Supermicron Monodisperse Styrene/Butyl Acrylate Latexes by A Novel Aggregative Emulsion Polymerization

by

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Abstract

A novel aggregative surfactant-free emulsion polymerization technique has been developed. It allows the synthesis, in one step or in sequential semi-continuous procedures, of poly(styrene-co-butyl acrylate) and poly(styrene-co-butyl acrylate-co-acrylic acid) monodisperse polymer particles with diameters in excess of three microns and with high solids contents.

In order to achieve stable (80:20) styrene/butyl acrylate (St/BA) micronsized particles, the one step reactions must be carried out with an ionic initiator in presence of electrolytes, while the polymerization system has to be under monomer *flooded* conditions.

The experimental data revealed that:

i. The increase of ionic strength by salt addition
    - slowed the polymerization rate
    - favored aggregative processes
    - increased the particle size.

ii. The increase of ionic strength by increasing the initiator concentration:
    - increased the polymerization rate
    - limited aggregative processes
    - decreased the particle size.

The largest particles resulted when the polymerizations were carried out at an initial pH < 8.0.

The styrene/butyl acrylate/acrylic acid (St/BA/AA) copolymerizations showed that monodisperse, stable, micronsized latex particles can be obtained in a one step synthesis if:

i. A semi-continuous monomer feeding procedure, with the AA comonomer completely distributed in the monomer phase, was employed.

ii. The polymerizations were performed in the presence of salts, under monomer *flooded* conditions, provided that the initial pH of the reaction medium (before the addition of the monomer mixture) was less than 8.5.

It was also found that the addition of acrylic acid (as an active comonomer with potential surface-activity) to the styrene/butyl acrylate copolymerization system led to:

i. A significant increase in the colloidal stability of the latex particles, due to an electro-steric stabilization mechanism.

ii. An increase in the polymerization rate, if the AA composition in the monomer mixture was higher than 1 wt %.

iii. No influence on the particle size of the final latex particles, when the AA composition was between 1 wt % to 5 wt %, since the polymerization was carried out salt-free.

iv. A change of the particle surface morphology.

All the reaction parameters investigated suggested that the St/BA/AA surfactant-free emulsion copolymerizations proceeded via a similar aggregative-polymerization mechanism as that found for the AA-free surfactant-free emulsion copolymerization of St/BA.

Different scenarios, based on the seed type, initiator type, composition of the monomer mixture feed and monomer feeding rate were investigated to find the best reaction parameters for growing St/BA and St/BA/AA micron particles from seed. Using a semi-continuos surfactant-free technique, stable, monodisperse latexes with a final particle size of up to 4 μm and solids content around 40 wt % could be produced. The experimental results strongly supported the limited capacity of the method to grow St/BA or St/BA/AA particles with diameters higher than 4 μm.

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To my daughter Cynthia Victoria

and

my wife Mariana

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CHAPTER 1

INTRODUCTION

1.1 THESIS OBJECTIVES

This thesis describes the synthesis and kinetic aspects of a novel aggregative surfactant-free emulsion polymerization process which allows one or two-stage preparation of monodisperse stable latexes with high solids content and particle size in the micron range. Two polymer systems, styrene/butyl acrylate (St/BA) and styrene/ butyl acrylate/acrylic acid (St/BA/AA) were studied in detail.

Three main objectives were associated with this project. The first one was to synthesize a one stage monodisperse latex with an average particle diameter greater than 1 micron at a solids content of at least 25 % wt/wt (solids content refers to the weight percent of polymer in the latex). This one stage synthesis of a stable, monodisperse latex with relatively large particles and a high solids content involved a novel experimental technique.

The second aim of the research was to understand the fundamentals of the new process, mainly from the kinetic point of view.

The final objective was to develop an experimental procedure which would allow further growth of supermicron seed made in the first stage, using a similar surfactant-free technique, to an average particle size of 2-8 μm.

1.2 SCOPE OF THE THESIS

The chapters of this thesis are self-contained. Each chapter possesses its own introduction, experimental, results and discussion sections which are followed by conclusions and references.

The thesis objectives and scope are described in Chapter 1. Chapter 2 gives the reader an introduction to emulsion polymerization. Chapter 3, the first experimental chapter, describes in detail the novel synthetic procedure and the characterization of supermicron, high solids contents styrene/butyl acrylate (St/BA) latexes. This chapter also focuses on kinetic aspects of the surfactant-free emulsion polymerization technique employed. By cross correlating the evolution of particle size (d_P) and particle size distribution (PSD), particle number density (N_p) and cumulative conversion (X%) with the experimental parameters, a novel aggregative emulsion polymerization process was developed to ensure the formation of monodisperse supermicron particles.

In order to improve latex characteristics, such as particle size distribution (PSD) and stability, as well as to avoid or to minimize coagulum formation, the influence a reactive co-monomer, such as acrylic acid (AA), was studied in Chapter 4. Control of the particle size and particle size distribution of the final latexes was accomplished through manipulation of main reaction parameters and experimental procedure. The influence of the co-monomer on the overall reaction mechanism was also studied.

Once monodisperse supermicron particles, with or without co-monomer, were synthesized, attempts were made to grow these particles in a second stage. Chapter 5 is devoted to this end. A mixed initiator approach, in systems with and without surfactants, was used to ensure that the particles could be grown to the desired size without secondary particle formation or coalescence of the latex.

Finally, the conclusions drawn from the thesis are summarized, and future work is suggested in Chapter 6.

CHAPTER 2

POLYMERIZATION IN AQUEOUS EMULSIONS

This chapter provides a brief overview of some fundamental aspects of emulsion polymerization processes in order to enable a better understanding of the areas covered by this thesis.

2.1 HISTORY OF EMULSION POLYMERIZATION

The beginning of emulsion polymerization is very closely linked with the first attempts to develop a process to imitate natural rubber during the First World War. Luther and Hueck[1] were the first to present a viable emulsion polymerization process in 1932. However, the major developments in emulsion polymerization were made during the Second World War, when the artificial rubber project was of paramount importance. At that time, and especially after the war, the first qualitative and quantitative theories of emulsion polymerization (Harkins's theory[2-4] or Smith-Ewart's theory[5,6]) were enunciated.

From the 1950s through to the 1980s, enormous efforts, especially in industrial research, were focused on the development of emulsion polymerization due to a rapid increase in the range and variety of products, and more demanding quality standards. The industrial efforts were frequently based on empirical trial and error. They nevertheless brought a huge accumulation of experimental data upon which the first mechanistic principles were formulated. Therefore, very soon, emulsion polymerization became a very competitive and attractive process, and the research efforts were directed both to industrial and academic laboratories. Many of the most important concepts and theories were developed during this time by authors such as Fitch *et al.*,[7,8] Gardon,[9-14] Ugelstad and Hansen,[15,16] Goodwin and Ottewill *et al.*,[17,18] Gilbert and Napper *et al.*.[19-22]

The present state of emulsion polymerization might be seen as a critical judgment of the previous scientific efforts, aided by the advent of new investigation techniques. By these means the fundamentals are now sufficiently well understood. Thus, the mechanisms governing emulsion polymerizations are re-formulated in new ways. All these contemporary efforts can lead to a quantum leap in performance and product characteristics.

For a better understanding of the future trends in emulsion polymerization it is worthwhile to recall both Gilbert's and Fitch's affirmations. Gilbert[23] believes that "*Intelligent, knowledge-based design is the way of the future for this important technology*"[5] while Fitch[24] supports the idea that the future of the emulsion polymerization stays in its "*state of the art*". Thus, both the systematic and intuitive approaches are supported by authorities in the field.

2. 2 ADVANTAGES AND DISADVANTAGES OF EMULSION POLYMERIZATION

Emulsion polymerizations are widely used industrial processes because it has many advantages for the commercial production of polymeric materials. However, this technique is not without drawbacks.

Emulsion polymerization is a free radical polymerization carried out in a heterogeneous, complex reaction system which essentially consists of: water, surfactant (emulsifier), monomers with varying degrees of water solubility (e.g., styrene, vinyl acetate), water-soluble initiator (e.g., ammonium persulfate) and other ingredients (e.g., modifiers, electrolytes). The end result of an emulsion polymerization process is a *latex* which is comprised of polymer particles, each containing many polymer chains, and a water phase.

The polymeric particles constitute a new dispersed phase, formed early in the polymerization. They are typically between 100 nm up to 600 nm in diameter. Polymer dispersions, also called polymer colloids or latices, play a key role in the production of synthetic elastomers, surface coatings, adhesives, lacquers and other applications.

2.2.1 Advantages

Some of the reasons for the industrial development of emulsion polymerization are as follows:

i. The exothermic effect generated by the free radical polymerization process can be both readily absorbed and dissipated by the aqueous phase (the reaction medium) - this means that the reaction temperature can be easily kept under control while less stringent precautions are required to avoid overheating of reactors.

ii. The reaction medium can have a high polymer content and still retain a relatively low viscosity which allows good mixing and, in some cases, simplifies post-reaction processing.

iii. The latex produced can be formulated directly into many final products without separation of the polymeric phase from the continuous phase; moreover, such products can be free of organic solvents which reduces both safety and environmental hazards.

iv. The rate of polymerization in emulsions is usually considerably greater than in an equivalent bulk process while, in absence of modifiers, the average molecular weight of the polymer formed in emulsion is higher than that obtained in bulk.

v. The average molecular weight can be easily controlled using chain transfer agents. This gives additional control of mechanical properties of the formed polymer, such as mechanical strength, glass transition temperature, or properties of the final latex, such as minimum film-forming temperature.

vi. Control of particle characteristics such as average size, size distribution, morphology, stability, reactivity and surface properties permits the design of products to satisfy special application needs.

vii. An emulsion polymerization process can easily be carried through to relatively high conversion.

viii. An emulsion polymerization process, despite its complexity, can be easily carried out in batch, semi-batch or continuous reaction systems.

2.2.2 Disadvantages

Among the emulsion polymerization disadvantages the following could be considered as most representative:

i. The emulsion polymerization process overall is very complex, sometimes less reproducible and hard to control.

ii. Due to its complexity the technical staff employed should be highly educated and very well trained.

iii. In some cases it is necessary to separate the polymer from the water phase, which causes increased production expenses.

2.3 AN OVERVIEW OF EMULSION POLYMERIZATION

A classical picture of an emulsion polymerization system is shown in Figure 2.1. The emulsion polymerization is a multistep process which mainly consists of:

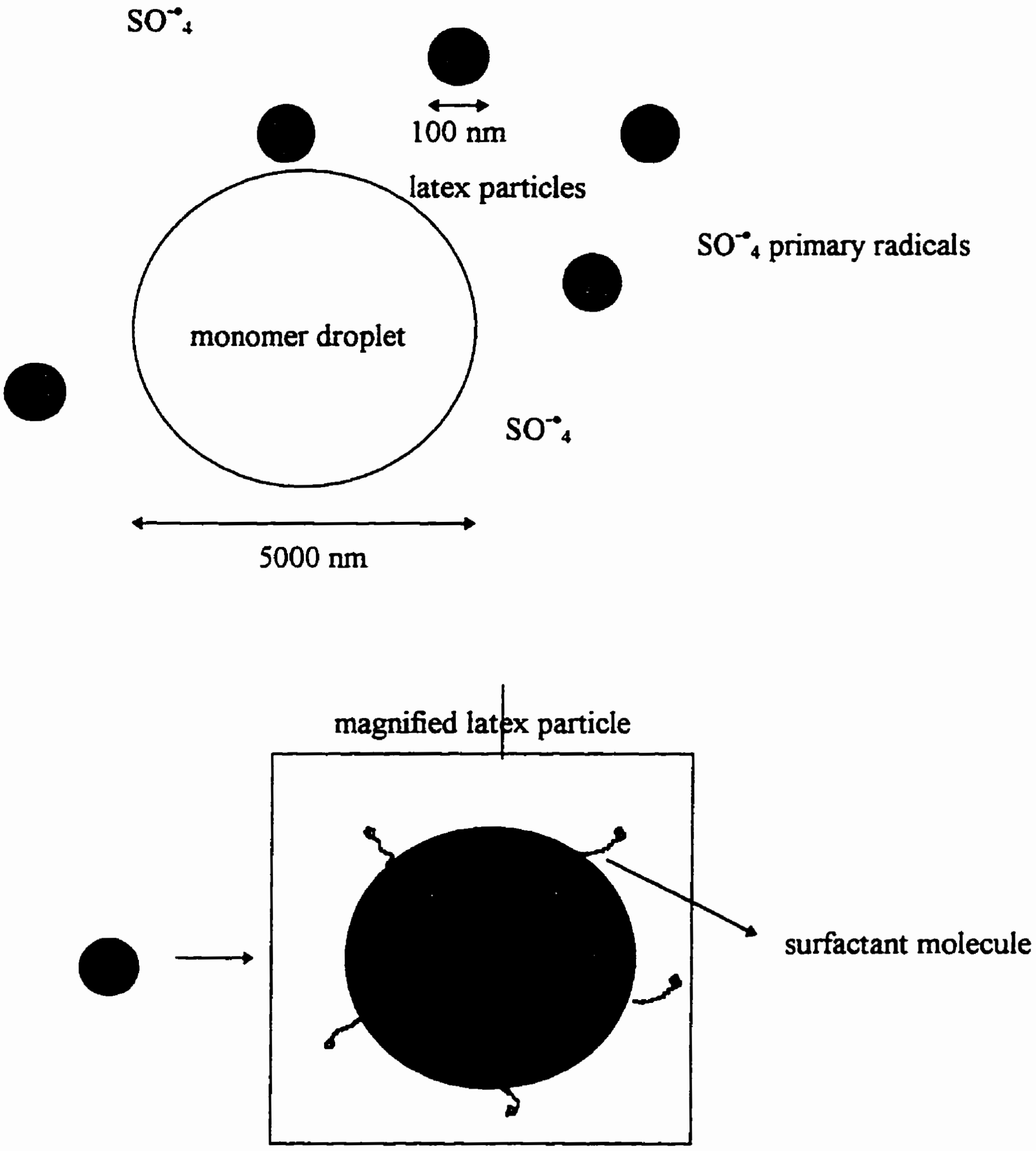
i. Particle formation.

ii. Particle growth: - after cessation of particle formation
- after the disappearance of monomer droplets.

Particle Formation

The first step of the particle formation process is the generation of primary radicals by thermal decomposition of the initiator. An ionic initiator, such as a peroxodisulfate (usually named, persulfate) $S_2O_8^{2-}$ which is completely water-soluble, generates primary radicals in the aqueous phase:[24]

Figure 2.1 The basic components of an emulsion polymerization system



$$S_2O_8^{2-} \rightarrow 2\ SO_4^{-\bullet} \qquad (2.1)$$

The primary radicals, $SO_4^{-\bullet}$, initiate polymerization with the monomer (M) dissolved in the water phase, and produce oligomeric radicals that are still soluble in water:

$$SO_4^{-\bullet} + M \rightarrow {}^{\bullet}M\ SO_4^{-} \qquad (2.2)$$

$${}^{\bullet}M\ SO_4^{-} + M \rightarrow {}^{\bullet}MM\ SO_4^{-} \qquad (2.3)$$

While the oligoradicals are propagating in the aqueous phase, they may become *surface-active* free radicals or undergo termination with other radical species, e.g.:

$${}^{\bullet}M\ SO_4^{-} + {}^{\bullet}MM\ SO_4^{-} \rightarrow M_3\ (SO_4^{-})_2 \qquad (2.4)$$

The oligomers which escape termination and reach a degree of polymerization at which they become surface-active, by subsequent aqueous phase propagation, can enter a pre-existing micelle or can form a new micelle by aggregation with surfactant molecules dissolved in the water phase.

Once the oligomeric radical is enclosed in a micelle, where the concentration of monomer is much higher than in the aqueous phase, it propagates rapidly. The "*stung*" micelle contains a long polymer chain which subsequently becomes a new young latex particle. At this time the distribution of particle sizes is broad. The first-born particles are large while the newest ones are small.

As the particles grow by propagation, a sufficient number of particles with a large enough size is formed. The new radicals produced in the aqueous phase enter pre-existing particles rather than nucleating new ones. During this stage there are at least three polymerization loci in the reaction system: the aqueous phase, the micelles, and the polymer particles.

Particle Growth

After cessation of particle nucleation, the formed *mature* particles, swollen with monomer, grow mainly by interior propagation, although other growth mechanisms, such as aggregation, are not excluded.

At the beginning of this stage of growth by inside-particle polymerization, the concentration of monomer in the particles is approx. 6 M, while the concentration of monomer in droplets is about 10 M. Further, the corresponding weight fraction of polymer in the latex particles is about 0.35. The thermodynamic equilibrium concentration of monomer in the particles is reached by water phase diffusion of monomer molecules from monomer droplets to particles. By interior polymerization the average size of particles increases whereas the polydispersity (the breadth of the distribution of particle sizes) decreases.

As the macroradical inside the particle continues to propagate, it is possible that its radical reactivity undergoes *transfer* to monomer, forming a monomeric radical:

$$M^{\bullet}_{n} + M \rightarrow M_{n} + M^{\bullet} \qquad (2.5)$$

The monomeric radical can continue propagating or it may diffuse out of the particle. The escape of monomeric radical into the aqueous phase is known as an *exit* phenomenon.

When an aqueous phase radical enters into a particle the process is known as *entry*. To be captured by a particle, the entering radical must have a sufficient degree of polymerization to give it surface-activity. If an entry event occurs into a particle which already contains a growing radical, termination takes place almost instantaneously; otherwise, a new growing chain results.

It can be appreciated that the overall result of these processes, *entry*, *transfer* and *exit* (Figure 2.2) is that the particle eventually contains a large number of dead chains by the time it has grown to a radius of 50 nm. While the molecular weight of these chains is high, in the order of 10^6,[24] no particle has more than one growing chain. Therefore, the average number of radicals per particle (denoted $\bar{n}$) is less than 0.5.

After all of the monomer droplets disappear, the only monomer left in the system is inside the particles. The monomer is consumed by propagation in particles and therefore the weight fraction of polymer increases. Thus, the viscosity inside the particle increases while the rate of termination decreases. In addition, as the particles grow, the exit of monomeric radicals is less likely. The overall result is that the particles can contain more than one growing chain; $\bar{n} > 1$. Thus, the decrease in termination rate and the increase of the average number of growing chains per particle can lead to an increase in the rate of polymerization, generally known as the "gel" or "Trommsdorff" effect.[24]

At very high conversion, however, when the fraction of polymer is about 0.85, the high viscosity inside the particle causes the rate of polymerization to drop rapidly. At this point the reaction slows down. The rate at which a monomer molecule can diffuse to the end of a growing chain becomes rate-determining. The polymerization ceases when virtually all of the monomer is consumed.

2.4 INITIATING SYSTEMS

The initiation in emulsion systems is a complex process which consists of:

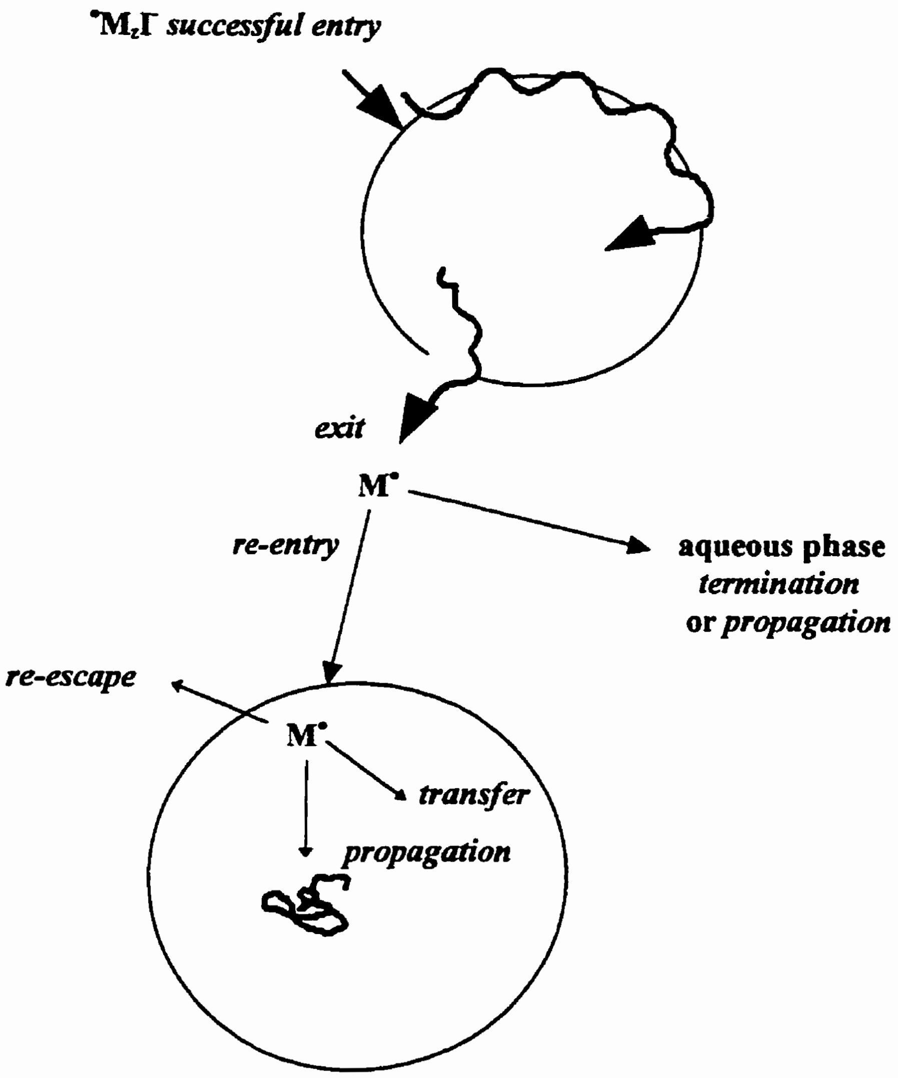
i. Decomposition of initiator in the water phase - formation of *primary radicals* ($R^\bullet$).

ii. Initiation of a radical polymerization reaction in the water phase with the soluble monomer(s) - formation of *free oligomeric radicals.*

iii. Nucleation of the first polymeric particles, *primary particles.*

iv. Nucleation of the *mature polymeric particles.*

Figure 2.2 The possible fates of free radicals in emulsion polymerization



v. The phase transfer processes: - *entry* of free radicals into *micelles* and/or *monomer-swollen polymer particles*
- *exit* (the escape) of free radicals from particles
- *re-entry* of free radicals into particles.[24]

The initiators used in emulsion polymerization systems can be divided into two groups: dissociation and redox[25]. Dissociation initiators generally decompose at higher temperatures (≥ 40 °C) into radicals mostly of ionic nature.

Redox initiators are two or multicomponent systems, which consist of components having different oxidation and reduction properties, by means of which radical species, suitable to initiate a polymerization reaction, are generated.

2.4.1 Dissociative Initiators

2.4.1.1 Peroxodisulfates

Peroxodisulfates, the most common *water-soluble initiators*, are extensively used for initiating the polymerization of monomers, both hydrophilic and lipophilic, in homogeneous or heterogeneous water phase disperse media. The most common peroxodisulfate initiators are ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, and potassium peroxodisulfate, $K_2S_2O_8$.

The most accepted mechanism for decomposition of peroxodisulfate was proposed by Kolthoff *et al.*[26,27] and is represented by the following equations:

$$S_2O_8^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2SO_4^{\bullet -} \tag{2.6}$$

$$SO_4^{\bullet -} + H_2O \xrightarrow{k_a} HSO_4^{-} + OH^{\bullet} \tag{2.7}$$

$$2\,OH^{\bullet} \xrightarrow{k_{OH}} H_2O + 1/2\,O_2 \tag{2.8}$$

It was found that the decomposition of peroxodisulfate in water is a first-order reaction with respect to its concentration.

The mechanism for decomposition of peroxodisulfate according to Equations 2.6 to 2.8 have been also experimentally supported by House[28] and Banerjee and Konar.[29] However, all these authors neglected the deactivation of ion radicals, $SO_4^{\bullet-}$, both inside and outside the cage, by recombination:

$$2SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \tag{2.9}$$

Other authors[26,27] considered that the decomposition reaction is strongly influenced by the pH (Equation 2.10) and the ionic strength of the water phase. An equation which can express the effect of the pH medium on the decomposition reaction of peroxodisulfate looks like Equation 2.10:

$$k_d = k_1 + k_2\,[H^+] \tag{2.10}$$

where k_d is the overall decomposition rate constant, k_1 is the uncatalyzed decomposition rate constant, and k_2 is the catalyzed decomposition rate constant.

Working in acid medium it was discovered that the decomposition rate constant rapidly decreases with increasing ionic strength while, in alkaline medium, the decomposition rate constant is unaffected by varying ionic strength[26,27]. Several other authors[28-30] supported the same conclusion.

In the radical polymerization of vinyl monomers in an aqueous phase, there is experimental evidence that the decomposition of peroxodisulfate initiators is somewhat influenced by the monomer type and concentration. The capture reaction of $SO_4^{\bullet-}$ radicals by the water-solubilized monomers (Equations 2.11 and 2.12) is suspected to be the main cause of this influence:

$$SO_4^{\bullet-} + M \rightarrow {}^{-}O_3S\text{—}O\text{—}M^{\bullet}\ (M^{\bullet}_1) \tag{2.11}$$

$$SO_4^{\bullet-} + M \rightarrow HSO_4^{-} + R^{\bullet} \tag{2.12}$$

where $R^{\bullet}$ is a water-soluble monomer radical.

Although the reaction described by Equation 2.11 has been experimentally confirmed (e.g., for the polymerization of acrylonitrile in water[192,193]), the transfer of radical to monomer (Equation 2.12) has not been confirmed yet.[31-34]

Adhikari *et al.*[195] studied the dependence of the rate constant for thermal decomposition of a peroxodisulfate on the concentration of ethyl acrylate dissolved in water. His experimental results showed that the rate of the initiator decomposition increased in proportion to the concentration of ethyl acrylate and of peroxodisulfate. The found reaction order with respect to monomer (0.92) could be considered direct evidence of the induced decomposition of peroxodisulfate by monomer. Furthermore, the increase in conversion of ethyl acrylate was accompanied by a decrease in the rate of decomposition of peroxodisulfate. This decrease was ascribed to a smaller contribution from the catalyzed decomposition of peroxodisulfate as a result of the decrease in monomer concentration.

The accelerating effect of monomer on the rate of decomposition of peroxodisulfate was also mentioned for the emulsion polymerization of a series of other vinyl monomers.[197]

In order to explain the mechanism for the monomer-catalyzed decomposition of peroxodisulfate, Dunn[198] has proposed the following reaction scheme:

- in the first step, monomer radicals are formed:

$$SO_4^{\bullet-} + RH(\text{monomer}) \rightarrow HSO_4^{-} + R^{\bullet} \tag{2.13}$$

- in the second step, the formed radical induces the decomposition of peroxodisulfate:

$$R^{\bullet} + S_2O_8^{2-} \rightarrow R\text{–}O\text{–}SO_3^{-} + SO_4^{\bullet-} \qquad (2.14)$$

Moreover, the author predicts the formation of radical $R^{\bullet}$ also to proceed in polymer particles, through chain transfer to monomer, which desorbs from the particles in the aqueous phase and takes part in reaction described by Equation 2.14. It was supposed that the course of these reactions should lead to a decrease in the pH of the water phase.

The surfactant is another component of an emulsion system that can affect the decomposition of a peroxodisulfate initiator. There is still a debate on the problem regarding which form of the surfactant (micellar or nonmicellar) contributes to the process more significantly. Jurzhenko *et al.*[35,36] supported the hypothesis that the rate enhancement of the decomposition reaction of peroxodisulfate initiators owing to the surfactants presence, is coming from the micellar surfactant. Their conclusion is based on the assumption that the surfactant catalyzed decomposition proceeds only on the micelle surface and that nonmicellar surfactant is not involved in this process.

In contrast to these assumptions, Ryabova *et al.*,[37,38] studying the effect of an anionic surfactant (potassium dodecyl sulfate), both below and above the CMC, on the decomposition reaction of a peroxodisulfate initiator, noted an increase in the decomposition reaction rate in both concentration ranges of surfactant. In addition, it was observed that the complexity of this mechanism follows from the fact that the activation effect of surfactant was eliminated by the presence of atmospheric oxygen. Furthermore, if the reaction contained styrene, the influence of oxygen on the decomposition reaction of the peroxodisulfate initiator was not observed.

Brooks and Makanjuola,[39] investigated the decomposition rate of potassium peroxodisulfate in the presence of sodium dodecyl sulfate (SDS) and found that the decomposition reaction rate of such initiators was greatly accelerated under the above reaction conditions. Other authors, Okubo and Mori [40] studied various aqueous solutions, pure water, SDS solutions, emulsifier-free poly(styrene) emulsions. They showed that "free" SDS molecules in their molecularly dispersed state increased the decomposition rate significantly, whereas those involved in micelle formation or adsorbed onto the polystyrene particles did not influence it. As well, in the former case the acceleration disappeared in the presence of a small amount of monomer.

All of these authors assumed that the acceleration of the peroxodisulfate decomposition reaction in presence of SDS is owed to the following reactions:

$$CH_3CH_2(CH_2)_{10}OSO_3^- + SO_4^{\bullet -} \rightarrow HSO_4^- + CH_3\overset{\bullet}{C}H(CH_2)_{10}OSO_3^- \tag{2.15}$$

$$CH_3CH_2(CH_2)_{10}OSO_3^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + [X]^{\bullet} \tag{2.16}$$

where $[X]^{\bullet}$ is a reactive intermediate.

Regarding the effect of cationic surfactants on the decomposition reaction of peroxodisulfate initiators in presence the vinyl monomers, Antonova *et al.*[41] and Capek *et al.*[42] have found out that the interaction between the anionic primary radicals, $SO_4^{\bullet -}$, and a cationic surfactant led to the formation of a water-insoluble product. In addition, the rate of polymerization was found to decrease with increasing concentration of this "adduct".

Working in aqueous phase only, Crematy[43] reported the formation of cationic surfactant radicals. Chain termination reactions due to reactions between the surfactant radicals and anionic primary radicals $SO_4^{\bullet -}$ were reported as well.

Regardless of the nature of the studied system (i.e. with or without monomer) these authors found that the decomposition reaction of the persulfate initiator was accelerated when the cationic surfactant concentration was above the CMC, whereas no effect was observed at a concentration below the CMC.

The decomposition reaction of peroxodisulfate initiators in emulsion polymerization processes is very complex and depends on many experimental variables. Consequently, the decomposition mechanism of such initiators in a real emulsion polymerization system is sometimes hard to follow. Although this problem is not resolved yet, the experimental data available so far provides a strong background for further studies in this domain.

2.4.1.2 Other Dissociative Initiators

Another category of common initiators for emulsion polymerization is represented by the *oil-soluble initiators* such as benzoyl peroxide and 2,2'-azobisisobutyronitrile (AIBN). Compared with the peroxodisulfate initiators, which are completely water-soluble, *the oil-soluble initiators* are less water-soluble but very soluble in the monomeric organic phase. Therefore, the majority of the initiator may be inactive for several reasons: the *cage effect*[23,25] can effectively deactivate the formed radicals and the diffusion of these radicals and initiator molecules through the aqueous phase is restricted because of their low water solubility.

Despite of their unfavorable water solubility, the small fraction of initiator dissolved in the water phase is active and influences the rate of initiation of emulsion polymerization greatly.[44-47]

It has been known to date that *oil-soluble initiators* can initiate polymerization in emulsion and follow a similar kinetic behavior to that of the emulsion polymerization system initiated by *water-soluble initiators*,[45] despite the difference in the principal loci of radical production. Although there is considerable experimental data[47,48] the reason why the kinetic behavior of the emulsion polymerization initiated by *oil-soluble initiators* is similar to that initiated by *water-soluble initiators*, has not yet been elucidated.

Among the *oil-soluble initiators* the group of azo initiators, typified by 2,2'-azobisisobutyronitrile (AIBN) and its derivates, is by far the most used. New classes of

AIBN initiators prepared via a reaction between AIBN and multifunctional alcohols, such as tetraethylene glycol or 1,6-hexanediol, or by modifying AIBN to structures with surface-activity, such as 4,4'-azobis-4-cyanovaleric acid and its salts, have become common.[25] These kinds of initiators, most of which show some surface activity, have wide applicability and are very useful for preparing special polymer dispersions with a reduced surfactant content or even without surfactant (surfactant-free).[49,50]

2.4.1.3 Redox Initiators

For the emulsion polymerizations run at lower temperatures (less than 40 °C) the initiation of polymerization is based on the use of redox initiating systems such as hydrogen peroxide/metal salt systems or peroxodisulfate/bisulfite.

The initiating system hydrogen peroxide/metal salt was studied in detail by Haber and Weiss.[51] The authors found that the rate of decomposition of hydrogen peroxide is catalyzed by iron(II) salts and, in order to explain this phenomenon, they proposed the following mechanism:

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + OH^{\bullet} + Fe^{3+} \qquad (2.17)$$

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet}_2 \qquad (2.18)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + OH^{\bullet} \qquad (2.19)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (2.20)$$

For this initiating system, the hydroxyl radical $OH^{\bullet}$ initiates the polymerization. Because of its very high reactivity $OH^{\bullet}$ can add to double bonds or abstract hydrogen from alkenes, generating radicals capable of initiating polymerization.

Other authors such as Marvel *et al.*[52], and Dixon *et al.*[53] found that not only does Fe^{2+} catalyze such initiating systems but Fe^{3+} and Ti^{3+} salts are effective catalysts capable of initiating polymerization in the water phase. In particular, iron (III) salts, such as nitrate, were successfully used in the catalytic decomposition of H_2O_2 when they were applied to the emulsion copolymerization of styrene and butadiene.[54,55]

One of the very common redox initiating systems is represented by the pair potassium peroxodisufate and potassium bisulfite ($K_2S_2O_8/KHSO_3$). Frank and Haber[56] have dealt with this initiating system. Based on their emulsion polymerization experiments carried out in acrylonitrile they have proposed for the decomposition of peroxodisulfate catalyzed by bisulfite the following mechanism:

$$S_2O_8^{2-} + HSO_3^{-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + {}^{\bullet}HSO_3 \qquad (2.21)$$

As well, the authors assumed that both sulfonate and sulfate radicals are initiating species. They also reported that the concentration of radicals formed via Eq.(2.21), radicals involved in the initiation of polymer chain propagation, is reduced by the competing reactions:

$$SO_4^{\bullet-} + HSO_3^{-} \rightarrow SO_4^{2-} + {}^{\bullet}HSO_3 \qquad (2.22)$$

$$2\ {}^{\bullet}HSO_3 \rightarrow H_2S_2O_6 \qquad (2.23)$$

The presence of sulfate ($-OSO_3H$) and sulfonate ($-SO_3H$) groups in the polymeric chains was supported experimentaly.[57,58]

The redox initiating system peroxodisulfate/sulfite was successfully used in emulsion polymerization of acrylonitrile, vinyl acetate [57,58] At the same time other redox initiating peroxodisulfate systems, such as (peroxodisulfate/bisulfite/iron(II) sulfate[59] or peroxodisulfate/iron(II) salt[59,60], were fruitfully used to initiate different polymerization systems.

2.5 KINETICS AND MECHANISM OF EMULSION POLYMERIZATION

2.5.1 The Rate of Emulsion Polymerization

Despite an enormous amount of experimental work devoted to kinetic and mechanistic aspects of emulsion polymerization, many mechanistic aspects are still unclear because of the complexity of these systems.

The complex character of emulsion polymerization follows from the heterogeneity of the reaction medium, the presence of several phases, and from variation of the kinetic parameters with the particularities of the processes involved such as diffusion, free radical addition, or adsorption/desorption. Moreover, in addition to the effect of the aqueous and monomer-organic phases on radical activity, the influence of the interface must also be taken into account.

The rate equation for an emulsion polymerization can expressed as:[23]

$$\frac{\mathrm{d}m_{\mathrm{M}}}{\mathrm{d}t} = -\frac{k_{\mathrm{p}}\, C_{\mathrm{P}}\, \bar{n}\, M_0\, N_{cr}}{\mathrm{N_A}} \tag{2.24}$$

where, m_{M} is the mass of monomer per unit reaction volume;

C_{P} is the monomer concentration in the latex particles;

$\bar{n}$ is the average number of free radicals per latex particle;

M_0 is the molecular mass of monomer;

N_{cr} is the number of particles per unit reaction volume;

$\mathrm{N_A}$ is Avogadro's number.

Although the above equation is always valid, care should be taken whenever it is used. For example, C_{P} invariably changes during polymerization, while k_{p} and $\bar{n}$ may also change. Moreover, this equation is based on the assumption that all polymerization takes place in the particles, and therefore, if the polymerization in the aqueous phase is significant, a second term, taking into account the kinetic parameters in that phase, must be also included. Certainly, these added parameters increase the complexity of the reaction analysis.

Very often it is convenient to look at emulsion polymerization as a three stage process. A qualitative description of these stages is summarized in Table 2.1.

Table 2.1

interval	typical % conversion range	micelles	monomer droplets	particle number N_p	particle size d_P	comments
I	0-10	present	present	increases	increases	nucleation period
II	10-40	absent	present	constant	increases	C_P constant
III	40-100	absent	absent	constant	roughly constant	C_P decreases

Interval I: represents the onset stage of the emulsion polymerization. In this stage, a new phase is formed, (a polymer phase) by particle nucleation. In most cases, Interval I is a rapid, transitory stage which always has a profound influence on the rest of the process, particularly with regard to the number of latex particles. From a kinetic point of view it is characterized by an increasing rate of reaction due to particle nucleation.

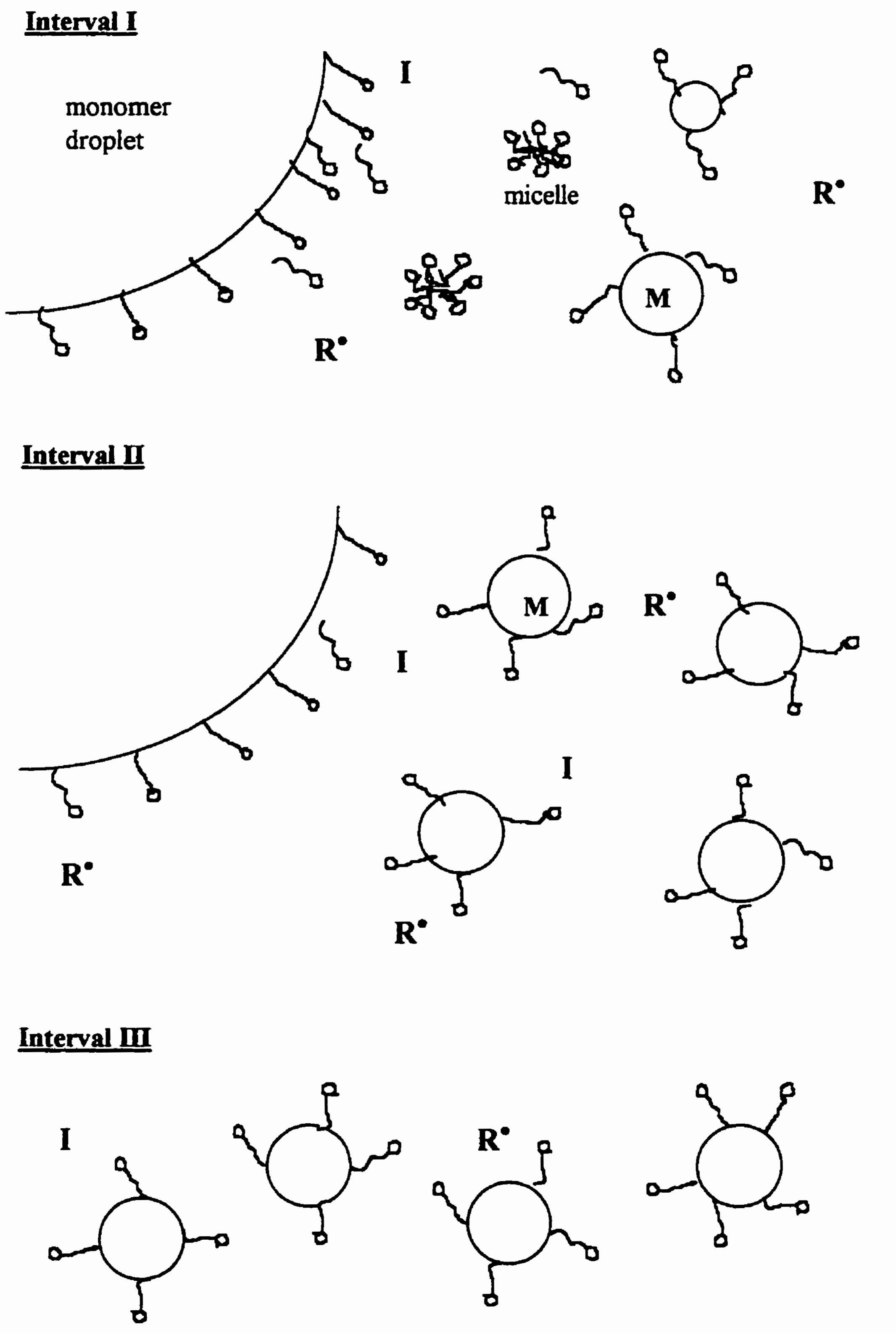
Interval II: otherwise known as the particle growth stage, succeeds Interval I and, theoretically starts when particle nucleation ceases. Practically, however, the particle nucleation and particle growth stages occur concurrently or at least overlap. In this stage, all three possible phases are present: an aqueous phase, a monomer droplet phase and latex particles.

In batch or *flooded* semi-batch polymerization (since monomer is accumulated in the reaction system during the feeding stage) during Interval II, the latex particles, which are monomer-swollen polymer particles, maintain an approximately constant monomer/polymer ratio. This "steady state" is maintained by monomer migration through a diffusional process through the aqueous phase from monomer droplets to the latex particles. The equilibrium monomer concentration inside the particles arises from the balance of the free energy of mixing of the monomer with polymer in the particle and the surface energy of the particle.[23] Since in most cases C_P and N_p are approximately constant during Interval II, the polymerization rate inside the latex particles is relatively constant. However, in some circumstances, $\bar{n}$ can increase, leading to an increase of polymerization rate (i.e. an acceleration).

Interval III: is the final stage of the process. Interval III commences as soon as the monomer droplets are depleted at the end of Interval II. At that time the reaction consists only of two phases, namely the latex particles and the aqueous phase. Moreover, the only monomer in the system is in the latex particles. Therefore, as polymerization proceeds the monomer concentration in the latex particles decreases monotonically with time. Thus, very often, in this stage the rate of polymerization is slowly decreasing. However, in some cases, a very pronounced increase in the rate of polymerization was found. This auto-acceleration, also known as the *Trommsdorff-Norrish gel effect*, is very common in emulsion polymerizations.
A detailed schematic of these three stages of polymerization are depicted in Figure 2.3.

One of the major differences between an emulsion polymerization system and a homogeneous bulk polymerization is the *compartmentalization* or *segregation* of the reaction system, regarding the locus of polymerization. In emulsion polymerization the main locus of polymerization is the latex particles, which are discrete entities. Thus, a radical in one particle will have no direct access to a radical from another particle without the implication of a phase transfer event.

Figure 2.3 The classical three intervals of an *ab initio* emulsion polymerization



By the segregation of the free radicals, the rate of termination is reduced and the average molecular weight of the formed polymer chains is enhanced. Moreover, the compartmentalization in emulsion polymerization leads to a simultaneous increase of both the polymerization rate and average molecular weight.

It is well known that the most common initiators in emulsion polymerization are the *ionogenic* initiators, e.g. ammonium persulfate $(NH_4)_2S_2O_8$, which are water-soluble. Therefore, the first free radicals are generated in the aqueous phase. Subsequently the formed free radicals can have different fates:

i. To migrate into pre-formed particle; this migration process is named *entry*.
ii. To terminate in the water phase.
iii. To propagate further.

As has already been shown in a previous paragraph, not all the free radicals formed can enter a pre-formed particle. To be able to enter a particle, the free radical must reach a critical degree of polymerization and become surface-active. The entry step involves three main steps: (1) the formation of surface-active free radicals; (2) the diffusion of these radicals to the particle surface; (3) the irreversible crossing of the particle/water interface.

Generally, it is accepted that the rate of entry is characterized by a pseudo-first order rate coefficient, ρ, and represents the average number of free radicals entering a latex particle per unit time (units: s^{-1}). The main parameters on which the rate of entry depends are: initiator type and concentration; particle number density; particle size and its surface charge density; surfactant type; ;

Nevertheless, entry is not the only possible fate for a water phase free radical. Sometimes, before successful entry, the free radical may undergo termination in the water phase, or it can grow further. Based on this, it is worthwhile to emphasize that not all the free radicals formed in the water phase undergo entry, and therefore the capture efficiency is always less than 100%.

A free radical inside a particle can have three fates:

i. To propagate.

ii. To transfer its reactivity to a monomer molecule.

iii. To escape from the particle to the water phase.

However, because both the surface-active free radicals and, basically, all the free radicals with a "reasonable" chain length have high free energy in the water polar phase, they will not escape from particles. Thus, the only species that can escape from particles are the small free radicals resulting from chain transfer. By exit the number of free radicals inside the particle, $\tilde{n}$, is reduced.

It is generally admitted that an exit process is a three-step mechanism:[20]

i. A monomeric free radical is generated by chain transfer; (if the monomer radical propagates it cannot exit).

ii. The monomeric free radical diffuses through the particle to its surface, the interface between the particle surface and the water phase, and thereupon undergoes desorption.

iii. The exited free radicals diffuse away from the latex particle/water interface into the bulk solution.

The desorption (exit) of free radicals from particles into the aqueous phase is described by a first-order rate constant, k (units: s^{-1}).

A free radical which has escaped from a particle does not represent a loss of free radical activity for the overall system, because this radical may re-enter another particle.[20] Nevertheless, an exited free radical may have other fates:

i. To re-enter another particle, which does not contain another free radical, or it may contain a free radical, but re-exit before termination can take place.

ii. To re-enter another particle which contains a free radical and to terminate with it.

iii. To terminate in the aqueous phase:

- with another exited free radical (aqueous phase homotermination)
- with an initiator-derived radical (aqueous phase heterotermination).

All of these possible fates of a desorbed free radical can have major influence on the overall kinetics.

It can be appreciated that the kinetic and mechanistic aspects of emulsion polymerization, such as polymerization rate and phase transfer events, represent a valuable starting point for a detailed study.

2.6 PARTICLE NUCLEATION

One of the most important processes in emulsion polymerization is the particle nucleation. Latex particles are formed during the early stages of polymerization. Although emulsion polymerization has been very well studied, because of its complexity many of the mechanistic aspects of the particle nucleation stage are still unclear and a matter of dispute.[23]

By understanding and controlling the particle formation process, the whole emulsion polymerization process can be kept under control. Fitch said that "what happens in the first few tens of seconds in an emulsion polymerization can have a profound influence on the rest of the reaction, particularly with regard to the number of latex particles"[24].

Moreover, Fitch[24] and Vanderhoff[61] have considered that the preparation of polymer colloids is both a science and an art. It is a science in that the kinetic principles of free radical-initiated vinyl addition polymerization and the principles of colloidal chemistry are superimposed on the heterogeneous polymer latex system. It is an art in that the researcher needs to use both his technical skills, experience and talent in order to figure the best recipe, which usually comprises several components whose small variations can result in drastic changes in the final latex quality.

The published literature covers a tremendous amount of work regarding the nucleation models, starting with the classical Harkins micellar model up to the current very sophisticated homogeneous-coagulative model of Gilbert and Napper. Regardless of their fundamentals, each of these models belongs to one of two reaction systems:

i. Particle formation in emulsion polymerization systems with surfactant concentration above the critical micellar concentration (CMC).

ii. Particle formation in emulsion polymerization systems with surfactant concentration below the CMC or without surfactant (surfactant-free systems).

2.6.1 Particle Formation Mechanisms Above The CMC: Micellar Entry Theories

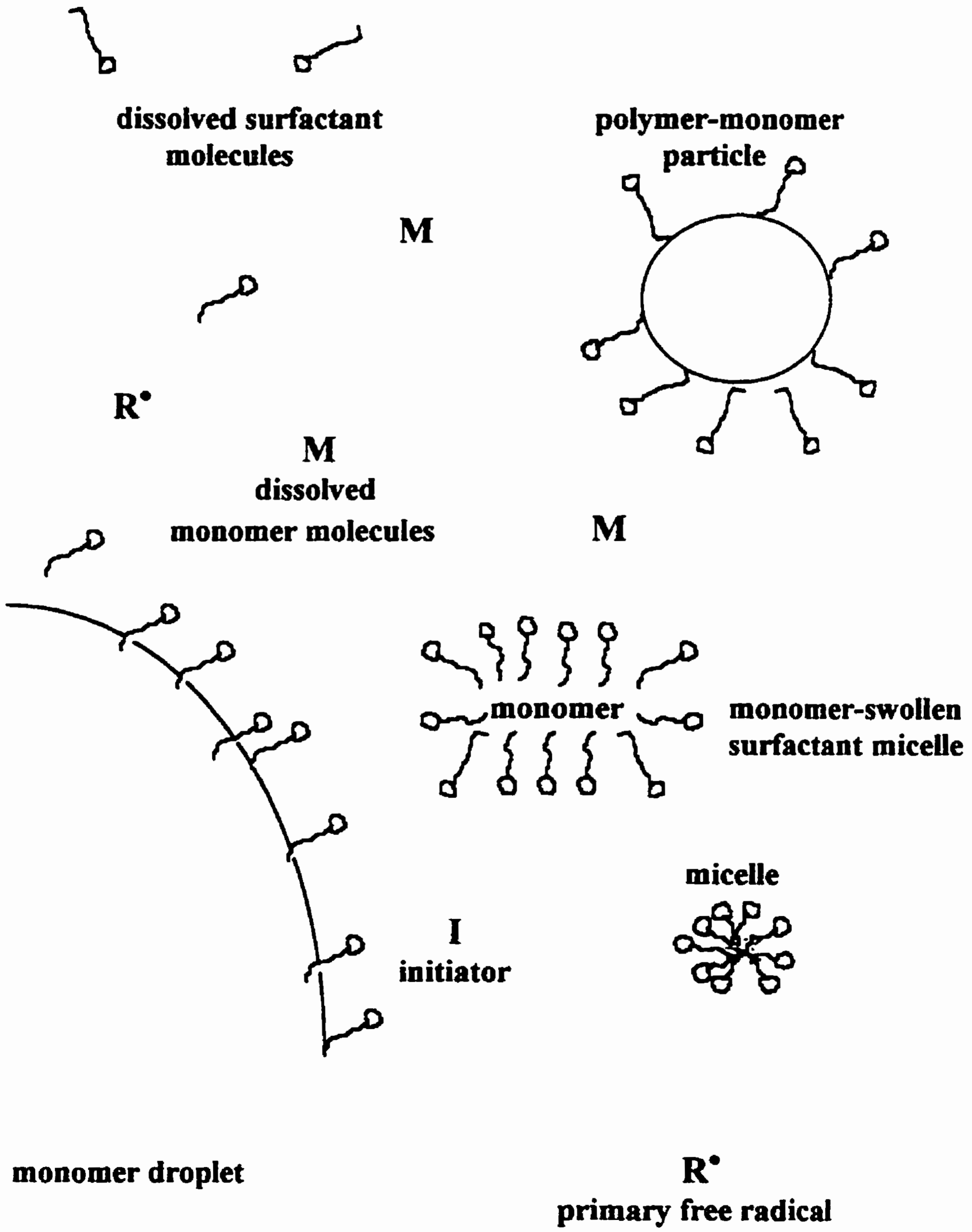
Generally, most commercial emulsion polymerizations involve surfactant at a concentration above the critical micellar concentration (CMC). Although the literature is abundant in different nucleation models for particle formation processes in emulsion systems whose surfactant concentration is above the CMC, only a few models are fundamentally important from a mechanistic point of view. These include the Harkins model[2-4] or the Smith-Ewart kinetic model.[5,6] In most cases, the other models have brought just more "mathematics".

2.6.1.1 Classical Harkins Model

The first hypotheses about the kinetics and mechanism of particle formation in emulsion polymerization were presented by Harkins as part of his detailed emulsion polymerization model in the early 1940s.

According to the Harkins model (Figure 2.4), before the polymerization process starts the reaction system consists of: monomer droplets, monomer solubilized in micelles, surfactant micelles, surfactant molecules dissolved in the water phase, and initiator molecules dissolved in the water phase.

Figure 2.4 The Harkins Model



In his model, Harkins assumed that the polymerization process starts by water phase decomposition of the ionic initiator into *primary radicals*. Afterwards, the primary radicals are absorbed into *monomer-swollen emulsified micelles*.

Once monomer-swollen emulsified micelles are "stung" by primary radicals a radical propagation reaction is initiated inside those micelles. As the reaction proceeds, the micelles become *monomer-swollen polymer particles*, or, briefly named, *polymer particles*.

The concentration of monomer in the polymer particles is maintained by diffusion of the monomer molecules from monomer droplets through the water phase to particles. In this diffusional process the monomer droplets act as a "monomer-feeding reservoir" by means of which the monomer dynamic equilibrium concentration in the polymer particles is maintained.

Interior polymerization occurs and the polymer particle surface grows. Thus, in order to keep their colloidal stability and integrity, the growing polymer particles have to adsorb more surfactant on their surface. The necessary surfactant molecules come from both the surfactant molecules dissolved in the water phase and/or from "inactive" micelles (micelles which were not "stung" by primary radicals). Therefore, in the Harkins model, the only role of surfactant is to stabilize the growing polymer particles.

When all the surfactant molecules are involved in stabilization of polymer particles, as opposed to micelles, then no further particles can be formed and the number of particles remains constant until the end of the polymerization process. Polymerization proceeds only inside the particles.

2.6.1.2 Elementary Smith-Ewart Model

The Smith-Ewart kinetic model for particle formation is based on Harkins' ideas about the micellar-entry model of emulsion polymerization.

The Smith-Ewart model starts by assuming that particles are nucleated whenever a primary radical, formed by initiator dissociation, enters a monomer-swollen micelle.

Micelles "stung" by primary radicals initiate a new polymerization reaction and so a new polymer particle is formed. It is assumed that initiator efficiency is 100%. This leads to:

$$R_i = \text{radical generation rate} = 2k_d[I] \qquad (2.25)$$

where, k_d is the initiator decomposition rate constant; [I] the initiator concentration.

The particle number N_P can be found by assuming that the particle formation ceases when micelles disappear. At that time the total surface area of the particles, A_P, is sufficiently large to adsorb all the surfactant molecules.

The total surface area of all particles at time t, $A_P(t)$, can be expressed as:

$$A_P(t) = 2k_d[I]\ \{(4\pi)^{1/2}\ 3K\}^{2/3}(3/5)t^{5/3} \qquad (2.26)$$

where K is the rate of volume growth per particle, for a particle containing one free radical.

In turn the total area of surfactant molecules is $a_S[S]$, where a_S is the surface area occupied by a single surfactant molecule and [S] is the surfactant concentration. Thus at the time t when nucleation ceases:

$$A_P(t) = a_S[S] \qquad (2.27)$$

Based on this model, the total number concentration of particles, N_p, is given by:

$$N_p(t{=}\infty) = 0.70\ (k_d[I]/K)^{2/5}\ (a_S[S])^{3/5} \qquad (2.28)$$

As can be seen, Eq.(2.28) gives the dependence of the final particle number on [S] and on [I] based on the assumption that free radical capture efficiency is 100%. However, free radical capture efficiency is always less than 100% which is why more sophisticated models were developed. Moreover, the simple Smith-Ewart model contained a number of error sources and major limitations, such as ignoring of the aqueous phase kinetics and (possibly) direct nucleation by exited radicals, compartmentalization and kinetics of exit, and the impossibility explaining the particle nucleation process in reaction systems with no surfactant.

Despite its limitations and error sources the simple Smith-Ewart model represented the first complete picture of particle formation at a surfactant concentration above the CMC. Therefore, this model has been a very useful source of inspiration for other authors, such as Gardon,[9-14] Napper and Gilbert,[23] Ugelstad *et al.*,[15,16] Schlueter,[62] who developed and put modern findings into it.

2.6.1.3 The Micelles and The Nucleation Mechanism: Emulsion Systems With Surfactant Above The CMC

The modern models of nucleation at a surfactant concentration above the CMC start from a fundamental question: are micelles the only place directly involved in particle nucleation processes? This question arose from the experimental evidence that in polymerization systems with surfactant concentration near and above the CMC the experimental data are *consistent* with both an homogeneous nucleation mechanism and a micellar entry model. In addition, it is very hard to find data by means of which it is possible to *reject* either model. For example, looking at the dependence of particle number (N_p) on surfactant concentration ([S]) the same dependence has been obtained from both the homogeneous nucleation mechanism and the micellar entry model.

Several authors, including Morrison *et al.*,[63] Lichti *et al.*,[64] Napper and Gilbert,[65] and Hansen and Ugelstad[10] have tried to find out ways of bringing out particular evidence for one nucleation mechanism or another.

An attempt to discriminate between a micellar entry mechanism and homogeneous nucleation was made by Gilbert and Napper.[63,64] Their rejection criteria were based on *the early-time particle size distribution*.

On one side it was observed that just after nucleation has ceased, most particles have very small volumes. This suggested that most particles must have been formed late in the nucleation stage. This behavior was thought to be specific of a coagulation process, where the formation of colloidally stable polymer particles is achieved through coagulative growth, which is autoaccelerating. This means that the rate of particle formation has to increase with time (until there are enough particles of sufficient size to be able to capture all newly-formed oligoradicals).

On the other hand, from the micellar entry nucleation mechanism point of view, formation of particles from micelles would be expected to show a decrease with time of the rate of particle formation (i.e as micelles disappear). This inference was supposed to represent valuable evidence to refute the micellar entry assumption. Nevertheless, Napper and Gilbert[65] pointed out that these results are also consistent with a homogeneous nucleation mechanism.

Schlueter[62] assumed that specific agglomeration catalysts (catalysts with restricted activity to the particle formation phase only) can be used to distinguish experimentally whether or not a homogeneous nucleation mechanism takes place, even in polymerization systems whose surfactant concentration is above the CMC.

Agglomeration catalysts must possess the following properties:

i. They must not be active when the precursor particles have formed in micelles and, in the early stage of polymerization, when they are still completely saturated with surfactant molecules. In other words, the catalysts do not operate in particle formation in the case of a micellar entry mechanism.

ii. In a homogeneous nucleation mechanism the catalysts must be very selective active in the particle formation towards only the unstable precipitating precursor particles and induce no agglomeration of more stabilized particles.

Schlueter based his study on three characteristic differences between the micellar entry nucleation and homogeneous nucleation models:

i. When particle formation is due to a micellar entry mechanism the end of particle nucleation is characterized by complete disappearance of the micelles. When particle nucleation follows a homogeneous mechanism, the nucleation process is continuous during the course of polymerization but is moderated by capture of precipitated oligomer radicals and by agglomeration of primary and secondary particles. Therefore, the rate of particle formation, dN_p/dt, is only initially the same as the rate of radical formation, R_i. That means, within a short period of time, a steady state is reached between initiation and capture of precipiting oligomeric radicals, R_C, and agglomeration of primary and secondary particles, R_a:

$$dN_p/dt = R_i - R_C - R_a = 0 \tag{2.29}$$

$$R_i = R_C + R_a \tag{2.30}$$

The steady state equation (2.29) shows the condition for the number of particles to remain unchanged.

ii. In the micelle entry model monomer droplets act as reservoirs providing the micelles with monomer by diffusion through the aqueous phase. Whereas in homogeneous nucleation, the micelles provide the surfactant for stabilization of the newly generated polymer particles from the aqueous phase.

iii. Micellar entry nucleation is generally considered to be applicable to those monomers that have a poor water solubility, such as styrene, and butadiene, whereas the homogeneous nucleation is postulated as the mechanism for those monomers that are considerably more water soluble, such as vinyl acetate, methyl acrylate. For monomers with intermediate water-solubility (ethyl acrylate, butyl acrylate) both mechanism have been proposed.

