CHAPTER 2

THEORY and LITERATURE REVIEW

2.1 Superabsorbent Polymers (SAPs)

Superabsorbent polymers are the materials that can absorb or retain liquid or fluid greater than 15 times their dry weight and that cannot release the retained liquid out in a liquid or fluid form but only diffuse through the gel membrane as water vapor or moisture.

2.1.1 Classification of Superabsorbent Polymers

Classifications of SAPs based on composition and preparation methods (network formation, introduction of hydrophilic groups and product form) are shown in Table 2.1.

Table 2.1 Four Classifications of Superabsorbent Polymers

A. Polymer composition	
a) Starch	Graft polymerization
	Carboxymethylation
b) Cellulose	Graft polymerization
	Carboxymethylation
c) Synthetic polymer	Poly(acrylic acid)
	Poly(vinyl alcohol)
	Polyacrylamide

Table 2.1 Four Classifications of Superabsorbent Polymers (continued)

A. Polymer composition

   c) Synthetic polymer   Polyoxyethylene

B. Network formation

   a) Graft polymerization

   b) Crosslinked copolymerization

   c) Network forming reaction of water-soluble polymers

   d) Self-crosslinked polymerization

   e) Radiation crosslinking

   f) Introduction of crystal structure

C. Hydrophilic groups

   a) Polymerization of hydrophilic monomers

   b) Carboxymethylation of hydrophilic monomers

   c) Graft polymerization of hydrophobic polymers with hydrophilic monomers

   d) Hydrolysis of nitrile or ester group

D. Product form

   a) Powder   Globular

                           Amorphous

   b) Film

   c) Fiber   Short fiber

                           Long fiber

                           Nonwoven fiber

2.1.2 Properties

Materials which are of increasing interest in SAPs show high capacity for immediate swelling on pouring water onto them, and they have properties of gelling and holding the water absorbed. At the high level of absorption, their water-absorbing power ranges from several hundred to many thousand times their weight.

2.1.2.1 Water Absorption Mechanism in Superabsorbent Polymers

       The factors that supply absorbing power to polymers are considered to osmotic pressure based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure [2].
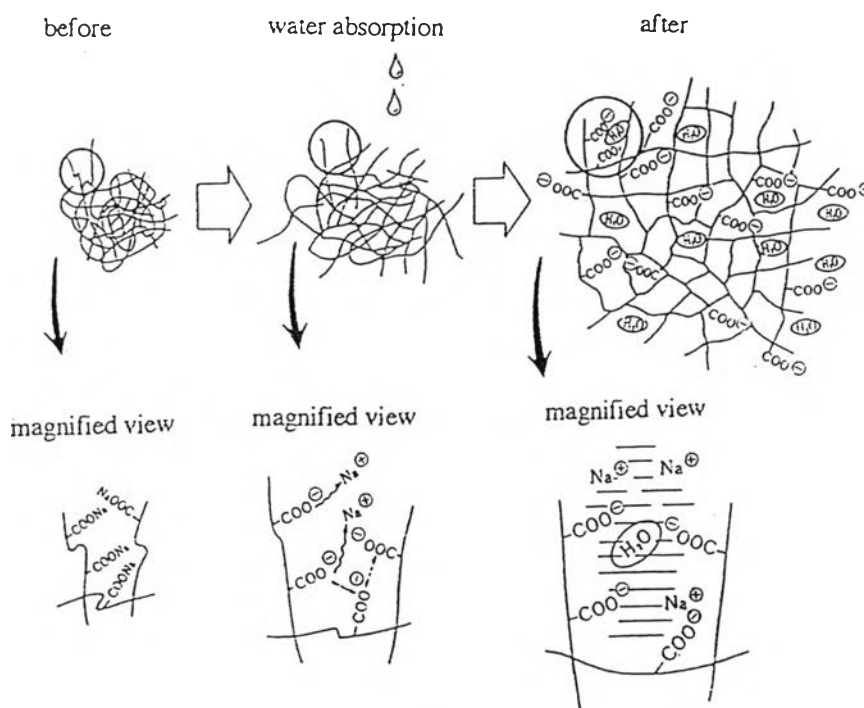

Figure 2.1 Water Absorption in Ionic Polymer Network

       Figures 2.1 and 2.2 show the water absorption mechanism of a type of SAP, which is a crosslinking polymer with sodium carboxylate groups. Before absorption, long chains of polymers are interwoven, and polymers make a three-dimentional structure by crosslinking between the chains to make a dense phase. In contact with water, the hydrophilic polymer backbone containing hydrophilic functional groups, interacts with the solvent accompanied by energy decrease and

entropy increase. Hydration and the formation of hydrogen bonds are two sources for such polymer/solvent interactions. The polymer chains also tend to disperse in the given volume of solvent. This leads to a higher number of allowed configurations for the system, which is equivalent to a higher degree of entropy.

