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-ray 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 the 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 a 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 an indirect ionization of water,

$$H_2O \xrightarrow{} e^- + H_2O^+ \tag{2.1}$$
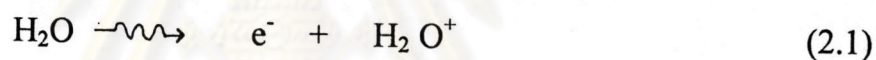
as well as a direct excitation,

$$H_2O \xrightarrow{} H_2O^* \tag{2.2}$$
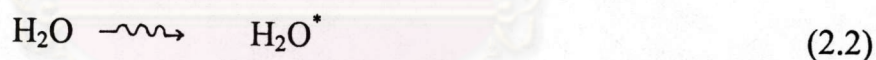
*The physicochemical stage consists of processes, which lead to the establishment of thermal equilibrium in the system. Its duration is usually taken to be of the order of 10^{-11} sec or less. Electron ejected in the ionization process becomes thermalized and hydrated:

$$e^- \longrightarrow e^-_{therm} \longrightarrow e^-_{eq} \tag{2.3}$$

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

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \tag{2.4}$$
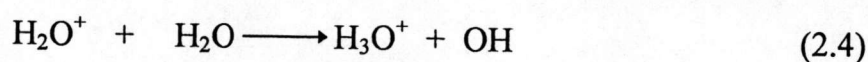
and the H_3O^+ becomes hydrated; hence, the point of formation and the initial spatial distribution of $H_3O^+_{aq}$ and OH are essentially the same and different from those for e^-_{aq}. If the volume in which they arose is considered to be spherical, then the radius for the initial distribution of 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,

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

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 of 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,

$$H_2O \rightsquigarrow H_3O^+_{aq}, {}^\bullet OH, e^-_{aq}, H^\bullet, H_2O_2, H_2O \qquad (2.6)$$
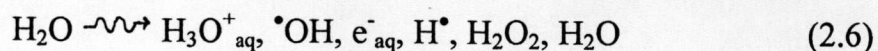
represents the state in irradiated water about 10^{-9} sec after the passage of high energy radiation, when the reactions in the spurs, blobs, and

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 yield $(G_{H_3O_{aq}^+}, G_H, G_{OH}, G_{e_{aq}^-}, G_{H_2},$ 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 absorbed 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 excited molecules are necessarily located close to the path of the ionizing particle. Thus, the initial distribution of primaty active species is very similar to the distribution of the water droplets around the track of charged particles. Figure 2.1 shows schematic diagram of the presumed distribution of primary events along the track of a fast electron(3).

Table 2.1 Reactions of Free Radicals in Irradiated Water.

| Reaction	Rate constant, $M^{-1} sec^{-1}$	pH
$e_{aq}^- + e_{aq}^- \xrightarrow{2H_2O} H_2 + 2OH^-$	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
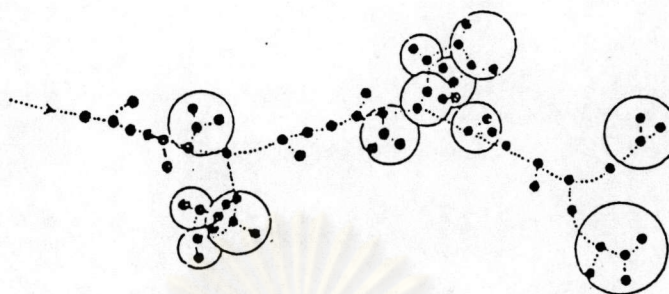
Figure 2.1 Schematic diagram of the presumed distribution of primary events along the track of a fast electron.

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 "cluster" 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, $\cdot$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

$$R + S \longrightarrow P \qquad\qquad (2.7)$$

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 reaction 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 reactivily is sufficiently high, the scavenger S also competes for the species R from the intraspur reactions. Then the increase in G(P) begins to occur on account of G_M (3).

2.3.3 Effect of pH

pH markedly influences the reactions occuring in irradiated water. This is true to an even greater extent in the case of irradiated aquesous 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 (3):

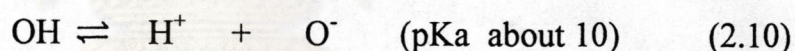(i) Conversion of a solvated electron to a hydrogen atom in acid solutions,

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

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

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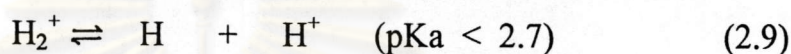
Other pH -dependent equilibria are:

(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,

$$H_2O \rightleftharpoons H^+ + O_2^- \quad (pKa \text{ probably } 2) \qquad (2.11)$$
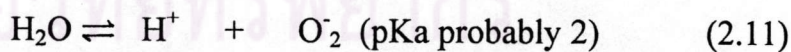
The O_2^- ion formed by this reaction can act as a reducing agent.

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

$$H + OH^- \longrightarrow e^-_{aq} \qquad (2.12)$$

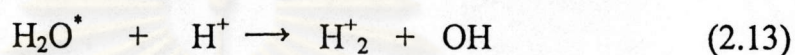(vi) At pH below about 3 and above about 11, the yields of reducing and hydroxyl radicals increase without any corresponding decrease in the yields of molecular hydrogen and hydrogen peroxide (Fig 2.2). The increase in radical yield in acid solutions may be due to an attack upon the acid by an intermediate that would otherwise revert to water.

$$H_2O^* \ + \ H^+ \longrightarrow \ H_2^+ \ + \ OH \qquad (2.13)$$

Similar reactions of the intermediate with hydroxyl ions are postulated to account for the increase in radical yield at high pH (4).
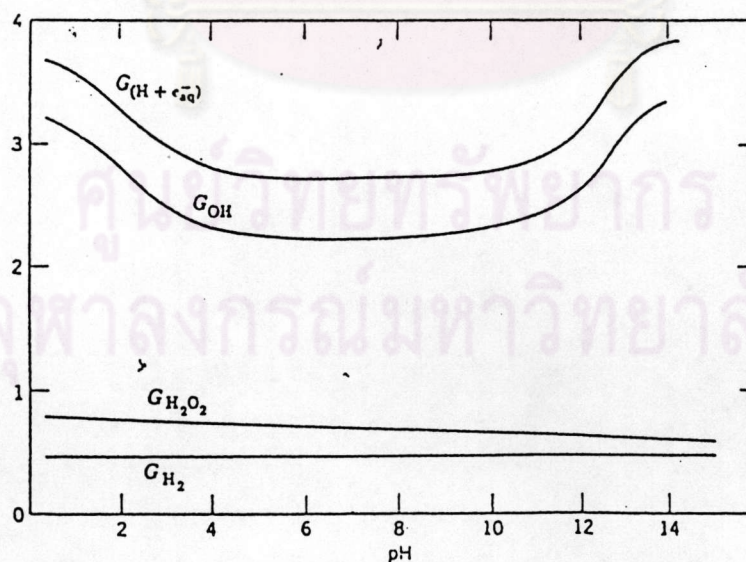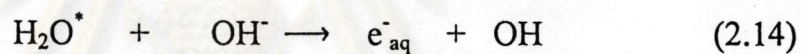
$$H_2O^* \ + \ OH^- \longrightarrow \ e^-_{aq} \ + \ OH \qquad (2.14)$$

Figure 2.2 Variation with pH of primary yields in γ-irradiated water

2.3.4 <u>Effect of linear Energy Transfer</u>

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 by 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 (4).

