CHAPTER II
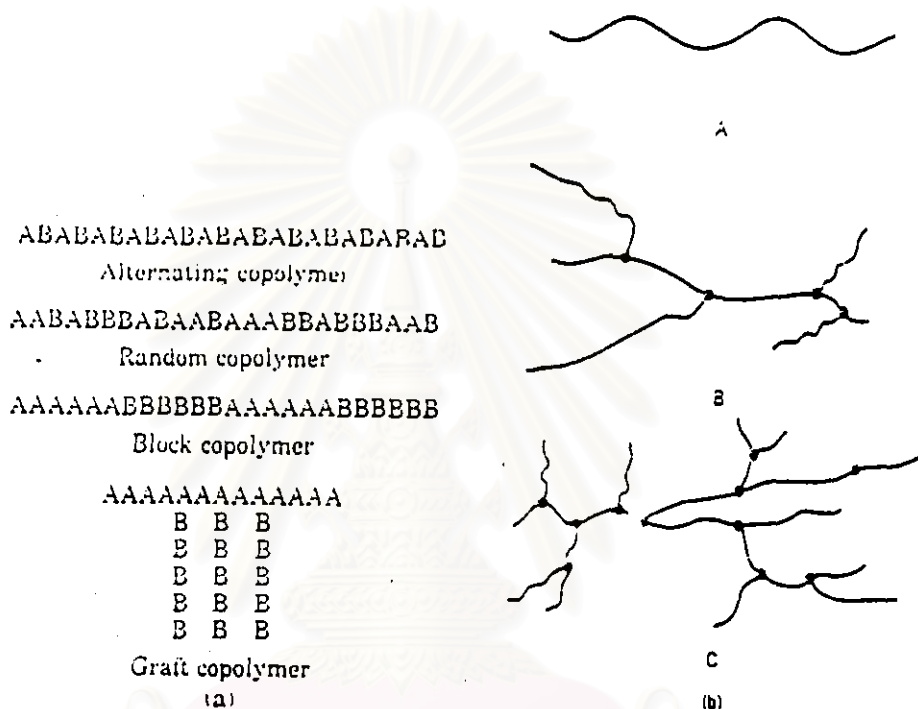
THEORY AND LITERATURE REVIEW
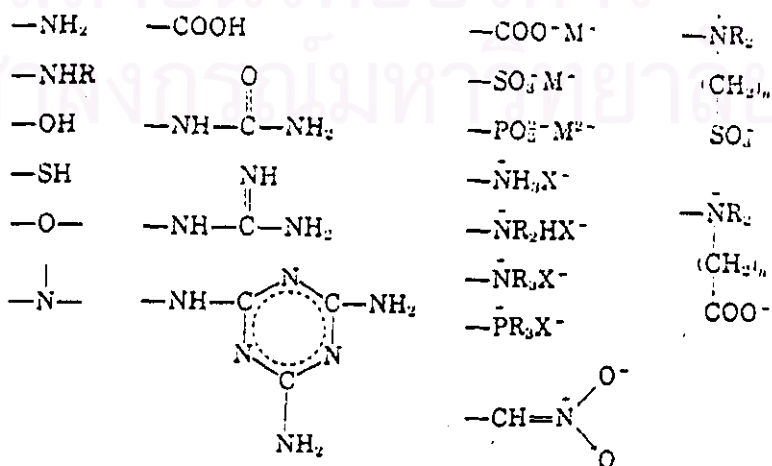
2.1 Water Soluble Polymers

Water soluble polymers are obviously dissolved in water to form polymer aqueous solutions. They can be crosslinked to form water absorbable polymers. Some of water soluble polymers are totally or partially dissolved in saline solutions. Water soluble polymers represent a diverse class of polymers ranging from biopolymers that mediate life process to synthetic resins of immense commercial utility.

Solution properties and performance of water soluble polymers are dictated by structural characteristics of solvated substituents on polymer chains and the polymer chains itself (2). The former determines the solubility of polymer (Fig 2.2). For the latter four categories should be accounted on. Firstly , polymer structure depends on the monomer repeating units, effective monomer compositions and their locations along the backbone (Fig.2.1 a). In addition, the polymer structure relies on the segmental disposition in the polymers (Fig 2.1 b). Secondly , the structure in the polymers is related to config-uration, conformation and intramolecular effects. Thirdly , the structure includes

intermolecular and water to polymer interactions. Finally ,the structure
involves multiple chain aggregation or complexation.

ABABABABABABABABABABABAB
Alternating copolymer

AABABBBABAABAAABBABBBAAB
Random copolymer

AAAAAABBBBBBAAAAAABBBBBB
Block copolymer

AAAAAAAAAAAAA
B B B
B B B
B B B
B B B
B B B

Graft copolymer

(a)

(b)

Fig. 2.1 (a) Monomer distributions ; (b) segmental disposition of soluble
copolymers : A, linear; B, branched-long branches ;
C, branched - branches protruding from branches give a
dendritic structure. (2)

—NH₂   —COOH   —COO⁻M⁺   —NR₂

—NHR   O   —SO₃⁻M⁺   (CH₂)ₙ
                                         |
—OH   —NH—C—NH₂   —PO₃⁻M²⁻   SO₃⁻

—SH   NH   —NH₃X⁻
         ||
—O—   —NH—C—NH₂   —NR₂HX⁻   —NR₂
                                         |
         |N   N| (CH₂)ₙ
—N—   —NH—C   C—NH₂   —NR₃X⁻ |
              | | COO⁻
              N   N   —PR₃X⁻
               C
               | O⁻
               NH₂   —CH=N
                                         O

Fig.2.2 Functional groups imparting water solubility (2)

