Strategic aspects of the incorporation of acrylic acid in emulsion polymers

Citation for published version (APA):
Slawinski, M. (1999). *Strategic aspects of the incorporation of acrylic acid in emulsion polymers*. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Universiteit Eindhoven. https://doi.org/10.6100/IR526315

DOI:
10.6100/IR526315

Document status and date:
Published: 01/01/1999

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
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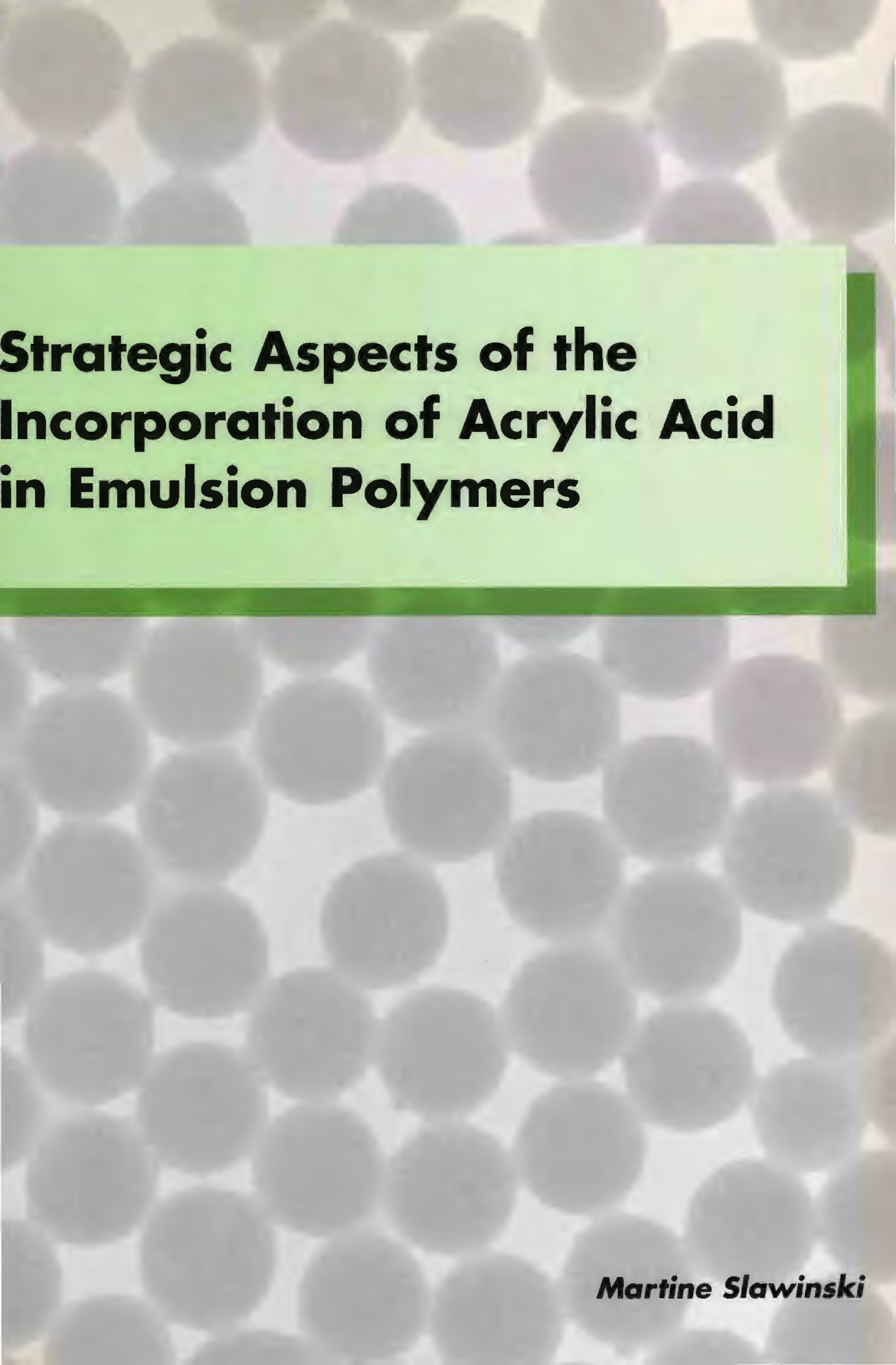

Strategic Aspects of the Incorporation of Acrylic Acid in Emulsion Polymers

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Slawinski, Martine

Strategic aspects of the incorporation of acrylic acid in emulsion
polymers / by Martine Slawinski. - Eindhoven : Technische Universiteit
Eindhoven, 1999.
Proefschrift. - ISBN 90-386-2671-1
NUGI 813
Trefwoorden: emulsie-polymerisatie
Subject headings: emulsion polymerization

Druk: Universiteitsdrukkerij Technische Universiteit Eindhoven

Strategic Aspects of the Incorporation of Acrylic Acid in Emulsion Polymers

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Technische Universiteit Eindhoven, op gezag van de
Rector Magnificus, prof. Dr. M. Rem, voor een
commissie aangewezen door het College voor
Promoties in het openbaar te verdedigen
op woensdag 20 oktober 1999 om 16.00 uur

door

Martine Slawinski

geboren te Somain (Frankrijk)

Dit proefschrift is goedgekeurd door de promotoren:

prof. dr. ir. A. L. German

en

prof. dr. G. Riess

Copromotor:

dr. J. Meuldijk

Les gens ont des étoiles qui ne sont pas les mêmes.
Pour les uns, qui voyagent, les étoiles sont des guides.
Pour d'autres elles ne sont rien que de petites lumières.
Pour d'autres, qui sont savants, elles sont des problèmes.
(...)
Mais toutes ces étoiles là se taisent.
Toi, tu auras des étoiles comme personne n'en a ...
(...)
Tu auras, toi, des étoiles qui savent rire!

Antoine de Saint-Exupéry
"Le Petit Prince" (1946)

Pour mon père...

SAMENVATTING

Het doel van dit proefschrift was om de kennis te verbeteren omtrent inbouw van carbonzuurfunctionele monomeren in polymeren gemaakt in emulsie. Zodoende is de invloed van acrylzuur op het verloop van de emulsiecopolymerisatie met styreen en met styreen en butadieen onderzocht. De aandacht is voornamelijk gericht op de hoeveelheid carboxylgroepen die worden ingebouwd gedurende het proces. De invloed van de pH van het reactiemengsel op het verloop van de reactie en de inbouw van acrylzuur in de polymeerdeeltjes is onderzocht zowel aan de hand van *ab-initio* experimenten als met experimenten met een kiemlatex.

Er zijn diverse analytische methoden ontwikkeld en toegepast om de carboxylgroepen in de latex te karakteriseren. Het is mogelijk gebleken de conductometrische titratie in waterig milieu van verdunde latexmonsters na dialyse te combineren met de potentiometrische titratie van de corresponderende opgeloste deeltjesfase in niet-waterige oplosmiddelen. Door middel van deze werkwijze kon de verdeling van polymeren met carboxylgroepen over de verschillende plaatsen in het reactiemengsel, dat wil zeggen begraven in de latexdeeltjes, aan het oppervlak ervan of in de waterfase, worden achterhaald. Voor de bepaling van de intermoleculaire chemische samenstellingsverdeling is gradiënt hoge druk vloeistof chromatografie ontwikkeld voor copolymeren van styreen en butadieen enerzijds en copolymeren van styreen en acrylzuur anderzijds. Er is aangetoond dat bij het gebruik van deze methode de invloed van molecuulmassa van de corresponderende solutie- en emulsiecopolymeren op het chromatografische scheidingsproces de interpretatie van de resultaten emstig bemoeilijkt.

De invloed van pH op de polymerisatiekinetiek van carbonzuurfunctionele monomeren in water is onderzocht met behulp van gepulseerde laser polymerisatie in combinatie met 'size exclusion chromatography' aan polymeren die gemodificeerd zijn door verestering van de carboxylgroepen. Voor dit deelonderzoek is methacrylzuur gebruikt bij verschillende pH-waarden en een constante ionensterkte. Het bleek dat de propagatiesnelheidsconstante van methacrylzuur hoog was onder zure condities, dat wil zeggen pH 2. De reactiesnelheidsconstante daalde vervolgens met toenemende pH en vertoonde een minimumwaarde bij een pH van 7. Dit gedrag is geëxtrapoleerd naar de emulsiepolymerisatie van styreen met acrylzuur als comonomeer. De invloed van zowel de pH als de hoeveelheid acrylzuur op enerzijds de propagatiesnelheidsconstante en anderzijds de chemische samenstelling van de gedurende het proces in de continue fase gevormde copolymeren is aangetoond. Echter, als gevolg van een lage verdelingscoëfficiënt tussen de organische en de waterfase heeft acrylzuur slechts een kleine invloed op de totale polymerisatiesnelheid. Dit gedrag werd ondersteund door afschatting van de gemiddelde propagatiesnelheidsconstante in de deeltjesfase.

Emulsiepolymerisatie experimenten met styreen of met styreen en butadieen zijn uitgevoerd. Het gebruik van acrylzuur in de polymerisatiereceptuur, tezamen met de pH van het reactiemengsel, bleek een sterke invloed te hebben op zowel het deeltjesvormingsproces als de effectiviteit van inbouw van de zuurgroepen. Relatief hoge acrylzuurconcentraties, alsmede een lage pH, resulteerden in een hoge concentratie latexdeeltjes en een relatief grote fractie van de carboxylgroepen ingebouwd in de polymeermoleculen die zich aan het oppervlak van de uiteindelijke latexdeeltjes bevinden. Kinetisch onderzoek aan emulsiepolymerisatiesystemen met een kiemlatex heeft geen duidelijkheid verschaft over de invloed van acrylzuur en de pH op de polymerisatiesnelheid per latexdeeltje in aanwezigheid van monomeerdruppels. Zowel *ab-initio* als experimenten met een kiemlatex hebben aangetoond dat acrylzuur voornamelijk wordt ingebouwd aan het oppervlak van de latexdeeltjes. Deze inbouw vindt bij voorkeur plaats gedurende de laatste fase van het emulsiepolymerisatieproces bij lage pH en bij een hoog specifiek oppervlak van de latexdeeltjes. De verkregen resultaten leverden een helderder beeld op van de optredende mechanismen in de produktie van gecarboxyleerde latices. Experimenten waarbij acrylzuur strategisch werd geïntroduceerd in de laatste fase van de emulsiepolymerisatiereactie bij lage pH resulteerden in een optimale inbouweffectiviteit van carboxylgroepen aan het oppervlak van de latexdeeltjes.

RESUME

Le but du travail entrepris est l'amélioration de nos connaissances concernant l'incorporation de monomères carboxyliques dans les polymères préparés suivant le procédé de polymérisation en émulsion. Le rôle de l'acide acrylique durant sa copolymérisation en émulsion avec le styrène et avec un mélange de styrène et de butadiène a été étudié. La quantité de groupes carboxyliques incorporée dans les polymères formés au cours de la polymérisation a retenu une attention toute particulière. Le pH a été étudié en tant que paramètre principal des expériences conduites *ab-initio* ou en présence d'un latex semence.

Des méthodes analytiques ont été développées afin de caractériser les produits de polymérisation contenant des fonctions carboxyliques. Le dosage des groupes acide a pu être effectué par conductimétrie pour les latex dilués et par pH-métrie pour les polymères en solution dans un solvant organique. De cette manière, la distribution des groupes carboxyliques entre l'intérieur des particules de latex, leur surface ainsi que la phase continue a pu être déterminée. La séparation chromatographique des copolymères par gradient de solvants permet d'établir leur distribution intermoléculaire de compositions chimiques. La méthode a été développée avec succès pour les copolymères de styrène et butadiène ainsi que les copolymères de styrène et d'acide acrylique. Cependant il a été noté que la séparation était également fonction de la masse moléculaire des polymères analysés. La validation de la méthode pour l'étude des polymères formés en solution et en émulsion n'a donc pas été possible.

Le rôle joué par le pH sur la cinétique de polymérisation des monomères carboxyliques en solution dans l'eau a été étudié grâce à des expériences de polymérisation par impulsion laser. Les polymères formés ont été analysés par chromatographie d'exclusion stérique après que les fonctions carboxyliques aient été estérifiées. L'étude a été menée avec l'acide methacrylique à différentes valeurs de pH et force ionique constante. Les expériences ont montré que la constante de vitesse de propagation est élevée en milieu acide, i.e. pH 2. Cette constante décroit considérablement lorsque le pH augmente et passe par un minimum à pH 7. Ce comportement a été transposé au cas de la polymérisation en émulsion du styrène avec l'acide acrylique. L'influence du pH et de la concentration en acide sur à la fois la constante de vitesse de propagation et la composition chimique des copolymères formés dans la phase continue a été démontrée. Cependant, à cause d'un faible coefficient de partage entre les phases organique et aqueuse, l'acide n'a qu'un effet très limité sur la vitesse globale de polymérisation en émulsion. Cette affirmation découle de l'estimation de la constante moyenne de vitesse de propagation dans la phase particulaire du latex.

Des expériences de polymérisation en émulsion du styrène et du mélange styrène butadiène ont été menées. Le processus de nucléation et l'efficacité de l'incorporation des groupes acides on été fortement influencés par l'introduction de l'acide acrylique dans les recettes de polymérisation ainsi que par le pH du milieu réactionnel. Des concentrations en acide relativement élevées de même que des valeurs faibles de pH ont géneré des concentrations de particules de latex élevées. Une fraction relativement élevée des groupes acides initiaux a également été incorporée à la surface des particules de polymère dans les latex finaux. L'étude de la cinétique de polymérisation en émulsion dans les systèmes ensemencés a montré que la concentration en acide acrylique et le pH ont peu d'effet sur les vitesses de polymérisation. Les expériences menées *ab-initio* ou en présence de latex semence ont montré que l'acide acrylique est en majeure partie incorporé à la surface des particules de polymère. L'incorporation a lieu de préférence à faible pH pendant le dernier intervalle de la polymérisation en émulsion. Les résultats obtenus permettent une meilleure compréhension des mécanismes gouvernant la synthèse des latex carboxylés. Les expériences au cours desquelles l'acide acrylique a été stratégiquement introduit dans le milieu réactionnel à faible pH durant le dernier intervalle de la polymérisation ont permis d'obtenir une incorporation optimale des groupes carboxyliques à la surface des particules dans le cadre de cette étude.

SUMMARY

The objective of this thesis was improving our knowledge about incorporation of carboxylic monomers in polymers prepared in emulsion. Therefore, the influence of acrylic acid on the course of emulsion copolymerisation has been investigated with styrene as well as with styrene and butadiene. Attention was focused on the amount of carboxylic groups incorporated into the latex products during the process. The pH of the reaction mixture was studied as the main parameter and ab-initio as well as seeded experiments were performed.

Analytical tools were developed to characterise emulsion polymerisation products containing carboxylic groups. It was shown that the aqueous conductometric titration of diluted latex samples after cleaning could be combined with the non-aqueous potentiometric titration of the dissolved corresponding particle phase. So, the amount of carboxylic groups incorporated into polymer chains present in the core and in the outer layer of the latex particles as well as in the continuous phase could be obtained. Gradient Polymer Elution Chromatography® was used to investigate the intermolecular chemical composition distribution of copolymers. The method was successfully developed for copolymers of styrene and butadiene as well as copolymers of styrene and acrylic acid. It was shown that the validation of the method for the analysis of corresponding solution and emulsion polymerisation products was hampered by the influence of the molecular weight on the chromatographic separation process.

The influence of pH on the polymerisation kinetics of carboxylic monomers in water was investigated with Pulsed Laser Polymerisation experiments in combination with Size Exclusion Chromatography on the polymer product modified by esterification of the carboxylic groups. The investigation was carried out with methacrylic acid at different values of the pH and a constant ionic strength. The experiments revealed that the propagation rate constant is high under acidic conditions, *i.e.* pH 2. The propagation rate coefficient decreases strongly on increasing the pH and passes a minimum at pH 7. This behaviour was extrapolated to emulsion polymerisation of styrene with acrylic acid as comonomer. The influence of pH together with the acrylic acid level on the propagation rate constant as well as on the composition of the copolymer formed in the continuous phase during the process was demonstrated. However, because of a low partition coefficient between the organic and the aqueous phase, acrylic acid has only a limited influence on the overall emulsion polymerisation rate. This behaviour was supported by the estimation of the average propagation rate constant in the latex particle phase.

Emulsion polymerisation experiments with styrene or with styrene and butadiene were performed. The use of acrylic acid in polymerisation recipes together with the pH of the reaction mixture had a strong influence on both the nucleation process and the acid incorporation efficiency. Relatively high acrylic acid concentrations as well as a low pH resulted in high latex particle concentrations, and a relatively large fraction of the initially present carboxylic groups was incorporated at the surface of the polymer particles in the final latex products. The investigation of the kinetics of emulsion polymerisation in seeded systems did not show a substantial influence of acrylic acid concentration or pH on the rate of polymerisation per particle in the presence of monomer droplets. With both *ab-initio* and seeded experiments it was demonstrated that acrylic acid was preferentially incorporated at the surface of the polymer particles. Incorporation preferentially occurs during the last stage of the reaction at low pH. The results obtained provided more insight into the mechanisms obeyed during the production of carboxylated latexes. Experiments in which acrylic acid was strategically introduced in the last stage of the emulsion polymerisation reaction performed at low pH resulted in the optimal incorporation efficiency of carboxylic groups on the surface of the latex particles observed in the study.

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1

Introduction

1.1. General introduction to Emulsion Polymerisation

Polymerisation reactions cover a wide range of mechanisms, reactants, polymerisation media and product structures. Amongst all possible combinations, emulsion polymerisation is a free-radical-initiated polymerisation reaction in which a monomer or a mixture of monomers emulsified in water is polymerised by a, usually, water-soluble initiator. The product of the reaction consists of a colloidal dispersion of submicron synthetic polymer particles in an aqueous medium, also known as latex. Since the beginning of its development in the early 1930s, the process has received a constant industrial interest. The interest is mainly driven by the numerous advantages offered by the reaction in terms of processing and product properties. Initially developed for the manufacturing of synthetic rubber, emulsion polymerisation is nowadays an economically important process applied to a wide variety of monomers to produce elastomers, thermoplastics, and numerous speciality polymers.

The advantages of emulsion polymerisation processes are numerous and mainly arise from the absence of organic solvents and the compartmentalisation of the reaction. Water constitutes an inert and harmless continuous phase, acts to maintain a relatively low viscosity of the end products and provides a proper heat transfer. The polymerisation actually takes place in the latex particles that act as numerous microreactors for bulk polymerisation. The process is characterised by the possibility to produce high-molecular-weight polymers at a polymerisation rate higher than in homogeneous systems. Furthermore, the molecular weight of the polymer can be controlled by the addition of chain transfer agents. The polymerisation can usually be carried out up to high conversion minimising the amount of residual monomer. The relevant disadvantages of emulsion polymerisation are related to the compartmentalisation of the reaction as well. The reaction mixtures usually contain a lot of additives like surfactants and initiator fragments. These substances are difficult to remove and can affect the final product quality. In case the polymer itself is needed, the aqueous continuous phase has to be removed causing additional expenses.

The monomers used in emulsion polymerisation processes are generally slightly to moderately water-soluble and can be selected according to the end-use application requirements. Some of the monomers most commonly used as main components in emulsion polymerisation recipes are styrene, butadiene, vinyl acetate, acrylates and methacrylates and vinyl chloride. Functional monomers are usually used together with the main monomers to tune the bulk polymer properties or the latex colloidal properties or to allow post-polymerisation reactions. Functional monomers are added in very small quantities and are characterised by numerous types of reactive groups, see Upson [1985] and Snuparek [1994].

The emulsion polymerisation products can be used as latex or as raw material after removal of the continuous phase. A review of the current common final applications of polymer latexes has been made by DeFusco *et al.* [1997]. Amongst them and most visible since part of our daily life, let us quote latex paints, paper coatings, textile coatings and adhesives. Of major industrial interest, speciality emulsion polymers also include cement additives, rheology modifiers and biomedical latexes.

Emulsion polymerisation is a complex process and gives therefore rise to scientific challenges in addition to industrial interests. Harkins [1947] first gave a qualitative description of emulsion polymerisation processes before Smith and Ewart [1948] developed the corresponding mathematical model. Since then, extensive work has been carried out to better understand and quantitatively describe the mechanisms involved during the process, see van Herk *et al.*, [1998]. The key issues are control of the polymerisation reactions and design of emulsion polymers. Overviews on emulsion polymerisation kinetics and emulsion polymers can be found in literature [Piirma, 1982, Gilbert, 1995; Lovell and El-Aasser, 1997].

1.2. Aims of the investigation

Carboxylic monomers bearing carboxylic acid groups are often used as functional monomers in emulsion polymerisation recipes. The final emulsion products are referred to as carboxylated latexes and carboxylated polymers. Carboxylic monomers like acrylic, methacrylic or itaconic acids are actually miscible with water and cannot be used in emulsion polymerisation processes unless they are used together with a monomer or mixture of monomers with a low water-solubility. The amount of carboxylic monomer is usually low compared to the total amount of monomer: up to 10% by weight. The purpose of incorporating carboxylic groups in polymer products is manifold: to provide the final products with sites for post-polymerisation reactions, in particular crosslinking reactions, to enhance the chemical and mechanical stability of the latex particles and their adhesion to polar substrates and to control the rheology of the latexes. A complete review of the production of carboxylated latexes has been written by Blackley [1983]. Most of the advantages actually result from the in situ formation of surfactant during polymerisation.

Water-soluble carboxylated copolymer molecules may indeed have some surface activity and act as surfactant species for the latex particles. Moreover, some carboxylated copolymer molecules might be incorporated into the latex particles during the process and their carboxylic rich part preferentially resides in the outer shell of the particles. In that case, additional stabilisation is provided by surfactant-like species which are chemically bound to the particles and cannot be removed easily.

The use of water-miscible monomers like carboxylic acids in emulsion polymerisation is somewhat contradictory with the heterogeneous aspect of a process that leads to water-insoluble polymers. One can expect the mechanisms usually controlling the process to be much more complicated. Numerous studies have been performed to find out how carboxylic monomers are incorporated into emulsion polymers and to understand the role these monomers play in emulsion. The main challenge is to optimise the incorporation of the functional monomer into the polymer molecules since the incorporated carboxylic groups will ultimately reside in the outer shell of the particles [Ceska, 1974; Egusa and Makuuchi, 1982]. In addition to the conventional parameters to be defined in emulsion polymerisation, the nature of the water-soluble carboxylic monomer makes that the course of the process and its outcome are very sensitive to pH. Not only colloidal stability is influenced but also the kinetics and the phase equilibria. The pH strongly influences the polymerisation behaviour of carboxylic monomers in water [Kabanov *et al.*, 1973] and their partitioning between the organic and aqueous phase of an emulsion system. The affinity of the polar monomer for the aqueous phase or the particle phase depends indeed on the degree of dissociation of the carboxylic groups [Shoaf *et al.*, 1990].

Carboxylic monomers were found to play a major role in the process of latex particle nucleation. The number of particles formed during the reaction is closely related to the amount and type of the carboxylic monomer, to the pH and to the ionic strength [Sakota *et al.*, 1976]. In addition, the particle growth process is also affected by the presence of carboxylic monomers. Shoaf *et al.* [1991] developed a model which describes the kinetics of particle growth in emulsion copolymerisation systems with carboxylic acids. These authors confirmed the influence of the events taking place in the aqueous phase on the basic mechanisms operating in the particle growth stage. In the presence of a completely water-miscible monomer, the events in the water phase should be emphasised on.

Despite a long history of investigation, the production of carboxylated latexes remains very often more a matter of know-how than know-why. The investigation described in this thesis aims at a better understanding and a possible control of the processes leading to the incorporation of carboxylic groups into latex products. Acrylic acid has been chosen as the carboxylic monomer in a study of styrene and styrene-butadiene emulsion polymerisation. The original approach consists in the combination of information obtained from the emulsion polymerisation kinetics and acid group distribution in polymerisation products. With a better insight into the important mechanisms involved in the process, the parameters governing the efficiency of the ultimate acid incorporation are determined.

1.3. Outline of the thesis

Chapter 2 is a more detailed introduction into emulsion polymerisation mechanisms and kinetics. Attention is focused on the use of functional monomers like carboxylic acids in emulsion copolymerisation processes and its consequences with respect to the production of carboxylated polymers and latexes.

Chapter 3 deals with the ingredients and the experimental procedures used throughout the investigation. Latex cleaning is an important technique for the characterisation of latex products and is presented in chapter 3 as well.

Chapter 4 describes the methods developed to characterise carboxylated polymers and latexes. Attention is focused on the experimental determination of the acid group distribution between the different phases of latex systems. This is achieved by means of aqueous and non-aqueous titrations. Attempt is made to determine the chemical composition distribution of emulsion copolymerisation products by means of Gradient Polymer Elution Chromatography®.

Chapter 5 deals with important kinetic aspects in emulsion copolymerisation with carboxylic monomers. The influence of pH on the polymerisation of methacrylic acid in water is investigated. Estimations of the propagation rate constants controlling the particle phase and aqueous phase polymerisations in latex systems are made using the copolymerisation terminal model. The copolymerisation terminal model is also used to determine the chemical composition of the polymer molecules formed in the aqueous phase.

Chapter 6 describes and discusses the emulsion polymerisation of styrene, butadiene and acrylic acid. The acid content and the pH of the reaction mixture are investigated with regard to their influence on the progress of the polymerisation process and on the nature of the latex products. Both particle nucleation and particle growth are studied.

Chapter 7 describes and discusses the emulsion polymerisation of styrene and acrylic acid. Attention is focused on the particle growth processes only by performing seeded emulsion polymerisation. Evidence is found for the participation of acrylic acid into mass transfer phenomena leading to the incorporation of acid groups into latex particles. The mechanisms involved in the process are pointed out and attempt is made to control the final acid incorporation efficiency.

2

Emulsion Polymerisation Mechanisms

ABSTRACT: The mechanisms involved in emulsion polymerisation processes are described. The influence of carboxylic monomers in some of the mechanisms is introduced as well as the specific characteristics of carboxylated latexes with respect to the distribution of carboxylic groups over the particle phase and the aqueous phase of latex systems.

2.1. Emulsion polymerisation kinetics

2.1.1. A three interval process

A batch emulsion polymerisation process can commonly be divided into three time separated intervals as suggested by the classic Harkins' theory [1947]. The reaction mixture initially consists of monomer droplets and monomer swollen surfactant micelles dispersed in a continuous aqueous phase. When polymerisation starts, a third phase is formed consisting of monomer swollen polymer particles. This step is called the nucleation step, also referred to as Interval I, and ends when all micelles have disappeared. After nucleation and throughout Interval II, the polymer particles grow at the expense of monomer droplets. Interval III starts later on in the process when the monomer droplets have disappeared as well. Polymerisation continues in Interval III until the monomer present in the particles or dissolved in the aqueous phase is depleted and the polymerisation is complete. This scheme distinguishes between two main stages: the nucleation stage (Interval I) and the particle growth stage during which the number of latex particles is ideally constant (Intervals II and III).

2.1.2. Free radical oligomers

In fact, the first important process before nucleation is the generation of free radical species. This process remains actually a crucial issue throughout the whole course of emulsion polymerisation reactions. The initiator introduced in the recipe is usually water-soluble, e.g. persulfate. It dissociates in the aqueous phase and two free radical species are formed. The monomers used in emulsion polymerisation are usually sparsely water-soluble. However, a sufficient amount of enough monomer is dissolved in the continuous phase where it is available for reaction with the freshly formed radical. The "monomeric" radicals so-formed can undergo in first instance all reactions related to a free radical solution polymerisation scheme: propagation with dissolved monomer units, cross-propagation in case of a copolymerisation system, termination and transfer. Additional processes inherent to the heterogeneous nature of emulsion polymerisation systems can occur as well. These specific processes include all mass transfer phenomena between the continuous aqueous phase and the dispersed organic phase. The small oligomeric radicals may enter surfactant micelles, monomer droplets or already existing polymer particles. The first two events account for particle nucleation whereas the entry of radicals in the particle phase is one of the key issues in latex particle growth and emulsion polymerisation kinetics. Entry first includes the diffusion of free radical species through the bulk phase onto the surface of one of the above mentioned discrete phases. Note that radical entry in monomer droplets is usually neglected because of the low specific surface area. In case the free radical species are irreversibly captured, the free radical reactivity is then transferred to the organic phase [Hansen *et al.*, 1982]. The water-solubility and the surface activity of the oligomeric radicals play a very important role with regard to mass transfer phenomena [Priest, 1952; Penboss *et al.*, 1983]. The incorporation of monomer units into oligomeric radicals growing in the aqueous phase is limited by a critical degree of polymerisation z above which the polymer chains become surface active and irreversible entry occurs [Maxwell *et al.*, 1991]. For a degree of polymerisation below z, the oligomeric radicals are soluble in water but a dynamic equilibrium between the aqueous phase and the dispersed organic phase probably exists, each oligomeric radical being characterised by its own partition coefficient. Therefore, entry may occur as well [Hansen, 1993]. Note that the critical degree of polymerisation z depends of course on the nature of the monomers available for polymerisation in water.

2.1.3. Particle nucleation

Nucleation introduced as Interval I of emulsion polymerisation in section 2.1.1 is the period during which latex particles are formed. In his description of emulsion polymerisation processes Harkins [1947] suggested a nucleation mechanism dominated by micellar nucleation *i.e.* the entry of oligomeric radicals in surfactant micelles as described in section 2.1.2. Smith and Ewart [1948] reported a quantitative treatment of this model that proved to be successful in describing emulsion polymerisation kinetics. The number of particles, N_p, formed during Interval I is predicted by $N_p \propto [I]^{0.4}\ [S]^{0.6}$ where [I] and [S] are the concentrations of respectively initiator and surfactant.

However, this model is not obeyed by a wide range of monomers, more particularly the monomers with a significant water-solubility, and nucleation can obviously occur in surfactant-free systems as well. Jacobi [1954] and Priest [1952] were the first authors to propose a homogeneous nucleation mechanism, quantitatively treated by Fitch *et al.* [1971] and Ugelstad *et al.* [1976] and known as the HUFT theory (Hansen-Ugelstad-Fitch-Tsai theory). According to this model, radicals add monomer units in the aqueous phase until they exceed their water solubility, precipitation occurs and a precursor polymer particle is formed. Precipitation actually stands for the clustering of the hydrophobic tails of the oligomeric radical which may also contain a hydrophilic initiator derived end group. The monomer diffuses from the droplet phase to swell the newly formed latex particles and polymerisation proceeds further. If present, surfactant molecules contribute to the colloidal stability of the freshly nucleated particles.

The coagulative nucleation mechanism was proposed by Napper *et al.* [1987] as an extension of the homogeneous nucleation model. According to the coagulative mechanism, the precursor particles formed by homogeneous nucleation are not colloidally stable and can hardly be swollen by monomer because of their very small size [Morton *et al.* 1952]. Therefore, the precursor particles aggregate or coagulate to form mature stable latex particles which may grow further from monomer absorption and eventually surfactant adsorption. Note that coagulation of precursor particles onto already existing latex particles can occur as well.

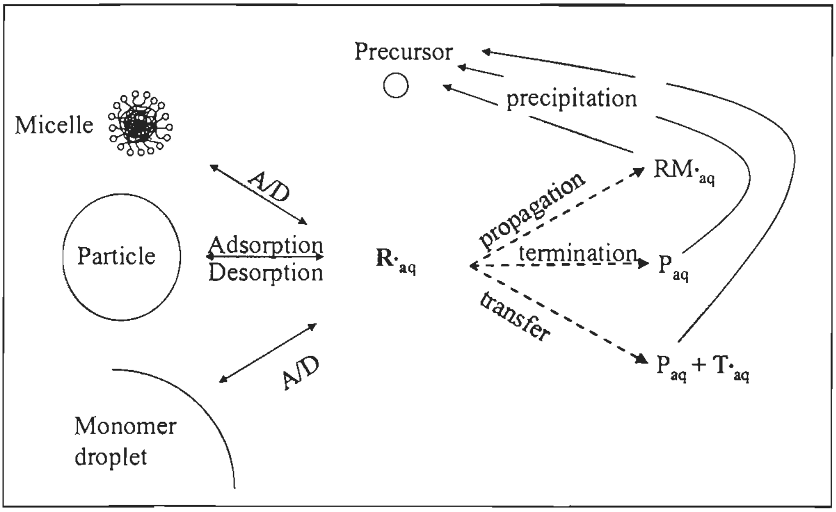


Figure 2.1: Schematic representation of relevant mechanisms and species involved in emulsion polymerisation processes. Solid lines: adsorption/desorption and coagulation process, dotted lines: aqueous phase kinetics.

Nucleation is a very complex but important part of the emulsion polymerisation process. Actually, all mechanisms described above may occur simultaneously. Droplet nucleation which has not been introduced in the present discussion should also be considered but is mainly predominant in mini and microemulsion polymerisations [Sudol *et al.*, 1997; Candau, 1997]. The parameters determining which mechanism may dominate the others are the monomer solubility, the surfactant level and the quality of monomer emulsification [Meuldijk *et al.*, 1998]. For instance, homogeneous nucleation is considered to be the primary mechanism for monomers with high water-solubilities and/or low surfactant levels. A unified model is difficult or even impossible, see Van Herk *et al.* [1998]. Elucidation of nucleation mechanisms is still an active area [Hansen, 1993; Casey *et al.* 1993]. A schematic representation of relevant events occurring during emulsion polymerisation is proposed in Figure 2.1.

2.1.4. Particle growth

Particle growth occurs during the Intervals II and III defined in section 2.1.1. Ideally, nucleation has ceased and the number of particles is constant and equal to the value reached at the end of Interval I. Each particle behaves as a microreactor and the polymerisation rate in the particle phase expressed in moles monomer converted per unit volume of the aqueous phase per unit of time is given by:

$$R_p = \frac{k_p \bar{n} N_p C_{Mp}}{N_{av}} \tag{2.1}$$

where k_p is the propagation rate constant in the particle phase, $\bar{n}$ is the average number of growing chains per particle, C_{Mp} is the overall monomer concentration in the particles, N_p is the number of latex particles per unit volume of the aqueous phase and N_{av} is Avogadro's number.

The value of $\bar{n}$ is determined by three processes: entry of free radicals from the aqueous phase, exit of free radicals from the particles and bimolecular termination inside the particles. $\bar{n}$ follows form the solution of the radical population balance over the latex particle size distribution, see Smith and Ewart [1948], O'Toole [1965] and Ugelstad *et al.* [1967]. Smith and Ewart [1948] discussed three different limiting cases:

Case 1: $\bar{n} \ll 0.5$

Case 1A: termination in the aqueous phase is dominant. This situation is unlikely to occur in conventional emulsion polymerisation systems where the radical population in the particles is high compared to that in the aqueous phase. This is not the case any more if there is a strong hindrance to radical entry.

Case 1B: termination in the particles is dominant and instantaneous upon entry of a second radical in a particle containing already one.

Case 2: $\bar{n} = 0.5$.

Termination in the particle phase containing already one radical is instantaneous upon entry of a second radical and exit is negligible. Since entry randomly occurs, half of the latex particles contain 0 radical while the other half contain 1 radical.

Case 3: $\bar{n} \gg 1$

Termination in the particles is not instantaneous any more compared to radical entry and more than one radical can coexist in a particle.

Case 1 and Case 2 are usually referred to as Zero-One kinetics since the particles contain only zero or one radical. Case 2 is also known as the Smith-Ewart theory and result in a simplified expression of Equation 2.1.

Figure 2.2 gives two examples for the numeric solution reported by Ugelstad *et al.* [1967]. α' and m can be respectively related to the rate of radical production in the aqueous phase and the rate of radical desorption from the particle phase while Y quantifies the occurrence of termination in the aqueous phase. When carboxylic monomers are used in emulsion polymerisation, termination in the aqueous phase may be significant and $Y \neq 0$. The plots in Figure 2.2 are often referred to as the Ugelstad plots. The three limiting cases introduced by Smith and Ewart appear clearly in Figure 2.2 where for given m and Y values $\bar{n}$ is successively smaller, equal and larger than 0.5 as α' increases.

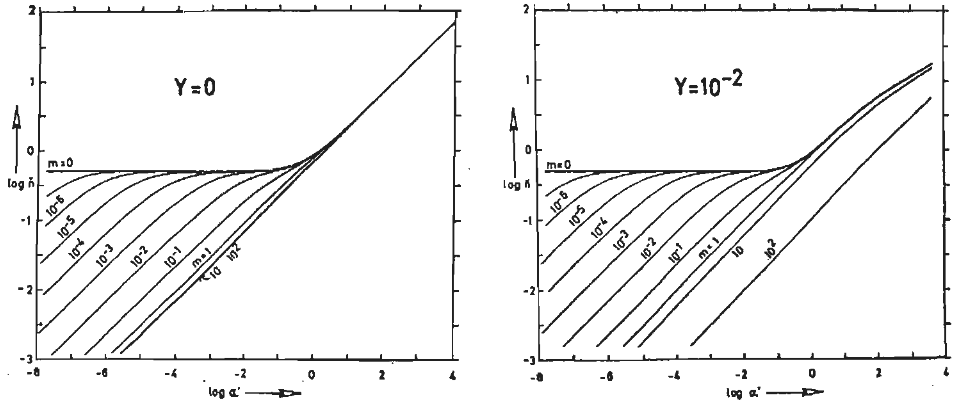


Figure 2.2: Average number of radicals per particle as a function of the parameters α' and m for different values of Y as defined by Ugelstad *et al.* [1967]

2.2. Carboxylated latexes

2.2.1. Mechanisms involved

All mechanisms described in section 2.1 apply since all monomers involved in the emulsion process partition between the continuous aqueous phase, the monomer droplets and the latex particles. However, due to the hydrophilic nature of carboxylic monomers and polymers, all fundamental reaction steps and equilibria in the aqueous phase must be emphasised on.

Initiation takes place in the aqueous phase where the monomer concentration is higher than in conventional systems and depends on the recipe. Cutié *et al.* [1997] investigated the influence of the monomer concentration on the persulfate initiated polymerisation rate of acrylic acid in water. These authors reported the interaction of the monomer with the initiator itself or with the initiator derived radicals trapped in a solvent cage. This behaviour may have a significant influence on the rate of free radical generation. Carboxylic monomers are always used as functional comonomers in the emulsion polymerisation of monomers with a low water-solubility. The polymerisation scheme in the aqueous phase is therefore complicated by the presence of more than one monomer and by the relatively high overall monomer concentration in the continuous phase.