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 (4).

2.3.5 <u>Effect of Dose Rate</u>

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.

2.3.6 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. Chain Copolymerization

Chain copolymerizations can be carried out with mixtures of two monomers to form polymeric products with two different structures in the polymer chain. This is not the case for chain polymerizations where only one monomer needs to be used to produce a polymer. However, chain polymerizations can be carried out with mixtures of two monomers to form polymeric products with two different structures in the polymer chain. This type of chain polymerization process in which two monomers are simultaneously polymerized is termed a *copolymerization* and the product is a *copolymer*. It is important to stress that the copolymer is not an alloy of two homopolymers but contains units of both monomers incorporated into each copolymer molecule. The process can be depicted as

$$M_1 + M_2 \longrightarrow M_1 \, M_2 \, M_2 \, M_1 \, M_2 \, M_2 \, M_2 \, M_1 \, M_1 \, M_2 \, M_2 \, M_1 \, M_1 \, M \quad (2.15)$$
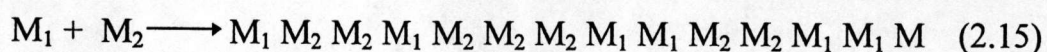
The two monomers enter into the copolymer in overall amounts determined by their relative concentrations and reactivities. The simultaneous chain polymerization of different monomers can also be carried out with mixtures

of three or more monomers. Such polymerizations are generally referred to as *multicomponent copolymerization*; the term *terpolymerization* is specifically used for systems of three monomers.

3.1 Importance of Chain Copolymerization

Chain copolymerization is important from several considerations. Much of our knowledge of the reactivities of monomers, free radicals, carbocations, and carbanions in chain polymerization comes from copolymerization studies. The behavior of monomers in copolymerization reactions is especially useful for studying the effect of chemical structure on reactivity. Copolymerization is also very important from the technological viewpoint. It greatly increases the ability of the polymer scientist to tailor-make a polymer product with specifically desired properties. Polymerization of a single monomer is relatively limited as to the number of different products that are possible. The term *homopolymerization* is often used to distinguish the polymerization of a single monomer from the copolymerization process.

3.2 Types of Copolymerization

The copolymer described by Eq. 2.15, referred to as a *statistical copolymer*, has a distribution of the monomer units along the copolymer chain that follows some statistical law, for example, Bernoullian (zero-order Markov) or first - or second - order Markov. Copolymers formed via Bernoullian processes have the two monomer units distributed randomly and are referred to as *random copolymers*. There are three other types of copolymer structures-*alternating*, *block*, and *graft*. The alternating copolymer contains the two monomer units in equimolar amounts in a regular alternating distribution,

$$M_1 \, M_2 \, M_1 \, M_2 \, M_1 \, M_2 \, M_1 \, M_2 \, M_1 \, M_2 \, M_1 \, M_2 \, M_1 \, M_2$$

I

Block and graft copolymers differ from the ether copolymers in that there are long sequences of each monomer in the copolymer chain. A block copolymer is a linear copolymer with one or more long uninterrupted sequences of each polymeric species,

$$M_1 \ M_1 \ M_1 \ M_1 \ M_1 \ M_1 \ M_2 \ M_2 \ M_2 \ M_2 \ M_2 \ M_2$$

II

while a graft copolymer is a branced copolymer with a backbone of one monomer to which are attached one or more side chains of another monomer,

$$\sim\!\!M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1\!\!\sim$$

III

3.3 Copolymer Composition

The composition of a copolymer is usually different from the composition of the comonomer feed from which it is produced. In other words, different monomers have differing tendencies to undergo copolymerization. It was observed early that the relative copolymerization tendencies of monomers usually borne little to resemblance to their relative rates of homopolymerization. Some monomers are more reactive in

copolymerization than indicated by their rates of homopolymerization; other monomers are less reactive.

The composition of a copolymer thus cannot be determined simply from a knowledge of the homopolymerization rates of the two monomers. The determinants of copolymerization composition have been elucidated by several workers by assuming the chemical reactivity of the propagating chain (which may be a free radical, carbocation, or carbanion) in a copolymerization is dependent only on the identity of the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit. This is referred to as the *first-order Markov* or *terminal model* of copolymerization. Consider the case for the copolymerization of the two monomers M_1 and M_2. Although radical copolymerization has been more extensively studied and is more important than ionic copolymerization, we will consider the general case without specification as to whether the mode of initiation is by a radical, anionic, or cationic species. Copolymerization of the two monomers leads to two types of propagating species; one with M_1 at the propagating end and the other with M_2. These can be represented by M_1^* and M_2^* where the asterisk represents either a radical, a carbocation ion, or a carbanion as the propagating species depending on the particular case. If it is assumed that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain (referred to as the *end* or *ultimate* unit), four propagation reactions are then possible. Monomers M_1 and M_2 can each add either to a propagating chain ending in M_1 or to one ending in M_2, that is,

$$M_1^* + M_1 \xrightarrow{\ k_{11}\ } M_1^* \qquad (2.16)$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^* \qquad (2.17)$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^* \qquad (2.18)$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^* \qquad (2.19)$$
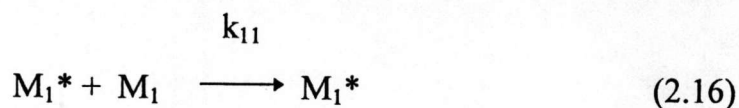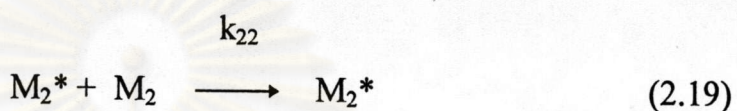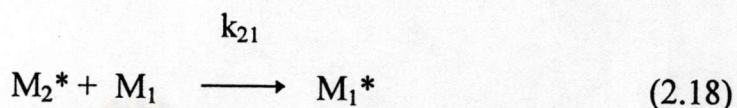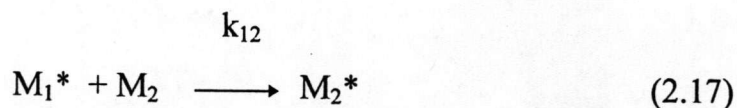
where k_{11} is the rate constant for a propagating chain ending in M_1 adding to monomer M_1, k_{12} that for a propagating chain ending in M_1 adding to monomer M_2, and so on. The propagating of a reactive center by addition of the same monomer (i.e., Reactions 2.16 and 2.19) is often referred to as *homopropagation* or *self-propagation*; propagation of a reactive center by addition of the other monomer (Reactions 2.17 and 2.18) is referred to as *cross-propagation* or a *crossover* reaction. All propagation reactions are assumed to be irreversible.

