

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Superabsorbent Polymer (SAPs)

##### 2.1.1 General Properties of Superabsorbent Polymers

Superabsorbent polymers, otherwise known as SAPs, absorbent polymers, absorbent gels, super soakers, super slurpers, or gel crystals, are materials that swell in water to form a clear gel made up of separate, individual particles. SAPs possess a number of attributes that make them attractive in many different applications. SAPs have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties (6).

The basic property of water absorption has suggested the use of superabsorbent polymers in many other applications, including paper towels, surgical sponges, meat trays, disposable mats for outside doorways and in bathroom, and for household pet litter, bandages and wound dressings. The ability of swollen gels to release the water to the surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. Superabsorbent polymers may also be used to release water-soluble substances from within the network structure into the surroundings as a solution. For example, pharmaceuticals and fertilizers may be incorporated into the superabsorbent polymer to yield controlled release products. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse

as cosmetics or concrete or to contribute a soft yet dry feel to a product like a hot or cold pack for some muscles. The soft, rubbery nature may also be employed to impart sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables.

As mentioned above superabsorbent polymer can absorb water up to several thousand times of its own weight and keep this water under pressure. The absorbed water can be released slowly when the SAP is put in dry air to maintain the moisture of the environment. Most SAPs are in principles crosslinked hydrophilic polymers.

Because of these unique properties, SAPs have many novel potential applications in various areas. For example, they can be used in baby diapers, sanitary towels, athletic garment, as carrier of contamination prevention agent used as ship bottom painting to prevent the formation of microorganism, adhesives and food packing, etc. In agriculture and horticulture, it is being used as a plant growth medium to improve the water retaining property of sandy soil, in civil engineering as a friction reducing material for placing pipe for sewage transport, in environmental protection, as a sludge dehydrating treatment agent for solidifying waste and to absorb heavy metal ions such as  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$ .

There are many kinds of methods to prepare SAP with various starting materials, such as copolymerizing a hydrophilic monomer with a crosslinking agent, grafting monomer with starch, cellulose, synthetic fiber, and polysaccharide, cross-linking linear hydrophilic polymer with polyvalent metal ions or organic multifunctional group materials, etc. The product of SAP can be in the form of small particles, powder, fiber, membrane, microbeads and even liquid.

The SAPs can be classified with different methods. From a morphological point of view they can be divided into particle, powder, spherical, fiber, membrane and emulsion types etc. The morphology of SAP is designed to respond the different requirements of the applications. For example, the powder product can be put in the multilayers sheet to form sanitary napkins and diapers, the particle and spherical product can be used as a deodorant, fiber product can be used as an antistatic electric fiber, membrane product can be used as an antifrost sheet and emulsion product can be used in soaking and painting.

From a material resource point of view, SAP can also be divided into natural macromolecules, semi-synthesized polymer, and synthesized polymers. From a preparation method point of view, it can be classified as graft polymerization, cross-linking polymerization, networks formation of water-soluble polymer and radiation cross-linking, etc. There are many types of SAPs in the present market. Mostly, they are crosslinked copolymer of acrylates and acrylic acid, and grafted starch-acrylic acid polymer prepared by reverse suspension and emulsion polymerization, aqueous solution polymerization, and starch graft polymerization.

Water absorption capacity (WAC) is the most important characteristic of SAP. There are many ways to measure WAC, however, there is no standard yet. Usually, the WAC is measured using volumetric method, gravimetric method, spectroscopic method and microwave method. The volumetric method is to measure the volume changes of SAP (or the water) before and after the absorption, the gravimetric method is to measure the weight changes of SAP, the spectrometric method is to measure the changes in the UV spectrum of the SAP and the microwave method is to measure the microwave absorption by energy changes.

The water absorption capacity (WAC) of the SAPs depends upon its composition and structure generated from the preparation method, as well as the presence of electrolytes in the water. For example, the WAC of SAP can be thousand gram water/gram SAP when in contact with pure water, but when it is put into water containing urine, blood and metal ions, the WAC will be reduced to only one tenths of its maximum value.

The principle of water absorption by polymer can be illustrated by the Flory theory of an ionic network.

$$Q^{5/3} = \left\{ \left( \frac{1}{2} \times \frac{i}{V_u} \times 1/S^{1/2} \right) + \left( \frac{1}{2} \cdot X_1 \right) / V_1 \right\} \times V_0/v \quad (2.1)$$

where  $Q$  is maximum swelling ratio of SAP,  $i$  is electronic charge on the polymer structure per polymer unit,  $V_u$  is polymer repeating unit volume,  $S$  is ionic strength of solution,  $X_1$  is interaction parameter of polymer with solvent,  $V_1$  is molar volume of solvent, in a real network,  $V_0$  is un-swollen polymer volume,  $v$  is effective number of chains. These parameters in the equation formed a balance of the swelling which can be further defined as follows:  $\frac{1}{2} \times \frac{i}{V_u} \times 1/S^{1/2}$  is ionic strength on both polymer structure and in the solution,  $(\frac{1}{2} \cdot X_1) / V_1$  is the affinity of network with solvent,  $V_0/v$  is cross-linking density. The equation shows that the water absorption power mainly from the osmotic pressure, the affinity of water and polymer, and the cross-linking density of the network.

The swelling process of SAP can be explained as follows: the solvent tries to penetrate the polymer networks and produce the 3D-molecular network expanding, at the same time, the molecular chains between the crosslinked points thus decrease the

configuration enthalpy value. The molecule network has an elastic contractive force which tries to make the networks contract. When these opposed forces reach an equilibrium, the expansion and contraction reach a balance too. In this process, the osmotic pressure is the driving force for the expansion of swelling, and the network elastic force is the driving force of the contraction of the gel.

At present, hydrophilic crosslinked superabsorbent polymers (SAP) such as modified acrylates and acrylamides are under scrutiny to develop a variety of products for industrial applications including chemomechanical ("intelligent") materials that convert chemical energy into mechanical motion. The equilibrium swelling of such hydrogels is sensitive to environmental stimuli of either chemical or physical nature such as changes in pH, ionic strength of the surrounding solution, temperature, photo-irradiation and electric field that may influence the size, shape, solubility and degree of ionization of the gel. By applying an electric field to a swollen gel in a solution, the gel can be made to contract and expand reversibly, thus simulating a muscle action. Also, research is ongoing worldwide to develop sensors and actuators based on those materials to monitor biochemical activity, pressure and strain rate.