As described in sections 2.1.2 and 2.1.3 the water-solubility and the surface activity of the oligomeric radicals formed in the aqueous phase play a very important role in the nucleation process and in the radical transfer from the aqueous phase to the particle phase.

The pH of the reaction mixture has a very strong influence on aqueous phase phenomena. However, aqueous phase polymerisation is difficult to study in emulsion polymerisation from an experimental point of view. The obvious reasons are the presence of the discontinuous particle phase and the partitioning of all (oligomeric) species between the phases involved. Further, the relatively low concentrations of the oligomeric species hamper a detailed mechanistic study because these species cannot be isolated and characterised. Therefore mechanistic information about the emulsion polymerisation processes cannot generally be directly obtained.

2.2.2. Acid group distribution

Acid groups are present in the latex products in five different forms, see Figure 2.3:

- incorporated into copolymer chains inside the polymer particles, *i.e.* buried
- incorporated into copolymer chains but residing in the outer shell of the polymer particles, *i.e.* at or near the particle surface
- incorporated into surface active copolymer chains physically adsorbed onto the polymer particle surface, *i.e.* acting as surfactant molecules
- incorporated into water-soluble copolymer chains with a low surface activity, *i.e.* dissolved in the aqueous phase
- homopolymerised in the aqueous phase

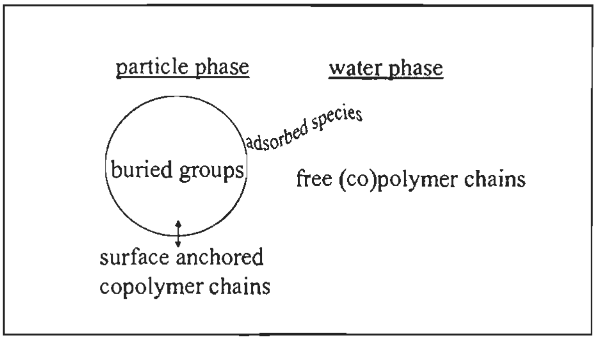


Figure 2.3: Carboxylic acid group distribution in carboxylated latexes

The final distribution of acid groups in latex products is controlled by several factors of which the most important are:

- the reactivities of the monomers
- the hydrophilicity of the carboxylic acid monomer and its partitioning behaviour
- the pH of the reaction mixture
- the way in which the monomers and more particularly the functional carboxylic ones are supplied to the reaction mixture

Valuable mechanistic information can be obtained form the determination of the acid distribution. Indeed, effective entry of acid rich oligomeric radicals will mainly result in the incorporation of acid groups chemically bound to the polymer molecules in the latex particles. Monomer units partitioned into the latex particles will copolymerise and remain buried inside the particles. After transfer or termination in the aqueous phase oligomeric radicals will remain dissolved in the aqueous phase or will adsorb onto the surface of the latex particles depending on their surface activity and therefore on their chemical composition.

3

Experimental Techniques

ABSTRACT: A wide variety of experimental techniques has been used to study carboxylated latexes. Two main types can be distinguished: the procedures used in the synthesis and preparation of carboxylated latexes and those used in the characterisation of the latexes. The routinely used chemicals, experimental set up, general reaction conditions and sampling procedures are outlined in detail in this chapter. The most frequently applied experimental procedures including the measurement of overall conversion time history, the determination of particle size distribution and latex particle concentration as well as the latex cleaning are also described in this chapter.

3.1. Latex synthesis

3.1.1. Materials

Monomers:

Butadiene (B) was supplied by Air Products and Chemicals. Before polymerisation the monomer was purified in the distillation unit depicted in Figure 3.1 by condensing the gaseous monomer from a 27 dm^3 storage vessel into a cooled (T = -5°C) stainless steel recipient. A 3 dm^3 stainless steel dosage vessel was filled with the freshly distilled butadiene. Styrene (S) inhibited with 20 ppm 4-tert-butyl-pyrocatechol was supplied by Merck. Acrylic Acid (AA) inhibited with 20 ppm hydroquinone monomethyl ether was supplied by Fluka. Before polymerisation, AA and S were distilled under reduced pressure and stored at 5°C.

Chemicals for emulsion polymerisation experiments:

Sodium dodecylsulfate (SDS, p.a., Merck), sodium persulfate (SPS, p.a., Fluka), sodium carbonate (SC, p.a., Merck), sodium chloride (NaCl, p.a., Merck), acetic acid (p.a., Merck), all laboratory grade, were used in the standard emulsion polymerisation recipes without further purification. Hydroquinone (p.a., Merck) was used to stop polymerisation for conversion measurements.

Distilled deionised water was used directly from the deionisation unit and purged with nitrogen to remove oxygen before use in emulsion polymerisation experiments.

3.1.2. Polymerisation procedures

Copolymerisation with Styrene and Butadiene:

The emulsion polymerisations were carried out in a 1.2 dm^3 jacketed cylindrical stainless steel reactor equipped with a six-bladed turbine impeller. In Figure 3.2 a cross-section of the reactor is shown. The reactor was charged under nitrogen at room temperature with all ingredients, except for B. The inert gas in the head space was evacuated. The correct amount of freshly distilled liquid B was then added to the reactor from the weighed steel dosage vessel under pressure, see Figure 3.1. The pressure never exceeded 5 bars in the reactor during polymerisation.

The initiator was added together with all other chemicals at the beginning of the procedure or after the reaction temperature was reached by connecting a stainless steel pressure proof syringe to the reactor and giving a pulse of an initiator solution.

During polymerisation samples of about 10 ml were withdrawn from a valve at the bottom of the reactor with a pressure tight glass syringe, model B-D Cornwall from Becton Dickinson & Co., equipped with a Luer Lock Stopcock from Alltech.

Polymerisation with Styrene:

A jacketed cylindrical stainless steel reactor, volume 5 dm^3, equipped with a twelve bladed turbine impeller was used to produce the seed latexes. The distance of the impeller from the bottom of the vessel was 1/3 of the liquid height.

The seeded experiments were carried out in a jacketed cylindrical stainless steel/glass reactor with the same configuration as the one used for the copolymerisation of S and B, see Figure 3.2.

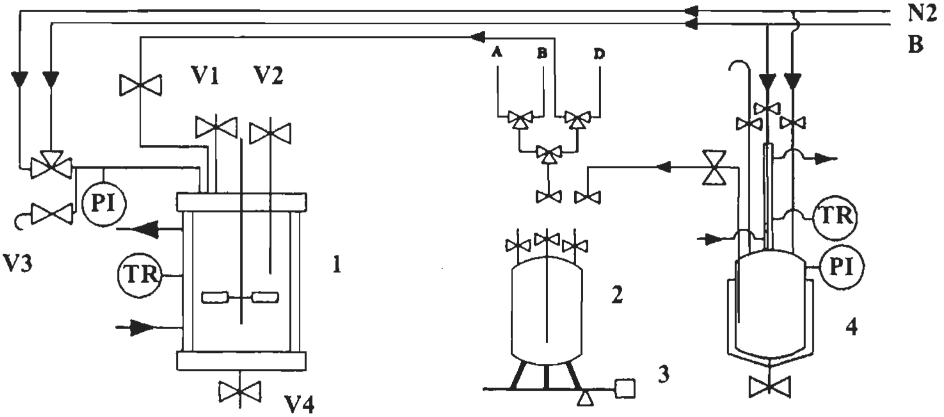
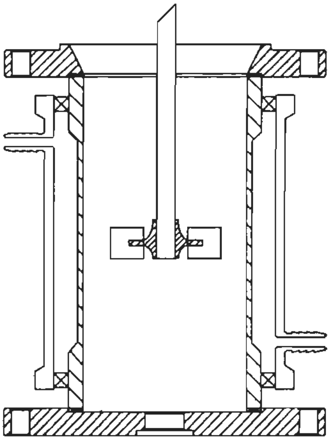


Figure 3.1: Flow diagram of the butadiene experimental set up. 1: reactor (see Figure 3.2), 2: dosage vessel, 3: balance, 4: distilled monomer recipient, V1: ingredient inlet, V2: connection to the stainless steel pressure proof syringe, V3: pressure outlet and connection to vacuum, V4: sampling valve connected to pressure proof sampling syringe, PI: pressure indicator, TR: temperature regulation, N2: nitrogen line, B: butadiene line from the 27 litre storage vessel.



Reactor dimensions (mm):	
reactor diameter	96
reactor height	205
turbine diameter	60
turbine position (from bottom)	68
blade length	18
blade height	15

Figure 3.2: Cross-section of the reactor used for emulsion polymerisation experiments

In all seeded experiments, all ingredients except the initiator were supplied to the reactor and the reaction mixture was equilibrated for about 30 minutes at reaction conditions expressed in temperature and a stirring speed of 300 rpm before the initiator was added. In order to avoid secondary nucleation during seeded emulsion polymerisation experiments the excess of emulsifier was removed from the seed latexes by the dialysis procedure described in section 3.2.

3.1.3. Conversion analysis

The overall conversion was determined by gravimetry on samples collected from the reaction mixture. The reaction was stopped immediately after sampling by using hydroquinone. The overall conversion X_{ov} was calculated with the following equation:

$$X_{ov}(t) = \frac{SC(t) - SC_{initial}}{SC_{final} - SC_{initial}} \tag{3.1}$$

where SC(t) is the fractional solid content determined at time t of the reaction, $SC_{initial}$ and SC_{final} the fractional solid contents respectively at the beginning of the reaction and after complete conversion, both calculated from the recipes. The conversions could be measured with an accuracy of 2% conversion. In the seeded experiments, the seed polymer introduced in the reaction mixture was included in $SC_{initial}$ so that the conversion corresponded to the conversion of the freshly added monomers only.

In experiments with B, a limited amount of B monomer was present as a gas phase in the reactor even though the gas cap was as small as possible. The resulting systematic error in the measurement of conversion by gravimetry was neglected provided excessive sampling was avoided. The pressure in the reactor during polymerisation with B gave a good indication of the progress of the reaction. The pressure was constant as long as butadiene was present in a monomer phase separate from the particle phase *i.e.* Intervals 1 and 2 of an emulsion polymerisation process, see Chapter 2. In Interval 3 of the polymerisation process, the latex particles are in equilibrium with the monomer dissolved in the water phase which is itself in constant equilibrium with the monomer present in the gas cap. So, the pressure decreased with conversion in the last stage of the emulsion polymerisation.

The overall rate of polymerisation per unit volume of the continuous phase in a batch emulsion polymerisation experiment can be calculated with the relation:

$$R_p(t) = C_{M,0} \frac{dX_{ov}(t)}{dt} \tag{3.2}$$

where $C_{M,0}$ is the initial total monomer concentration per unit volume of the aqueous phase and X_{ov} the overall conversion. Although the aqueous phase plays a crucial role in the polymerisation process, the main locus of polymerisation is the particle phase. The contribution of the aqueous phase polymerisation to R_p has therefore been assumed negligible in all our calculations. R_p, can also be expressed by the equation introduced in Chapter 2:

$$R_p = \frac{\bar{k}_p \, \bar{n} \, N_p \, C_{Mp}}{N_{av}} \tag{3.3}$$

where $\bar{k}_p$ is the average propagation rate constant at the locus of polymerisation *i.e.* the particle phase, $\bar{n}$ is the average number of growing chains per particle, C_{Mp} is the overall monomer concentration in the particles, N_p is the number of latex particles per unit volume of the aqueous phase and N_{av} is Avogadro's number. The appropriate estimation of $\bar{k}_p$ in emulsion copolymerisation systems will be discussed in Chapter 5.

3.1.4. Particle size analysis

The average particle diameter and the particle size distribution (PSD) were measured by Transmission Electron Microscopy (TEM, Jeol 2000 FX). TEM was preferentially performed to get accurate values of the PSD and was used as a check for secondary nucleation in the seeded experiments. The PSD and average particle size were determined from the electronmicrographs by counting at least 500 particles. Prior to TEM the polybutadiene containing latexes were stained with osmium-tetraoxide (OsO_4). Staining with OsO_4 results in less deformation of the soft polybutadiene-rich latex particles in the electron beam of the microscope and a better contrast due to the high OsO_4 electron density, see Kato [1966]. Relevant definitions are given in Table 3.1.

Table 3.1: Definition of particle size diameters, n_i represents the number of particles with diameter d_i

d_n Number-average	d_s Surface-average	d_v Volume-average	d_w Weight-average	P Polydispersity
$\frac{\sum_i n_i d_i}{\sum_i n_i}$	$\frac{\sum_i n_i d_i^2}{\sum_i n_i}$	$\frac{\sum_i n_i d_i^3}{\sum_i n_i}$	$\frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3}$	$\frac{d_w}{d_n}$

The average particle number density per unit volume of continuous phase can be calculated with the relation:

$$N_p = \frac{6\frac{P}{W}}{\frac{\rho_p}{\rho_w}\pi d_p^3} \tag{3.4}$$

where P/W is the polymer to water weight ratio in the reaction mixture, ρ_P the average density of the polymer, ρ_W the density of water and d_p the average particle diameter given by TEM. P/W is a function of the initial monomer to water ratio, the conversion and in seeded systems the amount of initial seed polymer. Table 3.2 gives an overview of the specific data used in all the calculations. The amount of AA was neglected in the calculation of N_p since the total AA content in the recipe was usually low and AA was only partly incorporated in the particle phase.

Table 3.2 Densities of monomers (ρ_M) and polymers (ρ_P).

Monomer	**ρ_M (kg m^{-3})**	**ρ_P (kg m^{-3})**	**Reference**
Styrene	878 (50°C)	1044 (50°C)	Hawkett *et al.* [1980]
Butadiene	570 (60°C)	860 (60°C)	Verdurmen [1993]

The monomer swollen particle diameter can be calculated with the relation:

$$d_{pswol.}^{\,3} = d_p^{\,3}\left(1 - \frac{M_M\, C_{Mp}}{\rho_M}\right)^{-1} \tag{3.5}$$

where d_{pswol} is the swollen particle diameter, M_m the molecular weight of the swelling monomer, C_{Mp} the monomer concentration in the swollen particles and ρ_m the density of the swelling monomer. In intervals I and II of emulsion polymerisation monomer is still present as a separate phase and C_{Mp} depends on the particle diameter only. In interval III the monomer phase has disappeared and C_{Mp} depends also on the overall conversion.

In seeded systems where no secondary nucleation takes place, the particle diameter during polymerisation is a function of both the seed particle diameter and the conversion:

$$d_p^{\,3} = d_{pseed}^{\,3} + \frac{6\dfrac{M}{W}X_{ov}}{\dfrac{\rho_P}{\rho_w}\pi N_p} \tag{3.6}$$

where M/W is the initial monomer to water ratio in the reaction mixture and d_{pseed} the initial seed particle diameter.

3.2. Cleaning procedures

Together with polymer particles, a latex system contains a number of other ingredients such as electrolytes, buffer, emulsifier molecules and water-soluble oligomer molecules. These ingredients are introduced in the recipe or are formed during the course of the polymerisation process. These components are present in the aqueous phase or can be adsorbed on the surface of the latex particles in the case of the emulsifier and the water-soluble polymer. The cleaning process consists in removing the above mentioned species which are present in a latex system but do not belong to the bulk polymer phase. The objectives of cleaning can be multiple and have been reviewed by El-Aasser [1983]. In our work cleaning is an essential step in the analysis and quantification of chemically bound polymer end groups present on the surface of latex particles [Vanderhoff *et al.*, 1970; Van den Hul *et al.*, 1970] and in the control of the amount of emulsifier molecules adsorbed on the surface of the latex particles [Ahmed *et al.*, 1980; Vijayendran *et al.*,1981]. We indeed used the cleaning process to remove the excess surfactant in seed latexes and therefore avoided secondary nucleation. We also used the cleaning process to remove the water-soluble species produced during the synthesis of carboxylated latexes, see Chapter 2, and therefore have the possibility to study the particle phase only and to determine the distribution of carboxylic groups over the particles and the aqueous phase.

3.2.1. Dialysis

Several cleaning methods have been developed: dialysis [Edelhauser, 1969; Everett *et al.*, 1979; McCarvil *et al.*, 1978], serum replacement / ultrafiltration [Labib *et al.*, 1978; El-Aasser *et al.*, 1980; Ahmed *et al.*, 1980; Wilkinson *et al.*, 1981]. The method we used in our study is based on the one described by Vanderhoff *et al.* [1970] and consists of dialysis followed by ion-exchange.

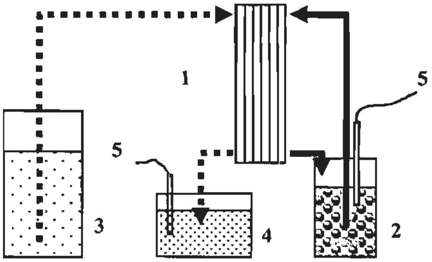


Figure 3.3: Schematic representation of the experimental setup for the dialysis of latexes. 1: dialysis cell, 2: latex sample, 3: deionised water, 4: serum collector, 5: conductivity cell

Hollow fiber membranes proved to be efficient for the dialysis of latexes, see McCarvill [1978]. The membrane used in this study consists of a commercially available dialyzer (Lun Dia® Pro 500 from Gambro, Sweden). It has the following characteristics: polyether carbonate membrane in polycarbonate casing, 1.2 m^2 absolute effective membrane area, membrane thickness of 15μm, molecular weight cut-off of 15000 kg/kmol. The latex was diluted to about 5% solids and pumped loop-wise along the shell side of the membrane.

Figure 3.3 schematically shows the dialysis set-up used. The water-soluble species were removed from the latex product which was pumped through the membrane. The diluted serum could therefore eventually be collected for further analysis.

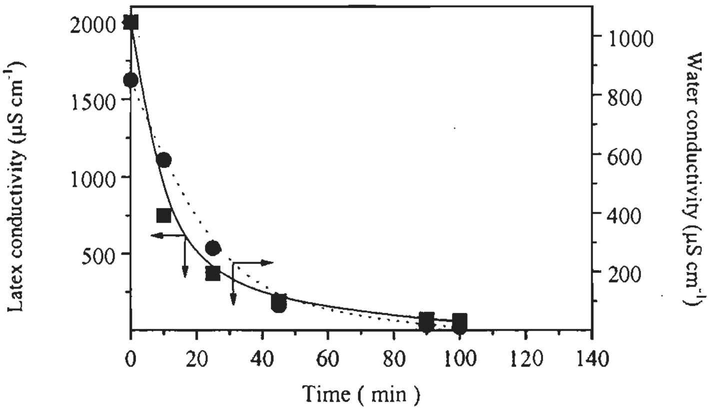


Figure 3.4: conductivity as a function of time during dialysis of a styrene/acrylic acid latex. ■ latex pumped through the dialyzer, ● water effluent.

The conductivity of both the latex and the effluent dialysate were monitored (conductimeter model CDM80 with conductivity cell PP1042 from Radiometer, Copenhagen). An example of the conductivity as a function of time is shown in Figure 3.4. The cleaning process was governed by mass transfer through the membrane and proved to be very efficient in removing a considerable amount of electrolytes within a short period of time. A level of low conductivity was reached at the end of the cleaning process. Dialysed latexes could be used in seeded experiments with a controlled level of additional surfactant and in most cases no secondary nucleation occurred.

3.2.2. Ion Exchange

The dialysis method suffers from several disadvantages, see Vanderhoff *et al* [1970], Everett *et al.* [1979] and Wilkinson *et al.* [1981], Goodall *et al.* [1978 and 1979] and Hearn *et al.* [1980]. These authors reported that the method is slow and inefficient in removing low molecular weight polymer and oligomeric weak acids. This is obviously a major disadvantage for the characterisation of carboxylated latexes. In our study on the acid group distribution over the aqueous phase and the polymer particles in carboxylated latexes, cleaning was therefore completed by ion exchange as described by Vanderhoff *et al.* [1970 and 1972]. This method proved to be very efficient in removing the remaining polyelectrolytes and charged oligomers dissolved in the aqueous phase of the latex products and adsorbed on the surface of the latex particles, see McCarvil *et al.* [1978]. In addition, ion exchange also ensured a complete exchange of Na^+ counterions by H^+ ions after contact with the functionalised ion-exchange resins. Ion exchange therefore enabled the accurate determination of protonated weak acid groups by titration.

Thoroughly cleaned Dowex 50Wx8 (sulfonic acid active groups, 20-50 mesh size, exchange capacity = 1.7 meq / ml wet resin) and Dowex 1x8 (trimethyl ammonium active groups, 20-50 mesh size, exchange capacity = 1.33 meq / ml wet resin) resins (Fluka) were used. The purity of the resins is very important since small amounts of polyelectrolytes can be leached from the commercial ion exchange resins and contaminate the latex samples, see Schenkel *et al.* [1958]. The method developed by Vanderhoff *et al.* [1970] was therefore used to clean the ion exchange resins. The volume of resins necessary to thoroughly clean latex samples was based on the recipes producing the carboxylated latexes. Typically 100 to 150 ml of the dialysed latex (5% solids) was stirred for 2 hours with an excess of mixed-bed resin, which consisted of an equivalent amount of cationic and anionic ion-exchanger. The latex was then separated from the resin beads by filtration. The efficiency of the whole process including dialysis and ion-exchange was checked by comparing the amount of surface acid groups detected in a carboxylated latex sample by titration, see Chapter 4, after successive ion exchange cycles. The results showed that provided the dialysis was carried out until a constant conductivity level was observed in the latex loop, a constant charge level was obtained already after the first ion exchange cycle with about a five fold excess of ion exchange resins. So these charges could be attributed to non-removable surface charges. This procedure was applied prior to all surface weak acid group determination.

The effect of cleaning on the latex particle size distribution was investigated since significant changes in particle size distributions due to preferential flocculation of small particles with resin beads has been reported by McCann *et al.* [1971]. We studied the effect of both dialysis and ion exchange on a carboxylated polystyrene latex with a broad particle size distribution with TEM. No effect of dialysis and ion exchange on the particle size distribution could be observed in our latexes.

We did not investigate the influence of ion exchange resins on the hydrolysis of sulfate groups originating from the initiator and built on the surface of latex particles. Ahmed *et al.* [1980] reported that no hydrolysis occurred by prolonged contact with ion exchange resins. However, Fitch *et al.* [1978] did report that the sulfate end groups of their polystyrene latexes could undergo hydrolysis reactions during the ion exchange process. In our study hydrolysis would hardly introduce a systematic deviation in the amount of carboxylic groups detected on the latex surface. In fact the amount of sulfate groups eventually incorporated onto the surface of the latex particles is relatively low as compared with acid groups originating from the carboxylic monomer. It is therefore assumed that the cleaning processes do not alter the chemical characteristics of the surface of the latex particles except for counterion exchange.

4

Characterisation of Carboxylated Latex Products

ABSTRACT: Analytical tools have been developed to characterise carboxylated latex products. In this chapter attention is focussed on the distribution of the carboxylic acid groups over the different phases of latex systems and in the copolymer chains formed during polymerisation reactions. The aqueous conductometric titration of latexes and the non-aqueous potentiometric titration of polymerisation products are described. Gradient Polymer Elution Chromatography (GPEC) applied to model copolymers of styrene and butadiene and of styrene and acrylic acid is described. The behaviour of the corresponding emulsion copolymerisation products is presented.

4.1. Introduction

A latex consists of a heterogeneous system with water as the continuous phase and submicron polymer particles as the dispersed phase. This roughly results in the presence of three distinct main loci: the aqueous phase, the particle phase and the interface between the two. All components present in the emulsion polymerisation reaction mixture for the synthesis and more particularly the monomers distribute over all these three different loci. The carboxylic groups present in a carboxylated latex can therefore be present after polymerisation in the particle phase as "buried" species, in the aqueous phase as oligomers or at the surface of the latex particles. Surface groups can be divided into two types:

- water-soluble surface active polymer chains which are adsorbed at the interface between the particles and the continuous phase
- polymer chains grown in the particle but with a chain end rich in carboxylic groups that have the tendency to stretch out of the particle into the aqueous phase.

The first type can eventually be removed from the surface whereas the second type is chemically bound to the polymer particle and remains as so-called surface-acid.

The way the carboxylic acid groups end up in a certain locus depends on the mechanisms governing the synthesis of the latex. Three processes contribute to the distribution:

- the partitioning of the carboxylic monomer which allows its presence in the polymer particle and contributes to the formation of copolymer in which the acid groups belong to the "buried" population,
- the aqueous phase polymerisation which produces oligomeric radicals and water-soluble oligomers. Those species can precipitate on existing latex particles, participate to the formation of new latex particles or adsorb as surface-active species onto the surface of the latex particles. The carboxylic acid groups carried by those species can end up as "buried" groups or removable "surface" acid groups
- the effective entry in the latex particles of oligomeric radicals rich in carboxylic acid groups. These radicals can propagate further inside the latex particles and contribute to the anchored "surface" population.

A detailed description of the distribution of the carboxylic groups over the different locations in the reaction mixture may contribute to a better understanding of the mechanistic aspects of the emulsion polymerisation process in the presence of hydrophilic monomers.

4.2. Conductometric titration of surface acid groups

4.2.1. Objective

Several authors described the characterisation of the surface of carboxylated latex particles in terms of amount of chemically bound carboxylic acid groups, see e.g. Gran [1952], Hen [1974], Everett *et al.* [1979], Vijayendran [1979], Labib *et al.* [1980] and Stenius *et al.* [1983]. All the methods include as a first step the removal of all the species simply adsorbed onto the surface. The next steps are usually the protonation of the remaining anchored surface carboxylic acid groups and the quantification of those groups by means of titration. The titration methods are based on the reactions between the functional groups and a titrant: carboxylic acid groups with a strong base or carboxylate groups with a strong acid.

4.2.2. Method

In this study, the titrants were aqueous solutions of sodium hydroxide, NaOH, or hydrochloric acid, HCl, with a well-known concentration (Titrisol®, Merck). The concentration of the titrants was checked by performing an acid-base titration of potassium hydrogen phthalate, KHP, (p.a., Merck). It is a hygroscopic powder and was therefore dried before use in a vacuum oven at 50 °C for 12 hours. It was rapidly weighed and titrated with both the NaOH and the HCl titrant. The concentration of the two titrants could therefore be accurately obtained. All the acid base titrations were performed in a closed jacketed glass vessel in which the titrants were added with automatic burettes, model Dosimat 665 from Metrohm.

After measuring the solid contents by gravimetry, a known amount of latex (corresponding to 0.5 to 1g of polymeric material) was diluted with deionised water in the titration vessel. The total volume of the diluted latex sample was about 150 ml. Argon was bubbled through the latex sample for at least 20 minutes under mild stirring. The titrant NaOH (0.05N) was added stepwise at regular time intervals and the conductivity of the mixture was measured continuously (conductometer model 160 with conductivity cell model 016010 from Orion). This procedure is called the forward titration. After the equivalence point was reached NaOH was replaced by the titrant HCl 0.05N and the procedure was repeated again. This second procedure is called the back titration. A typical plot giving the conductivity as a function of volume titrant added during the forward titration is shown in Figure 4.1. Kamel *et al.* [1980 and 1982] reported the influence of carbon dioxide (CO_2) during conductometric titrations. The formation of hydrogen carbonate upon dissolution of CO_2 in water can lead to errors in the interpretation of the titration results. Therefore all the titrations have to be performed in a CO_2-free atmosphere.

4.2.3. Interpretation of the conductometric titration curves

The conductivity κ is given by the sum of the contributions from each individual ionic species in the solution:

$$\kappa = \sum C_i \lambda_i \tag{4.1}$$

where C_i is the concentration and λ_i the molar conductivity of ion i. Our latexes carry typically two types of surface groups: a weak acid functionality (carboxylic acid groups from the functional monomer) and a strong acid functionality (sulphate groups from the initiator fragments). Both functionalities react with NaOH during the titration and the conductivity is given by:

$$\kappa = C_H{}^+ \lambda_H{}^+ + C_{Na}{}^+ \lambda_{Na}{}^+ + C_{OH}{}^- \lambda_{OH}{}^- \tag{4.2}$$

Note that in this discussion we only take into account the mobile free ions and the counterions of the surface anchored species and do not consider the contribution of the immobile functional groups chemically bound to the surface of the latex particles.

NaOH reacts first with the strong acid groups. Note that the dissociation constants of the initiator-derived acid and the carboxylic acid are different, see Table 4.1. $C_H{}^+$ decreases by reaction with the titrant NaOH while $C_{Na}{}^+$ increases. Since $\lambda_H{}^+ > \lambda_{Na}{}^+$, see Table 4.1, κ decreases with the amount of added NaOH as demonstrated by the negative slope AB in Figure 4.1. When all the strong acid groups are consumed, NaOH reacts with the weak acid groups and contributes to their dissociation. The conductivity is then given by Equation (4.2) with:

$$C_H{}^+ = K_{aCOOH} \frac{1-\alpha}{\alpha} \tag{4.3}$$

where Ka_{COOH} is the dissociation constant, see Table 4.1, and α the degree of dissociation of the weak acid given by:

$$\alpha = \frac{[COO^-]}{[COOH]+[COO^-]} \tag{4.4}$$

Table 4.1: Dissociation constants of acids and Molar conductivities of some ions present during the titration of carboxylated latexes. Source: Atkins [1998]

	OH^-	Cl^-	H^+	Na^+	$-HSO_4^-$	$-COOH$
Molar Conductivity λ (10^{-4}S m^2 mol^{-1})	174	65.4	329.8	43.6	-	-
pK$_a$	-	-	-	-	2.0	4.6

C_H^+ still decreases but its contribution to the conductivity is now so small that the decrease of the contribution of protons to the conductivity is compensated by the increase in C_{Na}^+. So κ increases with the amount of added NaOH as demonstrated by the slope BC in Figure 4.1. Finally when all the weak acid groups have reacted, NaOH is added in excess and the OH^- ions contribute strongly to the conductivity κ resulting in a steep increase as demonstrated by the slope CD in Figure 4.1. The back titration with HCl can be interpreted in a similar way.

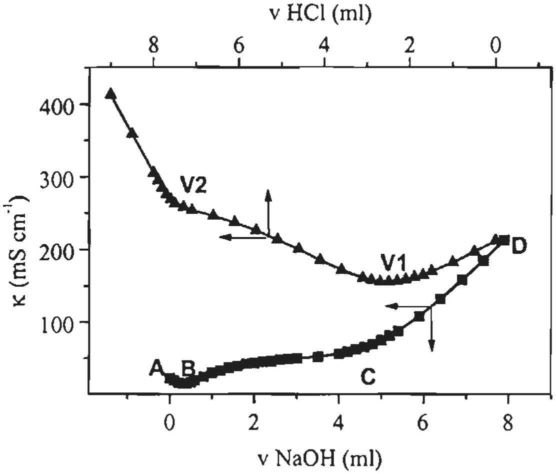


Figure 4.1: Conductivity as a function of volume titrant added during the titration of a carboxylated polystyrene latex after cleaning.
■ NaOH titrant, forward titration,▲ HCl titrant, back titration.

The global shape of the titration curves is straightforward but some factors have an influence on the actual slopes and stoichiometric points observed in the different parts of the curve:

- the relative low mobility of the functional ionised groups chemically bound to the surface of the latex particles which contributes also to the conductivity
- the influence of the degree of dissociation on the dissociation constant Ka_{COOH} for the weak acid groups anchored on the surface. It is known that the apparent dissociation constant of weak acid groups in a polyacid decreases with an increasing degree of dissociation of the polyacid, see Mandel [1970] and Bloys van Treslong [1978]. The slope BC in Figure 4.1 is probably affected by this behaviour since the weak acid groups titrated in this part of the curve are likely to belong to longer polymer chains bearing more than one acid group and behaving like a polyacid
- the reduced mobility of the counterions in the double layer surrounding the latex particle and the changing distribution of ions between the bulk liquid and the surface during the titration due to both dissociation and double layer effects.

This resulted in the case of forward titration curves in smaller slopes and poorly defined stoichiometric points in comparison with titration of free acids in solution. As reported by several authors, reliable quantitative results could however be obtained from the back titration curves, see e.g. Vijayendran [1979]. Unfortunately, strong acid groups do not give any equivalence point in back titration curves. Nevertheless, the amount of weak acid groups could still be obtained accurately from the two stoichiometric equivalence points V1 and V2 in Figure 4.1.

The amount of surface acid groups $C_{AAsurf.}$ obtained by titration is usually expressed in terms of equivalents (moles) per gram polymer. It can be compared to the initial amount of acrylic acid groups in the emulsion polymerisation recipe, $C_{AAtot.}$ also expressed in terms of equivalents per gram polymer theoretically formed after complete reaction. The Degree of Surface Incorporation, D.S.I., defined as:

$$\text{D.S.I.} = \frac{C_{AAsurf.}}{C_{AAtot.}} \qquad (4.5)$$

is used as a measure of the efficiency of the surface incorporation process.

The modelling of the titration curve shape and equivalence points can give interesting information about the surface of the particles in terms of number of carboxylic monomer units per polymer chain anchored at the particle surface. This study requires the exact determination of the dissociation constant of carboxylic acid groups in a copolymer chain as a function of the degree of dissociation and the exact contribution of the surface anchored dissociated carboxylic groups to the conductivity of the latex sample. However, there is probably a distribution of surface anchored acid-rich polymer chains in terms of length and composition. The determination of the number of anchoring points is therefore difficult to achieve.

4.3. Potentiometric titration of polymers

4.3.1. Objective

In this section a method is described which has been used to detect the carboxylic acid groups present in a clean latex but not detected as surface groups. Note that the free oligomers and adsorbed species are assumed to be completely removed from the surface. The groups detected belong to the "buried" population, see section 4.1. They are present inside the particle core or close to the surface and cannot be reached by the titrant during the conductometric aqueous titration described in section 4.2. To detect the buried groups a potentiometric titration method has been used. This titration method is also based on the reactions between the functional carboxylic acid groups and a titrant but unlike the surface acid groups characterisation, the titration mixture was homogeneous. During this process, the latex particles were dissolved in an appropriate solvent and therefore the total amount of carboxylic acid groups present both on the surface (anchored) and inside the latex particles (buried) could be titrated. The solvent had to be chosen with care: it must dissolve the polymer, be miscible with the titrant and it should allow potentiometric measurements [Uminski, 1995; Dos Santos, 1997]. Copolymers of styrene and butadiene (PSB) prepared in emulsion could not be analysed in this way because of their high gel content, see section 4.5.3. For PSB latexes, no homogeneous solutions could indeed be obtained with any solvent. Carboxylated polystyrene latexes could be dissolved completely in tetrahydrofuran (THF) which was chosen as a solvent for titration.

4.3.2. Method

A pH electrode suitable for non-aqueous solutions was used (ROSS®SURE-FLOW™ model 8172 from ORION Research) and water was added as a co-solvent to optimise the performance of the electrode.

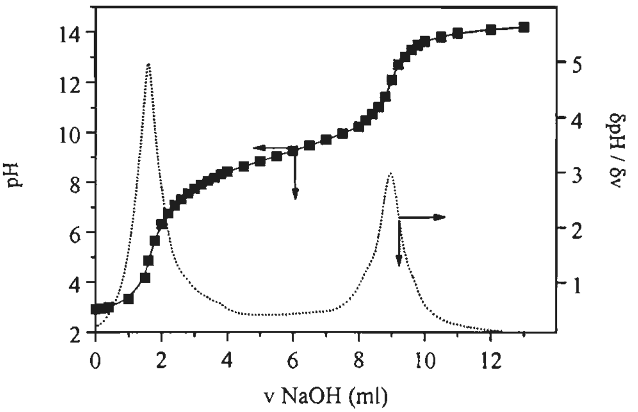


Figure 4.2: Potentiometric titration of a carboxylated polystyrene latex. pH (■) and first derivative (dots) as a function of volume titrant added. The carboxylated polystyrene latex is dissolved after cleaning in a mixture of THF and water acidified with HCl 1N. Aqueous solution of NaOH 0.05N is used as titrant.

A proper amount of latex was dissolved in THF and water to get 150 ml of a mixture containing between 0.5 and 1g of polymer in a 80/20 volume ratio THF/water. In order to get a distinct strong acid equivalence point and ensure the complete protonation of all the acid groups in the sample, the slightly cloudy solution was acidified with 0.1 ml of a 1N solution of HCl in water. After equilibration during 30 minutes, a homogeneous solution was obtained. The mixture was titrated with a 0.05N solution of NaOH in water. Incremental volumes were added at constant time intervals and the pH was recorded. This procedure ensured that the drift in pH often occurring in non-aqueous potentiometric titrations was minimised. Figure 4.2 shows the pH as a function of the volume titrant added in a typical potentiometric titration.

4.3.3. Interpretation of the potentiometric titration curves

All the titration curves showed two equivalence points revealed better when plotting the first derivative of the curve *i.e.* δpH/δvNaOH as a function of the added titrant volume, see Figure 4.2. The first equivalence point corresponds to the neutralisation of the strong acid groups present in the emulsion polymers and from the HCl solution added previously. The second equivalence point corresponds to the weak acid groups. No flat area could be seen between the two equivalence points as it would be the case in an aqueous solution of a mixture of acids. This is due to the drift in pH observed in non-aqueous systems and also to the pH-dependent dissociation constant of polyacids ("drifting" pKa) already discussed. From the difference between the two equivalence points in the titration curve, the amount of weak acid groups present in the particle phase of the latex $C_{AApart.}$ could be computed. $C_{AApart.}$ is usually expressed in terms of mole equivalent per gram of polymer like $C_{AAsurf.}$.

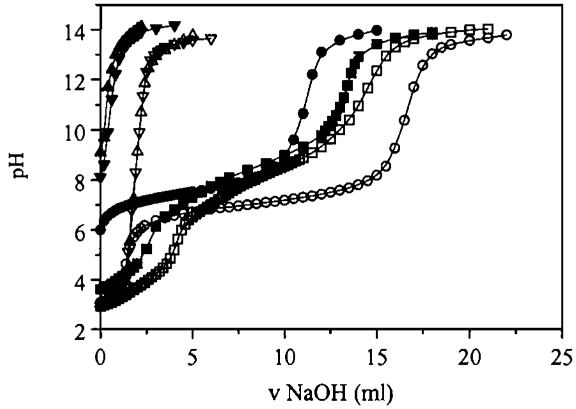


Figure 4.3: Non aqueous potentiometric titration of latexes. pH as a function of volume titrant added. Conditions: see Table 4.2.
▲: reference, solvent only; ▼: S1; ●: S2; ■: S3. Open symbols: solvent 1; solid symbols: solvent 2.

