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Improved Superabsorbent Polymers

by

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Abstract

This work is devoted to the synthesis, characterization and modification of a class of acrylic-based superabsorbent polymers. The techniques of inverse suspension and solution polymerisations were used for synthesis. Each absorbent was mainly characterised by its equilibrium capacity of water absorption and by the rate of absorption.

The swelling characteristics of the polymers were evaluated in terms of change in polymerisation variables which include, type and amount of crosslinker, monomer composition, process of polymerisation, temperature, initiator concentration, monomer concentration and particle size of the product. The swelling dependency on salinity was also examined. In some cases, the base polymer was blended with certain polymers in order to upgrade the swelling properties.

A swelling model was devised based on a simple viscoelastic model, *i.e.* Voigt model, to obtain a better understanding of the effect of the above-mentioned variables on the swelling behaviour.

Finally, our materials of choice were compared with some commercial analogues and some further comments have been made for continuing the work.

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An extended summary of the work

The work presented here explores the effects of a number of variables on the swelling properties of a class of acrylic-based superabsorbent polymers. The variables have been considered among the most important polymerisation parameters and included a couple of external parameters, *i.e.* the parameters which manifest themselves in service.

In order to produce superabsorbent polymers, two main techniques were used here, *i.e.* inverse suspension and solution polymerisation. The product obtained from these polymerisations were expected to be respectively in particle and bulk form. But this has not been the case and the product was obtained in different shapes, including granule and lump.
So, the first part of the work was devoted to produce a superabsorbent in particle form. This step was crucial to survey the effects of the variables on the swelling properties of the products, since the swelling was found to be quite sensitive to the size of the particles to be examined.

We experimented with various concentration of the surfactants, the rate of agitation, the change in surfactant, applying vacuum distillation, incorporating a variety of additives, changing the method of dewatering and finally incorporation of another class of stabilising systems, to produce the polymer in particle form. The last approach proved to be best for resolving the problem.

The effect of the various concentrations of ethylene glycol dimethacrylate on swelling was surveyed. The swelling as well as the crosslink density were affected. A polymer of high absorption capacity and gel strength was obtained, although the rate of absorption was low, *i.e.* the equilibrium swelling was attained in a fraction of an hour.

The effect on swelling of another class of crosslinkers, *i.e.* a water soluble type, was also examined. Again, the swelling in the various media and the structural properties of the polymers were affected by the crosslinker concentration. A decreased swelling was obtained at the expense of an increase in the crosslink density. Here again, a polymer of high absorption capacity was obtained, but at a very low loading of crosslinker concentration and still having a low rate of absorption.

Incorporating to the polymer structure of a non-ionic monomer led to a decrease in the equilibrium swelling, but the rate of water absorption was much improved. This observation was accounted for in terms of the increased mobility and the screening effect on the anionic repeating units, as well as the effect of drying on the morphology of the polymer chains.

The inverse suspension was replaced by a solution technique, in order to convert it into a simple method of synthesis and to make the product cheaper. Although the swelling capacity at the same crosslinker concentration was reduced to some extent, the rate of absorption was still poor.

To be able to predict the swelling properties, we devised a model which was based on the two element Voigt model, already used for explaining the creep behaviour of typical viscoelastic materials. The spring and the dashpot elements of the model were considered respectively as the resistance to expansion and to permeation for an absorbent system. A very good fit of the experimental swelling data was achieved using a two variable exponential relationship, showing the strain behaviour of the model under any applied stress. A wide range of the values was obtained for these two parameters which characterise any absorbent studied so far. Based on the model parameters, we justified the effect on absorption rate of an increase in the crosslinker concentration and of using acrylamide.

The solution polymerisation process is extensively used industrially to produce acrylic-based superabsorbent polymers. Using a simple, small scale laboratory version of the polymerisation part of this process, which permits contact with air and evaporation of water, the effect of varying the heat input to the reaction mixture and the initiator concentration were also explored. The presence of oxygen resulted in an inhibition period which lengthened the time for completing the polymerisation and consequently increased evaporative losses of water. The absorbency of the reaction products was higher under the conditions which gave short reaction times. Long reaction times resulted in long inhibition periods, runaway polymerisations and low absorbency. These effects were accounted for in terms of oxygen participation in the reaction and extensive losses of water.

The existence of an inhibition period and observation of a sudden normal polymerisation was confirmed by simulating the bench-scale polymerisation through the use of a differential scanning calorimeter. A variety of micropolymerisations was run with DSC, at different set temperatures and initiator concentrations.

The particles obtained from various inverse suspension and solution systems were expected to impose certain effects on the swelling properties, because of their sizes. This was assessed through measuring the swelling properties of selected particles which differed in size. A higher swelling capacity and rate were observed for the smaller particles. These observations were accounted for in terms of the increased surface area and the excessive capillary effect within the smaller particles.

The effect on the swelling properties of the ionic strength of the swelling media was also surveyed. The change in the crosslinker concentration showed some effect. This observation was accounted for in terms of a change in the rigidity of the polymer structure.

For running polymerisations at higher monomer concentration, the initiator and the neutraliser were replaced by their more water soluble counterparts. An increase in monomer concentration led to a decrease in the swelling capacity, but to an improved rate of absorption. The resulting porous structure was partly responsible for this observation.

In other work, we tried to create a superabsorbent of a porous structure. For this purpose, a variety of absorbent formulations containing poly (vinyl chloride) emulsion powder was polymerised. No improvement in the capacity and in the rate of absorption was obtained with these formulations, except that a vigorous foaming in the reacting medium occurred. But in an attempt to etch by a suitable solvent of the PVC particles embedded in the superabsorbent matrix, the rate of absorption was increased to some extent, while the equilibrium swelling was unchanged.

Finally, we compared our superabsorbents with a number of commercially available types, which were similar in their structure and the method of synthesis. If a better swelling property is defined as the higher water uptake at a shorter period of time, the sample of solution polymerisation of a highly monomer-loaded system showed better properties than the commercials.

Chapter 1: INTRODUCTION

1.1 Definition

Hydrophilic polymers having ability to absorb large quantities of pure water, saline or physiological solutions are named superabsorbent polymers (SAP)[1] . To qualify as a superabsorbent, a dry material should spontaneously imbibe about twenty times or more of its own weight of aqueous fluid. Moreover, the swollen material should retain its original shape, *i.e.* a swollen bead is still recognizable as a bead, a swollen fiber as a fiber, and a swollen film as a film (*Fig. 1.1*). The 'hydrogel' resulting from the transformation of the dry superabsorbent must have sufficient physical integrity to resist flow and fusion with neighboring particles. When exposed to an excess of water, true superabsorbent hydrogel particles swell to their equilibrium volume and do not dissolve. The mechanisms driving swelling are exactly the same as those for dissolution. The swollen polymer is prevented from actually dissolving by some form of network tie-points generally provided by crosslinking [2].

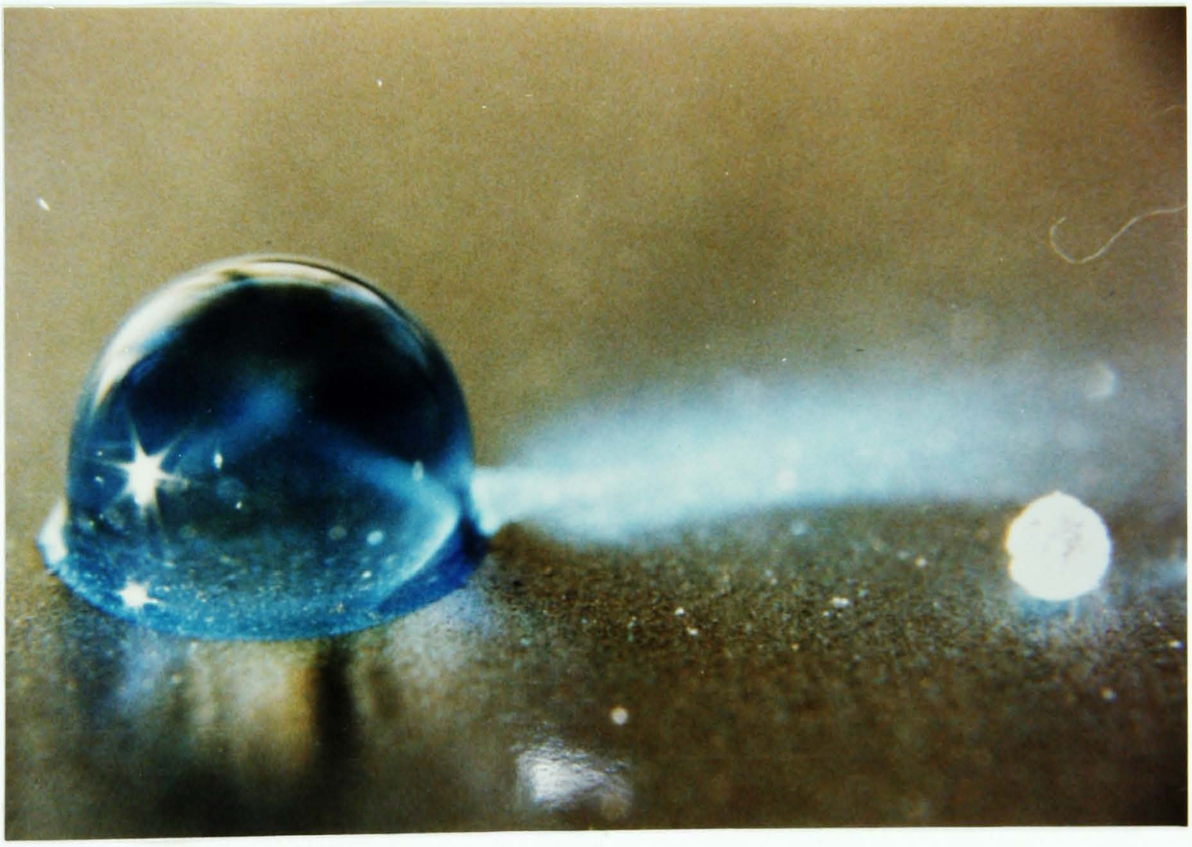


Figure 1.1 A dry particle of superabsorbent against its swollen counterpart

This class of material originated in the U.S during the late 1950's and was designed for very focused applications, such as water retention agents in agriculture and fire-fighting aids. But their real industrial-scale development took place in Japan in the mid-70's in the personal care area. It appeared that SAP could be a competitively-priced alternative for wood fluff, traditionally-used in baby diapers and catemanial items[3].

Superabsorbent polymers have revolutionized the personal care industry over the past decade and nearly 450,000 tons of SAP are now produced annually[4].

1.2 Analysis of superabsorbents

Desired features of SAPs are: high water absorbency (they should absorb and retain huge amounts of water even under load or in contact with other materials), high absorption rates (a large amount of fluid must be absorbed per unit of time) and good gel strength (the material should not become 'slimy' and flow away after swelling). These requirements are dependent on the final use of material. For some applications, fluid absorption should be reversible (the polymer must be able to absorb and desorb the fluid several times without degradation). Moreover, they must be non-toxic and should not contain traces of unreacted monomers and, finally the cost of the raw material and the production process should be low.

In practice it is difficult for a polymer structure to meet all of these requirements simultaneously. How these properties are measured is optional and generally is as follows:

1.2.1 Absorption capacity

Absorption capacity is measured by putting a dry polymer sample in excess water for a time sufficient to saturate it and then after removing the excess of water, *e.g.* with a sponge, weighing the gel obtained. Synonymous terms used to describe swelling are, gel capacity, water absorbency, ratio of absorption, swelling ratio, swelling, swelling index, water retention value and so forth. The same definitions are also adopted for saline or physiological solutions (*e.g.* synthetic urine).

1.2.2 Absorption rate

The absorption rate can be expressed in two ways: either through the amount of fluid absorbed by a weighed amount of the polymer in a fixed short time (a rate factor) or through the time required by the polymer sample to absorb a given amount of fluid.

1.2.3 Gel strength

Gel strength measurement methods are even more exotic and in many cases a qualitative observation is preferred. Typical methods used include, the maximum diameter of a steel ball required to settle through the gel, the amount of gel free-flowing through a screen, or the pressure to be applied to the gel in order to force it to flow through a certain screen [1].

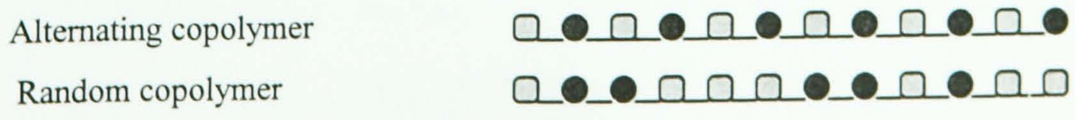
1.3 Structural design of superabsorbent polymers

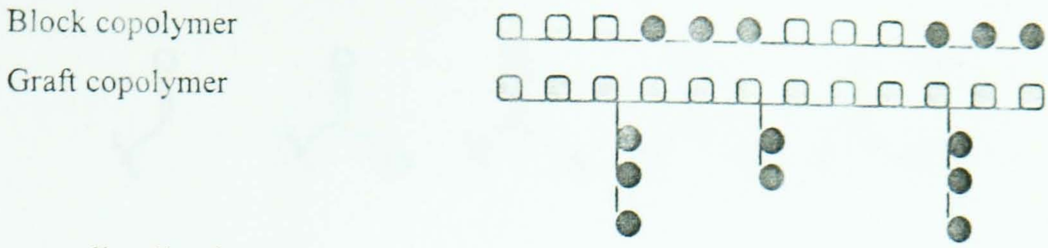
Macromolecules exhibiting solubility in aqueous solutions represent a diverse class of polymers ranging from biopolymers that direct life processes to synthetic systems with enormous commercial utility. This class of materials can be regarded as a base to produce superabsorbing polymers. Therefore, to design a desired superabsorbent polymer, a deep knowledge on hydrophilic polymers is fundamental. Solution properties and ultimate performance of water-soluble polymers are determined by specific structural characteristics of the solvated macromolecular backbone which can be explained as follows.

1.3.1 Polymer structure

The primary structure depends upon the nature of the repeating units (bond length and valence bond angles) as well as composition, location and frequency. In terms of monomer distribution, repeating units of a macromolecule may be arranged in a random, alternating, block or graft mode (*Fig. 1.2a*). On the other hand, a macromolecule may be linear, branched or dendritic (*Fig. 1.2b*) in terms of its segmental distribution.

a: Monomer distribution





b: Segment distribution

(1). Linear

(2). Branched-long branches

(3). Branched-branches protruding from branches (dendritic)

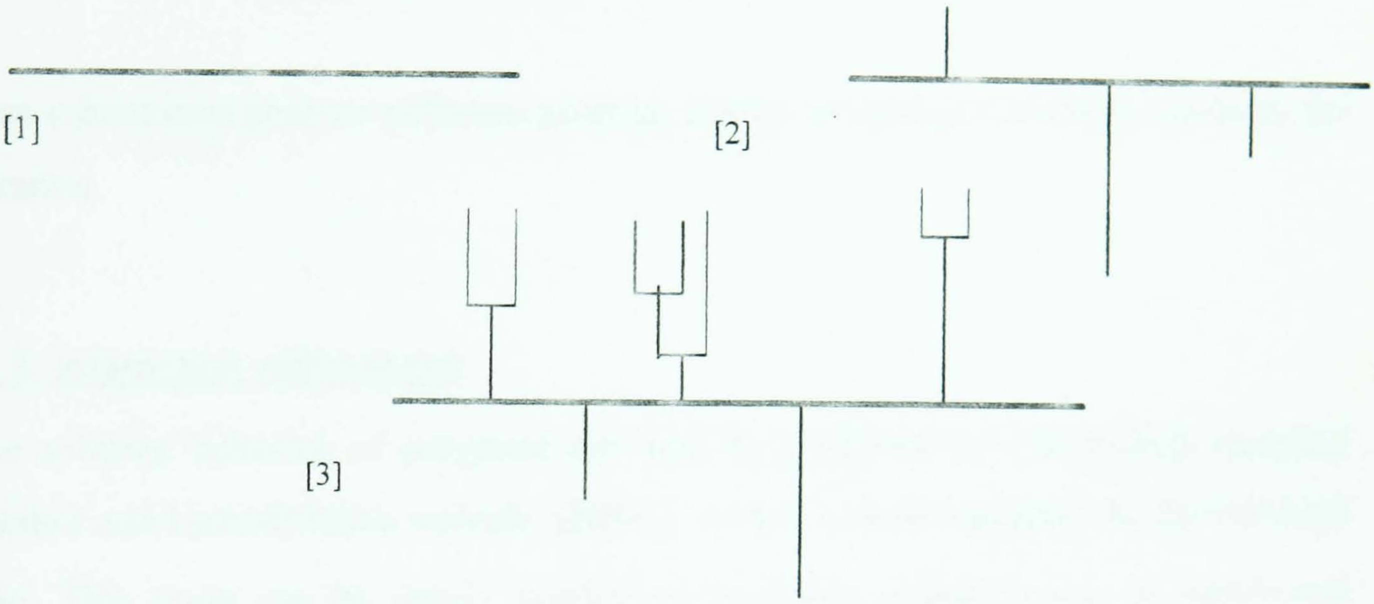


Figure 1.2 Primary structures of a typical macromolecule.

Secondary structure is related to configuration, conformation and intramolecular effects such as hydrogen bonding and ionic interactions. Tertiary structure is defined by intermolecular interactions while quaternary structure is governed by multiple-chain complexation.

1.3.2 Functional groups on polymer structure

For a desired polymer structure to be soluble in water, sufficient amounts of hydrophilic functional groups should be positioned along the backbone or side chains of the polymer. Examples of functional groups imparting water solubility include the following (*Fig. 1.3*):

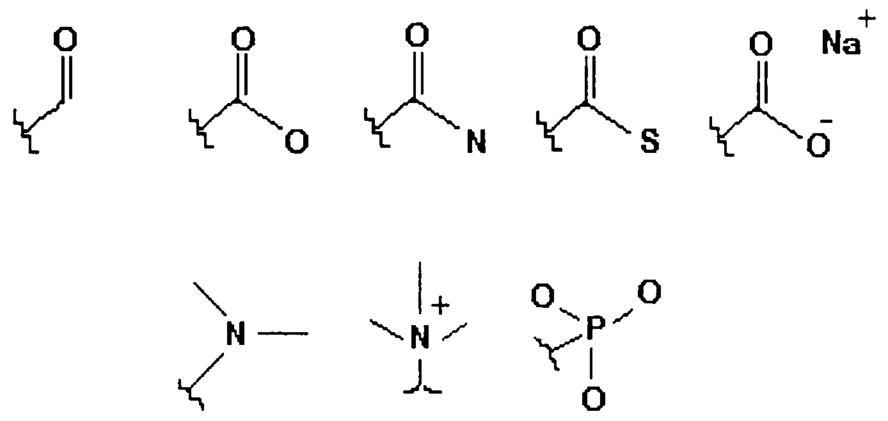


Figure 1.3 Typical functional groups impart water solubility

These substituents possess sufficient polarity, charge or hydrogen bonding capability for hydration.

1.3.3 Interaction with solvent

The solution behavior of polymers can best be predicted by considering chemical structure and hydrodynamic volume (**HDV**) or that volume occupied by the solvated chain. This chain can be simply considered as freely jointed having an end-to-end distance of, $\mathbf{r}$. The latter parameter can be related to the number of bonds, $\mathbf{n}$, and the length of each bond, $\mathbf{l}$, according to *Equation.* 1.1.

$$< \mathbf{r}^2 > = \mathbf{n}\mathbf{l}^2 \qquad (1.1)$$

However, more realistic nature of this typical chain is provided by taking into account the valence bond angle, θ, and conformational angle, φ. These two exhibit restriction or stiffening characteristics which are necessary to impose directionality to the chain (*Equation.* 1.2):

$$< \mathbf{r}^2 > = \mathbf{n}\mathbf{l}^2 \left(\frac{\mathbf{1} - \cos\theta}{\mathbf{1} + \cos\theta}\right)\left(\frac{\mathbf{1} + \cos\varphi}{\mathbf{1} - \cos\varphi}\right) \qquad (1.2)$$

In a macromolecular chain, additional expansion is predicted since segments cannot spatially occupy sites filled by other segments. Reasonably good approximation of the end-to-end distance can be obtained by including an expansion factor (α) (*Equation.* 1.3):

$$< r^2 > = nl^2 \left(\frac{1-\cos\theta}{1+\cos\theta}\right)\left(\frac{1+\overline{\cos\varphi}}{1-\overline{\cos\varphi}}\right) \alpha^2 \qquad (1.3)$$

In addition to the excluded volume and solvating effects, longer range molecular interactions, charge-charge repulsions (or attractions), hydrogen bonding, etc. may contribute to the value of (α).

1.3.4 Approaches to increase chain expansion in solvent

a) Increase in number of bonds "$\mathbf{n}$".

Potential synthetic approaches for increasing the average end-to-end distance and thus **HDV** of macromolecules are revealed by *Equation.* 1.3. The number of bonds, $\mathbf{n}$, can be increased by increasing the degree of polymerization **(DP)**. Choice of appropriate monomers and mechanisms (free-radical, anionic, cationic, coordination or template) can lead to high molecular weights. Polymers obtained by step polymerization usually have low molecular weight and rely on other interactions for reasonable values of **HDV**.

b) Increase in bond length "$\mathbf{l}$".

The effective bond length, $\mathbf{l}$, may be increased by the appropriate choice of monomers. Introduction of cyclic rings (polysaccharides), double or triple bonds increase rigidity by affecting valence bond angle, θ, changes. Likewise, rotational bond angles φ might be changed by introducing steric bulk along the backbone. Temperature, of course, determines the availability of various rotational states and thus **HDV**.

Adjacent polymer units may act in concert if associated by hydrogen bonding (partially-hydrolyzed acrylamide) or ionic charge interactions to yield longer effective bond lengths with restrictive rotations. In some cases, configurational restrictions lead to chain stiffening by helix formation (polypeptides, polynucleotides and polysaccharides).

c) Increase affinity to solvent

Finally, chain expansion may be realized by increasing the polymer-solvent interaction and by introducing like charges along or pendant to the macromolecular backbone. Extremely large **HDV** s are attainable for flexible polyelectrolytes in deionized water, although addition of simple electrolytes dramatically reduces **HDV**.

Viscosity, which is directly related to **HDV**, can yield a valuable insight into structure/performance relationships and can be defined by the Mark-Hawink-Sakurada expression (*Equation.* 1.4):

$$[\eta] = \mathbf{k.M}^{\alpha} \qquad (1.4)$$

where **M** is the molecular weight and **k** and α are characteristic of a particular polymer chain under specified conditions of solvent and temperature.
Of significance is the extension of the coil in dilute solution indicated by the value of α which can range from **0.5** for random coils in theta conditions to nearly **2.0** for extended rods. The higher the value of α is, the higher the extension of the coil will be. In semi-dilute and concentrated solutions, macromolecules are no longer isolated. Intermolecular interactions above a critical concentration lead to an increased value of viscosity[5].

For a polymer structure of desired associated prescribed parameters, including backbone molecular weight and the stiffening parameter, to be water swellable, provisions should be made to prevent the chains from attaining infinite solubility. This job can be done by crosslinking.

1.4 Crosslinking

1.4.1 In bulk

Crosslinking of polymer chains is basically carried out in two ways (*Fig.* 1.4). The first involves free-radical copolymerization with small amounts of polyvinylic comonomers (*Fig.* 1.4a). The use of polyunsaturated comonomers is by far the most common method for obtaining crosslinked poly(acrylates). In this case, crosslinking takes place simultaneously with chain growth. Diacrylates or bisacrylamides are the most frequently used polyunsaturated crosslinkers, although trifunctional acrylates and di-or triallyl compounds are sometimes employed. The second way consists of a nucleophilic or condensation reaction between the carboxylate or carboxylic pendant group of the linear polymer respectively, with suitable polyfunctional compounds (*Fig.* 1.4b); poly (epoxides), halo-epoxides and polyols are the most common. Spontaneous thermal crosslinking or auto-crosslinking without using crosslinker molecules occurs through hydrogen abstraction from the polymer backbone followed by radical combinations or involves intermolecular reactions between chemical functionalities already present in the polymer chains as pendant groups such as carboxyls and hydroxyls. These types of crosslinking reactions render covalent crosslinks.

Another way to produce crosslinks is treatment of polymerization mixtures with polyvalent metallic cation solutions. Multivalent metal ions can function as ionic bridges between carboxylate groups of two or more different poly(acrylate) chains. Zinc, calcium, strontium or barium acetates are used for this purpose at the end of (after) polymerization.

As in thermoplastic elastomers, crystalline domains (hard segments) act as crosslinks. Block copolymers of an acrylic monomer and a crystallisable monomer such as vinyl alcohol are apparently rendered insoluble through poly(vinyl alcohol) crystalline regions.

Hydrophobic association of pendant long chain hydrocarbon groups obtained by copolymerization of an acrylic monomer with a small amount of an oil-soluble comonomer, such as lauryl methacrylate, can prevent the polymer chains from dissolving. Hydrophilic association via hydrogen bonding may also be the mechanism by which some absorbents form gel.

1.4.2 Crosslinking at surface

In fact when a water-absorbent resin which crosslinked by any method described above is contacted with water, swelling first occurs at the surface of the particles and further penetration of water into the core, or toward the central parts of the particles, is retarded. Moreover the particles become sticky and form agglomerates (lumps), which block the diffusion of water toward particles into the agglomerates. As a result a low absorption rate is achieved. The phenomenon is sometimes referred as "fish-eyes" formation or "gel-blocking". A method of obviating these inconveniences is to render the gel surface structure more rigid; hence the effectiveness of surface crosslinking was found valuable.

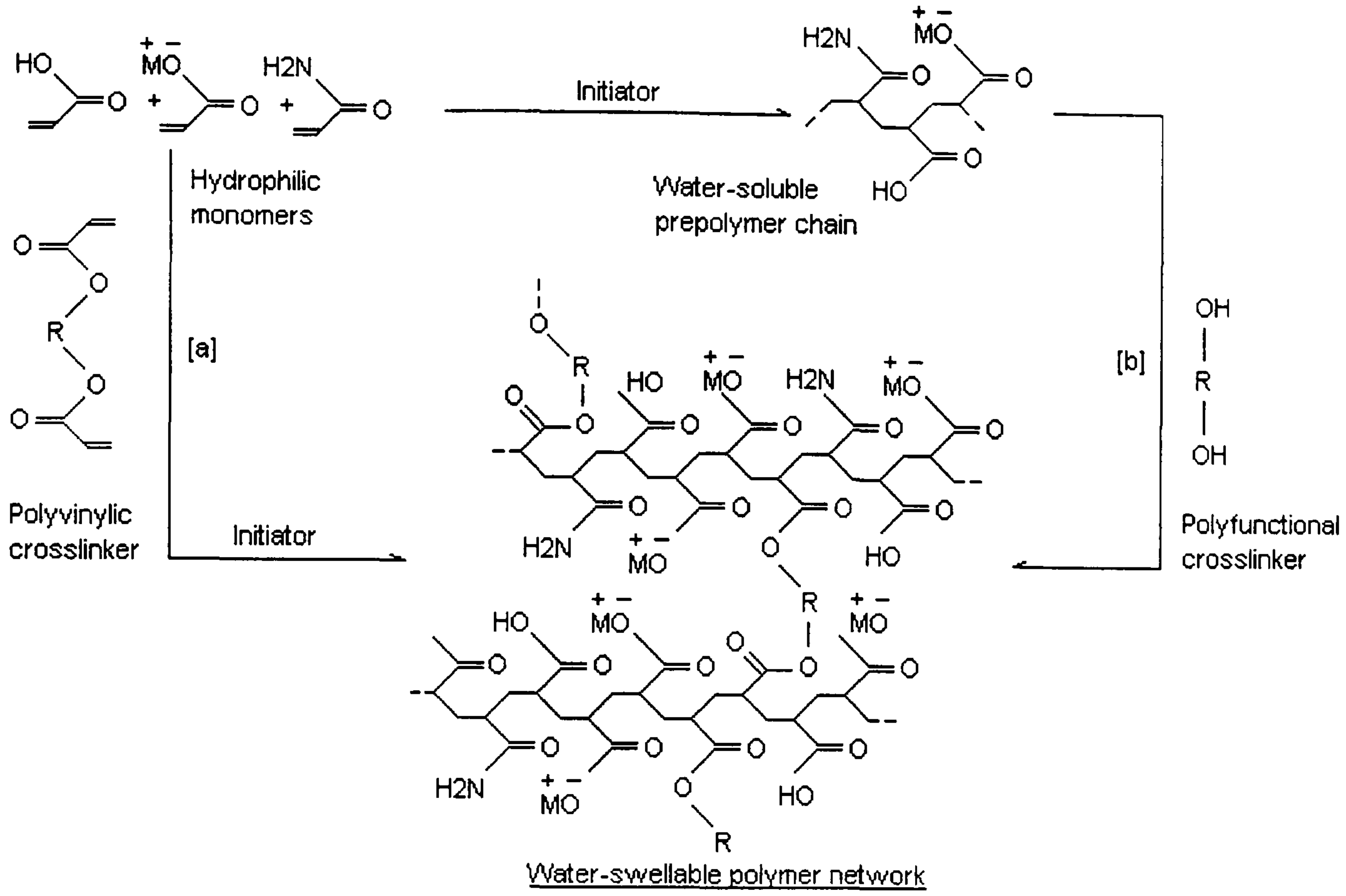


Figure 1.4 Two essential routes to crosslink polyacrylate superabsorbents.
a) simultaneous polymerization and crosslinking via radical mechanism.
b) crosslinking after polymerization via functional groups condensation.

Treatment with polyvalent metal salts or electrophilic polysubstituted compounds can also be applied to induce surface crosslinking of already crosslinked superabsorbent polymers recovered from the reaction system. Surface crosslinking of crosslinked acrylic-based superabsorbents is also accomplished by coating the particles with glycerin or other polyols. Adding peroxide at the end of the polymerization to the polymer slurry and heating the mixture at 50-100 °C above the decomposition temperature of the peroxide also leads to surface crosslinking [1,6,7].

1.5 Swelling

1.5.1 Non-ionic gels

When such a polymer is contacted with water or an aqueous solution, free energy of mixing comes to play because of polymer- solvent interaction which renders the polymer soluble in water. The infinite solubility can be prevented by the elastic response of the network which is provided by some crosslinking. Balancing these two forces determine the swelling capacity of non-charged networks.

1.5.2 Ionic gels

Most synthetic SAPs are polyelectrolyte gels, *i.e.* gels which bear ionic or ionisable moieties and active sites for crosslinking. When immersed in a high dielectric constant medium, such as aqueous fluids, these ionic moieties will dissociate and create an overall charge density along the chains as well as a high concentration of mobile ions in the gel (*Fig.* 1.5).

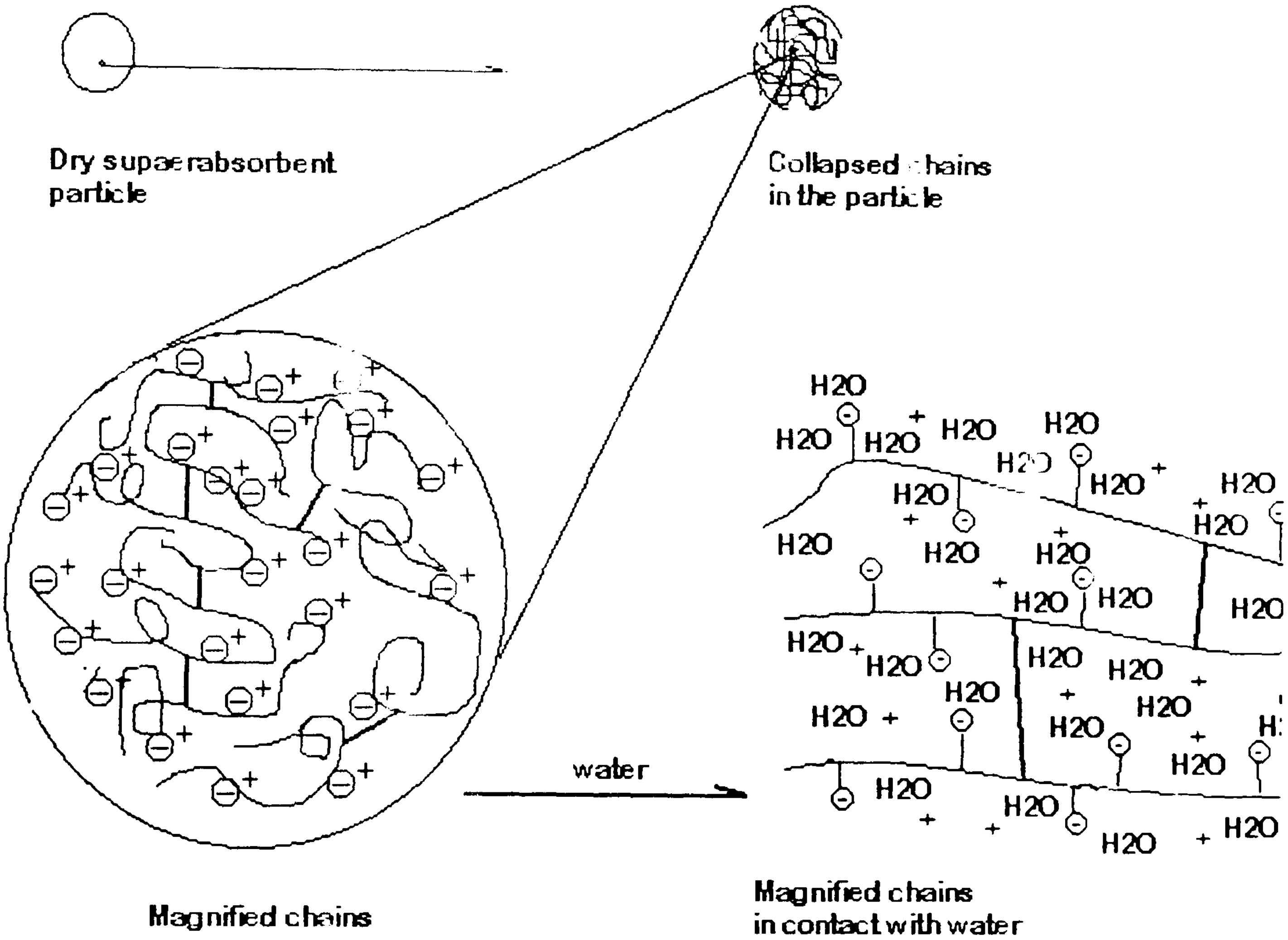


Figure 1.5 Schematic swelling of a typical ionic superabsorbent.

Compared to classical (non-charged) gel behavior, this ionic character will bring two "new players" forces to the system: (a) the osmotic pressure resulting from differences in ion concentration between the swollen gel and the external solution (for "macroscopic" electroneutrality reasons, mobile ions belonging to the gel cannot leave it and minimization of this osmotic pressure can only be achieved through dilution of the network charge density, *i.e.* swelling) and (b) the net charge density along the chains will generate some electrostatic repulsions between chain segments. Therefore the resulting expansion of the network is determined by the four forces and because of the latter two, the non-ionic absorbents are not as effective as ionic ones in pure-water absorbency[3].

It should be noted that the amount of crosslinker incorporated into the polymer chains is substantially lower than of the conventional thermoset resins. This is critical for facile diffusion of water into the polymer chains. Although increased superabsorbent strength in its gel form results from incorporating of higher dosage of crosslinker, it usually leads to decrease in water absorption capacity.

1.6 Synthetic methods

Water soluble or swellable polymers or copolymers are prepared by step growth or chain-growth polymerization of appropriate monomers or by post-reaction procedures. Distribution of the units along the backbone or on the side chain may be accomplished in different ways. In nearly all procedures, proper sequencing can be obtained by carefully controlling monomer reactivity, concentration, orders of addition and reaction conditions.

The major mechanisms for preparation of such polymers in commercial sense are direct chain growth or ring-opening of functionalised alkenes, carbonyl monomers or strained ring systems. Initiation may be accomplished free-radically, anionically, cationically or by coordination catalysis depending on monomer structure[5].

1.6.1 Homogenous polymerization

Commercial syntheses of high molecular weight water-soluble polymers employ monomer loadings of approximately 50% of the aqueous phase. Under such circumstances some relatively specialized technology is required to overcome the high exothermicity of the polymerization and to maintain a mobile reaction mixture.

The solution process is based on a copolymerization carried out in aqueous solution of the monomers. Due to crosslinking, the viscosity as well as elastic modulus increases very rapidly, affording small gel particles formed under high shear agitation. To overcome this, either dilute solutions(associated with an economic trade-off, due to insufficient reactor utilization) or a heterophase water-in-oil polymerization can be employed (*Fig.* 1.6). The final solid product is collected, dried and ground up in order to obtain the desired particle size distribution. The solution polymerization process is limited since the extreme viscosities generated at high conversions(>1,000,000 cp.) result in agitation and heat transfer difficulties, which lead to thermal instabilities. Thus polymerisations are usually performed between 40 and 60°C.

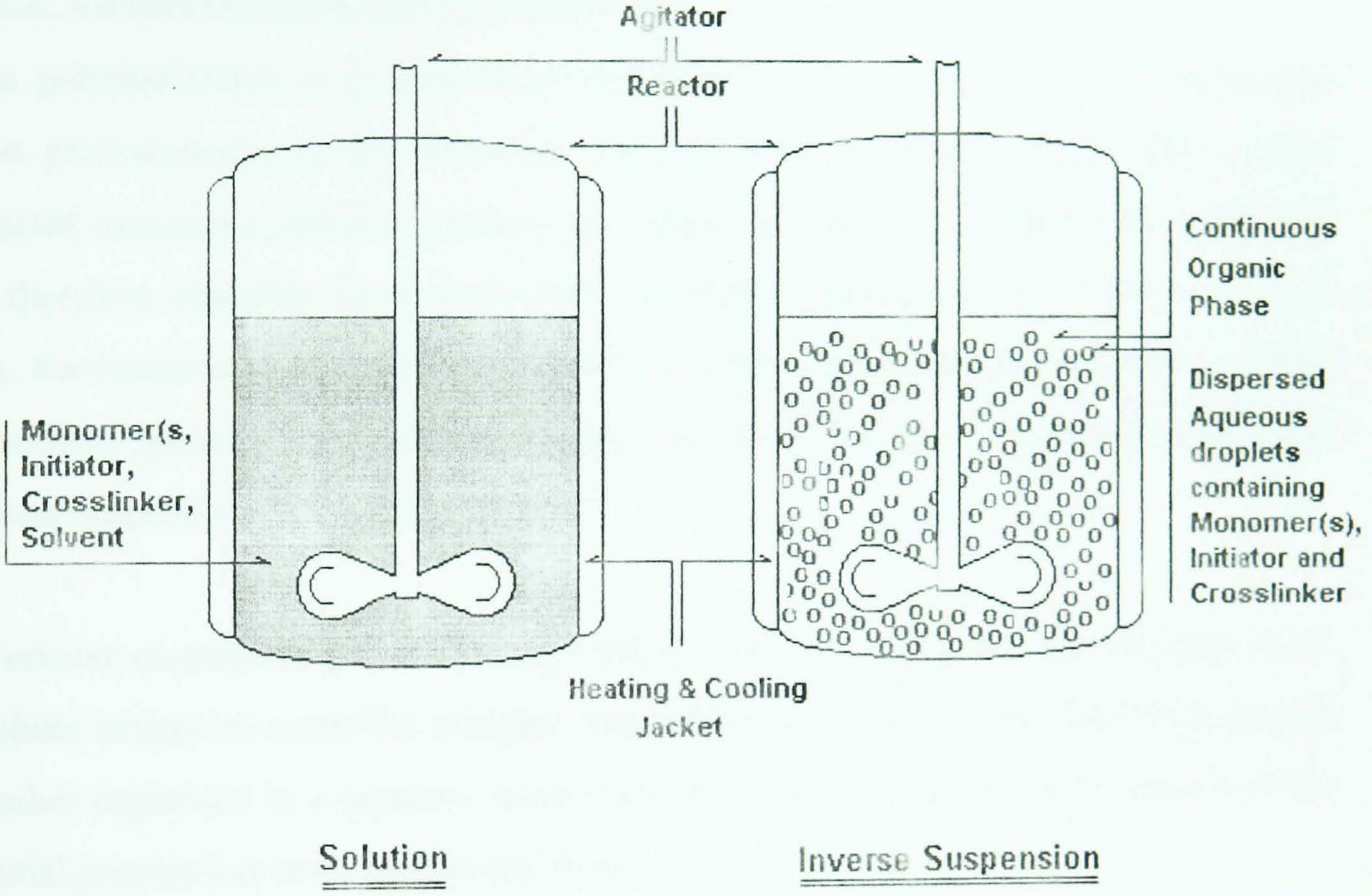


Figure 1.6 Set up of the two most common polymerization systems for SAP synthesis.

1.6.2 Heterophase polymerization

Into the typical reactor of heterophase polymerization shown in *Fig.* 1.6, the various heterophase synthetic procedures (*Fig.* 1.7) can be performed according to two primary thresholds: the onset of thermodynamic stability and the surface tension driving force. The former relates to the emulsifier concentration, while the latter is determined by the surface tensions of hydrophilic and lipophilic moieties within the emulsifier molecule. So, four polymerization regimes may be identified: I, macroemulsion; II, inverse-macroemulsion; III, microemulsion; IV, inverse-microemulsion. The macroemulsion domains can be further subdivided by a secondary transition at the critical micelle concentration (c.m.c).

1.6.2.1 Emulsion and Inverse-emulsion

For surfactant levels above the c.m.c, micelles or inverse-micelles are formed which can have a role in particle nucleation. Such polymerisations are referred to as “emulsion”(Ib) and “inverse-emulsion”(IIb) respectively.

1.6.2.2 Suspension and Inverse-suspension

If the polymerization is performed at emulsifier levels below the c.m.c, nucleation occurs predominantly in the monomer droplets. Each monomer droplet will contain unreacted monomers, solvent, primary and macroradicals and dead polymer chains and will therefore resemble an independent microbatch polymerization reactor. In such cases, the continuous phase serves primarily as a heat sink, although it can also contain the initiator species. These polymerisations are designated as “suspensions”(Ia) and “inverse-suspensions”(IIa) respectively [8].

The inverse suspension process is successfully carried out if the surface tension of the lipophilic moiety of emulsifier is higher than of its hydrophilic counterpart. This process is further explained in a separate section and the other sections as well, since it is the essential process has been used in our work.

Thermodynamically unstable **Thermodynamically stable**

I: Macroemulsion		**III**
(a) **Suspension**	**(b)** **Emulsion**	**Microemulsion**

*** $\Delta\gamma$ ↕ 0.0**

II: Inverse- Macroemulsion		**IV**
(a) **Inverse suspension**	**(b)** **Inverse emulsion**	**Inverse microemulsion**

0.0 → **cmc** **↑ Thermodynamic threshold**

Emulsifier concentration

*Surface tension driving force $\Delta\gamma = \gamma_{A.H} - \gamma_{O.L}$

γ = Surface tension

A.H = Aqueous phase – Hydrophilic moiety of emulsifier

O.L = Organic phase Lipophilic moiety of emulsifier

Process is oil in water if $\Delta\gamma > 0$

Process is water in oil if $\Delta\gamma < 0$

Figure 1.7 Features of various heterophase systems of polymerisations.

1.7 Inverse suspension polymerization

Inverse-suspension polymerization involves the dispersion of a solution of water-soluble monomer in a continuous organic phase. The latter can be either paraffinic or aromatic. Emulsifier levels are typically 2-5 wt.% of the organic phase and below the c.m.c thus polymerization proceeds in monomer droplets. The dispersion is thermodynamically unstable and requires both continuous, vigorous agitation and the addition of a low *HLB* (hydrophilic-lipophilic balance) steric stabilizer. This forms a condensed electrically-neutral interface layer and prevents coalescence. The monomer droplets are typically 1-100 microns in diameter and are controlled predominantly by the Weber number of the mixture.

When particles with nominal diameter of one micron are formed, the process is referred to as "inverse-microsuspension". The prefix "micro" designates the particle size and is needed to distinguish polymerisations including inverse-emulsion where interfacial reactions occur [8, 9].

The resulting spherical particles from this process are easily removed by filtration or centrifugation from the continuous organic phase. Upon drying, these particles or beads will directly provide a free-flowing powder. Apart from the unique flowing properties of the beads, this process displays some further advantages compared to the alternative gel or solution process. These include better control of reaction exotherms, regulation of particle size distribution and further possibilities for adjusting particle structure or morphology [6, 10].

1.8 Previous studies on hydrophilic polymers

1.8.1 Introduction

According to literature, superabsorbent polymers are water-insoluble hydrophilic polymers able to absorb an aqueous solution, as high as 10-1000 times their own weight. These are usually polyelectrolytes which bear crosslink sites and contain carboxylic groups. Dissociation of the latter groups helps the polymer coils to extend, because of electrostatic forces and osmotic pressure. Based on chemical structure, SAPs can be grouped into three main classes according to patent literature.

1. Crosslinked poly (acrylate)s or poly (acrylamide)s.
2. Cellulose or starch acrylonitrile graft copolymers.
3. Crosslinked maleic anhydride copolymers.

Other hydrophilic polymers, including poly (ethylene oxide), poly (vinyl alcohol) and poly (N-vinyl pyrrolidone) have been used as superabsorbents after special treatments like crosslinking or blending to prevent them from dissolving.

An up-to-date survey on the state of the art concerning the industrial research activities on SAPs has recently been done by Riccardo Po`[1]. This survey covers all the published United States (US), European (EP) and World (WO) patents on both chemical and application aspects in SAP production appeared in *Chemical Abstracts* on-line data bank through volume 119, 1993.

Regarding acrylic superabsorbents, subjects including synthetic procedures, monomers used, methods of crosslinking, various modifications on the polymers have been reviewed in detail.

Starch graft copolymers, modified cellulose copolymers and miscellaneous poly (saccharide) derivatives constitute the second topic of this survey. More than 300 patents has been covered in this survey.

Another recent and detailed review on hydrogels and superabsorbents has been written by Scranton et al [11].This review is concerned with methods of hydrogel synthesis including poly (hydroxyethyl methacrylates), (N- isopropylacrylamide), 2-oxazolines, poly (acrylic/ methacrylic acid) as well as preparation of hydrogel microspheres by emulsion/ suspension techniques. The second topic of this review was devoted to hydrogel synthesis by polymer modification. Unlike the patent survey done by Po`, this review is essentially based on academic activities done in this area. This review covers near 90 references.

Under the topic on preparation of hydrogel microspheres by emulsion/ suspension polymerisations, one of our works regarding synthesis and characterization of acrylic-based superabsorbents has been referenced (*Ref. 62. p422*). It should be noted, this is the only reference about SAP which has been used by Scranton et al to introduce inverse suspension techniques of polymerization.

Another recent review which is also based on industrial activities has been written by Buchholz [12]. This review contains 35 references which is devoted to recent advances in superabsorbent polyacrylates.

Finally general topics on superabsorbent polymers can be found in two books published in 1990 [2] and 1994 [13] which are the sole available books written on this field up to now.

Although, industrial research publications on SAPs are very extensive, the academic counterpart is quite poor. To avoid any redundant work, our literature survey was devised to be based on latest academic publications regarding in-use or potential materials which are promising to be used as superabsorbent polymers.

To prepare this survey, up to the latest publications (1996) contained mainly in *"Chemical abstracts", "RAPRA"* and *"Polymer Contents"* as well as miscellaneous references have been viewed.

This survey was sub-classified according to the structural nature of the polymers which are used or promising to be used as superabsorbent polymers.

1.8.2 Natural polymers

Among the naturally-occurring water-soluble polymers, *i.e.* polynucleotides, polypeptides and polysaccharides, derivatized polysaccharides are potentially important in absorbent technology. All of them have high values of stiffening parameter which can lead to large values of **HDV** in solutions. The three most abundant, naturally-occurring saccharides, cellulose, chitin and starch have been derivatized to yield water solubility.

Common derivatives include use of hydroxyethyl-, hydroxypropyl-, carboxymethyl-, sulfate-, and phosphate functions.

Xanthan is the extracellular polysaccharide produced by the microorganism *Xanthomonas campestris*. Xanthan (anionic) primary structure is based on a linear (1→ 4)- β- D- glucose backbone, as in cellulose, with charged (COO^-) trisaccharide side chains on every second residue, that impart semi-rigidity or a worm-like behaviour into its structure. The strong current interest in xanthan is its large potential for use as an additive to injection fluids for enhanced oil recovery. It can be used in its solution or crosslinked form, for which, in the latter case, the trivalent chromium ion is added to the commercial polymer commercially as a crosslinker. Several studies on xanthan have indicated good viscosity retention in seawater at temperatures up to 90 °C. The excellent stability of xanthan solutions in the presence of salts is probably due to the maintenance of order [14-15].

The high viscosity of these polymers at low solution concentrations, is due to both their high molecular weight and their high structural chain rigidity. The molecular reason for the high stiffness is most likely the multistranded nature of the polymers. The prevalence of the ordered, probably double-stranded, conformation of xanthan at high salt concentrations and low temperature, and the triple-stranded conformation of scleroglucan also provide a molecular basis for the enhanced long-term stability of these polymers under harsh conditions against to that observed for single-stranded polysaccharides [16-17].

Fungi of the genus *Sclerotium* secrete scleroglucan. The polymer is present both in fibre form and in aqueous solution in a triple helical conformation. A polycarboxylate has been obtained from this polymer through a selective and quantitative oxidation of the glucopyranosyl side chains and its conformational changes were reviewed [18]. This polymer has recently achieved much attention because of its potential as a thickening agent. Semi-dilute solutions of entangled scleroglucan show a thermoreversible gelation which occurs about 6 °C [19].

Schizophyllan is a nonionic extracellular polysaccharide coming from fungal fermentation and has been employed as an anti-tumor agent. It exists as a more rigid triple helix in aqueous solutions and consists of a main chain of (1→3)- β- linked D-glucose residues with one (1→ 6)-β- linked D- glucosyl group for every three glucose residues. The intrinsic viscosity of the latter polymer is not influenced by the ionic strength which is opposed to the observations for the xanthan polymer [20].

Although the biopolymers such as xanthan gums are suitable for low to moderate temperature and high salinity conditions the polyacrylamide and partially hydrolyzed polyacrylamide are suitable for low temperature and low salinity conditions. Specially tailored synthetic copolymers, such as HE polymers (HE is a trade name) are suitable for high salinity and high temperature reservoir conditions [21-22].