Monomer M_1 disappears by Reactions 2.16 and 2.18 while monomer M_2 disappears by reactions 2.17 and 2.19. The rates of disappearance of the two monomers, which are synonymous with their rates of entry into the copolymer, are given by

$$\frac{-d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \qquad (2.20)$$

$$\frac{-d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \qquad (2.21)$$

Dividing Eq. 2.20 by Eq. 2.21 yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{k_{11}\,[M_1{}^*]\,[M_1] + k_{21}\,[M_2{}^*]\,[M_1]}{k_{12}\,[M_1{}^*]\,[M_2] + k_{22}\,[M_2{}^*]\,[M_2]} \qquad (2.22)$$

In order to remove the concentration terms in $M_1{}^*$ and $M_2{}^*$ from Eq. 2.22, a steady-state concentration is assumed for each of the reactive species $M_1{}^*$ and $M_2{}^*$ separately. For the concentrations of $M_1{}^*$ and $M_2{}^*$ to remain constant, their rates of interconversion must be equal. In other words, the rates of reactions 2.17 and 2.18 are equal,

$$k_{21}\,[M_2{}^*]\,[M_1] = k_{12}\,[M_1{}^*]\,[M_2] \qquad (2.23)$$

Equation 2.23 can be rearranged and combined with Eq. 2.22 to yield

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{\dfrac{k_{11}k_{21}\,[M_2{}^*]\,[M_1]^2}{k_{12}\,[M_2]} + k_{21}\,[M_2{}^*]\,[M_1]}{k_{22}\,[M_2{}^*]\,[M_2] + k_{21}\,[M_2{}^*]\,[M_1]} \qquad (2.24)$$

Dividing the top and bottom of the right side of Eq. 2.24 by $k_{21}\,[M_2{}^*]\,[M_1]$ and combining the result with the parameters r_1 and r_2, which are defined by

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \qquad (2.25)$$

one finally obtains

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]\,(r_1\,[M_1] + [M_2])}{[M_2]\,([M_1] + r_2\,[M_2])} \qquad (2.26)$$

Equation 2.15 is knows as the *copolymerization equation* or the *copolymer composition equation*. The copolymer composition, $d[M_1]/d[M_2]$, is the molar ratio of the two monomer units in the copolymer. $d[M_1]/d[M_2]$ is expressed by Eq. 2.26 as being related to the concentrations of the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameter r_1 and r_2. The parameters r_1 and r_2 are termed the *monomer reactivity ratios*. Each r as defined above in Eq. 2.25 is the ratio of the rate constant for a reactive propagating species adding its own type of monomer to the rate constant for its addition of the other monomer. The tendency of two monomers to copolymerize is noted by r values between zero and unity. An r_1 value greater than unity means that M_1^* preferentially adds M_1 instead of M_2, while an r_1 value less than unity means that M_1^* preferentially adds M_2. An r_1 value of zero would mean that M_1 is incapable of undergoing homopolymerization.

The copolymerization equation can also be expressed in terms of mole fractions instead of concentratons. If f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed, and F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer, then

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \qquad (2.27)$$

and

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \qquad (2.28)$$

Combining Eqs. 2.27 and 2.28 with Eq. (2.26) yields

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (2.29)$$

Equation 2.29 gives the copolymer composition as the mole fraction of monomer M_1 in the copolymer and is often more convenient to use than the previous form (Eq. 2.26) of the copolymerization equation.

4. Polyacrylamide (PAM).

Polyacrylamide is distinguished by its highly hydrophilic character, which is grater than that of most other nonionic water-soluble polymers. This shows itself, e.g., by the ready absorption and tenacious retention of water by the bulk polymer, by the absence of phase separation in aqueous solution over the normal temperature range(which is in accordance with the estimated value of the ideal temperature of this system, $\theta = -38^{\circ}C$ and by its relatively high resistance to precipitation from aqueous solution by electrolytes. A further reflection of this character is that its solubility in nonaqueous liquids is limited to hydrophilic ones such as ethylene glycol, glycerol, and formamide, while it is insoluble in most other common organic liquid such as methanol, ethanol, acetone, diethyl ether, and aliphatic and aromatic hydrocarbons.

Paradoxically, however, despite this highly hydrophilic character, the main technical application of PAM is for the flocculation of aqueous suspensions and allied purposes, where it is therefore required to have a relatively high affinity to the surface of the suspended solid if the necessarily strong adsorption of the polymer is to take place; in practice, however, this adsorption is often enhanced by using modified (anionic or cationic) forms of PAM.
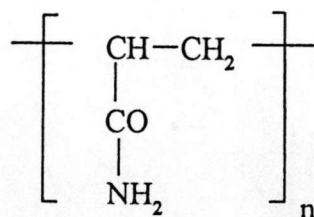
$$\left[\begin{array}{c} CH-CH_2 \\ | \\ CO \\ | \\ NH_2 \end{array} \right]_n$$

Figure 2.3 The primary chain structure of polyacryamide(PAM).

4.1 Production and Purification

Polyacrylamide may by produced from its monomer by free radical polymerization using a wide variety of initiation methods. The purely thermal polymerization at 140°C has been studied, as well as the polymerization in aqueous solution initiated by free radical sources such as hydrogen peroxide, persulfate and an azo compound (where the reaction was followed to high conversion). The azo-initiated polymerization has been studied in benzene and diglyme (diethylene glycol dimethyl ether) in the latter case at temperatures of 60, 100 and 140°C, similarly initiated polymerization in ethanol leads to the precipitation of the polymer during the course of the reaction.
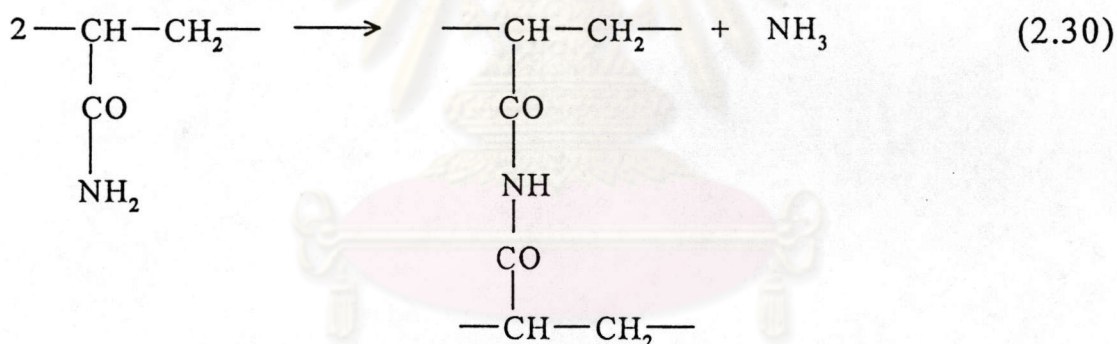
For the production of PAM by one of these thermal methods, the initiator of choice would seem to be hydrogen peroxide, since it allows the reaction to be carried out at convenient temperatures (40 to 67°C) to give a high molecular weight polymer free of contaminants; if needed the molecular weight can be controlled (i.e, reduced) by including methanol in the reaction medium as a chain transfer agent.

Redox systems have also been used as free radical initiators in aqueous solution, such as permanganate + tartaric acid, chlorate + sulfite, and persulfate + thiosulfate.

The electro-initiated reaction in aqueous solution with perfluoroacetic acid and potassium perfluoroacetate leads to only relatively short-chain polymers.

Irradiation methods for polymerization in aqueous solution that have been studied include those using uv or visible light through the photodecomposition of hydrogen peroxide, or via photosensitizers such as ferric ions or riboflavin, using ultrasonic irradiation, or using x- or γ-rays.

Minsk and co-workers(7) have investigated to give suggestions that the apparent low nitrogen content of PAM produced by the free radical mechanism arises from an imidization crosslinking during the course of the reaction.

$$
2\;-\overset{|}{\underset{\underset{NH_2}{|}}{\underset{CO}{|}}{CH}}-CH_2- \quad\longrightarrow\quad -\overset{|}{\underset{\underset{-CH-CH_2-}{|}}{\underset{CO}{\underset{NH}{|}}}{CH}}-CH_2-\; +\; NH_3 \qquad (2.30)
$$

They showed, however, that this imidization is not likely to occur to any appreciable extent during the polymerization, and that the apparent low nitrogen content is more likely due to the presence of retained water or other solvent in the polymer finally isolated.

