CHAPTER II

THEORY and LITERATURE REVIEW

Theoretical Background

1. Gamma Rays

    Gamma rays are high-energy photons and as such carry no charge or mass. X-rays and gamma rays are the same except for their source. X-rays are the result of an extranuclear process, i.e., the energy released when an electron falls into an unfilled orbital of an atom. Gamma rays are the result of nuclear processes; they are released in the fission process and also in the decay process of radioactive isotopes.

    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.

    a) Photoelectric Process

    In the photoelectric process a photon is completely absorbed in a collision with an orbital electron and the electron is ejected from the atom. This can happen whenever the energy of the photon is greater than the binding energy of the electron. The difference between the electron binding energy and the photon energy is carried away by the electron.

    The photoelectric effect is greatest for radiation of low energy and for material of high atomic number.

b) Compton Process

The Compton process is the result of an elastic collision between a photon and an orbital electron in which part of the photon energy is transferred to the electron. The electron causes further ionization and excitation, while the photon is scattered with reduced energy.

The Compton scattering process is often the principal effect for γ-rays in radiation Chemistry: for example, it is the only important process occurring when Co^{60} γ-rays (1.17 and 1.33 MeV) interact with water or other substances of low atomic number.

c) Pair Production

If a photon has an energy greater than twice that equivalent to the rest mass of an electron then the pair-production process can occur. Since the rest mass of an electron is 0.51 MeV, the minimum energy for pair production is 1.02 MeV. In this process the photon interacts with a nucleus and disappears with the production of two particles, a positive and a negative electron. The energy of photon in excess of the minimum 1.02 MeV appears primarily as kinetic energy of the pair of particles.

The positron so formed usually is annihilated by an electron. When this occurs, two annihilation photons occur travelling in opposite directions and carrying one-half of the energy, 1.02/2 MeV, or 0.51 MeV (2).

2. Interaction of Radiation with Water

2.1 The Formation of Primary Free-Radical Products in Water Radiolysis

The overall process of producing chemical changes by the use of ionizing radiation starts with the bombardment of water or aqueous solution by the radiation and terminates with the reestablishment of chemical equilibrium. This process is usually divided into three stages.

• The physical stage consists of energy transfer to the system. Its duration is of the order of 10^{-15} sec or less. The incident radiation produces, indirectly, ionization of water,

$$H_2O \rightsquigarrow e^- + H_2O^+ \qquad (2.1)$$
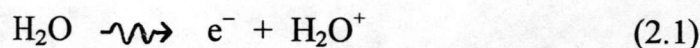
as well as directly excitation,

$$H_2O \rightsquigarrow H_2O^* \qquad (2.2)$$
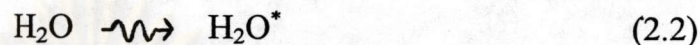
• The physicochemical stage consists of processes which lead to the estalishment of thermal equilibrium in the system. Its duration is usually taken to be of the order of 10^{-11} sec or less. Electron ejected in the ionization process become thermalized and hydrated:

$$e^- \rightarrow e^-_{therm} \rightarrow e^-_{aq} \qquad (2.3)$$

The H_2O^+ ions undergo a proton transfer reaction with neighboring water molecules,

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (2.4)$$
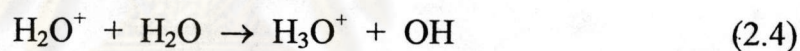
and the H_3O^+ becomes hydrated; hence, the point of formation an the initial spatial distribution of $H_3O^+_{aq}$ and OH are essentially the same and different from those for e^-_{aq}. If the volume in which they arose is considered to be spherical, then the radius for the initial distribution of the hydroxyl radicals and $H_3O^+_{aq}$ is about three times smaller than that of the hydrated electrons.

The dissociation of excited water molecules gives the hydrogen atom and hydroxyl radical as main products,

$$H_2O^* \rightarrow H^\bullet + {}^\bullet OH \qquad (2.5)$$

It also gives a low yield of hydrated electrons and, eventually, molecular hydrogen. It seems, however, that the contribution of excited water molecules to the formation of primary free-radical products in water radiolysis is of minor importance in comparison with that of the ionization processes.

• The chemical stage consists of diffusion away from the point of origin and chemical reaction of primary species (e^-_{aq}, ${}^\bullet OH$, $H_3O^+_{aq}$, and $H^\bullet$),

and leads to the establishment of chemical equilibrium. It begins in the spur about 10^{-11} sec after the passage of the radiation and about 10^{-10} sec in the bulk of the solution. Table 2.1 summarizes important chemical reactions of the primary species.

The expression for radiation-induced water decomposition,

$$H_2O \rightsquigarrow H_3O^+_{aq}, \cdot OH, e^-_{aq}, H \cdot, H_2O_2, H_2 \qquad (2.6)$$
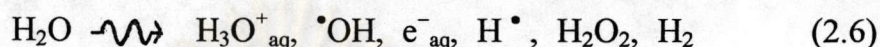
represents the state in irradiated water about 10^{-9} sec after the passage of high-energy radiation, when the reactions in the spurs, blobs, and short tracks are practically terminated. These products are found in irradiated water irrespective of the type and energy of radiation. Their amounts per 100 eV absorbed, the so-called primary product yields ($G_{H_3O^+_{aq}}$, G_H, G_{OH}, $G_{e^-_{aq}}$, G_{H_2}, and $G_{H_2O_2}$) depend, however, on the LET of radiation and on other parameters that will be discussed.