Due to the presence of the crosslinks, the polymer chains are restricted in swelling by elastic retraction forces of the network. The more the chains separate from each other, the more stiffness the originally coiled polymer chains become. This decreases the entropy of the chains. Finally there is a balance between the infinite dilution of the chains and the retractive forces. Higher crosslink densities give networks with stronger retractive forces and with lower degrees of swelling at equilibrium.
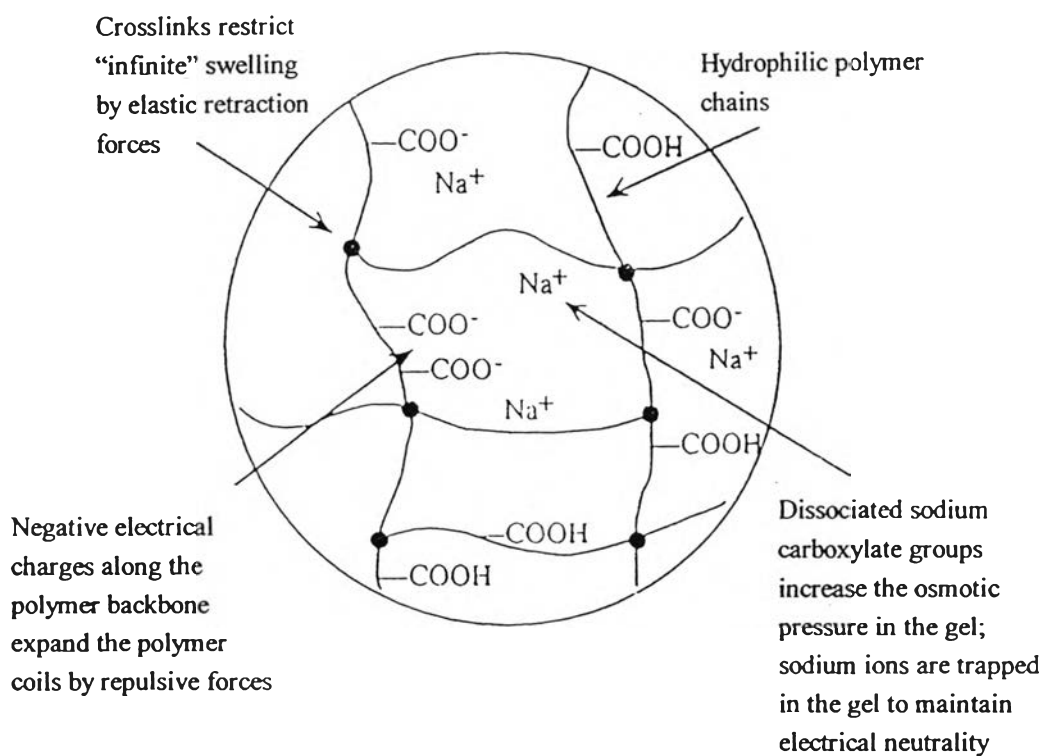
Figure 2.2 Mechanisms of Swelling of Superabsorbent Polymers

For ionic polymers, the solvent/polymer interactions include more than a simple mixing term. These gels bear electrical charges along the polymer chains. The negative charges of the carboxyl groups repel one another and are compensated for by the positive charges of the sodium ions, in order to maintain electrical neutrality. When the polymer comes into contact with water, the solvent diffuses into the polymer network and solvates the sodium ions. Water with its high dielectric constant lowers the attractive forces between the sodium ions and the negatively charged carboxylate groups. As in solutions of simple salts, the sodium ions are released and become freely movable within the gel. Hence they contribute to the osmotic pressure. It is consequently impossible to leave the gel region due to the attraction forces of the negative charges, which are fixed along the polymer backbones. The sodium ions therefore behave as if trapped by an invisible, semi-permeable membrane. The driving force for swelling is then the difference between the osmotic pressure in- and outside of the gel. Increasing the salinity and by this the osmotic pressure of any external aqueous solution lowers the absorption capacity of the gel for that fluid [3].

The water absorbency and the strength of SAPs can be expressed by Equation 2.1 (Flory's equation) and Equation 2.2, respectively.

$$Q^{5/3} = [(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/v_1] / (v_e/V_0) \qquad (2.1)$$

$$G = RT \, v_e/V_0 \qquad (2.2)$$

where Q is degree of swelling, i/v_u is charge density of polymer, S^* is ionic strength of solution, $(1/2 - \chi_1)/v_1$ is polymer-solvent affinity, v_e/V_0 is crosslinking density, and G is rigidity.

The water absorbency, therefore, increases with increasing number of hydrophilic and ionic functional groups, and with decreasing in the crosslinking density of the polymer network and in the concentration of ionic solutions (NaCl solution, urine, etc.).

2.1.2.2 Water Absorption Capacity and Absorbing Rate

Water absorption capacity is generally a term employed to indicate capacity to retain as much absorbed fluid as possible (retention). In addition, this term also has two other meaning. One is the capacity to swell by absorbing fluid (absorption), and the other is the capacity to gel and decrease flowability by absorbing fluid (gelation). These three types of water absorption capacity can be influenced by modifying the composition and the product form. Table 2.2 shows the methods for measuring water absorption capacity according to each definition.

The water absorption rate is more influenced by the product form than by the composition of the SAP. Fundamentally, the larger the surface area the higher the water absorption rate. However, lumps are produced in the case of fine powders, and tend to obstruct absorption. A way to eliminate this obstacle is to have coarse particles and to increase the surface area by making the resin porous or scaly.

Table 2.2 Measurement of the Water Absorbing Capacity

Required performances	Measurement method	Outline of the method
Absorption power	Capillary method (Demand Wetability method)	The resin is placed on a porous sheet or on a sheet with small holes. and put in contact with the fluid.
Water retention	Filtration method	After making the resin sufficiently swell in an excess of fluid, the excess fluid is filtrated by a screen.
	Centrifugal dehydration method	After making the resin sufficiently swell in an excess of fluid, it is placed in a bag, and centrifugal dehydration is performed.
	Tea-bag method	The resin is inclosed in a nonwoven bag, and after dipping it in the fluid for a certain time, it is weighed after draining water.
	Sheet method	The polymer is inserted between two layers of tissue paper in order to obtain a sheet, and is then immersed in the liquid.
	UV absorbance	The polymer swells in aqueous Blue Dextrin solution, and UV absorbance is measured in comparison to a blank.
Gelation	Vortex method	A fixed volume of liquid is put in a beaker, the polymer is introduced while stirring, and time is measured until the disappearance of the vortex.
	Flow method	The polymer is put in a beaker, liquid is added to make it swell, and the point at which the gel starts to flow constitutes the end point.

2.1.3 Application

Table 2.3 indicates the application of the SAPs classified from the market fields and the properties of polymers.

Materials with high absorbing capacity for water or other aqueous fluids were used in large number of sanitary products in the early years, and then uses as agricultural-gardening agents and in civil engineering as the next follower. Further applications in cosmetic-toiletries, medical, and other fields also have been developed recently. These applications are based on the material's ability to soak up liquid and also immobilized it. Here, some characteristics of new applications are discussed.

Although hard contact lenses with 10% moisture content were used in the past, lenses containing 70 to 80% moisture, superior in properties such as transparency, strength, oxygen permeability, and low irritation to eyes, have been developed using such polymers as silicone acrylate, fumaric acid diester, and alkylene glycol monoacrylate.

