# CHAPTER 2

# THEORY AND LITERATURE REVIEW

## 2.1 Superabsorbent Polymers (SAPs)

The materials that their absorbing capacity is greater than 15 times their own weight in the aqueous fluids, water, electrolyte solution, including synthetic urine, brines, and biological fluids such as urine sweat, and blood have so many called-names as superabsorbent polymers, (SAPs), or hydrogel, or water containing gels, or highly water absorbing polymers, (HWAPs), etc. Not only they are high fluid absorbing capacity, but the absorbed fluid is hard to release also, as they merely immobilize the fluid by entrapment rather than by holding it in their structure [5]. They are polymers which were characterized by hydrophilicity, insolubility in water [6], and cross-linked polyelectrolytes. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving [7].

Many kinds of SAPs have been commercialized since the hydrolyzed starch-polyacrylonitrile graft copolymer, superslurper was first developed by the Northern Regional Laboratory of the United States Department of Agriculture in the early 1970's. They are widespreadly applied not only in the fields of personal care products, biosorbent, bio-materials, but also in agriculture and industrial applications, and for many of them, dealing with leaking water is also a common theme. For example, leaking water is often a problem in the construction industry. One new product is a sealing composite that swells slightly in water. It is made by blending a superabsorbent powder into rubber with the aid of a surfactant-like substance [4]. Leaking water can also degrade the performances of fiber optic communication cables and power transmission cables [8]. Water-blocking tapes, made by applying a superabsorsbent polymer and a polymeric binder onto a non-woven fabric were wrapped around the cable, beneath the plastic covering, and intercept any water that gets through them [9].

In addition to their liquid-water absorption characteristic, super-absorbents can absorb and release moisture from the air more effectively than silica gel. This property can be used to prevent damage due to moisture condensing on walls and ceilings in humid buildings, help maintain a constant humidity in vegetable and fruit storage buildings, and prevent spotting of the produce caused by water dripping from the surface of the structure. They have been developed to be superabsorbent sheets or superabsorbent fiber. Not only that but they can also help conserve water in agriculture and horticulture and improve the air content of the clay soil [4].

As mentioned above, SAPs have been mainly used and developed only in the limited field of disposable absorbing materials such as diaper and sanitary napkin, in recent their applications are being extended into others industrial areas as shown in concluding Table 2.1 [5].

Generally, SAPs are classified into the four categories as shown in Table 2.2 [5]. By the raw materials, SAPs are divided into starch and cellulose based polymers and synthetic polymers. The physical properties of SAPs are dependent upon the methods of insolubilization and hydrophilization introduced into the SAPs and upon the appearance of products, powder, film, and fiber.

TABLE 2.1

APPLICATIONS OF SAPs [5]

1. Disposable Absorbing Materials:
    - Sanitary Napkins,
    - Diapers for Infants & Adults,
    - Medical Sheets,
    - Paper Towel & Non woven.
2. Agriculture & Horticulture:
    - Soil Conditioners for Water Retention,
    - Coatings for Seed Germination,
    - Hydro-Mulching Formulations.
3. Industries:
    - Dehydrating Agents for Fuels,
    - Blocking Agents for Underground Cables,
    - Sludge Dewatering,
    - Sealing Gaskets.
4. Others:
    - Swellable toys,
    - Fire Fighting Fluids

TABLE 2.1

APPLICATIONS OF SAPs [5] (continued)

4. Others(continued):
    - Wallpapers for Humidity Control,
    - Ice pack,
    - Debris Flow Control [4],
    - Artificial Snow [4],
    - Gel Actuators [4],
    - Matrices for Controlled release devices [10].

TABLE 2.2

CLASSIFICATION OF SAPs [5]

1. By Raw Materials
    a) Starch grafts, carboxymethylated.
    b) Cellulose graft, carboxymethylated.
    c) Synthetic polymer : poly(acrylic acid), poly(vinyl alcohol) poly(oxymethylene)
2. By Method on Insolubilization
    a) Graft polymerization.
    b) Chemical Cross-linking.
    c) Self-cross-linking.
    d) Radiation cross-linking.
    e) Introduction of crystalline structure or hydrophobic groups.

TABLE 2.2

CLASSIFICATION OF SAPs [5] (continued)

3. By Method of Hydrophilization
    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.
4. By Product Form
    a) Powder.
    b) Film.
    c) Fiber.

Because SAPs belong to the group of hydrogel, which can be further classified as shown in Table 2.3 [11].

TABLE 2.3

CLASSIFICATION OF HYDROGELS [11]

1. By Hydrogels' charge
    a) neutral hydrogels;
    b) anionic hydrogels;
    c) cationic hydrogels;
    d) ampholytic hydrogels.
2. By Method of preparation
    a) homopolymer networks;
    b) copolymer networks;
    c) multi-polymer networks;
    d) interpenetrating polymeric networks.
3. By Physical structural features of the system
    a) amorphous hydrogels;
    b) semi-crystalline hydrogels;
    c) hydrogen-bonded structures;
    d) super-molecular networks structures;
    e) hydrocolloidal aggregates.
4. By their mechanical and structural characteristics
    a) affined networks;
    b) phantom networks.

Commercially available products are summarized in Tables 2.4-2.5. In a point of view by the raw materials used, cross-linked polymers of partially neutralized acrylic acid and graft copolymers of cross-linked poly(acrylic acid) and starch are the most popular in use worldwide [5].

TABLE 2.4

COMMERCIALLY AVAILABLE PRODUCTS [5]

| Maker | Trade Name | Composition | Form |
|---|---|---|---|
| **Japan** | | | |
| Sanyo Kasei | SUNWET | HSPAA, PAA | Powder |
| Seitetsu Kagaku | AQUAKEEP | PAA | Powder |
| Kao | TURFINE | PAA | Powder |
| Sumitomo Kagaku | SUMIKAGEL | PVA-b-PAA | Powder |
| | | PEO | Powder |
| | IGETAGEL P | Vinyl alcohol | Powder |
| | | Sodium polyacrylate | Powder |
| Arakawa Kagaku | ARASORB | PAA | Powder |
| Nippon Shokubai | AQUALIC | PAA | Powder |
| | ACRYHOPE | PAA | Powder |
| Kurareisoprene | KI gel | MA-co-IB | Powder |
| Exlan | LANSIL | HPAN | Fiber |
| Nippon Synthetic Chemical Industry | MIZUMOCHI ICHIBAN | PVA | granules & powder |
| Mitsubishi Petrochemical | DIAWET | PAA | granules |
| Kurita Water Industries | GRASSPOWER | PAA | granules |
| Meisei Kagaku | AQUAPLEN P 840 | PEO | granules |
| **USA** | | | |
| Dow Chemical | DRYTECH | PAA | Powder, film |
| Grain Processing | WATER-LOCK | HSPAN | Powder |
| Hercules | AQUALON | CMC | Fiber |

## TABLE 2.4

## COMMERCIALLY AVAILABLE PRODUCTS [5] (continued)

| Maker | Trade Name | Composition | Form |
|---|---|---|---|
| **EUROPE** | | | |
| BASF | LUQUASORB | PAA | Powder |
| Stockhausen | FAVOR | PAA | Powder |
| Enka | AKUCELL | CMC | Fiber |

HSPAA : Hydrolyzed Starch-Poly(acrylic acid) Graft Copolymer
HSPAN : Hydrolyzed Starch-Polyacrylonitrile Graft Copolymer
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

Many water insoluble gel-forming polymers are known for their usefulness as absorbents because of their ability to imbibe and bind or immobilize aqueous fluids. These polymeric materials find applications in industry for various de-watering and fluid immobilization uses, such as water retaining agents in agricultural/horticultural fields, dehydrating of oil, and like purposes. In recent years absorbent polymer having large capacities for absorbing aqueous fluids have been developed and found use in personal care product for absorbing aqueous biological fluids. In a typical personal care product, such as a diaper, the aqueous fluid absorbent polymer is utilized in a powder form, and is often mixed with cellulosic fibers that help initially absorb and distribute the fluid load. The

## Table 2.5

## Major superabsorbent polymers and their features

| Name | Manufacture | Major components | Absorbent capacity (cc/g) | | Remarks |
|---|---|---|---|---|---|
| | | | Pure water | 1% saline solution | |
| Turfine KP 6201 | Kao | Poly(acrylic acid) | 400 | 60 | White powder |
| Mizumochi ichiban | Nippon Synthetic chemical Industry | Poly(vinyl alcohol) | | | |
| OKS 7703 | | | 150 | 25 | Pale yellow granules |
| OKS 7702 | | | 150 | 25 | Pale yellow powder |
| KI gel 201 K | Kuraray | Isobutylene Maleic anhydride | 200 | 56 | White powder |
| Sunwet | Sanyo Chemical Industries | Starch Poly(acrylic acid) | | | |
| IM 1000 | | | 1,000 | 80 | White powder |
| IM 1000 BG | | | 1,000 | | White granules |
| IM 1500 BG | | | 500 | | White granules |
| Igetagel P | Sumitomo Chemical | Vinyl alcohol Sodium polyacrylate | 500 | 50 | Pale wellow spherical powder |
| Arasorb G KR 713 | Arakawa Kagaku | Poly(acrylic acid) | 650 | 80 | White powder |
| Acryhope GH-1 | Nippon Shokubai | Sodium polyacrylate | 300 | 30-40 | Pale yellow particles |
| GH-5 | | | 600 | | White granules |

## Table 2.5

## Major superabsorbent polymers and their features (continue)

| Name | Manufacture | Major components | Absorbent capacity (cc/g) | | Remarks |
|---|---|---|---|---|---|
| | | | Pure water | 1% saline solution | |
| Acryhope CS | Nippon Shokubai | Sodium polyacrylate | 200 | | Pale yellow powder |
| Diawet BA | Mitsubishi Petrochemical | Poly(acrylic acid) | 500 | 50 | White granules |
| Grasspower G 200 | Kurita Water Industries | Poly(acrylic acid) | 250 | 30-40 | Sloghtly yellowish granules |
| Aquaplen P 840 | Meisei Kagaku | Poly(etylene oxides) | 40 | 38 | White granules |
| Gelfine 107 | Daical Chemical Industries | Cellulose | 600 | 50 | White powder |
| Aquakeep 4S | Seitetsu Kagaku | poly(acrylic acid) | 400 | 40 | White powder |

water absorbent compositions may be made from a variety of polymers or copolymers. Basically, any water-soluble ethylenically unsaturated monomer or mixture thereof that cross-links to form a substantially water insoluble gel or particle is suitable. Cross-linked structures may be obtained by the copolymerization of a water soluble monomer, and a cross-linking monomer possessing at least two polymerizable double bonds in a molecular unit. The polymeric materials of interest such products are based upon a variety of polymers including those derived from water soluble ethylenically unsaturated monomers or graft polymers in which unsaturated monomers are graft polymerized onto a polysaccharide (such as starch or cellulose) or other polymeric backbone [12]. Examples of such polymer are cross-linked, partially neutralized, polymers, and copolymers of acrylic acid, starch grafted polymers, and copolymers of acrylic acid polymers, starch-polyacrylonitrile grafted polymers [13], a saponification product of a vinyl acetate/ an acrylate ester copolymer, a hydrolyzate of an acrylonitrile copolymer, and a hydrolyzate of an acrylamide copolymer [14].