One example of a hydrogel with an intelligent (smart) property responding to an environment stimulus is the pH-response polymer gel. Usually, the pH responsive gel is a molecular structure composed of a crosslinked network and ionizable groups in the network. These groups ionize in different pHs and ionic solution. During the changing of the network structure and the ionic concentration with the environmental pH, effects arise such as the generation of osmotic pressure, changes of the ionic groups and changes of the ionization degree. The hydrogen bond is changed, which in turn causes the gel to change in volume and mass. Besides the homogeneous polymer, the pH responsive gel can also be a block polymer (or

interpenetrating polymer) composed of physically crosslinked non-polar rigid and soft structures such as block polymers containing polyurea (a rigid portion) and polyethyleneoxide (a soft portion)

Another example is a temperature-sensitive gel which can respond to a temperature stimulus to change its conformation. At low temperature the gels swell as the large molecular chains extend by hydration. When the temperature reaches to a certain value, a rapid dehydration takes place. Because of attraction of hydrophobic groups, the molecular chain contracts. A typical hydrogel with a temperature-responsive property is polyisopropylacrylamide (PIPAM). Poly(acrylic acid) and poly(*N, N'*-methylene bisacrylamide) inter-penetrate polymer network gels also contract at low temperature due to hydrogen bond formation. At higher temperature, the hydrogen bonds weaken and the gel swells. Phase transition of the gel is a phenomenon of discontinuous change of the volume of the gel with the change of the environmental factors.

The commercially important SAPs are prepared by redox and thermal free-radical initiated polymerizations of acrylic acid and its salts, with small quantities of a crosslinker containing two (or more) polymerizable double bonds such as *N,N'*-methylenebisacrylamide, triallylamine and analogs of the aforementioned acrylates, in aqueous solution or as a suspension of drops of aqueous solution in a hydrocarbon. Some of the commercially available polymers are graft terpolymers with starch or poly(vinyl alcohol) as the graft substrate. As mentioned above, SAPs have been mainly used and developed only in the limited field of disposable absorbing materials such as primarily in diapers and feminine hygiene applications.

### 2.1.2 Physical Behavior of Superabsorbent Polymers

Superabsorbent polymers (SAPs) are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. SAPs function by means of a diffusive mechanism. Diffusion is a molecular phenomenon wherein molecules move in a random, nonorganized manner as a result of their thermal energy. Increasing the temperature makes the molecules move faster, and the diffusive processes occur therefore at a faster rate. The molecules are in a constant motion and will move from their average position in space toward regions of lower activity by purely statistical means. The absorption mechanism before and after swelling in a dilute salt solution of an example of a superabsorbent resin, in the case of a crosslinked polymer with sodium carboxylate groups is shown in Figures 2.1 and 2.2. Before absorption, long chain of polymers is interwoven and polymers make a three-dimensional structure by crosslinking between the chains to make a dense phase. These SAPs instantaneously absorb water and swell with dissolution of  $\text{Na}^+$ , owing to the hydrophilic ionic groups, and becoming a gel (7).

In Figure 2.1, sodium carboxylate groups are present in a stable salt form (before). Sodium cations ( $\text{Na}^+$ ) leave carboxylate anions ( $-\text{COO}^-$ ) bound to polymer chains, which then extend as a result of repulsion between anionic charge (during). Water molecules are taken in and retained in the polymer network (after).

Figure 2.2, similar to Figure 2.1 the polymer backbone in SAP is hydrophilic i.e. 'water loving' because it contains water loving carboxylic acid groups ( $-\text{COOH}$ ). When water is added to SAP there is a polymer/solvent interaction; hydration and the formation of hydrogen bonds are two of these interactions

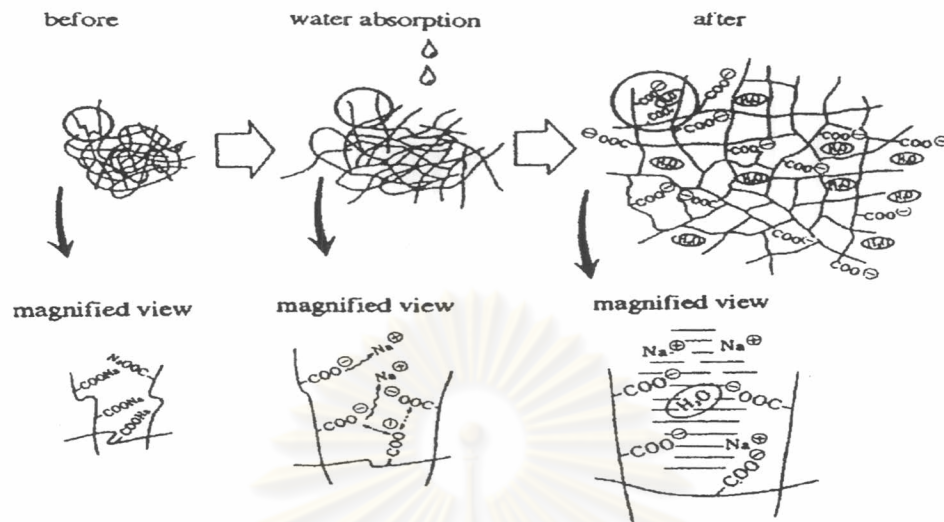


Figure 2.1 Water absorption in ionic polymer network.

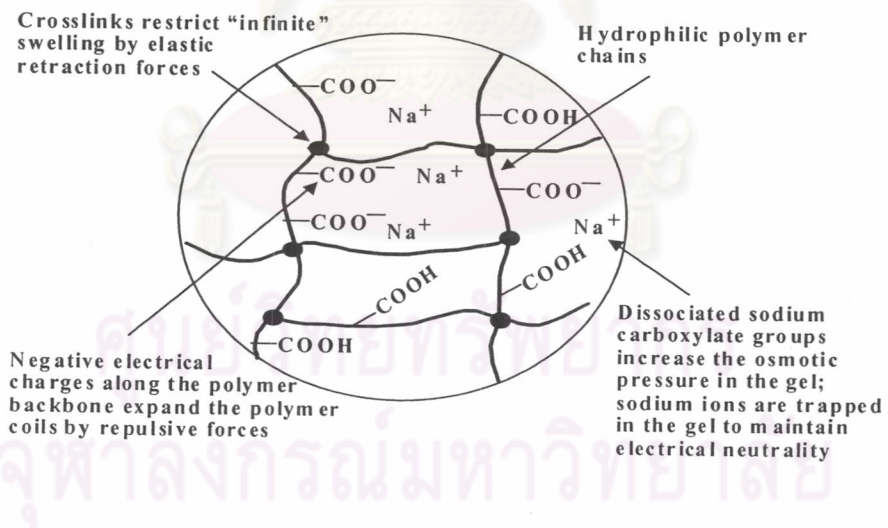
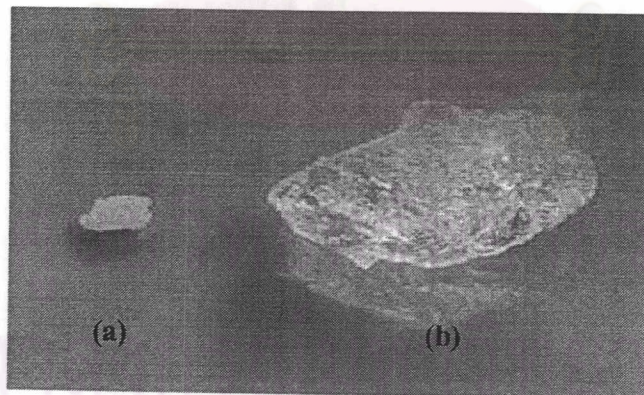