Schlueter suggested that a homogeneous nucleation mechanism is operative even for polymerization systems with monomers having low water solubility, such as styrene and butadiene, for which a micellar entry mechanism is generally accepted at a surfactant concentrations above the CMC. However, it is still difficult to say that in such polymerization systems the only nucleation mechanism is a homogeneous one and to completely exclude the operation of the micellar-entry nucleation mechanism.

An in-depth quantitative description of particle nucleation above the CMC has been developed by Napper and Gilbert et *al.*,[19-21] as shown in Figure 2.5.

Although their nucleation model is based on the main assumptions of the Smith-Ewart micellar entry, some modern mechanistic considerations are involved as follows:

i. The primary radicals ($SO_4^{-\bullet}$) propagate in water until they reach a critical degree of polymerization (z) and become z-mers with surface activity.

ii. Any of these free radicals can undergo water termination.

iii. The z-mers may enter micelles, or equivalently, aggregates covered with surfactant molecules, whereupon they become precursor particles.

iv. Surfactant molecules are adsorbed onto formed particles which are growing, thus the amount of free surfactant is reduced.

v. The z-mers may also propagate further to reach their critical size j_{crit}, to form j_{crit}-mers, (j_{crit} is the degree of polymerization at which the oligomers become insoluble and precipitate) although this is kinetically insignificant while there is sufficient free surfactant to be above the CMC.

vi. The free radicals within these micelle-like species propagate rapidly and transform them into precursor particles.

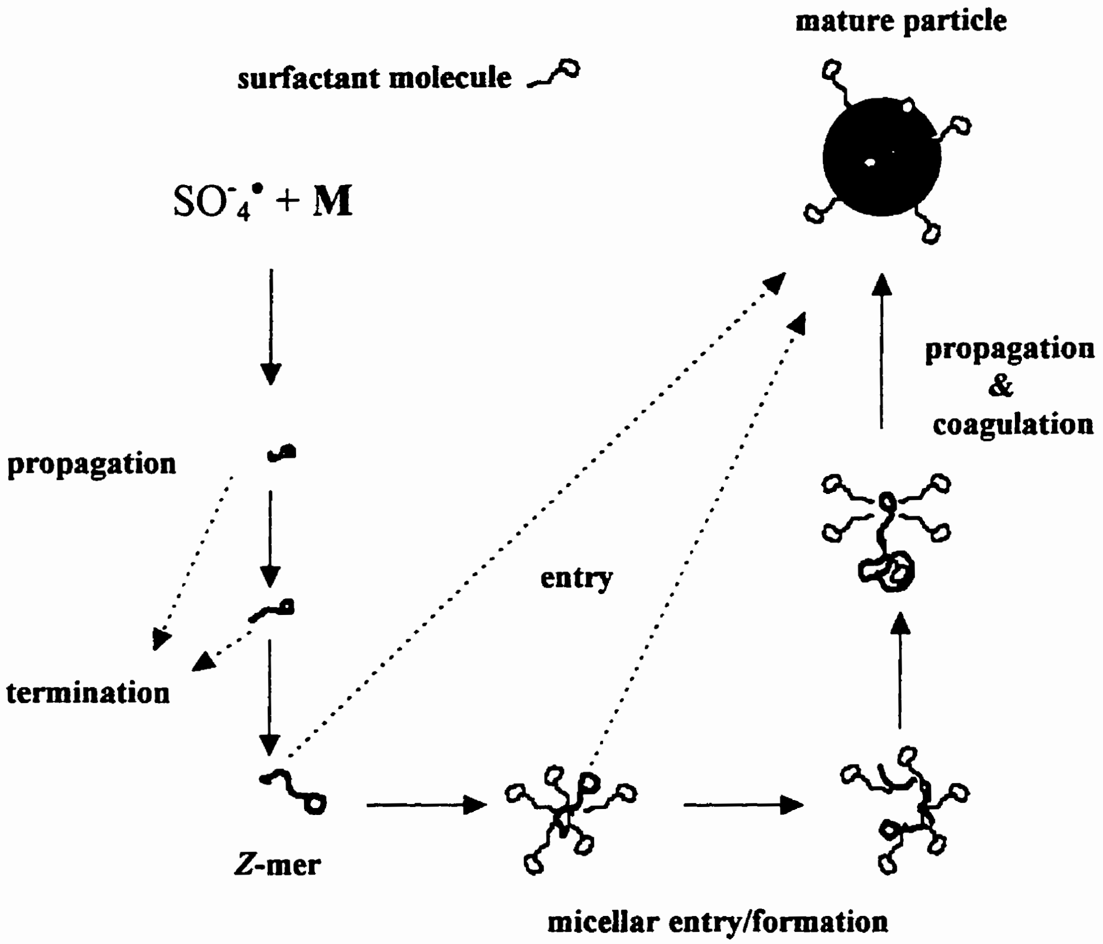
vii. The precursor particles might undergo limited coagulation among themselves.

viii. Although colloidally unstable, entry into, and exit from, these precursor particles can also take place; the desorbed radical might form a new particle.

ix. In time, the precursor particles grow sufficiently large in size and number to capture all newly formed aqueous phase free radicals so that new particle nucleation is avoided.

Nucleation processes cease when the rate of capture of the new formed free radicals by the pre-formed particles and termination greatly exceeds the rate at which newly born aqueous phase free radicals can themselves generate new particles.

Figure 2.5 The Extended Gilbert & Napper Micellar Model (above the CMC)



The particle nucleation mechanism proposed by Gilbert and Napper combines aspects of both homogeneous and micellar entry mechanisms. Despite its quantitative limitation this nucleation model is useful in order to understand and control the particle formation stage in polymerization systems in which surfactant concentration are above the CMC.

2.6.2 Particle Formation Below The CMC and Surfactant-Free Emulsion: Homogeneous Nucleation Theories

The fundamentals of the particle formation mechanism in both emulsion polymerization systems with surfactant concentration below the CMC and without surfactant (surfactant-free systems) are covered by the principles of the homogeneous nucleation theory. Some authors consider that the first ideas about the particle nucleation by a homogeneous mechanism belong to Roe.[66]

Working in polymerization systems with partially water-soluble monomers and using a water-soluble initiator, Roe found that no surfactant is necessary for the initiation of polymerization. In such cases, the surfactant molecules only act as stabilizers of the formed polymer particles. Roe assumed that the newly formed polymer particles had resulted from interaction between oligomeric radicals and surfactant molecules (or micelles). The process takes place until the complete depletion of free surfactant. It was supposed that early in the particle nucleation stage, *primary particles* are formed by the association of oligomeric radicals and their swelling with monomers, and are stabilized by the surfactant molecules present in the system. Meanwhile, the unstabilized oligomeric radicals are absorbed into polymer particles where they initiate or terminate chain propagation. From a kinetics point of view, Roe accepted the classical Smith and Ewart[5,6] model ($\bar{n}$=0.5).

Later on, Fitch *et al.*[7,8] looked in-depth into emulsion polymerization systems with hydrophilic monomers and worked out the first principles of the theory of the homogeneous nucleation model. One of the main assumptions of their theory was that the initiation of polymerization is in the aqueous phase. By a thermal decomposition reaction (Eq. 2.31), the water soluble initiator molecules generate ionogenic radicals known as *primary radicals*, $R^{\bullet}$ (i.e example $SO_4^{\bullet-}$):

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \tag{2.31}$$

By subsequent water phase polymerization the primary radicals can reach a particular critical chain length. On exceeding this limited length, the formed macroradicals become water insoluble and collapse to give *primary particles*. It was supposed that at this stage of polymerization, with conversion at ~ 0 %, the rate of particle formation equals the rate of radical generation:

$$dN_p/dt = R_e = fR_d \tag{2.32}$$

where R_e represents the effective rate of radical formation, while f is the efficiency of initiation, and R_d the rate of decomposition of initiator in the aqueous phase.

Once the system contained monomer-polymer particles the rate of particle formation becomes more complicated. The primary particles, bearing only one stabilizing ionogenic surface charge, flocculate, and thus the rate of particle formation becomes:

$$dN_p/dt = R_e - R_C - R_{fl} \tag{2.33}$$

where, R_C is the rate of absorption of oligomeric radicals from the water phase into polymer particles, and R_{fl} is the rate of flocculation of polymer particles.

The first stable primary polymer particles are formed once their surface potential reaches a critical value which offers enough colloidal stability to avoid further flocculation. At that point flocculation stopped, $R_{fl} = 0$, and:

$$dN_p/dt = R_e - R_C \tag{2.34}$$

Particle nucleation ceases, $dN_p/dt = 0$, when an equilibrium between the rate of radical formation in the aqueous phase and the rate of their absorption by already formed polymer particles is attained:

$$R_e = R_C \tag{2.35}$$

Fitch's homogeneous nucleation model is mainly formulated on the basis of processes which take place in the aqueous phase, as shown in Figure 2.6.

More recently, Hansen and Ugelstad[15-16] developed another model, using the DLVO theory to calculate R_C and R_{fl}, starting from the same main assumptions of the classical homogeneous nucleation model. At almost the same time, around 1980, Goodall *et al.*[67] considered an alternative nucleation mechanism.

In their mechanism, Goodall *et al.*[67] considered that the aqueous phase oligoradicals can undergo three events in the water phase:

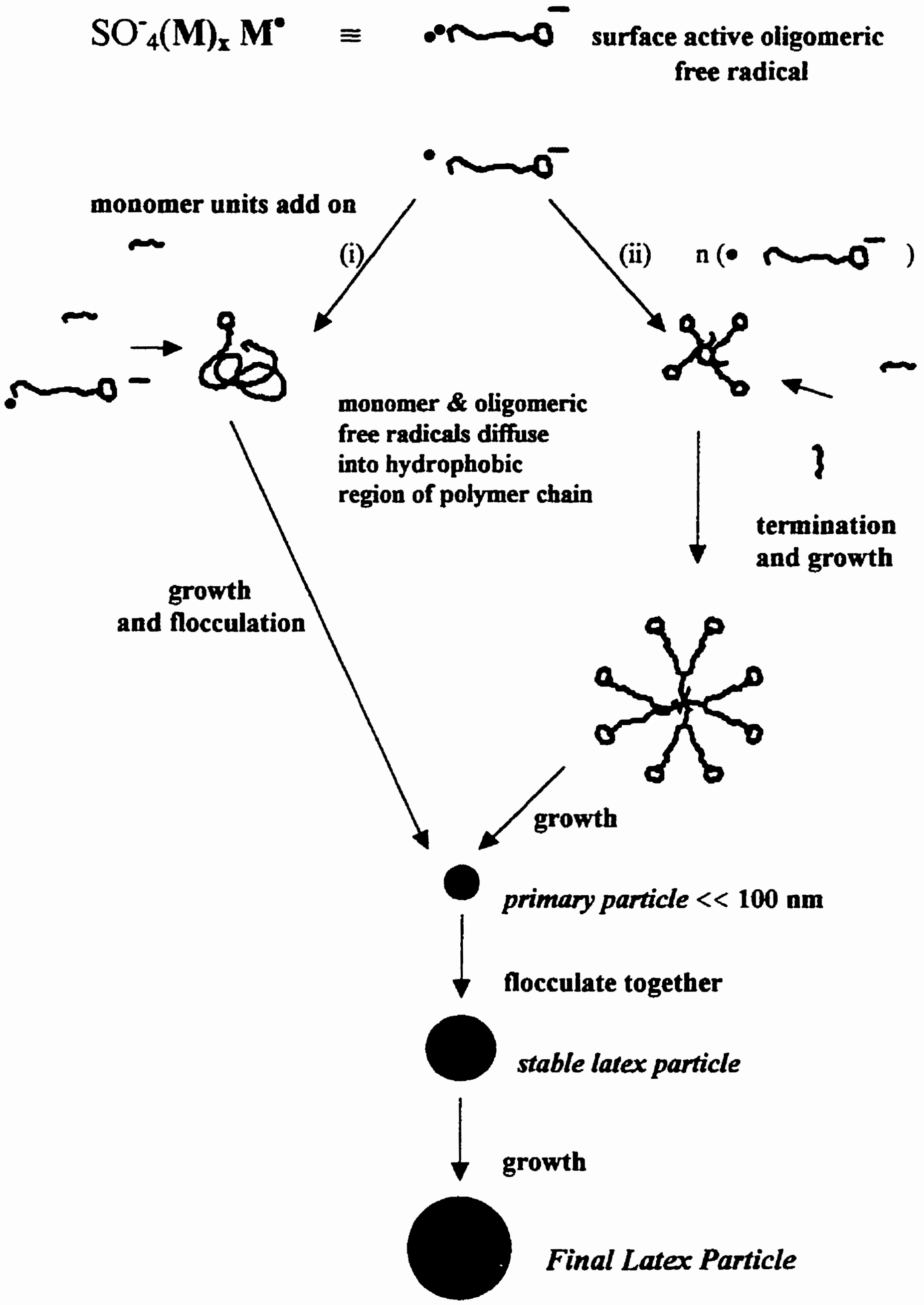
i. The growing free radicals terminate, generating dead species: therefore, the primary nuclei are formed by coagulation of these "dead" chains.

ii. The growing free radicals achieve a size and concentration at which they become surface active and associate by a mechanism similar to micellization. However, unlike true micellization their aggregation is irreversible.

iii. The oligomeric free radicals continue to grow until they attain a critical size, when they become water-insoluble and precipitate.

Any of the above mechanisms lead to particles consisting of low molecular weight polymer and having a high surface charge density. By monomer swelling, these polymer particles become the main polymerization loci, and high molecular weight polymeric chains are generated inside them. Moreover, a few new charged end groups are incorporated on their surface as well, which improves their colloidal stability. Nevertheless, during the initial growth, a part of the particles undergoes coagulation, because of the great increase of their volume and decrease of their particle surface charge density.

Figure 2.6 The Fitch Homogeneous Model



2.6.2.1 HUFT Model

One of the most accepted theories concerning particle nucleation by a homogeneous mechanism is represented by the *H*ansen-*U*gelstad-*F*itch-*T*sai (HUFT) theory.[7,68] Mathematical formulation of this model takes into account the competition between entry (capture) of newly formed radicals and the formation of precursor particles.

The entry model is based on the aqueous phase propagation and termination of an initiator-derived radical, followed by the diffusion of the aqueous phase free radicals to the particle surface. It is stated that a true entry occurs if and only if the aqueous phase radical has achieved a critical degree of polymerization *z* which confers surface activity. Small species may encounter the surface of particles but will not reside there. Moreover, the new theory has postulated that the growth of the aqueous phase free radicals to a particular degree of polymerization is the *rate-determining* step for free radical capture by latex particles.

The next aqueous phase reactions represent the main events which lead to entry of a *z*-mer into a particle:

i. Initiator decomposition: $$\text{Initiator} \xrightarrow{k_d} 2R^{\bullet} \tag{2.36}$$

ii. Initial propagation step: $$R^{\bullet} + M \xrightarrow{k_{pi}} RM^{\bullet}_1 \tag{2.37}$$

iii. Subsequent propagation: $$RM^{\bullet}_i + M \xrightarrow{k^i_{p,aq}} RM^{\bullet}_{i+1} \tag{2.38}$$

iv. Termination: $$RM^{\bullet}_i + T^{\bullet} \xrightarrow{k_{t,aq}} \text{dead species, } i < z \tag{2.39}$$

v. Entry: $$RM^{\bullet}_z + \text{latex particle} \xrightarrow{\rho} \text{entry} \tag{2.40}$$

where, $R^{\bullet}$: primary radical and k_d the decomposition rate constant;

M: monomer molecule;

$RM^{\bullet}_1$: water-soluble free radical which incorporated one monomer molecule;

k_{pi}: initial propagation rate constant;

$k_{t,aq}$ termination rate constant of water-soluble oligomer, $i < z$;

$k^{i}_{p,aq}$: propagation rate constant for water phase reactions;

$T^{\bullet}$: any water phase free radical;

$k_{t,aq}$: termination rate constant in water phase;

$RM^{\bullet}_z$: surface active z-mer;

ρ: entry rate constant.

One of the main assumptions of the above model is that k_{pi} is many orders of magnitude higher than the rate constant k_p. Therefore, the initial propagation step is not rate-determining, which leads to the resulting rate equations:

$$\frac{d[RM^{\bullet}_1]}{dt} = 2\,k_d[I] - C_w\,k^{1}_{p,aq}\,[RM^{\bullet}_1] - k_{t,aq}[RM^{\bullet}_1][\,T^{\bullet}] \tag{2.41}$$

$$\frac{d[RM^{\bullet}_i]}{dt} = C_w\,\{k^{i-1}_{p,aq}\,[RM^{\bullet}_{i-1}] - k^{i}_{p,aq}[RM^{\bullet}_1]\} - k_{t,aq}[RM^{\bullet}_1][\,T^{\bullet}],\ i < z \tag{2.42}$$

where, [I] is the initial concentration of the initiator.

In the entry model developed above, it is assumed that the entry of a z-mer into a latex particle is not rate-determining and no new particles are nucleated. That is why the postulated hypothesis of this model will no longer be valid when entry competes with a nucleation process.

As a conclusion, it can be appreciated that at the very early stage of polymerization, where no particles are formed yet, a z-mer must undergo other fates than entry. Later on, when particles start to appear, these fates compete with the entry, and in time become insignificant.

Regarding the formation of precursor particles, it is stated that the growing aqueous phase radicals must achieve a critical degree of polymerization, j_{crit}, at which point they become water-insoluble and precipitate from the system generating precursor particles. Always, z will be significantly less than j_{crit}, and oligomers of degree of polymerization z or less cannot form precursor particles. Therefore, one of the main postulates of the homogeneous nucleation model is that any aqueous phase oligoradical can have different fates up to a degree of polymerization above z until a precursor particle is formed from an oligoradical which attained the critical size j_{crit}. Then, the entry process is rate-determining, and the entry model becomes:

$$RM^{\bullet}_i + \text{latex particle} \xrightarrow{k^i_e} \text{entry}, \quad i = z, \ldots, j_{crit} \tag{2.43}$$

The actual particle-formation stage comprises:

$$RM^{\bullet}_{jcrit} \rightarrow \text{new particle} \tag{2.44}$$

The new kinetic equations are:

$$\frac{d[RM^{\bullet}_i]}{dt} = C_w \{k^{i-1}_{p,aq}[RM^{\bullet}_{i-1}] - k^i_{p,aq}[RM^{\bullet}_i]\} - k_{t,aq}[RM^{\bullet}_i][T^{\bullet}] - k_e^i[RM^{\bullet}_i]N_p/N_A$$

$$i = z, \ldots, j_{crit} - 1; \tag{2.45}$$

Finally, *the rate of particle formation*, in molar units, $d(N_p/dN_A)/dt$, is given by:

$$d(N_p/dN_A)/dt = k_{p,aq}C_w[RM^{\bullet}_{jcrit}] = \text{total formation rate of precursor particle} \tag{2.46}$$

where, C_w represents the monomer concentration in the water phase and N_A is Avogadro's number.

Because (j_{crit} - 1) is sufficiently large, the dependence of $k_{p,aq}$ on chain length can be ignored for degrees of polymerization above (z - 1).

Applying the steady-state approximation to Eqs. 2.41-2.46, the entry model is described by the following rate equations:

$$[RM^{\bullet}_{1}] = \frac{2k_d[I]}{k^{1}_{p,aq}C_w + k_{t,aq}[T^{\bullet}]} \tag{2.47}$$

$$[RM^{\bullet}_{i}] = \frac{k^{i-1}_{p,aq}C_w[RM^{\bullet}_{i-1}]}{k^{i}_{p,aq}C_w + k_{t,aq}[T^{\bullet}]}, \quad i = 2,\ldots, z\text{-}1 \tag{2.48}$$

$$[RM^{\bullet}_{i}] = \frac{k^{i-1}_{p,aq}C_w[RM^{\bullet}_{i-1}]\, C_w}{k^{i}_{p,aq}C_w + k_{t,aq}[T^{\bullet}] + k_e^{i}(N_p/N_A)}, \quad i = z,\ldots, j_{crit}-1 \tag{2.49}$$

$$[T^{\bullet}] = \sum_{i=1}^{z-1} [RM^{\bullet}_{i}] \tag{2.50}$$

As can be seen, because of their very high reactivity (k_{pi} very large) the first species formed directly from the initiator decomposition are excluded from this model.

The above entry model can be solved numerically using an iterative method.

In conclusion, a useful mathematical model related to a homogeneous-nucleation mechanism has been developed. However, certain mechanistic aspects of the particle nucleation stage, such as the positively skewed variation of the early-time particle size distribution (PSD) with the particle volume, cannot be explained. Despite of these limitations the model remains a valuable start for the most recent homogeneous-coagulative nucleation theory developed mainly by Gilbert and Napper[23].

2.6.2.2 In Situ Micellization Model

Some authors, such as Goodall *et al.*[69] or Song & Poehlein[70-72] have supported the idea that in emulsion polymerization systems with no surfactant or low amounts of surfactant, the particle nucleation mechanism is based on *in situ* micellization.

In this mechanism it is believed that sufficient surface-active species (i.e. *in situ* surfactants) are formed by aqueous phase termination of initiator-derived oligoradicals. The *in situ* surfactant molecules form micelles which take part in the nucleation of polymer particles by a micellar-entry mechanism.

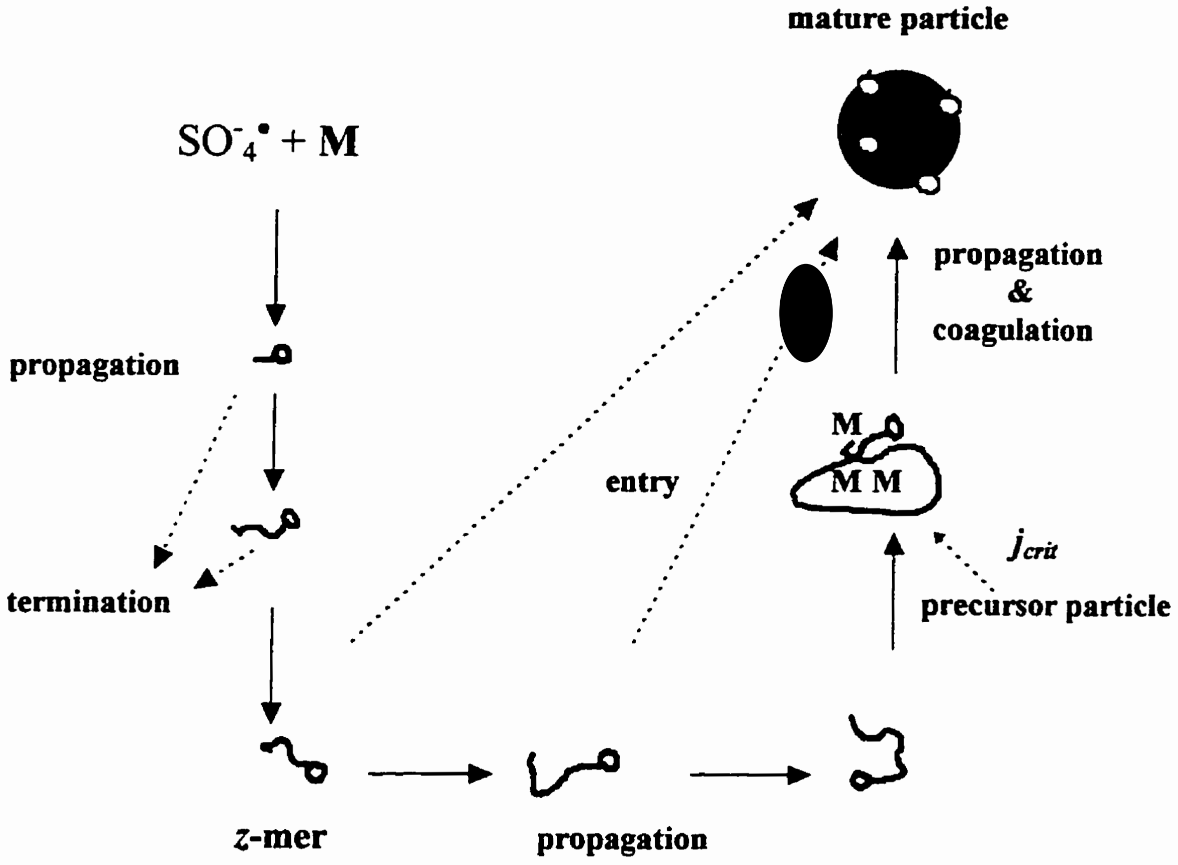
However, *in situ* micellization is thought to be rare since the total amount of the formed surface-active species is unlikely to exceed the CMC on a time scale commensurate with that of particle formation. This conclusion has been supported by experimental data and verified by calculations.[63]

2.6.2.3 Homogeneous-Coagulative Nucleation Model

Recent experimental studies[49,58,19-21,73-75] carried out in emulsion polymerization systems without surfactant (surfactant-free) or with low surfactant concentration (below the CMC) have reported the formation of particles with a maximum value of the number of particles during the nucleation stage. Moreover, in the conventional emulsion polymerization of styrene it was found that the time evolution of the particle size distributions are in qualitative and quantitative conflict with the predictions of any single-step nucleation mechanism, regardless of whether it is micellar-entry or homogeneous nucleation.

Based on these experimental observations Napper & Gilbert et *al.*[19-21] were the first to have proposed a *multistep particle nucleation mechanism* (Figure 2.7). Based on this hypothesis, they postulated a new coagulative nucleation theory, whose predictions have been confirmed by experimental results regarding the emulsion polymerizations with surfactant below CMC or without surfactant.

Figure 2.7 The Gilbert and Napper Homogeneous-Coagulative Model for surfactant concentration below the CMC or surfactant-free



Napper and Gilbert began their theoretical treatment of homogeneous coagulative nucleation from a critical point of view of the already known "simple" homogeneous nucleation model.

In the first step, they revealed insufficiencies of some assumptions related to this model which are very important in quantitative modeling:

i. All particles are assumed to contain growing radicals and exit is not taken into account.

ii. All particles have the same size, rather than a distribution of sizes, although a number of rate modeling parameters (e.g. C_p, k^i_e, the exit rate coefficient), depend on particle size.

iii. Coagulation among newly formed particles is completely ignored, although a lot of experimental evidence, such as the time evolution of particle number, $N_p(t)$, or the influence of the ionic strength change on the particle number, supports this process.

This new homogeneous-coagulative theory was a simple extension of the HUFT model. The new model takes into account both the coagulative and the volume dependence of the various kinetic events. In this sense the homogeneous-coagulative mechanism considers in more detail the particle formation process, starting from the fate of precursor particles, rates of entry into and exit from polymer particles, up to the rearrangement of the double layer between particles of greatly differing curvatures and its influence on coagulative process.

Briefly, the basic mechanistic assumption in homogeneous-coagulative theory is that the coagulation of "*precursor*" particles is involved in the formation of *mature* latex particles. Each precursor particle is composed of one or more *primary precursor* particles, which have been formed by the propagational events that primary free radicals undergo in the aqueous phase after being generated by initiator decomposition.

In the homogeneous-coagulative mechanism the term *primary precursor* denotes a newly formed precursor particle which has not undergone significant propagation or coagulation growth, whereas *precursor* particle refers both to a primary precursor and to a particle of any size that is unstable to coagulation.

It must be kept in mind that both primary precursors and subsequently formed precursor particles:

i. Are usually electrostatically stabilized, by means of the charged end-groups arising from initiator (if the latter is ionic) and distributed on their surface, and/or as a result of surfactant adsorption (when it is the case).

ii. Are colloidally unstable.

iii. Imbibe only relatively small amounts of monomer compared with mature latex particles (thus, they mainly grow by aggregation).

The primary precursors are thought to arise by homogeneous nucleation from the water phase oligomeric species whose chain lengths exceed the critical degree of polymerization, j_{crit}, required to precipitate from solution. When primary precursors have a deficient amount of surface charge density, they become unstable to *homo*-coagulation (*homo*-coagulation is a coagulation process among particles with roughly the same size) and generate nuclei.

Once the nuclei have grown sufficiently (by both propagation and homo-coagulation, in systems without surfactant or with surfactant below the CMC), they will start to *hetero*-coagulate with smaller more recently formed precursors.

When sufficient colloidally stable large particles have been formed in significant numbers, aqueous phase oligoradicals undergo entry into these particles as soon as the oligomers become *z*-mers. Such *z*-mers have surface-activity and are captured by the already formed polymer particles rather than undergoing further propagational growth to j_{crit}-mers and to nucleate new particles. At that time the particle nucleation process ceases.

In homogeneous-coagulative nucleation theory, the rate of particle formation is calculated from:

i. The rate of homogeneous nucleation and formation of primary precursors, based on the HUFT theory.

ii. The kinetics of coagulation among precursor particles, combining the Smoluchowski-Müller-Fuchs theory with the DLVO theory.

iii. Propagational growth.

One of the very common expressions of the rate of particle formation, based on homogeneous-coagulative nucleation theory, is given by:[25]

$$dN_p/dt = \sum_{i=1}^{m} v_i \left(\sum_{j=m-1+i}^{m} B_{ij} v_i \right) \tag{2.50}$$

where v is the rate of coagulation; B_{ij} is Müller's rate of coagulation between i-fold and j-fold flocculated particle.

The mathematical model of the homogeneous-coagulative nucleation mechanism is considerably more complex than the above equation. It involves a large number of equations, most of them nonlinear. However, using some appropriate assumptions it is possible to simplify the model.

Although complex, the homogeneous-coagulative model contains a relatively small number of adjustable parameters, such as k_t (termination rate constant) for the oligomeric species, or other parameters concerning the monomer concentration in oligomers and particles, and $\bar{n}$. Generally, however, the model predictions are in satisfactory agreement with the experimental data of emulsion polymerization systems carried out at a surfactant concentrations below the CMC, including surfactant-free reaction.

As will be seen in the experimental part of this thesis, the main assumptions of the homogeneous-coagulative theory have been successfully applied in the kinetic studies regarding the surfactant-free emulsion copolymerization of styrene with butyl acrylate. Moreover, based on this model a novel aggregative emulsion polymerization process has been developed.

2.7 COLLOIDAL STABILITY OF POLYMER LATICES

The stability of polymer latices is governed by the same principles as colloidal sols. In general, the balance between the electrostatic and steric repulsion forces and the London-van der Waals attraction forces[23] is taken into account as shown in Figure 2.8.

An electrostatic stabilization mechanism was initially proposed by Deryaguin-Landau-Verwey-Overbeek in the 1940's, known as the DLVO theory.[76]

The stability arises from the double layer of ions on the latex particle surface and the diffuse counterion layer. Once two particles come close enough, the double layers overlap and cause a repulsive force to develop. The forces causing particles to coagulate are Van der Waals forces which increase as the particle distance decreases. This gives rise to a net energy of attraction or repulsion depending on their separation distance, as shown in Figure 2.8.

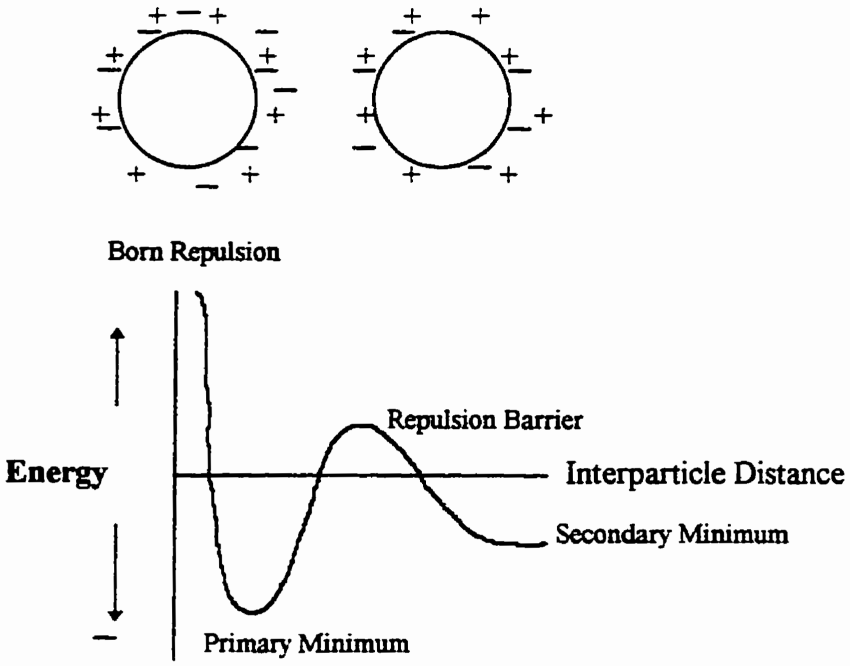
It is well recognized that the electrical double layer structure of the particle surface gives particles sensitivity towards ionic species from the dispersive phase. Thus, the repulsive barrier for particles in a medium of high ionic strength is lower than one in pure water. Therefore, coagulation of particles may be induced if the ionic strength is high enough. A critical coagulation concentration (c.c.c) is defined as the minimum ionic species concentration for onset of coagulation.

The effect of the increase of the ionic strength on the latex particle size was investigated by Goodwin *et al.*[17]. They proposed that by shrinking the electrical double layer of the particles, by raising the ionic strength, the precursor particles become less stable. This decrease in stability causes the precursor particles to coagulate more often, increasing the latex particle size.

Steric stabilization arises from nonionic water soluble polymeric material adsorbed or chemically attached to the surface of latex particles (Figure 2.8). As two particles

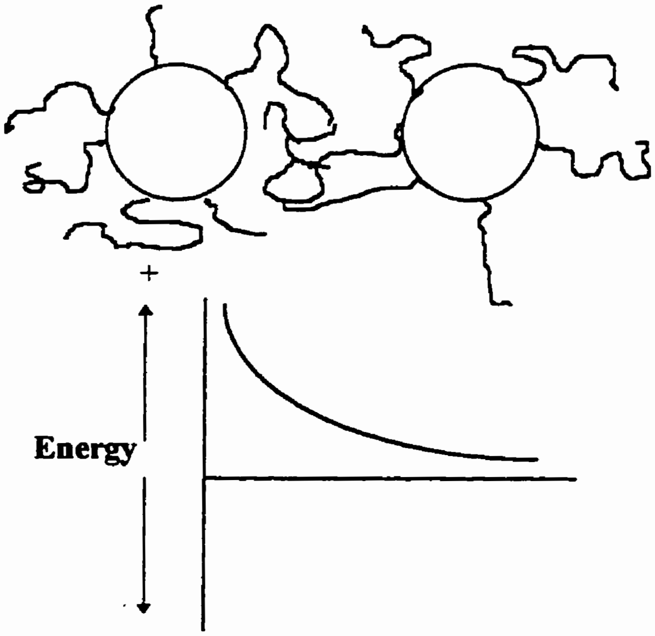
Figure 2.8 Stability of latex particles

Stabilization by Ionic Surfactant
DLVO - theory



Stabilization by polymeric surfactant

Steric Stabilization



come together, this water soluble polymeric material begins to overlap. When these layers overlap the aqueous solvent is forced from the overlapping region, leading to an increase in free energy causing the particles to be repelled. This is known as the mixing or osmotic aspect of steric stabilization. Another aspect is the elastic or volume restriction term which arises when the stabilizing chains are actually compressed.

Examples of steric stabilizers commonly used are ethoxylated nonyl- or octyl-phenols and poly(acrylic acid) under acidic conditions. A major characteristic of the steric repulsion forces is that they are less affected by other parameters of the system than the electrostatic forces. Although there is no unifying theory for steric stabilization mechanism, the effect of steric stabilization forces in combination with other forces has been summarized.[23]

Electro-steric stabilization is a combination of both electrostatic and steric stabilization.[77] The electrostatic and steric portions can be varied independently as with the addition of a nonionic surfactant to an anionic surfactant or they may be dependent on the degree of neutralization of soluble poly(acrylic acid) with sodium hydroxide, for example.

Generally, stabilization of latex particles is reached by means of surfactants. There are three basic types of surfactants:[23,25]

i. Electrostatic surfactants, anionic or cationic.
ii. Uncharged polymeric (steric) surfactants (non-ionic).
iii. Electrosteric surfactants.

Even if the most common procedures of polymerization in emulsion involve surfactants, stable latexes also have been made in emulsion polymerization without surfactant (surfactant-free systems) by using an ionogenic initiator, e.g. a persulfate salt. [23,25] In such polymerization systems it is well accepted that early during the beginning of the initiation stage an *in situ* surfactant, having a sulfate end group, is produced. This case will be discussed in more detail in the experimental part Chapters 3 and 4.

Regardless of whether surfactant is used in a polymerization system, three main mechanisms account for stabilization of latex particles:

i. Stabilization due to the adsorbed groups.
ii. Stabilization due to chemically bound groups.
iii. Stabilization due to polar-but-uncharged groups of monomer molecules.

The adsorbed groups may be any conventional surfactant (anionic or cationic, e.g. sodium lauryl sulfate, or nonionic, e.g. nonylphenol-polyoxyethylene adducts) or polymeric surfactant (e.g. methylcellulose). It should be emphasized that under specific circumstances the adsorbed surfactants may desorb from the particle surface, bringing destabilization. The stability of an adsorbed surfactant molecule onto a particle surface is governed by an adsorption-desorption equilibrium.

Instead of stability, the polymeric surfactants may bring flocculation of the latex by "bridging" in some circumstances. Usually, very low concentrations of the polymeric surfactant give flocculation, whereas higher concentrations give stability.

It must be emphasized that such polymeric surfactants may be generated *in situ* using an active (functional) co-monomer (e.g. acrylic acid, 2-sulfoethyl methacrylate, sodium styrenesulfonate).[23]

The chemically bound stabilizing groups may be:

i. Polymer end groups, (e.g. sulfate end groups, $-SO_4^-$, arising from persulfate initiator).
ii. Reaction products of these end groups (e.g. hydroxyl or carboxyl groups) incorporated functional groups, such as sulfate or carboxyl.

As a major specific characteristic, the chemically bound groups cannot desorb from the particle surface without removing the surface layer of the particle.

2.8 SUMMARY

Emulsion polymerization is a very versatile technique which allows the synthesis of particles with both desired sizes and morphologies. The experimental work presented in the next chapters of this thesis supports the fascinating "state of the art" of the emulsion polymerization and enriches the already impressive literature of that domain with new experimental data.

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CHAPTER 3

ONE STAGE SURFACTANT-FREE EMULSION POLYMERIZATION OF SUPERMICRON MONODISPERSE STYRENE/BUTYL ACRYLATE PARTICLES

3.1 INTRODUCTION

This chapter describes the one stage surfactant-free semi-batch polymerization processes carried out to synthesize styrene/butyl acrylate (St/BA) particles up to approximately 3 microns in diameter. Following a study of the influence of initiator concentration and monomer addition strategy, ionic strength, and initial pH a novel synthetic method was devised to produce stable monodisperse latexes with high solids contents (at least 25 % wt/wt) and particle sizes in the micron range. The latexes were characterized with respect to their particle size distribution, coagulum level and final yield.

Monodisperse polymer particles with diameters in the micron range have many applications in fields such as biology, medical analyses, chromatography and xerography. The most common methods of preparing such large particles are based on the non-aqueous dispersion polymerization procedures, as well as by stepwise and/or surfactant-free emulsion polymerization techniques.

Vanderhoff *et al.*[1], Ober and Lok[2] and Paine[3] have prepared particles in the 1-10 μm range, in a single step dispersion polymerization reaction in an organic medium and with a steric stabilizer grafted to the polymer particles. However, the particle size distribution and disposal of the organic diluent are still major problems.

Surfactant-free emulsion polymerization techniques are very attractive for producing "model polymer colloids" in the micron size domain. This method has been widely described in the literature for the surfactant-free homopolymerization of styrene, especially due to the pioneering work of Vanderhoff *et al.*[4,5], and Goodwin *et al.*[6-8]. It was shown that the ionic strength of the aqueous-phase plays a major role in order to get monodisperse polystyrene latexes and to control the particle size.

Goodwin *et al.*[6] presented qualitative arguments which clearly showed that the size of the first stable colloidal particles formed is controlled to a large extent by the ionic strength of the water phase. Their experimental observations revealed that for the same initial monomer concentration and for the same percentage conversion of monomer to polymer the final particle size produced in the higher ionic strength medium was larger than that at the lower ionic strength. Moreover, indirect experimental evidence supported a controlled coagulation process in the early stages of the reaction.

When an *ionogenic* water-soluble initiator, such as a persulfate salt ($(NH_4)_2S_2O_8$) is used, the free radicals produced by thermal decomposition of the initiator become incorporated as end-groups on the polymer chains and hence form the surface groups on the particle. The surface-anchored sulfate groups impart colloidal stability[9,10].

For a similar polymerization system, Fitch *et al.*[11] and Goodall *et al.*[12] suggested both homogeneous and *in situ* micellization mechanisms. The same mechanisms were also proposed by several authors, such as Poehlein *et al.*[13-15] and Kim *et al.*[16] working on surfactant-free emulsion copolymerization of styrene with different ionogenic co-monomers, such as acrylic acid, methacrylic acid or sodium styrenesulfonate.

Although there is considerable experimental data for surfactant-free styrene homopolymerization, only a few reports have been published about surfactant-free copolymerization[17-23]. It is worthwhile to mention the extensive work done by Guillaume *et al.*[17-19] on batch surfactant-free copolymerization of styrene with butyl acrylate. Using different techniques, including a completely surfactant-free polymerization system, polymerization in presence of a surface-active co-monomer (e.g., sodium acrylamido undecanoate)[18] or ionogenic co-monomers (e.g., methacrylic acid)[19] they prepared monodisperse latexes with a particle size up to, but less than 1 μm (micron). Moreover, the solids content was less than 10% wt/wt.

Another very attractive technique used in emulsion polymerization to prepare micron-sized particles is the swelling of seed particles. The work done by Ugelstad *et al.*[24,25] is of great interest. These authors employed a two step swelling technique. In the first step, before polymerization was initiated, the seed particles were swollen with a water insoluble low molecular weight compound and subsequently, with monomer and initiator. The resulting particles covered the 2-20 μm range. However, the polydispersity of the final latexes and the low solids contents makes the method restrictive. There have also been difficulties in reproducing Ugelstad's experimental procedures.

In the early 1990s two US Patents[26,27] of Fuji Xerox Co., Ltd., Tokyo, Japan described a multi-step procedure to synthesize vinyl monodisperse latexes. The geometric standard deviation of size distribution of the polymer particles was ≥ 1.09 (measurements made on the Coulter Counter) with a final number-average particle size from 1.0 to 10.0 μm. The inventors emphasized the vital role played by the type of surface active agent, as well as the kind and concentration of the polymerization initiator and electrolyte used. The maximum reported yield of the final latex was 81%.

In the present work the homogeneous-coagulative mechanism[28-30] was recognized as the most likely mechanism of surfactant-free emulsion polymerization. A novel synthetic procedure was developed for the one step synthesis of monodisperse latexes (PSD ≤ 1.028, where PSD is defined as d_W/d_n) with a particle size from 1.0 to 3.0 μm and a solids content of at least 25 % wt/wt.

Both the concentration of initiator and electrolyte were crucial in the polymerization mechanism, and particularly in the coagulative processes during the particle growth stage. Using a versatile semi-continuous (or a semi-batch) technique, it was possible to keep the whole polymerization process under control.

3.2 EXPERIMENTAL

3.2.1 Chemicals

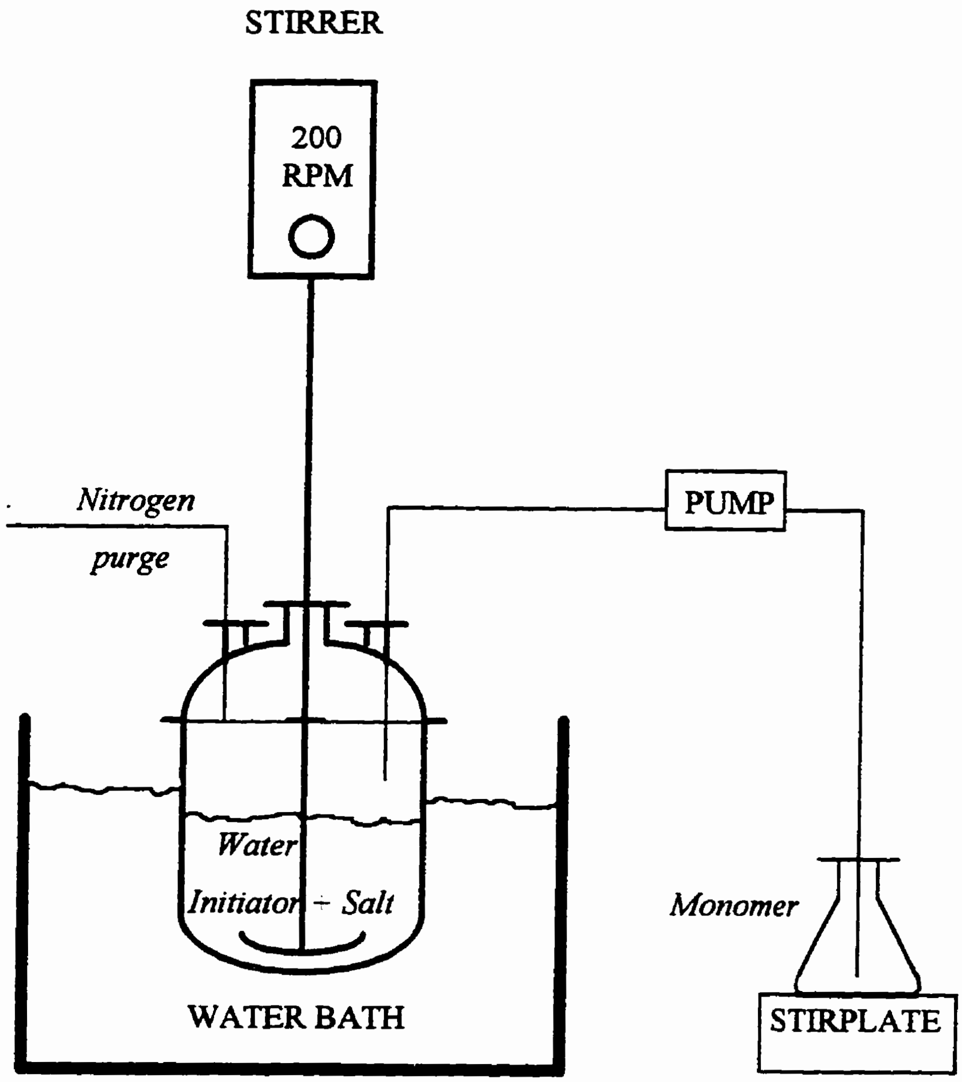
Reagent-grade styrene and butyl acrylate monomers were purchased from the Aldrich Chemical Company and used without further purification. Analytical-grade ammonium persulfate, and all the salts used were also purchased from the Aldrich Chemical Company and used as received. Deionized water was used throughout.

3.2.2 Synthesis of St/BA Latexes

Typical emulsion polymerization recipes are presented in Table 3.2.1. The St/BA (80/20 by wt.) latexes were prepared by a semi-continuous procedure. The syntheses were carried out in a four necked 1-L reactor equipped with a condenser, stirrer, thermometer, and nitrogen inlet. The reactor was thermostatted at 70 °C in a water bath. The reaction setup is shown in Figure 3.2.1. Agitation was kept constant at 200 RPM. A slow nitrogen purge was maintained throughout the polymerization at a slow rate in order to minimize evaporation.

Prior to the start of the polymerization reaction, the water was charged into the reactor and purged with nitrogen for approximately 1 h in order to eliminate the dissolved oxygen. The water-soluble initiator, ammonium persulfate $(NH_4)_2S_2O_8$, was dissolved in nitrogen-purged water and added to the reactor under nitrogen prior to the monomer feed. The reaction mixture was allowed to re-equilibrate thermally for 10 minutes. At this point, the monomer mixture, which was previously prepared by mixing the monomers under nitrogen, was fed into the reactor continuously, usually over a period of five hours, by means of an FMI QSY-1 piston pump. The reaction time was 12 h, except where noted. In some cases the reaction was allowed to proceed for 24 h in order to reach the highest possible conversion. At the end of the reaction the latex was cooled and filtered through glass wool to remove any coagulum formed.

Figure 3.2.1 Schematic of reaction setup



3.2.3 Latex Characterization

Particles larger than 1.5 μm were characterized using a 256 channel Coulter Multisizer II, while smaller ones were measured with an ICI-Joyce Loebl Disk Centrifuge equipped with a photodetector and supported by a Brookhaven Instruments DCP-1000 Data System. In the former case the latex was dispersed into Isoton II^{TM} solution, while in the latter, the spin fluid and dilution solvent for latexes was a 80/20 wt/wt water/methanol mixture. All samples were sonicated for 15 minutes in an ultrasonic water bath (Bronson-2200) before the measurements.

Particle size and uniformity, as well as the particle shape and particle surface morphology were confirmed by both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

The Scanning Electron Microscope was an Hitachi S-570. The measurements were performed at an accelerating voltage of 15 keV. The samples were adhered and dried on aluminum sample holders and coated with a thin layer of gold prior to viewing. When looking for secondary particle populations, it was found that the edge of the sample was the best place to examine.

The Transmission Electron Microscopy measurements were made using a Philips 300 TEM. The latexes were prepared for analysis by dilution to 0.1% solids and then adhered onto Formvar coated copper grids. These were then dried and subjected to RuO_4 vapors (0.5 % wt aqueous solution, from Polysciences) for less than two minutes. More than 300 particles per grid were counted.

Surface tension was measured with a Cenco-DuNuoy Interfacial Tensiometer using the ring method.

The initial pH of the aqueous phase, just before starting the monomer feeding, and the final pH of the reaction mixture were always measured. In some experiments the pH was monitored throughout the reaction as well.

Table 3.2.1

Typical emulsion reaction recipes (amounts in grams).

REACTION:		***S-168***	***S-171***	***S-205***
PRECHARGE - I	Deionized Water [g]	400.0	400.0	400.0
	Salt Type:	NaCl	$NaHCO_3$	None
	-Sodium Chloride [g]	0.65		
	-Sodium Bicarbonate [g]		0.93	
PRECHARGE - II	Deionized Water [g]	50.0	50.0	50.0
	Initiator (AP) [g] $(NH_4)_2S_2O_8$	1.2	1.2	1.2
CONTINUOUS FEED	Styrene (St) [g]	160.0	160.0	160.0
	butyl acrylate (BA)[g]	40.0	40.0	40.0
FEED DURATION	t_F [h]	5	5	5
PARTICLE SIZE	d_W [nm]	2705	2228	717
PSD	d_W/ d_n	1.014	1.014	1.006

Both the cumulative and instantaneous conversions were determinated gravimetrically. Samples (~ 2 mL) were removed from the reaction mixture at different times, diluted with 2 mL saturated hydroquinone solution, weighted into tared aluminum pans and dried at 70 °C to a constant weight.

The percentage conversion was obtained from the experimental solids content by means of the following formulas:

$$X_{\text{cum.}}(t) = \frac{\text{Reacted monomer from } t\text{=0 to } t}{\text{Total monomer added}} \tag{3.1}$$

$$X_{\text{cum.}}(t) = \frac{V(t)\ \mathrm{SOC}(t) - V(0)\ \mathrm{SOC}(0)}{R_a\ t_F} \tag{3.2}$$

$$X_{\text{inst.}}(t) = \frac{\text{Reacted monomer from } t\text{=0 to } t}{\text{Monomer added from } t\text{=0 to } t} \tag{3.3}$$

$$X_{\text{inst.}}(t) = \frac{V(t)\ \mathrm{SOC}(t) - V(0)\ \mathrm{SOC}(0)}{R_a\ t} \tag{3.4}$$

where: - SOC(0) is the solids content at time t=0, [g solids/mL latex];

- t_F is the time at the end of the monomer addition, [min.];
- R_a is the monomer addition rate, [g/min.];
- V(t) is the reaction volume at time t; [mL]: $V(t) = V(0) + R_a\ t$.
- V(0) is the initial reaction volume, [mL], just before starting the monomer addition.

The particle number density, N_p, was determined from the solids content and the average particle diameter, as follows:

$$N_p(t) = \frac{6\text{x}10^{21}\,\mathrm{SOC}(t)}{\pi d_W{}^3(t)\,\rho} \qquad (3.5)$$

where: - ρ is the polymer density; $\rho = 1.05$ [g/mL];

- $d_W(t)$ is the weight average particle diameter, [nm];
- $N_p(t)$ is the particle number density, [number of particles/mL latex].

3.3 RESULTS AND DISCUSSION

3.3.1 Experimental Method for St/BA Latex Synthesis

The first step of this research explored the possibility of a one-shot synthesis of a stable (80/20) styrene/butyl acrylate monodisperse latex with a particle size in the micron domain ($d_P > 1\mu$m) and a solids content higher than 25 % wt/wt.

A surfactant free emulsion polymerization route was selected after recognizing the potential advantages of this method to prepare latexes with larger particle [6,17].

All the preliminary trials carried out in a batch reaction system were unsuccessful, the polymerization failing early in the reaction because of catastrophic gross coagulation.

In order to give more versatility to the synthetic method, several semi-continuous techniques were designed. All the experiments were carried out using the procedure described in Section 3.2.2.

3.3.2 The Analysis of A Typical Experiment - Reaction S-168 (Table 3.2.1)

The reaction was performed in the absence of surfactant using an ionogenic water soluble initiator (ammonium persulfate $(NH_4)_2S_2O_8$) and in the presence of NaCl. As shown in Figure 3.3.2.1, the conversion-time curve was concave upward until about 80 % conversion, after which the curve suddenly leveled off.

During the monomer feeding stage (the time during which 100% of monomer had been added) the overall cumulative conversion was less than 20%. This very low conversion level revealed that at the end of the monomer feeding stage most of the monomer was still in monomer droplets, or in the particles. Thus, these reactions were definitely not starve-fed.

The variation of the particle number density, N_p, with time and conversion (Figure 3.3.2.1 and Figure 3.3.2.3 respectively) exhibited two distinct periods. During the first 30 % conversion N_p decreased by a factor of about 10, and after the monomer feeding period, N_p remained constant at $X_{cum.} \cong 30$ %. At the end of the monomer feeding stage the formed polymer particles were larger than 1 μm (Figure 3.3.2.3), while the corresponding conversion was less than 20 %.

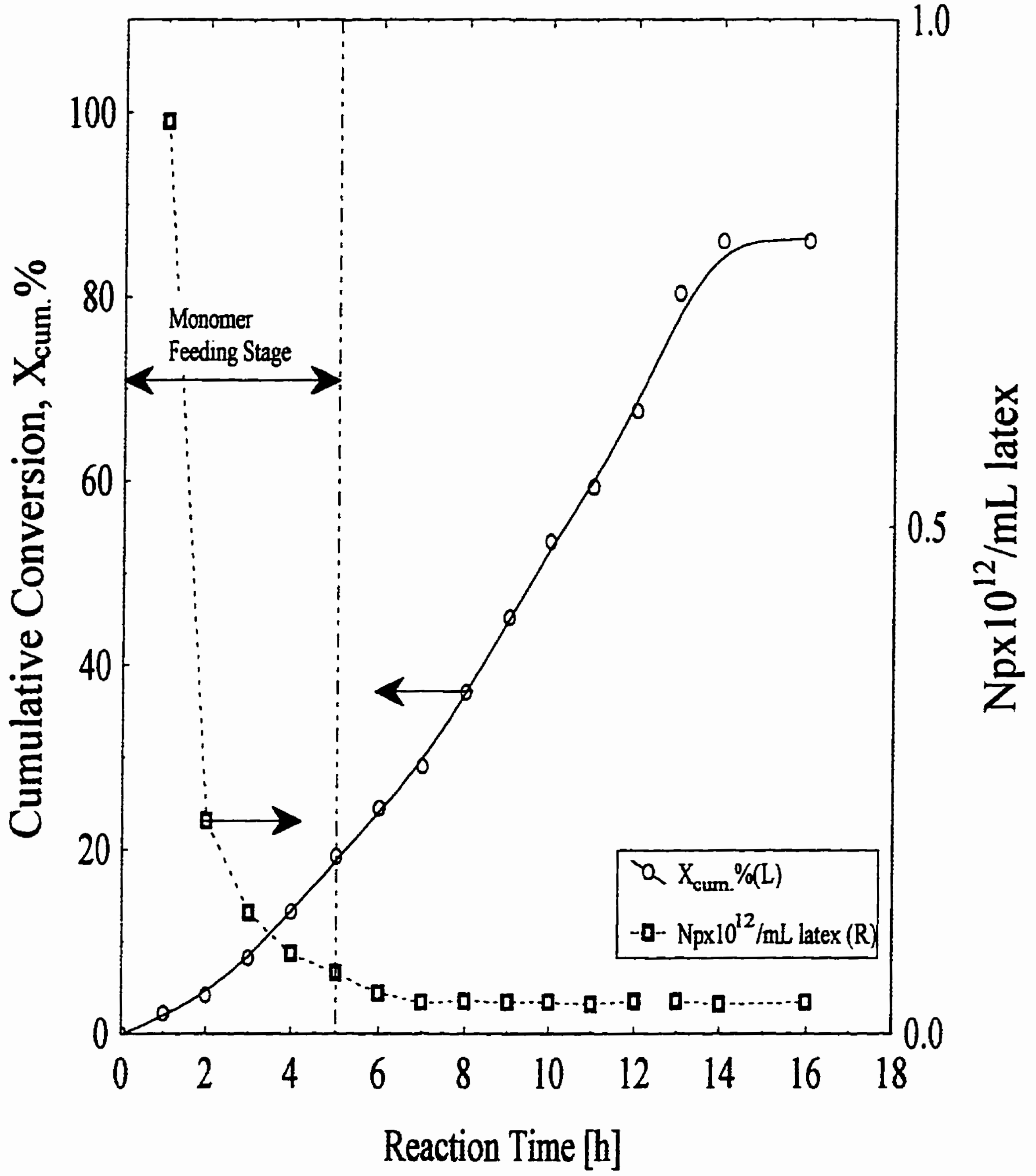
Also, the time evolution of the particle size showed two distinctive regimes which can be linked with the time-variation of the particle number density (Figure 3.3.2.3). In the first stage, during the flocculation period, the particle size increased at a faster rate than during the postflocculation stage when the number of particles was constant.

It is also interesting to note that after the first rapid flocculation stage, within the conversion range 10-80 %, the log/log plot of conversion versus reaction time gives a straight line with the slope very close to 1.5 (Figure 3.3.2.4). From a theoretical standpoint, for the "Smith-Ewart case III", the slope of log/log plot of conversion versus time is 2, while for the " Smith-Ewart case III applied to the shell reaction model " it is 1.5.[31-33] Accordingly, the experimental results shown in Figure 3.3.2.4 are consistent with the Smith-Ewart case III applied to the shell reaction model[33].

Chen *et al.*[21] found similar results working in the polymerization system styrene/acrylamide. They also suggested a shell reaction model.

Figure 3.3.2.1

The time-variation of cumulative conversion and particle number density in St/BA surfactant-free emulsion copolymerization in presence of NaCl (Run S-168).



Mechanistic Interpretation of The Behavior of A Typical Run

Latex particles with a diameter larger than 1.5 μm at a cumulative conversion of less than 30 % (Figure 3.3.2.3) strongly suggest a particle growth mechanism based mainly on a controlled aggregation. Figure 3.3.2.3 shows that during this stage, the latex particles can mainly grow by two different mechanisms:

i. By inside particle polymerization and perhaps, by capturing oligomers from water phase (heteroaggregation).

ii. By particle aggregation (homoaggregation).