In general, water-soluble monomers include ethylenically unsaturated amides such as acrylamide, methacrylamide, and fumramide as well as their N-substituted derivatives. Ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, and crotonic acids and their salts are preferred. Suitable poly(carboxylic acids) include maleic acid, fumaric acids, and itaconic acid. Preferred ethylenically unsaturated carboxylic acid esters include hydroxyethylacrylate, hydroxyethylmethacrylate, and esters of acrylic and methacrylic acids with poly(ethylene oxide). Vinyl amines such as vinyl pyridine and vinyl morpholine, and diallyl amines are also useful.

The ethylenically unsaturated monomer may be partially neutralized as set forth below. In such cases, the monomer mixture will further comprise a salt of the ethylenically unsaturated monomer. The monomer mixture may also include components that graft polymerize onto one or more other additional monomers of the monomer mixture. Polysaccharides, such as starch and cellulose are examples of graft-polymerizable components. Particularly suitable is a graft-polymerizable poly(vinyl alcohol). Not only that, poly(styrene sulfonic acid), PSSA can be used also. This PSSA is a strong acid, which ionizes completely in aqueous solution, very hygroscopic, reactive and decomposes on storage. Therefore, the polymer is normally stored as the Na or K salt.

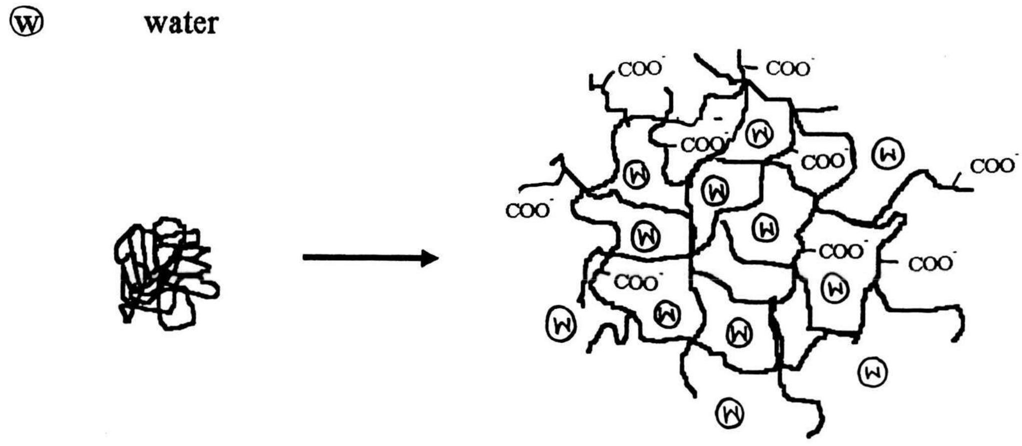
The monomer mixture typically includes one or more cross-linking monomer which comprises organic compounds having two or more ethylenic groups copolymerizable with the water-soluble monomers of the monomer mixture. Exemplary cross-linking monomers include diacrylate or dimethacrylate of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, trimethylol propane and pentaerythritol, triacrylates or tetramethacrylate of pentaerythritol, N,N′-methylenebisacrylamide, N,N′-methylenebis-methacrylamide, and triallyl isocyanurate. Preferred cross-linkers include methylenebisacrylamide, trimethylol propanetriacrylate and diethlene glycol diacrylate and tetraethylene glycol diacrylate [12].

The synthetic polyacrylates derived from acrylic acid, and the graft copolymers from starch and acrylic acid have emerged as the absorbent polymers of choice. This is in no small part due to economic factors, at a glance at any chemical marketing periodical will show acrylic acid as one of the least expensive water soluble monomers. In addition, the properties of acrylic acid make it relatively easy to polymerize, and to polymerize to products of high molecular weight.

Superabsorption acrylic polymers belong to the group of hydrogel, i.e. water-retaining gel, which are water insoluble polymers with a high hydrophilicity resulting from hydrophobic groups such as -OH, -COOH, $-CONH_2$, -CONH-, $-SO_3H$, and -COONa, etc. present in the main chain. The high molecular linear chain is sparsely cross-linked with covalent bonds but, additionally, with hydrogen bonds and Van der Walls forces. Water may freely enter into the polymer structure, which swells up to a volume equilibrium [15]. The insolubility and stability of shape are due to the presence of three-dimensional network. The swollen state results from a balance between the dispersing force acting on hydrated chains and cohesive force, that do not prevent the penetration of water into the network. Cohesive forces are most important often due to covalent cross-linking. Others are electrostatic, hydrophobic, or dipole-dipole in character. The degree and nature of cross-linking and the tacticity and crystallinity of the polymer are responsible for its characteristics in the swollen state [6].

As illustrated in Figure 2.1, the polymer, in the absence of water, has its long, high molecular chains intertwined with each other. These chains join with each other at certain points (to form a three-dimensional structure), forming a closely-bound molecule as a whole. If this polymer, which has hydrophilic group (-COO-) on its individual chains, is placed in water, it starts to expand for dissolution in water. Concurrently, these hydrophilic groups, which are negative ions, repel each other, helping the polymer expand further.

Such expansion of the polymer allows its chains to be completely diffused in water, making it soluble in water as a water-soluble, high molecular compound. The polymer, however, has a three-dimensional structure which allows it to expand only to a certain point, at which it stops expanding in a state similar to that of an expanded fishing net. The opening of the resultant net holds water to provide the polymer with a highly water absorbing power. This actually appears as a swelling of visible particles in water, which are formed by gathering of an infinite number of high polymers as shown in Figure 2.1, [6].



1. Before water absorption

2. After water absorption

Figure 2.1 Diagram of water absorption [6].

Figure 2.2 [16] shows that the driving force for polyacrylate networks that enable them to absorb huge amounts of aqueous solution. In contact with water the hydrophilic polymer backbone, containing hydrophilic functional groups, interacts with the solvent accompanied by energy decrease and entropy increase. Hydration and the formation of hydrogen bonds are two sources for such polymer/solvent interactions. The polymer chains also tend to disperse in the given volume of solvent. This leads to a higher number of allowed configurations for the system, which is equivalent to a higher degree of entropy.

Due to the presence of the cross-links the polymer chains are restricted in swelling by elastic retraction force of the network. The more of chains separate from each other, the more stiffened the originally coiled polymer chains become. This decrease the entropy of the chains. Finally there is a balance between the trend toward infinite dilution of the chains and the retractive forces. Higher cross-link densities give networks with stronger retractive forces and superabsorbent polymer with lower degrees of swelling at equilibrium.

For ionic polymers the solvent/polymer interactions include more than a simple mixing term. These gels bear electrical charges along the polymer chains. The negative charge of the carboxyl groups repel one another and are compensated for by the positive charge of the sodium ions, in order to maintain electrical neutrality. When the polymer comes into contact with water, the solvent diffuses into the polymer network and solvates the sodium ions. Water with its high dielectric constant lowers the attractive forces between the sodium ions and the negatively charged carboxylate groups. As in solutions of simple salts, the sodium ions are released and become freely moveable within the gel.

Hence they contribute to the osmotic pressure. But for them it is impossible to leave the gel region due to the attraction forces of the negative charges, which are fixed along the polymer backbones. The sodium ions therefore behave as if trapped by an invisible, semi-permeable membrane. The driving force for swelling is then the difference between the osmotic pressure in- and outside of the gel. Increasing the salinity and by this the osmotic pressure of any external aqueous solution lowers the absorption capacity of the gel for the fluid.

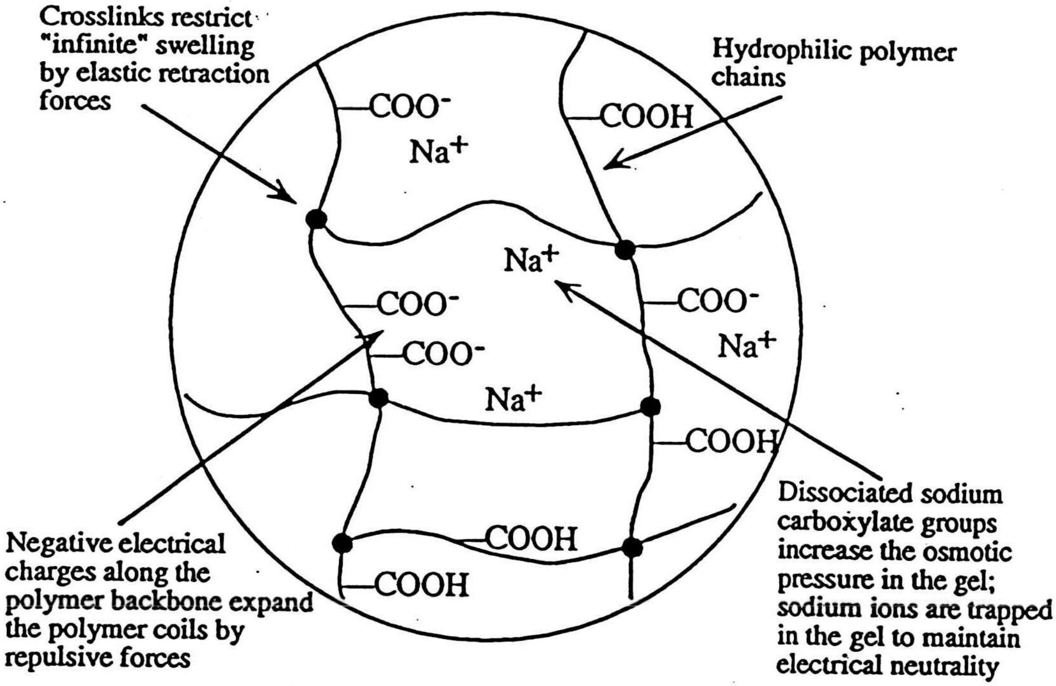


Figure 2.2 Mechanism of swelling of superabsorbent polymers [16].

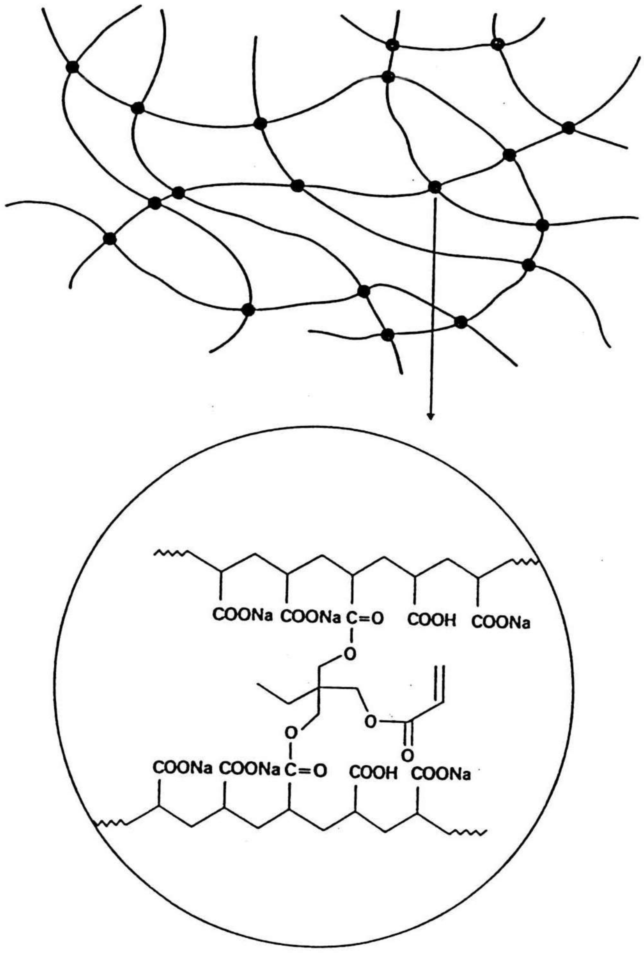


Figure 2.3 The cross-linked, network structure of superabsorbent polymer and structure of cross-linking (in detail) [17].

