed in the swelling studies at different temperatures. The water transport mechanism throughout hydrogels was evaluated by kinetic behavior using Fickian and non-Fickian diffusion, and Case II transport. The PAAm-co-PNIPAAm/CS obtained is not pH-sensitive; however, they may be used to remove either proteins or other chemicals from aqueous solutions[79].

Novel pH sensitive carboxymethyl (CM) chitosan/acrylic acid hydrogels were prepared. CM-chitosan and acrylic acid (AA) in aqueous solution were copolymerized and crosslinked by using vinyltriethoxysilane (VTESi). Different amounts of AA and crosslinker were incorporated in CM-chitosan/AA hydrogel. IR analysis confirmed the presence of pyranose ring as well as Si-O-Si linkage within the hydrogel. Thermogravimetric analysis showed an increase in the stability of hydrogel either having high AA ratio or high crosslinker ratio. The swelling of the hydrogels was carried out by investigating the effect of time, pH (buffered and nonbuffered) and ionic media. In non-buffered media the overall swelling was found to be high as compared to buffered media. Maximum swelling was observed in hydrogel having mass ratio of 7.0 (AA : CM-chitosan). This hydrogel showed low swelling in low pH similar to that of the stomach and high swelling in neutral pH similar to that of the small intestine and can be used in drug delivery applications[80].

N-vinylpyrrolidone (VP)/methacrylic acid (MAA) copolymers have been prepared at three different mole percents for which the methacrylic acid composition is around 5, 10, and 15%. MAA and VP monomer mixtures have been irradiated in a $^{60}$Co-γ source at different irradiation doses and percent conversions have been
determined gravimetrically. ~80% conversion of monomers into hydrogels were performed at 3.4 kGy irradiation dose. Poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) hydrogels have been used for the adsorption of some dyes such as Safranine-O, Methylene Blue from aqueous solutions. These hydrogels were swollen in distilled water and in aqueous solutions of dyes at pH 4.0, 7.0, and 9.0. P(VP/MAA) hydrogel which contains the higher methacrylic acid content showed the maximum % swelling at pH 9.0 in water and swelling increased in the order of Safranine-O>Methylene Blue. Diffusion of water and aqueous solution of dyes within hydrogels was found to be of non-Fickian character. Diffusion coefficients of water and aqueous dye solution in P(VP/MAA) hydrogels were calculated. In the dye adsorption experiments, the effects of pH, concentration of aqueous dye solution and the composition of hydrogels on adsorption process were investigated. When the pH and concentration of aqueous solutions of dyes and the MAA content in hydrogels increased, the adsorption increased as well. From the adsorption studies, the cationic dyes could be repeatedly adsorbed and desorbed with P(VP/MAA) hydrogel without significant loss in their adsorption capacity[81].

Poly(N-hydroxymethylacrylamide), PHMA, hydrogels were prepared by using N-hydroxymethylacrylamide, HMA, monomer and polyethyleneglycol (400) diacrylate as a crosslinking agent in aqueous medium and then amine groups were incorporated onto PHMA hydrogels by amination reaction with different diamines. The obtained hydrogels were characterized by determination of amine value, hydroxymethyl group content and FTIR spectra. The amine value of hydrogels changed from 2.23 to 4.64 mmol/g by depending on the amine compounds used in amination reaction. Their swelling degree increased at acidic pH values and they
showed pH dependent swelling behavior. They were used as sorbent for removal of indigo carmine and Cu(II) ion, as a model dye molecule and metal ion, respectively, from aqueous solutions. The adsorption properties of the hydrogels were investigated by depending on pH, time and initial indigo carmine or Cu(II) ion concentration. It was seen that the amine group incorporated hydrogels have quite high adsorption rate and adsorption capacity, and their adsorption capacities changed with pH of the solution. Langmuir isotherm model was the best fit for adsorption of both indigo carmine and Cu (II) ion[82].