The over all structural characteristics of water soluble polymer dictate the hydrodynamic volume (volume occupied by the solvated chain), therefore dramatically affecting solution behaviors of polymers. Polymers dissolved in water can have structures ranging from random coils to microheterogeneous polymeric vesicles (see Fig. 2.3) (2).
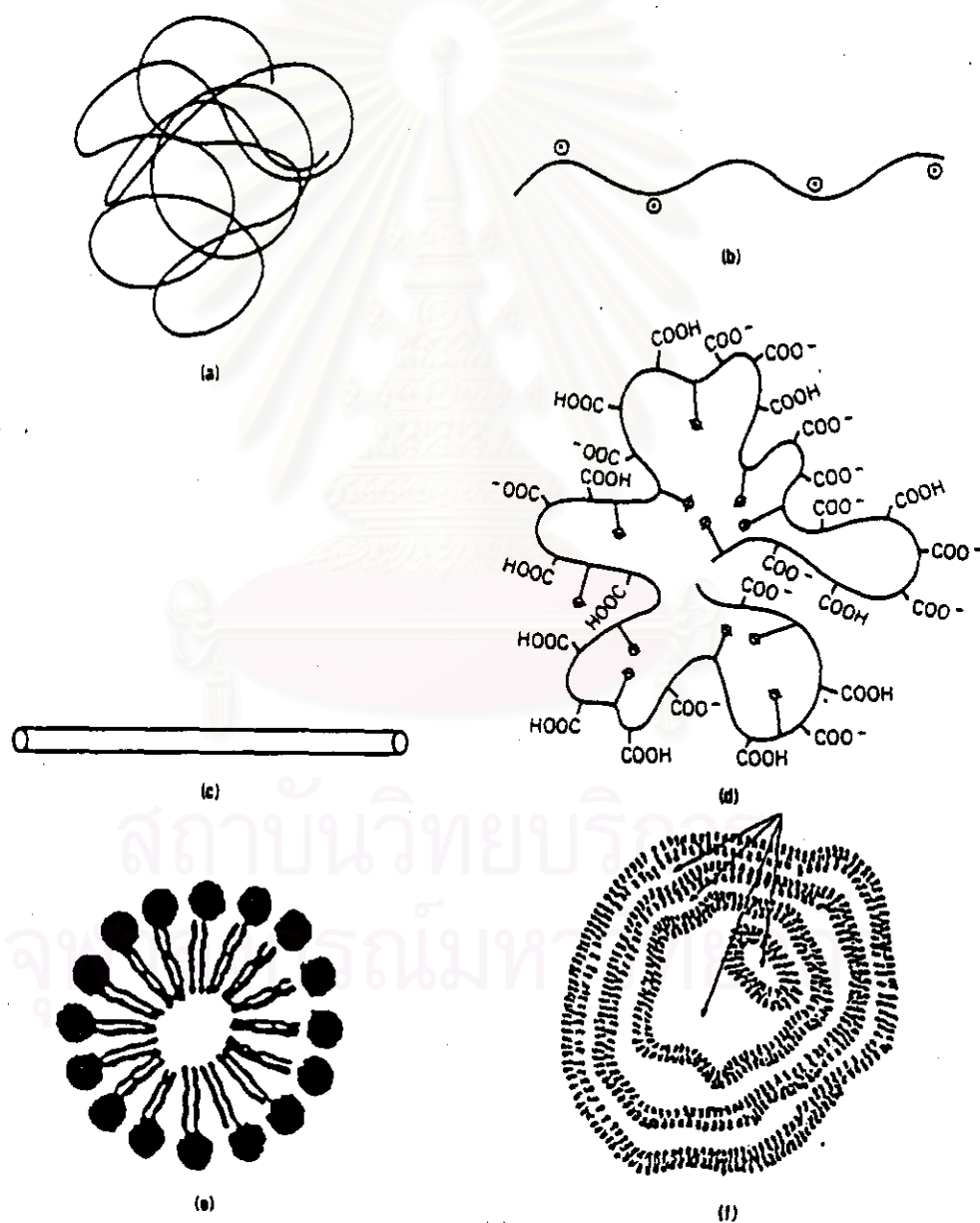

Fig.2.3 Structural dependence upon molecular shapes of copolymers in aqueous media. (a) Solvated random coil; (b) extended coil; (c) rod-like polymer; (d) hypercoil; (e) polymeric micelle; (f) vesicle. (2)

A number of synthetic strategies are usually employed to increase hydrodynamic volume of water soluble polymers. These include the synthesis of ultra-high molecular weight polymers, introduction of chain stiffening elements on the backbone, grafting of hydrophilic monomer on the hydrophobic polymer backbone and others. Because of the various types of polymer solution behaviors, water soluble polymers are often used in various applications.

Water plays a considerable role in determination of the properties and extreme utilities of polymer in solutions. In the solvation of polymer chains, it may be the interaction of palar site of hydrophilic segments with water (Figs.2.3 a and b) or more complicated solvation of amphiphilic structures (Figs.2.3 d-f).

The polymer solubility and precipitation behavior involves the entropy or enthalpy-dominated events (4). The total free energy of the polymer and water is considered to predict phase behavior. Disposition of polymer chain solution is usually evaluated from viscosity of very dilute solution (5). The intrinsic viscosity relates directly to hydrodynamic volume in according to the Mark-Houwink-Sakurada equation shown below.

$$[\eta] = KM^a \quad (2.1)$$

where [η] is the intrinsic viscosity and a is related to chain

extension in dilute solution which implies the hydrodynamic volume.

Rheological characteristics of water soluble polymers are also dictated by molecular structure, solvation and by inter and intrachain association (4). Parameters are taken into account and used to illustrate rheological behavior. The major behavioral patterns involving these parameters are shown in Fig.2.4 .
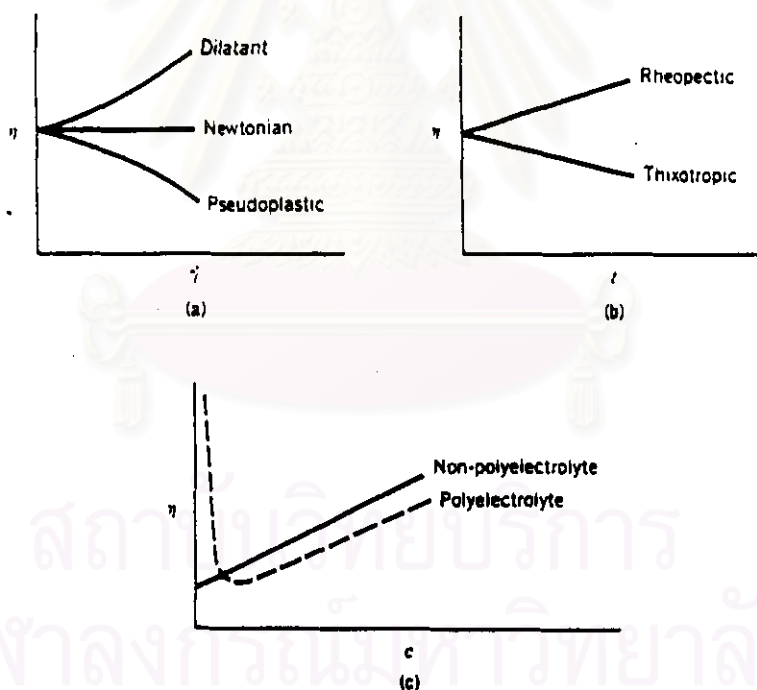
Fig.2.4 Rheological characteristics of water soluble polymers.
All variables other than those on the axes are held constant.
(a) Viscosity (η) vs. shear rate (γ); (b) viscosity vs. time ;
(c) viscosity vs concentrations (2).