Figure 2.2 Diagrammatic representation of part of the polymer network.



Water moves into a particle of superabsorbent polymer because the activity of water is initially lower in the interior of the particle. As water diffuses into the particle, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move, generally in a direction opposite to that of the molecules of water. The change in volume is apparent in Figure 2.3, which shows a particle of superabsorbent polymer before and after swelling in a dilute salt solution. Because polymer molecules are much larger than water molecules, they diffuse much more slowly. Not only are the polymer molecules larger, but they are also connected one to the other by the crosslinks, so that the polymer does not eventually dissolve in the water and become useless as a superabsorbent polymer. Therefore, to move in a certain direction, the polymer chains must move cooperatively, requiring more time than if each polymer chain, or each monomer segment, moved individually. The slow polymer motion is in principle a rate-limiting phenomenon in polymer swelling.



**Figure 2.3** Water absorption by the superabsorbent polymer: (a) dry granule and (b) swollen gel.

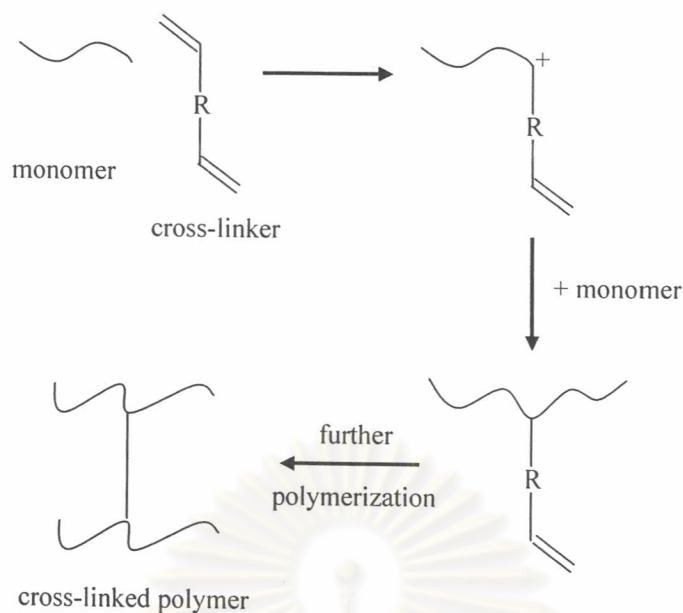
### 2.1.3 Cross-linking in Superabsorbent Polymers

There are two main types of crosslinking in most superabsorbent polymers (7).

- a) **Bulk or core crosslinking** – Such a crosslinking polymer normally takes place during the polymerization stage of superabsorbent production.
- b) **Surface crosslinking** – This type of surface crosslinking is a newer process that improves the absorption against a pressure profile of the polymer. In depth details for both types of crosslinking are given in the following sections.

#### 2.1.3.1 Core Crosslinking

Crosslinking is the joining of molecules – generally joining two or more macromolecules with a smaller molecule. The most important type in the case of superabsorbents, and the most common, is the covalent cross-link. In SAP manufacture the most common types of cross-linker are organic molecules that contain two or more polymerisable double bonds. These molecules are incorporated into the backbone of the polymer chains as they grow during the polymerization reaction shown in Figure 2.4. Several factors determine the incorporation of the cross-linkers in to the polymer and their distribution along the polymer backbone. The molecules of monomer and polymerization double bonds are incorporated into the backbone of the polymer chains as they grow during the polymerization reaction.



**Figure 2.4** Schematic illustration of core crosslinking reaction.

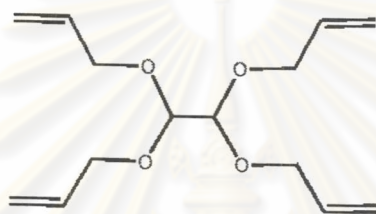
#### a) Reactivity Ratios

Reactivity ratios are a measure of the affinity for each of the reaction components to react with each other. If the cross-linker has a high reactivity ratio then most of it will be consumed in the early stages of the polymerisation and any polymer chains made during the latter stages will be less likely to cross-link and end up as extractable chains. Cross-linkers with low reactivity ratios have the opposite tendency. The choice of cross-linker or mixture of cross-linkers determines the structure of the final polymer network.

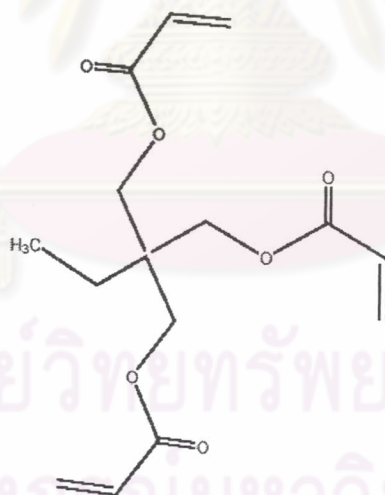
#### b) Extractables

Generally low molecular weight polymer chains, that are not incorporated in to the polymer network are called the soluble or extractable fraction. These chains can be readily extracted from the polymer when the polymer is swollen in excess

liquid, hence the name *extractables*. The degree of soluble polymer is important in determining the optimum cross-linker level and performance of the product. Too little a cross-linker concentration and the polymer will have a high swelling capacity, low strength against pressure and a tacky feel due to high extractables, and too much a cross-linker level will give low extractables, low tackiness but a low swelling capacity. The amount of the extractables and swelling capacity data is useful in optimising the quality of the polymer.