The phase transition behaviour of the water-xanthan system was investigated as a function of water content. Water content can be classified into 'free' and 'bound' water. The latter is further classified as 'freezing' and 'non-freezing' water. The 'non-freezing' water can be calculated from heat of fusion of water using a differential scanning calorimeter. The glass transition behaviour and the transition from the mesophase to isotropic liquid can be analyzed as a function of the non-freezing water content. It has been found that increase in water content results in an increase in bound water content and a decrease in the glass transition temperature [23].

Graft copolymerization of vinyl monomers onto cellulose can be carried out in both heterogeneous and homogeneous solvent systems to improve its water solubility properties. The desired solubility properties can be achieved through grafting acrylamide monomer onto the ethylcellulose backbone [24]. Hydrogels based on hydrophilic cellulose ethers can be obtained by crosslinking hydroxyethyl cellulose (HEC) or carboxymethyl cellulose (CMC) with divinylsulphone. The crosslinking reaction is much more efficient with HEC of nonionic character. The crosslinker reacts with the hydroxyl groups on the cellulose ethers.

With CMC, the majority of the hydroxyl groups at the C_6 position are substituted by carboxymethyl groups. Only a few hydroxyl groups at C_6 as well as most of the less reactive hydroxyl groups at C_2 and C_3 remain available for the crosslinking reaction. The electric charges carried by the CMC impede intermolecular contacts because of the electrostatic repulsion. Hence, the divinylsulphone could mostly be used to link two hydroxyl groups of the same macromolecule instead of forming effective crosslinks. On the other hand, the ionic CMC gels show larger swelling, particularly in solutions of low ionic strength. In the swollen state , the mechanical behavior of the gels is largely influenced by non-Gaussian effects. With the cellulosic gels, these become noticeable at considerably lower degrees of swelling than with gels made from acrylic polyelectrolytes. The enhancement of the modulus due to non-Gaussian behavior is a highly desirable effect. when such gels are considered a potential material for superabsorbents [25].

The fundamental properties of the HEC superabsorbents including viscosity, the state of the sorbed water and moisture absorption has been compared with some commercial ones. The investigated absorbents were HEC graft copolymers containing partially hydrolyzed polyacrylamide, partially hydrolyzed polymethacrylate. sodium polyacrylate and polydimethylaminopropyl acrylamide [26].

The influence of several structural parameters on the swelling behaviour in water or in saline water of starch-based superabsorbent gels has been deeply explained. Anionic gels were obtained by saponification of grafted poly (acrylonitrile) onto starch. Crosslinks and sodium acrylate units are formed during the alkaline hydrolysis. Cationic gels have been synthesized by graft copolymerization with a cationic monomer (trimethylaminoethylacrylate chloride) and a crosslinking agent, such as methylene bisacrylamide. The degree of swelling decreases drastically with the crosslink density. Among these properties the polymerization rate depends on monomer concentration. The higher the dilution of the reaction mixture, the higher the water retention of the gel. However the material obtained has a poor consistency. The percentage of linear copolymers formed increases with dilution and of very high dilutions gel formation can even be prevented. On the other hand, highly concentrated mixtures lead to gels with low swelling capacity. Hydrolysis of starch grafted PAN with LiOH leads to gels with higher absorbency compared to NaOH and KOH. The decrease of the network expansion through increase in ionic strength was ascribed to screening of the ionic charges bound to the network and to the decrease of the osmotic pressure difference between the gel and the external solution.

The ionic strength of the solution was found to be dependent on both the mobile ion concentration and their valency. Small quantities of divalent or trivalent ions can drastically decrease the swelling values, due to the complexing ability of carboxylate groups inducing intramolecular and intermolecular complex formation. Thus the 'effective' crosslink density of the network increases. The swelling capacity was also drastically reduced at a certain range of NaCl concentrations. This transition was due to polymer/polymer affinity which induces the expulsion of free water from the network. When the crosslink density of the gel increased, the characteristic time for swelling or retardation time decreased as well, indicating a faster rate of swelling [27].

Superabsorbent polymers were prepared using acrylonitrile grafted to corn starch employing low levels of gamma ray radiation as initiator. In the evaluation of superabsorbents as desiccants, data obtained reveal the superiority of superabsorbent over silica gel as a desiccant [28].

Graft copolymerization of acrylamide onto starch initiated by a redox system of Ce^{4+} to Ce^{3+} ions was also examined [29].

1.8.3 Inorganic polymers

Inorganic polymers are another class of water-soluble or potential water -swellable materials. Among the most important are poly (meta-phosphoric acid) and poly (silicic acid) [5].

1.8.4 Synthetic polymers

1.8.4.1 Non-ionic polymers

Synthetic water-soluble polymers can be classified into non-charged and charged polymers. Polar, nonionic functional groups can impart water-solubility if present in sufficient amounts along or pendant to the backbone. Amide, lactam, hydroxyl and ether groups are the most important ones. Corresponding polymers have similar solution behaviour in pure water and in saline. Attention was concentrated on hydrogels prepared by gamma-irradiation of aqueous mixtures of vinyl pyrrolidone with various hydrophobic monomers, methyl methacrylate and methyl acrylate. Applications of hydrogels are usually limited to materials with a water content up to about 80%. Increased water content results in unacceptable mechanical properties. The latter can be

improved by control of chemical (covalent) and physical (especially hydrophobic) crosslinking. It was observed that small clusters of hydrophobic groups in a predominantly hydrophilic network may serve to increase load bearing, yet with avoidance of the embrittlement caused by carbon-carbon crosslinks. [10, 30]
The monomer is frequently copolymerised with hydrophobic monomers in the presence of a crosslinker to produce xerogels. The crosslinked form of PVP (using ethylene glycol dimethacrylate) has a very high water absorbency but it is rarely used as a hydrogel because of its fragility. With these polymers, an increase in crosslinker results in: decrease in sol fraction, increase in modulus, an increase in polymer-solvent interaction parameter (due to the hydrophobicity of the crosslinker), a decrease in molecular weight between two successive crosslinks, a decrease in water content, a decrease in freezing water, and non-freezing water remains rather constant [31].

Partially-hydrolyzed polyacrylamide can form gels as the result of the formation of the crosslinks between added chromium ion Cr^{+3} and pendant carboxylate groups of the polymer. The de-gelation reaction is rather more complex, as the starting solution contains not only the elements necessary for gelation, but also a third reagent, sodium salicylate, which is a thermodynamically-strong complexing agent for the chromium ion Cr^{+3}. To promote gelation, the pH and the salicylate concentration can be optionally adjusted.[32-33] .

The nonionic poly (N-vinylacetamide), poly NVA, hydrogels were prepared by the copolymerization of NVA with divinyl compounds such as methylene bisacrylamide, methylene bisNVA, and butylene bisNVA in high yield. The resulting hydrogels are more stable than polyacrylamide gel and show quite a high swelling property in a wide range of pH (1-12) and even in a 5M NaCl solution. They show not only the typical characteristics of nonionic hydrogels (10-35g/g in distilled water) but also an amphiphilic property and they swell well in some organic solvents.
The partially hydrolyzed gels, *i.e.* cationic crosslinked poly (NVA-*co*-vinylamine) can take water up to 400g/g which depends on the percent of hydrolysis. Moreover, when the total concentration of NVA and crosslinker decreases in the polymerization system, the gel swelling ratio may increase. With nonionic crosslinked polyNVA, the swelling does not change with pH. In the case of cationic gel, it has a maximum value at pH 4.5 since the pK_b value of polyvinylamine is about 4.0, the amino group of hydrogels is not

ionized at high pH. The maximum in the swelling curve with pH is typical in behavior of ionic hydrogels such as polyacrylamide-acrylic acid and crosslinked polyelectrolytes copolymers. The reduction in swelling at higher pHs is due to the decrease in ionization of the network. The decline in swelling at a low pH is considered to be due to the elimination of Donnan ion exclusion at a high ion concentration [34].

The preparation of non-ionic hydrogels based on star-shaped polyoxazoline by means of partial hydrolysis of this polymer followed by crosslinking reaction or the copolymerization with the bifunctional oxazoline monomer was reported. The gels form stable dispersion in water and saline solutions. The swelling degrees in two latter solution was obtained the same about 6-7 g/g. Moreover the equilibrium degree of swelling was increased with increase in the feed ratio of the initiator to the monomer. Taking into account of the wide range of the 2-oxazoline monomers, a wide variety of hydrogels having various functional groups in the side chains can be expected by this preparative method [35].

1.8.4.2 Ionic polymers

Polymers possessing charges can be classified into two main groups based on their behavior in aqueous electrolyte solutions. Polyelectrolytes, such as polyanions (negative charges for carboxylate, sulfonate and phosphonate groups) or polycations (positive charges such as ammonium or quaternary ammonium salts) with their associated counter-ions normally collapse to smaller hydrodynamic dimensions upon addition of electrolytes, while ampholytes (having both positive and negative charges along the chain) expand in dilute electrolyte solutions. Electrostatic effects, counter-ion binding, solvating and local dielectric effects determine this phase behaviour and solubility.

Hydrogels containing phosphate groups were prepared by copolymerization of 2-methacryloyloxyethyl dihydrogen phosphate (phosmer) and various hydrophilic monomers [N,N-dimethylacrylamide (DMAAm), acrylic acid (AAc) and 2-hydroxyethyl methacrylate (HEMA). These hydrogels are thermo-sensitive. Phosmer-DMAAm and phosmer-HEMA hydrogels deswell with increasing temperature, but for the phosmer-AAc hydrogel the swelling ratio increases with temperature. The swelling ratio decreases with an increase in phosphate group content, because the latter is acting both as the functional group and the crosslinking agent [36].

Various classes of hydrogels, their polymerization and processing, properties, test methods, health and safety factors and uses have been reviewed [37]. Polymeric hydrogels of methacrylic acid monomer characterized by a high crosslink density (through 1,4-butanediol dimethacrylate) show relatively low swelling in water and are suitable for use as ion-exchange resins, where some swelling is necessary but high swelling ratio must be avoided [38]. Swelling equilibria of ionized poly (methacrylic acid) gels was studied in the absence of salt [39].

A copolymer in powder form with a particle size of <2mm and water absorbency of 500-1000 g/g was synthesized by suspension polymerization of an aqueous solution of a mixture of acrylic acid, sodium acrylate and a crosslinking agent in toluene in the presence of dispersing agent. Increase in ethyl cellulose content at a certain range as dispersant resulted in a decrease in the mean particle size. With a constant stabilizer content in the region of strong stabilization, a reduction in mean particle size was observed with an increase in agitation rate. In the intermediate regime the stability of the system starts to fall at a high level of mixing, since this decreases the strength of the protective layer in this region. The water/ oil ratio is also important. An increase in the water phase leads to a reduction in the emulsion stability due to an increase in the probability of collision between the particles which is linked with growth in mean particle size. With an increase in the crosslinker, MBA, water absorption diminishes. Partial neutralization of the acid groups results in an increase water uptake but with neutralizations of >90% of the carboxyl groups, water absorption was reduced [40].

The isoionic dilution method, in which there would be no configurational change if the polyelectrolyte solution is diluted with salt solution so that the effective ionic strength is kept constant, has been used to measure the intrinsic viscosity of a poly (acrylic acid) sample as a function of neutralization degree at low ionic strength. The viscosity increases linearly with neutralization in the region 0.06 to 0.35 with a large slope, which decreases abruptly after 0.35 neutralization. The results are in good agreement with the Manning theory in which a critical value of 0.35 ionic content for ion binding is predicted [41].

Samples of poly (acrylic acid) neutralized to varying degrees with sodium hydroxide were subjected to gamma-irradiation to yield insoluble crosslinked hydrogels. For all samples, gel formation only occurred above a certain minimum concentration of the polymer solution and above a critical irradiation dosage. Crosslinking is less efficient at higher neutralization levels. It has been suggested that the polyion charges act cooperatively to exert long-range electrostatic forces in solution. At high levels of neutralization, the macromolecule could expand to such an extent, that the distance between neighboring charges becomes too great for optimum cooperation effects between the charges. As these cooperative electrostatic effects are thought to play a major role in structuring water within the gel, a reduction in these cooperative forces could explain reduced water uptake of the gel at high levels of neutralization.

The electrostatic effects have been shown to play a major role in water sorption. An electric charge applied across a swollen gel causes the gel to collapse above a particular potential, the volume of the collapsed gel being up to several hundred times smaller than that of the swollen gel. This indicates that the electrostatic forces are much more responsible than osmotic pressure in swelling [42].

Diallyl ammonium chloride (DAAC) was radically copolymerised with acrylamide (AAm). The rate of polymerization increased with an increase in the mole fraction of AAm in the feed. The insoluble fraction of the polymer sample was separated using a typical phase transition phenomenon of hydrogel. The polymer sample containing both soluble and insoluble fractions was swollen in water and then acetone added until the gel or insoluble fraction drastically shrunk to give a precipitate. The latter, separated by centrifuging, was swollen again in water, followed by acetone addition, and this swell-shrunk process was repeated at least three times until no sol was extracted in the supernatant liquid. The reduction of sol content was achieved by increasing the mole fraction of AAm in the monomer mixture. With a 50:50 mixture of DAAC: AAm the swelling ratio was decreased by conversion or the progress of gelation. The quite high volume swelling value was observed at 37% conversion [43].

The polyelectrolyte network of sodium methacrylate/acrylamide copolymer forms complexes with oppositely charged surfactants, cetylpyridinum bromide in mixed water-alcohol media. This interaction results in gel shrinking or collapse. The complexes of charged networks with surfactants are good absorbers for different organic compounds, dyes, phenols etc.[44]

The kinetics of swelling of sodium polyacrylate has been studied by gravimetric, microscopic observation and calorimetric methods. The swelling process followed a first-order kinetics and the rate constant was of the order of 0.01 s. The rate constant was depressed by the addition of sodium chloride. The activation energy of the swelling was 46.0±6.2 kJ/mol and decreased with the increase in sodium chloride concentration. The swelling is an exothermic process in which 196±17 J/g is released and this quantity did not vary with the addition of sodium chloride[45-46].

The rheological behavior of a water soluble polymer can be altered by copolymerization with various monomers to fit the service requirements. The added monomers usually contain ionic groups (ion pairs) to create charges along the backbone, or hydrophobic groups which can associate to alter solubility behavior.

1.8.4.3 Amphoteric polymers

Amphoteric water-soluble polymers contain zwitterions on the same monomer (*i.e.* betaines) or along the same backbone (ampholytes). In some cases water-solubility can be obtained by preparing interpolymer complexes of polyanions and polycations. Amphoteric polymers are generally prepared by copolymerization of betaine monomers or ampholytic monomer pairs with appropriate comonomers, mainly acrylamide. Polyamphoterics have unusual solution properties. Unlike typical polyelectrolytes, they are more soluble with significantly higher viscosities in aqueous salt solutions than in deionized water. For this reason, these polymers are called "anti-polyelectrolytes".

For a polyelectrolyte containing one type of charge, the addition of salt decreases hydrodynamic volume of the polymer. However, a polyampholyte will expand in the presence of added electrolyte. The addition of salt breaks up intramolecular and intramonomer interactions allowing the hydrodynamic volume of the polymer coil to increase. In other words, this is an increased polymer-solvent interaction, allowing the chains to behave more freely. The unusual properties of these polymers may find utility in brine viscosification, enhanced oil recovery, drag reduction [47-79] and superabsorbency.

A number of naturally occurring materials, such as pulp and sponge retain water, but release the water under mechanical application of pressure, because a capillary effect is involved in the absorption. However, the water absorbency of ionomers is based on electrostatic interactions and water is not as easily removed by the application of pressure. In one study, a mixture of ion pair comonomer (3-methacrylamidopropyl trimethyl ammonium 2-acrylamido-2-methylpropanesulfonate, acrylamide and hydroxyethyl cellulose with 100 ml distilled water was degassed by a freeze-thaw cycle and sealed *in vacuo*. A ^{60}Co gamma ray source of radiation was utilized for initiation of polymerization. Water absorbency of the product in distilled water and 1M NaCl solution is 15 and 22g/g respectively [6].

In another study, three hydrogels were prepared using the same monomer and crosslinker concentration: first, an ampholytic hydrogel by using ion pair monomer, methacrylamidopropyl trimethyl ammonium chloride and sodium styrene sulfonate; a second ampholyte hydrogel using the zwitterionic sulfobetaine monomer and, third, an uncharged polyacrylamide hydrogel as a blank. The betaine-based hydrogel is insensitive to changes in NaCl concentration below 0.01M, as expected, because of the balance between positive and negative fixed charges in the gel. One advantage of using betaine for creating an ampholytic hydrogel is that the molar ratio of cationic to anionic charges in the hydrogel is automatically unity. Water absorbency of these hydrogels in 1M NaCl aqueous solution was 60, 33 and 22 g/g respectively. Apparently, some of the increase in swelling at appreciable salt concentration (>0.1M) for the ampholytic hydrogels may be attributed to salting-in of the polymer [80].

The graft copolymers, of the ampholytic ion pair comonomer 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methyl propanesulphonate with acrylamide onto starch and hydroxyethyl cellulose, by both ceric ion and ^{60}Co irradiation, have been prepared and show promising use as viscosity modifiers in oil recovery and superabsorbents for saline media. It has been shown that the polyampholyte has a greater affinity for salt solutions than for pure water, thus higher absorbency can be expected in the former than in the latter [81].

1.8.4.4 Hydrophobically-modified polymers

Hydrophobically modified polymers are water soluble synthetic polymers containing non-polar groups which aggregate in polar media. Aggregation may result in increased viscosity of polymer solution and hence an increased **HDV** of the polymer chains. These polymers can be placed into one of two categories: those that form intramolecular association and those that form intermolecular association. Both in reality, form micro-heterogeneous solutions in water [82-95].

1.8.4.5 Rod-like polymers

Finally, rod-like polymers are potentially suitable for increasing the viscosity of aqueous solutions provided that some hydrophilicity can be introduced in their structures. These types of polymers may be useful in the field of saline superabsorbency [96-104]

1.9 Industry status

1.9.1 Applications

The commercially important superabsorbent polymers are sodium salts of crosslinked poly(acrylic acid) and graft copolymers of cellulose or starch-acrylonitrile. Superabsorbent polymer technology has been available since the early 1970's, but the market potential of superabsorbent polymers was not realized until the Japanese used them extensively for personal care products. Commercial production started in Japan in 1978. In the United States, until a few years ago, these materials were only used in some adult incontinence products. These absorbing polymers were reintroduced to the United States after Procter & Gamble test marketed its "Ultra Pampers" disposable baby diaper in 1985. Superabsorbent polymers are used in non-woven presentations in three particular segments of personal care products: infant disposable diapers, adult incontinence briefs and feminine pads. In disposable baby diapers, the superabsorbent polymer is used at the rate of 5 to 6g per diaper, whereas in the adult incontinence diapers 12-14g of superabsorbent is used per pad. In the external feminine hygiene products, only about 1.0-1.5g of superabsorbent is used per pad. Personal hygiene products accounts for more than 95% of the market for superabsorbents manufactured [7]. Other uses of superabsorbent polymers are in civil engineering, *e.g.* mud conditioners, lubricants, sealing material, wall covering to prevent drops of condensation from forming, and in agriculture/ gardening, *e.g.* water retention material, artificial culture soil, etc. A tiny fraction of the total superabsorbent can be used in following areas, according to the patents [105-162]:

- Artificial snow [105-109].
- Water scavenger pouches to absorb water from hydrocarbon fuel and oil [110].
- Artificial soils for hydroponics [111-115].
- Drilling fluid additive usable in wellbores [116-117].
- Sealing underground formations, joints in water-supply pipes, building constructions, fibre optic cables [118-121].
- Polymer concrete compositions [122-123].
- Static demolition agent for destroying rock structures [124].
- Thickening sewage [125].
- Absorbing moisture from powder of coking coal [126].
- Biomass support and carrier [127].
- Antifouling coating for watercraft [128].
- A thermal energy storage [129].
- A dew-preventing coating [130].
- Preventing electrolyte leakage and electrode drowning [131-132].
- Thixotropic agent in poly(vinyl chloride) paste [133].
- Protecting wires carrying dc currents and healing shorts caused by moisture in such wires [134].
- Preserving biological specimens in formaldehyde solution [135].
- Preserving the freshness of packed fruit and vegetables [136].
- Towels, bandages and absorbent laminates [137-144].
- Bubble-free phantoms for NMR diagnosis [145].
- Biosensors for determination of biochemical analytes [146].
- Controlled release of drugs [147-148].
- Wound dressing gel and foam [149-150].
- Laminated articles coming into contact with body fluids, prosthesis implants, artificial kidneys, membranes and tubing [151].
- Emulsions with moisturizing activity toward human skin [152-153].
- Gelling materials in suction equipment to absorb medical wastes and body fluids (blood, lymph liquid, medullary fluid, amniotic fluid, urine) [154].

- Deodorizing air [155].
- Desiccant materials in refrigeration systems [156].
- Aqueous gel for fire-fighting [157-158].
- Water desalination media [159].
- Filtration media [160].
- Enhancing water absorption in poly(urethane) foams [161].
- Absorbent fibrous materials [162].
- Viscosifying agent.
- Fluidity control agent.
- Sludge conditioning agent.
- Grouting agent.
- Asphalt cement additive.
- Friction reducing material.
- Antidrying agent specially for drilling muds.
- Fluid solid water.
- Sludge conditioning.
- Anticondensational agent for paint and wall paper.
- Imparting water swellability to rubber, plastics, etc.
- Imparting hydrophilicity to films, urethanes, etc.
- Imparting water absorbency to paper, nonwoven fabrics [163].

1.9.2 Price and main manufacturers

Large volume prices of superabsorbent polymers are generally in the range of $2.20 to $3.00 per kg.

The largest producer of superabsorbents in the US is Dow, with Hoechst Celanese, Stockhausen, and Nalco sharing the second position. Nippon Shokubai and Chemdal are also big producers in Japan and Western Europe respectively [164-165].

1.10 Aims

The physical and chemical phenomena involved in the swelling of superabsorbent polymers are very complex. The knowledge and understanding of the chemistry and polymerization characteristics leading to superabsorbents is poor, despite the large amount of patent literature published in this field (for example, [166-182]). Thus it was necessary to study the mechanisms of synthesis based on a simple structure, such as acrylic acid, which is also the principal starting monomer for most commercial SAPs. As the literature shows, the inverse-suspension polymerization method is apparently a suitable way to control the parameters affecting superabsorbency. Only one comprehensive work in this area has been published [3], but the underlying reasons and explanations for the events are not fully explained and some parameters, such as initiator and temperature and the mechanism of the swelling were not discussed in their work.

Following Trijasson's work, the present work was aimed at obtaining a deeper understanding of the effects of inverse-suspension variables on the swelling behaviour of superabsorbent polymers.

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Chapter 2: EXPERIMENTAL

2.1 General procedure for the synthesis of superabsorbent polymers

2.1.1 Inverse suspension polymerisation

2.1.1.1 Preparation of the dispersed phase

[a] Monomer solution

Glacial acrylic acid was diluted with the prescribed amount of doubly-distilled water at room temperature with mild magnetic agitation. The same procedure was applied to prepare acrylamide solutions. The acrylic acid and the acrylamide are liquid and solid respectively at room temperature, thus the latter needs longer time to pass into solution. These two clear solutions were stored in tightly-stoppered bottles at room temperature until required. Solutions were left for a maximum of a couple of hours before starting the reactions.

[b] Initiator solution

To a prescribed amount of doubly-distilled water contain in a 100ml beaker, a defined amount of recrystallised initiator was added at room temperature while shaking, until a clear solution was obtained and the solution stored in cool place (0-5 °C) away from light.

[c] Crosslinker solution

To a magnetically-stirred prescribed amount of doubly-distilled water contained into a 100ml beaker, a defined amount of crosslinker was introduced at room temperature and stirred until it passed into solution, as indicated by a clear appearance. The solution was stored in cool place (0-5 °C) away from light.

[d] Neutraliser solution

To a pre-determined amount of doubly-distilled water, the required amounts of sodium hydroxide or potassium hydroxide pellets was added over an ice-water bath to suppress any exothermicity. The mixture was agitated magnetically until a clear cold solution was obtained. The solution was stored at room temperature until required.

2.1.1.2 Preparation of the continuous phase

[e] Surfactant solution

To a defined amount of an aromatic hydrocarbon. an appropriate amount of a water in oil surfactant was added and heated under stirring up to 80 °C while bubbling nitrogen through the solution over a period of 15 min.

[f] Crosslinker solution

To a certain part of an organic hydrocarbon, the oil-soluble crosslinker was incorporated at room temperature while stirring magnetically.

2.1.1.3 Sequence of addition

The sequence of addition and treatment to prepare aqueous dispersion phase was conducted as follows:

-The acrylic acid solution, prepared as in [a] was treated with the neutraliser solution, prepared as in [d]. The latter was added dropwise through a dropping funnel to the former under mild magnetic stirring over an ice-water bath to attain a prescribed, partial degree of neutralisation. The treatment was completed shortly after a clear solution was obtained.

-To the acrylamide solution, prepared as in [a], the crosslinker solution of [c], was introduced. This step is essential to avoid any crosslinker nonhomogenity.

-The next step was to combine the two above solutions, *i.e.* [a] plus [d] with [a] plus [c].

-The initiator solution [b] was left aside until starting the reaction in order to prevent any premature polymerisation.

-To prepare a continuous organic phase, the crosslinker solution, as prepared in [f], was introduced to the surfactant solution, as prepared in [e].

2.1.2 Solution polymerisation

While the inverse suspension polymerisation is a heterogeneous or a two-phase, water in oil polymerisation, the solution polymerisation is a one-phase or homogeneous polymerisation. The preparative procedure of the medium in which polymerisation occurs is quite similar as to the preparation of the dispersed phase for the inverse-suspension technique.

2.2 Materials

Acrylic acid **($C_3H_4O_2$): m.w 72.1, m.p 13 °C, b.p 30 °C/3mm, d 1.051.** Normally being stabilised with 0.02% hydroquinone monomethyl ether, this was purified by steam distillation through a column packed with copper gauze to inhibit polymerisation. Heat of polymerisation of acrylic acid is about 77 KJ/mol [1].

Acrylamide **(C_3H_5NO): m.w 71.1, m.p 84 °C, b.p 125 °C/25mm.** The material crystallised from methanol, then vacuum dried and kept in dark place under vacuum. The acrylamide was then recrystallised from chloroform (200g dissolved in 1L heated to boiling and filtered, without suction, in a warmed funnel through a Whatman 541 filter paper. Allowed to cool to room temperature and kept at -15 °C overnight). Crystals were collected with suction in a cooled funnel and washed with 300ml of cold methanol. Crystals were air-dried in a warm oven (30 °C). Heat of polymerisation for acrylamide monomer is about 82.8 KJ/mol [2].

Ethylene glycol dimethacrylate ($C_{10}H_{14}O_4$): m.w 198.2, b.p 98-100 °C/5mmHg, n 1.456, d 1.053. This was distilled through a short Vigreux column at about 1mm pressure, in the presence of 3.0 w/w % of phenyl-β-naphthylamine, before use.

Bisacrylamide ($C_7H_{10}N_2O_2$): m.w 154.2. Recrystallised from methanol (100g dissolved in 500ml boiling methanol and filtered without suction in a warm funnel. Allowed to stand at room temperature and then at -15 °C overnight. Crystals were collected with suction in a cooled funnel and washed with cold methanol). Crystals were air-dried in a warm oven (30 °C) . The toxicity of bis-acrylamide is similar to that of acrylamide.

Ammonium peroxydisulphate [$(NH_4)_2S_2O_8$]: m.w 228.2. Recrystallised at room temperature from ethanol/water mixture.

Potassium peroxydisulphate ($K_2S_2O_8$): m.w 270.3. Crystallised twice from distilled water (10ml/g) and dried at 50 °C in a vacuum desiccator.

All the purification procedures has been followed according to the reference no 3.

Ethyl cellulose The degree of substitution of the material (type N 14) was 2.42-2.53 and was purchased from Hercules Incorporated.

Commercial superabsorbent This was obtained from Softron International Company. The material is based on acrylic acid and used as supplied.

Other ingredients Commercial grades of carboxymethyl cellulose (obtained from toothpaste manufacturer) and poly (vinyl chloride, emulsion type which is used to produce PVC plastisols) were used as supplied. Poly (vinyl alcohol), reagents including sodium hydroxide and potassium hydroxide as well as solvents were used as supplied from Merck.

2.3 Experiments

2.3.1 Inverse suspension polymerisations

2.3.1.1 Preliminary trials (Expts. 1-17)

These preliminary experiments were devised to obtain the polymer product as particles. The summary of the formulations can be seen in *Table*. 2.1.

Expt. 1

To a 1l round-bottomed five-necked flanged flask fitted with a mechanical stirrer, dropping funnel, an efficient condenser, nitrogen inlet and a thermocouple (heated in a stream of nitrogen up to setting temperature for a period of 5 min.), 200g of toluene and a toluene solution of sorbitan monostearate (0.75g in 23.6g solvent) were poured in and heated while mechanically stirring over an oil bath set at 80 °C for a period of 15 min. and constant purging with a stream of nitrogen until a light yellow solution was obtained. The agitation rate was set at 400 rpm. Separately, an aqueous solution of acrylic acid (30g in 7.5g water) neutralized with an aqueous solution of sodium hydroxide (12.52g in 36.18g water), the neutralized monomer solution was then combined with an aqueous solution of potassium persulphate (0.15g in 4g water). Shortly after incorporating the latter solution, the whole aqueous solution of the neutralised monomer and initiator was added dropwise over a 10 min. period to the above organic toluene solution. This addition was carried out immediately after incorporating the toluene solution of ethylene glycol dimethacrylate (0.036g in 20g solvent) to the well-stirred preheated surfactant-loaded toluene solution contained in the flask. In the first few seconds of the dispersed phase addition, the clear solution changed to cloudy, since the system is a typical water in oil polymerisation. The reaction mixture was left stirring in the oil bath set at 80 °C for a total period of 90 min. the timing being started when the first droplet of the aqueous solution of the monomers was poured into the continuous toluene phase. When the reaction was completed, the oil bath was removed and the flask was allowed to reach room temperature. The supernatant liquid was decanted to a separate vessel and rejected. The precipitated solid polymer was dried overnight in an air-circulated oven adjusted at 60 °C . The tightly-attached water-swollen granules of the superabsorbent polymer (see *Fig.* 3.1) were stored in sealed, stoppered bottles until required for the swelling measurements. (**Note**: a granule is defined as a cluster of microparticles which is typically 2-3 mm in diameter.).

Expt. 2

Repeat of Expt. 1, *except* that the amount of sorbitan monostearate used was 2.0g rather than 0.75g. The product was obtained as a lump. The latter is a mass consisted of tens of granules, each contains numerous fine particles. In this case, the granules within the lump were loosely attached to each other.

Expt. 3

Repeat of Expt. 1, *except* that the amount of sorbitan monostearate used was 2.0g rather than 0.75g and that the rate of agitation was set at 600rpm. rather than 400rpm. The polymer was obtained as in Expt. 2.

Expt. 4

Repeat of Expt. 1, *except* that the amount of sorbitan monostearate used was 2.0g rather than 0.75g and that, during the last 45min of the total period of reaction, the dropping funnel was replaced by a vacuum line (300mmHg), fitted with a water trap, and the vacuum was switched on. The polymer was obtained as in Expt. 2.

Expt. 5

Repeat of Expt. 1, *except* that the amount of sorbitan monostearate used was 2.0g rather than 0.75g, that xylene (246.6g) was used in place of toluene (243.6g). and that, during the last 45 min. of the total period of reaction, the dropping funnel was replaced by a vacuum line (300mmHg), fitted with a water trap, and the vacuum was switched on. The polymer was obtained as in Expt. 2, but the granules were more separated.

Expt. 6

Repeat of Expt. 1, *except* that sorbitan monooleate (2.0g) was used in place of the stearate, that xylene (246.6g) was used in place of toluene (243.6g), and that, during the last 45 min. of the total period of reaction, the dropping funnel was replaced by a vacuum line (300mmHg), fitted with a water trap, and the vacuum line was switched on. The product was obtained as a fine, water soluble powder.

Expt. 7

Repeat of Expt. 1, *except* that sorbitan monooleate (0.4g) was used in place of the stearate, that xylene (246.6g) was used in place of the toluene (243.6g) and that, during the last 45 min. of the total period of reaction, the dropping funnel was replaced by a vacuum line (300mmHg), fitted with a trap, and the vacuum line was switched on. The product was obtained as coarse, star-shaped, water swollen granules (see *Fig.* 3.2).

Expt. 8

This experiment was carried out to explore the effect of adding a commercial sample of poly (sodium acrylate), as a superabsorbent, to the polymerisation mixture. The idea was to try to remove as much water as possible from the reaction medium as the new granules of polymer formed. Thus as in Expt. 1, *except* that sorbitan monooleate (0.4g) was used in place of the stearate, that xylene (246.6g) was used in place of toluene. Just after 45 min. of the total reaction period, a sample (0.08g) of a commercial poly (sodium acrylate) superabsorbent was poured into the reaction mixture. The polymer obtained was of uniformly-sized, water-swollen but separate granules (see *Fig.* 3.3).

Expt. 9

Repeat of Expt. 1, *except* that sorbitan monooleate (0.4g) was used in place of stearate and that, just after 45 min. of the total reaction period, a sample (0.08g) of a commercial poly (sodium acrylate) superabsorbent was poured into the reaction mixture. The polymer obtained was similar in appearance to that obtained in Expt. 8.

Expt. 10

Repeat of Expt. 1, *except* that sorbitan monooleate (0.8g) was used in place of the stearate. The polymer was obtained as separate, coarse, water-swollen granules in wider size distribution.

Expt. 11

Repeat of Expt. 1, *except* that sorbitan monooleate (2.0g) was used in place of the stearate. The polymer was obtained as an amorphous, water-soluble gel.

Expt. 12

Repeat of Expt. 1, *except* that sorbitan monooleate (0.8g) was used in place of the stearate and that an aqueous solution of poly (vinyl alcohol) (0.4g in 10g H_2O) was added to the reaction mixture at the beginning, before heating. The product polymer was obtained as a sticky gel.

Expt. 13

Repeat of Expt. 1, *except* that sorbitan monooleate (0.8g) was used in place of the stearate and that an aqueous solution of sodium carboxymethylcellulose (0.17g in 5g H_2O) was initially added to the aqueous dispersed phase. The polymer was obtained as a sticky gel.

Expt. 14

Repeat of Expt. 1, *except* that sorbitan monooleate (0.8g) was used in place of the stearate. The coarse granules obtained (see Expt. 10) were dehydrated after decanting off the supernatant liquids. To methanol (400ml), used as the dehydrating agent, was dispersed the polymer granules and the mixture was left stirring for a period of 30 min. The mixture was allowed to settle and the supernatant was decanted off. The solid precipitate was dried overnight at 60 °C in an air-circulating oven. The separate granules were obtained as the polymerisation product (see *Figs.* 3.4 *and* 3.5).

Expt. 15

Repeat of Expt. 1, *except* that, to a portion (50ml from the 200ml) of the original toluene solvent used, was added ethyl cellulose (0.45g) and this was stirred for 30 min. to effect dissolution and this solution was added to the remainder before continuing the polymerisation, using sorbitan monooleate (0.8g) in place of the stearate. The product polymer was dehydrated with methanol, using the procedure described in Expt. 14. The sign of granule segragation into particles was observed (see *Figs.* 3.6-3.9).

Expt. 16

Repeat of Expt. 1, *except* that, to a portion (50ml from 200ml) of the original toluene solvent used, was added ethyl cellulose (1.5g) and this was stirred for 30 min. to effect dissolution and this solution was added to the remainder before continuing polymerisation, using sorbitan monooleate (0.8g) in place of the stearate. The product polymer was dehydrated with methanol, using the procedure described in Expt. 14. More particles than observed for the Expt. 15, were separated from granules.

Expt. 17

Repeat of Expt. 1, *except* that to a portion (50ml from 200ml) of the original toluene solvent used, was added ethyl cellulose (3.0g) and this was stirred for 30 min. to effect dissolution and this solution was added to the remainder before continuing the polymerisation, using sorbitan monooleate (0.8g) in place of the stearate. The product polymer was dehydrated with methanol, using the procedure described in Expt. 14. The number of segragated granules increased, so that, a lot amount of isolated particles was observed in the product (see *Figs.* 3.10-3.13).

Table. 2.1 Formulations for the Experiments 1-21.

Expt	*Acrylic acid (g)*	*Sodium hydroxide (g)*	*Potassium persulfate (g)*	*EGDMA^a mol% to monomers*	*SMS^b (g)*	*SMO^c (g)*	*c.p^d*	*rpm*	*Features*
1	30	12.52	0.15	0.045	0.75		t^1	400	
2	30	12.52	0.15	0.045	2.0		t	400	
3	30	12.52	0.15	0.045	2.0		t	600	
4	30	12.52	0.15	0.045	2.0		t	400	Vacuum distilled
5	30	12.52	0.15	0.045	2.0		x^2	400	Vacuum distilled
6	30	12.52	0.15	0.045		2.0	x	400	Vacuum distilled
7	30	12.52	0.15	0.045		0.4	x	400	Vacuum distilled
8	30	12.52	0.15	0.045		0.4	x	400	SAP^3
9	30	12.52	0.15	0.045		0.4	t	400	SAP
10	30	12.52	0.15	0.045		0.8	t	400	
11	30	12.52	0.15	0.045		2.0	t	400	
12	30	12.52	0.15	0.045		0.8	t	400	PVA^4
13	30	12.52	0.15	0.045		0.8	t	400	CMC^5
14	30	12.52	0.15	0.045		0.8	t	400	Methanol
15	30	12.52	0.15	0.045		0.8+0.4 EC^e	t	400	Methanol
16	30	12.52	0.15	0.045		0.8+1.5 EC	t	400	Methanol
17	30	12.52	0.15	0.045		0.8+3.0 EC	t	400	Methanol
18	30	12.52	0.15	0.055		0.8+3.0 EC	t	400	Methanol
19	30	12.52	0.15	0.24		0.8+3.0 EC	t	400	Methanol
20	30	12.52	0.15	2.30		0.8+3.0 EC	t	400	Methanol
21	30	12.52	0.15	4.58		0.8+3.0 EC	t	400	Methanol

a) ethylene glycol dimethacrylate. b) sorbitan monostearate. c) sorbitan monooleate. d) continuous phase. e) ethyl cellulose. 1) toluene. 2) xylene. 3) superabsorbent. 4) poly (vinyl alcohol). 5) carboxymethyl cellulose.

2.3.1.2 Effect of the oil-soluble crosslinker concentration (Expts. 18-21)

Expt. 18

Repeat of Expt. 17, *except* that the amount of crosslinking agent, ethylene glycol dimethacrylate, was increased from 0.045 mol% to 0.055 mol%.

Expt. 19

Repeat of Expt. 17, *except* that the amount of crosslinking agent, ethylene glycol dimethacrylate, was increased from 0.045 mol% to 0.238 mol%.

Expt. 20

Repeat of Expt. 17, *except* that the amount of crosslinking agent, ethylene glycol dimethacrylate, was increased from 0.045 mol% to 2.30 mol%.

Expt. 21

Repeat of Expt. 17, *except* that the amount of crosslinking agent, ethylene glycol dimethacrylate, was increased from 0.045 mol% to 4.58 mol%.

2.3.1.3 Effect of the water-soluble crosslinker concentration (Expts. 22-25)

Expt. 22

Repeat of Expt. 17, *except* that the preparation step for the toluene solution of ethylene glycol dimethacrylate was eliminated and that, into 4.0g of doubly distilled water, the methylene bisacrylamide (0.016 mol% to the total monomer) was dissolved at room temperature with frequent shaking for a period of 30 min., to effect dissolution. The combined toluene solutions for this preparation were, the pure toluene (170g), a solution of sorbitan monooleate (0.8g in 23.6g toluene) and a solution of ethyl cellulose (3.0g in 50g toluene).

Expt. 23

Repeat of Expt. 22, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.016 mol% to 0.047 mol%.

Expt. 24

Repeat of Expt. 22, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.016 mol% to 0.078 mol%.

Expt. 25

Repeat of Expt. 22, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.016 mol% to 0.11 mol%.

2.3.1.4 Effect of the comonomer replacement (Expts. 26-29)

Expt. 26

To a 1l. round-bottomed, five-necked flanged flask fitted with a mechanical stirrer, dropping funnel, an efficient condenser, nitrogen inlet and a thermocouple, 145.6g of toluene with a toluene solution of sorbitan monooleate (0.72g in 23.6g solvent) and a solution of ethyl cellulose (2.7g) in toluene (50g) was poured in and heated while mechanically stirring to 80 °C over an oil bath for a period of 20 min. and constant purging with the stream of nitrogen until a light yellow solution was obtained. The agitation rate was set at 400 rpm. Prepared combined aqueous solutions of the acrylic acid monomer (15g in 7.5g water) neutralized with sodium hydroxide (6.26g in 18.11g water), acrylamide monomer (15g in 13.39g water), methylene bisacrylamide (0.016 mol% to the total monomer in 4.0g water) and potassium persulphate (0.15g in 4g water) was added dropwise over 10 min. times to the well-stirred preheated solution in the flask. Shortly after addition of the dispersed phase, the clear solution changed to cloudy. The reaction mixture was left stirring over the oil bath set at 80 °C, for a total period of 90 min. The timing was started , when the first droplet of the aqueous solution of the monomers was poured into the continuos toluene phase. When the reaction was completed (1.5h), the oil bath was removed and the flask was allowed to reach room temperature. The supernatant liquid was decanted to a separate vessel and rejected. The precipitated solid polymer particles were dispersed, after decanting the supernatant, into 400 ml methanol as a dewatering agent. The mixture was left stirring for a period of 30 min., then allowed to settle followed by decanting the supernatant off. The solid precipitate was dried overnight at 60 °C in an air-circulating oven.

Expt. 27

Repeat of Expt. 26, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.016 mol% to 0.047 mol%.

Expt. 28

Repeat of Expt. 26, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.016 mol% to 0.078 mol%.

Expt. 29

Repeat of Expt. 26, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.016 mol% to 0.11 mol%.

2.3.2 Solution polymerisation

2.3.2.1 Effect of the change in the crosslinker concentration (Expts. 30-33)

Expt. 30

First, an aqueous solution of acrylic acid monomer (15g in 7.5g water) was prepared. The acrylic acid was partially neutralised with sodium hydroxide solution (6.26g in 18.11g water). The degree of neutralisation was 75 mol/mol % which was obtained through an acrylic acid titration curve (see *Sec.* 2.4.1). Thus in the neutralisation vessel, the components are acrylic acid, sodium acrylate and water in a 1: 3: 3 mol ratio. This water remains in the reaction mixture and accounts for some of the water originally present as a diluent in the reaction mixture. Acrylamide was also diluted with water at room temperature while stirred (15g in 13.39g water). Methylene bisacrylamide (0.0078 mol% to the total monomer) was used as a tetrafunctional crosslinker and diluted with water (4.0g). Potassium persulfate was recrystallised twice, diluted with water (4.0g) and used as the thermally decomposing initiator (0.15g). In highly concentrated aqueous solutions especially when a salt is present, the crosslinker is sparingly soluble. Thus, it was added to the acrylamide solution first. The latter was mixed with the neutralised acrylic acid solution. So the mixture of the reaction contains acrylic acid, sodium acrylate and acrylamide as monomers in a 1: 3: 4 mol ratio, besides the crosslinker. The prepared initiator solution was poured into the latter mixture of solutions just before putting the reaction mixture into the bath.

A 1l open beaker was used as reactor. An oil thermostating bath was also used as heating source. A digital thermocouple was also used to monitor the reaction temperature. The bath was allowed to reach the desired temperature, *i.e.* 80 °C. The prepared mixture was poured into the beaker at room temperature. The beaker was immersed into the bath and the mixture was continuously stirred magnetically (400rpm). The reaction mixture was continuously warmed up due to heat transfer from the hot bath to the cold beaker. The reaction mixture was left stirring until the so-called *gel point,* when the magnetic stirrer follower bar was stopped due to the sudden rise in viscosity of the reaction medium. At the end of the gel formation, the oil bath was removed and the beaker content was freely allowed to reach room temperature. The resulting product was removed from the reaction vessel and cut to small pieces (dimensions of 2-5 mm) by a pair of scissors. The cut pieces were spread over an aluminum foil and heated overnight into an air-circulating oven at 60 °C to rather constant weight. The, presumably, dried gels were ground by a hammer type minigrinder (laboratory scale), then screened using a robot sifter. The classified particles were stored in tightly-stoppered bottles until further measurements.

Expt. 31

Repeat of Expt. 30, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.0078 mol% to 0.016 mol%.

Expt. 32

Repeat of Expt. 30, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.0078 mol% to 0.047 mol%.

Expt. 33

Repeat of Expt. 30, *except* that the amount of crosslinking agent, methylene bisacrylamide, was increased from 0.0078 mol% to 0.078 mol%.

2.3.2.2 Effect of the temperature in solution polymerisation (Expts. 34-47)

Expts. 34-47

Repeat of Expt. 30, *except* that the amount of crosslinker, methylene bisacrylamide, was increased from 0.0078 mol% to 0.078 mol%, and that the bath temperature (in degrees of Centigrade) was varied as follows:

Expt.	*34*	*35*	*36*	*37*	*38*	*39*	*40*
$T\,^{o}C$	75	90	97	105	112	120	127

Expt.	*41*	*42*	*43*	*44*	*45*	*46*	*47*
$T\,^{o}C$	135	142	150	157	165	172	180

2.3.2.3 Effect of the initiator concentration in solution polymerisation (Expts. 48-56)

Expts. 48-56

Repeat of Expt. 30, *except* that the amount of crosslinker, methylene bisacrylamide, was increased from 0.0078 mol% to 0.078 mol%, that the bath temperature was held at 120 °C and that, the molar ratio of initiator to total monomer was varied as follows:

Expt.	*48*	*49*	*50*	*51*	*52*	*53*	*54*	*55*	*56*
$[I]/[M] \times 100$	0.010	0.021	0.044	0.087	0.176	0.264	0.325	0.441	0.529

2.3.2.4 DSC studies on the effect of initiator concentration (Expts. 57-66)

Expts. 57-66

First, sodium hydroxide (2.51g) was diluted with prescribed amount of doubly distilled water (4.30g), under mild agitation and ice-cooling, until a clear cold solution was obtained. The latter was poured dropwise onto the acrylic acid (4.40g), while ice-cooling. The crosslinker, methylene bisacrylamide (0.0067g) was added into doubly distilled water (1.43g), under shaking, until a clear solution was obtained. The latter solution was added to the neutralised acrylic acid solution. The initiator solution (0.0043g-0.0616g in 2g water) was similarly prepared as the crosslinker solution, then it was added to the combined solutions of crosslinker and monomers. A sample of about 15-20mg of this original formulation was withdrawn by a disposable syringe and put into DSC pan at room temperature. The pan was quickly put into the DSC heating chamber, again at room temperature. The chamber was closed and heating rate was set at 40 °C/min. to attain an isothermal reaction, with the least delays to reach a setting temperature. The total period of reaction was 1h. The polymerisations were carried out under normal atmosphere and at constant temperature of 80 °C.

Expt.	*57*	*58*	*59*	*60*	*61*	*62*	*63*	*64*	*65*	*66*
[I]/[M]×100	0.014	0.02	0.029	0.033	0.034	0.064	0.076	0.091	0.137	0.21
Initiator g	0.004	0.006	0.009	0.010	0.010	0.02	0.024	0.028	0.042	0.065

2.3.2.5 DSC studies on the effect of temperature (Expts. 67-72)

Expts. 67-72

Repeat of Expts. 57-66, *except* that 0.0118g of the potassium persulphate was diluted with 2.0g water and used as the initiator solution, and that, the temperature was varied ranging from 70-95 °C.

Expt.	*67*	*68*	*69*	*70*	*71*	*72*
T °C	70	75	80	85	90	95

2.3.2.6 Change in initiator and neutralizer (Expt. 73)

Expt. 73

Repeat of Expt. 30, *except* that the acrylic acid solution (15g in 7.5g water) was neutralised with potassium hydroxide (8.75g in 18.39g water) in place of sodium hydroxide and that, ammonium peroxydisulphate (0.16g in 5.0g water) was used in place of the potassium peroxydisulphate. The polymer obtained as in Expt. 30, *i.e.* in rubbery form.

2.3.2.7 Change in monomer concentration (Expt. 74)

Expt. 74

The acrylic acid monomer was used undiluted (15g). The aqueous solution of acrylamide monomer was prepared as follows: Into 7.0g of magnetically-stirred (400 rpm) double distilled water contained in a 400 ml bolt-capped beaker over a water bath held at 50 °C, was added 15g acrylamide crystals and the mixture heated for a period of 30 min. until a clear, water white solution was obtained. The same procedure was applied to prepare aqueous caustic potash solution (8.75g in 7.0g water), *except* that stirring was performed without heating but over an ice-water bath. Aqueous solutions of the crosslinker, methylene bisacrylamide (0.0078 mol% to the total monomer in 2.0g water) and the initiator, ammonium peroxydisulphate (0.16g in 1.0g water) were prepared as described under general procedure of synthesis (*Sec.* 2.1.1.1). To help to solubilise the crosslinker, its aqueous solution was added to the aqueous acrylamide solution in the cold under magnetic stirring for a period of 30 min. or until a clear mixture was attained. Acrylic acid was poured into the latter solution, while swirling and finally the initiator solution was added. The reaction was started as in Expt. 30. At the early stage of the reaction (say, 5 min. or gel point) an excessive foaming (up to 10 times of the original volume) occurred and the resulting mass retained its spongy shape until the end of the reaction. The foamed product which was excessively dry and brittle was removed from the beaker and then easily ground to a powder. The powder was spread over an aluminum foil and heated overnight in an air- circulating oven held at 60 °C to complete the drying. The dried powders were classified according to their mesh sizes and stored individually into well-sealed bottles.

2.3.2.8 Using PVC emulsion powder (Expts. 75-80)

Expts. 75-79

The same formulation and procedure as considered for the Expt. 73 was applied to run present reactions. The Expt. 73 was considered as a blank to observe the effect of introducing such a filler into the reaction medium. The poly (vinyl chloride) was used in its free flowing powder form, which is a dried product of poly (vinyl chloride) emulsion polymerisation. The latter was incorporated portionwise through a dropping funnel (with occasional shaking) into the prepared combined aqueous solutions (20.0g of the blank formulation of the Expt. 73) contained in a bolt-capped flask while stirring magnetically (800 rpm applied to prevent the filler particles forming agglomerates) at room temperature for a period of 30 min. These experiments differ in terms of their blank formulation of the Expt. 73) contained in a bolt-capped flask while stirring magnetically (800 rpm applied to prevent the filler particles forming agglomerates) at room temperature for a period of 30 min. These experiments differ in terms of their PVC loading (2.5, 5.0, 7.5, 10, 12.5 and 15 w/w % respectively for the Expts. 75-79. Into the same, open flask (loosely covered by aluminum foil) fitted with a thermocouple, the resulting milky suspension was subjected to polymerisation as for the blank experiment. After a short period of time, an excessive foaming was happened to the reaction mixture. After spontaneous collapse of the foamed product. it was withdrawn from the flask and cut into 2-3 mm pieces. The latter was put into an air-circulating oven set at 60 °C, for overnight. The dried pieces of product were ground by a hammer type minigrinder, followed by classified. Amount of the materials evaporated during the exothermic reaction was calculated by difference, just after the completion the reaction.