When dilute aqueous solutions are irradiated practically all the energy absobed is deposited in water molecules and the observed chemical changes are brought about *indirectly* via the molecular and, particularly, the radical products. *Direct* action due to energy deposited directly in the solute is generally unimportant in dilute solutions. At higher solute concentrations direct action may be significant, and there is some evidence that excited water molecules may transfer energy directly to the solute (3).

2.2 Spatial Distribution of Primary Species

Most radiation-chemical changes result from various secondary processes involving ions and excited molecules produced by the direct interaction of the radiation with matter. Since the process of ionization or excitation requires a strong interaction between a fast-moving charged particle and a molecule of the absorbing medium, such primary ions and

Table 2.1 Reactions of Free Radicals in Irradiated Water

Reaction	Rate constant, $M^{-1} sec^{-1}$	pH
$e_{aq}^- + e_{aq}^- \xrightarrow{2H_2O} H_2 + OH$	5.5×10^9	13.3
$e_{aq}^- + H \xrightarrow{H_2O} H_2 + OH^-$	2.5×10^{10}	10.5
$e_{aq}^- + OH \longrightarrow OH^-$	3.0×10^{10}	11
$e_{aq}^- + O^- \longrightarrow 2OH^-$	2.2×10^{10}	13
$e_{aq}^- + H_3O^+ \longrightarrow H + H_2O$	2.06×10^{10}	2.1-4.3
$e_{aq}^- + H_2O_2 \longrightarrow OH + OH^-$	1.23×10^{10}	7
	1.36×10^{10}	11
$e_{aq}^- + HO_2^- \longrightarrow O^- + OH^-$	3.5×10^9	13
$e_{aq}^- + H_2O \longrightarrow H + OH^-$	16	8.3-9.0
$H + H \longrightarrow H_2$	7.75×10^9	3
$H + OH \longrightarrow H_2O$	3.2×10^{10}	0.4-3
$H + OH^- \longrightarrow e_{aq}^-$	2.2×10^7	11-13
$H + H_2O_2 \longrightarrow H_2O + OH$	1.6×10^8	0.4-3
$OH + OH \longrightarrow H_2O_2$	6×10^9	0.4-3
	4×10^9	7
$O^- + O^- \longrightarrow O_2^{2-}$		
$\xrightarrow{H_2O} HO_2^- + OH^-$	1×10^9	13
$OH + H_2O_2 \longrightarrow HO_2 + H_2O$	4.5×10^7	7
	1.2×10^7	0.4-3
$O^- + HO_2^- \longrightarrow O_2^- + OH^-$	7×10^8	13
$OH + H_2 \longrightarrow H + H_2O$	6×10^7	7
$O^- + H_2 \longrightarrow H + OH^-$	8×10^7	13

excited molecules are necessarily located close to the path of the ionizing particle. Thus, the initial distribution of primary active species is very similar to the distribution of the water droplets around the track of charged particles (4).
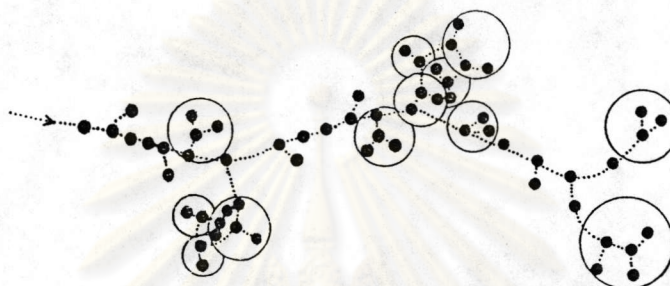

Fig. 2.1 Schematic diagram of the presumed distribution of primary events along the track of a fast electron.

Figure 2.1 shows isolated clusters of ions distributed like beads on a string along the path of a fast electron. Such sites of dense ionization and excitation are called "clusters" or "spurs". Once a cluster or a spur is formed, the local density (or concentration) of active species decreases rapidly as a result of both diffusion and chemical reaction.

Owing to the high local concentration of active species (e.g. free radicals) in a spur, recombination reactions are highly favoured, since the rate of these processes is proportional to the square of the concentration. Thus, in water, primary radicals OH and H can lead to the formation of hydrogen and hydrogen peroxide. The reaction products formed in the spur are called "molecular products".

2.3 Radiation-Chemical Yields of The Primary Products of Water Radiolysis and Their Dependence on Various Factors

2.3.1 Definition

The radiation-chemical yields of primary species is meant the number of free radicals, G_R (where R is $H^•$, $^•OH$, or e^-_{aq}), or molecules, G_M (where M is H_2 or H_2O_2), per absorbed 100 eV, present during the chemical stage of water radiolysis.