After achieving enough colloidal stability the formed particles can mainly grow by inside particle polymerization mechanism and by capturing water soluble oligomeric species.

It has long been known that stable monodisperse particles can be generated in surfactant-free emulsion polymerization, even with monomers known to be almost insoluble in water (e.g., styrene), provided that the initiator decomposition gives rise to charged primary free radicals[4,6-10]. Recently, mainly based on the extensive work done by Gilbert and Napper[10,28-30], most authors accepted that in such reaction systems an homogeneous-coagulative mechanism would take place.

Although, our experimental evidence exhibited most of the characteristics of an homogeneous-coagulative mechanism, some particularities, such as the comparative evolution of the size of particles and the particle number density versus conversion and time, suggest a very interesting new emulsion polymerization mechanism.

At the very beginning of the polymerization process, when no particles exist, the initiation of polymerization is assumed to take place exclusively in the water phase by reaction of ionogenic primary radicals and the St and BA monomer molecules, (M (aq.)), dissolved in the water phase.[4,9-10] Consequently, both the oligomers resulting from the aqueous termination and the propagating oligoradicals are electrically charged. Moreover, they could either be soluble in the aqueous phase or they could coagulate to form primary particles, depending on their degree of polymerization.

Figure 3.3.2.2

The time-variation of the weight-average particle size, d_W, and particle number density in St/BA surfactant-free emulsion copolymerization in presence of NaCl (Run S-168).

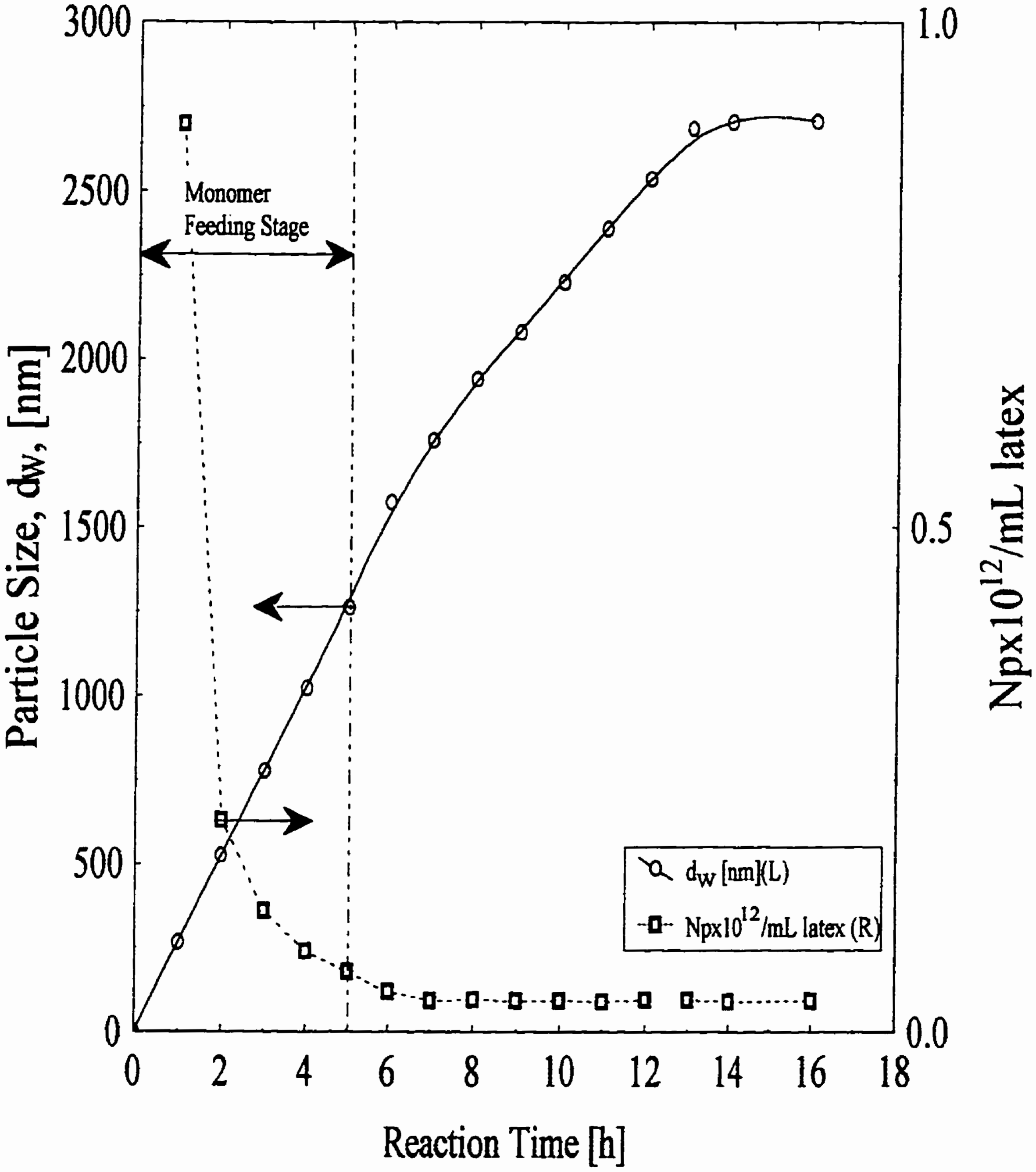


Figure 3.3.2.3

The variation of the weigh-average particle size, particle number density, and ln(N_p) versus conversion, in St/BA surfactant-free emulsion copolymerization in presence of NaCl (Run S-168).

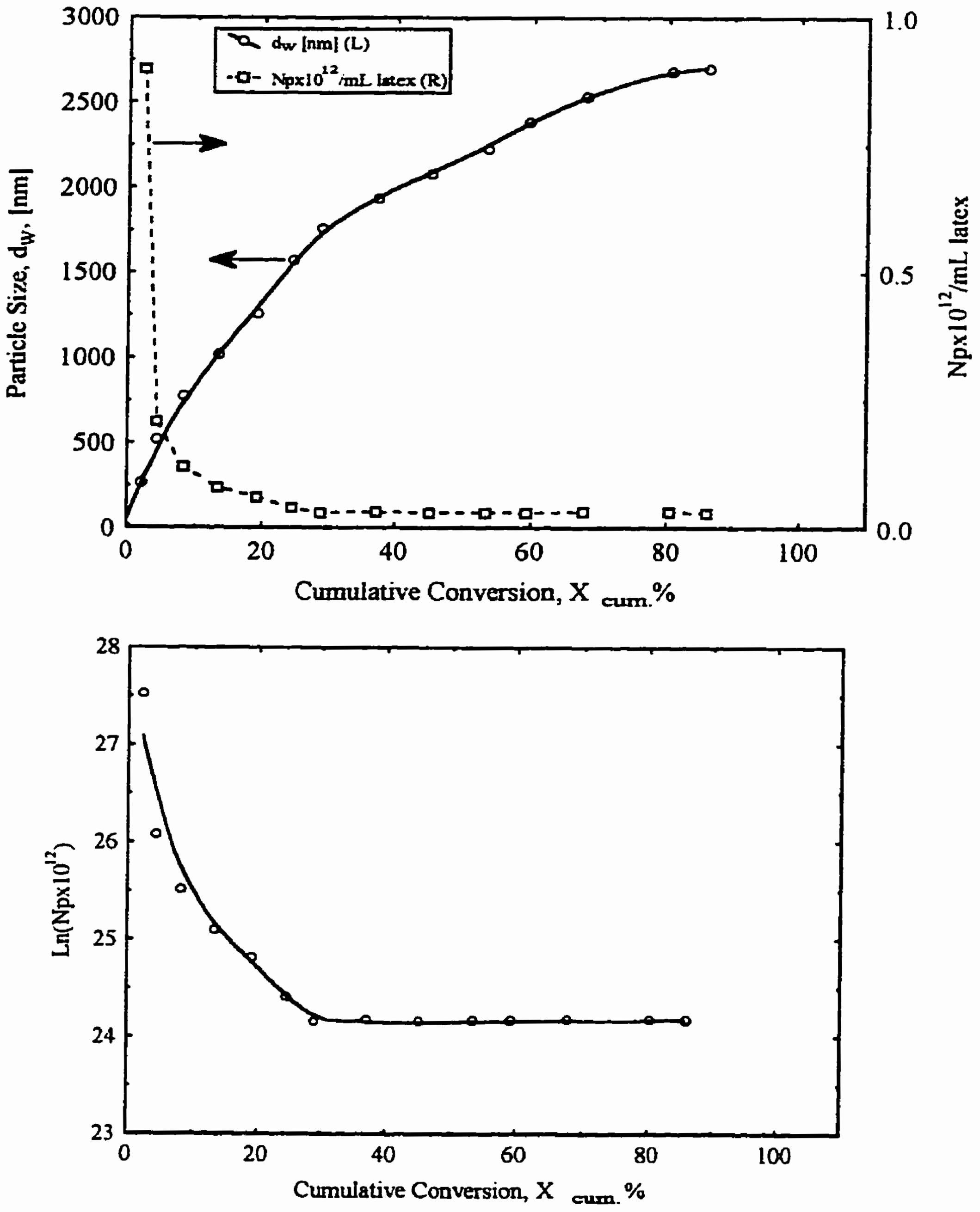
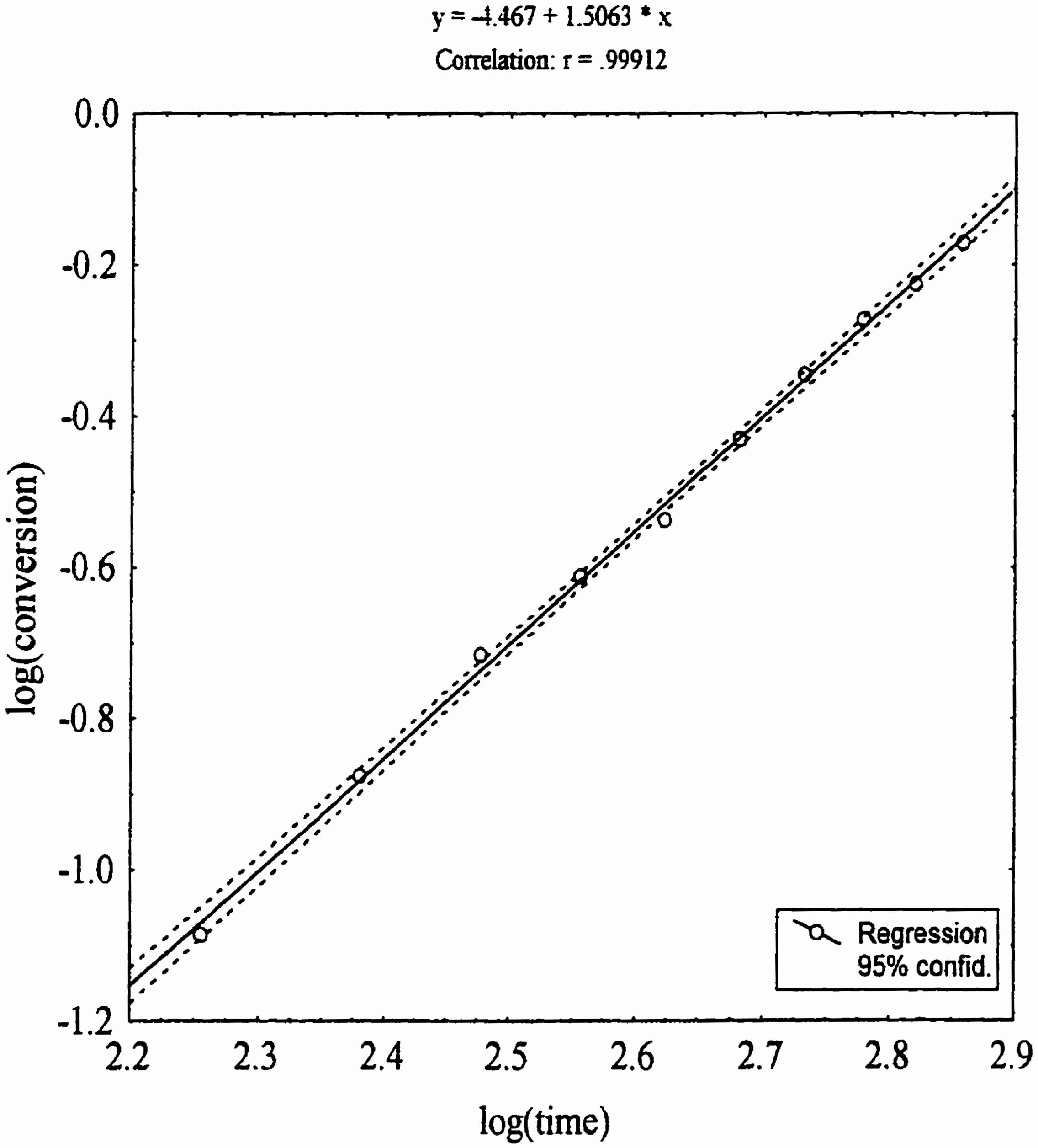


Figure 3.3.2.4

The log/log plot of conversion versus reaction time within the conversion range 10-80 %, in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.



According to the homogeneous nucleation theory[9,10], these oligoradicals add monomer molecules until they reach a critical chain length, $j_{crit.}$, at which they exceed their water solubility and precipitate. The precipitated oligoradicals collapse together as *nuclei* which undergo further aggregation to *primary particles*.

Because the first formed primary particles bear only a few stabilizing groups on their surfaces they are not stable. Thus, as collisions between the primary particles occur, particles flocculate due to insufficient surface charges. As a result of flocculation, the number of particles decreases, but they become more stable because of increased surface charge density. It can be assumed that during the flocculation process most of the stabilizing charges, because of their hydrophilicity, are mainly distributed on the surfaces of the newly formed particles.

As can be seen from Figures 3.3.2.1 and 3.3.2.2 respectively, in the first two hours of reaction, the cumulative conversion was less than 5 % while the corresponding size of particles was larger than 500 nm. Also, during this stage, N_p decreased sharply with time. These experimental observations strongly suggest that particles grew mainly by aggregation rather than by propagation.

It was clear that the successful key to reach micron-sized St/BA particles in a one-shot synthesis is to use a versatile semi-continuous surfactant-free emulsion polymerization technique and to find a means of controlling both the coagulative and aggregation processes which take place during different stages of reaction.

A detailed experimental program was carried out on the St/BA emulsion copolymerization system to determine the influence of the following experimental parameters: initiator concentration and its addition policy, ionic strength, the initial pH of water phase, and the monomer mixture composition and feeding rate.

3.3.3 The Influence of Initiator Concentration

Two series of experiments (series A and B in Table 3.3.3.1) were carried out to study the effects of initiator concentration on the St /BA surfactant-free emulsion copolymerization.

In order to avoid any other influence, the recipes for the two series were the same except for the following:

i. In series A, two sets of polymerizations were performed in the presence of two different salts:

- NaCl in the A1 set, in which case the initial pH was acidic
- $NaHCO_3$ in the A2 set, when the initial pH was basic.

ii. In series B, no salt was used.

The minimum concentration of the initiator in this work was fixed by the amount required to produce a stable, monodisperse latex with the largest particle size. As can be seen in series B (Table 3.3.3.1), for the (80/20) St/BA polymerization system without salt addition, the minimum initiator concentration was 2.67 g/L water. When the polymerization was performed at lower initiator concentrations the final latex was polydisperse even if the final particles were bigger.

When A and B series polymerizations were carried out at the same minimum initiator concentration (Table 3.3.3.1) the final latex particles were in the micron domain. Although, in all these cases the final latexes were monodisperse (Figure 3.3.3.1) a lot of coagulum was found at the end of the polymerization process. This limited the final solids content and latex yield. However, in neither of these cases was the solids content less than the 25 % wt/wt limit.

Table 3.3.3.1

The influence of initiator concentration on St/BA surfactant-free emulsion copolymerization.

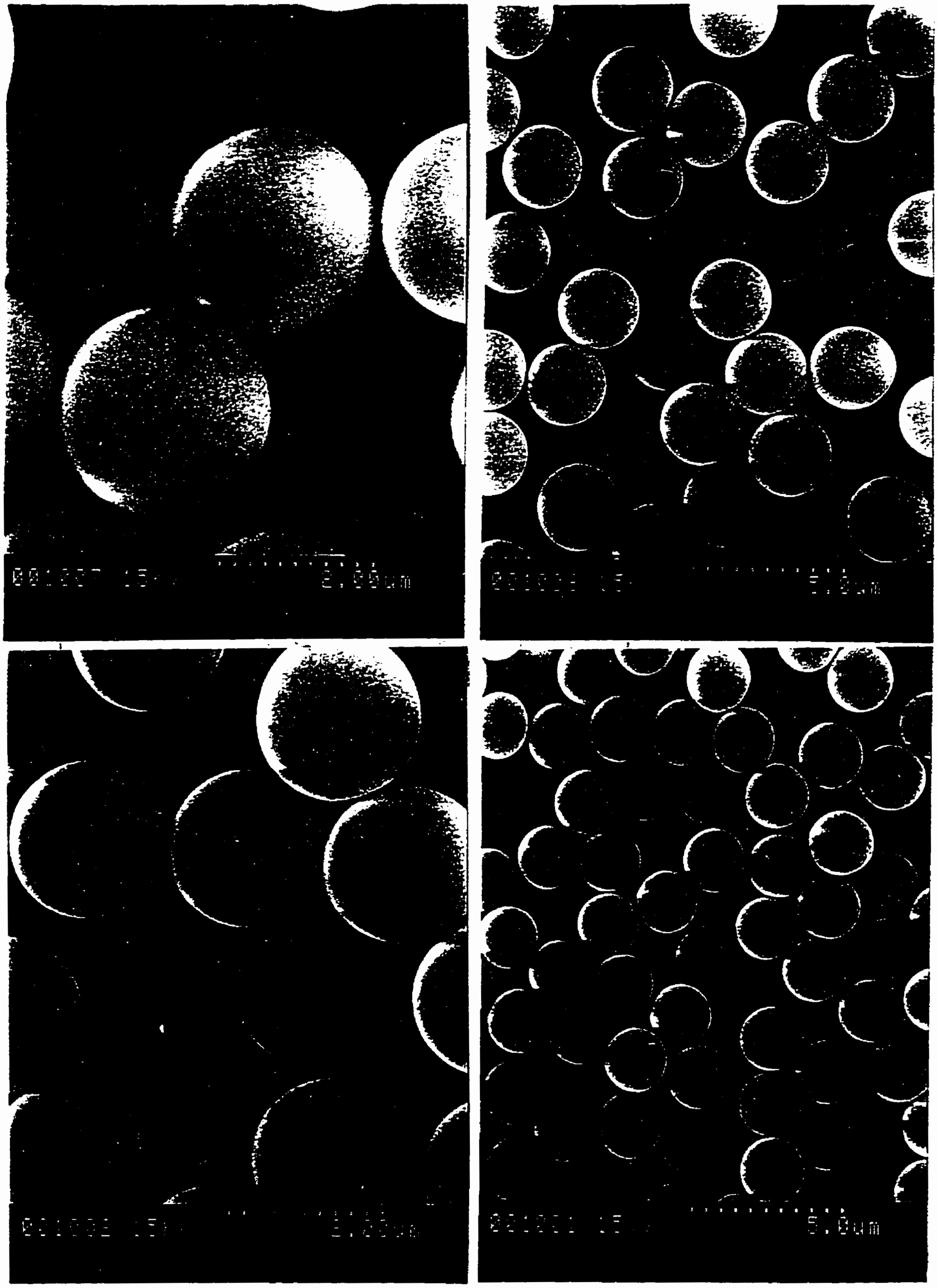
	A series					*B series*	
	NaCl		**$NaHCO_3$**			**No salt**	
Latex No.	***S-168***	***S-199***	***S-171***	***S-198***	***S-197***	***S-175***	***S-205***
Initiator Conc.[g/L water]	**2.67**	**5.56**	**2.67**	**3.55**	**5.56**	**2.67**	**1.78**
Salt Conc. [g/L water]	1.44	1.44	2.07	2.07	2.07	0	0
Ionic Strength [mol/L]	0.059	0.098	0.059	0.071	0.098	0.035	0.023
Initial pH	3.1	3.0	7.5	7.4	7.5	3.0	3.0
Particle Size [nm]	2705	1166	2228	1598	1025	717	824
Latex Polydispersity d_w/d_n	1.014**	1.006*	1.014**	1.013**	1.005*	1.006*	1.020*
Coagulum	much	little	much	little	little	little	much
Solids Content [% wt/wt]	26.5	29.8	27.6	29.6	31.0	30.2	28.9
Latex Final Yield [%]	80.6	94.6	85.6	92.8	94.8	93.6	89.7

St/BA = 80:20 wt/wt; Temp. = 70 °C; monomer feeding time, $t_F \cong 5$ h, constant; stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

Figure 3.3.3.1

SEM photographs of St/BA latexes made with different salts at a constant initiator concentration, $[(NH_4)_2S_2O_8]=2.67g/L$ water.



In order to overcome coagulum formation the initiator concentration was increased (Table 3.3.3.1). This led to a higher solids content and increased the final latex yield, regardless of the type of salt used. Nevertheless, in both polymerization sets of the A series, the increase of initiator concentration significantly decreased the latex particle size probably, because a higher number of particles were nucleated.

Furthermore, the experimental data (Table 3.3.3.1) reveal some interesting characteristics:

i. Increased initiator concentration decreased particle size in spite of increased ionic strength which would be expected to work in the opposite direction.

ii. Larger particles were obtained at lower pH at same initiator concentration and ionic strength.

iii. Particle size was more sensitive to initiator concentration at lower pH.

In most of the kinetic studies the time scale was reported to the reduced-time, t/t_F, (where t is the reaction time and t_F represents the total monomer feeding time).

In series A (Figure 3.3.3.2 and Figure 3.3.3.3) the conversion curves revealed an increase of the polymerization rate with the increase of the initiator concentration regardless of the initial pH value. In both cases the final conversion was enhanced as well. This evidence is in qualitative agreement with the well accepted equation of the polymerization reaction rate Eq. 3.6:[9,10]

$$R_p = k_P [M]\tilde{n}N_p/N_A \qquad (3.6)$$

where k_P is the propagation rate constant, N_p is the number of particles, $\tilde{n}$ is the number of radicals per particle, [M] the monomer concentration in the particle, and N_A is Avogadro's number.

Figure 3.3.3.2

The influence of initiator concentration on the polymerization rate and time-variation of particle number density in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.

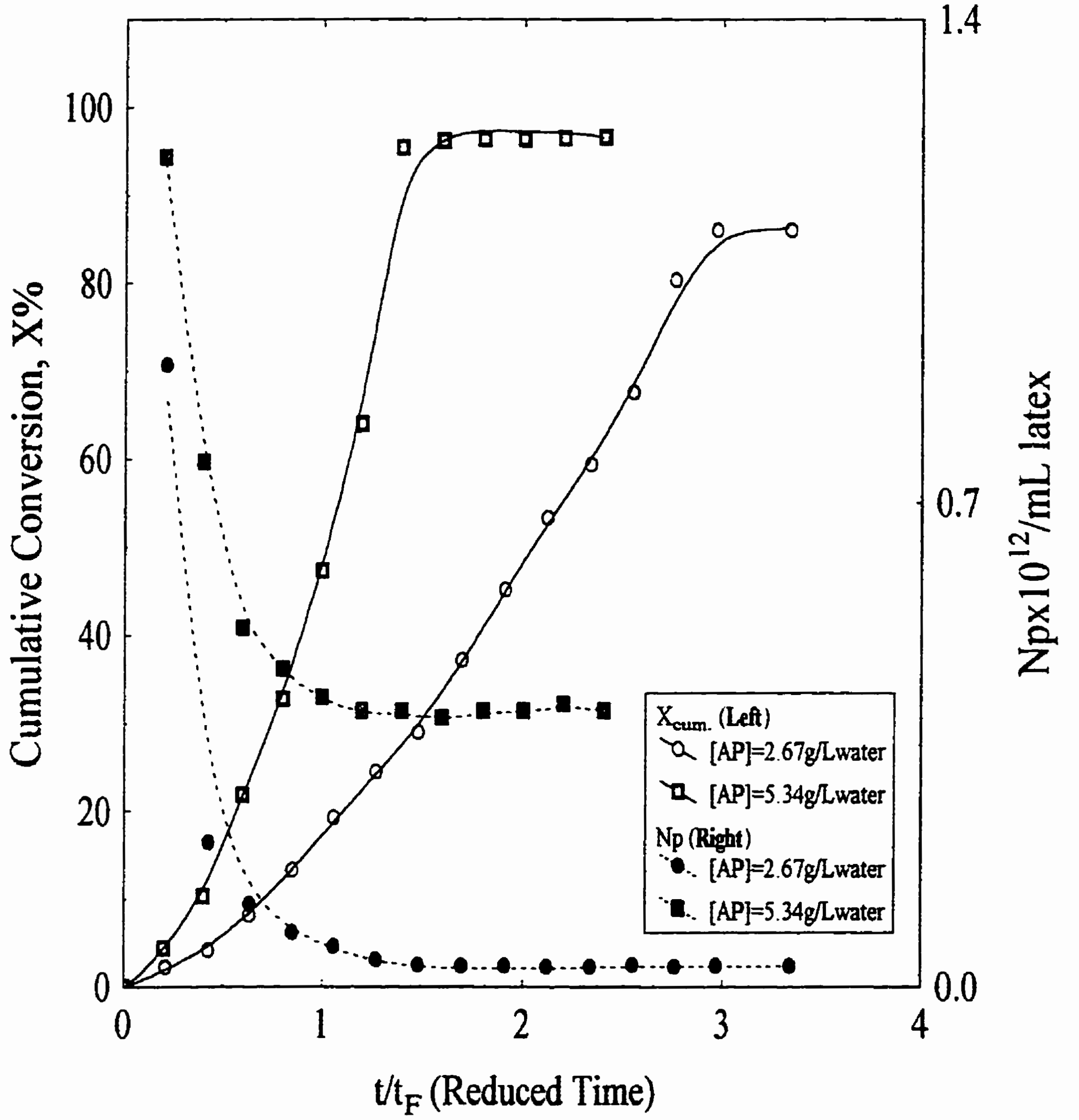
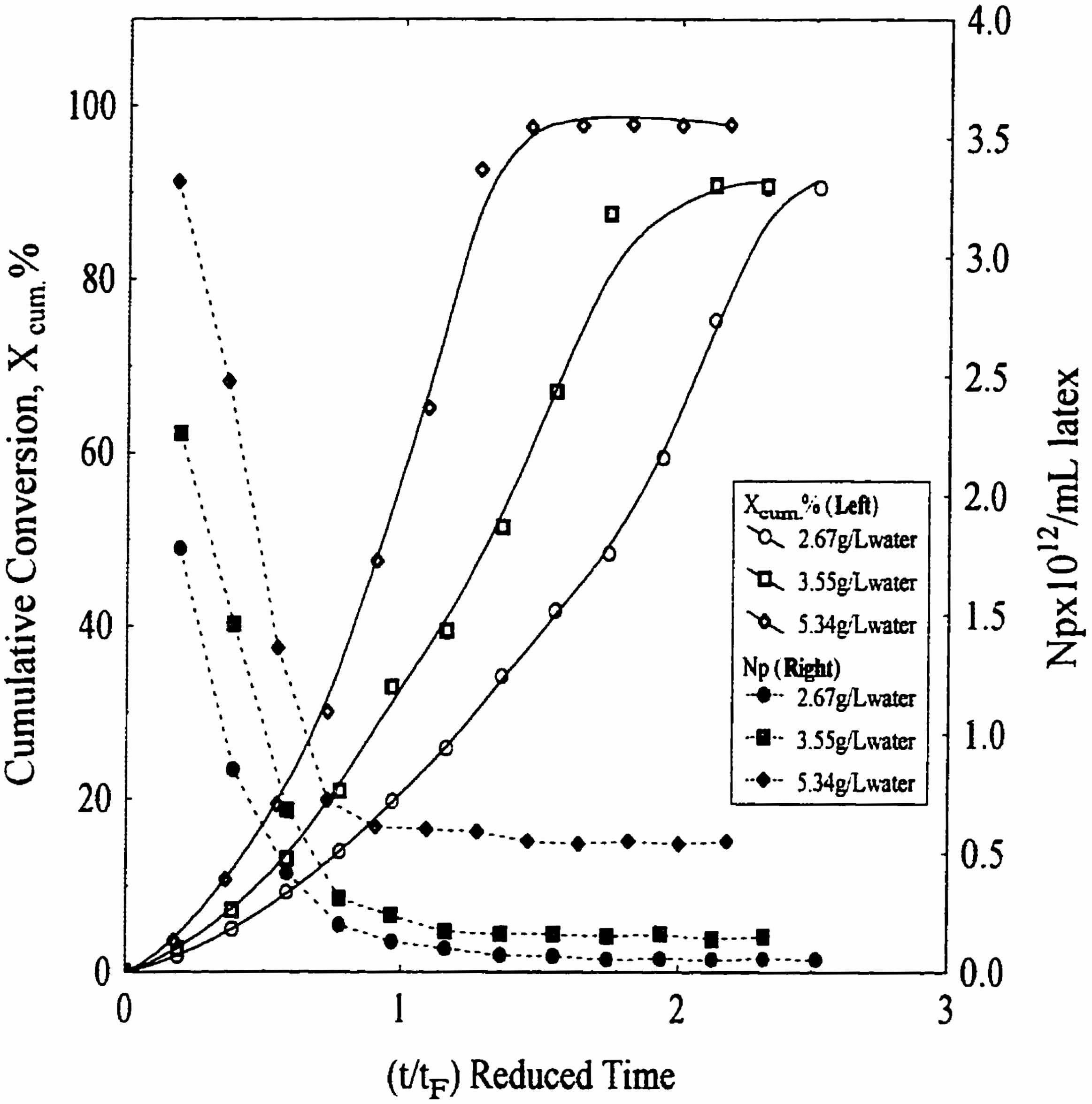


Figure 3.3.3.3

The influence of initiator concentration on the polymerization rate and the time-variation of particle number density in St/BA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.



Very early during the reaction ($X_{cum} < 10$ %) the particles were unstable and flocculated continuously (Figure 3.3.3.2 and Figure 3.3.3.3). Thereafter, N_p reached a constant level at $1.5t_F$. The conversion at which the number of particles became constant depended on both the initiator concentration and the initial pH (Figures 3.3.3.2 - 3.3.3.3 and Table 3.3.3.2 respectively). Higher conversion levels were obtained at higher initiator concentration and a higher pH.

In both series, the increase in the initiator concentration shortened the time when the particle number density became constant (Figure 3.3.3.2). As well, the final particle number density was higher at a higher initiator concentration, regardless of salt type, reflecting greater nucleation (Figure 3.3.3.2 and Figure 3.3.3.3). In all cases, larger particles were formed in the early stage of reaction (average sizes larger than 1 μm at $X_{cum} > 20$ %).

The increase of the initiator concentration can have two main competing effects:

i. To increase the concentration of the primary radicals in the water phase which favors the nucleation of more particles and leads to smaller particles.

ii. To increase the ionic strength of the water phase, which favors the coagulation and aggregation processes, and by that to reduce the number of formed particles which leads to larger particles.

Table 3.3.3.2

The influence of initial pH and initiator concentration on the conversion level of St/BA emulsion copolymerization.

	NaCl $pH_{init.} \cong 3.1$		*$NaHCO_3$* $pH_{init.} \cong 7.5$		
[AP] [g/L water]	2.67	5.56	2.67	3.55	5.56
$Np10^{12}$ = (constant level)	0.03	0.40	0.055	0.15	0.55
$X_{cum.}$%	24.5	47.5	48.3	51.4	65.1

Figures 3.3.3.4 - 3.3.3.5 reveal that the initial particle size growth was independent of initiator concentration. As a result, the main effect of increasing initiator concentration was to reduce the aggregation after about 0.5 t_F (Figure 3.3.3.4) and 0.6 t_F (Figure 3.3.3.5).

The experimental curves N_p versus time and N_p versus conversion (Figures 3.3.3.2 - 3.3.3.3 and Figures 3.3.3.6-3.3.3.7 respectively) reveal some interesting aspects related with the polymerization mechanism. The time-variation of the particle number density showed a faster decrease of N_p, to the final constant value, with the increase of initiator concentration. In contrast, the N_p variation with conversion showed a longer decrease period of N_p by increasing the initiator concentration.

It was already emphasized that by increasing the initiator concentration, more primary particles are nucleated and more stabilizing sulfate groups are anchored on their surface. Thus, in some circumstances, the resulting particle charge density is high enough to give sufficient colloidal stability and to counterbalance the particle aggregation process, which is favored by the increase of ionic strength, due to the increase of initiator concentration. Therefore, the size of the final particles is smaller for the latexes prepared at a higher initiator concentration than at lower initiator concentration, although the ionic strength is higher in the former case.

3.3.4 The Influence of Ionic Strength

The lower accessible limit of ionic strength, I, was determined by the minimum amount of initiator required to produce an effective stable monodisperse latex. For the (80/20) St/BA polymerization system, in the presence of ammonium persulfate, this limit was *c.a.* I=0.035 mol/L (Table 3.3.2.1), corresponding to [AP] = 2.67 g/L water.

The increasing of ionic strength (by salt addition), at constant initiator concentration, significantly increased the size of the latex particles (Table 3.3.4.1). However, if the overall ionic strength, based on initiator plus added salt, was too high, a polydisperse latex resulted, followed by a gross coagulation.

Figure 3.3.3.4

The influence of initiator concentration on the time-variation of particle size and particle number density in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.

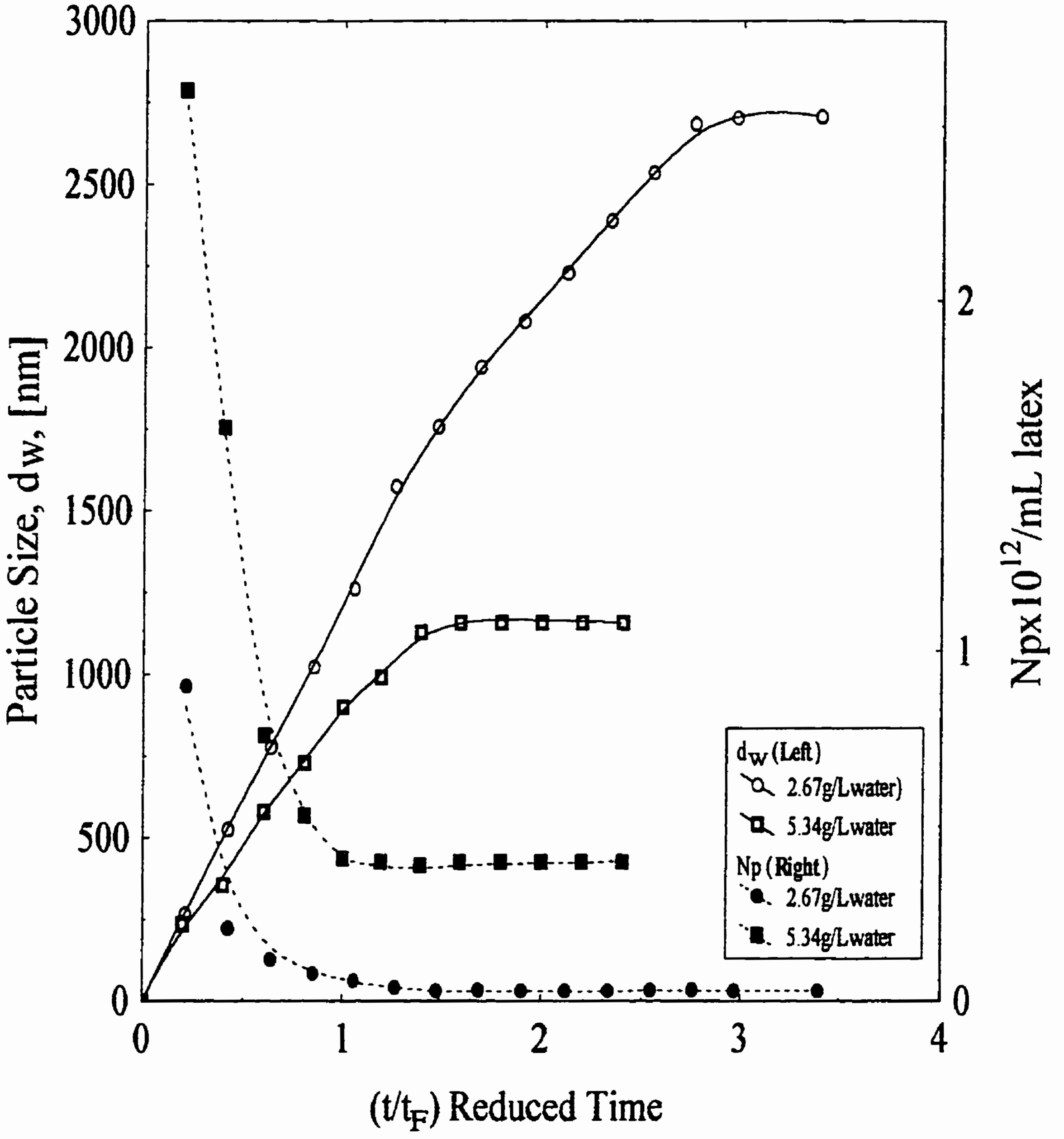


Figure 3.3.3.5

The influence of initiator concentration on the time-variation of particle size and particle number density in St/BA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

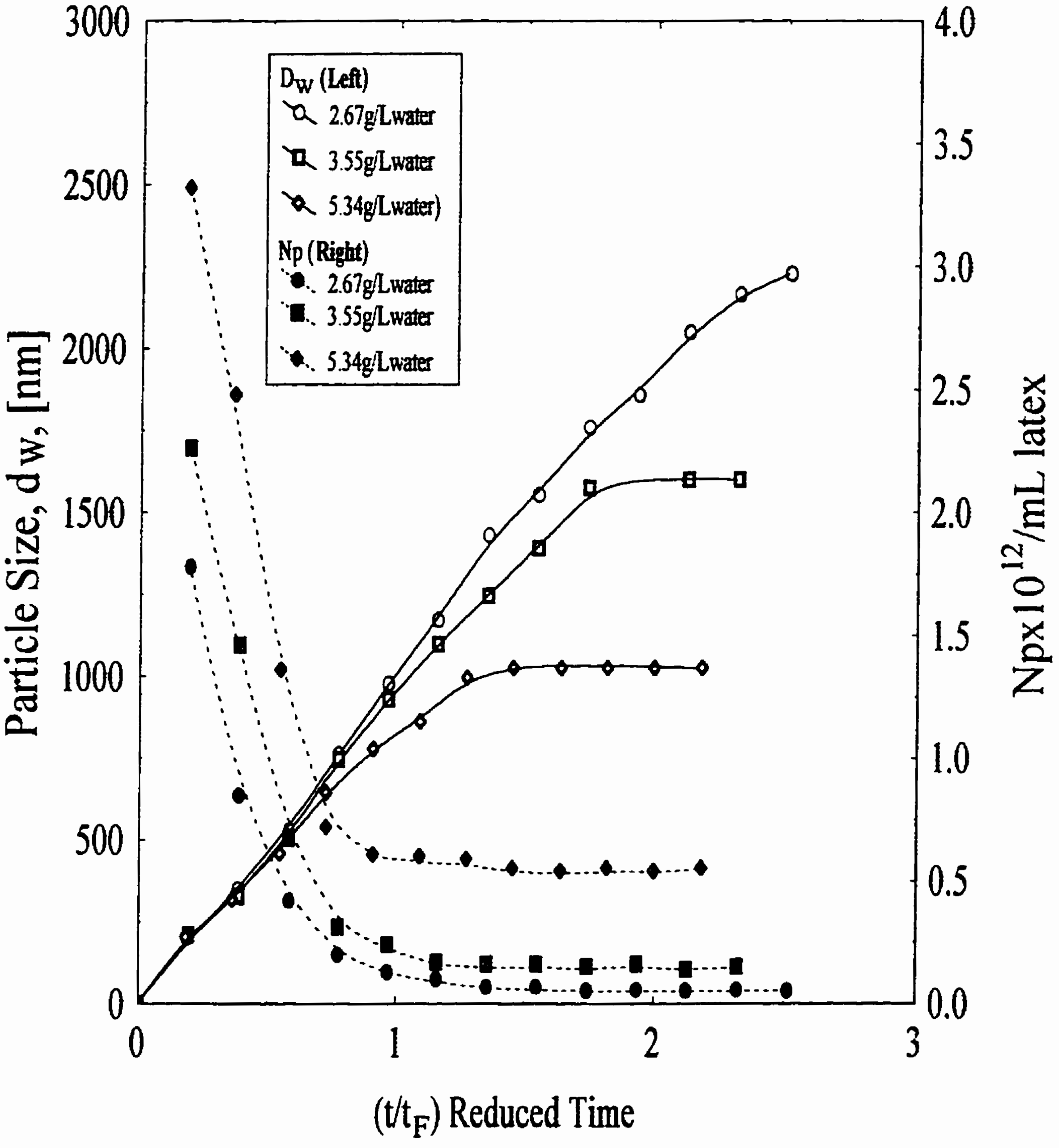


Figure 3.3.3.6

The influence of initiator concentration on the variation of particle size and particle number density with cumulative conversion in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.

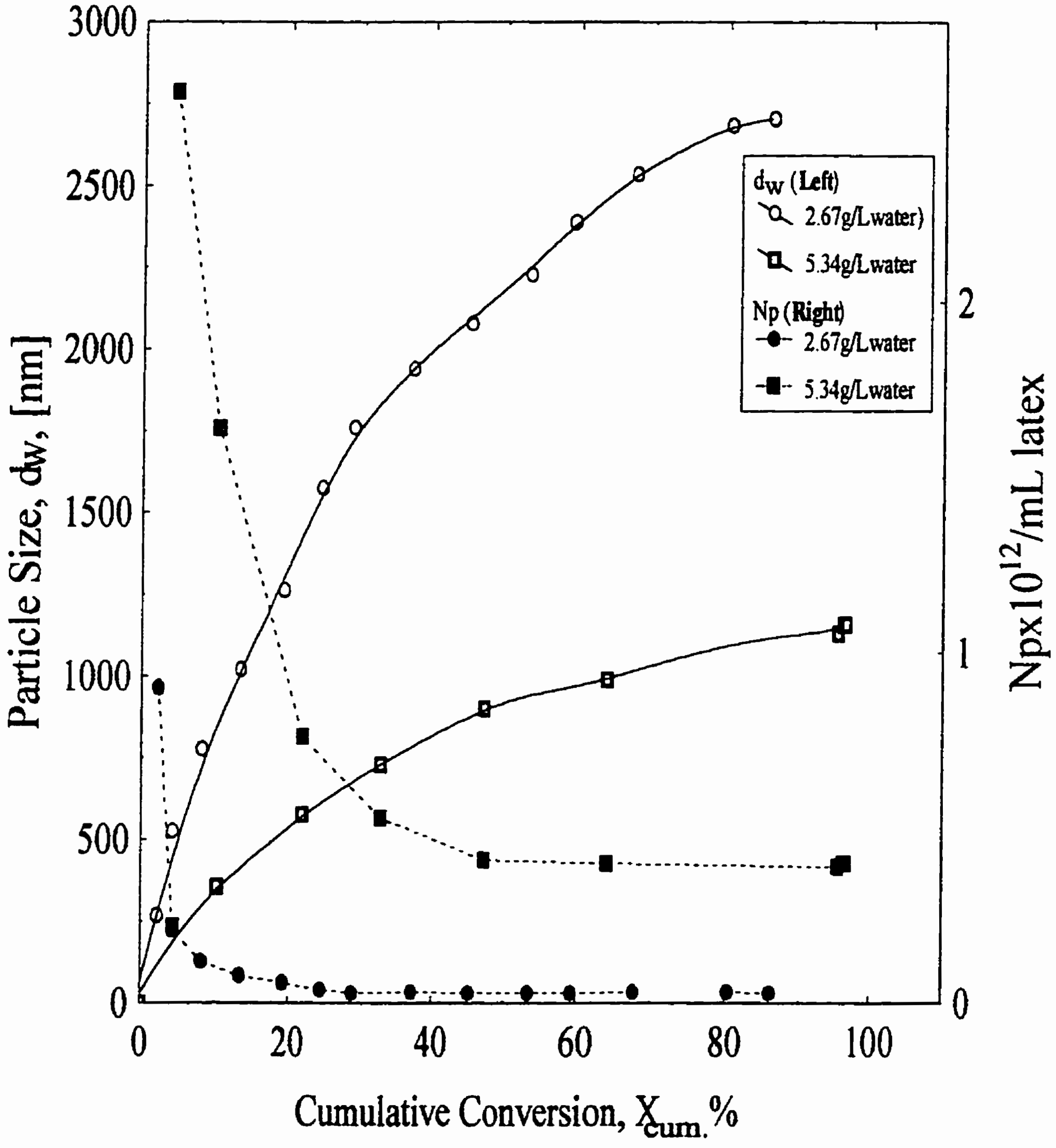
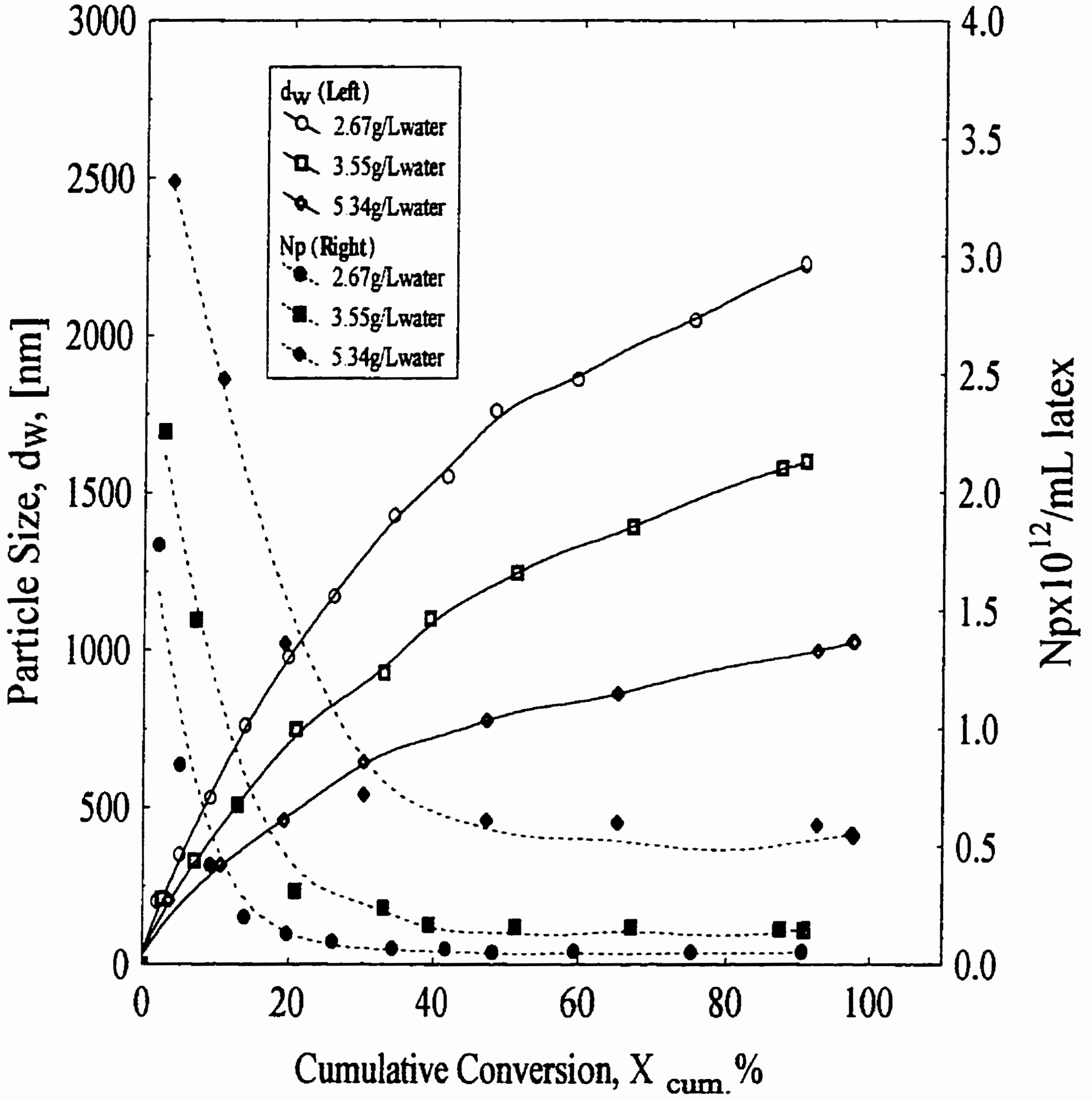


Figure 3.3.3.7

The influence of initiator concentration on the variation of particle size and particle number density with cumulative conversion in St/BA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.



When the polymerizations were carried out in presence of NaCl (Table 3.3.4.1). a slight increase of ionic strength led to a sharp increase of the final latex particle size. At highest ionic strength the colloidal stability of latexes decreased. Thus, a lot of coagulum was formed, while the final latex yield and the solids content dropped off below 90 % and around 26% wt/wt respectively.

Above the highest ionic strength value, I=0.059 mol/L, the synthesis failed because of a gross coagulation which occurred during the monomer feeding stage.

Polymerizations carried out in the presence of $NaHCO_3$ showed similar trends to those performed with NaCl. However, the upper ionic strength limit was almost two times higher than that for polymerization carried out in presence of NaCl (Table 3.3.4.1).

In order to find more about the influence of ionic strength on the polymerization mechanism, a more detailed analysis was made based on the experimental data resulted from the polymerization carried out in presence of NaCl as added inert salt (Table 3.3.4.1).

The time-variation of cumulative conversion, $X_{cum.}$ %, at different initial ionic strengths and constant initiator concentration (Figure 3.3.4.1) revealed a decrease in the polymerization rate with increase of ionic strength. The limiting conversion was also lower with increase ionic strength.

In the early stage of the polymerization, regardless of the ionic strength, all the experimental curves of N_p versus time showed the now typical decreasing trend (Figure 3.3.4.1) which leveled off at about the end of the monomer feeding. In each of these cases, during the monomer feeding stage, the cumulative conversion was very low (less than 30 %) depending on the ionic strength. At a higher ionic strength the cumulative conversion was lower than that recorded at a lower ionic strength.

The constant value of the particle number density strongly depended on the ionic strength. Higher ionic strengths led to lower final particle number density. Therefore, the final size of the latex particles was larger (Figure 3.3.4.2).

Table 3.3.4.1

The influence of ionic strength on St/BA surfactant-free emulsion copolymerization.

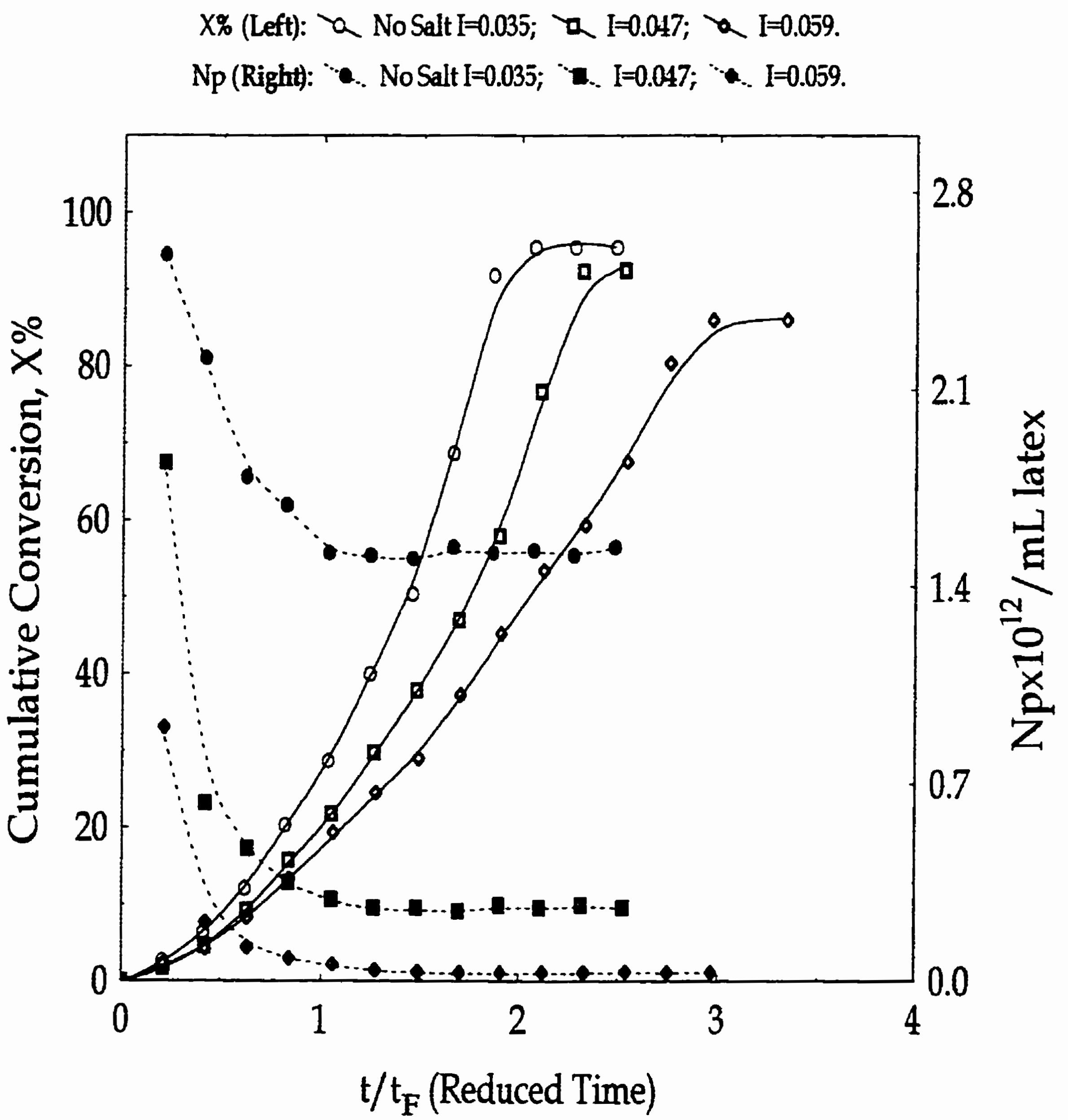
Series	NaCl			$NaHCO_3$	
Latex No.	***S-227***	***S-223***	***S-168***	***S-171***	***S-111***
Initiator Conc. [g/L water]	2.67	2.67	2.67	2.67	2.67
Salt Conc. [g/L water]	0	0.71	1.44	2.07	8.27
Ionic Strength [mol/L]	**0.035**	**0.047**	**0.059**	**0.059**	**0.111**
Initial pH	3.0	3.1	3.1	7.5	8.2
Particle Size [nm]	717	1279	2705	2228	2820
Latex Polydispersity d_w/d_n	1.006*	1.006*	1.014**	1.014**	1.026**
Coagulum	little	little	much	much	much
Solids Content [% wt/wt]	30.2	30.0	26.5	27.6	25.0
Latex Final Yield [%]	93.6	92.6	80.6	85.6	82.2

St/BA = 80:20 wt/wt; Temp. = 70 °C; monomer feeding time ≅ 5h;
stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

Figure 3.3.4.1

The influence of ionic strength on the polymerization rate and time-variation of particle number density in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.



Moreover, the time-evolution of the particle size revealed that throughout the polymerization carried out at a higher ionic strength, the latex particles attained their final size much more slowly than during the polymerization performed at a lower ionic strength (Figure 3.3.4.2).

The experimental curves from Figure 3.3.4.3 revealed a decreasing trend of N_p versus conversion, while the corresponding variation of the particle size versus conversion is increasing.

In the early part of the reaction (within the conversion range 0-10 %) a very rapid particle flocculation process was observed (Figure 3.3.4.4) followed by a slight decrease of the particle number density until N_p became constant. The higher the ionic strength was, the stronger the particle flocculation process was and the faster the number of particles became constant. Moreover, the conversion at which N_p became constant was lower at a higher ionic strength, while the corresponding particle size was higher in that case. Throughout these polymerizations, at the same conversion level, the size of the latex particles recorded at a higher ionic strength was much larger than that which resulted at a lower ionic strength.

All these experimental arguments support the well accepted theory which suggests that at constant initiator concentration the size of particles generated in a surfactant-free emulsion polymerization process increases in parallel with the increase of the ionic strength of the aqueous phase[6-8,10,35-38]. This is because colloid stability is affected by ionic strength. An electrolyte destabilizes the electrostatically stabilized lattices obtained by surfactant-free emulsion polymerization, and causes them to aggregate or coagulate.

Goodwin *et al.*[6-8] suggested that the size of the first stable colloidal particles formed is controlled to a large extent by the ionic strength of the aqueous phase. Consequently, for the same initial monomer concentration and the same percentage conversion of monomer to polymer, the final particle size attained in the higher ionic strength medium will be larger. Moreover, if the final particle size distribution is

Figure 3.3.4.2

The influence of ionic strength on the time-variation of particle size in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.