Expt. 80

Into a well-stoppered 100 ml dark bottle, 1 g of the dried product obtained from the Expt. 78 was poured into 75ml of the solvent, tetrahydrofuran (THF) which has a same solubility parameter as the PVC and is a common solvent for PVC- based formulations. The mixture was set aside away from light at room temperature for a period of month. The dispersion was then filtered through a fluted filter paper and washed several times with fresh solvent to remove traces of extracted poly (vinyl chloride). The extract was oven-dried overnight at 60 °C, then weighted on a laboratory scale (to the nearest 0.001g). The dried extract was examined for its swelling behaviour.

2.4 Determination and characterization of polymers

2.4.1 Neutralisation

To obtain the desired, degree of partial neutralisation of acrylic acid, *i.e.* the required acid/salt ratio, the required amount of sodium hydroxide was estimated by the following diagram (*Fig.* 2.1). To draw the latter, dilute acrylic acid (30g in 7.5g double distilled water) was titrated with 25.4 w/w % NaOH solution. According to the diagram. 75% neutralisation degree (acid/salt molar ratio of 1/3) is obtained when the pH assumes a value of 5.73.

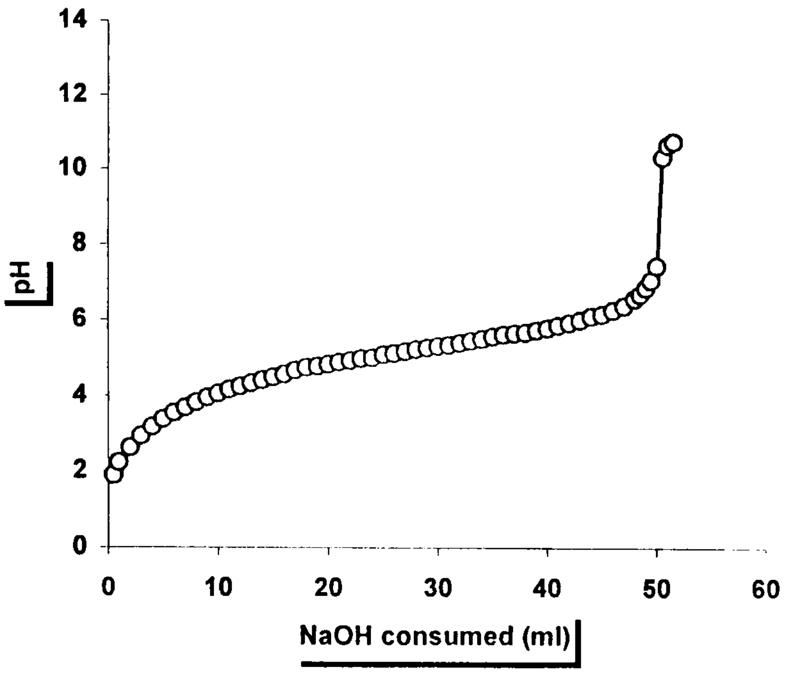

Figure 2.1 Titration curve for acrylic acid neutralization.

2.4.2 Assaying crosslink density, network chain density and M_c

The amount of water sorption is quantified by the degree of swelling, *i.e.* the ratio of the swollen polymer volume or mass to that of the dry polymer [4]. The volume degree of swelling of crosslinked polymers is simply the inverse of the polymer volume fraction, so the former can be readily predicted as a function of polymer-solvent interaction parameter, crosslink density and polymer ionic content, neglecting the electrostatic term (see *Sec.* 1.5.2) and assuming Gaussian chain statistics (see *Equation.* 2.1).

$$\left[\ln(1-\upsilon_{2,s})+\upsilon_{2,s}+\chi_1\upsilon_{2,s}^{2}\right]/V_1+ \\ \upsilon_{2,r}\rho_x\left[(\upsilon_{2,s}/\upsilon_{2,r})^{1/3}-0.5(\upsilon_{2,s}/\upsilon_{2,r})\right]+i\,\upsilon_{2,s}/V_m=0 \qquad (2.1)$$

where:

$\upsilon_{2,s}$ is Polymer volume fraction at equilibrium swelling

χ_1 is Polymer-solvent interaction parameter

V_1 is Solvent molar volume

$\upsilon_{2,r}$ is Polymer volume fraction at network formation

ρ_x is Crosslink density

i is Ionic content

V_m is Monomer molar volume

If non-Gaussian statistics are assumed (that is valid for highly swollen gels), the degree of swelling is predicted to level off with increased ionisation for a given level of crosslinking. Thus at a high degree of ionisation, the sorption capacity of a polymer is primarily a function of crosslink density [5]. For ionic gels at large degree of swelling, the influence of χ_1 becomes minor. Thus neglecting the mixing term, the *Equation.* 2.2. has been derived:

$$\upsilon_{2,r}\, \rho_x\, [(\upsilon_{2,s} / \upsilon_{2,r})^{1/3} - 0.5([(\upsilon_{2,s} / \upsilon_{2,r})] + i\, \upsilon_{2,s} / V_m = 0 \qquad (2.2)$$

This has been solved explicity for crosslink density as displayed in *Equation.* 2.3:

$$\rho_x = (i\, \upsilon_{2,s} / V_m\, \upsilon_{2,r}) / [(\upsilon_{2,s} / \upsilon_{2,r})^{1/3} - (\upsilon_{2,s} / \upsilon_{2,r})/2] \qquad (2.3)$$

Weight swelling degree, q has been related to the volume fraction in the gel, $\upsilon_{2,s}$ by the *Equation.* 2.4 [6].

$$1 + q(\rho_{polymer} / \rho_{liquid}) = 1 / \upsilon_{2,s} \qquad (2.4)$$

The following equation (*Equation.* 2.5) can be used to calculate monomer molar volume (*Equation.* 2.6)[7].

$$\rho = \rho_1 + (1 - \rho_1 / \rho_2^*)\, C_2 \qquad (2.5)$$

$$\text{and } V_m = M / \rho_2^* \qquad (2.6)$$

where:

ρ is Density of the sample

ρ_l is Density of water

C_2 is Monomer concentration in g/cm^3 of solution

M is Molecular weight of the monomer

ρ_2^* is Density of the monomer

The moles of crosslinks per unit volume or crosslink density can be related to the network chain molecular weight M_c by the *Equation.* 2.7:

$$\rho_x = (\mu / V) = 2\, \rho / \phi\, M_c \qquad (2.7)$$

where:

(μ / V) is Crosslink density

and ϕ is Functionality of the crosslinking agent

Finally, the moles of network chains per unit volume can be calculated according to the *Equation.* 2.8[8].

$$(v/V)=\rho/M_c \qquad (2.8)$$

where (v/V) and M_c are respectively network chain density and molecular weight between two successive crosslinks.

2.4.3 Density measurements

The density of the dried polymers were measured using solvent mixtures and densitometer at room temperature. The solvents used were, chloroform (*d,* 1.47), dichloromethane (*d,* 1.32) and carbon tetrachloride (*d,* 1.59).

2.4.4 Swelling measurements

A sieved sample of the polymer (1.0g ±0.001g, 50-60 mesh) was dispersed into 2L of doubly distilled water or accordingly saline solution, and allowed to swell with mild agitation. The steady state, or equilibrium swelling was determined by allowing overnight for absorption. The swollen samples were filtered through a 100-mesh wire gauze and surface water dried carefully using a piece of a soft open-cell polyurethane foam until they no longer slipped from the sieve when it was held vertical. For measuring swelling kinetics or rate of absorption, the water-absorbed samples were taken from the solution at prescribed periods and then exposed to swelling measurements through the above procedure. To obtain a reliable value for swelling at any time, five values were averaged, although the value of standard deviation for this method is ±2.1 g of water absorbed per g of dry superabsorbent. The quantitative figures of swelling were calculated as shown in *Equation.* 2.9:

$$q_t = [q_{ss} - q_{ds}] / q_{ds} \qquad (2.9)$$

where:

q_t is Swelling at time t.

q_{ss} is Weight of the swollen or water-absorbed polymer at time t.

q_{ds} is Weight of the original dry superabsorbent polymer.

All of the measurements were done on the original polymer without isolating its sol content.

This measurement recipe is for the dried products. For non-dried products, a same procedure was followed, except that 1g quantities of a bulk material (which still contains amounts of water), was immersed into 2L. of doubly distilled water.

2.4.5 Curve fitting

This has been done throughout the thesis to find the two parameters of the Voigt model (see p.109), which fit the experimental data. The values for the parameter no 1 are very close to the values for steady state swelling of the individual samples, since the water transport is diffusion controlled. To obtain parameter no 2, the values of $Ln\ [1 - q_t / q_\infty]$ were plotted against time. This showed a typical first order kinetics, thus the slope is a measure of the characteristic time of the polymer, or else the value of retardation time, which was calculated and named here as parameter no 2. The best fitting curves were used to obtain the values of the initial slopes and the time needed to reach constant swelling (*Sec.* 3.3, *Table.* 3.6). With the former, the slope of the line between the zero point and the point at 70% fractional swelling was determined. For the latter, the point at which the swelling value diverges from the value of the parameter no1 was selected.

2.4.6 Sol content measurement by spectroscopy (*Sec.* 3.3, *Table.* 3.6)

To a 1L beaker containing 500ml of 1.0 w/w % sodium chloride solution, 0.5g (±0.0001g) of dried superabsorbent (50-60 mesh) was poured. The dispersion was kept aside at room temperature for a period of 72h. After several shaking and standing cycles to homogenise the liquid phase, the dispersion was allowed to settle, then the supernatant liquid was filtered through a sintered glass, followed by withdrawing a known volume of it for UV spectroscopy. A PU 8800 UV/VIS (double beam) spectrophotometer was used, using quartz 10 mm cells. A 1.0 w/w % NaCl solution was used as reference and the scanning was performed through the range of 250-190 nm. With our acrylate superabsorbents the λ_{max} appears at about 206nm.

2.4.7 Water content (bound water) measurement (*Sec.* 3.3, *Table.* 3.6)

A thermal analyser, PL-TGA 1500 was used. The temperature was set at 200 °C (under nitrogen blanket) and held for a period of 30 min. By this time all the water contained into the polymer was isolated.

2.4.8 Gel time measurement

The gel time was measured as the time required to create first stable bubbles in the gel. The time just after initiator addition was considered as the starting point of the measurement. The timing was started after initiator addition (*Sec.* 3.4, *Table.* 3.8). In *Table.* 3.12, the gel time was considered as the time, required to create an exothermic peak on the DSC thermogram

2.4.9 Assaying particle size distribution (*Sec.* 3.6.2, *Table.* 3.17)

The particle size distribution of the samples obtained from the synthesis was found by automatic sieve analysis. A set of sieves was used with apertures of 300, 250, 180, 150, 106, 75, 53, 45 and 38 microns in diameter. The data obtained from the sieve analysis was used to determine the mean surface diameter of the particles (d_S) according to the *Equation.* 2.10:

$$d_S = \frac{\Sigma p_i}{\Sigma p_i / d_i} \qquad (2.10)$$

where p_i and d_i are the mass of the individual fractions and mean aperture diameter of the two successive sieves respectively.

2.4.10 Gel content measurement by gravimetry (*Sec.* 3.4, *Tables.* 3.7-3.8)

A saline solution of 1.0 w/w % sodium chloride (supplied from Merck) was used as the extracting medium. About 0.8 gram (±0.01g) of the dry superabsorbent polymer was immersed in the above solution (260g), then allowed to saturate for 72h at room temperature without any stirring. All of the samples were poured onto a sintered glass filter after the prescribed time, then the two phases were separated by gravity until observing no free-falling drops of water down the filter. The aqueous extracts were collected for further experiments. The wet gels on the filter were transferred onto a filter paper and subjected to drying for a period of 10 hr at 90 °C in a normal, air-circulating oven. The gel and the sol fraction of the samples were calculated according to *Equation.* 2.11:

$$G = [(A+B)-B+(C-D)]/E \times 100$$
$$S = 100-G \qquad (2.11)$$

where:

G is Gel content or gel fraction

A is Weight of residual dried gel on paper

B is Weight of filter paper

C is Weight of blank filter paper before heat treatment

D is Weight of blank filter paper after heat treatment

E is Weight of original dry superabsorbent

S is Sol content or sol fraction

2.5 References

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Chapter 3: RESULTS AND DISCUSSIONS

3.1 Introduction

Based on our aims in *Sec.* 1.10, we attempted at first for producing a product in powder form and in well-defined size as well as capable of showing normal superabsorbency. This step was crucial for investigating the key parameters involved in controlling the polymer function in swelling media. Thus we tried to synthesize a high quality superabsorbent polymer in particle form, in reproducible amounts and consistent quality, which was the aim for doing the Expts. 1-17 (*Sec.* 3.2.1.1).

The next step was investigating the effect of the influential variables including the crosslinker concentration and its type on the swelling characteristics of the products. This was the subject of the Expts. 18-21 (*Sec.* 3.2.1.2) and 22-25 (*Sec.* 3.2.1.3) respectively for the oil-soluble and the water-soluble crosslinkers. The final variable in inverse-suspension experiments was the effect of comonomer replacement, which was investigated through the Expts. 26-29 (*Sec.* 3.2.1.4).

At the end of these experiments, a suitable material was obtained in terms of its swelling characteristics. But, we tried for simplifying the method of polymerisation as well as for obtaining the materials at a cheaper price. Thus, the Expts. 30-33 (*Sec.* 3.2.2.1) were devised based on these requirements. For this purpose, a simple solution polymerisation was introduced after numerous trials for accomplishing it successfully.

According to our findings from these experiments, a simple and general model (*Sec.* 3.3) was devised in order to explain the principal factors responsible for the swelling. The step further was using our model for comparing the swelling characteristics of the materials obtained up to this stage.

The effects of other parameters including the amount of the heat supplied for starting the polymerisation reaction and the amount of the initiator used to start the kinetic chains were also examined respectively through the Expts. 34-47 and 48-56 (*Sec.* 3.4). We used our model to justify the swelling properties of the various materials obtained at different bath temperatures and the initiator concentration.

Effects of initiator concentration (Expts. 57-66) and of bath temperature (Expts. 67-72) were assessed in microsynthesis polymerisation using a Differential Scanning Calorimeter (*Sec.* 3.5). These experiments have been done in order to obtain more insight into the kinetics of solution polymerisation, especially at gel point.

The effects of the particle size and the ionic strength of the swelling media on the swelling properties of the products were also assessed in detail, as can be seen respectively in *Sec.* 3.6.2 and 3.6.3

With some experiments, the type of the initiator and of the neutralizer was changed for performing the solution polymerisation at higher monomer concentration. This is the subject of the Expts. 73-74.

Finally, we tried to use our model to obtain superabsorbents of higher quality and, if possible of superior properties to those are commercially available. Thus, the Expts. 75-80 were devised based on this objective.

3.2 Polymerisations

The first step was to find a suitable preparative procedure to produce a typical polymer in particle form, which displays normal superabsorbency. To obtain the desired superabsorbency, we required a rather full knowledge of the polymerisation system. According to the literature survey, two general approaches could be adopted to make superabsorbent polymers, *i.e.* inverse suspension and solution polymerization; both methods have their own advantages and disadvantages. Although, for economic reasons, the industrial method of superabsorbent preparation is by solution polymerization, the material dosenot lend itself to the study the effects of changing parameters.

On the other hand, the inverse suspension material does allow one to investigate subtle changes in variable parameters and learn the major effects involved in the properties of the final superabsorbent material. By these reasons, we started by developing a suitable laboratory method first by carrying out the versatile inverse suspension polymerisation.

3.2.1 Inverse suspension polymerisation

A typical *suspension* polymerisation consists of two immiscible phases (an organic phase and an aqueous phase). The organic phase, containing a single monomer (or mixed monomers) and a radical initiator, which is soluble in the monomer but not in water, is added to a reaction vessel containing water, fitted with an impeller until the volume fraction of the organic phase is of the order 0.2 to 0.35. The impeller breaks this phase into drops; each of which becomes a miniature chemical reactor in which monomer is converted to polymer by the radicals generated within[1].

On the other hand, the *inverse suspension* polymerisation (*Fig. 1.6*) involves the suspending of a water-miscible monomer (or monomers), usually in aqueous solution, into the continuous oil medium using a water in oil emulsifier. Polymerisation is carried out using a water-soluble initiator to give a dispersion of water-swollen particles in a continuous oil phase [2]. Thus, with suspension method, which is suitable for producing hydrophobic polymers, the dispersed phase is an oil-miscible monomer(s) and the continuous phase is water. For its inverse version, *i.e.* inverse suspension polymerisation, which is flexible and is a suitable method for producing hydrophilic polymers, the dispersed phase and the continuous phase are water-miscible monomer(s) and an oil respectively. All other features are similar for the two methods of polymerisation.

Therefore the basic ingredients in inverse-suspension polymerisation could be adopted as follows:

a) Ingredients for the dispersed phase

Monomer (or monomers): These are the basic starting ingredients or building blocks of a superabsorbent structure. Superabsorbent polymers are generally hydrophilic materials which can surprisingly swell up to thousands times of their own weight in water. Thus regarding the swellability as a matter of solubility, the more hydrophilic the monomer, the more the swelling of the polymer. There is a wide variety of the available hydrophilic monomers, possessing various functionality (see *Fig.* 1.3) but, consideration of features such as structural simplicity, cheapness, low toxicity and availability are all prerequisites. Although different classes of the monomers are available that lead to various types of polymers; *e.g.* anionic, cationic and amphoteric materials, our literature survey suggested that the anionic classes are best suited to prepare high quality superabsorbents (in terms of absorption capacity and rate as well as gel strength). Acrylic acid is a readily available and inexpensive monomer and was therefore our first material of choice.

Initiator: In any polymerisation systems, starting a kinetic chain of monomers can be accomplished by using an initiator. Among a very wide initiating systems, a thermal one using potassium peroxydisulfate was attempted.

Water: There is a need for a matrix to dilute the monomers to obtain a desired monomer concentration. Water is the material of choice, since the monomer(s) are miscible with it. Therefore, the aqueous monomer solution forms the dispersed phase of the polymerisation system.

b) Ingredients for the continuous phase

Oil (a typical hydrocarbon): Any liquid or low melting hydrocarbon could be considered as the dispersing medium for the aqueous phase. This can be selected among aliphatic, aromatic and cycloaliphatic hydrocarbons. For our studies, toluene was chosen, otherwise indicated.

c) Ingredients for the interface

Emulsifier: The dispersed and the continuous phases which being prepared in this way are immiscible. Therefore, to render miscibility, there is a need to use certain emulsifying stabilizers. The most commonly used stabilizers are monoesters of sorbitol. These are defined according to their characteristic "HLB", Hydrophilic-Lipophilic Balance values. The HLB value indicates the hydrophilic-lipophilic balance of a particular emulsifier and is a useful guide to the selection of a suitable emulsifier system for a given dispersed phase particularly when nonionic emulsifiers are to be used.

Most of the commonly encountered nonionic and ionic surfactants lie in a HLB range from one to twenty [3-4]. Moreover, the solubility characteristics of many surface active materials in water roughly follows their HLB classification [5].Thus an HLB value of one indicates oil solubility, while an HLB value of twenty indicates a high degree of water solubility [3].*Table.* 3.1 shows some features of the common commercial emulsifiers. Stabilizers of sorbitan monostearate and sorbitan monooleate were used in our study.

Table. 3.1 The features of the common commercial stabilizing emulsifiers.

HLB range	*Dispersibility in water*	*Suitable application*	*Some commercial samples (HLB values)*
1-4	Nil		Span 85 (1.8), Span 65 (2.1)
3-6	Poor	W/O emulsifier	Span 60 [1] (4.7), Span 80 [2] (4.3)
6-8	Milky dispersion on agitation	Wetting agent	Span 40 (6.7)
8-10	Stable milky dispersion	Wetting agent, O/W emulsifier	Span 20 (8.6)
10-13	Translucent to clear dispersion	O/W emulsifier	Tween 65 (10.5)
>13	Clear solution	O/W emulsifier, Solubilising agent	Tween 21 (13.3), Tween 60 (14.9), Tween 20 (16.7)

1) Sorbitan monostearate 2) Sorbitan monooleate

d) Other provisions

The foregoing materials are considered as an integral part of the formulation of the system, but a few auxiliary compounds are also needed to achieve superabsorbency: these are crosslinking agent(s) (to render the polymer swellable) and a monomer neutralizer (to increase swellability).

The acrylic acid monomer can be neutralized by a variety of hydroxides of the group I elements of the periodic table. Generally, the aqueous solubilities of the alkali acrylates increase with increasing atomic weight of the alkali metal as is expected. Poly (acrylic acid) itself is not a practically useful absorbent, since the excess of hydrogen bonding prevents the macromolecular chains from diffusing in water and indeed very little water can be absorbed. A similar behaviour is expected for fully-hydrolyzed poly (vinyl alcohol) polymers. In such circumstances, the polymers behave like a non-ionic materials. As the degree of neutralization is introduced, so does water absorption. This is due to the creation of higher salt content which in turn increase the osmotic pressure and intra/inter chain ionic repulsions. At the extreme, that is, presumably full neutralization, these polymers tend to dissolve in water and this property can only be overcome by increasing the degree of crosslinking. When this is achieved, the polymers swell as much as possible without actually dissolving, *i.e.* they behave as superabsorbents. Thus we tried to investigate the parameters controlling the "solubility" and "swellability" in superabsorbent polymers.

The amount and the nature of the crosslinker unit is also crucial. When the polymerization is simultaneously being carried out in the presence of crosslinker (crosslinking), as is the case for common procedure of superabsorbent manufacturing, the crosslinker efficiency should also be taken into consideration. This parameter determines the number of the efficient ties between the polymer chains. Generally speaking, more ties result in less water absorption due to more hindrance of the network to swell. Among the variety of crosslinkers, one could select either water soluble or oil soluble crosslinkers, but different polymer properties could be expected.

Another parameter of importance in determining the properties of final polymer is the concentration of the monomer used in the polymerization reaction. Polymerization is exothermic. By using a lower concentration of monomer, there is less risk of thermal runaway, better chances for process control and, generally, more homogeneity in the final product but less yield. High heat output of the highly concentrated reaction medium results in undue polymerization and to high viscosity of the reaction medium and both these factors give lower control on the process and higher heterogeneity with product. The advantage of using a higher monomer concentration is to obtain commercial economic value.

Although a big list of other variables, including the water/oil ratio, the rate of agitation and the type of the stirrer would be expected, we focused on the main variables which could remarkably affect polymer properties.

To perform polymerisation, the two phases should be intimately contacted with each other through a mechanical mixing. To deoxygenate the reacting medium which is accessible to the atmospheric oxygen, a blanket should be provided throughout the system, *e.g.* *nitrogen blanket*. Otherwise, the polymerisation is prevented or retarded due to inefficient monomer consumption.

The reaction starts after establishing the temperature. According to the nature (in terms of solubility in water or in oil) and concentration of the materials used and associated operating conditions, products of various physical shapes (powder, bead and lump) could be obtained. These conditions are also responsible for producing a polymer of the desired swelling properties (*i.e.* swelling amount, swelling rate and gel strength after swelling). Thus the effect of the individual parameters should be interrelated and balanced to attain a polymer with the desired appearance and swelling properties.

3.2.1.1 Preliminary trials (Expts. 1-17)

After numerous trials and errors, a basic preparative procedure (Expt. 1) was adopted following methods described in patents [6-23].

One of the basic requirements for a successful inverse suspension polymerisation, in order to produce separated, well-defined particles was the use of a surfactant of very low hydrophilic-lipophilic-balance (HLB). The sorbitan monostearate (HLB, 4.7) [24] was used for this purpose in Expt. 1. A characteristic feature of this typical stabiliser was its hydrophobicity which brought it to partition mainly in the organic hydrocarbon solvent (hence it is very sparingly soluble in water, as indicated by forming a milky mixture between water and the stabiliser).

On the other hand, the total monomer (including acrylic acid and sodium acrylate) concentration was set at 40.0 w/w % of the reaction mixture. Following the preparative procedure described in Expt. 1, the product was obtained as a swollen lump. The lump itself was constituted by the number of granules which were tightly attached to each other and each granule had incorporated very numerous smaller particles in different sizes (see *Fig.* 3.1).

After oven-drying, weight of the lump was reduced. This was due to the amount of the water originally present in the reacting medium, which was taken up by the resulting reaction product, that was potentially a super water-absorbent. What we needed was obtaining the material in particle form not as a big lump or even a granular mass. The latter was not a useful material in service, since most of the potentially superabsorbent particles were occluded into the granule, thus not being accessible to water in a relatively short periods of time. Therefore there was a need to first separate the lump into the granules and then break the latter up to give the effective particles. The most usual method to obtain discrete particles was to increase the surfactant concentration and speed of agitation. The former is essential to separate the particles physically, by, presenting the more surface tension along the interfaces, although the latter helps to segregate the granules and the particles mechanically through increasing the stress between them.

Increasing the stabilizer or surfactant concentration (Expt. 2) led to the same product, as before, except that the granules within the lump were loosely attached to each other.

A similar result was obtained from Expt. 3 for which the agitation speed was increased while the surfactant concentration was kept high as in Expt. 2. This modification showed that the increased agitation rate does not help to separate the swollen granules anymore.

After the latter experiments failed, the possible reason for the granules adhering to one another seemed to be a consequence of the water present in the system, since water presumably adhered the particles (through solvent-binding), which are hydrophilic in nature as well as a swelling medium. Thus vacuum distillation was attempted to remove water. However this experiment (Expt. 4) failed due to the partial miscibility of water and toluene [toluene/water mixture containing 20% water forms an azeotrope of boiling point 85 °C [25] which is very near to the reaction temperature] which perturbed the water/oil ratio due to evaporation.

Based on this assumption, toluene was then replaced by xylene (Expt. 5) which has a higher boiling point than toluene (138-142 °C compared to 111 °C) and forms an azeotropic mixture at temperature [93 °C when the mixture contains 33% water [25]] well above the reaction temperature (80 °C). The result was the formation of non-uniform (in size), swollen and rather separated granules, which was not satisfactory.

Carrying out more experiments with same formulation as in Expt. 5, but incorporating higher dosages of surfactant led to the water soluble products. This meant any attempts to increase the stabiliser concentration in order to produce separate polymer granules and particles was complicated by the increased solubility of the polymer, which is undesirable.

Thus a few experiments were devised using sorbitan monooleate as a more powerful, lower HLB stabilizer than sorbitan monostearate (4.3 compared to 4.7) [24]. The product of the latter modification (Expt. 6) was obtained as a fine, water-soluble but non-swellable powder.

Attempts to increase the size of the latter particles through a decrease in the surfactant concentration (Expt. 7) led to coarse, star-shaped, rather separated, swollen granules (see *Fig.* 3.2).

As an alternative to removing water by vacuum distillation, use of a commercial water-absorbent polymer was attempted (Expt. 8). In this case, more uniform, separated, swollen granules were obtained (see *Fig.* 3.3) which demonstrated more water removal efficiency of the superabsorbent polymer compared to the vacuum distillation procedure. The average size of 2-3 mm was measured for the granules, which were constituted of aggregated particles of 50-500μm. One of the outstanding feature of using the absorbent appeared to be the very rapid rate of water uptake, which takes too much time using the vacuum process. Another feature is that the particles of the superabsorbent additive which was liberally added, acts presumably as seeds on which polymerisation proceeds. This is the same procedure to produce seeded poly (vinyl chloride) emulsion powders. And, finally, there is an advantage of maintaining the system intact, *i.e.* evaporation of the phases is no longer experienced.

Nearly a similar result was obtained under the conditions by replacing xylene with toluene (Expt. 9). Deleting the superabsorbent from this formulation as well as increasing the surfactant concentration (Expt. 10) led to rather coarser granules. Attempt to break the granules again through an increase in surfactant concentration (Expt. 11) afforded a water soluble powdery gel.

The material obtained from Expt. 10 was appeared to be a good starting point for our work, exhibiting a 416 times absorbency, although it was obtained relatively coarser than the product of the Expt. 9. Moreover, compared to the latter, there was no need to apply another ingredient, like a superabsorbent which complicates formulation and results.

Attempts to use auxiliary emulsifiers, such as partially-hydrolyzed poly(vinyl alcohol) (Expt. 12) and CMC (carboxy methyl cellulose) (Expt. 13) in order to break the granules resulted in formation of sticky gels, although their effects on absorption capacity was quite remarkable, giving values of 610 and 720 g/g respectively.

Another modification was to use methanol as a precipitant (non-solvent or insolubiliser) and dewatering agent for the polymer granules, as detailed in Expt. 14. The resulting product had better handling properties and was obtained in the form of a coarse and separated granules, white in color. This led us to choose methanol as dehydrating agent.

An examination of ground up and as-synthesised product of Expt. 14, by scanning electron microscopy (SEM), without any attempts to break the granules into their constituted particles, is shown in *Fig.* 3.4 and *Fig.* 3.5 respectively.

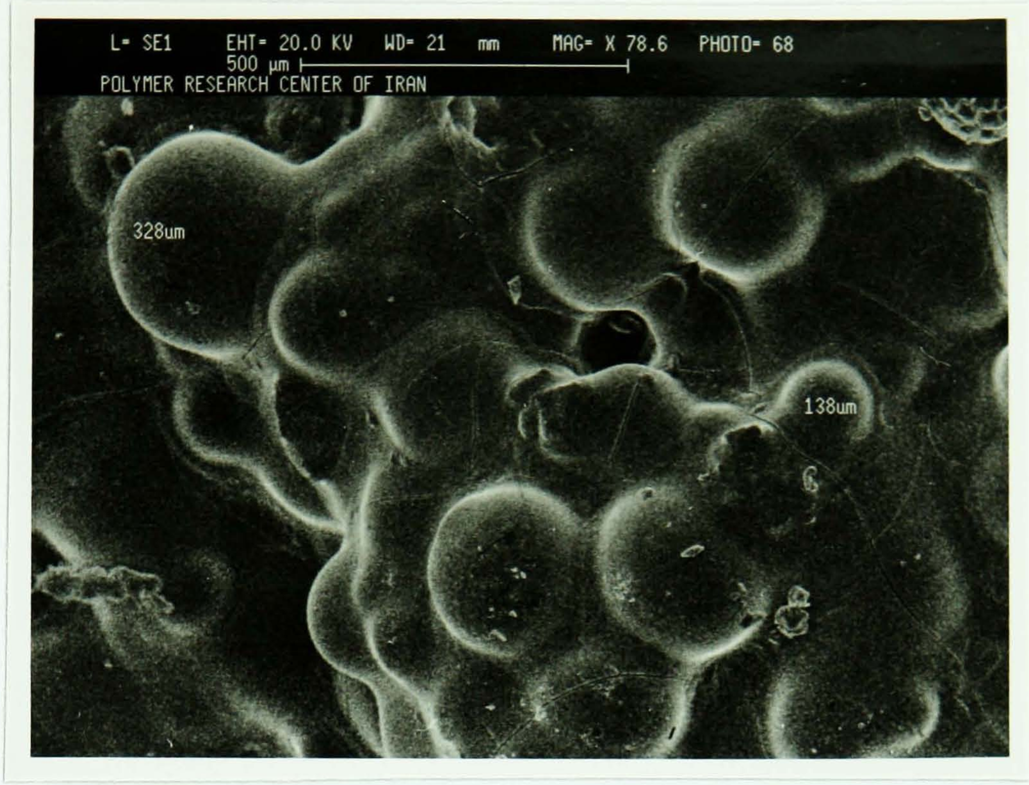

***Figure* 3.1** SEM micrograph of the product obtained from the Expt. 1, shows aggregation of granules consisting numerous fine particles.

***Figure* 3.2** SEM micrograph of an isolated star-shaped granule obtained from the Expt. 7.

***Figure* 3.3** SEM micrograph of an isolated round granule obtained from the Expt. 8.

***Figure* 3.4** SEM micrograph of ground-up absorbent obtained from the Expt. 14.

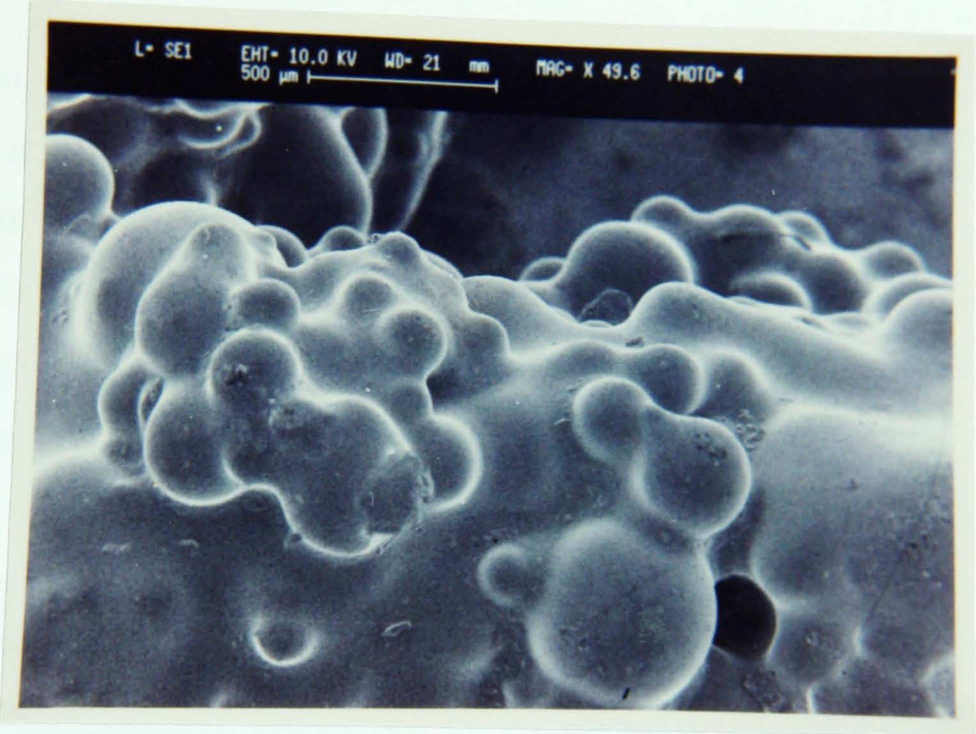

Figure **3.5** SEM micrograph of as-synthesised product obtained from Expt. 14.

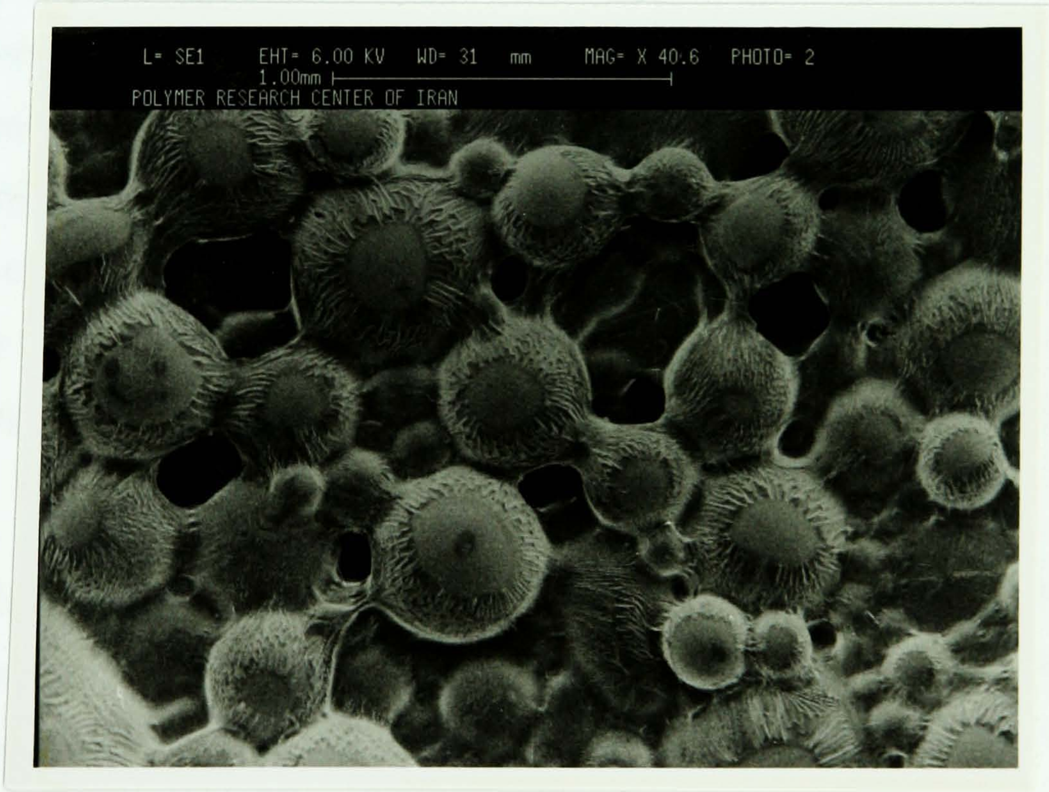

Figure **3.6** SEM micrograph of a sample obtained in Expt. 15, clearly shows the presence of ethyl cellulose over the polymer surface.

There was no remarkable feature (*e.g.* porosity) onto the surface of the product. Up to this point, we were only successful to break the lump into the separated granules of reasonable amount of absorption capacity.

From our preliminary results it appeared that a single low molecular weight surfactant like sorbitan monostearate or even sorbitan monooleate, and in some cases a combined surfactant [together with high molecular weight materials like poly (vinyl alcohol) or carboxy methyl cellulose] did not produce materials with all the required characteristics, mainly obtaining the material as particles. This enforced us to make some further trials. The final experiments, to reinforce or modify the performance of the principal emulsifier was attempted by using ethyl cellulose as an auxiliary macromolecular emulsifying agent in order to produce reasonable particle sizes (Expts. 15,16 and 17) (***Note***: low and high molecular weight emulsifiers can be termed micromolecular and macromolecular respectively). *Figure* 3.6 shows the product obtained from the Expt. 15. It can be observed, that a layer of ethyl cellulose covered the surface of the particles and as an abhesive, preventing them from adhering to each other. A typical contraction was occurred and can be observed for the ethyl cellulose surface layer, which reshaped it as a drape or a wrinkled sheet. The surface contraction was due to the particle shrinkage, which was caused by the water removal from the polymer particle through applying a methanol dewatering procedure. *Figure* 3.7 displays this phenomenon under higher magnification. The evidence for the presence of the ethyl cellulose barrier over the surface of the polymer particles was obtained when the particles shown in *Fig.*3.6 were simply treated with fresh toluene. As clearly be seen in *Figs*. 3.8 and 3.9 with two levels of magnification, the particles were obtained bare and free from any coating.

A better solution was obtained from Expt. 16, in which more separated particles were obtained. Increased dosage of ethyl cellulose (Expt. 17) led to highly separated particles as can be seen in *Fig.* 3.10. The mean surface diameter of the latter particles, with almost a 800 times absorption capacity, was about 300 microns. *Figures* 3.11 and 3.12 show a completely separated particle in non-swollen and swollen form in water. It should be mentioned that, a few bigger particles still show something like aggregation, *i.e.* adhering of smaller particles onto the surface of the bigger ones. This can clearly be seen in *Fig.* 3.13. For simple observation of such aggregation, one of the particles was allowed to swell in doubly distilled water to high extent (left-hand side of the picture).

The properties of the material from the foregoing experiment were, an extraordinary amount of absorption, reasonable swollen gel strength (rather hard and tough) and relatively low rate of absorption which takes near an hour to reach equilibrium or steady state swelling. The other advantage was its shape, *i.e.* particle, after synthesis, the shape we required to assay various system variables on polymer properties. The swelling properties of the superabsorbents are critically dependent on the size of the particles to be assessed. Therefore, any attempts to survey the effect of system variables on the swelling properties should be done on particles of well-defined size, *e.g.* 50-60 mesh or something else. But how sensitive the swelling parameters mainly, absorption capacity and absorption rate are to the system parameters and how they inter-relate is of crucial importance and should be cleared. Thus a variety of experiments were designed to study the effect of the system parameters on the swelling characteristics of the polymers. The selected parameters of the former, reviewed here in turn, are the crosslinker type and amount (oil and water soluble crosslinkers in a variety of concentrations), the comonomer other than present structural units, methods for superabsorbent manufacturing other than the inverse suspension method, temperatures and initiator, particle size, ionic strength of the swelling media, monomer concentration and filler.

Figure 3.7 SEM micrograph of the product from Expt. 15, at higher magnification.

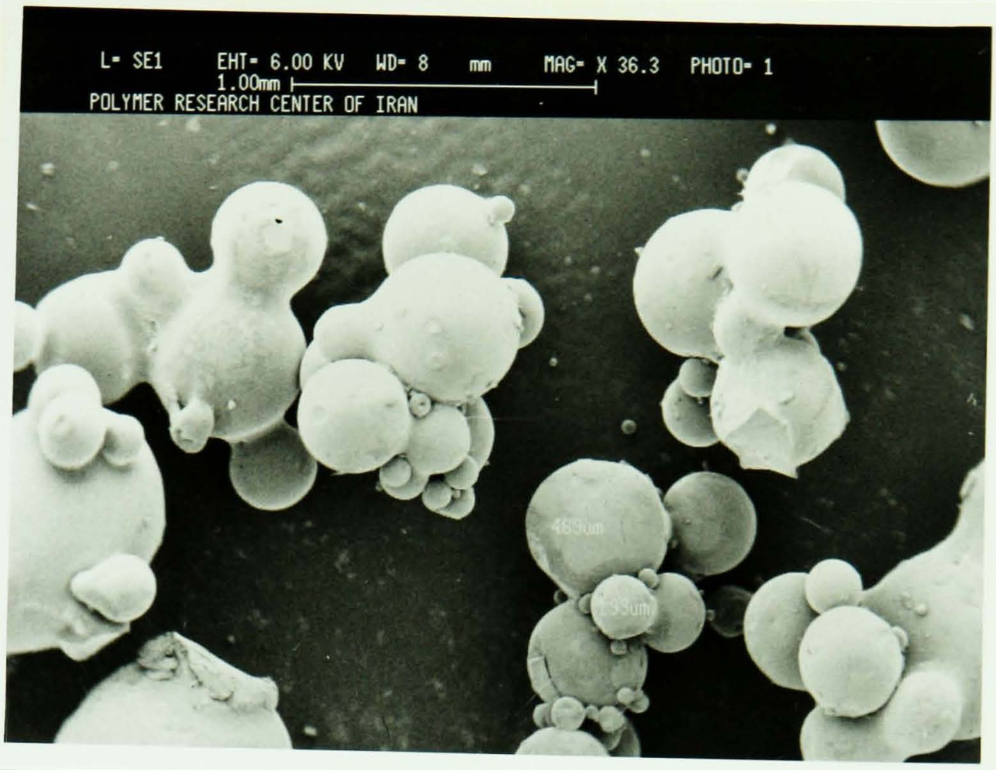

Figure 3.8 SEM micrograph of the product obtained from Expt. 15, after washing with fresh toluene.

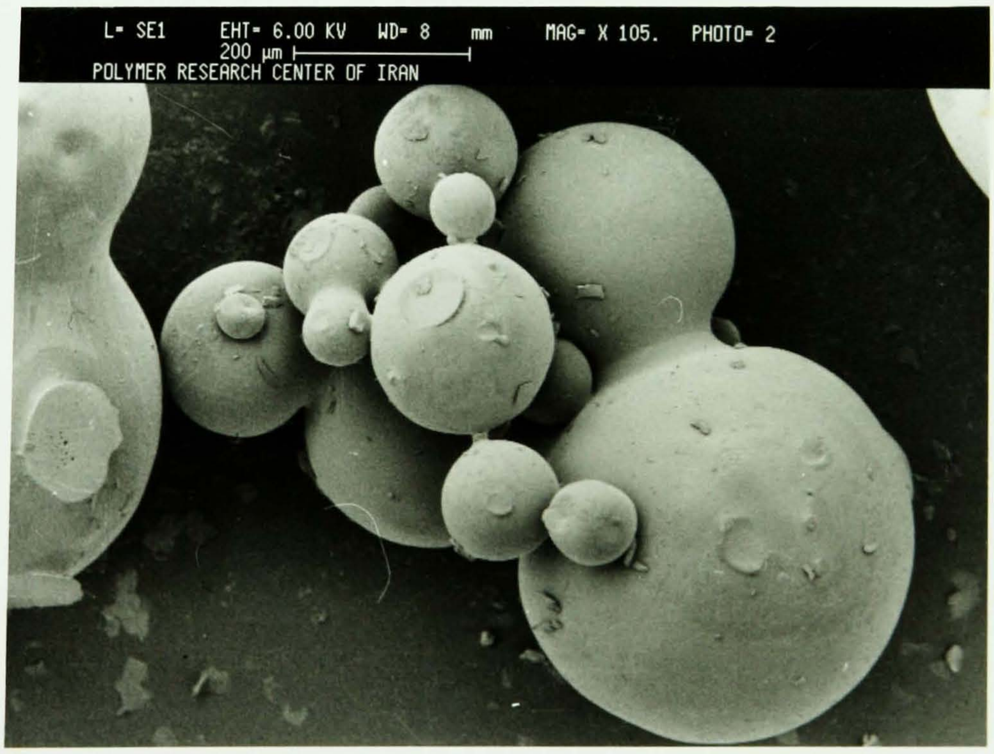

Figure 3.9 SEM micrograph of the product obtained from Expt. 15, after washing with fresh toluene, at higher magnification.

***Figure* 3.10** Photograph of a product obtained from the Expt. 17.

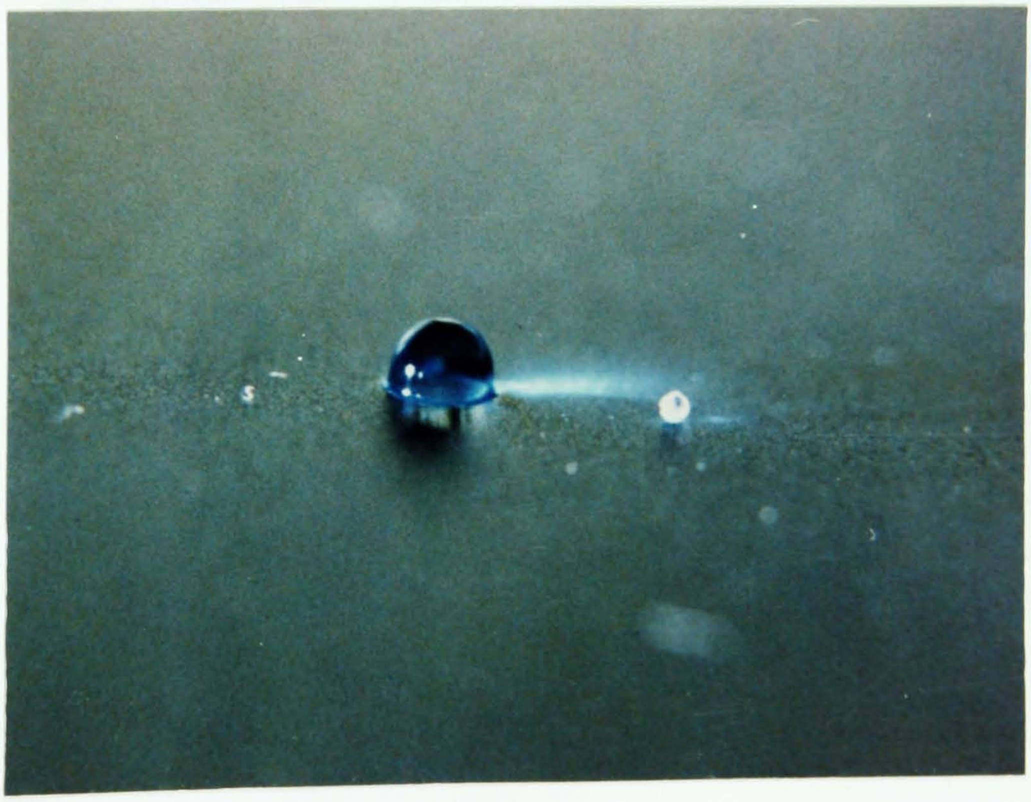

***Figure* 3.11** Photograph of a particle (from Expt. 17) in its swollen and non-swollen form.

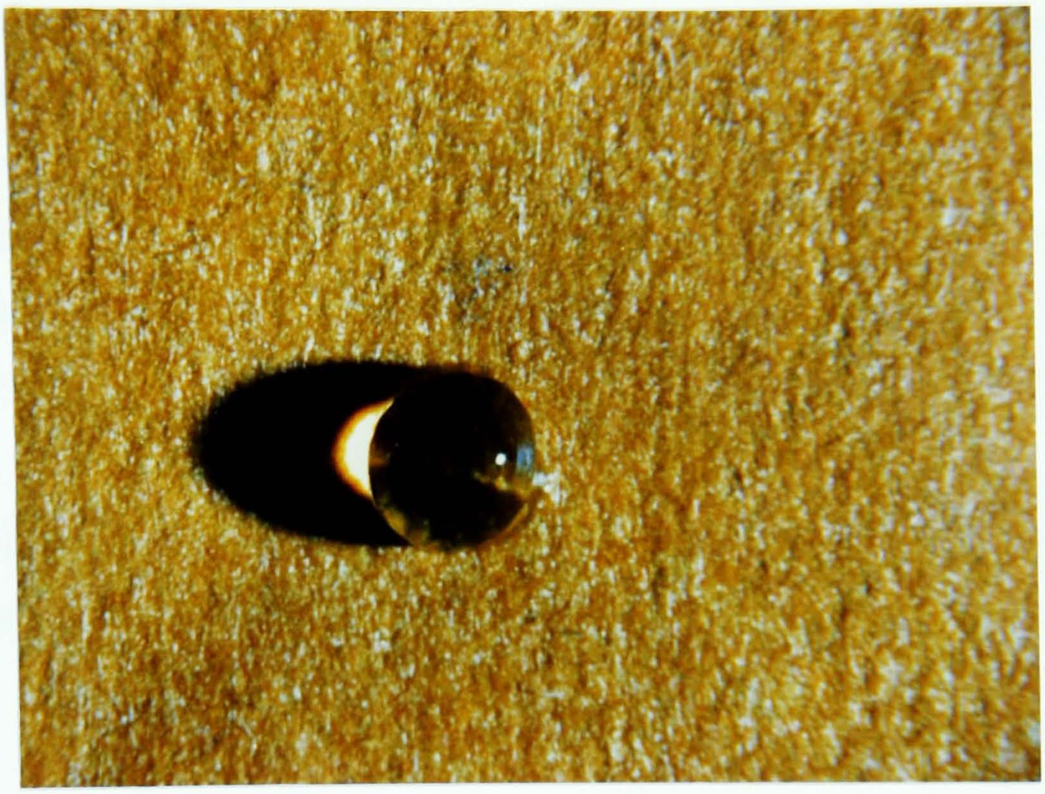

***Figure* 3.12** Photograph of an isolated particle (Expt. 17) in its slightly swollen form.

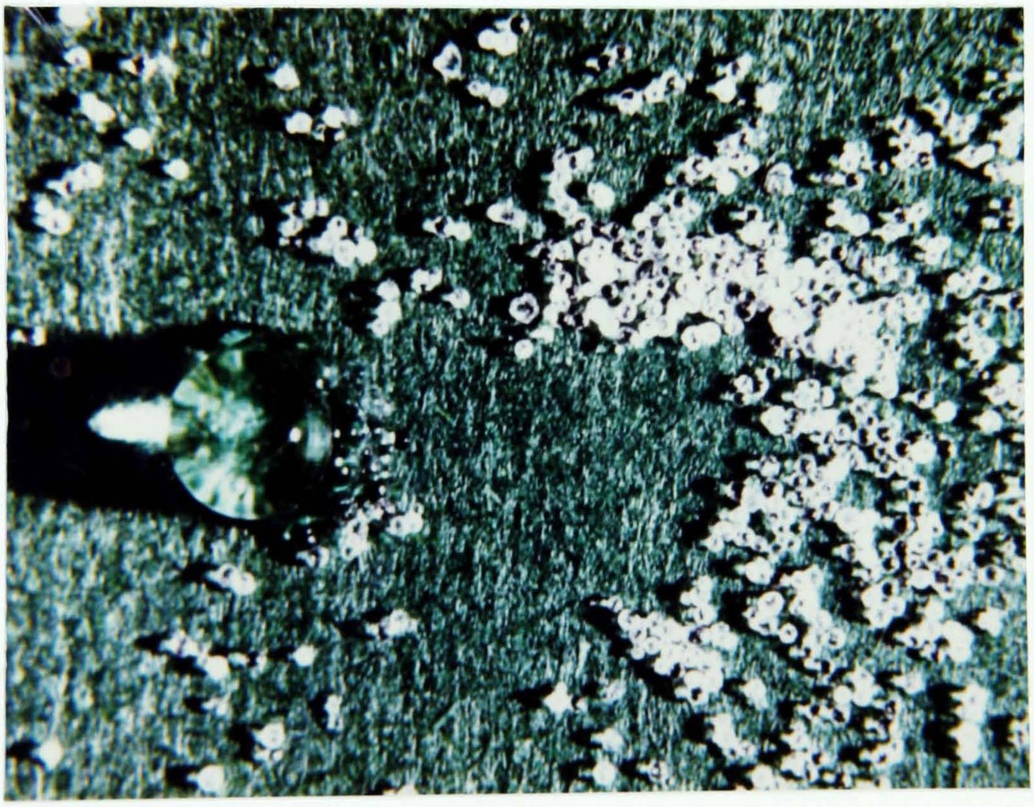

***Figure* 3.13** Photograph showing a typical aggregation of finer particles (Expt. 17) onto a big particle, in swollen state.