(a) Tetraallylethoxy ethane



(b) 1,1,1-Trimethylolpropanetricrylate (TMPTA)

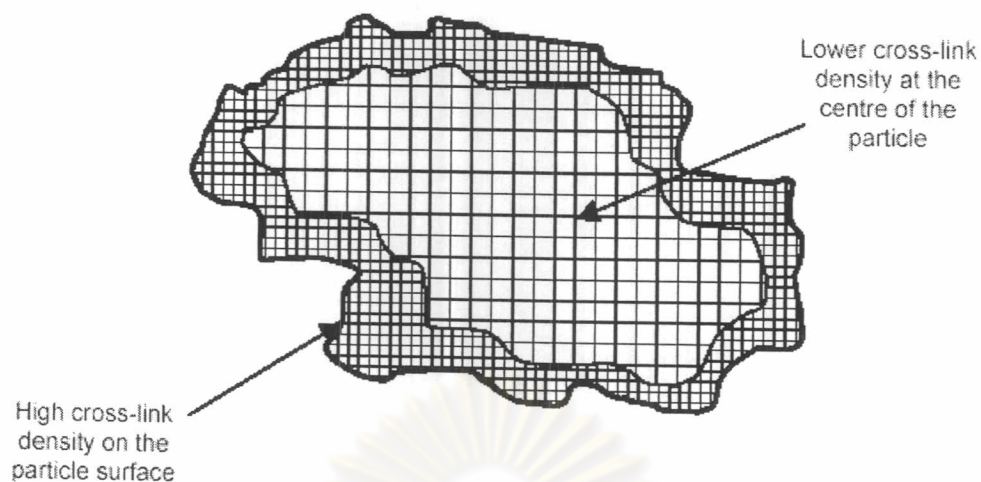
**Figure 2.5** Some common types of cross-linker.

### 2.1.3.2 Surface Crosslinking of Superabsorbent Polymers

Historically it is known that SAPs with no surface treatment and low internal cross-linking tend to show high swelling capacities but poor absorption against pressure. Improving the swelling capacity of SAP by decreasing the core crosslinking, i.e. decreasing the crosslinking density, is limited by the accompanying increase in extractable polymer content of the gel. Likewise the increase in capacity would lead to a decrease in the uptake of liquid when the SAP was under load, for example a baby sitting on its diaper. This means that when a pressure is applied on the SAP, liquid is not absorbed effectively in these areas. Moreover the pressure on the semi-swollen gel can cause a blockage in the area preventing further liquid entering the gel bed and being absorbed by dry SAP underneath. This phenomenon is called gel blocking and causes diapers to leak. Hence increasing the swelling capacity using conventional means (lowering core crosslinker) leads to an overall decrease in capacity under load.

Improving the absorption against pressure and the swelling rate of a SAP can be achieved by crosslinking the surface of the particles. Post crosslinking is normally performed on the dried, milled and sized SAP as the final stage of the process. A crosslinking solution is applied to the particles, which are then 'cured' normally through heating. The chemicals that perform the crosslinking usually have at least two functional groups capable of reacting with the carboxyl groups on the polymer backbone for example polyhydric alcohols such as glycerine.

The result of this process is an increase in the density of cross-linking on the surface of the particles giving what can be described as a core-shell particle. The core of the particle is the lightly crosslinked polymer and the shell represents the higher cross-linking density on the surface. This is visually described in Figure 2.6.



**Figure 2.6** A surface crosslinked superabsorbent particle.

Manipulation of the surface coating on SAP particles is one of the key steps in tailoring the properties of the product. With a good quality base polymer (i.e. low extractable, low residual and desired capacity) different types of coating solution and cross-linker can be applied to give the polymer many different performance characteristics.

#### 2.1.4 Applications of Superabsorbent Polymers

Superabsorbent polymers possess a number of attributes that make them attractive in many different applications. Superabsorbent polymers have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. The basic property of water absorption has suggested the use of superabsorbent polymers in many other applications, including paper towels, surgical sponges, meat trays,

disposable mats for outside doorways and in bathrooms, and for household pet litter, bandages and wound dressings. The ability of the swollen gels to release the water to the surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. Superabsorbent polymers may also be used to release water-soluble substances from within the network structure into the surroundings as a solution. For example, pharmaceuticals and fertilizers may be incorporated into superabsorbent polymer to yield controlled release products. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse as cosmetics or concrete or to contribute a soft, yet dry, feel to a product like a hot or cold pack for sore muscles. The soft, rubbery nature may also be employed to impart sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables (8). Their applications are being extended into other industrial areas as shown in Table 2.1.



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**Table 2.1** Possible Applications of Superabsorbent Polymers (9)

Properties Fields	Water absorption and retention	Swelling in volume	Gelling ability	Increase in Viscosity
Sanitary products	Sanitary napkins, Diapers, Breast pads			
Agriculture gardening	Water-retaining agent in soil, Dry preventives for samplings		Cultivation plot for mushroom, Seed beds in fluid	
Civil engineering, architecture	Artificial moss, Dew preventing agents in walls	Water sealing agents, Substitutes for sandbags	Sludge solidification agents	
Cosmetics, Toiletries	Water-retaining agents in concretes, Sweat		Gelaromatics, Pocket warmers, Disposal chamber pots	Mud shielding work
Medical	Wound dressings, Sheets for surgical operation	Control release agents for drug, Disintegrators in tablets	Gelation of blood wastes	Wet plasters
Food industry	Agents for preservation of freshness		Gelling agents, Cold keeping hydrogels	Viscosity enhancing additives
Others	For preventing film, Dehydration agents in oil, Moisture sensor	Control release agents for drug, Disintegrators in tablets	Hydrogel for fire fighting, Artificial snow, Water bed	Wet plasters



## 2. 2 Mechanism for Free Radical Polymerization

### 2.2.1 Initiation, Propagation, and Termination

Before the unique aspects of the polymerization of acrylic and methacrylic acids are discussed, the essentials of free radical addition polymerization of vinyl monomers are summarized. Several excellent texts on this subject exist, and the reader is directed to one of these for more comprehensive information.

Steps of a typical free-radical polymerization comprise initiation, propagation, and termination. Typical free-radical initiators are peroxides or diazenes, which thermally decompose to form two radical species:



These radicals may add to monomer molecules (Eq. 2.3), forming a new radical:



Additional monomer units add rapidly to this growing end, depicted in Eq. 2.4. This step is called *propagation*:



Finally, two of these highly reactive radical chains find one another and combine, resulting in termination of the radical chain:



Two possible termination reactions exist, recombination and disproportion. Both are identical kinetically, but recombination results in the formation of a single polymer chain, while disproportion results in two chains, each with half the molecule weight of the product from recombination.