The classification of water soluble polymer based on key features is shown in Table 2.1.

TABLE 2.1

Classification of Water Soluble Polymers

1. Biopolymers

   a) Polynucleotides

   b) Polypeptides and Proteins

   c) Polysaccharides :   Storage Polysaccharides e.g. Starch,

                              Algal Polysaccharides e.g. Alginic Acid,

                              Pectin, Plant Gums,

                              Seed Mucilages e.g. Guar Gum,

                              Extracellular Polysaccharides e.g:

                                   Dextran,

                              Bacterial and Fungal Polysaccharides

                                   e.g.Xanthan,

                              Mucopolysaccharide of Higher Animals

                                   e.g.Hyaluronic acid, Heparin,

                              Synthetically Modified Polysaccharides

                                   e.g.   Carboxymethylcellulose (CMC),

                                          Hydroxyethylcellulose (HEC),

                                          Cellulose Sulfates/ Phosphastes

                                          Chitin/Chitosan

2. Nonionic Polymers

   a) Polyacrylamide (PAM)

TABLE 2.1 (Continued)

Classification of Water Soluble Polymers

b) Poly (acrylic acid)

c) Poly (ethylene oxide)

d) Poly (vinyl alcohol)

e) Poly (N-vinylpyrrolidinone) (PNVP)

3. Polyelectrolytes

a) Anionic polyelectrdyte :   Poly (acrylic acid) and Its Salts

Poly (methacrylic acid) and Its Salts

Poly (vinylsulfonic acid) and Its Salts

Poly (styrenesulfonic acid and Its Salts

Other Sulfonic or Carboxylic Acids and Other

Anionic Types

b) Cationic Polyelectrolyte :   Poly Acrylamide-Based Cationics.

Polyamines, Polyimines, and Polyvinylpyridines

c) Amphoteric Polyelectrolyte : Polybetaines, Polyampholytes and Inter-

Polymer Complexes

4. Hydrophobically Associating Polymers

e.g. Maleic Anhydride-Styrene Copolymer

a Terpolymer of Styrene-Maleic Anhydride - Vinylbenzyl Polyglycol Ether

Acrylamide-Alkyl Acrylate Copolymers

5. Inorganic Water-Soluble polymers

e.g. Poly (metaphosphoric acid) and Poly (silicic acid)

As shown in Table 2.2 , water-soluble polymers have a wide ranges of applications, specially, polyacrylamide which is commercially the most important synthetic water-soluble polymer.

TABLE 2.2

Applications of Water Soluble Polymers

Function	Application	Industry
Flocculation	Solid recovery	Mining
	Waste removal	Municipal services
	Water clarification	General
	Retention aid	Paper making
	Drainage aid	Paper making
Rheology control	Waterflooding	Petroleum
	Drilling muds	Petroleum
	Viscous drag reduction	Petroleum, Marine
	Turbulent friction	Fire fighting
	Reduction	Irrigation pumping
	Secondary recovery fluids	Petroleum
	Well-completion fluids	Petroleum
	Thickener	Food , Cosmetic,
	Viscosifier	Coating , Personal-care products

TABLE 2.2 (continued)

Applications of Water Soluble Polymers

Function	Application	Industry
Adhesion	Dry strength	Paper
	Wallboard cementing	Construction
	Denture fixative	Personal-care products
	Binder	Paint, Coating
Coating / Sizing	Sizing agent	Textile, fiber glass
	Microencapsulated ink	Printing
	Fiber formation aid	Paper
	Tablet coatings	Pharmaceutical
Lubricant	Detergents, Soaps	
	Toothpaste, Creams, Lotions	Personal care product
	Ophthalmic solution	Pharmaceutieal
	Tire-mounting lubricant	Industrial supplies
Thermoplastic	Seed tape	Agriculture
	Water-soluble packaging	Agriculture
Water retention	Catamenial device	
	Diaper, Sanitary napkin	Personal care products
	Soil amendment/ stabilization	Agriculture
	Absorbent, Surgical powder	Medical
Biologic function	Therapeutic agent	Medical
	Tissue culture	Agriculture

2.2 The Foamed Polymerization Process (3)

The foamed polymerization process was discovered by Zhang, L.S. et al. in 1990 (3). Graft copolymers and other water-soluble polymers were synthesized via this process , which is in the other words a type of the free-radical chain polymerization under foamed aqueous solution system.

The foamed polymerization process has several distinct advantages. The polymerization can be achieved at high monomer concentration in the reactant mixture while the other processes such as suspension or emulsion polymerization could not be. As the result of the high monomer concentration , autoacceleration reaction occurs at the very short period of time rendering high monomer conversion to polymer as well as highly exothermic reaction , which sometimes lead to the high temperature over the boiling point of water. In effect the drying of polymer synthesized may be unnecessary. The autoacceleration reaction here occurs when the polymerization rate is accelerated under the non-isothermal condition ; gel effect involves the autoacceleration in polymerization rate under isothermal condition (10). In the foamed polymerization process, the physical state of the foamed aqueous solution system makes it better to control. The polymerization mixture, on a microscale, is in intimate contact with gas bubbles. The heat of the polymerization exotherm can therefore easily be transferred into the bubbles, so as to minimize the risk

of overheating. This transfer is promoted by the evaporation of water from the aqueous mixture into bubbles, thereby absorbing the polymerization exotherm as latent heat.

The high concentration of monomer in the aqueous mixture, above 60% and often 70 to 90% by weight of monomer plus water, is preferred, since the gas bubbles will result in the isolation of the polymerization mixture (like gel) into very small gel-like particles, thus promoting the autoacceleration reaction. It is preferable to allow the exotherm to raise sufficiently for water to be driven off as steam out of the polymerization mixture. Consequently ,the final polymer obtained is more dried than that obtained from other polymerization processes.

Nevertheless the monomer concentration can be lower, generally 20 to 50% by weight. Even if the concentration is typical of those appearing normal aqueous solution polymerization the foamed process has two distinguished advantages. Firstly, a substantial amount of water is evaporated into the bubbles of foam and out of the foamed mixture during the polymerization, so that the communitable mass has a lower water content than would be obtained in conventional aqueous solution polymerization. Secondly, the foamed and communitable mass is much easier to crush than the bulk polymer, specially low molecular weight polymer that is sticky.

The typical main components in the foamed polymerization process are monomers, backbone polymers, initiators, foaming agents and

viscosifiers, chain tranfer agents, and crosslinking agents. Details are the followings.