In certain cases, the polymerization of acrylamide does not lead to polyacrylamide; with Grignard reagents(in the presence of an inhibitor of free radical polymerization) or with alkali metal alkoxides, there is an "anionic transition polymerization" leading to poly (β- alanine).

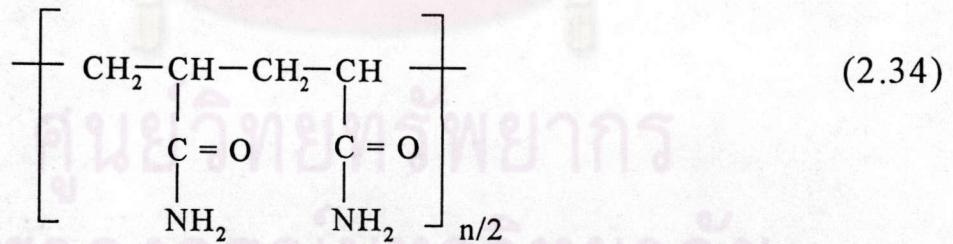$$CH_2 = CH-CO-NH_2 \longrightarrow \left[CH_2-CH_2-CO-NH \right] \qquad (2.31)$$
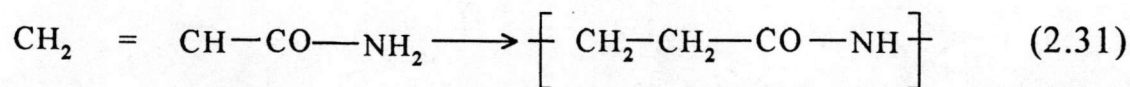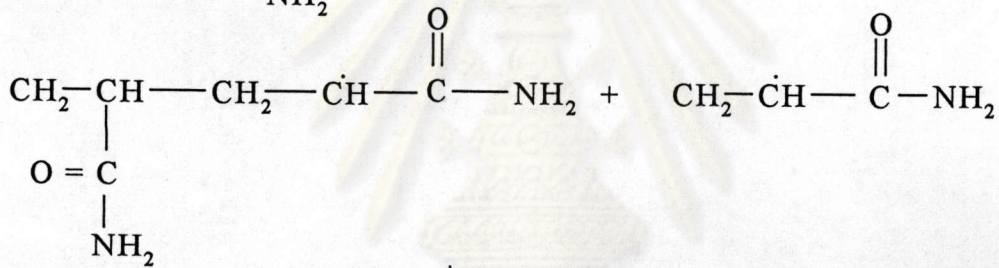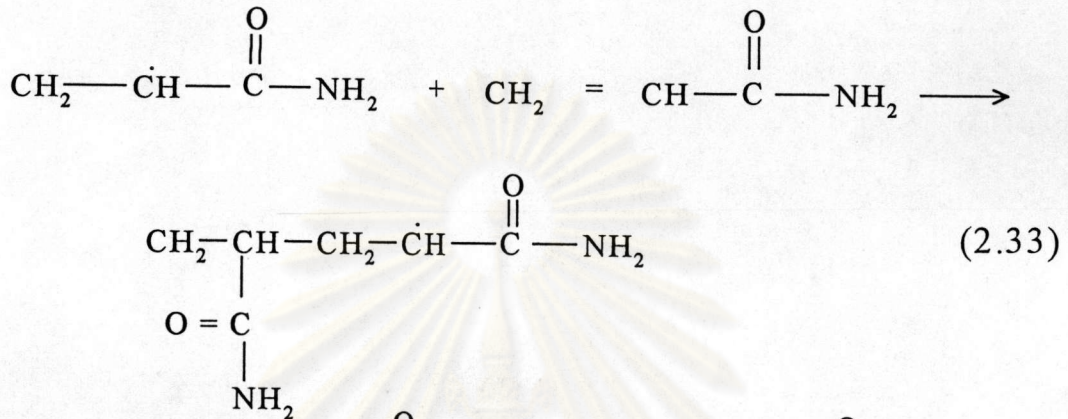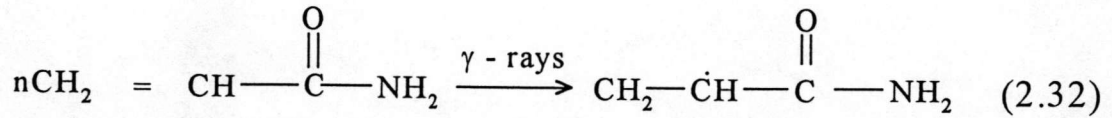
Polyacrylamide is also available commercially, e.g. in the form of Cyanamer P-250 produced by the American Cyanamid Co. (other grades of Cyanamer such as A-370 or p-35 are modified forms of PAM) or of Separan and Purifloc produced by the Dow Chemical Co. (where again only certain grades are truely unmodified PAM). Where such commercial products (or indeed, and other sample is thought to have an appreciable carboxylic acid content due to hydrolysis of some of the amide groups, these may by reconverted back to amide groups by treatment with thionyl chloride and ammonia.

The polymer may be purified by precipitating it from aqueous solution with methanol, ethanol or acetone.

Various grades of cross-linked polyacrylamide in a form of bead, with different degrees of cross-linking and different particle sizes, are available commercially for use in gel permeation chromatography. The cross-linked polymer is also used in gel electrophoresis, where it is generally prepared in situ in water-swollen form using methylene-bis-acrylamide as the cross-linking agent.

The direct free-radical polymerization to produce polyacrylamide (PAM) is by gamma irradiation. This may by represented as follows:

$$nCH_2 = CH-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \xrightarrow{\gamma\text{-rays}} CH_2-\overset{\cdot}{C}H-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \qquad (2.32)$$

$$CH_2-\overset{\cdot}{C}H-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \ + \ CH_2 = CH-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \longrightarrow$$

$$CH_2-CH-CH_2-\overset{\cdot}{C}H-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \qquad (2.33)$$
$$\underset{\underset{\textstyle NH_2}{|}}{O=C}$$

$$CH_2-CH-CH_2-\overset{\cdot}{C}H-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \ + \ CH_2-\overset{\cdot}{C}H-\overset{\overset{\textstyle O}{\|}}{C}-NH_2$$
$$\underset{\underset{\textstyle NH_2}{|}}{O=C}$$

$$\left[\begin{array}{c} CH_2-CH-CH_2-CH \\ \underset{\underset{\textstyle NH_2}{|}}{C=O} \quad \underset{\underset{\textstyle NH_2}{|}}{C=O} \end{array}\right]_{n/2} \qquad (2.34)$$

Polyacrylamide (PAM)

4.2 Fractionation and characterization

PAM may be fractionated by conventional stepwise precipitation methods with the solvent/nonsolvent system water/acetone. The molecular weight distributions of whole polymer samples have been studied by GPC.

4.3 Bulk Polymer

The glass transition temperature, T_g, of PAM has been given as 165°C (without further details) and 188°C (by differential thermal analysis). Whichever value is correct, this shows that up to these relatively high temperatures the polymer is in the glassy state and thus relatively resistant to the ingress or egress of small-molecule penetrants (such as retained solvent), and that it is necessary to use higher temperatures to put the polymer in the rubbery state where absorbed solvent molecules are sufficiently mobile to be desorbed.