3.2.1.2 Effect of the oil-soluble crosslinker concentration (Expts. 18-21)

A series of experiments (Expts. 18-21) was designed to assay the effect of the oil-soluble crosslinker concentrations on the absorption behaviour of the polymers obtained as in Expt. 17. The starting conditions were variants of those described for Expt. 17 using various crosslinker dosages as quoted in *Table.* 2.1 and 3.2. No difference in nature of polymerisation of these formulations was observed, moreover, all the products were mainly obtained in particle form. The swelling measurements carried out on particles range in size, 50-60 mesh. Typical properties of these hydrogels are presented in *Table.* 3.2.

The samples for Expts. 18-21 differ only in terms of crosslinker amount. Parameters recorded in the table have been found according to the equations introduced in *Sec.* 2.4.2.

Table. 3.2 Properties measured for the samples crosslinked using ethylene glycol dimethacrylate.

Expt.	*18*	*19*	*20*	*21*	*Change*
Molar percent of crosslinker to monomer	*0.055*	*0.238*	*2.30*	*4.58*	*84 ×*
Degree of swelling (g/g)					
in double distilled water	789	756	617	487	-38.2%
in 0.009% NaCl solution	452	439	390	333	-26.3%
in 0.09% NaCl solution	196	191	174	144	-26.5%
in 0.9% NaCl solution	71	70	65	57	-19.7%
Polymer volume fraction in the gel	8.2 E-4	8.6 E-4	1.03 E-3	1.3 E-3	+58.5%
Crosslink density (mol/cm^3)	7.2 E-5	7.4 E-5	8.4 E-5	9.8 E-5	+36.1%
Network chain density (mol/cm^3)	1.44 E-4	1.48 E-4	1.68 E-4	1.96 E-4	+36.1%
Network chain molecular weight (g/mol)	10763	10472	9226	7908	-26.5%

Note: According to the Sec. 2.4.3, the density of the samples was found 1.55 g/cm^3.

In the *Table.* 3.2, the degree of swelling has been measured according to the *Sec.* 2.4.4. It should be mentioned that this parameter was expressed as a weight ratio. Polymer volume fraction in the gel means, the volume of the polymer within the polymer and water combination after swelling. Thus, it is reciprocal of the volume degree of swelling. Hence, the higher the swelling, the lower will be the polymer volume fraction. The crosslink density is the measure of the amounts of the ties connected the free chains to each other. On the other hand, the network chain density is the density of the chains between two junction points, which is simply twice the crosslink density value, if the crosslinker is tetrafunctional. In general, network chains exhibit a distribution of molecular weights about an average, which serves as a reference quantity in describing a network structure [26]. Thus, the parameter measured as network chain molecular weight is the average value for the molecular weights of different chains between two crosslink points. To calculate these parameters, at first, we obtained the amount of the weight swelling, q , by the method described in *Sec.* 2.4.4. Then, with known density value of the polymer (*Sec.* 2.4.3), the polymer volume fraction in the gel was obtained through *Equation.* 2.4. By substituting the parameters in *Equation.* 2.3 with appropriate quantities, the crosslink density was found. Knowing the density of the polymer and the functionality of the crosslinker, the molecular weight between two crosslinks and the network chain density were calculated using equations 2.7 and 2.8 respectively.

With these experiments, the crosslinker dosage was substantially increased, *i.e.* the crosslinker in the Expt. 21 was 84 times greater than in the Expt. 18. The highest equilibrium swelling was observed for the lowest loaded product. Any increase in the crosslinker led to a decrease in the corresponding equilibrium swelling value. Thus, the minimum amount of steady state or equilibrium swelling was observed for the product containing the highest amount of the crosslinker.

Generally speaking, an increase in the crosslinker concentration resulted in a decrease in equilibrium swelling (in each swelling medium), an increase in the polymer volume fraction in the gel, an increase in crosslink or network chain density as well as a decrease in the molecular weight between the two successive crosslinks.

The degree of the swelling for the individual samples was plotted against time, as shown in *Fig.* 3.14. A similar trend was generally observed for the dynamic swelling values of other samples. Thus, three regions could be distinguished in the plot of the swelling against time. The swelling increased sharply, then continued smoothly to finally a constant value.

Considering a same acid/salt molar ratio of 1/3 (means 75% neutralisation degree) for all the samples, this was the molar percent of the crosslinker to the monomer , which remarkably determined the equilibrium water-retaining capacity of these absorbents.

The time taken by the samples to reach their final swelling state was different. The longest time was recorded for the sample from the Expt. 18 (about 40 min.). An increase in the crosslinker led to a decrease in time, so that, the value of 23 min. was obtained for the sample from the Expt. 21. This means, the higher crosslinker loaded material reaches faster to its equilibrium swelling capacity than the lower loaded counterpart. This observation will be further discussed under the heading "A Swelling Model" (see *Sec.* 3.3).

On the other hand, for each sample, a decrease in the equilibrium swelling was observed with salt concentration. The highest swelling was observed in doubly-distilled water, whilst the swelling medium of the highest salt concentration led to the lowest amount of swelling. The effect of the ionic strength of the swelling medium on the absorbent properties will be discussed under the heading "Effect of the Ionic Strength" (see *Sec.* 3.6.3).

When we plotted the equilibrium swelling values of the samples obtained at different crosslinker concentrations, against salt concentration of the swelling medium, a sharp transition in the swelling curve was generally observed. Finally, the swelling values converged nearly to the same point at high saline concentration (see *Fig.* 3.15).

The plots of the equilibrium swelling values against crosslinker concentration were different for the various swelling media (see *Fig.* 3.16). The swelling in doubly-distilled water was reduced sharply with the crosslinker. But this trend became smoother with an increase in the ionic strength of the swelling medium. A conclusion could be simply made that, the amount of the equilibrium swelling became independent of the crosslinker concentration at high saline concentration.

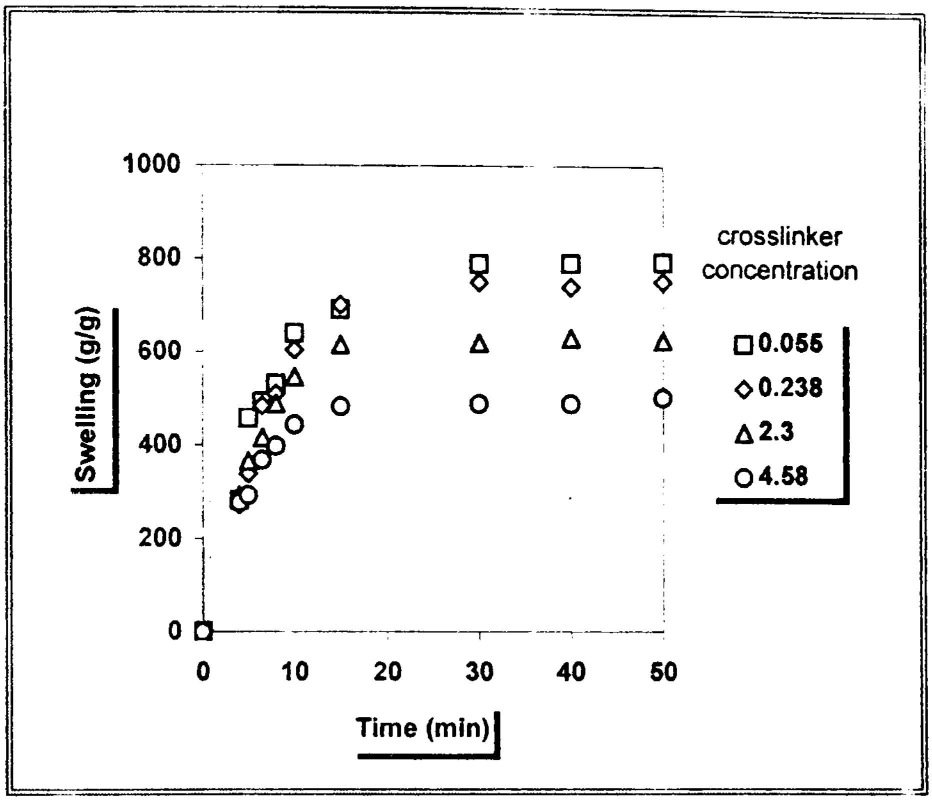

***Figure* 3.14** Dynamic swelling curves for the samples obtained from Expts. 18-21, at different crosslinker concentration.

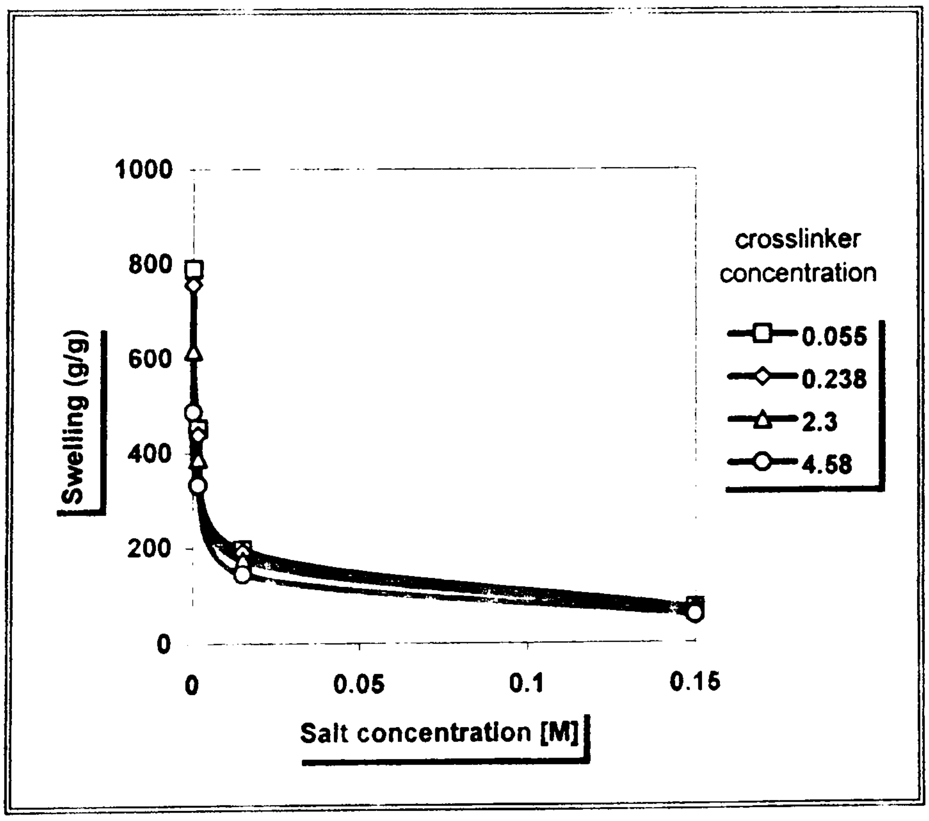

***Figure* 3.15** Equilibrium swellings at different crosslinker concentration, against saline concentration of the swelling medium (Expts. 18-21).

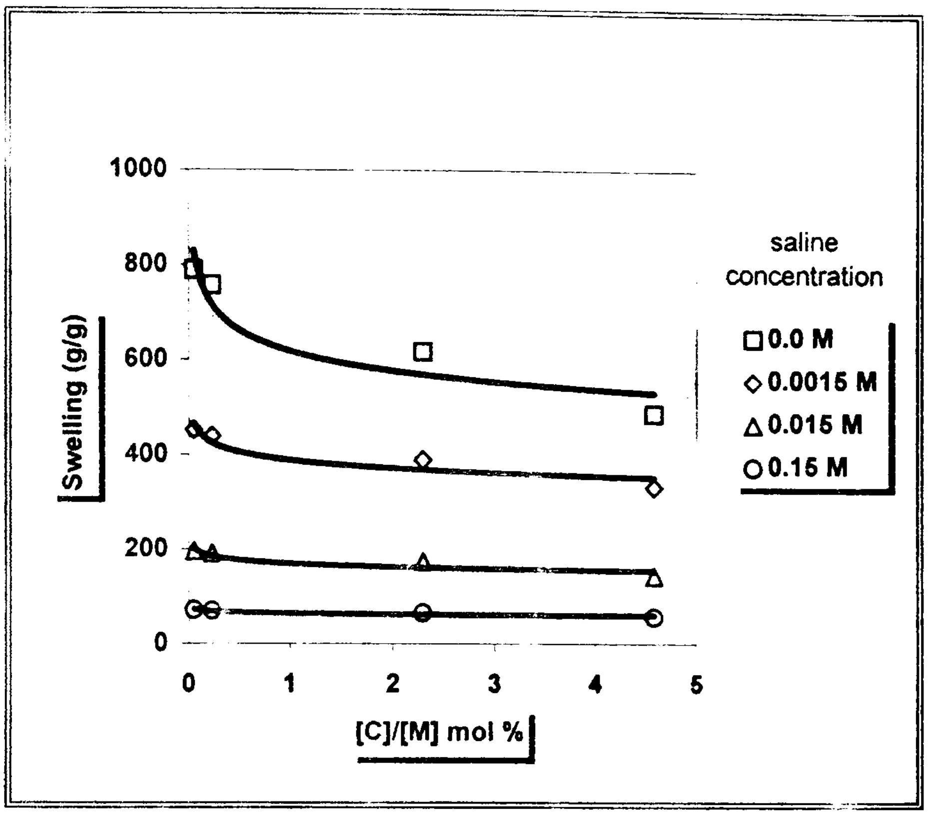

Figure 3.16 Equilibrium swellings in different swelling media, against crosslinker concentration (Expts. 18-21).

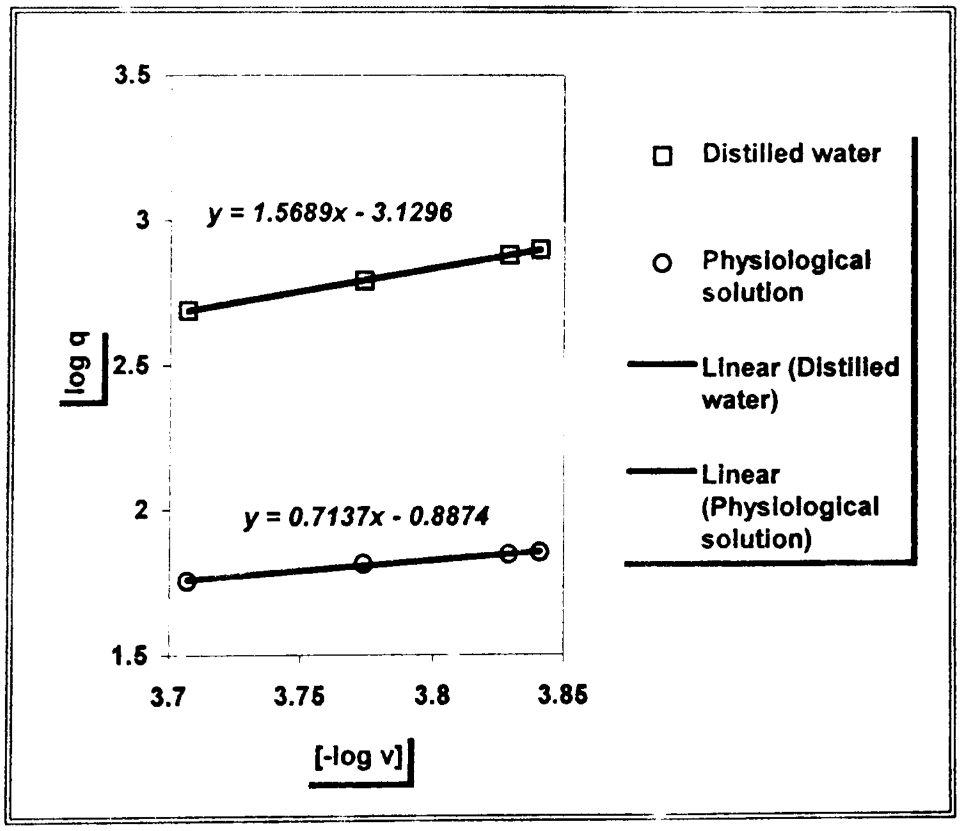

Figure 3.17 Logarithmic relationships between equilibrium swelling and corresponding network chain density (Expts. 18-21).

According to the *Fig.* 3.17, the logarithms of the equilibrium swelling values versus the logarithms of the network chain density, showed a power law behaviour, $q = a\, \upsilon^{n}$, in two extremes of the swelling media, *i.e.* in doubly-distilled water and in physiological solution. The experimental exponent, n, for these two solutions was found to be 1.57 and 0.71 respectively. These figures also indicate that the swelling capacity was much more dependent on the crosslinker concentration in the salt-free water than in the brine. Finally, with the Expt. 18, the ratio of the equilibrium swelling values in distilled water and the swelling medium of highest salt concentration was found 11.1. This ratio decreased with crosslinker concentration. So that, the ratios of 10.8, 9.5 and 8.5 were calculated respectively for the Expts. 19, 20 and 21.

Although the superabsorbents obtained from the Expts. 17-21 were able to absorb huge amounts of water, they suffer from a few disadvantages. Firstly, there was a need to apply high crosslinker dosage to obtain a reasonable capacity of water absorption. Secondly, a remarkable increase in crosslinker concentration had a very small effect on reducing the swelling capacity. Finally, the rate of absorption was very slow, so that, a fraction of an hour was required for the samples to reach their equilibrium capacity, although the rate was increased with crosslinker concentration.

For baby diapers and personal care products, these absorbents are potentially useful, since they have a well-defined particle size. But for some fields of application, such as agricultural and horticultural use, the requirement for the particle size can be pursued by grinding the superabsorbent in bulk form (lump), followed by classifying the particles. Therefore, the material obtained from the Expt. 14 can potentially be used in such applications.

3.2.1.3 Effect of the water-soluble crosslinker concentration (Expts. 22-25)

Another way to make a hydrophilic polymer, useful as a superabsorbent was the use of a water-soluble crosslinker. For this purpose, we adopted, among a family of the bisacrylamide compounds, a compound containing two identical double bonds. This was N, N'- methylene bisacrylamide. This crosslinker is much more soluble in water than ethylene glycol dimethacrylate. So, we run a couple of experiments (Expts. 22-25), as a way similar to the latter experiments, *except* that, the nature and amount of the crosslinker was varied. The crosslinker concentration changed from 0.016 to 0.11 molar percent to the total monomer present in the reacting medium. The swelling data, as well as some structural properties are quoted in the *Table.* 3.3.

Here again, the highest value of swelling was observed for the material contain the lowest amount of the crosslinker. The equilibrium swelling decreased with the crosslinker.

Table. 3.3 Properties measured for the samples crosslinked using methylene bisacrylamide.

Expt.	*22*	*23*	*24*	*25*	*change*
Molar percent of crosslinker to monomer	*0.016*	*0.047*	*0.078*	*0.11*	*7 x*
Degree of swelling (g/g)					
in double distilled water	752	517	288	254	-66.2%
in0.009% NaCl solution	403	290	212	196	-51.4%
in 0.09% NaCl solution	179	142	106	105	-41.4%
in 0.9% NaCl solution	61	53	41	39	-36.0%
Polymer volume fraction in the gel	8.56 E-4	1.25 E-3	2.25 E-3	2.54 E-3	+196%
Crosslink density (mol/cm^3)	7.4 E-5	9.57 E-5	1.42 E-4	1.55 E-4	+109%
Network chain density (mol/cm^3)	1.5 E-4	1.9 E-4	2.8 E-4	3.1 E-4	+109%
Network chain molecular weight (g/mol)	10333	8157	5535	5000	-51.6%

Note: According to the Sec. 2.4.3, the density of the samples was found 1.55 g/cm^3.

A similar behaviour was observed in other swelling media. The polymer volume fraction in the gel, the crosslink and the network chain density increased with the crosslinker, but the molecular weight between the two successive crosslinks decreased. With previous experiments, a 84 times increase in the crosslinker concentration led to the 36% increase in the crosslink density, whilst a corresponding 7 times increase , in case of present experiments resulted in about 110% increase in the crosslink density. In a same way, the effect of the amount of the crosslinker was twice that of the latter experiments on the molecular weight between two crosslink points (compare the values -26% and -52% in *Tables.* 3.2 and 3.3).

The swelling data of the individual samples plotted against time is shown in *Fig.* 3.18. Nearly the same trend can be seen as for the Expts. 18-21. The effect of the crosslinker on the swelling capacity was clear through the swelling curve, but it was hardly possible, observing this effect on the rate of the swelling or absorption rate. This will be discussed under the heading "A Swelling Model" (*Sec.* 3.3). Considering a same acid/ salt ratio for the samples, the crosslinker showed a remarkable effect on the equilibrium swelling capacity. Thus, at a certain degree of neutralisation of the acid, the crosslinker concentration determined the equilibrium water retaining capacity of the absorbents.

According to the swelling values in the *Table.* 3.3, with each crosslinker concentration, swelling reduced with the salt concentration of the swelling medium.

The plot of the swelling data against salt concentration of the swelling medium was similar in trend for the various crosslinker concentrations (see *Fig.* 3.19). A very sharp transition was observed at saline concentration near to the doubly distilled water. The swelling values converged to nearly a same point at high saline concentration.

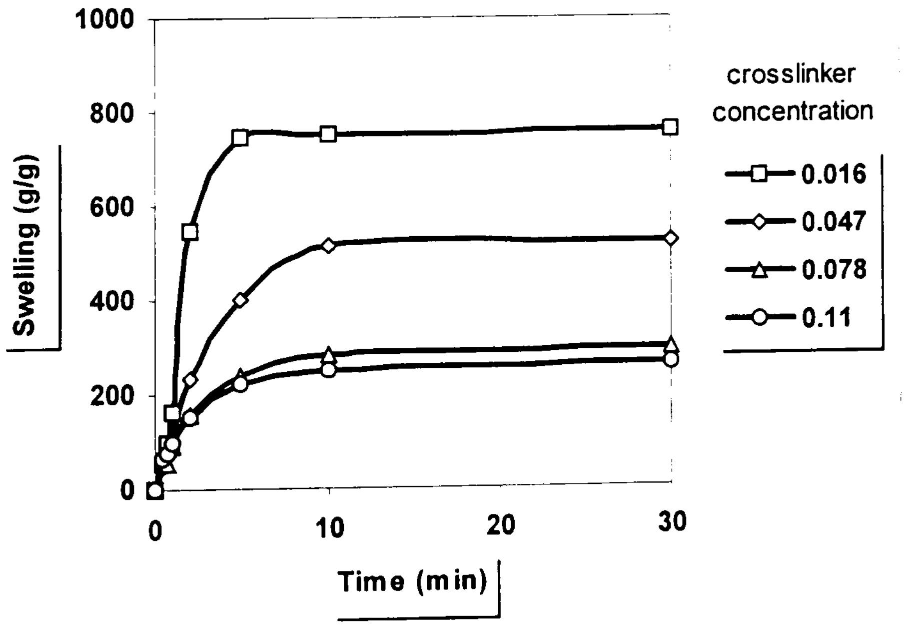

***Figure* 3.18** Dynamic swelling curves for the samples obtained from Expts. 22-25.

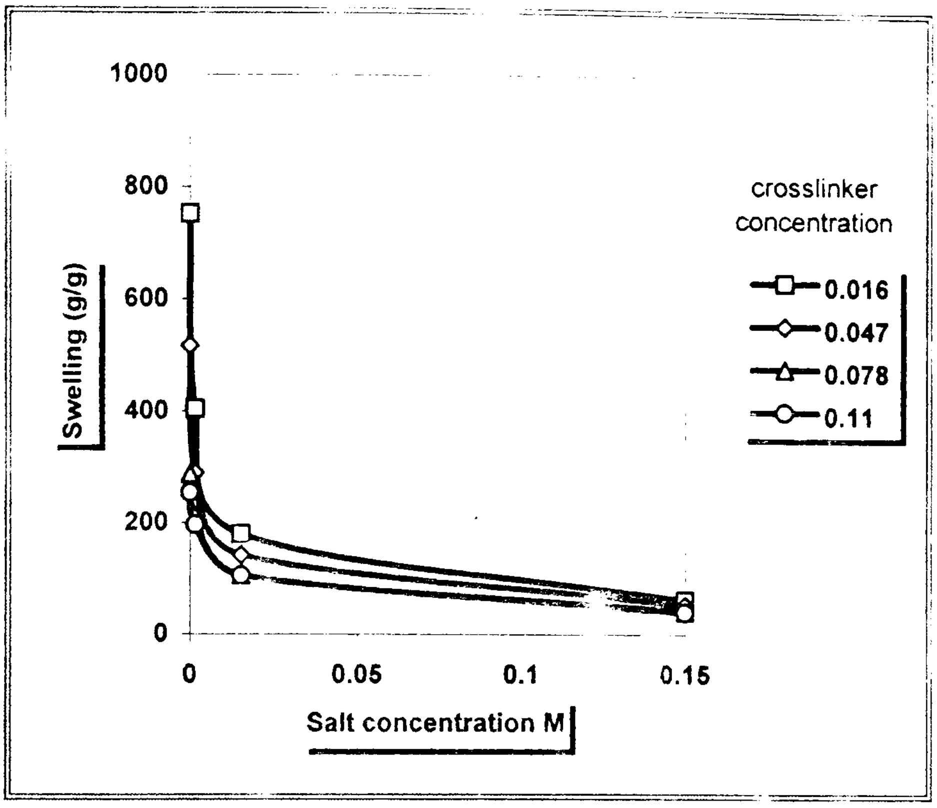

Figure 3.19 Equilibrium swelling data against saline concentration of the swelling medium, for the samples obtained from Expts. 22-25.

On the other hand, the plot of the equilibrium swellings against the crosslinker concentration was different in trend for the various swelling media. A sharp variation was observed for the lowest crosslinker loaded material, whilst with the highest loaded counterpart, the swelling variation was very low with an increase in the crosslinker (see *Fig*. 3.20).

The plot of the logarithms of the equilibrium swelling against the logarithms of the network chain density showed again a power law relationship. The experimental exponent, n , was 1.50 and 0.63 respectively for the swelling in doubly distilled water and physiological solution (see *Fig*. 3.21). These exponents were lower than the corresponding figures for the superabsorbents crosslinked with the ethylene glycol dimethacrylate. This observation reinforced that, the swelling sensitivity to the crosslinker in doubly distilled water was higher than in the salt contained swelling medium.

Another outcome was obtained by dividing the ultimate swelling values in doubly distilled water and physiological solution. With the lowest crosslinker case (Expt. 22), the ratio of about 12.3 was found. Here again, an increase in the crosslinker led to a decrease in the corresponding ratio. So that, with the highest crosslinker case (Expt. 25), the corresponding ratio was 6.51. This will be discussed under the heading "Effect of Ionic Strength " (*Sec.* 3.6.3).

Although the general behaviour of these absorbents was similar to the absorbents crosslinked by the EGDMA, they showed a distinct behaviour in some respects, which can be described according to the *Figs.* 3.22 and 3.23.

With these figures, the ultimate swelling values of the absorbents obtained from the two series of experiments, *i.e.* Expts. 18-21 and 22-25 are plotted against the molar percent of the crosslinker to monomer. The suitably fitted mathematical relationships revealed the relative efficiencies of the two types of crosslinker. With both, a power law behaviour was observed, but with quite different exponent. As in *Fig.* 3.22, the exponent for the EGDMA case was about -0.1, whilst the corresponding figure for the case of MBA was near to -0.6 according to the *Fig.* 3.23. This showed us, that MBA was much more efficient than the EGDMA to affect swelling capacities.

It should be noted that, a different particle size distribution was obtained for the two series of experiments, although a well-defined size, *i.e.* 50-60 mesh was considered for the swelling assessments. The swelling dependency on the particle size was considered as a separate section under the heading " Effect of the Particle Size" (*Sec.* 3.6.2).

A remarkable achievement through replacing the oil-soluble crosslinker by the water-soluble one was attaining a rather, high swelling material by incorporating a minute amount of a water soluble crosslinker. Moreover, the time required to reach equilibrium swelling improved down to 13 min. which was still poor and needed to be modified.

To cope with the latter requirement, another series of experiments (26-29) was designed by performing a basic change in the backbone chemical structure.

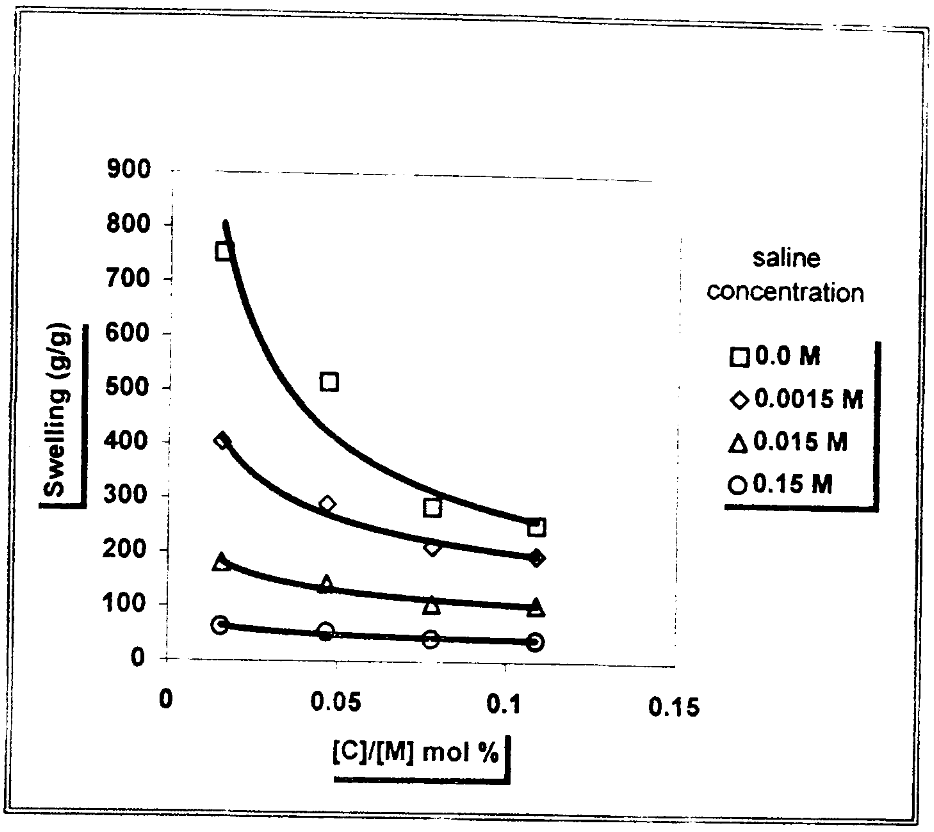

***Figure* 3.20** Equilibrium swellings in different saline, against crosslinker concentration, for the Expts. 22-25.

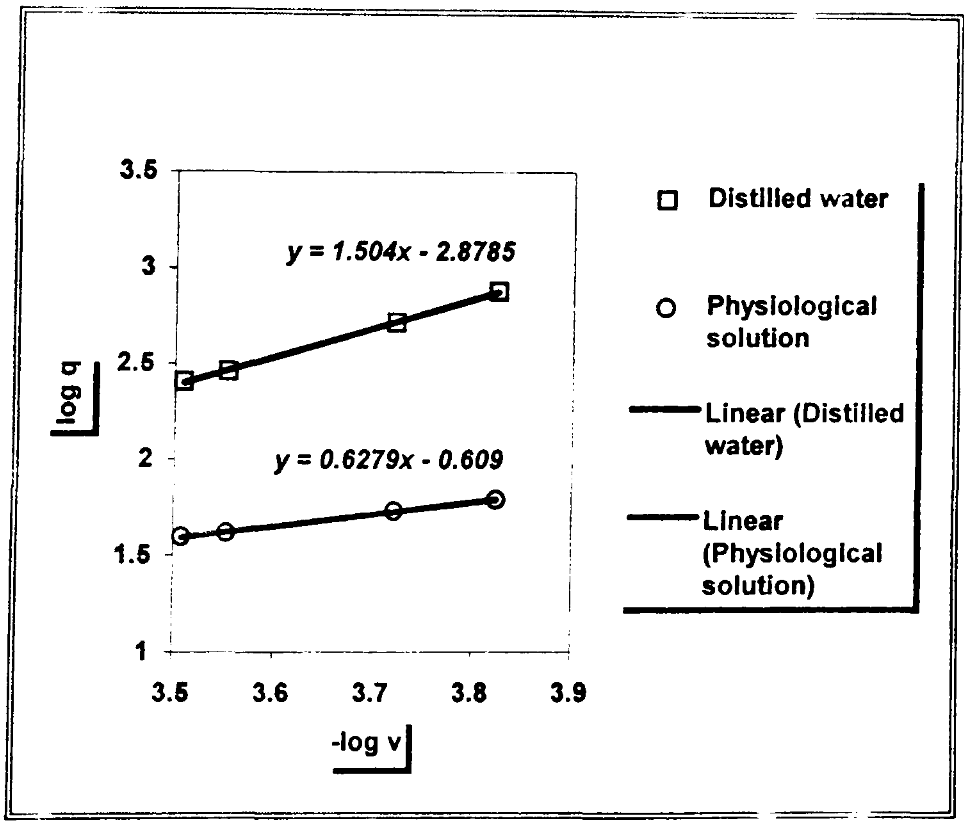

***Figure* 3.21** Power law relationship between equilibrium swelling and corresponding network chain densities, for the Expts. 22-25.

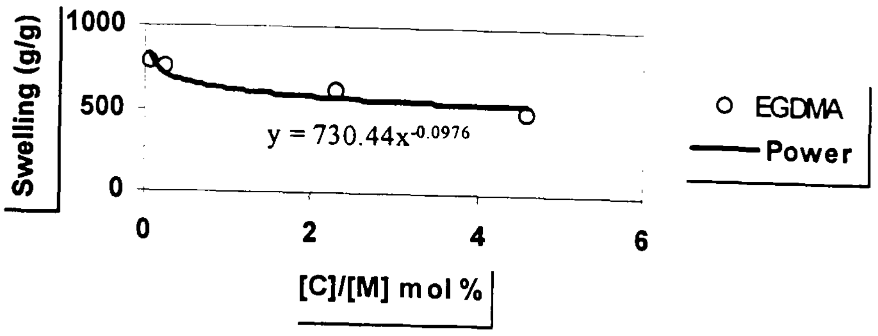

***Figure* 3.22** Equilibrium swellings of the materials obtained from the Expts. 18-21, against EGDMA concentration.

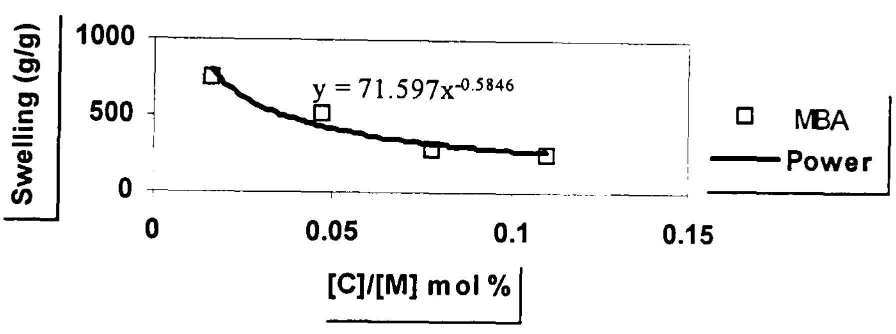

***Figure* 3.23** Equilibrium swellings of the materials obtained from the Expts. 22-25, against MBA concentration.

3.2.1.4 Effect of the comonomer (Expts. 26-29)

The basic starting monomers in foregoing experiments (22-25) was altered to include another hydrophilic but nonionic monomer, *i.e.* acrylamide. So that, three monomers participated in the polymer backbone, *i.e.* acrylic acid, sodium acrylate and acrylamide in molar ratio of 1/3/4. A same crosslinker and its concentration applied as used for the Expts. 22-25.

Table. 3.4 displays some information on the polymer properties. It should be added, that a couple of experiments were carried out with different acid/amide ratio, to find the optimum value of this ratio. With the high acid value, the swelling behavior of the product was approached to that of the materials obtained in Expts. 22-25, which suffered from a low rate of water absorption. On the other hand, with high amide value, the absorbency was remarkably decreased, so that the molar ratio of 1:1 (acrylic acid plus sodium acrylate: acrylamide) was obtained as nearly as an optimum value.

Table. 3.4 Properties measured for the samples prepared by using additional comonomer.

Expt.	*26*	*27*	*28*	*29*	*Change*
Molar percent of crosslinker to monomer	*0.016*	*0.047*	*0.078*	*0.11*	*7 ×*
Degree of swelling (g/g)					
in double distilled water	573	423	219	204	-64.4%
in 0.009% NaCl solution	328	261	183	142	-56.7%
in 0.09% NaCl solution	134	99	85	65	-51.4%
in 0.9% NaCl solution	60	50	31	23	-60.4%
Polymer volume fraction in the gel	1.2 E-3	1.61 E-3	3.2 E-3	3.4 E-3	+183%
Crosslink density (mol/cm^3)	5.3 E-5	6.5 E-5	1.0 E-4	1.1 E-4	+107%
Network chain density (mol/cm^3)	1.0 E-4	1.3 E-4	2.0 E-4	2.18 E-4	+107%
Network chain molecular weight (g/mol)	13792	11246	7310	6706	-51.0%

Note: According to the Sec. 2.4.3, the density of the samples was found 1.462 g/cm^3.

The swelling decreased with crosslinker as before. This observation was independent of the types of the swelling medium.

A 7 times increase in the crosslinker led to nearly a same change as for the Expts. 22-25 in polymer volume fraction in the gel (+183% against +197%), the crosslink density (+107% against +109%) and the molecular weight between the two crosslinks (-51%

against -51.6%). This showed us, that the crosslink density is a matter of the type of the crosslinker used.

At a same crosslinker concentration, a lower value of the equilibrium swelling was observed, compared to the corresponding swellings of the latter experiments (22-25). This was clearly due to a lower ionic nature of the polymer structure.

The effect of the salt was a decrease in swelling with each experiment. Here again, a sharp transition in the plot of the swelling against salt concentration of the swelling medium could be seen, as shown in *Fig.* 3.24. The swelling variation with crosslinker was more pronounced in a salt free swelling medium (see *Fig.* 3.25).

Although a power law relationship fitted the logarithms of the equilibrium swellings against the logarithms of the network chain density, the exponents were different from the corresponding value of the latter experiments. So that, the first exponent, *i.e.* the value of , n , in doubly distilled water was reduced down to 1.37. But in physiological solution, the exponent was remarkably increased from a value of about 0.63 (Expts. 22-25) to the value of 1.12 (see *Fig.* 3.26). This means, through the range of the crosslinker used, the swelling behavior of the polymers in doubly distilled water and physiological solution approached to each other. This could be attributed to incorporating a nonionic building block. Further discussions will be made under the heading "Effect of the Ionic Strength" (*Sec.* 3.6.3).

The plots of the swelling against time, *i.e.* the dynamic swelling at different crosslinker concentration can be seen for the samples without and with acrylamide (see *Fig.* 3.27). The swelling characteristics, *i.e.* the capacity and the rate of absorption, of these two series of experiments was quite different. In the absence of acrylamide, the swelling capacity was relatively higher than of their counterparts contain acrylamide. But, the rate of absorption for the latter was much faster than of the former. In fact, the superabsorbents modified with the acrylamide, could absorb water (up to their equilibrium capacities) in a fraction of a minute. For instance, the sample from the Expt. 27, absorbed doubly distilled water more than 420 times of its own weight, just in a period of about 30 sec.

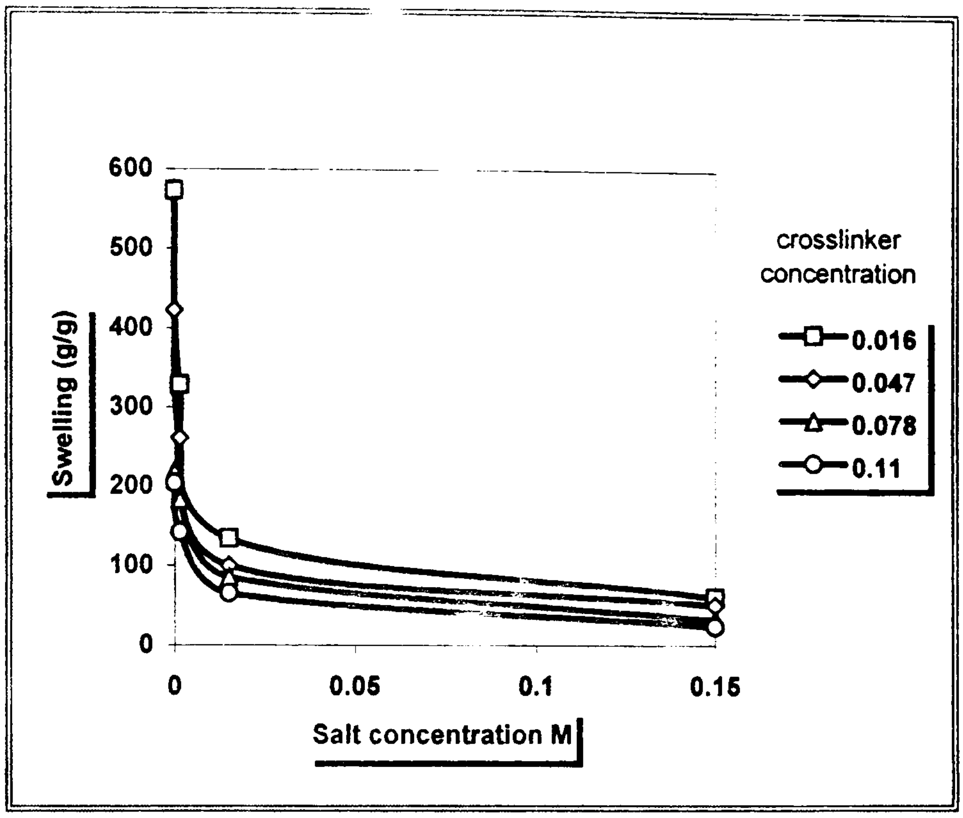

Figure 3.24 Equilibrium swellings against saline concentration of the swelling medium. for the materials obtained from Expts. 26-29.

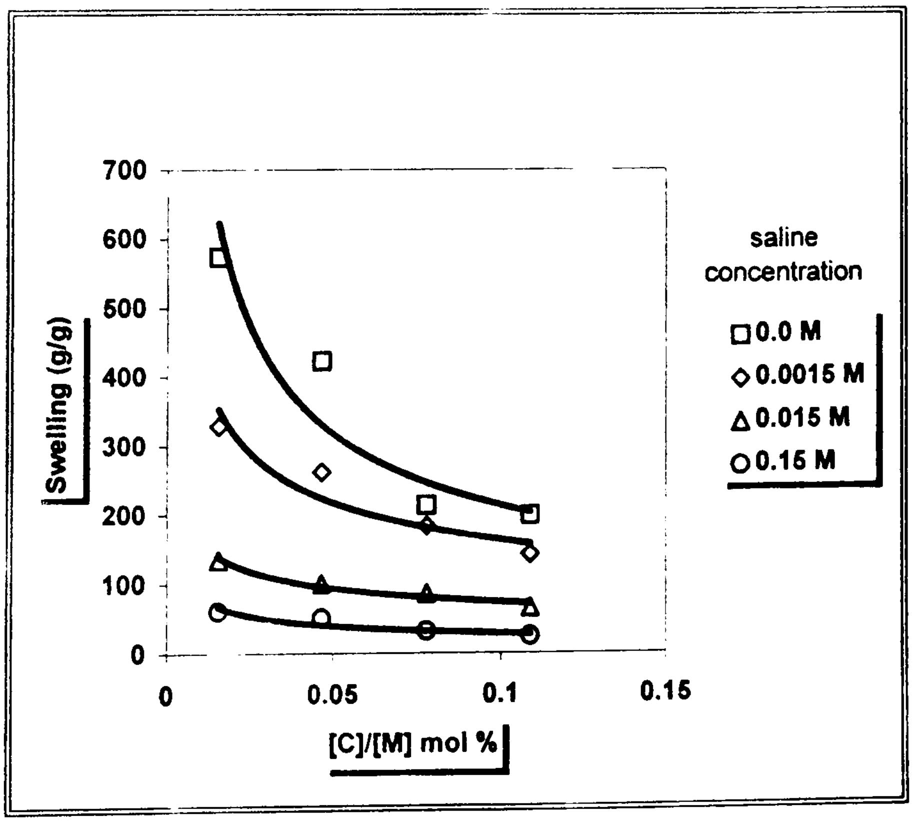

Figure 3.25 Equilibrium swellings at different swelling media (Expts. 26-29), against crosslinker concentration.

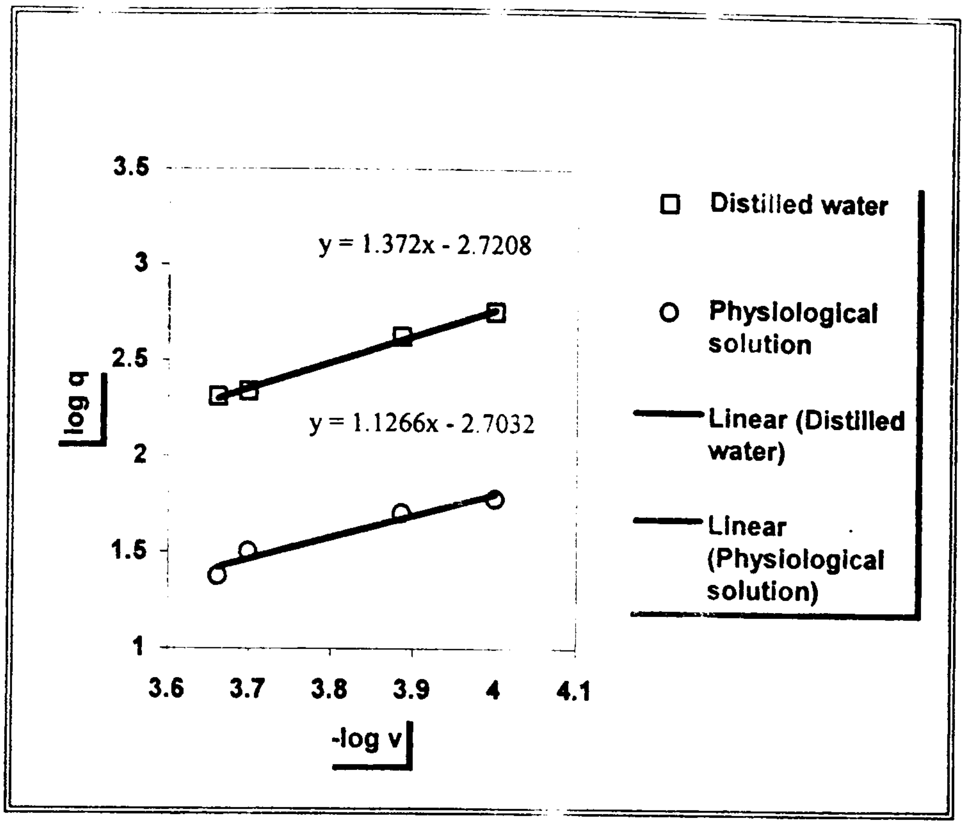

Figure 3.26 Power law relationship between equilibrium swellings and corresponding network chain densities, for the Expts. 26-29.

