

CHAPTER II

THEORY and LITERATURE REVIEW

2.1 Water Absorbing Polymers

A high-water absorbing polymer (HWAP) is defined as the material that its absorbing capacity is greater than 15 times its own weight in the fluids such as water, electrolyte solution, or body fluid, and the absorbed fluid is hard to release, for it merely immobilizes the fluid by entrapment rather than by holding it in its structure (2).

Many kinds of HWAPs have been commercialized since the hydrolyzed starch-polyacrylonitrile graft copolymer (Super Slurper) was first developed by the United States Department of Agriculture. They are being widely used not only in the fields of disposable absorbing materials such as sanitary napkin, diaper and medical care but also in agriculture and industrial uses.

The classification of HWAPs is shown in Table 2.1 (2). By raw materials used, HWAPs are divided into starch- and cellulose-based polymers and synthetic polymers. The physical properties of HWAPs depend upon the methods of insolubilization and hydrophilization introduced into HWAPs and upon the appearance of products, i.e. in a form of powder, film and fiber.

Commercially available products are summarized in Table 2.2. In a point of view by raw materials used, poly(acrylic acid)-based HWAPs are most popular in usage worldwide (2).

TABLE 2.1
Classification of HWAPs

<p>1. <u>by Raw materials</u></p> <ul style="list-style-type: none">a) Starch grafts, Carboxymethylated.b) Cellulose grafts, Carboxymethylated.c) Synthetic polymers: Poly(acrylic acid), Poly(vinyl alcohol), Poly(oxyethylene).
<p>2. <u>by Method of Insolubilization</u></p> <ul style="list-style-type: none">a) Graft polymerization.b) Chemical crosslinking.c) Self-crosslinking.d) Radiation crosslinking.e) Introduction of crystalline structure or hydrophobic groups.
<p>3. <u>by Method of Hydrophilization</u></p> <ul style="list-style-type: none">a) Polymerization of hydrophilic monomers.b) Carboxymethylation of hydrophilic polymers.c) Graft copolymerization of hydrophilic polymer on hydrophobic polymer backbone.d) Hydrolysis of nitrile groups and ester groups.
<p>4. <u>by Product form</u></p> <ul style="list-style-type: none">a) Powder.b) Film.c) Fiber.

TABLE 2.2
Commercial Available Products

Maker	Name [®]	Composition*	Form
<u>Japan</u>			
Sanyo Kasei	SANWET	HSPAA	Powder
		PAA	Powder
Seitetsu Kagaku	AQUAKEEP	PAA	Powder
Kao Soap	WONDERGEL	PAA	Powder
Sumitomo Kagaku	SUMIKAGEL	PVA- <i>b</i> -PAA	Powder
		PEO	
Arakawa Kagaku	ARASORB	PAA	Powder
Nippon Shokubai	AQUALIC	PAA	Powder
Kurareisoprene	KI-GEL	MA- <i>co</i> -IB	Powder
Exlan	LANSIL	HPAN	Fiber
<u>U.S.A.</u>			
Dow Chemical	DRYTECH	PAA	Powder
			Film
Grain Processing	WATER-LOCK	HSPAN	Powder
Hercules	AQUALON	CMC	Fiber
<u>Europe</u>			
BASF	LUQUASORB	PAA	Powder
Stockhausen	FAVOR	PAA	Powder
Enka	AKUCCELL	CMC	Fiber

* HSPAA: Hydrolyzed Starch-Poly(acrylic acid) Graft Copolymer;
HSPAN: Hydrolyzed Starch-Polyacrylonitrile Graft Copolymer;
HPAN: Hydrolyzed Polyacrylonitrile; PAA: Partially Crosslinked Poly
(acrylic acid salt); PVA: Poly(vinyl alcohol); PEO: Poly(ethylene
oxide); CMC: Carboxymethyl Cellulose; MA-*co*-IB: Maleic acid-
Isobutylene Copolymer

Figure 2.1 depicts the structure of a partially crosslinked poly(acrylic acid salt), a representative of HWAP. As shown in Figure 2.2, HWAP is composed of a type of mobile ion (a counter cation) as a source of water absorption, and an ion network made from electrolyte anions in the polymer chains.



— : crosslinking network

Na : mobile ion

FIGURE 2.1 Structure of Crosslinked Poly(acrylic acid salt)

(The figure is reproduced from Reference 2.)

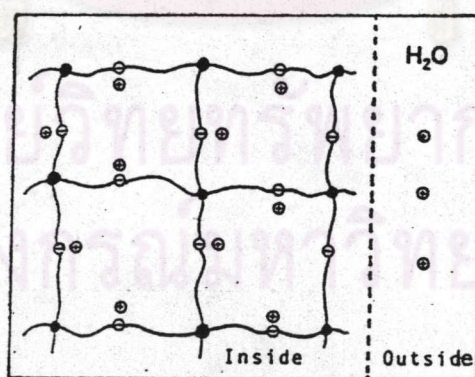


FIGURE 2.2 Theoretical Model of HWAP Structure:

(-), Polymer electrolyte (anion)

(+), Mobile ion (cation)

(•), Crosslinking point

(The figure is reproduced from Reference 2.)

Therefore, the absorbency is mainly dependent upon three factors: a) the osmotic pressure; b) the molecular chain expansion resulting from electrical repulsion between the electrolyte anions in the polymer chains; and c) the extent of crosslinkage affecting the degree of swelling of the polymer.

The recent developments in HWAP preparation process were summarized as follows:

1. Graft Copolymerization

The hydrolyzed starch-polyacrylonitrile graft copolymer (HSPAN), the first product of HWAPs, was prepared by the graft copolymerization of acrylonitrile onto gelatinized starch using ceric ammonium nitrate as an initiator and then by hydrolysis (USDA Method). However, this process is almost not used for the preparation of HWAP because of complicated process and high viscosity phenomenon at the hydrolysis stage.