The method was checked with a few model systems consisting of a PS latex, a mixture of PS latex with AA monomer and a carboxylated PS latex shortly after reaction, see Table 4.2. The curves are plotted in Figure 4.3. $C_{AApart.}$ was computed from the determination of the equivalence points in the titration curves and was compared to $C_{AAtot.}$, the total amount of acid groups initially introduced in the systems, see Table 4.2. In all cases, all the weak acid groups could be detected within experimental accuracy. The slope of the titration curve between the two equivalence points for a PS latex mixed with some additional AA monomer was smaller compared to the carboxylated PS latex due to the drift in pK_a for polyacids see Figure 4.3.

Table 4.2: Potentiometric titration of model systems.

System	**Description**	**Solvent** [a)]	$C_{AAtot.}$ [b)] ($\mu eq/g_{pol.}$)	$C_{AApart.}$ [c)] ($\mu eq/g_{pol.}$)
S1	PS latex	1	0	0
S1		2	0	0
S2	PS latex + AA monomer	1	543	558
S2		2	830	810
S3	Carboxylated PS latex	1	740	720
S3		2	740	700

a) Solvent 1 = THF / water (0.8/0.2 in volume), Solvent 2 = THF / water (0.8/0.2 in volume) + 0.1 ml HCl (1N)

b) Calculated from the amount of acrylic acid introduced in the system

c) Calculated from the titration curves

4.4. Acid group distribution

The results of the conductometric titration of the latex combined with the results of the potentiometric non-aqueous titration of the particle phase provides sufficient information to set up a mass balance in acid groups over the different locations, namely the aqueous phase, $C_{AAaq.}$, (free and physically adsorbed species) the particle surface, $C_{AAsurf.}$ (anchored species only) and the particle interior, $C_{AAint.}$. Actually, only $C_{AApart.}$ and $C_{AAsurf.}$ are experimentally measured and the mass balance is given by the following relations:

$$C_{AAtot.} = C_{AAaq.} + C_{AAsurf.} + C_{AAint.} \quad (4.6)$$

$$C_{AApart.} = C_{AAsurf.} + C_{AAint.} \quad (4.7)$$

Note that C_{Aaaq} has to be expressed in terms of equivalents per gram polymer as well.

The analysis of the aqueous phase products and the determination of $C_{AAaq.}$ can provide information and verify the mass balance. However, this is difficult to achieve in most cases since the aqueous phase polymer cannot be easily isolated and characterised. The conductometric titration of the original latex before cleaning could give information about the amount of acid groups present in the aqueous phase but only if no buffer or weak acid initiator fragments are present.

An important question is the origin of the acid groups in the different locations and the distinction between the outer limits of the particles and the interior. The assumption is generally made that the surface acid groups originate from oligomeric radicals entered into the particle, see section 4.1. All the carboxylic acid groups present in the outer layer of the latex particles and being part of polymer chains anchored to the particles should be considered as surface acid groups. However, after protonation of all the surface acid groups by ion exchange, the layer is eventually compressed onto the particle surface due to the less hydrophilic nature of the protonated acid groups and some of the surface acid groups can become artificially "buried". The consequence would be that these groups become invisible for the titrant in the conductometric forward titration. On the contrary, at the beginning of the back titration process all the acid-rich chains are ionised and stretch out into the aqueous phase. Therefore it can be assumed that all the surface functional groups can be detected. It can also be assumed that the titrant in the surface back titration process do not diffuse into the latex particles. The results of the conductometric back titrations are therefore restricted to the accurate determination of $C_{AAsurf.}$ only.

It is also worth noting that carboxylic acid groups incorporated by copolymerisation in the latex particle core can eventually move close to the surface during the emulsion polymerisation process itself. These groups will be detected as surface acid groups although their presence on the particle surface is not due to oligomeric radical entry. Additionally, acid groups incorporated onto the surface of the latex particles via oligomeric radical entry during the latex particle growth process can become buried by the growth of the particle over the anchoring point. These acid groups will be detected as buried species although they originate from effective entry. Although all these processes are expected to be negligible, they show the difficulty to draw and mechanistically interpret an accurate mass balance in acid groups over the different locations of a latex system.

4.5. Polymer chemical composition analysis

4.5.1. Introduction

The use of more than one monomer in polymerisation processes often results in a heterogeneous product in terms of inter molecular chemical composition. Monomer partitioning and different reactivities in terms of the reactivity ratios of the monomers involved lead to composition drift. As a consequence, the products of an emulsion polymerisation process show an intermolecular Chemical Composition Distribution (CCD) [van Doremaele, 1990; Verdurmen-Noel, 1994]. Gradient Polymer Elution Chromatography (GPEC®) [Staal, 1996] is a form of High Performance Liquid Chromatography and a powerful tool for the determination of copolymer CCD [Mori, 1989; Glöckner *et al.*, 1991; Sparidans *et al.*,1990; van Doremaele *et al.*, 1991; Schoonbrood, 1994]. The method has been applied to a large number of copolymers, see Glöckner [1991], and is based on the elution of the polymer chains with a solvent/non-solvent eluent mixture in which the ratio of solvent to non-solvent is gradually changed. The key elements of a GPEC® system are properties of the the column, the solvent/non-solvent system as well as the gradient speed. For each type of copolymer a specific combination should be developed.

The copolymer is dissolved in a good solvent and is injected in the GPEC system while the eluent is very rich in non-solvent. Phase separation occurs and the copolymer chains are retained in the system while the dilute phase is taken up by the eluent. The ratio of solvent to non-solvent is then gradually increased. The polymer chains will redissolve and be taken up by the eluent at a given eluent composition determined by their chemical composition and molar mass. Provided the gradient speed and the retention behaviour of copolymers with a well-defined chemical composition are known, the CCD of any copolymer sample can be obtained.

The procedure used to determine the solvent/non-solvent combination is based on the solubility of the homopolymers. Solvent and non-solvent should of course be miscible. The Cloud Point Composition (CPC) *i.e.* the solvent/non-solvent composition at which a polymer dissolves, is measured for the corresponding homopolymers in different solvent/non-solvent combinations. The difference between the CPC of the homopolymers should be large enough to obtain a proper separation.

The copolymer samples should be prepared carefully before injection. The solvent used to dissolve the copolymer should indeed provide optimum precipitation conditions upon injection to avoid breakthrough. Breakthrough can be seen as a peak normally due to the not retained sample solvent and is caused by a cloudy polymer solution eluting simultaneously with the solvent molecules. To minimise breakthrough one should optimise the amount of solvent molecules in the sample in order to have a good exchange of the solvent molecules in the sample with the non-solvent molecules in the eluent and therefore optimise the initial precipitation of the polymer chains. The solutions are to decrease the injection volume, to increase the concentration of the sample, optimise the exchange with the eluent with a mixing step (introduction of a mixing unit before the column) or dissolve the copolymer sample with a mixture of solvent and non-solvent close to the CPC.

4.5.2. Description of the Set-up

The set-up consists of HPLC pumps, a gradient controller (Waters 600E), a Waters Intelligent Sample Processor (WISP), a HPLC column, a UV detector (Waters 486 set at a wavelength of 260 nm) and an Evaporative Light Scattering Detector (ELSD, 750/14 from Applied Chromatography Systems Ltd). The eluent is nebulized in the ELSD with a nitrogen flow and heated to 80°C in the evaporating tube. The eluent evaporates and an aerosol is formed from the non-volatile solutes (polymer) present in the eluent. A light-scattering photometer detects the non-volatile solutes and the scattering intensity is related to their concentration in the eluent resulting in the CCD. The chemical composition dependence of the detector response was not taken into account in this work.

4.5.3. GPEC on copolymers of Styrene and Butadiene

Calibration with Standards

Tetrahydrofuran (THF, HPLC grade unstabilised, Merck) as solvent and Acetonitrile (ACN, gradient grade, Merck) as non-solvent were chosen according to the work of Willems [1993], Cools *et al.* [1996] and Staal [1996]. The gradient profile given in Table 4.3 was applied for the separation of copolymers of styrene and butadiene. The column was a C18 column (Delta pack® C18, Waters, 3.9mm*15 cm) with a C18 precolumn (Delta pack® C18, Waters, 3.9mm*1 cm). The columns were kept at a temperature of 35°C. The eluent flow rate was 1 ml min^{-1}.

The set of standards we used is the following: Polystyrene, PS (TSK standard, Tosoh, Mw=3.84 10^{6} g mol^{-1}), Polybutadiene, PB (Scientific Polymer Products inc. M_w=2.72 10^{5} g mol^{-1}), copolymers of styrene (S) and butadiene (B) with a styrene mole fraction of 0.05, 0.23 and 0.45, respectively SB5, SB23 and SB45 (Scientific Polymer Products inc., unknown molecular weights). The samples were prepared by dissolving about 10 mg of polymer in 1 ml THF. Some samples containing B were only partially soluble in solvent due to the presence of crosslinked material. Only the soluble part obtained after filtration was then injected in the system. The injection volume was 10 or 15 µl.

Table 4.3: Gradient for the analysis of copolymers of styrene and butadiene (volume fraction)

% Solvent (THF)	%Non-Solvent (ACN)	Time (min)
0	100	0
40	60	5
80	20	45
100	0	50
100	0	55
0	100	60
0	100	65

Figure 4.4 shows a collection of the chromatograms corresponding to all the standards used for the calibration. The gel content of PB and SB5 was large, therefore these polymers could only partially be dissolved in THF. The copolymer standards showed a broad distribution and in some cases PS homopolymer could be observed. Nevertheless the gradient

was able to separate the different copolymers according to their chemical composition and an attempt was made to compose a calibration curve. Figure 4.5 shows the retention time or solvent composition at the maximum peak height as a function of F_S the mole fraction of S in the copolymers. A linear calibration line could be drawn. However, this line does not fit the data very well.

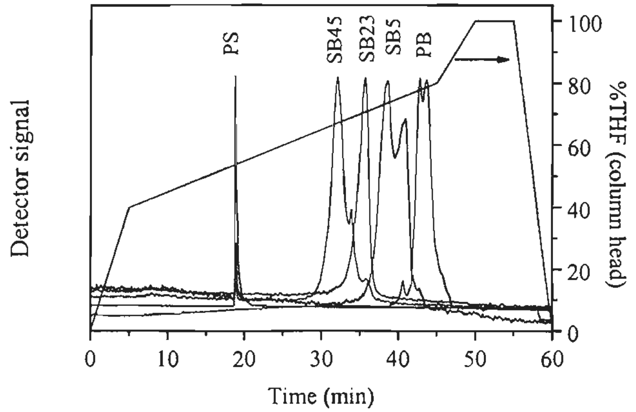


Figure 4.4: GPEC chromatograms of standards, styrene/butadiene copolymers. Normalised detector signal and eluent composition as a function of analysis time.

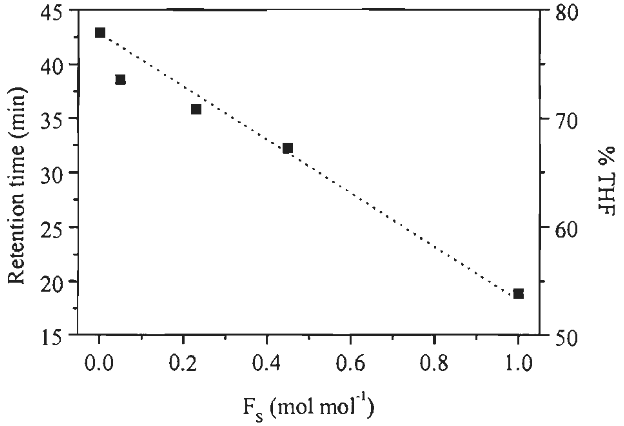


Figure 4.5: Calibration for the GPEC analysis of copolymers of styrene and butadiene. Retention time as a function of the styrene mole fraction in copolymer.

Characterisation of emulsion products

Two copolymers of S and B were prepared in emulsion and analysed in terms of CCD by means of GPEC with the system previously described. The recipes are summarised in Table 4.4. In experiment MSE6, the latex was prepared in the presence of acrylic acid and the final latex products were characterised in terms of acid group distribution. Since the polymer could not be completely dissolved in THF, no potentiometric titration could be carried out and only surface acid groups could be accurately quantified by means of surface titration, see section 4.2. The amount of AA groups incorporated on the surface of the latex particles, $C_{AAsurf.}$, is given in Table 4.4 as well.

For experiment MD8, samples were withdrawn from the reaction mixture at intermediate overall conversions to determine the CCD of the copolymer whereas the CCD of the copolymer formed in experiment MSE6 was determined for the final latex products only. The corresponding CCD curves are shown in Figure 4.6.

Table 4.4: *Ab-initio* Emulsion Copolymerisation of Styrene and Butadiene

Components	**MD8**	**MSE6**
S/B mole ratio	0.6/0.4	0.52/0.48
S/B/AA mole ratio	0.6/0.4/0	0.5/0.45/0.05
Fraction Solids	0.3	0.1
Sodium Dodecyl Sulfate (10^{-3} mol dm^{-3})	50	5
Sodium Persulfate (10^{-3} mol dm^{-3})	10	10
$C_{AAsurf.}$ (μeq $gpol^{-1}$)	0	170

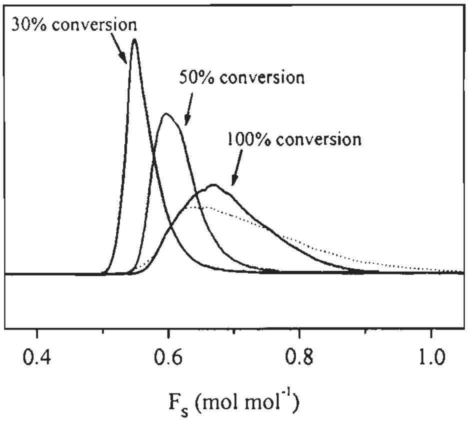


Figure 4.6: CCD of Emulsion Copolymers of Styrene Butadiene and Acrylic Acid. Influence of conversion and acid content.
— MD8, ··· MSE6. Conditions and recipes are given in Tables 4.4 and 4.5.

The copolymer formed at low conversion in experiment MD8 had a narrow CCD with a maximum peak height at F_S=0.55, see Figure 4.6 and Table 4.5. This value can be compared to the chemical composition calculated with the terminal copolymerisation model, see equation 5.19, and the reactivity ratios r_S=0.58 and r_B=1.35 reported in literature, see

Meehan [1946]. Figure 4.7 shows F_S the mole fraction of S momentary built into the copolymer as a function of f_S the mole fraction of free S at the locus of polymerisation. The copolymerisation of S and B is not ideal ($r_S.r_B=0.78$) and the occurrence of composition drift during copolymerisation is expected since B reacts faster in time than S. An initial F_S value of 0.50 can be expected for the experimental conditions of the study, see Table 4.4. This value is in good agreement with the value given by the GPEC analysis at low conversion.

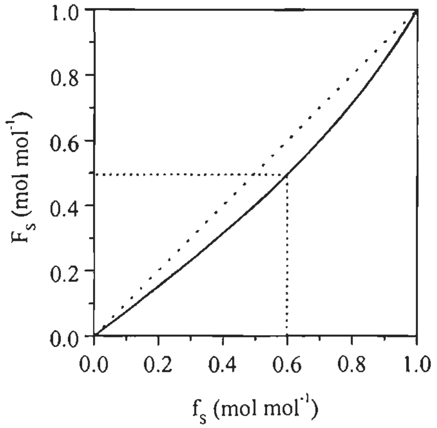


Figure 4.7: Copolymerisation of Styrene and Butadiene: instantaneous copolymer composition as a function of the mole fraction of the free monomer at the locus of polymerisation, calculated with terminal model and $r_S=0.58$, $r_B=1.35$, Meehan [1946].

A broadening of the CCD was observed as conversion increased in experiment MD8, see Figure 4.6. The CCD showed that the fraction of S built-in into the copolymer increased with conversion. This behaviour is caused by the occurrence of composition drift, see Figure 4.7. However, in addition to broadening, the whole CCD curve was shifting towards the S-rich area. The average S fraction in the copolymer was larger than that calculated from the recipe.

In order to get more information concerning the latex samples analysed by GPEC, the gel content in the samples (*i.e.* the fraction of insoluble crosslinked polymer) was measured by toluene extraction. The polymer was obtained by freeze-drying the latex. About one gram of the dry copolymer was then brought into a previously weighed Soxhlet thimble and extracted for 24 hours with Toluene (p.a., Merck) in a Soxhlet set-up. The amount of undissolved copolymer was determined by drying and weighing the thimble after extraction. Although it is difficult to extract the free polymer chains from the matrix of copolymer of infinite molecular mass, the method gives a good estimation of the gel fraction. The results given in Table 4.5 show that the polymer in the latex samples had a high gel content. The gel content was increasing with conversion up to very high levels.

Table 4.5: Emulsion Copolymerisation of Styrene and Butadiene. Copolymer composition and Gel Content. See recipes in Table 4.4

Latex	**Overall conversion (kg kg^{-1})**	**F_S peak (mol mol^{-1})**	**Gel fraction (kg kg^{-1})**
MD8-30	0.3	0.55	0.05
MD8-50	0.5	0.60	0.2
MD8-100	1	0.67	0.6
MSE6	1	0.63	0.6

Since only the soluble part of the polymer was analysed by means of GPEC, the resulting CCD was not representative for the whole corresponding latex sample. The results show that the CCD shift towards the S-rich copolymer region meaning that the soluble copolymer chains extracted from the latex samples were the ones with a large fraction of S units. This behaviour can be explained by the gel formation via crosslinking of the unsaturated bond in the B units.

Figure 4.6 shows the CCD of the copolymer in the latex product of experiment MSE6. The average chemical composition resulting from the CCD curve of the final product did not match the average composition following from the recipe, see Table 4.4. The CCD was very broad and slightly overlapped the value of $F_S=1$. Moreover, the lowest fraction of S in the copolymer detected by means of GPEC was 0.55 whereas the recipe gives an average S/B ratio of 0.52/0.48 which means that copolymer chains with S fractions lower than 0.52 have to be expected.

The selectivity of the analysis towards S-rich copolymer chains not incorporated into the insoluble crosslinked copolymer material was again the limiting factor for a reliable analysis of the copolymer formed during S, B, AA copolymerisation. The final polymer formed in experiment MSE6 had a very high gel content, see Table 4.5. No influence of the presence of AA groups in the copolymer on the CCD could be clearly recognised because observation of a possible effect of AA on the CCD is completely hampered by the crosslinked material in the samples. Although the amount of acid groups buried inside the latex particles was not quantified, some evidence was obtained for the presence of acid groups on the surface of the latex particles, see Table 4.4. AA groups incorporated into the SB copolymer chains may also have influenced the separation in GPEC giving additional interaction of the carboxylic acid functional groups with the column material and therefore contributing to the retarded elution of the emulsion polymer products. Other factors like the molecular weight distribution, the branching density, the nature of the polymer end groups can also considerably affect the interaction of the polymer chains with the stationary phase and therefore the separation.

4.5.4. GPEC on copolymers of Styrene and Acrylic Acid

The determination of the carboxylic acid group distribution gives relevant information about the formation of carboxylated latexes, see Chapter 2. However, the carboxylic acid group mass balance determined by titration gives no information about the chemical composition of the polymer chains bearing the carboxylic acid groups.

The separation of copolymer chains with GPEC is based on different elution times for homopolymers and the principle is straightforward for systems containing two monomers, see section 4.5.1. When S, B and AA monomer units are present in a terpolymer, a single linear calibration with SB copolymer standards is no longer valid and the interpretation of the GPEC chromatograms to obtain the CCD of a polymer sample is not possible. Furthermore, to get a better understanding of emulsion polymerisation processes in the presence of AA both S/B/AA and S/AA systems have been studied. Therefore, it was necessary to develop a proper GPEC analysis procedure applicable for both SBAA terpolymers and SAA copolymers.

The principle of the method we developed is based on a separation of the polymer chains by using a gradient optimised towards the AA content in the polymeric material only. This requires a system in which no distinction can be made between PS and PB in terms of retention behaviour. This is possible since the two homopolymers are similar in polarity as compared to PAA. In such a system, only the AA content has an influence on the retention time of the polymer molecules in the system and information can be obtained concerning the incorporation of AA units in the polymer chains. The development of the method requires:

- a proper combination of a stationary phase and an eluent system that allows co-elution of PS and PB as well as a different elution behaviour of PAA
- proper model compounds and calibration of the system
- investigation into the influence of the molecular weight distribution on the copolymer elution process
- robustness towards the analysis of emulsion co- and terpolymers of SAA and SBAA.

Method development

As already mentioned in section 4.5.1, a complete GPEC system consists of a column and a combination of a solvent (S) and a non-solvent (NS). In the present case the solvent system must allow the co-elution of PS and PB. Data on Cloud Point Composition (CPC) of PS and PB in different solvent combinations were therefore used to choose an appropriate solvent system, see Table 4.6. The gradient was then tested with PS, PB and PAA homopolymer standards.

Table 4.6: Cloud Point Composition (CPC) for Polystyrene and Polybutadiene standards*) determined by titrimetry. Source: Staal [1996]

Non-Solvent(NS)/Solvent(S)	**CPC PB % NS**	**CPC PS % NS**	**Δ% NS**
Acetonitrile/Tetrahydrofuran	26	58	32
Acetonitrile/Toluene	26	58	32
2-propanol/Tetrahydrofuran	48	53	5
Methanol/Chloroform	25	30	5
2-propanol/Chloroform	47	47	0
Water/Tetrahydrofuran	7	13	6

*) M_w: PB=120 10^3 $gmol^{-1}$, PS=200 10^3 $gmol^{-1}$.

System 1:

A gradient from 2-propanol to Chloroform on a C18 column was applied. PS and PB were co-eluted as expected whereas PAA showed no retention in the system. Some copolymer standards were analysed and promising results were obtained. Unfortunately after several sample injections the results were difficult to reproduce. Acid groups present in the samples probably interacted with the column material and altered the separation properties of the column.

System 2

The choice was then made for a completely hydrophobic organic styrene-divinylbenzene (SDVB) column with tetrahydrofuran (THF) as the solvent and water as the non-solvent (with regard to PS and PB). The eluent was acidified with 200 μl tetrafluoro acetic acid (TFA, Merck, p.a.), per dm^3 water. TFA is a very strong acid and ensured a complete protonation of the AA groups during the analysis. PS and PB standards were eluted in a reasonably narrow solvent composition range and so co-elution of the two homopolymers was closely approximated. In addition, PAA did not show any retention in the system whereas a little amount of AA in a copolymer with S had a tremendous influence on the retention behaviour. The following experimental conditions were used for further investigation: a SDVB column (styragel® from Waters, length 3 or 15 cm) operating at 35°C with a flow rate of 1 ml per minute. In Table 4.7 the applied gradient profiles are given.

Table 4.7: Gradient applied for the analysis of all S-AA copolymers

% S (THF)	**%NS (Water)**	**Time (min) 3 cm Column**	**Time (min) 15 cm Column**
75	25	0	0
100	0	25	33
100	0	30	38
75	25	35	40
75	25	40	60

Synthesis and characterisation of model compounds

SAA copolymer model compounds with a well defined narrow chemical composition distribution are needed as references to calibrate the GPEC system. Preparation of these copolymers was performed by low conversion bulk polymerisation with different AA fractions in the monomer feed, see Table 4.8.

Table 4.8: Model compound retention times in GPEC

	f_{AA} a)	F_{AA} b)	$F_{AA\,corr}$ c)	**Retention time (min) column 15cm**	**Retention time (min) column 3cm**
SAA2	0.03	0.13	0.09	22.8	15.3
SAA4	0.06	0.15	0.12	21.2	14.2
SAA6	0.09	0.21	0.17	19.4	12.6
SAA8	0.11	0.23	0.19	18.6	12.0
SAA10	0.14	0.29	0.22	17.5	13.3
SAA12	0.16	0.29	0.24	16.0	10.5
SAA20	0.26	0.38	0.33	13.9	8.6
SAA30	0.38	0.43	0.38	11.7	6.8
SAA40	0.48	0.48	0.40		
SAA90	0.93	0.68	0.62		

a) AA fraction in the monomer feed (mol mol^{-1})

b) fraction of AA built-in into the copolymer chains (mol mol^{-1}), results obtained by considering only one equivalence point in the titration curves

c) idem, correction is made for the presence of free AA unit in the samples

The general procedure for the synthesis is as follows: a mixture of freshly distilled S and AA was introduced together with α,α'-azoisobutyronitrile (AIBN, Fluka, p.a.) as initiator (0.1 wt% of the total reaction mixture) in a thermostated reaction vessel equipped with a reflux condenser. The reaction was carried out at 70°C in a nitrogen atmosphere for about 30 minutes. The polymerisation was stopped by pouring the reaction mixture in a large amount of heptane in which the formed polymer precipitated. The polymer was then redissolved in a mixture of acetone and ethanol (with various volume fractions of both solvents depending on the AA content in the copolymer) and precipitated with heptane again. This procedure was repeated twice. Finally, the copolymer was gently dried in a vacuum oven. The conversion was determined by gravimetry and never exceeded 5% in all cases.

For calibration of GPEC it was necessary to have the disposal of copolymers with a very narrow and accurate chemical composition distribution. A method based on conductometric titration was developed. This method is thought to be more accurate than other analytical methods like ^{1}H-NMR used by Kim [1990] to determine the AA fraction in the copolymer.

The dried copolymer (between 0.02 g and 0.2 g) was dissolved into 80 ml dimethylsulfoxide (DMSO, Merck). DMSO was a proper solvent for the titrations: all the copolymers were completely soluble in DMSO and the conductivity of the solutions could be measured accurately (conductometer model 160 with conductivity cell model 016010 from Orion). After an equilibration period, the polymer was titrated with increments of a 0.05 N solution of NaOH in methanol (calibrated with the potassium hydrogen phtalate procedure, see section 4.2) added with an automatic burette (model Dosimat 665 from Metrohm). A total of 15 ml NaOH solution was added stepwise and the conductivity was measured after a constant equilibration period following each addition (20 seconds). Some of the titration curves are shown in figure 4.8. The increase in conductivity during the titration followed the same trend for all the copolymers: fast at the beginning (slope AB in Figure 4.8), relatively small for the following additions (slope BC) and finally fast again (slope CD) after the complete neutralisation of all the acid groups.

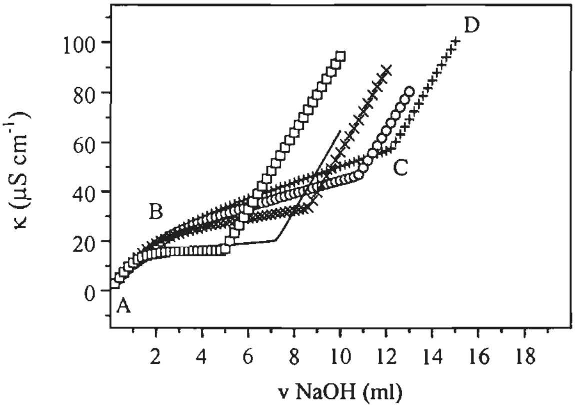


Figure 4.8: Bulk copolymerisation of styrene and acrylic acid. Conductometric titrations of the polymerisation products in DMSO. Acrylic acid fractions in the recipes: + 0.06, ○ 0.08, × 0.12, — 0.2, □ 0.4.

The presence of two equivalence points (B and C in Figure 4.8) was somewhat surprising. The first part of the curve corresponded actually to free AA in the sample. Indeed, AA is a stronger acid in the monomer from than when surrounded with other AA monomer units in a polymer chain, see Bloys van Treslong [1978]. Free AA units will therefore be titrated before AA built in a polymer chain. AA is actually known to give H-bonding, see Chapiro *et al.* [1977] and to be very difficult to remove from its own polymer. The purification of the copolymers after low conversion polymerisation might not have been sufficient to remove all the monomer units. To confirm this point, the conductometric titration of a copolymer sample was performed after the addition of 0.01 g of pure AA. The titration curves are shown in Figure 4.9.

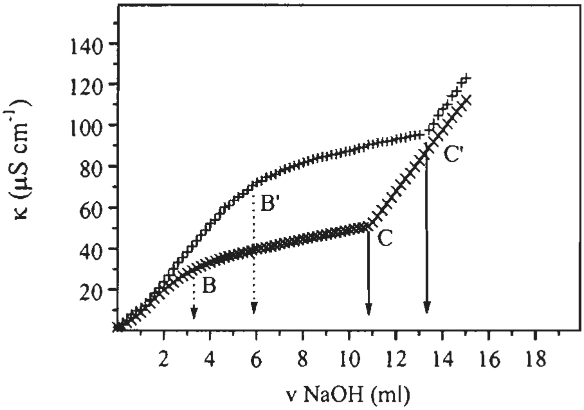


Figure 4.9: Conductometric titrations of styrene-acrylic acid bulk copolymers. Titration of: × polymer in DMSO, + polymer in DMSO with additional acrylic acid monomer.

The first equivalence point (B and B' in figure 4.9) shifted in perfect agreement with the amount of free AA added while the distance between the two equivalence points (BC and B'C') was not affected. An interesting point is that the method developed allowed the distinction between the two kinds of acid groups. An appropriate correction could therefore be made in the computation of the average chemical composition of the copolymers, see Table 4.8.

Accurate observation of the titration curves might even provide additional information. The slope in the intermediate part of the curves (slope BC in Figure 4.8) decreases with an increasing AA content in the copolymer. Since the slope of a titration curve can be related to the acid strength (dissociation constant) of the carboxylic acid groups it might perhaps be possible to disclose some information about the microstructure of the copolymers from the titration curves.

The low conversion bulk copolymerisation experiments of S and AA experiments performed to synthesise the model compounds were used to determine the reactivity ratios of the monomer pair S/AA. A wide range of S/AA molar ratios was used in the recipes so that a wide range of copolymer compositions was availble for both the calibration of the GPEC and the determination of reactivity ratios. It was realised that this method is not the best statistical method for parameter estimation according to Tidwell and Mortimer [1965]. The best estimation would be obtained by replicating experiments at two well-chosen monomer feed compositions. Furthermore, no attempt was made to discriminate between different copolymerisation models. In this case the terminal model was used, see Chapter 5.

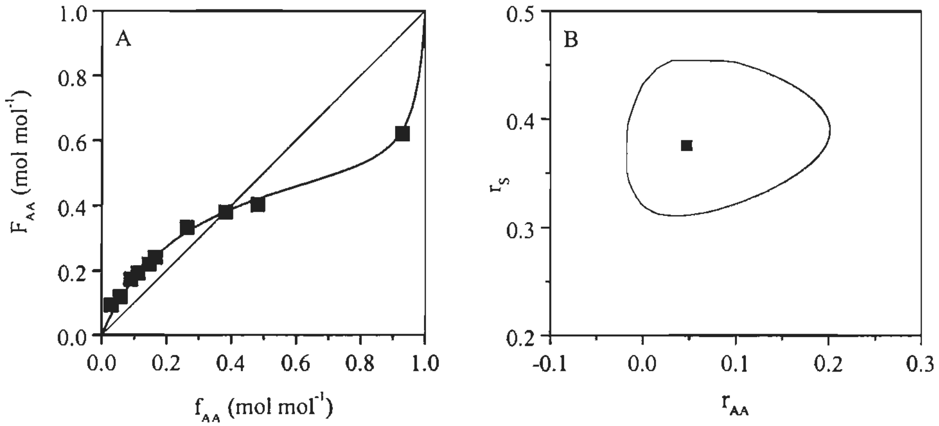


Figure 4.10: Bulk copolymerisation of Styrene and Acrylic Acid.
A: Instantaneous copolymer composition as a function of the mole fraction of the free monomer at the locus of polymerisation, experimental data and fitted line, calculation with terminal model. B: reactivity ratios and 95% joint confidence interval.

The program Contour based on the non-linear least-squares method, see van Herk [1995], was used to calculate reactivity ratios and joint confidence intervals from the data collected in Table 4.8. Figure 4.10 shows the reactivity ratios with the 95% confidence intervals, the experimental data and the fitted curve. The resulting values of r_{AA}=0.0473 and r_S=0.375 are in good agreement with the values reported in literature, see Table 4.9.

Table 4.9: Reactivity ratios for the monomer pair Styrene/Acrylic Acid in bulk

r_{AA}	r_S	**Reference**
0.0473	0.375	This study
0.04	0.4	Kim [1990]
0.07	0.25	Kerber [1966]
0.05	0.25	Ryabov *et al.*[1970]

The well defined S/AA copolymers were analysed with GPEC in the system previously described. The samples were dissolved in THF to a concentration of about 1 mg/ml and filtrated before injection. Figure 4.11 shows a collection of the GPEC chromatograms obtained with a column of 15 cm. In addition to the model compounds, homopolymers of AA ($M_w = 450\ 10^3$ gmol^{-1}, Aldrich) and S ($M_w = 156\ 10^3$ gmol^{-1}, Polymer Laboratories) were also analysed.

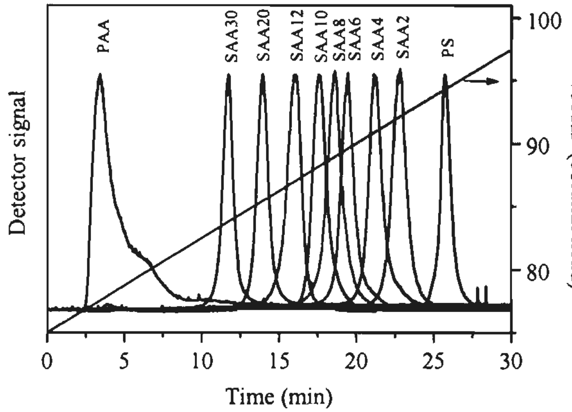


Figure 4.11: GPEC chromatograms of model compounds. Normalised detector signal and eluent composition as a function of analysis time. Column 15cm.

The separation was very good for most of the copolymers. Only the copolymers with a high AA fraction (PAA, SAA40 and SAA90 in Table 4.8) could not be separated. They did not show any retention in the column and all were eluted within few minutes. Figure 4.12 shows the copolymer retention times as a function of the chemical compositions for the two different columns. A linear relation between FAA and the retention time was observed for both columns. The calibration curves show that for $F_{AA} > 0.6$ no separation can be observed.

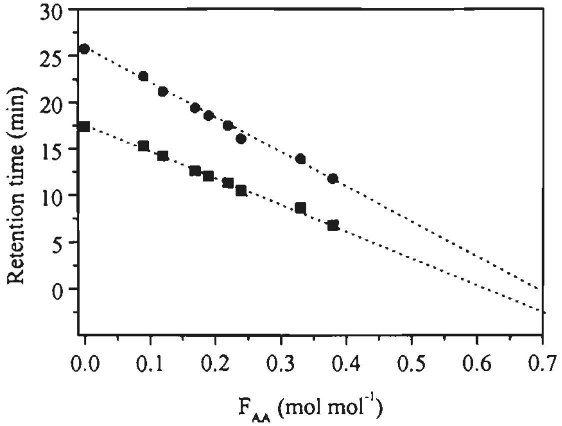


Figure 4.12: Calibration curve for the GPEC analysis of copolymers of styrene and acrylic acid. ■ column 3 cm, • column 15 cm.

Characterisation of solution polymers

Some solution copolymerisation experiments were carried out in dimethyl formamide (DMF) to investigate the influence of molecular weight on the elution behaviour of S-AA copolymers during GPEC analysis. Kim [1990] reported that the solution copolymerisation of S and AA could be carried out in DMF without precipitation. Figure 4.13 shows the instantaneous copolymer composition as a function of the free monomer composition, using the terminal model and the reactivity ratios found in literature for copolymerisation in DMF [Kim, 1990; Ryabov *et al.* 1970].

Note the difference between Figures 4.13 and 4.10 and the strong influence of solvent on the copolymerisation of S and AA. For low AA fractions in the free monomer (<0.2) the copolymer formed has about the same composition as the monomer feed and no composition drift occurs, see Figure 4.13. Therefore recipes with AA mole fractions lower than 0.2 were used to prepare copolymers for the investigation of molecular weight on elution behaviour during GPEC.

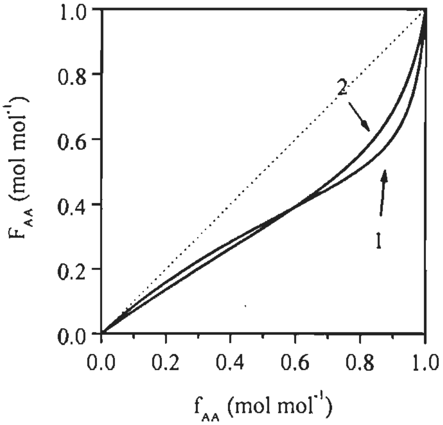


Figure 4.13: Solution Copolymerisation of Styrene and Acrylic Acid in DMF: instantaneous copolymer composition as a function of the mole fraction of the free monomer at the locus of polymerisation. Calculation with terminal model and different sets of reactivity ratios. 1: $r_{AA}=0.08$, $r_S=1.1$, 2: $r_{AA}=0.17$, $r_S=1.4$, see Table 4.9.

The solution polymerisation experiments were performed at 70°C with AIBN as initiator. Both the S/AA ratio in the recipe and the initiator concentration were varied. The experimental set-up used for the polymerisation experiments was similar to the one used for the preparation of the model compounds. An overview of the recipes is given in Table 4.10. The conversion was measured by gravimetry. For this purpose, samples were taken from the reaction mixture, weighed, poured in a mixture of water (4 parts) and methanol (1 part) to precipitate the polymer. The polymer was redissolved in acetone, precipitated again and gently dried in a vacuum oven before weighed again. Simultaneously, samples were taken for

CCD determination. No attempt was made to isolate the polymer and the whole sample was dissolved in THF before injection in the GPEC system. The molecular weight of the polymer products was measured by means of Gel Permeation Chromatography with the method developed by Loenen [1996]. The results are given in Table 4.10.

Table 4.10: Formulations of the batch solution copolymerisations of Styrene and Acrylic Acid in DMF. f_{AA} represents the AA fraction in the free monomer and M_w the weight average molecular weight of the final copolymer

Experiment	**DMF (g)**	**S (g)**	**AA (g)**	**AIBN (g)**	**T (°C)**	**f_{AA}**	**M_w (10^3 gmol^{-1})**
SOL3	144	62.0	2.3	1.61	70	0.05	20
SOL4	143	52.9	6.5	1.61	70	0.15	20
SOL5	145	124.0	4.7	0.80	75	0.05	50
SOL6	144	105.5	13.1	0.80	75	0.15	50

Figure 4.14 shows the GPEC chromatograms of the solution copolymers at different overall conversions. As expected, hardly any composition drift could be observed during the polymerisation and the CCD remained the same throughout the whole polymerisation process. In most cases, a peak could be observed in the first minutes of the analysis beyond the separation limits determined by the calibration curve, see Figure 4.12. This peak corresponded to free monomer still present in the samples directly withdrawn from the reaction mixture. As conversion increased the monomer peak decreased. The observed CCDs were in all cases in good agreement with the composition in the recipe.