The IR absorption spectrum of PAM has been given for the range 200-4000 cm^{-1} by Chapiro and Perec, for 625-4000 cm^{-1} by Nuquist, and for 600-4000 cm^{-1} by Kulicke and Klein, accompanied in the last case by an interpretation; the section over the more limited range 3,000-37,00 cm^{-1} has been given by Griot and Kitchener in connection with the adsorption of the polymer from aqueous solution with the adsorption of the polymer from aqueous solution onto silica. The IR spectrum may be used to distinguish true PAM (which has a primary amide band at 1655 cm^{-1}) from the alternative polymerization product poly(β-alanine) (which has instead a secondary amide band at 1555 cm^{-1}).

5. Partially Hydrolyzed Polyacrylamide (HPAM)

Polyacrylamide, in its partially hydrolyzed form (HPAM), has been used in oil recovery processes far more frequently than xanthan biopolymer. Although HPAM had been used in other industries, it was the pioneering studies of Pye, Sandiford, Mungan et al. and Gogarty that established this polymer as a potential mobility control agent in improving waterflooding operations. HPAM is a synthetic straight-chain polymer of

acrylamide monomers, some of which have been hydrolyzed, as shown in Figure 2.3

Figure 2.4 The primary chain structure of polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM).

The fraction of backbone acrylamide units which have been hydrolyzed may be established by a potentiometric titration. The degree of hydrolysis may be important in certain physical properties such as polymer adsorption shear stability and thermal stability. However, even though commercial polymers are supplied with a stated degree of hydrolysis, it is well known that at elevated temperatures the hydrolysis of the amide wil continue.

The HPAM molecule is a flexible chain structure sometimes known as a random coil in polymer chemistry. There is essentially no permanent secondary structure in polyacrylamide which affords it some degree of rigidity in the way that the helical structure acts in xanthan.

HPAM is a polyelectrolyte, and as such it will interact quite strongly with ions in solution. However, since the polyacrylamide chain is flexible, it may respond much more to the ionic strength of the aqueous solvent, and its solution properties are much more sensitive to salt / hardness than are those of xanthan. This is illustrated schematically in Figure 2.4, in which the effect of ionic strength on the hydrodynamic size of the molecule is shown.
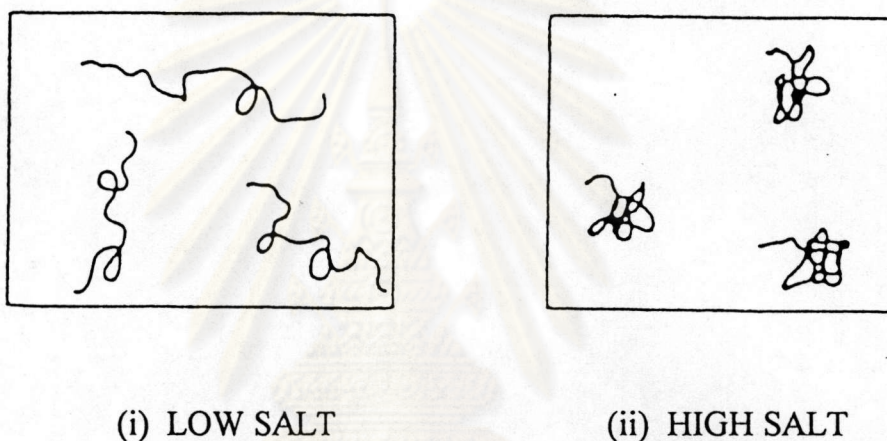

(i) LOW SALT   (ii) HIGH SALT

Figure 2.5 Schematic presentation of the effect of solution ionic strength on the conformation of flexible coil polyelectrolytes such as HPAM.

Holzwarth et al. used a combination of band sedimentation and low-angle laser light scattering (LALLS) in order to examine the molecular weight distribution of HPAMs. One result of their work is depicted in Figure 2.6, in which the MWD is shown to have a very long high molecular weight tail up to 40 x 10^6, which is well beyond the limit of currently available SEC Columns. In this work, polydispersity indices in the range of 1.6 - 2.5 are also reported for the HPAMs which were studied by Holzwarth et al. Langhorst et al. used a combination of hydrodynamic chromatography (HDC) and LALLS detection to measure the molecular weight distributions of PAMs and HPAMs. Using this method, they studied some very high molecular

weight HPAMs which are used for polymer flooding applications $(M_w = 9 \times 10^6)$ and show tails of up to $50 - 60 \times 10^6$ in the MWD.
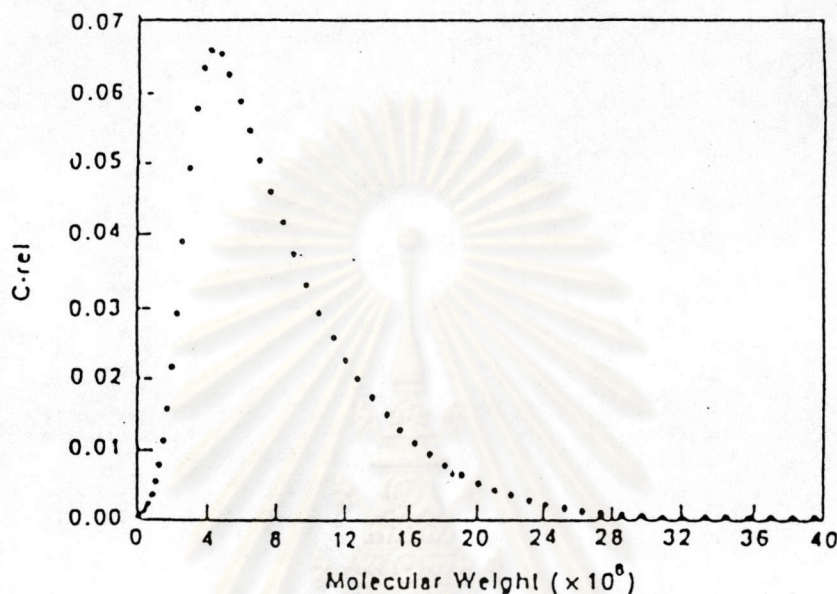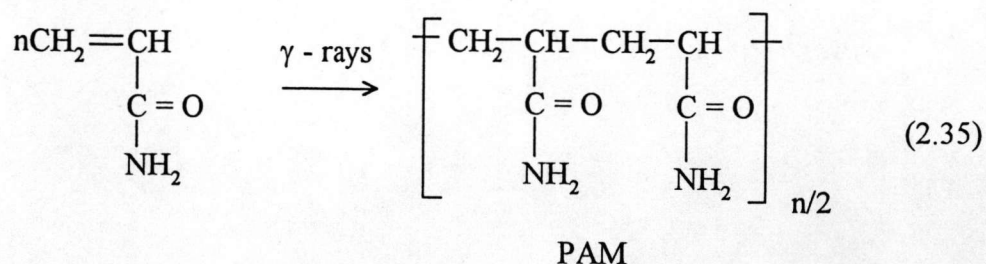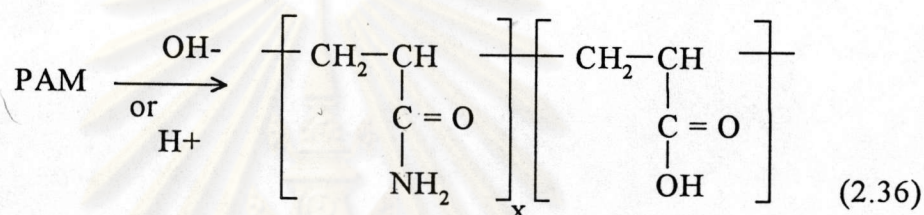

Figure 2.6 Normalised molecular weight distribution (MWD) of an HPAM sample using band sedimentation and LALLS (from Holzwarth et al., 1988).