An amphiphilic colloidal copolymer containing methyl methacrylate (MMA) and sodium acrylate at different compositions was prepared by a free-emulsion polymerization method with potassium persulfate as an initiator, and it was then doped in HCl solution to obtain the acid form poly(methyl methacrylate-co-acrylic acid) (PMMAA) copolymer. The copolymers were characterized by means of gel permeation chromatography, \(^1\)H- nuclear magnetic resonance spectrometer, \(^{13}\)C solid-state nuclear magnetic resonance spectrometer, infrared spectra, and differential scanning calorimeter. The copolymers have only a single, and nearly constant, glass transition temperature of 124°C, at which there is no observable effect on the structure of the copolymer. The monomer reactivity ratios \(r_{\text{NaAA}}\) and \(r_{\text{MMA}}\) were \(r_{\text{NaAA}} = 1.06\), \(r_{\text{MMA}} = 0.70\) and \(r_{\text{NaAA}} = 1.02\), and \(r_{\text{MMA}} = 0.63\) estimated respectively by using the classical Fineman-Ross and the Kelen-Tüdös methods. The results revealed that the copolymer had a tendency towards the formation of small acrylic acid blocks that have very short segments of MMA. The proton spin-lattice relaxation time in the rotating frame \(T_1^H\) indicated single composition-dependent for all copolymers, which
imply dynamic homogeneity and a good miscibility with chain dynamics on the upper spatial scale of 3 nm existed in the PMMAA copolymer. An increase of the thermal stability of the copolymers was shown from the apparent activation energy of the thermal degradation process for the copolymers relative to the homopolymers[83].

Hydrogels comprising of zwitterionic repeat units were synthesized. The amine groups of the poly (ester amine) were quaternized with 1,3-propane sultone. The gelation was observed on treatment with sultone. The hydrophilic gel thus formed is sensitive to temperature, pH, ionic strength and nature of electrolytes in aqueous solution. In absence of any electrolyte, the extent of swelling decreased with temperature, but in the monovalent salt solution the equilibrium swelling diminished with temperature and the contrary behavior was experiential in bivalent electrolytes[84].

The swelling behavior of hydroxyethyl cellulose-acrylamide hydrogels at different pH and temperatures was studied. The absorption increased for the first 12 hours and then decreased. Several hydroxyethyl cellulose-acrylamide ratios were studied. Increasing hydroxyethyl cellulose amount decreased swelling, indicating that swelling was affected by increase in crosslinking. Three different levels of crosslinking agent were studied. Hydrogels exhibited a thermal and pH sensitive behavior. Highest swelling capacity was found at pH 7.0 and 30 °C. All samples were characterized by means of infrared spectroscopy (FTIR). Characteristic absorbance peaks for both materials were found, showing the presence of hydroxyethyl cellulose and acrylamide on hydrogel[85].
A novel series of copolymer hydrogels of 2-(dimethylamino) ethylacrylate (DMAEA)/ 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were prepared by solution free radical polymerization at different feed monomer mol ratios. The monomer reactivity ratios were determined by Kelen–Tüdös method. According to that, the monomer reactivity ratios for poly(DMAEA-co-AMPS) were $r_1 = 0.125$ and $r_2 = 2.85$, $(r_1 \times r_2 = 0.356)$. The effect of reaction parameters, including the concentration of cross-linking reagent $N,N'$-methylene-bis-acrylamide (MBA) and initiator ammonium persulfate (APS), the monomer concentration, pH, temperature, salt solutions, and solvent polarity on the water absorption have been also studied. The hydrogels achieved water-absorption values of $430 \text{ g of water/g of xerogel}$ for the copolymer 1:2 richest in AMPS moiety. This copolymer is also very stable to the temperature effect. The optimum pH for the copolymers is 7. Aqueous solutions of the copolymers showed lower critical solution temperature behavior (LCST). The phase transition temperatures of aqueous solutions of these copolymer increased with increasing of hydrophilic AMPS unit content in the copolymers. The glass transition temperature (Tg) of hydrogels showed a decrease by increasing of comonomer DMAEA content[86].