2.2.1 Monomers

A single or a blend of water soluble monomer is used. It is preferred to use a blend of nonionic and anionic monomers or a blend of nonionic and cationic monomers. The preferred nonionic monomer is acrylamide but others can be used, such as methacrylamide, vinyl pyrollidone and hydroxyalkyl(meth)acrylates. Suitable cationic monomers are diallyldimethyl aluminium chloride, and dialkylaminoalkyl(meth) acrylates and dialkylaminoalkyl(meth)acrylamides and their quaternary ammonium salts. Suitable anionic monomers are carboxylic monomers, e.g. crotonic acid, itaconic acid, maleic acid or, preferably, (meth) acrylic acid. The others are ethylenically unsaturated sulphonic monomers, e.g. AMPS, alkyl sulphonate and vinyl sulphonate (usually in form of sodium salts or other water soluble salts).

In general, the polymerisable mixture is preferably formed from 3-30% ethylenically unsaturated sulphonic monomers, 70-97% of a blend of ethylenically unsaturated carboxylic monomer and acrylamide in an amount of 1 to 3 times the weight of carboxylic monomer. All percentages are by weight of total monomeric material.

2.2.2 Backbone Polymers

For the production of graft copolymers, it is preferred to use backbone polymers including the water soluble polyhydroxy materials, e.g. polyvinyl alcohol, polysaccharide (water soluble starch, dextrin, dextran or carboxymethyl cellulose and its salts), and other water soluble polymers (lignin, polyethylene oxide, polypropylene oxide, polyethylene imine).

In the preparation of graft copolymer, the polymerization mixture is preferably formed from 3 to 70% water soluble polyhydroxy polymer, 3 to 10% ethylenically unsaturated sulphonate monomer and 25 to 95% of a blend of acrylamide with sodium acrylate or other water soluble salt of acrylic acid and in which, in the blend, the amount of acrylamide is 50 to 75% and the amount of sodium acrylate is 25 to 50% by weight.

2.2.3 Initiators

The conventional thermal initiators are used but is preferably a redox system, for instance, potassium persulphate or other peroxy compounds, polyvalent metals, e.g. ceric.

2.2.4 Foaming Agents and Viscosifiers

The foamed system can be created by bubbling an inert gas of carbon dioxide or nitrogen through the aqueous polymerization mixture and can be developed by including surfactant.

Generally, foaming may be made from carbon dioxide produced from the reaction of an inorganic carbonate, e.g. sodium carbonate with a protonic acid incorporated in the mixture.

The foaming also can de-oxygenate from the polymerization mixture. The viscosifiers may be used to stabilize the initial foamed system whereby they may be inert polymer or polyhydroxy polymer in grafting polymer. The stability of foam can be improved after polymerization has proceeded sufficiently to give the desired viscosity.

2.2.5 Chain Transfer Agents

Conventional chain transfer agents, e.g. propylene glycol, may be used. The amount added is 0.01-15% based on total monomer weight. This results in lowering of polymer molecular weight and in minimizing chain branching.

2.2.6 Crosslinking Agents

When water swellable polymers are obtained the crosslinking agent is included in the mixture. The crosslinking agents used may be

polyethylenically unsaturated monomer, e.g. methylene(bis)acrylamide which an suitable amount generally is 10-5,000 ppm. A polyvalent metal salt such as caesium or aluminum salt crosslinking agent may be used.

The solvent used in the system is usually water and may depend on initiator and monomer types. The chelating agent such as EDTA is preferably included to eliminate metal ion inhibitor in the polymerization mixture.

The foamed aqueous polymerization mixture is formed by blending water soluble monomeric materials (and polyhydroxy backbone polymer if the graft copolymer is obtained) with the chosen amount of water and chemical foaming agent and auxiliary agents.

The polymerization in foamed system is initiated by adding initiator in the mixture at a given temperature. The free radicals from the decomposition of the initiator attack the monomer molecules on very small gel-like particles taking place by foaming and the polymerization goes further on the particles while the particles are separated all time by gas bubble and agitation. The heat of polymerization can be transferred to bubbles, thus, resulting in the temperature and viscosity of system increase slowly at this stage. The polymerization is subsequently allowed to accelerate due to a rapid increase in temperature and viscosity. The heat of polymerization is transferred not only into gas bubbles but also by the evaporation of water from the aqueous mixture into bubbles and out of the foamed mixture. The polymerization is allowed to

complete for further 15 minutes and the temperature of system falls off.

The product obtained by the polymerization is porous gel and can be comminuted easily in conventional manner. After that, the product may be dried, for example by fluid bed drying.

Watchalayan, K. et al. (6) studied the synthesis of starch graft polyacrylamide, poly(acrylic acid) and poly(acrylamido-2-methyl propane sulphonic acid) using potassium persulphate as initiator by the foamed polymerization process in laboratory scale. They found that increasing in reaction temperature and the amount of NaEDTA chelating agent affected the faster reaction time, and that water soluble starch was suitable for use as backbone polymer.

Tripattanasuwan, S. et al. (7) studied the synthesis of crosslinked starch graft polyacrylamide, poly(acrylic acid) which was used as water absorbable polymer by the foamed polymerization process. The crosslinking agents used were methylene(bis)acrylamide and divinyl benzene. In the studies, the water absorbency and reaction time in various conditions were investigated. They found that the suitable reaction temperature was 30 °C and the water soluble starch at 10% based on monomer weight, the mole ratio of acrylamide and acrylic acid equal to 6:4 can be used to produce the highest water absorbency copolymers. The suitable crosslinking agent was methylene(bis) acrylamide, which improved the absorbing rate and gel strength of water absorbable polymer produced.

Charoensirisomboon, P. et al. (8) studied the synthesis of quaternary cationic graft copolymer of starch and comonomer (acrylamide, acrylic acid and acrylamido-2-methyl propanesulfonic acid), used as flocculant for paper pulp, by the foamed polymerization process. The quaternizing process of the graft copolymer was made by Mannich reaction ; the optimum condition of the reaction was also studied. The characterization of polymeric product and its flocculation properties were investigated.

Kaihirun, M. et al. (9) studied the synthesis and characterization of relating biopolymer. The chelating biopolymer was prepared by synthesizing graft copolymer of hydrolyzed starch with comonomers (acrylamide and acrylic acid) using the foamed polymerization process, introducing thioglycolate group (ligand) on methoxy group of starch backbone using esterification and transesterification reaction. The chelating ability of polymeric product was investigated.