Therefore, the absorbency is mainly dependent upon three factors [5]:

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 cross-linkage affecting the degree of swelling of polymer.

The absorbency (Q) can be expressed by the Flory's equation [5] shown below.

$$Q^{5/3} = \left( (I / 2V_u S^{*1/2})^2 + (\tfrac{1}{2} - X_1) / V_1 \right) (\upsilon_c / V_0) \qquad (2.1)$$

Where, $I$ = degree of ionization of polymer electrolyte

$S^*$ = ionic strength of salt solution added

$(\tfrac{1}{2} - X_1) / V_1$ = affinity between ionic network and the absorbed water

$V_u$ = molar volume of polymer repeating unit

$\upsilon_c / V_0$ = cross-linking density

Figure 2.4 shows the relationships between the absorbency(Q) and the factors mentioned above.

The important physical properties of absorbent polymers depend on the precise structure of the polymer network. Of key importance for use in personal care applications are the equilibrium swelling capacity, the rate of swelling and the modulus of the swollen gel. These properties of the product both are related to the cross-link density of the network : modulus increases and swelling capacity decrease with increase cross-link density [11].

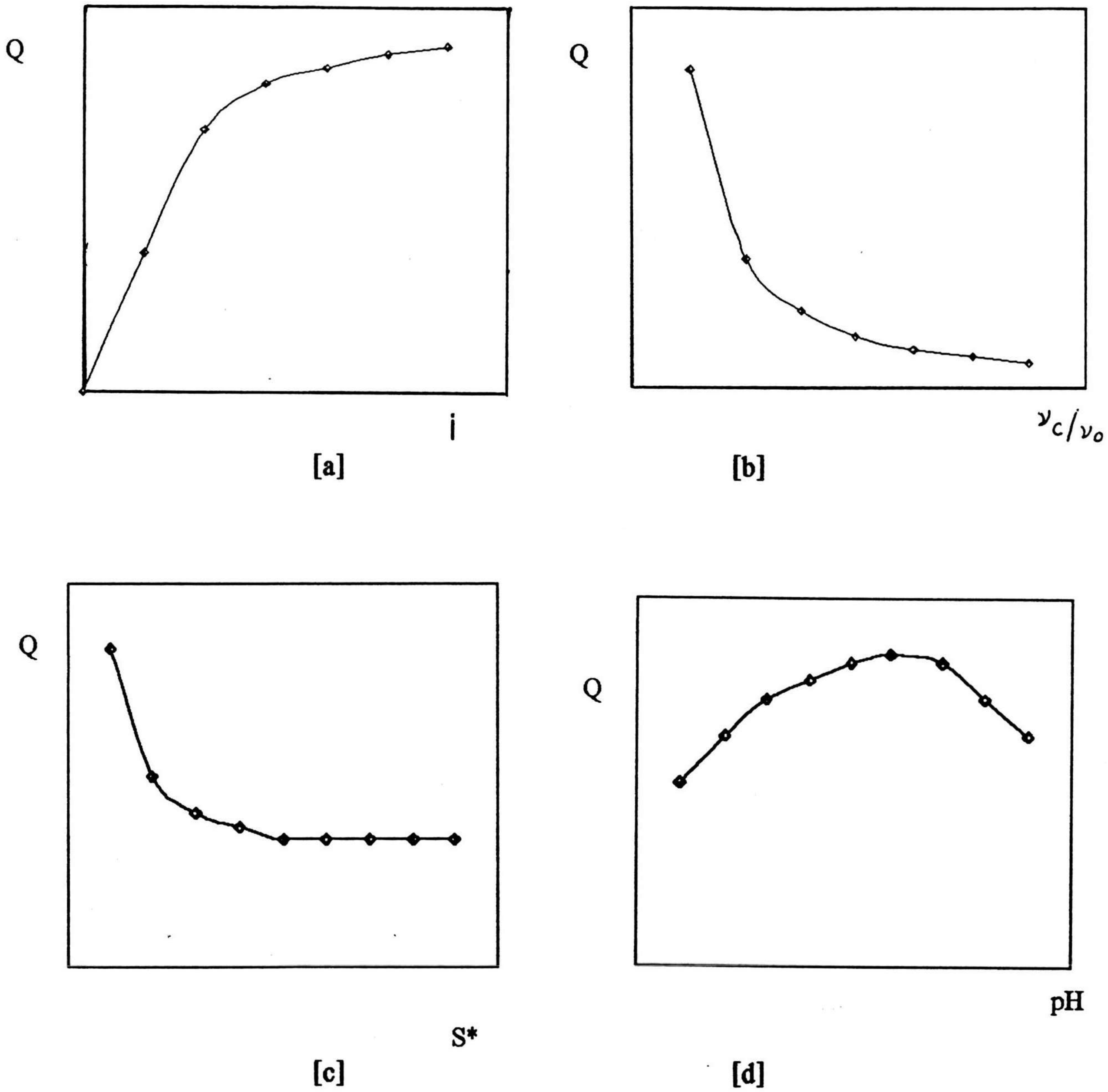


Figure 2.4 Relationships between swelling degree [5]

[a] with ionization degree of polymer electrolyte

[b] with cross-linking density of polymer network

[c] with ionic strength of salt solution

[d] with pH of polymer solution

## 2.2 Polyacrylates by Free Radical Chain Polymerization

The structure of the polymeric network is ultimately determined by the method of synthesis. The monomer and cross-linker concentrations, the initiator type and concentrations, the relative reactivities of the monomers, the specific solvent and reaction temperature are all significant factors. Commercially, the rate of the polymerization reaction is also of importance, since it directly affects the volumetric efficiency of the production equipment. Fortunately, many of the important structural parameters are determined by the polymerization kinetics and by the various stoichiometries of the reaction.

The kinetics of the free radical chain polymerization are well understood. In general, very small concentration of free radicals are generated by any number of chemical or photochemical reactions, which then initiate the polymerization by reacting with the carbon-carbon double bond present in the monomer. The original radical-containing fragment is added to the double bond, generating a single bond and a new free radical. This radical quickly adds to another monomer molecule, and another, in the propagation step. Finally, the new macromolecular radical reacts with another macromolecular radical to stop, or terminate, the kinetic chains. The entire process is generally complex because many radicals from different sources are present at any time, giving the possibility of many different termination reactions, which affect the polymer structure.

The derivation of the kinetics of individual steps of free radical polymerization is available. Key results give the rate of polymerization in terms of the concentrations of monomers and initiators, for bimolecular termination [1]:

$$R_p = k_p [M] \{ f k_d[I] / k_t \}^{1/2} \qquad (2.2)$$

(for polymerization with thermal initiator)

$$R_p = k_p [M] [\underline{(f k_d[\text{oxidant}][\text{reductant}])} / 2 k_t]^{1/2} \qquad (2.3)$$

(for polymerization with redox initiators)

$R_p$ is the polymerization rate, $k_p$ is the rate of constant for the propagation step, $k_d$ is the rate constant for initiator decomposition, $k_t$ is the rate constant for the termination step, [M] is monomer concentration, f is efficiency factor for the initiators and [I], [oxidant], and [reductant] are concentrations of the initiators. The general first-order dependence of rate on monomer concentrations is altered when the macroradicals are terminated by radicals directly formed from the initiator, and when the monomer is involved in the initiation step.

In any free radical chain polymerization, a given initiator radical will start a polymer chain which will propagate until it is terminated by another radical. The conditions of solvent, type of monomer, temperature, additives and impurities will determine how long the chain will grow. This length is the kinetic chain length. Derivation of the kinetic chain length in terms of these polymerization conditions yields the following equation where $\upsilon$ is the kinetic chain length [1].

$$\upsilon = k_p [M] / 2 \{f k_d k_t [I]\}^{1/2} \qquad (2.4)$$

The dependence of the kinetic chain length on polymerization rate is given by

$$\upsilon = k_p^2 [M]^2 / 2 f k_t R_p \qquad (2.5)$$

The molecular weight of the polymer formed is also derived from kinetic chain length and the particular termination mechanism. If two macroradicals couple to form a polymer molecule, the number of monomer units is twice the kinetic chain length. If two macroradicals terminate by disproportionation into a molecule with a terminal double bond and another molecule with a hydrogen atom end-group, the number of monomer units in each is equal to the kinetic chain length. The molecular weight of the final molecule is just the monomer molecular weight times the average number of monomers per molecule. For networks formed by free radical, cross-linking copolymerization, this gives the backbone molecular weight of chains if somehow the cross-links were removed.

Normally, superabsorbents are prepared by free-radical initiated polymerization of acrylic acid and its salts, with a cross-linker, in aqueous solution or in suspensions of aqueous solution drops in a hydrocarbon medium. These two principal processes, bulk solution polymerization and suspension polymerization, share many features. The monomer and cross-linker concentrations, the initiator type and concentrations, polymerization modifiers, the relative reactivities of the monomers, the basic polymerization kinetics and the reaction temperature are all significant factors in both processes [18].

### 2.2.1 Monomer concentration

The concentration of monomer in the reaction solution affects the properties of the resulting polymer, the kinetics of the reaction and the economics of the process. High monomer concentration results in increasing toughness of the intermediate gel polymer as the polymerization progresses. The toughness of the gel affects the design of equipment, the size of gel particles produced during agitation of the reaction mass and the method of heat removal. In addition, chain transfer to polymer increases with monomer concentration, especially at a high extent of conversion, and this results in increasing amounts of branching and self-cross-linking reactions that affect product properties. Chain-transfer agents are useful to combat these side-reactions [19]. Another factor influencing the choice of monomer concentration is that the efficient use of the cross-linker increases with monomer concentration because the solubility of cross-linkers typically not very water soluble often increases with monomer concentration due to the increasing organic content of the monomer phase.

The factor of considerable importance to the polymerization in large quantity and at high monomer concentration is the large heat of polymerization of acrylic acid. The monomer yields 18.5 kcal/mole upon polymerization, making a temperature control an important parameter. Lower monomer concentration lessens the potentially adiabatic temperature rise but also lowers the volumetric efficiency of the reaction equipment and affects the polymerization kinetics. Evaporative cooling at reduced pressure may be used to remove the heat of polymerization [20]. The heat has also been used to dry the polymer to a foamy mass [21]. If the suspension process is used, traditional methods of heat transfer can be used because a lower viscosity, liquid state is maintained. This can be an advantage when a precise temperature control is desired.