Sanyo Chemical Company developed the modified graft copolymerization process and industrialized in 1978. The process is to copolymerize acrylic acid onto starch directly using a specific initiator.

2. Acrylic Acid Polymerization

Recently, a partially crosslinked poly(acrylic acid salt) was being mainly used as HWAP because of its simple process and easy quality control of the product compared with the hydrolyzed graft copolymers.

2.1 Solution Polymerization in Water

Using a redox initiator, the acrylic acid neutralized with sodium hydroxide is polymerized in water as a solvent without any additives at a low temperature. Although, this is a simplest method for the preparation of acrylic-based HWAP, it is very difficult to dry the swelled gel produced after polymerization.

2.2 Thin Layer Polymerization

The process of thin layer polymerization was recently developed by Arakawa Kagaku Company in Japan.

The monomer solution with more than 70% of acrylic acid is prepared with a mixture of water soluble initiator, water and sodium hydroxide; and then sprayed on the surface of the conveyor belt to make a thin layer. It is polymerized and simultaneously dried by the heat of polymerization generated during the polymerization.

2.3 Inverse Suspension Polymerization

The monomer solution is prepared with a mixture of water soluble initiator and acrylic acid neutralized with sodium hydroxide. After the solution is dispersed into the organic solvent containing surfactant; it is polymerized and then crosslinked to give a desirable property. The physical properties are dependent on the concentration of monomer, the degree of neutralization, the kind and concentration of surfactants. This process is an ideal process in the control of heat of polymerization, because microsuspensions have lower viscosities, provide easier heat removal and can be used at higher monomer concentrations than the solution process (3).

Table 2.3 summarizes chemical factors affecting the physical properties of HWAPs (2).

TABLE 2.3
Factors Affecting Physical Properties of HWAPs

Physical Property	Factor
Absorbency	a) In Graft Copolymers: <ul style="list-style-type: none"> - MW of grafted PAN, - grafting frequency, - grafting percentage, b) MW of Synthetic Polymers, c) Hydrophilicity of Functional Groups in Vinyl Monomers, d) Composition of Hydrophilic Monomer in Acrylic Copolymers.
Water Retention (Gel Strength)	a) Degree of Crystallinity, b) Degree of Crosslinking, c) Selection of Crosslinking Agent.
Absorbing Rate	a) Degree of Crosslinking; b) Crosslinking Density (gradient), c) After-Treatment: <ul style="list-style-type: none"> - Particle size and Porosity, - Wetting Agent and Filler, - Appearance: Powder, Film, Sheet, Foam.

Although HWAPs have been mainly used only in the limited fields of disposable absorbing materials such as diaper and sanitary napkin, their use is being extended recently into agriculture and industrial areas as shown in Table 2.4 (2).

TABLE 2.4
Applications of HWAPs

<p>1. Disposable Absorbing Materials:</p> <ul style="list-style-type: none"> - Sanitary Napkins, - Diapers for Infants & Adults, - Medical Sheets, - Paper Towels & Non-Wovens.
<p>2. Agriculture & Horticulture:</p> <ul style="list-style-type: none"> - Soil Conditioners for Water Retention, - Coatings for Seed Germination, - Hydro-mulching Formulations.
<p>3. Industries:</p> <ul style="list-style-type: none"> - Dehydrating Agents for Fuels, - Blocking Agents for Underground Cables, - Sludge Dewatering, - Sealing Gaskets.
<p>4. Others:</p> <ul style="list-style-type: none"> - Swellable Toys, - Fire Fighting Fluids, - Ice Packs, - Wallpapers for Humidity Control.

2.2 Polymerization Techniques

Polymers are macromolecules built up by linking together of large numbers of much smaller chemical units. The small molecules that combine with each other to form polymer molecules are known as monomers, and the reactions by which they combine are termed polymerization. Polymers and their polymerization process or reactions can be classified in two ways. Based on the composition or structure of the polymers, they may be condensation or addition polymers and the corresponding polymerization reactions, as follows. They can be called step or chain polymerization, based on the mechanism of the polymerization reactions. Since polymers of the same structure can be obtained under different conditions through different mechanisms, the use of these two classifications is not always interchangeable. For polymerization, the classification based on mechanism is natural, therefore, polymerization can be either a chain or a step reaction.

Chain polymerization proceeds by a distinctly different mechanism from step polymerization. The most significant difference is that high molecular weight polymer is formed immediately in a chain polymerization. A radical, anionic, or cationic reactive center, once produced, adds many monomer units in a chain reaction and grows rapidly to a large size. The monomer concentration decreases throughout the course of the reaction as the number of high polymer molecules increases. At any instant the reaction mixture contains only monomer, high polymer, and the growing chains. The molecular weight of the polymer is relatively unchanged during the polymerization, although the overall percent conversion of monomer to polymer increases with reaction time.

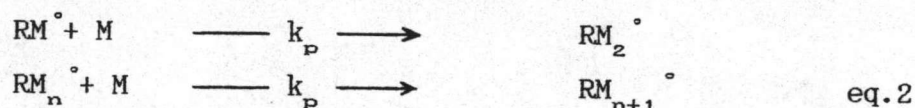
The situation is quite different for a step polymerization. Whereas only monomer and the propagating species can react with each other in chain polymerization, any two molecular species present can react in step polymerization. Monomer disappears much faster in step polymerization as one proceeds slowly to produce dimer, trimer, tetramer, and so on. The molecular weight increases throughout the course of the reaction and high molecular weight polymer is not obtained until the end of the polymerization. Long reaction times are necessary for both high percent conversion and high molecular weights (4).