2.3 Kinetics of Radical Chain Polymerization (10)

Water soluble polymers can be prepared by step-growth or chain-growth mechanisms but major commercial synthetic water-soluble polymers are created by the chain-growth polymerization of functionalized alkenes, carbonyl monomers, or strained ring compounds. These may be initiated free radically , anionically or cationically , depending on the monomer structure. In this present research work,

the most   commercially important synthetic water soluble polymer, polyacrylamide, was prepared by the radical chain polymerization, which is therefore mentioned in details hereafter.

2.3.1 Polymerization Mechanism

Radical chain polymerization mechanism consists of a sequence of three steps; *initiation, propagation, and termination.*

The initiation step involves two types of reactions. One is the production of free radicals by any one of a number of reactions. In general is the homolytic dissociation of an initiator or catalyst species I to yield a pair of radicals $R \cdot$ (primary radical)

$$I \xrightarrow{\ k_d\ } 2R \cdot \qquad\qquad (2.2)$$

where k_d = the rate constant for the catalyst dissociation reaction. The last is the addition of primary radical to the first monomer molecule to produce the propagating radical containing one monomer molecule, $M_1 \cdot$

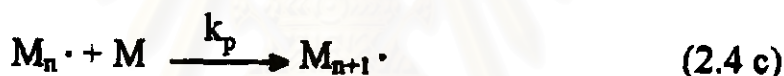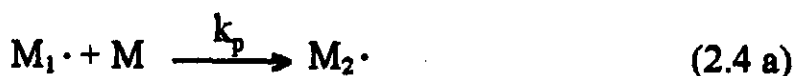$$R \cdot + M \xrightarrow{\ k_i\ } M_1 \cdot \qquad\qquad (2.3)$$

where   M = a monomer molecule

k_i = the rate constant for the initiation reaction.

The propagation step consists of the growth of $M_1 \cdot$ by

the successive addition of large numbers of monomer molecules, which can be presented by

$$M_1 \cdot + M \xrightarrow{k_p} M_2 \cdot \qquad (2.4\ a)$$

$$M_2 \cdot + M \xrightarrow{k_p} M_3 \cdot \qquad (2.4\ b)$$

$$\cdot \qquad \cdot \qquad \cdot$$
$$\cdot \qquad \cdot \qquad \cdot$$
$$\cdot \qquad \cdot \qquad \cdot$$
$$\cdot \qquad \cdot \qquad \cdot$$

$$M_n \cdot + M \xrightarrow{k_p} M_{n+1} \cdot \qquad (2.4\ c)$$

where k_p = the rate constant for the propagation reaction

$M_{n+1} \cdot$ = the propagating radical containing n+1

monomer molecules.

The values of k_p for most monomers are in the ranges of 10^2-10^4 L/mol-s (10).

The termination step relates to the bimolecular reactions between radicals. Two radicals react with each other by *combination (coupling)* or by *disproportionation* in which a hydrogen radical that is beta to one radical center is transferred to another radical center, resulting in the formation of two polymer molecules, i.e.,one saturated and one unsaturated chain ends.

$$M_n \cdot + M_m \cdot \xrightarrow{\ k_{tc}\ } M_{n+m} \qquad (2.5\ a)$$

$$M_n \cdot + M_m \cdot \xrightarrow{\ k_{td}\ } M_n + M_{mu} \qquad (2.5\ b)$$

where k_{tc} and k_{td} are the rate constants for the termination by combination and disproportionation, respectively.

The termination step can be also expressed by

$$M_n \cdot + M_m \cdot \xrightarrow{\ k_t\ } \text{dead polymer} \qquad (2.6)$$

where $k_t = k_{tc} + k_{td}$.

The term dead polymer signifies the cessation of growth of the propagating radical. Typically k_t value is in the ranges of 10^6-10^8 L/mol-s (10).

The growing radical can be subjected to the premature termination by the transferring of a hydrogen or other atoms or species presented in the system (e.g. the monomer, initiator or solvent, as the case may be). These radical displacement reactions are termed as *chain-transfer* reactions.

$$M_n \cdot + XA \xrightarrow{\ k_{tr}\ } M_n\text{-}X + A \cdot \qquad (2.7)$$

where k_{tr} is the chain-transfer reaction rate constant , and

XA may be monomer, initiator, solvent, polymer, or other chain transfer agents and X is the atom or species transferred. The chain transfer agent is the chemical adding deliberately to lower of polymer

molecular weight and minimize chain branching. If A· is active radical, the polymerization by this radical can be continued.

2.3.2 Rate of Polymerization

The rate of polymerization is synonymous to the rate of monomer disappearance. The monomer disappears by the initiation reaction (Eq. 2.3) and by the propagation reactions (Eq. 2.4)

$$- \frac{d[M]}{dt} = R_i + R_p \qquad (2.8)$$

where R_i and R_p are the rates of initiation and of propagation respectively. Compared with the number of monomer molecules in the propagating step, the one reacting in the initiation step is negligible. At the steady state assumption, R_i can be omitted from Eq.(2.8) to give

$$- \frac{d[M]}{dt} = R_p \qquad (2.9).$$

The rate of propagation is the sum of many individual propagation steps and the rate constants for all steps are the same, thus, the rate of polymerization can be expressed as

$$R_p = k_p [M\cdot] [M] \qquad (2.10)$$

where $[M]$ = the monomer concentration ,and

$[M\cdot]$ = the total concentration of all growing radicals.

From the *steady-state assumption*, the concentration of radical increases initially, but almost instantaneously reaches a constants, steady-state value. The rate of change of concentration of radicals quickly becomes and remains zero during the course of the polymerization. That means the rates of initiation R_i and of termination R_t of radicals are equal

$$R_i = R_t \qquad (2.11).$$

The initiation reaction in polymerization is compassed of two steps (Eq. 2.2 and 2.3). The second step is usually much faster than the first step. The homolysis of the initiator is the rate determining step in the initiation sequence and the rate of initiation is then given by

$$R_i = 2fk_d [I] \qquad (2.12)$$

where $[I]$ = the concentration of the initiator ,and

   f = the initiator efficiency.

The termination reactions by combination or by disproportionation follow the same kinetic expression. The rate of termination is then given by

$$R_t = 2k_t [M\cdot]^2 \qquad (2.13).$$

The use of the factor of 2 in those equations above follows the generally accepted convention for tha reaction creating or destroying radicals in pairs. Substitution of Eq. 2.12 and 2.13 into Eq. 2.11 yields

$$[M\cdot] = \left(\frac{fk_d [I]}{k_t} \right)^{1/2} \qquad (2.14).$$

Substitution of Eq. 2.14 into Eq. 2.10 yields

$$R_p = k_p [M] \left(\frac{fk_d [I]}{k_t} \right)^{1/2} \qquad (2.15).$$

The rate of polymerization, R_p, can be experimentally followed by measuring the change in any property that differs for the monomer and polymer, for example, solubility, density, refractive index and spectral absorption. The utility of any particular techniques depends on its precisions and accurancy at low, medium and high percentages of conversion.