Because acrylic acid is inhibitedly stored against a premature polymerization with *p*-methoxyphenol and oxygen, either the *p*-methoxyphenol and oxygen must be removed from the monomer solution before a polymerization will proceed. The simplest method is to strip the dissolved oxygen from the solution with a stream of nitrogen gas. Alternatively, the oxygen must be reacted from the solution by a metal ion catalyzed reaction that forms hydroperoxides from the oxygen and monomer.

### 2.2.2 Initiators

The polymerization is initiated by a free radical in the aqueous phase, using thermally decomposable initiators, redox initiators or combinations. Redox systems used for the cross-linking copolymerization include couples of persulphate/bisulfite, persulphate/thiosulphate, persulphate/ascorbate and hydrogen peroxide/ascorbate. Thermal initiators include persulphates, 2,2′-azobis-(2-amidinopropane)-dihydrochloride, and 2,2′-azobis(4-cyanopentanoic acid). Combinations of initiator are used when the polymerization takes place over a broad temperature range. In this case, it may be desirable to maintain a constant rate despite the change in temperature. Appropriate concentration of multiple initiators can achieve the desired constant rate of polymerization [22].

In graft copolymerization of vinyl monomers to polysaccharide substrates, initiation is accomplished using a redox reaction of an oxidant, such as the oxidized form of a metal ion, with oxidizable groups of the polysaccharide. When the metal ion is reacted with the graft substrate before monomer is added, grafting efficiency is increased. In addition to initiating the polymerization reaction, initiators are a factor in reducing the levels of unreacted monomer during the drying step [23], and can contribute to undesirable chain cleavage reactions at occur when the gel is handled at higher temperatures. For example, a higher content of soluble polymer is found when sodium polyacrylate gels made by ammonium persulphate initiator are dried in a very hot oven [24].

### 2.2.3 Neutralization

The monomer and cross linker are dissolved in water at a desired concentration, usually from about 10%-70%. The acrylic acid usually is partially neutralized before the polymerization is initiated [25], but the cross-linked polymer can be neutralized after polymerization is complete [26]. In suspension processes, neutralization of the monomer is required due to the appreciable solubility of acrylic acid in hydrocarbons (a continuous phase).

Inexpensive bases, such as sodium hydroxide and sodium carbonate, are used as neutralizing agents. A choice would be made based on consideration of the pH of the base solution and the resulting potential for hydrolyzing cross-linker, the solubility limits of the base in water and on the solubility of the monomer salt in water. For example, potassium acrylate is more soluble in water than is sodium acrylate.

### 2.2.4 Other polymerization additives

Chain transfer agents may be used to control network properties through a control of polymer backbone molecular mass. A variety of chain transfer agents are known for water soluble monomer systems [27]. Examples are mercapto compounds [28-31], formic acid [32], carbon tetrachloride, isopropanol [33], monobasic sodium phosphate and hydropersulfite salts [34]. Some of these have also been used in a cross-linking system [35-37]. Typically, a higher swelling capacity is obtained when chain transfer agents are used, as predicted by theory [19]. Chain transfer agents and other radical scavengers can also help prevent oxidative degradation of the polymer after it has been hydrated during use [38]. In addition, chain transfer may be used to minimize the branching and self-cross-linking reactions that have been reported during polymerization at a higher monomer concentration [39].

Chelating agents are useful to help control the variable concentrations of metal ions that are present in the water used as reaction solvent. These metal ions, notably iron, catalyze many free radical reactions. When their concentration is variable, initiation is irregular and possibly uncontrollable. Metal ions can also catalyze reactions of the initiators that lead to non radical products; this wastes the initiator and can cause incomplete conversion of the monomer to polymer.

### 2.2.5 Kinetics

The polymerization kinetics are affected by monomer and initiator concentrations, pH, and ionic strength of the reaction medium. Most, if not all, of the commercial processes use persulphate salts as one of the initiators. In this case, the kinetics of the polymerization are proportional to the 1.5 power of acrylic acid concentration and to the square root of the concentration of persulphate. Polymerization rates decrease with an increasing extent of neutralization, but this effect is moderated in industrial processes by the high ionic strength of the monomer solution when the acrylic acid is partially neutralized at high concentrations.

### 2.2.6 Cross-linkers

Relatively small amounts of cross-linkers play the major role in modifying the properties of superabsorbent polymers. The cross-linkers typically used in superabsorbent polymers are di- and tri-acrylate ester such as 1,1,1-trimethylolpropanetriacrylate or ethylene glycol diacrylate. In addition to modifying the swelling and mechanical properties, the cross-linker affects the amount of soluble polymer formed during the polymerization. The tendency of a cross-linker to be depleted earlier in the polymerization is reflected in its reactivity ratio with acrylic acid or sodium acrylate. Early depletion of cross-linkers should cause higher soluble fraction in the product.

Unfortunately, reactivity ratios have not been directly determined for the cross-linker typically used in making superabsorbent polymers. However, these can be estimated from the reactivity ratios of structurally analogous monomers, using the Alfrey-Price Q-e scheme. This has been done for several cross-linker analogs, using the available Q-e values [18]. The results, shown in Table 2.6, suggest that cross-linkers similar to triallylcitrate should yield polymers with a lower amount of soluble polymer while a cross-linker similar to ethyl methacrylate should yield higher amounts of soluble polymer. This prediction is confirmed in the results from polymerizations, shown in Tables 2.6-2.7 [18].

Table 2.6

Cross-linker Reactivity Effect on Gel Fraction [18].

| Cross-linker | $r_1$ [a] | gel fraction [b] |
|---|---|---|
| Methylenebisacrylamide | 2.8 | 0.986 |
| Triallycitrate | 2.8 | 0.981 |
| Ethyleneglycol diacrylate | 1.56 | 0.955 |
| Ethyleneglycol dimethacrylate | 0.74 | 0.789 |

[a] Taken as the average of the $r_1$ values for acrylic acid and sodium acrylate with the respective cross-linker analogs.

[b] Identical polymerizations of 65 mole% neutralized acrylic acid with 0.145 mole% cross-linker, in aqueous solution at 32 mass% monomer, initiated with a sodium persulphate and sodium erythorbate redox couple at 28°C.

Table 2.7

Reactivity ratios for structural analogs of cross-linkers [18].

| Monomer/Cross-linker analog | $r_1$ | $r_2$ |
|---|---|---|
| 1. Acrylic acid | | |
| triallycitrate | 5.636 | 0.049 |
| acrylamide(bisacrylamide) | 2.676 | 0.324 |
| ethyl acrylate(diacrylate) | 1.514 | 0.576 |
| ethyl methacrylate(dimethacrylate) | 0.585 | 1.024 |
| 2.Sodium acrylate | | |
| acrylamide | 2.852 | 0.355 |
| ethyl acrylate | 1.598 | 0.631 |
| ethyl methacrylate | 0.902 | 1.173 |

The choice of cross-linker will also depend on the method used to neutralize the carboxylic acid groups. A high pH process step may require a hydrolytically stable cross-linker, such as tetraallyoxyethane, rather than a diacrylate ester. In a suspension polymerization process, the availability of the cross-linker in the aqueous phase will be controlled by the partition coefficient of the cross-linker between the aqueous phase and the hydrocarbon, a continuous phase. The partition coefficient will depend on the extent of neutralization and on the nature of the hydrocarbon e.g., whether aromatic or aliphatic. The solubility of the cross-linker in the monomer solution also affects the efficiency of cross-linking in solution polymerization. Efficiency of cross-linking will also depend on steric hindrance and reduced mobility at the site of pendent double bond, the tendency of a given cross-linker to undergo intermolecular addition (cyclopolymerization) and the solubility of the cross-linker that can depend on the extent of neutralization, as noted above. As a result of a combination of factors such as these, different cross-linkers can exhibit much different effectiveness in the cross-linked product. An example is given in Figure 2.5. Here, the effectiveness of cross-linking is compared for triallyamine and 1,3-butyleneglycol diacrylate. The amount of cross-linker has been normalized in each case for the functionality of the cross-linker, using the normalizing factor (1-2/f) where f is the functionality of the cross-linker. In Figure 2.5, the functionality of 1,3-butyleneglycol diacrylate is 4 and the functionality of triallyamine is 6. Several times more triallyamine is needed than diacrylate to achieve the same swelling ratio.

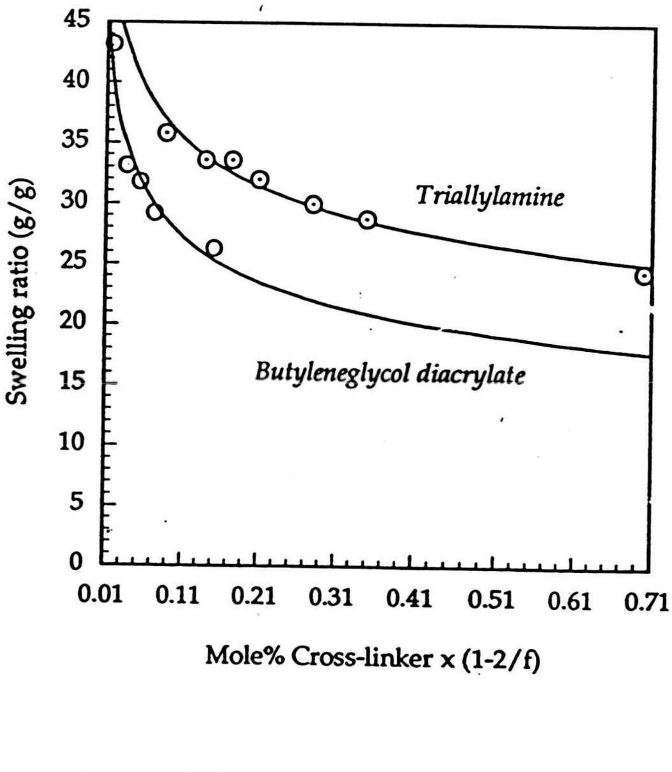


Figure 2.5 Dependence of the swelling ratio on the cross-link density and the functionality of the cross-linker. The two cross-linkers differ in efficiency [18].

## 2.3 Specific Polymerization Techniques

Commercial polyacrylate superabsorbent polymers are prepared using a large variety of techniques, but they can be grouped into five general categories: solution cross-linking copolymerization, inverse suspension cross-linking copolymerization, suspension polymerization, graft copolymerization and cross-linking after polymerization (curing). Occasionally, a combination of two of these is practised to obtain a specific set of product properties. For example, a polymer formed in a cross-linking copolymerization may be further cross-linked at the surface of polymer particles to change the absorption rate characteristics of the product [40].

### 2.3.1 Solution Polymerization

The polymerization of acrylic acid or sodium acrylate with a cross-linker in aqueous solution would seem to be a straightforward process. The monomer and cross-linker are dissolved in water at a desired concentration, usually from about 10% - 70%, since polymerization of undiluted acrylic acid is extremely dangerous due to the high heat of polymerization and rapid polymerization kinetics. The monomer solution is deoxygenated by bubbling an inert gas through the solution, or by a series of evacuations and repressurizations with an inert gas, the desired free radical initiator is added and the temperature is brought to the appropriate point for polymerization to begin. However, the use of this technique in industrial practice is complicated by a variety of factors, the solution to which is the subject of numerous patents.