For the purpose of discussions on an organic polymerization, free radicals can be defined as organic segments containing odd or unpaired electrons(5). Free radical polymerization comprises four main reactions: (i) initiation, in which an initiator, e.g., a peroxide, decomposes to form primary radicals; (ii) propagation, in which a free radical adds monomer molecules in succession to form a large polymeric radical; (iii) termination, in which the polymeric radicals react to form a dead polymer; (iv) transfer, in which a polymeric radical abstracts an active hydrogen or halogen from a compound to terminate the growing radical and form a radical which may initiate a new chain reaction. These four main reactions are presented in the following equations (4,6,7):-

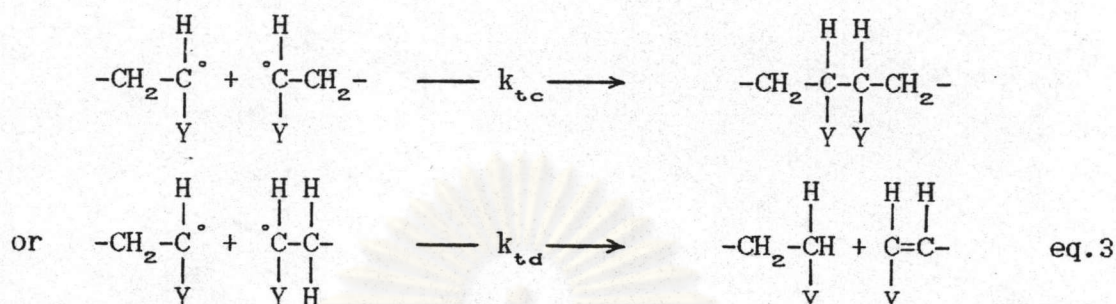
Initiation:



Propagation:



Termination:



Chain transfer:



2.3 Suspension Polymerization

In suspension polymerization a monomer or mixture of monomers is dispersed by strongly mechanical agitation into droplets suspended in a second liquid phase in which both monomer and polymer are essentially insoluble. The monomer droplets, which are larger than those in a true emulsion, are then polymerized the dispersion of which is maintained by continuous agitation. To the suspending liquid, which is almost always water, are added suspending agents which hinder the coalescence of the droplets during polymerization, the details of which are presented in the following section. Polymerization initiators or catalysts soluble in the monomer phase are generally used. According to the particular monomer employed, hard or soft spheres, beads, pearls or less often irregular granules, which normally separate easily from the aqueous phase when stirring is discontinued, are formed. Aside from cast resins and the synthetic rubbers, suspension polymerization has become the most important commercial method for polymerization of olefinic monomers. Despite

the prominent industrial role of the method, relatively few publications have appeared and the scientific aspects have been little explored (8).

Reasons for the industrial development of suspension polymerization are clear. Most importantly, the large heat of polymerization can be dissipated, and granules easily filtered products can be obtained directly from many polymers, otherwise, difficulties to break up from the tough, hard adhesive or rubbery masses may arise. The necessity for coagulation of latex and intensive washing of emulsion polymers is consequently avoided.

Several other types of polymerizations are carried out in an aqueous medium. These must be distinguished from the suspension and pearl polymerization, and they give different types of end products. An outline of these processes of polymerization is presented in Table 2.5 (8). Suspension polymerization has been little used outside the field of vinyl-type or ethylenic monomers.

2.3.1 The Aqueous Phase and Suspending Agents

The aqueous phase maintains the monomer in the form of droplets and serves as a heat exchange medium. It is the vehicle for monomer and polymer. Water is seldom used alone but is modified by an addition of various suspending agents. The most important types of additive are:

- (a) water-soluble organic polymers (so called protective colloids), and
- (b) inorganic compounds in the form of water-insoluble powders.

TABLE 2.5

Polymerization Processes in Heterogeneous Aqueous Dispersions

Process	Monomers	In aqueous phase	Initiator	Type of polymer product	Examples of commercial polymers and copolymers
Emulsion polymerization	Largely water insoluble	Initiators, emulsifiers, etc.	Water soluble, e.g., persulfates, redox systems	Latex of particles 0.05-0.2 microns	Methacrylate and acrylate, ester, vinyl acetate, styrene, butadiene
Dispersion polymerization	Largely water insoluble	Initiator and >1% water-soluble polymeric dispersant, e.g., PVA	Water soluble, e.g., H ₂ O ₂	Viscous, latexlike dispersions, 0.5-10 microns	Vinyl acetate
Bead-type suspension polymerization	Largely water insoluble	<1% water-soluble polymer or inorganic powder	Monomer-soluble peroxides or azo compounds	Clear beads	Styrene, methacrylate, acrylate, vinyl acetate
Powder-type suspension polymerization	Polymer insoluble in monomer	With or without suspending agents	Monomer-soluble peroxides or azo compounds	Opaque pearls or powders	Vinyl chloride, high-acrylonitrile, fluoroethylenes

Surface active agents may be added in small concentrations. A survey of the materials used as suspending agents is given in Table 2.6 (9).

If a layer of water-insoluble liquid monomer is poured over water and then the liquids are stirred, monomer droplets are formed. After the agitation is stopped, less dense monomer droplets rise, and again unite to form a homogeneous layer. But this coalescence does not occur instantaneously. Instead, the monomer droplets move about among each other for some time, and on collision they may rebound like billiard balls. There is a tendency to maintain the originally spherical droplet which results from an effect of interfacial tension. The lower the interfacial tension, the more easily are the monomer droplets deformed under the influence of the moving water as judged by the intensity of agitation required for forming lens-shaped or elongated drops. On the other hand, a high surface tension has the effect of greatly increasing the stability of the large spherical drop. In that case, on collision a deformation of the spherical drop can hardly occur, but there is an elastic reaction instead which leads to rebounding. When the interfacial tension is low, the tendency to maintain a spherical shape is comparatively low. A deformed drop on collision will then be further deformed, giving a larger surface area. Thus, a low interfacial tension leads, with agitation, to breaking up the monomer into very small droplets; too much surfactant, of course, gives true emulsions.