The copolymer samples of experiment SOL4 were titrated and the AA content was calculated from the titration curves. The resulting F_{AA} values not corrected for the presence of free AA monomer units are compared with those obtained by GPEC at the maximum peak height in the chromatograms, see in Table 4.11. As already mentioned, the GPEC analysis did not show any significant composition drift and the copolymer compositions were in good agreement with the recipe at any conversion. The F_{AA} values obtained by titration were in good agreement with the ones obtained by GPEC except at low conversion where a significant difference was observed. This difference at low conversion was probably the result of the presence of free AA monomer units in the corresponding titration samples. Free AA monomer units do not interfere with the copolymer analysis in GPEC since they are not retained in the system and come out as a separate peak at the beginning of the gradient.

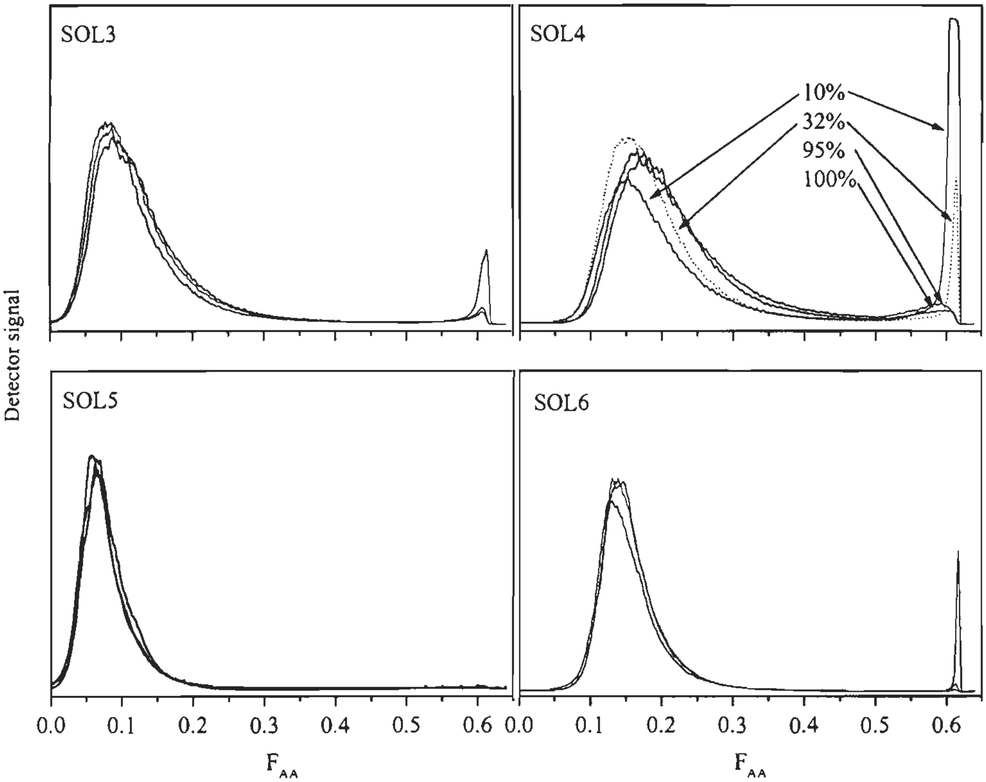


Figure 4.14: Solution copolymerisation of Styrene and Acrylic Acid in DMF. GPEC chromatograms as a function of conversion, see recipes in Table 4.10 and peak assignments in Table 4.11.

Table 4.11: Solution Copolymer Compositions determined by titration and GPEC.

Experiment	f_{AA}	Conversion	F_{AA} titration	$F_{AA\ peak}$ GPEC
SOL4	0.15	0.1	0.27	0.150
		0.32	0.18	0.153
		0.95	0.15	0.166
		1	0.15	0.172
SOL6	0.15	1	-	0.142
SOL3	0.05	1	-	0.093
SOL5	0.05	1	-	0.066

At equivalent molecular weights (experiments SOL3 and SOL4 or SOL5 and SOL6), the GPEC analysis is able to separate the copolymers according to chemical composition, see Table 4.11. However a significant influence of molecular weight on retention behaviour of copolymers with the same chemical composition but different molecular weights was observed, see Table 4.11 and Figure 4.15 which shows a collection of the chromatograms of all solution copolymers after complete conversion.

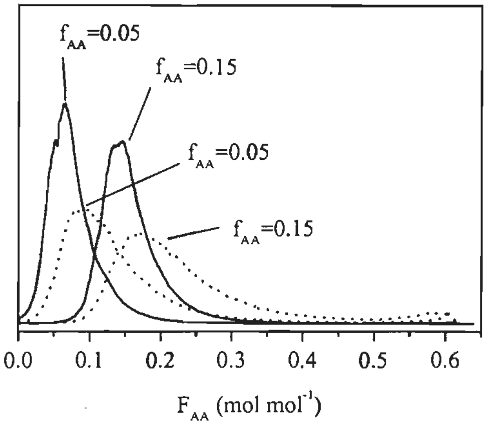


Figure 4.15: Solution Copolymerisation of Styrene and Acrylic Acid in DMF. CCD of polymerisation products after complete conversion.
— M_w=50 10^3gmol^{-1}, ··· M_w=20 10^3 gmol^{-1}.

Increasing the molecular weight at a given monomer composition in the recipe resulted in sharper peaks with a better approach to the chemical composition calculated from the recipe. The molecular weight of the model compounds was measured with the same method as for the solution copolymers and therefore the results could be qualitatively compared. All the model compounds showed a molecular weight between 120 10^3 and 250 10^3 g mol^{-1}. The calibration with model compounds was therefore probably more appropriate for the solution polymers with the largest molecular weight. This can explain the variation in F_{AA} obtained by GPEC for solution polymers differing in molecular weight only. This can also explain the broad CCD observed in GPEC for low molecular weight solution polymers.

The following concluding remark can be made: analysis of solution copolymers of S and AA by means of GPEC is possible but the observed CCDs are influenced by the molecular weight and molecular weight distribution of the polymer chains. This can be explained by the molecular weight dependency of a copolymer redissolution point in a mixture of solvent and non-solvent and by the additional interactions of the copolymer chains with the stationary phase after redissolution (adsorption, exclusion), see Klumperman *et al.* [1996]. Increasing the molecular weight of the copolymer resulted in an increase in the retention time (and as a consequence a decrease in F_{AA}). It indicates that in this particular case adsorption of the polymer chains on the stationary phase probably controlled their elution after redissolution.

Influence of molecular weight in GPEC

To investigate more into detail the influence of molecular mass on retention in GPEC, PS standards with a narrow molecular weight ranging from 1700 to 2.25 10^6 gmol^{-1} (Polymer

Laboratories, M_w/M_n=1.05) were analysed in the same system as the one used in the previous sections. The PS standards were dissolved in THF to a concentration of about 1mg ml^{-1} filtrated and injected in the GPEC system. Figure 4.16 shows a collection of the chromatograms. The peaks showed a significant broadening for low molecular masses and the retention time was very strongly molecular weight dependent. Figure 4.17 shows the retention time of the PS standards in the GPEC system (value at maximum peak height) as a function of their molecular mass, see data in Table 4.12.

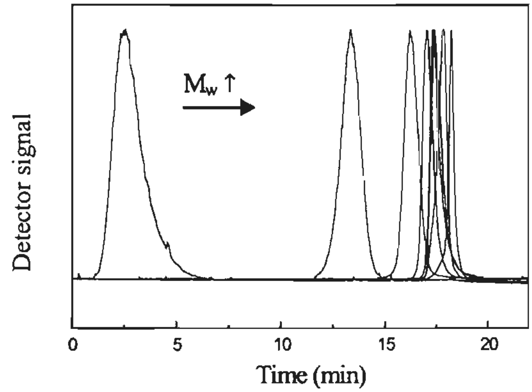


Figure 4.16: GPEC Chromatograms of Polystyrene Standards. Influence of molecular weight, see data in Table 4.12.

Table 4.12: Polystyrene Standards.

Mw ($gmol^{-1}$)	**Time (min)**
1.7 10^3	2.35
9.2 10^3	13.15
28.5 10^3	16.05
66 10^3	16.85
156 10^3	17.35
570 10^3	17.35
1.03 10^6	17.65
2.25 10^6	18

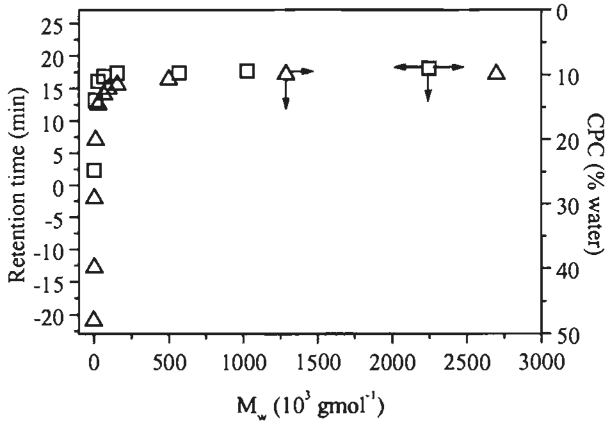


Figure 4.17: Polystyrene Standards. Influence of molecular weight on Cloud Point Composition in THF/water mixture and on retention time in GPEC.
□ this study, △ data from Staal [1996].

The retention time in the system can also be expressed in terms of eluent solvent composition passing through the detector This actually corresponds to the Cloud Point

Composition (CPC) of the eluting polymer. A correction for the gradient system time (t_{sys}) needs to be done. t_{sys} corresponds to the time interval necessary for the gradient to reach the detector. It was determined by looking at the UV absorption signal when the gradient was applied during a "blank" run in which no polymer was injected. The change in the eluent solvent composition resulted in a delayed variation in the baseline of the UV signal. The results obtained in this work are compared in Figure 4.17 with CPC values obtained by Staal [1996] for PS with various molecular weights in Water-THF mixtures.

The two sets of data are in very good agreement with each other. The molecular weight dependency of the CPC which affects the retention time in GPEC is very strong for molecular weight below 0.5 10^6 $gmol^{-1}$. In the molecular weight range from 10^5 to 10^6 $gmol^{-1}$, no significant influence of the molecular weight on the retention time in our system could be observed. A molecular weight range from 10^5 to 10^6 g mol^{-1} is therefore the most appropriate to study separation according to chemical composition only. Furthermore, the molecular weight of our model compounds fall into that range (between 120 10^3 and 250 10^3 $gmol^{-1}$) which makes the calibration curve reliable. Above a value of about 2 10^6 $gmol^{-1}$, the molecular weight influenced again the retention time in our system although no effect was reported concerning the CPC. The retarded elution of high molecular weight PS in our system limits the suitability of our method for the CCD determination of emulsion polymers with a commonly high molecular weight and a broad molecular weight distribution.

Characterisation of emulsion products

SAA emulsion copolymerisation experiments were carried out according to different reaction conditions and the resulting copolymers analysed by means of GPEC in the eluent/column combination previously described. An overview of the recipes and conditions is given in Tables 4.13 and 4.14.

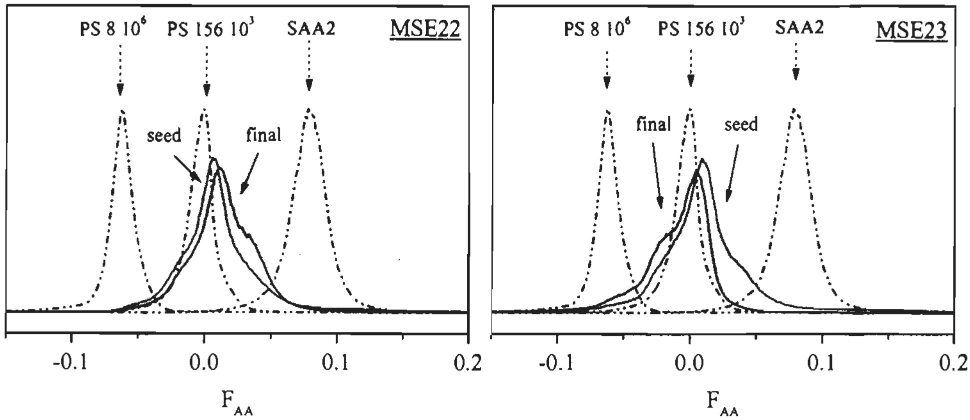
Table 4.13: Emulsion polymerisation of styrene and acrylic acid. Recipes are given in Table 4.14.

Latex	Experimental conditions
MSE22	Seeded emulsion polymerisation of S and AA
MSE23	Seeded emulsion polymerisation of S Addition of AA at an overall conversion of 0.9
MSE30	Semi continuous seeded emulsion polymerisation of S and AA AA mole fraction in the monomer feed = 0.083
MSE31	*Ab-initio* batch emulsion copolymerisation of S and AA

Table 4.14: Emulsion polymerisation of styrene and acrylic acid. Process conditions are given in Table 4.13.

Components (g)	**MSE22**	**MSE23**	**MSE30**	**MSE31**
Water	144	145	185	185
Polystyrene seed	30	30	4	0
Styrene	27	27	16	20
Acrylic acid	3	3	1	1
Sodium Persulfate	0.5	0.5	0.4	0.4
Sodium Dodecyl Sulfate	0.6	0.6	0.5	0.5
Temperature °C	70	70	60	60
Final solids fraction	0.3	0.3	0.1	0.1
Overall AA mole fraction	0.07	0.07	0.07	0.07

The CCDs of the emulsion products are shown in Figure 4.18. The chromatograms of two PS standards of different molecular weight and the SAA model compound with the lowest AA fraction are displayed as references in Figure 4.18 as well. The seed polymer in experiments MSE22 and MSE23 gave a broad peak probably due to a broad molecular weight distribution of the polymer. However, the peak corresponded to an AA fraction in the polymer of 0 (the seed material consists of PS only). The CCD of the final products in experiment MSE22 was even broader. The maximum peak height did not shift significantly from the one observed for the seed polymer. A shoulder in the AA region was observed which was due maybe to the presence of AA-containing copolymer chains but more probably to the molecular weight difference between the seed polymer and the polymer formed in the seeded experiment. In experiment MSE23, the CCD presented a shoulder in the region below the F_{AA} value of 0. This was probably due to the formation of very high molecular weight polymer as suggested by the elution behaviour of the high molecular weight PS standard. No clear evidence was therefore found in the CCD of the latex products for the presence of AA-rich copolymer chains. Neither the final products in experiment MSE31 nor the ones in experiment MSE30 showed any evidence in terms of effective AA incorporation in the copolymer chains. No effect of specific process conditions could therefore be observed on the CCD of emulsion copolymers of S and AA.



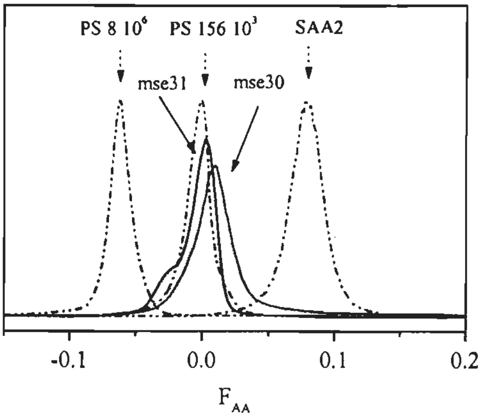


Figure 4.18: CCD of emulsion copolymers of styrene and acrylic acid, experiment MSE22, MSE23, MSE30 and MSE31.
— emulsion products
··· reference polymers.

Conditions and recipes are given in Tables 4.13 and 4.14.

The analysis of emulsion products by means of GPEC is not straightforward and is very strongly influenced by the broad molecular weight distribution of the copolymer chains. Few additional remarks can be made. Since the GPEC eluent/column combination we used is very sensitive to molecular weight and does not allow the separation of copolymers with high AA fractions, it is not suitable for the analysis of oligomers present in the water phase of the carboxylated latexes. The oligomers are likely to have a low molecular weight (< 20,000) and be rich in incorporated AA groups since otherwise they would not be water-soluble. The GPEC system we used in this work can therefore only be used for the analysis of the polymer present in the particle phase. An investigation of the mechanisms involved in the incorporation of AA in emulsion polymers will be given in the following chapters. Two main processes are responsible for the presence of AA in the particle phase of a latex:

- the copolymerisation of AA monomer units present in the monomer swollen latex particles
- the effective entry of AA-rich oligomeric radicals in the latex particles followed by further propagation in the monomer swollen polymer phase resulting in chemically anchored AA groups on the surface of the particles.The first process forms copolymers

similar to the ones obtained in bulk but the amount of AA present in the particle phase will be low due to partitioning reasons. The sensitivity of the GPEC system used to characterise the particle phase products should therefore be very high. The second process forms copolymers rich in AA at one side of the chain at least, the one which stretches out into the water phase. The influence of such a "block"-like structure on the separation of copolymer chains in a GPEC system should be investigated before any reliable analysis of emulsion polymers can be undertaken.

4.6. Conclusions

Conductometric aqueous and potentiometric non-aqueous titrations are powerful techniques for the determination of the acid group distribution in latex systems. Provided the latex products can be dissolved in a proper solvent for potentiometric titration, the complete mass balance in acid groups can be drawn from the combination of these two techniques. Therefore information can be obtained concerning the relative amounts of acid groups buried in the particle interior, chemically attached onto the particle surface and free in the aqueous phase. Contrary to non-aqueous potentiometric titrations, aqueous titrations of the surface groups can always be performed and give valuable insight into the efficiency of the acid incorporation into latex products at the preferred location with respect to the final latex properties.

Gradient Polymer Elution Chromatography was successfully used for the determination of chemical composition distribution of copolymers of styrene and butadiene and copolymers of styrene and acrylic acid. The accurate determination of the chemical composition distribution of the corresponding polymerisation products was hampered by the formation of crosslinked material during the polymerisation. Additionally, a significant influence of molecular weight on the separation of copolymers in GPEC was observed. Therefore, the analysis of emulsion products with low acrylic acid contents with GPEC could not be used in combination with acid group titration to obtain more information concerning the incorporation of carboxylic groups into latex products.

5

Kinetic Aspects in Emulsion Polymerisation with Carboxylic Monomers

ABSTRACT: This chapter supports the assumptions and simplifications used in a further discussion of the phenomena involved in the emulsion polymerisation with acrylic acid. After an overview of the dissociation behaviour of carboxylic monomers and their polymers in water, the propagation rate constant of methacrylic acid in water as a function of pH is determined. The combination of Pulsed Laser Polymerisation, esterification of polymer chains and Size Exclusion Chromatography generates valuable k_p data and confirms that an increase from pH 2 to pH 7 results in a significant decrease in k_p values (at 25°C $k_{p,pH\,2} = 3150$ dm^3 mol^{-1} s^{-1}, $k_{p,pH\,7} = 918$ dm^3 mol^{-1} s^{-1}). Next, the polymerisation kinetics during emulsion copolymerisation with acrylic acid is investigated. The copolymerisation terminal model is used together with acrylic acid partition coefficients to estimate the average propagation rate constant and the instantaneous copolymer composition in the particle phase and in the aqueous phase of emulsion systems. The results show that the role of acrylic acid in the particle phase is very small. On the other hand, the acrylic acid level and the pH have a significant influence on the formation of polymer in the aqueous phase.

5.1. Introduction

Due to their heterogeneous nature, emulsion polymerisation processes involve many kinetic events not only in the particle phase generally described as the main locus of polymerisation, but also in the aqueous phase. These fundamental reaction steps belong to the usual free radical polymerisation scheme and include initiation (generally in the aqueous phase), propagation, termination and transfer reactions. All these fundamental reation steps are individually characterised by a rate coefficient. The use of more than one monomer in emulsion recipes has a significant influence on the polymerisation scheme since all the monomers may differ in reactivity. Moreover, when one of the monomers is to a large extent soluble in water, the kinetic events in the aqueous phase become of particular interest. Therefore, valuable mechanistic information with respect to the various emulsion polymerisation processes including reaction rates and polymer composition can only be obtained if reliable kinetic parameters are known.

5.2. Influence of pH on the polymerisation of carboxylic monomers

5.2.1. Some features of carboxylic monomers

Numerous carboxylic monomers are commonly used as functional monomers in polymerisation processes. The present discussion will be limited to acrylic acid (AA, CH_2=CH–COOH) and methacrylic acid (MAA, CH_2=C(CH_3)–COOH) since these acids are the ones typically used in latex formulations. For the same reason, attention will be focused on water as solvent. Both AA and MAA are monomers which are completely miscible with water. AA and MAA can be polymerised via free-radical polymerisation. The polymers formed are water-soluble as well.

An important and fundamental characteristic of these functional monomers is the presence of a carboxylic acid group in the molecule which makes AA and MAA weak acids according to the Brønsted-Lowry theory. This carboxylic acid group provides the monomers and the corresponding polymers with special features. The carboxylic acid group in the monomer, polymer or free radical form in solution can ionise or dissociate by donating or transfering its H atom to a proton acceptor species, *i.e.* a base B, according to the following equilibrium between the acid-base conjugate pairs:

$$\text{-COOH} + \text{B} \rightleftharpoons \text{-COO}^- + \text{BH}^+ \quad (\text{K})$$

where K is the equilibrium constant of the reaction.

For solutions in water which can act as a base by accepting a proton from the carboxylic acid group, the equilibrium is rather described by the ionisation constant of the carboxylic acid group K_a defined by:

$$K_a = \frac{[COO^-][H_3O^+]}{[COOH]} \tag{5.1}$$

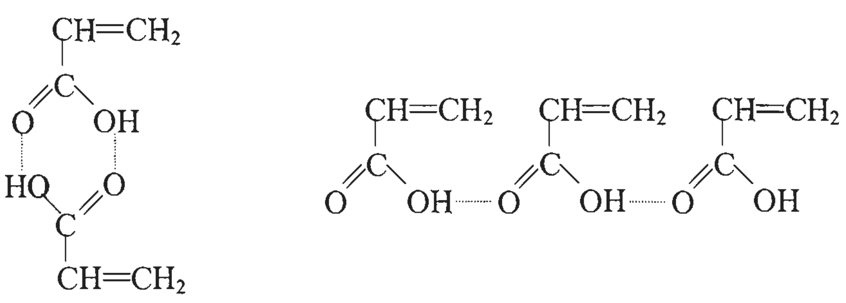
where [COOH] and [COO$^-$] are the concentrations of respectively protonated and ionised acid groups in solution and [H_3O^+] is the concentration of hydronium ions.

The extent of ionisation or degree of dissociation, α, is defined as the ratio of the concentration of the ionised form of the acid to the initial concentration of the non-ionised acid:

$$\alpha = \frac{[COO^-]}{[COOH]+[COO^-]} \tag{5.2}$$

The features of carboxylic acid monomers depend very much on their degree of dissociation since the ionised and non-ionised acid groups may differ in reactivity and hydrophilicity.

Additionally, it is well established [Davis *et al.*, 1960, Constant *et al.*, 1962 and Pimentel *et al.*, 1960] that carboxylic acids associate via hydrogen bonds to form cyclic or open oligomers as depicted in Figure 5.1. The hydrogen bonds exist in the polymers of carboxylic monomers as well, see Coleman *et al.* [1991] and Dong *et al.* [1997], and control the conformation of the polymer chains, see Davenport *et al.* [1980]. The association of monomer units with the carboxylic acid groups in polymer chains has been reported by Massif [1973] and the influence of the associated monomer units on polymerisation has been investigated by Chapiro *et al.* [1977]. Polymers of AA and MAA can be considered as polyacids and the hydrogen bonds eventually formed between adjacent pairs of carboxylic groups in the polymer chain can affect their dissociation constant. This behaviour known as the "neighbour effect" has a strong influence on the acidic properties *i.e.* on the probability to transfer the H atom [Annenkov *et al.*, 1998]



Cyclic dimer

Open oligomer

Figure 5.1: Associations of Acrylic Acid

5.2.2. Dissociation constants of carboxylic monomers and polymers

Combining Equations 5.1 and 5.2 results in a relation between pH, pK_a and α:

$$pH = pK_a - \log_{10}\left(\frac{1-\alpha}{\alpha}\right) \tag{5.3}$$

Equation 5.3 is one form of the Henderson-Hasselbach equation and is true in any solution in which COOH and COO^- groups coexist, *i.e.* $0 < \alpha < 1$.

It has been observed [Katchalsky *et al.*, 1947, Leyte *et al.*, 1964] that the behaviour of polyacids upon addition of strong base which reacts quantitatively with the acid groups cannot be described by Equation 5.3 unless an apparent pK_a value is defined:

$$pH = pK_a^{app.} - \log_{10}\left(\frac{1-\alpha}{\alpha}\right) \tag{5.4}$$

where $pK_a^{app.}$ is dependent on α. This result indicates that the ionisation behaviour of weak acid groups in a polymer chain depends on the overall degree of dissociation of macromolecule as a consequence of the "neighbour effect", see Bloys van Treslong [1978]. Leyte *et al.* [1964] and Mandel [1970] studied the potentiometric titration curves (pH as a function of α) of polyacrylic acid (PAA) and polymethacrylic acid (PMAA) and calculated $pK_a^{app.}$ as a function of α according to Equation 5.4. The plots in Figure 5.2 clearly show the dependence of the apparent dissociation constant on α.

Mandel [1970] reported that for PAA with a molecular weight below 10^6 $gmol^{-1}$, $pK_a^{app.}$ can be expressed by a second degree polynomial dependency on α:

$$pK_a^{app.} = pK_{a0} + \Phi_1\,\alpha + \Phi_2\,\alpha^2 \tag{5.5}$$

Mandel [1970] reported that the coefficients of the polynomial are strongly dependent on ionic strength and molecular weight, see Table 5.1, but only very moderately dependent on polymer concentration.

The behaviour of PMAA during potentiometric titrations is more complex because of the occurrence of a conformational transition from dense coil to expanded chain at a given degree of dissociation, see Arnold *et al.* [1950] and Leyte *et al.* [1964]. Each configuration can actually be characterised by a different relation between $pK_a^{app.}$ and α. This behaviour can clearly be seen in Figure 5.2. No general expression for $pK_a^{app.}$ that covers the whole range $0 < \alpha < 1$ could be found.

Table 5.1: Parameters for the calculation of $pK_a^{app.}$ for PAA and PMAA and true pK_a values of the corresponding monomers, see Kortüm *et al.* [1961], Leyte [1964] and Mandel [1970].

Polymer	**[polymer] (mol dm^{-3})$^{a)}$**	**[salt] (mol dm^{-3})**	**pK_{a0}**	**Φ_1**	**Φ_2**	**pK_a monomer**
PAA (790 10^3 g mol^{-1})	4.71 10^{-3}	0	5.2	4.3	-1.8	4.86
		3.3 10^{-3}	4.3	1	0.5	
PAA (120 10^3 g mol^{-1})	6.04 10^{-3}	0	4.8	3.8	-1.5	4.86
		5 10^{-3}	4.68	3	-0.8	
PMAA (870 10^3 g mol^{-1})	4.81 10^{-3}	3.3 10^{-3}	5.2			5.05
		1	5.1			

a) expressed in terms of monomer units

The $pK_a^{app.}$ dependence on α has a considerable influence on the co-existence of protonated and ionised acid groups in water as a function of pH. Figure 5.3 shows that the pH range corresponding to the co-existence of the two groups is much broader in the case of polymer molecules but is very much dependent on ionic strength and molecular weight.

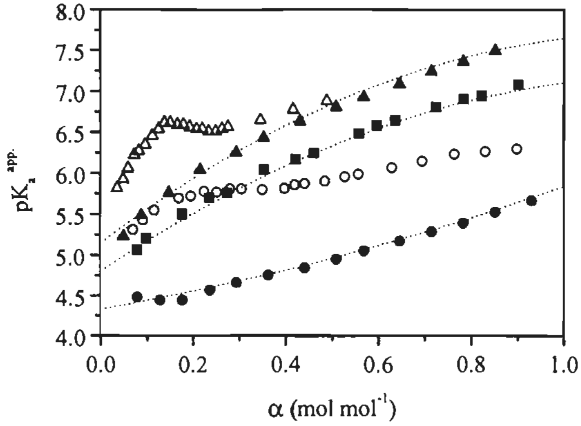


Figure 5.2: $pK_a^{app.}$ dependence on α for PAA and PMAA. Data obtained from Leyte *et al.* [1964] and Mandel [1970]. [PMAA] = 4.81 10^{-3} mol dm^{-3}, M_w = 870 10^3 g mol^{-1}, △: [$NaNO_3$] = 3.3 10^{-3} mol dm^{-3}; ○: [$NaNO_3$] = 1 mol dm^{-3}; [PAA] = 4.71 10^{-3} mol dm^{-3}, M_w = 790 10^3 g mol^{-1}, ▲: [$NaNO_3$] = 0 mol dm^{-3}, ●: [$NaNO_3$] = 3.3 10^{-3} mol dm^{-3}; [PAA] = 6.04 10^{-3} mol dm^{-3}, M_w = 120 10^3 g mol^{-1}, ■: [NaCl] = 0 mol dm^{-3}. The data for PAA are fitted with Equation 5.5, see parameters in Table 5.1 (dotted lines).

The extrapolation of the curves $pK_a^{app.}$ vs α in Figure 5.2 to α = 0 results in pK_{a0} values which can be compared to the dissociation constant of the carboxylic monomers, see Table 5.1. Since for $0 < \alpha < 1$, $pK_a < pK_a^{app.}$ the monomer can be considered as a stronger acid compared to the corresponding polymer. This consideration is of major importance when dealing with mixtures of monomers and polymers.

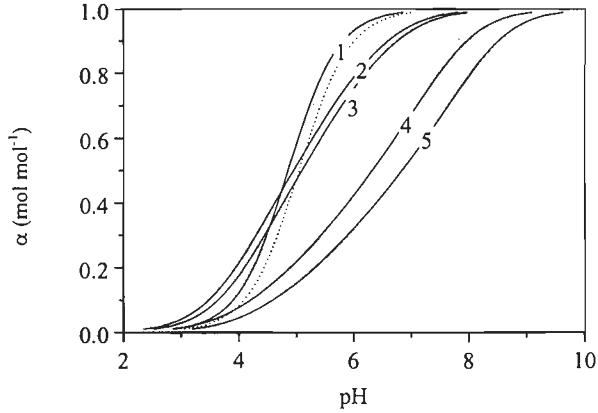


Figure 5.3: Degree of dissociation of carboxylic groups of acrylic acid and polyacrylic acid in water as a function of pH. Curves obtained with Equations 5.4 and 5.5 and parameters in Table 5.1. 1: monomer (dotted line : methacrylic acid); **2**: $M_w = 790\ 10^3$ g mol^{-1}, no salt added; 3: $M_w = 120\ 10^3$ g mol^{-1}, [NaCl] = 0.2 mol dm^{-3}; 4: $M_w = 120\ 10^3$ g mol^{-1}, no salt added; 5: $M_w = 790\ 10^3$ g mol^{-1}, [NaNO$_3$] = 3.3 10^{-3} mol dm^{-3}.

5.2.3. Potentiometric titration

The $pK_a^{app.}$ dependence on α can influence potentiometric titration curves. Figure 5.4 represents the expected evolution of the pH of an aqueous solution of AA or PAA upon addition of a strong base (NaOH). The parameter x is defined by:

$$x = \frac{n_{NaOH}}{n_{COOH\,tot}} \tag{5.6}$$

where n_{NaOH} is the amount of strong base added to neutralise the $n_{COOHtot}$ carboxylic acid groups (in polymer or monomer form) initially present in solution. The amount of carboxylic acid groups present in solution can also be expressed by the overall concentration C. The pH of the solution is calculated on the basis of conservation of mass and charge with the following equations:

$$K_a = \frac{[COO^-]\,[H_3O^+]}{[COOH]} \tag{5.1}$$

$$K_w = [H_3O^+]\,[OH^-] \tag{5.7}$$

$$C = [COOH] + [COO^-] \tag{5.8}$$

$$[Na^+] = C\,x \tag{5.9}$$

$$[Na^+] + [H_3O^+] = [COO^-] + [OH^-] \tag{5.10}$$

The titration curves are therefore described by the following situations:

- $x = 0$, $[OH^-] \ll [H^+]$ and $[COOH] \approx C$
  $$\alpha = 0 \text{ and } pH = 0.5\,(pK_a - \log_{10} C) \tag{5.11}$$
- $0 < x < 1$, $[OH^-] \ll [COO^-]$ and $[Na^+] \gg [H^+]$
  $$\alpha = x \text{ and } pH = pK_a - \log_{10}\left(\frac{1-x}{x}\right) \tag{5.12}$$
- $x = 1$, $[Na^+] \gg [H^+]$
  $$\alpha = 1 \text{ and } pH = 0.5\,(pK_w + pK_a + \log_{10} C) \tag{5.13}$$
- $x > 1$, $[Na^+] \gg [H^+]$ and $[OH^-] \gg [COOH]$
  $$\alpha = 1 \text{ and } pH = pK_w + \log_{10} C + \log_{10} (x-1) \tag{5.14}$$

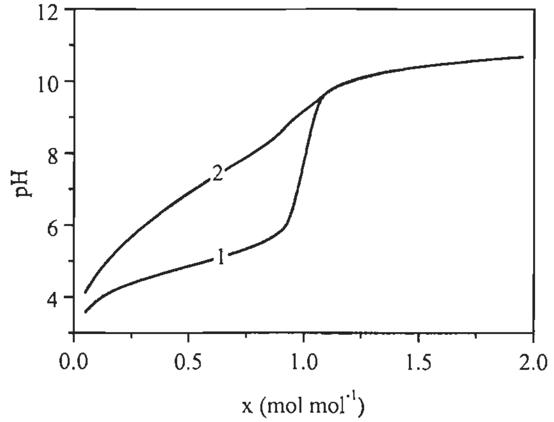


Figure 5.4: Simulated potentiometric titration curves of aqueous solutions of acrylic acid (1) and polyacrylic acid, $M_w = 790\ 10^3$ g mol^{-1}, (2). pH as a function of added NaOH as defined in Equation 5.6. Calculations with Equations 5.5, 5.11 to 5.14 and parameters given in Table 5.1 assuming no salt is present. Total concentration of carboxylic acid groups C is $5\ 10^{-4}$ mol dm^{-3}.

The pH vs x curves in Figure 5.4 have been calculated for $C = 5.10^{-4}$ mol dm^{-3} with Equations 5.5, 5.11 to 5.14 and the values given in Table 5.1 assuming no salt is present and $M_w = 790\ 10^3$ g mol^{-1}. K_w, the autoionisation constant of water is 10^{-14}. The slope of the titration curves shown in Figure 5.4 is strongly influenced by the type of acid. Polymeric acid shows a much steeper slope in the region corresponding to the consumption of the weak acid groups by the strong base ($0 < x < 1$) because of the apparent dissociation constant. As a result, a less pronounced pH-jump at the equivalence point ($x = 1$) can be observed. Experimental examples of this particular behaviour are given in Chapter 4. Note the sensitivity of x on the pH at the equivalence point where the first derivative of pH to x passes a maximum value.

5.2.4. Polymerisation of carboxylic monomers

The previously reviewed physico-chemical properties of carboxylic acid monomers and their polymers are very important to study the solution polymerisation of carboxylic acid monomers in water. The physico-chemical properties suggest that the carboxylic acid groups in a reaction mixture consisting of monomer units, polymer molecules and corresponding free radicals are in constant dynamic acid-base equilibrium. An overall degree of dissociation, α, as well as a degree of dissociation for the monomer, α_m, and for the polymer, α_p, should therefore be defined. As the polymer is a (somewhat) weaker acid than the monomer, see Figure 5.2, three main situations can occur during polymerisation depending on the overall degree of dissociation of all the acid groups in the reaction mixture:

- Case A: $pH < 5$, $0 < \alpha_m < 1$ and $\alpha_p = 0$

Dissociated monomer units are converted to protonated acid groups when incorporated into a polymer chain. Indeed, the monomer units behave as stronger acid than the polymer molecules and transfer their acidic hydrogen atom to the carboxylic groups in the polymer chains. Therefore, α_m increases with conversion. Since the monomer is present in two different forms this process can be regarded as a copolymerisation. Note however that the polymer formed is a homopolymer.

- Case B: $5 < pH < 8$, $\alpha_m = 1$ and $0 < \alpha_p < 1$

All the monomer units are completely in the dissociated anionic form and the arrangement of dissociated and protonated acid group in the polymer chains may vary with conversion. The nature (protonated or dissociated) of the polymer ultimate unit, *i.e.* the radical chain end, is a very important parameter since it may influence the incorporation of additional monomer units. Upon addition of a dissociated monomer unit, a protonated propagating radical may or may not transfer its proton to the new ultimate unit. The existence of a specific dissociation constant for the ultimate unit of the propagating radical may be considered, see Wojnarovits [1999], and the fraction of protonated end groups probably govern the polymerisation rate. The polymerisation resembles the homopolymerisation type although the resulting polymer is a copolymer. The pH range covered by Case B is very difficult to predict accurately since the dissociation behaviour of polyacids strongly depends on experimental conditions, see Figure 5.3. The ionic strength is expected to play a considerable role.

- Case C: pH > 8, $\alpha_m = 1$ and $\alpha_p = 1$.

Both monomer and polymer are completely dissociated and the influence of ionic strength and counterion type definitely have to be taken into account. The polymerisation resembles a conventional homopolymerisation.

The actual polymerisation behaviour of such a system is, of course, much more complex for the following main reasons. The above distinction between three cases implicitly assumes that the monomer is a stronger acid than the polymer, behaviour that in practice depends strongly on the experimental conditions. The transition situations where $\alpha_m \approx 1$ or $\alpha_p \approx 1$ are difficult to describe and achieve from an experimental point of view. The molecular weight dependence of $pK^{app.}$ and therefore α_p at a given pH should also be considered. Finally, solvent effects and the influence of e.g. hydrogen bonding and shielding of negative charges by positively charged ions are of considerable importance as well.