The foregoing description is based on a thermally decomposing initiator. Redox couples are another class of radical initiators that are particularly useful for preparing superabsorbent polymers. In such cases an oxidizing agent and a reducing agent react to form at least one active radical, which then initiates polymerization (10):



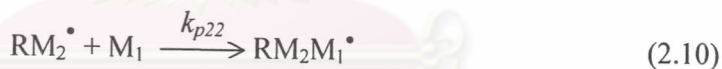
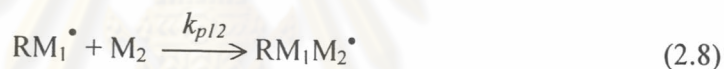
### 2.2.2 Crosslinked Gels by Copolymerization

To be useful as superabsorbents, linear polymers must be crosslinked to form gels. Two general approaches exist for crosslinking. The first method is through copolymerization of acrylic acid with a second monomer, which has multiple vinyl groups, to form a gel directly during the polymerization process. The second approach is via crosslinking of a polymer by reaction with a di-functional molecule, similar to a rubber curing reaction (11).

Adequate description of a crosslinking copolymerization requires at least a summary of copolymerization in general. The model outlined here was developed by Alfrey and Goldfinger and extended to systems containing many monomers by

Walling and Briggs (12). The model itself is known as the Mayo-Lewis model and is the most widely used model for copolymer systems.

The model is based on the concept that the nature of the very last monomer added to the growing chain controls its reactivity. In a simple copolymerization of two monomers,  $M_1$  and  $M_2$ , there are four possible propagation events. The growing chain with a monomer 1 moiety on the end  $RM_1\cdot$  can react with another molecule  $M_1$  with a rate constant  $k_{p11}$  or with a molecule  $M_2$  with a rate constant  $k_{p12}$ . Likewise, when monomer 2 moiety  $RM_2\cdot$  is at the end of the growing chain, it can add to  $M_1$  with a rate constant  $k_{p21}$  or to  $M_2$  with a rate constant  $k_{p22}$  as shown in Eqs. 2.7-2.10



The reactivity ratios  $r_1$  and  $r_2$  are defined by Eqs. 2.11 and 2.12

$$r_1 = \frac{k_{p11}}{k_{p12}} \quad (2.11)$$

$$r_2 = \frac{k_{p22}}{k_{p21}} \quad (2.12)$$

When  $r_1 > 1$ , radical  $RM_1\cdot$  preferentially reacts with monomer  $M_1$  (i.e., homopolymerized), instead of monomer  $M_2$ . Very frequently  $r_1 < 1$ , which indicates

$RM_1$  preferentially reacts with monomer  $M_2$ . This latter behavior can lead to alternating copolymers. The reactivity ratio can also be zero, indicating that a monomer will not homopolymerize. The composition of a co-polymer is controlled by both the reactivity ratios of the monomers and their concentration (11).

### 2.2.2.1 Chemical Crosslinking

The most severe mechanism for decreasing molecular freedom is chemical crosslinking-linking the polymer chain together through covalent or ionic bonds or form a network. Occasionally the term curing is used to denote crosslinking. There are a number of ways for crosslinking can be brought about, but basically they fall into two categories: (1) crosslinking during polymerization by use of polyfunctional instead of difunctional monomers, and (2) crosslinking in a separate processing step after the linear (or branched) polymer is formed. The crosslinks may contain the same structural features as the main chains, which is usually the case with the former, or they may have an entirely different structure, which is more characteristic of the latter.

A number of extreme changes accompany crosslinking. If previously soluble, the polymer will no longer dissolve (except in the case of some ionically crosslinked polymers). In the presence of a solvent, a crosslinked polymer swells as solvent molecules penetrate the network. The degree of swelling depends on the affinity of solvent and polymer for one another, as well as on the level of crosslinking. It may be recalled that a solvent-swollen crosslinked polymer is called a gel. Covalently crosslinked polymers also lose their flow properties. They may still undergo deformation, but the deformation will be reversible; that is, the polymer will exhibit

elastic properties. Ionically crosslinked polymers will flow at elevated temperatures, however.

With network polymers it is common to speak of the crosslink density, that is the number of crosslinked monomer units per main chain. The higher the crosslink density, the more rigid the polymer. Very high crosslink densities lead to embrittlement. Because crosslinking reduce segmental motion, it is frequently employed to increase the glass temperature.

#### **2.2.2.2 Physical Crosslinking**

When polymer chemists use the term crosslinking, they invariably mean covalent chemical crosslinking. Covalent crosslinking has certain disadvantages, however. Once crosslinked, a polymer cannot be dissolved or molded. One approach has been to investigate thermally labile crosslinks, that is, chemical crosslinks that break apart on heating and reform in cooling. Ionic crosslinks fall into this category. The other approach has been to introduce strong secondary bonding attraction between polymer chains such that the polymer exhibits properties of a thermosetting material while remaining thermoplastic. Crystalline polymers fit into this category. Because of the very strong secondary forces arising from close chain packing, many of the mechanical and solution properties of crystalline polymers resemble those of crosslinked amorphous polymers. Certain materials intermolecularly associated through hydrogen bonds also behave like crosslinked polymers (13).

### 2.2.2.2 Crosslink Density

One of the most important structural parameters characterizing crosslinked polymer is  $\bar{M}_c$ , the average molecular weight between crosslinks, which is directly related to the crosslink density. The magnitude of  $\bar{M}_c$  significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine  $\bar{M}_c$ . Early research by Flory and Rehner laid the foundations for the analysis of equilibrium swelling. According to the theory of Flory and Rehner, for a perfect network (14),  $\bar{M}_c$  can be expressed as shown in Eq. 2.13:

$$\bar{M}_c = -V_1 d_p \frac{v_s^{1/3} - v_s/2}{\ln(1-v_s) + v_s + \chi v_s^2} \quad (2.13)$$

where,

$\bar{M}_c$  is the number-average molar mass of the chain between crosslinks,

$V_1$  is the molar volume ( $\text{cm}^3 \text{mol}^{-1}$ ),

$d_p$  is the polymer density ( $\text{g cm}^{-3}$ ),

$v_s$  is the volume fraction of the polymer in the swollen gel,

$\chi$  is the Flory-Huggins interaction parameter between the solvent and the polymer.

The swelling ratio (S) is equal to  $1/v_s$ . Here, the crosslink density,  $q$ , is defined as the mole fraction of crosslinked units:

$$q = \frac{M_o}{\bar{M}_c} \quad (2.14)$$

where  $M_o$  is the molecular weight of the polymer repeating unit. We defined  $q$  in Eq (2.14) in order to simplify direct comparison with the mole fraction of divinyl monomers in copolymerization.