Under the unique conditions of pearl polymerization, the droplets easily blend with one another without change of size. Among good suspending agents are found polymeric substances such as starch, proteinaceous materials and poly(vinyl alcohol), which are only very weak surface active substances. Pronounced surface active agents such

TABLE 2.6
Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
1. Natural polymeric agents:	Unsaturated esters of organic acids, such as acrylate esters and vinyl esters.
-Carbohydrates: starch, agar, tragacanth, pectin, plant gums. such as acacia, sodium alginate.	
-Proteinaceous materials: glue, gelatin, isinglass.	Vinyl esters, vinyl chloride, etc.
-Alginic acid and salts.	Methyl methacrylate.
-Starch with buffer.	Vinyl acetate.
2. Modified natural polymeric agents:	
-Methyl cellulose.	Acrylic and vinyl esters.
-Methyl hydroxypropyl cellulose with 0.05-0.2 hydroxypropyl group per C 6 unit.	Vinyl compound: vinylidene chloride, vinyl chloride, acrylonitrile, etc.
-Carboxymethyl cellulose sodium salt.	Vinyl compounds.
-Hydroxyethyl cellulose.	Vinyl chloride.
3. Synthetic polymeric agents:	
(a) Containing carboxyl groups:	
-Salts of poly(acrylic acid) and of poly(methacrylic acid).	Acrylic and vinyl esters and homologs.
-Above at pH 5.5-8 with buffers.	Acrylic compounds.
-Sodium salts of copolymers of	Dichlorostyrene, acrylonitrile,

TABLE 2.6 (continued)
Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
methacrylic acid with dichloro- styrene.	methylmethacrylate.
-Salts of copolymers of maleic acid, crotonic acid, with styrene, vinyl ethers, vinyl acetate, etc.	Unsaturated polymerizable organic compounds generally.
-Salts of acrylic acid copolymers with acrylic ester or vinyl ester.	Vinyl chloride, etc.
-Copolymers of maleic acid, maleic anhydride with vinyl acetate.	Vinyl halides and comonomers.
-Copolymers of vinyl methyl ether and maleic anhydride.	Vinyl halides and comonomers.
-Polymers of itaconic, fumaric, maleic, citraconic, aconitic acids also partial esters or their salt.	Vinyl compounds including acrylic compounds.
-Sodium salts of copolymers of 1- alkoxybutadiene and maleic acid.	Polymerizable vinyl compounds.
(b) Containing nitrogen:	
-Poly(vinyl pyrrolidone).	All polymerizable organic compounds.
-Polymeric reaction products of methylmethacrylate with ammonia.	Acrylic, vinyl esters and mixtures.
-Above at pH 5.5-8 with buffers.	Acrylic compounds, homologs.

TABLE 2.6 (continued)
Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
-Polymethacrylamide with NaH_2PO_4 and Na_2HPO_4 as buffers.	Monomers in general.
(c) Containing alcoholic OH groups:	
-Poly(vinyl alcohol).	Acrylic and vinyl esters.
-Poly(vinyl acetate) partially saponified, mixtures of different mol.wt. and degrees of saponification.	Vinyl acetate.
(d) Containing sulfonic acid groups:	
-Sulfonated polystyrene with 0.15-0.5 SO_3H group per ring.	Vinyl chloride with less vinylidene chloride.
-Reaction products of poly(vinyl alcohol) with aldehyde sulfonic acids.	Polymerizable vinyl compounds.
4. Low molecular compounds	
-Ester of organic hydroxyacids, e.g., octyl lactate.	Polymerizable vinyl compounds generally.
-Aliphatic acid esters of poly(ethylene glycol).	Vinyl chloride.
-Partial esters of polyalcohols with fatty acids, e.g., pentaerythrityl laurate.	Vinyl chloride, vinylidene chloride and other vinyl compounds.

TABLE 2.6 (continued)
Materials Used in Suspension Polymerization

Suspending agent	Monomer suggested
-Phthalate esters.	Vinyl chloride.
5. Condensation polymers:	
-Urea-formaldehyde.	Vinyl chloride, vinylidene chloride, acrylonitrile.
-Water-soluble phenol-formaldehyde.	Vinyl chloride polymers.
6. Inorganic agents:	
-Powders such as kaolin, barium sulfate, talcum, aluminum hydroxide.	Polymerizable vinyl and vinylidene compounds.
-Addition of powders produced by precipitation together with monomers.	Polymerizable vinyl and vinylidene compounds.
-Tricalcium phosphate.	Polymerizable vinyl and vinylidene compounds.
-Difficultly soluble neutral phosphates of 0.2-0.005 μ .	Polymerizable vinyl and vinylidene compounds.
-Hydrated complex magnesium silicates.	Polymerizable vinyl and vinylidene compounds.
-Bentonite (colloidal clay).	Polymerizable vinyl and vinylidene compounds.

as wetting agents and soaps are not useful alone as suspending agents. However, in certain cases they may be used in combination with other agents for reducing bead size, e.g., along with strongly dissociated inorganic salts which raise the surface tension of the water phase, thus compensating to some extent for the wetting action. The surface activity of salts alone is sufficient in the case of some monomers such as lower acrylic esters for carrying out suspension polymerization. Salt addition is often used also in polymerization in combination with regular suspension stabilizers.

It is easy to understand how the increase of viscosity of the aqueous phase by dissolved organic polymers has a stabilizing action in suspension polymerization. The molecules of water layer which exist between two colliding droplets are easily pushed aside. But, if the thin layer of water contains dissolved polymer such as poly(vinyl alcohol) or protein, imparting increased viscosity, there is substantially more resistance to coalescence of droplets. For this reason, it is important that the organic polymers serving as suspension stabilizers be soluble in water but completely insoluble in the monomer phase. The increased viscosity imparted to the aqueous phase is directly important in delaying the process of coalescence.

In the case of the inorganic materials used in a fine powder form as outstanding suspension stabilizers, the viscosity of the aqueous phase is not affected. Powders suspended in water are wetted by the aqueous phase. When two monomer droplets approach each other, their recombination may be prevented by the powder particles which lie between them. This can be observed distinctly under a microscope.