Most chain polymerizations involve considerable changes in refractive index between monomer and polymer. The refractive index measurement needs a good control of temperature. The heat of polymerization, ΔH, can be measured quite accurately by differential scanning calorimetry and is measurement of conversion. From the conversion profile, one can determine the rates of polymerization (11), (12), (13), (14), (15).

Equation 2.15 shows the polymerization rate to be dependent on the square root of the initiator concentration. This dependency has been abundantly confirmed for many different monomer-initiator combinations over a wide ranges of monomer and initiator concentrations. The typical data illustrating the square-root dependence on [I] is shown in Fig. 2.5. In addition, the rate expression Eq. 2.15 requires a first order dependence of the polymerization rate on the

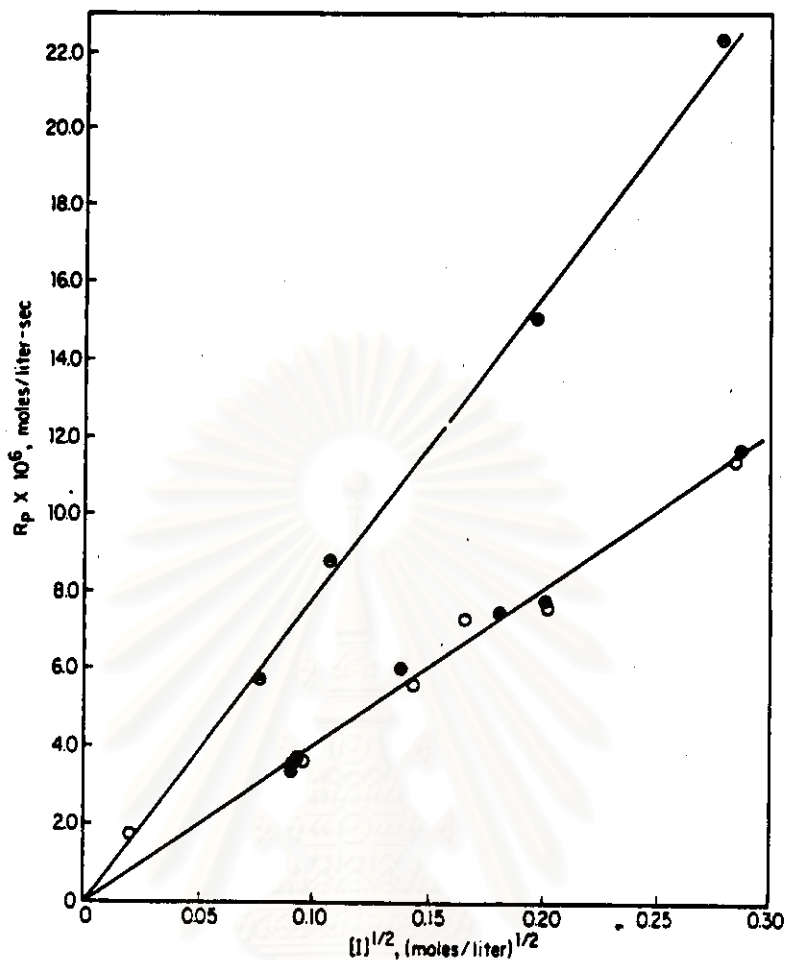Fig. 2.5 Square-root dependence of the polymerization rate R_p on the initiator concentration [I]. ⊖ = Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke [1942] (by permission of Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). ○, ● = Vinyl benzoate, azobisisobutyronitrile, 60°C. After Santee et al. [1964] and Vrancken and Smets [1959] (by permission of Huthig and Wepf Verlag, Basel) (10) .
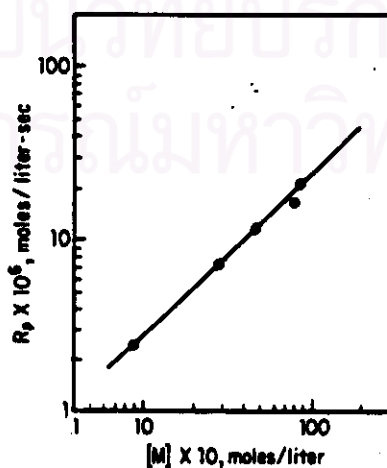

Fig. 2.6 First-order dependence of the polymerization rate R_p of methyl methacrylate on the monomer concentration [M]. The initiator is the t-butyl perbenzoate–diphenylthiourea redox system. After Sugimura and Minoura [1966] (by permission of Wiley-Interscience, New York) (10) .

monomer concentration. This is indeed found to be the general behavior for many polymerizations. Figure 2.6 shows the first-order relationship for the polymerization of methyl methacrylate (10).

The polymerization rate depends on the ratio of three rate constants k_p $(k_d / k_t)^{1/2}$ in accordance to Eq. 2.15. Each of rate constants can be expressed by an Arrhenius relationship

$$k = Ae^{-E/RT} \qquad (2.16),$$

or $$\ln k = \ln A - \frac{E}{RT} \qquad (2.17)$$

where A = collision frequency factor, E = activation energy, T = Kelvin temperature dependence of k_p $(k_d/k_t)^{1/2}$, obtained by combining three separate Arrhenius-type equations, i.e.,

$$\ln\left[k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right] = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{[E_p + (E_d/2) - (E_t/2)]}{RT} \qquad (2.18)$$

The overall activation energy for the rate of polymerization E_R is $[E_p + (E_d/2) + (E_t/2)]$. Since R_p is given by Eq. 2.15, one can rewrite Eq. 2.18 as

$$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[(f[I]^{1/2}[M]\right] - \frac{E_R}{RT} \qquad (2.19).$$