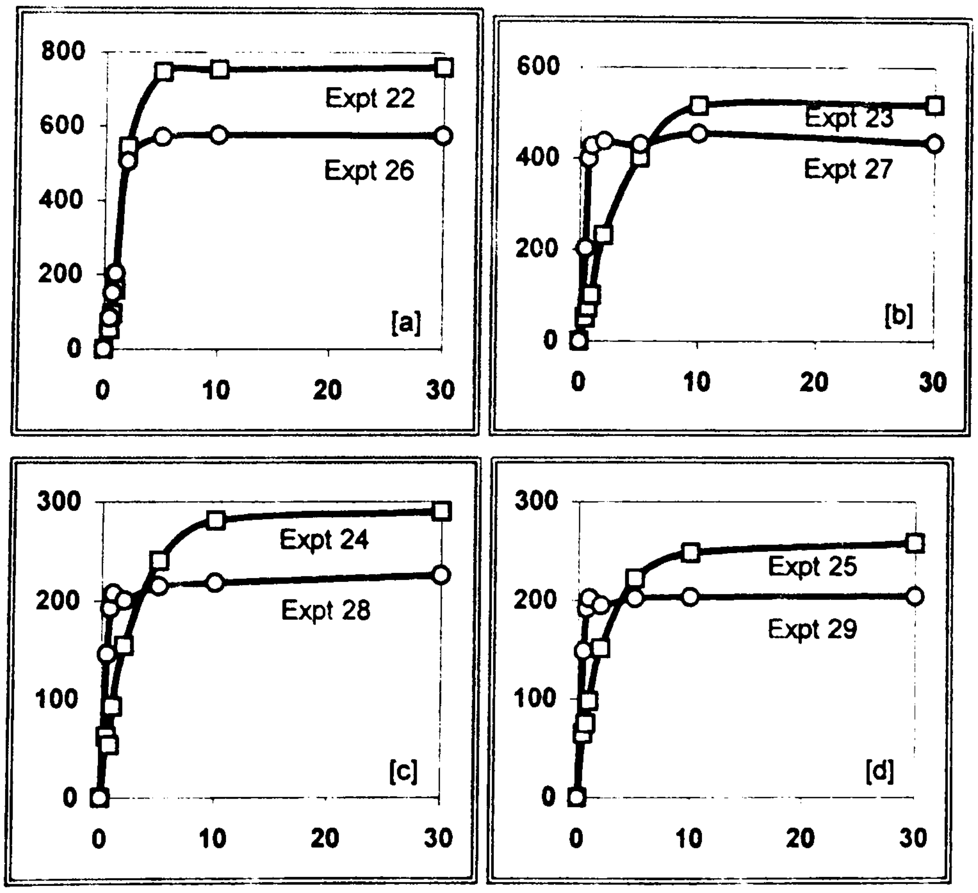

Figure 3.27 Dynamic swellings of the two series of experiments, Expts. 22-25 against Expts. 26-29.

Up to this point, we examined the effect of the different crosslinker and their concentrations, as well as of the comonomer, on the swelling properties of a specific class of superabsorbent polymers. Moreover, we were successful to produce absorbents of reasonable amount of swelling characteristics.

All the previous experiments were carried out under the inverse suspension conditions, but, it was interesting to know, what is happening to the polymer properties, when the polymerisation is carried out under other circumstances. So, our attention turned to the development of a solution process.

3.2.2 Solution polymerisation

A distinct difference between solution and inverse suspension polymerisation, seemed to be the nature of the polymerising system, *i.e.* being homogenous or heterogeneous. In addition to a couple of remarkable advantages of the inverse suspension technique, there were some disadvantages, when we were dealing with this system. These include the following:

- The need for the extra materials and equipment, *e.g.* for the solvent and its recovery.
-The need for surfactant or co-surfactant, which are expensive ingredients.
-The fire danger of using hydrocarbons as a continuous phase.
- The need for an efficient vapor-condensing system, for the material escaping during heating and reaction.
- Need for a continuous agitation to keep the dispersed phase stable.
- Need for a controlled addition of the dispersed phase to the continuous matrix.

These all complicate the process and increase the price of the end-product. On the other hand, the polymerisation of acrylic acid or sodium acrylate with a crosslinker in an aqueous solution would seem to be a straightforward process. The monomers and crosslinkers are dissolved in water at a desired concentration, usually from about 10 wt.% to 70 wt.%, since the polymerisation of undiluted acrylic acid is extremely dangerous, because of the heat of polymerisation and rapid polymerisation kinetics. The monomer solution is normally deoxygenated by bubbling an inert gas; then a desired free radical initiator is added and the temperature is brought to an appropriate point to start the polymerisation. Using this technique in industrial usage is also potentially complicated by a variety of factors [27]. This is the subject of the following sections.

In order to explore the effect of the change in polymerisation system, on the swelling characteristics, we devised a solution process after performing a numerous trials to run it successfully. The first effort was, running a same experiment as for the Expts. 26-29, but under the conditions of solution polymerisation. For this purpose, a same range of water soluble crosslinker, MBA, was used.

3.2.2.1 Effect of the water soluble crosslinker concentration (Expts. 30-33)

According to the experimental section (see Expt. 30 as a base experiment), the reaction was deliberately stopped at gel point. This period was nearly equal for the individual experiments 30-33. So that, we were not able to distinguish the gel times, if they were different. All the parameters were considered constant for these experiments.

Data of swelling and other polymer properties, quoted in *Table.* 3.5. The qualitative effect of the amount of crosslinker was as before on the degree of swelling, the polymer volume fraction in the gel, the crosslink density and the molecular weight between two successive crosslinks. Moreover, at a same crosslinker concentration, nearly a same density of crosslinks was obtained as obtained in case of inverse suspension counterparts (compare the corresponding values in *Tables.* 3.4 and 3.5).

Table. 3.5 Properties measured for the samples produced by a solution polymerisation.

Expt.	*30*	*31*	*32*	*33*	*Change*
Molar percent of crosslinker to monomer	*0.0078*	*0.016*	*0.047*	*0.078*	*10 ×*
Degree of swelling (g/g)					
in double distilled water	779	505	323	228	-70.7%
in 0.009% NaCl solution	440	337	245	188	-57.1%
in 0.09% NaCl solution	162	138	109	90	-44.5%
in 0.9% NaCl solution	56	51	38	37	-34.2%
Polymer volume fraction in the gel	8.9 E-4	1.37 E-3	2.0 E-3	2.96 E-3	+232%
Crosslink density (mol/cm^3)	4.4 E-5	5.8 E-5	7.57 E-5	9.9 E-5	+125%
Network chain density (mol/cm^3)	8.8 E-5	1.1 E-4	1.5 E-4	1.98 E-4	+125%
Network chain molecular weight (g/mol)	16613	13290	9746	7383	-55.0%

***Note:** According to the Sec. 2.4.3, the density of the samples was found 1.462 g/cm^3.*

The equilibrium swelling data (*Table* 3.5) against salt concentration of the swelling medium clearly displayed a phenomenon of a typical phase transition from sol to gel. It means, the swelling capacity was dramatically changed with the composition of the swelling medium. In other words, there is a critical amount of salt, which is required to force the transition.

As before, the water absorbency increased with time generally in exponential form to equilibrium (see *Fig.* 3.28). In this figure, the dynamic swellings of the two different series of samples were compared at a same crosslinker concentration. The absorption capacities of the solution samples were very close to that of their inverse suspension counterparts. But, the rate of absorption for the latter was higher than of the former. In other words, suspension samples could reach their equilibrium in water, at a fraction of a minute, whilst the time taken by the solution samples was considerably longer (say, minimum 10 min.).

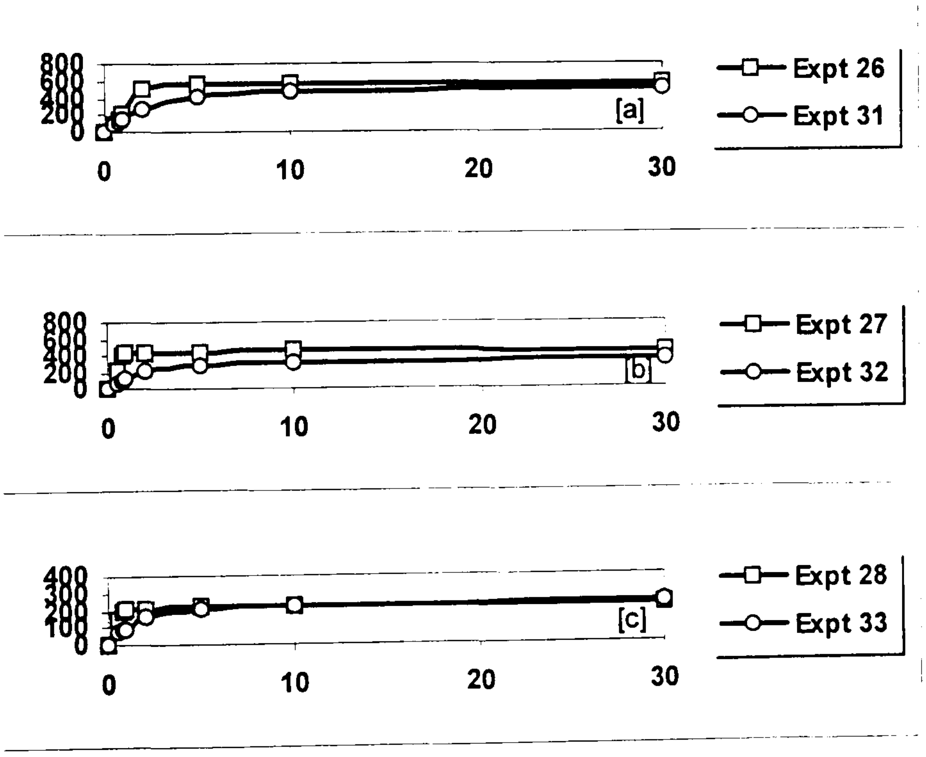

***Figure* 3.28** Dynamic swelling curves of the solution polymerised samples (Expts. 30-33), against of their inverse suspension counterparts (Expts. 26-29). a) 0.016, b) 0.047, c) 0.078 molar percent of crosslinker to monomer

The advantage taken here was obtaining a reasonable swelling characteristics and a very short period of polymerisation, of course, the polymerisation system was also quite simple (using no extra materials and equipment).

Generally speaking, according to our findings from the experiments done up to now, the inverse suspension was found a method of choice, if an exact particle size distribution and a very fast rate of absorption is required. However, in order to produce superabsorbing polymers of high swelling capacity, but without stringent requirement on the size of the particles, a much less expensive, faster manufacturing technique is suitably applicable. Examination of some commercial samples, which are introduced later show a behaviour of the materials obtained by a solution polymerisation.

Based on our outcomes, we decided to find a systematic way, *i.e.* modeling, to predict and justify the swelling properties of our absorbents.

3.3 A swelling model

3.3.1 Introduction

The swelling behaviour of superabsorbent polymers, which can swell up to hundreds of times their own weight in an aqueous media [28], is characterized mainly by the amount of water they absorb and the rate of absorption [29-32]. Both are important in practice and most applications, such as diapers, require them to be optimized [33]. The reason for optimization is, these two parameters so far showed an opposite relationship with increase in the crosslink density. In other words, the swelling decreased with crosslinker at the expense of obtaining a faster rate to reach equilibrium swelling (this was obvious, by looking at T_{eq} values at each crosslinker concentration).

Although the swelling parameters are dependent on thermodynamic and kinetic factors, we and others [34-35] have found that, among the factors, the crosslink density was particularly influential.

The superabsorbents have been commercialized for some time, but there would appear to be a considerable scope for gaining more insight than has been published so far, into relationships between swelling characteristics and molecular structure. Thus, we reviewed our exploratory investigations of the influence of some critical variables (mainly of crosslinker) on the swelling characteristics.

The water retaining capacity and the rate of absorption of our superabsorbents was changed with, the amount and nature of crosslinker, *e.g.* water soluble or oil soluble. the monomer composition, *e.g.* the ratio of acrylic acid/ sodium acrylate/ acrylamide and the type of polymerisation, *e.g.* inverse suspension or solution.

Based on above findings, we devised a model to show the swelling phenomenon, to compare and justify swelling characteristics and finally, to use it for possibly producing higher qualified absorbents. Before going into this subject, we shortly review the foregoing results to highlight the effect of the crosslinker.

3.3.2 Swelling dependency on the crosslinkers

The features of the samples have been gathered in *Table.* 3.6. For convenience, another nomenclature was used as follows:

Table. 3.6 Feature of inverse suspension and solution methods as well as parameters fitted to experimental swelling data.

Expt.	*Process Type*	*X* Type*	*M** Present*	*C/M Mol%*	*Initial Slope g/min.*	*Time to Cons. Swelling min.*	*Steady State Swelling g/g*	σ_o/E *g/g*	τ_o *sec*	*Sol*** cont.*	*Water cont. %*
S1.1/19	I.S	O.S	AAc ,NaA (1/3)	0.238	89.7	38. 7	756	760	438	-	6.25
S1.2/20				2.30	99.0	28.1	617	620	318	1.93	5.28
S1.3/21				4.58	86.0	23.8	487	490	270	1.83	5.32
S2.0/@	I.S	W.S	AAc ,NaA (1/3)	0.0	-	-	-	-	-	2.08	-
S2.1/23				0.047	123	16.9	517	520	192	1.05	5.17
S2.2/24				0.078	82.5	15.4	288	290	174	0.96	4.81
S2.3/25				0.11	86.0	13.2	254	255	150	0.90	4.65
S3.0/@	I.S	W.S	AAc ,NaA ,AAm (1/3/4)	0.0	-	-	-	-	-	2.65	-
S3.1/27				0.047	1178	1.6	423	425	18	1.62	8.6
S3.2/28				0.078	825	1.8	219	220	21	0.87	6.7
S3.3/29				0.11	785	1.7	204	205	19.8	0.79	7.7
B1.0/@	S	W.S	AAc ,NaA ,AAm (1/3/4)	0.0	-	-	-	-	-	4.44	6.11
B1.1/30				0.0078	162	21.2	779	783	258	3.70	6.41
B1.2/31				0.016	144	15.9	505	508	180	-	6.42
B1.3/32				0.047	123	12.2	323	325	138	2.68	6.8
B1.4/33				0.078	95	10.6	228	230	120	2.65	6.34

@ The same formulation without using crosslinker.
** Crosslinker   ** Monomer(s)   *** As UV absorbance in arbitrarily unit*
Abbreviations: I.S (Inverse suspension), S (Solution), O.S (Oil- Soluble), W.S (Water- Soluble).

S1: for the materials obtained by inverse suspension, crosslinked by *EGDMA*.

S2: for the materials obtained by inverse suspension, crosslinked by *MBA*.

S3: for the materials contain acrylamide, obtained by inverse suspension, crosslinked by *MBA*.

B1: for the materials of same formulations as in S3, obtained by solution polymerisation.

In this *Table.*, the degree of swelling ranged from about 200 to 800g/g, whereas, the time to reach a steady state varied more widely from about 1.6-40 min. and the initial rate of swelling ranged from about 90-1200g/min. The highest degrees of swelling were obtained for inverse suspension polymerisation with an oil soluble crosslinker at its lowest concentration and for solution polymerisation at the lowest concentration of crosslinker.

3.3.3 Comparing polymers in terms of their swelling characteristics

The first two sets of polymerisations (see *Table.* 3.6), S1 and S2, differed only in the nature of the crosslinker. Ethylene glycol dimethacrylate and N, N'- methylene bisacrylamide were used as oil soluble and water soluble crosslinkers respectively. A much higher concentration of the oil soluble crosslinker was required to form a gel and prevent the polymer from dissolving, presumably because it partitioned primarily into the oil phase. Comparing sample S1.3 and S2.1 indicates that about 100 times as much oil soluble crosslinker was required to give a steady state swelling of 500 g/g. Also, increasing the concentration of oil soluble crosslinker by a factor of 10 decreased the steady state swelling to 65 % of its previous value, whereas increasing the concentration of water soluble crosslinker by a factor of only 2.3, in the S2 set of polymerisations, cut the swelling by half.

The S2 and S3 polymerisations differ only in that acrylamide was present in S3 and not in S2. Although the steady state swelling was somewhat higher for S2, there was a much more striking difference of an order of magnitude, in the initial rate of increase of swelling and in the time taken to reach a steady state, *i.e.* acrylamide speeded up swelling by this extent. The S3 and B1 polymerisations both contained acrylamide but differed in the type of process. This affected the rate of swelling much more than the final degree of swelling. Polymer made by the inverse suspension process swelled faster than obtained from the solution process by a factor of about 8.

3.3.4 Mathematical relationships between swelling and crosslinker concentration

For each set of polymerisations, the steady state swelling decreased as the ratio of crosslinker to monomer was increased. The relationship was explored further by testing different mathematical functions. For this purpose, the extent of swelling was assumed to be zero when only crosslinker was present and not monomer. This was done to obtain a more reliable fit, by adding another point. It is evident from the data for S1 polymerisations in *Table*. 3.6, that any relationship between crosslinker concentration and swelling was quite indirect. The best fit (*Equation*. 3.1) was obtained with an exponent of 0.1 (see *Fig*. 3.29).

$$q = 616 / \{[C]/[M]\}^{0.1}\ g/g \qquad (3.1)$$

For the S2 and S3 inverse suspension and B1 solution polymerisations, with a water soluble crosslinker, the following relationship was obtained in which the power law exponent was found about 0.6 (*Equation*. 3.2):

$$q = A / \{[C]/[M]\}^{0.6} g/g \qquad (3.2)$$

where A = 64 g/g for S2, 49 g/g for S3 and 41g/g for B1. The relationships plotted in *Fig*. 3.30 for the two first and in *Fig*. 3.31 for the last one.

The finding that, the steady state swelling was inversely proportional to about 0.6 power exponent of the molar ratio of crosslinker to monomer for S2, S3 and B1 polymerisations is quite close to the 0.6 relationship derived thermodynamically [36] .The relationship between steady state swelling and crosslinker to monomer ratio was different for inverse suspension polymerisation in the presence of an oil-soluble crosslinker. When the crosslinker was oil soluble, swelling became less dependent on the amount of crosslinker than for the water-soluble counterpart, presumably as a result of most of the crosslinker existing in the oil phase.

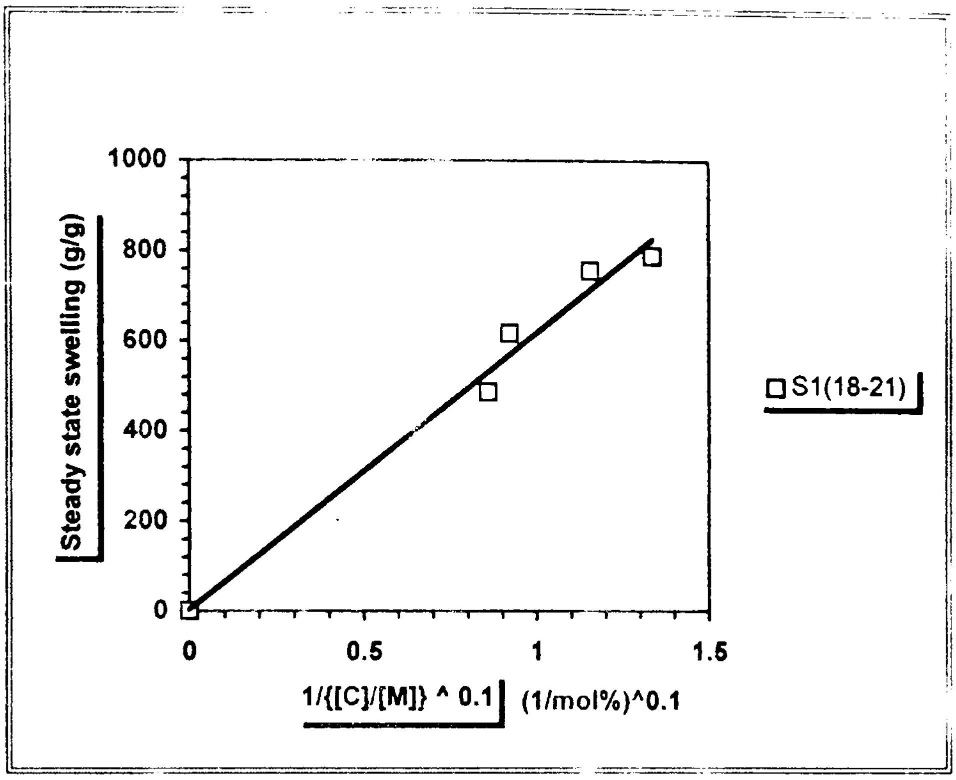

Figure 3.29 Curves fitted the equilibrium swellings against crosslinker concentration, for S1 series of experiments.

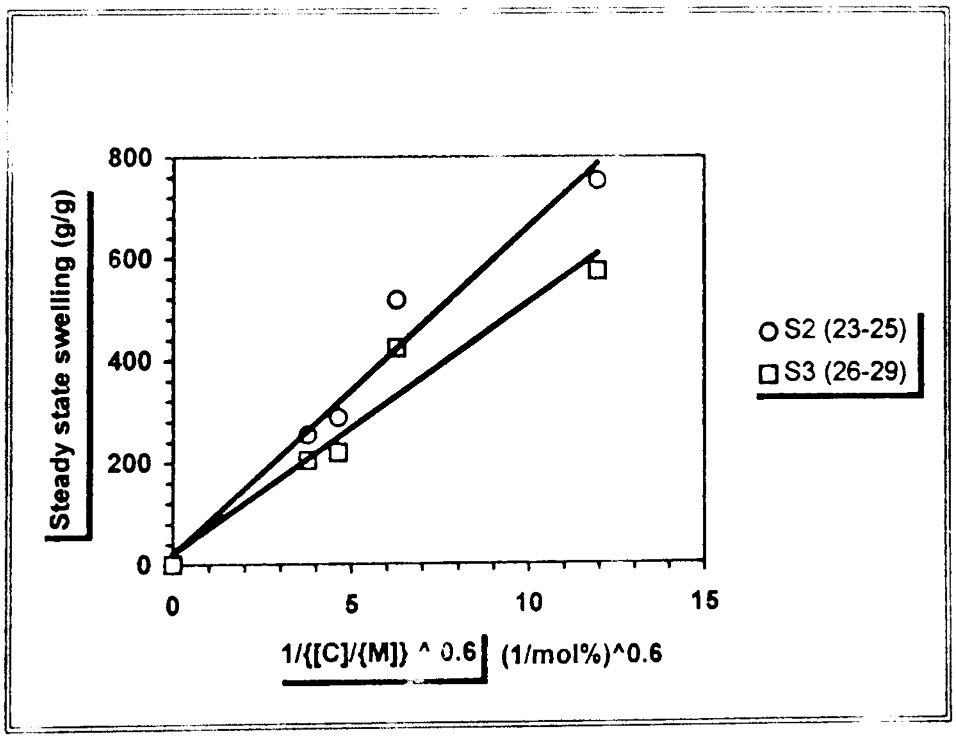

Figure 3.30 Curves fitted the equilibrium swellings against crosslinker concentration, for S2 and S3 series of experiments.

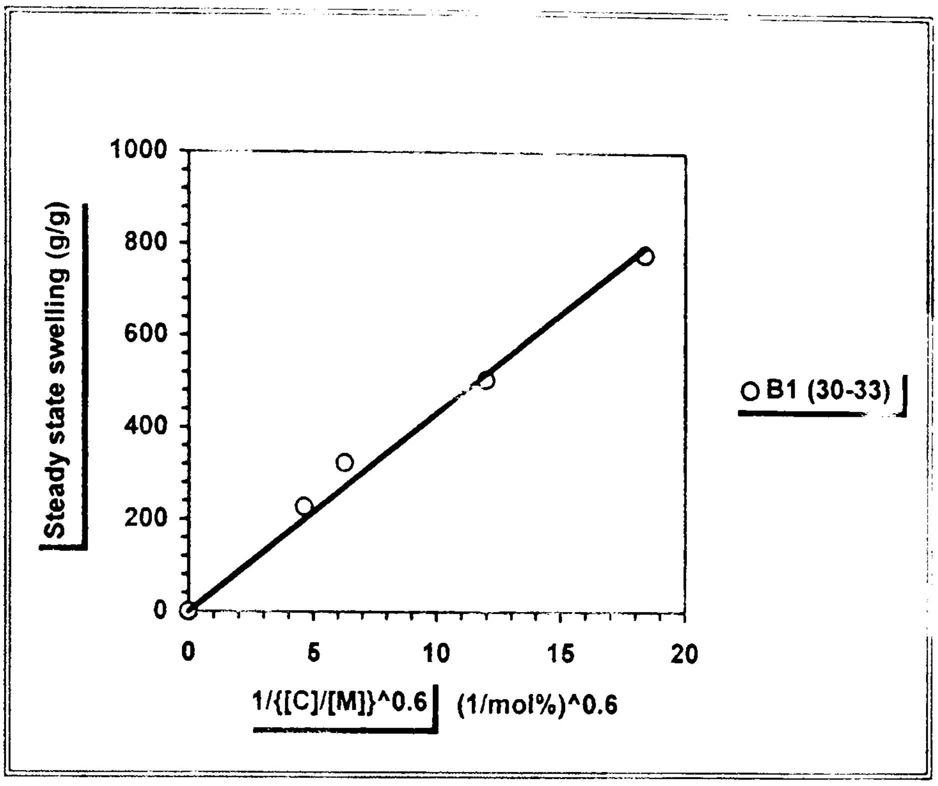

Figure 3.31 Curves fitted the equilibrium swellings against crosslinker concentration, for B1 series of experiments.

3.3.5 Viscoelastic models

The rate of change of swelling with time falls off rapidly (see *Figs.* 3.14, 3.18, 3.27, 3.28), but simple power law expressions did not fit the experimental data satisfactorily. A sharper transition from the high initial rate to the slow rate towards the end of the swelling process needed to be explained.

In the polymer field the spring and dashpot model is best known for its use in modeling creep and relaxation in viscoelastic materials. The spring and dashpot elements respectively provide the immediate elastic and delayed viscous strain responses to an externally applied stress. Any number of arrangements of these elements can be devised to simulate a particular kind of time dependence, however complex. In molecular terms the elastic responses are the fast, reversible changes in bond length, shape and orientation which occur when stress is applied to a polymer chain. The viscous responses are the slower, irreversible, energy dissipating processes which occur as a result of the molecular movements. Elastomers show particularly large effects.

3.3.5.1 Voigt model

One of the simplest arrangements of these elements, a spring and a dashpot in parallel, is known as the Voigt model [37-38] (see *Fig.* 3.32).

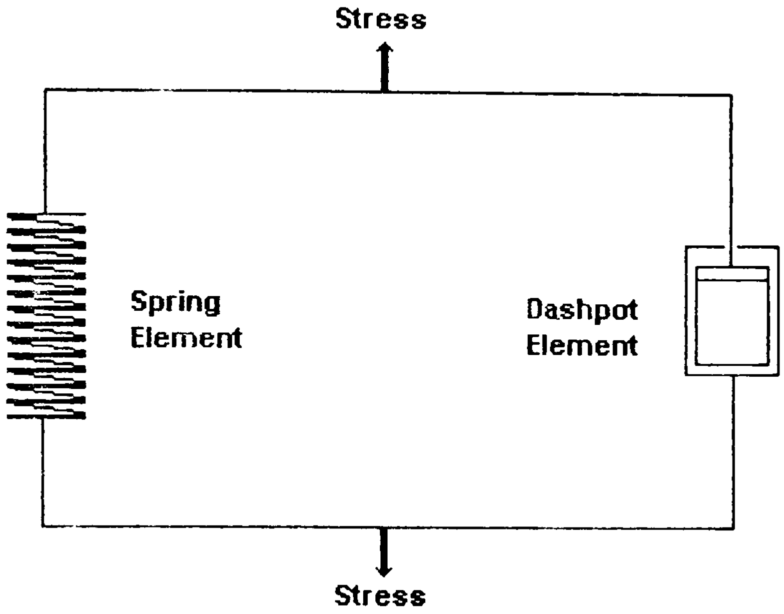

***Figure* 3.32** Schematic diagram showing a Voigt model.

When a stress σ_0, is applied at time t_0, the strain response ε, of the model with Young's modulus E, is given at time t, by an expression of the form (*Equation.* 3.3):

$$\varepsilon(t) = \sigma_0/E\,[1 - \exp\{(t_0 - t)/\tau_0\}] \qquad (3.3)$$

where τ_0 is known as the retardation time and determines the influence of the dashpot.

There are two variables, *i.e.* σ_0/E *and* τ_0, in this equation, which determines the behaviour of the whole assembly to any stress applied. The quantitative effect of these two parameters on the strain, which the model experiences under the stress applied, can be clearly seen in *Figs.* 3.33-3.34.

In *Fig.* 3.33, change in σ_0/E was assessed, considering a constant value for the other variable, τ_0. The effect was the increase in strain with increase in parameter no 1. Moreover, the shape of the curves was obtained quite similar.

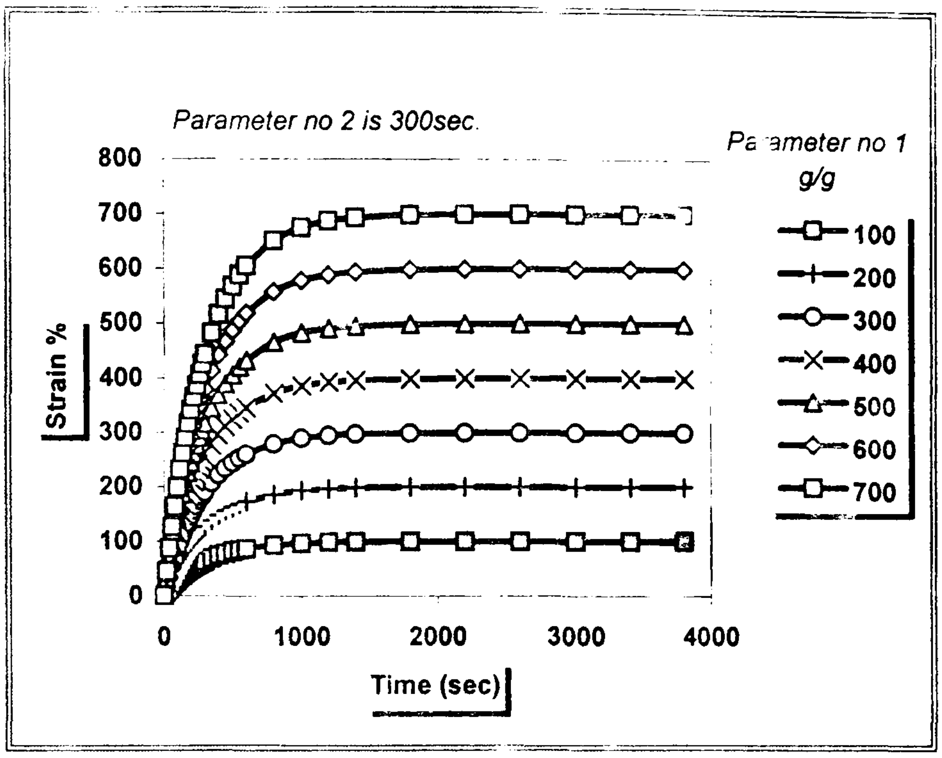

Figure 3.33 Strain variation of a Voigt model against time, evaluation with change in parameter no 1.

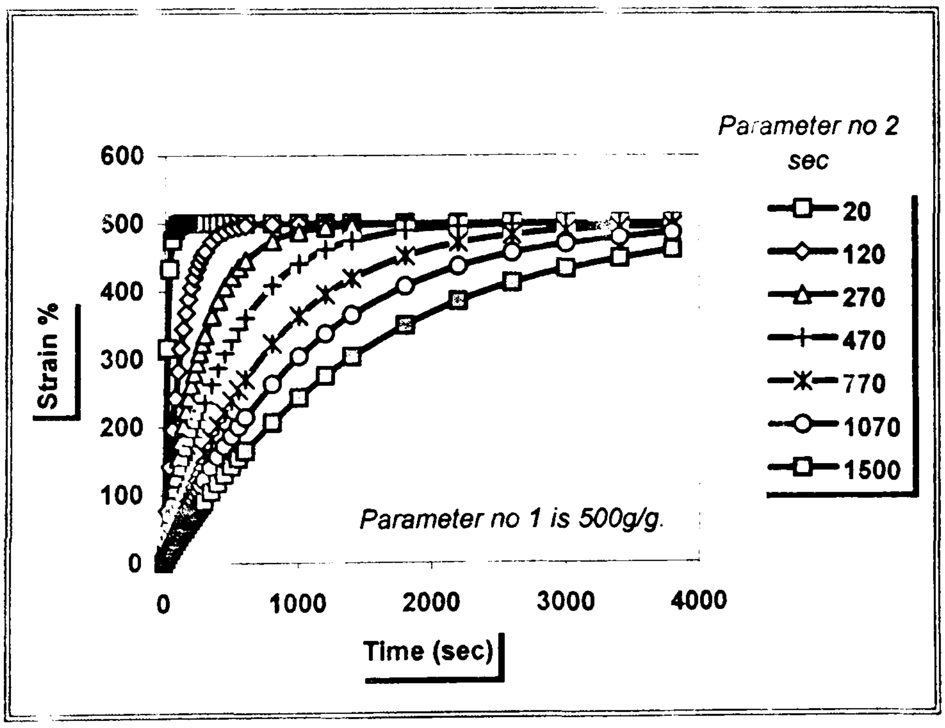

Figure 3.34 Strain variation of a Voigt model against time, evaluation with change in parameter no 2.

Another assessment was made in *Fig.* 3.34, assuming a constant value for the parameter no 1. The ultimate strain did not change with increase in parameter no 2, but a quite different trends to ultimate strain experienced by the models, which differed only in their dashpot nature. The effect of dashpot progressively decreased with a decrease in retardation time. So that, the effect was nearly nil, when the retardation time approached zero (assuming infinite elastic nature). This indicates, approaching to a perfect elastic material, which respond immediately to any stress applied. Increase in retardation time, led to a big delay to reach ultimate strain.

3.3.6 Curve fitting

Using *Equation.* 3.3, a better fit was obtained to the experimental swelling data for all the polymerisations (see *Figs.* 3.35-3.38). The quantitative values of the two parameters in *Equation.* 3.3 have been found for the individual samples through curve fitting (*Sec.* 2.4.5) and quoted in *Table.* 3.6.

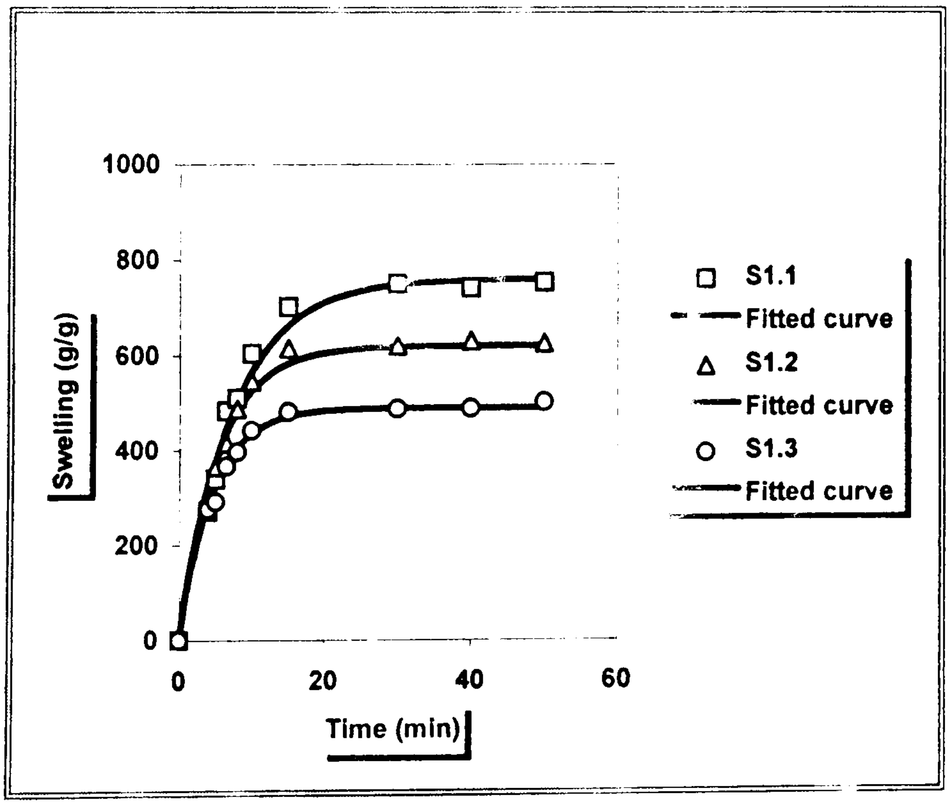

***Figure* 3.35** Theoretical and experimental dynamic swelling curves for S1 series of samples.

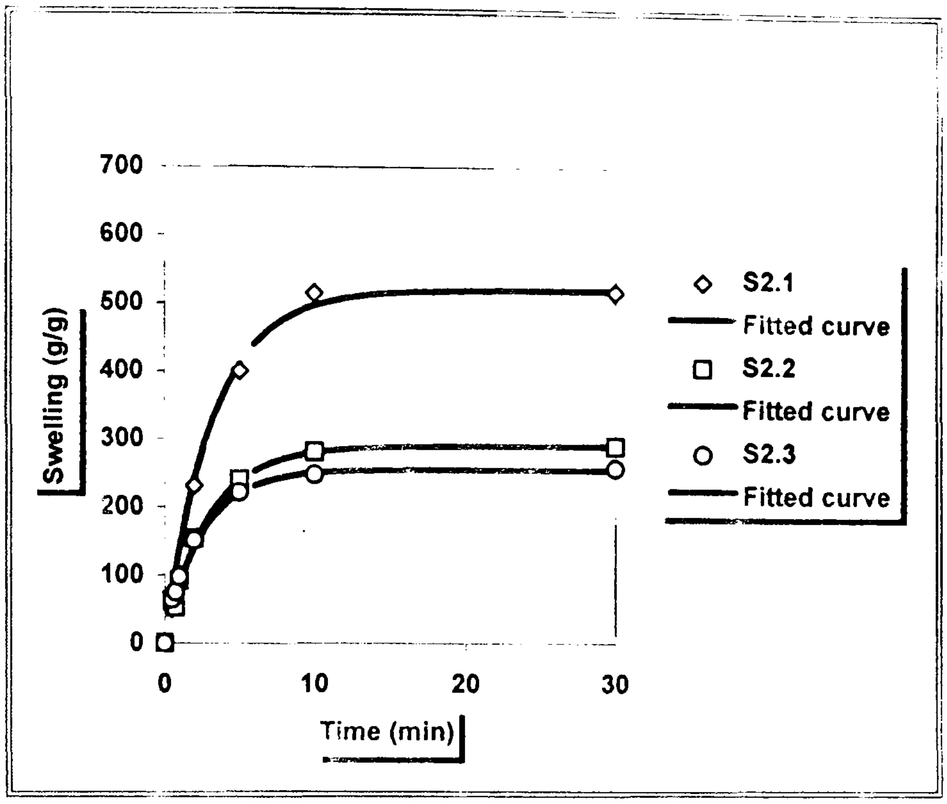

Figure 3.36 Theoretical and experimental dynamic swelling curves for S2 series of samples.

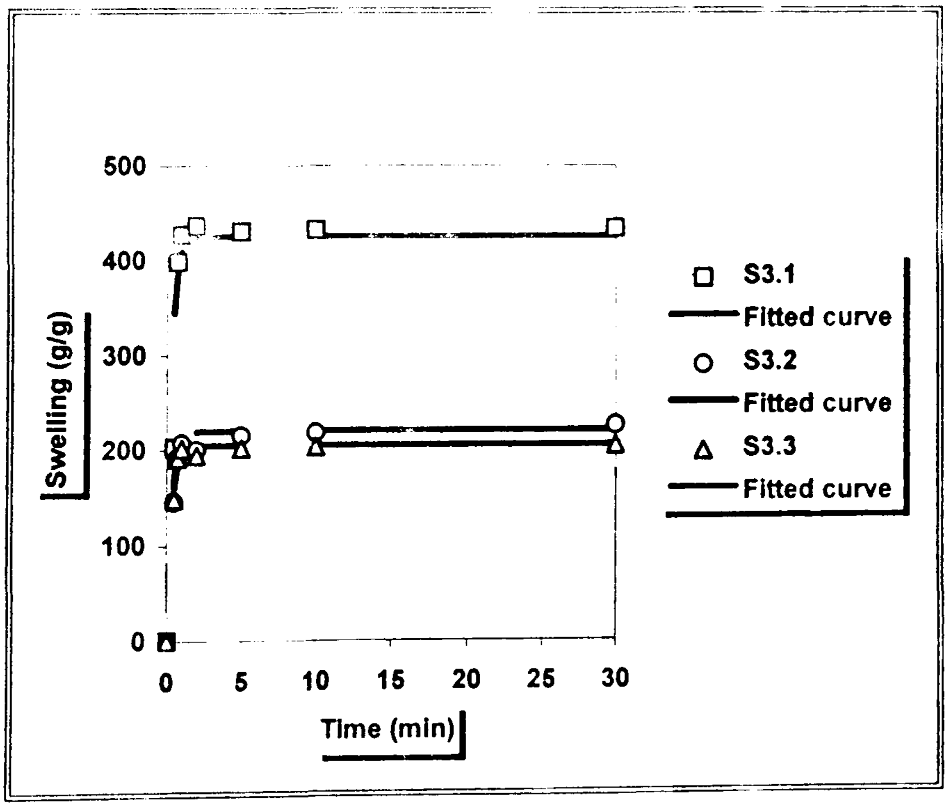

Figure 3.37 Theoretical and experimental dynamic swelling curves for S3 series of samples.

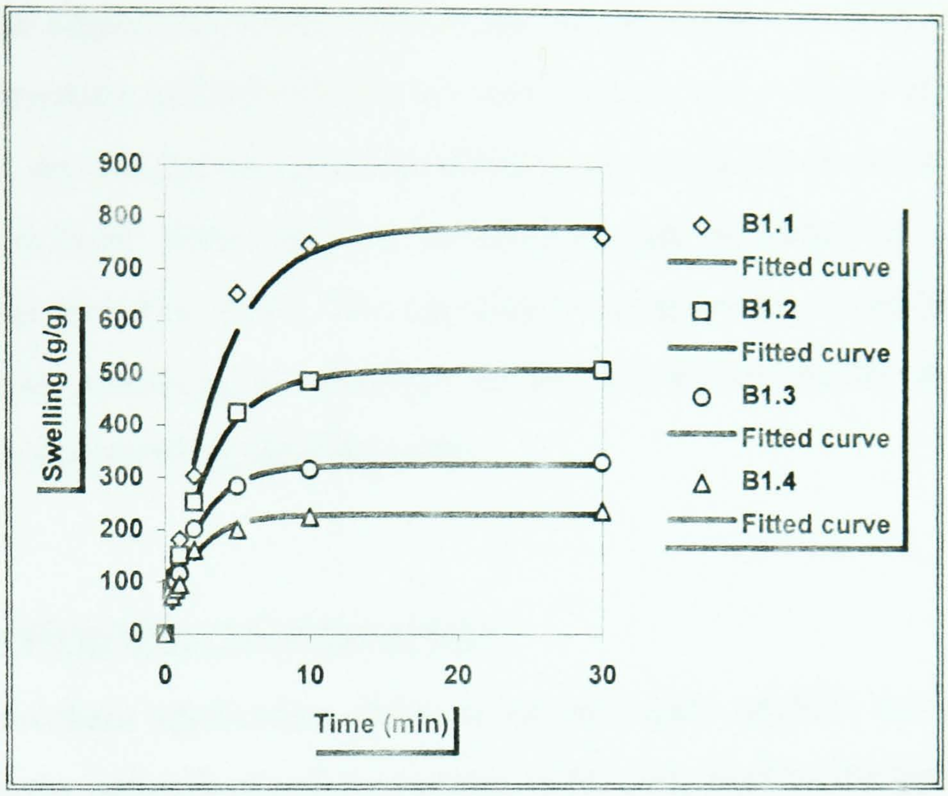

Figure 3.38 Theoretical and experimental dynamic swelling curves for B1 series of samples.

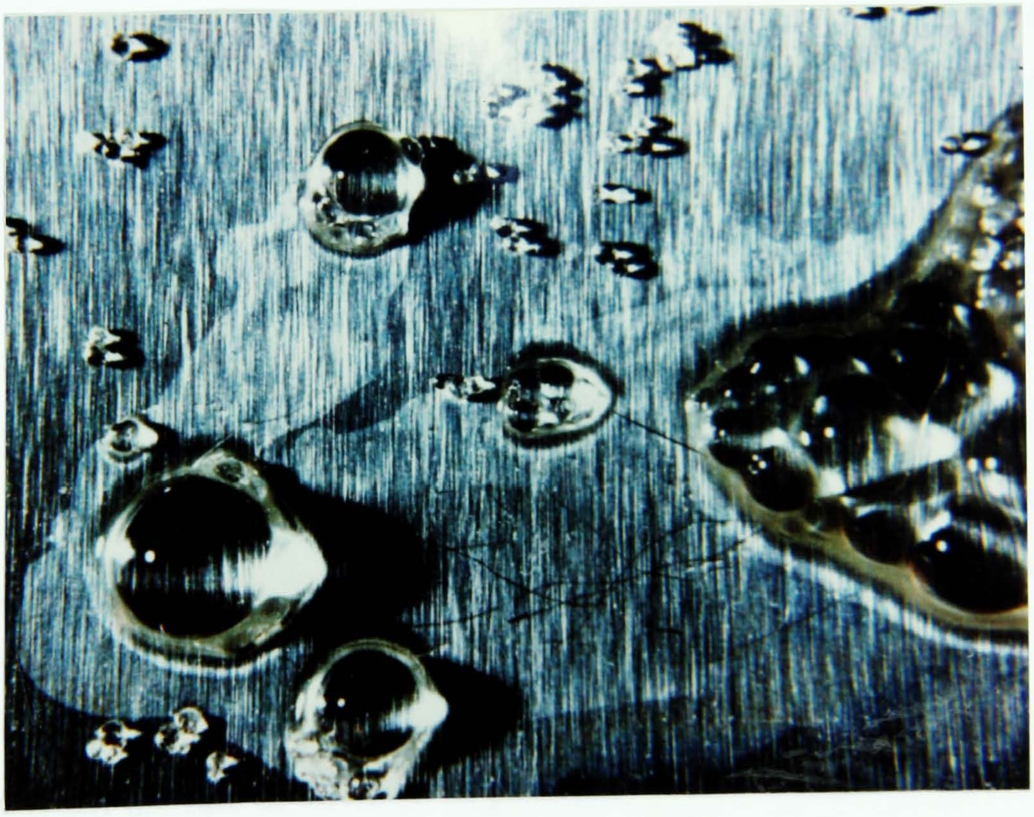

Figure 3.39 Photograph of a slightly water-swollen particle, clearly shows a swollen sheath around the particle.

3.3.7 Swelling picture

When water comes into contact with an absorbent, which is initially in the glassy state, it has to penetrate between the chains and separate and mobilise them for swelling to occur. The process becomes self accelerating and a sheath of swollen polymer can be envisaged to form. Water then has to travel through the sheath to reach the interior of dry polymer (see *Fig.* 3.39). This description suggests the possibility of replacing the resistance to stretching, or modulus, in the viscoelastic model with a resistance to permeation and swelling for absorbents.

3.3.8 Swelling in terms of expansion

For an absorbent application, there is no externally applied stress. Instead stress is exerted on the network of polymer chains in the absorbent by the interaction with water. The system differs fundamentally from the stretching of a dry rubber in that the volume increases a lot with time and the chains become separated from each other. Consequently the modulus in *Equation.* 3.3 cannot have the same significance for absorbents. Although Flory [36], in describing the thermodynamics of swelling, referred to an inverse relationship between the equilibrium swelling of a rubber by a solvent and the "modulus" of the rubber, this was for a dry rubber [36] and the time dependence of swelling was not discussed. Also the absorbents were dried before coming into contact with water and were ,therefore, presumably in a glassy state.

3.3.9 Swelling in terms of diffusion

In general, permeation is governed by Fick's laws of diffusion and the degree of absorption by a material obeying these laws is proportional to the square root of time. This is known as Case I sorption but, in some cases the amount of absorption is observed to be directly proportional to time and this is known as Case II sorption. Case I occurs when the rate of advance of permeant is determined by the rate of diffusion and Case II occurs when the rate of advance is determined by the rate of expansion of the material [39]. In Case II sorption the permeant front is much sharper than in Case I and high stresses are generated at the sharp boundary between the swollen and non-swollen material. By identifying the type of diffusion which takes place when absorbents swell, the rate limiting factor becomes known and this is what has to be tackled for absorption to be made faster.

The rate of swelling for all of the absorbents can readily be obtained from *Equation.* 3.3 for the Voigt model and is given by the *Equation.* 3.4:

$$d\varepsilon/dt = (\sigma_o/E\tau_o)\,exp\{(t_o - t)/\tau_o\} \qquad (3.4)$$

In the early stages of swelling, when $t_o - t << \tau_o$, the exponential term is close to 1 and so the rate changes slowly with time, *i.e.* it approximates to Case II sorption.

For the B1 series of polymers (in *Table.* 3.6), which were prepared by the solution process at the lowest crosslinker ratio of 0.0078g/g, the degrees of swelling calculated using the parameters given in *Table.* 3.6 for *Equation.* 3.4 at times of $\tau_o/4$ and $\tau_o/8$ are respectively 22.2 % and 11.75 % of the steady state value. These values are much closer to being proportional to time^1 than to time$^{1/2}$ and they demonstrate that Case II sorption applies over a substantial part of the swelling. The same applies to the other members of this series B and to the other series as well, because it is only the ratio $(t_o - t)/\tau_o$ that matters. At longer times the ratio increases and swelling changes more slowly with time. For example at times of τ_o and $2\tau_o$ the degrees of swelling for the same B1 polymer as before become 63.2 % and 86.5 %. These values are close to a square root relationship and so it follows that the overall swelling behavior changes progressively from Case II in the early stages to Case I in the second half. The same Case II sorption process might even persist to a late stage of swelling for the last dry material to be reached by the water but on too small a scale to be detected.

It also follows that the rate of swelling is restricted in the early stages by the resistance of the polymer molecular structure to diffusion or expansion. Diffusion could be resisted by unfavorable interactions between the water and polymer chains or by close packing and low chain mobility. Expansion could be opposed by bonding between chains and by lack of mobility within chains. These factors may also be expected to influence the polymer behavior at an earlier stage when, it is dried prior to testing and because this comes before the swelling stage, their influence in the drying process may well predetermine the swelling behavior. The experimental data provide information about the effect of changes in crosslinking, monomer composition and type of polymerisation process on the degree and rate of swelling.