Additions of surface active agents to the aqueous phase have great influence along with powders as suspending agents, because of the reduction of surface tension. Very small additions of such surface active agents can promote the fine dispersion of the insoluble powder without changing the surface tension of the water very much. If these wetting agents are only used in an extremely small concentration, they are practically adsorbed completely upon the powder surface, so that few freely diffusing wetting molecules are present in the aqueous phase. Because of the better dispersion of the suspending powder, smaller polymer granules are formed.

The suspension stabilizers must perform their function during the whole course of the polymerization. The most critical phase of each polymerization, however, is that when the droplets contain enough dissolved polymer to become syrupy, and because of their higher viscosity they can no longer be broken up as readily by the agitation as when they were mobile pure monomers. At this stage also, the droplets are not yet sufficiently solidified to prevent sticking together on collision. It is possible that this critical phase is also influenced by the changes in interfacial tension between the aqueous and organic phases occurring during the progress of polymerization. The monomer and the polymeric product may possess widely different values of surface tension. When the polymer is insoluble in the monomer, as in the case of vinyl chloride, of course no sticky, viscous condition can cause coalescence.

2.3.2 The Monomer Phase

Generally, those monomers which are insoluble or only slightly soluble in water are polymerized by suspension processes. However, where the solubility of the monomers or the products is too

great, electrolytes such as alkali salts of strong acids, which have a salting-out effect, may be added. Mixtures of different monomers also may be copolymerized in suspension where a difficultly soluble monomer acts as an extracting agent for a second more soluble monomer. In this way, copolymeric pearls from relatively water-soluble monomers may be obtained, especially in the presence of salts. Similar action can be exerted by plasticizers which have been occasionally added initially to the monomers in order to facilitate a uniform pearl formation.

In pearl or bead polymerization, the monomer phase usually contains the dissolved polymerizable initiator or catalyst. Practically, the same initiators are used as in ordinary bulk and solution polymerizations of unsaturated monomers, i.e., organic peroxides, and less frequently used azo compounds.

2.4 Inverse Suspension Polymerization

Inverse suspension polymerizations, which recently have attained commercial importance, begin with concentrated aqueous solutions of monomers dispersed in hydrophobic organic solvents. The technique is particularly useful with acrylamide, methacrylamide, acrylic acid, methacrylic acid, salts of the corresponding acids, and quaternary ammonium monomers such as quaternized diethylaminoethyl methacrylate and vinylbenzyl trimethylammonium chloride and their mixtures. Generally 50-80% monomer in concentrated solution with water is dispersed along with water-soluble initiators such as persulfates, hydrogen peroxide, and redox activators of these. As external phases one may use aliphatic hydrocarbons or less frequently toluene, xylene or chlorinated hydrocarbons(8).

This process provides many advantages, due to the compartmentalization of the reactive loci it associates a high polymerization rate to a high average degree of polymerization, low viscosities and good heat removal(10).

Heide, W., Hartmann, H., and Vamvakaris, C.(11) disclosed an inverse suspension polymerization process for the preparation of bead polymers of water-soluble ethylenically unsaturated monomers, such as acrylamide, methacrylamide, acrylic acid, methacrylic acid, alkali metal and ammonium salts of vinylsulfonic acid. The monomers can be employed in the polymerization either alone or as a mixture with one another, so that either homopolymers or copolymers are obtained. Preferred monomers are acrylic acid, methacrylic acid, acrylamide and/or methacrylamide. These monomers can be copolymerized with one another in any ratio.

The polymerization can also be carried out in the presence of crosslinking agents. The crosslinking agents contain two or more ethylenically unsaturated double bonds, examples of suitable crosslinking agents being N,N'-methylenebisacrylamide, poly(ethylene glycol diacrylates) and poly(ethylene glycol dimethacrylates), each of which is derived from a poly(ethylene glycol) having a molecular weight of from 126-8500, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethylene glycol diacrylate, propylene glycol diacrylate, butanediol diacrylate, hexanediol diacrylate, hexanediol dimethacrylate, diacrylates and dimethacrylates of block copolymers of ethylene oxide and propylene oxide, adducts of ethylene oxide and/or propylene oxide with trimethylolpropane, the said adducts being diesterified or triesterified with acrylic acid or methacrylic acid, poly(hydric alcohols), such as glycerol or pentaerythritol, which are diesterified or polyesterified with acrylic acid or methacrylic acid,

and triallylamine, tetraallylethylenediamine, divinylbenzene, diallyl phthalate, poly(ethylene glycol divinyl ether), trimethylolpropane diallyl ether, butanediol divinyl ether, pentaerythritol triallyl ether and/or divinylethyleneurea. Water-soluble crosslinking agents are preferably used, for example N,N'-methylenebisacrylamide, poly(ethylene glycol diacrylates), poly(ethylene glycol dimethacrylates), pentaerythritol triallyl ether and/or divinylurea. The crosslinking agents are used in an amount of from 0.001 to 5%, preferably from 0.01 to 2%, by weight, based on the mixture of monomers.

The polymerization may be carried out in the presence or absence of the conventional polymerization regulators. Examples of suitable polymerization regulators are thiol compounds, such as thioglycollic acid, mercaptoalcohols, e.g. 2-mercaptoethanol, mercaptopropanol and mercaptobutanol, dodecylmercaptan, formic acid and ammonia.

The polymerization is carried out in the presence of a conventional polymerization initiator, e.g. ammonium, sodium or potassium peroxydisulfate, a peroxide, such as dibenzoyl peroxide, dilauryl peroxide, di-2-ethylhexyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, bis(4-tert-butylcyclohexyl) peroxydicarbonate, tert-butyl perpivalate, tert-butyl perbenzoate, tert-butyl permaleate, di-tert-butyl peroxide, tert-butyl hydroperoxide or hydrogen peroxide, and redox catalysts, suitable reducing components being iron(II) ammonium sulfate, ascorbic acid, sodium methylsulfinate, disodium bisulfite and sodium bisulfite. Azo initiators, such as azobisisobutyronitrile, 2,2'-azobis-(N,N'-dimethylisobutyramidine) dihydrochloride, 2,2'-azobis-(2-amidinopropane) dihydrochloride, 2,2'-azobis-(N,N'-dimethyleneisobutyraniline), 4,4'-azobis(4-cyanopentane carboxylic acid) and 2-carbamylazoisobutyronitrile, are also suitable.