The quoted molecular weights of partially hydrolyzed polyacrylamide samples are usually in the range $\overline{M}_w = 2 - 20 \times 10^6$, although occasionally higher values are given. This is rather higher than the M_w values stated for commercially available xanthans. The polydispersity index of these HPAMs is usually higher than that of xanthan, which might be expected since the specificity of microbes in a fermentation process is much higher than that in an industrial synthetic polymerization reaction.
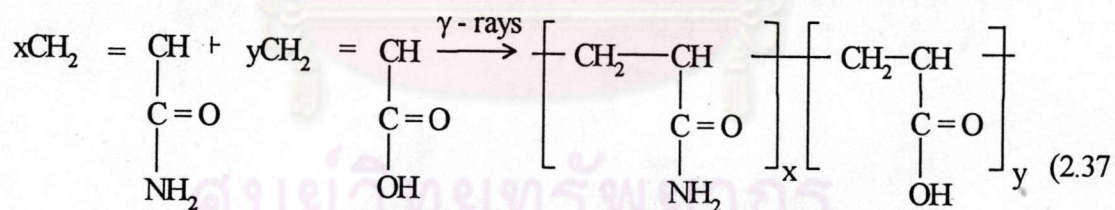
There are three main chemical approaches which may, in theory, be used to synthesise HPAMs. Firstly, there is the direct free-radical polymerization to produce polyacrylamide (PAM):
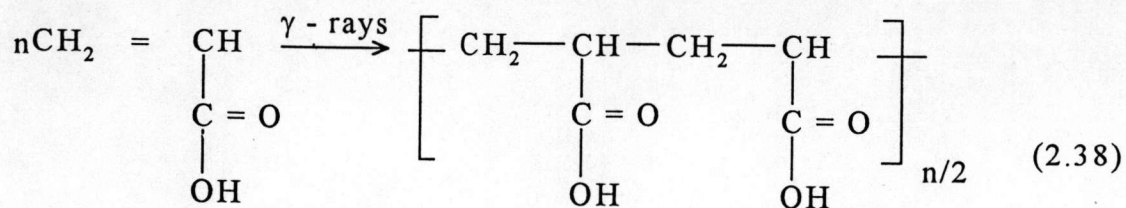
$$nCH_2{=}CH \xrightarrow{\gamma \text{ - rays}} \left[\begin{array}{cc} CH_2-CH-CH_2-CH \\ \quad | \qquad\qquad | \\ \quad C=O \qquad\quad C=O \\ \quad | \qquad\qquad | \\ \quad NH_2 \qquad\quad NH_2 \end{array} \right]_{n/2} \quad (2.35)$$

<div align="center">PAM</div>

followed by the acid or base hydrolysis of some of the amide groups along the PAM backbone to produce HPAM:

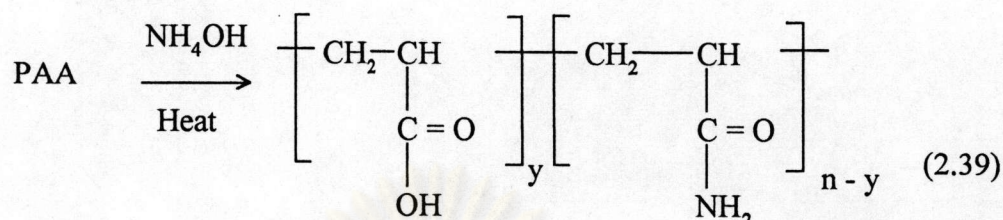$$PAM \xrightarrow[\substack{\text{or} \\ H+}]{OH\text{-}} \left[\begin{array}{c} CH_2-CH \\ | \\ C=O \\ | \\ NH_2 \end{array} \right]_x \left[\begin{array}{c} CH_2-CH \\ | \\ C=O \\ | \\ OH \end{array} \right] \quad (2.36)$$

A second approach is to co-polymerize chosen proportions of acrylamide and acrylic acid directly :

$$xCH_2 = CH + yCH_2 = CH \xrightarrow{\gamma \text{ - rays}} \left[\begin{array}{c} CH_2-CH \\ | \\ C=O \\ | \\ NH_2 \end{array} \right]_x \left[\begin{array}{c} CH_2-CH \\ | \\ C=O \\ | \\ OH \end{array} \right]_y$$

$$\begin{array}{ccc} \quad | \qquad\qquad | \\ \quad C=O \qquad\quad C=O \\ \quad | \qquad\qquad | \\ \quad NH_2 \qquad\quad OH \end{array} \quad (2.37$$

The third chemical route to HPAM would be to polymerize acrylic acid to give polyacrylic acid (PAA)

$$nCH_2 = CH \xrightarrow{\gamma \text{ - rays}} \left[\begin{array}{cc} CH_2-CH-CH_2-CH \\ \quad | \qquad\qquad | \\ \quad C=O \qquad\quad C=O \\ \quad | \qquad\qquad | \\ \quad OH \qquad\quad OH \end{array} \right]_{n/2} \quad (2.38)$$

followed by the aminolysis of the PAA as follows:

$$PAA \xrightarrow[\text{Heat}]{NH_4OH} \left[\begin{array}{c} CH_2-CH \\ | \\ C=O \\ | \\ OH \end{array} \right]_y \left[\begin{array}{c} CH_2-CH \\ | \\ C=O \\ | \\ NH_2 \end{array} \right]_{n-y} \quad (2.39)$$

of the three reaction paths above, commercial processes usually use the first two. When any of these reactions are used industrially, they are applied as a one-step process, even in the first and third methods, which are shown as being two-step. It is sufficient to note here that the conditions in the industrial processes used to obtain HPAM can be adjusted to produce polymers with a given percentage hydrolysis. Since there are reactive side groups along the polymer chain (−COOH or −CONH$_2$), then side branching and cross-linking of polymers can occur under certain reaction conditions. This too can be controlled by suitable choice of reaction conditions.

In addition to the chemical procedure used to produce HPAMs, there are different possible media or phases in which the polymerization process can be carried out. All of the above three chemical reactions can be carried out as :

- Aqueous solution polymerization.

- Mixed solvent solution polymerization.

- Dispersed-phase polymerization.

The aqueous solution polymerization is the commonest and cheapest method used in the production of HPAM. Initiators such as peroxide, persulphate, azo-compounds or uv radiation are commonly used, and the pH of the reaction medium governs the final degree of hydrolysis of the product. This process may produce a viscous liquid product containing

up to about 20% by weight of polymeric solids. Mixed solvent systems, using water and alcohol, are usually used to obtain lower molucular weight materials with a rather well-defined and narrower MWD. This is possible because the solvent mixture is chosen to cause the growing polymer chain to precipitate. When it reaches a certain size. Dispersed-phase, or latex, polymerization is when the aqueous reactants are dispersed in an inert carrier fluid (such as paraffin, xylene or tetrachloroethylene) before the reaction is initiated. In this more expensive process, the HPAM product is obtained as beads, typically containing 50% polymer and 50% water. This type of reaction tends to lead to less branching and cross-linking of polymer chains. Thus, more uniform straight-chain, gel-free polymers are produced.