Drug-release-control agents using appropriate SAPs have been devised to facilitate gradual drug dissolution at specific sites within the patient's body. Crosslinked polymer materials composed of poly(N-vinylpyrrolidone) are particularly suitable with regard to biocompatibility and safety. N-substituted acrylamide, cellulose ether, and poly(vinyl alcohol) derivatives are also used for the same application.

Wound dressings and artificial skins as cure supporters for burns or external wounds are made from the crosslinking of alcoholic soluble nylon with gelatin, sodium polyacrylate, and from porous films of chitin as polysaccharide coated with hydrophilic polymer [2].

Table 2.3 Possible Applications of Superabsorbent Polymers

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 agents in soil • Seed coatings • Drying preventives for samplings • Artificial moss		• Cultivation plot for mushrooms • Seed beds in fluid	
Civil engineering, architecture	• Dew preventing agents in walls • Water-retaining agents in concrete	• Water sealing agents • Substitutes for sandbags	• Sludge solidification agents • Lubricants in drilling works • Slurry explosives	•Mud shielding works
Cosmetics, Toiletries	• Sweat absorbing and kitchen papers		• Gelaromatics • Pocket warmers • Disposable chamber pots	
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 • Drip absorbents • Dehydrating agents		• Gelling agents • Cold keeping hydrogels	• Viscosity enhancing additives
Others	• Fog preventing film • Dehydrating agents in oil • Moisture sensor • Ink jet for printer	• Toys swelling when soaked in water	• Hydrogel for fire fighting • Artificial snow • Water bed	• Emulsion paints

2.2 <u>Starch</u>

Starch, $(C_6H_{10}O_5)_n$, the principal reserve polysaccharide in plants, constitutes a substantial portion of human diet. It is the principal component of most seeds, tubers, and roots and is produced commercially from corn, wheat, rice, tapioca, potato, sago, and other sources [4].

2.2.1 <u>Granular Nature and Cooking Properties</u>

Starch occurs in plants in the form of granules. The size and shape of granules are specific for the plant of origin and can be identified microscopically. Diameters (in micrometers) of some commercial starches are in the following ranges: rice, 3-8; corn, 5-25; tapioca, 5-35; potato, 15-100.

Starch granules do not dissolve in cold water. They reversibly imbibe water and swell slightly, but remain as granules until the suspension-slurry is heated. When heated in water, starch granules gelatinize. Gelatinization is the collapse (disruption) of molecular orders within starch granules manifested in irreversible changes in properties such as granule swelling, native crystallite melting, loss of birefringence, and leaching of soluble components (primarily amylose).

Pasting is the phenomenon following gelatinization when a starch slurry containing excess water is heated. It involves further granule swelling, additional leaching of soluble components, and eventually, especially with the application of shear, total disruption of granules, resulting in molecules and aggregates of molecules in dispersion or solution, although in most, if not all cases, granule remnants remain [5].

The temperature at which this drastic change occurs is usually termed the gelatinization or, more correctly, the pasting temperature of starch [6]. The gelatinization temperature is recorded as a temperature range that depends on starch type [4].

Starch	Range, °C
potato	59-68
tapioca	58.5-70
corn	62-72
waxy corn	63-72
wheat	58-64

2.2.2 Molecular Components

Although commercial starch granules contain small amounts of protein, lipids (especially phosphoglycerides), and other components, the principal components are amylose and/or amylopectin.

1) *Amylose*

Amylose is an essentially linear polysaccharide composed of $(1 \rightarrow 4)$-linked α-D-glucopyranosyl units. Its degree of polymerization (DP) is 1,000-16,000 (MW 160,000-2,650,000), depending on the source and method of preparation. Amylose can have several conformations. In the solid state, it probably exists most often as a left-handed, sixfold helix. In solution, it seems to be a loosely wound and extended helix that behaves as a random coil [5].
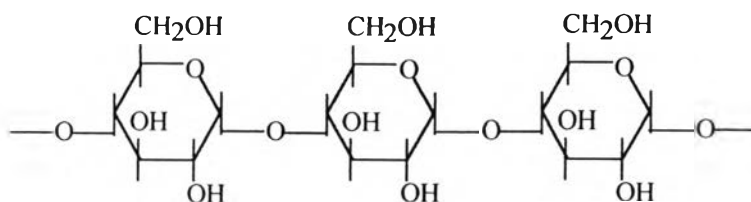
Figure 2.3 Chemical Structure of Amylose Chain

Amylose, because of its special helical structure, is able to complex with hydrophobic molecules. When iodine becomes lodged within this helix, a deep blue starch-iodine complex results [7]. This characteristic blue color has been used both as a qualitative and quantitative test for starch in various systems [4].
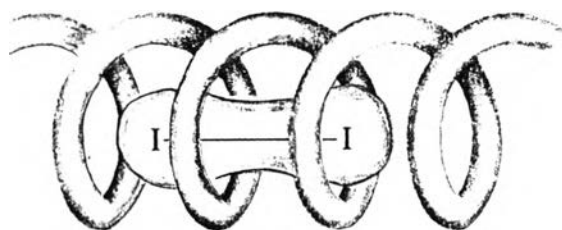
Figure 2.4 Formation of the Amylose Helix as a Blue Charge-transfer Complex with Molecular Iodine

2) *Amylopectin*

Amylopectin has a branch-on-branch structure. Amylopectin molecules are composed of chains of $(1 \rightarrow 4)$-linked α-D-glucopyranosyl units; branches are formed by joining these chains with α-D-$(1 \rightarrow 6)$ linkages. The molecular weight of amylopectin has been measured as $5 \times 10^7 - 4 \times 10^8$ (DP $3 \times 10^5 - 2.5 \times 10^6$), depending on the source and method of preparation [5].