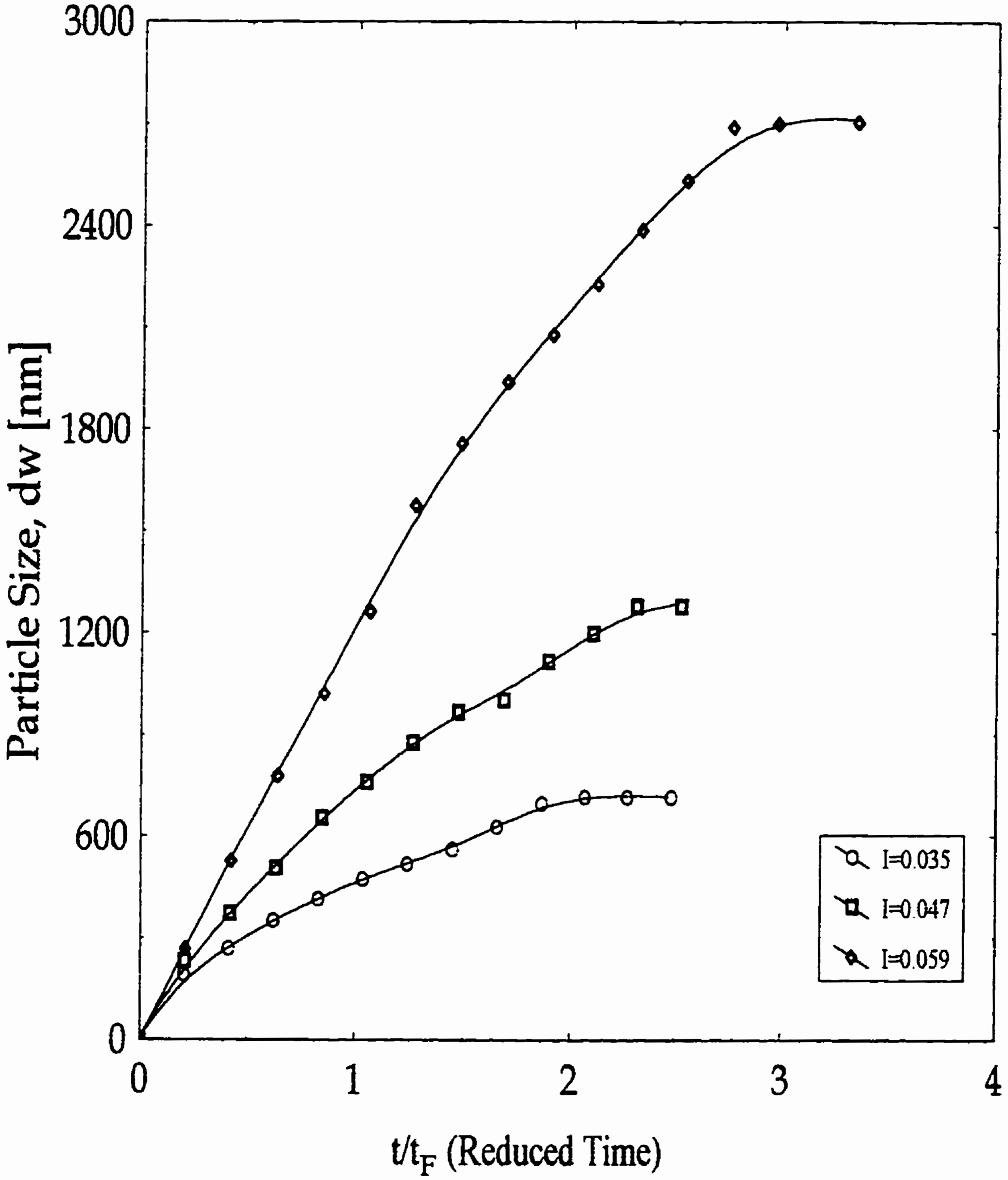
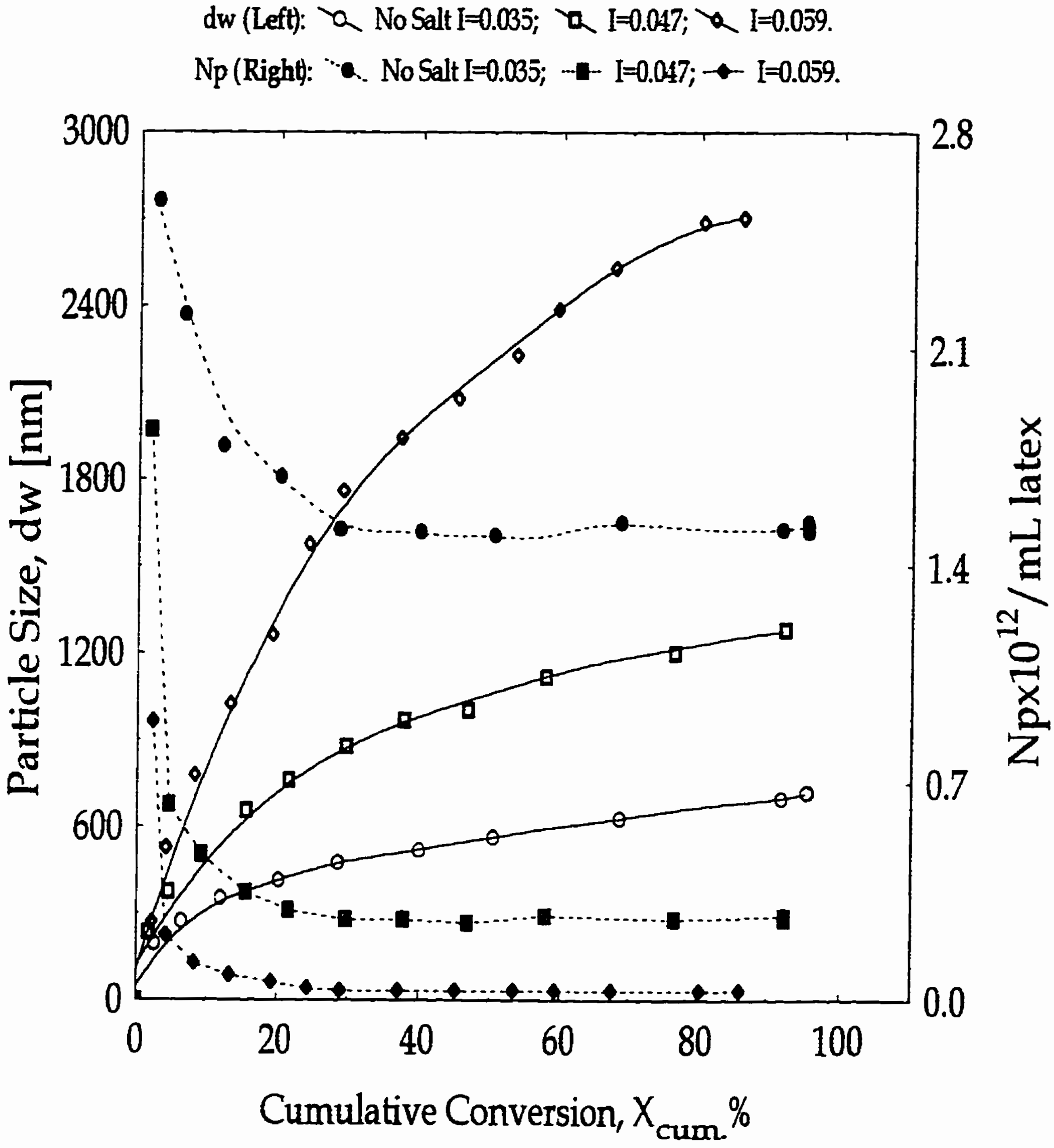


Figure 3.3.4.3

The influence of ionic strength on the conversion-variation of particle size and particle number density in St/BA surfactant-free emulsion copolymerization in presence of sodium chloride.



monodisperse, this means that any aggregative process must occur in the early stages of the reaction.

This trend is consistent with the generally well accepted points of view of the DLVO theory concerning the influence of the ionic strength on the colloidal stability of latexes[39]. Thus, the DLVO theory considers that the increase of the ionic strength shrinks the electrical double layer of particles and by that reduces the repulsive electrostatic barrier between particles. The particles become less colloidally stable and more liable to coagulate. However, up to a certain limit of the ionic strength, mainly depending on the initiator concentration and type of electrolyte, both the aggregative and coagulative processes can be kept under control. In this case, the final latexes will be stable enough to remain monodisperse. Once the ionic strength exceeds this limit the latexes become polydisperse, more coagulum is formed and finally, the reaction system fails by gross coagulation.

3.3.5 The Influence of Initial pH

For the semi-continuous surfactant-free emulsion copolymerization of (80/20) St/BA system it was found that an increase in the initial pH (resulting from initiator and salt addition influence) decreased the size of latex particles and strongly influenced the latex properties, such as monodispersity, solids content and final yield (Table 3.3.5.1).

In order to investigate the influence of pH on the polymerization system, some experiments were carried out using a constant monomer composition (80/20 St/BA), initiator concentration ($[(NH_4)_2S_2O_8]$ = 2.67 g/L), ionic strength (I = 0.059 mol/L), feeding rate (Ra ≅ 0.68 g/min.- corresponding to approx. 5 h monomer feeding), stirring rate (~ 200 RPM) and reaction temperature (T = 70 °C).

Except when the experiments were carried out at pH ≅ 3.0, the initial pH of the reaction medium was controlled by salt addition: $NaHCO_3$ for neutral/weak-basic range: pH ≅ 7.5, and NaOH for basic range: pH ≅ 11.0.

Table 3.3.5.1

The influence of initial pH on St/BA surfactant-free emulsion copolymerization.

Latex No.		***S-168***	***S-171***	***S-174***
Initiator Conc.	[g/L water]	2.67	2.67	2.67
Salt Type		NaCl	$NaHCO_3$	NaOH
Salt Conc.	[g/L water]	1.44	-	-
		-	2.07	-
		-	-	2.00
Ionic Strength	[mol/L]	0.059	0.059	0.059
Initial pH		**3.1**	**7.5**	**10.9**
Particle Size, d_W,	[nm]	2705	2228	621
Latex Polydispersity, d_W/d_n		1.014**	1.014**	1.025*
Solids Content	[% wt/wt]	26.5	27.6	31.2
Latex Final Yield	[%]	80.6	85.6	94.0

St/BA = 80:20 wt./wt.; Temp. = 70 °C; monomer feeding time ≅ 5 h;
stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

The conversion versus time plots for these pHs are shown in Figure 3.3.5.1. As can be seen, as the initial pH increased from 3.0 to 8.0, the polymerization rate increased slightly, while at a pH $\cong$ 11.0, the polymerization rate was significantly higher. As well, at the end of the monomer feeding stage, the conversion level was also higher in polymerizations carried out in basic pH. The significantly higher polymerization rate within the basic pH range was well supported by the 100-fold higher number of particles generated in this case.

What is more interesting from the point of view of the polymerization mechanism is the variation of the particle number density versus time and cumulative conversion, see Figures 3.3.5.1 and 3.3.5.2, respectively.

For both the NaCl and $NaHCO_3$ runs, the particle number density decreased substantially as the reaction proceeds. Moreover, the formation of polymer particles with average particle size larger than 1 μm at a cumulative conversion less than 20 %, can be only explained by an ongoing particle aggregation process. As a result, instead of particles with diameter in the nanometer domain (the normal particle size range for a classical emulsion polymerization process) supermicron, monodisperse, particles were obtained.

In contrast, for the NaOH run (S-174), the experimental curves N_p versus time and conversion respectively, revealed two main trends:

i. Np decreased to some extent in the first 3 hours of reaction (up to ~15 % conversion) indicating some aggregation.

ii. At 15 % conversion N_p increased up to about 25 % conversion and remained constant. This suggests that additional particles were formed (secondary nucleation). Further aggregation did not occur.

The recorded changes in the particle number density evolution correspond to the generation of a new particle population (Figure 3.3.5.3) and consequently, to decreasing the latex monodispersity (Figure 3.3.5.4).

Figure 3.3.5.1

The influence of initial pH on the time-variation of conversion and particle number density in St/BA surfactant-free emulsion copolymerization.

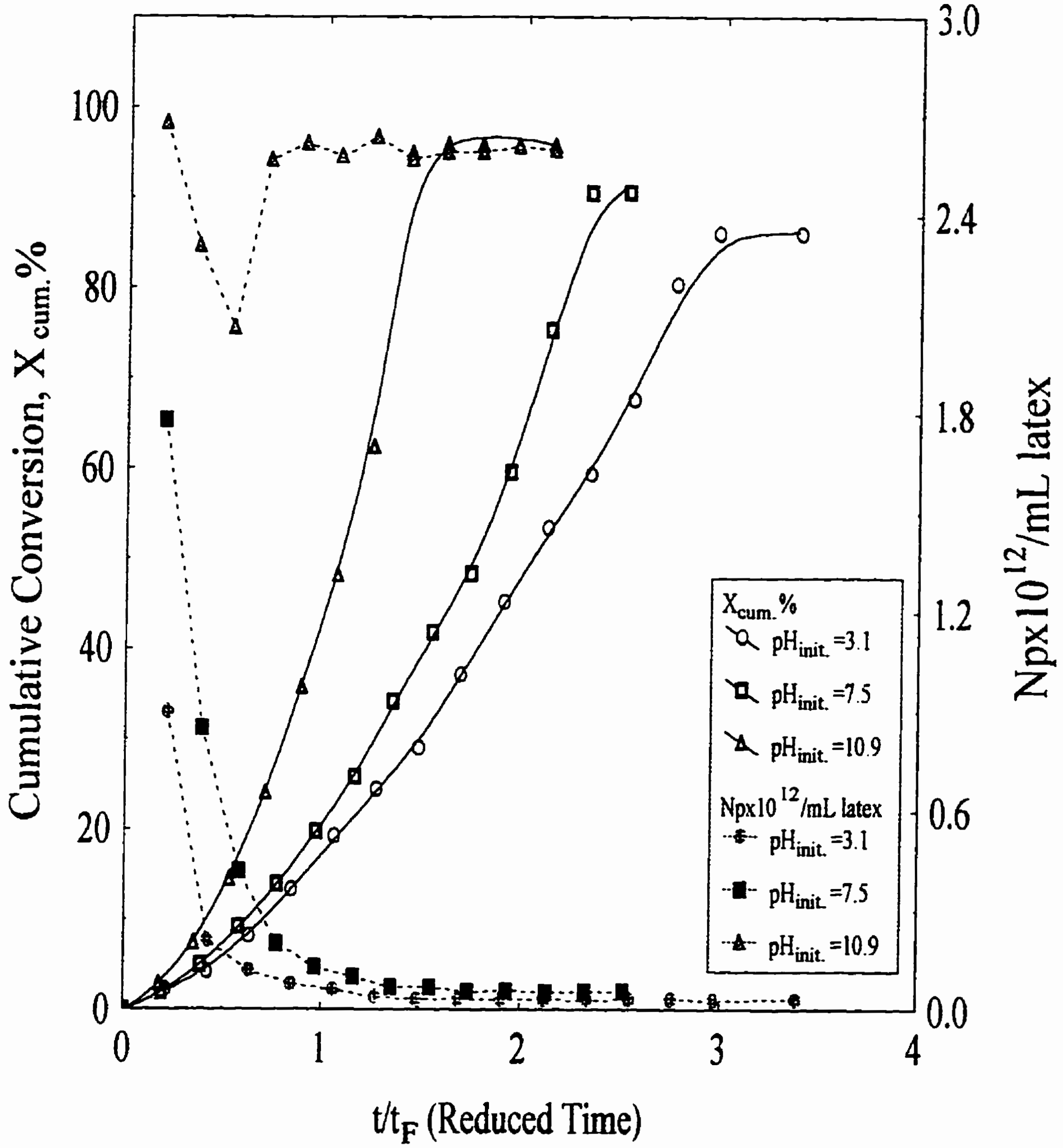
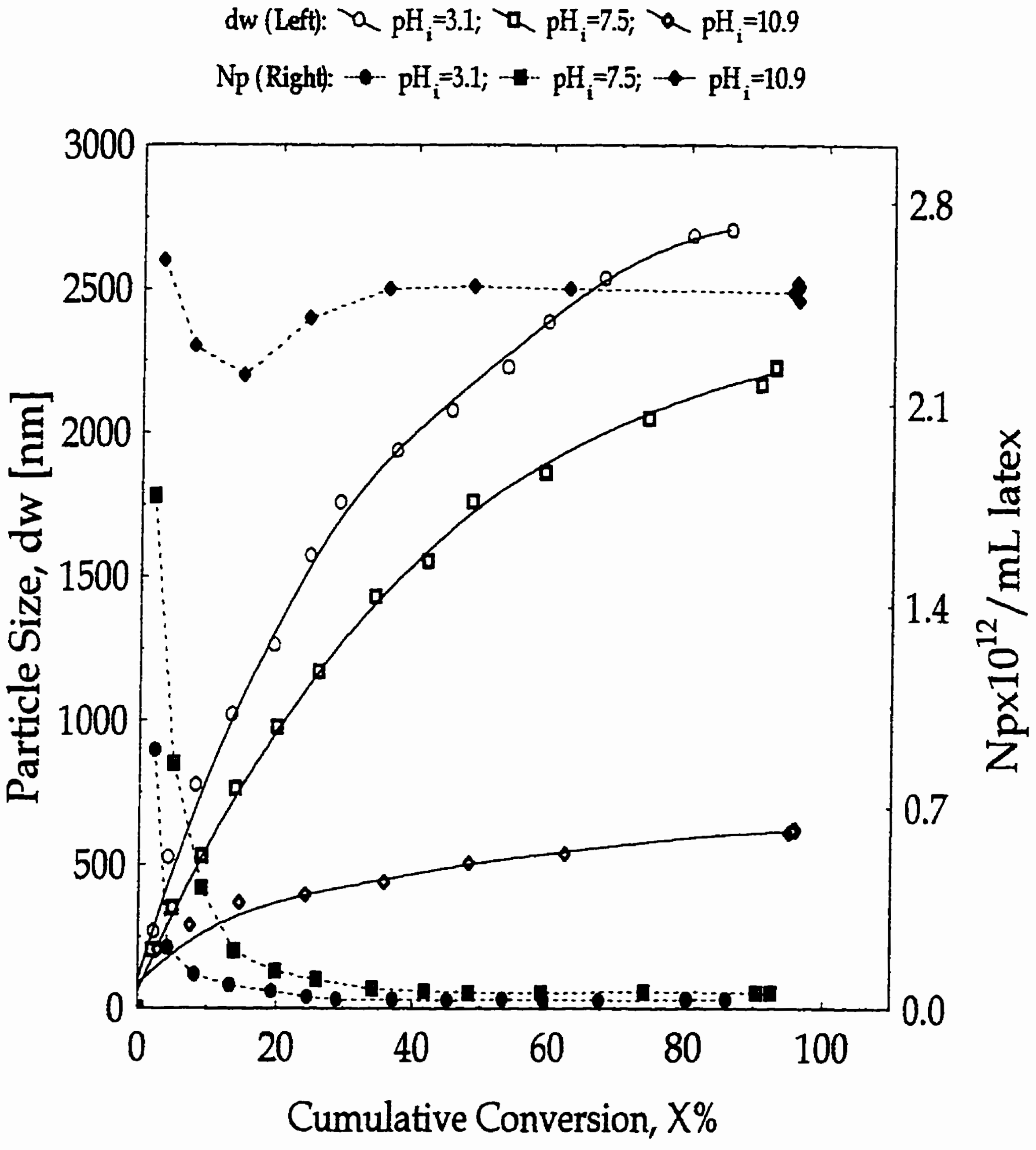


Figure 3.3.5.2

The influence of initial pH on the variation of particle size and particle number density with conversion in St/BA surfactant-free emulsion copolymerization.



The observed increase in the particle number density at the generation point of the new particle population suggested that the newly formed population was that with smaller particles. At the end of polymerization, the same two main populations were also recorded. However, at that time, the population with smaller particles was slightly higher (Figure 3.3.5.3).

The multiple role played by aqueous phase pH in emulsion polymerization is well recognized. This is due to its influence over the decomposition of water soluble initiators[34-36], colloidal behavior of particles[40], monomer solubility, polarity and co-monomer reactivity ratio[41-42].

It is well known that persulfate decomposition in aqueous solution is strongly dependent upon temperature and pH.[34-36]

Kolthoff and Miller[35] showed that when the initiator used is ammonium persulfate its decomposition reaction is strongly accelerated by hydrogen ions at pHs less than 3. They also found that in alkaline solutions the rate was independent of the ionic strength but in acid solution there is a negative salt effect. Therefore, they postulated different mechanisms for the AP decomposition including one uncatalyzed and one catalyzed by hydrogen ions. However, Santos *et al.*[34] reported that in the pH range from 3 - 7, the AP decomposition is first order and the reaction was not catalyzed by hydrogen ions.

The most widely accepted theory supports the idea that $SO_4^{\bullet-}$ anionic radicals are mainly formed by thermal decomposition in neutral and alkaline solutions, although the formation of the hydroxyl radicals $OH^{\bullet}$ is not excluded. It is also accepted no influence of the ionic strength on the decomposition rate of $S_2O_8^{2-}$.

In contrast, in acidic solutions it is supposed that the $OH^{\bullet}$ radicals are the main radical species[34-36] while the concentration of the $SO_4^{\bullet-}$ ionic radicals sharply decreases. Therefore, at lower pHs, less $SO_4^{\bullet-}$ radicals are available to initiate the polymerization while more $OH^{\bullet}$ radicals are generated. By that, the number of sulfate groups on the particles surface (stabilizing groups), will be smaller and thus, the formed particles are less stable against aggregation and coagulation. The lower pHs make the particles more

Figure 3.3.5.3

The time evolution of particle population throughout St/BA surfactant-free emulsion copolymerization in presence of sodium hydroxide.

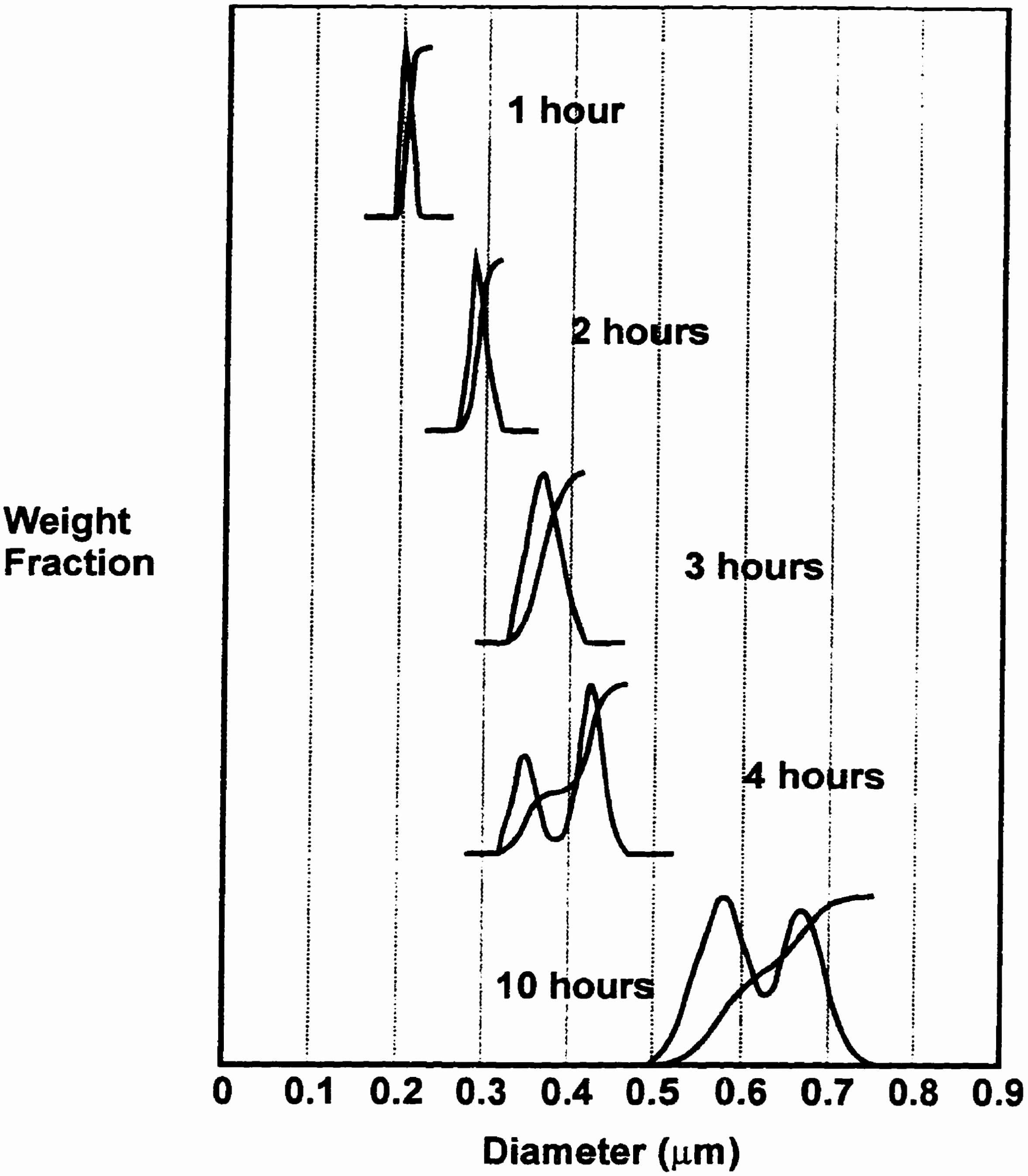
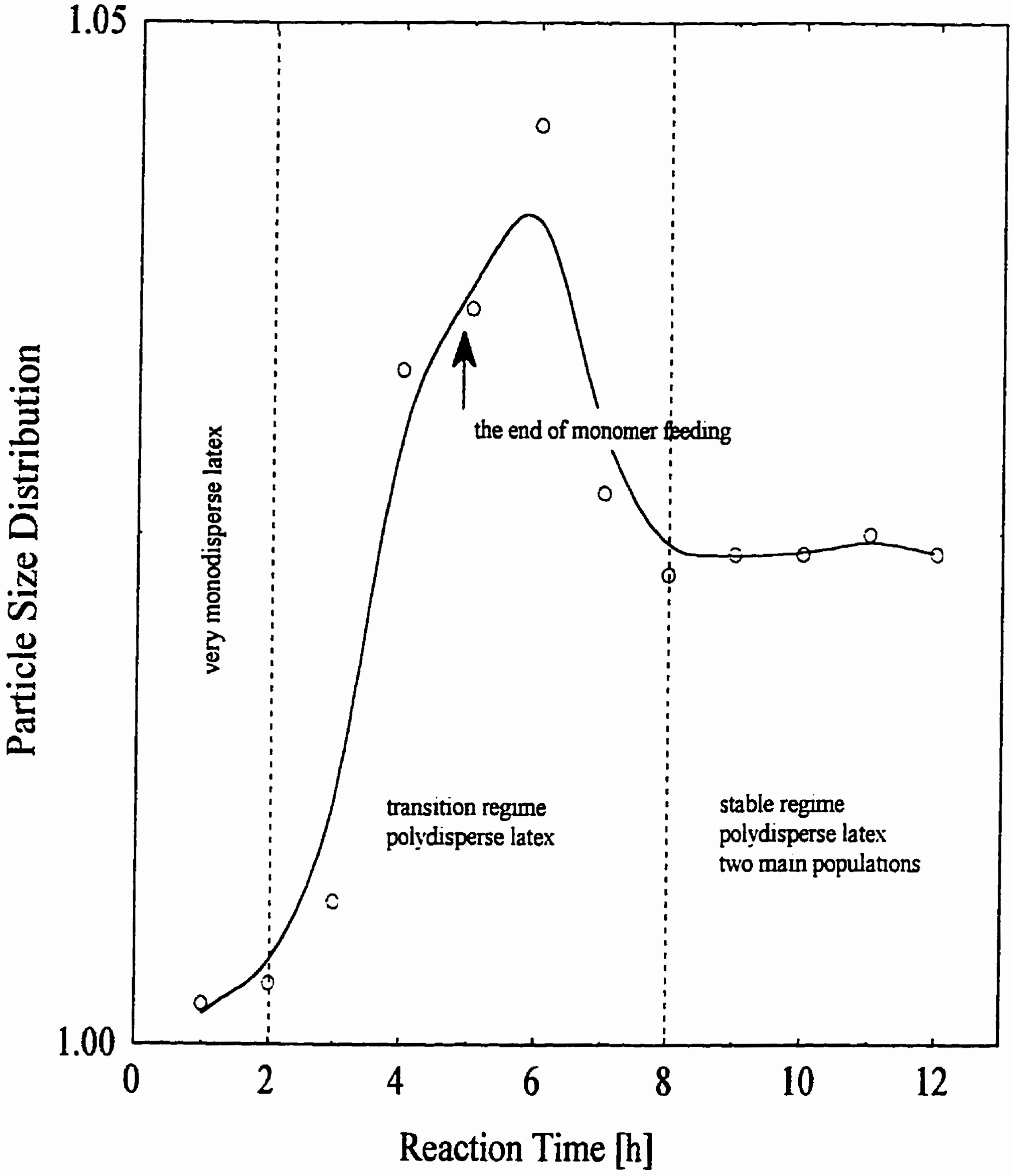


Figure 3.3.5.4

The time evolution of particle size distribution in St/BA surfactant-free emulsion copolymerization in presence of sodium hydroxide (Run S-174).



prone to aggregation (Figure 3.3.5.5), and sometimes to coagulation. That is why the final particle size at lower pHs is larger than at higher pHs.

Because coagulation cannot be avoided, more coagulum is formed in the acidic range which decreases the solids content and reduces the yield of the final latex.

The experimental data (Table 3.3.5.1) show that the increase of the initial pH (resulting from initiator and salt addition influence) led to a decrease of the final particle size whereas, above a critical pH limit the latex size distribution became broadened. As well, the quality of the final latex, the solids content, and the latex yield strongly depended on the initial pH.

An interesting pH influence on the polymerization mechanism was found when the pH-values were in the neutral and the alkaline domains. The experimental curves corresponding to the polymerization carried out at an initial pH between 3.0 to 8.0 (Figure 3.3.5.1 and Figure 3.3.5.2) supported the same polymerization mechanism. The only significant difference between these polymerization processes was that more particles were nucleated and/or less aggregation occurred at a higher pH. Therefore, the polymerization rate was significantly higher and the final particle size was smaller at higher pHs.

The larger number of particles produced at a higher initial pH strongly supports the favorable influence of the basic pHs on the generation of stabilizing sulfate groups. The increase of the amount of sulfate groups generated leads to the increase of the sulfate groups onto the particle surface which also increases the particle surface potential barrier. These particles are somewhat less prone to aggregation and coagulation, and the final particle size of the latex slightly decreased and the coagulum level drops.

The unexpected change in the evolution of the number of particles at very basic pHs caused by the generation of a new particle population (see Figures 3.3.5.1-3.3.5.2) could be explained by taking into account the above mentioned assumptions concerning the influence of pH on the initiator decomposition mechanism.

It can be assumed that at very alkaline pHs the concentration of $SO_4^{\bullet -}$ radicals significantly increases. Consequently, many more primary particles with a very high surface charge density can be nucleated. Therefore, throughout the polymerization carried out at a very basic pH, at the "secondary nucleation point", both the recorded number of particles and the corresponding conversion were significantly higher than that recorded during the polymerization carried out at a lower pH. Consequently, the final particle size was significantly smaller too.

It can be suggested that the first particles generated at very high pH had a very high charge density distributed on a very small surface. Therefore very high repulsive forces arose among these particles and secondary nucleation occurred readily.

Throughout the polymerization process carried out at a very high initial pH, a prolonged unstable particle formation process was suggested by the transition regime on the time evolution of the particle size distribution (Figure 3.3.5.4) and the time evolution of the fraction of the two populations (Figure 3.3.5.3).

Based on the experimental evidence, we recognized in St/BA surfactant-free emulsion copolymerization two pH regimes:

i. At pH $\cong$ 3 - 8 there was a slight effect of pH on the particle stability. However, higher pH values slightly enhanced the particle stability.

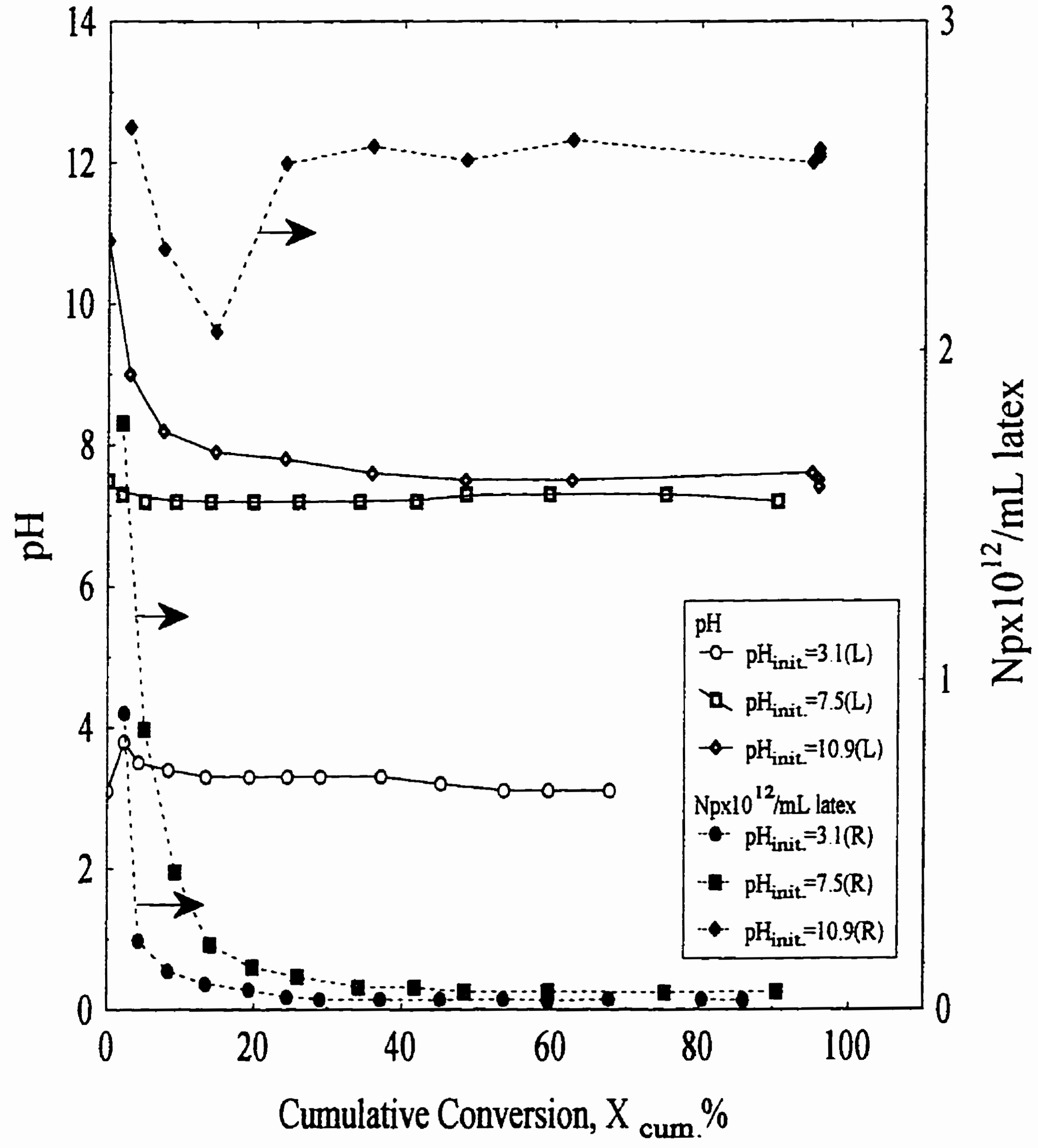
ii. At high pHs secondary nucleation took place and caused particle size to decrease.

3.3.6 The Influence of Monomer Feeding Time

The experimental results (Table 3.3.6.1) show that large particle size was a consequence of higher monomer feeding rates regardless of the other reaction parameters. However, monomer feed time cannot be reduced to less than 3 hours because of gross coagulation. For large particles, the optimal monomer feeding time was around 5 hours (~ 0.68 g monomer/min.). This was the time for most polymerizations in

Figure 3.3.5.5

The evolution of pH and particle number density versus conversion in St/BA surfactant-free copolymerization in presence of different salts.



this thesis. In addition, it has been found that the influence of the monomer feeding time seems to be significantly higher when the polymerizations were carried out in presence of salt.

It is generally accepted that the semi-continuous emulsion polymerization process has wide practical use because of its advantages regarding convenient control of the polymerization exotherm[42-44], rate of polymerization[44-45], particle morphology[46], and the composition[7-49].

The experimental technique employed in our study was based on the feeding of monomers at constant given flow-rate into a water phase containing initiator molecules, and optionally electrolytes.

Since the reactivity ratios and the water-solubility of styrene and butyl acrylate are significantly different (Table 3.3.6.2) it was necessary to consider the competition between the rate of polymerization (R_p) and the rate of monomer addition (R_a), which determined the rate of monomer accumulation in the polymerization system. It is well known that both the nature and the reactivity of the first formed polymeric radicals and precipitated dead chains strongly depend on the amount and composition of accumulated monomers. Moreover, the composition and the reactivity of these polymeric species are very important in the polymerization fate.

Since we have not been primarily concerned with particle morphology control, the corresponding monomer feeding rate was chosen such as to provide a monomer *flooded* reaction system. However, in order to avoid gross coagulation and to maintain both the stability and monodispersity of the resultant latex, the accumulated monomer must be well dispersed into the reaction medium and cannot exceed a certain limit value against the water phase amount.

In all of these polymerizations, regardless of whether salts were or not added, a coagulative-polymerization mechanism was observed. The final size was higher at faster rates due to more aggregation (less stability).

These hypotheses will be supported in the next section which is dedicated to the analysis of the influence of the monomer composition on the surfactant-free emulsion copolymerization mechanism of St/BA.

Table 3.3.6.1

The influence of monomer feeding time on St/BA surfactant-free emulsion copolymerization.

No Salt $I = 0.035$ [mol/L] $pH_{init.} \cong 3$			*Sodium Chloride* $I = 0.059$ [mol/L] $pH_{init.} \cong 3$			*Sodium Bicarbonate* $I = 0.059$ [mol/L] $pH_{init.} \cong 7.5$		
Feeding time	d_W [nm]	d_W/d_n^{*}	*Feeding time*	d_W [nm]	d_W/d_n^{**}	*Feeding time*	d_W [nm]	d_W/d_n
4h 00min.	843	1.004	4h 27min.	2981	1.028	4h 46min.	2259	1.028**
4h 37min.	827	1.004	4h 59min.	2705	1.014	5h 02min.	2228	1.014**
5h 01min.	717	1.003	5h 54min.	1598	1.014	6h 00min.	1372	1.006*

Temp. = 70°C; stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

Table 3.3.6.2

Data from the literature regarding the reactivity ratio and solubility of styrene (St) and butyl acrylate (BA).

Styrene		***Butyl-acrylate***		***References***
r_2	*water solubility*	r_1	*water solubility*	
0.62		0.24		[48]
0.76		0.19		[50]
0.76		0.15		[50]
0.68		0.19		[50]
0.64		0.19		[50]
1.03		0.34		[50]
0.59	0.4 [g/L] at 70°C	0.23	1.55 [g/L] at 70 °C	[17]
	0.3 [g/L] at 70°C		1.2 [g/L] at 70 °C	[48]

3.3.7 The Influence of Monomer Feed Composition

Experimental evidence, as presented in Table 3.3.7.1, supported a strong influence of the monomer composition on the final particle size and on the polymerization rate (indirectly expressed by the overall reaction time, t_R). The increase of BA content in the monomer mixture led to a significant decrease in the average particle size, and a sharp increase in the polymerization rate.

The experimental curves conversion versus time (Figure 3.3.7.1) exhibited a sharp increase in the polymerization rate with an increase in BA content. An autoacceleration effect seemed to take place by increasing the BA content (Figure 3.3.7.1 and Figure 3.3.7.2). It is, indeed, well known that an autoacceleration occurs very early in conversion for pure acrylates[17,50].

In the BA homopolymerization two main trends were recorded:

i. During the monomer feeding stage the overall instantaneous conversion, $X_{inst.}$, sharply increased up to ~ 85 % wt and remained constant until the end of monomer feeding.

ii. After the monomer addition, the overall instantaneous conversion, $X_{inst.}$, slightly increases to the final value of ~ 96.5 % wt (Figure 3.3.7.2).

The time evolution of $(X_{inst.}\%)_{BA}$ during the monomer feeding stage bordered on a starve-fed regime, while the linear increase in the overall BA cumulative conversion supported a constant polymerization rate. Based on these observations, it can be concluded that the BA homopolymerization took place under a steady-state regime.

Styrene addition significantly reduced the conversion both during and after the monomer feeding stage. A limiting conversion was observed as well.

For the polymerization with 20/80 St/BA, $X_{inst.}$ was higher than 60 % at the end of the monomer feed stage while for the polymerization with 80/20 St/BA $X_{inst.}$ was less than 30 %. At the end of the monomer feed stage $X_{inst.}$ was less than 20 % for styrene homopolymerization.

Figure 3.3.7.1

The influence of monomer feed composition on the variation of cumulative conversion with time in St/BA surfactant-free emulsion copolymerization.

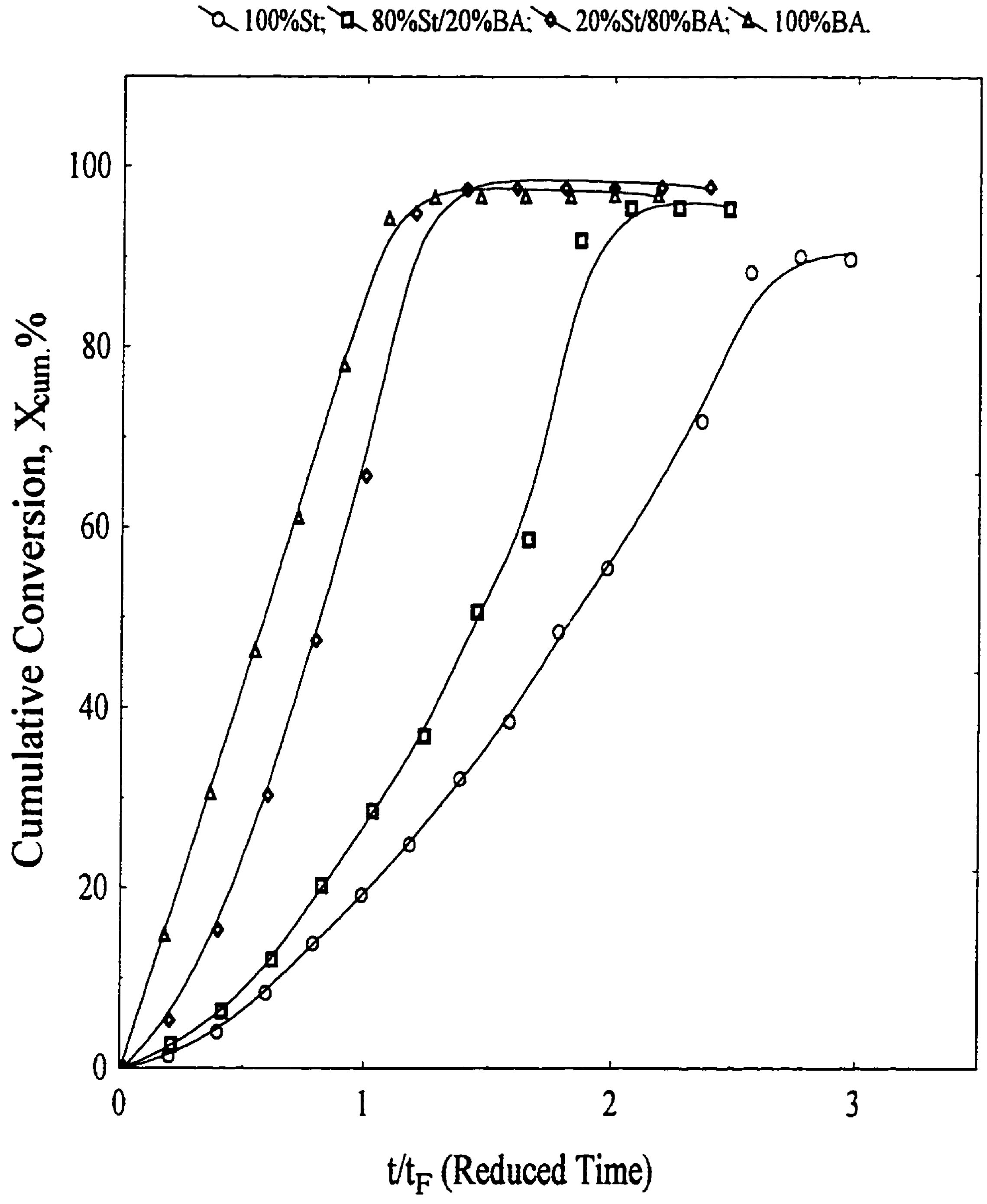
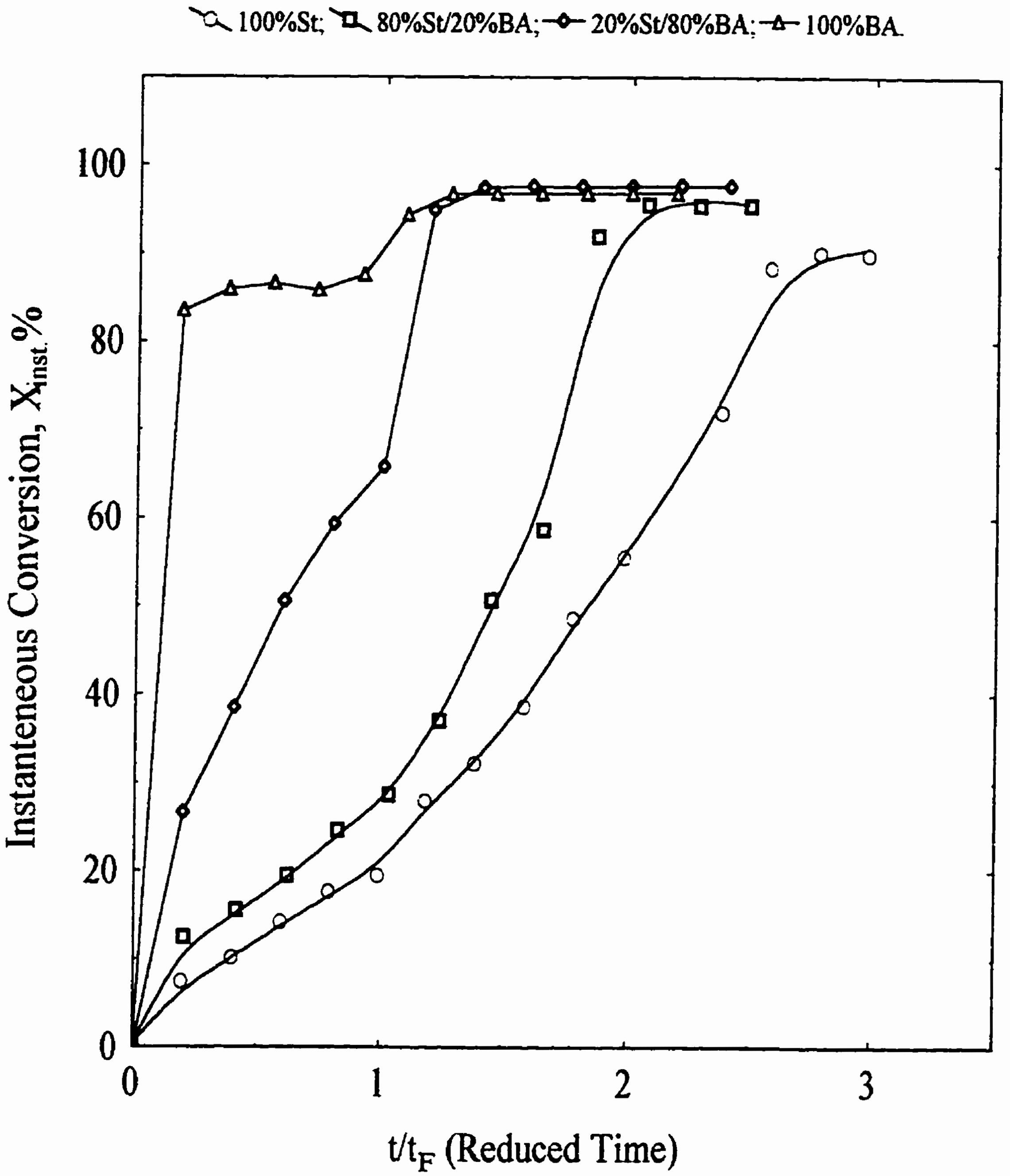


Figure 3.3.7.2

The influence of monomer feed composition on the time-variation of instantaneous conversion in St/BA surfactant-free emulsion copolymerization.



At the given polymerization pH, the butyl acrylate is thought to have an accelerating effect on the initiator decomposition rate[52]. Because of BA's water solubility, which is approximately four times higher than that of styrene[17] and the close reactivity ratios of St and BA (r_{St}=0.59 and r_{BA}=0.23)[17] it is likely that, very early, during polymerization with a higher BA content more nuclei were generated in a shorter period of time. Consequently, more primary particles were nucleated and hence more polymerization loci (polymer particles) were created (Figure 3.3.7.3 and Figure 3.3.7.4). In addition, the experimental plots in Figure 3.3.7.4 exhibit a prolonged aggregation process during the BA homopolymerization. The styrenic systems seem to stabilize shortly after feeding ends.

According to the homogeneous-coagulative mechanism[9,10], the final particle number is directly determined by the number of primary particles formed at the very beginning of the polymerization and by their coagulation rate with the precursor particles.[10] The number of primary particles depends on the time, $t_{crit.}$, required for an oligomer to reach its critical degree of polymerization, $j_{crit.}$, at which time a new polymer particle can be nucleated. Basically, $t_{crit.}$ can be estimated by the following expression[17]:

$$t_{crit.} = j_{crit.} / R_p^{aq} \tag{3.7}$$

where, R_p^{aq} represents the copolymerization rate of one oligoradical in aqueous phase (molecule/s/radical).

A means of estimating $j_{crit.}$ can be deduced by comparing the hydrophobic free energy of the tail associated with (for persulfate initiator) a sulfonated surfactant that has a Krafft temperature which is the same as the temperature of the emulsion polymerization system under consideration.[10] Since the Krafft temperature is the temperature below which micelles cannot form, then the hydrophobic free energy of a surfactant that is just hydrophobic enough not to form a micelle and so is poised to collapse should also be that for a z-mer. Therefore[10]:

Figure 3.3.7.3

The influence of monomer feed composition on the time-variation of particle number density in St/BA surfactant-free emulsion copolymerization.

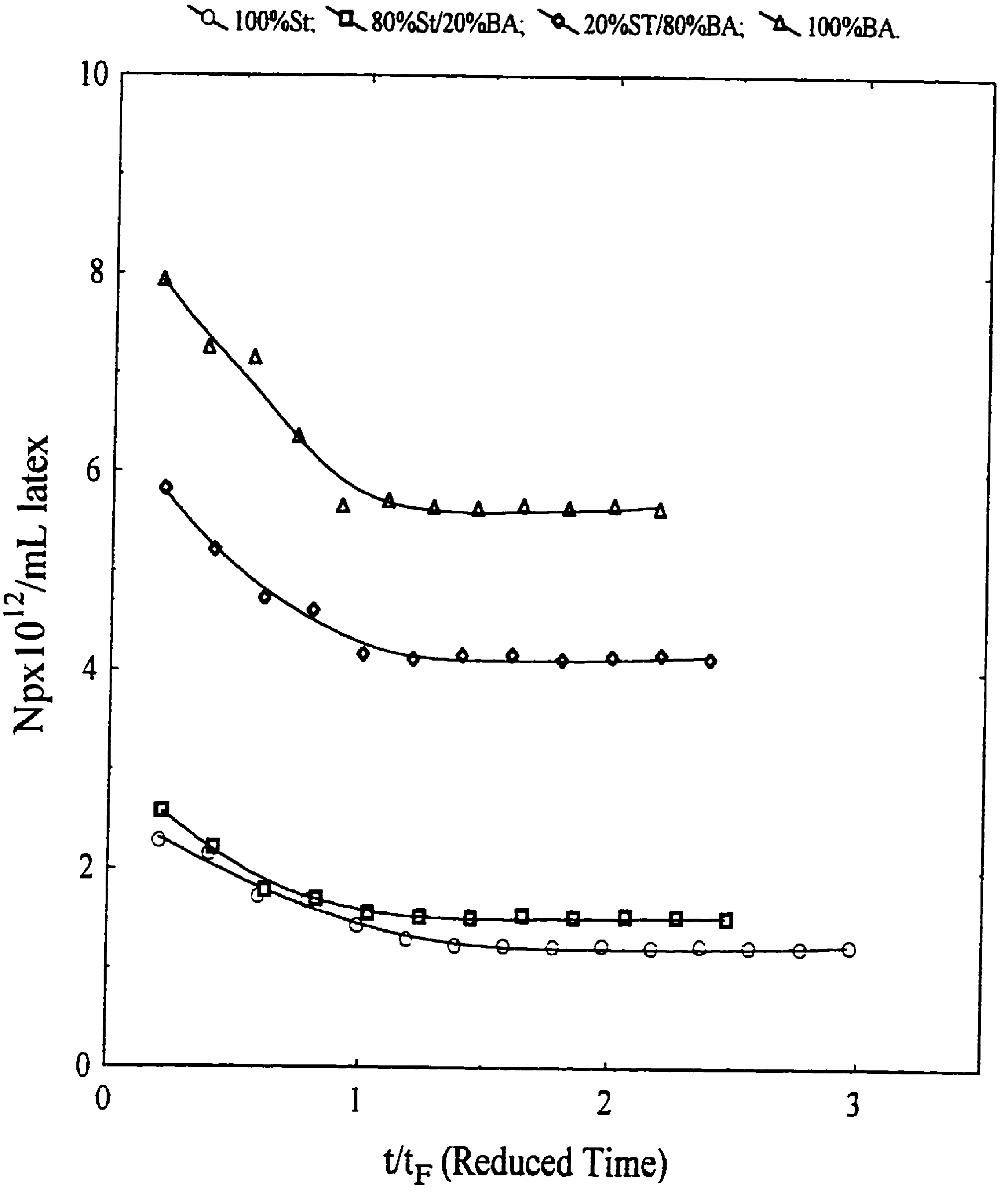
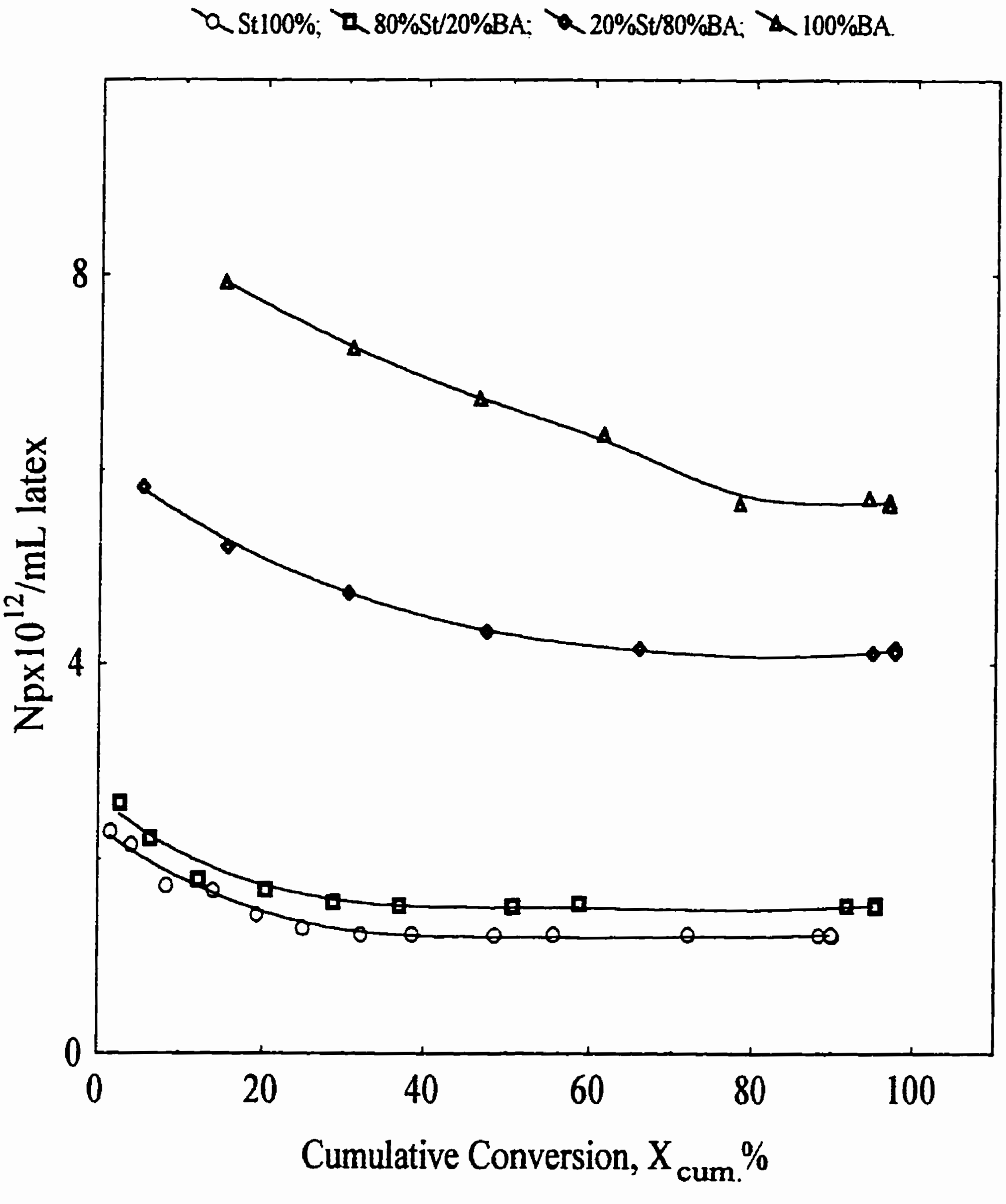


Figure 3.3.7.4

The influence of monomer feed composition on the variation of particle number density versus cumulative conversion in St/BA surfactant-free emulsion copolymerization.



$$j_{crit.} = 1 - \frac{55 \text{ kJ mol}^{-1}}{RT \ln[M^{aq}]_{sat.}} \qquad (3.7)$$

Based on literature data,[17] it was considered that the water solubility at 70 °C of styrene and butyl acrylate are 0.4 and 1.55 g/L respectively, which means:

- styrene water solubility $\cong$ 3.12 mM, and so $[M^{aq}]_{sat.St} \cong 3.12$ mM;
- butyl acrylate water solubility $\cong$ 14.9 mM, and so $[M^{aq}]_{sat.BA} \cong 14.9$ mM.

The critical degree of polymerization that can be calculated for St and BA is 5 and 6 respectively. Therefore, the influence of the critical degree of polymerization on the formed oligoradicals is insignificant versus $t_{crit.}$.

The significant increase in the polymerization rate with the increase in the BA content (Figure 3.3.7.1) suggested a higher water phase polymerization rate R_p^{aq} at a higher BA content. Consequently, these two effects led to a decrease in $t_{crit.}$ when the polymerization was richer in BA. Thus, an increase in BA content in the feed monomer mixture led to an increase in the number of particles, and therefore, a higher polymerization rate at a higher BA content.

These results are in contradiction with those of Mangaraj and Ruth[48] and Snuparek[49] who found that the maximum copolymerization rate of styrene with butyl acrylate appears at a ratio of 80/20 St/BA. Both Snuparek and Mangaraj *et al.* performed their polymerizations semi-continuously with surfactant.

On the other hand, these results agree with those of Guillaume *et al.*,[17] who performed the polymerization in a batch surfactant-free system. However, they reported no influence of BA content on the particle size which was always less than 500 nm. In that case the particle number density did not change drastically upon variation of BA content. The authors considered that the increase in polymerization rate by increasing BA content was caused by an increase in the average number of radicals (ñ) per particle, in the case of BA-rich copolymerizations.

Table 3.3.7.1

The influence of monomer feed composition on the final size of latex particles and overall reaction time.

Monomer-ratio	d_W *[nm]*	t_R *[h]*
100% Styrene	775.5	~ 12
80%St : 20%BA	717.0	~ 10
20%St : 80%BA	513.1	~ 7
100% Butyl-acrylate	460.8	~ 5

Initiator (AP) conc. = 2.67 [g/L water]; T = 70 °C; ionic strength, I = 0.035 mol/L; pH = 3.0; stirring rate = 200 RPM; monomer feeding time = 5h.

At the same cumulative conversion, $X_{cum.}$, but at a higher BA content in the feed monomer mixture, the size of the particles was smaller (Figure 3.3.7.5). The increase in BA content also prolonged the particle aggregation up to a very high cumulative conversion. Both the slight decrease in N_p and the variation of the particle size, d_W, with cumulative conversion, $X_{cum.}$% (Figure 3.3.7.4 and Figure 3.3.7.5 respectively) suggested a particle growth mechanism by both inside-particle propagation and particle aggregation.

3.3.8 The Influence of Initiator Addition Policy

Taking into account the double role of the initiator (as initiator and ionic strength modifier), its step-wise addition is a potential approach for controlling both the coagulation and aggregative process (especially during the particle nucleation stage) as well as the stability of latex particles.