2.3.2 Effect of Scavenger Reactivity

If a substance S reacts with a short-lived species R which is a primary product of water radiolysis, to give the product P according to the reaction

$$R + S \longrightarrow P \tag{2.7}$$

then the increase of the concentration of S should be followed by the increase of G(P). This increasing process should continue until all the species R escaping the recombination (R + R = M) are scavenged. The effectiveness with which the substance S reacts with the species R also depends on the reaction rate constant k_{R+S}.

At very low concentrations, the scavenger cannot react with all radicals because their other reactions with molecular products or impurities are also effective; at moderately low concentrations is removes all those R's which are in the bulk of the solution. When the reactivity is sufficiently high, the scavenger S also competes for the species R from the intraspur reactions. Then increase in G(P) begins to occur on account of G_M (3).

2.3.3 Effect of pH

pH markedly influence the reactions occurring in irradiated water. This is true to an even greater extent in the case of irradiated aqueous solutions. In some solutions pH will determine the structure of the solute, but in all solutions changes in pH may alter the nature and reactivity of the primary radicals. Some of these changes have been mentioned already but for convenience all the pH-dependent reactions of the primary radicals are collected here. Those already mentioned are (5):

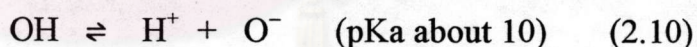(i) Conversion of a solvated electron to a hydrogen atom in acid solutions,

$$e^-_{aq} + H^+ \rightleftharpoons H \qquad (2.8)$$

(ii) The relatively slow association of a hydrogen atom and a hydrogen ion in acid solutions

$$H_2^+ \rightleftharpoons H + H^+ \quad (pKa < 2.7) \qquad (2.9)$$
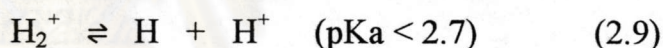
Other pH-dependent equilibria are:

(iii) Dissociation of the hydroxyl radical in alkaline solutions

$$OH \rightleftharpoons H^+ + O^- \quad (pKa \text{ about } 10) \qquad (2.10)$$

(iv) Dissociation of the perhydroxyl radical in neutral or alkaline solutions

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad (pKa \text{ probably } 2) \qquad (2.11)$$
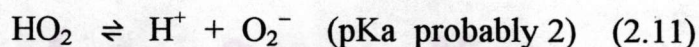
The O_2^- ion formed by this reaction can act as a reducing agent

(v) Conversion of a hydrogen atom to a solvated electron in alkaline solutions,

$$H + OH^- \rightarrow e_{aq}^- \qquad (2.12)$$

(vi) At pH below about 3 and above about 11, the yields of reducing and hydroxyl radicals increase without any corresponding decrease

in the yields of molecular hydrogen and hydrogen peroxide (Fig.2.2)   The increase in radical yield in acid solutions may be due to attack upon the acid by an intermediate that would otherwise revert to water.

$$H_2O^* + H^+ \rightarrow H_2^+ + OH \qquad (2.13)$$
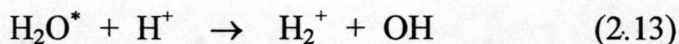
Similar reactions of the intermediate with hydroxyl ions are postulated to account for the increase in radical yield at high pH (4).

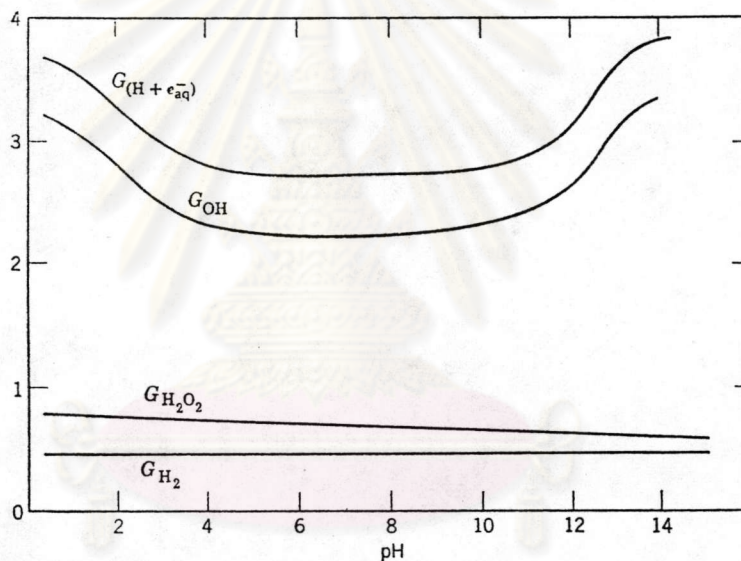$$H_2O^* + OH^- \rightarrow e_{aq}^- + OH \qquad (2.14)$$
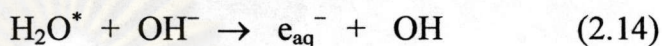
Fig. 2.2 Variation with pH of primary yields in γ-irradiated water

2.3.4 Effect of Linear Energy Transfer

All types of high-energy radiation interact with matter by giving rise to energetic charged particles (electrons or heavy particles) and that these react in essentially the same way to produce ionizations and excitations close to the track. However, it is found in practice that different types of radiation often produce different effects due to differences in the linear density of events along the track. When the ionized and excited molecules are

close together (α-particles), the reactive entities to which they give rise are formed sufficiently close to each other to react together, whereas when the ionizations and excitations are further apart (γ-rays), the reactive entities are less likely to react together and are hence able to react more effectively with substances in the medium.