E_R can then be obtained from the slope of a plot of $\ln R_p$ versus 1/T, similar to Fig. 2.7.
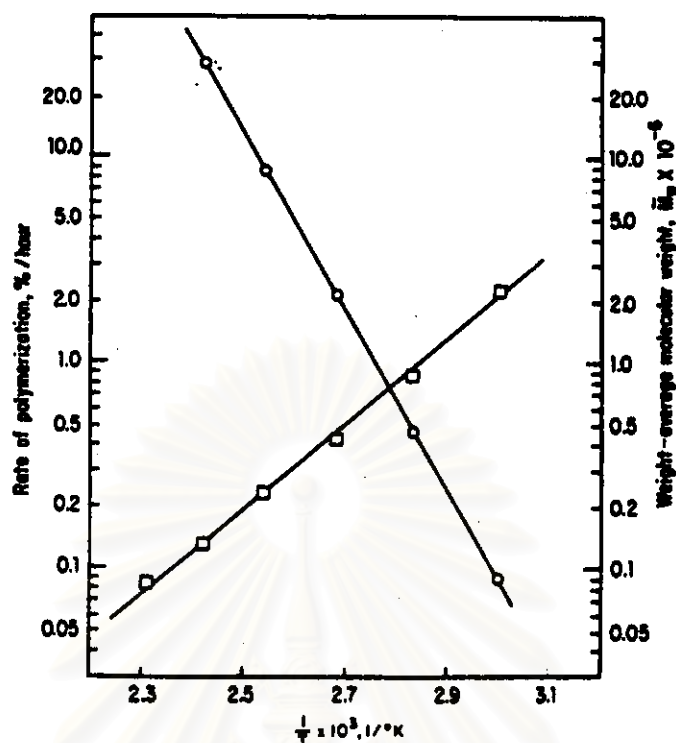
Fig. 2.7   Dependence of the polymerization rate (○) and polymer molecular weight (□) on the temperature for the thermal self-initiated polymerization of styrene. After Roche and Price [1952] (by permission of Dow Chemical Co., Midland, Mich.)   (10) .

2.3.3   Autoacceleration

In   many   polymerizations ,   the polymerization   rate increases rapidly with conversion during the course of reaction. This is named *autoacceleration reaction*.   A typical example is shown in Fig. 2.8. the curve for the 10 %   methyl   methacrylate solution shows the behavior that would generally be expected. The curve for pure monomer shows a dramatic autoacceleration in the polymerization rate. Such behavior in referred to as to as *gel effect*. The terms *Trommsdorf effect* and *Norrish-Smith effect* are also commonly used. It turns out that the gel effect is the normal behavior for
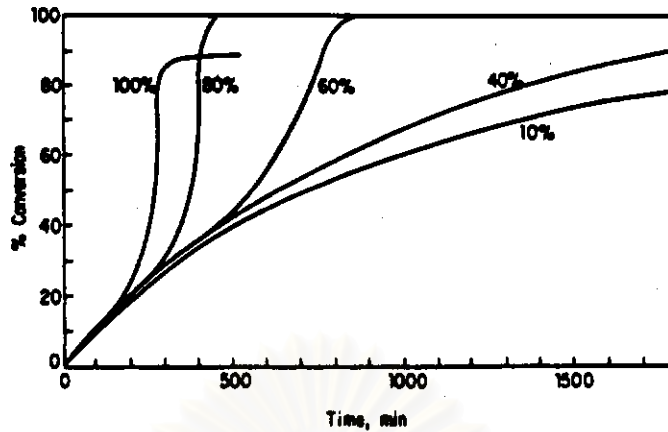
Fig. 2.8 Autoacceleration in the benzoyl peroxide initiated polymerization of methyl methacrylate in benzene at 50°C. The different plots represent various concentrations of monomer in solvent. After Schulz and Haborth [1948] (by permission of Huthig and Wepf Verlag, Basel) (10) .

most polymerizations and is observed under isothermal reaction condition

Gel effect is a diffusion-controlled process, which is related to the decrease of the termination rate constant caused by a decrease in mobility of polymer chains due to the increase of the viscosity of the reaction medium. It is generally assumed that segmental diffusion and translational diffusion are expected to be affected differently with conversion (16).

At low conversion, the viscosity of reaction medium increases slowly and the polymer chain radicals in gradually crowded and entangled with each other. Chain entanglement leads to a faster decrease in tranlational diffusion relative to the decrease with increasing viscosity. However, the decrease in translational diffusion is apparently exactly counterbalanced by the increase in segmental diffusion. The termination reaction is controlled by segmental diffusion. The radical chain ends can rearrange in the proper orientation so that collision of radical ends is possible. That allows the termination reaction to take place. The

polymerization proceeds normally and the rate of polymerization is still constant.

At high conversion, the increase in viscosity of the system is faster with subsequent chain entanglement. The translational diffusion decreases faster than the increase in segmental diffusion. The termination rate is dominated by translational diffusion and becomes increasingly slower. Therefore the rapid autoacceleration in polymerization rate occurs (the gel effect). The propagation reaction is also hindered but the effect is smaller than the one on the termination reaction. Termination involves the reaction of two large polymer radicals, while propagation involves the reaction of small monomer molecules and only one large radical. High viscosity affects the former much more than the latter. Therefore, the result is an increase in polymerization rate with conversion. That shows the increase in the radical lifetime with increasing conversion also.

At very high conversion, the polymerization rate decreases or becomes constant. This shows *glass effect*. The glass transition temperature of a polymerization reaction mixture increases with conversion. Polymerization can stop appreciably short of full conversion if the reaction system has a percent conversion whose glass transition temperature exceeds the reaction temperature. Like the gel effect, glass effect is also diffusion controlled process. For the polymerization of a reaction mixture below the glass transition temperature, at the glassy

state, the propagation rate constant and the polymerization rate fall effectively to zero because of the presence of strong diffusion effect hindering even the movement of individual monomer molecules (16).

2.4 Literature Survey

No informations about the kinetics of foamed polymerization process are found since it is rather new. Since acrylamide was a dedicated monomer use for the studies of the foamed polymerization kinetics, the relevant literatures reviewed hereafter are not limited to any polymerization processes.

Kay, T.A. and Rodriguez, F. (17) investigated the kinetics of free radical polymerization of acrylamide using the hydrogen peroxide-hydroxylamine hydrochloride couple as redox initiator in aqueous solution system. In this work the temperature of polymerization of acrylamide risen in an adiabatic reaction was used to obtain conversion . The adiabatic reactor was an aluminium beaker with a thin internal organic liner. The reactor was insulated and shielded. Approximate reactor charge was 100 g. The initiator monomer concentration in the reaction medium ranged from 0.2 to 0.8 mol/kg while the concentration to the two initiator components was varied from 1 to 100 mmol/kg. The dependence of rate on initiator concentrations was found to be proportional to the peroxide and hydroxylamine concentration raised to

0.44 and 0.52 power respectively. The rate was found to be proportional to the monomer concentration raised to the 1.03 power. Iron was found to have a pronounced accelerating effect on the rate. The predominant reaction appeared to be the iron-catalyzed decomposition of hydrogen peroxide in the presence of small amounts of hydroxylamine hydrochloride. The activation energy was lowered by the addition of iron from 18.7 kcal/mol. with no added iron to 4.5 kcal/mol when the system contained 1 ppm iron.