### 2.3.2 Graft Copolymerization

Water soluble polymers such as starch and poly(vinyl alcohol) are grafted into superabsorbents in order to modify the properties. Certain processes benefit from increased viscosity of the monomer solution, and the water soluble, graft substrates can serve this purpose[41, 42]. Historically, the "superslurper" absorbents were made from acrylonitrile grafts to starch, and the currently used acrylic acid grafts to starch appear to have developed from the earliers work. Special initiators are useful to increase grafting efficiency with polymers containing hydroxyl sites. Metal ions, such as cerium, complex with the hydroxyl sites and serve as a locus for the nascent free-radical formed by oxidation of the substrate. For example, starch has been reacted with a partially neutralized acrylic acid and a diacrylate ester cross-linking agent, using $Ce^{4+}$ as a free radical initiator. The gel like reaction product was dried and pulverized[43]. Graft copolymers can also be prepared using an inverse suspension polymerization [44].

### 2.3.3 Cross-linking after polymerization.

In this technique, the polyacrylate is formed in a first step, as a soluble polymer, which is then reacted in a second step with a suitable cross-linking agent. These are any of a hung variety of compounds which can react with carboxyl groups including amines, alcohols, epoxides and polyvalent metal ions. A benefit of this technology is that the absorbent polymer can be formed in to a desired shape by mixing the soluble polymer and cross-linker and curing in place, for example onto fibers or onto the surface of a sheet of tissue. Drawbacks to this technology are the handing of the viscous solutions of polymer and their thorough mixing with the cross-linker and any catalysis required [18].

### 2.3.4 Suspension polymerization [45]

The term suspension polymerization refers to a system in which monomers are suspended as the discontinuous phase of droplets in a continuous phase and polymerized. The reactor product is a slurry of suspended polymer particles. The monomer suitable for suspension polymerization usually can be polymerized by free-radical mechanisms. The continuous phase is usually water, as most monomers are relatively insoluble in water. The terms pearl polymerization and bead polymerization describe the smooth, spherical particles from some suspension polymerization.

Suspension particle morphology (the particle size, shape, and internal structure) affects how the resin performs in many mixing operations and applications and affects its economic value. Suspension particles are 50-200 μm in diameter, with the exact size depending on the monomer type, surfactants, and agitation in the reactor. The range can be extended to 400 μm for some products. These particles are much larger than those formed in emulsion polymerization(20-1000 nm) and usually move as a free-flowing powder when dry and are relatively easy to recover from air streams. The small average particle size produced by suspension processes aids in mixing other components with the resin, such as in compounding operations. In many cases, particle morphology makes important contributions to the value of suspension polymer products.

Several characteristics of the suspension polymerization method are common to most systems. The weight ratio of the continuous water phase to the discontinuous monomer phase varies from 1:1 to 4:1 in most commercial processes. The bulk viscosity of the slurry is near that of water during most of the polymerization. The low bulk fluid viscosity allows good mixing of the reactor contents at modest energy inputs and can improve heat transfer in the polymerization reactor. Water is a good medium for removing heat from polymerizing droplets because it has both a high heat capacity and high thermal conductivity. However, suspension polymers must be separated and dried from the water phase. Suspension droplets are not thermodynamically stable, and their coalescence is controlled by balancing the agitation system and the suspending agents.

Aside from cast resins and the synthetic rubbers, suspension polymerization has become the most important commercial method for polymerization of olefinic monomer, commodity polymers. Because the potential engineering advantages over bulk , solution, and emulsion polymerization are

a) Low cost of conversion with flexibility to vary the particle properties.

b) Excellent heat transfer. When coalescence is controlled, heat is easily transferred from the beads to the water phase and then to heat transfer surfaces in the reactor. The high heat capacity of the water phase relative to the monomer polymer phase provides a "reservoir" for absorbing rapid increase in energy being released. In addition, control of pressure can permit vaporization of monomer or water as another mechanism for removing energy from the reactor.

c) Particle-size control. Average particle size and particle-size distribution can be controlled to a fairly narrow range. The particles are relatively easy to recover from water or gas streams. The particle morphology can affect its performance in mixing and applications.

d) Low levels of additives in the polymer. Suspension products have a lower additive content than emulsion polymerization products, but more additives than solution and bulk polymerization products.

The chemical properties of suspension polymers may differ from those prepared by bulk or emulsion polymerization techniques. The suspending agents can become incorporated into the polymer particles and can affect properties such as particle fusion during mixing and blending. Water, used as the continuous phase is a potential source of contaminants, e.g., metal ions, which can affect the thermal stability of the product. The solubility of monomers and initiators in the water phase is low, but not zero. Water-phase polymer can form and have different properties from the normal resin.

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 2.8 [46]. Suspension polymerization has been little used outside the field of vinyl type or ethylene monomers.

The steps of a typical polymerization process are preparation of the suspension agents, buffers, and initiators; formation of the monomer suspension

## TABLE 2.8

### Polymerization Process in Heterogeneous Aqueous Dispersions [46]

| 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., persulphates, redox System | Latex of particles 0.05-2.0 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., $H_2O_2$ | 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 powder | Vinyl chloride, high-acrylonitrile, fluoroethylenes |

in the water continuous phase; initiation and polymerization; monomer recovery dewatering, and powder storage. However, the details vary among the polymers produced and among different commercial manufactures. Suspension droplets are thermodynamically unstable, unlike emulsion systems in which monomer and polymer particles can remain dispersed for long periods of time. A suspension of monomer droplets in the size range 50-200 μm coalesces rapidly in the absence of agitation to form a distinct monomer phase. Particle coalescence depends in part on monomer solubility in the polymer phase. The particle-size distribution achieved is often considered to represent a dynamic equilibrium between particle dispersion by shear or turbulence forces in the reaction vessel and coalescence by impingement or wetting of reactor surfaces. Droplets that wet reactor surfaces can polymerize and result in polymer buildup or adhesions.

Each particle can be considered a mini-bulk reactor modeling purposes. Except near the completion of the polymerization, most of the unreacted monomer is in the droplets or polymerizing particles because it is sparingly soluble in the water phase. Initiators soluble in the monomer phase are used to begin the polymerization. Polymerization usually are conducted above room temperature but below the boiling point of the continuous phase, 100°C for water.

A suspension polymerization system is combined with two important phases, aqueous phase, and monomer phase, organic phase:

### 2.3.4.1 The aqueous phase and Suspension 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.

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 drops. In that case, on collision a deformation of the spherical drops 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.

The monomer must be relatively insoluble in water for the droplets to form. A typical water-insoluble organic monomer has a lower surface tension than water. When such a monomer is mixed continuously as a dispersed phase in a continuous phase of water with no surfactants present, an unstable dispersion forms due to the continuous breakup and coalescence of monomer droplets. If the agitation stops, the monomer-water system will separate into its two phases. Particle coalescence is not prevented but is controlled by a combination of surfactant and agitation-system design.

The tendency of droplets to coalescence or particles to agglomerate varies during the reaction. During the initial stage of polymerization, monomer droplets tend to remain in a fairly stable dispersion. At moderate conversion levels, about 20% when the droplets contain polymer and monomer, their surfaces become "tacky" and the particles can agglomerate if they collide. The tacky stage occurs in systems in which the monomer is soluble in the polymer and in systems in which the monomer swells the polymer. As monomer is consumed further, the particles become more solid-like and their tendency to agglomerate is reduced. Large agglomerates are difficult to dry and may be difficult to process. Accumulation of agglomerates on reactor surfaces can result in poor heat transfer and possible loss of temperature control. The surfactant agitation package chosen should be able to form the desired initial dispersion and to control agglomeration during the tacky stage.

The condition for a stable dispersion of liquid droplets in a continuous liquid medium are [45]

a) A protective film must be present at the surface of the water-organic droplet interface to prevent immediate coalescence. The film is normally established by using surfactants and other additives. The properties of the surfactant system, i.e., the hydrophilic-lypophilic balance or HLB and its solubility in the monomer and water phases, determine droplet size, droplet coagulation, and particle agglomeration for a specific agitation system.

b) Agitation must be sufficient to redisperse droplet pairs and clusters. For the dispersion of two immiscible liquids in a vessel with a specific agitation system design and operation, there is a minimum droplet size above which stabilization by agitation becomes possible. If the average size is much small than this, the droplets coalesce as in an unstabilized dispersion until they reach the minimum size.

c) Agitation must be sufficient to prevent a separation of the dispersion caused by of the difference in specific gravity between two phases.

The surfactant system helps establish the initial monomer droplet size distribution, controls droplet coalescence, and reduce particle agglomeration. The suspension stabilizer affects particle size and shape as well as the clarity, transparency, and film-forming properties of the resin. In some system, suspending aids can be used to control resin porosity. The solubility of water in the monomer and possible solubilization of water in the monomer due to the suspension stabilizer can also affect the bead clarity.

Nonionic surface-active agents and polymeric suspension stabilizers are thought to promote a steric or solvation barrier because of their adsorption at the interface. Evidence for adsorbed surfactant stabilizing the suspension system includes

a) Small amounts of specific high polymers offer adequate suspension protection for specific monomer-polymer systems. Higher concentrations of other specific protective colloids, which increase the aqueous viscosity to a greater degree, may fail to provide sufficient protection to the polymerizing system. The affinity for adsorption seems to be more important than an increase in viscosity.

b) Small amounts of suspension stabilizers can be observed to be incorporated into the surface of the granular resin particles under microscopic examination.

c) The method of dispersion can affect the stabilization of the particles.

d) A comonomer droplet containing, e.g., 90% of the one monomer may need a different type or much larger concentration of suspension stabilizer than does the homopolymer. This may be due the monomer mixture having adsorptive properties different from the homopolymer. Differences in solubility of the copolymer in the monomers can also be important factor.

Several other chemical techniques are available for influencing particle size. Electrolytes are used as a complement to surfactants. Buffers and other electrolytes usually increase the interfacial tension between the monomer and water phases. They also reduce the solubility of monomers in the water phase and often result in smaller particles at the same surfactant level. The density of the aqueous phase can be adjusted to that of the monomer-polymer phase so that the polymerizing mass is neutrally buoyant. This technique may be useful only in certain systems, because there is usually a density increase in the droplet as it polymerizes. Additives can be used to increase the aqueous phase viscosity in order to reduce the number of droplet collisions resulting in coalescence or agglomeration. Some suspension stabilizers may result in foam formation in the reactor or in downstream processing [45].

#### 2.3.4.2 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 a relatively water-soluble monomer 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 an 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 monomer, i.e., organic peroxides, and less frequently used azo compounds.

### 2.3.5 Inverse Suspension Polymerization

Inverse suspension polymerizations, which recently have attained commercial importance, begin with concentrated aqueous solution 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 persulphates, hydrogen peroxide, and redox activators of these. As external phases one may use aliphatic hydrocarbons or less frequently toluene, xylene or chlorinated hydrocarbons [46].

This system is different from suspension polymerization in phase of monomer solution, solubility of initiator in organic phase and aqueous phase as shown in Figure 2.6.