### 2.3 Free Radical Polymerization Techniques

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion. Ionic and other nonradical polymerizations are usually confined to solution techniques. Each of the methods has advantages and disadvantages, as outlined in Table 2.2. In addition, work has also been done on solid- and gas-phase polymerizations of vinyl monomers, but these are of lesser importance. Because polymers are not volatile, the term *gas-phase polymerization* means, in effect, bulk polymerization in which monomer vapors diffuse to the polymerization site (15).



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**Table 2.2** Free radical Polymerization Techniques (15)

<b>Method</b>	<b>Advantages</b>	<b>Disadvantages</b>
Bulk	Simple; no contaminants added	Reaction exotherm difficult to control; high viscosity
Suspension	Heat readily dispersed; low viscosity; polymer obtained in a granular form and may be used directly	Washing and/or drying required; agglomeration may occur; contamination by stabilizer
Solution	Heat readily dispersed; low viscosity; may be used directly as solution	Added cost of solvent; solvent difficult to remove; possible chain transfer with solvent; possible environmental pollution
Emulsion	Heat readily dispersed; low viscosity; high molecular weight obtainable; may be used directly as emulsion; works on tacky polymers	Contamination by emulsifier and other ingredients; chain transfer agents often needed to control DP; washing and drying necessary for bulk polymer

### 2.3.1 Bulk

Bulk polymerization is the simplest from the standpoint of formulation and equipment, but it is also the most difficult to control, particularly when the polymerization reaction is very exothermic. This, coupled with problems of the heat transfer as the monomer-polymer solution increases in viscosity, limits the use of the bulk methods in commercial production, although more efficient bulk processes have been developed in recent years.



In cases where a polymer is insoluble in its monomer, the polymer precipitates and the viscosity of the medium does not change appreciably. Problems still arise, however, as a result of free radicals (detectable by ESR) being occluded in the polymer droplet, which can lead to *autoacceleration*, that is, a rapid increase in the polymerization rate. In some instances, particularly with diene monomers, this occlusion effect may lead to formation of insoluble crosslinked nodules and usually of light weight and occupy considerably more volume than the monomers from which they are derived, which may cause fouling and even fracture of the polymerization apparatus.

The major commercial uses of bulk vinyl polymerization are in casting formulations and low-molecular-weight polymers for use as adhesives, plasticizers, tackifier, and lubricant additives.

### 2.3.2 Suspension

Suspension polymerization involves mechanically dispersing monomer in a noncompatible liquid, usually water, and polymering the resultant monomer droplets by use of a monomer-soluble initiator. The monomer is kept in suspension by continuous agitation and the use of *stabilizers* such a poly(vinyl alcohol) or methyl cellulose. If the process is carefully controlled, polymer is obtained in the form of granular beads, which are easy to handle and can be isolated by filtration or by spraying into a heated chamber (spray drying). A major advantage is that heat transfer is very efficient and the reaction is therefore easily controlled. Suspension polymerization cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles. From the standpoint of kinetics and mechanism, suspension polymerization is identical to bulk polymerization.

Suspension methods are used to prepare a number of granular polymers, including polystyrene, poly(vinyl chloride), and poly(methyl methacrylate).

### **2.3.3 Solution**

Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions may severely limit the molecular weight. Apart from the environmental concerns associated with organic solvent, a major problem in solution polymerization is that it is often difficult to remove solvent completely from the finished polymer. As a result there is considerable interest in using supercritical carbon dioxide as a polymerization solvent. Advantages are that carbon dioxide is nontoxic, inexpensive, and easily removed from the polymer recycled.

### **2.3.4 Emulsion**

Emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient; but there are the similarity ends. Monomer is dispersed in the aqueous phase by an emulsifying agent such as a soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into micelles to continue the reaction. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination extremely high molecular weights are obtainable, generally too high to be of practical value unless compounds

called *chain transfer* agent are added that control the degree of polymerization. The overall process is complex, with reaction kinetics differing significantly from that of bulk or solution process.

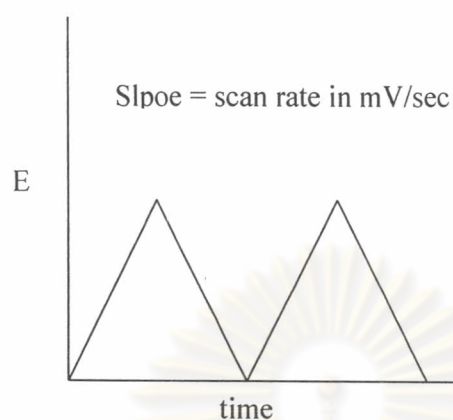
## 2.4 Electrochemical Techniques

Electrochemical techniques are concerned with the interplay between electricity and chemistry. These techniques are the important methodology for following up the reaction. Many chemical measurements, which involve homogeneous bulk solution, electrochemical processes take place at the electrode-solution interface. Typically, the substance is fixed at the surface of electrode and electrons are transferred in system of electrochemical cell. One advantage of electrochemical techniques is the examination of catalytic properties which could be further used for the selection of a catalyst (16).

Cyclic voltammetry, one type of electrochemical techniques, is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox processes.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode, using a triangular potential wave-form as shown in Figure 2.7 (17).

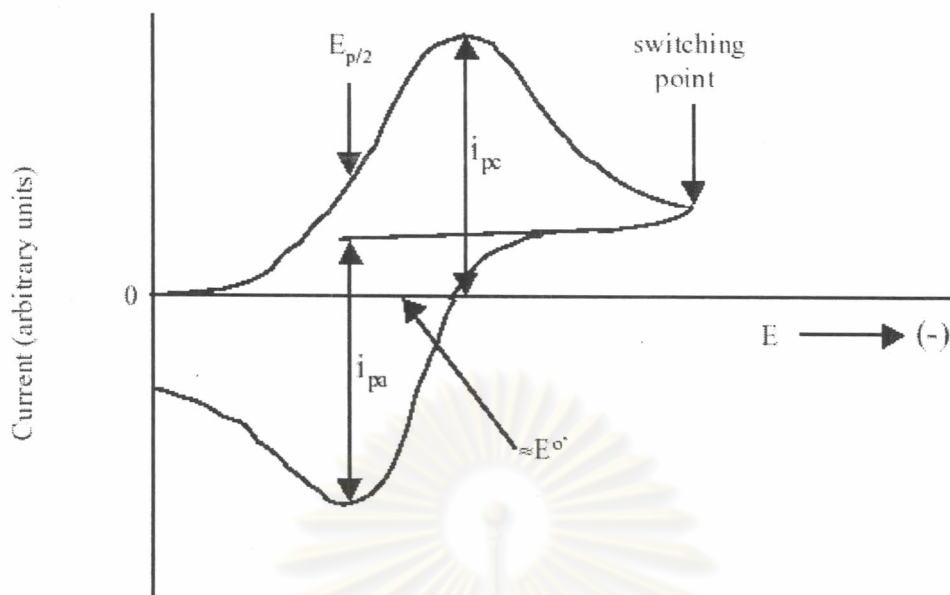
## Applied Signal for Linear Scan Voltammetry



**Figure 2.7** Potential-time excitation signal in a cyclic voltammetric experiment

During the potential sweep, the potentiostat measures the current resulting from the applied potential. The relationship between the potential applied and the current obtained is called cyclic voltammogram as shown in Figure 2.8.