5.2.5. Influence of pH on polymerisation rate

Free-radical solution polymerisation of AA and MAA has been studied by several workers who reported the influence of reaction medium, see Galperina *et al.* [1975], Chapiro *et al.* [1977], Gromov *et al.* [1980], Plochocka [1981] and Gao *et al.* [1996]. The pH dependence of AA and MAA polymerisation rate in water has been investigated as well, see Katchalsky *et al.* [1951], Kabanov *et al.* [1971, 1973 and 1975], Guillot *et al.* [1990], Shoaf *et al.* [1991] and Anseth *et al.* [1996].

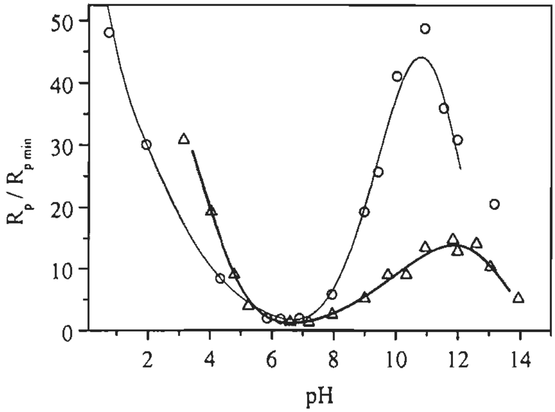


Figure 5.5: Polymerisation of carboxylic monomers in water. Influence of pH on the polymerisation rate. Reactions carried out with Methacrylic Acid (o) and Acrylic Acid (△) at 60°C with AIBN as initiator, see Kabanov *et al.* [1973].

Kabanov *et al.* [1973] studied the polymerisation of AA and MAA in water at 60°C in the pH range from 0 to 14. The pH was adjusted by the addition of strong acid or base. The reaction was initiated by AIBN using UV irradiation. The resulting relative polymerisation rates R_p/R_{pmin} as a function of pH are depicted in Figure 5.5. According to Kabanov *et al.*, the polymerisation behaviour upon addition of strong base follows successively Cases A, B and C described in section 5.2.3. The authors describe the reaction by assuming that there are three polymeric radical species (R_n) able to react with either the protonated (HA) or the dissociated (A^-) form of the monomer:

$$HR_n + HA \rightarrow HR_{n+1} \qquad (5.a)$$

$$R_n^- + HA \rightarrow R_{n+1}^- \qquad (5.b)$$

$$R_n^{-/+} + HA \rightarrow R_{n+1}^{-/+} \qquad (5.c)$$

$$HR_n + A^- \rightarrow HR_{n+1} \qquad (5.d)$$

$$R_n^{-/+} + A^- \rightarrow R_{n+1}^{-/+} \qquad (5.e)$$

$$R_n^- + A^- \rightarrow R_{n+1}^- \qquad (5.f)$$

where HR represents the protonated polymer radical (*i.e.* the propagating acid group is protonated), R^- represents the dissociated one and $R^{-/+}$ represents the radical associated with a cation e.g. Na^+.

According to Kabanov *et al.* [1973], reactions 5.a, 5.b and 5.c are dominant at low pH but when NaOH is added a larger amount of monomer becomes dissociated and the reactions 5.d, 5.e and 5.f contribute more and more to the overall polymerisation rate. The decrease in the polymerisation rate can therefore be attributed to a lower reactivity of the monomer in the dissociated form and the electrostatic repulsion between dissociated monomer and propagating radical, see Case B in section 5.2.3. At pH > 7, most of the acid groups are dissociated (α_m and $\alpha_p \approx 1$). The concept of "ion pair formation was suggested by the authors to interpret the increase in polymerisation rate observed experimentally. The "ion pair" formation is attributed to the binding of cations to the polyacid. It is the result of an increase in the local cation concentration in the vicinity of dissociated propagating radicals. The formation of such an ion pair might diminish the electron repulsion between the monomer and propagating radical and therefore increase the probability of further growth of the polymer chain, see Figure 5.6.

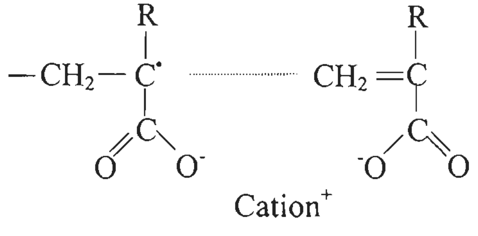


Figure 5.6: Ion-pair in the polymerisation of carboxylic monomers

The decrease in polymerisation rate observed at very high pH has to be related to the large amount of NaOH necessary to achieve the experimental conditions pH > 12, see Figure 5.4. The excess NaOH results in a considerable increase in the ionic strength and therefore in a decrease in the electronic interactions between all the species involved in the reaction mixture.

Several authors confirmed with their results the polymerisation scheme proposed by Kabanov *et al.*, see Manickam *et al.* [1979], Hruska *et al.* [1985] and Anseth *et al.* [1996]. Gao *et al.* [1996] used experimental results reported in literature and developed a model based on the theory proposed by Kabanov. These authors managed to simulate the polymerisation rate of AA in water in the range 1 < pH < 7. However, no model accounting for the "ion pair" formation process can be found. The polymerisation of carboxylic monomers in water is very complex and not yet fully understood. The complexity mainly arises from the numerous parameters involved in the process. In the present section the known influence of pH was discussed as well as the expected influence of ionic strength. Other parameters that have to be considered in an accurate and reliable study of the polymerisation of carboxylic monomers include the conformation of the polymer chains, the auto-association behaviour, *i.e.* H bonding, of the polymer and monomer, the monomer concentration and the counter-ion type. Finally, the modelling of the polymerisation rate is still hampered by the lack of information about the rate coefficients of the fundamental reaction steps controlling the process, *i.e.* propagation, termination, transfer, in relation to the above mentioned physico-chemical aspects.

5.2.6. Propagation rate coefficient of methacrylic acid homopolymerisation in water

On the basis of the discussion presented in section 5.2.4, the possibility to get more information concerning the polymerisation of carboxylic monomers in water as a function of their degree of dissociation was investigated. The work in this field was more specifically aimed at the determination of propagation rate constants by means of Pulsed Laser Polymerisation.

PLP/SEC

Pulsed Laser Polymerisation (PLP) combined with Size Exclusion Chromatography (SEC) is a powerful technique to investigate free radical polymerisation kinetics. PLP is more particularly useful for the accurate determination of propagation rate coefficients, see e.g. Buback *et al.* [1995] and van Herk [1997]. The polymerisation in a PLP experiment is initiated by radicals generated after irradiation with a laser pulse of a photoinitiator dissolved in a reaction mixture. After propagation, the so-formed polymer chains terminate with the freshly formed radicals generated by the subsequent laser pulses. The length of the polymer chains can therefore be directly related to the value of the propagation rate coefficient (k_p) provided the monomer concentration [M] and the time between two pulses τ are known:

$$L_i = i \cdot k_p \cdot [M] \cdot \tau \qquad (5.15)$$

L_i represents the chain length of the polymer formed by termination after i laser pulses. Note that growing chains can survive more than one subsequent pulses. Accurate determination of the polymer molecular weight distribution is therefore crucial for a successful application of this technique. It has been shown that the first inflection point on the low molecular mass side of the SEC curve actually corresponds the best to L_1, see Olaj *et al.* [1987]. A typical molecular weight distribution obtained in a PLP experiment is shown in Figure 5.7.

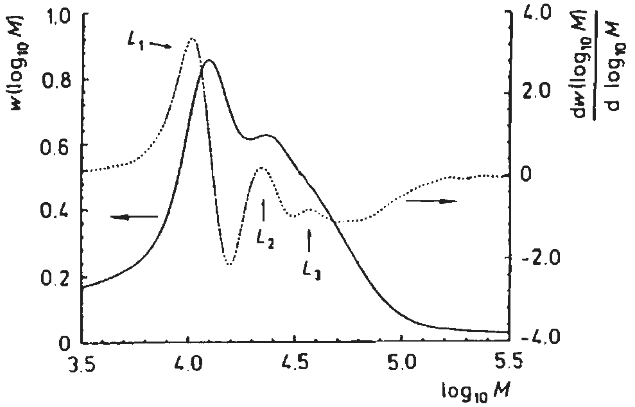


Figure 5.7: Molecular weight distribution of polystyrene obtained by PLP/SEC method. The overtone inflection points are indicated as maxima of the derivative. See Buback *et al.* [1995].

The polymerisation of methacrylic acid in organic solvents, *i.e.* methanol, tetrahydrofuran, acetic acid, iso-propanol and toluene, has been investigated with the PLP/SEC technique by Beuermann *et al.* [1997]. The use of the PLP/SEC technique to determine propagation rate constants of carboxylic monomers in water is possible and presents few requirements, see Loenen [1996] and Kuchta [1997]. One of the most important requirements concerns the SEC analysis of the polymer formed during the PLP experiment. Indeed, a conventional SEC setup operating with THF as eluent is not suitable for the polymer bearing very polar functional groups. The functional carboxylic acid groups adsorb on the stationary phase of the column and no accurate analysis can be done. Esterification of the carboxylic acid groups prior to SEC analysis provides good results since the analysis then concerns the corresponding methylmethacrylate polymer. A general procedure used for the methylation of carboxylic acid containing polymer is described in the following section.

Other requirements directly related to the polymerisation medium concern the type of photoinitiator used in the PLP experiment and the control of the ionic strength of the reaction mixture. The initiator should be active at the wavelength provided by the laser and should have a relatively high water solubility. Proper control of the pH, or more exactly the degree of dissociation of the acid groups, together with the ionic strength is of major importance since pH and ionic strength are expected to play a major role in the polymerisation behaviour, see section 5.2.5.

Kuchta [1997] reported additional problems when performing PLP experiments with AA in comparison to MAA. The determination of PAA molecular weight distributions was less straightforward. PLP experiments with AA required a very high pulse repetition rate to be sure that termination was controlled by successive laser pulses only and obtain the molecular weight distribution typical for PLP. MAA was therefore chosen for our investigation of the influence of pH on k_p.

Modification of carboxylic acid groups

Diazomethane (CH_2N_2) is the most common methylating reagent for carboxylic acids and has found wide application in the methylation of phenols, alcohols, enols and hetero-atoms such as nitrogen and sulfur, see Black [1983]. The most common and convenient method for generating diazomethane is the base-catalysed decomposition of N-methyl-N-nitroso-amines and amongst them N-methyl-N-nitroso-p-toluenesulfonamide (Diazald® from Aldrich, see Figure 5.8) which has good shelf life and can be handled safely.

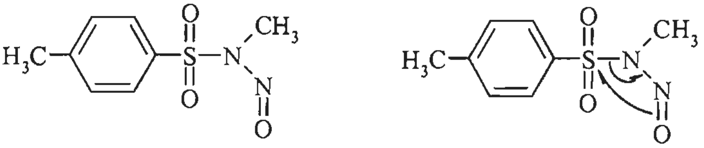
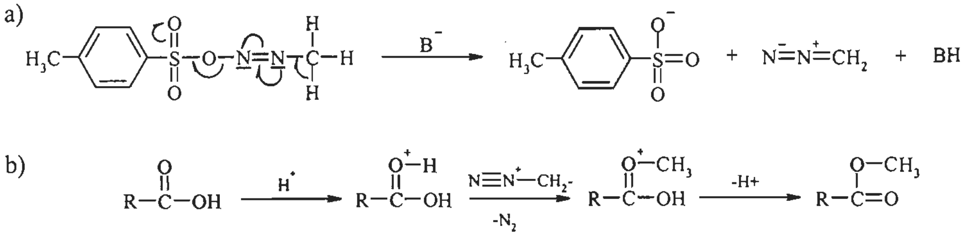


Figure 5.8: Diazald structure.

In the usual procedure described by Aldrich [1993], the diazomethane is generated in a special "Diazald Kit" glassware. A solution of Diazald in dry diethyl ether is slowly added to a solution of potassium hydroxide in a mixture of water and ethanol heated at 65°C. The reaction proceeds and a yellow solution of diazomethane in ether is slowly distilled, see reaction scheme 5.1a. Due to the high toxicity of diazomethane and since diazomethane is known to explode quite unexpectedly. Therefore rough surfaces have to be avoided and the reaction must be performed in a well-ventilated fumehood with an additional protecting screen. The solution of diazomethane in ether is added dropwise to a solution of the carboxylated polymer. Nitrogen is formed upon methylation of the carboxylic acid groups with diazomethane, see reaction scheme 5.1b. The solubility of the modified polymer strongly depends on its composition and proper solvent has to be used to avoid or at least to control the precipitation of the polymer chains upon the addition of the methylating agent. Mixtures of THF and methanol are generally used. The reaction is very fast and the addition of diazomethane is proceeded until the nitrogen generation stops and the polymer solution remains yellow. After about 15 minutes additional reaction time, the excess diazomethane in the polymer solution is destroyed with acetic acid.



Scheme 5.1: Generation of diazomethane from Diazald (a) and esterification of carboxylic acid groups (b).

In order to check the reaction yield, methylation was carried out on homopolymers of acrylic acid (M_w = 2000 g mol^{-1} and M_w = 450 10^3 g mol^{-1}, Aldrich) and on a copolymer of styrene and acrylic acid obtained by low conversion bulk polymerisation. The copolymer was used as model compound in the development of Gradient Polymer Elution Chromatography, see Chapter 4, and was characterised in terms of acid content by means of non-aqueous titration, see 4.5.4., before and after methylation. Titration of the polymers after methylation did not provide any evidence for the presence of carboxylic acid groups. Furthermore, infra-red spectra of the copolymer before and after methylation were recorded on a Mattson Polaris FT-IR spectrometer. The results obtained by titration and FT-IR spectroscopy showed that the methylation of the carboxylic acid groups in acrylic acid homopolymers and co-polymers with styrene was complete within the detection limits of these techniques. The effect of the eventually not methylated carboxylic acid groups in the polymer on the SEC analysis is therefore negligible.

SEC analysis was performed on the methylated compounds. The SEC setup consisted of a Waters 510 pump, a Waters autosampler (WISP 712), four columns Plgel MIXED-B (Polymer Laboratories, 10μm, 300*7.5 mm, 40°C) and a Waters 410 differential refractometer (40°C). THF (stabilised, Biosolve, A.R.) was used as eluent at a flow rate of 1 ml min^{-1}. Narrow molecular weight polystyrene standards (Polymer Laboratories) were used to calibrate the system. The molecular weights of the methylated polyacrylic acid samples corresponded well with the values given by the supplier. For the copolymer of styrene and acrylic acid, a weight average molecular weight (M_w) of 290 10^3 g mol^{-1} and a polydispersity of 1.86 were found. These values agree with those reported in Chapter 4 section 4.5.4.

PLP experiments

Methacrylic acid (MAA, Aldrich) was distilled under reduced pressure. To avoid polymerisation during the distillation, the distillation column was fitted with copper wires and copper powder was added to the distillation vessel. Distilled deionised water was used to prepare the solutions of MAA and initiator. 2,2-dimethoxy-1,2-diphenylethane-1-one (Irgacure 651, Ciba-Geigy) was used as initiator for which a water solubility of 2.5 10^{-4} mol dm^{-3} at 20°C was measured. Accurate amounts of sodium hydroxide were added to the solutions to vary the degree of dissociation α of the carboxylic acid groups in the initial reaction mixture, see Equation 5.2.

Since NaOH reacts quantitatively with the acid groups, Equation 5.2 can also be written:

$$\alpha = \frac{n_{NaOH}}{V.C} \tag{5.16}$$

where n_{NaOH} is the amount of NaOH added (mol), V is the volume of the solution and C the overall concentration of carboxylic groups.

Stock solutions were prepared with V = 100 ml, C = 1.8 mol dm^{-3} and an initiator concentration of 1.7 10^{-3} mol dm^{-3}. The pH of the reaction mixture was measured as an indication of the degree of dissociation. The ionic strength was adjusted with NaCl over the whole range of α and approximated by the total concentration in sodium ions. The monomer solutions were prepared in opaque flasks and purged with argon to remove oxygen prior to polymerisation. The PLP experiments were performed with a Lambda Physik LPX 110iMC excimer laser operating at the XeF line at 351 nm with a pulse width of 20 ns. The polymerisations were carried out in a quartz cell directly placed in the laser beam and thermostated at a temperature of 25.0 $\mp$ 0.1 °C. The energy per pulse was set at 50mJ, the pulse frequency was 20 Hz and the reaction time was chosen between 20 and 40s. After polymerisation, hydroquinone (Merck, fotopur) was added as inhibitor to avoid post polymerisation. The samples prepared at an initial degree of dissociation $\alpha > 0$ were acidified with a 1N solution of HCl in water to ensure complete protonation of all the acid groups and therefore a complete solubility and a proper reactivity of the polymer chains during the methylation step. Residual monomer and water were evaporated in a vacuum oven at 50°C. The conversion was measured by gravimetry and never exceeded 7%. The polymer was redissolved in mixtures of THF and methanol and subsequently methylated with diazomethane.

A good control of the degree of dissociation and the ionic strength is of great concern in this study. However, it is very difficult to combine all the prerequisites for a reliable interpretation of the PLP experiments. The conversion should be kept low to allow the approximation C = [M] in Equation 5.15. The monomer concentration should therefore be high enough to obtain a sufficient amount polymer for analysis. Note that the volume of the PLP cell is about 10^{-3} dm^{-3}. A high monomer concentration requires larger amounts of NaOH for neutralisation and therefore higher ionic strengths are involved. With a monomer concentration of 1.8 mol dm^{-3}, an ionic strength ($[Na^+]$) of 1.8 mol dm^{-3} is reached upon complete neutralisation of the acid with NaOH *i.e.* $\alpha = 1$. This means that the investigation of the influence of pH on k_p at constant ionic strength requires sodium ion concentrations of about 2 mol dm^{-3} throughout the whole pH range studied. For polymerisations performed at $\alpha < 1$, a constant sodium ion concentration of 1.8 mol dm^{-3} should therefore be used.

This was the main problem to cope with during the experiments. For $\alpha = 0$ *i.e.* completely protonated methacrylic acid, the addition of NaCl to control the ionic strength resulted in a separation of the reaction mixture into an aqueous phase and an organic phase (salting out effect) which impeded any PLP experiment. Therefore the highest NaCl concentration at which no phase separation occurred was measured. For a concentration of MAA in water of 1.8 mol dm^{-3} (15.5 wt %), $[Na^+]_{max} = 0.7$ mol dm^{-3}. The PLP experiments were therefore divided into two series: one series with $0 < \alpha < 1$ with $[Na^+] = 0.68$ mol dm^{-3} and one series with $\alpha = 1$ and $[Na^+] = 2$ mol dm^{-3}. In the series with $\alpha = 1$ the pH was varied between 6 and 11 by addition of NaOH. An overview of all the recipes is given in Table 5.2. The pH was measured with a calibrated pH meter (Orion Research).

Table 5.2. PLP experiments, recipes

Experiment	**NaOH added** (mol dm^{-3})	**NaCl added** (mol dm^{-3})	α	**Initial pH** (measured)	**$[Na^+]$** (mol dm^{-3})
01	0	0	0	2.3	0
31	0	0.67	0	2.0	0.7
32	0.04	0.64	0.02	2.7	0.7
33	0.10	0.58	0.05	3.1	0.7
34	0.30	0.38	0.15	3.6	0.7
35	0.70	0	0.40	4.1	0.7
22	1.50	0.5	0.85	5.2	2.0
23	1.70	0.30	0.95	5.8	2.0
25	1.80	0.20	1	6.6	2.0
26	1.82	0.20	1	9.4	2.0
27	1.83	0.20	1	10.7	2.0

Results and Discussion

After methylation all the polymer samples were analysed by SEC, see conditions described for the esterification check. The SEC chromatograms were converted into a differential weight distribution on logarithmic weight scale ($w(\log_{10}M)$ vs $\log_{10}M$) according to a computer program developed by Manders [1997], see Figures 5.9 and 5.10. The molecular weight distributions all exhibited the features of a PLP experiment. The shoulder on the low molecular weight side which indicates the free radical termination between two successive pulses was however more pronounced and additional overtone appeared clearly for the series performed with the lowest sodium ion concentration and pH < 7.

The peak maxima of the first derivative gave L_i values which were used together with Equation 5.1 to calculate k_p. The results are summarised in Table 5.3. Due to the shape of the distribution at a sodium ion concentration of 2 mol dm^{-3}, only L_1 was taken into account.

The results presented in Table 5.3 and Figure 5.11 confirm that the propagation rate constant for the polymerisation of MAA in water strongly depends on the degree of dissociation and therefore on the pH of the reaction mixture. The values we obtained for the propagation rate constant of MAA in water at 25°C are in good agreement with those reported in literature, see Table 5.4.

Table 5.3: Propagation rate constant of methacrylic acid in water at 25°C.
[MAA] = 1.8 mol dm^{-3}, [initiator] = 1.7 10^{-3} mol dm^{-3}, laser pulse repetition rate = 20 Hz and energy = 50 mJ, polymerisation time = 20 s

Experiment	**pH**	**[Na^+]** mol dm^{-3}	**L_i**	**k_p** dm^3 mol^{-1} s^{-1}
01	2.3	0	$L_1 = 284$	3260
			$L_2 = 577$	3316
			$L_3 = 920$	3524
31	2.0	0.7	$L_1 = 288$	3199
			$L_2 = 579$	3219
			$L_3 = 827$	3062
32	2.7	0.7	$L_1 = 284$	3155
			$L_2 = 583$	3238
			$L_3 = 823$	3049
33	3.1	0.7	$L_1 = 293$	3251
			$L_2 = 606$	3365
			$L_3 = 907$	3359
34	3.6	0.7	$L_1 = 281$	3121
			$L_2 = 571$	3173
			$L_3 = 954$	3533
35	4.1	0.7	$L_1 = 248$	2760
			$L_2 = 516$	2868
			$L_3 = 797$	2954
22	5.2	2.0	$L_1 = 163$	1811
23	5.8	2.0	$L_1 = 109$	1216
25	6.6	2.0	$L_1 = 83$	918
26	9.4	2.0	$L_1 = 178$	1974
27	10.7	2.0	$L_1 = 236$	2626

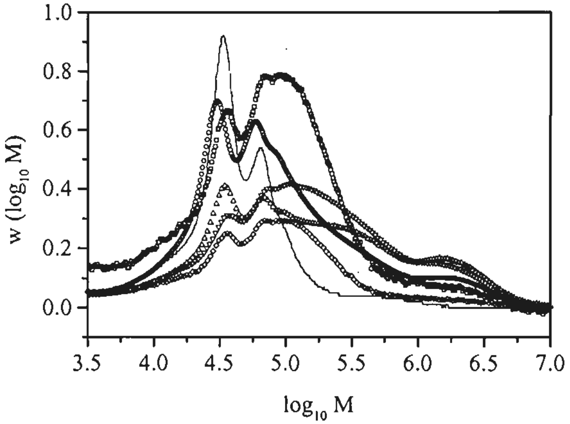


Figure 5.9: Molecular weight distributions (MWD) of polymer formed in a pulsed laser polymerisation of methacrylic acid in water at (25±0.1)°C after methylation to polymethyl-methacrylate. Influence of pH on the MWD. The laser pulse repetition rate is 20Hz, laser pulse energy 50mJ, initiator concentration 1.7 mol dm^{-3}, monomer concentration 1.8 mol dm^{-3}, sodium cation concentration 0.7 mol dm^{-3} and the pH varies between 2.0 and 4.1. Experiments numbers :- 01, □ 31, ◇ 32, ▽ 33, △ 34, ○ 35.

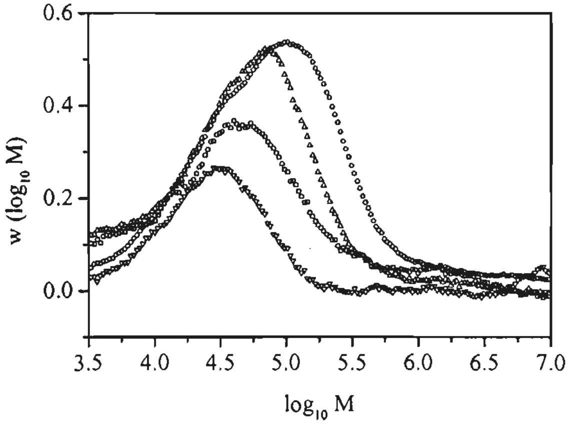


Figure 5.10: Molecular weight distributions (MWD) of polymer formed in a pulsed laser polymerisation of methacrylic acid in water at (25±0.1)°C after methylation to polymethyl-methacrylate. Influence of pH on the MWD. The laser pulse repetition rate is 20Hz, laser pulse energy 50mJ, initiator concentration 1.7 mol dm^{-3}, monomer concentration 1.8 mol dm^{-3}, sodium cation concentration 2 mol dm^{-3} and the pH varies between 5.8 and 10.7. Experiments numbers: □ 23, △ 25, ○ 26, ▽ 27

Below pH 3.5, there is no evidence for the influence of pH on k_p. In these conditions of pH, the fraction of protonated acid groups in both the monomer and the polymer form is higher than 80%, see Figure 5.3. An additional experiment, see experiment 01 in Table 5.2, was performed at pH 2.3 without any addition of NaCl. The resulting k_p value was not significantly different from that obtained at the same pH and a sodium ion concentration of

0.7 mol dm^{-3}. This behaviour indicates that ionic species in a system with α_m and α_p close or equal to zero have hardly any influence on k_p.

At pH ~ 4, k_p slightly decreased. This result is in good agreement with a significant degree of dissociation of the carboxylic monomer, $\alpha_m \neq 0$, and the expected lower reactivity of the dissociated monomer. The decrease in k_p is further observed when pH increases from 4 to 7. In this pH range, $0 < \alpha < 1$, α_m increases but we expect α_p close to zero as long as $\alpha_m \neq 1$. Therefore, the polymerisation between a protonated radical and dissociated monomer units becomes dominant. The apparent continuity in k_p between the series performed at [Na$^+$] = 0.7 (pH < 4) and 2.0 mol dm^{-3} (pH > 5) has to be interpreted with care but is consistent with the limited influence of ionic species on k_p observed at low pH. For pH > 7, all acid groups are initially completely dissociated, $\alpha = 1$. An increase in k_p with pH has been observed, see Figure 5.11. This increase of k_p with increasing pH is in line with the results reported by Plochocka [1981]. However, in our experiments, the occurrence of "ion pair" formation between dissociated species and cations in solution upon increasing pH from 6 to 10 is questionable since the sodium ion concentration was kept constant by the addition of NaCl to the reaction mixture. The increase in k_p with increasing pH is therefore difficult to relate to variations in the ionic strength of the reaction mixture

Table 5.4: Reported k_p values for methacrylic acid in water at a temperature of about 25°C.

k_p (dm^3 mol^{-1} s^{-1})	pH	[M] mol dm^{-3}	Reference
4100	2.5 (estimation)	0.3-0.5	Gromov *et al.* [1980]
3940	2.5 (estimation)	1.7	Kuchta [1997]
670	8.6	0.92	Kabanov *et al.* [1973]
1950	13.6	0.92	"
3150	2.7	1.8	This study
1974	9.4	1.8	"
2626	10.7	1.8	"

No clear evidence for the occurrence of "ion pair formation" can be observed in our results. The present work nevertheless points to a dominant role of dissociation equilibria in the polymerisation behaviour of carboxylic monomers. However, the results obtained at pH > 6 have to be cautiously interpreted. Indeed, the PLP products obtained at pH > 6 were difficult to analyse and characterise. We observed that some polymerisation products could remain trapped in the NaCl precipitate formed when preparing the samples for methylation. It is therefore difficult to ensure the non-selectivity of the whole procedure. The differences observed in the SEC analysis of the polymer formed at low and intermediate pH, see Figures 5.9 and 5.10, can eventually be a consequence of the difficulties met during the isolation of the product after the PLP experiment. Further investigation should include the development of an accurate and reliable analytical procedure to characterise the polymerisation products. Experiments should then be designed to investigate the influence of polymer chain conformations and cation type and to determine the nature of the propagating radical.

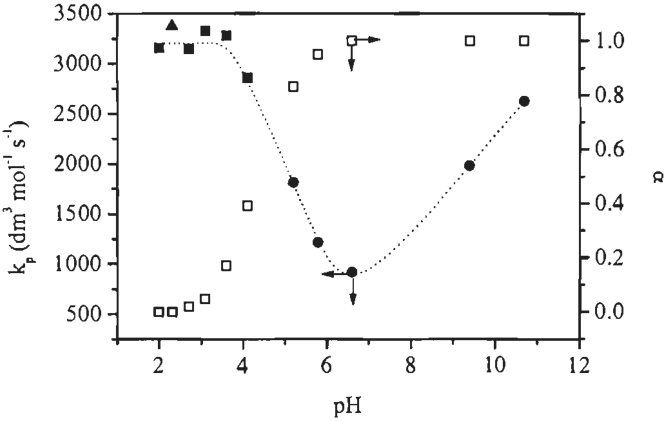


Figure 5.11: Polymerisation of methacrylic acid in water at 25°C determined by the PLP/SEC technique. Influence of pH on k_p. The laser pulse repetition rate is 20Hz, laser pulse energy 50mJ, initiator concentration 1.7 mol dm^{-3}, monomer concentration 1.8 mol dm^{-3}, sodium ion concentration 0 (▲), 0.7 (■) and 2 (●) mol dm^{-3}. The open symbols represent the initial overall degree of dissociation. Recipes, see Table 5.2.

The results obtained by PLP on methacrylic acid confirm the influence of pH on the polymerisation behaviour and more particularly on the propagation rate constant of carboxylic acid monomers in water. This subject is of major interest for the proper understanding of the kinetic events taking place during emulsion polymerisation. We generally performed emulsion polymerisation experiments at the two different but well-defined pH values of 2.5 and 7. The PLP results qualitatively confirm that the k_p of acrylic acid can be expected to be much higher at low pH than at intermediate pH. The consequence of this behaviour will be discussed in the following section.

5.3. Estimation of average propagation rate constants and copolymer composition in emulsion systems containing acrylic acid

5.3.1 Copolymerisation kinetics

The most frequently used model describing copolymerisation kinetics and copolymer chemical composition is the terminal model introduced and developed by Alfrey and Goldfinger [1944] and Mayo and Lewis [1944]. The model is based on an ultimate kinetic scheme, see Table 5.5.

Table 5.5: Copolymerisation scheme according to the terminal model

Terminal group	Added monomer	Rate	Result
$\sim M_i^\bullet$	M_i	$k_{p,ii}\,[M_i^\bullet]\,[M_i]$	$\sim M_iM_i^\bullet$
$\sim M_i^\bullet$	M_j	$k_{p,ij}\,[M_i^\bullet]\,[M_j]$	$\sim M_iM_j^\bullet$
$\sim M_j^\bullet$	M_i	$k_{p,ji}\,[M_j^\bullet]\,[M_i]$	$\sim M_jM_i^\bullet$
$\sim M_j^\bullet$	M_j	$k_{p,jj}\,[M_j^\bullet]\,[M_j]$	$\sim M_jM_j^\bullet$

The monomer addition to a radical chain only depends on the nature of the radical end group, *i.e.* terminal or ultimate unit, and the propagating monomer. The reactivity ratios of the monomers i and j are defined as:

$$r_i = \frac{k_{p,ii}}{k_{p,ij}} \tag{5.17}$$

and

$$r_j = \frac{k_{p,jj}}{k_{p,ji}} \tag{5.18}$$

where $k_{p,ii}$ is the propagation rate coefficient for homopolymerisation of monomer i and $k_{p,ij}$ is the rate coefficient for propagation of a terminal unit i with monomer j.

Combining the equations for monomer consumption and a steady-state assumption for the radicals, the instantaneous copolymerisation equation can be derived:

$$F_i = \frac{r_i f_i^2 + f_i f_j}{r_i f_i^2 + 2 f_i f_j + r_j f_j^2} \tag{5.19}$$

where F_i and f_i are the instantaneous mole fractions of monomer i units in the formed copolymer and in the locus of polymerisation. In general, as a result of the different reactivities of the monomers involved, $F_i \neq f_i$ and the composition of the monomer feed and the copolymer formed changes with conversion. This behaviour is referred to as "composition drift".

The average propagation rate constant $\bar{k}_p$ is given by:

$$\bar{k}_p = \frac{r_i f_i^2 + 2 f_i f_j + r_j f_j^2}{\dfrac{r_i f_i}{k_{p,ii}} + \dfrac{r_j f_j}{k_{p,jj}}} \tag{5.20}$$

For emulsion copolymerisation, the rate in the particle phase is given by:

$$R_p = \frac{\bar{k}_p\,\bar{n}\,N_p\,C_{Mp}}{N_{av}} \tag{5.21}$$

where $\overline{k}_p$ is the average propagation rate constant in the particle phase, $\overline{n}$ is the average number of radicals per particle, C_{Mp} is the overall monomer concentration in the particles, N_p is the number of latex particles per unit volume of the aqueous phase and N_{av} is Avogadro's number. $\overline{n}$ can in principle be calculated by solving the radical population balance over the particle phase using the pseudo homopolymerisation approach reported by Storti *et al.* [1989]. The contribution of the aqueous phase polymerisation to the overall polymerisation rate in emulsion can usually be neglected since the main locus of polymerisation is the particle phase. Therefore, Equation 5.21 can be used to describe the course of emulsion polymerisations and, provided $\overline{k}_p$ and C_{Mp} are known, valuable information concerning $\overline{n}$ can be obtained from the polymerisation rate.

5.3.2. Particle phase propagation rate constant

5.3.2.1. Copolymerisation of Styrene and Butadiene

The copolymerisation of S and B in the particle phase of an emulsion polymerisation system can be treated as equivalent to bulk copolymerisation. The copolymerisation equation, i.e. Equation 5.19, is applied to the polymerisation of S and B to calculate the instantaneous copolymer composition as a function of the monomer composition in the locus of polymerisation i.e. the free S mole fraction in the (partially) monomer swollen latex particles. The reactivity ratios are given in Table 5.6a and the results are shown in Figure 5.12.

Table 5.6 a: Bulk Copolymerisation. Kinetic Parameters.

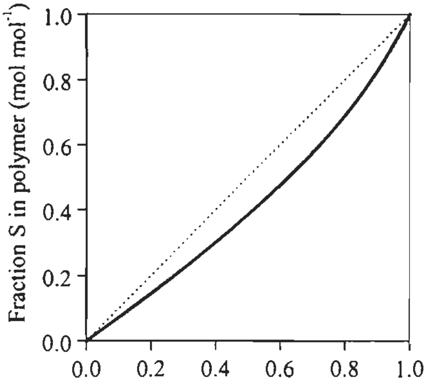
Monomer	k_p at 70°C ($dm^3\ mol^{-1}\ s^{-1}$)	E_A ($kJ\ mol^{-1}$)	**Reference**
S	477	32.5	Buback *et al.* [1995]
B	290	35.7	Deibert *et al.* [1992]
AA	41000$^{a)}$	18.0	Kuchta [1997] Gromov *et al* [1980]

a) value extrapolated from k_{pAA} in acetic acid at 25°C

Table 5.6 b: Bulk Copolymerisation. Reactivity ratios.

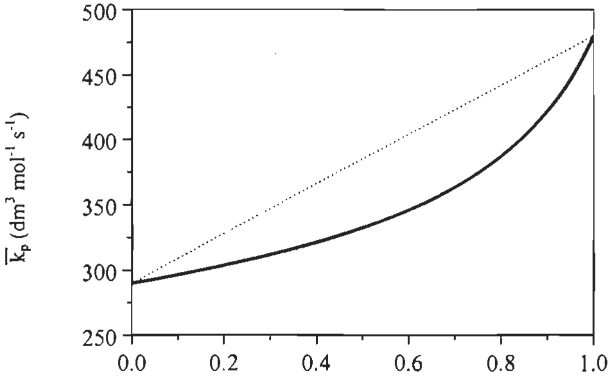
Monomer Pair	**r**	**Reference**
S, B	0.5, 1.4	Meehan [1946]
S, AA	0.4, 0.05	This thesis, Table 4.9
B, AA	0.49, 0.36	Yuan [1996]

The copolymerisation of S and B is non-ideal with the product $r_S.r_B$ being 0.7. Composition drift can occur since the instantaneous fraction B built-in into the copolymer is larger than the fraction free B in the locus of polymerisation. However, note that the copolymerisation is quite close to the ideal type.



Fraction free S (mol mol^{-1})

Figure 5.12: Copolymerisation of Styrene and Butadiene. Calculated instantaneous copolymer composition as a function of the mole fraction of the free monomer at the locus of polymerisation. Calculation with Equation 5.19 and the parameters given in Table 5.6.



f_S (mol mol^{-1})

Figure 5.13: Copolymerisation of Styrene and Butadiene (70°C). Calculated average propagation rate constant as a function of the mole fraction of free styrene at the locus of polymerisation. Calculation with Equation 5.20 and the parameters given in Table 5.6.

For the copolymerisation of two monomers with a low water-solubility, the ratio of the mole fractions of the two monomers in the droplet phase is equal to the corresponding ratio in the particle phase and a single overall free monomer composition can be defined, see Verdurmen-Noel [1994]. Therefore, Equation 5.20 is used together with the parameters in Table 5.6a and b to investigate the influence of the instantaneous free monomer composition on the average propagation rate constant of the S-B copolymerisation in the particle phase.

The results shown in Figure 5.13 indicate that composition drift occurring during the emulsion copolymerisation of S and B has only a limited influence on $\bar{k}_p$. Therefore $\bar{k}_p$ calculated with the initial molar ratio between S and B can be used as reasonable estimation for the $\bar{k}_p$ value determining the kinetics in the particle phase throughout the whole polymerisation process.

5.3.2.2. Influence of Acrylic Acid

The copolymerisation equation, *i.e.* Equation 5.19, applied to the copolymerisation of AA with S or with B results in the instantaneous copolymer composition as a function of the free monomer composition in the locus of polymerisation shown in Figure 5.14. The copolymerisation is in both cases non-ideal. All reactivity ratios are lower than 1, see Table 5.6 and the copolymerisation presents azeotropic conditions with $f_{AA} = F_{AA}$, see Figure 5.14.

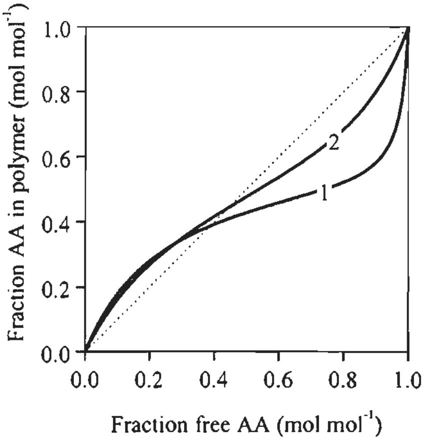


Figure 5.14: Copolymerisation with Acrylic Acid. Calculated instantaneous copolymer composition as a function of the mole fraction of the free monomer at the locus of polymerisation. 1: copolymerisation with Styrene; 2: copolymerisation with Butadiene. Calculation with Equation 5.19 and the parameters given in Table 5.6.