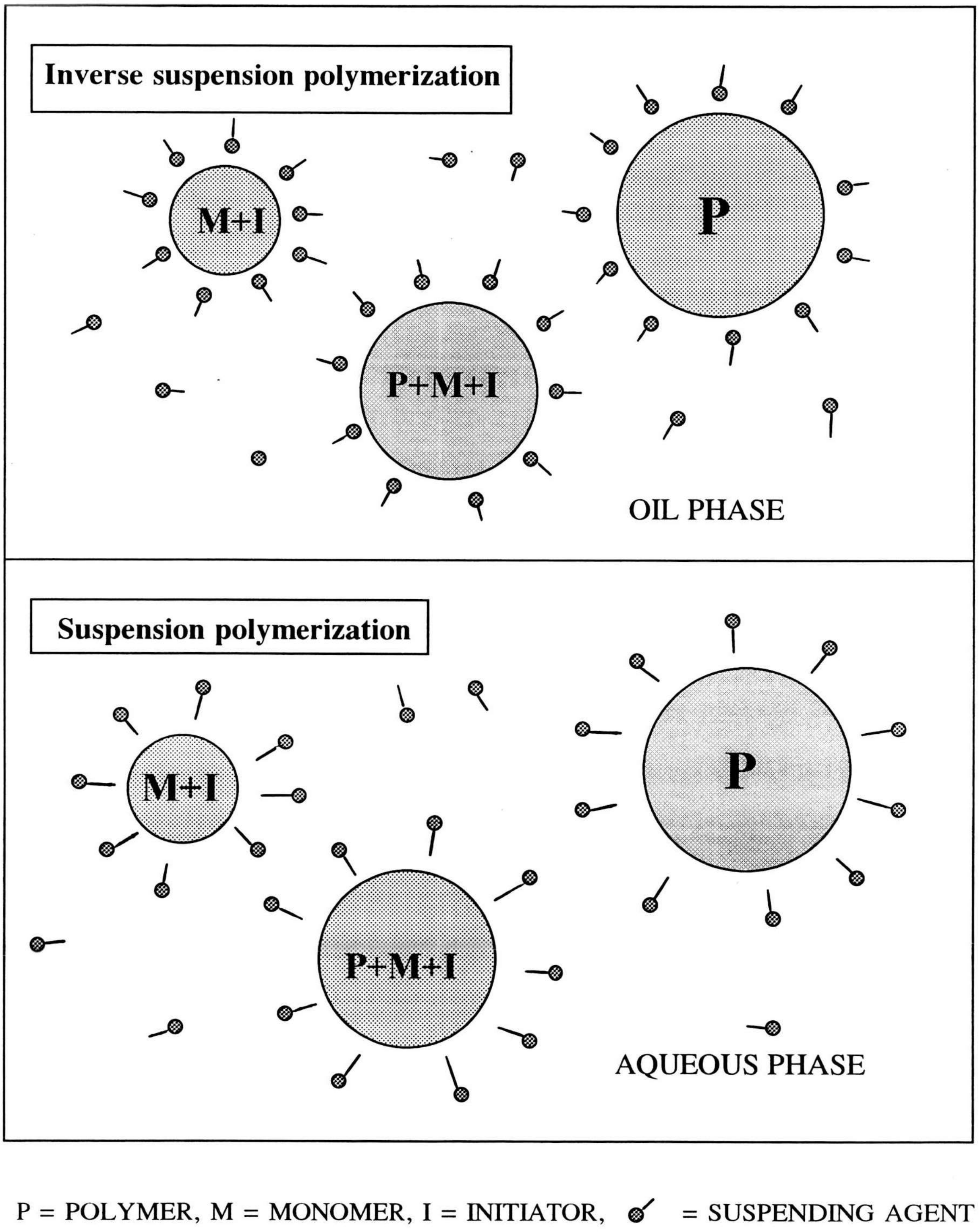
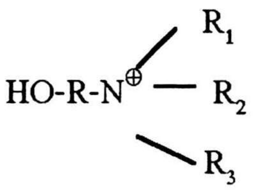


Figure 2.6 : Comparison the difference of inverse suspension polymerization and suspension polymerization.

Heide, W., Hartmann, H., and Vamvakaris, C. [47] disclosed a process for preparation of bead polymers by inverse suspension polymerization based on water-soluble ethylenically unsaturated monomer, for example ethylenically unsaturated C3-C5-carboxylic acids, their amide and esters with amino alcohols of the formula:



The formula of ethylenically unsaturated amino alcohol.

where R is $C_2$-$C_5$-alkylene, and $R_1$, $R_2$, and $R_3$ are each H, $CH_3$,$C_2H_5$ or $C_3H_7$. These compounds are, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, acrylamide, methacrylamide, crotonamide, dimethylaminoethyl acrylate, diethyaminoethyl acrylate, diethyaminopropyl acrylate, dimethylaminobutyl acrylate, diethylaminoethyl methacrylate, dimethylaminoethyl methacrylate, dimethyl aminopropyl acrylate, dimethylaminoneopentyl acrylate and dimethylaminoneo pentyl methacrylate. The basic acrylates and methacrylate are used in the form of their salts with strong mineral acids or carboxylic acids or in a quaternized form. Other water-soluble monomers are N-vinylpyrrolidone, acrylamidopropane sulfonic acid, vinylphosphonic acid, and alkali metal or ammonium salts of vinylsulfonic acid. The other acids can likewise be used in the polymerization either in an unneutralized form or in a partially or a completely neutralized form. The monomer of these examples 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 methacrylamide. These monomer can be copolymerized with one another in any ratio.

This process, an aqueous solution of the monomers is first dispersed in an aliphatic hydrocarbon using an inorganic suspending agent based on a modified finely divided mineral to give a water-in-oil suspension, and this suspension is then polymerized in the presence of the polymerization initiator with the formation of a water-in-oil polymer suspension, if the polymerization is additionally carried out in the presence of from 0.1 to 5% by weight, based on the monomers used, of a nonionic surfactant having an HLB value of from 2 to 16.

The polymerization can also be carried out in the presence of cross-linking agents. The cross-linking agents contain two or more ethylenically unsaturated double bonds, example of suitable cross-linking agents being N,N′-methylenebisacrylamide, polyethylene glycol diacrylate, and poly(ethylene glycol) dimethacrylates, each of which is derived from a poly(methylene glycol) having a molecular weight of from 126 to 8500, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethylene glycol diacrylate, propylene glycol diacrylate, butanediol diacrylate, hexandiol diacrylate, hexanediol dimethyacrylate, diacrylates and dimethacrylates of block copolymers of ethylene oxide and propylene oxide, adducts of ethylene oxide and 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, diallylphthalate, poly(ethylene glycol divinyl ether), trimethylolpropane diallyl ether, poly(ethylene glycol divinyl ether), butanediol divinyl ether, pentaerythritol triallyl ether and divinylethyleneurea. Water-soluble cross-linking agents are preferably used, for example N,N′-methylenebisacrylamide, poly(ethylene glycol dicarylates), poly(ethylene glycol dimethacrylates), pentaerythritol triallyl ether and divinylurea. The cross-linking 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 monomer and cross-linking agent. The amount of the cross-linking agent used for obtaining a water absorbent polymer may be changed in a board range; if the amount of the cross-linking agent is large, the swelling property to water is reduced or lost.

The water-soluble monomer can be modified not only with the aid of the cross-linking agent, but where a change in properties of the polymer is desired, additionally with suitable monomers, such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, acrylonitile and methacrylonitrile. These monomers are used for modifying the water-soluble polymer, they are employed in an amount of from 2 to 10 % by weight, based on the monomer mixtures, the total percentage for the monomer mixtures always sum to 100.

This polymerization may be carried out in the presence or absence of the conventional polymerization regulators. Examples of suitable polymerizaion regulators are thio compound, such as thioglycollic acid, mercaptoalcohols, e.g., 2-mercaptoethanol. Mercaptopropanol and mercaptobutanol, dodecylmercaptan, formic acid, and ammonium.

In the polymerization, organic phase, a hydrocarbon having 6 to 10 carbon atoms or a halogenated aromatic hydrocarbon is preferably used as the dispersion medium. For example, there can be mentioned, aromatic hydrocarbons such as benzene, ethylbenzene, toluene, and xylene; alicyclic hydrocarbons such as methylcyclohexane, cyclooctane, and decalin; aliphatic hydrocarbons such as hexane, heptane, octane, and pentane; and halogenated hydrocarbons such as chlorobenzene, bromobenzene, and dichlorobenzene; toluene, xylene, cyclohexane, methylcyclohexane, hexane, heptane, chlorobenzene, and dichlorobenzene are especially preferred. A mixture of two or more of the foregoing solvents may be used as the dispersion medium according to the kind of the cellulose ester or cellulose ether used. Furthermore, a single solvent may be used as the dispersion medium when a certain cellulose ester or cellulose ether is selected and used. In this case, recycling of the dispersion medium is facilitated, and the process is carried out very advantageously from the industrial view point [48].

When dichlorobenzene. toluene, xylene, or chlorobenzene is used singly as the dispersion medium, ethyl cellulose having an ethoxy group content of 43 to 47% by weight or cellulose acetate butyrate having a butyryl group content of 20 to 50% by weight is preferably used as the cellulose derivative. When cyclohexane, cyclopentane, methylcyclohexane or decalin is used singly as the dispersion medium, ethyl cellulose having an ethoxy group content of 47 to 50% by weight is preferably used as the cellulose derivative. When n-hexane, n-heptane or n-octane is used singly as the dispersion medium. Ethylhydroxyethyl cellulose is preferably used as the cellulose derivative. The protecting colloid is used in an amount of 0.05 to 10% by weight, preferably 0.5 to 5% by weight, based on dispersion medium [48].

The volume ratio between the dispersion medium and the aqueous solution of the monomer can be changed in a broad range, but from the viewpoints of removal of the polymerization heat and control of the polymerization temperature, the above volume ratio is preferably controlled within the range of from 1:1 to 5:1 [48].

For polymerization of the monomer, a known amount of a water-soluble radical polymerization initiator is used. As for polymerization initiators, for example, persulphates, such as potassium persulphate, and ammonium persulphate, hydroperoxides, such as t-butyl hydroperoxides and cumene hydroperoxide, and azo compounds such as 2,2′-azobis-2-amizinopropane hydrochloride are preferred. A mixture of two or more of these initiators may be used, and these initiators may be used in a form of redox type initiators. The rate of decomposition of peroxides, which decompose at high temperatures can be reduced by using organic metal complexes, such as copper acetylacetone, so that the decomposition rate of the peroxides can be adapted to a particular polymerization temperature choosen. The polymerization initiator is used in an amount of from 0.01 to 5%, preferably from 0.2 to 3%, by weight, based on the monomers used in the polymerization [47].

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, are the agents conventionally used in inverse suspension polymerization processes. The mineral component of these substances is formed for example, by betonite, 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 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 organosilicon compound is, for example, trimethylsilyl chloride [48].

The objective 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 μm, in general from 0.5 to 5 μm. The silicas reacted with organo-silicon 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 suspension, which contains 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 monomer used, of a nonionic surfactant so that the polymerization batches do not undergo coagulation or agglomeration.

The cellulose ester or cellulose ether oil-soluble at the polymerization temperature, which is used as the protecting colloid for the W/O suspension polymerization is a cellulose ester or cellulose ether which is insoluble or hardly soluble at room temperature in the hydrocarbon or halogenated aromatic hydrocarbon used as the dispersion medium but becomes soluble in the dispersion medium at the polymerization temperature, higher than 40°C [47].