Amylopectin also forms a complex with iodine, but its color is purple to reddish-brown, depending on the source of amylopectin. This color reaction is usually obscured by the amylose-iodine blue [4].
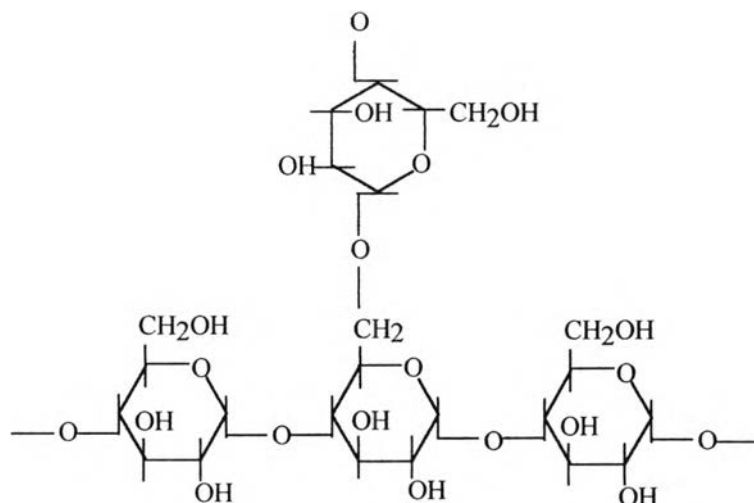
Figure 2.5 Branched Structure of Amylopectin

Starch properties are greatly influenced by the ratio of amylose to amylopectin. This ratio varies according to the type of starch and the fractions may range from 70% amylose and 30% amylopectin, in recently developed high amylose starches, to practically 100% amylopectin in the so-called waxy starches. Common starches, however, such as corn, wheat, rice, barley, tapioca, sago, and potato, contain 17-27% amylose and 73-83% amylopectin. For any one species of starch, the ratio is constant [8].

2.3 Free-Radical Graft Copolymerization by Radiation Methods

A graft copolymer consists of a polymeric backbone with covalently linked polymeric side chains. In principle, both the backbone and side chains could be homopolymers or copolymers. Graft copolymers are of great interest in the field of absorbency in a number of aspects. Grafting can be carried out in such a way that the properties of the side chains can be added to those of the substrate polymer without greatly changing the latter [9].

In free-radical-initiated graft copolymerizations, a free radical produced on the backbone reacts with monomer to form a grafted copolymer. One of the free radical initiation methods is irradiation.

2.3.1 Radiation-Induced Synthesis

When electromagnetic radiation passes through matter, its intensity decreases, primarily as a result of scattering and energy absorption by some of the irradiated molecules. Three major processes are operative.

1) The photoelectric effect

2) Compton scattering

3) The production of electron pairs

For gamma rays from Co^{60} the predominant effect in organic materials is Compton scattering. In the Compton effect the incident gamma ray interacts with an orbital electron ejecting the electron from its orbit and producing another photon of lower energy. Both the electron and photon subsequently interact with the material or the surroundings giving rise to essentially two processes, one of ionization and the

other of excitation. In the case of ionization the Compton electron transfers sufficient energy to the orbital electron of another atom to overcome the forces binding it to the nucleus. The electron is therefore ejected, leaving behind a positive ion. If the energy transferred is insufficient to cause ejection of an electron, the energy level of the atom is raised and the atom is said to be in an excited state. The ions and excited molecules are very reactive; they either react with other materials present in the system or decompose into radicals and atoms or molecules. The free radicals produced upon irradiation of polymeric systems may be used to initiate graft copolymerization.

2.3.2 The Different Methods of Radiation Grafting

Radiation synthesis of graft copolymers can be accomplished by the following methods.
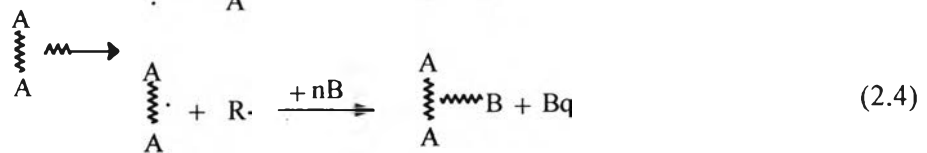
1) *The Direct Grafting Method*

In its simplest form the direct grafting method involves the irradiation of a polymeric substrate in the presence of a monomer and in the absence of oxygen. Graft copolymerization of the monomer to the polymer is then initiated through the free radicals generated in the latter.

A number of important factors must be considered, however, before applying the direct radiation method to a given polymer-monomer system. Ionizing radiation as such is unselective. One must therefore consider not only the effect of radiation on the polymeric substrate but also the effect on the monomer, the solvent, or any other substance present in the system.

The radiation sensitivity of a substrate is measured in terms of its G_r value or free radical yield which is the number of free radicals formed per 100 eV energy absorbed per gram. The highest grafting yields will occur for polymer-monomer

combinations in which the free radical yield of the polymer is much greater than for the monomer.

Together with the radiation sensitivity of the polymer-monomer combination, one must also consider the effect of the radiation on the actual polymeric substrate. In general, polymers either degrade or crosslink under irradiation. If the polymer degrades then irradiation in the presence of a monomer will lead predominantly to block-type copolymers (eq. 2.3); if the polymer crosslinks, graft structures will result (eq. 2.4). This may be represented schematically as follows:

$$
\begin{array}{cc}
A & \\
\xi & + \\
\xi &
\end{array}
\quad + \quad nB \quad \longrightarrow \quad
\begin{array}{cc}
A & B \\
\xi & + \xi \\
B & A
\end{array}
\qquad (2.3)
$$

$$
\begin{array}{c}
A \\
\xi \quad \text{ww} \longrightarrow \\
A
\end{array}
$$

$$
\begin{array}{c}
A \\
\xi \cdot + R\cdot \\
A
\end{array}
\quad \xrightarrow{+ nB} \quad
\begin{array}{c}
A \\
\xi\text{www}B + Bq \\
A
\end{array}
\qquad (2.4)
$$
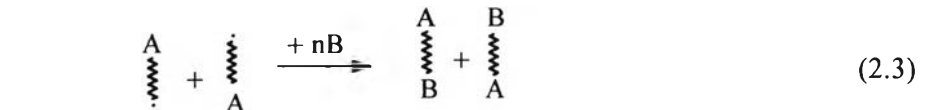
Here A ww· and A ww A represent polymeric free radicals derived from Ap, and R represents a low molecular weight radical or hydrogen atom.