Balakrishnan, T. and Subbu, S. (18) studied the kinetics of polymerization of acrylamide (AM) initiated by manganese (III) (Mn^{3+}) acetate-ethoxyacetic acid (EAA) redox system in aqueous sulphuric acid in the temperature ranges of 35 to 45°C. The effects of variations in concentration of AM, Mn^{3+}, EAA, acid and ionic strength on the rate of polymerization were studied. The polymerization process is initiated by the free radical arising from the oxidation of ethoxy-acetic acid by Mn^{3+} and terminated by the mutual combination of growing polymer radicals. The rate of polymerization was determined by finding out the concentration of monomer bromometrically in the reaction mixture before and after the polymerization. The dependence of rate on concentration of AM, EAA, Mn^{3+} were found to be raise to the 1.0, 0.5 and 0.5 power respectively. There were no significant effects of acid and ionic strength on the rate. A suitable reaction scheme was proposed and the rate expressions are derived. The study on degree of polymerization supported the proposed

scheme. The overall activation energy for this system was 13.9 kcal /mol.

Mishra, M.K. and Bhadani, S.N. (19) reported a study of the kinetics of polymerization of acrylamide initiated with nitrogen dioxide in tetrahydrofuran. The investigation showed that the rate of polymerization was first order in the monomer and half order with respect to the initiator. The overall activation energy of the polymerization was found to be about 11.5 kcal/mol, which is lower than the ones for the polymerization of acrylamide with NO_2 in other solvents. Also the molecular weight measured by dilution viscometry was found to be higher. That showed the effect of interaction between monomer and solvent on polymerization mechanism was shown. The ranges of monomer and initiator concentrations studied were 1.0-4.0 mol/L and 1.0×10^{-2} - 4.0×10^{-2} mol/L, respectively. The polymerization temperature studied ranged from 15 to 40°C.

Behari, K, Raja, G.D. and Agarwal, A. (Km) (20) studied the kinetics of aqueous polymerization of acrylamide under an inert atmospheres at 30 ± 1°C using potassium perphosphate as initiator with different activators including mercaptosuccinic acid and cystiene hydrochloride. The ranges of monomer concentration studied were 0.66-4.00 × 10^{-1} mol/L. The initiator concentration ranges used was 1.25-12.50 × 10^{-3} mol/L. The activator concentrations mercaptosuccinic acid and cysteine hydrochloride, were 3.33 - 10.00 × 10^{-3} and 1.42-2.50 ×

10^{-3} mol/L ,respectively. The order with respect to perphosphate and acrylamide was found to be one-half and unity, respectively, in both redox systems. Mercaptosuccinic acid had a half-order dependence on the rate of polymerization, whereas cysteine hydrochloride had the first-order dependence. The overall energy of activation was 42.5 ± 2 kJ /mol and 38.3 ± 1 kJ /mol for perphosphate/ mercaptosuccinic acid and perphosphate/cysteine hydrochloride redox systems, respectively. Polyacrylamide samples collected under different kinetic conditions were used for the determination of the intrinsic viscosity also.

Bajpai, U.D.N., Bajpai, A.K., and Bajpai, J. (21) investigated the kinetics of aqueous polymerization of acrylamide with potassium peroxydiphosphate/sodium metabisulfite redox pair at 35 ± 0.2°C under atmospheric oxygen. The rate of polymerization was found to be of the first power to monomer, a half-power to catalyst and a 0.75 power to activator concentration. The overall energy of activation was calculated to be 11.0 kcal/deg. mol between 25 and 45°C. They found also that the addition of organic solvents and dinitrobenzenes was the retardation on the rate of polymerization in those systems.

Rapp, T.L. et al. (22) investigated the polymerization kinetics of aqueous acrylamide solution in gel electrophoresis capillaries by Raman microprobe spectroscopy. The systems studied were the formation of 3.5 % T (total monomer concentrations), 3.3 % C (cross-linker) crosslinked polyacrylamide in 75μm-i.d. electrophoresis cappillaries. The

disappearance of the acrylamide at 1292-cm^{-1} band was followed with 60-s time resolution for 30 min. Polymerization was 98 % complete in 1.5 h. and greater than 99 % complete after 2h. In the 900-1700 cm^{-1} region no bands attributable to cross-linking were observable. Reaction in the cappillaries followed the second-order kinetics.

Candau, F. and Leong, Y.S. (23) investigated the kinetics of the polymerization of acrylamide in inverse microemulsions stabilized by Aerosol OT emulsifier and initiated with azobisisobutyronitrile (AIBN) or potassium persulphate ($K_2S_2O_8$). The inverse polyacrylamide latexes formed were clear and highly stable. A dilatometric technique was used to follow the conversion of monomer at T = 45°C The rate of polymerization was first order with respect to the initial monomer concentration in the presence of AIBN and 1.5 order to $K_2S_2O_8$. An inverse relationship between molecular weight and emulsifier concentration was found and suggested participation of the emulsifier in the initiation reaction. This was confirmed by the independence of the molecular weight of poly acrylamide on the concentration of the initiators. High values of the rate of polymerization were obtained in combination of the high molecular weights. Each final latex particle consists of one single molecule of poly-acrylamide in a collapsed state. This suggested kinetics do not follow the the Smith and Ewart theory.

Ghosh, S.K. and Mandal, B.M. (24) studied the kinetics of the

inverse emulsion photopolymerization of acrylamide using a water soluble photoinitiator, α-ketoglutaric acid, sorbitan monooleate (Span 80) as the emulsifier and toluene as the oil phase. The rate of polymerization (R_p) was represented by : $R_p \propto [I]^{0.5} [C]^{0.5} [M]^{1.28} [E]^{-0.42}$ where I, C, M and E represented the light intensity (313 nm U.V. light), photoinitiator, monomer and emulsifier, respectively, The over all activation energy is 10.20 ± 1.58 kJ /mol. The presence of gel effect was evident from the increase of molecular weight with conversion and also from the nature of the percentage of conversion versus time curves.

Hunkeler, D. (25) investigated the kinetics of aqueous solution polymerization of acrylamide at high monomer concentrations (25-50 wt % or 3.54-7.04 mol/L) at temperatures between 40 and 60°C using potassium persulfate as initiator. The rate of polymerization was found to be proportional to the monomer concentration to the 5/4 th power, and to the initiator concentration to 0.5 power. The rate order was invariant to acrylamide concentration up to its solubility limit in water. Limiting conversions observed were reciprocally related to the initial monomer concentration. Both the high rate orders and limiting conversion was found to be manifestations of the same phenomena : the monomer-enhanced decomposition of potassium persulfate. A "hybrid cage-complex" mechanism was derived. This postulated that the monomer-initiator associate led to donor-acceptor interactions between amide and the persulphate.