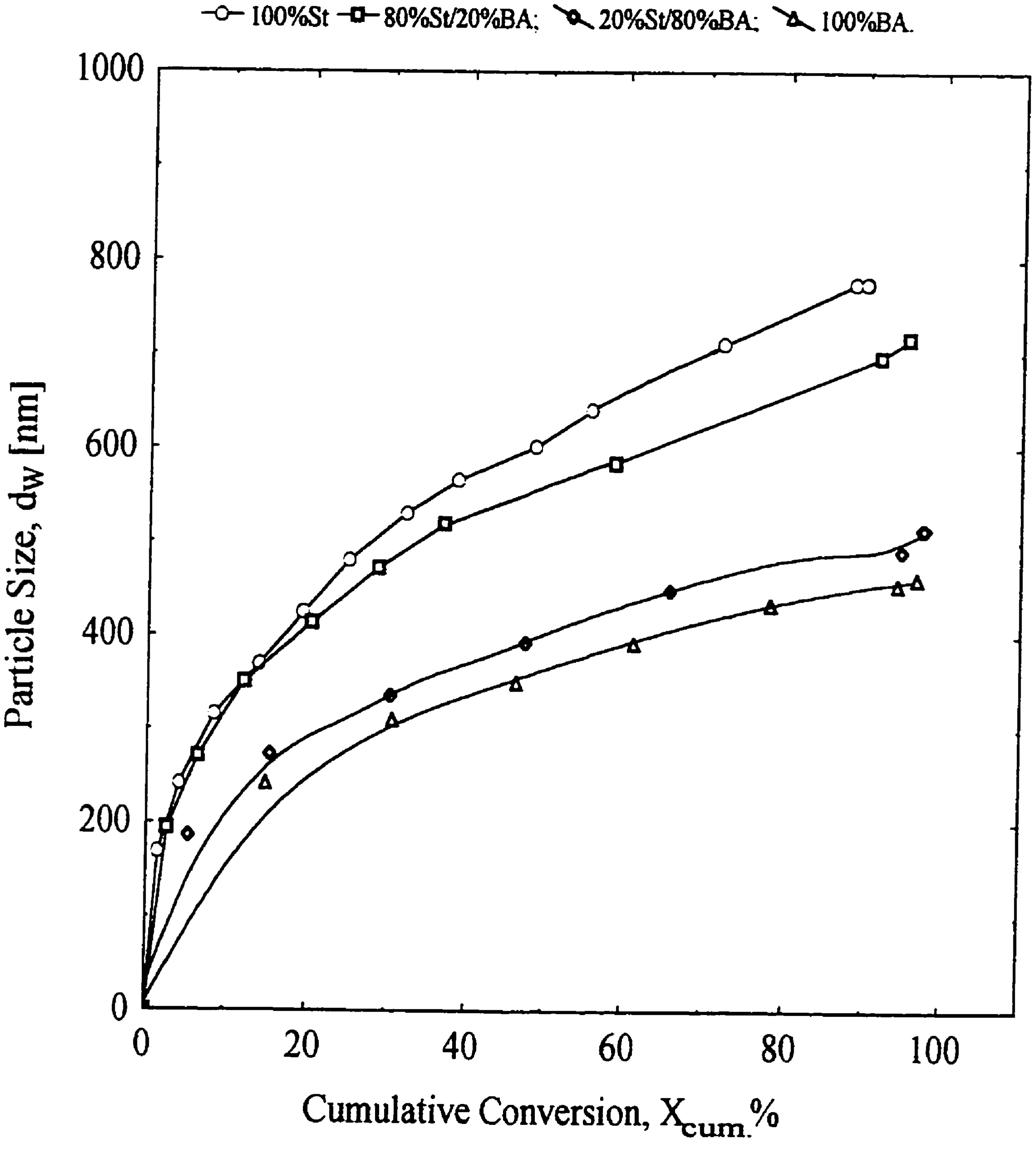
In Section 3.3.4 it was experimentally supported that in some circumstances a second addition of initiator can significantly improve the colloidal stability of particles against coagulation. The particle size was less affected, compared with a similar polymerization in which the same initial amount of initiator was added in one shot at the beginning of the reaction. This is an interesting fact, since in the first case, the overall concentration of initiator was higher (Table 3.3.8.1).

On the other hand, when the polymerization was carried out at the same overall initiator concentration but using a different addition strategy the polymerization in which a second shot of initiator was added led to much larger particles. In all the cases the final latex showed almost the same characteristics as the latex obtained with all the initiator added at the beginning of reaction (Table 3.3.8.2).

In order to keep the latex monodisperse, it was found that the second shot of initiator should be added early during the particle nucleation process when the colloidal stability of existing particles is low and particle aggregation/coagulation processes still

Figure 3.3.7.5

The influence of monomer feed composition on the variation of particle size versus cumulative conversion in St/BA surfactant-free emulsion copolymerization.



occur. It is worth noting that in both experimental sets the evolution of the curves reveals both common and particular trends.

In the series B1 (experiments carried out at different overall amounts of initiator- Figure 3.3.8.1) the second shot of initiator significantly speeded up the polymerization rate and reduced the time at which the particle number density became constant.

In the series B2 (experiments carried out at a similar overall amount of initiator), when all the amount of initiator was added in one shot at the beginning of the reaction, the polymerization rate was higher than that of a polymerization based on a second addition of initiator (Figure 3.3.8.2). Moreover, in the former case the particle number density became constant sooner.

In both experimental sets two main trends can be observed: an early flocculation and polymerization followed by a slightly aggregation (Figure 3.3.8.3 and Figure 3.3.8.4). The early particle growth stage was prolonged throughout the polymerization in which all the initiator was added at the beginning of the reaction.

It is noteworthy that similar trends were also recorded in the variation of the particle size with the cumulative conversion (Figure 3.3.8.5 and Figure 3.3.8.6).

Throughout the B1 polymerizations, after the second addition of initiator and at the same cumulative conversion (less than 20 %) the size of the particles was only slightly lower than that of particles obtained when the initiator was added at the beginning of polymerization. In the B2 polymerizations, the difference of the particle size was much more significant. In the latter experiments the particle size was much higher than that which results from the polymerization in which the initiator was added in two shots. Once the cumulative conversion increased above 20 %, the differences between the corresponding particle size became more significant.

Even though, in all these polymerizations, the variation of the particle number density decreased with increasing cumulative conversion, some particular trends were recorded.

Table 3.3.8.1

The influence of a second shot addition of initiator on St/BA surfactant-free emulsion copolymerization at different overall initiator concentrations.

	B1 series	
Latex No.	***S-168***	***S-204***
Overall Initiator Concentration [g/L water]	5.33	5.33
- second addition after ***1h*** [g]	1.2+**0.0**	1.2+**1.2**
Salt Conc. [g NaCl/L water]	1.44	1.44
Initial Ionic Strength [mol/L]	0.059	0.059
Initial pH	3.1	3.1
Particle Size, d_W, [nm]	2705	2022
Latex Polydispersity, d_W/d_n	1.014**	1.011**
Solids Content [% wt/wt]	26.5	30.4
Latex Final Yield [% wt./wt.]	80.6	94.8

St/BA = 80:20 wt./wt.; Temp. = 70 °C; monomer feeding time ≅ 5 h;
stirring rate = 200 RPM.

**Measurements on Coulter Multisizer.

Table 3.3.8.2

The influence of a second shot addition of initiator on St/BA surfactant-free emulsion copolymerization at the same overall initiator concentration.

	B2 series	
Latex No.	***S-199***	***S-204***
Overall Initiator Concentration [g/L water]	5.33	5.33
- second addition after ***1h*** [g]	2.4+**0.0**	1.2+**1.2**
Salt Conc. [g NaCl/L water]	1.44	1.44
Initial Ionic Strength [mol/L]	0.098	0.059
Initial pH	3.0	3.1
Particle Size, d_W, [nm]	1166	2022
Latex Polydispersity, d_W/d_n	1.006*	1.011**
Solids Content [% wt/wt]	29.8	30.4
Latex Final Yield [% wt./wt.]	94.6	94.8

St/BA = 80:20 wt./wt.; Temp. = 70 °C; monomer feeding time ≅ 5 h; stirring rate = 200 RPM.

*Measurements on disc centrifuge. **Measurements on Coulter Multisizer.

Figure 3.3.8.1

The influence of a second shot addition of initiator on the polymerization rate and time-variation of particle number density in St/BA surfactant-free emulsion copolymerization at a different overall amount of initiator.

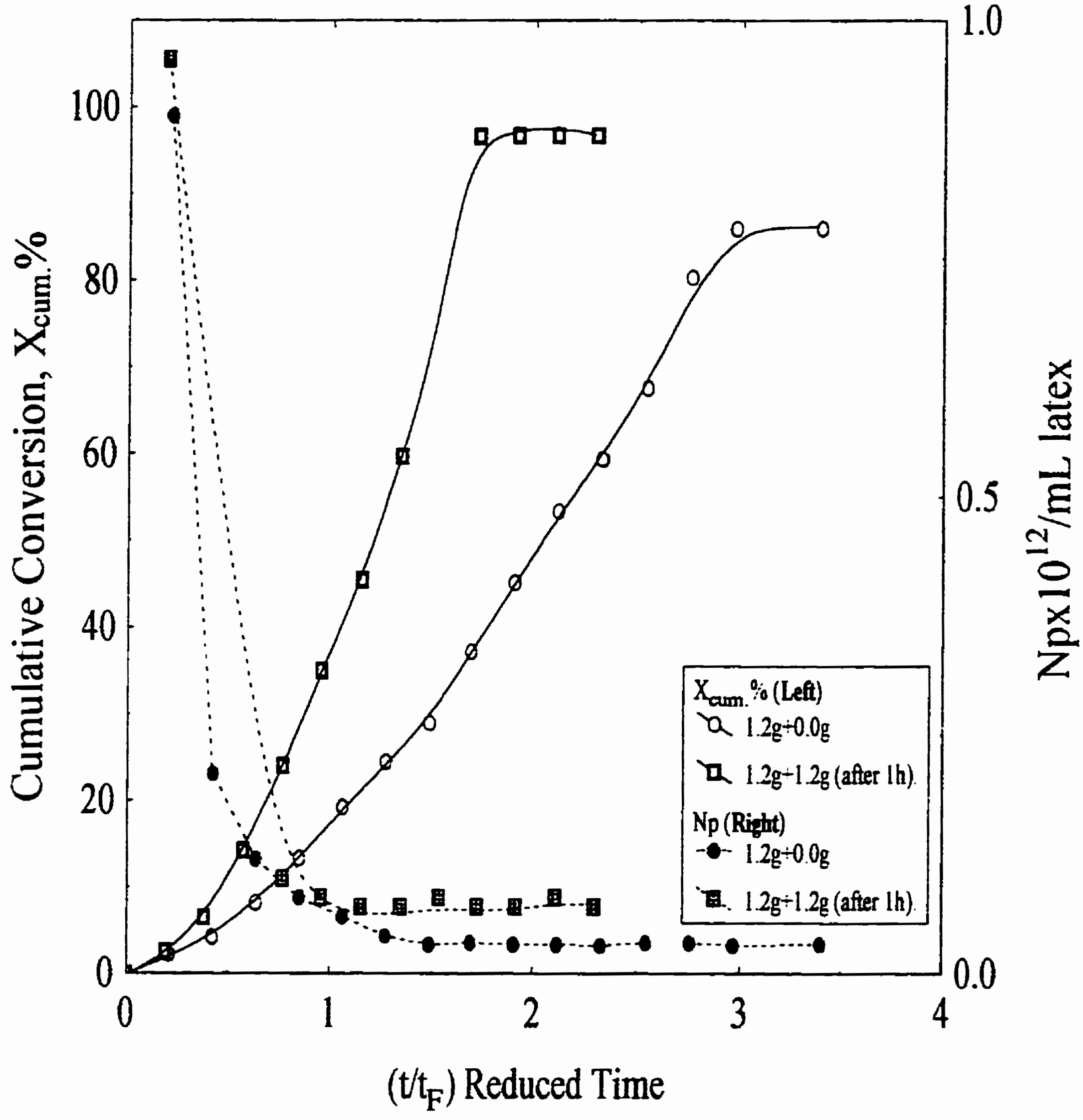


Figure 3.3.8.2

The influence of a second addition of initiator on the polymerization rate and time-variation of particle number density in St/BA surfactant-free emulsion copolymerization at a similar overall amount of initiator.

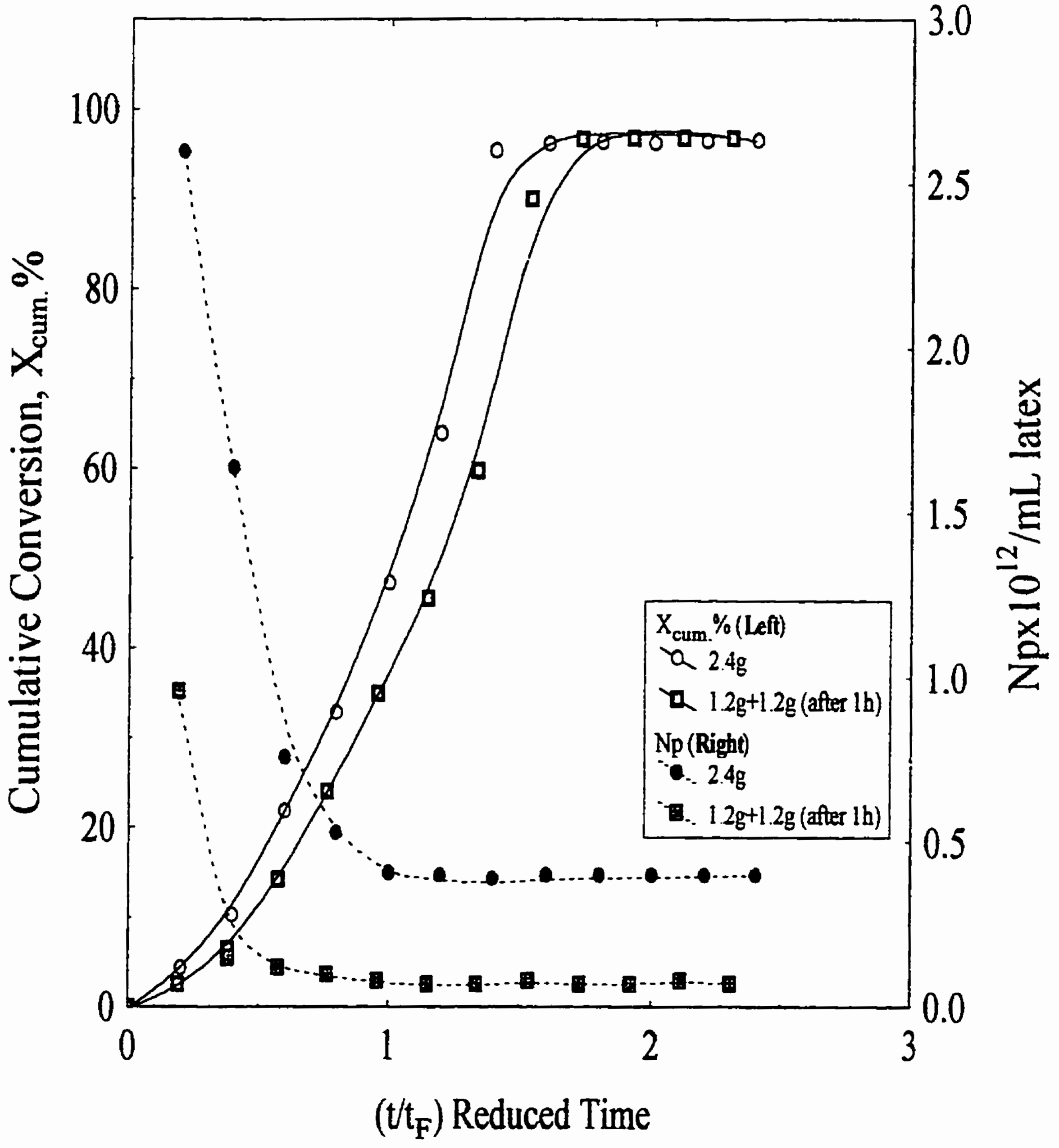


Figure 3.3.8.3

The influence of a second shot addition of initiator on the time-variation of particle size and particle number density in St/BA surfactant-free copolymerization at a different overall amount of initiator.

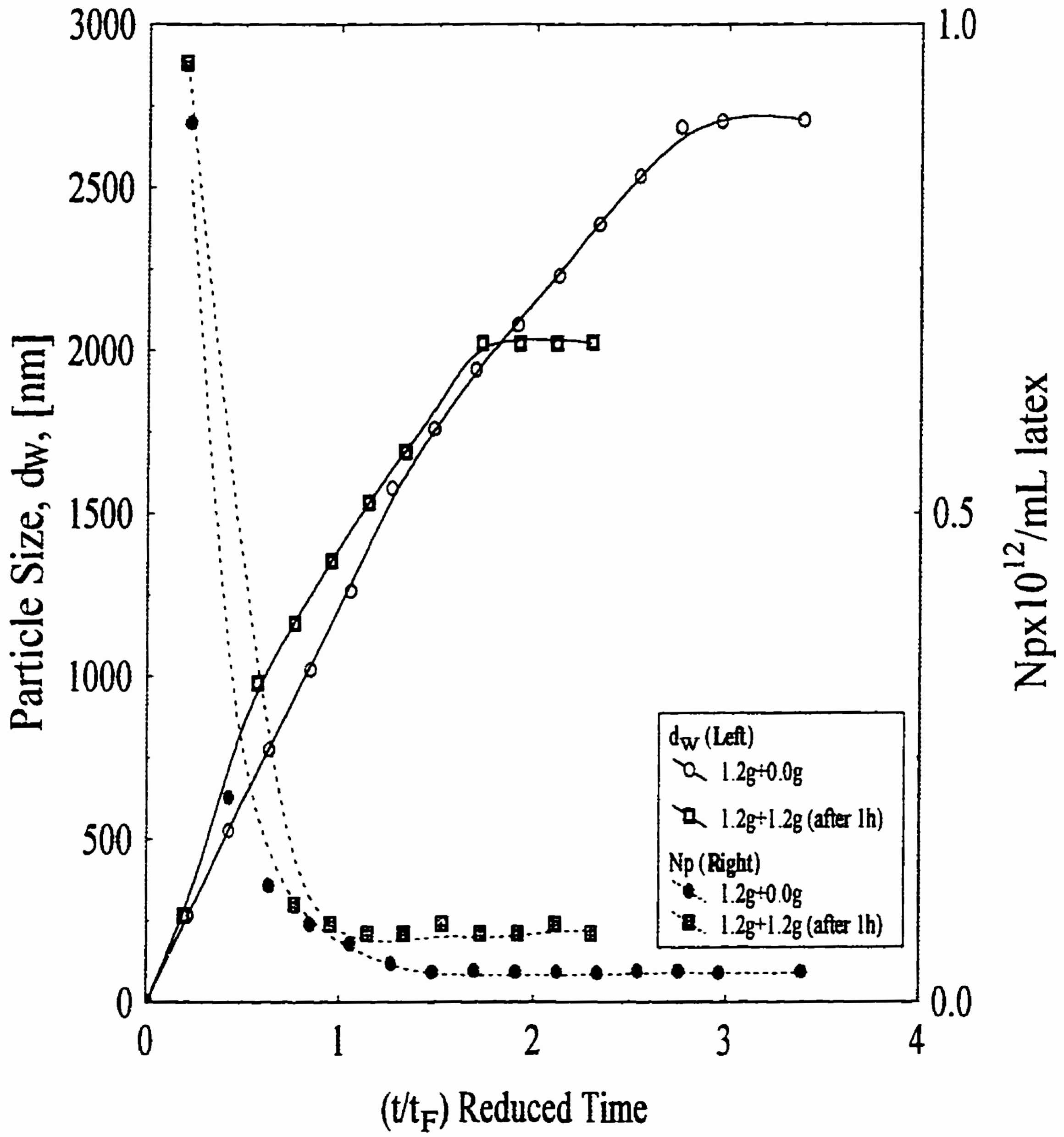


Figure 3.3.8.4

The influence of a second shot addition of initiator on the time-variation of particle size and particle number density in St/BA surfactant-free emulsion copolymerization at a similar overall amount of initiator.

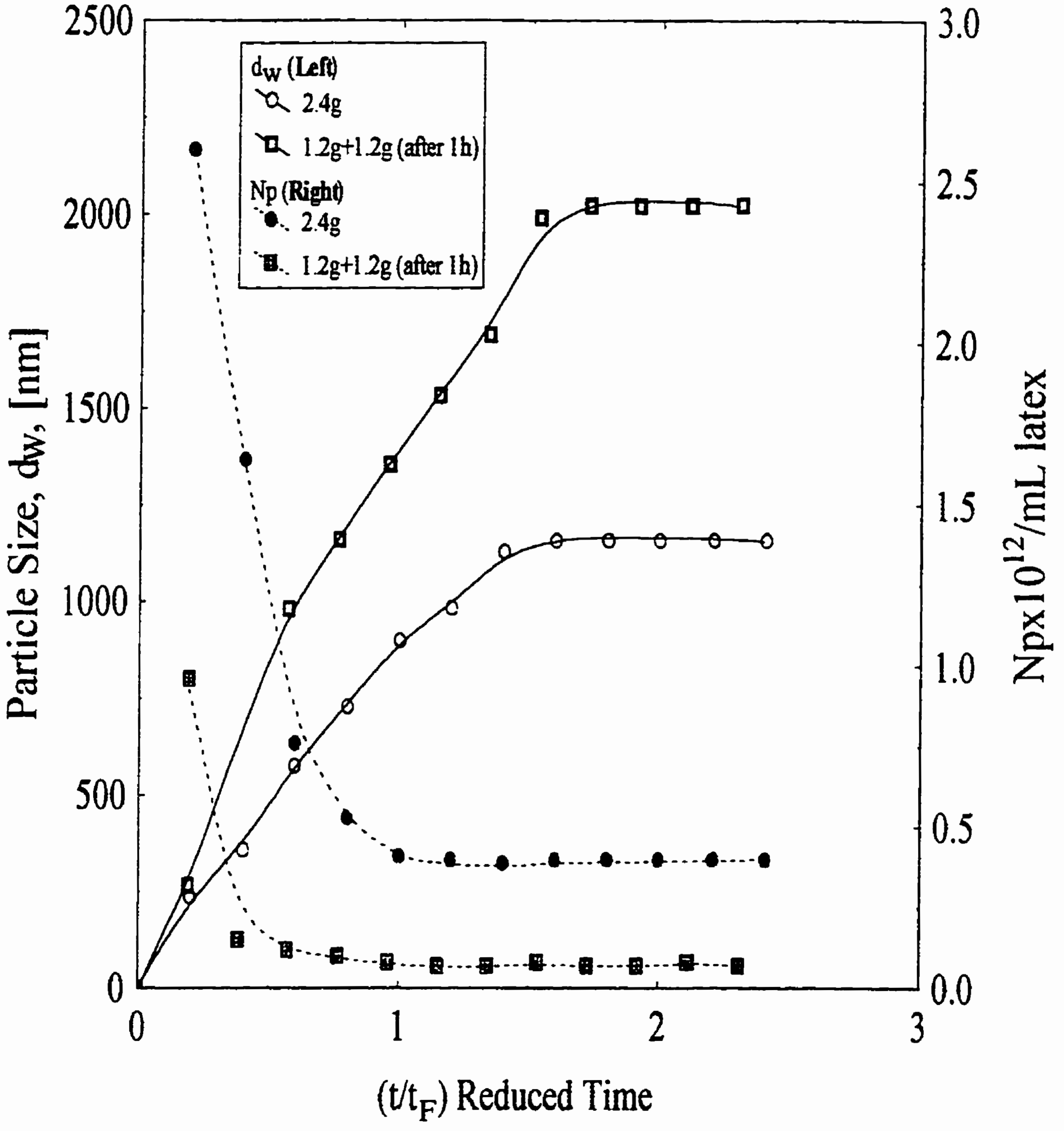


Figure 3.3.8.5

The influence of a second shot addition of initiator on the particle size and particle number density variation with cumulative conversion in St/BA surfactant-free emulsion copolymerization at a different overall amount of initiator.

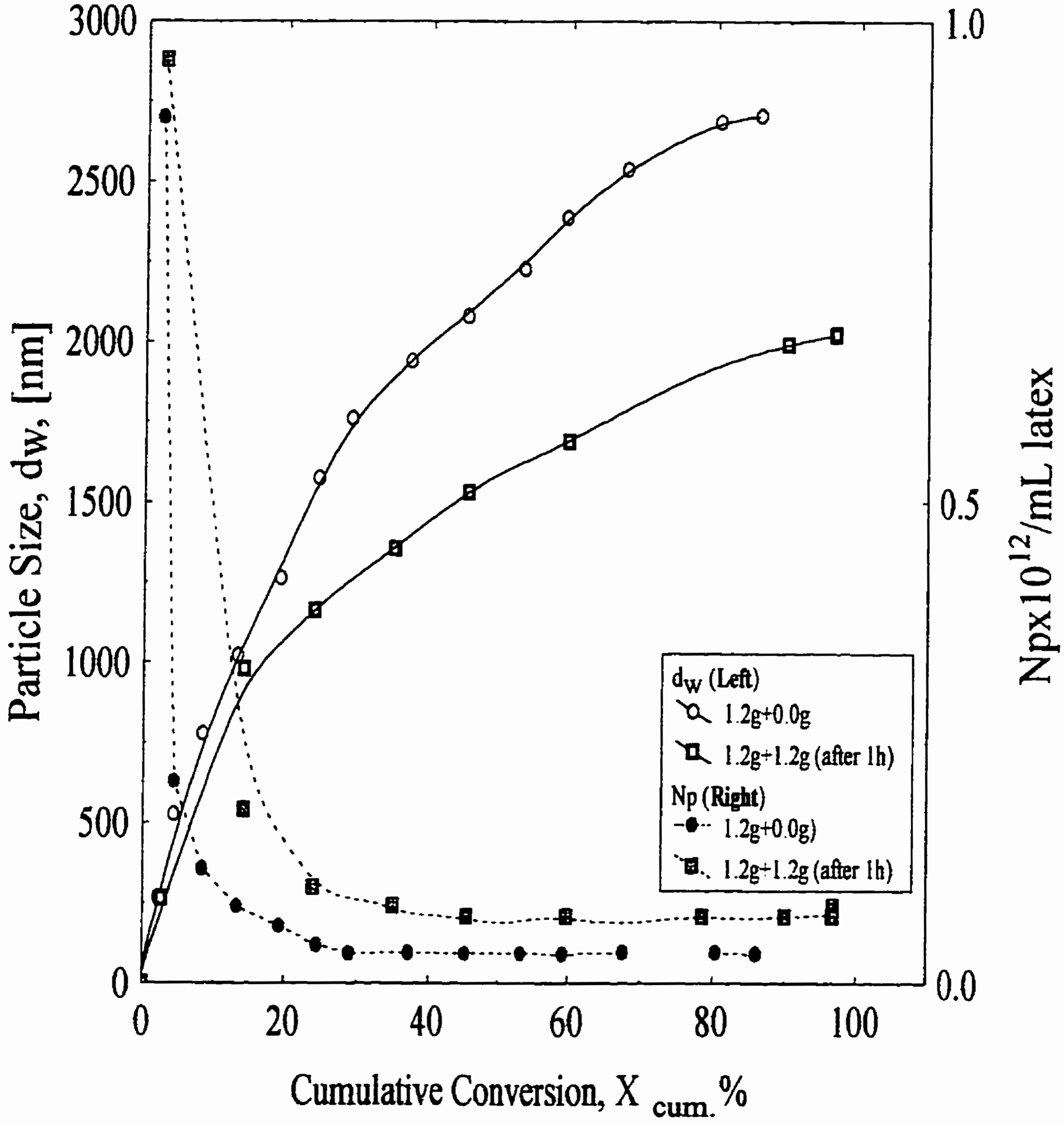
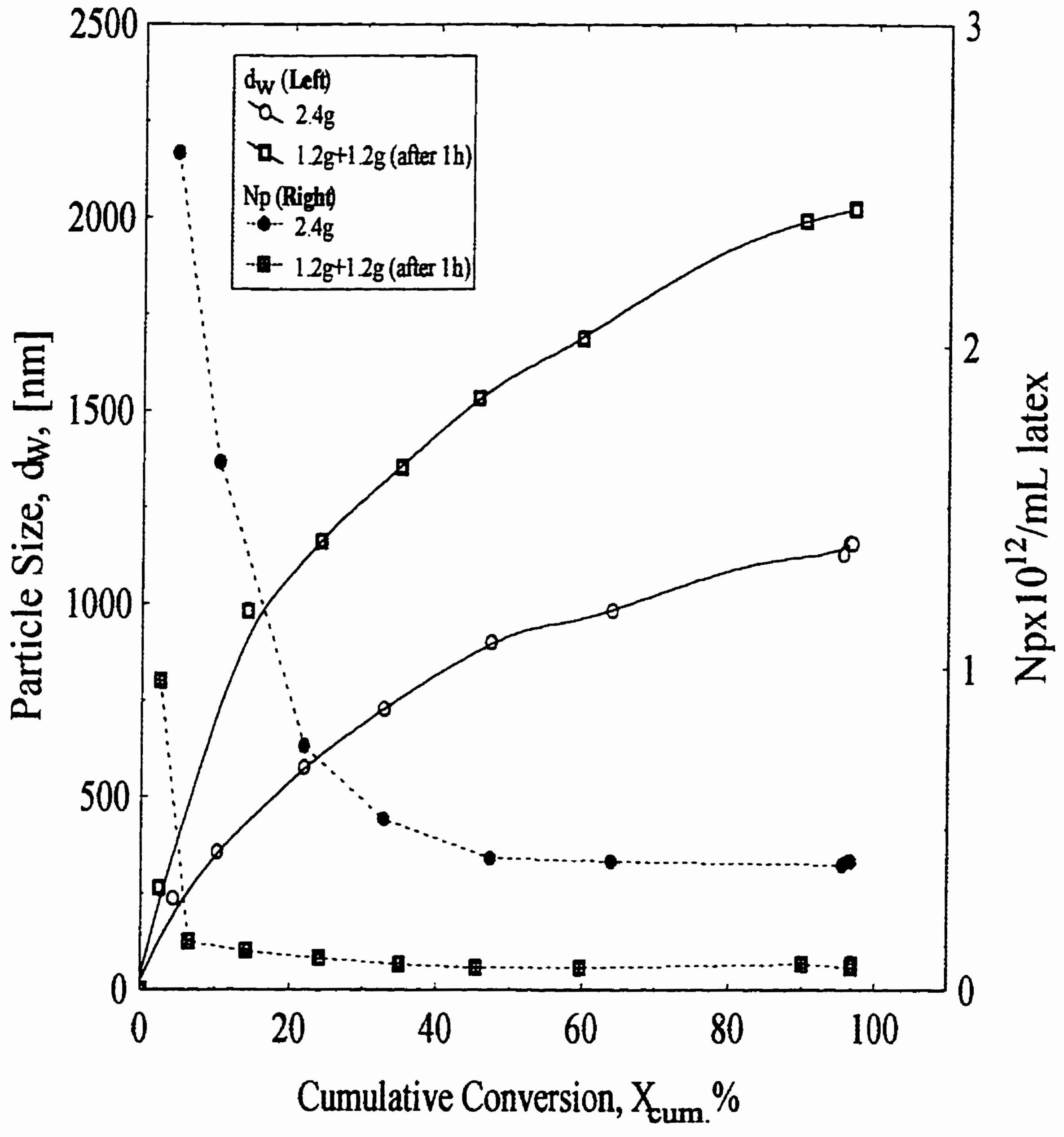


Figure 3.3.8.6

The influence of a second shot addition of initiator on the particle size and particle number density variation with cumulative conversion in St/BA surfactant-free emulsion copolymerization at a similar overall amount of initiator.



In the polymerizations of the series B1, the number of particles became constant (Figure 3.3.8.5):

i. At a cumulative conversion below 30 %, when all the amount of initiator was added at the beginning of reaction.

ii. At a cumulative conversion above 30 %, when the initiator was added in two shots.

In the former case the particle number density was also lower and therefore larger particles resulted.

In the polymerizations of the series B2, the trends were more significant (Figure 3.3.8.6):

i. The second shot of initiator led to a much lower cumulative conversion, below 30 %, at the point to the onset of a constant number of particles.

ii. When all the amount of initiator was added at the beginning of reaction, the cumulative conversion was higher than 40 % at the point to the onset of a constant number of particles.

In the former case less particles were nucleated and therefore the particles obtained were much larger than in the latter case.

3.4 CONCLUSIONS

A novel aggregative surfactant-free emulsion polymerization technique was developed, which allows the synthesis of stable styrene/butyl-acrylate (80:20 wt/wt) monodisperse latexes with a particle size in the micron range (d_W = 1- 3 μm), and a solids content higher than 25 % wt/wt.

In order to achieve micron-sized particles, the polymerization had to be carried out under monomer *flooded* conditions.

Based on a comparative analysis of the ionic strength influence (at the same initial pH, all the other parameters being maintained constant), by varying the amount of salt, and respectively, by increasing the initiator concentration, while the salt concentration was kept constant, it can be appreciated that:

(a) the increase of ionic strength by salt addition	(b) the increase of ionic strength by increasing the initiator concentration
- slowed the polymerization rate	- increased the polymerization rate
- favored aggregative processes	- limited aggregation processes
- increased the particle size	- decreased the particle size

The largest particles resulted when the polymerizations were carried out at an initial $\mathrm{pH} < 8.0$.

Following a step-wise addition procedure for the initiator, the size of particles obtained in a one-step synthesis was bigger than 2 μm, while the quality of the final latex (monodispersity, stability, coagulum level) was significantly improved.

The investigation of the role and influence of the above reaction parameters, in the semi-continuous surfactant-free emulsion copolymerization of St/BA using a persulfate initiator, strongly suggested an aggregative polymerization mechanism.

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CHAPTER 4

ONE STAGE SURFACTANT-FREE EMULSION POLYMERIZATION OF SUPERMICRON MONODISPERSE STYRENE/BUTYL ACRYLATE/ACRYLIC ACID PARTICLES

4.1 INTRODUCTION

In the past years an increasing interest has been focused on the synthesis of functionalized latexes in order to give chemical reactivity to polymer particles and to enhance the stability of polymer emulsions.

One of the most useful preparative routes to modify the surface properties of latex particles is the surfactant-free emulsion polymerization of a vinyl monomer, or any co-monomer mixture, in the presence of a monomer containing surface-active functional groups (e.g., acrylic acid, methacrylic acid, sodium styrene sulfonate).[1-6]

Usually, these functional monomers are highly soluble in water and therefore a large amount of hydrosoluble chains result when using a batch process. The chains, in addition to representing a waste of functional monomer, may also act as flocculating or stabilizing agents, depending upon their molecular weight and concentration.[7]

In the case of ionogenic co-monomers such as carboxylic monomers, it is possible to reduce the formation of hydrosoluble chains by controlling, for example, the pH of the aqueous phase. Thus, several authors[2-4] have reported that using acrylic and methacrylic acids in their unionized form the concentration of hydrosoluble chains was lowered.

Okubo *et al.*[2-3] reported that when carboxylic acid monomers were used, the hydrophilic carboxyl groups tend to be anchored predominantly on the surface rather than being buried in the particles. The favorable surface distribution of carboxyl groups contributes to the improvement of the colloidal stability of latexes.

Several published reports[1,8-10] emphasized a different contribution of the carboxylic monomers (e.g., acrylic acid, AA, or methacrylic acid, MAA) to the particle stabilization mechanism, which was mainly due to their differences in solubility inside the particles and in the water phase. AA is more hydrophilic than MAA and its distribution at the surface between the polymer particle and the water phase is more favored than that of MAA.[1,3,8-10] Nevertheless, it was found that the absolute amount of carboxyl groups is greater inside the particle rather than at the surface. This may be because the volume of the inside is larger than that of the surface layer.

In most cases it has been considered that only carboxyl groups distributed at the surface layer are useful in particle stabilization. Therefore a lot of experimental work was done in order to anchore the carboxyl groups onto the surface of polymer particles.[2-3,8-10] In addition, some reports[2-3,8] underlined that not only the carboxyl groups on the particle surface are important but also their degree of ionization.

Some authors[1-2] suggested that when the carboxyl monomer was not ionized, it did not promote a better particle stability and therefore the size of particles could not be controlled by the functional monomer concentration.

Recently, Guillaume *et al.*[1,11] studied the batch surfactant-free copolymerization of styrene and butyl acrylate in the presence of some ionogenic monomers such as methacrylic acid and potassium sulfopropylmethacrylate. The copolymerizations were performed in the presence of MAA at pH > 6. Guillaume *et al.*[1] found that the introduction of this co-monomer led to a higher particle number and a smaller particle diameter, at the same solids content, as compared with copolymerizations carried out without any addition of co-monomer. Better particle stabilization and a good control of the particle size was obtained using MAA as a co-monomer, provided that the polymerization was carried out at a pH > 6.5.

The aims of the present chapter are to present experimental data concerning the one step generation of micron sized monodisperse St/BA/AA latex particles and, to further elucidate the polymerization mechanism of surfactant-free, semi-continuous, emulsion polymerizations.

Based on the previous work done on St/BA surfactant-free emulsion copolymerization (Chapter 3), without any co-monomer addition, and the published data in the literature,[1-3,8-10] it was supposed that the addition of AA would improve the colloidal stability of polymer particles. The quality of latexes such as monodispersity, percent of solids content, and final yield would be subsequently improved.

Following a study of the influence of the monomer addition strategy, monomer concentration, monomer feeding time, ionic strength, and initial pH a novel synthetic procedure was devised to produce stable monodisperse St/BA/AA micron sized latex particles.

The latexes were characterized with respect to their particle size and particle size distribution, coagulum content and final yield.

4.2 EXPERIMENTAL

4.2.1 Chemicals

The monomers, initiator and salts used are mentioned in Section 3.2.1. Those described for the first time in this chapter include acrylic acid (AA) and methacrylic acid (MAA) obtained from Aldrich, used as received.

4.2.2 Synthesis of St/BA/AA Latexes

The syntheses of St/BA/AA latexes were carried out surfactant-free by a semi-continuous emulsion polymerization procedure which follows the same steps as in St/BA copolymerization without co-monomer addition, Section 3.2.2. However, as will be described below, the co-monomer addition procedure is critical for the course of the polymerization process.

4.2.3 Latex Characterization

In addition to the already presented characterization methods, Section 3.2.3, whenever it was interesting to do so, the pH variation was measured throughout the polymerization to complement the initial and final pH measurements.

4.3 RESULTS AND DISCUSSION

4.3.1 Co-monomer Addition Strategy

In general, carboxylated latexes can be prepared by copolymerizing carboxylic monomers with the main monomer, or a co-monomer mixture, using classical batch, semi-continuous, or continuous procedures.

The addition strategy of AA as a co-monomer is important in the St/BA copolymerization because of the higher water solubility of AA compared with that of styrene and butyl acrylate. While styrene is a highly hydrophobic molecule (0.3 g/L solubility in water at 70 °C)[1] and butyl acrylate is somewhat more polar and more water soluble (1.2 g/L water at 70 °C),[1] the acrylic acid is much more hydrophilic and almost completely water miscible.

Using a semi-continuous procedure, the AA addition could proceed in three main ways:

i. All the AA is dissolved in the reaction medium at the beginning of polymerization.

ii. All AA is fed with the main monomers as a common mixture (St/BA/AA).

iii. AA is divided between the reaction medium and the organic monomer phase (St and BA) - a combination of the above scenarios.

For reactions in which all the AA was dissolved in the reaction medium, time zero was defined as the moment when the initiator solution was poured into the reactor and the monomer feeding was started. In this case, after four hours of monomer feeding, but before the depletion of the amount of monomers fed, the reaction failed because of a catastrophic coagulation (Table 4.3.1.1 Run S-65).

On the other hand, when the added AA was distributed equally between the initial reactor mixture and the monomer feed, the polymerization proceeded without any problem. However, the final latex comprised of small polydisperse particles (Table 4.3.1.1 Run S-67). It is worth noting that the particle size obtained was typical for a polymerization carried out at a surfactant concentration higher than its CMC (100-300 nm).

When the polymerization was performed with all the AA dissolved in the monomer feed mixture, the results were successful with respect to latex size and monodispersity, although the final particle size was not yet in the desired micron range (Table 4.3.1.1 Run S-69).

The significantly larger size of the final latex particles (Table 4.3.1.2) was very close to that of the particle size measured for an AA-free St/BA surfactant-free emulsion polymerization process (Run S-69). The evolution of the experimental curves of d_w and N_p versus the reduced time, t/t_F, and $X_{cum.}\%$, percent cumulative-conversion, given in Figure 4.3.1.1 and Figure 4.3.1.2 respectively, suggested a similar aggregative-polymerization growth mechanism as found in the AA-free St/BA surfactant-free emulsion copolymerization.

Even though the concentration of acrylic acid was less than 5 wt % against the main monomers, the experimental evidence strongly supported the ideas that both the fate of the polymerization and the properties of the final latex were greatly dependent on the method of introduction of the carboxylic co-monomer.

Table 4.3.1.1

The influence of AA addition strategy on the surfactant-free emulsion copolymerization of St/BA by a semi-continuous procedure.

AA ***reactor***	***100%***	***50%***	***0%***
feed	***0%***	***50%***	***100%***
Run	**S-65**	**S-67**	**S-69**
AA Concentration [wt % on monomer]	2.00	2.00	2.00
AP Concentration [g/L water]	2.67	2.67	2.67
Ionic Strength [mol/L]	0.035	0.035	0.035
Initial pH	2.3	2.4	3.1
Particle Size, d_W, [nm]	polymerization failed after 4h	243.0	723.1
Latex Polydispersity d_W/d_n	-	1.024*	1.002*
Solids Content [% wt/wt]	-	30.0	32.0
Latex Final Yield [% wt/wt]	-	~92.0	>94.0

St/BA = 80:20 wt./wt.; Temp. = 70 °C; monomer feeding rate = 0.68 g/min; stirring rate = 200 RPM.

*Measurements on disc centrifuge.

Table 4.3.1.2

The influence of AA addition on St/BA surfactant-free emulsion copolymerization by a semi-continuous procedure.

Latex Type	*No AA*	*2 wt % AA*
Initiator Conc. [g/L water]	2.67	2.67
Ionic Strength [mol/L]	0.035	0.035
Initial pH	3.0	3.0
Final pH	2.0	1.9
Particle Size, d_W, [nm]	717	723
Latex Polydispersity d_W/d_n	1.006*	1.002*
Solids Content [% wt/wt]	30.2	31.3
Latex Final Yield [% wt./wt.]	90.6	94.6
Relative Surface-Tension**	1.062	0.829

St/BA = 80:20 wt./wt.; Temp. = 70 °C; monomer feeding rate = 0.68 g/min; stirring rate = 200 RPM.

*Measurements on disc centrifuge.

**Values calculated against the experimental average water surface-tension measurement, $S_f = 71.20$.

For polymerizations in which all the AA was completely charged into the reactor at the beginning of the process (Run S-65), most of the primary radicals will initiate polymerization of the solubilized AA molecules due to the very high water-solubility of AA. It is very likely that a relatively large number of oligoradicals were formed which mainly had a polyacrylic structure. These very hydrophilic oligoradicals can undergo, to a high extent, water-termination reactions and form *in situ* "dead" polyacrylic species. Because of their high water-solubility, these species were mainly wasted in the aqueous phase. Not only did the AA molecules produce useless polymer, but they also wasted the primary radicals from the initiator. As a result, the growing particles remained colloidally unstable and finally coagulated. Adding all the AA to the reactor did not result in AA incorporation.

Several published papers have emphasized similar trends.[12-14] It was suspected that the polymeric species formed *in situ* (depending on their molecular weight and concentration) could increase particle stability or also cause flocculation of the latex by "bridging".

Keeping the same amount of monomers and the same ratio between AA and the monomer feed, a second scenario was used with AA distributed between the reactor and the monomer feed.

When AA was distributed equally between the reactor and the monomer feed, the experimental evidence suggested an homogeneous nucleation mechanism based on the *in situ* formation of surfactant.

The third experiment (Run S-69 in Table 4.3.1.2) supported the useful contribution of AA molecules to particle stability when the AA was completely in the monomer feed. The AA addition enhanced the latex monodispersity, while the particle size remained almost unaffected. As well, significantly less coagulum was formed, which suggested a higher colloidal stability. This influence of AA moieties on particle stabilization is also supported by the experimental curves of Figure 4.3.1.1 and Figure 4.3.1.2.

Figure 4.3.1.1

The influence of AA addition on the time-variation of cumulative conversion and particle number density in St/BA surfactant-free emulsion copolymerization.

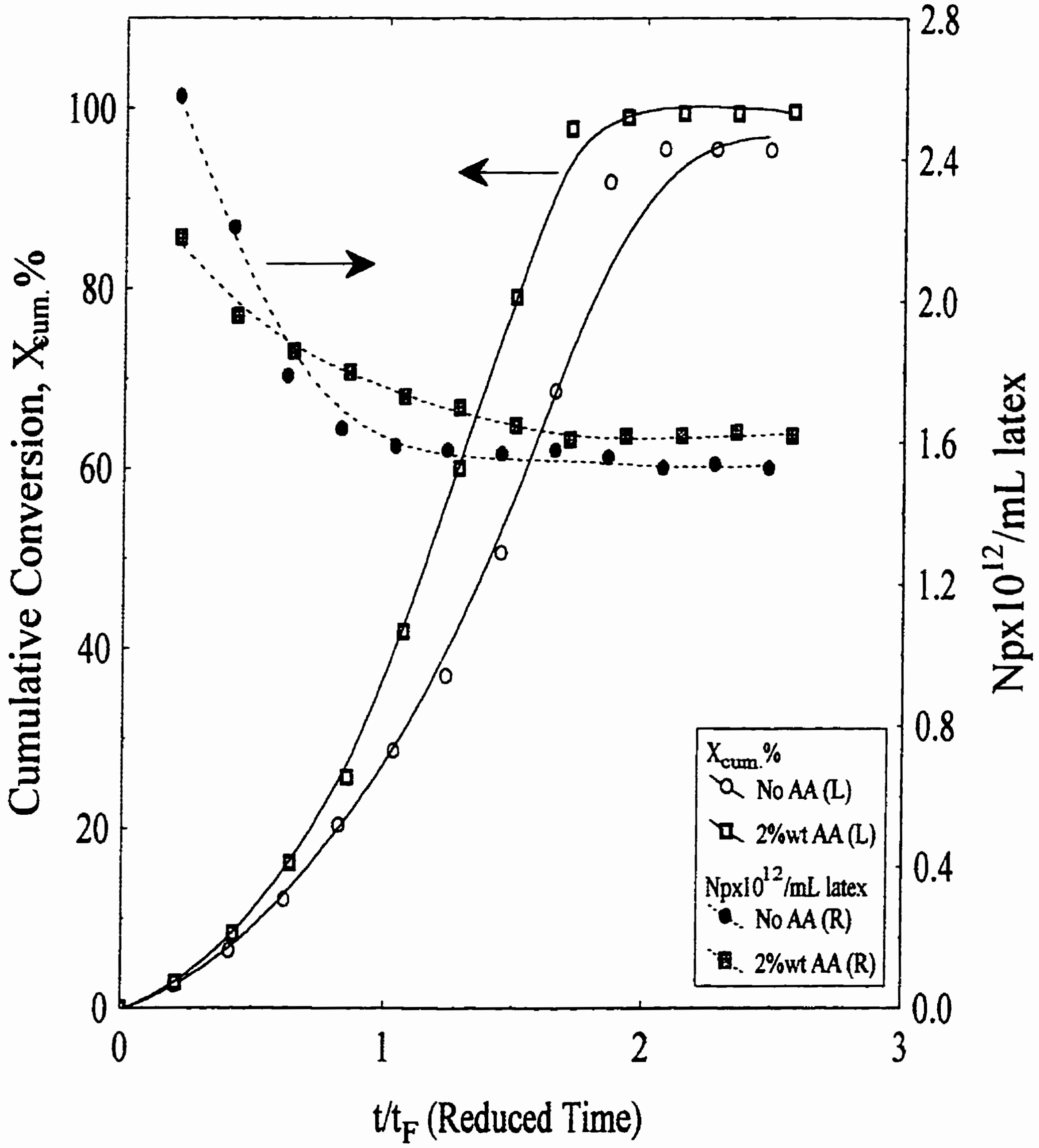
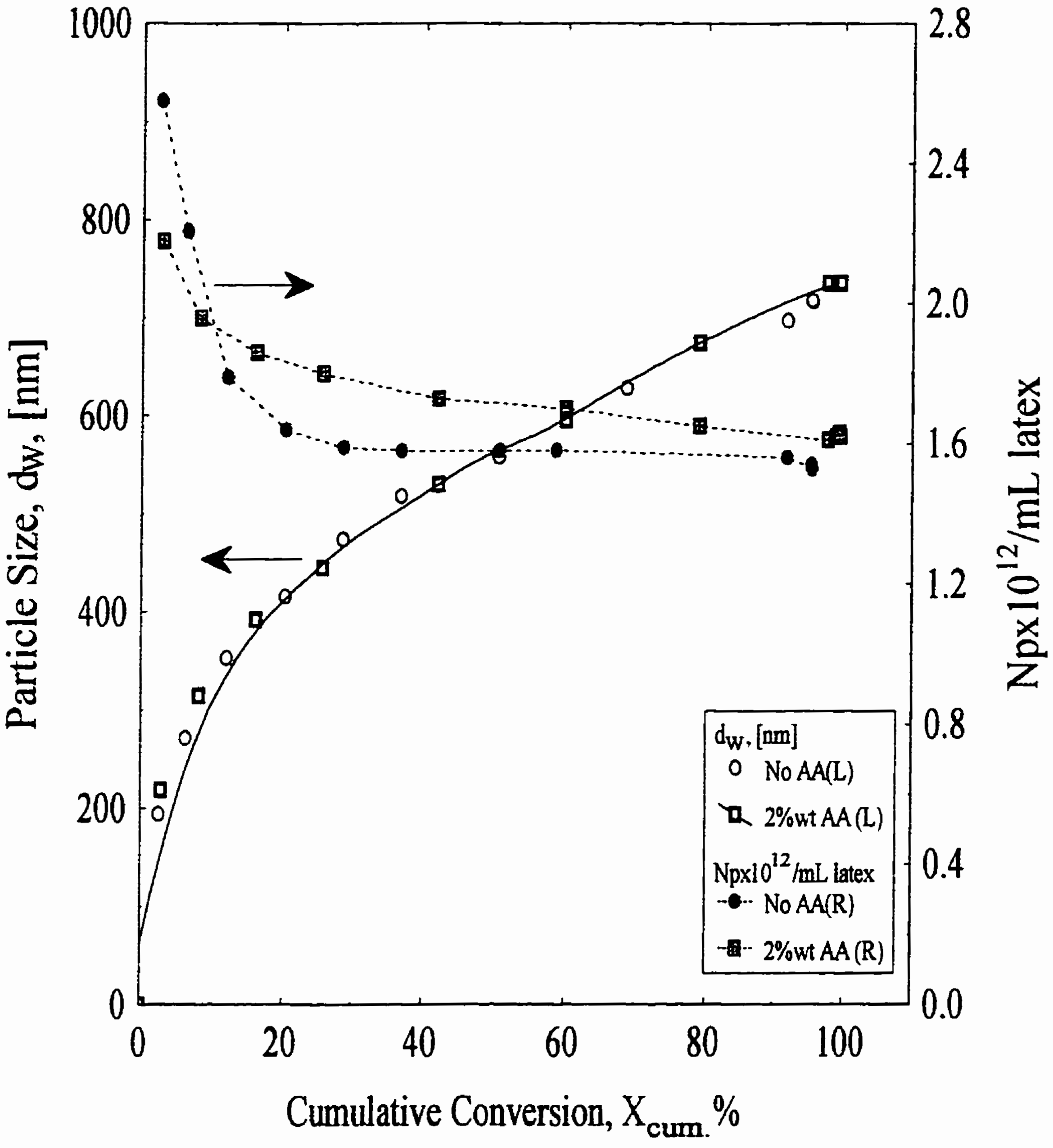


Figure 4.3.1.2

The influence of AA addition on the variation of particle size and particle number density versus conversion in St/BA surfactant-free emulsion copolymerization.



Throughout the polymerization carried out with AA completely distributed in the monomer feed, the time-evolution of the particle number density (Figure 4.3.1.1) exhibited a slight particle-aggregation process which extended until the end of polymerization. Whereas, during AA-free polymerization, the particle-aggregation process was complete by the end of the monomer feeding stage.

In both cases, the recorded final number of particles was almost the same. Consequently, the same final particle size was found. However, a different time-evolution of N_p was observed throughout the St/BA/AA copolymerization compared with that in AA-free polymerization (Figure 4.3.1.3). In the former case the increase rate of the particle size was slightly higher.

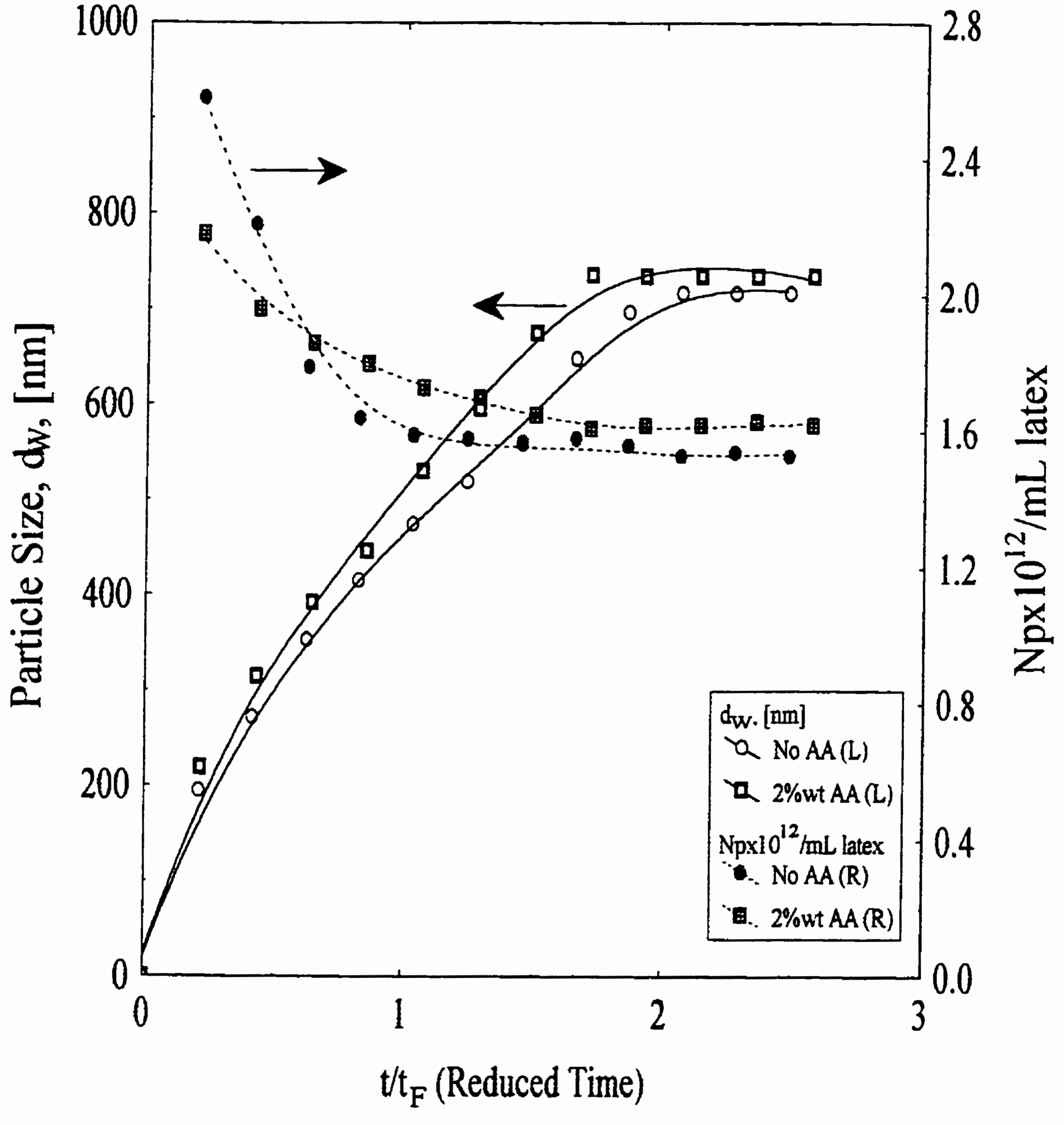
The experimental plots of particle size versus conversion (Figure 4.3.1.2) revealed a similar trend and an almost identical evolution with or without AA. The conversion level corresponding to the end of variation in the number of particles was higher than 90 % throughout the St/BA/AA copolymerization and less than 30 % in the AA-free St/BA copolymerization (Figure 4.3.1.2). Moreover, after an early particle flocculation corresponding to a conversion lower than 10 % and at the same conversion level, the recorded size of particles was the same in both polymerizations. However, the number of particles was higher in the St/BA/AA copolymerization than in AA-free St/BA copolymerization.

During the AA-free St/BA copolymerization the particle growth mechanism by aggregation was limited up to 30 % conversion. While, throughout the St/BA/AA copolymerization, the aggregative growth mechanism takes place until the end of the polymerization process. This evidence suggests that AA addition leads to fewer nuclei and more stable primary particles because of a lower aggregation rate which extends over a long time (Figure 4.3.1.3). Consequently, the AA addition led to a prolonged aggregative-polymerization process and also to a different particle stabilization mechanism.

The nature of the particle stabilization mechanism can be revealed by means of the influence of the ionic strength on the colloidal stability of electrostatically stabilized

Figure 4.3.1.3

The influence of AA addition on the time-variation of particle size and particle number density in St/BA surfactant-free emulsion copolymerization.



latexes. The DLVO[15] theory recognizes that sufficiently large electrolyte concentrations can destabilize electrostatically stabilized particles and cause them to flocculate and/or coagulate, whereas sterically stabilized particles are unaffected. The qualitative test performed consisted of the drop-wise addition of a water saturated solution NaCl (approx. 6 M) to 100 mL of latex under stirring. The first series of latexes was made without AA and the second series with AA.

Two types of latexes made with AA were tested: one resulted from polymerizations carried out in the acidic range (pH ≅ 3.0) and another one from a polymerization carried out in the presence of sodium bicarbonate (pH ≅ 8).

The latexes resulting from an AA-free copolymerization process coagulated quickly after the addition of ~12 mL of salt solution. The latexes prepared with AA, regardless of pH, did not coagulate even after the addition of 100 mL of salt solution. Moreover, the decrease in the latex surface tension (Table 4.3.1.2) by AA addition also supports this enhancement of the latex stability.

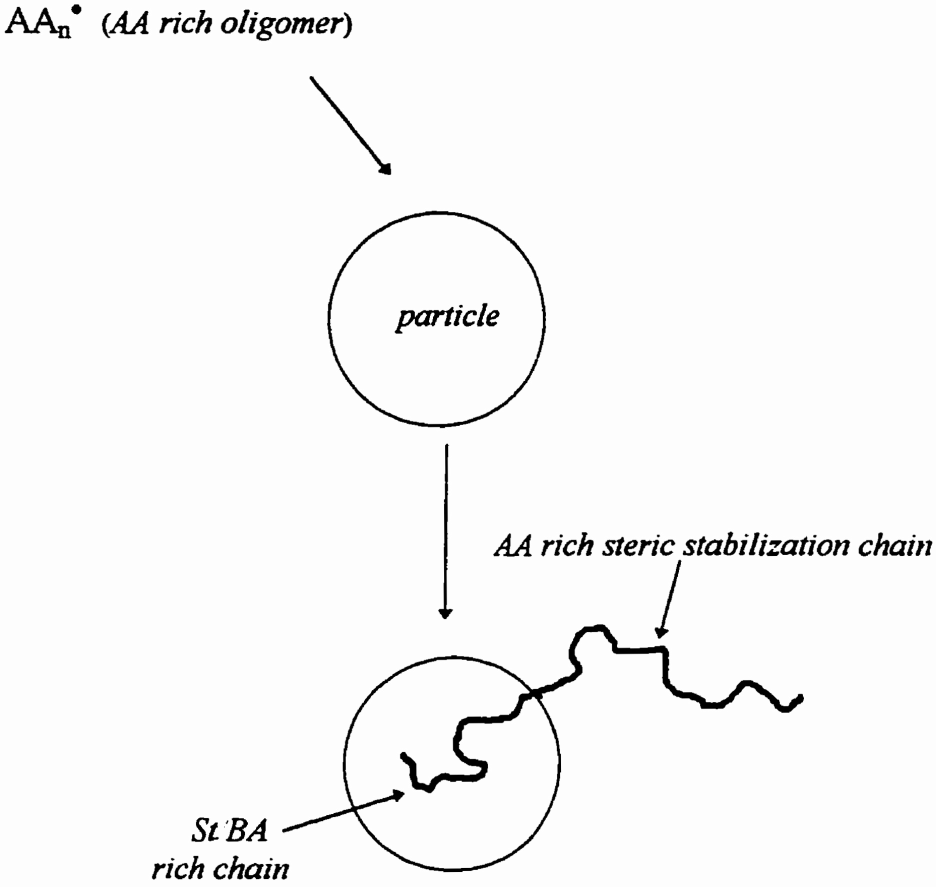
These experimental results suggested an expected electrostatic stabilization mechanism for the latex prepared without AA and an electro-steric stabilization mechanism for those latexes prepared with AA.