Equation 5.20 is used together with the parameters in Table 5.6 to investigate the influence of the instantaneous free monomer composition on the average propagation rate constant of AA and S or B. The results presented in Figure 5.15 show that two situations can be expected. For f_{AA} values up to about 0.9, the influence of f_{AA} on $\bar{k}_p$ is rather limited for both copolymerisation systems. However, for very high f_{AA} values $\bar{k}_p$ strongly increases with f_{AA}. This behaviour is mainly due to the very large difference between the homopolymerisation rate constants of AA and S or B. Note that the homopolymerisation rate coefficient of AA strongly depends on solvent, see Chapiro *et al.* [1977]. We assume that the course shown in Figure 5.15 agrees qualitatively with reality although no accurate k_{pAA} value corresponding to bulk polymerisation, *i.e.* best description of particle phase polymerisation, has been reported.

The polymerisation behaviour of AA with either S or B seems very similar and the copolymerisation kinetics of S and B is not very much influenced by the ratio of the two monomers, see Figure 5.13. Therefore, no attempt is made to describe the terpolymerisation rate constant involving the three monomers together. Attention is rather focused on the influence of the AA content on the particle phase kinetics during the emulsion polymerisation of S only.

The results shown in Figure 5.15 indicate that the kinetics in the particle is controlled by the local AA concentration and therefore by the partitioning of AA monomer in emulsion systems. The partitioning of monomers between the different phases present in emulsion polymerisation always occurs and can usually be described by thermodynamic considerations [Flory, 1942; Huggins, 1942, Morton *et al.*, 1954]. Numerous attempts to model and to predict the partitioning of monomers and therefore the swelling of latex particles by one or more monomers can be found in literature [Maxwell *et al.*, 1992; Noel *et al.*, 1993, Kurja, 1997]. The models can usually only be applied to monomers with a limited water-solubility. When water-soluble or water-miscible monomers are used, the partitioning behaviour becomes much more complicated [Schoonbrood, 1994] and hardly any information is available.

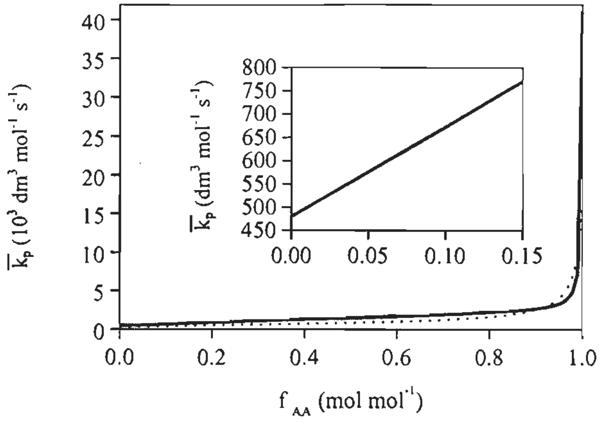


Figure 5.15: Copolymerisation with Acrylic Acid (70°C). Calculated average propagation rate constant as a function of the mole fraction of the free monomer at the locus of polymerisation. Solid line: copolymerisation with Styrene; dotted line: copolymerisation with Butadiene. Calculation with Equation 5.20 and the parameters given in Table 5.6.

Shoaf *et al.* [1990] investigated the partitioning of AA or Methacrylic Acid (MAA) in mixtures of S and water as a function of the monomer to water ratio. These authors experimentally determined x_A^{org}, the fraction of acid in the organic phase. x_A^{org} is defined by:

$$x_A^{org} = \frac{n_A^{org}}{n_A^{ov}} \tag{5.22}$$

where n_A^{org} is the absolute amount of acid in the organic phase (mol) and n_A^{ov} is the absolute amount of acid in the mixture (mol). Shoaf *et al.* [1990] reported that the distribution of the carboxylic monomer (A) between the aqueous phase and the organic phase is different for MAA and AA, see Figure 5.16.

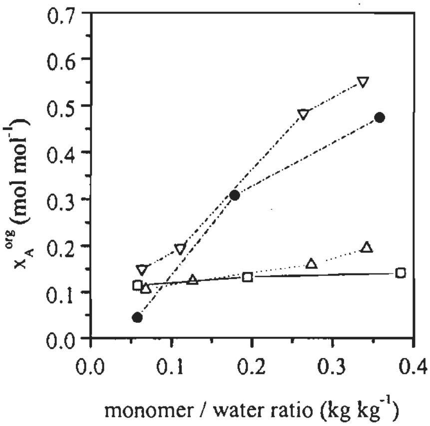


Figure 5.16: Partitioning of carboxylic monomers in mixtures of Styrene and water. Fraction of acid in the organic phase as a function of the monomer to water ratio for different carboxylic monomer weight fractions of total monomer. □: AA, 0.1; △: AA, 0.25; •: MAA, 0.1; ▽: MAA, 0.25.

This behaviour can be attributed to differences in hydrophobicity. Indeed, due to the presence of the methyl group, MAA is (somewhat) more hydrophobic than AA. Therefore, on increasing the monomer to water ratio, more MAA is taken-up by the organic phase. In addition, the partitioning of the acidic monomers is further complicated by the formation of hydrogen-bonded aggregates in both the organic and the aqueous phase, see Prausnitz *et al.* [1986] and Chapiro *et al.* [1977]. So, the development of a model describing the partitioning behaviour of carboxylic monomers in latex systems is not straightforward.

Shoaf *et al.* [1990] also used a partition coefficient PC to describe the partitioning of acid between the aqueous and the organic phases. PC is defined as the ratio of the acid concentrations in the two phases:

$$PC = \frac{[\text{acid}]^{org.}}{[\text{acid}]^{aq.}} \tag{5.23}$$

PC can also be related to x_A^{org} and the overall monomer to water weight ratio (M/W):

$$PC = \frac{1}{\frac{M}{W}} \frac{x_A^{org}}{1 - x_A^{org}} \tag{5.24}$$

Shoaf *et al.* [1990] reported that for both acids PC is strongly influenced by α, the degree of dissociation of the acid groups in the aqueous phase, see Figure 5.17. Other parameters reported to have an influence on PC are the ionic strength of the solution and the total amount of carboxylic monomer. These authors also studied the partial swelling, *i.e.* without monomer droplets, of polystyrene seed latex particles with styrene and carboxylic monomer. This situation corresponds to Interval III of the emulsion polymerisation process.

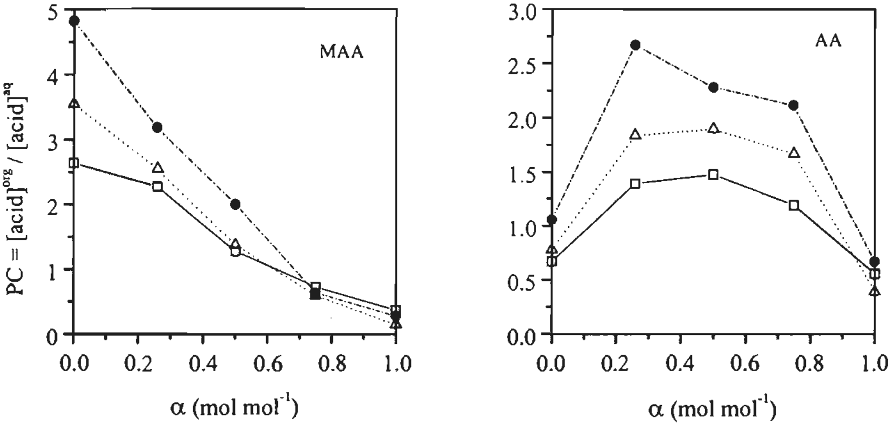


Figure 5.17: Partitioning of carboxylic monomers in mixtures of styrene and water. Partition coefficient of Methacrylic Acid and Acrylic Acid as a function of the degree of dissociation. Acid weight fractions of total monomer: •: 0.35; Δ: 0.25; □: 0.14.

No reliable information could be obtained about the partitioning of AA between polystyrene latex particles, S monomer droplets and water, *i.e.* interval II of emulsion polymerisation. However, because of the hydrophilicity of carboxylic acids and because AA is a poor solvent for polystyrene, only a small amount of AA can be expected to dissolve in polystyrene unless it is swollen with S. Indeed, according to Shoaf *et al.* [1990] the interaction between AA or MAA and polystyrene are characterised by relatively high interaction parameters as defined by the Flory-Huggins theory. Therefore it is assumed that there is no specific "bonding" between AA and the polymer and so the molar ratio of the two monomers in the particle phase can be approximated to be the molar ratio of the two monomers in the droplet phase. Note that experimental evidence for this behaviour has been reported for monomers with a low water-solubility [Verdurmen-Noël, 1994]. On the basis of this assumption, our emulsion systems can be treated as if AA would partition between the aqueous phase and a single organic phase consisting of S monomer in general. The instantaneous AA mole fraction in the monomer swollen polymer or in the monomer droplets, f_{AA}^{org}, can therefore be expressed by the relation:

$$f_{AA}^{org} = \frac{x_A^{org}}{x_A^{org} + \frac{1 - f_{AA}^{ov}}{f_{AA}^{ov}}} \qquad (5.25)$$

where f_{AA}^{ov} is the instantaneous AA mole fraction in the overall free monomer. The amount of S partitioned in the aqueous phase has been neglected.

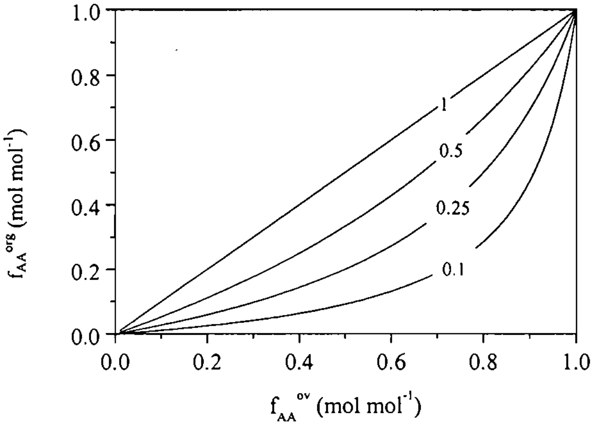


Figure 5.18: Partitioning of Acrylic Acid in a mixture of Styrene and water. Free AA mole fraction in the organic phase as a function of the AA mole fraction in the overall free monomer. Calculations with Equation 5.25 with different values for x_A^{org}.

Figure 5.18 shows the influence of f_{AA}^{ov} on f_{AA}^{org} for different values of x_A^{org}, see Equation 5.22. The upper limit $x_A^{org} = 1$ is very unrealistic because it would mean that all AA is dissolved in S and no AA is present in the aqueous phase. The range $0.10 < x_A^{org} < 0.5$ is more realistic, see Figures 5.16 and 5.17, and covers most of the experimental conditions met in Chapter 6 and 7 in terms of monomer to water ratio, acid level and degree of dissociation. When performing emulsion polymerisation experiments with low amounts of carboxylic monomer, f_{AA}^{ov} is expected to remain low throughout most of the process and more particularly during the particle growth in the presence of monomer droplets *i.e.* during interval II of emulsion polymerisation. Commonly in our work, the initial value of f_{AA}^{ov} ranges between 0 and 0.2. For recipes with small amounts of AA, Figures 5.18 and 5.15 point to a very limited influence of AA on $\overline{k}_p$ in the particle phase during the stage of particle growth. $\overline{k}_p$ can therefore be estimated by taking only the main hydrophobic monomers into account. Note that the influence of dissociated acid groups on the determination of $\overline{k}_p$ in the particle phase has not been discussed here. Since the amount of dissociated acid units in the particle phase is expected to be very low and because of the low reactivity of the dissociated monomer, no significant influence on $\overline{k}_p$ is expected.

5.3.3. Aqueous phase polymerisation

Although the main locus of polymerisation remains the particle phase, the chemical reactions taking place in the aqueous phase play a very important role in emulsion polymerisation processes, see Priest [1952], Roe [1968] and Casey *et al.* [1993]. The chemical events include the complete polymerisation scheme in water, *i.e.* initiation, propagation, termination and transfer. Also included are aqueous phase phenomena with a physico-chemical character such as the diffusion in the continuous phase of the so-formed species, and more particularly the free-radicals, their aggregation and their capture by the dispersed phase. All those events have been reviewed in Chapter 2. When using at least one monomer with a high water-solubility, one can expect the role of aqueous phase events to be even more important. In this section we will focus on the influence of carboxylic monomers on the copolymerisation kinetics in the aqueous phase. The emulsion copolymerisation of S and AA is the model system to be discussed in the following sections.

5.3.3.1. Free monomer composition in the aqueous phase

In the previous section, it was demonstrated that the free AA fraction in the particle phase of an emulsion polymerisation system was generally very low. Therefore, the average propagation rate constant $\bar{k}_p$ in the particle phase could be reasonably approximated by the propagation rate constant for the homopolymerisation of the predominant hydrophobic monomer only. However, due to the large amount of AA present in the water phase compared to the limited concentration of hydrophobic monomers, see Table 5.7, this assumption is not valid any more for the determination of $\bar{k}_{p,aq}$, the average propagation rate constant in the aqueous phase. The aqueous phase polymerisation corresponds actually to a solution copolymerisation with a roughly constant but small concentration of hydrophobic monomer units (at least as long as monomer droplets are present *i.e.* in intervals I and II) and a finite overall amount of AA. AA partitions between the different phases where it can polymerise and therefore its concentration in the aqueous phase can vary throughout the whole process. The simple terminal model introduced in section 5.3.1 to describe copolymerisation kinetics can be used to improve insight into the influence of AA on the aqueous phase polymerisation during the emulsion polymerisation of S and AA. With the terminal model, the instantaneous copolymer composition and the average copolymerisation rate constant can be related to the instantaneous free monomer composition in the aqueous phase, the monomer reactivity ratios and the homopolymerisation rate constants, see Equations 5.19 and 5.20.

Table 5.7: Values of aqueous-phase solubility, $[M]_{aq}^{sat}$, for hydrophobic monomers at 50°C

Monomer	$[M]_{aq}^{sat}$ (mol dm-3)	**Reference**
Styrene	$4.5\ 10^{-3}$	Lane *et al.* [1946]
Butadiene	$37\ 10^{-3}$	Reed *et al.* [1959]

The monomer droplets in an emulsion polymerisation system act as a reservoir and ensure a constant concentration of S in the aqueous phase corresponding to the S solubility in water, $[S]_{aq}^{sat}$. The influence of AA on $[S]_{aq}^{sat}$ is not considered here. The instantaneous AA mole fraction in the aqueous phase based on the total amount of monomer in the aqueous phase can be expressed by:

$$f_{AA}^{aq} = \frac{1}{1 + \frac{[S]_{aq}^{sat}}{[AA]_{aq}}} \tag{5.26}$$

where $[AA]_{aq}$ is the instantaneous concentration of AA in the aqueous phase. Additionally:

$$[AA]_{aq} = \frac{M\,\rho_W}{W}(1 - x_A^{org})\frac{f_{AA}^{ov}}{M_s\,(1 - f_{AA}^{ov}) + M_{AA}\,f_{AA}^{ov}} \tag{5.27}$$

where M_S and M_{AA} are the molecular weight of S and AA respectively and ρ_W is the density of water.

The results shown in Figure 5.19 have been calculated with Equations 5.26 and 5.27 and the x_A^{org} values reported by Shoaf *et al.* [1990] at low pH, see Figure 5.16. Only the range $0 < M/W$ (kg kg^{-1})< 0.4 with $0 < f_{AA}^{ov} < 0.4$ has been covered by the investigation of these authors. Higher values for M/W are not expected in practice. The limited range of f_{AA}^{ov} is not appropriate here because f_{AA}^{ov} depends on the relative consumption of the monomers during the process. Although the relative amount of functional monomer introduced in the recipe is usually low (commonly $0 < f_{AA}^{ov,initial} < 0.15$), it has been observed experimentally by several authors that the concentration of unreacted carboxylic acid usually remains high up to the last stage of the emulsion process [Shoaf *et al.*, 1991; Yuan, 1996]. So, one can expect high values of f_{AA}^{ov} during the last stage of the polymerisation. Therefore the results presented in Figure 5.19 rather describe situations encountered during the first two stages of emulsion polymerisation.

In contrast to conventional emulsion polymerisation of monomers with a low water-solubility, Figure 5.19 shows that the monomer concentration in water is high and is strongly influenced by the monomer to water ratio. Due to the difference in water-solubility between AA and S, $f_{AA}^{aq} \sim 1$ except for very low f_{AA}^{ov} values.

Additionally, AA is present in its dissociated form at pH values above its pK_a value, $pK_a = 4.86$, see section 5.2.2. As already discussed in section 5.2.4., completely protonated AA and dissociated AA can actually be seen as two different monomers with their own characteristics in terms of hydrophilicity and polymerisation behaviour. The pH of the emulsion polymerisation mixture is therefore one of the key process parameters as well. The situation pH = 7 is also described in Figure 5.19. The calculations have been done with $x_A^{org} = 0$ in Equation 5.26 since dissociated acids remain preferably in the aqueous phase, see Figure 5.17. pH has only a small influence on f_{AA}^{aq} since the concentration of non-dissociated AA in the organic phase is intrinsically low.

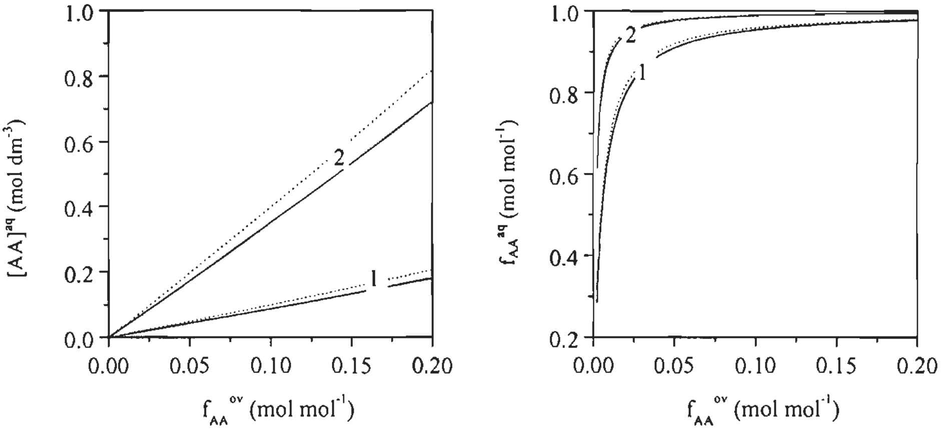


Figure 5.19: Emulsion polymerisation of Styrene with Acrylic Acid. Free monomer composition in the aqueous phase as a function of the overall monomer composition for different values of M/W. **1** = 0.1:1; **2** = 0.4:1. Solid lines: pH = 2.5. Dotted lines : pH = 7. Calculations with Equations 5.26 and 5.27 and the data shown in Figure 5.16.

The free monomer composition in the aqueous phase definitely differs from that in the particle phase. Indeed, the particle phase polymerisation is characterised by f_{AA} rather close to zero while the aqueous phase polymerisation proceeds with f_{AA} close to one. No influence of pH on the free monomer composition in the aqueous phase can be expected, see Figure 5.19. Note that the discussion is limited to relatively low f_{AA}^{ov} values. Due to the lack of experimental data covering a larger f_{AA}^{ov} range, the prediction of the aqueous phase composition and therefore the modelling of the whole emulsion polymerisation process is hardly possible.

5.3.3.2. Estimation of copolymerisation rate constants

Equation 5.20 can be applied to the solution polymerisation of AA and S in water. The parameters used in the calculations are collected in Table 5.8 a and b. Note that most of the kinetic parameters for AA are debatable because of the lack of accurate experimental data. The results for MAA as obtained by PLP confirmed the influence of pH on the polymerisation behaviour and more particularly on the propagation rate constant of carboxylic acid monomers in water, see section 5.2.6. The emulsion polymerisation experiments discussed in this thesis are generally performed at the two different but well-defined pH values of 2.5 and 7. Although AA is used instead of MAA in emulsion, our PLP results confirm that the homopolymerisation rate constant of AA, $k_{p,AA}$, can be expected to be much higher at pH 2.5 than at pH 7, see Kabanov *et al.* [1973].

Kim [1990] reported the strong dependence of solvent on the reactivity ratios of the monomer pair AA/S. To the best of our knowledge, the copolymerisation behaviour of S and

AA in water has not been reported. Note that the generation of experimental results in water is very tedious because of the low solubility of S. Therefore, the values collected in Table 5.8b correspond to the copolymerisation in methanol which was believed to be the best equivalent for water. Additionally and of major importance, even less information is available concerning the dissociated form of the monomer, AA^-, in terms of reactivity ratios. The assumption is made that S reacts in the same way with both forms of carboxylic monomers and that $r_S = k_{pS}/k_{pS,AA} = k_{pS}/k_{pS,AA^-}$. The estimation of r_{AA^-} is more difficult and two situations will be considered: $r_{AA^-} < r_{AA}$ and $r_{AA^-} > r_{AA}$. Using the Q-e scheme introduced by Alfrey *et al.* [1952] with Q = 1.00 and e = -0.8 for S and Q = 1.18 and e = - 0.37 for sodium acrylate [Bourdais J., 1955], results in $r_S = 0.6$ and $r_{AA^-} = 1.3$ and indicates that $r_{AA^-} > r_{AA}$ is probably the best estimation.

Table 5.8a: Bulk Copolymerisation. Kinetic Parameters.

Monomer	**k_p at 70°C** ($dm^3\ mol^{-1}\ s^{-1}$)	**E_A** ($kJ\ mol^{-1}$)	**Reference**
AA, pH 2.5	58000	18.0	Gromov *et al* [1980]
AA^-, pH 7	660	18.0	Kabanov *et al.*[1973] Gromov *et al* [1980]
S	477	32.5	Buback *et al.* [1995]

Table 5.8b: Bulk Copolymerisation. Reactivity ratios.

Monomer Pair	**r**	**Reference**
S, AA, pH 2.5	1.1, 0.13	Kim [1990]a)
S, AA^-, pH 7	0.6, 1.3	Bourdais [1955]b)
	1.1, 0.01	Estimation 1
	1.1, 1	Estimation 2

a) values obtained in methanol
b) Q-e scheme

Figure 5.20 shows the average propagation rate constant calculated with Equation 5.20 and the parameters collected in Table 5.8a and b as a function of f_{AA}^{aq} for both conditions of pH. f_{AA}^{aq} has only a limited influence on $\overline{k}_p$ except at pH 2.5 and for $f_{AA}^{aq} > 0.95$. This situation is only possible when almost all the S has been depleted in the aqueous phase that is, in the very last stage of the process and provided AA monomer units are still present. In the range $0 < f_{AA}^{aq} < 0.95$, hardly any influence of pH on $\overline{k}_p$ can be observed as well. The average propagation rate constant in the aqueous phase is therefore only moderately dependent on the process conditions considered here. Recall that a similar behaviour is observed for the particle phase propagation rate constant.

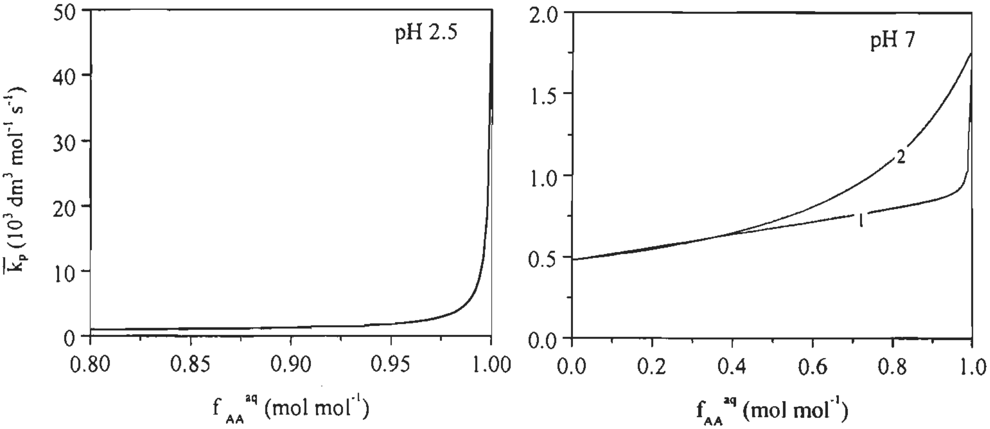


Figure 5.20: Styrene Acrylic Acid Solution Copolymerisation in Water (70°C). Calculated average propagation rate constant as a function of the mole fraction of the free monomer in the aqueous phase at different pH values.
pH = 2.5: (r_S, r_{AA}) = (1.1, 0.13); pH = 7: **1**, (r_S, r_{AA^-}) = (1.1, 0.01); **2**, (r_S, r_{AA^-}) = (1.1, 1).
Calculation with Equation 5.20 and the parameters given in Table 5.8a and b.

5.3.3.3. Estimation of copolymer composition

The nature of the copolymer formed in the aqueous phase is one of the parameters controlling the mass transfer phenomena between the phases involved and therefore the overall kinetics of emulsion polymerisation processes. Equation 5.19 is used together with the parameters in Table 5.8b to describe the influence of some of the process conditions on the instantaneous copolymer composition. Figure 5.21 shows the instantaneous AA mole fraction in the copolymer as a function of the instantaneous mole fraction of free AA for the copolymerisation of S and AA in water.

Unlike the copolymerisation of S and AA in the particle phase, the copolymerisation in the aqueous phase does not show azeotropic conditions, see Figure 5.14. The instantaneous AA fraction built-in into the copolymer chains is always lower than the instantaneous mole fraction of free AA in the aqueous phase. Information obtained from the copolymerisation equation and from Equations 5.26 and 5.27 are combined in Figure 5.22 which represents the instantaneous copolymer composition as a function of the overall instantaneous free monomer composition during the early stage of the process, *i.e.* $0 < f_{AA}^{ov} < 0.20$.

Typical emulsion polymerisation recipes are considered and the corresponding F_{AA}^{aq} and $\overline{k}_p$ values are calculated, see Table 5.9. Important information can be extracted from the results collected in Table 5.9 and Figure 5.22. F_{AA}^{aq} are usually high but always below 1 which means that a significant number of S units are incorporated into the polymer chains formed in the aqueous phase. The significant S fraction in the polymer chains in the aqueous phase is of major importance since it shows that the oligomeric radicals are likely to possess some surface activity which is believed to be a key issue for nucleation processes and mass transfer events, *i.e.* entry.

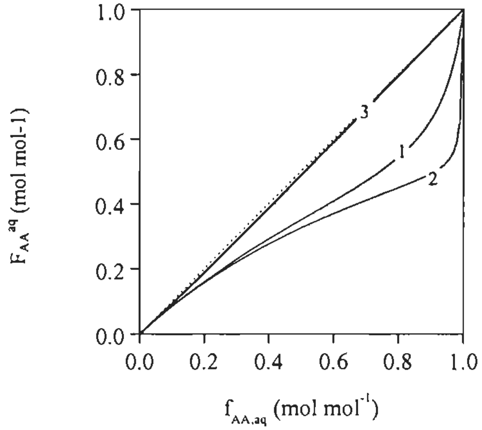


Figure 5.21: Styrene Acrylic Acid Solution Copolymerisation in water. Calculated instantaneous copolymer composition as a function of the mole fraction of AA in the free monomer in the aqueous phase.
1: pH = 2.5, (r_S, r_{AA}) = (1.1, 0.13); **2**: pH = 7, (r_S, r_{AA^-}) = (1.1, 0.01); **3**: pH = 7, (r_S, r_{AA^-}) = (1.1, 1). Calculation with Equation 5.19 and the parameters given in Table 5.8.

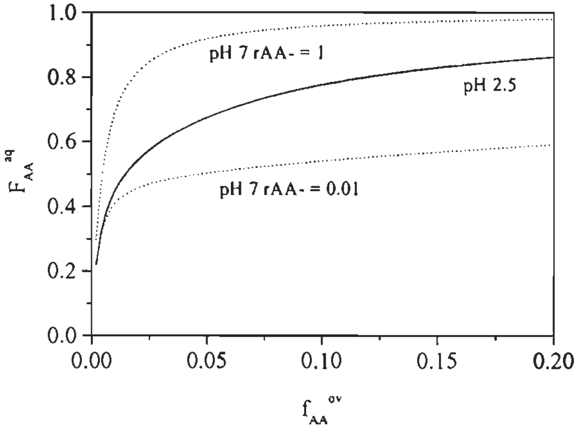


Figure 5.22: Styrene Acrylic Acid Solution Copolymerisation in Water. Calculated instantaneous copolymer composition as a function of the overall monomer composition for different pH. Calculations with Equations 5.19, 5.26 and 5.27 and the data in Table 5.8b and Figure 5.16. Monomer / water ratios = 0.1 (kg kg^{-1}); pH 2.5: (r_S, r_{AA}) = (1.1, 0.13), x_A^{org} = 0.12; pH 7: (r_S, r_{AA^-}) = (1.1, 0.01 or 1), x_A^{org} = 0.

Table 5.9: Composition of the aqueous phase polymer in emulsion polymerisation at different pH. $\bar{k}_p$ in $dm^3\ mol^{-1}\ s^{-1}$.

AA (g)	$f_{AA}^{ov\ c)}$	f_{AA}^{aq}	F_{AA}^{aq} pH 2.5	$\bar{k}_p$	F_{AA}^{aq} pH 7 $^{a)}$	$\bar{k}_p$	F_{AA}^{aq} pH 7 $^{b)}$	$\bar{k}_p$
0.5	$8.42\ 10^{-3}$	0.60	0.40	770	0.38	720	0.65	815
1	$1.67\ 10^{-2}$	0.75	0.53	900	0.44	780	0.77	1020
2.5	$4.07\ 10^{-2}$	0.90	0.64	1300	0.49	855	0.90	1390
5	$7.80\ 10^{-2}$	0.95	0.73	1870	0.52	900	0.95	1575

a) $r_{AA^-} = 0.01$
b) $r_{AA^-} = 1$
c) The calculations are based on 85 g Styrene and 900 g Water

F_{AA}^{aq} moderately increases with f_{AA}^{ov} except for very low f_{AA}^{ov} values. Predictions concerning the influence of $f_{AA}^{ov} > 0.2$ on F_{AA}^{aq} are difficult since the AA partitioning behaviour is not known in detail. However, one can expect very high f_{AA}^{aq} values. Nonetheless, the F-f curves in Figure 5.22 show that F_{AA}^{aq} remains smaller than one and S units can be incorporated.

The pH of the reaction mixture has a very strong influence on the composition of the instantaneous copolymer formed. However, at a given f_{AA}^{ov} value the difference between the instantaneous composition of the copolymer at pH 2.5 or pH 7 is dependent on the set of r-values used in the calculations. If the hypothesis $r_{AA^-} = 0.01$ is selected, *i.e.* dissociated AA preferentially copolymerises, the S and AA fractions in the copolymer are similar and F_{AA}^{aq} is much lower at pH 7 than 2.5. Opposite conclusions can be drawn if the other hypothesis is selected. The ion-pair formation model introduced by Kabanov *et al.* [1973] to explain the influence of pH on the polymerisation behaviour of AA suggests $r_{AA^-} \neq 0.01$. Indeed, the cation concentration in emulsion polymerisation systems is generally high and induces formation of ion-pairs and shielding of negative charges. Therefore, F_{AA}^{aq} probably increases with pH.

The previous discussion holds at the beginning of the process. It is very difficult to predict what happens exactly when conversion increases since it requires a good knowledge of the individual monomer consumption and monomer partitioning behaviour. As long as monomer droplets are present, the hypothesis that f_{AA}^{aq} decreases when conversion increases seems realistic (AA is consumed in the aqueous phase but the S concentration remains the same). Therefore, a decrease in the acid fraction in the aqueous phase copolymer can be expected. Further discussion is hardly possible without considering the rate of consumption of AA in the aqueous phase. Due to the compartmentalisation of emulsion polymerisations processes, the main locus of polymerisation is the particle phase and the polymerisation rate is much lower in the aqueous phase than in the particle phase, see Shoaf *et al.* [1991]. Since

AA is poorly soluble in the organic phase, a significant amount of free AA is likely to be present in the aqueous phase at the beginning of Interval III. Shoaf *et al.* [1991] and Yuan [1996] found experimental evidence for this behaviour. Therefore f_{AA}^{aq} increases again with conversion and less and less S units are incorporated in the aqueous phase polymer.

5.4. Conclusions

Pulsed Laser Polymerisation can be used to determine the propagation rate constant of carboxylic monomers in water. The molecular weight of the polymer formed during the PLP experiments can be determined by Size Exclusion Chromatography provided the carboxylic acid groups are converted into ester groups. The results on the polymerisation of methacrylic acid confirm the role of pH in the process with a significant decrease of the propagation rate constant when pH increases. The trend is, however, not easy to interpret. One should consider ionic association and the possible difference in reactivity of the species bearing protonated or dissociated carboxylic groups, more particularly with respect to the propagating radicals. Experimental issues like an accurate control of pH and ionic strength during the polymerisation or the isolation of the polymer chains prior to analysis must be solved before further mechanistic investigation is carried out.

Using the copolymerisation terminal model, it is demonstrated that the incorporation of carboxylic monomers in emulsion polymerisations has only a limited influence on the propagation rate constant in the particle phase since the mole fraction of the carboxylic monomer in the organic phase is usually low. The propagation rate constant can therefore be approximated by the propagation rate constant of the hydrophobic monomers.

The copolymerisation terminal model applied to the aqueous phase polymerisation gives valuable qualitative information. It is shown that the monomer concentration in the aqueous phase and the pH of the reaction mixture have a considerable influence on the average propagation rate constant and a significant influence on the chemical composition of the polymers formed in the aqueous phase. This is of major importance for the investigation of emulsion polymerisation mechanisms with respect to the mass transfer phenomena controlling the process. The calculations show that the fraction of the hydrophobic monomer built-in into the oligomeric radicals is significant and high enough to expect the species to be at least surface active and to interact with the dispersed organic phase.

More accurate data concerning the partitioning behaviour of carboxylic monomers in latex systems and their reactivity towards other monomers are necessary to further investigate and quantitatively describe the influence of pH, ionic strength and monomer to water ratio on the production polymer in the aqueous phase. Then, the other reactions involved in the polymerisation scheme (*i.e.* termination and transfer) together with physico-chemical aspects (i.e. surface activity) and thermodynamic aspects (i.e. adsorption equilibria) should be considered to be able to correctly describe mass transfer phenomena.

6

Emulsion Polymerisation of Styrene, Butadiene and Acrylic Acid

ABSTRACT: **The emulsion copolymerisation of styrene, butadiene and acrylic acid is investigated. Results from *ab-initio* experiments show that acrylic acid and pH play a very important role in the particle nucleation process resulting in different final latex particle concentrations and therefore different reaction rates. The incorporation of carboxylic groups into latex products is strongly dependent on the pH of the reaction mixture as well. Particle growth is investigated by performing seeded emulsion polymerisation experiments. It is shown that the average number of radicals per particle $\overline{n}$ increases with the particle size diameter. The amount of acrylic acid introduced in the recipes, the pH and the ionic strength of the reaction mixture have a significant influence on the polymerisation rate and can be explained by variations in the rate of entry. No consequent effect is reported with respect to the incorporation of carboxylic groups in latex products. The results indicate that pH is the dominating parameter for the incorporation process. An optimal incorporation on the surface of the particles is observed for a low value of pH. In that case all the acid groups are protonated.**

6.1. Introduction

In the previous chapter it was demonstrated that the introduction of a carboxylic acid monomer in emulsion polymerisation recipes leads to changes in the basic kinetic parameters controlling the course of the reaction. Not only the changes are very complex, but they mutually influence each other during the emulsion polymerisation process. In this chapter experimental results of the emulsion polymerisation of styrene and butadiene is reported. Attention is focussed on the polymerisation rate and the incorporation of carboxylic acid groups into latex products. pH, ionic strength, initiator level and acrylic acid level are used as experimental parameters and their influence is investigated in the processes of formation and growth of latex particles.

6.2. Emulsifier free batch emulsion polymerisation

6.2.1. Experimental

Emulsion polymerisation experiments were carried out in the experimental set up for butadiene monomer described in Chapter 3, see Figure 3.1.3.2. All recipes were emulsifier free and contained 900 g of distilled deionised water, 100 g of a styrene/butadiene/acrylic acid monomer mixture and 10.10^{-3} mol dm^{-3} of persulfate initiator (based on water). The weight ratio of styrene and butadiene monomers was kept constant in all the experiments, *i.e.* 70/30 equivalent to a mole ratio of 0.55/0.45. Only the amount of acrylic acid monomer and therefore $f_{AA}^{ov,initial}$, the initial acrylic acid mole fraction in the monomer mixture, was varied. Two types of counterions were used in the recipes. The initiator was therefore either sodium persulfate ($Na_2S_2O_8$) or potassium persulfate ($K_2S_2O_8$). A variable amount of sodium (Na_2CO_3) or potassium carbonate (K_2CO_3), in accordance with the initiator type, was used to control the pH of the reaction mixture. Sodium (NaCl) or potassium chloride (KCl) was added to correct for the variation in ionic strength (based on the total concentration in Na^+ or K^+ cations in the recipe). The recipes are summarised in Table 6.1. For the reactions carried out at pH 7, all acid groups were supposed to be dissociated. All concentrations are given per unit volume of the aqueous phase.

After reaction, the latexes were characterised in terms of particle size and acrylic acid distribution according to the procedures described in Chapters 3 and 4. Table 6.2 gives the average particle diameter (d_p) of the final latexes measured by TEM and the amount of surface weak acid groups on the surface ($C_{AAsurf.}$) determined by aqueous conductometric titration of latex samples after cleaning, see section 4.2. The average number of particles per unit volume of the continuous phase (N_p) is calculated with Equation 3.4:

Table 6.1: Recipes for surfactant free batch emulsion copolymerisation of styrene, butadiene and acrylic acid.