The term used nowadays to describe the linear density of events along the track is "linear energy transfer" or LET, which may be expressed in keV absorbed per micron of track in the medium. The value of LET increases with the square of the charge on the particle and decreases as its speed increases (6).

It is easy to predict qualitatively the effect of LET on the yield of a radiation-chemical reaction. The increase of LET leads to the increase of the density of primary events per unit space and unit time. This should favor reactions of recombinations of primary species. The value of G_M is expected to increase, while G_R should decrease. If the product P comes mainly from the solute reactions with free radicals (H, OH, and e_{aq}^-), then G(P) should decrease (3).

2.3.4 Effect of Dose Rate

The increase of dose rate should, in a way, have an effect similar to that observed in the case of the increase of LET, since in both cases an increase in density of primary events is involved. This means that a favoring of recombination reactions and an increase in G_M, with a simultaneous decrease in G_R, are to be expected. The yields of stable reaction products should increase or decrease, depending on whether these are formed by reactions with molecular or radical primary products.

2.3.5 Effect of Temperature

The increase of temperature might lead to a broader distribution of primary species and thereby to an increase in G_R and a decrease in G_M (3).

3. Starch

Starch is the most abundant constituent in the human diet. Starch occurs naturally in most plant tissues, including roots and tubers, cereal grains, green vegetables, and fruits. It is a carbohydrate, a very large group of compounds containing carbon, hydrogen, and oxygen in the ratio of 6:10:5 as an empirical formula of $C_6H_{10}O_5$. The latter two elements are essentially in the same ratio as they exist in water, namely, two atoms of hydrogen to one of oxygen. Hence the name "carbohydrates," or hydrates of carbon. Besides starch, carbohydrates include such important substances as cellulose, sugars, and gums, all of which are widely distributed as natural plant products. Carbohydrates furnish the basic material for most buildings, paper, explosives, foods, alcoholic beverages, clothing, fuel, etc.

Carbohydrates are classified as monosaccharides, disacchrides, trisaccharides, and polysaccharides. Monosaccharides are simple sugars with six carbon atoms, which cannot be hydrolyzed to smaller molecules. Dextrose (glucose) is a monosaccharide, while disaccharides contain twelve carbon atoms and can be hydrolyzed to two simple sugars. Disaccharides include sucrose (common sugar), lactose, and maltose. Trisaccharides contain eighteen carbon atoms and yield three molecules of simple sugars on hydrolysis. Raffinose is the best known trisaccharide. Polysaccharides, which are very numerous, do not have the sweet taste of the other carbohydrates, are insoluble, and are of high molecular complexity. On hydrolysis, a polysaccharide

molecule yields many molecules of monosaccharide sugars. Starch, cellulose and glycogen are polysaccharides (7).

Starch is abundantly available, inexpensive, a desirable source of calories, and occurs in the form of granules with a density of approximately 1.5 g/cm^3. In granule form, starch is semi-crystalline, dense, insoluble in cold water, and only slightly hydrated. The granules themselves vary considerably in shape (from spheres to rods) and size (from a diameter of 2 μm in the pollen starch of amylomaize to 175 μm for canna starch), depending on the source. For cassava starch, the size of the granules ranges from 5 to 35 μm. The largest sizes are usually 25 to 35 μm and the smallest ones are 5 to 15 μm (8).

3.1 Molecular Component

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

Amylose is an essentially linear polysaccharide composed of (1→4)-linked ∝-D-glucopyranosyl units (often called anhydroglucose units, or simply AGU) (Figure 2.3). 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, six-fold helix. In solution, it seems to be a loosely wound and extended helix that behaves as a random coil.
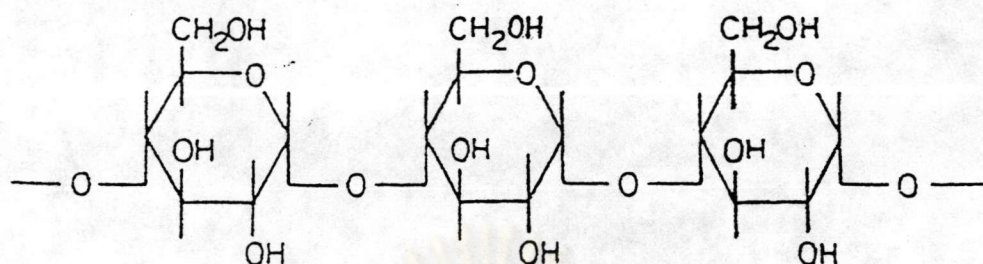
Figure 2.3 Chemical structure of amylose chain