A number of literature reports[1,7] suggested that polymeric surfactants may be obtained *in situ* when a monomer containing a functional group (e.g., acrylic acid) is used in the polymerization. In this case, the polymeric surfactant is adsorbed on the particle surface imparting steric stabilization. The steric stabilization mechanism augments the electrostatic stabilization mechanism offered by the already anchored sulfate end-groups. A combination of electrostatic and steric stabilization forces can be accounted for[1,7] (Figure 4.3.1.4).

Even if there is no unifying theory for an electro-steric stabilization mechanism, it is well accepted that such a stabilization mechanism offers the particles more colloidal stability and less sensitivity to the salt addition than stabilization by an electrostatic mechanism only. This is the reason why the latex obtained by copolymerization in presence of AA did not coagulate.

Figure 4.3.1.4

St/BA/AA particle stabilized by an electro-steric stabilization mechanism.



These data strongly suggested that the most successful experimental procedure for the polymerization system under study would be that in which AA is fed into the reactor with the monomer mixture.

4.3.2 The Influence of Acrylic Acid Concentration

It has been emphasized, in the previous section, that the main contributions of AA addition to the monomer mixture consist of:

i. The improvement of latex colloidal stability.
ii. The increase of the polymerization rate.

Experimental evidence supports the enhancement of the latex stability by adsorption of the surfactant formed *in situ*. It is very likely that this species would have a poly(acrylic acid) block structure. In this case, the latex stabilization changes from an electrostatic mechanism to a more complex electro-steric mechanism.

The effect of AA concentration was studied to find the optimum amount which should be used in the polymerization process of St/BA because the *in situ* polymeric surfactants formed, depending on their molecular weight and concentration, can increase the particle stability.

In the aqueous phase the AA molecules undergo acid-base equilibria. Therefore, depending on the pH, the equilibrium of the reaction (4.1) can be forced to favor the formation of one or the other acrylic species:

$$CH_2{=}CH{-}COOH + H_2O \rightleftharpoons CH_2{=}CH{-}COO^- + H_3O^+ \qquad (4.1)$$

$$AA \quad + H_2O \rightleftharpoons \quad AA^- \quad + H_3O^+$$

Two sets of surfactant-free emulsion copolymerizations with varying levels of AA were performed at a constant concentration of initiator and ionic strength. The first set was carried out in the acidic pH domain, $pH_{init.} \cong 3.0$ (Table 4.3.2.1) while the second set was, in the neutral/weakly-basic range, $pH_{init.} \cong 8.1$ (Table 4.3.2.2). In both experimental sets, the AA concentration was varied between 1 wt % and 5 wt % AA based on the monomer amount.

Results at pH ≅ 3.0

Depending on the initial pH, the variation in the final particle size versus AA content (Figure 4.3.2.1) showed a completely different influence of AA molecules on the final size of latex particles. When the polymerizations were carried out in the acidic range, $pH_{init.} \cong 3.0$, particle size measurements (illustrated in Table 4.3.2.1) yielded an almost constant particle size and particle size distribution for an AA concentration in the 0-4 wt % range. The final quality of the latexes made in the presence of AA was significantly improved with respect to coagulum content. The final latex yield increased from 90.0 % (no AA) to 94.3 % (4 % AA) (Table 4.3.2.1).

It is also worthwhile to mention the change of the particle surface morphology (Figure 4.3.2.2) as a function of the AA concentration in the monomer feed. An increase in AA concentration caused a change from spherical smooth particles (AA-free) to spherical "moon-like" particles (1 wt % AA), to slightly irregular "cracked" particles (2 wt % AA) up to very irregular "stone-like" particles (4 wt % AA). This is probably because the AA incorporated in the particles increased their water swellability. Water removed during SEM preparation below T_g leads to cracks.

Conversion-time curves for these polymerizations are plotted in Figure 4.3.2.3 together with that of the AA-free styrene/butyl acrylate. The addition of small amounts of the functional carboxyl monomer resulted in a significant increase in the polymerization rate over that found for St/BA, except when the AA content in the monomer feed is 1 wt %. The polymerizations carried out AA-free and with 1 wt % AA showed an almost identical polymerization rate and particle size variation versus conversion. The time-variation of N_p revealed similar trends but a different evolution during the monomer

Table 4.3.2.1

The influence of AA concentration on St/BA/AA surfactant-free emulsion copolymerization without salt addition.

Latex No.	*No AA*	*0.5% AA*	*1.0% AA*	*2.0% AA*	*3.0% AA*	*4.0% AA*
AP Conc. [g/L water]	2.67	2.67	2.67	2.67	2.67	2.67
Ionic Strength [mol/L]	0.035	0.035	0.035	0.035	.035	0.035
Initial pH	3.0	3.0	3.0	3.0	3.0	3.0
Final pH	2.0	1.9	1.9	1.9	1.9	1.9
Particle Size, d_W, [nm]	717	716	731	723	730	751
Latex Polydispersity d_W/d_n	1.006*	1.004*	1.003*	1.003*	1.003*	1.004*
Solids Content [% wt/wt]	30.2	30.5	31.7	31.3	31.4	31.6
Latex Final Yield [%]	90.6	92.6	92.9	94.6	94.2	94.2
Relative Surface-Tension***	1.062	0.904	0.864	0.829	0.830	0.819

St/BA = 80:20 wt./wt.; Temp. = 70 °C; feeding rate = 0.68 g/min;
stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

***Values calculated against the experimental average water surface-tension measurement, $S_f = 71.20$.

Table 4.3.2.2

The influence of AA concentration on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

Latex No.	***No AA***	***0.5% AA***	***1.0% AA***	***2% AA***	***4% AA***	***5% AA***
Initiator Conc. [g/L water]	2.67	2.67	2.67	2.67	2.67	2.67
Bicarbonate [g/L water]	8.27	8.27	8.27	8.27	8.27	8.27
Ionic Strength [mol/L]	0.133	0.133	0.133	0.133	0.133	0.133
Initial pH	8.1	8.1	8.1	8.1	8.1	8.1
Final pH	8.5	7.9	7.3	6.5	5.05	4.8
Particle Size, d_W, [nm]	2820	1887	1297	1203	1005	957
Latex Polydispersity d_W/d_n	1.014**	1.013**	1.005*	1.003*	1.005*	1.007*
Solids Content [% wt/wt]	24.0	30.5	30.7	31.3	31.3	28.7
Latex Final Yield [% wt/wt]	82.3	91.1	92.9	94.6	93.2	86.2
Relative Surface-Tension***	-	0.796	0.782	0.777	0.780	0.797

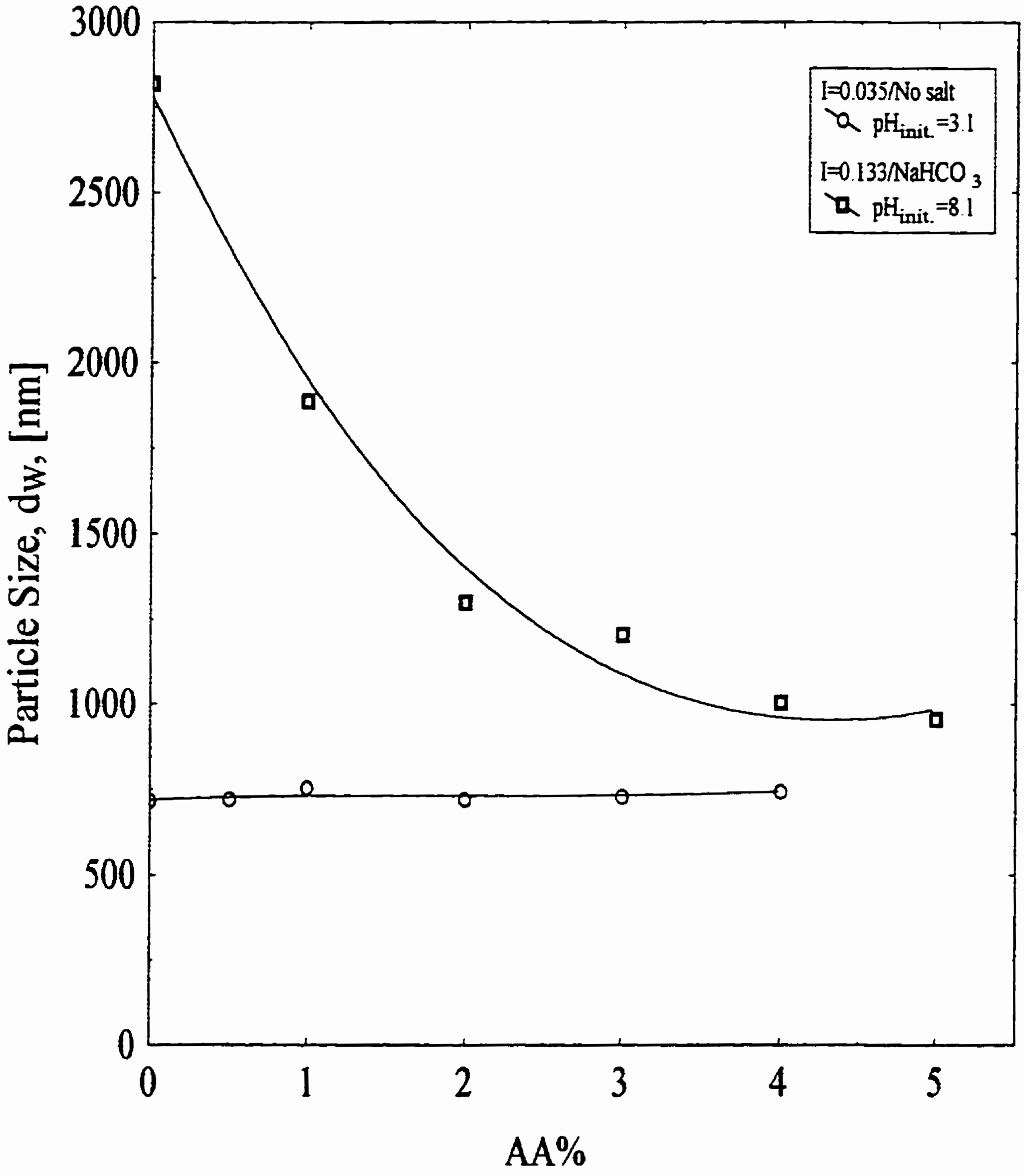
St/BA = 80:20 wt./wt.; Temp. = 70 °C; feeding rate = 0.68 g/min;
stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

***Values calculated against the experimental average water surface-tension measurement, S_f = 71.20.

Figure 4.3.2.1

The influence of AA concentration on the particle size of St/BA/AA latexes.



feeding stage.

The experimental plots in Figure 4.3.2.4 exhibited a stronger flocculation process in the very early stage of the polymerization, due to the increase in AA concentration. The decrease in the number of particles after this followed an almost identical trend (within experimental error limits). This suggested an aggregative polymerization process similar to the AA-free surfactant-free emulsion polymerization of St/BA, regardless of the AA concentration between the limits mentioned.

Results with Bicarbonate Buffer

The copolymerizations carried out in the weakly-basic range (in presence of $NaHCO_3$) revealed a completely different behavior compared with the copolymerizations performed at pH = 3 (Figure 4.3.2.1). When copolymerizations were performed with $NaHCO_3$, by increasing the AA concentration from 1-5 % of monomer, the size of the final latex particles decreased.

The St/BA/AA copolymerization carried out in presence of $NaHCO_3$ revealed two main trends which depend on AA concentration (Table 4.3.3.2):

A) regarding the particle size variation:

i. A sharp decrease in particle size with increasing AA concentration from 0 % (no added AA) to 1 wt %.

ii. A slightly decrease in particle size by increasing AA concentration from 1 % to 5 wt %.

B) regarding the latex quality:

i. A lot of coagulum formed and a very low latex yield, less than 90 %, when:
  - the polymerization process was carried out without AA
  - the polymerization process was carried out with 5 wt % AA.

ii. Clean, stable latexes with a final yield above 90 %, if [AA] $\in$ [1 wt % to 4 wt %].

Figure 4.3.2.2

SEM analysis of St/BA/AA latexes obtained with different AA concentrations.

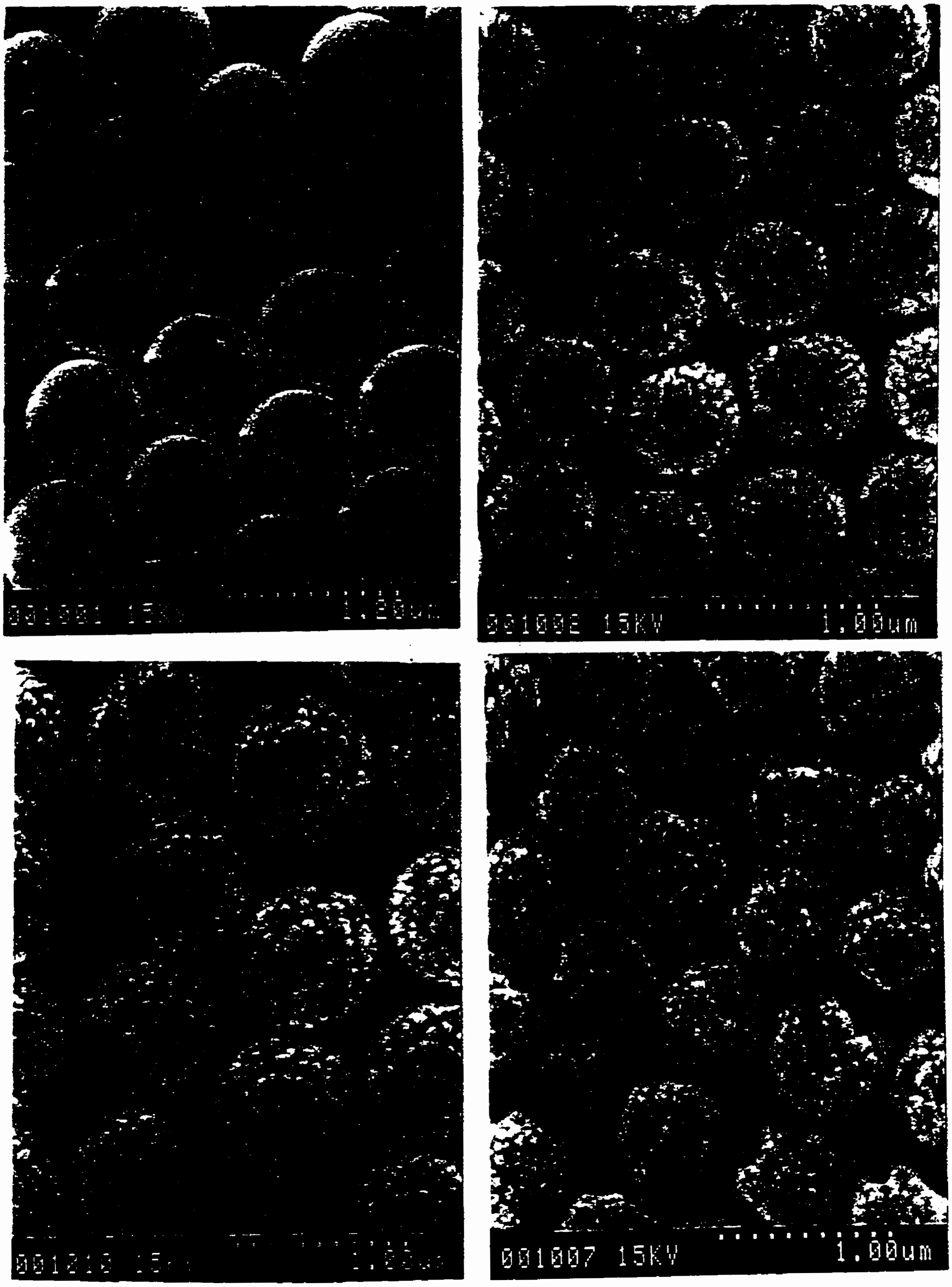


Figure 4.3.2.3

The influence of AA concentration on the overall polymerization rate in St/BA/AA surfactant-free emulsion copolymerization at an initial pH = 3.

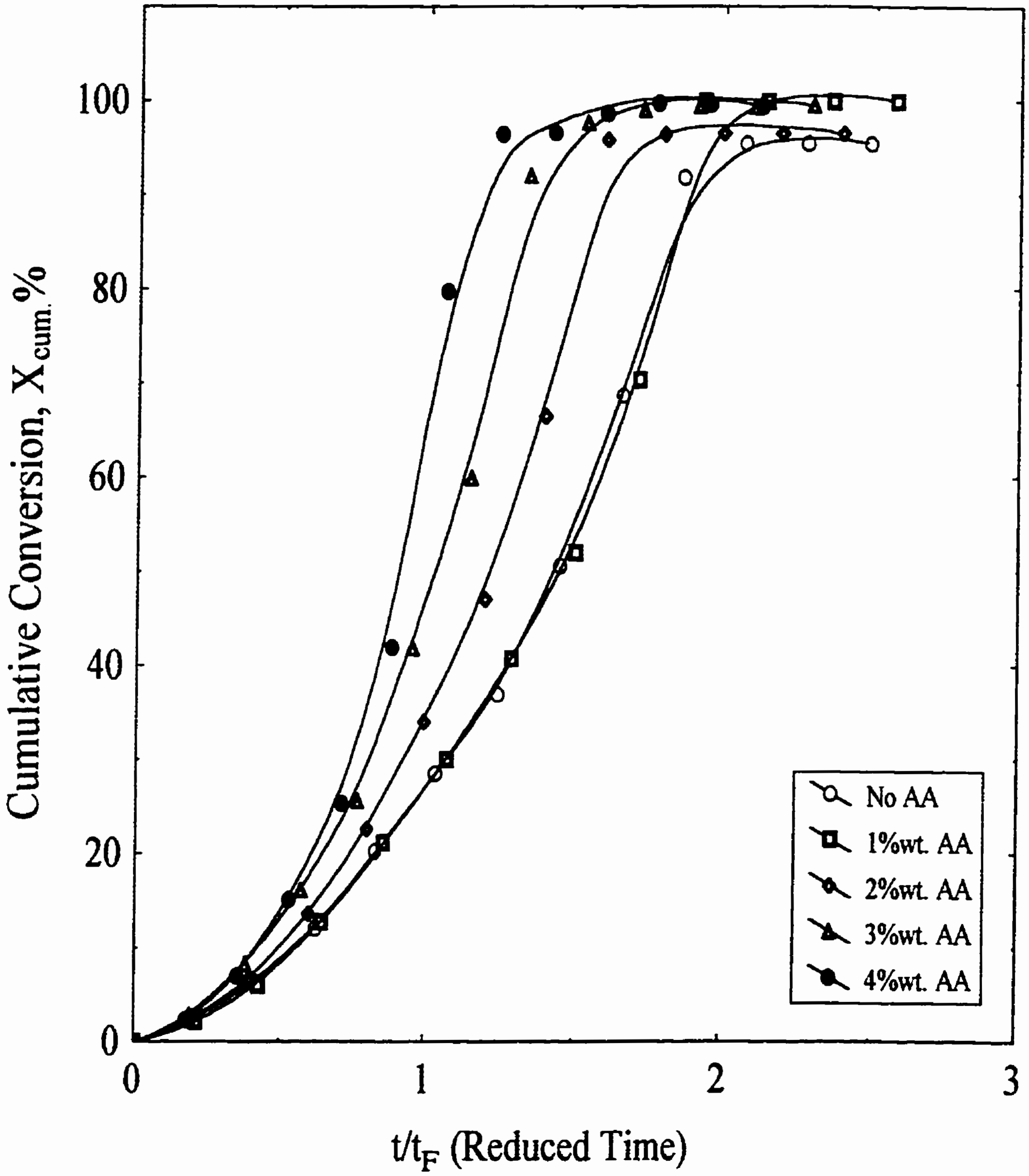


Figure 4.3.2.4

The influence of AA concentration on the variation of particle number density with time in St/BA/AA surfactant-free emulsion copolymerization at 70 °C.

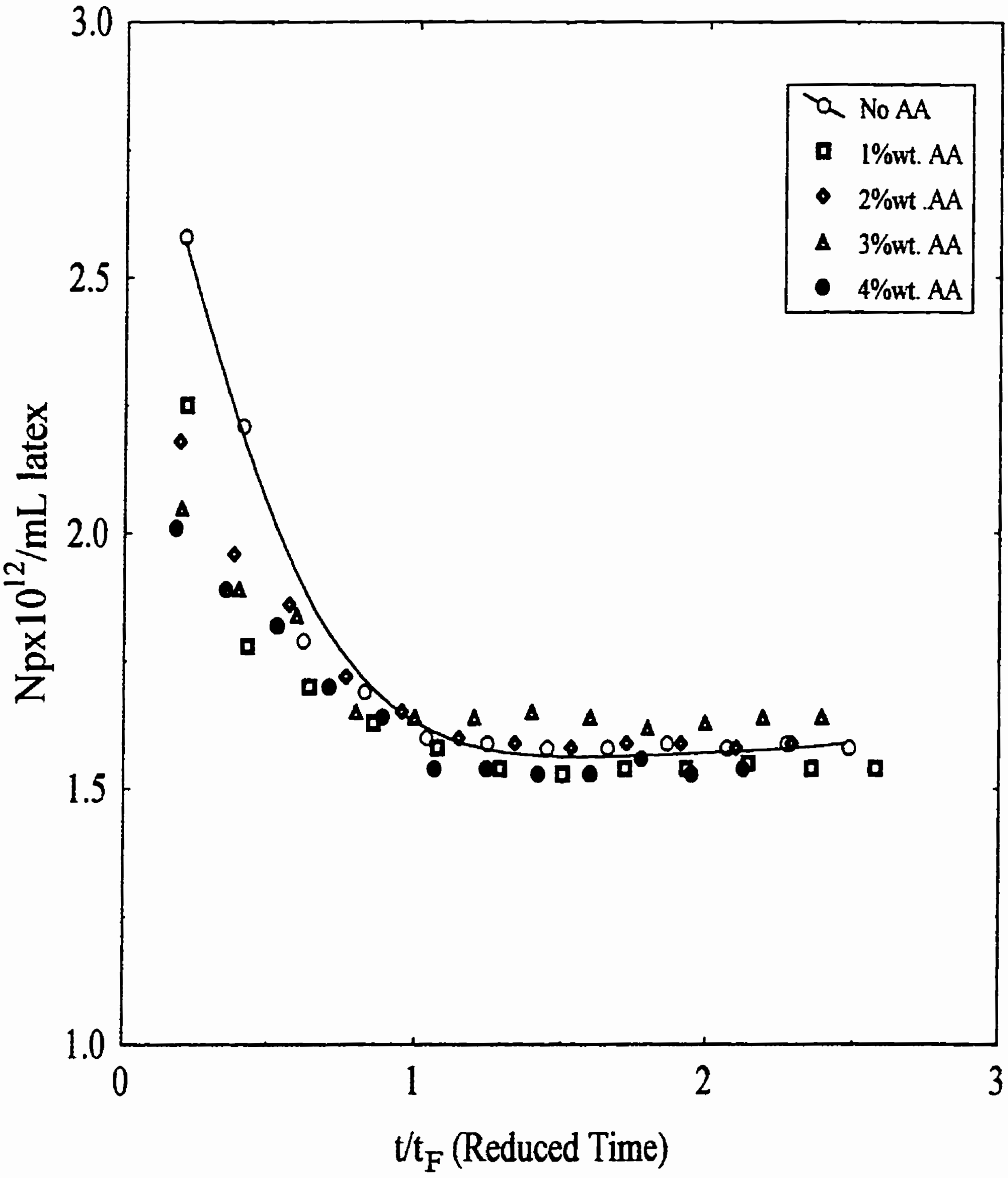
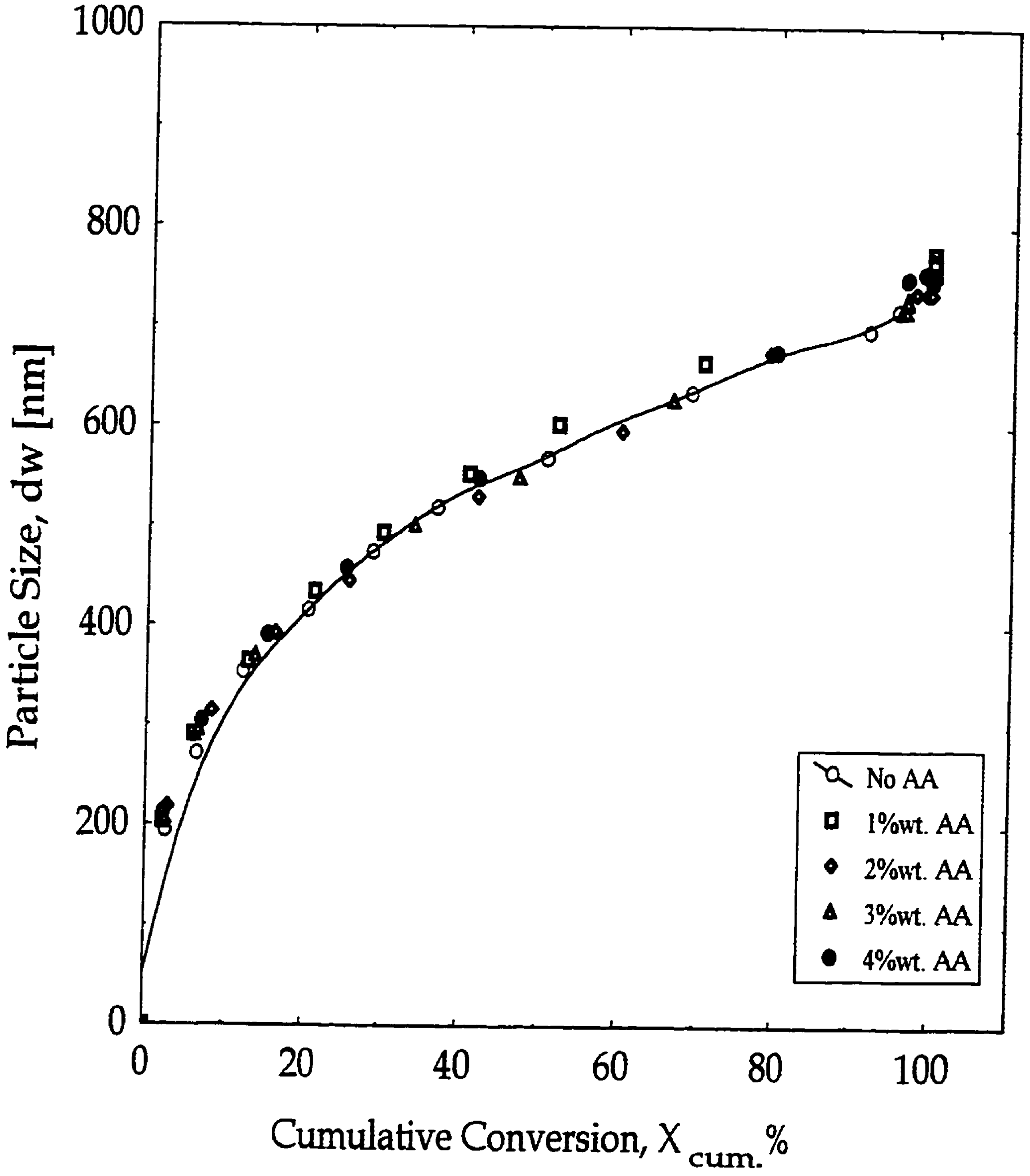


Figure 4.3.2.5

The variation of particle size versus cumulative conversion at different AA concentrations in St/BA/AA surfactant-free emulsion copolymerization at 70 °C.



The particular behavior of the St/BA/AA polymerization system in presence of $NaHCO_3$ can be explained by considering the acid base equilibrium of the AA (Eq. 4.1) and by postulating the hypothesis that *in situ* surfactant may result.

By undergoing water-phase polymerization, both the ionized and the unionized AA species are incorporated into the polymeric chain via oligoradicals formed in the water phase. These oligoradicals are more or less hydrophilic, depending on the number of ionized and unionized acrylic monomer units on the chains. By increasing the number of acrylic units into a polymeric chain one increases the hydrophilicity. Therefore these species stay dissolved in the water phase longer. They are more suitable to undergo water-phase propagation and consequently reach a higher molecular weight. Thus, an increase in AA concentration in the monomer mixture led to an increased *in situ* surfactant concentration. More primary particles can be nucleated and the final size of the latex particles was smaller.

The presence of a charge on some of the AA units of an AA^- rich surface active chain has two effects:

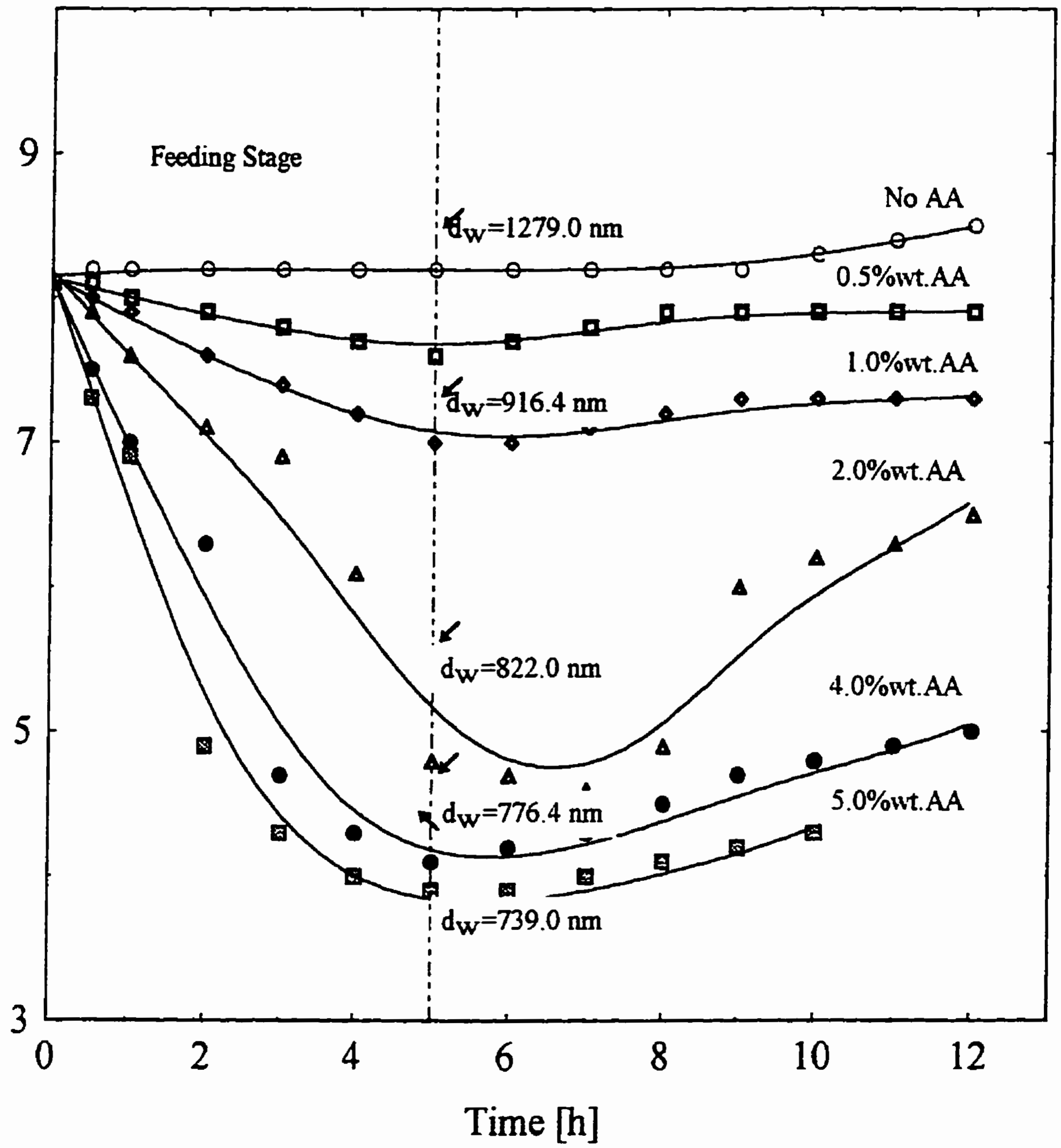
i. Electrostatic repulsion between charged centers makes it difficult for new species to get to the surface of existing particles, so they may be more likely to nucleate (stabilize) new particles - resulting in a much higher particle count.

ii. Electrostatic effects keep the AA groups near the surface of existing particles so they are less likely to be buried during the growth process, like the undissociated –COOH at low pH (if this is true, titration to find –COOH would find more buried groups at a lower pH).

The literature[7] emphasizes that any polymeric emulsifier which adsorbs on the latex particles to increase the colloidal stability may also cause particle flocculation. This, however, depends on the concentration and molecular weight. The bridging effect of several polyelectrolytes, such as a high molecules weight poly(acrylic acid) is well known. Therefore, the increase in the coagulum content at the end of polymerization carried out with 5 wt % AA might be the result from a bridging effect.

Figure 4.3.2.6

The time-variation of pH function of AA concentration in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.



The fact that the time-evolution of the pH during the polymerization (Figure 4.3.2.6) depended on the feed AA content (since it is a source of protons) also supported the above hypotheses. As can be observed, the sodium bicarbonate buffer capacity sharply decreased within increasing AA content, especially at a concentration higher than 1 wt %. This suggested an increase in the concentration of the polyelectrolyte species in the water phase. The increase in pH during the late stages of the reaction could suggest that a part of the species were adsorbed from the water phase onto the particle surface. Alternatively, some –COOH groups may have been buried in the particles.

4.3.3 The Influence of Ionic Strength

The studies dedicated to the analysis of the ionic strength influence on the St/BA surfactant-free emulsion copolymerization system (Section 3.3.4) revealed a specific effect on both the size of latex particles as well as on the kinetic behavior. The ionic strength came from initiator concentration variation or from an added salt.

The effects of increasing ionic strength by salt addition:	The effects of increasing ionic strength by increasing the initiator concentration:
- increased the particle size	- decreased the particle size
- broadened the particle size distribution	- enhanced the monodispersity
- slowed the polymerization rate	- increased the polymerization rate
- favored aggregative processes	- limited aggregative processes

When the polymerizations were carried out with AA (2 wt % on monomer) and the same amount of salt (Table 4.3.3.1), a decreased initiator concentration led to a polydisperse latex and increased the coagulum level.

The polymerizations were carried out in the presence of the same salt ($NaHCO_3$) and the initiator concentration ranged over the same concentration limits. The size of the final particles obtained from the polymerizations carried out with AA (Table 4.3.3.1) were similar each other, while those resulting from AA-free polymerizations were very

Table 4.3.3.1

The influence of initiator concentration on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

Latex No.	*S-144*	*S-145*	*S-142*
Initiator Conc. [g/L water]	1.33	2.67	5.55
Salt Conc. [g $NaHCO_3$/L water]	8.27	8.27	8.27
Ionic Strength [mol/L]	0.115	0.133	0.171
Initial pH	8.3	8.1	7.8
Particle Size, d_W, [nm]	1280	1203	1098
Latex Polydispersity d_W/d_n	1.104[*]	1.005[*]	1.003[*]
Solids Content [% wt/wt]	28.7	31.3	31.5
Coagulum	much	little	little
Latex Final Yield [% wt/wt]	87.3	91.6	94.6

T = 70 °C; feeding rate = 0.68 g/min; stirring rate = 200 RPM.

[*] Measurements on disc centrifuge.

different (Table 3.3.3.1). This effect could be correlated to the influence of AA molecules on the particle stabilization mechanism.

It has already been shown that St/BA/AA particles are less likely to aggregate compared with AA-free St/BA particles. The St/BA/AA particles were stabilized by an electro-steric mechanism, which makes the particles more stable against aggregation than the St/BA particles which were stabilized by an electrostatic mechanism only.

At a constant initiator concentration, the influence of ionic strength was confounded with a strong pH effect, because of the ability of AA molecules to be ionized (Figure 4.3.3.1). Therefore, experiments which will elucidate the influence of ionic strength on the particle size of the latex particles resulting from the St/BA/AA copolymerization were carried out with NaCl (initial pH ≅ 3.1), $NaHCO_3$ (initial pH ≅ 7.4 - 8.1) and NaOH (initial pH ≅ 11.1). In order to minimize any side effects, the AA concentration was kept constant at 2 % wt/wt on the monomers, and all the other experimental conditions were the same.

4.3.3.1 The Influence of Ionic Strength Changes by NaCl Addition

When the polymerizations were performed with NaCl (pH ≅ 3, constant during the reaction) the increase in ionic strength led to a constant increase in particle size until the system reached the critical coagulation concentration (c.c.c.) (in this case 6.67 > c.c.c.> 5.55 g NaCl/L water) and failed due to gross coagulation. At a higher ionic strength the particle size distribution of the latexes broadened, but remained monodisperse. Moreover, a higher level of coagulum was found at the end of the polymerization (Table 4.3.3.2).

For the St/BA/AA copolymerization performed in the ionic strength interval yielding stable monodisperse latexes, the time-variation of the overall cumulative conversion revealed two trends (Figure 4.3.3.2 and Figure 4.3.3.3):

Figure 4.3.3.1

The influence of ionic strength, by salt addition, on St/BA/AA surfactant-free emulsion copolymerization.

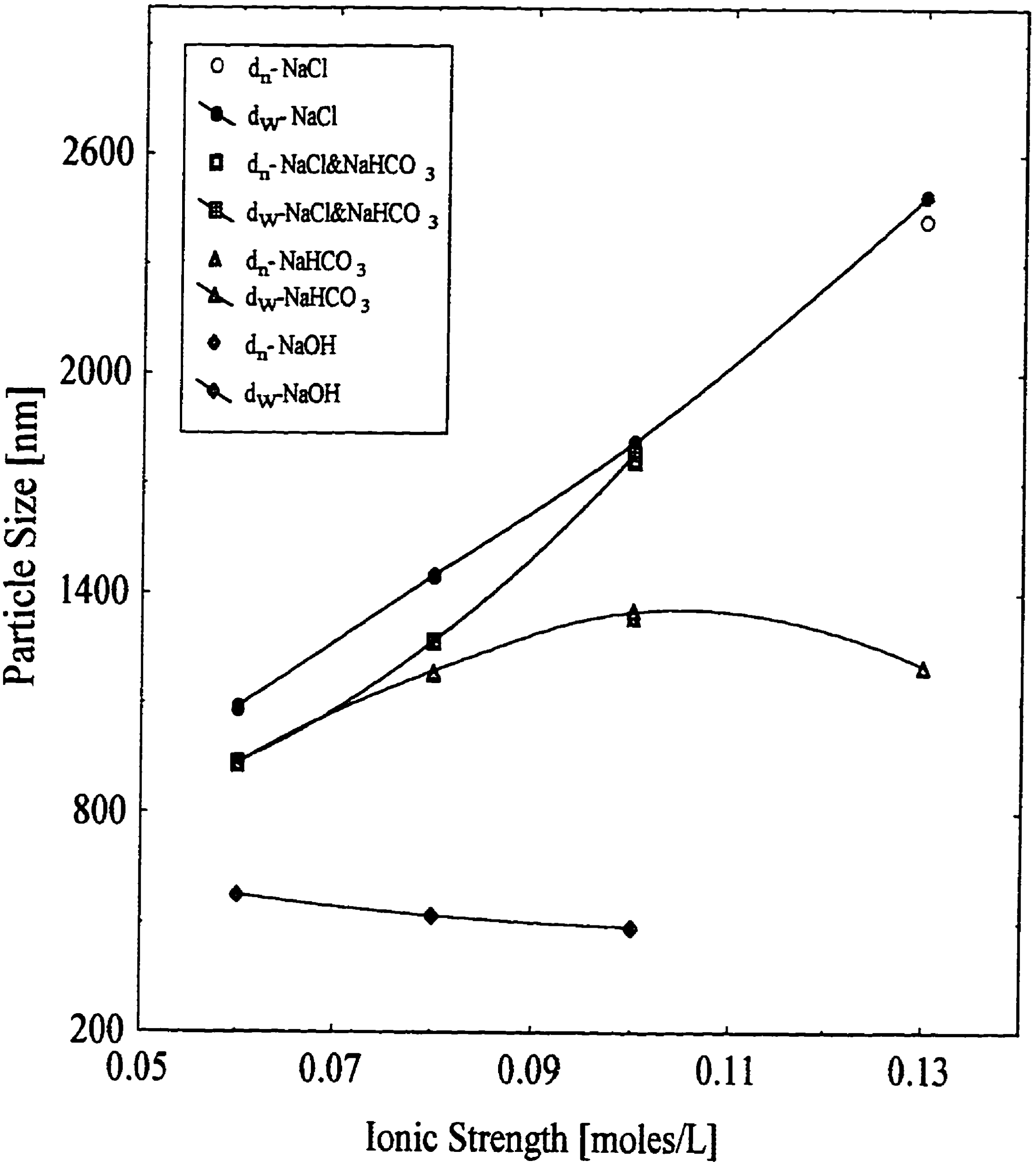


Table 4.3.3.2

The influence of initiator concentration on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride.

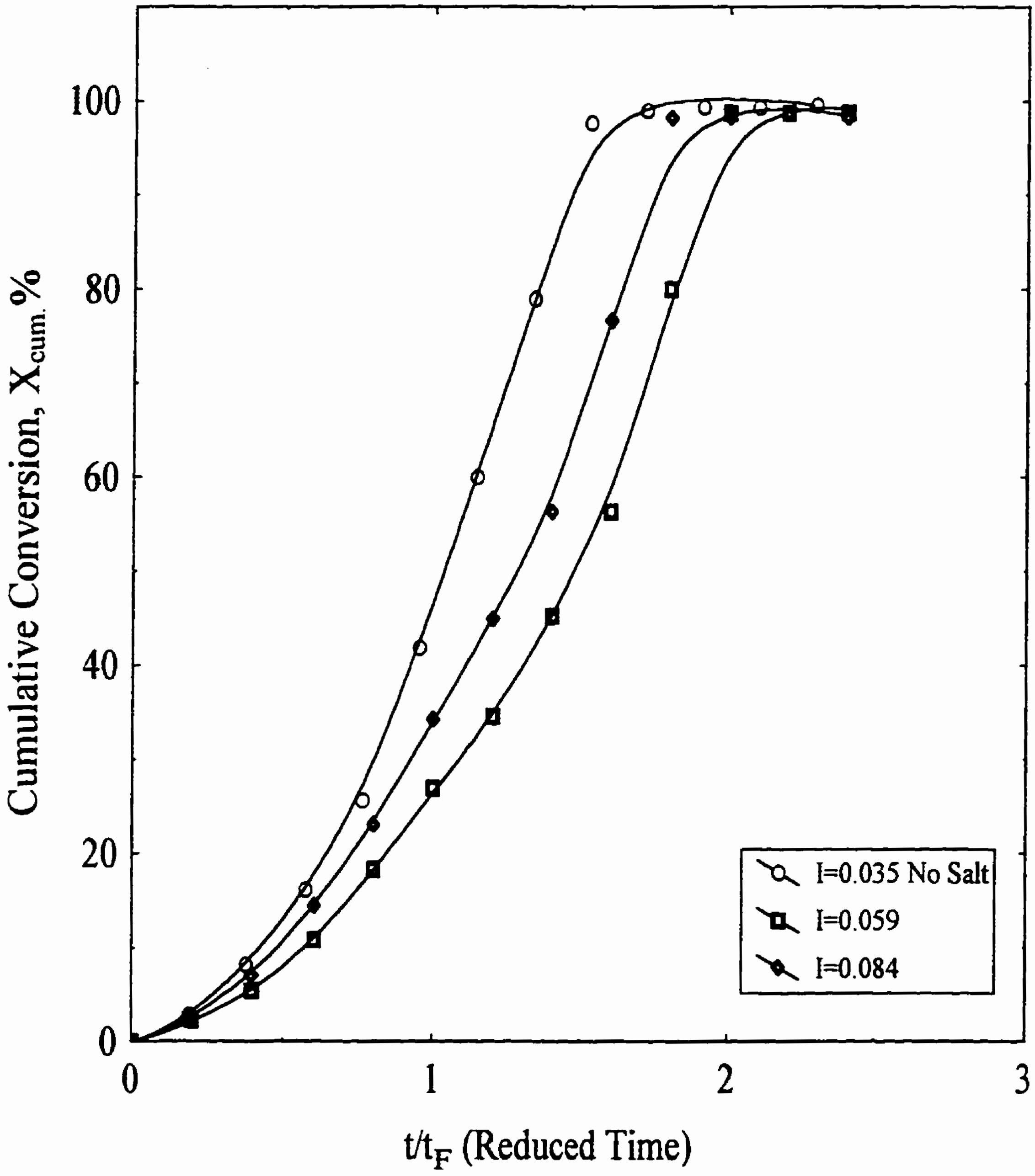
Latex No.	*S-144*	*S-145*	*S-148*	*S-149*
Initiator Conc. [g/L water]	2.67	2.67	2.67	2.67
Salt Conc. [g NaCl/L water]	1.44	2.89	4.44	5.55
Ionic Strength [mol/L]	0.059	0.084	0.111	0.130
Initial pH	3.1	3.0	3.1	3.1
Particle Size, d_w, [nm]	1091	1451	1815	2489
Latex Polydispersity d_w/d_n	1.003*	1.004*	1.013**	1.028**
Solids Content [% wt/wt]	31.0	31.3	29.8	27.8
Coagulum	little	little	much	much
Latex Final Yield [% wt/wt]	92.3	93.6	88.6	86.7

Temp.= 70 °C; feeding rate = 0.68 g/min; stirring rate = 200 RPM.

*Measurements on disc centrifuge. **Measurements on Coulter Multisizer.

Figure 4.3.3.2

The influence of ionic strength on the polymerization rate of surfactant-free St/BA/AA emulsion copolymerization at 70 °C in presence of sodium chloride.



i. An expected lower polymerization rate in the presence of NaCl compared to the electrolyte-free polymerization.

ii. An unexpected increase of polymerization rate with an increase in ionic strength throughout the polymerization performed with NaCl.

The increase in ionic strength by NaCl addition led as well to an increase in the particle size (Figure 4.3.3.3).

If the classical Smith-Ewart polymerization equation (Eq. 3.6) is accepted to describe the polymerization system studied, the time-evolution of the number of particles (Figure 4.3.3.4) clearly supported the first trend. As can be seen, throughout the salt-free St/BA/AA polymerization system the number of particles, N_p, was higher than during the polymerization carried out in presence of NaCl.

During the particle nucleation stage, in the electrolyte free polymerization, aggregation of the *precursors* and *primary particles* was limited compared with the polymerization based on salt addition. In the former case more particles were nucleated and therefore the polymerization rate increased.

The unexpected increase of the polymerization rate at a higher ionic strength (by NaCl addition) suggested a more complex polymerization mechanism. Throughout these polymerizations it could be assumed that two opposite effects of ionic strength are balanced:

i. An obvious decrease in N_p with the increase in ionic strength which, always leads to a decrease in R_p.

ii. A less certain, based on limited experimental data, increase in R_p by increasing the ionic strength (by means of NaCl addition) due to:

- the decrease in fk_d of the initiator with an increase in ionic strength
- the increase in ionic strength might increase capture efficiency of dead oligomers formed by water-termination (not seen in other experiments).

Another approach to explain this unexpected evolution of R_p with the increased in ionic strength could be based on the Smith-Ewart equation by accepting that:

Figure 4.3.3.3

The influence of ionic strength, by sodium chloride addition, on the St/BA/AA polymerization rate.

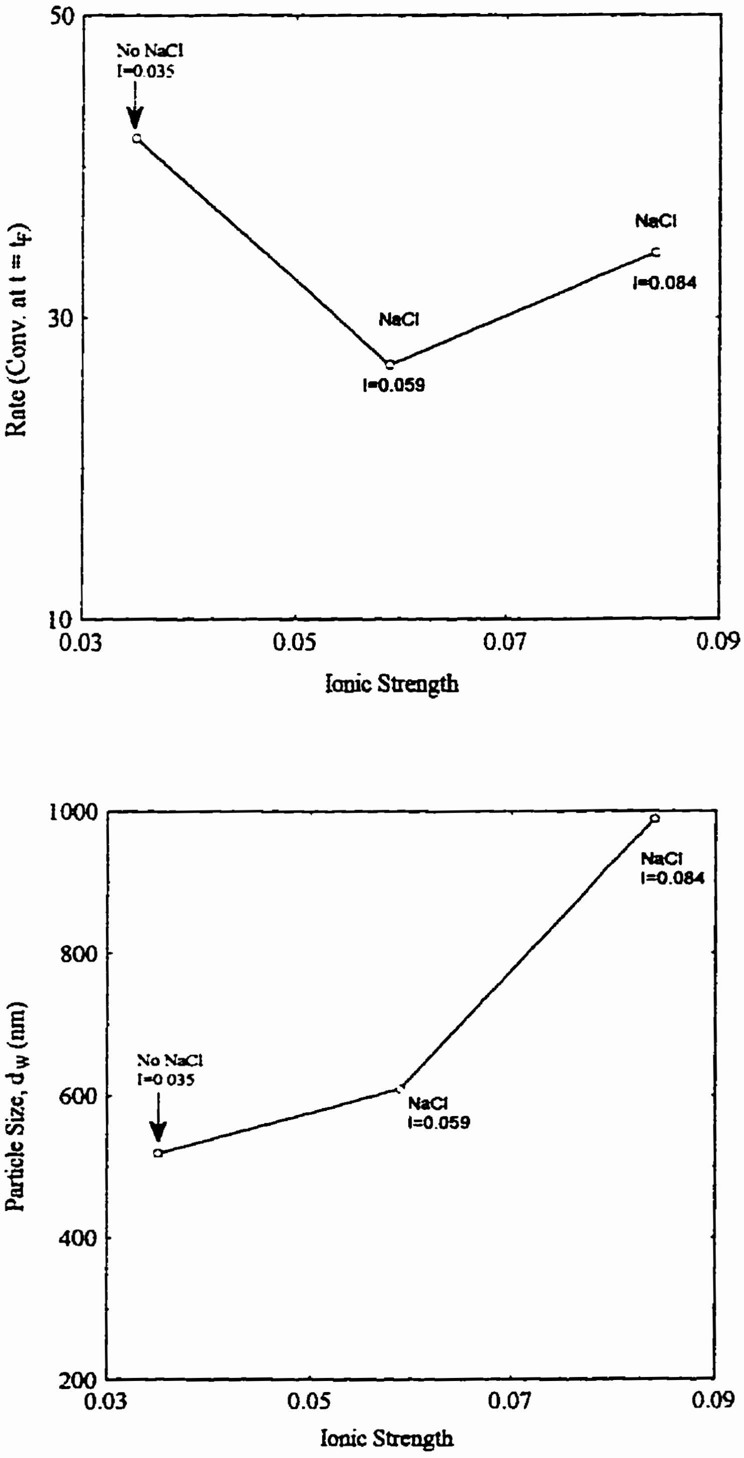


Figure 4.3.3.4

The influence of ionic strength on the particle number density variation versus time in St/BA/AA surfactant-free emulsion copolymerization at 70 °C in presence of sodium chloride.

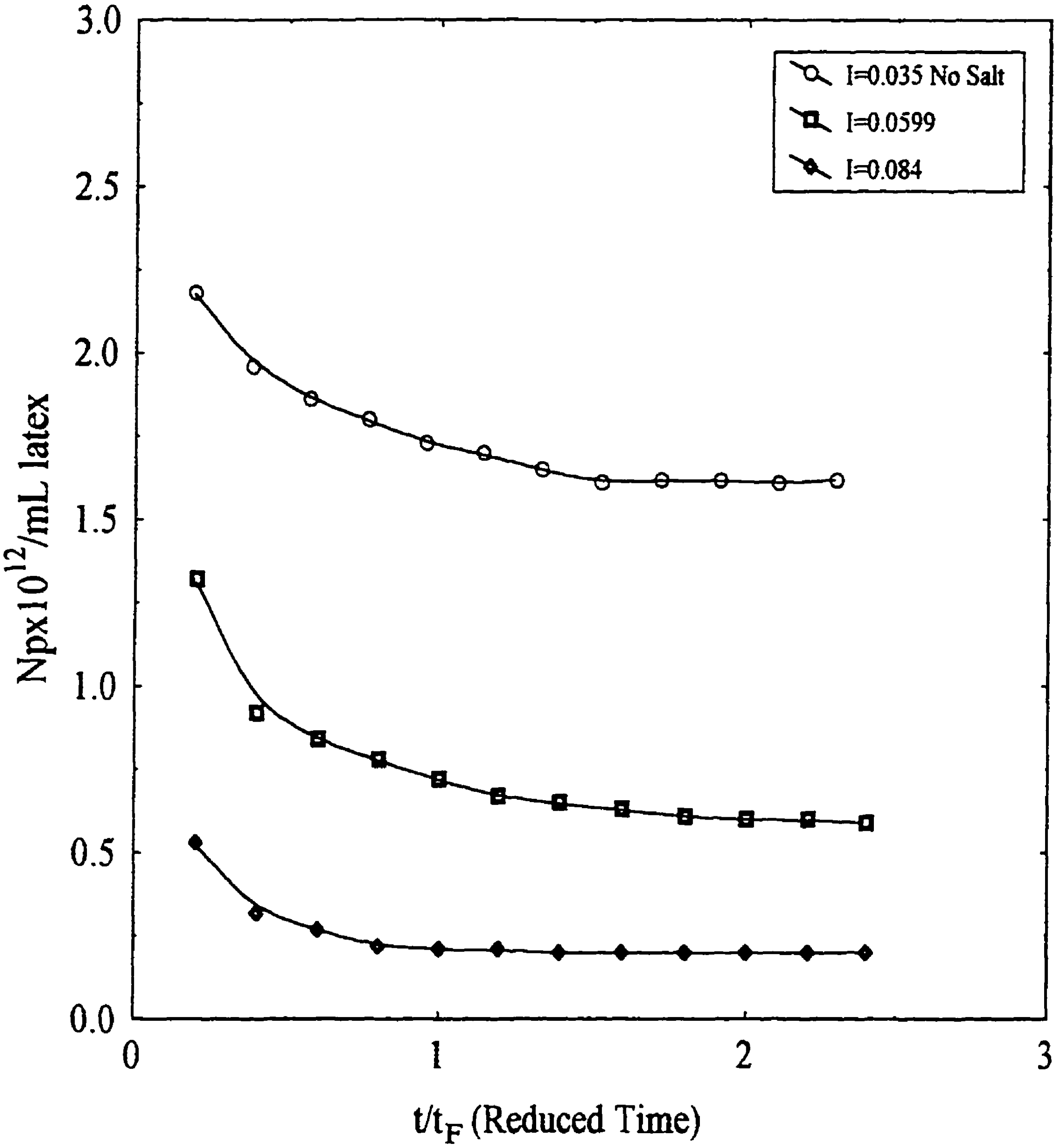
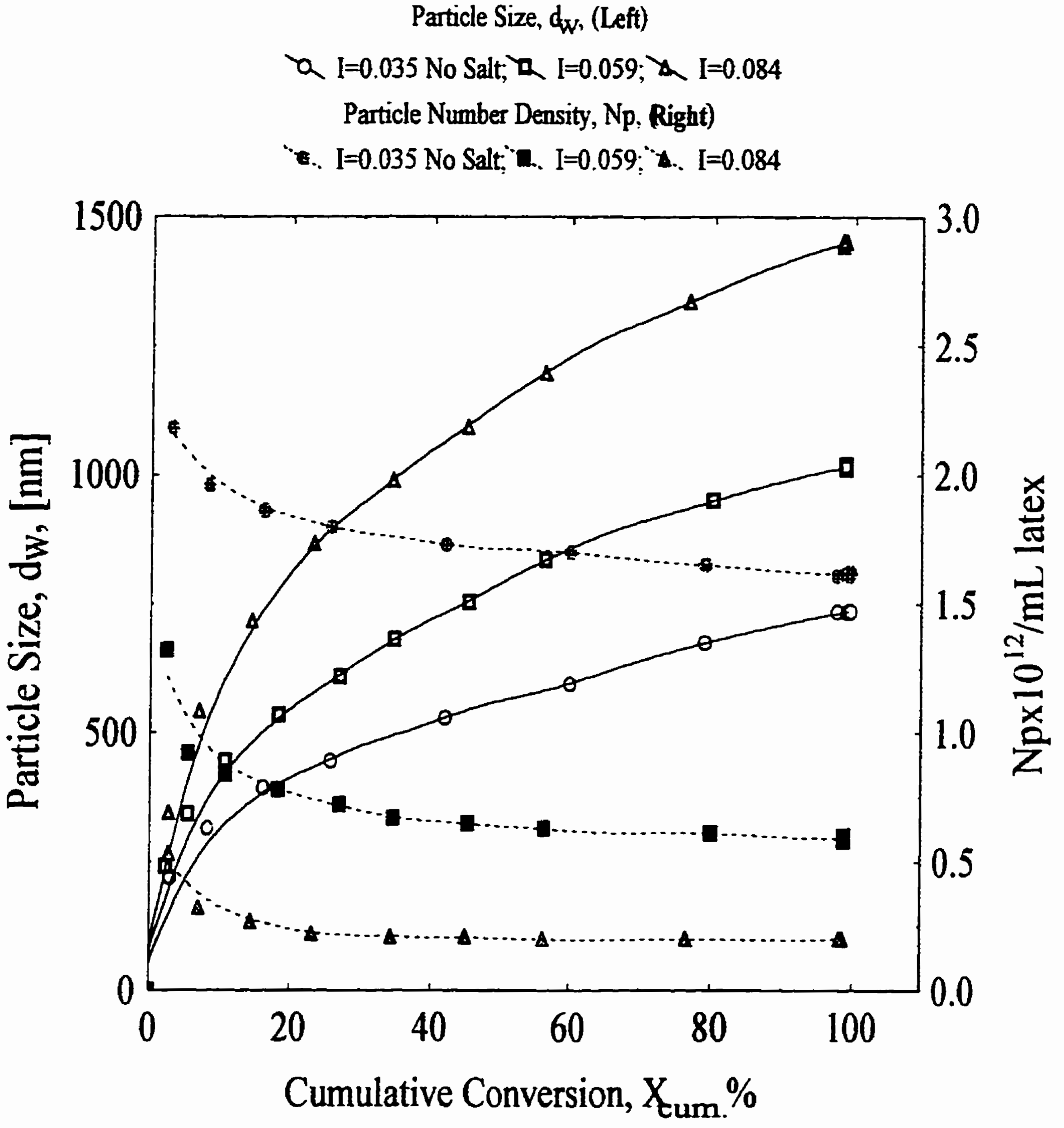


Table 4.3.3.5

The influence of ionic strength on the conversion variation of particle size and particle number density in St/BA/AA surfactant-free emulsion copolymerization at 70 °C in presence of sodium chloride.



$$\{ [M]_P \bar{n} \}_{\text{higher ionic strength}} > \{ [M]_P \bar{n} \}_{\text{lower ionic strength}} \qquad (4.2)$$

where, $[M]_P$ and $\bar{n}$ represent the monomer concentration and the number of radicals in a particle respectively.