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$i_{pa}$  = anodic peak current

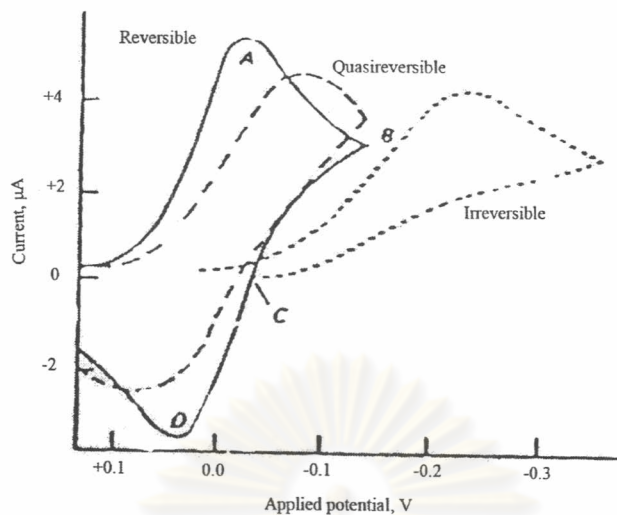
$i_{pc}$  = cathodic peak current

$E_{pa}$  = anodic peak potential

$E_{pc}$  = cathodic peak potential

**Figure 2.8** The relationship between the potential and the current

In addition, cyclic voltammetry can inform the kinds of redox reactions occurred. The redox reaction can be classified into three types: reversible, quasi-reversible and irreversible shown in Figure 2.9, which gives the information in a system.



**Figure 2.9** The cyclic voltammogram of three types of redox reaction

For a reversible process, the separation between the peak potentials is given by

$$\Delta E_p = E_{pc} - E_{pa} = 0.059/n$$

where  $E_{pc}$  = cathodic peak potential

$E_{pa}$  = anodic peak potential

$n$  = number of electrons transferred

In addition, the ratio of the reverse-to-forward peak currents,  $i_{pc}/i_{pa}$ , is unity.

For a quasi-reversible system, the voltammograms are more drawn out and exhibited a larger separation in peak potentials compared with a reversible system. For an irreversible process, the individual peak was reduced in size and widely separated

(18).

## 2.5 Literature Survey

Recent researches on the synthesis of superabsorbent polymer and important physical property development are listed as below:

Karadag et. al.(19) synthesized and characterized acrylamide-crotonic acid hydrogels which were prepared by copolymerization of acrylamide and crotonic acid with crosslinkers, such as ethylene glycol dimethacrylate, 1,4 butanediol dimethacrylate (BDMA) and *N,N'* methylenebisacrylamide (N-MBA), with  $\gamma$ -irradiation. After swelling tests were performed, the influence of the applied  $\gamma$ -ray dose, the amount of crotonic acid and the type and amount of crosslinking agents on the swelling properties of the gel, the diffusion behaviour of water, and the diffusion coefficients and network properties of the hydrogel systems were examined. Water diffusion in the hydrogels was non-Fickian.

Karadag and Saraydin (20) prepared AAm/CA hydrogels by free radical polymerization in aqueous media. Some multifunctional crosslinkers such as trimethylolpropane (TMPTA) and 1,4 butanediol dimethacrylate (BDMA) used in the polymerization process. Equilibrium water content (EWC%) of AAm/CA hydrogels were calculated in the range of 88.73-96.75%. This result showed that AAm/CA hydrogels would be used as a biomaterial on some biomedical applications, because equilibrium water contents were bigger than the percent water content value of the body about 60%. The diffusion type of hydrogels was a non-fickian diffusion characteristic.

Caykara et. al. (21) studied the equilibrium swelling behavior of copolymeric hydrogels containing monoprotic acid moieties and considering the presence of ionization, a modified new equation has been derived. Hydrogels with various ionic

group contents were prepared from acrylamide and crotonic acid (CA) monomers with 0-12.9 mol% CA in aqueous solution by radiation-induced polymerization and gelation with  $\gamma$ -rays. The volume swelling ratio of the poly(acrylamide/crotonic acid) hydrogels was investigated as a function of the pH and ionic strength of the swelling medium and type of counterion in the swelling medium.

Duran et. al. (22) synthesized and characterized acrylamide(AAm)-acrylic(AAc) acid hydrogels and adsorption of some textile dyes. The AAm-AAc hydrogels have been prepared at AAm initial compositions of 15%, 20% and 30%. AAm-AAc monomer mixtures have been irradiated in a  $^{60}\text{Co}$ -source at different doses and percent conversions have been determined gravimetrically. The results of swelling tests at pH 8.0 indicated that poly(AAm-AAc) hydrogels have been considered for the removal of some textile dyes from aqueous solutions. Among the two common textile dyes tested, Janus Green B (JGB) has shown the highest adsorption capacity while Congo Red (CR) was not adsorbed by these hydrogels.

Solpan et. al. (23) studied adsorption of methyl violet in aqueous solutions by poly[acrylamide-*co*-(acrylic acid)] hydrogels which contain different quantities of acrylic acid irradiated to form hydrogels with  $\gamma$ -radiation. Diffusions of water and methyl violet within the hydrogels were found to be non-Fickian in character. Adsorption capacity of poly(AAm-*co*-AAc) hydrogels was changed with pH of the aqueous solution of dye and adsorption isotherms of poly(AAm-*co*-AAc) hydrogels were S type. Poly(AAm-*co*-AAc) hydrogel adsorbed methyl violet, while poly(AAm) hydrogel did not adsorb any dye. Thermodynamic parameters such as G, H and S for poly(AAm-*co*-AAc) dye system were calculated and H values were  $<20 \text{ kJ mol}^{-1}$  so adsorption process is a physical adsorption. These results show that poly(AAm-*co*-



AAc) hydrogels can be used as a sorbent for water pollutants such as dyes and treatment of organic contaminants from wastewater.