The polymerization initiators can be used either alone or as a mixture. The rate of decomposition of peroxides which decompose at high temperatures can be reduced by using organic metal complexes, such as copper acetylacetonate, so that the decomposition rate of the peroxides can be adapted to the particular polymerization temperature chosen. The polymerization initiators are used in an amount of from 0.01 - 5%, preferably from 0.2 - 3%, by weight, based on the monomers used in the polymerization.

For the polymerization, the monomers are dissolved in water, the monomer concentration in the aqueous solution being from 10% by weight to the saturation concentration, preferably from 30% by weight to the saturation concentration. The aqueous solution is then suspended in an aliphatic hydrocarbon. Suitable aliphatic hydrocarbons are C_5 - C_{10} alkanes, e.g. pentane, n-hexane, cyclohexane, heptane, n-octane, isooctane, nonane and decane, as well as mixtures of aliphatic hydrocarbons. The aliphatic hydrocarbon preferably used as the oil phase in the inverse suspension polymerization is cyclohexane. The weight ratio of the aqueous phase to the oil phase in the inverse suspension polymerization is from 1:9 to 7:3.

In order to disperse the aqueous monomer solution in the aliphatic hydrocarbon, inorganic suspending agents based on modified finely divided minerals or nonionic surfactants are required. The inorganic suspending agents, which have a low hydrophilic-lipophilic balance (HLB), are the agents conventionally used in inverse suspension polymerization processes. The mineral component of these substances is formed for example, by bentonite, montmorillonite or kaolin. The finely divided minerals are modified by treating them with salts of long-chain amines, e.g. C_8 - C_{24} amines or quaternary ammonium salts, the amine salts or the quaternary ammonium salts being incorporated

between the individual layers of the finely divided minerals. The unquaternized or quaternized ammonium salts used for the modification preferably contain 1 or 2 $C_{10}-C_{22}$ alkyl radicals. The other substituents of the ammonium salts are C_1-C_4 alkyl or hydrogen. The content of free ammonium salts in the amine-modified minerals is not more than 2% by weight. Finely divided minerals modified with ammonium salts are commercially available.

The inorganic suspending agents for the inverse suspension polymerization also include silica which has been reacted with organosilicon compounds. A suitable organosilicone compound is, for example, trimethylsilyl chloride.

The object of modifying the finely divided inorganic minerals is to improve the wettability of the minerals with the aliphatic hydrocarbon used as the outer phase of the inverse suspension polymerization. In the case of the natural minerals having a layer structure, e.g. bentonite and montmorillonite, modification with amines results in the modified minerals swelling in the aliphatic hydrocarbon and thus disintegrating into very fine particles. The particle size is about $1\ \mu\text{m}$, in general from 0.5 to $5\ \mu\text{m}$. The silicas reacted with organosilicon compounds have a particle size of from about 10 to 40 nm. The modified finely divided minerals are wet by both the aqueous monomer solution and the solvent and consequently accumulate at the phase boundary between the aqueous phase and the organic phase. They prevent coagulation when two aqueous monomer droplets collide in the suspension.

The stability of water-in-oil suspensions which contain a modified finely divided mineral as the suspending agent and an aliphatic hydrocarbon as the oil phase can surprisingly be increased

by adding from 0.1 to 5% by weight, based on the monomers used, of a nonionic surfactant, so that the polymerization batches do not undergo coagulation or agglomeration.

The nonionic surfactants which are used in the inverse suspension polymerization process have an HLB value of from 2 to 16. Examples of suitable nonionic surfactants are C_8 - C_{12} alkylphenols which are oxyalkylated with ethylene oxide and/or propylene oxide. Examples of commercial products are octyl- and nonylphenols which have been reacted with from 4 to 20 moles of ethylene oxide per mole of phenol. Other nonionic surfactants which are used according to the invention are oxyethylated C_{10} - C_{24} fatty alcohols and/or polyhydric C_3 - C_6 alcohols which are partially esterified with C_{10} - C_{24} fatty acids. These may additionally be reacted with from 2-20 moles of ethylene oxide. Examples of suitable fatty alcohols are palmityl alcohol, stearyl alcohol, myristyl alcohol, lauryl alcohol, oxo alcohols and unsaturated alcohols, e.g. oleyl alcohol. The fatty alcohols are oxyethylated to such a degree that they are soluble in water. In general, 1 mole of alcohol is reacted with from 2-20 moles of ethylene oxide in order to obtain surfactants having the HLB value stated above.

Examples of C_3 - C_6 alcohols which are partially esterified and may be oxyethylated are glycerol, sobitol, mannitol and pentaerythritol. These polyhydric alcohols are partially esterified with C_{10} - C_{24} fatty acids, e.g. oleic acid, stearic acid or palmitic acid. The esterification with the fatty acids is carried out so that one or more OH groups of the polyhydric alcohol remain unesterified. Examples of suitable esterification products are sobitan monooleate, sorbitan tristearate, mannitol monooleate, glycerol monooleate and glycerol dioleate. The stated fatty acid esters of polyhydric alcohols, which may contain one or more free OH groups, can then be

reacted with ethylene oxide and/or propylene oxide. From 2 to 20 moles of ethylene oxide are used per mole of fatty acid ester. The degree of oxyethylation is known to affect the HLB value of the nonionic surfactants. By a suitable choice of the oxyethylation, it is possible to prepare surfactants which have a HLB value in the stated range. The nonionic surfactants can be used either alone or as a mixture with one another. This permits a large number of possible variations; for example, it is possible to employ surfactants having different degrees of oxyethylation, or oxyalkylated phenols together with oxyethylated fatty alcohols or oxyethylated fatty alcohol derivatives. From 0.2 to 3% by weight, based on the monomers used in the polymerization, of a nonionic surfactant are preferably used for stabilizing the suspension.