The number of radicals might be higher in larger particles than in the smaller ones. Thus, the increase in the number of radicals inside the particle-aggregates (newly formed particles) can compensate for the decrease in the particle number density and lead to an increase in the polymerization rate.

At the same cumulative conversion (Figure 4.3.3.5), the particle number density recorded in the polymerizations carried out at a higher ionic strength was lower than that in polymerizations performed at a lower ionic strength. In the former case, the particle size was also larger. In order to support one or another of the above assumptions concerning the influence of ionic strength on R_p by NaCl addition, more experimental work should be done.

A comparison of the influence of NaCl addition on the polymerization rate of polymerizations carried out with and without AA revealed several fundamental differences (Figure 4.3.3.6). In the St/BA/AA polymerization, the increase in ionic strength led to an increase in the polymerization rate. In the AA-free St/BA polymerization, the polymerization rate decreased with increasing ionic strength. In all cases, both the particle number density and particle size evolution showed similar trends (Figure 4.3.3.6 and Figure 4.3.3.7).

The polymerization carried out with AA, at the same ionic strength (Figure 4.3.3.6 and Figure 4.3.3.7) revealed that:

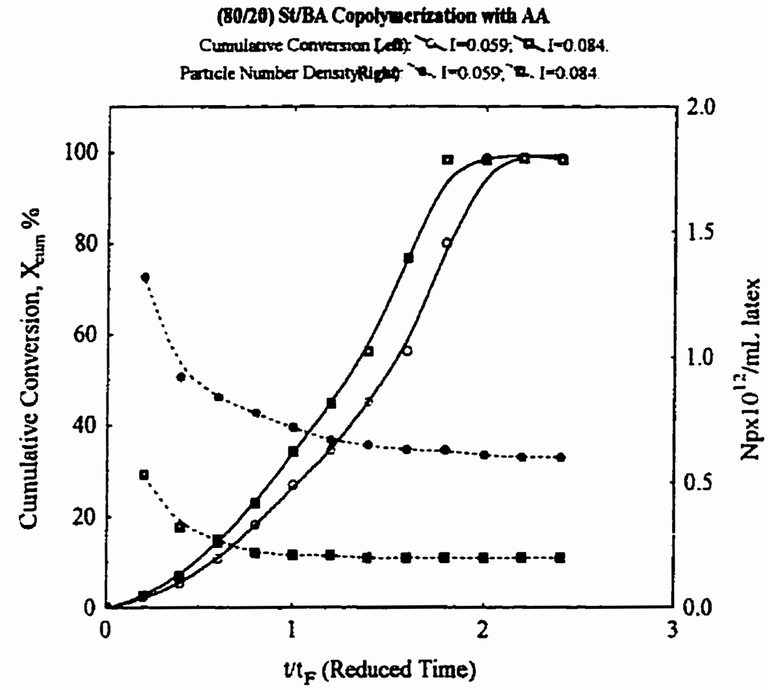
i. A higher polymerization rate than the AA-free copolymerization - already explained in another section.

ii. A slower rate decrease of the particle number density than in the corresponding AA-free copolymerization - same explanation as in prior section.

iii. A smaller latex particle size at a specific cumulative conversion than in AA-free copolymerization - which caused (i).

Figure 4.3.3.6

The time evolution of cumulative conversion and particle number density in St/BA and St/BA/AA surfactant-free emulsion copolymerization at a different ionic strength in presence of sodium chloride.


(80/20) St/BA Copolymerization with AA

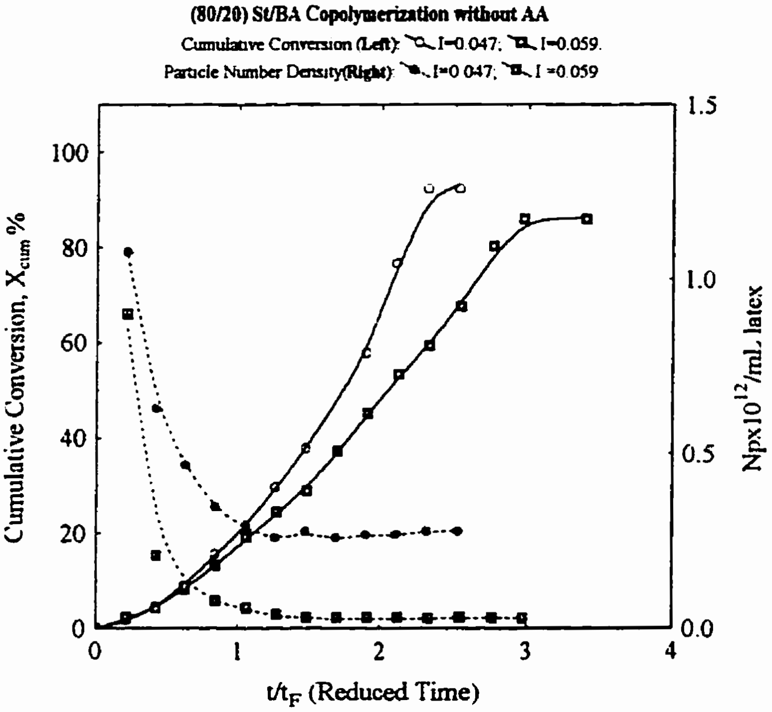
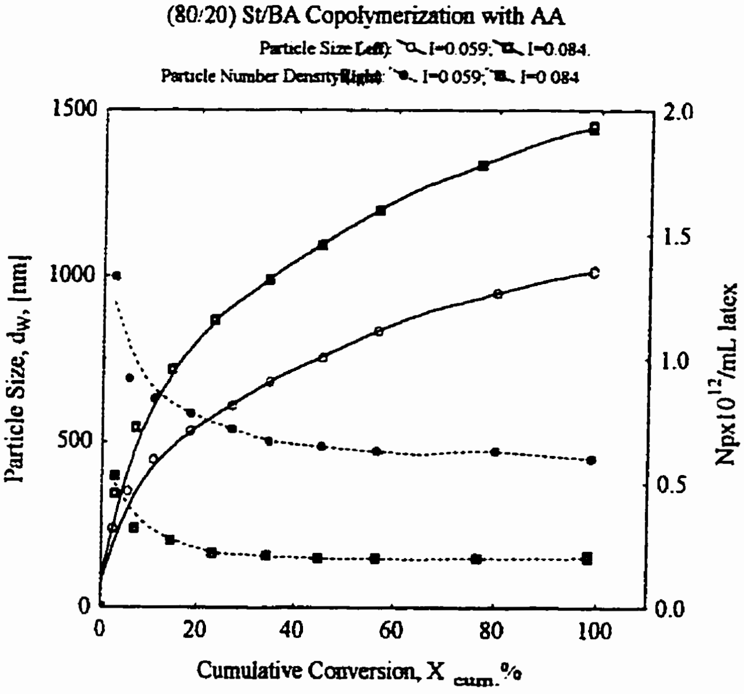
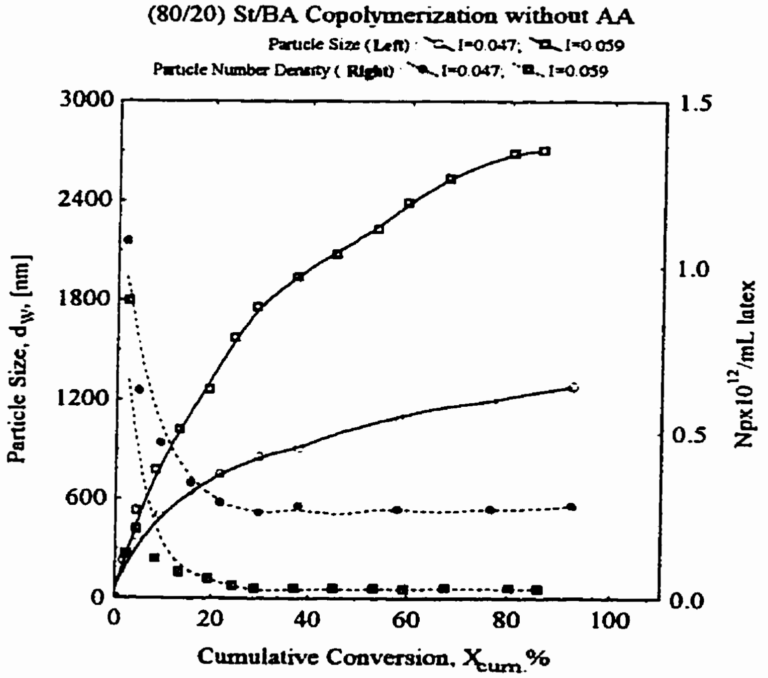

(80/20) St/BA Copolymerization without AA

Figure 4.3.3.7

The influence of ionic strength on the particle size and particle number density in St/BA and St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride.





4.3.3.2 The Influence of Ionic Strength Changes by NaCl & $NaHCO_3$ Addition

The polymerization medium was buffered at an initial pH ≅ 7.5 using a salt mixture which consisted of sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl) (Table 4.3.3.3). At this pH, the AA molecules can easily ionize.

Larger particles resulted due to increasing the ionic strength. In the ionic strength range studied, all the latexes were monodisperse. However, the increased ionic strength led to a higher coagulum level at the end of the polymerization.

The conversion-time plots (Figure 4.3.3.8) revealed a slight decrease in the polymerization rate with increasing ionic strength. This is due to a higher particle number density. By increasing the ionic strength the colloidally unstable primary particles are more likely to coagulate. Thus fewer particles, which become the main polymerization loci, were nucleated. The decrease in the number of polymerization loci led to a decrease of polymerization rate. The higher the ionic strength, the lower the conversion at which the number of particles reached a constant level (Figure 4.3.3.9). Moreover, after an early rapid flocculation at a conversion less than 5 %, the size of the particles, at the same conversion level, was significantly larger at a higher ionic strength.

The above mentioned experimental trends are normal for a surfactant-free emulsion copolymerization process in which the particle nucleation process is based on an homogeneous-coagulative mechanism and particle growth by an aggregative-polymerization mechanism.

4.3.3.3 The Influence of Ionic Strength Changes by $NaHCO_3$ Addition

When the polymerizations were performed with $NaHCO_3$ (Figure 4.3.3.1) the particle size increased with increasing ionic strength up to a certain ionic strength (I ~ 0.1 mol/L) and then slowly decreased. The latex particle monodispersity was unaffected up to a very high ionic strength value. A low level of coagulum was also found at the end of

Table 4.3.3.3

The influence of ionic strength on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride and sodium bicarbonate

Latex No.	*S-191*	*S-196*	*S-194*
Initiator Conc. [g/L water]	2.67	2.67	2.67
Ionic Strength [mol/L]	0.059[a]	0.084[b]	0.097[c]
Initial pH	7.2	7.4	7.4
Final pH	3.8	3.6	3.6
Particle Size, d_W, [nm]	939	1270	1785
Latex Polydispersity d_W/d_n	1.004*	1.003*	1.013**
Solids Content [% wt/wt]	31.7	31.3	31.5
Latex Final Yield [% wt/wt]	94.3	94.6	94.2

Temp. = 70 °C; feeding rate = 0.68 g/min; stirring rate = 200 RPM.

*Measurements on disc centrifuge. **Measurements on Coulter Multisizer.

[a] Ionic strength resulted from 2.06g $NaHCO_3$/L water;

[b] Ionic strength resulted from (2.06g $NaHCO_3$ + 1.44g NaCl)/L water;

[c] Ionic strength resulted from (2.06g $NaHCO_3$ + 2.22g NaCl)/L water.

Figure 4.3.3.8

The influence of ionic strength on the polymerization rate and time-variation of particle number density in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride and sodium bicarbonate.

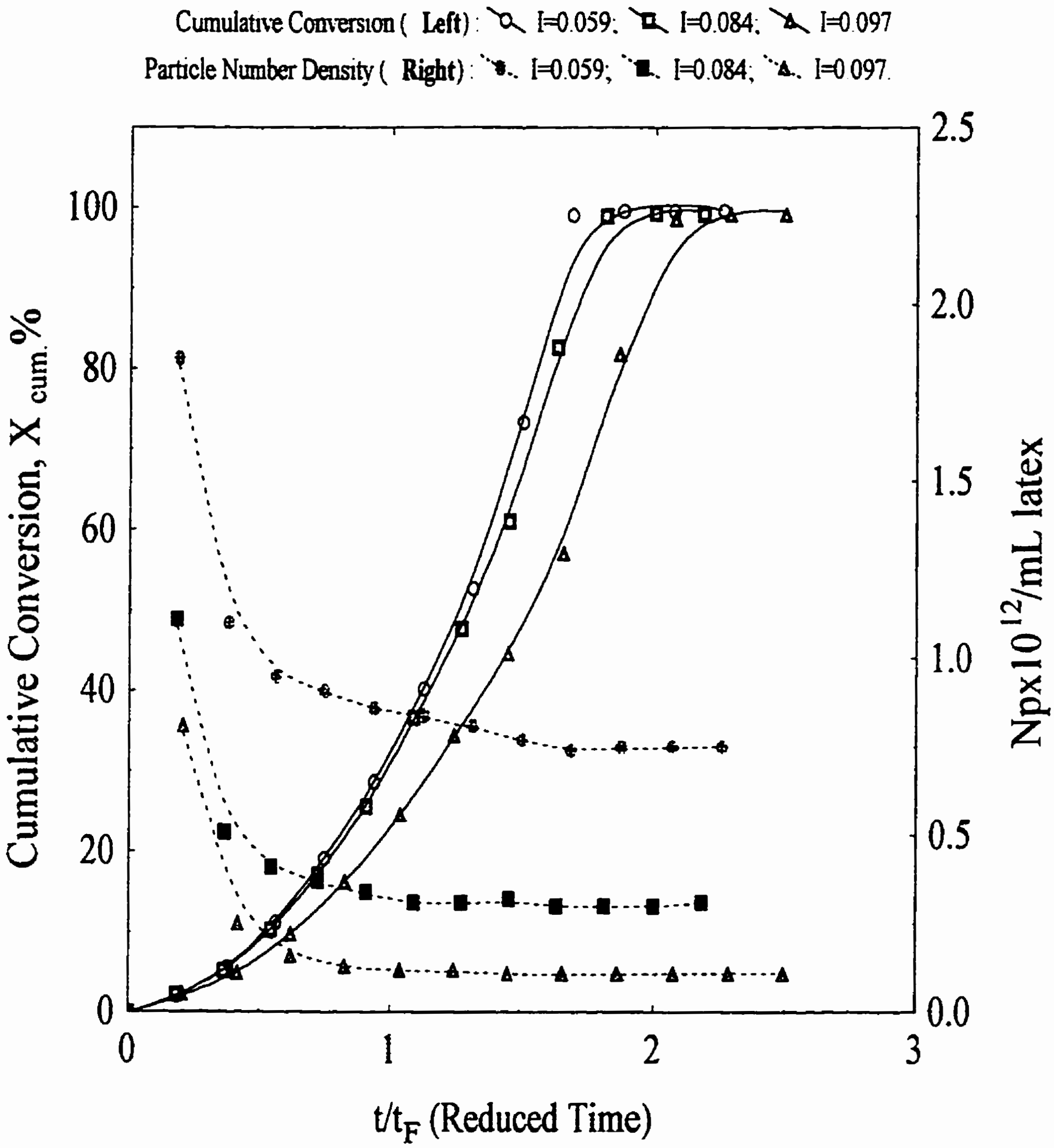
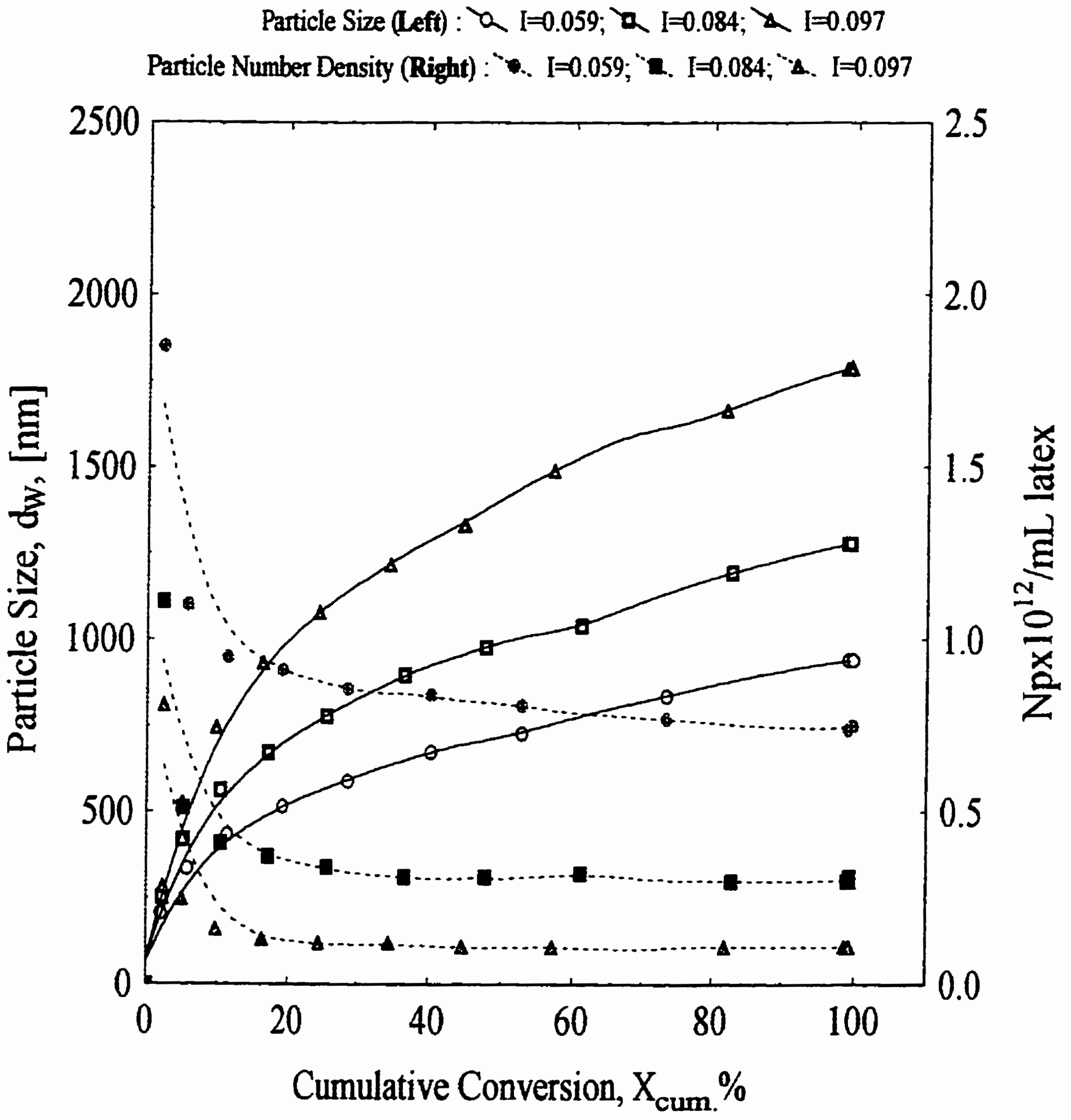


Figure 4.3.3.9

The influence of ionic strength on the particle size and particle number density variation with conversion in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride and sodium bicarbonate.



the polymerization (Table 4.3.3.4). Therefore, in all cases the particle colloidal stability covered a larger ionic strength range. The critical coagulation concentration found was higher than 10.8 g $NaHCO_3$/L water.

It is well known that the addition of bicarbonate has a double role: to increase the ionic strength and to buffer the reaction medium to a certain pH.

Both the time-evolution and the conversion-evolution of the particle number density, N_p, revealed two distinctive trends (Figure 4.3.3.10 and Figure 4.3.3.11):

i. When I < 0.111 [mol/L], corresponding to an initial pH < 8.0, an expected decrease in the number of particles at lower ionic strength.

ii. When I > 0.111 [mol/L], corresponding to an initial pH > 8.0, an unexpected increase in the number of particles at a higher ionic strength.

At higher ionic strengths, the time-variation of the pH during the polymerization (Figure 4.3.3.12) showed a prolonged decreasing period which suggested a higher buffering capacity of $NaHCO_3$.

In polymerizations carried out at I > 0.111 [mol/L] (Figure 4.3.3.10) the conversion followed the same time-variation, regardless of ionic strength. However, the variation in the particle number density revealed different pathways and a similar trend. At conversion less than 10 %, the particle number density of the first particles formed was higher in the reaction medium with a higher ionic strength (Figure 4.3.3.11). The corresponding sizes of particles were almost the same, $d_W \cong 400$ nm.

These results emphasize that above a certain ionic strength limit, the buffering capacity of the bicarbonate plays an equally important, but opposite role on the whole polymerization mechanism as ionic strength.

At the beginning of the reaction when no particles exist, the polymerization takes place only in the aqueous-phase. Because of the difference in water solubility of the monomers (St and BA are only sparingly water soluble, while AA is completely water soluble) it is very likely that the first oligoradicals and oligomers are richer in AA units. Therefore this oligomeric species are more water soluble. Hence, their concentration in

Table 4.3.3.4

The influence of ionic strength on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

Latex No.	***S-144***	***S-145***	***S-148***	***S-149***
Initiator Conc. [g/L water]	2.67	2.67	2.67	2.67
Salt Conc. [g $NaHCO_3$/L water]	2.06	4.13	6.35	8.26
Ionic Strength [mol/L]	0.059	0.084	0.111	0.133
Initial pH	7.2	7.8	8.0	8.1
Final pH	3.8	4.6	5.2	5.6
Particle Size, d_W, [nm]	939	1194	1353	1316
Latex Polydispersity d_W/d_n	1.004*	1.004*	1.014**	1.014**
Solids Content [% wt/wt]	31.7	31.3	31.4	30.6
Coagulum	little	little	little	little
Latex Final Yield [% wt/wt]	94.3	93.6	92.6	92.6

Temp.= 70 °C; feeding rate = 0.68 g/min; stirring rate = 200 RPM.

*Measurements on disc centrifuge. **Measurements on Coulter Multisizer.

Figure 4.3.3.10

The influence of ionic strength on the polymerization rate and the time-variation of particle number density in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

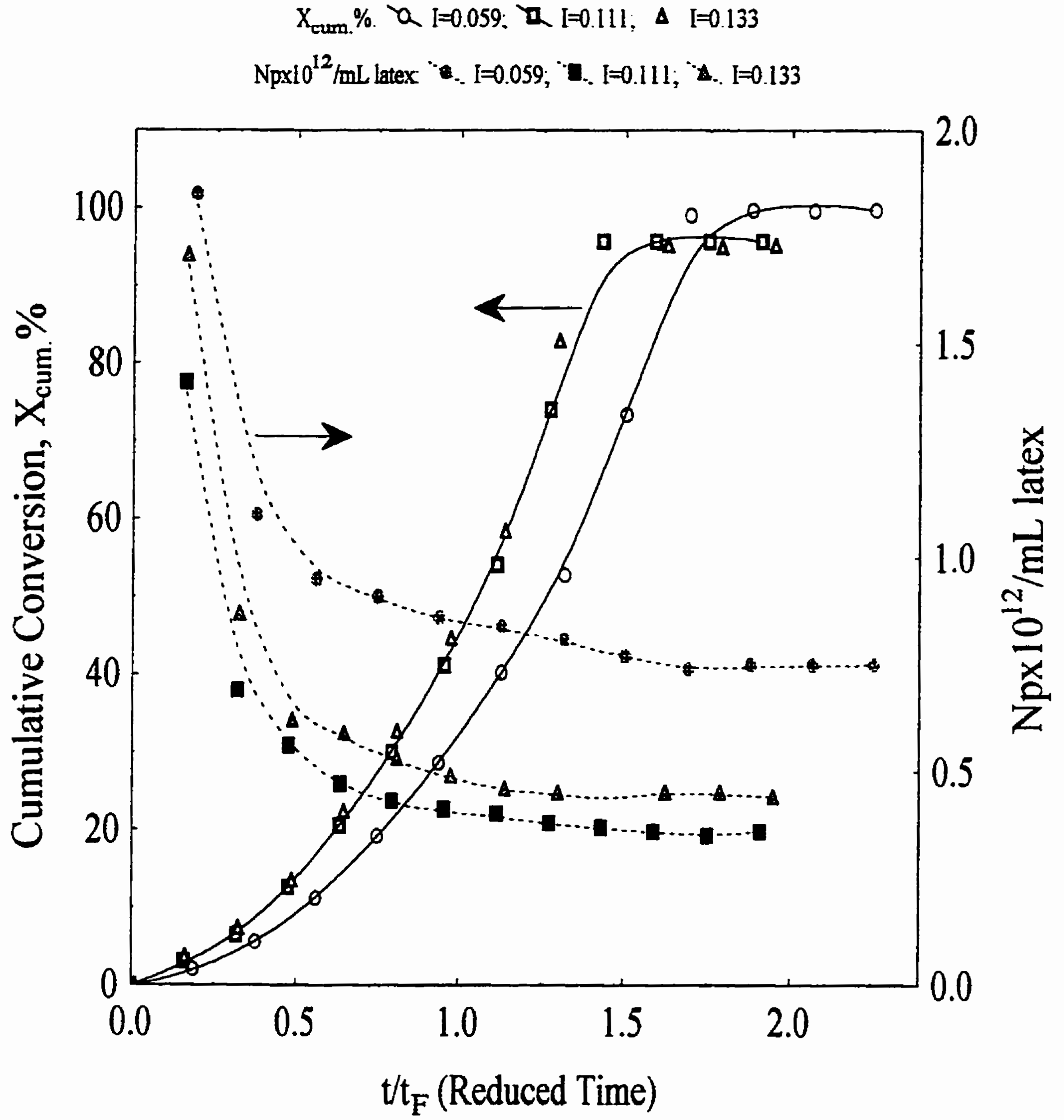


Figure 4.3.3.11

The influence of ionic strength on the variation of particle size and particle number density with conversion in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

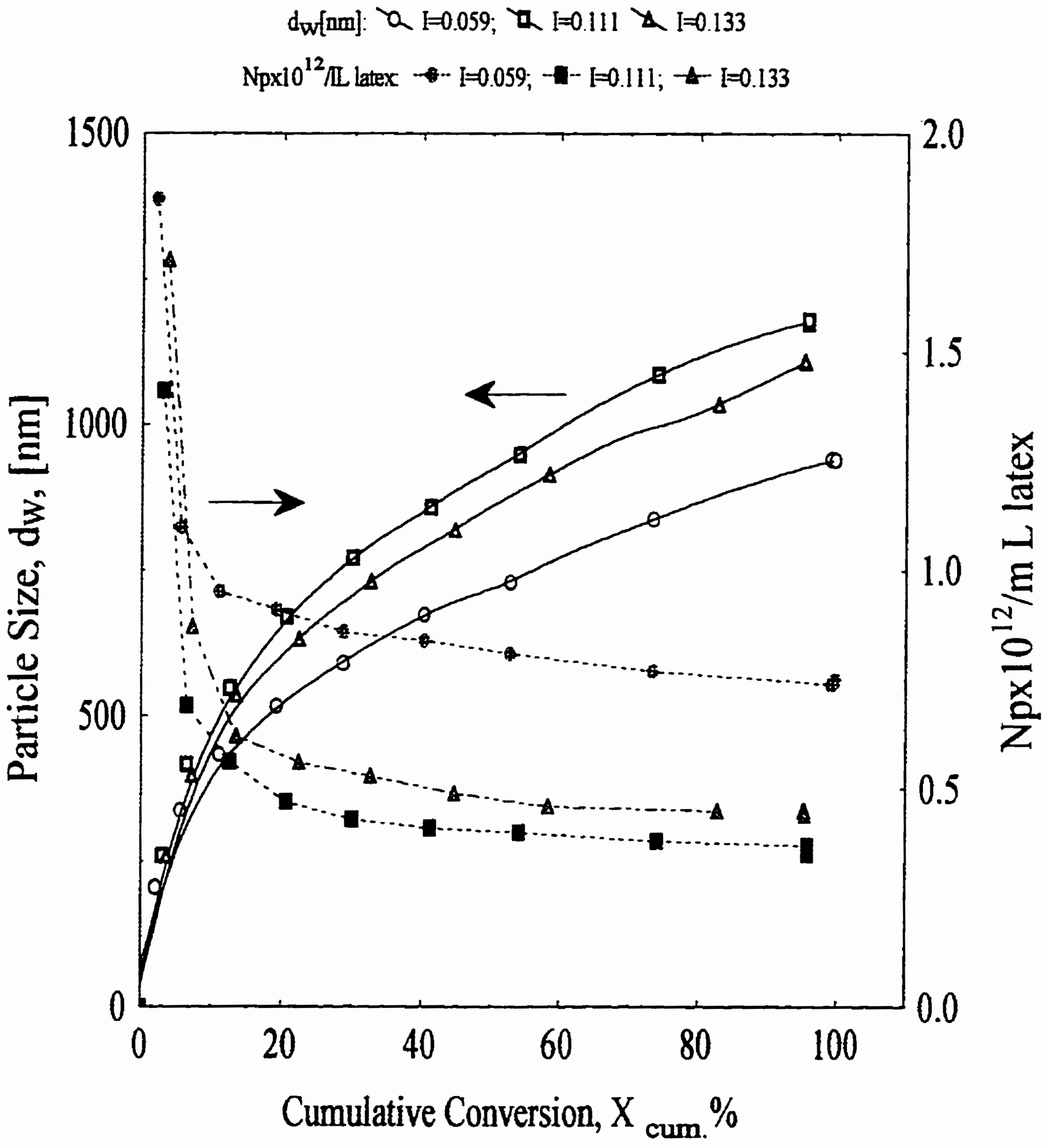
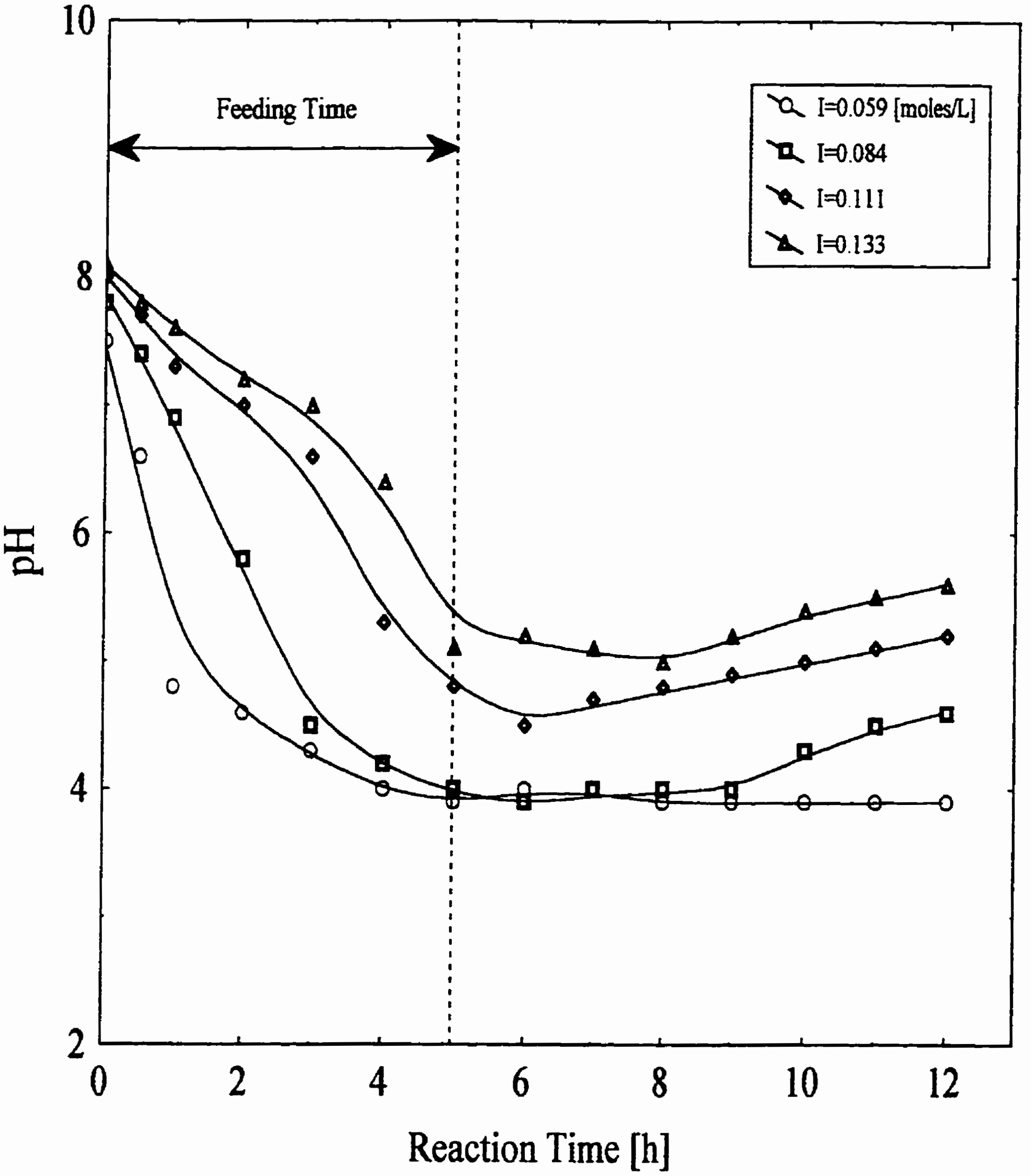


Figure 4.3.3.12

The influence of ionic strength on the time-variation of pH in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.



in the water phase increased. Consequently, more primary particles were nucleated.

Most of carboxyl groups are likely distributed at the primary particle-aqueous phase interface because of the AA^- hydrophilicity. This distribution interface leads to a higher charge density, which favors particle repulsion. Thus, more colloidally stable particles were generated at higher pH. The higher the charge density on the particle surface, the more electrolyte has to be involved to shrink the electrical double layer of the particles, and to make them more suitable to coagulate.

Therefore, above a certain ionic strength limit, an increase in the amount of bicarbonate was not enough to reduce the colloidal stability of the formed particles even if the ionic strength increases. Consequently, the particles remained stable.

These inferences were supported by the experimental evidence found during the surfactant-free emulsion copolymerization of St/BA/AA (Figure 4.3.3.11).

Using NaOH, the particle size dramatically dropped into the submicron range (Table 4.3.3.5) similar to classical emulsion polymerization. A very slight decrease in particle size was observed while the latex size distribution broadened with increasing ionic strength. At the end of all the polymerizations performed with NaOH, two main particle populations, very close in size, were observed (Figure 4.3.3.13).

This behavior can only be understood and explained by an analysis of pH variation with the time-variation of particle number density. This analysis is made in the next section, which is dedicated to the influence of the pH on the polymerization system studied.

4.3.4 The Influence of Initial pH

It is well recognized that the pH strongly influences the surfactant-free polymerization of latexes based on acidic co-monomers, such as an carboxyl acid (e.g., AA). This is mainly due to of the acid-base equilibrium associated with Eq. 4.1.

Table 4.3.3.5

The influence of ionic strength on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium hydroxide.

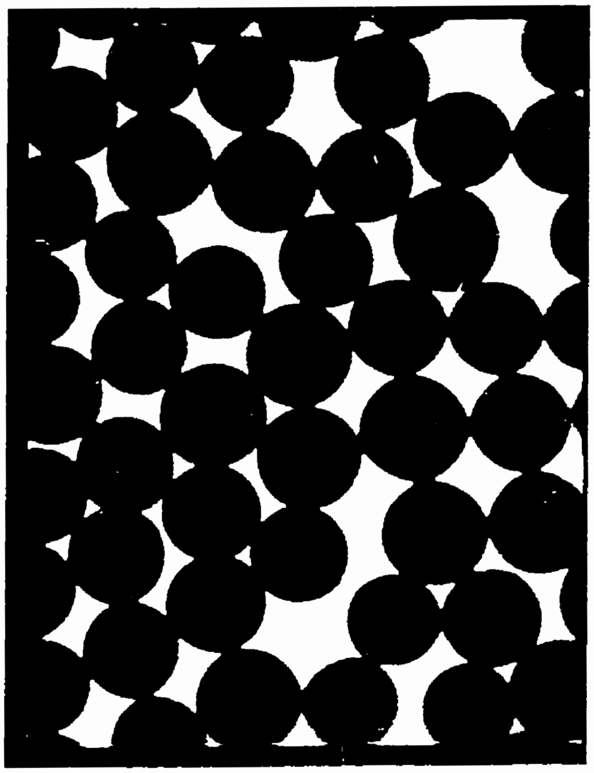
Latex No.	***S-191***	***S-196***	***S-194***
Initiator Conc. [g/L water]	2.67	2.67	2.67
Salt Conc. [g NaOH/L water]	2.00	2.88	3.96
Ionic Strength [mol/L]	0.059	0.084	0.110
Initial pH	11.1	11.3	11.5
Final pH	4.3	5.1	5.6
Particle Size, d_w, [nm]	578	516	495
Latex Polydispersity d_w/d_n	1.006*	1.007*	1.010*
Solids Content [% wt/wt]	31.7	31.3	31.5
Latex Final Yield [% wt/wt]	94.3	94.6	94.2

Temp. = 70 °C; feeding rate = 0.68 g/min; stirring rate = 200 RPM.

*Measurements on disc centrifuge.

Figure 4.3.3.13

TEM analysis of a St/BA/AA latex prepared in presence of sodium hydroxide.



The ionized and the unionized AA molecules are characterized by very different polarities (which controls monomer partition between polymer/monomer phase and water phase), reactivity ratios and propagation rate constants (k_P). Therefore, a complex tertiary copolymerization becomes a complicated quaternary copolymerization due to the existence of this equilibrium.

In order to "simplify" the polymerization, except for the initial pH, all the other experimental parameters (such as procedure, monomer feeding time, temperature, stirring rate, amount of water, monomer amount, AA content, initiator concentration, ionic strength) were kept constant for all the polymerizations carried out in this study, as follows:

- monomer feeding time ~ 5 h; T = 70 °C; stirring rate 200 RPM;
- amount of water 450 g; monomer amount 200 g (80 wt % St and 20 wt % BA);
- AA co-monomer 2 wt % against monomer amount;
- initiator, ammonium persulfate, 2.67 g/L water; ionic strength 0.084 mol/L.

The initial pH was fixed using different salts, such as NaCl for pH $\cong$ 3, NaH_2PO_4 for pH $\cong$ 5, a mixture of NaCl and $NaHCO_3$ for pH $\cong$ 7.5, $NaHCO_3$ for pH $\cong$ 8, Na_2CO_3 for pH $\cong$ 10, and NaOH for pH $\cong$ 12.

The experimental curve of particle size versus initial pH (Figure 4.3.4.1) revealed two main trends:

i. A very slight decrease in the particle size, which remains in the micron range, when pH values covered the acidic range up to a weakly/basic limit (pH = 8).

ii. A significant sharp decrease of the particle size to submicron values, when pH values were in a basic range, pH > 8.

Moreover, the experimental data (Table 4.3.4.1) indicated a broad particle size distribution at higher pHs. Both the particle size variation and the broadening of the particle size distribution with pH variation suggest a different effect of ionized AA^-, compared with the unionized AA, on the polymerization mechanism.

Figure 4.3.4.1

The influence of initial pH on the particle size of St/BA/AA latexes at a constant ionic strength, I=0.084 [mol/L].

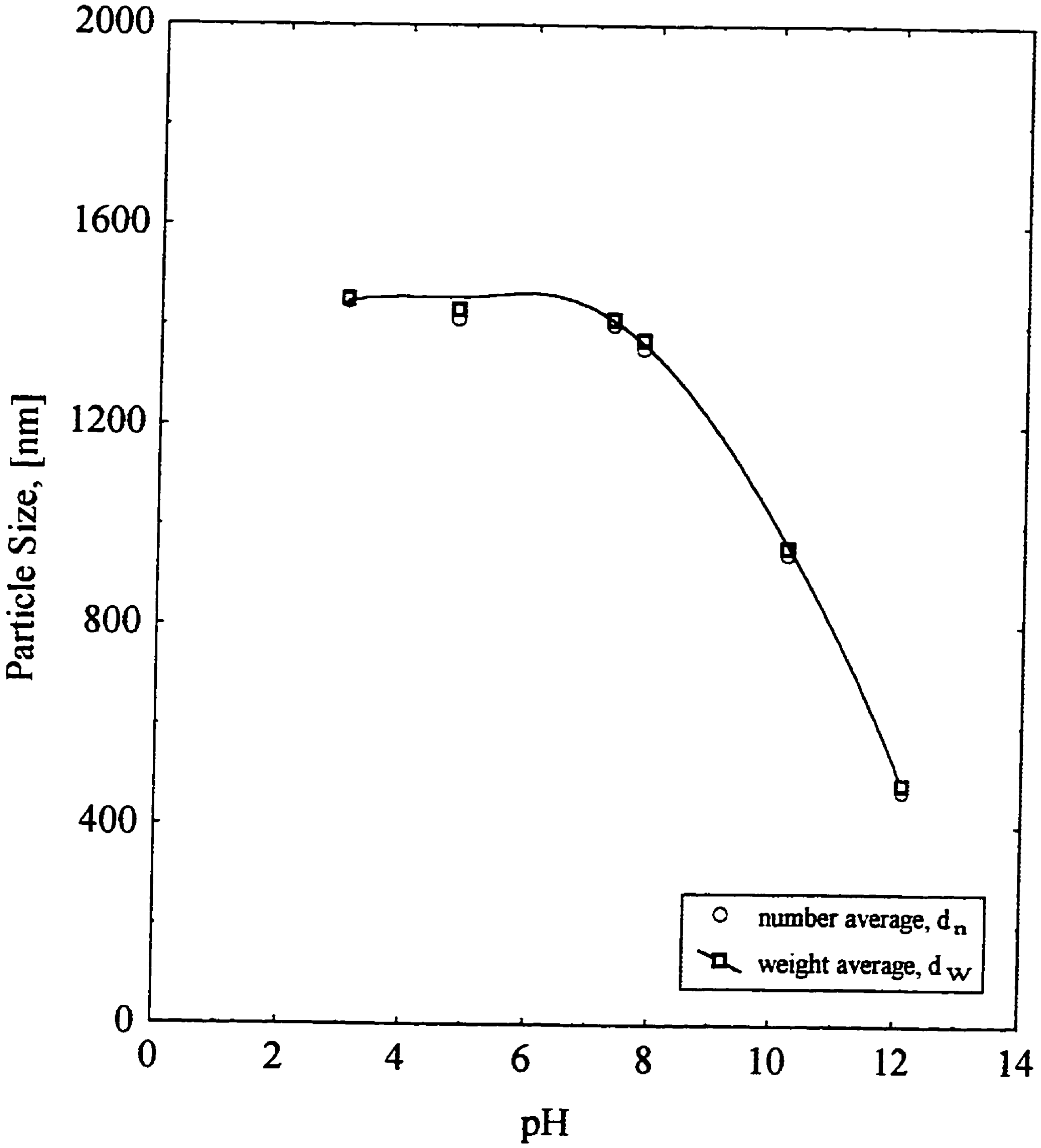


Table 4.3.4.1

The influence of initial pH on the quality of St/BA/AA latexes obtained by surfactant-free emulsion polymerization.

Latex No.	*S-160*	*S-156*	*S-196*	*S-164*	*S-163*	*S-162*
Initial pH	**pH=3.1**	**pH=4.8**	**pH=7.6**	**pH=7.9**	**pH=10**	**pH=12**
Initiator Conc. [g/L water]	2.67	2.67	2.67	2.67	2.67	2.67
Salt Conc. [g/L water]	1.30	3.26	1.58	2.86	3.81	1.26
Ionic Strength [mol/L]	0.083	0.083	0.083	0.083	0.083	0.083
Final pH	8.5	7.9	7.3	6.5	5.05	4.8
Particle Size, d_W, [nm]	1451	1430	1410	1371	956	484
Latex Polydispersity d_W/d_n	1.014**	1.014**	1.014*	1.012**	1.015*	1.014*
Solids Content [% wt/wt]	31.5	31.0	31.7	31.6	29.3	31.7
Latex Final Yield [% wt/wt]	96.0	92.6	92.9	92.6	89.7	96.4

(80/20) St/BA with 2 wt % AA; Temp. 70 °C; monomer feeding time $\cong$ 5h; stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

For an initial pH = 3.0 - 8.0, the evolution of the conversion versus time curves showed almost the same variation. However, in the very basic domain (pH $\cong$ 12), the polymerization rate was significantly higher than in former cases (Figure 4.3.4.2). These trends were well supported by the time-variation of N_p.

An increase in the initial pH in the very basic range led to a significantly higher number of particles. This means the presence of more polymerization loci and therefore, the polymerization rate increased as well.

The time-evolution of the particle number density (Figure 4.3.4.2) also revealed two interesting trends:

i. When the pH values covered the acid range up to a weakly/basic limit (pH = 8), the number of particles continuously decreased to a constant value. This trend is characteristic of the polymerizations in which a homogeneous-coagulative mechanism is involved (surfactant-free polymerizations, or polymerizations with surfactant at levels below the CMC).

ii. In the very basic pH range, the time-variation of the particle number density looked similar to polymerizations carried out in the presence of surfactant at a concentration above the CMC, when a micellar nucleation mechanism is very likely to take place At the beginning the number of particles increased with time and then it decreased slightly to a final value.

The unexpected time-variation of the particle number density throughout polymerization carried out at pH $\cong$ 12.1 (Figure 4.3.4.2) suggests a secondary nucleation. In the *in situ* surfactant polymerization systems, it is generally accepted that a secondary nucleation occurs when surfactant generation is faster than new surface generation. In this case, secondary nucleation increases N_p and hence R_p, but decreases the final particle size. The time evolution of the particle size distribution (Figure 4.3.4.4) strongly supported the formation of *in situ* surfactant and suggested the possibility of a homogeneous nucleation mechanism.

Figure 4.3.4.2

The influence of initial pH on the polymerization rate and time-variation of particle number density in St/BA/AA surfactant-free emulsion copolymerization.

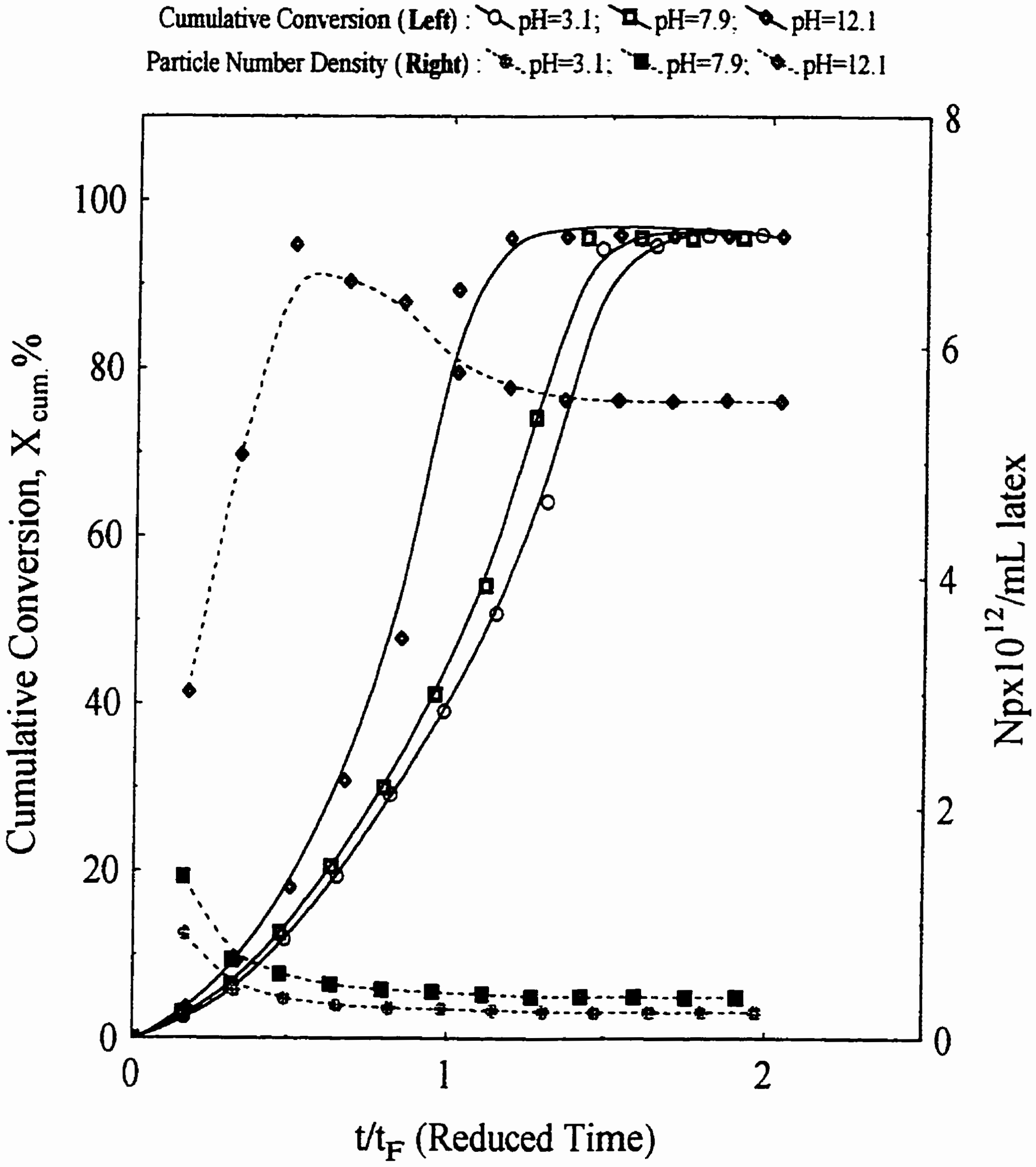
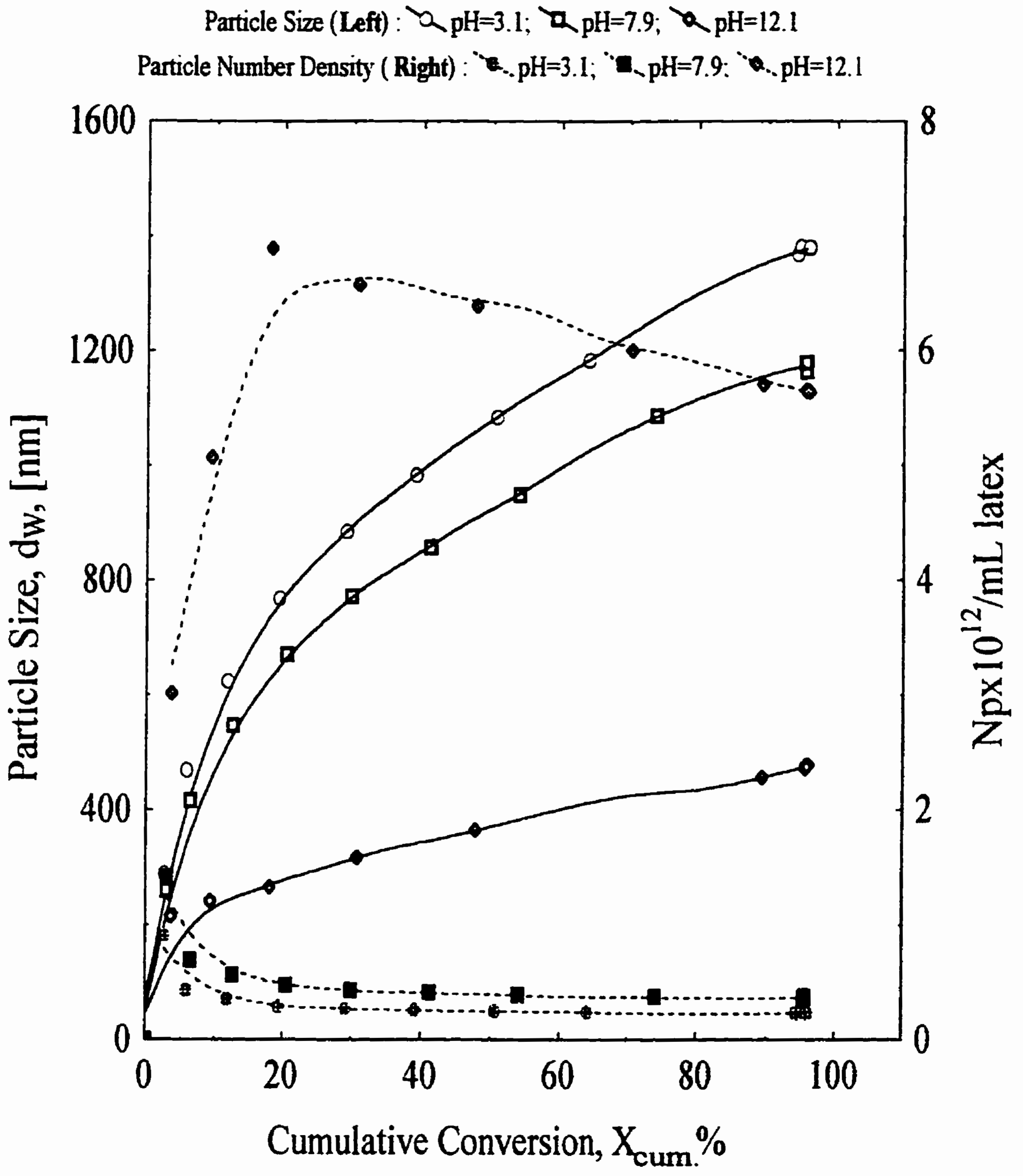


Figure 4.3.4.3

The influence of initial pH on the variation of particle size and particle number density with cumulative conversion in St/BA/AA surfactant-free emulsion copolymerization.



For the polymerizations carried out at pHs 3.1 and 7.9 respectively, the evolution of the particle size with cumulative conversion (Figure 4.3.4.3) revealed a very rapid flocculation at a conversion level less than 5%, followed by a very slowly particle aggregation process. The number of particles remained constant at approx. 20% conversion. At this point, the size of the particles was larger than 600 nm.

On the other hand, in the polymerization performed at pH = 12.1, continuous nucleation increased the number of particles up to a conversion higher than 80% and the corresponding particle size was less than 500 nm.

The oligoradicals formed at higher pHs become more hydrophilic, because more AA^- units are incorporated in their backbone. By that the external electrical field significantly increased and the particles become more colloidally stable. These oligoradicals can stay dissolved in the reaction medium for a longer period of time, and are less likely to coagulate with each other. They can grow until they become *z-mers*, becoming surface-active. The formation of *in situ* surfactant led to smaller latex particles. The secondary nucleation suggested that too much *in situ* surfactant formed, which broadened the PSD (Figure 4.3.4.6).

Moreover, by increasing the initial pH of the aqueous phase to an unbuffered value of 12, the reaction medium becomes richer in AA^- species and the initial pH decreased sharply with the monomer addition (Figure 4.3.4.5). Based on this experimental evidence it can be supposed that by increasing the initial pH more particles were nucleated. Therefore, the final particle size of the latex was also smaller than that obtained from the polymerization carried out at a lower pH.

In the first hours of reaction carried out with NaOH, the particle number density, N_p, increased to a maximum and then decreased to a constant value. As can be seen in Figure 4.3.4.6, secondary nucleation took place during the monomer feeding stage (after 2 hours of reaction). Subsequently, a competitive particle growth process took place. At the end of polymerization, the particle size of the two populations was very similar (Figure 4.3.3.13).

Figure 4.3.4.4

The time-variation of the particle size distribution throughout the St/BA/AA surfactant-free emulsion copolymerization in presence of sodium hydroxide.

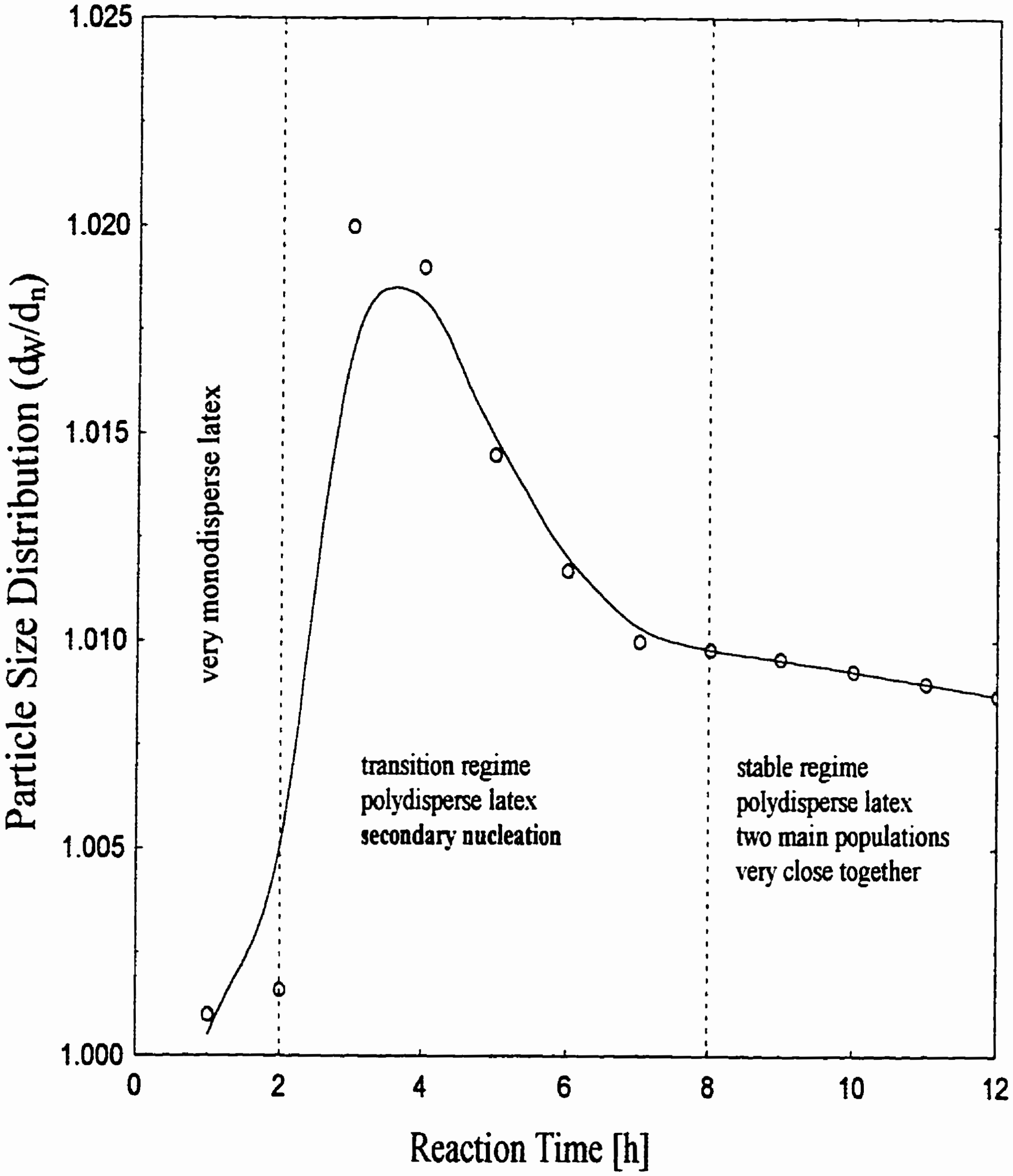


Figure 4.3.4.5

The pH variation with time for St/BA/AA surfactant-free emulsion copolymerization in presence of different salts.