As a general empirical rule, it may be stated that when the structure of a vinyl polymer is such that each carbon atom of the main chain carries at least one hydrogen atom, the polymer crosslinks (case I), whereas if a tetrasubstituted carbon atom is present in the monomer unit, the polymer degrades (case II).

$$
\left[-CH_2 - \underset{R}{\overset{H}{C}} - \right]
\qquad
\left[-CH_2 - \underset{R_2}{\overset{R_2}{C}} - \right]
$$
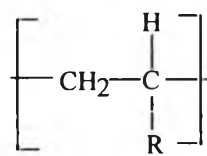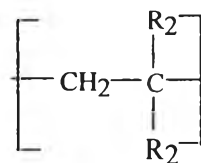
(I)   (II)

The dose and dose-rate of irradiation are important factors in any radiation grafting system. In the direct method, the total dose determines the number of grafting sites while the dose-rate determines the length of the grafted branches. The length of the branches is also controlled by other factors, such as the presence of chain transfer, the concentration of monomers, the reaction temperature, the viscosity of the reacting medium, diffusion phenomenon, etc.

Diffusion of the monomer into the polymer plays an important role in the direct radiation method as it is by this means that the monomer reaches the active sites within the polymer. It would be expected that the rate of graft polymerization would be directly proportional to the radiation dose-rate. In some cases, however, the diffusion of monomer cannot satisfy the increased rate of initiation within the polymer.
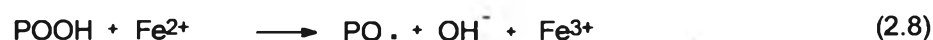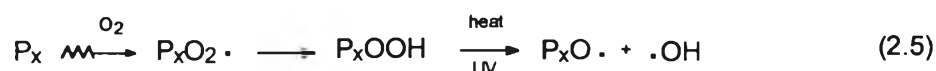
It will be appreciated that in the direct radiation method a certain amount of homopolymer will always be formed both because of the effect of the radiation on the monomer and as a normal consequence of the grafting reaction (eq. 2.4). Contamination of the grafted product with homopolymer can be quite inconvenient as by large most polymers are incompatible and due to a segregative tendency, the presence of physically mixed polymer impurity can yield a product with poor physical, optical, and electrical properties. The direct radiation method is, on the other hand, by far the most efficient technique since it involves rapid utilization of the accessible backbone polymer radicals as they are formed. It is not surprising then that numerous techniques have been developed in an effort to reduce the amount of homopolymerization formed during the reaction.

2) *Preirradiation in Air*

In this method the polymeric substrate is irradiated in air or oxygen to produce peroxide bonds. These peroxide groups are reasonably stable and the polymer

can be stored in the cold without loss of activity. If heated subsequently in the presence of monomer (as liquid or vapor) to about 150°C in the absence of air, the peroxide groups decompose liberating free radicals which can then initiate graft polymerization.

In principle the preirradiation method should not yield homopolymer because the monomer is never directly exposed to radiation. In some cases, however, there is evidence that irradiation in air leads to the formation of hydroperoxides on the polymer backbone. These, on heating, decompose giving a hydroxyl radical which can initiate the homopolymerization of the added monomer (eqs. 2.5-2.7). Homopolymer formation can, however, be reduced considerably by the incorporation of a redox system during irradiation to convert the hydroxyl radicals to hydroxyl ions (eq. 2.8).

$$P_x \xrightarrow{O_2} P_xO_2 \cdot \longrightarrow P_xOOH \xrightarrow[UV]{heat} P_xO \cdot + \cdot OH \qquad (2.5)$$

$$P_xO \cdot + M \longrightarrow P_xOM \cdot graft\ copolymer \qquad (2.6)$$

$$\cdot OH + M \longrightarrow HOM \cdot homopolymer \qquad (2.7)$$

$$POOH + Fe^{2+} \longrightarrow PO \cdot + OH^- + Fe^{3+} \qquad (2.8)$$

3) Grafting Initiated by Trapped Radicals

One of the primary effects of ionizing radiation on polymers is the formation of free radicals. Although free radicals are highly reactive it has been demonstrated that they can become trapped for extremely long periods (several days or months) in a viscous medium such as that encountered in a polymer at a temperature below its glass transition point. If the polymer is partly crystalline, the free radicals formed within the crystalline regions upon irradiation are still more firmly trapped, since the mobility of polymeric segments is much lower if these are involved in an organized structure. Although the free radicals are trapped they are still highly reactive

and provided the monomer can diffuse through the polymer to reach the reactive sites, the trapped radicals can be used to initiate graft copolymerization.

The grafting yield obtained by this method will depend directly on the efficiency of radical trapping. Radical mobility is a function of temperature and the physical state of the system; it follows therefore that the most efficient radical trapping will occur for crystalline polymers irradiated at low temperature. The concentration of free radicals in an irradiated polymer has been shown to increase linearly with dose but tends to reach a limiting value for a certain dose. This limiting dose is apparently a function of the particular polymer system and has to be determined experimentally.

As with the peroxidation technique, homopolymer formation should not occur in this process as the monomer is not exposed to radiation. Moreover, low molecular weight radicals, which would also initiate homopolymerization, are not expected to remain trapped at ordinary temperatures.

The efficiency of the trapped radical method of grafting is not as good as for the peroxidation method because of the very low concentration of frozen-in radicals that can be achieved. The limited lifetime of these radicals also means that the grafting reaction must be carried out almost immediately after the irradiation. Perhaps the only advantage of this method over the peroxidation technique is the fact that the temperature required for the grafting reaction to occur is much lower. This makes the method useful for polymers with a poor heat stability.

### 2.3.3 Kinetic Features of Radiation Grafting

In principle, the conventional free radical polymerization scheme should be applicable to radiation-grafting systems as, in general, the reaction involves the polymerization of a vinyl monomer initiated by a polymeric radical. In practice, however, the situation is not quite as straightforward as this because of the number of

specific features that result from the special reaction conditions prevailing in most grafting systems. The gel effect, chain transfer, phase separation, and diffusion effects are but a few of the many factors which can seriously affect the reaction kinetics.