Amylopectin has a branch-on-branch structure. Amylopectin molecules are composed of chains of (1→4)-linked ∝-D-glucopyranosyl units; branches are formed by joining these chains with ∝-D-(1→6) linkages. A schematic diagram of the amylopectin molecule is shown in Figure 2.4 (9).
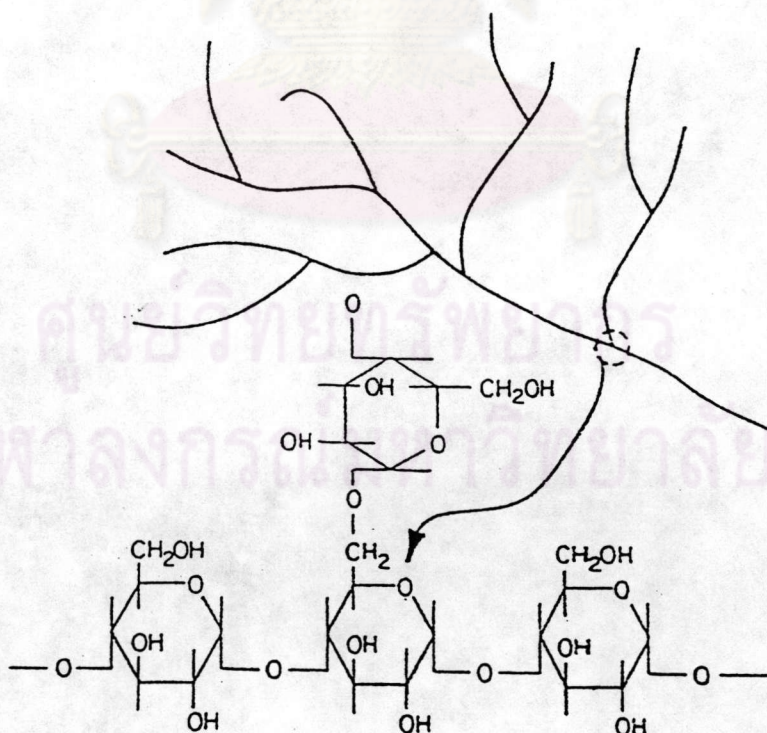
Figure 2.4 Branched structure of amylopectin

3.2 Gelatinized Starches

Occurrence in a granular form makes starch unique. Starch granules can be dispersed in water, producing low viscosity slurries that can be easily mixed and pumped. They can then be isolated by filtration or centrifugation, resuspended, reacted, and recovered.

When heated in water, starch granules absorb water, increase manyfold in size, swell, and gelatinize. Concurrently, the initially thin, opaque starch suspension becomes at a certain point viscous, semiopaque, and finally transparent. The temperature at which this drastic change occurs is usually termed the *gelatinization* or, more correctly, the *pasting temperature* of starch. More exactly, the gelatinization temperature is recorded as a temperature range in which the starch granules lose their birefringence. With cassava starch, gelatinization sets in at about 60°C and the process is completed below 85°C. The point of gelatinization to a certain extent depends on granule size, the smaller granules being more resistant to swelling (10).

As a result of cooking, starch forms a continuous system, referred to as *starch cook* or *starch paste*. In a starch cook or paste, there is a mixture of hydrated; swollen granules and granule particles, held together by a typical maze of associative forces (Figure 2.5)

Figure 2.5 Structure of molecules in a cooked starch paste

4. <u>Free-Radical Graft Copolymerization of Starch by Radiation Methods</u>

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.

In free-radical-initiated graft copolymerizations, a free radical produced on starch reacts with a monomer to form a grafted copolymer. One of the free radical initiation methods of starch is *irradiation* (11).

4.1 The Different Methods of Radiation Grafting

As indicated above, the irradiation of organic macromolecules leads predominantly to the formation of free radicals. If the irradiation is carried out in air, an effective free radical scavenger, peroxides and

hydroperoxides are formed within the polymer. If, however, the polymeric substrate is highly crystalline and in particular if the irradiation is carried out at low temperature and in the complete absence of air, the free radicals can be trapped in the system and can remain "active" for a considerable time. The free radicals, peroxides, and hydroperoxides formed or trapped in polymeric substrates upon irradiation can be used quite conveniently to initiate block and graft copolymerizations. Experimentally then, radiation synthesis of graft and block copolymers can be accomplished by the following methods.
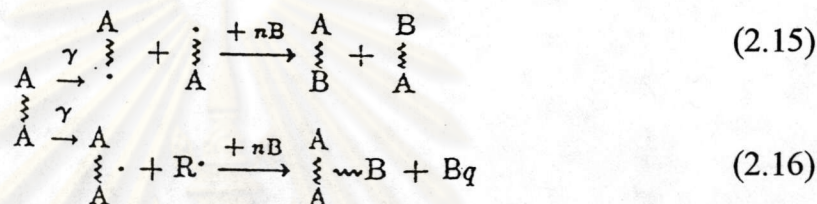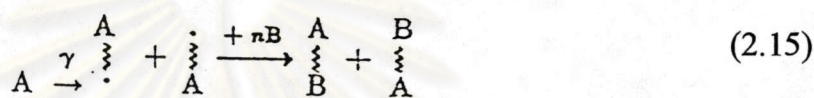
4.1.1 The Direct Grafting Method

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. It also follows that the grafting yield will increase with the lower the monomer concentration. The free radical yield of a monomer can be directly derived from the kinetics of its radiation polymerization and from experiments with free radical scavengers.