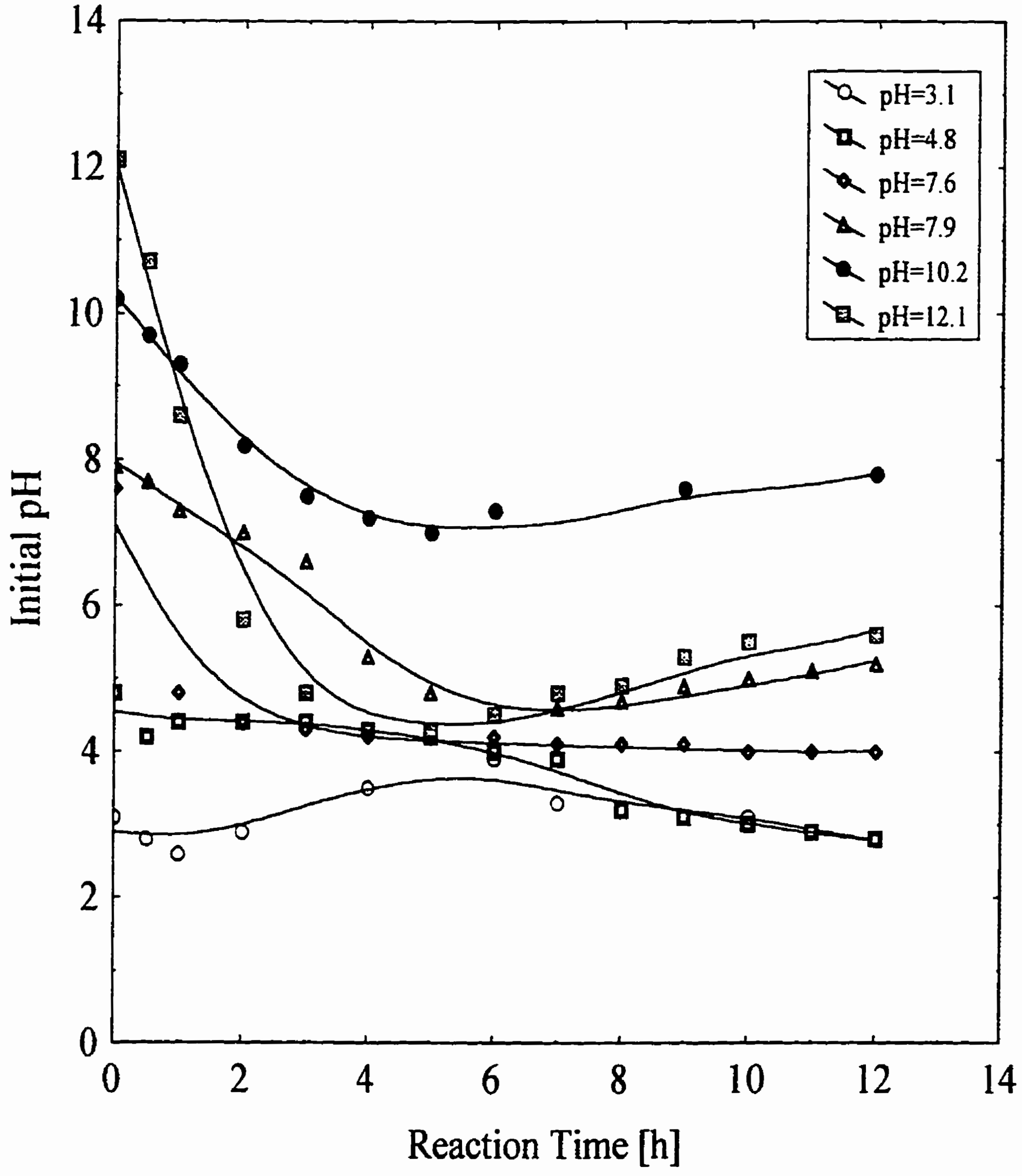
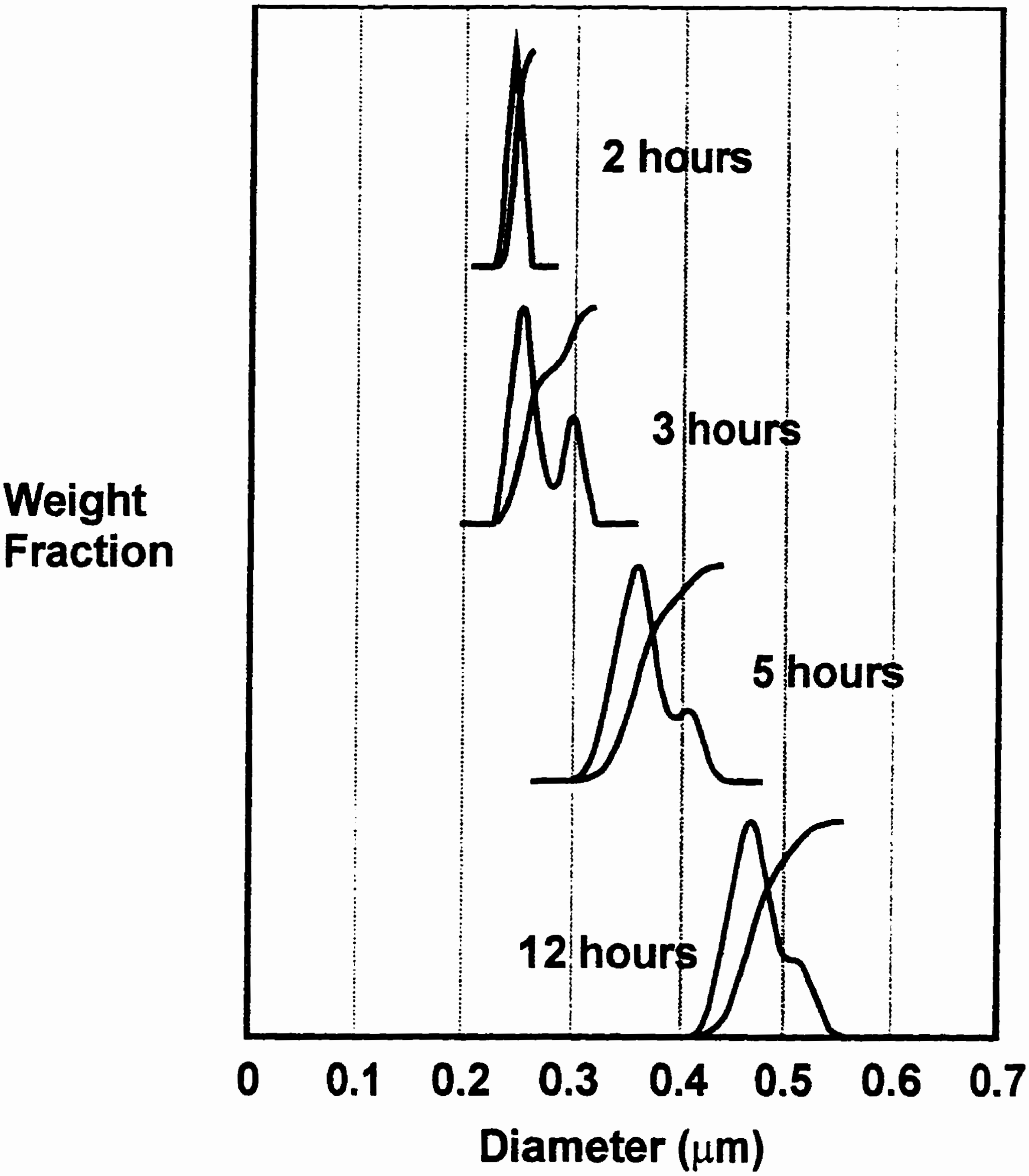


Figure 4.3.4.6

The time evolution of St/BA/AA particle population during surfactant-free emulsion polymerization in presence of sodium hydroxide.



4.3.5 The Influence of Monomer Feeding Time

Recall that in Section 3.3.6, the monomer feeding time can affect the size of the final latex and even its monodispersity of the St/BA surfactant-free emulsion polymerization system, even though, in all the cases studied the polymerization medium was monomer-flooded.

In order to avoid any other influence, all the experiments were carried out at constant reaction parameters, except for the monomer feeding time. In addition, several polymerizations were performed at different initial pHs (Table 4.3.5.1).

As can be seen in Table 4.3.5.1, the monomer feeding time significantly influenced the latex particle size when polymerization was performed at an initial pH of up to 8.1. The influence of the variation of the monomer feeding time was more significant at higher pHs, although a limiting behavior appeared.

When the surfactant-free St/BA/AA copolymerization was performed in presence of an inert salt (NaCl, Table 4.3.5.2) an increase in the monomer feeding time led to a pseudo-starve-fed reaction regime (Figure 4.3.5.1 and Figure 4.3.5.2). Moreover, for polymerizations carried out under a nearly starve-fed regime, a substantial difference was recorded between the cumulative conversion and instantaneous conversion.

In polymerizations carried out with a longer monomer feeding time (even if the particle number density was significantly higher than that recorded during the polymerization carried out at a lower monomer feeding time) the overall polymerization rate and the monomer concentration were lower. Since at a lower monomer feeding rate the polymerization system was "poor" in monomer, the monomer concentration into particles drops off as well. Therefore, the polymerization rate decreases.

When the polymerizations were carried out in presence of $NaHCO_3$, almost no influence on the polymerization rate was found by increasing the monomer feeding time

Table 4.3.5.1

The influence of monomer feeding time on St/BA/AA surfactant-free emulsion copolymerization.

Sodium Chloride *I = 0.084 [mol/L]* $pH_{init.} \cong 3$			***Sodium Bicarbonate*** *I = 0.084 [mol/L]* $pH_{init.} \cong 8$			***Sodium Hydroxide*** *I = 0.084 [mol/L]* $pH_{init.} \cong 12$		
Feeding time	d_W *[nm]*	d_W/d_n	*Feeding time*	d_W *[nm]*	d_W/d_n	*Feeding time*	d_W *[nm]*	d_W/d_n
5h.00min.	1451	1.014^{**}	5h 00min.	1371	1.014^{**}	5h 02min.	484	1.014^{*}
6h.00min.	1378	1.014^{**}	5h 29min.	1316	1.014^{**}	6h 02min.	475	1.014^{*}
17h.00min.	1060	1.003^{*}	6h 07min	1191	1.004^{*}			

(80/20) St/BA with 2 wt % AA; Temp. = 70 °C; stirring rate = 200 RPM.

*Measurements on disc centrifuge; **Measurements on Coulter Multisizer.

Table 4.3.5.2

The influence of monomer feeding time on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride.

Latex No.	*S-160*	*S-165*	*S-166*
Feeding Time [h]	5.0	6.0	17.0
Initiator Conc. [g/L water]	2.67	2.67	2.67
Salt Conc. [g NaCl/L water]	2.89	2.89	2.89
Ionic Strength [mol/L]	0.084	0.084	0.084
Initial pH	3.1	3.1	3.1
Solids Content [% wt./wt.]	31.6	31.5	30.3
Latex Final Yield [% wt./wt.]	96.00	96.00	90.00
Particle Size, d_w, [nm]	1451.0	1378.0	1060.0
Polydispersity Index	1.014**	1.013**	1.003*

Temp.= 70 °C; stirring rate = 200 RPM.

*Measurements on disc centrifuge. **Measurements on Coulter Multisizer.

Figure 4.3.5.1

The influence of monomer feeding time on the polymerization rate and particle number density variation with time in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium chloride.

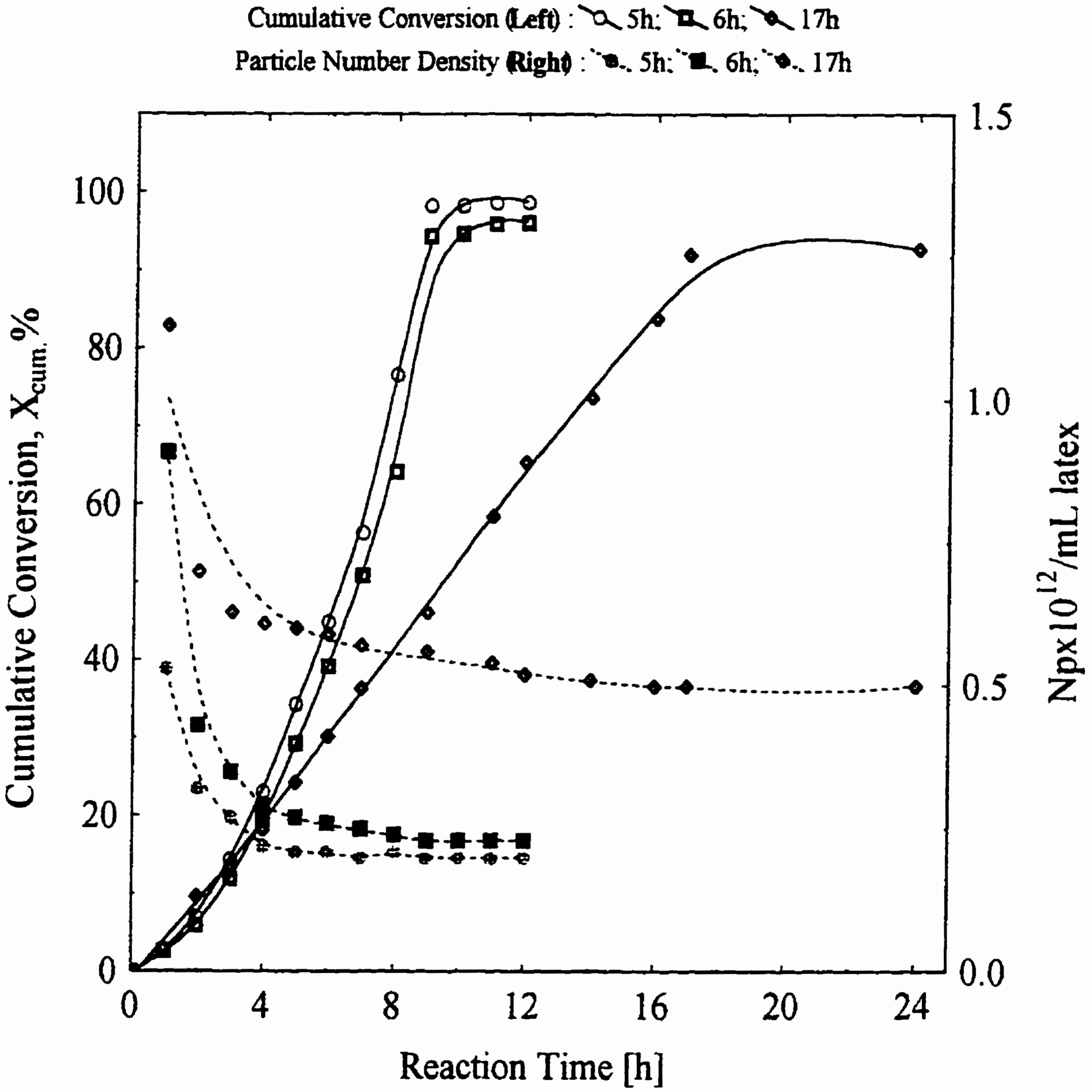


Figure 4.3.5.2

The influence of monomer feeding time on the time-variation of instantaneous conversion in St/BA/AA surfactant-free emulsion copolymerization.

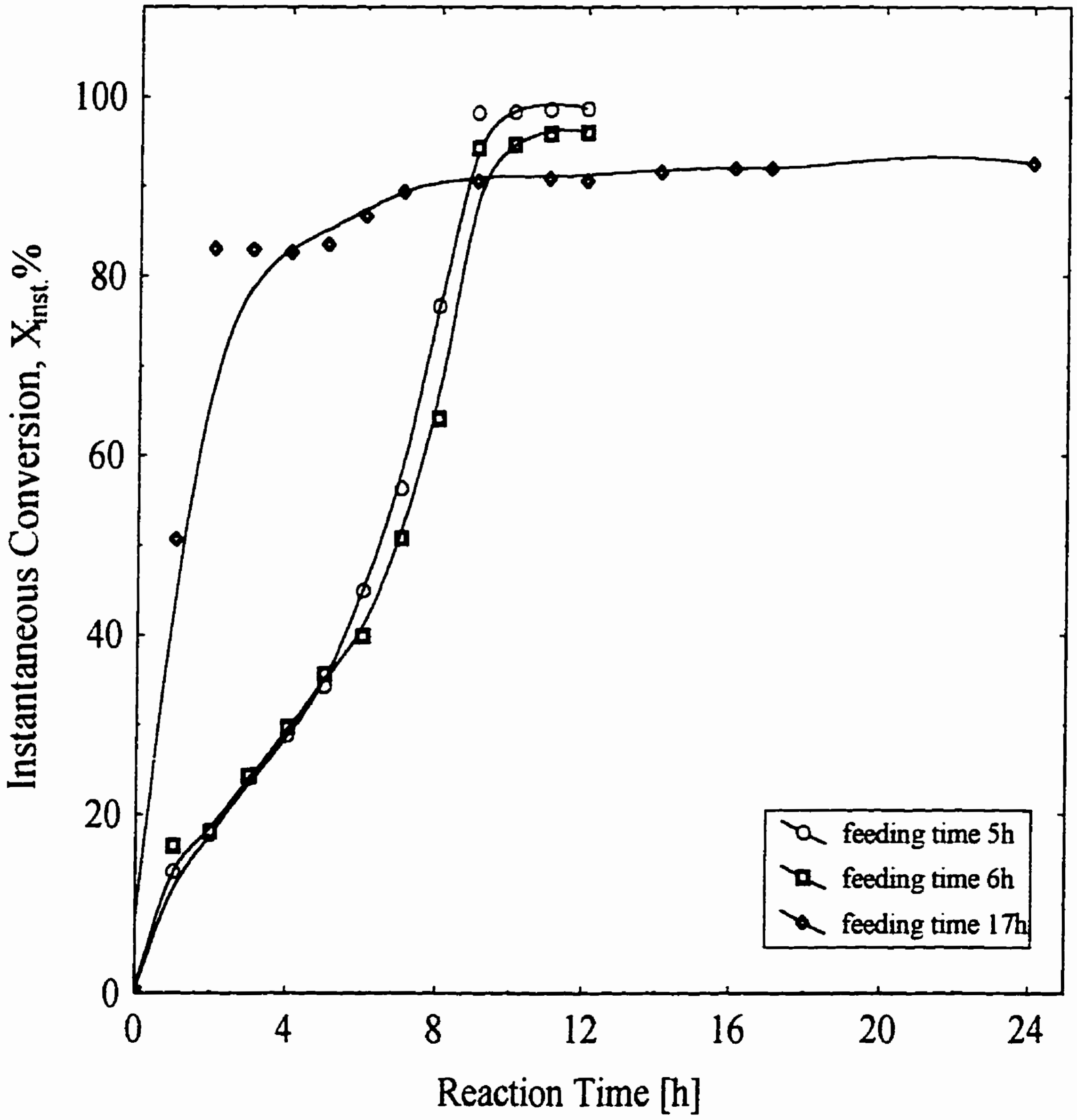


Figure 4.3.5.3

The influence of monomer feeding time on the polymerization rate and particle number density variation with time in St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

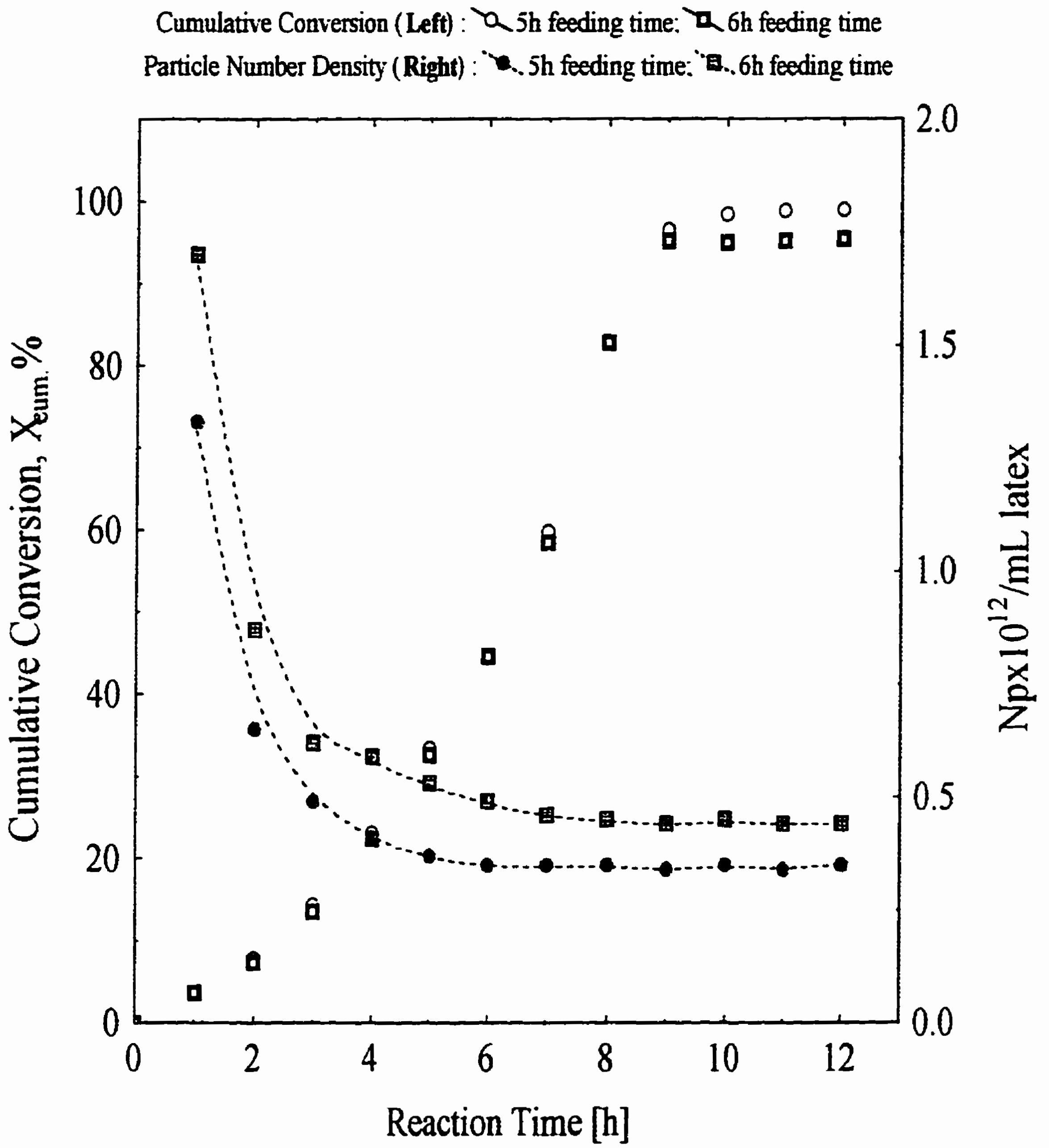


Table 4.3.5.3

The influence of monomer feeding time on St/BA/AA surfactant-free emulsion copolymerization in presence of sodium bicarbonate.

Latex No.	*S-162*	*S-161*
Feeding Time [h]	5.0	6.0
Initiator Conc. [g/L water]	2.67	2.67
Salt Conc. [g $NaHCO_3$ /L water]	8.26	8.26
Ionic Strength [mol/L]	0.133	0.133
Initial pH	8.1	8.1
Particle Size, d_w, [nm]	1203.0	1109.0
Latex Polydispersity d_w/d_n	1.004*	1.005*
Solids Content [% wt/wt]	31.3	31.5
Latex Final Yield [% wt/wt]	93.60	91.2

St/BA = 80:20 wt/wt; Temp. = 70 °C;

*Measurements on disc centrifuge;

from 5 h to 6 h. The particle number density was also lower in the former case. As well, the final cumulative conversion was higher at a lower monomer feeding time (Figure 4.3.5.3). As can be seen, in this case, the polymerization was far from a starve-fed regime. The experimental data in Table 4.3.5.3 exhibited a smaller difference between the final particle size of these latexes and an almost no influence on latex quality.

For our purposes, the best monomer feeding time at which the St/BA/AA copolymerization system should be carried out is that in which the polymerization takes place under monomer *flooded* regime.

4.4 CONCLUSIONS

Monodisperse, stable, carboxylated St/BA/AA latexes, with a particle size in the micron domain ($d_W \cong 1.0 - 2.0$ μm) and a solids content higher than 30 % wt/wt, were synthesized in one step, by a novel surfactant-free aggregative polymerization method.

The experiments showed that monodisperse, micron latex particles (Figure 4.4.1) can be obtained in one step synthesis when:

i. A semi-continuous monomer feeding procedure, with the AA co-monomer completely distributed in the monomer phase, was employed.

ii. The polymerization system was carried out under monomer *flooded* conditions.

iii. The polymerization was performed in presence of salts, provided that the initial pH of the reaction medium (before the addition of the monomers mixture) was less than 8.5, to minimize secondary nucleation.

Based on comparative analysis of the experimental data it has been found that the addition of AA to the St/BA copolymerization system led to:

i. A significant increase in the colloidal stability of the latex particles, due to an electro-steric stabilization mechanism.

ii. An increase in the polymerization rate, when the AA content of the monomer mixture was higher than 1 wt %.

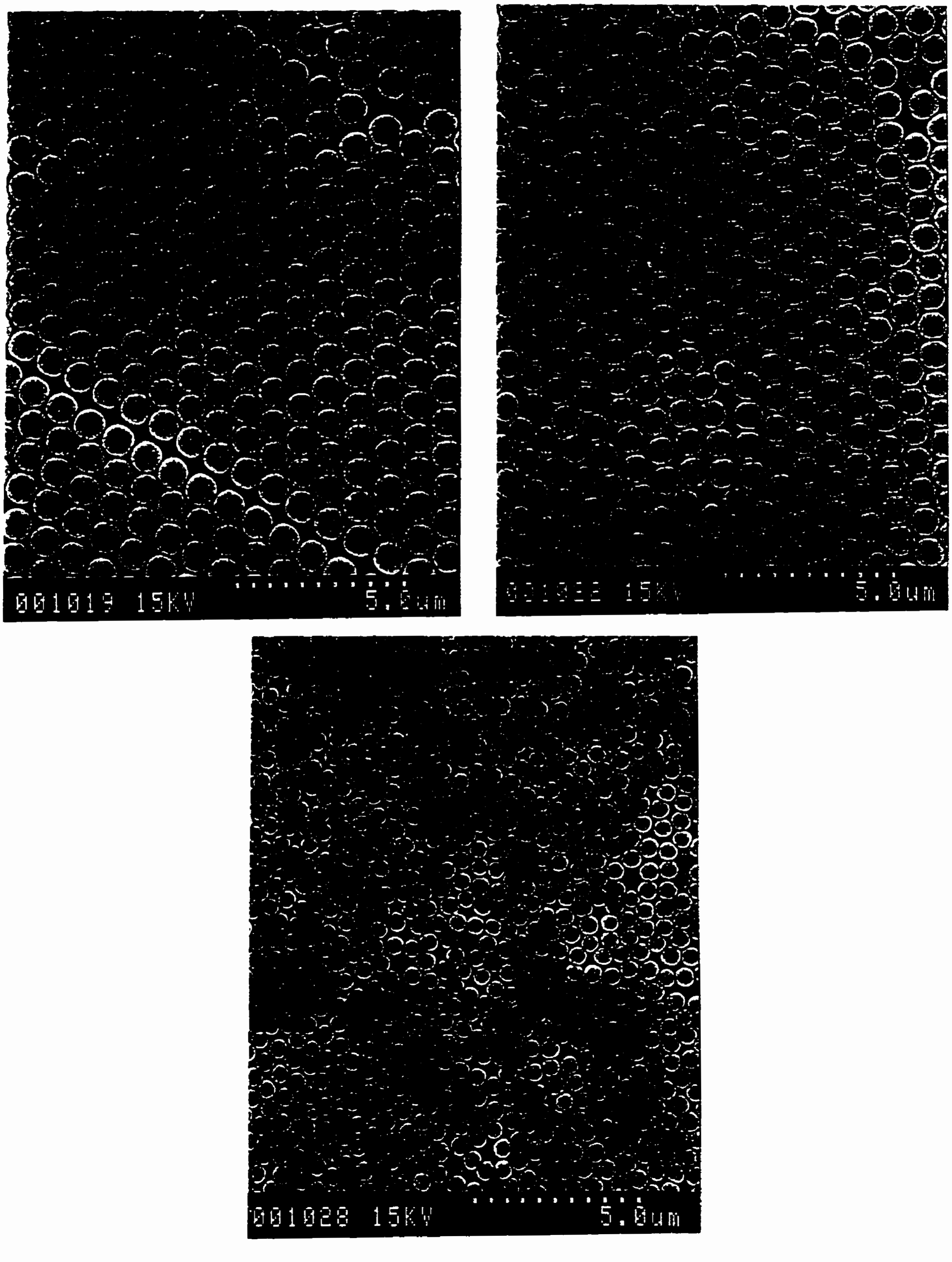
iii. No influence on the particle size of the final latex particles, when the AA composition was in the ranges of 1 wt % up to 5 wt %, since the polymerization was carried out salt-free.

iv. A change in the particle surface morphology from spherical smooth particles (AA-free), to spherical "moon-like" particles (1 wt % AA), to slightly irregular "cracked" particles (2 wt % AA) up to very irregular "stone-like" particles (4 wt % AA).

For the St/BA/AA surfactant-free emulsion copolymerization system studied all the investigated reaction parameters suggested a similar aggregative-polymerization mechanism to that found to be operative in the AA-free St/BA surfactant-free emulsion copolymerization.

Figure 4.4.1

SEM photographs of St/BA/AA latexes obtained in presence of different salts.



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CHAPTER 5

GROWTH OF St/BA AND St/BA/AA LATEXES BY SEMI-CONTINUOUS, SEEDED EMULSION POLYMERIZATION

5.1 INTRODUCTION

The main goals of the present thesis were:

i. To generate monodisperse St/BA or St/BA/AA latex particles in the 2 - 8 μm size range via a surfactant-free emulsion polymerization process.

ii. To understand the fundamentals of the processes in order to control them.

This chapter of the thesis follows O'Callaghan's research[1] where he tried a sequential buildup in size from 500 nm to 3 or 4 μm, doubling the size at each stage. He used only electrostatic stabilization and found a "limit" in size of around 3-4 μm, beyond which monodispersity was lost either to secondary nucleation or to aggregation.

Starting from O'Callaghan's results, the possibility to obtain very large stable, monodisperse seed particles with steric colloidal stability which allows successful particle growth was studied.

In emulsion polymerization the most common technique of particle growth is by seeding the reaction medium with small monodisperse particles followed by subsequent polymerization.[1-10] By seeding the reaction system, the most random, irreproducible and hard to control step in emulsion polymerization, the particle nucleation step can also be avoided.[2-5] Nevertheless, the major problem which appears in a seeded emulsion polymerization is the secondary particle nucleation process. In order to overcome this drawback different experimental procedures and techniques have been designed.[11-16]

Swelling of seed particles is a very attractive technique which allows the synthesis of micron particles by a batch polymerization procedure. This technique could be applied in the desired aqueous medium, such as Ugelstad's two step swelling technique[6,7], in non-aqueous medium such as Okubo's dynamic swelling technique[8,9], or by sequential seeded polymerization.[6,11]

Ugelstad's two step swelling technique[6] allows the synthesis of 2-20 μm particles in water based system. In the first step, the seed particles are swollen with a low molecular weight compound and then, the swollen seed particles undergo a consequent polymerization by initiation inside the particle. However, the particle size distribution and reproducibility make this method unattractive.

In Okubo's method[8,9] water is added slowly to an ethanol dispersion of seed particles, monomer, stabilizer and initiator. The monomer becomes increasingly insoluble in the continuous phase thereby swelling the seed particles. Although particles up to 6.0 μm have been produced, smaller secondary particles are also formed.

The use of sequential seeded polymerization can also produce very large particles.[6,11] Cook *et al.*[11] employed such a technique in order to build, by a semi-continuous emulsion polymerization procedure, poly(butyl acrylate) particles up to 6.0 μm. However, the latex monodispersity was maintained only up to 1.22 μm.

The first two experimental chapters revealed that we have successfully made seeds up to 3 μm, which could represent an important advantage for the particle growth step.

This chapter is dedicated to the exploration of the possibility to grow, by a semi-continuous surfactant-free seeded polymerization technique, the size of the monodisperse surfactant-free micron St/BA or St/BA/AA latexes above the 3 μm diameter.

5.2 EXPERIMENTAL

5.2.1 Chemicals

Styrene (St), butyl acrylate (BA) and ammonium persulfate (AP) were obtained from Aldrich. 2,2'- Azobisisobutyronitrile (AIBN) was obtained from Polysciences Inc.. Sodium dodecylbenzenesulphonate (SDBS) was obtained from Rhone-Poulec. These chemicals were all used without further purification. All water was deionized. The seed used were prepared in previous chapters, by the procedures already described.

5.2.2 Seeded Reaction

The reactor vessel charged with water and seed latex, was placed in a water bath at 75 °C, and purged with nitrogen for not less than 45 minutes. The stirring rate was 200 RPM.

When AP was used as initiator it was dissolved in 50 g deionized water and added to the reactor vessel prior to starting the monomer feed. When only AIBN was used as initiator it was added in the monomer feed. The reactor vessel was purged with nitrogen for 10 minutes after adding AP.

Monomer feeding was initiated at a rate which depended on experimental conditions. In most cases when synthesis ran well, the monomer mixture feeding time was 12 hours, and the reaction time was up to 14 hours.

Typically used recipes for surfactant-free seeded polymerization of St/BA or St/BA/AA are presented in Table 5.2.2.1.

5.2.3 Latex Characterization

Particle size analysis was performed using a Coulter Multisizer II as described in Section 3.2.3. The SEM analysis, surface tension measurements and solids content determination used in this chapter were described in Section 3.2.3.

Table 5.2.2.1

Typical emulsion recipes (amounts in grams) for seeded polymerizations.

REACTION		***G-149***	***G-200***
PRECHARGE - I	Deionized Water [g]	330.00	330.00
	Seed Type:		
	- No AA/NaCl [g]	100.00	
	- No AA/$NaHCO_3$ [g]		100.00
	Seed Size [nm]	1492	2022
PRECHARGE - II	Deionized Water [g]	-	50.00
	Initiator (AP) [g]	-	0.60
CONTINUOUS FEED	Styrene [g]	160.00	160.00
	n-Butyl acrylate [g]	40.00	40.00
	AIBN [g]	0.90	0.90
	Acrylic acid [g]	4.00	4.00
PARTICLE SIZE	d_W [nm]	3151	3285
PARTICLE SIZE DISTRIBUTION	d_W/d_n	1.014	1.014

5.3 RESULTS AND DISCUSSION

5.3.1 Surfactant-Free Particle Growth

The previous chapters of this thesis have shown that, in the surfactant-free emulsion polymerization of styrene and butyl acrylate, the particle stabilization mechanism is electro-static, provided by the anchored sulfate end groups available from the initiator molecules. When the polymerizations were carried out with AA as an ionogenic comonomer, an electro-steric stabilization mechanism was found.

As long as the particles can maintain their colloidal stability, they are suitable for further growth. However, since the particle diameter is proportional to the cube root of the particle volume, a doubling of the particle diameter involves an eight-fold increase in the polymer volume. Thus at larger sizes, the diameter increase for a given amount of added polymer becomes small. In order to avoid length growth stages, which can lead to other problems, it is very important to determine the best particle number density of the reaction precharge (polymer particles per unit volume of aqueous phase).

A decrease in the particle number density at larger sizes increases the chances of secondary particle formation. Fewer particles exist and the ratio of polymer surface area to aqueous phase volume slowly decreases with growth. This makes the task of sweeping up any aqueous material before it is stabilized more difficult. In order to maintain a constant particle surface area to aqueous phase volume ratio, a corresponding solids content should be employed.

The surface charge density of the electrostatic stabilized particles only is also important. If there is not sufficient charge on the particle surface, the growing particles loose their colloidal stability and may flocculate and/or coagulate. On the contrary, if the growing particles attain a too high surface charge density, they might repel the charged oligoradicals ready to be adsorbed. These oligoradicals may stabilize polymer formed in the aqueous phase and prevent it from coalescing onto the seed particles. This leads to the formation of secondary particles which then grow at the expense of the larger seed particles, due to their greater surface area.

In our surfactant-free experiments, the particle surface charge density was controlled by the amounts of water soluble initiator and by the amount of ionogenic comonomer (AA) if present. The AA addition can control the hydrophilicity of the adsorbed oligomeric material with surface activity (acrylic acid copolymers generated *in-situ*). Moreover, because of the distinctive influence on the particle stabilization mechanism of the ionized units AA^-, compared with unionized AA molecules, the pH of the polymerization medium is another important parameter to be taken into account. Therefore, in order to maintain the latex monodispersity, the pH, and the concentrations of initiator and acrylic acid should be controlled carefully.

In order to avoid secondary particle nucleation from water phase initiation, the seeded emulsion polymerization should be carried out employing an oil-soluble initiator (such as AIBN) rather than a ionogenic water-soluble initiator (e.g., ammonium persulfate). The oil-soluble initiator may "push" the polymerization locus into the particle, while a water-soluble initiator favors reactions in the aqueous-phase, which may lead to nucleation of new young smaller particles.

Several AA seeded polymerizations using only ammonium persulfate as initiator were carried out at two different concentrations (Table 5.3.1.1). The polymerization process developed well, but in both cases, the final latexes were polydisperse (Figure 5.3.1.1). In these cases the initiator was added to the precharged reaction mixture as a water solution 10 minutes before the start of monomer feeding. The experimental results (Figure 5.3.1.1) clearly support the above expectation regarding the secondary particle nucleation.

In order to avoid secondary particle nucleation an oil-soluble initiator (AIBN) was

Table 5.3.1.1

Seeded polymerizations of St/BA/AA latexes carried out with ammonium persulfate.

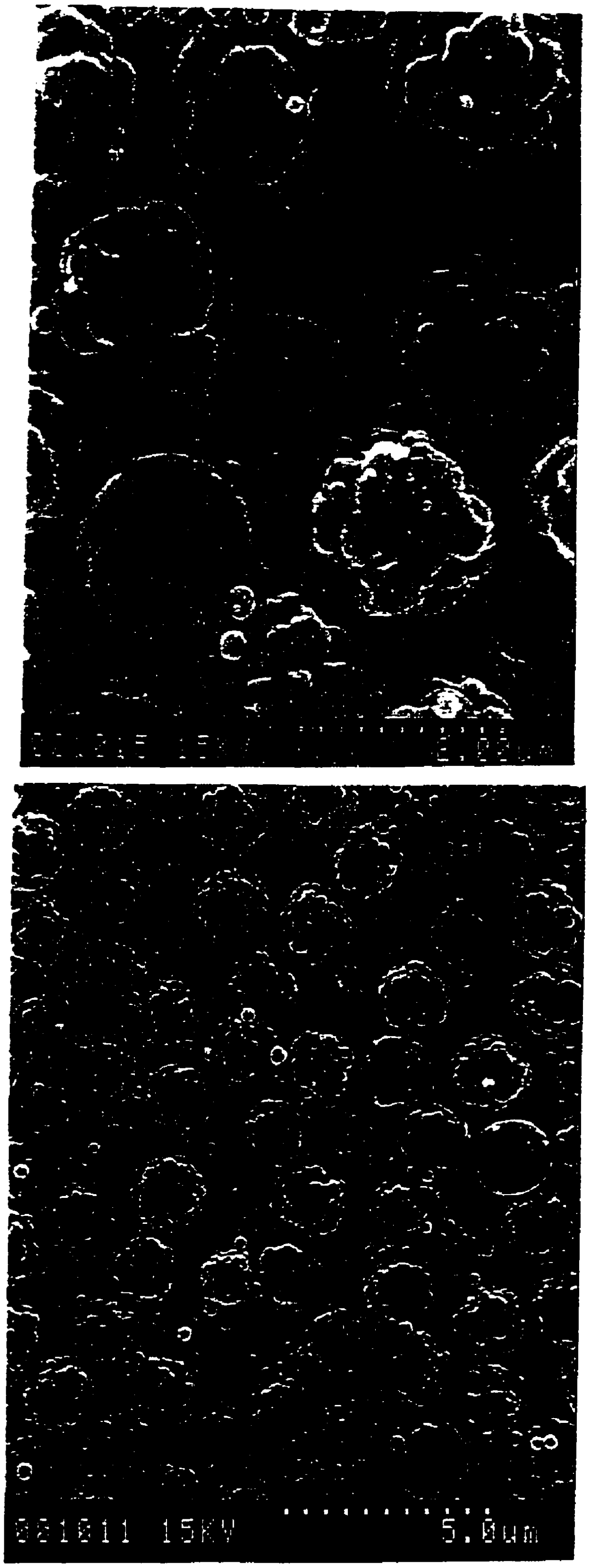
REACTION		*G-167-1*	*G-167-2*
PRECHARGE - I	Deionized Water [g]	300.00	300.00
	Seed Type:		
	- With AA/NaHCO$_3$ [g]	100.00	100.00
	- solids content [wt %]	31.60	31.60
	- particle size, d_W, [nm]	1178.0	1178.0
PRECHARGE - II	Deionized Water [g]	50.00	50.00
	Initiator [g]	0.60	1.00
CONTINUOUS FEED	Styrene [g]	160.00	160.00
	n-Butyl acrylate [g]	40.00	40.00
	AIBN [g]	-	-
	Acrylic acid [g]	4.00	4.00
PARTICLE SIZE	d_W [nm]	1939.0	1967.0
PARTICLE SIZE DISTRIBUTION	$d_W/\ d_n$ **	1.140	1.180
REMARKS	Polymerization failed when 84 % of monomer was fed.		

Temp. = 75 °C; feeding rate = 0.283 g/min; stirring rate = 200 RPM.

**Measurements on Coulter Multisizer.

Figure 5.3.1.1

SEM analysis of St/BA/AA latexes prepared by seeded surfactant-free emulsion polymerization with ammonium persulfate.



employed (Table 5.3.1.2). The initiator was previously dissolved in the monomer feed. In this case, the polymerization failed early during the monomer feeding stage, because of gross coagulation. The particle sizes in Table 5.3.1.2 were recorded one hour before coagulation.

When AIBN was used the particles grow by "inside" polymerization. Because the AIBN initiator cannot improve the particle stability throughout the growing stage, they lost their colloidal stability and coagulated.

A more successful way to carry out such a polymerization is to employ a combination of a ionogenic water-soluble initiator (AP), with an oil-soluble initiator (AIBN). The AP initiator may enhance the colloidal particle stability, by increasing the number of anchored sulfate groups on the particle surface throughout the polymerization (the increase in anchored sulfate groups balances the continuous increase in the particle volume because of polymerization), while AIBN favors the polymerization in particles. The experimental results (Table 5.3.1.3) support our expectations. Monodisperse, "raspberry-like" latex particles were obtained (Figure 5.3.1.2). However, a lot of coagulum was found at the end of polymerization.

Since a St/BA/AA seed latex could be more suitable for further growth because a better stabilization mechanism takes place, some polymerizations were carried out with such latexes. In all cases the polymerization failed during the monomer feeding stage due to gross coagulation, even though a mixture of initiators was employed.

All of these experimental results suggest limited opportunities to further growth of the micron St/BA or St/BA/AA seed particles by semi-continuous surfactant-free emulsion polymerization technique at 40 wt % solids.

When a small amount of anionic surfactant sodium dodecylbenzenesulphonate, SDBS, was employed, the seeded polymerization went well and the seed particles almost doubled their size (Table 5.3.1.4 and Figure 5.3.1.3). However, an appreciable level of coagulum was found at the end of the process.

Table 5.3.1.2

Seeded polymerizations of St/BA/AA latexes carried out with 2,2'-azobisisobutyronitrile (AIBN).

REACTION		***G-200-1***	***G-200-2***
PRECHARGE - I	Deionized Water [g]	300.00	300.00
	Seed Type:		
	- No AA/NaHCO$_3$ [g]	100.00	100.00
	- solids content [wt %]	30.40	30.40
	- particle size, d_W, [nm]	2022.0	2022.0
PRECHARGE - II	Deionized Water [g]	-	-
	Initiator [g]	-	-
CONTINUOUS FEED	Styrene [g]	160.00	160.00
	n-Butyl acrylate [g]	40.00	40.00
	AIBN [g]	0.60	0.90
	Acrylic acid [g]	4.00	4.00
PARTICLE SIZE	d_W [nm]	3151.0	2900.0
PARTICLE SIZE DISTRIBUTION	d_W/d_n **	1.014	1.028
REMARKS	Polymerization failed	after 5h	after 11h

Temp. = 75 °C; feeding rate = 0.283 g/min; stirring rate = 200 RPM.

**Measurements on Coulter Multisizer.

Table 5.3.1.3

Seeded polymerizations of St/BA/AA latexes carried out with ammonium persulfate and AIBN.

REACTION		*G-203-2*	*G-230-2*
PRECHARGE - I	Deionized Water [g]	300.00	300.00
	Seed Type:		
	- No AA/$NaHCO_3$ [g]	100.00	-
	- No AA/NaCl [g]	-	100.00
	- solids content [wt %]	29.50	29.80
	- particle size, d_W, [nm]	1357.0	1419.0
PRECHARGE - II	Deionized Water [g]	50.00	50.00
	Initiator [g]	0.40	0.40
CONTINUOUS FEED	Styrene [g]	160.00	160.00
	n-Butyl acrylate [g]	40.00	40.00
	AIBN [g]	0.90	0.90
	Acrylic acid [g]	4.00	4.00
PARTICLE SIZE	d_W [nm]	2291.0	2259.0
PARTICLE SIZE DISTRIBUTION	d_W/ d_n **	1.014	1.014
REMARKS	Final solids content [wt %]	37.80	37.50

Temp. = 75 °C; feeding rate = 0.283 g/min; reaction time 14h; stirring rate = 200 RPM.

**Measurements on Coulter Multisizer.

Figure 5.3.1.2

SEM analysis of St/BA/AA latexes prepared by seeded surfactant-free emulsion polymerization with ammonium persulfate and AIBN.

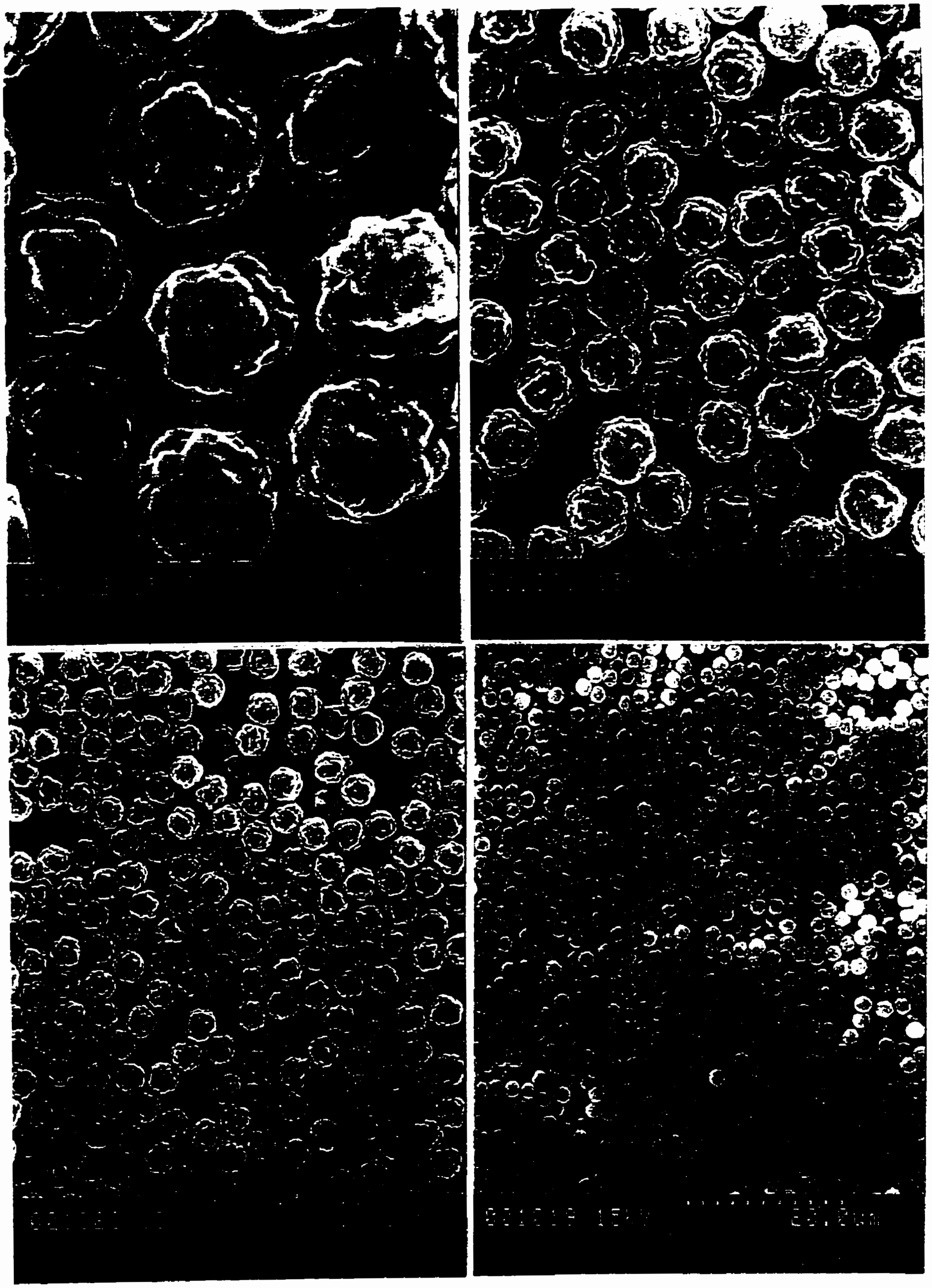


Table 5.3.1.4

Seeded polymerization of a St/BA latex carried out with AIBN in presence of SDBS surfactant.

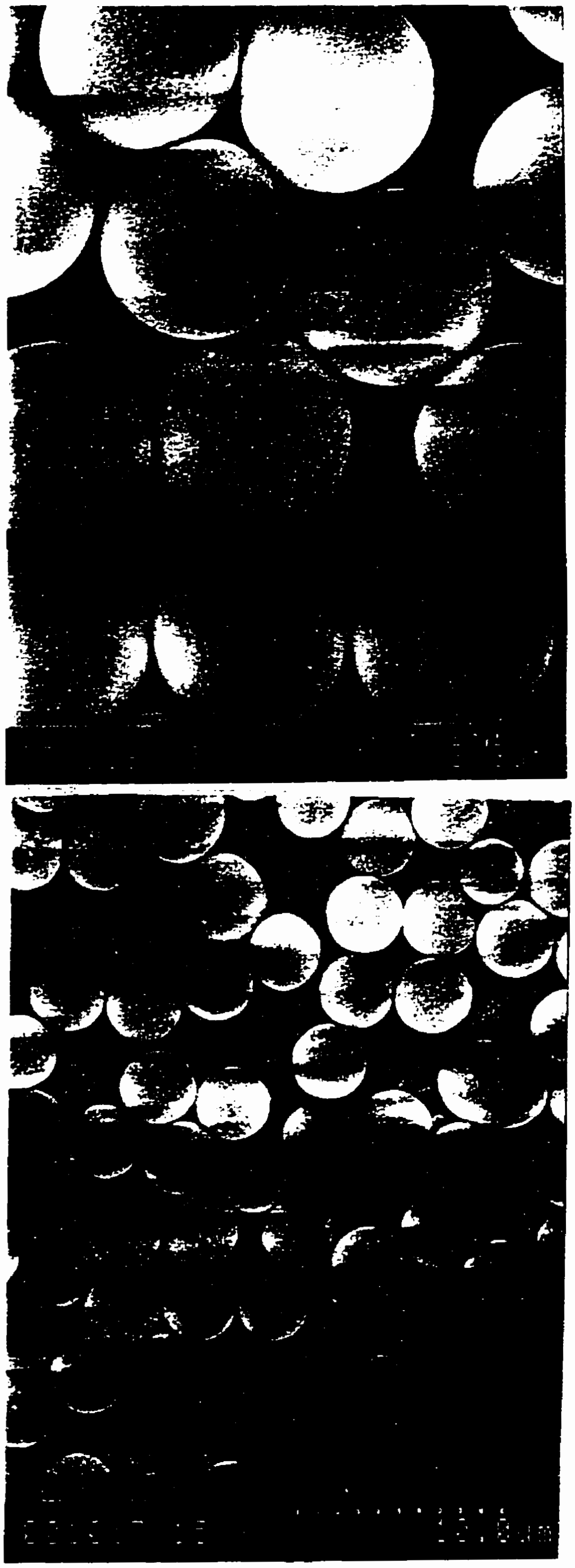
REACTION		*G-171-2*
PRECHARGE - I	Deionized Water [g]	300.00
	Seed Type:	
	- No AA/$NaHCO_3$ [g]	100.00
	- solids content [wt %]	29.80
	- particle size, d_W, [nm]	2228.0
PRECHARGE - II	Deionized Water [g]	-
	Initiator [g]	-
CONTINUOUS FEED	Styrene [g]	160.00
	Butyl Acrylate [g]	40.00
	AIBN [g]	0.90
	Acrylic acid [g]	-
PARTICLE SIZE	d_W [nm]	3989.0
PARTICLE SIZE DISTRIBUTION	d_W/d_n **	1.018
REMARKS	Coagulum	much

Temp. = 75 °C; feeding rate = 0.417 g/min; stirring rate = 200 RPM.

**Measurements on Coulter Multisizer.

Figure 5.3.1.3

SEM analysis of a St/BA latex prepared by seeded emulsion polymerization of a St/BA seed using SDBS surfactant and AIBN initiator.



5.4 CONCLUSIONS

These experimental results strongly support the limited capability of a surfactant-free emulsion polymerization technique to grow St/BA or St/BA/AA particles with diameters in the micronsize range. Nevertheless, since the particle growth stage was based on AA addition to the monomer feed, and an initiator combination of AIBN and AP was employed, the experimental results obtained could be considered more than encouraging for future experimental approaches.

It can be appreciated that more experimental work should be done using AA as a comonomer with potential surface-activity, in conjunction with an initiator combination of AIBN and AP. Because in the case studied, the most successful procedure seems to be that in which a controllable amount of anionic surfactant (SDBS) was employed, this possibility should also be taken into account.

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CHAPTER 6

SUMMARY AND FUTURE WORK

6.1 THESIS SUMMARY

The central theme of this thesis was to investigate the surfactant-free emulsion polymerization of St/BA and St/BA/AA as a potential technique to prepare, in one or a few steps, supermicron ($d_W > 1$ µm), monodisperse, stable latexes with high solid contents (higher than 25 % wt/wt).

A novel surfactant-free emulsion polymerization technique, which allows the one step synthesis of stable styrene/butyl acrylate (80:20 wt/wt) monodisperse latexes with a particle size in the micron domain ($d_W = 1$- 3 µm), and solid contents higher than 25 % wt/wt, was developed.

The investigation of the role and influence of the reaction parameters, throughout the semi-continuous surfactant-free emulsion copolymerization of St/BA, using a persulfate initiator, strongly supported an aggregative-polymerization mechanism.

The work outlined in Chapter 3 showed that micron particles can be obtained by a semi-continuous technique when the polymerization was carried out under monomer *flooded* conditions, using an ionogenic initiator such as ammonium persulfate.

A comparative analysis of the ionic strength influence (at the same initial pH and all the other parameters constant), by varying the amount of salt, while the initiator concentration was constant, and by increasing the initiator concentration, while the salt concentration was kept constant respectively, revealed that:

(a) the increase of ionic strength by salt addition	(b) the increase of ionic strength by increasing the initiator concentration
- slowed the polymerization rate	- increased the polymerization rate
- favored aggregative processes	- limited aggregative processes
- increased the particle size.	- decreased the particle size.

The largest particles resulted when the polymerizations were carried out at an initial pH < 8.0.

The novel procedure took advantage of the stabilizing effect gained from ionic initiator residues. These particles were stabilized by an electrostatic mechanism. Following a step-wise addition procedure of the initiator, the size of particles obtained in the one step-synthesis was bigger than 2 μm, while the quality of a final latex (monodispersity, stability, coagulum level) was significantly improved.

In most polymerizations the final latex yield was higher than 90 % and the final solids content around 30 wt %.

Based on a similar experimental technique as that employed in the synthesis of St/BA latexes, St/BA/AA monodisperse, stable carboxylated latexes, with a particle size in the micron domain ($d_W \cong 2$ μm) and a solids content higher than 30 % wt/wt, were also synthesized in one step.

The experiments show that St/BA/AA monodisperse, micron latex particles can be obtained in a one step synthesis if:

i. A semi-continuous monomer feeding procedure, with the AA comonomer added in the monomer phase, is employed.

ii. The polymerization system is carried out under monomer *flooded* conditions.

iii. The polymerization is performed in presence of salts, provided that the initial pH of the reaction medium (before the addition of monomers mixture) is less than 8.5 to minimize secondary nucleation.

Comparing St/BA to St/BA/AA system, the addition of AA led to:

i. Increased colloidal stability of the latex particles, due to an electro-steric stabilization mechanism.

ii. Increased polymerization rate, (for AA composition > 1 %).

iii. No influence on particle size, (for AA composition in the 1 - 5 wt % range; in salt-free polymerization).

iv. A variety of surface morphologies from spherical smooth particles (AA-free), to spherical "moon-like" particles (1 wt % AA), to slightly irregular "cracked" particles (2 wt % AA) up to very irregular "stone-like" particles (4 wt % AA).

The investigated reaction parameters for St/BA/AA surfactant-free emulsion copolymerization suggested a similar aggregative-polymerization mechanism as that found in the AA-free copolymerization of St/BA.

Chapter 5 presents the trials to grow St/BA and St/BA/AA micron particles using a "seed", by a sequential semi-continuous surfactant-free polymerization method. Different scenarios, based on the seed type, initiator type, composition of the monomer mixture fed, and monomer feeding rate were investigated in order to find the best reaction parameters. Using this technique, stable, monodisperse latexes with a final particle size up to 4 μm with solids content around 40 wt % were produced.

The experimental results strongly support the limited capacity of a surfactant-free emulsion polymerization technique to grow both St/BA and St/BA/AA particles with a diameter in the micronsize range. As well, the experiments revealed that the monomer feeding rate and the addition of AA, as a comonomer with potential surface-activity, to the monomer feed were crucial in order to keep under control the polymerization process.

6.2 FUTURE WORK

The novel aggregative-polymerization process, which was found out throughout the semi-continuous surfactant-free emulsion copolymerization of styrene with butyl acrylate, with and without acrylic acid added, opens new and very attractive opportunities in the synthesis of monodisperse micron particles.

The complex aggregative-polymerization mechanism has yet to be explained in order to define the "key" reaction parameters and the limiting factors affecting the process. A truly representative model must include an extensive analysis of both the particle nucleation and particle growth processes. The appropriate model must also consider the nature of monomers (water solubility, reactivity ratio, monomer/particle compatibility), the water phase reactions, such as the decomposition of the initiator, the water phase initiation of polymerization, propagation and termination (with a particular attention paid to the nature and the fate of the oligomer species formed). Further work needs to be done in this area.

A further study of the effects of AA addition in the polymerization reaction and particle stabilization mechanisms should also be performed. The experimental results reveal a very complex polymerization system which is somewhat between an art and a science. The AA concentration and addition policy emphasized a change in the polymerization mechanism as a function of ionic strength and electrolyte type (initial pH of the reaction medium). The contribution of AA molecules to the particle nucleation process and the distribution of the acrylic acid species formed during polymerization. Studies of the particle surface morphology and the nature of the particle surface charge should be also performed.

Although unsuccessful in obtaining monodisperse latex particles bigger than 4 μm, the experimental trials of the St/BA and St/BA/AA micron seeds revealed some interesting aspects regarding the importance of using AIBN (as an oil soluble initiator) in conjunction with AP (water soluble initiator). The AA addition to the monomer feed and the monomer feeding time are also of crucial importance to keep the polymerization process under control. Therefore, further experimental work related to the influence of these parameters on the seed particle growth stage should be assessed.