1) *The Direct Radiation Technique*

If one assumes that the graft copolymerization occurs by a radical chain process then the overall reaction scheme can be divided into three main steps: initiation, propagation, and terminaiton. This may be represented as follows:

Initiation:

$$P \rightarrow P\cdot \qquad (2.9)$$
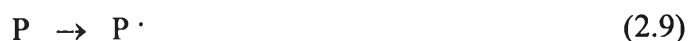
$$r = kI \qquad (2.10)$$

Propagation of initial radical:

$$P\cdot + M \rightarrow PM\cdot \qquad (2.11)$$

$$r_i = k_i [P\cdot][M] \qquad (2.12)$$

Propagation:

$$PM_n\cdot + M \rightarrow PM_{n+1}\cdot \qquad (2.13)$$

$$r_p = k_p [PM_n\cdot][M] \qquad (2.14)$$

Termination by two growing radicals:

$$PM_m\cdot + PM_n\cdot \rightarrow PM_{m+n} \text{ or } PM_m + PM_n \qquad (2.15)$$

$$r_t = 2k_t [PM\cdot]^2 \qquad (2.16)$$

If one makes the normal assumption that the length of the polymer chains is long, then reaction 2.11 can be neglected with respect to reaction 2.13, and one obtains the following relation for the rate of graft copolymerization:

$$r_p = k_p [PM_n \cdot][M] \qquad (2.17)$$

Introducing the conventional steady-state assumption that the rate of change in the radical concentration is small compared to its rates of formation and disappearance, then

$$k_i [P \cdot][M] = 2k_t [PM_n \cdot]^2 \qquad (2.18)$$

i.e.,

$$r_i = 2k_t[PM_n \cdot]^2 \qquad (2.19)$$

then

$$[PM_n \cdot] = (r_i / 2k_t)^{1/2} \qquad (2.20)$$

On combining Equations 2.17 and 2.20 one obtains for the rate of graft polymerization as the following:

$$r_p = k_p [M] (r_i / 2k_t)^{1/2} \qquad (2.21)$$

where

I = intensity of radiation.

P = backbone polymer.

P· = polymer radical.

PM_m, PM_n, or PM_{m+n} = graft copolymer.

M = grafting monomer.

r = rate of initiation of polymer radicals.

r_i = rate of initiation of graft reaction.

r_p, r_t = rate of propagation and termination respectively.

k = rate constant for initiation of polymer radicals.

k_i = rate constant for initiation of graft reaction.

k_p, k_t = propagation and termination rate constants, respectively.

2) *Grafting with More than One Monomer*

Deviations from normal copolymerization kinetics have also been noted in cases of the direct radiation grafting of more than one monomer to a polymeric substrate. On the basis of the normal copolymer composition equation,

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \qquad (2.22)$$

where

dM_1/dM_2 = ratio of monomer 1 to monomer 2 in the copolymer formed at any instant.

M_1, M_2 = concentrations of monomer 1 and 2, respectively, in the comonomer solution.

r_1, r_2 = relative reactivities of monomers 1 and 2, respectively.

one should then be able to predict the composition of the grafted copolymer provided the values of r_1 and r_2 are known [10].

2.4 Terminology and Definition

Before proceeding to the experimental part, several technical terms need to be clarified for the better understanding of readers.

1) Percentage Add-on

It is refered to as the weight percentage synthetic polymer in the graft copolymer and is determined as follows:

$$\%\text{add-on} = \frac{\text{weight of polymer grafted}}{\text{weight of the grafted copolymer}} \times 100 \qquad (2.23)$$

It is calculated by the acid hydrolysis method. The grafted polymers are seperated from the starch backbone by heating the graft copolymer under reflux in dilute acid solution.

2) Grafting Efficiency

It is a term often used to describe graft copolymerization reactions and is defined as the percentage of the total synthetic polymer formed that has been grafted to starch. High grafting efficiencies are desirable since a polymerizaton of the low grafting efficiency would afford mainly a physical mixture of starch and homopolymer. It can be calculated as follows:

$$\%\text{grafting efficiency} = \frac{\text{weight of polymer grafted}}{\text{weight of homopolymer + weight of polymer grafted}} \times 100 \qquad (2.24)$$

3) <u>Percentage Conversion</u>

It is used to describe the degree of the monomer, which undergoes graft copolymerization and homopolymerization. It can be evaluated by the following expression.

$$\%\text{conversion of monomer} = \frac{\text{weight of polymer formed}}{\text{weight of monomer charged}} \times 100 \qquad (2.25)$$

4) <u>Grafting Ratio</u>

It is a term used to describe graft copolymerization which is defined as the percentage ratio between polymer grafted starch and can be calculated by the following expression.

$$\%\text{graft ratio} = \frac{\text{weight of polymer grafted}}{\text{weight of starch}} \times 100 \qquad (2.26)$$

2.5 Literature Survey

Reyes et al., [11] studied the grafting of acrylic acid to preirradiated starch. The influence of acrylic acid concentration, irradiated starch concentration, and solvent on degree of grafting, molecular weight, and number of grafted branches were evaluated. They also found that higher degree of grafting was attained with electron-irradiated starch than with gamma-irradiated starch.

Garnett and Jankiewicz [12] studied the effect of acid in radiation polymerization. They found that the addition of mineral acid to solutions of styrene in dioxane enhanced the radiation polymerization yield of polystyrene. Gel permeation chromatographic analysis of the resulting homopolymer showed that $\overline{Mn}$ values was significantly reduced by acid inclusion. When radiation polymerization was carried out in the presence of a trunk polymer such as cellulose or polyethylene (i.e. grafting conditions), the same acid effect on $\overline{Mn}$ was observed in the monomer solution. A mechanism for this acid effect in both radiation polymerization and grafting was proposed based on the formation of shorter-chain oligomers.