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. 2.15); if the polymer crosslinks, graft structures will result (eq. 2.16). This may be represented schematically as follows:

$$
\begin{array}{ccc}
A & & \\
\gamma\ \substack{\} & + & \substack{\cdot\\} \xrightarrow{+\,nB} \substack{A\\\}} + \substack{B\\\}} \\
A \to \cdot & A & B \quad A
\end{array}
\tag{2.15}
$$

$$
\substack{\\A} \gamma \\
\substack{A \to A\\ \substack{\} \cdot + R^\cdot \xrightarrow{+\,nB} \substack{A\\\}} \leadsto B + B_q \\ A \qquad\qquad A}
\tag{2.16}
$$

Here $A\leadsto\cdot$ and $A\leadsto A$ represent polymeric free radicals derived from Ap, $R^\bullet$ represents a low molecular weight radical or hydrogen atom and B represent a monomer atom.

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 can not 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. 2.16). Contamination of the grafted product with homopolymer can be quite inconvenient, as 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 soon as they are formed.

To avoid homopolymer formation, Hugin and Johnson (12) attempted to overcome this problem by adding ferrous, ferric, and cupric salts in the aqueous solution of nylon 6 film-acrylic acid. The anions were found to have no effect on the grafting or homopolymerization, but both processes were suppressed by the cations.

4.1.2 Preirradiation Method

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. The hydroperoxides on heating, decompose to give hydroxyl radicals which can initiate the homopolymerization of the added monomer.

4.2 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.

Kinetic feature of the direct radiation technique, if one assumes that the graft polymerization occurs by a radical chain process then the overall reaction scheme can be divided into three main steps: initiation, propagation, and termination. This may be represented as follows:
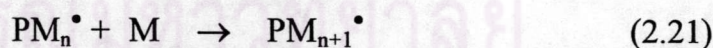
Initiation:

$$P \rightarrow P^\bullet \tag{2.17}$$
$$r = kI \tag{2.18}$$

Propagation of initial radical:

$$P^\bullet + M \rightarrow PM^\bullet \tag{2.19}$$
$$r_i = k_i[P^\bullet][M] \tag{2.20}$$

Propagation:

$$PM_n^\bullet + M \rightarrow PM_{n+1}^\bullet \tag{2.21}$$
$$r_p = k_p[PM_n^\bullet][M] \tag{2.22}$$

Termination by two growing radicals:
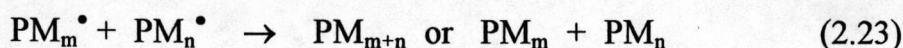
$$PM_m^\bullet + PM_n^\bullet \rightarrow PM_{m+n} \text{ or } PM_m + PM_n \tag{2.23}$$
$$r_t = 2k_t[PM_n^\bullet][PM_m^\bullet] \tag{2.24}$$

If one makes the normal assumption that the length of the polymer chains is long, then reaction 2.19 can be neglected with respect to reaction 2.21, and one obtains the following relation for the rate of graft polymerization:

$$r_p = k_p [PM_n^\bullet] [M] \tag{2.25}$$

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

$$k_i [P^\bullet] [M] = 2k_t [PM_n^\bullet]^2 \tag{2.26}$$

i.e.,

$$r_i = 2k_t [PM_n^\bullet]^2 \tag{2.27}$$

then

$$[PM_n^\bullet] = (r_i /2k_t)^{1/2} \tag{2.28}$$

On combining eqs. 2.25 and 2.28 one obtains for the rate of graft polymerization as the following:

$$r_p = k_p [M] (r_i /2k_t)^{1/2} \tag{2.29}$$

where

I = intensity of radiation

P = backbone polymer

$P^\bullet$ = 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 polylmer radicals

k_i = rate constant for initiation of graft reaction

k_p, k_t = propagation and termination rate constants, respectively

5. <u>Saponification of Starch-g-Polyacrylonitrile to Impart Water Absorbency</u>

To enhance the hydrophillic character of the starch-g-polyacrylonitrile, it will be hydrolyzed with an 8.5% potassium hydroxide causing the nitrile groups convert into a mixture of carboxamide and alkali metal carboxylate and ammonia. The intermediate colored products are formed. A deep red color is attributed to the formation of a partly hydrogenated naphtiridine type structure which is initiated by the nucleophilic attack of OH⁻ on the carbon atom of the nitrile group. Insolubility of the polymer is known to occur during this step and is explained by "propagation crosslinks" between interchain neighboring nitrile groups:

$$\text{(2.30)}$$
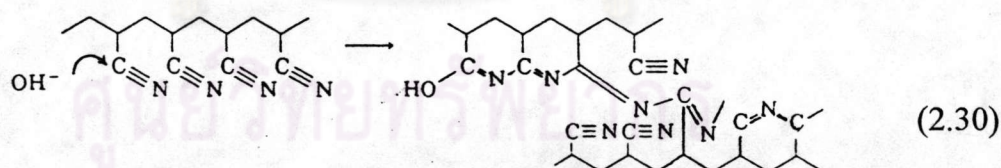
The end of the reaction is characterized by the light yellow color of the solution indicating the disappearance of the conjugated system $(C = N)_n$ and the formation of $CONH_2$ and CO_2^- groups. The product is recovered by precipitation in methanol and washed to neutrality. The hydrolyzed polyacrylonitrile grafted starch remains largely in the form of a highly swollen but insoluble gel after the saponification reaction (13).