Sodium alginate/acrylamide interpenetrating polymer networks ((NaAlg/AAm)IPN) have been prepared at definite composition. The aqueous solution of 3% (w/v) sodium alginate and 50% (w/v) acrylamide was irradiated with $^{60}\text{Co-\gamma}$ rays at a dose rate of 0.07 kGy/h up to 5 kGy. The percent conversion was determined gravimetrically and 100% gelation was achieved at 5 kGy dose. To understand whether the semi-interpenetrating polymer network of sodium alginate is performed, Fourier Transform Infrared (FTIR) spectra of polyacrylamide (PAAm),
sodium alginate, and the semi-interpenetrating polymer network were recorded. It is found that the FTIR spectra of PAAm, NaAlg, and the semi-interpenetrating polymer network are different. The thermograms of PAAm, sodium alginate, and the semi-interpenetrating polymer network were recorded for investigating their thermal character. (NaAlg/AAm)IPN hydrogels were immersed to swell in a solution of pH 7, at a temperature of 25°C. The swelling results at pH 7.0 indicated that (NaAlg/AAm)IPN hydrogel, containing 3% NaAlg showed maximum % swelling in water but swelling increased in the order of water > Magenta > Methylene Blue > Safranine-O > Methyl Violet. Diffusion of water and aqueous solution of dyes within (NaAlg/AAm)IPN hydrogels was found to be of Fickian character at the initial stage of swelling with regard to values calculated for diffusion coefficient of (NaAlg/AAm)IPN hydrogels in water and aqueous solution of dyes. Some diffusion parameters were calculated from swelling of (NaAlg/AAm)IPN in water and dyes and their adsorption isotherms were plotted. In the adsorption experiments, the efficiency of (NaAlg/AAm)IPN hydrogels to adsorb Magenta, Safranine-O, Methylene Blue, and Methyl Violet dyes from water was studied. (NaAlg/AAm)IPN hydrogels showed different adsorption for different aqueous solution of dyes at pH 7.0. Adsorption isotherms were constructed for (NaAlg/AAm)IPN-dye systems. S type adsorption in the Giles classification system was found. Thermal and spectroscopic characterization of semi-interpenetrating polymer network of sodium alginate and acrylamide and dye adsorbed semi-interpenetrating polymer network of sodium alginate and acrylamide was recorded[87].
Polymer-clay hydrogel composite was prepared on the basis of polyacrylamide (PAAm) gel containing the clay mineral sepiolite. The properties of swelling and dye adsorption of poly(acrylamide-sepiolite) (AAm/Sep) composite hydrogel were investigated. The parameters of swelling and diffusion in water and dye solutions were calculated for the AAm and AAm/Sep hydrogels. It was found that the equilibrium swelling degree of obtained composite higher than that of AAm gel. Spectroscopic analysis of composite and composite-dye systems was done with FT-IR method. Adsorption of monovalent cationic dyes such as Basic Blue 12 (BB-12) Basic Blue 9 (BB-9), and Basic Violet 1 (BV-1), was studied on the composite. In the adsorption experiments, S (Sigmoidal) type for composite gel adsorption isotherms in the Giles classification system was found. Adsorption studies indicated that the amounts of adsorbed dyes on the AAm/Sep composite hydrogel were increased with following order; BB-12 > BB-9 > BV-1. The composite hydrogel may be considered as good candidate for environmental application to retain more water and dyes[88].

Free radical copolymerization of styrene (S) and acrylonitrile (AN) in the ionic liquids (ILs) 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆), 1,3-dimethylimidazolium dimethylphosphate ([MMIM]Me₂PO₄) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]EtSO₄) were investigated. 2,2'-azobisiso butyronitrile (AIBN) and dibenzoyl peroxide (BPO) were used as initiators and dimethyl formamide (DMF) and methanol as reference solvents. The influence of the viscosity on the conversion and the molecular weights was studied by variation of the reaction temperature and the IL concentration. At reaction temperatures of 80 - 85 °C already after 30 minutes a conversion of about 80 % and almost a doubling of the molecular weights is reached for the S/AN (50/50 mol%) copolymerization. In
addition the copolymerization behavior of S/AN in [EMIM]EtSO₄ was investigated. With increasing concentration of AN in the monomer feed the polymerization rate as well as the molecular weights of the copolymers increase. The influence of the ionic liquid on the copolymer composition, glass-transition temperature and rheological behavior was studied[89].

L. Janovak et al., synthesized, thermo- and pH-sensitive gels and tested them as skin extenders. Our aim is the development of copolymer and composite hydrogels. When implanted under the human skin, swell osmotically and thereby induce skin growth. In the course of the polymerization reaction, we produced copolymers with variable compositions, starting from different acrylic compounds [N-isopropylacrylamide (NIPAAm), acrylamide (AAm), and acrylic acid (AAc)]. The mechanical strength and the swelling stability of the gels are enhanced by the addition of fillers [Na-montmorillonite and Na-montmorillonites organophilized with alkylammonium ions (C₄₅m.), n = 4, 12, 18]. They observed that in the case of composites synthesized with the addition of fillers, relatively low filler contents (1–5 wt.%) resulted in more extensive swelling and stronger gel structure. During the experiments, the monomer composition (0/100–100/0 mol% NIPAAm/AAm or AAc) and the cross-link density (50–1500 mol%) of the gels (M/C ratio) and, in the case of composites, the quality and quantity of fillers are varied. The filler content of composites varies between 1 and 25 wt.%. The extent of swelling and the viscoelastic properties can be manipulated through the ratios of these parameters. In the case of certain copolymer and composite gels, values of desorption enthalpy (ΔHₘ) corresponding to the actual water contents were also determined by thermoanalytical measurements (differential scanning calorimetry, DSC). Swelling values determined by gravimetry and
enthalpies calculated from DSC measurements were found to be in good correlation. Even in the case of the relatively hydrophobic poly(NIPAAm)-based gels, an enthalpy value of 98.41 kJ/mol was obtained, which is twice the value measured in pure water (41.74 kJ/mol). Evaluation and comparison of the rheological and DSC results also allowed conclusions to be drawn concerning the types of interaction operating among the three components of the system, i.e., the polymer skeleton and the filler and water molecules.[90].