3.3.10 Discussion on swelling in terms of model parameters

The fastest rates of swelling by far occurred for the inverse suspension polymerisation process with acrylamide present as a monomer, *i.e.* in the S3 series. The time taken to reach constant swelling (1.58 - 1.85 min.) and the initial rate of swelling (1178 - 785 g/min) were about an order of magnitude faster than for the S2 series (13.24 - 16.95 min. & 86.0 - 123 g/min) which, differed only in the absence of acrylamide. Clearly the presence of acrylamide (half the total molar monomer concentration) speeds up absorption. As may be seen in *Table.* 3.6, the first parameter of the Voigt model is a little lower for the S3 series than for S2 but, the second parameter for S3 is an order of magnitude lower than for S2 and so, although the effects are opposing, it is the second parameter which dominates and is associated with the higher rate of swelling for S3.

For viscoelastic systems the second parameter which is also known as the retardation time determines the magnitude of the viscous component in the Voigt model and the extent to which the spring element is retarded by the dashpot. This suggests that just as the spring element and first parameter in the model are thought to represent the resistance to expansion of the polymer network in the absorbent, the dashpot element and second parameter may represent the resistance to permeation by water. If so, it follows, from the values of the parameters for the S2 and S3 series, that introducing acrylamide into an acrylic acid/ sodium acrylate copolymer speeds up absorption by lowering resistance to permeation. The replacement of ionic monomer segments by non-ionic ones would be expected to reduce the stress responsible for the expansion of the polymer network by decreasing the number of ionic repulsions and accounts for the reduction in the first parameter since this is the ratio of stress to modulus for the absorbent system. Neither is measured on its own, unlike the viscoelastic system where the stress is applied externally and is readily measured.

Another feature of the S3 series is that the second parameter did not become smaller with more crosslinking as the others did. Since a decrease in the second parameter is interpreted as a lowering of resistance to permeation it follows that, crosslinking lowered this resistance for series S1, S2 and B1, presumably by preventing the chains from packing as closely in the drying step. Crosslinking also reduced the first parameter but this has the opposite effect of slowing the rate of absorption, presumably by increasing the resistance of the network to expansion. The net result of the opposing effects was for the initial rate of absorption to become slower with more crosslinking for all the series.

Comparison of the S3 and B1 series in *Table.* 3.6 shows that the solution process gave much slower absorption than the inverse suspension process. The data show that this was mainly associated with the second parameter being lower for S3 although the first parameter also contributed by being smaller at the same level of crosslinker. This indicates that permeation is slower for products made by the solution process. If the polymer particles formed in the inverse suspension process gave a porous structure after drying and the solution process gave a continuous mass then this would account for the difference.

The longest times to reach steady state swelling were taken by the S1 series in which the crosslinker was oil soluble. The last member, S1.3, of this series had almost the same steady state swelling as the first member, S2.1 of the S2 series, which differed only in the water solubility of the crosslinker. The first parameter was a little lower for S1.3 indicating less resistance by the polymer network to expansion since the monomer composition was the same. The retardation time for S1.3 was longer than for S2.1 indicating lower permeability. Overall the permeability effect was more pronounced and made swelling slower. Although some of this effect may be attributable to a lower degree of crosslinking, another factor may have been the distribution of crosslinker. As the crosslinker became consumed during polymerisation, more could diffuse from the oil phase in the case of the oil soluble crosslinker but not in the case of the water soluble one. This could have resulted in a higher degree of crosslinking at the outside of polymer particles than at the centre for the oil soluble crosslinker.

3.3.11 Increased permeability

With crosslinker: The general observation of increased rate of permeation of water (through decrease in parameter no 2) with increase in crosslinker concentration can be described as follows. If the polymer network acted only as a barrier against diffusing water molecules, the decreased mobility of water is expected for highly crosslinked networks. Thus, rate of water uptake should be increased by decreasing in crosslink density [40]. However, an acrylic-based superabsorbent is strongly hydrophilic polymer, which attracts water molecules instead of repelling them. It must generate a strong thermodynamic force that makes water diffuse so as to cancel the gradient. As a result, it may be expected that a denser network offers a higher rate for water uptake. Moreover, it has been described that the swelling process of a polyacrylamide gel is in fact the polymer network diffusion into water rather than by that of water molecules into the polymer network [41]. Since the local motion of a polymer network increases with increasing the elastic modulus of the network, the diffusion coefficient of water is expected to increase with increasing the crosslink density. This relationship has been already found for the sodium acrylate gels [42].

With acrylamide: The increase in permeability resulting from the introduction of acrylamide into the polymer is attributable to higher chain mobility or more free volume. On completion of polymerisation, there is sufficient water present to permit a high level of mobility but this changes as drying progresses. So, as the water level drops, the interaction between chains of different structures expected to become important. In such circumstances, the difference in polarity between the sodium acrylate and acrylamide groups suggests the likelihood of segregation which would affect chain packing and perhaps the free volume

The other point is the acrylamide screens the acrylate anions by which the polymer chain assumes more coiled conformations than extended alternative.

3.3.12 Effect of the local water in the absorbents

According to data quoted in the *Table.* 3.6, all the absorbents contain a substantial amount of water in their network even after drying process. This type of water can be called presumably bound water which can not be readily isolated from the polymer, because of excessive hydrogen bonding. In studying the thermal stability and degradation mechanism of poly (acrylic acid) and its salt, thermogravimetry analysis have indicated that, the initial weight loss below 100 °C is due to the release of water absorbed by the polymer which is free water [43]. But, in other work, the TGA curves of four different samples of polyacrylamide displayed one thing in common, *i.e.* the loss of water up to a temperature of approximately 250 °C [44]. Using the same technique (see *Sec.* 2.4.7), we found that this type of water can not escape from the network at temperatures below 200 °C, of course, in a short period of time.

On the other hand, the transition from glassy to rubbery state in the absorbent polymer is characterised by a threshold concentration of water which is the minimum local concentration of water required for the glassy state to be transformed into rubbery state [45]. At same crosslinker concentration, S3 samples contain larger amount of bound water than their S2 counterparts (1.6 times), *i.e.* 8.605, 6.707, 7.707 against 5.169, 4.812, 4.649 respectively. Thus below the threshold of water concentration (before immersing in water), it can be expected that the polymer which is originally contained higher amount of water assumes shorter times to reach its transition point, after immersing in water.

3.3.13 Effect of the extractable fractions in the absorbents

The semi-quantitative values of sol content of individual series of samples were also quoted in *Table.* 3.6. Generally speaking, the sol content decreases with increase in crosslinker amount as the swelling does. The initial rate of swelling can partly be related to the amount of soluble material in the network, although the rate also depends on the maximum capacity of absorption. This behavior can be attributed to an initially large chemical potential or osmotic driving force for swelling due to the presence of solute within the gel [46]. Through the range of crosslinker concentration which was studied here, samples were obtained by solution polymerisation offered higher concentration of soluble materials.

3.4 Effect of Temperature (Expts. 34-47) and Initiator (Expts. 48-56)

3.4.1 Introduction

An initiating system and temperature are integral parts of a recipe for a typical polymer synthesis. We theoretically know, that these both parameters can potentially affect the polymer properties, in terms of their influence on the polymer backbone molecular weight. So that, the high values for these variables, lead to lowering backbone molecular weight and vice versa. Superabsorbent polymers are not a linear or a branched chains of a hydrophilic structure. In fact, they are a complex network of infinite endless chains. In such circumstances, the term, polymer backbone molecular weight has no meaning; rather, the term, molecular weight between two successive crosslinks is much more meaningful. So, tracing the effect of initiator and temperature on polymer molecular weight does not seem to be straightforward. But, in simulating an industrial solution process to make superabsorbents, we found these two parameters can seriously affect the polymer properties.

We have already found that, a polymer obtained from the Expts. 30-33 has a reasonable swelling properties, although its kinetics of absorption is still low, compared to its inverse suspension counterpart. Considering a couple of advantages of the solution method, as well as its popularity in industry, we tried to simulate such a process in our laboratory, taking into account the effect of the heat input to the reaction mixture and the initiator concentration.

In a typical industrial process, the pre-heated solutions of monomers and the solutions of crosslinker and initiator are prepared separately, brought together in a nozzle type of mixer and spread on an endless conveyor belt [47] , and allowed to react. The reaction mixture is not agitated in anyway and is open to the atmosphere, providing unrestricted access to oxygen and loss of water vapor.

In our experiments, the presence of oxygen resulted in an inhibition period, which lengthened the time for completing polymerisation and consequently, increased evaporation losses of water. The water absorbency of the reaction products was obtained high, under conditions which gave short reaction time. Long reaction times resulted in long inhibition periods, runaway polymerisation and low absorbency. These effects were accounted for in terms of oxygen participation in the polymerisation and extensive losses of water as the solvent.

At best, we tried to use our model to justify the various swelling properties measured for the materials obtained at different bath temperatures and initiator concentration.

Detailed description of the synthesis can be seen in *Secs.* 2.3.2.2 and 2.3.2.3 respectively for the effect of temperature and initiator concentration. For each polymerisation reaction, the gel time was measured according to the *Sec.* 2.4.8.

The percent of water remained in undried products, at gel point, was obtained by difference. The swelling capacities of the samples were calculated according to the *Sec.* 2.4.4, except that 0.2g of each dried product was dispersed in 400ml of doubly distilled water. Finally, percent of water extractable materials within the individual products was measured according to the *Sec.* 2.4.10, except that 0.5g of each dried product was immersed in 500ml saline (1 w/w % aqueous NaCl solution).

3.4.2 General observations on the reaction

Gel times ranged from 1094 s to 42 s as the bath temperature was raised from 75 °C to 180 °C as shown in *Table.* 3.7 and from 709 s to 92 s as the initiator concentration was raised from 0.01 to 0.529 molar percent ratio as shown in *Table.* 3.8.

In each case there was an initial period when the temperature of the reaction mixture rapidly rose from ambient temperature towards the bath temperature. However the reaction mixture only reached the bath temperature at the low end of the range. The highest temperature observed was 110 °C. At the longer gel times reaction only became apparent near the end of the period. For example at a bath temperature of 75 °C nothing appeared to happen for the first 18 min. and then a vigorous reaction suddenly occurred within seconds, resulting in the stirrer slowing down and stopping as the viscosity increased and in foaming as the temperature rose to nearly 110 °C. On cooling to room temperature the reaction mixture was found to have been transformed to a glassy, white and porous state. At high bath temperatures and short gel times the reaction was much less vigorous, resulting in less foaming and in the final product being a soft, transparent and rubbery material. This was the case for bath temperatures in the range 120 - 180 °C.

<u>*Table. 3.7*</u> Absorption characteristics and extractables at the gel point for different bath temperatures and same initiator to monomer molar percent ratio of 0.295.

Expt.	*Bath Temp °C*	*Gel Time s*	Wt. % *Water in Undried Product*	*Equilibrium swelling of Undried Product g/g*	*Equilibrium swelling of Undried Product without Water g/g*	*Equilibrium swelling of Dried Product g/g*	Wt. % *Water-Extractables in Dried Product*
34	75	1094	1.1	267	269	331	-
35	90	720	4.2	296	309	355	22
36	97	500	16	270	322	319	-
37	105	345	23.5	325	423	340	12
38	112	200	34	505	765	420	-
39	120	128	38	615	994	588	14
40	127	108	37	615	980	569	-
41	135	88	37	593	942	686	6.5
42	142	74	37.5	650	1041	838	-
43	150	63	37	722	1142	848	9.8
44	157	56	37	622	985	826	-
45	165	48	37	641	1012	877	7.2
46	172	46	35.5	655	1015	827	-
47	180	42	35.5	621	961	833	-

Table. 3.8 Absorption characteristics and extractables at the gel point for different ratios of initiator to monomer, [I]/[M], and a bath temperature of 120 °C.

Expt.	*[I]/[M] (moles) x 100*	*Gel time s*	Wt.% *Water in Undried Product*	*Equilibrium swelling of Undried Product g/g*	*Equilibrium swelling of Undried Product without Water g/g*	*Equilibrium swelling of Dried Product g/g*	Wt. % *Water Extractables in Dried Product*
48	0.010	709	0.12	276	275	609.2	25.13
49	0.021	500	11.8	390	441	561.15	14.50
50	0.044	187	11.3	448	503	750.44	10.13
51	0.087	203	33.3	674	1008	749.81	3.63
52	0.176	122	37.2	642	1020	720.96	4.25
53	0.264	110	39.5	549	905	750.13	-
54	0.325	106	38.4	750	1215	808.33	6.13
55	0.441	94	39.7	926	1533	943.01	2.38
56	0.529	92	39.9	939	1562	930.22	-

as the temperature rose to nearly 110 °C. On cooling to room temperature the reaction mixture was found to have been transformed to a glassy, white and porous state. At high bath temperatures and short gel times the reaction was much less vigorous, resulting in less foaming and in the final product being a soft, transparent and rubbery material. This was the case for bath temperatures in the range 120 - 180 °C.

3.4.3 Results on water remained in undried product, after gel formation

Temperature case: Before reaction, the concentration of water in each reaction mixture for both series of reactions was 60 wt.%. As shown in *Table.* 3.7 the water contents in the reaction mixtures for the series of reactions at different temperatures dropped to 34 - 38 % after reaction for bath temperatures from 112 - 180 °C but dropped much more at lower bath temperatures and fell to just 1 % at the lowest. These contents correspond to losses of water ranging from 43 - 41 wt.% of the water originally present at the upper temperatures to 98 wt.% at the lowest temperature.

Initiator case: A similar pattern of water loss is evident in *Table.* 3.8 for the series of reactions at different initiator concentrations. At initiator to monomer ratios from 0.00529 to 0.00087 the water content dropped to 33 - 40 wt.% but at lower concentrations the water content dropped as far as 0.12 wt.%.

3.4.4 Results on evaporative losses of water and monomer concentration

Separate experiments were carried out to measure rates of evaporation of water caused solely by the heat from the bath, *i.e.* in the absence of any reaction. For each bath temperature and each initiator concentration in *Tables.* 3.7 and 3.8, the loss in weight due to evaporation was measured for the same amount of aqueous solution as used in the reaction mixture. These losses in weight, expressed as percentages of the original water present, are compared with the losses from the reaction mixtures in the temperature series in *Table.* 3.9 and with the losses from the initiator series in *Table.* 3.10.

Temperature case: In *Table.* 3.9, the evaporative losses from the aqueous solutions before reaction are in the range 5.4 to 9.1 wt.% of the water originally present for bath temperatures from 180 to 120 °C. They increase to 24.1 wt.% at 105 °C and reach 85.5 wt.% at 75 °C. The difference between the losses after reaction and the losses without reaction gives the losses due to reaction which are in the range 26 - 36 wt.% at temperatures of 105 - 180 °C and drop sharply to 13 wt.% at 75 °C. The ratio of the water lost before reaction to the water lost during reaction decreased rapidly as the bath temperature was raised from 75 °C and appears to have levelled off at about 0.18 at higher temperatures. At 75 °C the monomer concentration just before reaction increased to 83 wt.% from the original value of 40 wt.% because of water evaporation but at higher temperatures was almost unchanged. The increasing importance of the water loss before reaction with decreasing bath temperature is shown more strikingly in *Table.* 3.9 by the change in ratio of water lost before reaction to the loss during reaction from the lowest value of 0.16 to the highest value of 7.

Table. 3.9 Changes in concentration resulting from evaporative losses of water at different bath temperatures.

Temperature °C	*75*	*105*	*120*	*142*	*165*	*180*
wt.% water lost after reaction	98	60	35	38	39	41
wt.% water lost from aqueous solution without reaction	86	24	9	7	5	6
wt.% water loss due to reaction	13	36	26	31	33	35
water lost before reaction/ water lost during reaction	7	0.67	0.35	0.22	0.16	0.18
wt.% monomers in reaction mixture at gel point	83	47	42	42	41	41

Table. 3.10 Changes in concentration resulting from evaporative losses of water at different initiator concentrations.

[I]/[M × 100, moles	*0.01*	*0.021*	*0.044*	*0.087*	*0.176*	*0.264*	*0.325*	*0.441*	*0.529*
wt.% of original water lost after reaction	99.8	80	81	44.5	38	34	36	33.8	33.5
wt.% of original water lost at gel time without reaction	50.7	28.8	10.8	6.4	3.3	2.6	2.7	2.2	2.2
wt.% of original water lost during reaction	49.1	51.2	70.5	38.1	34.7	31.4	33.3	31.6	31.3
water lost before reaction/ water lost during reaction	1.03	0.56	0.15	0.16	0.09	0.08	0.08	0.07	0.07
wt.% monomers in reaction mixture at gel point	69	48	42	41	41	40	40	40	40

Initiator case: In the same way the variation of water loss with initiator concentration is shown in *Table.* 3.10. As the initiator concentration was increased from 0.01 to 0.525 mole % the loss in water after reaction, expressed as the proportion of the water originally present, dropped from 99.8 % to a steady value of about 34 % and similarly the amount of water lost before reaction dropped from 50.7 % to a steady value of about 2.5 %. The difference gave the amount of water lost during the reaction and apart from a high value of 70.5 % this ranged from about 50 % to 32 %. The ratio of the water lost before reaction to the water lost during reaction decreased from 1.03 at the lowest initiator concentration to a steady value of about 0.07 at the highest concentrations. The monomer concentration just before reaction was a little more than the original value of 13 mole % at higher initiator concentrations and rose to 23 mole % at the lowest concentration.

3.4.5 Results on swelling

Temperature case: The swelling characteristics of reaction products for bath temperatures ranging from 75 to 180 °C are given in *Table.* 3.7. Amounts of swelling for both undried and dried products increased with temperature but levelled off at about 140 °C. The amounts of swelling by the undried products are smaller than for the dried products at temperatures ranging from 135 to 180 °C and 75 to 97 °C but at temperatures in the range 105 to 127 °C the swelling by the undried products is similar to, or even higher than the swelling by the dried product. When allowance is made for the water contents in the undried products then the amount of swelling per unit mass of neat product becomes considerably higher for the undried product than for the dried product over the temperature range 105 - 180 °C but is still lower for the undried product at 75 and 90 °C.

Initiator case: Similarly the swelling characteristics of undried and dried reaction products for initiator: monomer ratios of 0.01: 0.529 mole % and at a bath temperature of 120 °C are listed in *Table.* 3.8. The amounts of swelling for dried product increased with increasing initiator concentration and ranged from 561 to 930 g/g. These values are higher than for the series of runs at different temperatures. The Expt. 39 in *Table.* 3.7 can be compared with the experiment which should be some - where between Expts. 53 and 54 in *Table.* 3.8. With nearly the same gel time and amount of water in undried product, the amount of swelling is higher for the latter. Although swelling for undried product at the highest initiator concentration is the same as for undried product, at the lowest concentration it is less than half. On allowing for the water content in the undried product as before, the highest amount of swelling for undried product, 1562 g/g, became considerably higher than for dried product whereas the lowest amount of swelling was still less than half.

3.4.6 Reaction kinetics

The experimental observation that the gel time was inversely proportional to the square root of the persulphate initiator concentration (*Fig.* 3.40) is as would be expected for a normal polymerisation [48] . However the polymerisation was not normal. There was no attempt to exclude oxygen and there was an inhibition period which became longer as the persulphate concentration was reduced. Precipitation of the reaction mixture in nonsolvent during this period showed that only small amounts of polymer were produced and there was no sign of an increase in viscosity. The existence of an inhibition period in the presence of oxygen is well established for free radical polymerisations in general [49] and for acrylic monomers in particular [50]. Studies carried out by Barnes and others [51-53] have shown that oxygen essentially forms an alternating copolymer with the monomer, *i.e.* a polyperoxide (-M-O-O-). Moreover the rate of addition of monomer to the peroxide radical formed by addition of oxygen to the polymer chain could be as slow as one thousandth of the normal rate of polymerisation. As described by Flory [49] the inhibition period is brought to an end by faster than normal polymerisation as a result of the polyperoxide decomposing and yielding initiator radicals.

If the polymerisations reported here proceeded in this manner then a possible reaction scheme can be formulated as follows:

(i) $K_2S_2O_8 \rightarrow 2OH^*$	Initiator radicals
(ii) $OH^* + M \rightarrow M^*$	Monomer radical
(iii) $M^* + M \rightarrow M^*$	Normal polymer radical
(iv) $M^* + O_2 \rightarrow O_2^*$	Peroxy radical
(v) $O_2^* + M \rightarrow M^*$	Polyperoxide radical
(vi) $2PP^* \rightarrow PP$	Recombination of polyperoxide radicals

The first step is as usual taken to be the decomposition of persulphate initiator (i), leading to the production of a pair of OH* radicals [54]. Polymerisation is then initiated by addition of these radicals to monomer and normal propagation would consist of addition of further monomer units (iii). During the inhibition period oxygen adds on to the monomer radical forming a peroxy radical. Addition of monomer to the peroxy radical is much slower than to the normal polymer radical, resulting in suppression of the normal propagation reaction and formation instead of a polyperoxide chain alternating in end group between monomer and peroxy radicals. Usually termination is attributed to combination or disproportionation of the polymer radicals. In this case the reaction is complicated by the two end groups for the polyperoxide, PP*, but would still be bimolecular.

If, as usual, the rate of initiation is assumed to be the same as the rate of termination for steady state conditions then the rate of production of polyperoxide in terms of number of moles of monomer segments is given by an expression with a square root dependence on the concentration of initiator [55] (see *Equation.* 3.5)

$$R_p = k_{iv} (e\, k_i [K_2S_2O_8] / k_v)^{1/2} [M] \qquad (3.5)$$

In this expression the subscripts of the rate constants, k , correspond to reactions in the above scheme and, e , is the efficiency of conversion of persulphate into active radicals.

The addition of monomer to the peroxy radical is taken to be the rate controlling step in the propagation reaction.

According to this reaction scheme the polyperoxide would accumulate at a rate inversely proportional to the square root of the persulphate concentration. The degree of polymerisation is reported by Flory [49] to be low, in the range 10 - 40. Nevertheless each peroxide link might be a potential source of free radicals for initiating polymerisation. If so then the concentration of initiating radicals would increase with time, leading to more polyperoxide and to a self accelerating process. At some point the concentration of initiating radicals might become high enough to enable significant amounts of normal polymerisation to occur, resulting in a rapid increase in viscosity, slowing of oxygen diffusion and rise in temperature.

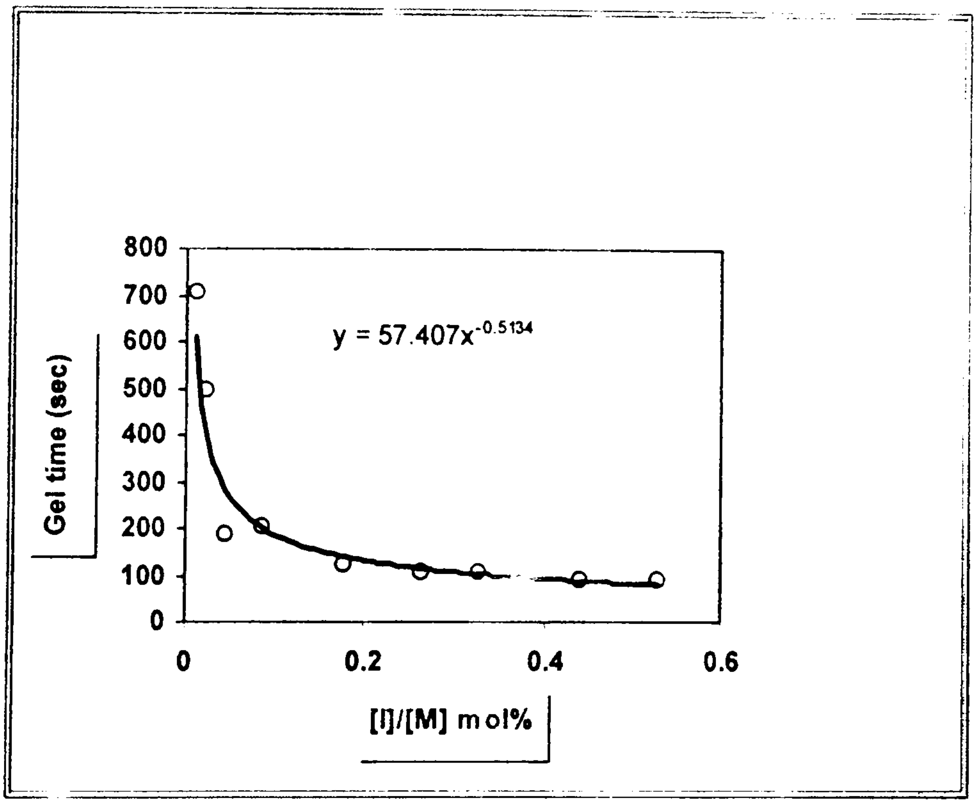

***Figure* 3.40** : Exponential relationship between gel time and initiator concentration.

Fig. 3.41 shows an Arrhenius plot of gel time against bath temperature. This would not be expected to fit the data accurately because the reaction temperature was not necessarily the same as the bath temperature but the data give a fair approximation to the following relationship (see *Equation.* 3.6):

$$Ln\ R_p = -8.2482 + 5280 / T \qquad (3.6)$$

and reducing the temperatures for runs at the upper end of the range would improve the linearity of the plot.

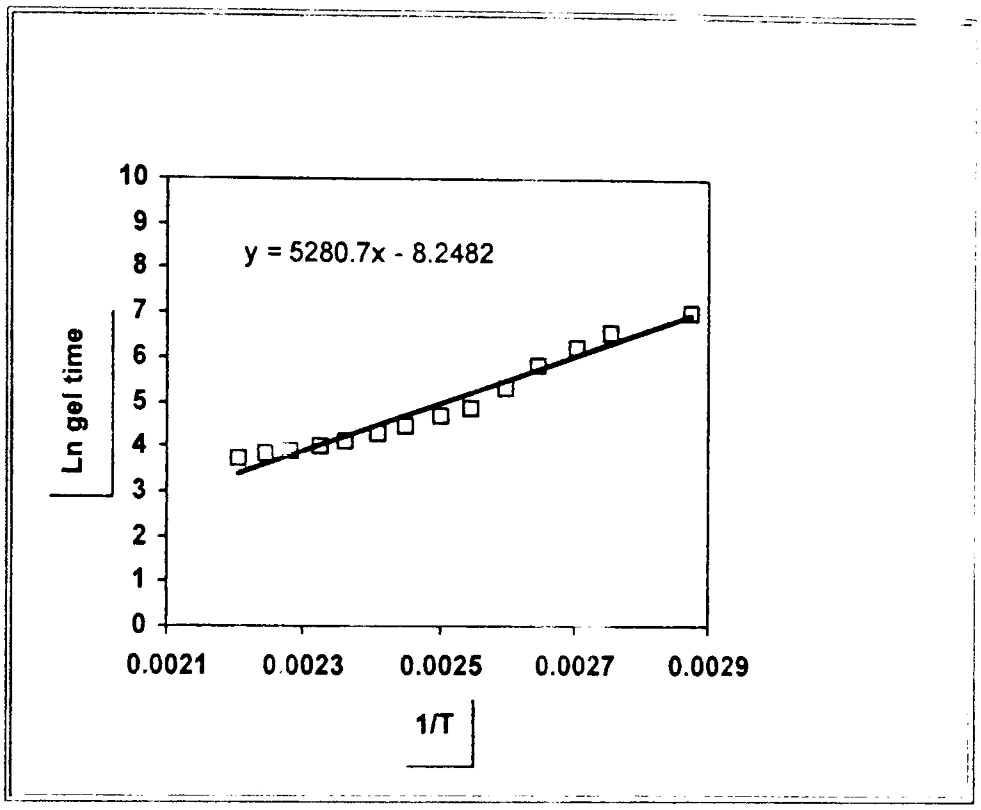

Figure **3.41**: Logarithmic relationship between gel time and absolute temperature.

3.4.7 Discussions on the effects of changes in water content before and after reaction

A complicating factor in the polymerisation process was the loss of water by evaporation. It is known that when the concentration of acrylic monomers exceeds a certain level [56] that runaway polymerisation occurs. However this has presumably been observed for normal polymerisation and is attributable to reduced heat transfer. A mechanism would still be required to account for oxygen inhibition being overwhelmed by normal polymerisation, despite free access to oxygen. Although the possibility cannot be excluded that the inhibition period ended as a result of water loss, polyperoxide is known to form under the conditions of polymerisation used here and it seems more likely to provide an explanation for the observed increase in reaction vigour with decreasing initiator concentration and decreasing temperature as a result of the accumulation of peroxide.

For both the temperature and initiator series of runs the water contents in the reaction products at the longest reaction times were so low (< 10 wt.%) that, they became glassy. This suggests the possibility that polymerisation was brought to a stop prematurely by lack of monomer mobility whereas polymerisations which lost less water stayed in a rubbery state and were able to continue polymerising to a higher degree of conversion, resulting in higher degrees of swelling. If so then some correlation might be expected between the water contents of the products and their degrees of swelling.

Temperature case: For the series of runs in which the temperature was varied the water contents of the reaction product were nearly constant over the range 180 - 120 °C and the degrees of swelling for the undried products were nearly constant too, apart from a high value at 150 °C. Although the degrees of swelling for dried products were also nearly constant over much of the range for dried products, they became smaller at temperatures below 142 °C. Most of the data for the temperature series therefore appear to be consistent with the degree of conversion of monomer to polymer depending on the water content in the reaction product.

The estimates of evaporative losses in *Table.* 3.9 show that the amount of water in the reaction mixture at the gel point for bath temperatures of 120 °C or more was only a little lower than it was before immersion in the bath because the reaction time was short. However as the bath temperature was reduced below 120 °C the reaction time became longer and at 75 °C the evaporative losses became so large that only 14 wt.% of the water originally present remained at the onset of rapid polymerisation. This can be expected to have affected the polymerisation considerably. It is reported [56] that acrylic acid undergoes runaway polymerisation when the monomer concentration is about 0.3-0.4 mol fraction. As shown in *Table.* 3.9, the monomer concentration at the gel point is estimated to have been close to 40 wt.% at bath temperatures of 120 °C or more but to have exceeded this at lower temperatures, reaching 86 wt.% at 75 °C. Runaway polymerisations could therefore be expected at bath temperatures below 120 °C and this seems to be consistent with experimental observations of smooth polymerisation at bath temperatures above 120 °C and noise-emitting polymerisation at lower temperatures. The low level of water remaining at the onset of rapid polymerisation when the bath temperature was 75 °C also suggests that conversion of monomer to polymer might be restricted by lack of water, as suggested by the lower degree of absorption than for higher bath temperatures.

Initiator case: For the series in which the initiator concentration was varied the water content in the reaction product was nearly constant over the initiator: monomer ratios in the range 0.00529 to 0.00176 but the degree of swelling for both undried and dried products became smaller. Evidently the degree of swelling was affected by other factors. If the degree of swelling depended solely on the degree of conversion of monomer to polymer then conversion at the lowest initiator concentration may have been less than one third of conversion at the highest concentration. Although the fifty-fold difference in initiator concentration is more than large enough to influence conversion to this extent, other factors may have been influential as well.

Conversion in the final product depended not only on when the mixture was removed from the bath but also on how much further conversion progressed as the mixture cooled. For products in a rubbery state, conversion may have increased considerably. Comparison of the highest degrees of swelling (926, 939 g/g) with those obtained previously for polymerisations where the degree of conversion was known to be nearly complete [31] indicates that conversion must have been high for Expts. 55 and 56 at the highest initiator concentrations. Given that the reaction mixture temperatures at the gel point did not exceed 110 °C and assuming that reaction stopped when the temperature dropped to a level at which initiator decomposition became too low to maintain propagation then it follows that the degree of conversion beyond the gel point depended on the rate of polymerisation at the gel point. For runs at the upper end of the initiator concentration range this additional conversion will have become smaller with decreasing concentration. For runs at the lower end of the range there was an increase in the rate of reaction at the gel point which has been attributed to the formation of polyperoxide but this was accompanied by loss of water. The resulting transformation from a rubbery gel to a rigid glass accounts for the failure of the acceleration in reaction to yield a high conversion.

3.4.8 Discussions on the effect of drying on swelling

Temperature case: Another feature of the results for the temperature series is the difference in the effect of drying the product on swelling at the two ends of the temperature range. Instead of the swelling of dried product being twice that for neat, undried product at the longest gel time it only increased by 23 % and instead of swelling increasing by 67 % at the longest gel time it only increased by 34 %. Although the highest bath temperature (180 °C) was well above the bath temperature in the initiator series (120 °C) there was much less difference in the reaction temperatures and the initiator ratio (0.00295) was well below the highest ratio in the initiator series. Under these conditions the rate of polymerisation at the gel point would have been slower and so less conversion of monomer to polymer could be expected in the final product. This deduction is consistent with the observed lower degrees of swelling for the temperature series.

Initiator case: Similar effects occurred in the initiator series but more markedly. Whereas swelling was more than doubled at the low end it was unchanged at the high end. Since the drying procedure involved heating the sample at 60 °C for 24 h the increase in swelling could be accounted for by resumption of polymerisation and increased conversion. This explanation is consistent with the substantial increases in swelling being restricted to the three products with low enough water contents to be glassy. At the upper end of the initiator concentration range the swelling of dried product might have been expected to exceed the value for undried product because of the higher active content in the dried product whereas the two values are the same and the swelling calculated for the active part of the undried product is higher by two thirds than for the dried product. It would therefore appear that drying reduced swelling by active product at high initiator concentrations, presumably by causing crosslinking. Although the swelling (549 g/g) for undried product of Expt. 53 was lower than expected from the data for neighbouring runs, the swelling for dried product (750 g/g) was in line with its neighbours, suggesting that the former value was in error.

Temperature case against initiator case: At the lowest bath temperature (75 °C) the degree of swelling by the dried product (267 g/g) was close to that (276 g/g) for the lowest initiator concentration, suggesting that the degree of conversion of monomer to polymer was similar. This is supported by the similar amounts of extractables in *Table.* 3.7 for Expt. 35 (22 wt.%) and in *Table.* 3.8 for Expt. 48 (25 wt.%).

Just as the evaporative losses at the onset of fast polymerisation for the temperature series were low for high bath temperatures, so were they also low for the higher initiator concentrations which gave short reaction times. At initiator concentrations from 0.529 to 0.044 mole % of the reaction mixture the evaporative losses were low enough (<11 wt.%) to expect little influence on the reaction at the gel point but at lower concentrations the losses became significant although they did not reach as low a level as for the temperature series because the reaction time was not as long. Consequently the smallest proportion of water remaining at the onset of rapid polymerisation (49 wt.%) was substantially higher than for the temperature series (14 wt.%). Nevertheless, nearly all of the remaining water was lost during polymerisation. As for the temperature series the monomer concentration at the onset of rapid polymerisation was close to 40 wt % for most of the reactions but was higher than this for the two longest gel times. Again these were the reactions which showed characteristics of runaway polymerisations and became glassy.

3.4.9 Application of Voigt model to rates of swelling

Rates of swelling for the absorbents in the temperature and initiator series were found to fit the same Voigt expression (*Figs.* 3.42 and 3.43), we found previously (see *Sec.* 3.3.5.1, *Equation.* 3.3). This expression related the degree of swelling, ε, to the time taken, t, using two parameters, one representing the resistance of the absorbent to expansion, σ_0/E, and the other representing the resistance to permeation, τ_o.

Values for these parameters are given in *Table.* 3.11 for the dried products. The effect of increasing the bath temperature and the initiator concentration was to increase both parameters, indicating that both the resistance to expansion and the resistance to permeation were becoming greater. These trends are consistent with increasing conversion of monomer to polymer since monomer would rapidly diffuse from the absorbent, speeding up absorption and would contribute little to resistance to expansion. More directly the data in *Tables.* 3.7 and 3.8 for extractables from the products provide evidence for significantly lower conversion of monomer to polymer at low bath temperatures and low initiator concentrations.

Table. 3.11a Model parameters for temperature variable system.

Expt.	*35*	*37*	*39*	*41*	*43*	*45*	*47*
Temperature ° *C*	90	105	120	135	150	165	180
σ_0/E *g/g*	355	351	578	710	850	900	870
τ_o *sec*	159	203	269	305	410	415	405

Table. 3.11b Model parameters for initiator variable system.

Expt.	*52*	*53*	*54*	*55*	*56*
$[I]/[M]$ *mol%*	0.176	0.264	0.325	0.441	0.529
σ_o/E *g/g*	730	730	810	960	950
τ_o *sec*	258	258	250	350	340

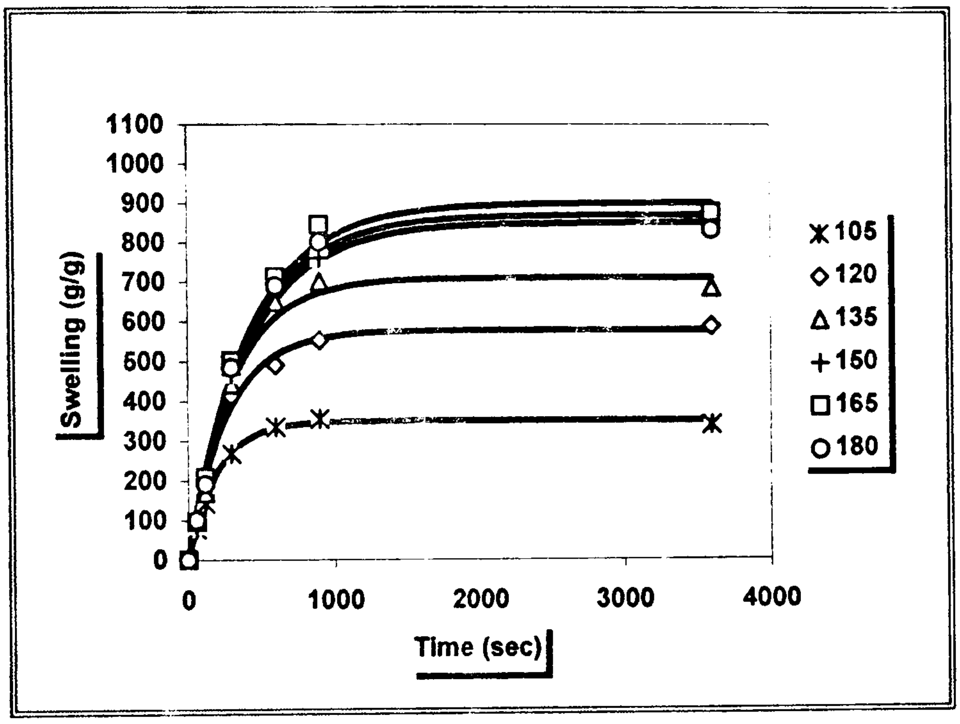

Figure 3.42: Experimental and modeled dynamic swelling figures for the materials obtained at different temperatures (°C).

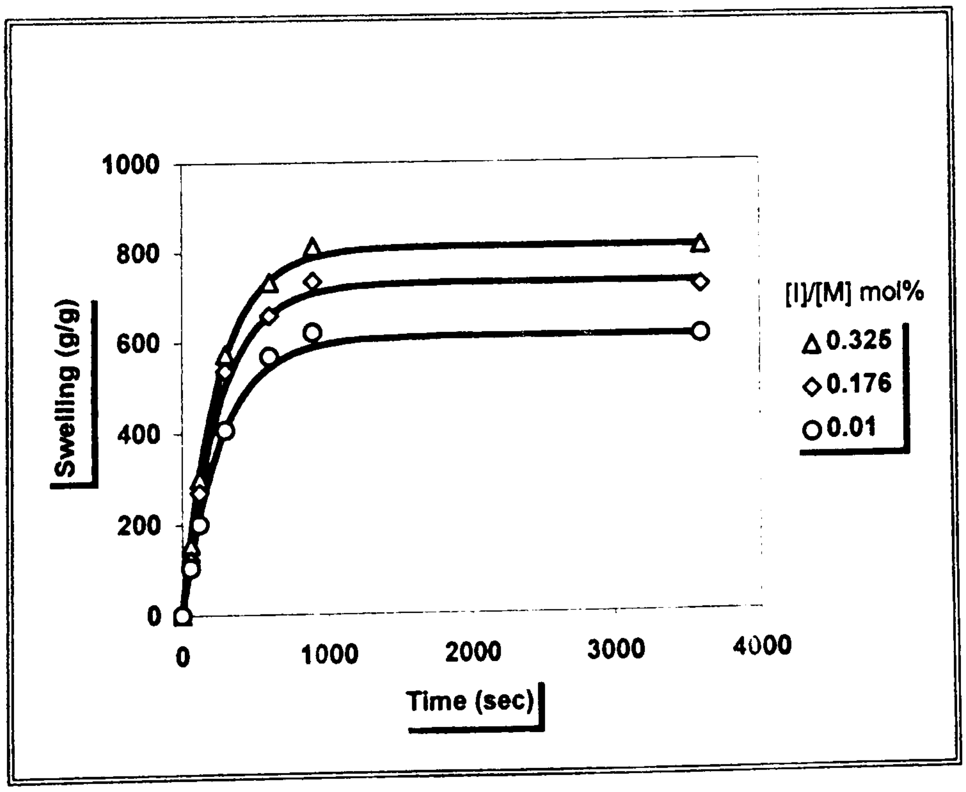

Figure 3.43: Experimental and modeled dynamic swelling figures for the materials obtained at different initiator loadings.

3.5 Monitoring the gel point through DSC studies (Expts. 57-66 and Expts. 67-72)

3.5.1 Introduction

With previous experiments, *i.e.* a simulation of an industrial solution process to make superabsorbents, the effect of the bath temperature and initiator concentration were assessed in the presence of oxygen. We observed an inhibition period, because of oxygen participation in the polymerisation reaction, and extensive losses of water, which seriously affected the final water-absorbency of our products. To obtain more insight into the events at the point of gel formation, we devised a few microsyntheses by the DSC.

Any exothermic or endothermic phenomenon could be monitored by this instrument. For instance, a typical polymerisation reaction and gel formation are familiar processes, which involve a definite amount of heat, thus, they can be detected by such a reliable instrument.

3.5.2 DSC results (see *Sec.* 2.3.2.4 for the preparative procedure)

Initiator case: Four regions were recorded on the thermograms (see *Fig.* 3.44). The first one relates to the heat transfer into the contents of the DSC pan to reach them to their set temperatures. This region which was observed within the time range of 0-2 min. can be seen as an endothermic peak and was same for all the reaction mixtures until they reached their set temperature. The first region was followed by a long and nearly straight region (slope 0.35 mcal/ sec ^{2}). The time range for this process was 10-12 min. (see *Table.* 3.12). A little bit difference in shape of the thermograms was observed through the whole range of initiator studied. One thing was common for all the thermograms. This was a little variation in the slope of the curves through the whole time interval of this region. Rate of heat transfer was ignorably variable (not appeared as a straight line or constant) in this time region for each individuals. At low initiator concentration in the range of 0.0139-0.0763 mol% to monomer, a very weak exothermic peak was observed within the midway of the second region. But, at high initiator concentration in the range of 0.0909-0.2101 mol% to monomer, the general endothermic peak was immediately followed by this weak exothermic peak within the time interval of 2-3 min. This peak appeared in its most intense form for the highest initiator concentration. The second region was completed after 12-14 min. Through the time range of 12-15 min., this relatively straight region was followed by a sudden and a very sharp exothermic peak. This was the third region which was observed on the thermogram. But this peak was appeared at different times and shapes. With the initiator range of 0.0139-0.0285 mol% to monomer, this peak was appeared at longer times but stronger. Time and intensity of the peak was decreased through the rest of the initiator range. So that, with the highest initiator concentration, no peak was observed in this region. On the other hand, this exothermic peak was accompanied with temperature rise within the reaction mixture. Rise in temperature was higher for the lower initiator concentrations in the range of 0.0139-0.0338 mol% to monomer and was nearly low and constant for the initiator range of 0.0640-0.2101 mol% to monomer. Through the time range of about 16-20 min. the fourth region was observed as a plateau for all the samples.

Temperature case: Again four regions can be distinguished on DSC thermogram (see *Fig.* 3.45). Within the first region, samples reached their set temperatures at slightly different times. This can be seen as different endothermic peak on the thermogram. Shortest (1.75 min.) and longest (2.375 min.) times were observed for low and high temperature respectively. After reaching the set temperature, the thermogram was changed in shape and smoother region was observed. This region appeared in different times and slopes. The longest time (20 min.) and lowest slope (0.15 mcal/ sec ^{2}) was observed for the lowest temperature and vice versa (6.12 min. for 1.66 mcal/ sec ^{2}). The shape of the thermogram was not exactly as a straight line, *i.e.* the rate of heat transfer was not constant through this region. Small rise in slope of the line which resembles a very weak exothermic peak can be seen for all the individuals but in different nature. This peak shifted to the shorter times with increase in temperature. So that, it was appeared as a shoulder for the high temperature extreme. At the end of this period, an exothermic peak suddenly appeared whose position was dependent on the end of the second period for each individual. The highest exotherm was observed for the low temperature system (see *Table.* 3.13). Through the temperature range of 85-95 ^{o}C, intensity of this exothermic peak was much weaker but nearly similar. The exotherm peak was followed by a plateau region for all the individuals.

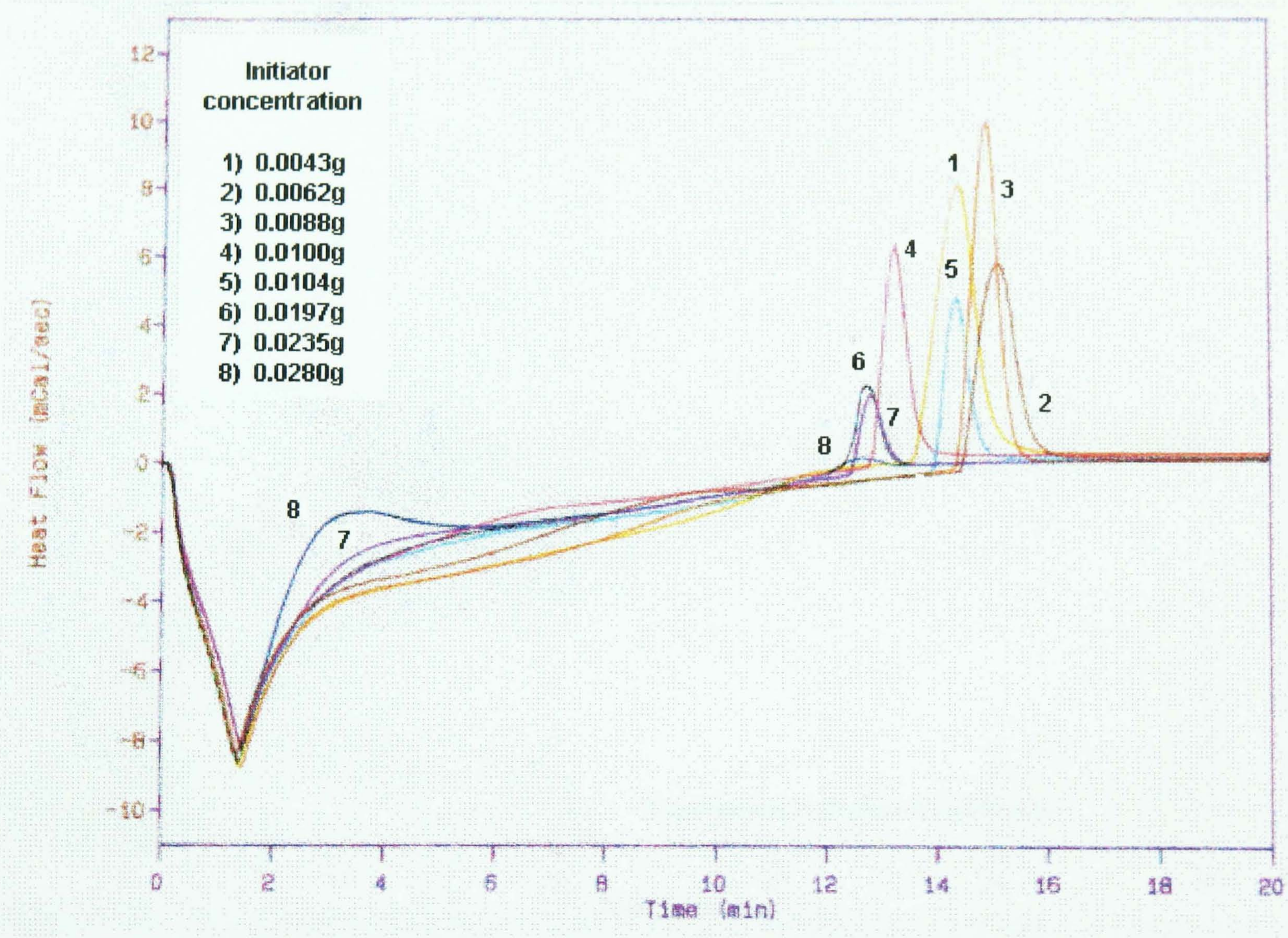

__Figure 3.44__: DSC curves of the samples in case of initiator change

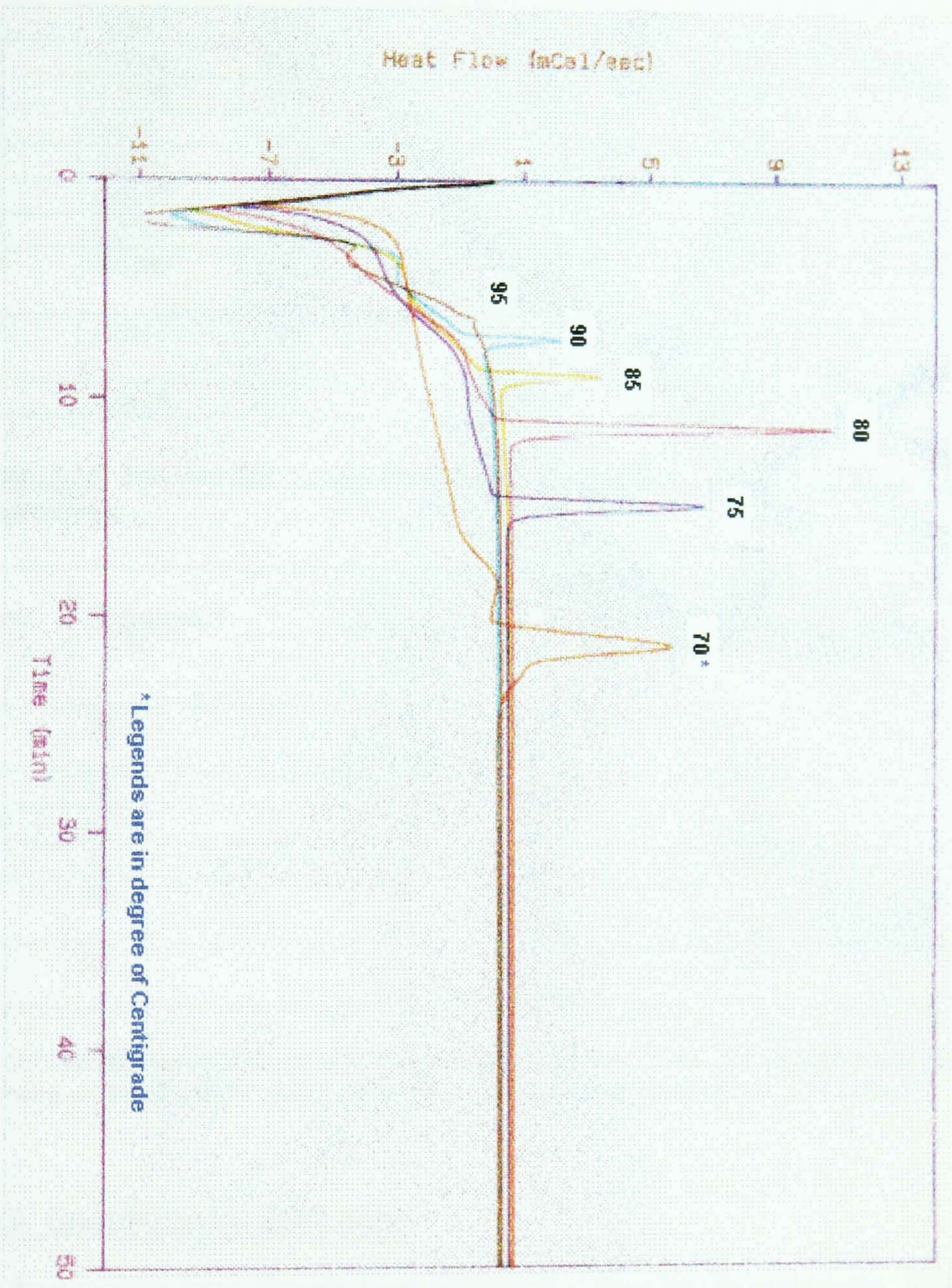

Figure 3.45: DSC curves of the samples in case of temperature change.