Terminology and Definition

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

Percent Add-on

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

$$\% \text{ add-on} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of the grafted copolymer}} \qquad (2.31)$$

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

Grafting Efficiency

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

$$\% \text{ grafting efficiency} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of homopolymer} + \text{weight of polymer grafted}} \qquad (2.32)$$

Percent Conversion

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

$$\% \text{ conversion of monomer} = \frac{\text{weight of polymer formed} \times 100}{\text{weight of monomer charged}} \qquad (2.33)$$

Grafting Ratio

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

$$\% \text{ grafting ratio} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of starch}} \qquad (2.34)$$

Grafting Frequency

It is defined as an average number of anhydroglucose units (AGUs) per high molecular weight graft that can be calculated by the following expression:

$$\text{grafting frequency (AGU/chain)} = \frac{\text{glucose (mole)}}{\text{PAN (mole)}} \qquad (2.35)$$

where

$$\text{PAN (mole)} = \frac{\% \text{ add-on}}{\text{molecular weight}} \qquad (2.36)$$

$$\text{glucose (mole)} = \frac{100 - \% \text{ add-on}}{\text{glucose molecular weight (162)}} \qquad (2.37)$$

Literature Survey

Erickson, R.E., et al. (14) prepared water swellable aerated films and laminates, made from solutions of carboxylic polyelectrolytes. The films and laminates were cured and crosslinked with a polyfunctional or difunctional crosslinking agent that was reactive with carboxylate groups by heating and removing substantially all of the water and alcohol from the precursor composition. The solutions were mechanically aerated prior to the curing step. The absorbent articles had a rapid water absorbency rate and were useful as components in diapers, tampons, bandages, dressings and the like.

Elmquist, L.F. (15) prevented the formation of gumballs (surface-wetted, dry-centered lumps) of absorbents, which occur when particles absorb liquid on their surface and swell to prevent passage of liquid into the center of the particle for additional absorption. He proposed that the treatment of the hydrolyzed starch polyacrylonitrile graft copolymer with aluminium ions provided a product having a substantially enhanced degree of wicking (absorption rapidly). The source of aluminium may be salts of aluminium such as aluminium chloride, aluminium acetate or aluminium hydroxide. He found that the treatment of product with aluminium slightly reduces the overall absorbency of the product, directly proportional to the increased aluminium level. However, the wicking time of the product is substantially improved through obtaining a product which has been modified throughout with the aluminium ions.

Makita, M., et al. (16) produced an improved water-absorbent resin having a high water absorbency and a high water absorption rate and capable of forming a gel having a high gel strength and nonstickiness. The water-absorbent resin particles which contained water and a crosslinking agent and were in the semi-swollen state were agitated at an elevated temperature in the presence of

an inert inorganic powder to conduct the crosslinking of the resin. The obtained water-absorbent resin contained a monomer units having a carboxyl group in the form of free acid or a metal salt.

Grushevskaya, L.N., Aliev, R.E., and Kabanov, V.Ya. (17) developed a method of grafting acrylamide onto low density polyethylene by the different methods and under different conditions: by the direct liquid phase method from this monomer solution in water (in neutral and acid media) and acetone, and by the pre-irradiation method from aqueous solution as well as from its sublimated vapor. A decreased rate of homopolymerization was noted when metal ions were presented.

Garnett, J.L., Jankiewicz, S.V., and Sangster, D.F. (18) found that the presence of either acid or neutral salt enhanced the radiation grafting that was attributed to a "salting out" of monomer from the solution into the grafting region within the polymer substrate. Measurements using a swelling/leaching technique and tritium labelled styrene, had shown that the rate of transfer and the equilibrium distribution are dependent on the polarities of the monomer, substrate and solvent as well as the concentrations of ionic solute and monomer. Molecular weight studies and the effect of other additives confirmed the proposed mechanism. A number of other additives exhibited specific radiolytic chemical effects. These usually reduced the grafting yield.

Gargan, K., Kronfli, E., and Lovell, K.V. (19) carried out an investigation to identify compounds that are 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, whilst

cupric sulphate or potassium ferrocyanide were favoured for use with methacrylic acid.

Iyer, V., Varadarajan, P.V., Sawakhande, K.H., and Nachane, N.D. (20) prepared superabsorbent polymers by 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 viscosity values of the dispersion of the final product were lower than that of the products prepared through ceric ion initiation and the product had high water absorbencies. Use of the superabsorbent as a desiccant had better than silica gel.