As is usual for polymerization processes, the inverse suspension polymerization is carried out in the absence of oxygen, preferably in a nitrogen atmosphere. The polymerization is carried out at from 35 to 100 °C under reduced or superatmospheric pressure. The polymerization is most simply carried out at the boiling point of the particular aliphatic hydrocarbon or of the particular aliphatic hydrocarbon mixture. In carrying out the polymerization, a water-in-oil suspension can first be prepared from the aqueous monomer solution and the aliphatic hydrocarbon. In this procedure, the inorganic suspending agent and the nonionic surfactant are used to promote dispersing of the aqueous solution in the hydrocarbon oil. The inorganic suspending agent and the nonionic surfactant can be added both to the aqueous monomer solution and to the aliphatic hydrocarbon. However, it is also possible to adopt a procedure in which the aliphatic hydrocarbon, the inorganic suspending agent and the nonionic surfactant are initially taken in a polymerization vessel, and an aqueous monomer solution is added with vigorous mixing so that a water-in-oil suspension is formed. The polymerization can then take

place. In another polymerization procedure, only one part of the aqueous monomer solution is first dispersed in the aliphatic hydrocarbon, the polymerization is initiated, and the aqueous monomer solution is then run in at the rate at which the polymerization progresses. In this procedure, a water-in-oil polymer suspension forms above a water-in-oil monomer suspension. This gives bead polymers which have a particle size of from 1 μm to 2 mm, preferably from 50 μm to 1 mm, depending on the reaction conditions. When the polymerization is complete, the water-containing bead polymers can be isolated (for example by filtration or centrifuging) from the water-in-oil polymer suspension. However, the bead polymers, which still contain water from the preparation, can first be dried (for example by means of azeotropic distillation) and then separated off from the aliphatic hydrocarbon.

Depending on the polymerization conditions and the monomers used, the polymers obtained have different molecular weights, which are characterized by the K value. The Fikentscher K values are from 50 to 300 (measured in 5% strength aqueous sodium chloride solution at 25 °C and at a polymer concentration of 0.1%). The low molecular weight polymers are useful, for example, as sizes. High molecular weight polymers are used as flocculants, for example water-soluble polymers of acrylic acid and of acrylamide, copolymers of acrylic acid and acrylamide or copolymers of acrylamide and dimethylaminoethyl acrylate hydrochloride. Crosslinked polymers, for example copolymers of acrylic acid and methylenebisacrylamide, are used either as thickeners in printing pastes or as a water-absorbing material in diapers, depending on the degree of crosslinking. In order to achieve rapid water absorption during use as an absorbent for water, the bead polymers can be dusted with finely divided inorganic materials, e.g. bentonite, montmorillonite, kaolin, china clay and silica as well as

with a thermally treated synthetic silica. Amounts as small as 0.2% by weight, based on the bead polymer, are sufficient to increase the rate of water absorption of the polymer compared with the untreated material.

Contrary to the case of conventional suspension polymerization where the polymerization mechanism is relatively well understood, no quantitative theory has actually been offered to date for the inverse polymerization process(12).

Dimonie, M.V., and et.al.(13) investigated the persulfate initiated polymerization of acrylamide in the presence of low emulsifier concentration (a nonionic surfactant, ethoxylated stearic acid, with 8 mole of ethylene oxide, 5-6 wt% based on the continuous phase, white spirit). They proposed an inverse suspension process with the following reaction steps as shown in Figure 2.3. First a water-in-oil type emulsion is formed (possibly a double emulsion, i.e., the organic medium can be microemulsified in an aqueous medium and

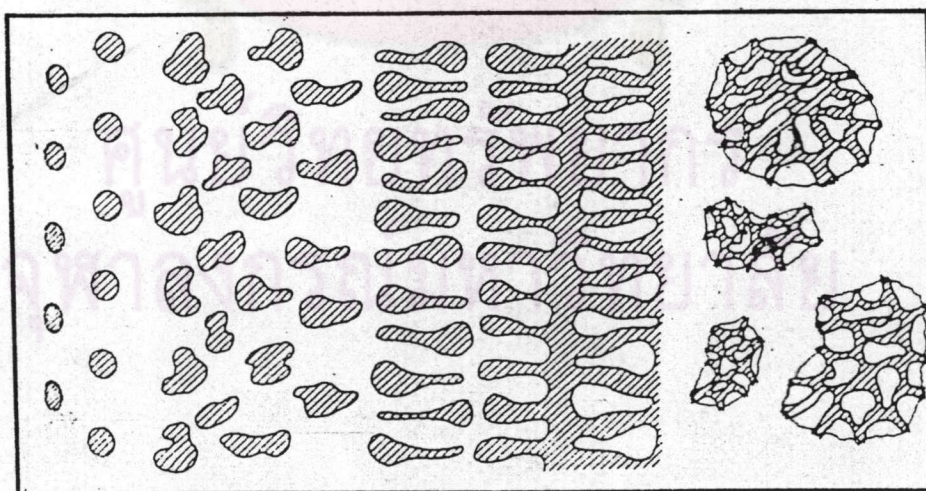


FIGURE 2.3 Schematic representation of acrylamide polymerization in inverse suspension.

(The figure is reproduced from Reference 14.)

this latter emulsified in turn as drops in an organic medium) which is unstable and tends to separate when stirring is stopped. Following the start of the reaction, the inversion of phases occurs (the monomer containing in aqueous phase becomes the continuous phase) and is accompanied to a marked increase in the viscosity of the medium which attains the consistency of a gel whose properties are those of a viscoelasticity. At higher conversion, under stirring, the gel breaks into small particles ranging from 0.5 to 1.5 mm in size, which remain as such at the end of the polymerization reaction(14).