Table. 3.12 DSC studies on superabsorbent microsynthesis in solution with different initiator concentration.

Expt.	*Initiator amount (g)*	*Gel time (min.)*	*Exotherm at gel point (m cal/mg)*	*Temperature during Exotherm °C*
57	0.0043	13.66	-36.79	82.08
58	0.0062	14.50	-25.73	81.72
59	0.0088	14.40	-30.63	83.67
60	0.010	12.84	-18.63	82.29
61	0.0104	13.97	-14.30	81.74
62	0.0197	12.32	-7.30	80.95
63	0.0235	12.38	-6.02	80.76
64	0.0280	2.42 12.01	-3.52 -1.71*	80.58 80.11
65	0.0410	2.70 11.81	-4.32 -1.89*	80.68 80.24
66	0.0616	2.25	-7.94*	80.78

Table. 3.13 DSC studies on superabsorbent microsynthesis in solution at different temperatures.

Expt.	*Temperature °C*	*Gel time (min.)*	*Exotherm at gel point (mcal/ mg)*	*Temperature during Exotherm °C*
67	70	16.34 20.41	-6.50 -37.24	70.10 71.14
68	75	14.50	-19.18	77.37
69	80	11.00	-23.78	84.22
70	85	8.58	-8.49	86.43
71	90	3.80 6.96	weak* -6.24	91.22
72	95	3.04 6.12	very weak* very weak	95.56

* *Is not readily measurable, since it is immediately followed by the endothermic peak. But, according to the figures for temperature rise, these exotherm values are more probable.*

3.5.3 Discussion on DSC data

The four regions have already been described in the DSC thermograms. Within the first region, the reaction mixture absorbed heat from the DSC chamber to reach its set temperature. This process appeared as an endothermic peak. The first region was followed by a another region, through which, the length and slope of the curve was varied. In this region the reaction was inhibited and temperature of the reaction mixture was sufficient to evaporate water from the system because the latter was open to atmosphere. This region was regarded as the evaporation and inhibition region. As already said, the rate of heat transfer was nearly constant for the initiator case. This means the rate of water evaporation from the reaction mixture was same and independent of the initiator concentration. In other words, the amount of water evaporated is only dependent on the time of evaporation. So for low initiator concentration higher amount of water is expected to evaporate compared to the high initiator case. On the other hand, various rates of evaporation was observed in case of temperature variation. For instance, the rate of water evaporation for the temperature 95 °C is 11.6 time faster than the corresponding value for the temperature 70 °C. So, the rate of water evaporation is critically dependent on the set temperature. The exothermic peak observed after any evaporation is a typical exothermic polymerisation reaction and the area under the peak is indicative of the heat of the reaction. Increase in temperature and initiator concentration led to suppressing the exothermicity.

3.5.4 DSC data against bench-scale data

The existence of an inhibition period in bench-scale Experiments (*Sec.* 3.4) was consistent with the DSC data, in which normal polymerisation commenced after a definite time. Moreover, a sudden rise in the viscosity of the reaction medium (*Sec.* 3.4), which was already ascribed to the onset of the normal polymerisation, was also clear through DSC data.

Nevertheless, the figures for the gel time and exotherm measured through DSC studies can not be compared with bench-scale experiments (*Sec.* 3.4) in quantitative terms, since the mass of the reaction for the latter case is about 1000 times bigger than the microscale reactor, thus the surface: volume ratio of the two reactors are quite different. On the other hand, the DSC instrument was equipped with cooling system to run isothermal polymerisation. So that, only 0-3 °C rise in temperature was recorded due to the exothermic reaction. This means runaway polymerisation was inhibited in our DSC experiments and this is the big difference with bench-scale experiments in which runaway polymerisation was led to glass materials at low temperature and initiator concentration.

3.6 Effect of the external parameters

3.6.1 Introduction

In our earlier works [30], to produce superabsorbing polymers by inverse suspension technique, a general procedure was introduced to obtain separate particles rather than obtaining coagulum. The other works in this series were studying the effect of monomer nature [31], the effect of process of manufacturing [32] and the effect of temperature and initiator concentration [57] on the swelling properties of superabsorbent polymers. What has been studied so far was the effect of presumably internal parameters on swelling properties. In other words, the study was limited to the effect of those parameters or variables which manifest their contributions on polymer structure or simply before obtaining the product. In the present work, the effect of so-called external parameters including the shape of the product and the presence of electrolyte in swelling media were also studied to obtain more knowledge of variables which affect superabsorbent properties.

The particles obtained from different inverse suspension and solution polymerisations were expected to impose certain effects on superabsorbent properties because of their size. This effect was studied here through measuring the swelling capacities of the selected particles which differed in size. Based on our observations, the finer particles showed higher swelling capacity and rate than of their coarser counterparts. The space between swollen particles and the surface area of the non-swollen particles were considered to be responsible for the swelling observations.

In a parallel study, the effect on the swelling properties of the ionic strength of the swelling media was also considered on swelling properties. The steady state swelling of the samples were measured in various media and the effect of salt present was studied. The crosslinker concentration showed a certain effect on the swelling capacity in these media which, was attributed to change in a rigidity of the polymeric network.

3.6.2 Effect of the particle size

3.6.2.1 Dynamic swellings

The inverse suspension product after classifying was spherical (see *Fig.* 3.12). The particles were normally isolated from each other, although some fine particles could form agglomorate through adhering to the other coarser particles (see *Fig.* 3.13). According to the sieve analysis, different sizes but in definite ranges were recorded for the particles of inverse suspension polymers. On the other hand, the solution polymerisation product was irregular in shape after classifying as shown in *Fig.* 3.4.

Generally speaking, surface area and volume of a typical particle determines respectively the rate by which mass transfer occurs and the ultimate capacity for mass transferred. On the other hand surface area and volume of a particle depends on its size. So it was expected that the particles which were different in size, impose various effects on mass transfer or absorption.

The following table (*Tables.* 3.14 a , b) displays the water uptake capacity of the particles of two different sizes at different time scales in double distilled water. Particles with size of 250-300μm and smaller than 250 μm were distinguished as coarse and small particles.

Table. 3.14a Dynamic swellings (in g/g) of the coarse particles.

Expt. *(code)*	*[C]/[M]* *mol%*	*0.5* min	*1.0* min	*2.0* min	*5.0* min	*10* min	*Equilibrium*
23 (S2.1)	0.047			231	400	514	517
24 (S2.2)	0.078			154	240	280	288
25 (S2.3)	0.11			151	221	247	254
27 (S3.1)	0.047	202	427		430	454	423
28 (S3.2)	0.078	146	207		214	217	219
29 (S3.3)	0.11	148	201		202	203	204
30 (B1.1)	0.0078	92	173	303		747	779
31 (B1.2)	0.016	85	150	252		485	505
32 (B1.3)	0.047	75	115	201		315	323
33 (B1.4)	0.078	71	94	160		225	228

Table3.14b Dynamic swellings (in g/g) of the small particles.

Expt. *(code)*	*[C]/[M]* *mol%*	*0.5* min	*1.0* min	*2.0* min	*5.0* min	*10* min	*Equilibrium*
23 (S2.1)	0.047			444	530	534	531
24 (S2.2)	0.078			290	322	323	323
25 (S2.3)	0.11			269	281	300	283
27 (S3.1)	0.047	512	539		521	517	531
28 (S3.2)	0.078	341	372		353	351	359
29 (S3.3)	0.11	296	314		301	306	306
30 (B1.1)	0.0078	406	433	538			
31 (B1.2)	0.016	204	348	410			
32 (B1.3)	0.047	199	226	266			
33 (B1.4)	0.078	139	161	196			

S2 series: At each crosslinker concentration, the swelling capacity of both coarse and small particles increased with time until approached a plateau region. By the time, difference in swelling capacities of the two particles became less. After 10 min. , the figures for swelling capacities of coarse particles becomes similar as for equilibrium. This was achieved after 5.0 min time for small particles.

At the lowest crosslinker concentration, through the time range of 0-2.0 min, the coarse particles were swollen up to 44.6% of their final swelling capacities. This figure was 83% for the small particles. For other crosslinker dosages, this figure was 53.4 and 59.4% for coarse particles and 90 and 95% for small particles.

Through the range of crosslinker used, equilibrium swelling capacity of small particles were 1.03, 1.12 and 1.11 times higher than of their coarser counterparts.

S3 series: After 1.0 min time, the figures for swelling capacity of coarse particles became similar to their equilibrium values. This could be achieved after about half a minute for smaller particles.

At lowest crosslinker concentration, the coarse particles were swollen up to 47.8% of their final swelling capacity after 0.5 min. This figure was 96.4% for the small particles. For other crosslinker dosages, this figure was 66.6% and 72.5% for coarse particles and 94.9% and 96.7% for the small particles after 0.5 min.

Through the range of crosslinker used, equilibrium swelling capacity of small particles were 1.25, 1.64 and 1.5 times higher than the coarse particles.

Generally the same behavior was observed for the B1 series in which finer particles showed more swelling capacity than their coarse counterparts through the time range of 0-2.0 min.

Generally speaking, according to the swelling figures at different intervals, rate of absorption for small particles was appreciably higher than their coarser ones. Moreover, the rate of absorption increased with the crosslinker concentration. The latter observation has been already observed and discussed under the heading *"A Swelling Model" (see Sec. 3.3.11)*. On the other hand, equilibrium swelling could be reached earlier for the smaller particles. For the whole range of crosslinker studied, equilibrium swelling capacities of the smaller particles were found higher than of their coarse counterparts for inverse suspension products and much higher was found in case of S3 series compared to S2 series.

Table. 3.15 displays the figures for ultimate swelling of the foregoing samples at the media of different ionic strengths.

3.6.2.2 Equilibrium swelling

At each crosslinker dosage, the swelling capacity decreased with the salt concentration. This was observed for all the samples independent of method of synthesis and whether coarse or small in size. The swelling capacity of small particles was found more than their coarse counterparts at different media. In other respects, the observations were similar for the two particle sizes. Detailed observations have been made in the next section under the heading " Effect of the Ionic Strength " (see *Sec.* 3.6.3).

To make convenience, the quantitative figures for relative increase or decrease in final swelling capacities of the two particles have been gathered in *Table.* 3.16. With any four vertical (in column) data set which differ in amount of crosslinker, the percent of increase in swelling was irregular. This indicates that increasing trend of ultimate swelling is independent of the crosslinker concentration. So each series of data (any four data in column) was averaged to help to make more reliable conclusions through increasing the number of our observations. The average values for S2 series were +9.80%, +15.9%, +15.22% and +16.6% at their corresponding saline media. The figures for the S3 series were +42.6%, +46.8%, +44.9%, +43.7%. The average values of each series at individual ionic strength were very close to each other. So the mean values of +14.37 and +44.5 was calculated for individual series of experiments.

So particles of different systems show a distinct behavior in terms of their swelling capacities. The above data shows that difference in swelling capacity between coarse and small particles is much more pronounced for S3 than for S2 series as already mentioned.

Table. 3.15 Steady state swelling features of different particles at different swelling media.

Size		*300-250 μm*				*Finer than 250 μm*			
		Swelling (g/g) in water of various salt concentration M				*Swelling (g/g) in water of various salt concentration M*			
Expt. (code)	*[C]/[M] mol %*	*0.0*	*0.0015*	*0.015*	*0.15*	*0.0*	*0.0015*	*0.015*	*0.15*
22 (S2.0)	*0.016*	752	403	179	61	850	483	215	74
23 (S2.1)	*0.047*	517	290	142	53	531	352	165	57
24 (S2.2)	*0.078*	288	212	106	41	323	234	123	47
25 (S2.3)	*0.11*	254	196	105	39	283	220	114	48
26 (S3.0)	*0.016*	573	328	134	60	750	544	197	68
27 (S3.1)	*0.047*	423	261	99	50	531	331	130	41
28 (S3.2)	*0.078*	219	183	85	31	359	247	115	42
29 (S3.3)	*0.11*	204	142	65	23	306	227	108	42

Table. 3.16 Percent of increase or decrease in steady state swelling of different particles traveling from coarse to fine particles in swelling media of different salt concentration M.

Expt. (code)	*[C]/[M] mol %*	*0.0 M*	*0.0015 M*	*0.015 M*	*0.15 M*	
22 (S2.0)	*0.016*	+13.03	+19.8	+20.1	+21.3	
23 (S2.1)	*0.047*	+2.70	+21.3	+16.2	+7.50	
24 (S2.2)	*0.078*	+12.1	+10.3	+16.0	+14.6	
25 (S2.3)	*0.11*	+11.4	+12.2	+8.6	+23.0	
Average		*+9.80*	*+15.9*	*+15.22*	*+16.6*	*+14.37*
26 (S3.0)	*0.016*	+30.9	+65.8	+47.0	+13.3	
27 (S3.1)	*0.047*	+25.5	+26.8	+31.3	-	
28 (S3.2)	*0.078*	+63.9	+34.9	+35.3	+35.4	
29 (S3.3)	*0.11*	+50	+59.8	+66.1	+82.6	
Average		*+42.6*	*+46.8*	*+44.9*	*+43.7*	*+44.5*

3.6.2.3 Mean particle size and particle size distribution

The data gathered in *Table.* 3.17 displays the weight fraction of individual particles ranging from 38-400 μm for the two first series of experiments. The samples were classified through eight mean particle sizes and weight of each fraction was measured by means of an automatic screener. With the first series the mean particle size was found 336 μm, while the number 268 μm was obtained with the second series. Nearly the same particle size distribution can be seen for each three individuals in S2 and each three individual in S3 series. Although each three are different in terms of amount of crosslinker used, the size distribution is similar which indicates particle size distribution is independent of crosslink density. But the two different series are quite different in terms of mean particle size and particle size distribution which can clearly be seen in *Fig.* 3.46. With S2, near 95% of the particles are in the range 250-400 μm, while for the S3 series, this figure is 67.2%. In other words, particle size distribution for the former is quite sharp, while the broad one is observed for the latter. The other thing is the presence of much finer particles in particle package of smaller than 250 μm which can be seen for the S3 series. The weight % distribution of fine and coarse particles within each particle packages (particles bigger and smaller than 250 μm) can be seen in *Figs.* 3.47 and 3.48 respectively. The average mass fractions were considered as the representative for each series. According to *Figs.* 3.47 and 3.48, weight contribution of coarser particles are bigger than smaller ones in case of S2 series. With S3 series, the contribution of smaller particles exceeds the coarser ones.

Table. 3.17 Particle size distribution of the two series of samples (the figures are in wt.%).

Particle size (µm)	*23 (S2.1)*	*24 (S2.2)*	*25 (S2.3)*	*27 (S3.1)*	*28 (S3.2)*	*29 (S3.3)*
400-300	83.80	81.87	85.82	50.79	40.35	48.32
300-250	10.91	12.83	9.84	23.71	20.07	18.36
total	*94.71*	*94.7*	*95.66*	*74.5*	*60.42*	*66.68*
250-180	2.18	2.24	2.16	4.54	9.25	6.30
180-150	1.91	2.03	1.57	13.04	12.40	11.95
150-106	0.72	0.61	0.39	3.75	10.82	6.52
106-75	0.18	0.20	0.00	4.15	4.72	5.86
75-53	0.00	0.00	0.00	0.00	0.19	1.18
53-45	0.09	0.20	0.19	0.00	0.00	0.00
45-38	0.21	0.02	0.03	0.02	2.20	1.51
total	*5.29*	*5.30*	*4.37*	*25.5*	*39.58*	*33.32*

Mean particle size (µm)	336	268
Coarser than 250 µm %	95.03 (averaged)	67.2 (averaged)
Finer than 250 µm %	4.97 (averaged)	32.8 (averaged)

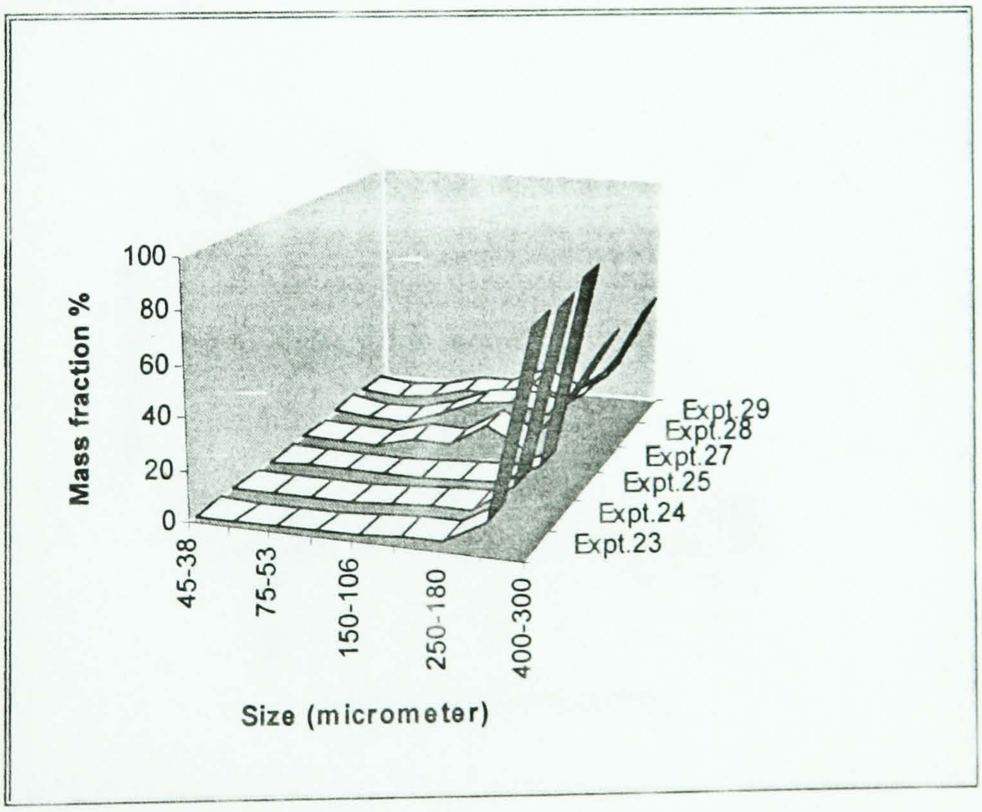

Figure 3.46: Particle size distribution of the individual samples.

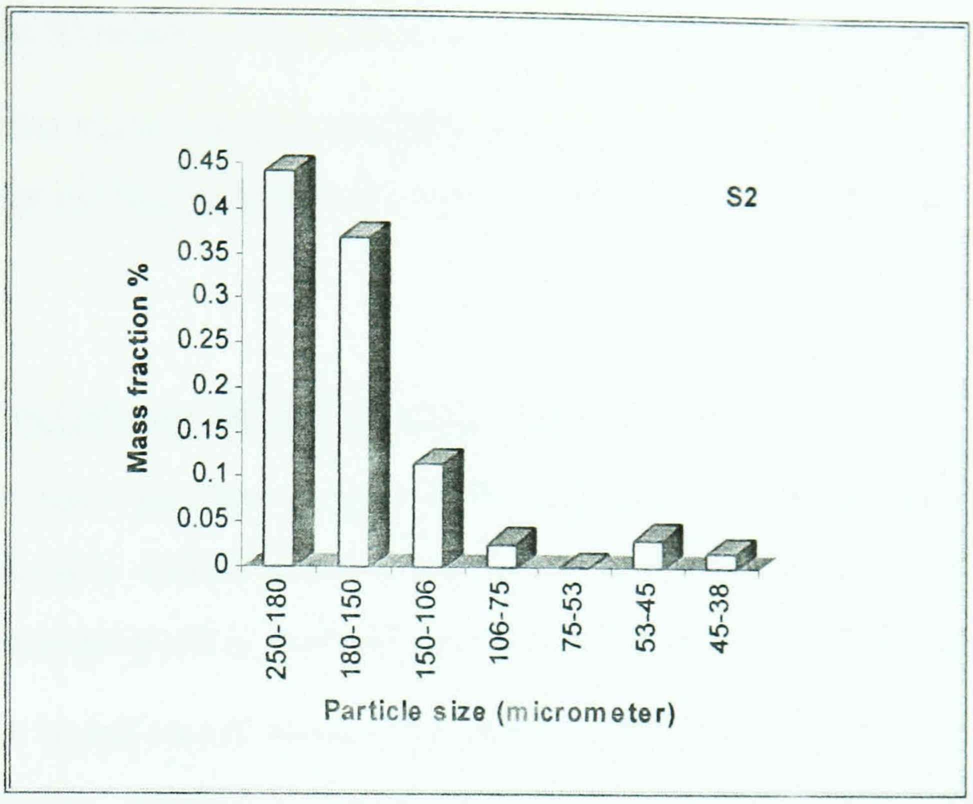

Figure 3.47: Distribution of the fine particles (smaller than 250μ) for S2 series.

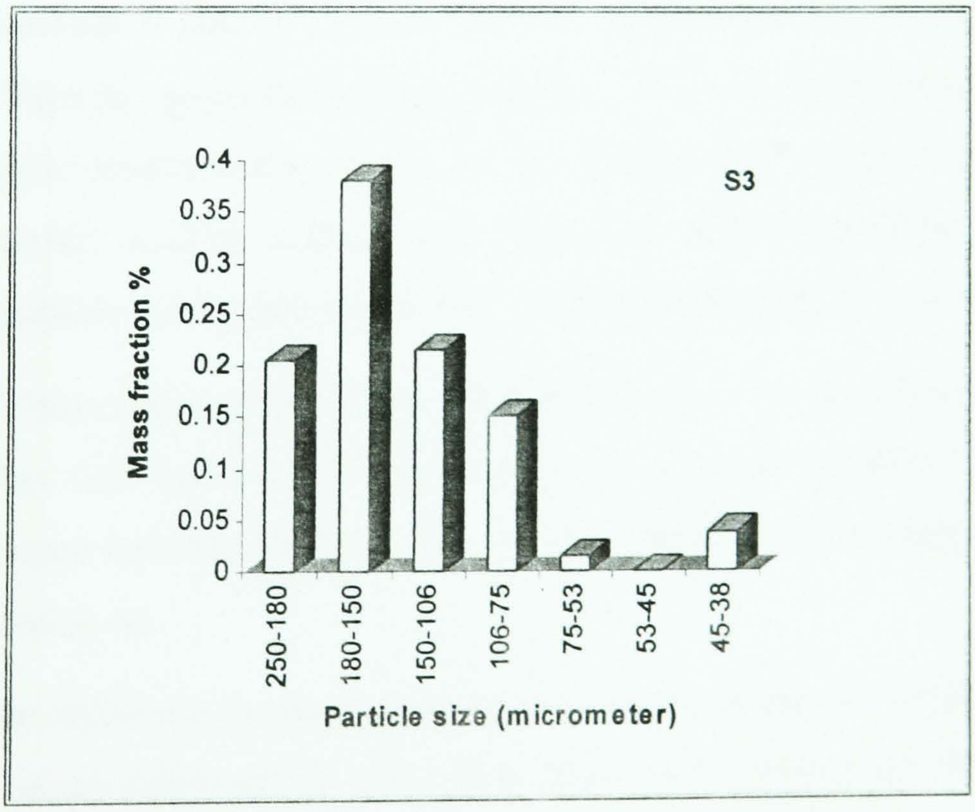

Figure 3.48: Distribution of the fine particles (smaller than 250μ) for S3 series.

Therefore, increased final swelling capacity of finer particles was consistent with their increased weight contribution in each package. As already said, this was much more pronounced for S3 series in which the contribution of finer particles were much higher.

This observation reinforces the assumption through which increased ultimate swelling was claimed for the finer particles in inverse suspension polymerisations.

3.6.2.4 An explanation for the swelling observations

The only difference between the two series of samples was the presence of acrylamide in the second series which indicates that the latter comonomer contributed to obtain firstly, smaller mean particle size and secondly, much wider size distribution.

As detailed in experimental section, the same stabilising system was used for the two series of inverse suspension experiments. The stabiliser concentration (sorbitan monooleate plus ethyl cellulose) at the threshold of stability for a system of acrylic acid and sodium acrylate mixture (S2 series) was found 0.33 w/w % based on toluene, otherwise coagulum occurred (see *Fig.* 3.5). But any change in chemical structure of the superabsorbent backbone alters the hydrophilic-lipophilic balance of the system which is typically between 9 and 10 for a number of acrylamide/sodium acrylate monomer mixtures [58]. Thus the optimum stabilising system which has been found earlier for the system of acrylic acid/its sodium salt is not an optimum but, a powerful system for the system of acrylic acid/its sodium salt/acrylamide which manifests itself through reduction in particle size by about 20% and creating a wide particle size distribution.

Scanning electron micrographs of the two particles of 2.5 times difference in size can be seen in *Figs.* 3.49 and 3.50. All the particles are spherical in shape and there is no serious difference between the two types of the particles, for example, difference in aggregation and so on.

To explain the difference in swelling behaviour, two packages of swollen particles can be imagined which differ only in terms of the size of the swollen particles. Assuming a same volume for the two packages, different patterns for laying the uniformly-sized swollen particles can be expected as be seen in *Fig.* 3.51.

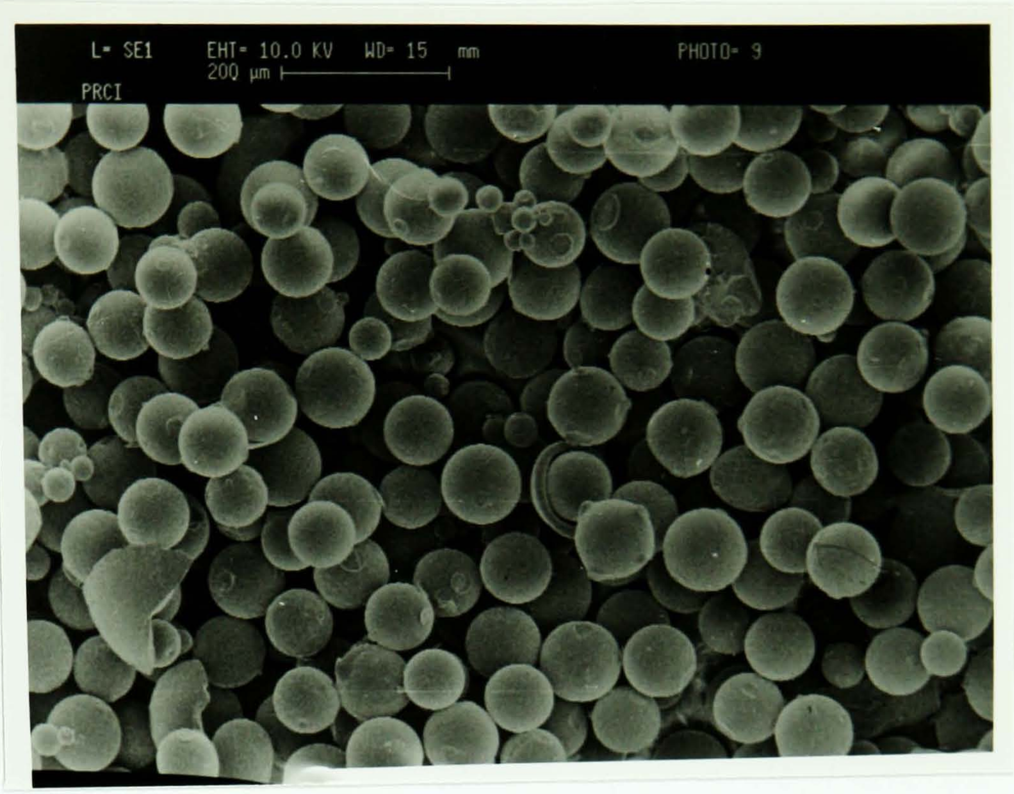

Figure 3.49: Micrograph of an inverse suspension batch of small particles.

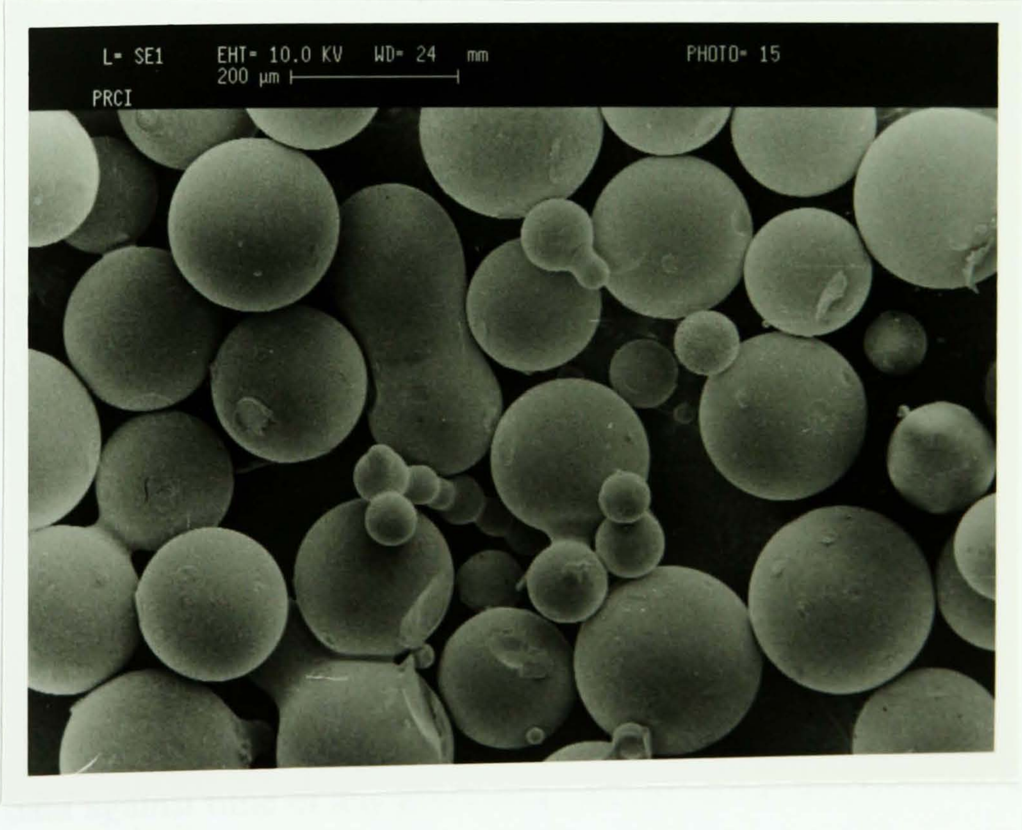

Figure 3.50: Micrograph of an inverse suspension batch of coarse particles.

If the particles laid side by side, some spaces could be left between the swollen particles, whether the particles are coarse or fine. This space can be called free volume which serves to accommodate additional water by a typical capillary action. So the capillaries are expected to be wide and narrow in bore for coarse and fine swollen particles respectively. Considering the two extremes for the size of the capillary bore, water drainage is presumably quite facile in case of extremely wide bore, *i.e.* coarser particles. With lowest size bores, *i.e.* finer particles, water is hardly drainable. If there are size distribution for the swollen particles, the finer swollen particles can easily accommodate within the free volume of the coarser ones and increase the number of capillaries. Therefore, absorption capacity of superabsorbents can be increased by creating numerous fine capillaries. Higher absorption capacity of the finer particles (in case of S2 series) against their coarser counterparts can be attributed to the presence of narrower capillaries between the finer swollen particles and is attributable to much more narrow- bore capillaries in case of S3 series of samples.

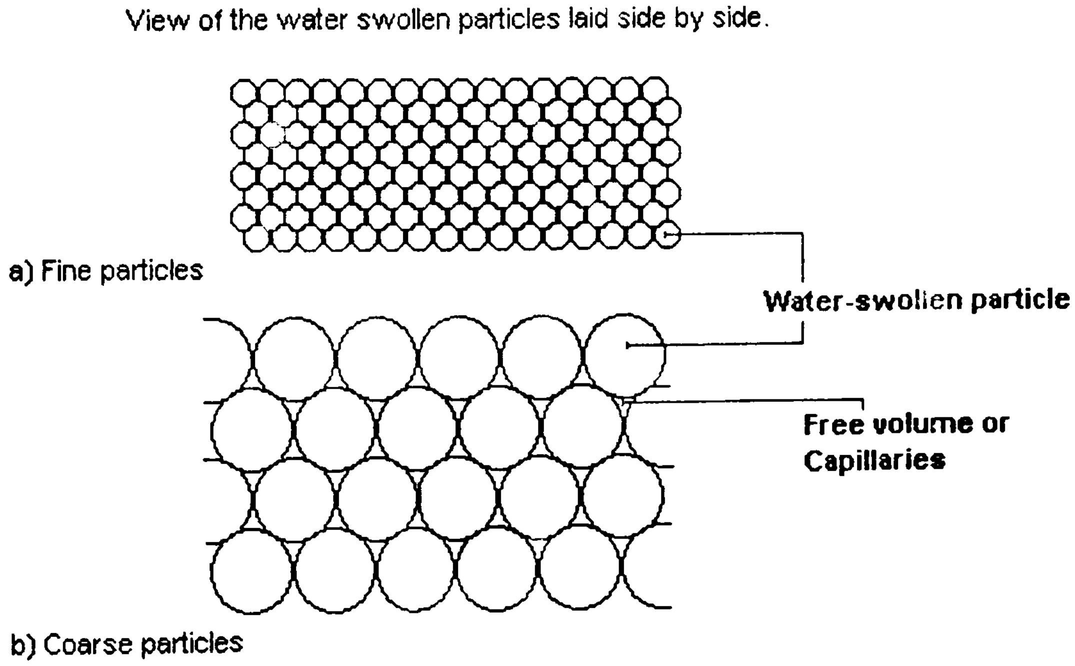

***Figure* 3.51**: A schematic diagram, showing capillaries between the water-swollen particles.

3.6.2.5 Model interpretation

The swelling data against time of any absorbent studied so far was followed a particular exponential relationship (see *Equation.* 3.3).

In this equation, there are two parameters which are unique to any absorbent and identify it. Parameter no 1 or σ_0/E is the measure of resistance to expansion of the polymer network which its value resembles the final swelling capacity. The parameter no 2 or τ_o is the retardation time which is the time required for fractional swelling to reach 0.632 times of its equilibrium or steady state swelling. This parameter represents the resistance to permeation which is a measure of permeation rate. Shortly speaking, the bigger the parameter no 1, the higher the swelling capacity. On the other hand, the smaller the parameter no 2, the higher is the rate of absorption. The quantitative values of σ_o/E and τ_o for the individual samples were tabulated in *Table.* 3.18. Moreover, the best fitted curves to experimental data can be seen in *Figs.* 3.52 and 3.53.

Table. 3.18 Corresponding values of the model parameters for the fine and coarse particles in case of S2 and S3 series of samples.

Particle size		*250-300 µm*		*Finer than 250 µm*	
Model parameters		*σ_o /E (g/g)*	*τ (sec)*	*σ_o /E (g/g)*	*τ (sec)*
23 (S2.1)	*0.0467**	520	192	530	65
24 (S2.2)	*0.0779*	290	174	325	60
25 (S2.3)	*0.109*	255	150	285	55
27 (S3.1)	*0.0467*	425	18	530	7
28 (S3.2)	*0.0779*	220	21	355	10
29 (S3.3)	*0.109*	205	19.8	310	10

* *Molar concentration of crosslinker to monomer (%).*

With each two series of experiments, the parameter no 1 decreased with crosslinker whether the particles were coarse or fine. At each crosslinker concentration, the parameter no 1 was higher for the finer particles against of their coarser counterparts. Difference between the values of parameter no 1 for the two particles was more pronounced with S3 series.

With S2 series, the parameter no 2 clearly decreased with crosslinker again, whatever was the size of the particles. The quantitative values of this parameter in case of S3 series did not change with crosslinker for both types of particles.

With S2 series, effect of particle size on the parameter no 1 was much lower than on the parameter no 2. Particle size had more effect on the parameter no 1 with the S3 series compared to the S2 series, although the effect on the parameter no 2 was nearly the same, more exactly, a little bit lower than of the S2 series. This indicated that much more accommodation for water should be available between the swollen particles in the case of S3 samples, because of distinct difference in particle sizes of the two series of samples. This was consistent with creation of much more spaces between finer swollen particles. Therefore, any increase in parameter no 1 for the finer particles could be ascribed to the creation of additional spaces for accommodating water. Moreover, decrease in parameter no 2 up to one third of the value for the coarser particles was attributable to an increase in the surface area of the finer particles.

With our previous works in studying the variables affecting absorption properties, it was found that each variable had similar effects on the values of the two parameters. In other words, an increase or a decrease in parameter no 1 was accompanied respectively with an increase or a decrease in parameter no 2. This means any attempt to increase swelling capacity of a typical superabsorbent was faced with a decrease in its rate of absorption. But according to the model data on particle size as another variable, it was surprisingly found that an increase in the swelling capacity was accompanied with an increase in the rate of absorption.

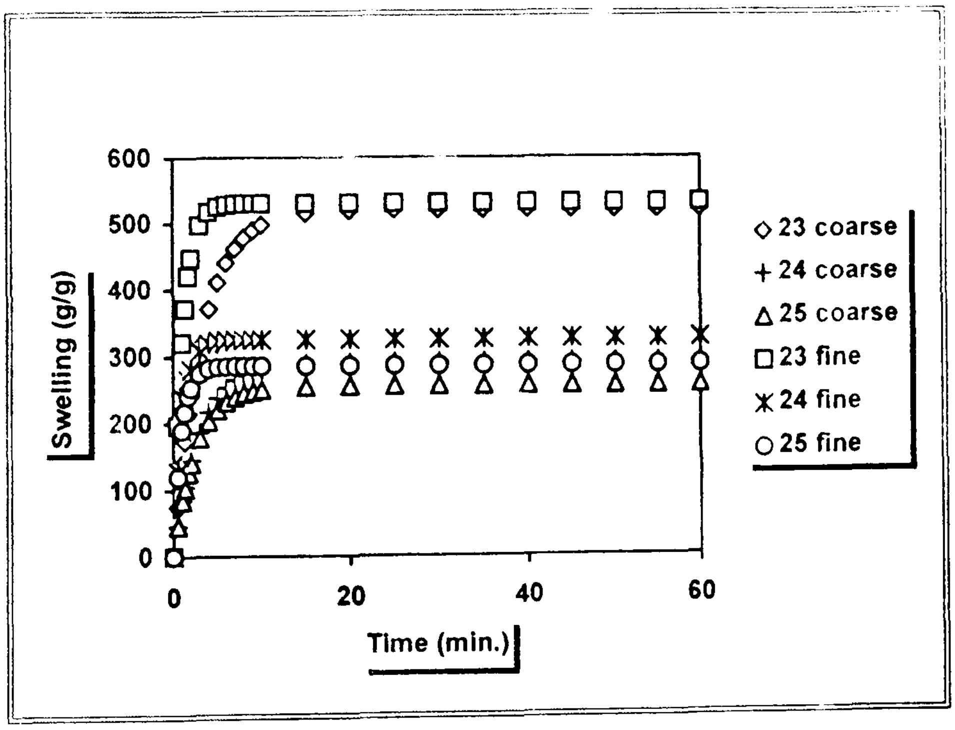

Figure 3.52: Modeled dynamic swelling curves for the fine and the coarse particles of the S2 series.

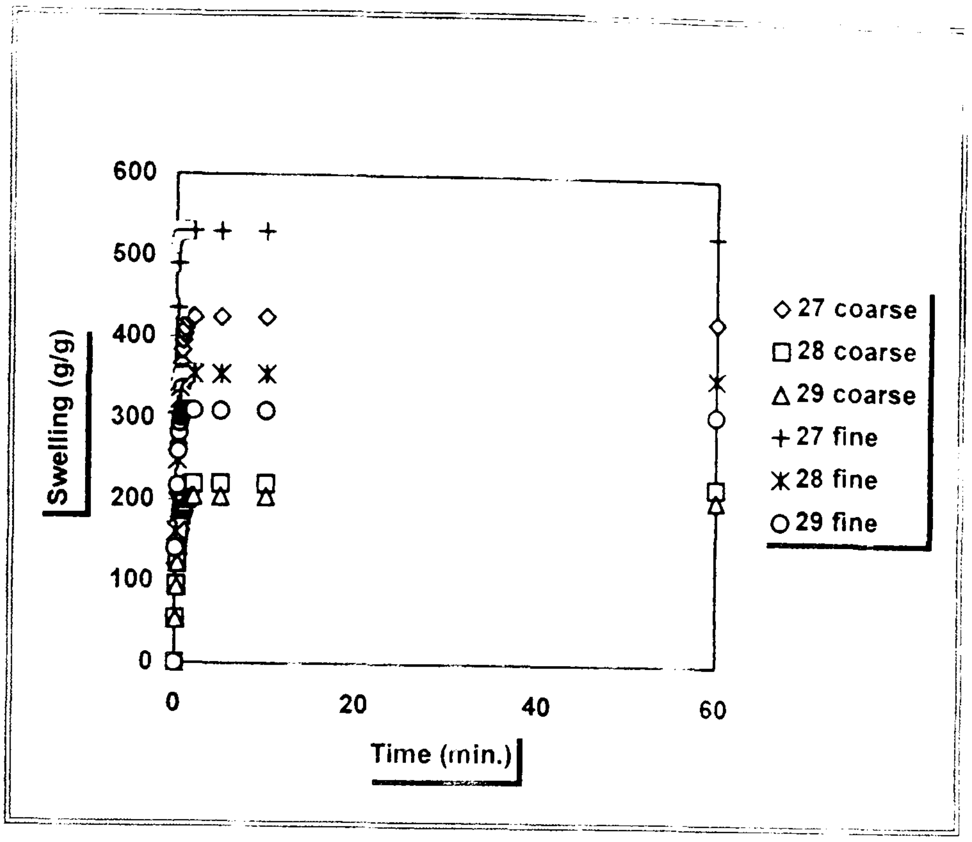

Figure 3.53 Modeled dynamic swelling curves for the fine and the coarse particles of the S3 series.

3.6.3 Effect of the ionic strength

The effect of other external parameters, *i.e.* pH, composition, temperature and ionic strength of the swelling media on swelling properties have been extensively studied [59-61]. All these effects are associated with conformational changes of the polymeric chains. The simultaneous effect of the ionic strength and the crosslinking on swelling in media of different ionic strengths was studied here.

3.6.3.1 Swelling-crosslinker relationship in various swelling media

For each sets of polymerisations the steady state swelling decreased as the ratio of crosslinker to monomer was increased as indicated before. Thus the relationship was explored further by testing different mathematical functions. Generally a power law behavior was obtained with different pair of constants. *Table.* 3.19 displays dependency of steady state swelling to crosslinker concentration in different swelling media.

__Table. 3.19__ Power law constants for swelling dependency of different samples to crosslinker concentration in different swelling media.

	0.0 M		*0.0015 M*		*0.015 M*		*0.15 M*	
Expts.	*k*	*n*	*k*	*n*	*k*	*n*	*k*	*n*
S1 (19-21)	619	0.1	388	0.063	169	0.06	64	0.04
S2 (23-25)	72	0.58	83	0.38	53	0.29	23	0.24
B1 (30-33)	63	0.51	78	0.35	49	0.25	22	0.19

With double distilled water, *i.e.* salt-free water, the power law exponent (n) was found to be 0.1, 0.51 and 0.58 which indicates that swelling capacities of the materials for the different systems have different sensitivity to crosslinker concentration. In other words a minute change in crosslinker concentration for the S2 and B1 series has a very big effect on the final swelling values, which is contrary to the observation for the S1 series. Qualitatively this observation is also valid for the swelling in other swelling media but in different quantitative terms. According to the figures, the dependency of swelling to crosslinker concentration changes with ionic strength of the swelling media. For instance, with the S1 series the value of the exponent (or sensitivity of swelling to crosslinker concentration) in salt free medium reduces down to 60% of its value in physiological solution which contains 0.9 w/w % NaCl. With the two other set of experiments the reduction in sensitivity was found to be 58% and 62% respectively which are very close to each other. This means that increase in ionic strength of the swelling medium results in decrease in dependency of swelling to crosslinker concentration. Moreover, with different series there is a similar point beyond which the swelling dependency to ionic strength of the swelling media is not appreciably changed. This occurs at about 0.0005M salt concentration.

3.6.3.2 Swelling-salt relationship at different crosslinker concentration

To make *Table.* 3.20, the ultimate swelling of each product was measured in a series of selected swelling media (presumably infinite, 0.15, 0.015 and 0.0015 M aqueous NaCl solutions) and related to its corresponding crosslinker concentration. Moreover, the amount of swelling in highly concentrated saline solution (or where the salt concentration is infinity) was truly assumed to be zero.

Table. 3.20 Power law constants for swelling dependency of different samples to salt concentration for different crosslinker concentration.

Expt. (code)	*[C]/[M] mol%*	*K*	*n*
19 (S1.1)	*0.238*	33.4	0.398
20 (S1.2)	*2.30*	31.48	0.389
21 (S1.3)	*4.58*	27.77	0.383
23 (S2.1)	*0.047*	27.43	0.366
24 (S2.2)	*0.078*	21.67	0.354
25 (S2.3)	*0.11*	21.05	0.348
30 (B1.1)	*0.0078*	24.48	0.445
31 (B1.2)	*0.016*	23.96	0.408
32 (B1.3)	*0.047*	18.29	0.402
33 (B1.4)	*0.078*	19.36	0.352

As generally be seen with each series of experiments, the value of the exponent reduced through the range of crosslinker studied. In simple statement, swelling capacity of the highly crosslinked samples show less dependency to the salt concentration of the swelling medium than the samples with lower crosslinker dosage.

3.6.3.3 Expansion factor

The effect of crosslinker concentration on swelling in different salt concentrations can be better seen in following table (see *Table.* 3.21).

Table. 3.21 Dependency of the dimensionless swelling factor to crosslinker concentration.

Expt.	*[C]/[M] mol%*	$\alpha^*_{0.0015}$	$\alpha_{0.015}$	$\alpha_{0.15}$
22 (S2.0)	*0.016*	0.53	0.24	0.08
23 (S2.1)	*0.047*	0.56	0.27	0.102
24 (S2.2)	*0.078*	0.74	0.37	0.14
25 (S2.3)	*0.11*	0.77	0.41	0.15
26 (S3.0)	*0.016*	0.57	0.23	0.1
27 (S3.1)	*0.047*	0.61	0.23	0.12
28 (S3.2)	*0.078*	0.83	0.39	0.14
29 (S3.3)	*0.11*	0.70	0.32	0.11
30 (B1.1)	*0.0078*	0.56	0.21	0.07
31 (B1.2)	*0.016*	0.67	0.27	0.1
32 (B1.3)	*0.047*	0.76	0.33	0.11
33 (B1.4)	*0.078*	0.82	0.39	0.16

Series	*[C]/[M] mol%*	$\alpha_{0.0015}$	$\alpha_{0.015}$	$\alpha_{0.15}$
S2	*0.016-0.11*	0.53-0.77	0.24-0.41	0.08-0.15
S3	*0.016-0.11*	0.57-0.83	0.23-0.39	0.1-0.14
B1	*0.0078-0.078*	0.56-0.82	0.21-0.39	0.07-0.16

**α: The ratio of swelling in saline to swelling in salt-free water. The subscripts denotes the molar salt concentration.*

For each absorbent, its swelling capacity in saline media was divided by its swelling capacity in double distilled water. The ratio was called expansion factor or parameter, α. This parameter can be varied within the range of 0-1.0 or even more . At lower extreme, the polymer should be highly sensitive to the salt present in swelling medium. In other words swelling decreases with salt concentration. This displays the swelling behaviour of anionic and cationic polymers. When the parameter approaching unity, the polymer structure is becoming inert to salt and its swelling capacity becomes similar in saline and salt-free water. This behaviour is limited to the non-ionic and rigid chain polymers. With the values greater than unity, again salt sensitivity of the polymer structure increases. In other words, swelling increases with salt concentration. This behaviour can be seen in amphiphilic or betaine polymers.

In each series and swelling medium, α was increased with increase in crosslinker concentration but its range of variation was distinctly different in various media. With S2 series, the parameter α was varied in the range of 0.53-0.77 for 0.0015 M saline solutions. An almost same range was also observed for the S3 and B1 series. This range was changed to 0.24-0.41 for 0.015 M saline in case of S2 series. Again, nearly similar range was observed for other series. For highly concentrated saline, the variation range of α was 0.08-0.15 which was closely repeated for other series. These observations indicate that the range of α is primarily dependent on the crosslinker concentration and the ionic strength of the swelling medium and, does not change with monomer composition and method of synthesis for the absorbents studied here.