Kiatkamjornwong, S., Dworjanyn, P.A., and Garnett, J.L. (21) reported grafting of styrene in methanol to cellulose in the presence of Ce(IV) for three systems namely thermal, photochemical and ionizing radiation induced processes. The role of additives such as acid and TMPTA in these systems is discussed for enhancing graft and minimizing homopolymer. In the presence of acid the concentration is higher in the backbone polymer, the higher concentrations of monomer are available for grafting at a particular backbone polymer site. The mechanism of the TMPTA effect was attributed to branching and crosslinking of the polystyrene chains which lead to accelerated grafting. The role of cationic salt like Ce(IV) in photografting and radiation grafting suppressed both homopolymer and grafting. However the addition of acid to these solutions containing cationic salt leads to enhancement in grafting due to the partitioning of monomer between grafting solution and backbone polymer.

Nakason, C. (22) prepared cassava starch-g-PAN by a grafting copolymerization reaction of acrylonitrile onto gelatinized starch backbone via gamma ray initiation method. Saponified starch-g-PAN was characterized in terms of the grafting efficiency and frequency, the percent add-on, the amount

of polyacrylonitrile formation, percent conversion of monomer, and the viscosity average molecular weight. This information provided a guideline to judge an optimum total dose (kGy), dose rate (gray/min), and ratio between starch/acrylonitrile. Water absorption was carried out in deionized distilled water, NaCl, $MgCl_2$, $K_3PO_4.3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ solutions. The results indicate that water absorption capacity in pure water was ranged 31 to 665 times their original dried weight. Water absorption capacity in saline solutions decreased with increasing the salt concentrations. Water retention in sand was also determined and showed that the increase in the water holding capacity of sand is proportional with the amount of absorbent used.

Hongfei, H., Xiaohong, L., and Jilan, W. (23) investigated the acid effect in mutual radiation grafting of acrylic acid (AA), 4-vinyl-pyridine(4-VP) and N-2-vinylpyrrolidone (N-NP) in methanol on silicone rubber and measured grafting yields as a function of dose. They found that acid in grafting system of 4-VP had enhancement effect, in N-VP system had 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.

Lokhande, H.T., Varadarajan, P.V., and Nachane, N.D. (24) 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 PAN add-on were 32.4, 48.5, and 66.2% 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 saponified samples were evaluated and the values were around 250 g/g.
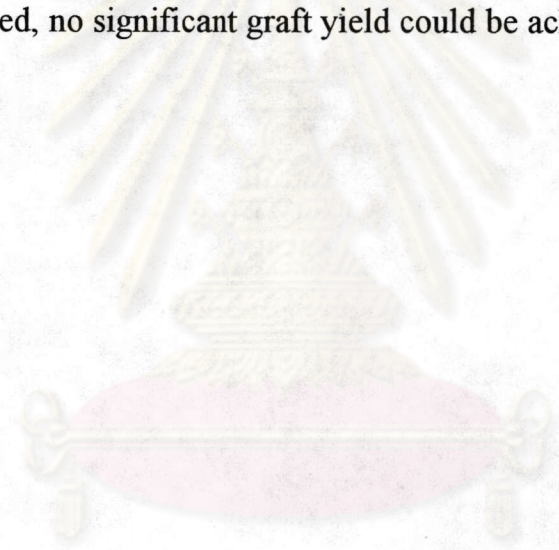
Le Ha, P., Canh, T.T., and Hai, L. (25) prepared chitosan by deacetylating irradiated chitin with 47% sodium hydroxide solution at the temperature of 80°C, 110°C, and 135°C. They found that irradiated chitin were deacetylated much more easily than the unirradiated control. The higher hydrolysis temperature, the higher degree of deacetylation. Acrylamide was grafted onto the prepared chitosan by gamma-ray irradiation. They found that at the dose of 0.75 Mrads was optimal for grafting copolymer. It was indicated the wettability of grafted chitosan powder increase with the grafting degree.

Dworjanyn, P.A., Garnett, J.L., Khan, M.A., Maojun, X., Meng-Ping, Q., and Nho, Y.C. (26) studied the role of additives including acids, inorganic salts, organic inclusion compounds like urea, multifunctional acrylates and methacrylates for increasing yields in radiation grafting reactions. They found that acids have efficiency in enhancing grafting sites by hydrogen abstraction reactions because of an increase in G(H). But multifunctional acrylates and methacrylates are superior to acids in accelerating grafting by chain branching.

Kiatkamjornwong, S., Chavajarernpun, J., and Nakason, C. (27) 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-ray. A thin aluminum foil was used to cover the inner wall of the reaction vessel that the homopolymer concentration was reduced to be less than 1.0% with a distilled water retention value of 665 g/g of the dry weight of the saponified grafted product.

Haddadi-asl, V., Burford, R.D., and Garnett, J.L. (28) 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. Metal-based homopolymerization inhibitors including Mohr's salt, Cu $(NO_3)_2$ and $FeSO_4$ were evaluated and found to prevent homopolymerization and significantly increased graft yield. Lithium nitrate was evaluted as a graft promoter. They found that replacing the oxygen with an inert gas such as nitrogen could significantly increase grafting yield. However, under all conditions studied, no significant graft yield could be achieved with AN.