Karadag et al. (24) studied interaction of some cationic dyes such as Union Green B (UG-B), Basic Blue 17 (BB-17), Basic Red 2 (BR-2), and Lauths Violet (LV) with acrylamide/itaconic acid hydrogels which were prepared by irradiating with  $\gamma$  radiation. The adsorptions of the dyes are increased with the content of itaconic acid (IA) in the hydrogels and irradiation dose. In the experiments of the adsorption, Langmuir type adsorption in the Giles classification system was found. Some binding and thermodynamic parameters for AAm/IA hydrogel-dye systems were calculated by using Klotz method. Adsorption studies indicated that monolayer coverages of AAm/IA hydrogel by these dyes were increased with the following order : BB-17 > UG-B > BR-2 > LV.

Oren et al. (25) studied the effect of gel composition, pH, ionic strength, and temperature in the uranyl ion ( $\text{UO}_2^{2+}$ ) adsorption capacity of poly[(N-vinyl 2-pyrrolidone-g-(tartaric acid))] (NVP-g-TA) hydrogels. It was found that not only the gel composition but also external stimuli, such as the pH, ionic strength, and temperature, play an important role in the adsorption behavior of NVP-g-TA hydrogels. These hydrogels are potential sorbents for the removal of  $\text{UO}_2^{2+}$  ions from waste-water and aqueous effluents.

Karadag et al.(26) investigated swelling equilibria and dye adsorption of chemically crosslinked superabsorbent acrylamide (AAm)/maleic acid (MA) hydrogels. AAm/MA hydrogels were prepared by free radical polymerization in solution with some multifunctional crosslinkers such as trimethylolpropanetriacrylate and 1,4-butanediol dimethacrylate. AAm/MA hydrogels were used in experiment on swelling and adsorption of a water-soluble monovalent cationic dye such as Basic

Blue 17 (Toluidin Blue). Hydrogel systems swelled in the range of 780-6050% in water. The values of equilibrium water content (EWC) were calculated in the range of 0.8873-0.9837. Water intake of hydrogels obeyed a non-Fickian type diffusion. The uptake of the cationic dye, BB-17 to AAm/MA hydrogels is studied by bath adsorption technique at 25°C Type S adsorption isotherm in Giles's classification system was found. The adsorptions of the dyes increased with increasing the content of MA in the hydrogels.

Saraydin et al. (27) studied a convenient method for removing some water-soluble monovalent cationic dyes from aqueous solutions by adsorption on a novel polymeric adsorbent such as AAm/MA superswelling hydrogels. The AAm/MA hydrogels prepared by irradiation with  $\gamma$  radiation were used in experiments on swelling, diffusion, and adsorption of some water-soluble monovalent cationic dyes such as basic red 5 (BR-5), basic violet 3 (BV-3), and brilliant cresyl blue (BCB). For this superswelling hydrogel, the swelling studies indicated that swelling increases in the following order: BR-5 > water > BV-3  $\geq$  BCB. Type-S adsorption isotherms in Giles' classification system were found. The adsorptions of the dyes increased with increasing the content of MA in the hydrogels and the  $\gamma$ -radiation.

Karadag et al. (28) studied a convenient method for removing some cationic dyes from water by adsorption on a new polymeric adsorbent as acrylamide/itaconic acid (AAm/IA) hydrogels. This study has shown that AAm/IA hydrogels can adsorb the basic dyes such as BR-5, BV-3, and BCB, while AAm hydrogels cannot. Type L3 (Langmuir) adsorption isotherms in Giles classification system were found. The adsorptions of the dyes are increased with increasing content of IA in the hydrogels and irradiation dose. As a result, it was shown that the AAm/IA hydrogels could be

used as a sorbent for the water pollutants such as cationic dyes, an important problem for the textile industry.

Karadag et al. (29) studied the swelling properties and some parameters controlling the diffusion and network of AAm/CA/salt and AAm/CA/Dalapon (sodium 2,2-dichloropropionate) hydrogel systems. The AAm/CA hydrogels containing these salts and agricultural drug could swell in water in the range of 2045-400% , while polyacrylamide hydrogels swelled in the range of 660-700%. Water intake of hydrogels obeyed a non Fickian-type diffusion.

Karadag et al. (30) investigated that swelling capability of acrylamide (AAm) hydrogels by adding a hydrophilic co-monomer such as crotonic acid (CA) during polymerization. Poly(AAm-co-CA) hydrogels were prepared by free radical polymerization. Some multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) and *N,N'*-methylenebisacrylamide (N-MBA) were added in polymerization. The hydrogel swelled in the range of 1729-2577 %. The EWCs were calculated and found in the range of 0.9473-0.9626. This result showed that poly(AAm-co-CA) hydrogels would be used as a biomaterial in some biomedical applications, because the equilibrium water contents were bigger than the percent water content of the body (about 0.60). The diffusion type of hydrogels was a non-fickian diffusion character. It was seen that the swelling of poly(AAm-co-CA) hydrogels increased with the increasing content of CA.

Naghash and Okay (31) copolymerized AAm and *N,N'*-methylenebisacrylamide in aqueous solution via free radical crosslinking reaction. About 80% of the pendent vinyl groups are consumed by cyclization reactions. When the monomer concentration was held at 1.8 w/v %, the critical conversion at the gel point was minimal at 7.5 mol % *N,N'*-methylenebisacrylamide. Average reactivity of

the pendant vinyls decreased abruptly with increasing *N,N'*-methylenebisacrylamide content and the equilibrium degree of swelling of PAAm gel was independent of the crosslinker content. All these results suggested a formation of PAAm microgels prior to the onset of macrogelation.

Kiatkamjornwong et al. (32) studied graft copolymerization of acrylamide and/or acrylic acid onto cassava starch by a simultaneous irradiation technique using gamma-rays as the initiator followed by alkaline saponification. The worker investigated various parameters of importance affecting the extent of water absorption : the monomer-to-cassava starch ratio, total dose (kGy), dose rate (kGy h<sup>-1</sup>), acrylamide-to-acrylic acid ratio, and the addition of nitric acid and maleic acid as the acid additives. The water absorption of the saponified graft copolymer in salt and buffer solutions of different ionic strength was measured, from which the superabsorbent properties are found to be pH sensitive. The starch graft copolymers of acrylamide and acrylic acid give higher water absorption than the starch graft copolymers of either acrylamide or acrylic acid alone. Ionic strength and multi-oxidation states of the saline and buffer solutions markedly decreased the water absorption of the saponified cassava starch grafted superabsorbent polymers.

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