2.5 Literature Survey

Recent works on the synthesis of water absorbing polymers by inverse suspension polymerization are listed below.

Aoki, S., and Yamasaki, H.(15) manufactured self-crosslinked alkali acrylate homopolymers which had a water absorption of 500 g/g dry polymer by dispersing a 40% aqueous solution of alkali acrylate containing a water-soluble radical polymerization initiator in hexane and polymerizing for 6 hours at 60-65°C in the presence of a sorbitan fatty acid ester with an HLB value of between 3-6, without an addition of a crosslinking agent. The product was easily powdered, nontacky when wet and had a pH of 7.4 in a form of 0.25% slurry.

Obayashi, S., and his coworkers(16) synthesized an alkali metal acrylate polymer by suspending an aqueous solution of acrylic acid and an alkali metal acrylate in cyclohexane containing a surfactant with an HLB value of between 8-12 and inverse suspension polymerizing the mixture in the presence of a water-soluble radical catalyst. The suspension was polymerized for 3 hours at 55-60°C to give a granular polymer with absorbency in deionized water of 1250

times its weight and in saline solution 120 times its weight. After 5 minutes in deionized water or saline, the absorbency was 300 and 25 times its weight respectively. The polymer showed no change in absorbency during long storage in the powdery state.

In 1981, Kao Soap Co., Ltd. (17,18) patented the synthesis of water-absorbing self-crosslinked polymers from acrylic acid by inverse suspension polymerization at 60-65°C for 3 hours, using potassium persulfate ($K_2S_2O_8$), hexane and sorbitan monostearate as an initiator, dispersing medium and emulsifier, respectively. The processes gave powdered copolymers having good absorption of 0.9% NaCl solution.

Polymers showing fast water absorption were prepared by polymerizing α,β -unsaturated carboxylic acids and/or their alkali metal salts with or without crosslinking agents in water-in-oil suspensions in the presence of nonionic surfactant having an HLB of between 6-9. The process revealed by Sumitomo Chemical Co., Ltd. (19) was carried out by dispersing a composition of water 30 parts, NaOH 6.7 parts, acrylic acid 15 parts, $K_2S_2O_8$ 0.0522 parts and 0.0085 parts of N,N'-methylenebismaleimide in a mixture of 0.9 parts sorbitan monolaurate (HLB 8.0) and 66 parts hexane at 60°C and stirring for 3 hours at 60°C to give copolymer beads having an average diameter of 20 μ and water absorption of 620 g/g in 12 seconds, compared with 50 μ diameter and water absorption of 500 g/g in 38 seconds, for a similar product prepared in the presence of sorbitan monostearate (HLB 5.1).

Polymers with high water absorption velocity were also developed by Sumitomo Chemical Co., Ltd. (20). Crosslinked poly(acrylic acids) and/or their alkali metal salts were contacted with mixtures of hydrophobic solvents and H_2O , separated from the solvents, dried, and pulverized to give polymers with a high rate of H_2O absorption.

For example, 6.7 parts NaOH in 30 parts H_2O was mixed under ice cooling with acrylic acid 15 parts, $K_2S_2O_8$ 0.052 parts, and 0.0085 parts of N,N'-methylenebisacrylamide, and polymerized for 3 hours at $60^\circ C$ with 0.9 parts of sorbitan monolaurate and 66 parts of hexane. The polymer was separated from hexane, mixed with 0.5 parts of poly(oxyethylene nonylphenyl ether) with an HLB value of 14.5, dried, and pulverized. The powders (177-250 μ grain size) had 620 g/g H_2O absorption within 10 seconds.

Makita, M. and Maeno, J. (21) prepared acrylic water absorbents which are useful as sanitary articles and in agriculture by inverse suspension polymerization of aqueous solutions of alkali salts of acrylic acid containing water-soluble polymerization initiators in hydrophobic organic solvents, optionally containing dispersing agents, using protective colloid copolymers and copolymerizable monomers. The polymer beads have water absorbency of 720 and 65 g/g for deionized water and 0.9% aqueous NaCl, respectively.

Makita, M., and Maeno, J. (22) also patented a process for preparing a highly water-absorbent resin by an inverse suspension polymerization method using an aqueous solution of a monomer containing an alkali metal salt of acrylic or methacrylic acid, water-soluble polymerization initiator, protective colloid, hydrophobic organic solvent and dispersing agent.

Cramm, J.R. and Bailey, K.M. (23) improved a process for producing an alkali metal acrylate or ammonium acrylate polymer having excellent salt solution absorbency of the type characterized by suspending an aqueous solution of acrylic acid and an alkali metal acrylate or ammonium acrylate, the mole ratio of the acrylic acid to the alkali metal acrylate or ammonium acrylate being 50/50 to 2/98, in

an alicyclic or aliphatic hydrocarbon solvent containing a surfactant having an HLB value of 8-12, subjecting the resulting suspension to inverse suspension polymerization in the presence of a water-soluble radical polymerization initiator and, if necessary, crosslinking the resulting polymer with a crosslinking agent, the improvement which comprises conducting the polymerization in the presence of a water-soluble chain transfer agent.

Cabestany, J. (24) developed water-insoluble hydrophilic acrylic acid-alkali metal acrylate copolymers, with a water absorption capacity of 650 g/g and physiological saline solution absorption capacity of 60 g/g by inverse suspension polymerization.

Han, Y-K and et al. (25) synthesized acrylic-acid based high-water absorbing polymers by inverse suspension polymerization of acrylic acid and followed by crosslinking reaction in a bench scale. The water absorbency of the polymer had several hundred times its weight. When the polymer was used as a soil conditioner in the pot and field test, both growth rate and harvest of crops such as soybean and red pepper were increased about 30 to 80% compared with the conventional seeding method depending on the class of soil and the concentration of the polymer added. This is considered to be due to the increase of water retention of soil, which helps the seed germination and growth.