Ranby and Rodehed [13] prepared the modified starch by Mn^{3+} initiated grafting of acrylonitrile onto starch followed by alkaline hydrolysis. At relative humidities (RH) up to 95-97% the modified starch showed normal water vapor absorption like cellulose and the other polysaccharides. At higher RH the water vapor absorption increased very rapidly. When in contact with liquid, distilled water, the modified starch formed a superabsorbent gel which retained very large amounts of water (up to 800 g g^{-1}). At low and high pH and in aqueous salt solutions (NaCl, $CaCl_2$ and synthetic urine), the water retention was strongly reduced.

Zicheng et al., [14] prepared three types of polyacrylamide hydrogel by radiation techniques. The first type, polyacrylamide hydrogels (PAM-HG1) were prepared by ^{60}Co γ-ray initiated polymerization acrylamide solutions and polyacrylamide (PAM) obtained with $\overline{Mw}$ = 5.7 x 10^6 was crosslinked under subsequent irradiation. PAM-HG1 formed had water retention value from 10 to 300 g g^{-1} depending on the gel content. The second type, anionic polyacrylamide hydrogels (PAM-HG2) were prepared by suspension hydrolysis of PAM-HG1 in the

hydrogenated gasoline with NaOH to convert part of the -CONH groups to -COONa groups in the polymer chains. The water retention value of PAM-HG2 was three times greater than the water retention value of PAM-HG1. The last type, copolymer hydrogels (PAM-HG3) were prepared by radiation polymerization and crosslinking of the mixture of acrylamide and sodium acrylate in aqueous solutions. PAM-HG3 had water retention value greater than 2000 g g^{-1}.

Iyer et al., [15] prepared superabsorbent polymers using acrylonitrile grafted to corn starch employing low levels of gamma-ray radiation as initiator. Various grafting parameters had been studied at these low dosages. The absorbency values for the final products were fairly good and comparable with those reported for various products prepared by chemical initiation methods. Use of the superabsorbent as a desiccant is better than silica gel.

Castel et al., [16] prepared starch graft superabsorbents by graft copolymerization either with polyacrylonitrile (PAN) and saponification of the resulting copolymer or with trimethyl-amino ethylacrylate chloride (CMA) and methylene bisacrylamide as crosslinking agent. The influence of several structural parameters on the swelling properties of those absorbents had been studied: crosslink density, ionic content, and composition of the starch. As expected, the absorbency decreased with an increase of the crosslink density. It increased with the ionic content of the graft copolymer up to a maximum, an excess of charges leading to a decreased swelling. The PAN branch length depended on the origin of the starch. High molar weight PAN was grafted onto waxy corn, a starch with high amylopectin content. The swelling increased with increasing molar weight of PAN up to 5×10^5. In saline solution the absorbency of both ionic gels decreased significantly. However, in the presence of

multivalent ions their behavior was different. For cationic absorbents the swelling depended on the ionic strength but not on the ion valency. On the other hand, anionic absorbents are significantly affected by multivalent cations.

Gargan et al., [17] carried out an investigation to identify compounds which were suitable for use as homopolymerization inhibitors when grafting acrylic acid or methacrylic acid onto pre-irradiated low-density polyethylene. It was found that certain transition metal compounds were able to suppress the formation of homopolymer whilst still allowing significant levels of grafting to take place. For acrylic acid the most suitable inhibitor found was ferrous sulphate as this compound allowed a high degree of grafting that was independent of inhibitor concentration. When grafting methacrylic acid either cupric sulphate or potassium ferrocyanide could be used and preferably at low concentrations (ca 0.01 M).

Hongfei et al., [18] investigated the acid effect in mutual radiation grafting of acrylic acid (AA), 4-vinyl-pyridine (4-VP) and N-2-vinylpyrrolidone (NVP) in methanol on silicone rubber and measured grafting yields as a function of dose. They found that acid in grafting system of 4-VP provided an enhancement effect, but in the NVP system had an inhibition effect with a wide absorbed dose range. But in the case of AA the relationship was more complex: below 6 kGy acid enhanced the grafting yield; while dose was up to 13 kGy the opposite results were obtained.

Kiatkamjornwong et al., [19] studied radiation modification on liquid retention properties of native cassava starch, gelatinized at 85°C by graft copolymerization with acrylonitrile, which was carried out by mutual irradiation to gamma rays. A thin aluminium foil was used to cover the inner wall of the reaction vessel, so that the

homopolymer concentration was reduced to be less than 1.0% with a distilled water retention value of 665 g g^{-1} of the dry weight of the saponified grafted product.

Lokhande et al., [20] reported the influence of different concentrations of the monomer acrylonitrile on the PAN add-on, the number average molecular weight of the PAN side chains, and the grafting frequency of the PAN side chains in the gamma-radiation induced grafting of acrylonitrile onto guar gum. They found that at 0.3 Mrad dosage, the extents of PAN add-on were 32.4, 48.5, and 66.2%, respectively; and the number average molecular weight of the PAN side chains were 59,100, 132,200, and 238,900, respectively, at three different reaction conditions. The frequency of grafting also showed considerable variation at 0.2 Mrad dosage, for all three sets of samples. The viscosity of the aqueous dispersions of the saponified samples at different concentrations decreased when the concentration of dispersion decreased. The water absorbency of the saponfied samples was evaluated and the values were around 250 g g^{-1}.

Dworjanyn et al., [21] reviewed the role of additives including acids, inorganic salts, organic inclusion compounds like urea, multifunctional acrylates and methacrylates for increasing yields in radiation grafting reactions. Synergistic effects in performance between the first three groups and the latter two had been observed. They also reported two new classes of compounds including oligomer acrylates and photoinitiators as additives in radiation grafting and compared their reactivities with the earlier series.