3.6.3.4 An explanation for the swelling observations

Linear polymers in solution usually display two types of configuration depending on the dielectric constant of the solvent. In a high-dielectric medium like water, the dissociable groups of the polymer chain are readily ionized and the macromolecules assume an extended configuration due to the repulsive electrostatic interaction between charged groups. Whereas in a low-dielectric medium such as saline or non-aqueous solvent, the ionization process is suppressed and the macromolecules remain in a random or coiled configuration. The latter is typical of many non-ionic polymeric systems[62].

The superabsorbents studied here were basically linear polymers which crosslinked by applying a tetrafunctional crosslinking agent. Although all the polymers obtained were ionic according to their different α values in various salines, but their swelling behaviour was changed towards the non-ionic and rigid-chain polymers, as α approached unity because of increase in the crosslinker concentration. This can be ascribed to an increased elastic modulus of the polymer network. In other words, because of more structural rigidity due to an increase in the crosslink density, the polymer chains are less perturbed in saline depending on the amount of crosslinker.

Thus the ratio of the two swelling values can presumably be a proper measure of chain rigidity and may be a hopeful device to assess, calibrate and classify the structures of various rigidity.

3.7 Creating a porous structure

Based on our model data in foregoing section, a decrease in size of the particle was led to a simultaneous increase in absorption capacity and rate. This was achieved through an increase in the parameter no 1 and a decrease in the parameter no 2. Moreover, this observation was ascribed to an increase in the free volume, which enlarges the capillary contribution of swelling. In other words, the swelling characteristics of the finer samples was improved, because of the capillary action of the free spaces between the water swollen particles. This conclusion brought us to try for creating absorbents of porous structure.

3.7.1 Increased monomer concentration

In most of the commercial manufacturing of superabsorbents [47], a high monomer concentration is desirable. The advantage taken here is the elimination of the drying process, by means of an increased heat of polymerisation. But, there is a serious need for using higher water-soluble ingredients, especially the crosslinker and the initiator, within the superabsorbent formulation. The insolubility problem is presumably due to saturation, increased ionic strength of the reacting medium and the very low amount of water present in highly concentrated formulations.

The solubility of potassium peroxy disulphate in water is limited, so that it requires 50 parts or 25 parts water at 40 °C, while the ammonium persulfate is freely soluble in water. [63] On the other hand the water solubilities of alkali acrylates increases with increasing atomic radius of the alkali metal (Na, 1.896 A° and K, 2.349 A°). It means that higher monomer concentration can be achieved by using potassium hydroxide rather than the sodium hydroxide as neutralizer. So the potassium persulphate and the sodium hydroxide were replaced by ammonium persulphate and potassium hydroxide respectively (see Expt. 73). It is not justified to compare swelling property of the present sample with its counterpart (Expt. 30), since although the initiator is different, it has been shown that monomer reactivity ratios, overall copolymerization rate and some electrochemical properties of the copolymers of acrylamide and acrylate salts depend on the nature of the cation in the acrylate salt [64]. Apparently, the water uptake of the copolymers is also related to the nature of the metal counter-ion in the acrylate salt.

Table. 3.22 shows the absorption behavior of the sample obtained from the Expt. 73.

Table. 3.22 Dynamic swelling feature of the samples from the Expts. 30 and 73-74.

Time min.	0.0	1.0	2.0	5.0	10.0	30.0
Swelling (g/g)						
Expt. 30	0	173	303		747	779
Expt. 73	0	181	313	534	651	626
Expt. 74	0	200	271	306	302	

As can be seen the time to reach equilibrium swelling is about 10 min. which is rather high as was for its counterpart. An increase in monomer concentration (Expt. 74) resulted in ultimate swelling of 300 g/g and the time needed to take water up to this point was about 5 min. A remarkable point here is their corresponding times to reach 0.632 of their final swelling values (retardation time) which as mentioned before is a measure of the rate of absorption. The quantitative values of the parameter for the products of Expt. 73 and 74were 170 and 45 sec respectively. This increase in absorption rate was obtained at the expense of a decrease in the final swelling value down to half. As quoted in detailed explanation of the Expts. 73 and 74, a big difference between these two samples was, their nature at the gel point. The former was obtained as a rubber, whilst the latter obtained in glassy state. According to the *Sec.* 3.4.7, the glass nature of the gel obtained from the Expt. 74, prevents the reaction from further facile polymerisation, which presumably results in less monomer conversion to polymer and hence lower swelling capacity. On the other hand, this modification, *i.e.* an increase in monomer concentration was led to an increase in the rate of absorption, which is in part due to the creation of a porous structure (see *Fig.* 3.54).

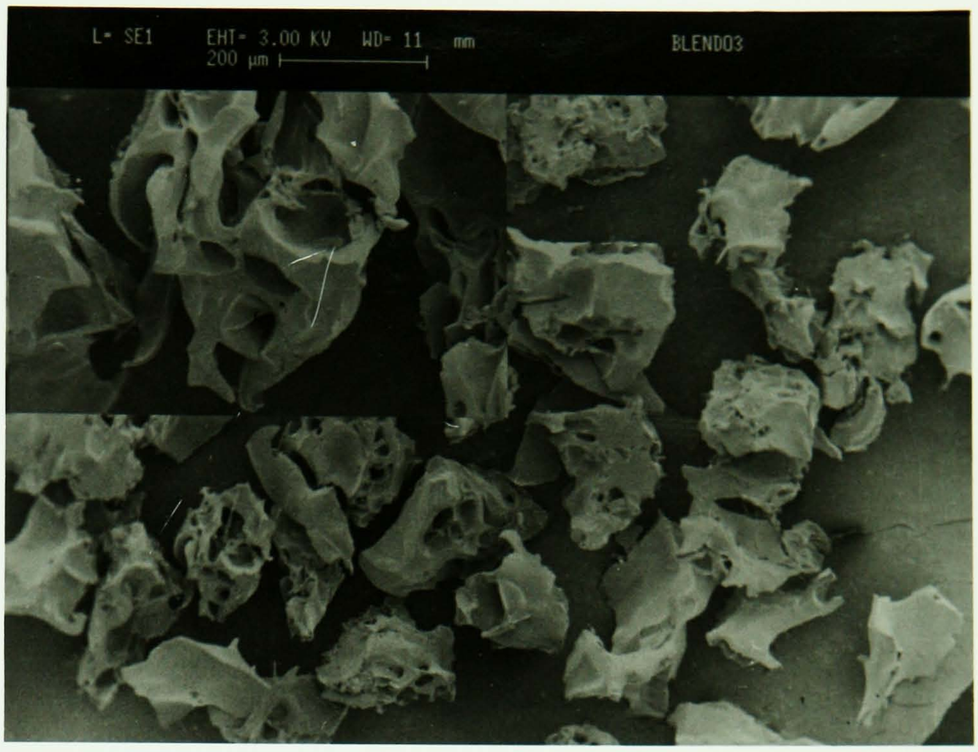

***Figure* 3.54**: SEM micrograph of the sample obtained from the Expt. 74.

3.7.2 Effect of introducing filler (non-etched samples)

The basic idea was to create porous structure in another way. It is common to polymer field, blending the compounds of various structures (*e.g.* one rather hydrophilic and the other rather hydrophobic or one plastic and the other one metal) followed by removing one of the components [*e.g.* etching with a suitable solvent or burning at the plastic decomposition temperature (as applied to manufacture cellular ceramics)] to produce cellular structure. This idea was conducted here with a hydrophilic polymer (say, superabsorbent) and a hydrophobic polymer [poly (vinyl chloride)]. The latter in its powder form was introduced into the superabsorbent formulation (before reaction). Although the basic idea taken here was removing by an appropriate solvent of the PVC particles from the superabsorbent matrix (etching), with our preliminary experiments, not indicated here, the foaming of the reacting medium was observed due to the presence of PVC powder which brought us to conduct some experiments without attempting to etch.

3.7.2.1 General observations on the reaction

The Expt. 73 was chosen as a reference matrix and various amounts of the poly (vinyl chloride) powder ranging 2.5-12.5 wt.% (based on matrix weight) was incorporated according to the Expts. 75-79.

Table. 3.23 displays the important features of the experiments. The data in column 5, is the temperature during the exothermic reaction. The time to reach gel point and amount of the materials evaporated during the reaction were recorded respectively in columns 6 and 7. The PVC powder was considered as a filler and its concentration in the matrix formulation can be seen in the column 3.

Table. 3.23 Features of the reaction in case of PVC-filled samples.

Expt.	*Matrix weight (g)*	*Filler weight (g)*	*Bath temperature °C*	*Temperature rise °C*	*Gel time Sec.*	*Evaporated material %*
73	*20*	*0.0*	80	114	113	20.5
75	*20*	*0.5*	80	99	91	14.7
76	*20*	*1.0*	80	103	90	15.9
77	*20*	*1.5*	80	103	106	14.5
78	*20*	*2.0*	80	101	104	11.8
79	*20*	*2.5*	80	100	93	12.2

With the Expt. 73, the reaction mixture temperature at gel point rose up to 20-34 °C based on the setting bath temperature. But the temperature rise was dropped by incorporating the filler, and remained almost the same through the rest of the reactions.

The remarkable difference between the blank (Expt. 73) and others was occurrence of foaming for the latter formulations. The foaming was visually observed more excessive for the higher filler-loaded formulations. The time required to change the nature of the reaction liquid to a rubbery viscous mass, so-called the gel time was not followed a regular trend. But the maximum gel time was observed for the blank formulation (Expt. 73). The amount of ingredients evaporated (presumably monomer/water mixture) during the synthesis was decreased by increasing the loading, which may be due to the suppressing exothermicity indicated by lowered temperature rise and also the physical obstruction of the PVC for the evaporation of volatile.

3.7.2.2 Swelling observations

The swelling behavior of the individual samples were recorded in *Table.* 3.24.

Table. 3.24 The swelling features of the PVC-filled samples.

Expt.	*Filler/matrix wt.%*	*Active material wt.%*	*Observed equilibrium swelling based on blend material (g/g)*	*Expected equilibrium swelling based on active material (g/g)*
73	0.0	100.0	450	450
75	2.5	97.56	448	459
76	5.0	95.24	421	442
77	7.5	93.02	354	381
78	10.0	90.90	393	432
79	12.5	88.88	400	450

Although the foaming of the reaction medium became more severe by increasing loading of filler, the amount of equilibrium swelling (for the filler-contained sample, column 3) followed a decreasing trend. It is clear from the data in last column of the *Table.* 3.24, that the PVC powder cannot absorb any water per se. In other words, the chosen filler was inert towards swelling and the swelling was apparently due to the active material present. These experiments were repeated thrice and overall trend observed was similar, although the figures recorded in the tables were not exactly reproduced.

3.7.3 Effect of etching

Another effort (Expt. 80) was to etch the superabsorbent matrix which was attempted with the sample of the Expt. 78 containing 10 wt.% filler. Unexpectedly 7.0 wt.% of the original material was removed by the solvent. Scanning electron micrographs of the original and treated sample can be seen respectively in *Figs.* 3.55 and 3.56. The swelling behavior of the blank (Expt. 78) and the etched material (Expt. 80) have been recorded in *Table.* 3.25.

Table. 3.25 The swelling features of the filler loaded and treated materials.

Expt.	*Active material wt.%*	*Observed swelling after 1 min.*	*Expected * swelling after 1 min.*	*Observed swelling after 24h*	*Expected * swelling after 24h*
78	90.90	46.1	50.7	466	512.6
80	97.90	58.2	59.4	504	514.8

* *Calculated based on the active material.*

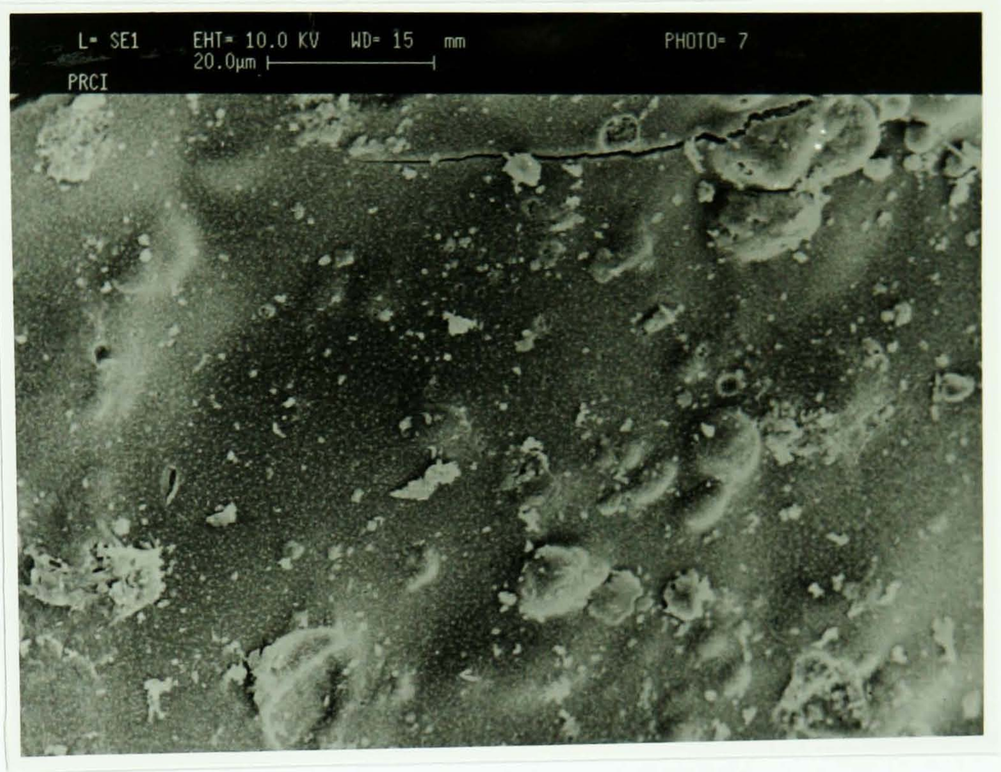

***Figure* 3.55**: SEM micrograph of the PVC-contained superabsorbent.

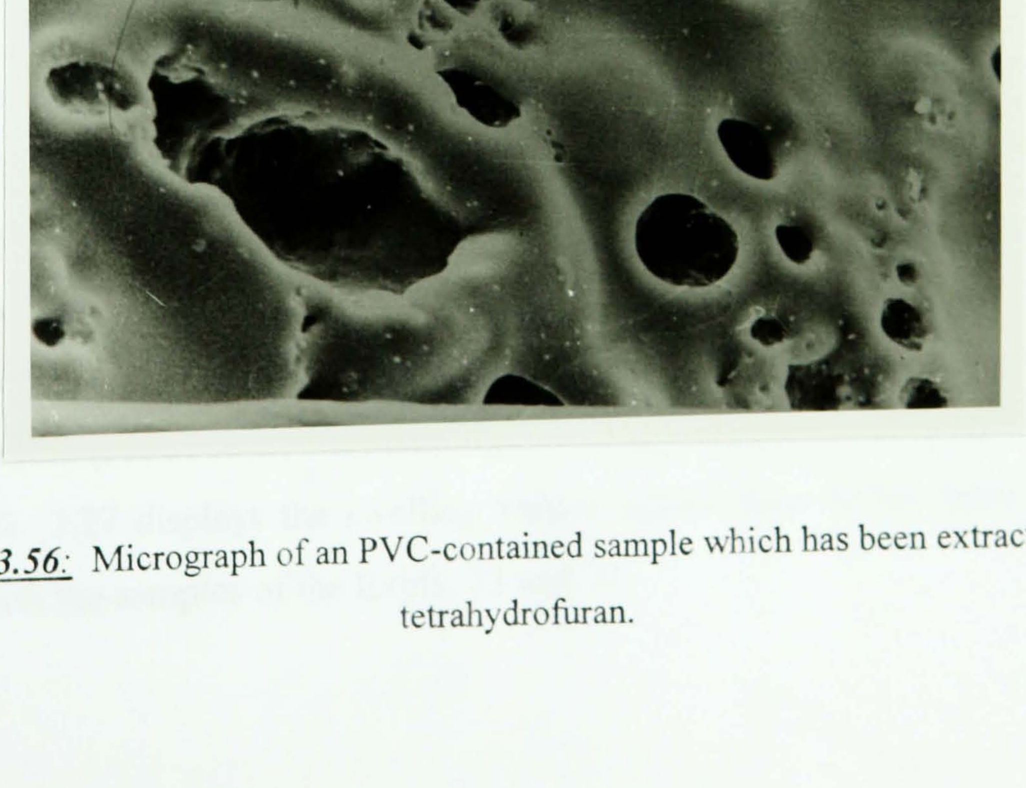

Figure 3.56: Micrograph of an PVC-contained sample which has been extracted with tetrahydrofuran.

Again assuming that swelling observed is only due to the superabsorbent present, it seems that etched material has no advantage over non-etched sample as indicated by their swelling values after 24 hours. Surprisingly this is not the case for the swelling values after 1 min. With the blank sample, expected value of swelling based on active material, after 1 min. was 50.7 g/g, while the corresponding value for the treated material was 59.4 g/g. Keeping the above assumption in mind, the same value (say, 50.7g/g) of swelling is to be expected for the treated sample which shows +17.1% increase in swelling within the period of 1 min. This is clearly due to the increased surface area obtained after etching treatment of the original material (see *Fig.* 3.56). Thus this typical treatment can help to attain faster rate of absorption, although the final swelling values are not being very affected.

3.8 Our samples against commercials

A number of commercial samples was selected among a series of marketed superabsorbents (see *Table.* 3.26) and examined for their swelling behavior.

Table. 3.26 Features of a number of commercial superabsorbents.

Trade name	*Company*	*Chemical name*	*Appearance of the dry material*	*Equilibrium water absorption*	*Water absorption rate*
Hydrosoil	Softron	Potassium polyacrylate	White powder	Medium	Very fast
Alcosorb 400			White powder	High	Medium
PR 3005 KB	SNF Floerger	Potassium polyacrylate	Off-white granules	Medium	Medium
PR 3005 B	SNF Floerger	Sodium polyacrylate	Off-white granules	Medium	Medium

Most members of the acrylic family of superabsorbents in the market are potassium or sodium based. The commercial types shown in *Table.* 3.26 are also based on potassium or sodium which are solution-polymerised. As assayed through the swelling measurements, a variety of swelling behavior can be observed *e.g.* medium amount of water uptake at very high rate (Hydrosoil), medium amount of water absorption capacity at medium rate (PR 3005 B, KB) and high swelling capacity in medium rate (Alcosorb 400). *Table.* 3.27 displays the swelling values against time of the latter commercials together with the samples of the Expts. 73 and 74.

As already found the swelling model is a valuable tool to predict and compare the swelling properties of different superabsorbents. Thus all the swelling figures were fitted with the best mathematical relationships to find the values of the parameters no1 and 2 as can be seen in *Figs*. 3.57-3.62. The model data were quoted in *Table*. 3.28.

Table. 3.27 Dynamic swelling features of a number of commercial superabsorbents together with of our laboratory counterparts.

Time sec	*Hydrosoil*	*Alcosorb 400*	*PR 3005 KB*	*PR 3005 B*	*Expt. 73*	*Expt. 74*
0	0*	0	0	0	0	0
15	78					96
30	114					
45	145					185
60	182	154	139	120	181	200
90	208					
120	227	262	218	188	313	271
180	240					
300	260	434	323	299	534	306
600	270	498	363	350	651	302
1800	258	583	373	349	626	
3600		552	330	334	590	

* *In terms of g/g.*

Table. 3.28 Corresponding model data for the commercial and synthesised superabsorbents.

Samples	σ_o/E *g/g*	τ_o *sec*	$\sigma_o/E\tau_o$ *g/g. sec*
Hydrosoil	265	56	4.73
Alcosorb 400	570	200	2.85
PR 3005 KB	370	140	2.64
PR 3005 B	350	140	2.50
Expt. 73	630	170	3.70
Expt. 74	300	45	6.66

According to the model, the best swelling properties are acquired at maximum and minimum values for the parameters no 1 and no 2 respectively. Thus the ratio of the two parameters can be a good indication of swelling properties. As far as the capacity of absorption (parameter no 1) is concerned, the materials are being ranked according to the following order:

Expt. 73> Alcosorb 400> PR 3005 KB> PR 3005 B> Expt. 74 > Hydrosoil

When the rate of absorption (value of the parameter no 2) is of importance, the above order can be rearranged to the following:

Expt. 74> Hydrosoil> PR 3005 KB,B> Expt. 73> Alcosorb 400

Finally the ratio of the two above seems to be a better approach to describe the swelling properties in which the capacity and rate of absorption are both included within a same term. The higher the ratio is, the better the swelling properties would be expected. Thus the following order is obtained:

Expt. *74> Hydrosoil>* Expt. *73> Alcosorb 400> PR 3005 KB> PR 3005 B*

Considering the ratio of the two parameters, the Expt. 74 is comparable with Hydrosoil and the Expt. 73 is comparable with the others. With the former in which the rate of absorption is highlighted, the Expt. 74 shows better performance over the commercial Hydrosoil, whilst its equilibrium swelling capacity is also rather higher. On the other hand where the capacity of absorption is highlighted, the Expt. 73 performs better than its comparable commercials.

3.9 Validity of the two parameters model

Based on the numerous experimental swelling data we have found throughout this work, followed by fitting them into an appropriate mathematical relationships, *i.e.* Voigt model expression (see *Equation.* 3.3), the standard deviation of the model was found about ±2.7. Although a very good fit of the experimental swelling data would be expected from our model, in some circumstances, we found that the model couldn't predict the swelling properties.

In some cases, as clearly be seen in *Figs.* 3.57-3.61, the experimental swelling rapidly approached to its maximum value, followed by a slight fall to the equilibrium value. The model couldn't appropriately follow the experimental data in this region of the dynamic swelling curve. This phenomenon has already been named, *overshoot sorption*.

Water uptake overshoot was observed in polymer gels containing water soluble salts in the form of either drugs or residual initiator. This behavior was attributed to an initially large chemical potential or osmotic driving force for swelling due to the presence of excess solute within the gel. Subsequently, the solute diffused out of the gel, thereby reducing this driving force and leading to deswelling of the network. Eventually the concentration inside and outside the network were equalised and the network reached its final equilibrium.

We expect that a polymer soluble fraction may lead to overshoot sorption behavior in a manner similar to the latter. At the gel point, there are enough crosslinks to produce a macromolecular network, which extends throughout the reaction mixture. Subsequently, the mixture contains a gel fraction, consisting of the polymer network, and a sol fraction, which contains unreacted monomer and polymer chains that have not become incorporated into the network. Before the gel point, the reaction mixture is 100% sol fraction. After the gel point the sol fraction decreases monotonically as material is incorporated in the network. At 100% conversion, most of the polymer is incorporated into the gel; however, a small fraction remains in the sol as we quoted in *Table.* 3.6.

The bigger difference between the overshoot sorption and the equilibrium swelling is expected, if a high amount of the extractable materials are occluded within the network [46].

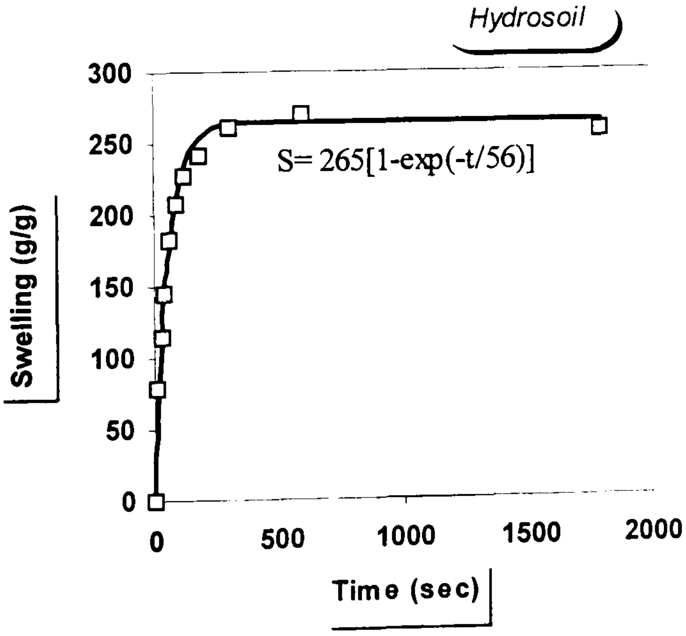

***Figure* 3.57**: Modeled and experimental dynamic swelling curves for Hydrosoil, a commercial superabsorbent.

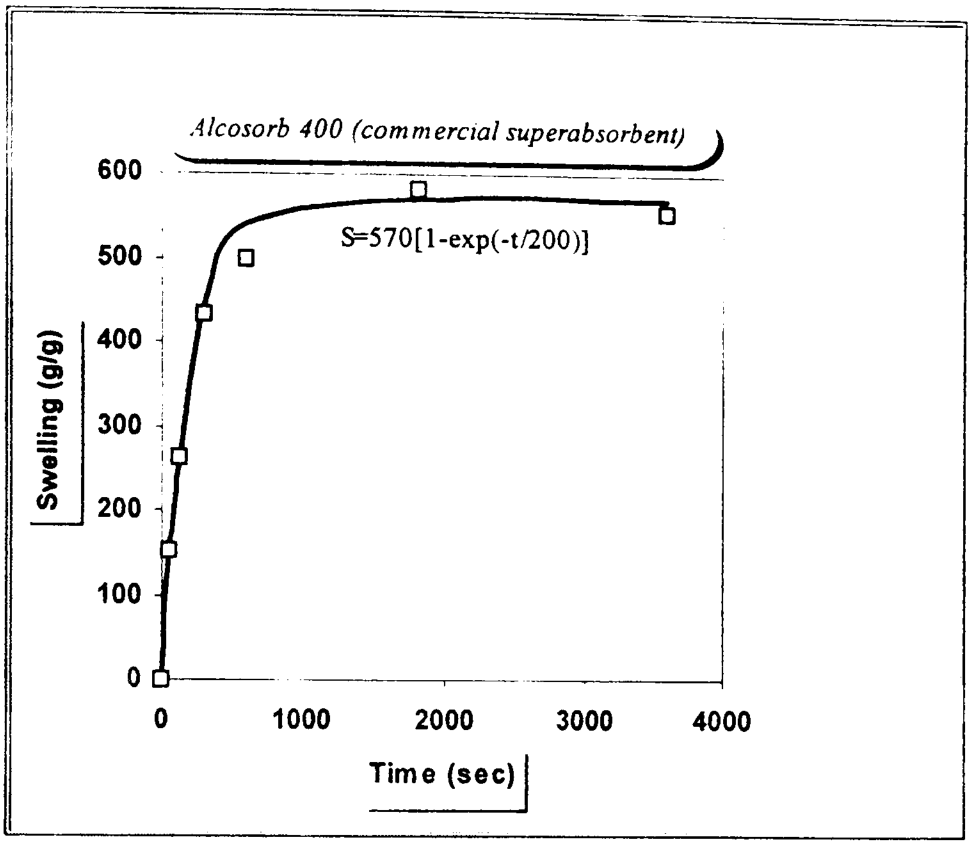

***Figure* 3.58**: Modeled and experimental dynamic swelling curves for Alcosorb 400, a commercial superabsorbent.

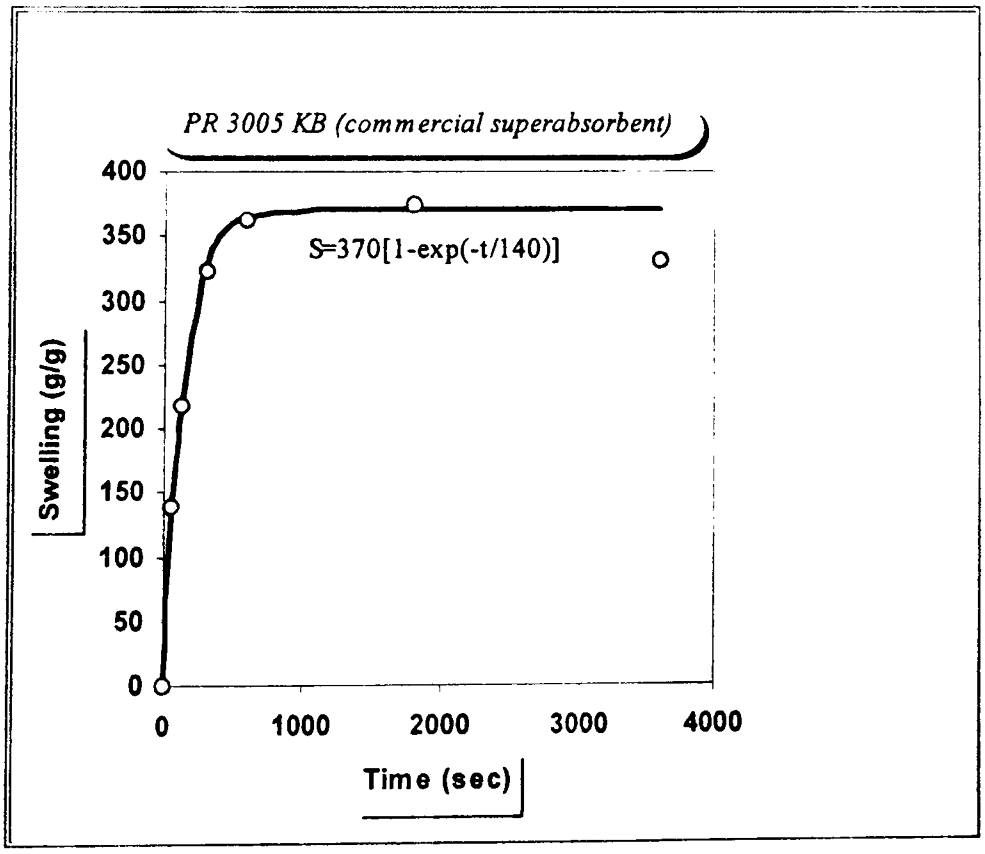

***Figure* 3.59**: Modeled and experimental dynamic swelling curves for PR 3005 KB, a commercial superabsorbent.

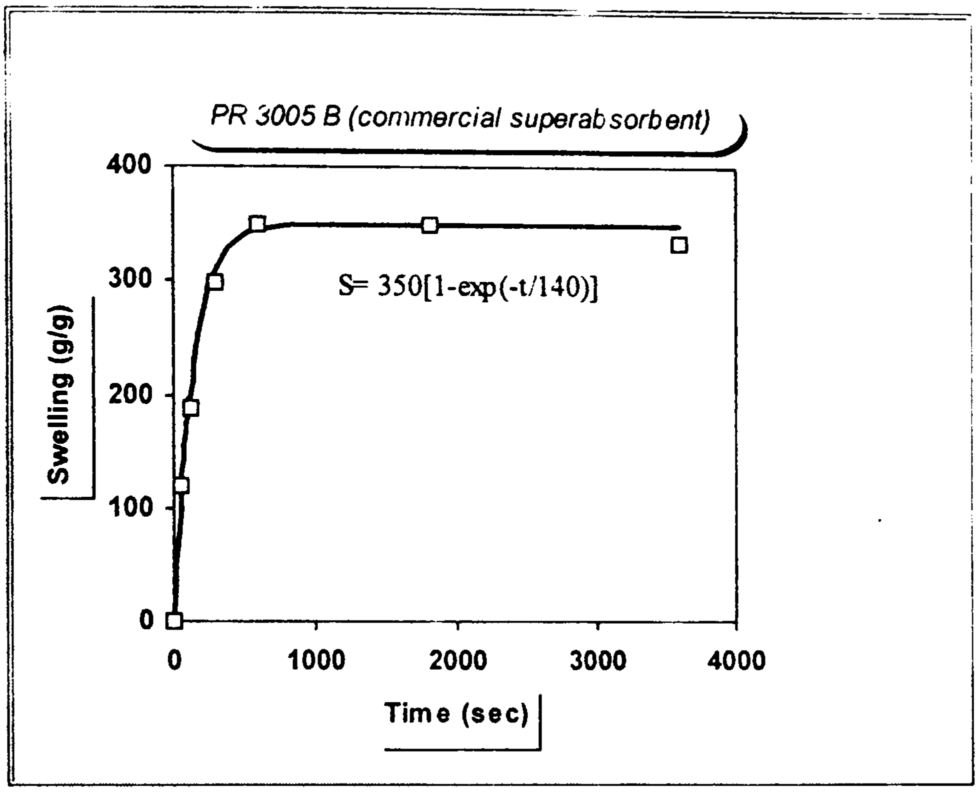

***Figure* 3.60**: Modeled and experimental dynamic swelling curves for PR 3005 B, a commercial superabsorbent.

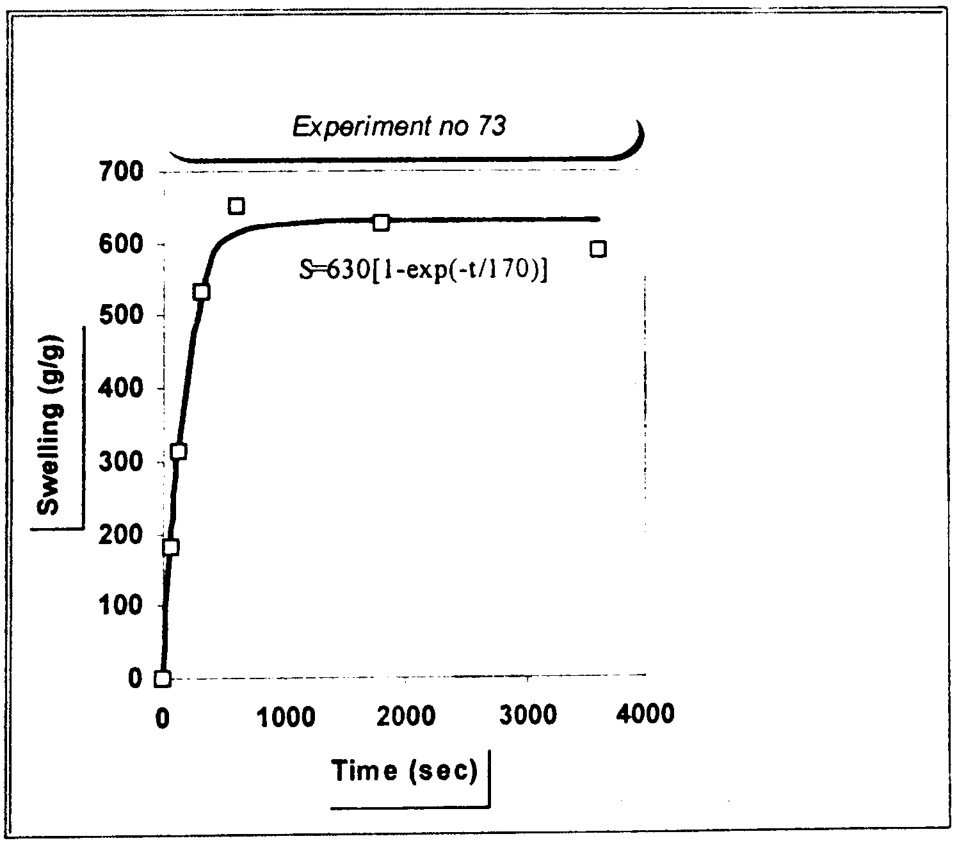

***Figure* 3.61**: Modeled and experimental dynamic swelling curves for the material obtained from the Expt. 73.

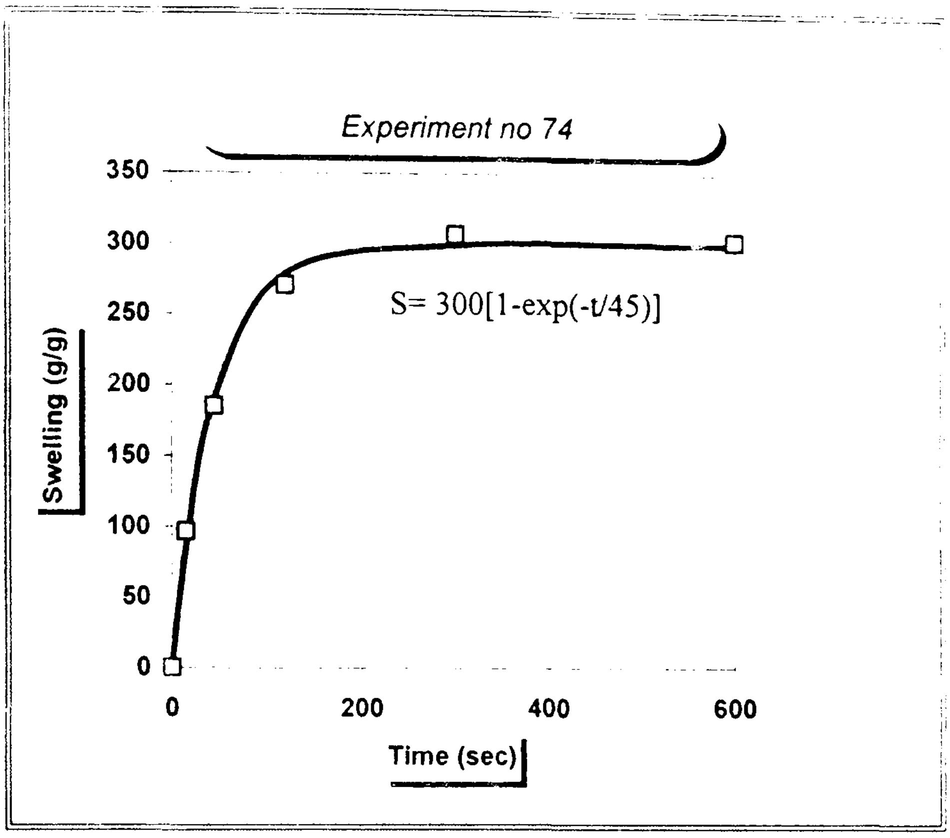

Figure **3.62**: Modeled and experimental dynamic swelling curves for the material obtained from the Expt. 74.

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Chapter 4: CONCLUSIONS

4.1 Preliminary trials

An inverse suspension polymerisation shows high degree of sensitivity to the variables of the reaction system. With our preliminary experimentals to produce a product in particle form, unexpectedly, the product was obtained in either a granular form or as lumps. Although a granule or a lump, as a reaction product could potentially act as a superabsorbent, a huge number of particles could be occluded in them which were not accessible to water. So, a long time is needed for water to reach to the center of a granule or a lump, which remarkably reduces the rate of absorption.

The sorbitan monostearate was not useful at all, to obtain the product in desirable shape. And, any further attempts with it was complicated by the solubility of the polymer in water. On the other hand, we thought that the water present in the reacting medium may be responsible for obtaining the product in undesirable shape. But, this was not the case according to unsuccessful dewatering attempts we made by vacuum distillation and using a super water absorbent.

The use of sorbitan monooleate as a more powerful water in oil surfactant than the sorbitan monostearate, brought us to conclude that, the former acts better and at least helps to break the lump into the granules. But, again, higher loading of it resulted in a water-soluble product.

Using a couple of so-called co-surfactants like poly (vinyl alcohol) or sodium salt of carboxymethyl cellulose also did not lead to a desirable product. Surprisingly, the amount of equilibrium swelling of the absorbent system increased by using them.

A desired product in particle form was obtained, using a certain amount of ethyl cellulose as a co-surfactant. So for the rest of inverse suspension experiments, a mixture of a micromolecular and macromolecular surfactants were used, as well as using methanol as a powerful dewatering agent. Therefore, the latter modifications were included within the preparation recipe, in order to survey the effects on swelling behaviour of the main variables.

4.2 Crosslinking by ethylene glycol dimethacrylate and methylene bisacrylamide

Crosslinking by ethylene glycol dimethacrylate resulted in a material of very high swelling capacity and visually of high gel strength. A major change in the crosslinker concentration led to only a small change in the amount of swelling. In a parallel study of the effect on swelling of a water-soluble crosslinker, it was found that a water soluble crosslinker is much more efficient than an oil-soluble counterpart to bring the swelling under effect. So that, a minute change in concentration of the former, led to a big change in the swelling capacity.

4.3 Inclusion of acrylamide

Increasing the non-ionic nature of the absorbent structure had a remarkable influence on the rate of absorption, although the absorption capacity was decreased. Moreover, polymerisation of a same formulation as in solution, led to a high swelling material, but still poor in rate and capacity of absorption compared to its inverse suspension counterpart.

4.4 The swelling model

These above-mentioned observations, constituted a base for devising a model to seek the relationships between the polymerisation variables and the swelling properties. For instance, in the case of EGDMA-crosslinked absorbents, the swelling smoothly increased to a very high constant value. On the other hand, with the acrylamide-containing absorbents, the swelling was abruptly increased to a moderate constant value. These two distinct swelling behaviours and also other dynamic swelling observations show a good fit to the strain response of a two parameter Voigt model to any applied stress. By assigning the spring parameter, the significance of resistance to expansion of the polymerised network and the dashpot parameter, the significance of resistance to permeation, the swelling characteristics of the different absorbents could be accounted for in more fundamental terms.

The model approximates to Case II sorption in the early stages of the swelling process and to Case I in the later stages. This shows that the rate -controlling process occurring in the early stages is the advance of a water front through the polymer with a sharp profile which generates high stresses on the polymer network and that swelling is restricted by the rate at which water can permeate into the dry polymer network or by the rate at which the network can expand.

Based on our observations, the water diffusion rate was increased by the two factors, *i.e.* the inclusion of acrylamide into the polymer structure and the crosslinker concentration. The first observation was mainly attributed to an increased mobility of the structure upon contacting with water (as the data for the water bound to the polymer indicated) and the screening effect of this comonomer on the carboxylate anions along the polymer backbone. The second observation was mainly attributed to an increased elastic modulus of the network and to restricting the collapse of the polymer network during the drying process, which presumably creates more free volume to accommodate water.

The inverse suspension products showed higher rate and capacity of absorption than of the solution counterparts, of course at a same crosslinker concentration. The reasons can be found somewhere in the process of manufacturing. The big difference was the atmosphere under which the polymerisation was carried out. With all the inverse suspension formulations, a nitrogen blanket was used, whilst with the solution systems, no inert blanket was provided. The other difference was the time of reaction, which was much longer for the suspension system. Moreover, at a same crosslinker concentration, the extractable materials within the solution products was more than for the inverse suspension products. These can be responsible for the decreased swelling characteristics in the solution products.

For the solution and inverse suspension polymerisation, in the presence of MBA as a crosslinking agent, the steady state swelling was inversely proportional to the square root of the molar ratio of the crosslinker to monomer. This is close to, but not identical, the thermodynamically derived 0.6 power relationship obtained by Flory, for the non-ionic polymers. In the case of EGDMA-crosslinked materials, the dependence was much weaker. This can be attributed to the partitioning of the oil-soluble crosslinker mainly into the continuous organic phase.

4.5 Temperature and Initiator

Regarding our preliminary investigations of the solution process, which is used industrially for producing superabsorbent polymers, we found that unrestricted access of the reaction mixture to oxygen and unrestricted evaporative losses of water can complicate the polymerisation of the acrylic monomers and the swelling characteristics of the products.

The existence of an inhibition period, especially at long reaction times was attributed to the formation of peroxy radicals with low reactivity, as has been established in the past for similar monomer systems. The ending of the inhibition period with the onset of rapid, apparently normal polymerisation is thought to result from the accumulation of polyperoxide which eventually yields enough active free radicals to overwhelm the inhibiting effect of the oxygen and set off a self accelerating process in which the heat released by normal polymerisation increases the rates of peroxide and initiator decomposition and the rise in viscosity restricts the inward flow of oxygen and outward flow of heat.

The delay caused by the inhibition period provided more time for water to be lost by evaporation and at lower temperatures and initiator concentrations the losses became large enough to raise the concentration of monomer into the range where runaway polymerisation has been reported for acrylic monomers, even in the absence of polyperoxide. Both effects may have combined to induce runaway polymerisations at long reaction times.

The highest degrees of swelling for reaction product were obtained at the higher temperatures (140 - 180 °C) and higher initiator concentrations (0.004 - 0.005 mole/mole of monomer) in the ranges covered. Substantial reductions in swelling with decreasing temperature or initiator concentration is attributed to two factors. One is the shortening of kinetic chain lengths as initiation by the polyperoxide became more important. The second is the loss of mobility when the remaining water level became so low at long reaction times that the product changed from a rubbery state to a glassy one. The resulting restriction in molecular mobility is believed to have limited the conversion of monomer to polymer and to have altered the swelling characteristics of the product. Drying the products by heating for a day at 60 °C had two effects. One was to reduce the swelling at short gel times compared with neat, undried product. This was attributed to crosslinking. The other effect was to increase the swelling at long gel times. This correlated with quantities of water extractables from dried products and is attributed to further conversion of monomer to polymer. Applying the Voigt expression to the time dependence of swelling provided further support for attributing decreases in swelling at lower temperatures and initiator concentrations to less conversion of monomer to polymer.

Overall it is clear that the highest degrees of swelling for products made by the solution process without restricting access to oxygen and evaporation are obtained when the reaction conditions such as temperature and initiator concentration favour a short reaction time. Further studies would be needed to check the explanations offered for the various effects of oxygen and evaporation. Usually precautions are taken to avoid these effects in studies of free radical polymerisations and they do not appear to be featured in publications on the subject, even though they might be important in applications such as coatings, adhesives and resin based products where polymerisation occurs in the presence of air. If similar effects occur in these applications as has been observed here then properties are likely to be downrated, particularly at surfaces.

4.6 DSC studies

The existence of an inhibition period and of a sudden rise in viscosity of the reaction medium in solution polymerisations were recognised in the parallel DSC studies. The effect of changing the initiator and temperature on the duration of inhibition period was the same as in bench-scale polymerisations.

4.7 Particle size

The effect of particle size on the swelling properties was also highlighted throughout the work. We showed that, any reduction in size of the particles obtained in inverse suspension systems is accompanied by an increase in capacity and the rate of absorption. With other variables, we found that any increase in the capacity of absorption is associated with a decrease in rate. Surprisingly, the size of the particles was the exclusive variable which simultaneously increased both the capacity and the rate of water uptake. In superabsorbents, the swelling is mainly favoured, because of diffusion. On the other hand, in materials like sponge, water can be absorbed by a capillary action of the pores within the matrix. The increased swelling characteristics in finer particles of a typical superabsorbent can be attributed to creating a capillary action within the superabsorbent matrix. This was presumably because of the existence of free volume between the finer swollen particles. Thus, the swellability of absorbent polymers can be enlarged by a supplementary action of capillaries.

4.8 Ionic strength

Another variable was the ionic strength of the swelling medium. We and others have already found that, the swelling decreases exponentially with the salt present in the swelling medium. This was not a surprising conclusion. But, the crosslinker had a certain effect on this dependency. It was found that, the crosslinker renders the polymer to be much less sensitive to the salt present in the swelling medium. This conclusion was achieved through introducing a dimensionless parameter named "expansion factor" which was seriously sensitive to the amount of crosslinker in a typical swelling medium. The crosslinker changed the swelling behaviour of our anionic superabsorbents into a non-ionic or a rigid chain material.

4.9 Porous structure

The effect of capillary on the swelling brought us to devise provisions to create a superabsorbent of porous structure. This was achieved with an increase in the monomer concentration of the reacting medium. This modification gave rise to the increased rate of absorption, but at the expense of reducing the capacity for absorption. The improvement in rate can be ascribed to the pores within the polymer. The adverse effect on the absorption capacity can be addressed back to the less conversion of monomer to polymer, which is evident from the characteristic odor of unreacted acrylic acid.

The final effort was producing a cellular structure by inclusion followed by removing the PVC particles from the superabsorbent-poly (vinyl chloride) blend. The filler had no effect on the rate and the capacity of absorption, but, it resulted in a severe foaming of the reaction mixture. Moreover, it led to a decreased amount of superabsorbent dusts. Etching by a suitable solvent of the blend, in order to create pores within the matrix, led to improving the rate of absorption to some extent. This treatment had no effect on the capacity for water uptake of the products.

4.10 Further works

After extensive investigation of the influence of the various parameters on the structure and the properties of the acrylic-based superabsorbent polymers studied here, a few areas of further work may prove particularly rewarding.

- Try to find other correlations between various parameters including change of the continuous phase, change in agitator speed, change in water/ oil ratio, change in initiating system of the inverse suspension polymerisation on the swelling properties of superabsorbent polymers and finding a replacement for the ethyl cellulose.

- More work is needed to understand the effect of oxygen and a typical inert blanket on the polymer swelling properties via the inhibition period. Differential Scanning Calorimeter can be useful in this respect.

-Attempting a high temperature synthesis of superabsorbent using a thermally resistant crosslinker like ethylene bisacrylamide.

- Using solid state NMR and neutron scattering techniques to understand the chemical structure of a superabsorbent in more fundamental terms.

- Try to modify the two-parameters model in order to predict the swelling properties at the very early and late of the swelling process to distinguish the characteristic time interval for the diffusion and the relaxation components of the swelling.

- Try to use diluent or volatile to create a porous structure like what we obtained via increasing the monomer concentration and incorporating followed by etching the filler.

- Producing a superabsorbent polymer on a microreticular matrix to make it spongy.

- Attempting various drying processes including, oven-drying, vacuum drying and freeze drying on the reaction product of inverse suspension polymerisation followed by observing the effects on the polymer swelling properties.

- Synthesizing superabsorbent polymers by microwave ovens in order to saving the time of the reaction.

- Synthesizing superabsorbent polymers in a supercritical fluid like supercritical carbon dioxide as a replacement for the continuous phase of the inverse suspension process. This modification potentially helps to have an environmentally friendly process of manufacturing by eliminating the hydrocarbon as a continuous phase.

List of publications

1- H. Omidian *et al.* Swelling and crosslink density measurements for hydrogels. *Iranian Polymer Journal*, 1994, **13** (2), 115-119.

2- H. Omidian *et al.* Synthesis and characterisation of acrylic-based superabsorbents. *Journal of Applied Polymer Science*, 1993, **50**, 1851-1855.

3- H. Omidian *et al.* Modifying acrylic-based superabsorbent polymers I, II. *Journal of Applied Polymer Science*, 1994, **54**, 241-249.

4- H. Omidian *et al.* Modifying acrylic-based superabsorbent polymers III. *Journal of Applied Polymer Science*, 1994, **54**, 251-256.

5- H. Omidian *et al.* Modified acrylic-based superabsorbent polymers (Effect of temperature and initiator concentration), *Polymer*, 1997, Accepted for publication.

6- H. Omidian *et al.* A model for the swelling of superabsorbent polymers. *Polymer*, 1997, Accepted for publication.

7- H. Omidian *et al.* Modified acrylic-based superabsorbent polymers (dependence on particle size and salinity), Submitted to *Polymer*, 1997.

8- H. Omidian *et al.* Synthesis, characterization and modification of superabsorbent polymers. A seminar presented at: *International Seminar on Polymer Science and Technology*, 1994, 2-4 May, Shiraz, Iran.

9- H. Omidian *et al.* Modeling of superabsorbents. A seminar presented at: *International Seminar on Polymer Science and Technology*, 1997, 3-5 November, Tehran, Iran.