	SB8	SB9	SB23	SB24	SB25	SB46	SB48
Temperature (°C)	80	80	80	80	80	70	70
AA weight fraction	0.05	0.05	0.05	0.05	0.05	0.05	0.015
$f_{AA}^{ov,initial}$ (10^{-2})	5.6	5.6	5.6	5.6	5.6	5.6	1.7
$C_{AAtot.}$ (μeq g_{pol}^{-1})	690	690	690	690	690	690	215
Final pH	2.5	7	6.5	4	2.5	2.5	2.5
[Na^+] (10^{-3} mol dm^{-3})	120	120				20	20
[K^+] (10^{-3} mol dm^{-3})			120	120	120		

Monomer ratio (weight %): S/B=70/30
Monomer to water ratio: 10 % by weight
[initiator] = 10 10^{-3} mol dm^{-3}, based on water

6.2.2. Influence of pH and acrylic acid content on the latex particle concentration

All the experiments produced stable surfactant free latexes. Electronmicrographs of the latex samples showed in all cases a narrow particle size distribution. Results collected in Figure 6.1 and Table 6.2 show the influence of pH, temperature, counterion type and acid content on the final latex products. Neither the temperature nor the type of cation present in the reaction mixture had a significant influence on N_p. However, the pH of the reaction mixture did have a significant influence on the final latex particle size which increased upon increasing pH. Consequently, the final latex particle concentration N_p decreased with increasing pH, see Figure 6.1. A similar behaviour was observed upon decreasing the amount of acrylic acid introduced in the recipe, see experiments SB46 and SB48 in Table 6.2.

Table 6.2: Results of the batch emulsion copolymerisation of styrene, butadiene and acrylic acid. See recipes in Table 6.1.

	SB8	SB9	SB23	SB24	SB25	SB46	SB48
Temperature (°C)	80	80	80	80	80	70	70
final pH	2.5	7	6.5	4	2.5	2.5	2.5
final dp (nm)	190	240	245	225	190	180	200
N_p (10^{16} dm^{-3})	2.8	1.4	1.4	1.8	3.0	3.5	2.6
$C_{AAsurf.}$ (μeq g_{pol}^{-1})	210	30	16	133	241	250	50
D.S.I. (%)	30	5	2.5	20	35	35	32

Increasing the amount of acrylic acid resulted in an increase in the latex particle concentration. Some evidence for this behaviour could also be found in the progress of the reaction, see Figure 6.2. The polymerisation performed with a smaller amount of acrylic acid had a significantly lower reaction rate. Table 6.3 gives R_p, the overall reaction rate calculated with Equation 3.2 between an overall conversion of 0.1 and 0.4 and R_p/N_p, the rate per particle. No significant difference in the polymerisation rate per particle could be observed between the two experiments. This result indicates that in this case the amount of acrylic acid monomer did not have a significant influence on the particle growth process but only on the nucleation stage and thus the number of particles.

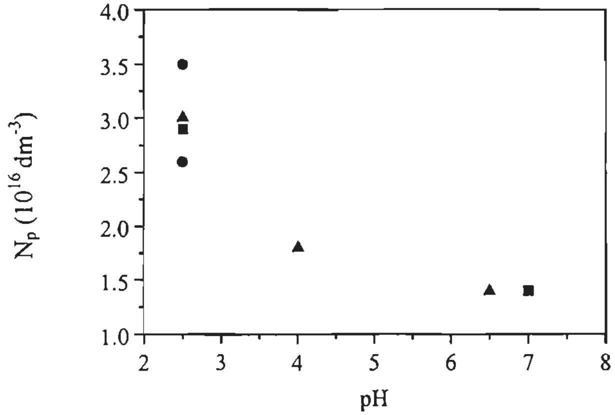


Figure 6.1: Batch emulsion polymerisation of styrene, butadiene and acrylic acid. Latex particle concentration for reactions performed at different pH.
■: SB8, SB9; ●: SB46, SB48; ▲: SB23, SB24, SB25, see recipes in Table 6.1

All our results show that both the degree of neutralisation of the acrylic acid groups in the latex system and the amount of water soluble monomer strongly influence the formation of particles during emulsion polymerisation. The particle nucleation process in emulsion polymerisation has been studied extensively since the basic theory of Smith and Ewart [1948] has been reported. An overview of the mechanisms involved in the formation of particles during emulsion polymerisation is given in Chapter 2. Several authors reported the influence of carboxylic monomers on nucleation mechanisms, see Ceska *et al.* [1974], Sakota *et al.* [1976], Guillaume *et al.* [1988], Lock *et al.* [1991], Yang at al. [1997] and Dos Santos *et al.* [1997]. All the studies indicate that the lower the ratio of surfactant to carboxylic acid monomer, the more important becomes homogeneous nucleation relative to micellar nucleation, see Chapter 2. In surfactant free systems, the main reported factors influencing the nucleation process are the hydrophobicity of the carboxylic acid monomer, the degree of neutralisation of the carboxylic acid groups and the amount of functional acid monomer introduced in the system.

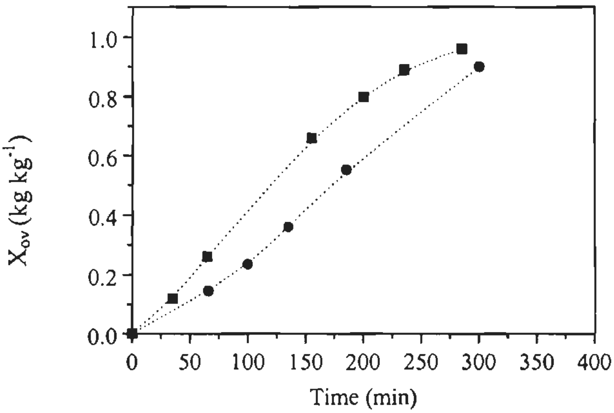


Figure 6.2: Batch emulsion polymerisation of styrene, butadiene and acrylic acid. Reactions performed with different amounts of acrylic acid.
■: SB46; •: SB48, , see recipes in Table 6.1.

Table 6.3: Emulsion polymerisation of styrene, butadiene and acrylic acid. Reaction rates.

	dX_{ov}/dt (10^{-5} s^{-1})	R_p/N_p (10^{-21} mol s^{-1})
SB46	7.4	2.9
SB48	5.2	2.7

In agreement with the results obtained by Ceska *et al.* [1974] and Sakota *et al.* [1976] our results show that upon increasing the pH of the reaction mixture and therefore increasing the degree of neutralisation of the carboxylic groups, less particles were nucleated. An explanation of this behaviour can be found in the influence of pH on both the copolymerisation in the aqueous phase and the hydrophilicity of the species formed in water. The distance L that an oligomeric radical travels after its start as a monomeric initiator radical in the aqueous phase of a latex system before it precipitates to form a primary particle has been given by Fitch *et al.* [1971]:

$$L = \sqrt{\frac{2\, D_f\, DP_{max}}{\bar{k}_{paq}\, [M]}} \tag{6.1}$$

where D_f is the diffusion coefficient of the oligomeric radical in the water phase, DP_{max} is the critical degree of polymerisation at which the oligomeric radical precipitates, $\bar{k}_{paq}$ is the average propagation rate constant in the aqueous phase and [M] is the overall monomer concentration in the aqueous phase. It is expected that an increase of pH from 2.5 to 7 results in a considerable decrease in the propagation rate constant for the homopolymerisation of acrylic acid in water, see section 5.2. Although reliable kinetic parameters for the terpolymerisation of styrene, butadiene and acrylic acid in water are not available, a similar influence of pH on $\overline{k}_{paq}$ can be expected although Figure 5.20 shows that the influence is probably limited. Equation 6.1 predicts that the resulting L value increases: it takes a longer time for the oligomeric radicals to precipitate and the latex particle concentration decreases. In addition to changes in the kinetics of the aqueous phase polymerisation, the pH has a considerable effect on DP_{max}. It has been shown in Chapter 5 that the chemical composition of the copolymers formed in the aqueous phase is pH-dependent, more acid groups being incorporated at higher pH values, see Figure 5.22 and Table 5.9. Moreover, neutralised carboxylic acid groups have a higher hydrophilicity and therefore more functional monomer can be incorporated in the oligomeric radicals before their solubility in water is exceeded. The resulting increase in DP_{max} upon increasing pH results in a larger value of L as well, see Equation 6.1.

Increasing the amount of carboxylic acid monomer in the recipe obviously results in an increase in the monomer concentration in the aqueous phase, see Figure 5.19, and results in an increase in F_{AA}^{aq}, see Figure 5.22, more particularly when the overall acrylic acid fraction in the monomer remains low. Therefore, a significant influence on DP_{max} should be expected since more carboxylic acid monomer units are likely to be incorporated into the oligomeric radicals before they exceed their water solubility. Therefore, the resulting effect on L can not be predicted with Equation 6.1 because in is not clear which effect on L is dominating: increase of concentration or increase of DP_{max}. Lock *et al.* [1991] studied the role of itaconic acid on the nucleation of polybutyl-methyl acrylate latex particles and reported that the final latex particle concentration decreased when more functional monomer was used in the recipe. On the contrary, Sakota *et al.* [1976] studied the nucleation of polystyrene latex particles in the presence of various amounts of acrylic acid and reported that the final particle concentration increased linearly with increasing amounts of functional monomer. Similar results were obtained by Guillaume *et al.* [1988] for the emulsifier-free emulsion polymerisation of styrene and butyl acrylate in the presence of methacrylic acid. Yuan [1996] studied the emulsion polymerisation of styrene and butadiene in the presence of acrylic acid, investigated the formation of latex particles and reported an increased latex particle concentration with larger amounts of acrylic acid. Our results confirm this particular behaviour and can be explained by an increased amount of acid rich radicals formed in the aqueous phase which provide the primary particles with a better stabilisation. The contradictory results obtained by Lock *et al.* [1991] are probably due to the nature of the carboxylic acid monomer used in their studies. Indeed, these authors reported that the copolymerisation of itaconic acid with methyl or butyl acrylate is much more favourable than its homopolymerisation. The probability of itaconic acid adding to its own radical is therefore very low and leads to the incorporation of low amounts of carboxylic acid groups in the oligomeric radicals.

6.2.3. Incorporation of acid groups

Distribution of acrylic acid groups

All the latex products were characterised in terms of the amount of weak acid groups located on the surface after cleaning and the Degree of Surface Incorporation (D.S.I) was calculated according to Equation 4.5. The results are collected in Table 6.2. During experiments SB8 and SB9, samples were also taken at intermediate overall conversions and characterised in terms of amount of surface weak acid groups after cleaning. The corresponding results are collected in Table 6.4.

Unfortunately, no data concerning the amount of buried acid groups in the latex particles could be obtained with the method described in Chapter 4. Indeed, due to the presence of crosslinked material in the copolymer formed during the process, see Chapter 4 section 4.3, the latex product could not be dissolved in THF and no reliable non-aqueous potentiometric titration could be carried out. Therefore, the distribution of carboxylic groups over the different locations in the latex could not be determined according to our standard procedure developed for S-AA copolymers.

Table 6.4: Emulsion copolymerisation of styrene, butadiene and acrylic acid. Incorporation of acrylic acid groups at intermediate conversions. Recipes given in Table 6.1

		SB8 **pH 2.5**			**SB9** **pH 7**	
Overall conversion	0.2	0.45	1	0.08	0.3	1
$C_{AAsurf.}$ (μeq g_{pol}^{-1})	460	225	210	300	65	30
D.S.I. [a)]	12	14	30	3	2.5	5

a) calculated with the values of $C_{AAtot.}$ corrected for the overall conversion

However, for experiments SB8 and SB9, it was tried to isolate the aqueous phase of the latex samples and investigate the presence of carboxylic groups in the water soluble species. An ultracentrifuge, model Centrikon T-2060 from Kontron Instrument, was used. Polycarbonate vials with a volume of 95 ml were filled with the latex samples and submitted to centrifugation at 30000 rpm at 20°C for about 2 hours. Under these conditions, a separation between the polymer phase (at the bottom) and the supernatant serum could be obtained. The clear serum was collected with a syringe while the polymer phase was redispersed with deionised water and submitted again to centrifugation. The clear serum after the second step was collected as well. The two serum samples were dried separately. Freeze-drying was preferred as a smooth drying method. So, there was s minimal chance for undesired chemical transformations of the water-soluble species. The samples were frozen with liquid nitrogen and dried for 24 hours under vacuum at a temperature of –30°C in a freeze dryer, model Hetosicc® from Heto (Denmark). The solid contents of the collected serum samples were measured gravimetrically.

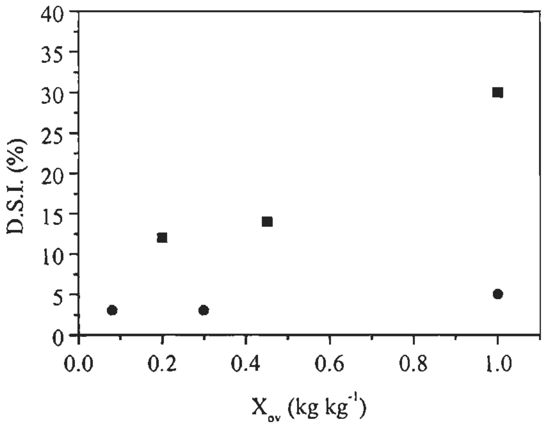


Figure 6.3: Batch emulsion polymerisation of styrene, butadiene and acrylic acid. Acrylic acid incorporation at intermediate conversion.

Table 6.5: Emulsion copolymerisation of styrene, butadiene and acrylic acid. Solid contents (weight %) of the aqueous phase after centrifugation of the latex samples.

		SB8 **pH 2.5**			**SB9** **pH 7**	
Overall conversion	0.2	0.44	1	0.08	0.3	1
Step 1	1.0	0.8	0.6	1.3	1.5	1.8
Step 2	0.2	0.1	0.1	0.2	0.1	0.1

The results collected in Table 6.5 show that centrifugation was not an efficient method for the complete isolation of water soluble species. The solid contents of the serum was still significant after redispersion of the sediment. The results in Table 6.5 reveal that during centrifugation, some water-soluble species are trapped by the particle phase which separates from the serum. These species are likely to be surface active polymer chains adsorbed on the surface of the latex particles. This appeared to be a serious problem and hampered a rigorous and non-selective analysis of the water-soluble products. Nevertheless, some attempts were made to characterise the products isolated from the serum by means of acid titration, infra-red spectroscopy (for the determination of the overall chemical composition) and Gel Permeation Chromatography (for the determination of the molecular weight). However, no reliable conclusion could, however, be drawn. Indeed, the quantities of isolated solids with the method were very small, and the products consisted not only of water-soluble polymer but also of various salts interfering in our analysis. Similar problems have been reported in section 5.2 during the determination of k_p values for methacrylic acid in water with Pulsed Laser Polymerisation.

To the best of our knowledge, the effect of successive cycles of centrifugation and redispersion on the isolation of water-soluble species in carboxylated latex systems has hardly been reported before. Our results show that the suitability of centrifugation is questionable although this method has been widely used, see e.g. Guillaume *et al.* [1988], Yuan [1996]. All the conclusions drawn from results obtained by centrifugation should therefore be interpreted with care. Alternative methods like dialysis or serum replacement might be less selective but are also known to result in incomplete removal of adsorbed species, see Chapter 4. Moreover, these cleaning methods require the use of large amounts of water in which the products will be diluted to a very large extend. An efficient non-selective and non-destructive method should then be applied to extract the products from the collected serum.

Acrylic acid groups incorporated at the surface

In the previous section it was concluded that only the information obtained from the conductometric titration of the surface carboxylic acid groups could be used. The results collected in Tables 6.2 and 6.4 and in Figure 6.3 show that the amount of acid groups incorporated on the surface of the latex particles was strongly dependent on the pH of the reaction mixture. The lower the pH, the more acid groups were incorporated onto the surface. These results are in good agreement with those obtained by e.g. Ceska [1974], Sakota *et al.* [1976 and 1977] and Dos Santos *et al.* [1997]. The amount of acrylic acid in the recipe had a significant effect on the absolute amount of acid groups on the surface, see $C_{AAsurf.}$ values for experiments SB46 and SB48 in Table 6.2, but hardly any effect on the efficiency of the incorporation, see the corresponding values of D.S.I which represents the ratio of acid groups built on the surface of the latex particles and the total initial amount of available acid groups. Similar results were also observed by Sakota *et al.* [1977] for emulsifier–free polystyrene latexes. No significant influence of temperature (latex SB25 compared to latex SB46) or counter ion (latex SB9 compared to latex SB23) on D.S.I of final latexes could be observed.

The preferential incorporation of carboxylic acid groups at low pH has to be related to the less hydrophilic nature of the functional monomer at pH values below the pK_a (pK_a = 4.86 for acrylic acid, see Kortüm *et al.* [1961]). Increasing the pH to values above 5 leads to higher concentrations of the dissociated form of the acid, see Figure 5.3, and affects the nature of the oligomeric radicals formed in the aqueous phase as it has already been discussed in Chapter 5 and in section 6.2.2. Our results show that not only the particle nucleation stage is affected by the pH but also the final amount of surface acid groups and therefore the overall efficiency of the process of acid group incorporation.

Table 6.4 gives valuable additional information about the incorporation of acid groups on the surface of the latex particles during the emulsion polymerisation process itself. At both pH 2.5 and pH 7 the (relative) amount of surface acid groups per unit of mass of the copolymer decreased with conversion. This means that the latex particles formed in the early stage of the reaction are very rich in surface acid groups. This result confirms the crucial role played by acrylic acid in the nucleation process, see Nuño-Donlucas *et al.* [1993]. However, the degree of surface incorporation, D.S.I., was low at intermediate conversions meaning that only relatively small amounts of acrylic acid were involved during the early stage of the process. Yuan [1996] studied the emulsion polymerisation of styrene, butadiene and acrylic acid and measured the amount of unreacted carboxylic monomer during the process. The process conditions were similar to ours. Yuan reported that about 20 to 30% of the initial acrylic acid reacted up to an overall conversion of 0.1, corresponding to the nucleation period. However, between overall conversions of 0.1 and 0.7, only 10 to 15% of the initial acrylic acid was consumed by reaction. The consumption of acrylic acid increased again in the last stage of the polymerisation process. Our results are in good agreement with the behaviour reported by Yuan [1996] although an accurate mass balance of the acid groups over the different locations in the reaction mixture is not available. Acrylic acid groups could eventually have been incorporated as surface acid throughout the latex particle growth process but buried simultaneously and are therefore hidden inside the polymer phase of the final latex particles. However, a remarkably large amount of surface acid groups could be detected at low pH in the final products, see Table 6.4 and Figure 6.3. This result actually supports our final conclusion that acrylic acid participated to a large extend to the formation of the latex particles. It was efficiently incorporated at low pH as surface acid as well via entry of acid rich oligomeric radicals in the last stage of the emulsion polymerisation since significant amounts of acrylic acid remain then available for polymerisation. For pH values significantly higher than pK_a, the incorporation efficiency was low throughout the whole process.

The amount of acrylic acid in the recipe had hardly any influence on the surface incorporation efficiency. Only the absolute amount of surface acid groups per particle was affected, see experiments SB46 and SB48 in Table 6.2. This behaviour can be explained by the aqueous phase polymerisation and the chemical composition of the entering oligomeric radicals which is strongly dependent on the acrylic acid concentration in water, see Figure 5.22. As already discussed in section 6.2.2., an increase in the acrylic acid concentration in water results in the incorporation of more acrylic acid units into the oligomeric radicals. Upon entry, the oligomeric radicals are therefore likely to provide more carboxylic groups to the latex particle surface. Sakota *et al.* [1977] studied the emulsifier-free emulsion polymerisation of styrene with various amounts of acrylic acid. In agreement with our results, these authors reported that the amount of acrylic acid in the recipe had hardly any effect on the acid group distribution which was substantially governed by the degree of neutralisation of acrylic acid, behaviour we also reported in the first part of the present section.

Due to the participation of acrylic acid to the nucleation mechanisms, it appears necessary to carry out the investigation of particle formation and particle growth processes separately. Attention is therefore focussed on the particle growth in order to get more insight into the mechanisms leading to the incorporation of acrylic acid on the surface via mass transfer phenomena. This can be achieved by performing seeded polymerisation experiments.

6.3. Seeded emulsion polymerisation

6.3.1. Experimental

The seed latexes were prepared by emulsion polymerisation of styrene and butadiene in the presence of sodium dodecyl sulfate as surfactant and sodium persulfate as initiator. The characteristics of the seed latexes are collected in Table 6.6. The seed latexes were submitted to dialysis to remove the excess surfactant before use in seeded emulsion polymerisation reactions, see section 3.2. The final seed latex particle diameter and particle size distribution were determined by Transmission Electron Microcopy.

All the seeded emulsion polymerisation reactions were performed at a temperature of 70°C according to the procedure described in section 3.1.2. The standard recipes contained 10 g seed polymer, 60 g styrene, 25 g butadiene, 900 g water and 10 10^{-3} mol dm^{-3} sodium persulfate (based on water). The pH of the reaction mixture was about 2.5 due to the presence of 1 to 5 g acrylic acid. In some experiments, the pH was increased to a value of about 7 with the addition of sodium carbonate (50 10^{-3} mol dm^{-3} based on water).

Table 6.6: Characteristics of the styrene-butadiene seed latexes

	S4	S7	S9
final diameter (nm)	60	75	45
S/B weight ratio	70/30	70/30	75/25
S/B molar ratio	55/45	55/45	60/40

Three series of experiments were performed. The parameters varied in the three series were the amount of acrylic acid in the recipe, the initiator concentration and the pH. Sodium chloride was added in some of the experiments performed at pH 2.5 to investigate the effect on ionic strength on the polymerisation process. The amount of acrylic acid introduced in the recipes was preferably expressed by $f_{AA}^{ov,initial}$, the initial overall acrylic acid molar fraction in the monomer mixture. The experimental conditions and results are summarised in Table 6.7 for all three series.

6.3.2. Influence of acrylic acid content content

Polymerisation rate

All experiments were characterised in terms of conversion time history and acrylic acid incorporation at the surface of the final latex particles according to the procedures described in Chapters 3 and 4. For reasons similar to those introduced in section 6.2.3 no acid distribution over the different locations in the latex systems could be determined. The overall polymerisation rate was calculated from the conversion time histories with Equation 3.2 in the overall conversion region between 0 and 0.5 corresponding to Interval II of emulsion polymerisation processes (no nucleation and particle growth stage in the presence of monomer droplets).

The latexes were checked with TEM for secondary nucleation and to determine the final particle diameter. All experiments produced stable latexes with a unimodal particle size distribution in very good agreement with the particle size distribution expected from the seed latex, see Equation 3.6. N_p was constant throughout the whole polymerisation and the rate per particle R_p/N_p during particle growth could be calculated.

The results collected in Table 6.7 and Figure 6.4 indicate that the amount of acrylic acid introduced in the recipe had a significant effect on the polymerisation rate. An increase in $f_{AA}^{ov,initial}$ resulted in higher value of R_p/N_p, see Figure 6.5 as well.

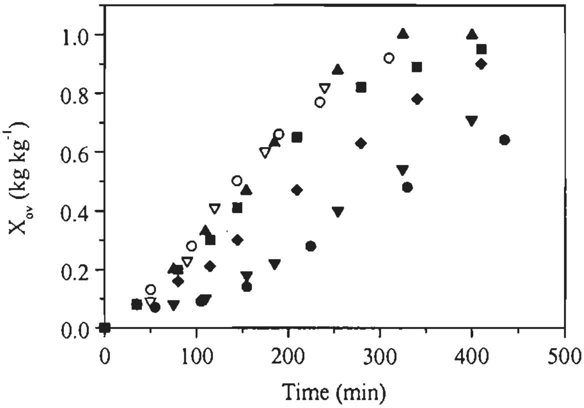


Figure 6.4: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Overall conversion time histories. Reactions performed at 70°C with a 60 nm seed latex with different amounts of acrylic acid. $N_p = 9.0\ 10^{16}$ dm^{-3}, [initiator] = 10 10^{-3} mol dm^{-3}, pH = 2.5, [Na$^+$] = 20 10^{-3} mol dm^{-3}, $f_{AA}^{ov,initial}$: ● 0, ▼ 1.6, ◆ 3.2, ■ 5.3, ▽ 6.3, ○ 6.3 + HCl, ▲ 6.6.

Table 6.7: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Reactions performed at 70°C with different seed latexes, acrylic acid content, initiator concentration and pH. Characteristics and results of all runs.

	pH	**$f_{AA}^{ov,initial}$ (10^{-2})**	**[initiator] (10^{-3} mol dm^{-3})**	**[Na^+]$^{a)}$ (10^{-3} mol dm^{-3})**	**R_p/N_p (10^{-22} mol s^{-1})**	**$\bar{n}$**	**$C_{AAsurf.}$ (μeq g_{pol}^{-1})**	**D.S.I. (%)**
	60 nm seed latex (S4), N_p = 9.0 10^{16} dm^{-3}, dp final = 120 nm							
SB13	3.0	0	10	20	4.0	0.13	0	0
SB14	2.5	6.6	10	20	7.5	0.24	290	40
SB15	3.0	1.6	10	20	4.7	0.15	80	50
SB16	2.5	3.2	10	20	5.1	0.16	180	50
SB17	2.5	5.3	10	20	7.0	0.22	250	43
SB18	2.5	6.3	10	20	8.1	0.26	-	-
SB20 $^{b)}$	1.8	6.3	10	20	8.0	0.26	-	-
	75 nm seed latex (S7), N_p = 4.6 10^{16} dm^{-3}, dp final = 160 nm							
SB31	2.5	6.3	10	20	9.7	0.31	320	45
SB32	2.5	6.3	0	20	No reaction	-	-	-
SB33	2.5	6.3	5	20	10.0	0.32	300	45
	45 nm seed latex (S9), N_p = 21 10^{16} dm^{-3}, dp final = 95 nm							
SB39	2.5	6.3	10	20	3.9	0.09	380	55
SB40	7	6.3	10	120	2.0	0.05	45	6
SB41	7	6.3	10	210	4.1	0.09	60	9
SB42	7	6.3	10	150	2.9	0.07	35	5
SB43	2.5	6.3	10	60	3.9	0.09	330	50

a) calculated with initiator, buffer, sodium chloride concentrations. The residual emulsifier in the seed latex has not been taken into account.

b) reaction performed with an additional amount of HCl (7.5 g of a 1 N solution in water)

R_p, can also be expressed by the relation already introduced in Chapter 2:

$$R_p = \frac{\bar{k}_p \, \bar{n} \, N_p \, C_{Mp}}{N_{av}} \qquad (6.2)$$

Equation 6.2 demonstrates that variations in R_p/N_p can be attributed to the influence of the acid content on either $\bar{k}_p$, the average propagation rate constant at the locus of polymerisation being the particle phase, or on $\bar{n}$, the average number of growing chains per particle. The influence of acrylic acid on C_{Mp}, the overall monomer concentration in the particles can be ruled out due to the low amounts of acrylic acid used in the recipes. No accurate data about the partitioning of acrylic acid are available for our systems. Nevertheless, variables such as the acid level, the monomer to water ratio, the ionic strength and the pH are expected to have a significant influence on the amount of acrylic acid monomer present in the particle phase, see Shoaf *et al.* [1990]. An influence of the overall acrylic acid fraction in the monomer on the composition of the monomer mixture in the swollen latex particles can therefore be expected. Higher acrylic acid fractions in the particle phase would affect the average propagation rate constant in the particle phase and results so in an increasing rate of polymerisation, see Figure 5.15. However, on the basis of the discussion presented in section 5.3.2.2, the influence of acrylic acid on $\bar{k}_p$ is probably very limited and it is questionable whether it could explain the differences in the polymerisation rates experimentally observed.

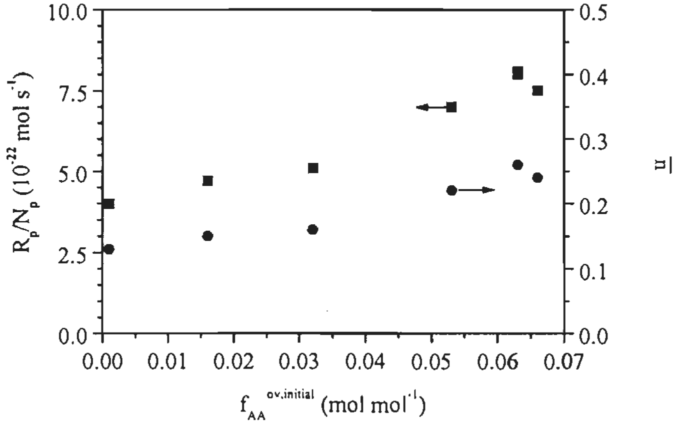


Figure 6.5: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Polymerisation rate per particle and average number of radicals per particle as a function of the initial overall acid content

The results were therefore attributed to a strong influence of the acrylic acid content on $\bar{n}$, *i.e.* on the emulsion polymerisation kinetic scheme according to which our systems proceed, see Chapter 2. $\bar{n}$ was estimated from the rate per particle with Equation 6.2 and with a $\bar{k}_p$ value corresponding to the copolymerisation of styrene and butadiene only, see section 5.3.2.1 and Figure 5.13: $\bar{k}_p = 340$ dm^3 mol^{-1} s^{-1}. The parameters used in the calculations are collected in Table 6.8.

Table 6.8: Values for parameters used in the calculation of the rate of polymerisation

Parameter	**Monomer**	**Value**	**Reference**
k_p at 70°C (dm^3 mol^{-1} s^{-1})	S	477	Buback *et al.* [1995]
E_A (kJ mol^{-1})		32.5	
	B	290	Deibert *et al.* [1992]
		35.7	
r_S, r_B	S, B	0.5, 1.4	Meehan [1946]
C_{Mp} (mol dm^{-3})		5.5	Hawkett *et al.*, 1980

The results collected in Table 6.7 show that the polymerisations obviously obey Smith Ewart Case 1 kinetics with $\bar{n} < 0.5$. In that situation, an increase in $\bar{n}$ when increasing $f_{AA}^{ov,initial}$ means that $f_{AA}^{ov,initial}$ had a strong influence on the mass transfer phenomena. Resulting in a higher entry rate of oligomeric radicals formed in the aqueous phase or a reduced free radical desorption rate from the latex particles. No comprehensive argument can actually support a lower exit rate when the acrylic acid content increases. Indeed, desorption mainly concerns radical species formed after transfer to monomer in the latex particle phase. The only consequence to be expected from an increased acrylic acid contents in the recipe may be a higher acrylic acid fraction in the latex particle phase. This would result in a higher probability of chain transfer to acrylic acid monomer. Exit into the aqueous phase of the highly water soluble newly formed monomeric radicals would also be higher unless the residence time of the radicals in the stabilisation layer is increased.

The influence of $f_{AA}^{ov,initial}$ on the rate of entry of oligomeric radicals in the latex particles has already been discussed in section 6.2.2. and is difficult to predict. Indeed, an increase in the acrylic acid concentration in the aqueous phase results in a moderate increase in $\bar{k}_{paq}$, see Figure 5.2 but also significantly affects the chemical composition of the oligomeric radicals, see Figure 5.22. In addition to the aqueous phase terpolymerisation kinetics, the efficiency of the persulfate decomposition might be influenced by the monomer concentration in water as well, see Cutié *et al.* [1997]. The use of larger quantities of water-soluble monomer might result in a larger free radical production rate in the aqueous phase.

The results concerning the influence of $f_{AA}^{ov,initial}$ on particle growth kinetics are different in seeded experiments as compared to the *ab-initio* batch emulsion polymerisation experiments presented in section 6.2.2, see experiments SB46 and SB48 in Table 6.3. The amount of acrylic acid did not have a strong influence on the kinetics of particle growth in *ab-initio* systems. The difference can be explained by realising that the two different series of experiments actually concerned latex particles with different diameters (final diameter > 180 nm for SB46 and SB48, final diameter = 120 nm for SB13 to SB20). $\bar{n}$ for the two *ab-initio* experiments can be estimated from the polymerisation rate per particle reported in Table 6.3

($Rp/Np \sim 2.8\ 10^{-21}$ mol s^{-1}) with the same assumptions as those made for seeded experiments. The estimation results in $\bar{n} \sim 0.9$ and indicates that the polymerisations were likely to proceed according to a transition from Smith Ewart Case 2 ($\bar{n} = 0.5$) to Case 3 ($\bar{n} > 0.5$) kinetics. The weak influence of entry rate in this kinetic regime is plausible and can explain the obtained results.

Other differences between the *ab-initio* and seeded systems are worth to be mentioned. In the case of *ab-initio* polymerisations, the reaction proceeded in the absence of surfactant molecules and the stabilisation of the latex particles was provided by the in-situ formed surfactant originating from effective entry of acid-rich oligomeric radicals formed in the aqueous phase. The particle growth occurred in the presence of this particular stabilisation layer which can have a significant influence on the oligomeric radical capture, see Coen *et al.* [1996]. In the case of the seeded systems, the seed latexes were prepared with emulsifier. Most of the emulsifier was removed by dialysis but the latex particles used in the seeded experiments were still partially covered with surfactant molecules. The particle growth occurred in this case in the presence of another type (more "conventional") of stabilisation layer which can also influence the oligomeric radical capture.

Acid incorporation

The results collected in Table 6.7 and Figure 6.6 show that the acrylic acid in the recipe had a significant influence on the amount of surface acid groups in the latex products. Like in the *ab-initio* systems, $C_{AAsurf.}$ increased with the amount of acid monomer introduced in the recipe. Figure 6.6 shows the relation between $C_{AAsurf.}$ and $f_{AA}^{ov,initial}$. The increasing amount of surface acid groups with acid content in the recipe is in good agreement with the expected variations in the aqueous phase polymerisation products (concentration and composition) already discussed, see section 6.2.2. The increasing amount of surface acid groups with the acid content in the recipe is also in good agreement with the observations reported in section 6.2.3 about the acid incorporation as a function of the overall conversion, see Table 6.4 and Figure 6.3. Actually from the acid incorporation point of view, there is hardly any difference between an emulsion polymerisation carried out *ab-initio* or with a seed latex. Indeed, it was found out that in an *ab-initio* process, most of the final surface acid groups were incorporated in the last stage of the reaction as well, see Figure 6.3.

The information about the presence of acid groups in the interior of the latex particles is however missing and no conclusion can be drawn about the possibility for surface acid groups to be buried during the process, by which those acid groups are not accessible for analysis. This means that no mechanistic interpretation of the results can be made in terms of relation between the surface acid groups and the rate of entry.

Greene [1973] studied the emulsion polymerisation of styrene, butadiene and acrylic acid in seeded systems. The experimental conditions in terms of particle diameter, temperature and solids used by this author were somewhat different than those in the present study but the results clearly indicate that the amount of acrylic acid chemically incorporated into the polymer phase was increasing with an increasing concentration of acrylic acid used in the polymerisation. Greene observed a constant ratio of the amount of acrylic acid in the serum phase and the amount of surface acid when the acrylic acid content in the recipe is varied. The ratio between the amount of surface acid and the amount of acid in the interior of the particles also remained constant on varying the acrylic acid content in the recipe. Our results are in good agreement with those reported by Greene as far as the influence of the acrylic acid concentration on the incorporation yield is concerned. The information about the overall distribution of the acid groups, however, has to be considered with care.

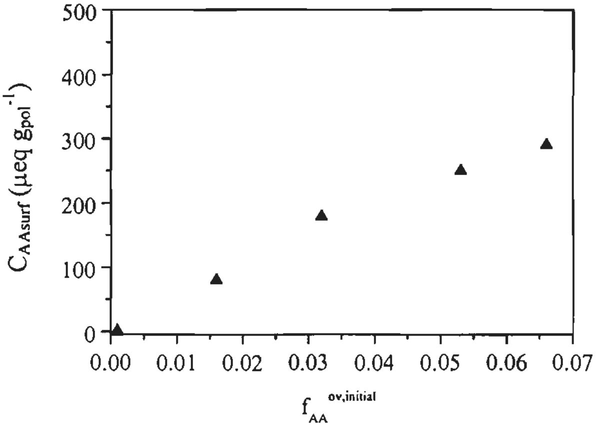


Figure 6.6: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Incorporation of surface acid groups as a function of the initial overall acid content for experiments SB13 to SB17. See latex characteristics in Table 6.7.

6.3.3. Influence of initiator concentration

Additional experiments were performed with different amounts of initiator, see experiments coded SB31, SB32, SB33 in Table 6.7. The conditions were similar to those used in the series discussed previously except for the seed latex which had a slightly larger particle size diameter. Therefore, the latex particle number was decreased to keep the seed polymer/water ratio the same for all the experiments. The results collected in Table 6.7 show that no reaction occurred in the absence of initiator ruling out the possibility of thermal initiation in the system. No influence of initiator concentration could experimentally be observed on the polymerisation rate per particle and on $\bar{n}$ calculated with the assumptions made in section 6.3.2. $\bar{n}$ was lower than 0.5 but slightly larger than in the series performed with various amounts of acrylic acid confirming the Smith-Ewart Case 1 kinetics and the dependence of $\bar{n}$ on the latex particle diameter. Figure 6.7 shows on a logarithmic scale the influence of the particle diameter on $\bar{n}$ calculated for the three seeded polymerisation series in Table 6.7 and the *ab-initio* polymerisations in Table 6.3 performed with an initiator concentration of 10 10^{-3} mol dm^{-3}. Note the resemblance between Figure 6.7 and the well-know Ugelstad plots shown in Figure 2.2. Actually, combining $\alpha' = \rho_i\ v / N_p\ k_t$ and $N_p = V / v$ results in $\alpha' \propto d_p^6$ for constant V and k_t (V is the volume of the polymer phase, v is the volume of a particle, k_t is the termination rate constant in the particle phase and ρ_i is the rate of radical production in the aqueous phase). At constant initiator concentration and acid content (ρ_i might be influenced by $f_{AA}^{ov,initial}$) Log α' can be replaced by Log d_p. Figure 6.7 therefore suggests the occurrence of different polymerisation schemes during the experiments performed with different particle diameters. It also confirms that the *ab-initio* experiments probably proceed according to Smith Ewart Case 3 kinetics whereas the seeded experiments cover Case 1 and 2 with an apparent limiting value for $\bar{n}$.

The independence of $\bar{n}$ on the initiator concentration is unclear if the hypothesis that the polymerisations proceeded according to Case 1 kinetics with $\bar{n} < 0.5$ is retained. Similar results have been reported by Weerts [1990] and Verdurmen [1993] in their investigation of the emulsion polymerisation of butadiene with initiator concentrations below about 10^{-2} mol dm^{-3}. These authors explained this behaviour by an increased radical loss via desorption from the latex particles. However, the limiting $\bar{n}$ value shown in Figure 6.7 indicates that the polymerisations performed with various initiator concentrations proceed close to Case 2 and therefore no initiator effect should be expected. Note that it should be realised that the initiator concentration was not varied over a large range (5 to 10 10^{-3} mol dm^{-3}).