As such cellulose ester or cellulose ether, for example, cellulose acetate, cellulose propinoate, cellulose acetate butyrate, cellulose acetate phthalate, ethyl cellulose, benzyl cellulose and ethylhydroxy ethyl cellulose can be mentioned. Cellulose acetate butyrate, ethyl cellulose and ethylhydroxyethyl cellulose are especially preferred.

Not only inorganic compounds, cellulose ether, and cellulose ester compounds, the nonionic surfactants also are used in the inverse suspension polymerization process with an HLB value of from 2 to 16. Examples of suitable nonionic surfactant are $C_8$-$C_{12}$-alkylphonols 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 are oxyethylated $C_{10}$-$C_{24}$-fatty alcohols and/orpolyhydric $C_3$-$C_6$-alcohols which are partially esterified with $C_{10}$-$C_{24}$-fatty acids. These may additionally be reacted with from 2 to 20 moles of ethylene oxide. Examples of suitable fatty alcohols are palmityl 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 to 20 moles of ethylene oxide in order to obtain surfactants having the HLB value stated above(2-16).

Examples of $C_3$-$C_6$-alcohols which are partially esterified and may be oxyethylated are glycerol, sorbitol, mannitol and pentaerythritol. These poly(hydric 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 poly(hydric alcohol) remain unesterified. Examples of suitable esterification products are sorbitan monooleate, sorbitan tristearate, mannitol monooleate, glycerol monooleate and glycerol dioleate. The stated fatty acid esters of poly(hydric alcohol), 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 surfactant. By a suitable choice of the oxyethylation, it is possible to prepare surfactants which have an HLB value in the stated range. The nonionic surfactant 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 it 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 a 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 nonionic surfactant are used to promote dispersion of 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 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 μm, 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 and then separated off from the aliphatic hydrocarbon.

Depending on the polymerization conditions and the monomer 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$^{\circ}$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 acrylamide, or copolymers of acrylamide and dimethylaminoethyl acrylate hydrochloride. Cross-linked polymers, for example, copolymers of acrylic acid and methylenebis-acrylamide, are used either as thickeners in printing pastes or as a water absorbing material in diapers, depending on the degree of cross-linking. 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 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.

## 2.4 Literature Survey

Recent research on the synthesis of superabsorbent polymer and important physical properties development are listed as below.

Dimonie, M.V., Boghina, C.M., Marinescu, N.N., Marinesou, M.M., Cincu, C.I., and Oprescu, C.G. [49] investigated the persulphate 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, by inverse suspension polymerization and compared with polymerization in solution. The influences of various factor upon the molecular weight of the polymer were studied, e.g., the concentration of initiator, the procedure of aqueous phase addition, the nature and concentration of emulsifier, the salt concentration, the time between mixing of phase and start of polymerization. Conductometer, NMR and electron microscopy were employed in order to establish the reaction stages and the characteristics of the polymers. The results indicated the importance of each factor and to an understanding of the polymerization.

Yamasaki, H., and Harada, S. [48] patented the process of preparation water-insoluble, high absorbent polymer beads which were prepared by dispersing and suspending an aqueous solution of a water-soluble, ethylenically unsaturated monomer containing a small amount of a cross-linking agent in a dispersion medium of a hydrocarbon or a halogenated aromatic hydrocarbon, carrying out the bead polymerization in the presence of a water-soluble radical polymerization initiator and a protecting colloid comprising a cellulose ester or cellulose ether which is oil-soluble at the polymerization temperature, that higher than 40$^{\circ}$C, and separating the resulting beads.

Cramm, J.R., and Bailey, K.M. [35], 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, a cross-linking agent. The resulting polymer with a cross-linking agent, the improvement which comprises conduction the polymerization in the presence of a water-soluble chain transfer agent was carried out.

Tsubakimoto, T., Shimomura, T., and Irie, Y., [14] synthesized an absorbent article by mixing 100 parts by weight of an absorbent resin powder having a carboxyl group, preferably, at least 0.01 equivalent of carboxyl groups were present per 100 g of the absorbent resin, with 0.001 to 0 Parts by weight of a cross-linking agent having at least two functional groups capable of reacting with the carboxyl group per molecule and reacting the absorbent resin powder with the cross-linking agent to cross-link the molecular chains existing at least in the vicinity of the surface of the absorbent resin powder. The absorbent resin powder and the cross-linking resin mixed by ordinary mixers such as a V-shaped rotating mixer, a ribbon mixer, a screw mixer, a rotating disc mixer and a fluidized bed mixer at various temperatures. The absorption article were obtained by this process had various advantages over the known conventional absorbent resins. Because it can be produced at a low cost by an industrially simple method which involved mixing the absorbent resin with the cross-linking agent and reacting them with each other. Since it was less susceptible to fish-eye formulation than the known conventional absorbent resins, it has a high speed of absorption. Furthermore, the absorbent resin in accordance with this process was difficult of caking upon moisture absorption.

Makita, M., and Maeno, J., [50] patented a process for preparing a highly water-absorbent resin by a reverse-phase suspension polymerization method using an aqueous solution of a monomer containing an alkali metal salt of acrylic or methacrylic acid, water-soluble polymerization initiator in hydrophobic organic solvent, optionally containing dispersing agents, using a protective colloid copolymer and a copolymerizable monomer. The synthesized polymer beads have maximum water absorbency at 900 and 65 times its dry weight for deionized water and 0.9 % aqueous NaCl, respectively. This product thus obtained had a high water absorbing rate, high gel strength and were very useful as water-absorbent resins, particularly as sanitary articles.

Heide, w., et al. [47] synthesized and patented bead polymer by inverse suspension polymerization by a process in which an aqueous solution of water-soluble ethylenically unsaturated monomer were polymerized in an aliphatic hydrocarbon using an inorganic suspending agent based on a modified finely divided mineral and, in addition, from 0.1 to 5 % by weight, based on the monomer used, of a nonionic surfactant, in the presence of a polymerization initiator, with the formation of a water-in-oil polymer suspension.

Patel, S.K., Rodriguez, F., and Cohen, C. [51] produced spheres of cross-linked acrylamide-methylene bisacrylamide copolymer by suspension polymerization. By introducing a vibrating stream of aqueous solution into an organic matrix, particles sizes of 0.33 ± 0.06 to 0.99 ± 0.41 mm in diameter resulted. The swelling of gel spheres in water was compared to that a larger bulk gels, and a significant amount of hydrolysis occurred in the spheres due to the presence of tetramethylethylenediamine(TEMED), used as an initiator. The dependence of the elastic modulus of the gel spheres upon the cross-linker concentration was non-linear, even in the regime when linearity is observed for bulk gels; this appears to be due to the varying amounts of TEMED that diffuses in the sphere and is known to affect the modulus of bulk gel.

Han,Y-K, Kim, Y.H., Kim, U.Y., No, Y-P., Jung, Y-T., and Chung, G-S., [52] synthesized acrylic acid based high water absorbing polymer by inverse suspension polymerization of acrylic acid and followed by cross-linking 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 condition in the pot and yield 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.

Abe, T., Egawa, H., Ito, H., and Nitta, A. [53] synthesized thermo-sensitive polymer beads by inverse suspension polymerization of aqueous monomer solution containing N-acryloylpyrrolidine(APR), N,N′-methylenebis-acrylamide, a cross-linking agent, and ammonium peroxysulphate(APS) and N,N,N′,N′-tetramethylethylenediamine(TMEDA) as redox initiator system. The polymerization temperature was contained at 20°C for 2 hrs. The polymerization condition such as dispersion medium, dispersing agent, monomer, and initiator concentration were investigated. Fine spherical gels with diameter of 50-500 μm were obtained in high yield. The swelling volume of these gels in water continually decreased by raising atmospheric temperature and vice versa. The degree of swelling increased for gel synthesized with lower degree of cross-linking or with lower monomer concentration. The degree of swelling was high in water and alcohols, but the gels swelled even in non-polar organic solvent, although the degree of swelling was low. The pore radius distribution of the gel was determined by aqueous size exclusion chromatographic method to investigate relation between pore characteristics of the gel and polymerization conditions. Monomer concentration has large effect on pore size, porosity, and pore volume of the gels. On the other hand, degree of cross-linking had little effect on these pore characteristics.

Dubrovskii, S.A., Afanaseva, M.V., Lagutina, M.A., and Kazanskii, K.S. [54] synthesized superabsorbent hydrogels(SAHs) by copolymerization of acrylamide(AA) and acrylic acid(AAc) in the presence of N,N′-methylenebis-acrylamide or by γ-radical cross-linking of high molecular AA-AAc copolymer in aqueous solution. The polymerization was initiated with ammonium persulphate-tetramethylethylendiamine(2:1) in 20 % aqueous solution of the monomer at

$45^{\circ}$C. The modified swelling theory had been used to develop a system of experimental and computational methods for the evaluation of supergels network parameter.

Qirong, L. [55] synthesizes hydrophilic network copolymers containing poly(ethylene oxide) and polyethyleneimine blocks by cross-linking polyethyleneimine with poly(ethylene oxide) terminated at both ends with Br atoms in DMSO. The experiment results showed that the network density of the copolymer and the water absorption power thereupon can be efficiently controlled by the change of the amount of DMSO in the reaction system. Further modification was obtained by converting these copolymers into quaternary ammonium salts. The resulting quaternary ammonium salts exhibit enormously enhanced water absorption power about 645 times its dry weight. The absorption power of these quaternary ammonium salts in ethanol was higher than in other organic solvents. In addition, the absorption power of these quaternary ammonium salts in aqueous solutions containing $Ca^{2+}$ and $Mg^{2+}$ were aqual at the same absorption time, and more than a system containing $Na^{+}$ and $Fe^{3+}$ salts.

Kiremitci, M., and Cukurova, H. [3] prepared highly cross-linked poly(2-hydroxyethylmethacrylate), (PHEMA) beads about 100 μm - 2 mm in diameter, by the suspension polymerization of HEMA monomer in an aqueous medium consisting only in magnesium oxide(MgO) as a suspending stabilizer and a salting-out agent. The procedure is so simple and the particles have excellent spherical geometry and very narrow size distribution compared to PHEMA beads prepared by other techniques. The effects of various factors such as MgO concentration, stirring speed and monomer phase/aqueous phase ratio on the particle geometry, size and size distribution were investigated. It was shown that the amount of MgO in the dispersion medium was the most important parameter, which affects the particle size and size distribution.

Stanly, F.W., Lamphere, J.C., and Wilson, L.R.[12] synthesized and patented highly wrinkled particles of superabsorbent polymer by means of an inverse suspension polymerization. The particles were not clusters but were discrete particles that have high surface areas and fast rates of absorption for aqueous liquids and high attrition resistant absorbent polymers, preferably of a cross-linked acrylic acid or acrylate. These absorbents had absorption rates superior to spherical absorbents. The particles were made by polymerization of aqueous droplets containing partially neutralized acrylic acid and a cross-linking agent that were suspended in a liquid hydrocarbon. The polymerization was initiated in the continuous oil phase, and the monomer concentration and the initial droplet size affect the extent of wrinkling. Larger droplet size and higher monomer concentration yield polymer particles with more wrinkles per particle and average diameter of absorbent particles were greater than 75 μm. Dispersing agents were nonionic surface active compositions having HLB values of 2 to 6 and the cross-linking agent was methylenebisacrylamide, diethyleneglycol diacrylate, tetraethyleneglycol diacrylate, trimethylolpropane triacrylate, or mixtures thereof.