6. New Polymers for IOR Application

Polyacrylamide and xanthans are not suitable for use in polymer floods under all reservoir conditions. The main thrust of current research into improving this situation is in two main areas; firstly, in cutting the cost of production and increasing product quality of the polymer, this is mainly a manufacturing or fermentation process modification; secondly, to search for polymers which have improved properties compared with those of commercially available biopolymers and synthetics. The more important polymer properties in which there is scope for improvement are the thermal and shear stability of the polymer, its salt/harness tolerance, control of its levels of adsorption and solubilisation and injectivity properties. Currently available polymers-both synthetics and biopolymers- can certainly be improved in some or all of the above ways. For example, both xanthans and polyacrylamides will degrade or precipitate in very high-temperature, high-salinity reservoirs (Akstinat, 1980; Davision and Mentzer, 1980). In addition, most synthetic polymers are sensitive to mechanical degradation when they pass through a porous medium at high flow rate. Polyacrylamides are also quite sensitive to brine hardness, and they may indeed precipitate in

very hard brines even at moderate temperatures (Zaitoun and Poitie, Moradi-Araghi and Doe). There is also some scope for improvement in lowering the adsorption levels observed in porous media for both xanthans and polyacrylamides, as high retention levels can seriously affect the economics of a polymer flood. It is also essential to have polyacrylamides and xanthans, which have good solubilisation and injectivity properties, although recent products are very much superior to those, which were available some years ago, as discussed above.

One thorough and systematic approach to the formulation of a new synthetic polymer for oil recovery processes is that of Stahl et al., who studied a wide range of synthetic and biopolymers at high temperatures and salinity (121°C in synthetic sea water at 33, 756 ppm of TDS-total dissolved solids). They found that PAM, a number of PAM co-polymer, and other synthetic systems, such as vinylether co-polymer, poly(vinyl pyrrolidone) and poly (ethylene oxide), all either precipitated or showed serious viscosity loss at 120°C. Likewise, xanthan and other biopolymers showed either precipitation or viscosity loss or both, although they noted that scleroglucan, the fungal biopolymer, showed a slower viscosity loss under these conditions.

However, they did find that co-polymers of n-vinyl-2-pyrrolidone (NVP) and acrylamide do not precipitate at this temperature. They also observed that NVP limited the level of acrylamide hydrolysis, which they claimed, gave this co-polymer its increased stability in the high salinity, high hardness and brine. They noted that neither the acrylamide nor the NVP homopolymer would be useful on its own. The notation structure of the NVP / PAM co-polymer is shown in Figure 2.7. Note that the distribution of NVP and PAM along the backbone in this figure will probably be random (unless a special technique has been empolyed in the polymer synthesis) and that the degree of hydrolysis (z) should be limited if the interpretation of Stahl et al. (1988) is correct.
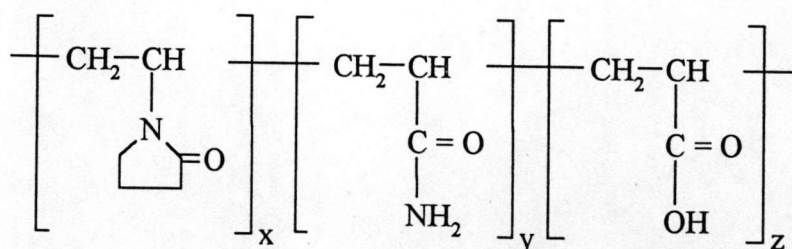
Figure 2.7 The notational primary structure of the co-polymer, poly (vinylpyrrolidone-co-acrylamide) (NVP / PAM).

Terminology and Definition

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

1 Percentage Conversion

Conversion of a monomer is defined as the extent of the monomer to which is charged to become a respective polymer (polymers). It can be evaluated by the following expression:

$$\% \text{ conversion of monomer} = \frac{\text{weight of polymer formed}}{\text{weight of monomer charged}} \times 100 \quad (2.40)$$

2 Determination of Nitrogen Content by Semi-Micro Kjeldahl Method

The method is based on the fact that digestion with sulfuric acid and various catalysts destroys the organic material and the nitrogen is converted to ammonium sulfate. When the reaction mixture is made alkaline, ammonia is liberated and removed by steam distillation, collected and titrated. Nitrogen content can be calculated by the following expression:

$$\text{percentage of nitrogen} = \frac{[(V_1 - V_2)N \times 0.0140 \times 100]}{W} \qquad (2.41)$$

where $\quad V_1$ = volume (cm^3) of H$_2$SO$_4$ required for titration of receiving flask.

$\qquad\qquad V_2$ = volume (cm^3) of H$_2$SO$_4$ required for titration of the blank.

$\qquad\qquad N$ = normality of H$_2$SO$_4$

and $\qquad\quad W$ = grams of sample used

3 Degree of Hydrolysis

Degree of hydrolysis was calculated by using the following formula:

$$\% \text{ degree of hydrolysis} = \frac{N1 - N2}{N1} \times 100 \qquad (2.42)$$

where $\quad N_1$ = nitrogen content before hydrolysis.

$\qquad\qquad N_2$ = nitrogen content after hydrolysis.

Literature Survey

Argabright, et al.(1) reported on an ultracentrifugation technique or determining the average molecular weight, $\overline{M}_w$, and distribution of HPAMs which were prepared in their laboratory. They prepared a number of samples with a range of molecular weights from 2.5 to 7 x 10^6, but the surprising feature of these was their very narrow molecular weight distribution, which they characterized by the quantity σ/M, where σ is the standard deviation of the molecular weight distribution, the widest distribution; that is, the lowest

molecular weight, has a σ/M value of 0.65, whereas the largest molecular weight species has a σ/M value of only 0.04.

Guerrero, S.J., Boldarino, P., and Zurimendi, J.A.(5) Characterized polyacrylamides by using techniques such as IR spectroscopy, ^{13}C-NMR, elementary analysis, TGA and x-ray diffraction. The first three techniques can also be used quantitatively to measure the degree of hydrolysis of the polymers, without the need to know accurately the weight of the sample. The presence of inorganic salts, such as Na_2SO_4, $Na_4(CO_3)SO_4$ and Na_2CO_3 is readily detected via IR or wide angle x-ray diffraction. No evidence of crystallinity is found in the samples studied.

Khune, G.D., Donaruma, L.G., Hatch, M.J., Kilmer, N.H., Shepitka, J.S., and Martin, F.D.(6) prepared copolymers of sodium acrylate and N-methyl-, N-iso-propyl-, N-n-butyl-, and N-t-butylacrylamide. The compared the viscosities of these copolymers in 0.01% and 2.00% NaCl and their resistances to shear with those of several partially hydrolyzed polyacrylamides. The poly(N-alkylacrylamide-co-sodium acrylate) demonstrated somewhat better retention of viscosity in brine than did analogous partially hydrolyzed polyacrylamides. N-alkyl substitution increased sensitivity to shear in low salt solutions.