Haddadi-asl et al., [22] studied radiation grafting of hydrophilic vinyl monomers onto ethylene-propylene elastomers (EPM rubbers) by the simultaneous

method. It was centered upon gamma radiation induced grafting of acrylamide (AAm), N-vinyl-2-pyrrolidone (NVP), 2-hydroxyethyl methacrylate (HEMA) and acrylonitrile (AN) onto four different EPM rubbers. They found that the graft efficiency of EPM rubber increased with increasing the ethylene content and molecular weight of the rubber, whilst attempts to graft EPM rubber in aqueous solution of AN, AAm, HEMA and NVP led to extensive homopolymerization. Metal-based homopolymerization inhibitors including Mohr's salt, $Cu(NO_3)_2$ and $FeSO_4$ were evaluated and found to prevent homopolymerization and sigificantly increased graft yield. Lithium nitrate was evaluated as a graft promoter. The effect of oxygen upon grafting was also studied. Replacing oxygen with an inert gas such as nitrogen could significantly increased grafting yield. However, under all conditions understudy, no significant graft yield could be achieved with AN.

Dung et al., [23] studied the grafting of acrylamide onto starch by radiation method. The effects of irradiated dose, dose rate and monomer concentration on grafting yield were investigated. The urease enzyme was then immobilized on the grafted starch. Some quantitative relationships between the percentage graft and the activity of immobilized enzyme were determined. The enzyme activity was maintained by more than seven batch enzyme reactions.

Kiatkamjornwong and Meechai [24] investigated the enhancement of the gamma radiation grafting of acrylonitrile onto gelatinized cassava starch. They found that addition of ionic salts at appropriate concentrations could reduce homopolymer formation to a certain extent, but they also caused deficiency in the product color and purity. The insertion of a clean aluminium foil to cover the inner wall of the reaction vessel could reduce efficiently the homopolymer with an improvement in the water

absorption. In addition, a total dose of 3.5 kGy at a dose rate 6.6×10^{-2} kGy min^{-1} for 20 cm^3 of acrylonitrile was found as the most effective in the simultaneous irradiation grafting of the gelatinized cassava starch and acrylonitrile under a specific condition. The aluminium foil was found to be the best metallic suppresser of homopolymer formation. Acid could be used to increase the number of grafted sites on the starch backbone and to improve water absorption capacity. Styrene comonomer hampered the grafting of acrylonitrile onto starch at this dose and dose rate. By a freeze drying the saponified starch-g-PAN, the water absorption capacity increased considerably compared with that using a 65°C oven. Aluminium trichloride hexahydrate improved the wicking time, but decreased water absorption capacity. The quality of homopolymer formed in the system of starch-acrylonitrile system lessened with increasing water absorption when a low dose rate was used.

Liu and Rempel [25] prepared superabsorbents comprising acrylic acid and acrylamide in the presence of formaldehyde by a solution polymerization technique using a potassium persulfite-potassium metabisulfite redox initiation system. The absorption behavior of superabsorbents was related to their chemical composition and the nature of the solvent. A superabsorbent (1.5% acrylamide) had a high water-absorption capacity and a fast rate of absorption. As expected, the absorption capacity decreased with increasing crosslink density. The addition of NaCl resulted in a continuous absorption capacity decreased for the superabsorbent (1.5% acrylamide). The decrease of absorption capacity was due to the decrease of the osmotic pressure difference between the gel and the external solution. The effects of initiator concentration, polymerization temperature, and amount of acrylamide in the copolymers were investigated. It was noted that absorption capacities decreased with increasing initiator concentration, polymerization temperature, and amount of

acrylamide in the copolymers. The swelling of the copolymer formed, which retained a 900 g water g^{-1} dry copolymer, was studied in alcohol/water mixtures of increasing alcohol content at 294, 304, and 314 K. The main transition for ethanol/water and methanol/water mixtures was a large decrease of retention capacity of the copolymer at 50-60 vol% ethanol and 55-65 vol% methanol, respectively.

Zhou et al., [26] prepared superabsorbent copolymers from acrylamide, sodium methallyl sulfonate, sodium acrylate, and N,N'-methylenebisacrylamide in aqueous solution using potassium persulfate/ N,N,N',N'-tetramethylethylenediamine as the redox initiator. The copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The experimental results showed that absorbency increased with an increase in crosslinker concentration but decreased with excessive crosslinking. The ionic groups in the polymer network significantly increased the equilibrium swelling. Water retention at pressures of 1-10 kg cm^{-2} and temperatures of 60 and 100°C were also reported.

Kiatkamjornwong and Suwanmala [27, 28] prepared partially hydrolyzed polyacrylamide-co-poly(n-vinyl pyrrolidone) used as a superabsorbent from acrylamide monomers exposed to γ-rays to become polyacrylamide that was subsequently partially hydrolyzed and was then copolymerized with n-vinyl pyrrolidone to obtain a terpolymeric superabsorbent. They found that a water absorption value was vitally dependent on the dose rate and total dose absorbed at each polymerization step, material concentration and the hydrolysis condition. The water absorption capacity could be improved by using a freeze dryer for drying the copolymer. The resulting copolymer could absorb distilled deionized water of 1100 g g^{-1}.

Kiatkamjornwong and Phunchareon [29] synthesized highly water-absorbing copolymers of poly(potassium acrylate-*co*-acrylamide) by an inverse suspension copolymerization. Acrylamide and potassium acrylate were used as comonomers, and *N,N'*-methylenebisacrylamide as a crosslinker polymerized by ammonium persulphate in *n*-hexane, each emulsified by a series of sorbitan surfactants with a relatively lower concentration of 1.0% w v^{-1} at 60°C for 2 h. The effects of influential reaction parameters on the water absorption of the newly synthesized copolymers were investigated. The obtained copolymer had high the water absorption (775 g g^{-1} dry weight) and liquid sorption rate (21.41 s). The water absorption depended highly on the pH of the buffer solution and the type and concentration of the saline solution. The copolymers exhibited a shear-thinning behavior at both low and high shear rates.

Diatao et al., [30] studied the grafting of acrylic acid onto powdered isotactic polypropylene by an electron beam preirradiation technique. All processes (including irradiation, storage of the samples, and grafting polymerization) were carried out in air. The effects of irradiation dose, storage time, reaction temperature, Mohr's salt, acid, and monomer concentration were investigated and discussed in detail. The results showed that the grafting could be achieved well without purging oxygen, and Mohr's salt was indispensable for initiating grafting reaction and decreasing the homopolymerization. Optimal reaction conditions could be generalized for a large-scale production of the desired polymer materials.