Akashi, M., Saihata, S., Yashima, E., Sugita, S., and Marumo, K. [56] synthesized poly(N-vinylacetamide), (polyNVA) by the copolymerization of N-vinylacetamide (NVA) with divinyl compounds such as methylene-bis-acrylamide, methylene-bis-NVA, and buthylene-bis-NVA in a high yield. The resulting hydrogels were more stable than polyacrylamide gel and showed quite a high swelling property in a wide range of pH(1-12) and even in a 5 *M* NaCl solution. They showed not only typical characteristics nonionichydrogels, but also an amphiphilic property and they swelled well in some organic solvents. When the gels were partically hydrolyzed, cationic hydrogels, i.e., crosslinked poly(NVA-co-vinylacetamide), were collected. The resulting superabsorbent hydrogels absorbed 400 times water.

Askari, F.,Nafisi, S., Omidian, H.,and Hashemi, S.A. [57] prepared and characterized superabsorbent polymers based on acrylic acid by carrying out by the inverse suspension polymerization in an aromatic hydrocarbon. The dispersion was stabilized by the mixture of micromolecular, sorbitan monooleate (Span 80), and macromolecule, ethylcellulose emulsifier. To obtain high swelling about 929 g/g dried polymer and appropriate absorption kinetic when the amounts of materials used and some characteristics of the system were the degree of acrylic neutralization, 75%; monomer concentration, 46.5% (based on aqueous phase); cross-linker concentration, ranging from 0.0545 to 4.58 % based on acrylic acid; initiator concentration, 0.5%/acrylic acid; surfactant concentration, 0.33% / organic phase; weight ratio of oil versus aqueous phase, 3:1. For all the polymerizations the monomer feed rate had been set to 10 g/min. to allow an isothermal polymerization. Water absorption rate of the obtained polymer was fast.

Woodrum, G.T., and Majette, T.H. [13], investigated a method of recycling superabsorbent polymer particles, which were selected from cross-linked, partially neutralized poly(acrylic acid) polymer, a cross-linked, partially neutralized starch-acrylic acid of graft polymer, a cross-linked, partially neutralized copolymer of isobutylene and maleic anhydride, a saponification product of a vinyl acetate-acrylic acid copolymer, a hydrolyzate of acrylamide polymer or acrylamide copolymer or a hydrolyzate of an acrylonitrile copolymer for converting fine particles into larger particles. The method was primarily directed to aqueous solution process for preparing superabsorbent polymers. In such aqueous solution polymerization methods, the polymerization reaction product was a high viscosity gel which was dried and ground into particles. In this grinding step, a portion of the product was produced as undesired fine particles having poor absorbency and poor fabrication properties; i.e., they gel block and dust. Then fine superabsorbent polymer particles were mixed with the high viscosity reaction product gel(100 parts) containing about 20 parts by weight of superabsorbent polymer and water(5 parts per part of recycle particles) to form a mixture with improved rheological properties. The resulting mixture could be processed at a high rate than a reaction product gel of equal solids content which results in a higher product yield and increased productivity.

Primoz, O., [15] patented a process for the manufacture of a superabsorption acrylic polymer by one-stage polymerization in a W/O type suspension. Wherein as the continuous phase a hydrophobic organic solvent or recycled organic solvent in a temperature range from 40 to 60°C were used to obtain a polymer product having an absorption for the physiological solution over 50 ml/g, a content of the monomer under 150 ppm, a natural to slightly acidic pH and the form of flowable granules suitable for use in sanitary products.

Chokwibulkit, P., and Kiatkamjornwong, S. [58, 59] synthesized high-water absorbing polymer(HWAPs) by inverse suspension polymerization. Beginning the synthesis copolymerization of acrylamide(Am) and potassium acrylate(KA) and N,N′-methylenebisacylamide(N,N′-MBA) as a cross-linker via the inverse suspension technique, the synthesized beads were collected by precipitation with excess methanol. The water absorbency of the synthesized copolymer was measured by swelling in distilled water.

The effects of the influential parameters on the synthesis of HWAPs were studied and the finding elucidated the following appropriate condition for the optimum water absorbency of the beads: The amount of the initiator ammonium persulphate,($(NH_4)_2S_2O_8$) was 1.4 g/l of the suspension, the polymerization temperature was 60°C for a thermal initiation of Am:KA at 71:29 molar ratio of the total monomer concentration of 7 molar in the absence of N,N′-MBA, which produced the best HWAP having water absorbency of 347 g/g. Cross-linking with N,N′-MBA by a thermal and a redox initiation did not improve the water absorbency of the copolymer. The synthetic copolymers were investigated for the functional groups, structure, thermal properties, and surface morphology by IR, NMR, DSC and SEM, respectively. The effects of KCl and $MgCl_2$ solutions on the water absorbency of the best copolymer were studied and found that the water absorbency decreases as the salt concentration increases, due to, the more rapidly decreasing osmotic pressure differential between the inside and outside of the gel, thus allowing less water to be absorbed.

Omidian, H., Askari, F., Nafisi, S., and Hashemi, S. A. [60] synthesized, characterized and modified acrylic based superabsorbents which were synthesized by carrying out the well-known process of inverse suspension polymerization. The dispersion was stabilized by using a mixture of micromolecular and macromolecular stabilizers. High swelling and appropriate absorption kinetics were obtained, provided that parameters, including initial monomer and cross-linking agent concentration, range of neutralization degree, initiating and stabilizing system, monomer addition rate, temperature and nature of the organic phase were being considered. The water absorbent efficiency of synthesized polymer, which cross-linking agent was soluble cross-linking agent, N,N′-methylenebisacrylamide(MBA) was higher than synthesized polymer, which cross-linking agent was oil soluble cross-linking agent, ethyleneglycol dimethacrylate (EGDMA). By replacing some of the base monomer in a modified system I with acrylamide, the rate of water absorption progressively increased at the expense of reducing absorption capacity.

Yao, K-J., and Zhou, W-J. [61] prepared a series of novel copolymer superabsorbents based on acylamide, sodium allylsulfonate, sodium acrylate, and N,N′-methylenebisacrylamide by copolymerization at 35°C. The resulting superabsorbents had a fast swelling rate. The absorbency increased to a maximum, 437 times its dry copolymer weight as the cross-linking agent concentration increased, $5 \times 10^{-3}$ mole/l, but an excess of cross-linking agent leaded to a decrease swelling. Their water retention was observed at pressures of 1-10 $kg/cm^3$ and temperatures of 60 and 100°C, respectively. The water retention of soil had been enhanced by using the poly(acrylamide-sodium allylsulfonate-sodium acrylate) superabsorbent; its use is for enhancement of bean growth.

Smith, S. J., and Lind, E. J. [62] improved absorption under pressure and fast absorption rate properties of superabsorbent polymer which was obtained by first providing a solution containing carboxylic acid monomers or water soluble salts thereof, and a cross-linking agent, the most preferred cross-linking agents were bis-acrylamide such as N,N′-methylenebisacrylamide, the di, tri or polyesters of unsaturated mono or polycarboxylic acid polyols such as trimethylolpropane triacrylate, the di or tri glycidyl ethers of polyols such as ethyleneglycol diglycidyl ether, the multi-substituted allyl amines such as diallyl amine and triallyl amine, or mixtures thereof. A blowing agent, preferred carbonate blowing agents was $MgCO_3$, $(NH_4)_2CO_3$, $Na_2CO_3$, and mixture thereof and a polymerization initiator are added, individually or in combination, to the solution to form a carbonated monomer solution. A polymerization initiator was then added to the carbonated monomer solution which was then polymerized at temperature ranging from about 0 to about 130°C, forming a microcellular hydrogel. The microcellular hydrogel was chopped or ground into gel pieces having a particle diameter ranging from about 0.1 mm to about 0.5 cm. The gel pieces were dried at temperatures ranging from about 85 to about 210°C, and were then ground to form a polymer having a particle size of from about 0.05 mm to about 5.0 mm. A mixture was formed from 100 parts by weight of the polymer and about 0.001 to about 30 parts by weight of a surface cross-linking agent. Preferably, the surface cross-linking agent included at least one compound selected from the group consisting of diethylene glycol, triethylene glycol, polyethylene glycol, glycerin, polyglycerine, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, oxyethylene-oxypropylene block copolymer, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid esters, trimethylolpropane, pentaerythritol, poly(vinyl alcohol), sorbitol, ethylene carbonate, and ethylene glycol diglycidyl ether. The polymer was reacted with the surface cross-linking agent to cross-link molecular chains existing on a surface of the polymer, forming the superabsorbent polymer.

Rebre, S.R., Collette, C., and Kowalik, A. [63] described particulates of a superabsorbent partially neutralized acrylic polymer, e.g., poly(acrylic acid), having a mean particle size ranging from 100 to 500 μm, essentially monodisperse and essentially devoid of fines having a particle size of less than 100 μm, having a nonuniformly surfaced spherical particle morphology but were lumpy and spherical, resembling the shape truffles and well suited for a variety of hygienic applications. They were prepared by the following steps

(1) polymerizing a suspension of an acrylic monomer charge I in an organic medium and producing a suspension of acrylic polymer gel particles, such acrylic monomer charge I having a degree of neutralization, ranging from 90 to 100%, greater than that desired in the final superabsorbent polymer, which have the neutralization degree about 75%.

(2) next absorbing a second acrylic monomer charge II into the gel particles, such acrylic monomer charge II having a degree of neutralization ranging from about 60 to 50% which were less than that desired in the final superabsorbent polymer, and

(3) polymerizing in the gel particles of the second acrylic monomer charge II. The superabsorbent polymer obtained according to not only economically provides large particles, but also an essentially monodisperse narrower particle size distribution. Moreover, the nonuniform geometry of the particles permits a better binding into a fibrous matrix or medium and, hence, greater ease of processing in the production, e.g., of sanitary napkins.

The suspension polymerization was advantageously carried out in the presence of an effective amount of a surfactant. The surfactants were in particular the nonionic surfactants such as the fatty acid esters of sorbitan, of polyglycerine and of sucrose, or poly(ethylene alkylphenyl ethers).

However, it was also conspicuously advantageous to formulate the inverse suspension polymerization of the first monomer charge using surfactants of poly(ethylene glycol)/dodecyl glycol block copolymer type which comprise a poly(ethylene glycol) backbone provided at either or both ends of the polymer with a number of hydrophobic end-groups comprising dodecyl glycol residues. The absorption of the second monomer charge by the polymer gel formed initially can then be accomplished without the need for cooling the reactor extensively and this absorption stage can be carried out at temperatures which were not less than 35°C, thereby very appreciably improving the profitability of the process.

Mizutani, Y. [64] reported that acrylic acid and cross-linking agent, poly(ethylene glycol)-diacrylate or divinylbenzene, were copolymerized in benzene in the presence of layered sodium silicate($\delta$-$Na_2Si_2O_5$) powder. Initiator of radical polymerization was a redox system: benzoyl peroxide(BPO)-p-toluyl-diethanolamine(PTEA). The copolymerization temperature was maintained at 40°C. The resultant poly(acrylic acid) complex showed large water absorbability, about 720 times its dry weight, for which dependency on cross-linking degree was investigated.