Mulier, G., Fenyo, J.C., and Selegny, E.(7) reported the temperature (100°C) and heating time (up to 384 h) on the physicochemical properties of high molecular weight ($\overline{M}_w \simeq 4 \times 10^6$) of partly hydrolyzed (31%) polyacrylamide(HPAM-25) solution with initial pH values near 4 and 7 respectively. Potentiometric and spectroscopy data indicate that upon heating the solutions for 16 days, the extent of hydrolysis is increased up to around 90%. The viscosity behavior, especially in the presence of bivalent salt ($CaCl_2$), can be explained by taking such an increase in hydrolysis into

consideration. Light scattering data showed that the conformational changes are not correlated with molecular weight degradation.

Durst, F., Haas, R., and Kaczmar, B.U.(8) reported experimental results on pressure losses of flows of dilute polymer solutions through porous media. The polymer products employed in their study consisted of partially hydrolyzed polyacrylamide(HPAM) with different degrees of hydrolysis. They studied the effect of the hydrolysis on the pressure drop in a porous media test section which designed to minimize polymer degradation. The investigations were carried out for various solvent conditions, and it is shown that the maximum increase in pressure drop is mainly dependent on the molecular weight of polymers. The results stress the importance of the solvent properties on the actions of the polymers and on the resultant pressure drop for porous media flows. The addition of salt ions to solutions of partially hydrolyzed polyacrylamides yields onset behavior previously observed for nonionic polymers. The differences measured between various solvent properties can be explained by the actual hydrodynamic molecular dimensions for a given molecular weight and polymer concentration. To quantify the influences of the solvent properties on the polymers, measurements were carried out in aqueous solutions for various pH values and therefore at various degrees of dissociation. The importance of separating polymer effects caused by their linear dimension in the solution from those that are introduced by an increase in solvent viscosity is shown. Measurements were performed to quantify the effects of solvent viscosity on the polymer action and to separate these effects from those due to changes in molecular dimensions.

Maltesh, C., Somasundaran, P., Kulkarni, R.A., and Gundiah, S.(9) investigated intermolucular interactions between polyacrylamides hydrolyzed to varying degrees and poly(vinyl pyrrolidone) or poly(ethylene oxide) by using fluorescence spectroscopy. At low degrees of hydrolysis, interactions between hydrolyzed polyacrylamide and poly(vinyl pyrrolidone) are weak, but at higher

degrees of hydrolysis, the interactions are strong and similar to that in the presence of poly(acrylic acid). At higher degrees of hydrolysis and low pH values, interpolymer complexation between the carboxylic acid group of the hydrolyzed polyacrylamide and the poly(vinyl pyrrolidone) is predominant over intramolucular complexation between the acid and the amide groups. There are no interactions between hydrolyzed polyacrylamide and poly(ethylene oxide) over the entire range of hydrolysis studied.

Hollander, A.F., Somasundaran, P., and Carl, C.G.(10) prepared polyacrylamide and its copolymer containing 6.8 mole% 2-acrylamido-2-methylpropane sulfonic acid by an irradiation-initiated precipitation polymerization technique. They characterized the polymer by intrinsic viscosity under conditions similar to those used during adsorption measurements. Hydrolytic degradation of the polyacrylamide was found to be negligible under conditions used. The adsorption substrate, sodium kaolinite, was prepared by an extensive ion exchange treatment. Equilibrium adsorption of the polymers on the sodium kaolinite was made as a function of polymer concentration, solution pH, ionic strength, and temperature.

Ahmed, I., and Moradi-Araghi, A.(11) reported polyacrylamide and partially hydrolysed polyacrylamide are suitable for low temperature and low salinity reservoir conditions. Biopolymer, such as xanthan gums, are suitable for low to moderate temperature and high salinity condition. Specially tailored synthetic copolymers, such as HE polymers(HE is a registered tradmark of the Drilling Specialties Company for stable synthetic polymers for hostile environments), are suitable for high salinity and high temperature reservoir conditions. These polymers are also used as drilling mud additives to reduce water loss from the mud, especially in higher temperature applications. While polyacrylamides are suitable for most reservoirs, they cannot withstand the higher temperature and salinity and/or hardness levels encountered in deeper reservoirs. Polyacrylamides undergo extensive hydrolysis at elevated

temperatures. The resulting hydrolyzed polymers precipitate with divalent cations, commonly present in oilfield water, leading to a substantial loss in viscosity. This seriously limits their use as mobility control agents in high temperature reservoirs.

Kharas, G.B.(12) studied copolymers of N-vinyl-2-pyrrolidone and 2-phenyl-1, 1-dicyanoethene. They discussed infrared, proton and carbon-13 spectra of the copolymers by comparison with poly(N-vinyl-2-pyrrolidone), model compounds, and various copolymers. Thermal behavior of the copolymers was investigated by using DSC, TMA and TGA mothods. Thermal as well as thermooxidative stability of the copolymers were found to be lower than those of poly(N-vinyl-2-pyrrolidone).

Burillo, S.(13) carried out the gamma-ray induced crosslinking of polyacrylamide under various conditions. The molecular weight of the polymer before irradiation was found to be the most important factor for crosslinking. When polymers have low molecular weight such as 80,000, the intensity of radiation, the external pressure applied and the water content of the polymer powder become important for crosslinking. Although the polyacrylamide hydrogel can be obtained directly by irradiation the monomer, it was obtained more conveniently by the irradiation of monomer-polymer mixtures. The hydrogels obtained by the radiation with a dose of over 50 kGy, absorb water by 1000 - 1500 wt %.

Kiran, E., and Rodriguez, F.(14) investigated the effect of ^{60}Co gamma radiation on aquesous solutions of poly(vinyl pyrrolidone), poly(vinyl alcohol), poly(ethylene oxide) and partially hydrolyzed polyacrylamide. They studied concentrations below and above the critical concentration for macrogel formation at radiation doses below and above the dose for incipient gelation. The changes in viscosity of solutions were followed to characterize the effect of radiation below the critical concentration. It was observed that, at a given fraction of the respective critical concentrations, the polymers behaved

similarly upon irradiation despite differences in atomic composition and molecular architecture. The dependence of reduced viscosity on absorbed dose showed three distinct regions which were asociated with intramolecular cross-linking and chain scission(decrease in viscosity), intermolecular cross-linking (increase in viscosity) and intramolecular cross-linking via ring formation(a second decrease in viscosity). The postgelation properties were characterized by dynamic mechanical measurements in a torsion pendulum using cone-plate geometry. For a given polymer system, storage modulus showed a linear increase with absorbed dose(after a small induction dose), indicating the formation of additional crosslinks. The efficiency of cross-link formation could be correlated in terms of the critical concentration. The logarithmic decrement showed a sudden drop at low doses(in the induction dose) and then leveled off with further irradiation indicating a rapid elemination of a loose chain ends. It was observed that the gels showed syneresis above a limiting dose. This phenomenon was associated with the creation of high internal stresses, which appear to develop more rapidly in polymers with bulky side groups.

Panarin, E.F., Ushakova, V.N., Leliukh, A.I., Kirukhin, D.P., and Munikhes, V.M.(15) studied the kinetics of the radiation-induced homopolymerization of VP in bulk, aqueous solutions and solutions in aliphatic alcohols with a normal structure($C_nH_{2n+1}OH$, where n = 2, 4, 6, 7, 8, 10, 12, 13) by differential scanning calorimeter(DSC), which makes it possible to carry out measurements of the process rate in a field of gamma radiation. The effect of polymerization conditions on the molecular weight characteristics of PVP was also investigated by viscometry and gel-permeation chromatography.