A novel hydrogel has been synthesized by grafting methacrylic acid (MAA) onto Gum arabic (GA) through free radical graft co-polymerization in the presence of potassium persulphate (KPS) as an initiator and hexamethylene tetramine (HMTA) as a cross-linker. Various reaction parameters like reaction temperature, reaction time, concentration of initiator, amount of solvent, pH, concentration of monomer and concentration of cross-linker were optimized. GACL-poly(MAA) was characterized by FTIR spectroscopy, SEM and TGA-DTA techniques. Optimized polymer was studied for its salt-resistant swelling behavior in different solutions: NaCl, MgCl₂, CaCl₂, FeCl₃, ZnCl₂ and BaCl₂ as a function of salt concentration, temperature and pH. It was observed that GACL-poly(MAA) exhibits following salt-resistant swelling trend in different salts: NaCl > ZnCl₂ > MgCl₂ > CaCl₂ > BaCl₂ > FeCl₃ [91].

Ionic Hydrogels were synthesized using N-cyclohexylacrylamide, acrylamide and AMPS Ionic Liquid by free radical polymerrization at 60°C. The swelling behavior increased with increasing amount of AMPS IL. The SEM analysis showed that the hydrogels are in rod like shape. XRD pattern exhibits more amorphous in nature[92].
A series of Poly(N-cyclohexylacrylamide -co -acrylamide / Sodium acrylate) Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N, N-methylenebisacrylamide (MBA) as a crosslinker at 600°C. The amount of N-cyclohexylacrylamide (NCA) and Acrylamide (AM) monomers was fixed and the amount of sodium acrylate(AcNa) was varied. The swelling behavior of Hydrogels showed that the degree of swelling was increased with increasing the amount of Ac Na. The surface morphology of hydrogels showed porous and well type structure[93].

Poly(N-tert-amylacrylamide -co -acrylamide / AMPS Na) Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N, N-methylenebisacrylamide (MBA) as a crosslinker at 600°C. The amount of N-tert-amylacrylamide (NTA) and Acrylamide (AM) monomers was fixed and the amount of 2-acrylamide-2-methylpropanesulfonic acid sodium salt was varied. The Hydrogels were characterized by IR spectroscopy. The swelling behavior of Hydrogels studied by Gravimetric method and degree of swelling was increased by increasing the amount of AMPS Na. The surface morphology was studied by SEM analysis.[94]

Poly(N-cyclohexylacrylamide -co -acrylamide / AMPS Na) Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide (MBA) as a crosslinker at 600C. The amount of N-cyclohexylacrylamide (NCA) and Acrylamide (AM) monomers was fixed and the amount of AMPS Na was varied. The
Hydrogels were characterized by IR spectroscopy. The swelling behavior of Hydrogels studied by Gravimetric method and the degree of swelling was increased when increasing the amount of AMPS Na[95].

A series of ionic poly(N-tert-amy lacrylamide -co -acrylamide / maleic acid) Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide (MBA) as a crosslinker at 600C. The amount of N-tert-amylacrylamide (NTA) and Acrylamide (AM) monomers was fixed and the amount of Maleic acid (MA) was varied. The swelling behavior of Hydrogels studied by Gravimetric method and degree of swelling was increased by increasing the amount of Maleic acid[96].

A series of ionic Poly (N-tert-amylacrylamide -co -acrylamide / Ac Na) Hydrogels were Synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide(MBA) as a crosslinker at 600C. These hydrogels showed up to 48% removal efficiency towards Methylene Blue dye adsorption study[97].
1.8 Aim of the study

Based on the above information from Literature study, we decided to synthesize the N-tert-amylacrylamide Hydrogels using different ionic monomers via free radical polymerization. The aim of the studies are as follows.


The above mentioned hydrogels were subjected to the following studies.

(a) FTIR characterization to conform the incorporation of Monomers in the Hydrogel.

(b) Swelling behavior by Gravimetric Method.

(c) To study the effect of Temperature and electrolytes on swelling behavior.

(d) Thermal stability by TGA

(e) XRD – amorphous nature.

(f) Surface Morphology by SEM analysis.
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