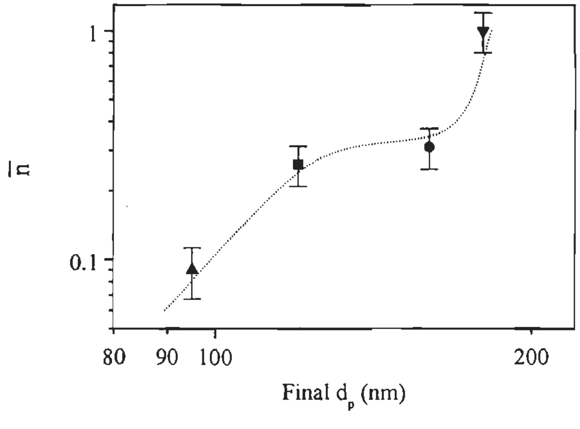


Figure 6.7: Batch emulsion polymerisation of styrene, butadiene and acrylic acid. Polymerisation rate per particle as a function of the final latex particle diameter. Reactions performed at 70°C with 5 g acrylic acid, [initiator] = 10 10^{-3} mol dm^{-3}, pH = 2.5, $[Na^+]$ = 20 10^{-3} mol dm^{-3}. ▲ SB39, ■ SB18, ● SB31, ▼ SB46. See detailed characteristics in Table 6.7.

The results about the acid incorporation on the surface of the latex particles did not show any influence of the initiator concentration used. $C_{AAsurf.}$ is solely dependent on the amount of functional monomer introduced in the recipe.

6.3.4. Influence of pH and ionic strength

In a third and last series of seeded emulsion polymerisation experiments the influence of pH and ionic strength on the rate of polymerisation and the acid incorporation was investigated. The influence of pH and ionic strength on colloidal aspects and on some of the kinetic parameters involved in latex systems has already been introduced in Chapters 2 and 5. The ionic strength is known to affect the colloidal stability, the particle size and particle number of latex systems, see e.g. Ottewill [1982] and Fitch [1997]. Additional sodium chloride was introduced into the reaction mixture to increase the concentration in ionic species. Table 6.7 gives the overall $[Na^+]$ in all experiments. $[Na^+]$ is used as a measure for ionic strength. All experiments resulted in stable latexes. In most cases, neither secondary nucleation nor coagulation (upon addition of sodium chloride) occurred. Figure 6.8 shows the Particle Size Distributions (PSD) of the seed latex and the final latexes obtained by seeded polymerisation. All particle size distributions were determined by TEM. The shape of the PSD of the latex products agree with the shape of the PSD of the seed latex except for latex SB40 which shows a broader and bimodal PSD compared to the other latexes.

Polymerisation rate

Figure 6.9 shows the overall conversion time histories of the series of experiments carried out at different values of the pH and the ionic strength. The overall polymerisation rate per particle was determined for each experiment from the conversion time histories in the overall conversion region between 0 and 0.5. The amount of surface weak acid groups was also determined for all the final latex products.

The results collected in Table 6.7 and in Figure 6.9 show that the pH had a significant effect on the polymerisation rate per particle. This effect cannot be attributed to different N_p since no secondary nucleation occurred in most cases. For experiment SB40, the lowest polymerisation rate per particle was observed. The final latex of experiment SB40 had the broadest PSD. Probably secondary nucleation occurred at the beginning of the process leading to the formation of new particles. However, the rate per particle was calculated with the value of N_p given in Table 6.7 corresponding to a polymerisation proceeding without secondary nucleation. Therefore the rate per particle was probably overestimated for experiment SB40.

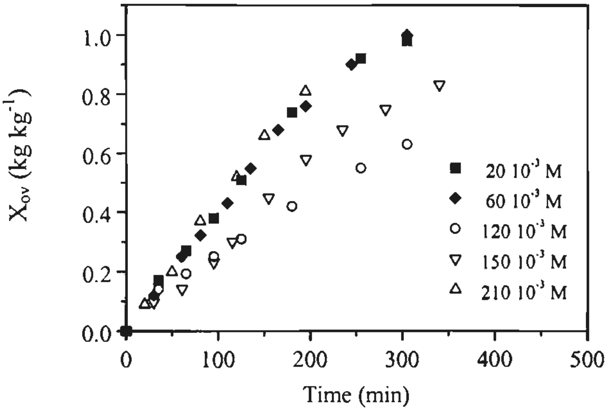


Figure 6.9: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Overall conversion time histories. Reactions performed at 70°C with a 45 nm seed latex, 5 g acrylic acid, $N_p = 21\ 10^{16}\ dm^{-3}$ and [initiator] = 10 10^{-3} mol dm^{-3}. Solid symbols: pH = 2.5; open symbols: pH = 7. [Na^+] = : ■ 20, ♦ 60, ○ 120, ▽ 150, △ 210 (10^{-3} mol dm^{-3})

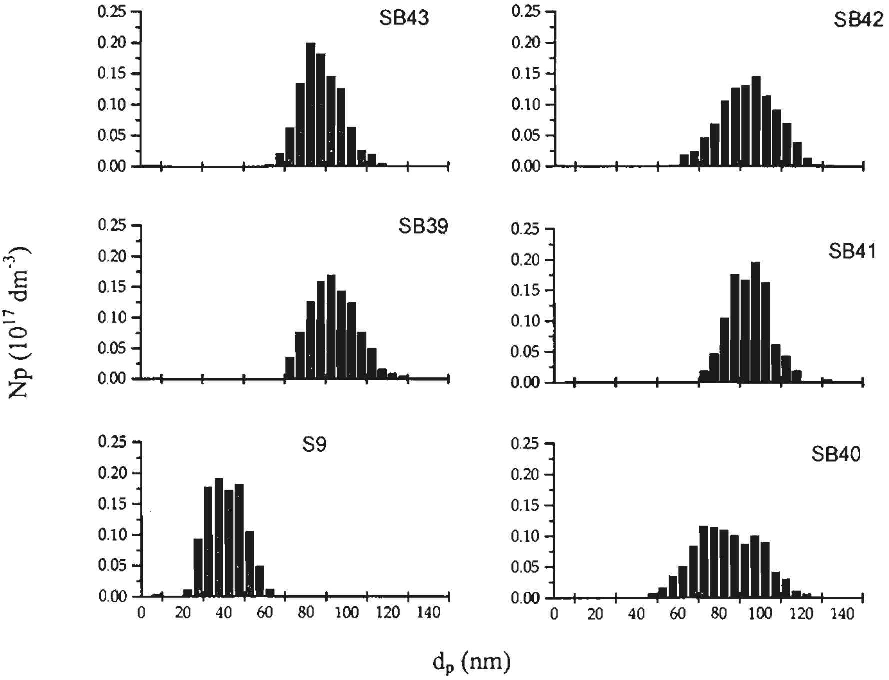


Figure 6.8: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Final particle size distributions of the latexes. Reactions performed at different pH and [Na^+], at 70°C with a 45 nm seed latex, 5 g acrylic acid, Np = 21 10^{16} dm^{-3} and [initiator] = 10 10^{-3} mol dm^{-3}. See latex characteristics in Table 6.7.

The results obtained indicate that for the experimental conditions of this study, the particle growth process depends on the pH of the reaction mixture: a low pH corresponds to a higher polymerisation rate. This can be explained by the decreased tendency of neutralised acid species to enter the organic particle phase leading to a lower rate of capture of oligomeric radicals at pH 7 as compared to pH 2.5. However, the results show that at pH 7 the polymerisation rate increased upon increasing the ionic strength (successively experiments SB40, SB42, SB41). As expected, the polymerisation rate at pH 2.5 was hardly affected by the introduction of additional salt in the reaction mixture. Note, however, that $[Na^+]$ was not varied over a wide range over a wide range, see Figures 6.9 and 6.10 as well as Table 6.7.

As already discussed previously, these results have to be related to the influence of the studied parameters on $\bar{k}_p$ in the particle phase and/or on $\bar{n}$. $\bar{k}_p$ in the particle phase is strongly influenced by the mole fraction of acrylic acid monomer in the latex particles, see Chapter 5, and therefore by the partition coefficient of acrylic acid. The influence of ionic strength on the partitioning of monomers between water and organic phase has been reported before. Klein *et al.* [1973] investigated the influence of ionic strength on the polymerisation rate for the emulsion polymerisation of vinyl acetate. These authors reported an increase in C_{Mp}, the monomer concentration in the particle phase, with increasing ionic strength. These authors attributed this effect to the decrease in interfacial tension upon condensation of the emulsifier. Shoaf *et al.* [1990] investigated the influence of ionic strength on the partitioning of acrylic acid and methacrylic acid between water and styrene. These authors reported a significant effect of ionic strength on the partitioning at low pH (all acid groups are protonated) with a larger partition coefficient of the carboxylic acid monomer at high ionic strength. Shoaf *et al.* did not investigate the influence of ionic strength at higher pH (all acid groups are dissociated) on the partitioning which can, however, be expected limited due to the high hydrophilicity of the dissociated acid species. We did not observe any influence of $[Na^+]$ on R_p at pH 2.5 which confirms that the presence of acrylic acid in the particle phase does not have a significant influence on $\bar{k}_p$, see section 5.3.3.2 and Figure 5.20. Similar results were obtained by Yuan [1996] in his investigation of the role of water-soluble oligomers in styrene-butadiene-acrylic acid emulsion polymerisation. The author did not mention any control of the pH of the reaction mixture and we therefore assume that the investigation was carried out at low pH values.

If the influence of $[Na^+]$ on $\bar{k}_p$ in the particle phase at any polymerisation pH is ruled out, the kinetic behaviour of our system must be attributed to variations in $\bar{n}$. The results collected in Table 6.7 and Figure 6.7 show that all polymerisations proceeded with $\bar{n} < 0.5$ according to Smith Ewart Case 1 kinetics. As already discussed in section 6.3.2, an increase in $\bar{n}$ as observed experimentally is therefore the result of a higher entry rate at pH 2 compared to pH 7 and an entry rate increasing with ionic strength at pH 7. Adams *et al.* [1988] studied the influence of ionic strength on the entry rate for the emulsion polymerisation of styrene with an ionic initiator and an ionic surfactant. These authors reported the adsorption of a radical into a particle is not governed by colloidal considerations involving the electrical double-layers around a latex particle and a charged oligomeric radical. However, Coen *et al.* [1996] investigated the influence of pH and ionic strength on the entry an exit rate coefficients in the emulsion polymerisation of styrene performed with an electrostatically-stabilised (sodium dihexyl sulfoccinate) and an electrosterically-stabilised (copolymer of acrylic acid and styrene) seed latex. These authors reported that a decrease in pH from 7 to 4 or an increase in the ionic strength had hardly any effect on the entry and exit rate coefficients in electrostatically-stabilised latexes. However, a significant increase of these coefficients in electrosterically-stabilised systems was observed. These authors suggested the presence of a "hairy layer", see Seebergh *et al.* [1995], in electrosterically-stabilised systems. This "hairy layer" makes that the diffusion of radical species becomes the rate-determining step in the polymerisation process.

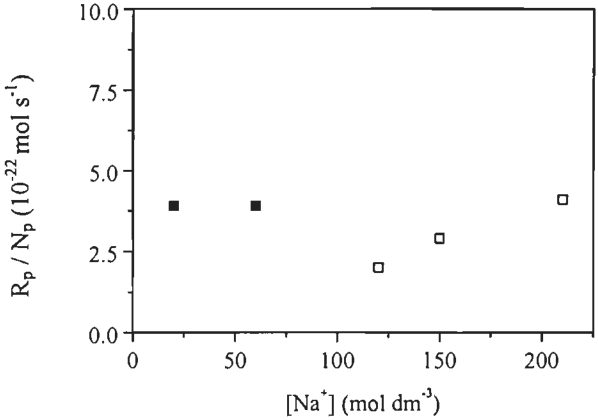


Figure 6.10: Batch seeded emulsion polymerisation of styrene, butadiene and acrylic acid. Polymerisation rate per particle as a function of [Na^+]. Reactions performed at 70°C with a 45 nm seed latex, 5 g acrylic acid, Np = 21 10^{16} dm^{-3} and [initiator] = 10 10^{-3} mol dm^{-3}. Solid symbols: pH = 2.5; open symbols: pH = 7.

Our system is actually more complex than those presented here above. We have investigated the fundamental steps taking place in the presence of seed latex particles initially totally electrostatically-stabilised but which build up carboxylic acid groups on the surface of the particles during polymerisation. Moreover, a completely water-soluble and pH-sensitive comonomer is used together with styrene as main monomer. The events taking place in water at pH 7 and various ionic strength are very complex as far as the polymerisation rate and the styrene and sodium acrylate reactivities are concerned, see Chapter 5 and the discussion concerning the polymerisation of acrylic acid in water as a function of pH. Undoubtedly, the formation of oligomeric radicals is affected. The oligomeric radicals ready to enter the latex particles may as well undergo a "salting-out" effect when increasing the ionic strength, see Chapter 5. This results in the enhanced entry rate of the radical species by the particles. The absence of "salting-out" effect at pH 2.5 is probably due to the different nature of the oligomeric radicals. Note however that $[Na^+]$ was not varied over a large range in these experimental conditions of low pH. The occurrence of secondary nucleation at pH 7 and low ionic strength indicates that instead of being captured by the particles, the oligomeric radicals can as well precipitate and form precursor particles.

In addition to these solubility considerations and as suggested by Coen *et al.* [1996], the events taking place at the interface between the particle phase and the water phase of our latex systems might also be affected by the pH and the ionic strength. After few acrylic acid units have been incorporated onto the surface of the latex particles, the so-formed in-situ surfactant can behave like the electrostatic-stabiliser investigated by Coen *et al.*. At low pH, the stabilising layer around the particles is compressed and no additional effect of $[Na^+]$ can be observed. At pH 7, the thickness of the stabilising layer depends on the ionic strength and the thickness of the layer might affect the effective capture of the oligomeric radicals by the latex particles. It is remarkable that for very high values of $[Na^+]$ at pH 7, the polymerisation rate per particle was similar to that observed at pH 2.5. This remarkable observation points to some kind of limiting value for the polymerisation rate per particle, see Figure 6.10. This result indicates that we reached in these situations some sort of optimal conditions for the polymerisation rate per particle.

Acid incorporation

The results summarised in Table 6.7 show that the pH of the reaction mixture had a significant influence on the amount of carboxylic acid groups incorporated onto the surface of the particles in the final latex product. The values obtained at pH 2.5 for this series of experiments are in good agreement with those obtained for the other series and show once again that effective entry of carboxylic acid-rich oligomeric radicals provided the latex particles with functional groups located on the surface. As already observed for the *ab-initio* reactions, see section 6.2.3, the amount of surface acid groups is much lower at pH 7 than at pH 2.5. This behaviour can be attributed to the more hydrophilic nature of the functional carboxylic monomer at pH values above the pKa. The ionic strength had hardly any influence of C_{AAsurf}. at low pH which is consistent with the kinetic results. However, at pH 7, only a small increase could be observed in C_{AAsurf}. when increasing the ionic strength although the effect on the kinetics was much more pronounced, see Figures 6.9 and 6.10. The increase in C_{AAsurf}. with ionic strength can be attributed to a more efficient capture of acid-rich oligomeric radicals as suggested by the polymerisation rate. However, although the polymerisation rate at pH 7 and high ionic strength was similar to the one obtained at pH 2.5, as a result of similar entry rates, the acid incorporation was far lower. This indicates that the chemical composition of the oligomeric radicals entering the latex particles might strongly depend on the pH of the reaction mixture. This can indeed be expected from a co-monomer like acrylic acid. A more detailed study of the process of acrylic acid incorporation in latex products combining acid distribution and polymerisation kinetics will be presented in Chapter 7 and Chapter 8.

6.4. Conclusions

Ab-initio emulsion copolymerisation experiments of styrene, butadiene and acrylic acid give information about the influence of acrylic acid and pH on the polymerisation kinetics and more particularly about the nucleation mechanism. The results can be qualitatively described by the amount of polymer chains formed in the aqueous phase, their expected chemical composition and the water-solubility.

Seeded emulsion polymerisation experiments give valuable information about the process of incorporation of carboxylic groups in latex products. The polymerisation rate in seeded system can be directly related to the average number of radicals per particle. The polymerisation proceed according to one of the three Cases distinguished by the Harkins' theory depending mainly on the size of the latex particles. Evidence is found that acrylic acid content, pH and ionic strength play a significant role in the particle growth kinetics by affecting the mass transfer phenomena more probably with respect to the rate of entry.

Additional information can be obtained from the amount of the carboxylic groups incorporated on the surface of the latex particles. However, no acid distribution can be determined since the amount of carboxylic groups buried in the interior of the latex particles is difficult to quantify. The determination of the surface incorporation in *ab-initio* experiments confirms the participation of acrylic acid to the nucleation process. During particle growth, hardly any consistency is found between the variations in reaction rate and the incorporation efficiency. Acrylic acid content and pH are the parameters which substantially control the amount of surface acid groups.

7

Seeded Emulsion Polymerisation of Styrene: Kinetics and Incorporation of Acrylic Acid in Latex Products

ABSTRACT: The batch seeded emulsion polymerisation of styrene in the presence of acrylic acid is studied. The progress of the reaction in terms of polymerisation rate is investigated. Attempt is made to evaluate the average number of growing chains per particle during Interval II of the emulsion polymerisation process. The final latex products are characterised by means of conductometric aqueous titration and potentiometric titration in an organic solvent mixture. The distribution of the acid groups over the aqueous phase, the particle surface and the particle interior during polymerisation is combined with the kinetic results to provide insight into the mechanisms governing the incorporation of acrylic acid in emulsion polymerisation products. The results indicate that pH is the main parameter affecting the process. An optimal incorporation on the surface of the particles is found for a low value of pH when all the acid groups are protonated. Two-step processes in which a shot of acrylic acid is performed in the last stage of the emulsion polymerisation reaction are investigated as a strategy to increase the surface incorporation efficiency.

7.1. Introduction

The present chapter attempts to provide insight into the influence of some reaction parameters on the course of the emulsion polymerisation of styrene (S) in the presence of acrylic acid (AA). Nucleation has been avoided by performing seeded experiments as suggested in chapter 6. The variables investigated include pH, temperature and particle diameter. Attention is focused on the effects on both the polymerisation rate and the ultimate distribution of the functional monomer over the latex particles. Therefore, the mechanisms leading to the incorporation of carboxylic groups during particle growth can be discussed.

7.2. Particle growth in the presence of acrylic acid

7.2.1.Experimental

The seed latexes were prepared by emulsion polymerisation of styrene in the presence of sodium dodecyl sulfate as surfactant and sodium persulfate as initiator. The characteristics of the seed latexes are given in Table 7.1. The seed latexes were submitted to dialysis to remove the excess surfactant before use in seeded emulsion polymerisation reactions, see section 3.2. The final seed latex particle diameter and particle size distribution were determined by Transmission Electron Microscopy.

Table 7.1: Characteristics of the polystyrene seed latexes

	MK2	MSS13	MSS10	MSS19
final diameter (nm)	34	50	97	100

The seeded experiments were carried out in a jacketed cylindrical stainless steel/glass reactor, described in Chapter 3. The parameters which were varied in the seeded emulsion copolymerisation of S and AA are the size of the seed latex particles, the pH and the temperature of the reaction mixture. Table 7.2 gives an overview of all the recipes. The amount of acrylic acid introduced in the recipes is expressed by $f_{AA}^{ov,initial}$, the overall initial acrylic acid mole fraction in the monomer mixture. $C_{M,0}$ represents the initial monomer concentration expressed per unit volume of the aqueous phase. A variable amount of sodium (Na_2CO_3) was used to control the pH of the reaction mixture. Sodium (NaCl) was added to correct for the variation in ionic strength (based on the total concentration in Na^+ cations in the recipe). All the ingredients except the initiator were supplied to the reactor. Before the addition of the initiator the reaction mixture was equilibrated for about 30 minutes at reaction conditions expressed in temperature and stirring speed. After reaction, the latexes were characterised in terms of particle size and acrylic acid distribution according to the procedures described in Chapters 3 and 4. TEM results showed that a secondary generation of latex particles was never formed and that the final particle diameter was in good agreement with the expected value calculated with equation 3.6.

Table 7.2: Standard recipe for batch seeded emulsion polymerisation of styrene and acrylic acid

Seed	10 g of solid polymer
Styrene	85 g
Acrylic acid	5 g
DI water	900 g
Sodium persulfate ($Na_2S_2O_8$)	10.10^{-3} mol dm^{-3}
Sodium dodecyl sulfate (SDS)	$5.5.10^{-3}$ mol dm^{-3}
Sodium carbonate (Na_2CO_3)	0 / 50.10^{-3} mol dm^{-3}
Sodium chloride (NaCl)	100.10^{-3} / 0 mol dm^{-3}
Temperature (°C)	50 to 80
$C_{M,0}$	0.985 mol dm^{-3}
$f_{AA}^{ov,initial}$	0.08
$C_{AAtot.}$ (μ_{eq} g_{pol}^{-1})	694

7.2.2. Influence of particle size on polymerisation kinetics

In our study, R_p is calculated with Equation 3.2 from the conversion-time histories in the conversion region between 0 and 0.4, see Figures 7.1 and 7.2. In the time interval corresponding to this conversion region unreacted monomer is still present in the reaction mixture as a separate phase and $C_{M,p}$ corresponds to the overall monomer in the particle phase. The assumption is made that $C_{M,p}$ is constant for conversions up to about 0.6, see Table 6.8.

The limited influence of acrylic acid on $\bar{k}_p$ in the particle phase has already been discussed in Chapters 5 and 6. Therefore $\bar{n}$ was estimated from the rate per particle with Equation 7.1 and with a $\bar{k}_p$ value corresponding to the copolymerisation of styrene only, see section 5.3.2.1 and Figure 5.13: $\bar{k}_p = 477$ dm^3 mol^{-1} s^{-1} at 70°C. The parameters used in the calculations are collected in Table 6.8.

$$R_p = \frac{\bar{k}_p \, \bar{n} \, N_p \, C_{Mp}}{N_{av}} \tag{7.1}$$

Table 7.3: Results from all runs. $f_{AA}^{ov,initial} = 0.08$

	T (°C)	**pH**	**R_p/N_p (10^{-21}mol/s)**	**$\bar{n}$**	**D.S.I. (%)**	**Buried AA [b)]**	**Free AA [b)]**
34 nm seed latex, $N_p = 5.4\ 10^{17}$ dm^{-3}, $dp_{swol.} = 75$ nm, $A_p = 9540$ m^2 dm^{-3}							
S34-50L	50	2.5	0.17	0.08	36	18	46
S34-50H	50	7.0	0.26	0.12	6		
S34-50L' [a)]	50	2.5	0.27	0.13	57	13	30
S34-50H' [a)]	50	7.0	0.26	0.12	9		
S34-75L	75	2.5	0.72	0.14	51	25	24
S34-75H	75	7.0	0.70	0.14	6	5	89
50 nm seed latex, $N_p = 1.7\ 10^{17}$ dm^{-3}, $dp_{swol.} = 110$ nm, $A_p = 6460$ m^2 dm^{-3}							
S50-60L	60	2.5	0.70	0.22	48	22	30
S50-60H	60	7.0	0.69	0.22	6	6	88
S50-60L' [a)]	60	2.5	0.82	0.26	51	19	30
S50-60H' [a)]	60	7.0	0.85	0.27	3	10	87
S50-70L	70	2.5	1.14	0.26	51		
S50-70H	70	7.0	1.11	0.25	8		
97 nm seed latex, $N_p = 2.3\ 10^{16}$ dm^{-3}, $dp_{swol.} = 210$ nm, $A_p = 3185$ m^2 dm^{-3}							
S97-70L	70	2.5	3.53	0.82	37	25	38
S97-70H	70	7.0	4.40	1.00	6		
S97-80L	80	2.5	7.50	1.20	41	25	34
S97-80H	80	7.0	4.56	0.75	6	5	89
100 nm seed latex, $N_p = 2.1\ 10^{16}$ dm^{-3}, $dp_{swol.} = 210$ nm, no AA added							
B100-70L [c)]	70	2.5	3.90	0.9			
B100-70H [c)]	70	7.0	3.90	0.9			

a) [initiator] = 20 mmol

b) expressed in % of the initial amount of acid groups

The results collected in Table 7.3 show that for an overall conversion of 0.4, the polymerisations started with a seed latex with a diameter of 34 nm or 50 nm obey zero-one kinetics with $\bar{n} < 0.5$. Polymerisations started with a seed latex with a diameter of 97 nm can roughly be approximated with Smith-Ewart Case 3 kinetics with $\bar{n} > 0.5$, see Chapter 2. Note that the polymerisations started with the seed latex with a diameter of 97 nm all showed an increase in the polymerisation rate for overall conversions higher than 0.6, see Figure 7.2. This increase should be attributed to a gel effect.

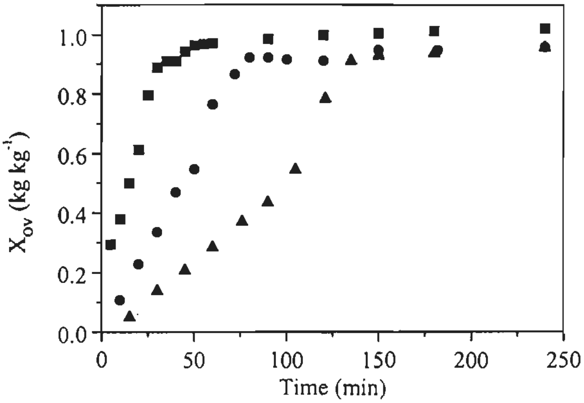


Figure 7.1: Overall conversion as a function of time for the batch seeded emulsion polymerisation of Styrene and Acrylic Acid.
pH=2.5, $[Na_2S_2O_8]=10.10^{-3}$mol dm^{-3}.
■ 34 nm, T=75°C, $N_p=5.4\ 10^{17}$ dm^{-3}; ● 50 nm, T=70°C, $N_p=1.7\ 10^{17}$ dm^{-3}; ▲ 97 nm, T=70°C, $N_p=2.3\ 10^{16}$ dm^{-3}

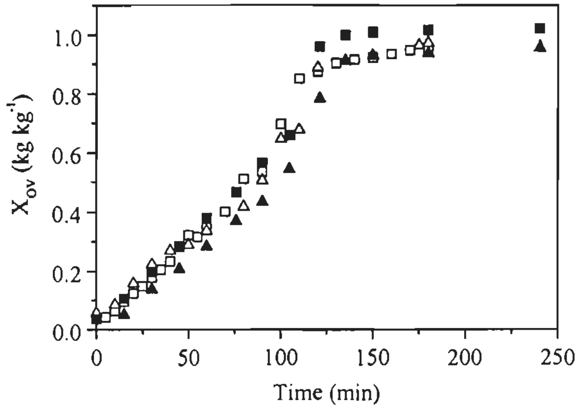


Figure 7.2: Overall conversion as a function of time for the batch seeded emulsion polymerisation of Styrene with (solid symbols) and without (open symbols) Acrylic Acid. ■ pH=2.5; ▲ pH=7.
97nm seed, $N_p = 2.3\ 10^{16}$ dm^{-3}, $[Na_2S_2O_8]=10.10^{-3}$ mol dm^{-3}, T=70°C.

Figure 7.3 shows $\bar{n}$ as a function of $d_{pswol.}$, the swollen particle diameter, for all the experimental conditions of pH, temperature and initiator concentration collected in Table 7.3.

$d_{pswol.}$ has been calculated at an overall conversion of 0.4, with a relation derived from combining Equations 3.5 and 3.6:

$$d^3_{pswol} = \frac{1}{1 - \frac{M_S\, C_{Mp}}{\rho_S}} \left(d_{pseed}^{\ 3} + \frac{6}{\pi} \frac{M_S\, X_{ov}\, C_{M,0}}{1000\, N_p\, \rho_{PS}} \right) \quad (7.2)$$

where d_{pseed} is the seed particle diameter, M_S (M_S=104g mol^{-1}) is the styrene molar mass, ρ_S and ρ_{PS} are the densities of respectively S and polystyrene, see Table 3.2. Figure 7.3 shows that $\bar{n}$ increases with particle size. This behaviour is in good agreement with values of $\bar{n}$ smaller or larger than 0.5 found experimentally, see section 6.3.3.

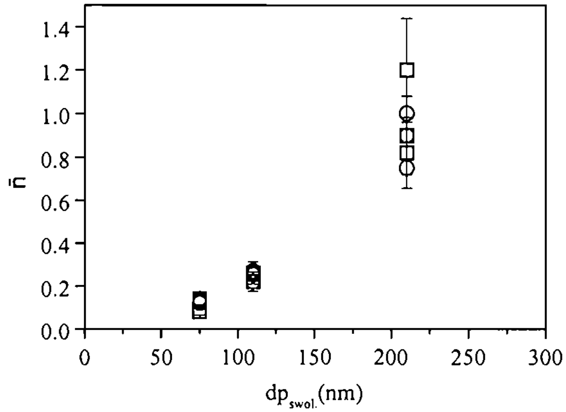


Figure 7.3: $\bar{n}$ as a function of the diameter of the swollen latex particles at x_{ov}=0 in the batch seeded emulsion polymerisation of styrene and acrylic acid for all the initiator concentrations and temperature listed in Table 7.3.
□ pH = 2.5, ○ pH = 7.

7.2.3. Influence of pH on the polymerisation kinetics

The pH is expected to have a strong influence on the course of the emulsion polymerisation process for the production of carboxylated latexes. Affecting the hydrophilicity of the functional monomer and of oligomers bearing carboxylic groups, the pH plays a considerable role in the kinetics of emulsion polymerisation, see Chapter 6. During the particle growth stage, the pH affects mainly the aqueous phase polymerisation and the mass transfer e.g., adsorption of oligomers, entry and exit. The use of persulfate as initiator in our systems further complicated the interpretation of the results since the decomposition rate of persulfate is known to be strongly dependent upon pH, see Kolthoff *et al.* [1951]. These authors showed that the initiator decomposition is accelerated by hydrogen ions when the pH is less than 3 due to an additional acid-catalysed decomposition reaction which does not produce any free radical. Dos Santos [1997] studied the decomposition of persulfate in the pH range from 3 to 7 and found no influence of hydrogen ion concentration on the decomposition rate. Henton *et al.* [1997] investigated the influence of AA on the decomposition of persulfate and observed an increased decomposition rate in the presence of AA and partially neutralised AA in comparison with the decomposition in water buffered at equivalent pH values. Similarly, Cutié *et al.* [1997] investigated the influence of monomer concentration on the persulfate initiated polymerisation rate of acrylic acid in water. These authors reported the interaction of the monomer with the initiator itself or with the initiator derived radicals trapped in a solvent cage. This behaviour can have a significant influence on the free radical generation rate. However, the limitation of all the methods ever used to study the thermal decomposition of persulfate is that neither the rate of free radical generation nor the efficiency can be directly measured. The effect of pH on the rate of free radical production in water is therefore still difficult to quantify.

In the present work, the experimental conditions were chosen to ensure a complete protonation, pH 2.5, or neutralisation, pH 7 of the carboxylic groups in both the monomer and the polymer, see section 5.2. As references, two polymerisation reactions were performed without the addition of AA, experiments B100-70L and B100-70H in Table 7.3. These reactions were performed with another seed latex having equivalent characteristics in terms of particle size and amount of surfactant than the one used for the S97 series. The results in terms of the influence of pH on the polymerisation rate in both series of experiments can therefore be compared. For the experiment performed at pH 2.5 without AA, the pH was adjusted by adding a proper amount of acetic acid to the initial reaction mixture. For the experiment at pH 7, sodium carbonate was used to adjust the pH. No difference was found in the overall polymerisation rate between experiments B100-70L and B100-70H. One interpretation of this result is that the polymerisation obeys Smith-Ewart Case 2 kinetics with $\bar{n}=0.5$. For Case 2 kinetics the initiator decomposition rate has indeed no influence on the polymerisation rate. However, the value of $\bar{n}=0.9$ calculated from the actual polymerisation rate using Equation 7.1 is larger than the Case 2 value of 0.5. Another interpretation is that the free radical generation process is hardly affected by the pH. In the absence of significant aqueous phase polymerisation, equivalent free radical generation rates result inevitably in equivalent overall polymerisation rates. The latter interpretation is supported by the molecular weight distribution of the final latex products which was not significantly different for the experiment carried out at pH 2.5 and the experiment performed at pH 7.

The presence of AA in the S97 series at a temperature of 70°C had only a limited influence on the overall polymerisation rate which was comparable to the rate of polymerisation observed in the B100 series at both pH-values investigated. The role of AA as well as the influence of pH on the course of the reaction in this particular situation was therefore questionable. Increasing the temperature to 80°C did not have the same influence on the polymerisation rate at pH 2.5 and pH 7. The increase in polymerisation rate at pH 2.5 was considerably larger than at pH 7. The different behaviour of the polymerisation rate at both pH values originates from a different influence of temperature on $\bar{n}$.

For the rest of the reactions performed in this study in the presence of AA, the pH appeared to have in most cases only a small influence on the polymerisation rate. The rate in experiment S34-50 was however significantly lower at pH 2.5 than at pH 7. An additional experiment was performed in which the amount of initiator was doubled. The results are also reported in Table 7.3. The polymerisation rate and so $\bar{n}$, increased a factor 1.5 at pH 2.5. Increasing the temperature to 75°C resulted in an increase in $\bar{n}$ as well. These results seem to confirm that the polymerisations started with seed particles with a diameter of 34 nm obeyed Smith-Ewart Case 1 kinetics with R_p increasing with the initiator concentration. However, at pH 7 hardly any influence of temperature or initiator concentration could be observed on $\bar{n}$. In polymerisations started with 50 nm seed particles $\bar{n}$ increased moderately upon temperature and initiator concentration at both pH-values indicating that the polymerisation rate is not very sensitive to the rate of free radical generation.

7.2.4. Incorporation of acid groups

The amount of acid groups present in polymer molecules which will ultimately reside in the outer shell of the surface, *i.e.* surface acid, as well as the amount of acid groups present inside the particles, *i.e.* buried acid, are strongly dependent on the pH of the reaction mixture, see Table 7.3. There are two distinct situations. In products produced at pH 7 most of the acid groups remained in the aqueous phase and both the amount of surface acid and the amount of buried acid were small. Generally less than 10% of the initial amount of AA was incorporated. This result is in agreement with the increased hydrophilicity of the functional monomer in its dissociated form. The carboxylic monomer concentration in the particle phase at pH 7 is considerably lower than at pH 2.5. Oligomeric radicals formed in water at pH 7 are also likely to be more hydrophilic than at pH 2.5 and therefore have a rather low tendency for entry. As a consequence, bimolecular termination of the oligomeric radicals in the aqueous phase at pH 7 may be expected to be more probable than at pH 2.5.

At pH 2.5 most of the acid was present as surface acid. Between 40 and 50% of the initial amount of AA was present in the outer shell of the particles. Additionally, a significant amount of AA, *i.e.* about 25%, was buried inside the particles. Experiment S34-50L showed clearly an increasing amount of surface acid when the initiator concentration was doubled and when the temperature was increased to 75°C, see Table 7.3. This behaviour is actually consistent with the simultaneously observed increase in $\bar{n}$. A higher rate of free radical generation results in more AA-containing oligomeric radicals entering the particles and therefore more AA incorporated. The influence of temperature or initiator concentration on the AA incorporation was far less significant within runs performed with the other two seed latexes.

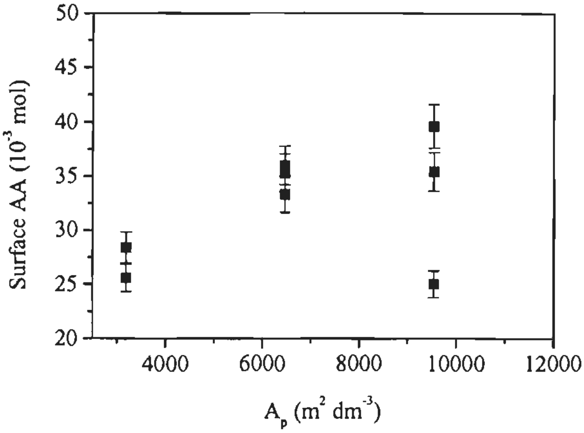


Figure 7.4: Amount of surface acid groups as a function of the total surface area of the swollen latex particles at x_{ov}=0 in the batch seeded emulsion polymerisation of styrene and Acrylic Acid at pH 2.5 for all the initiator concentrations and temperature listed in Table 7.3.

An influence of the seed particle diameter on the distribution over the outer surface of the particles and the surrounding continuous phase has been observed at low pH when going from rather small seed particles, *i.e.* 34 nm and 50 nm, to larger ones, *i.e.* 97 nm. The amount of surface acid decreases from about 50% to 40% while the amount of acid groups in the aqueous phase increases. The decrease in the amount of polymerised AA on the outer particle surface seems significant and is consistent with the difference in A_p the specific particle surface area per unit volume of the continuous phase, see Table 7.3. While changing the seed particle diameter we have chosen to keep the volume fraction of the seed particles in the reaction mixture at a constant value. So the number of particles as well as the total particle surface per unit volume of the continuous phase decreases on increasing the diameter of the seed particles. Figure 7.4 shows the amount of surface acid groups at pH 2.5 as a function of the initial surface area of the swollen particles A_p given in Table 7.3. The incorporation of the functional monomer on the surface increases with the particle surface area indicating that the rate of entry of oligomeric radicals in the particles increases with the surface area available.

7.2.5. Discussion

The role of AA in emulsion polymerisation has been reported in numerous papers, see e.g. Sakota *et al.* [1976], Egusa *et al.* [1982], Dos Santos *et al.* [1997]. Many authors reported that the polymerisation rate is influenced by the pH of the reaction mixture. Because most of the studies concern *ab-initio* reactions, the influence of pH on the polymerisation rate is generally related to different numbers of particles present after the nucleation period.

Shoaf *et al.* [1991] studied the S/AA system and developed a model to predict polymerisation rates for seeded emulsion copolymerisations in a batch reactor. These authors reported that the primary locus of polymerisation probably shifts from the particle phase to the aqueous phase after S has been consumed. This typical behaviour has been accounted for by the definition of an interval IV in the emulsion polymerisation process. However Shoaf and Poehlein did not include the influence of pH. Additionally the distribution of AA groups in the latex products was not investigated although this distribution gives valuable information. These authors however attempted to model the styrene/methacrylic acid system at various degrees of neutralisation. The evidence was found that the acid concentration in the organic phase decreases as expected when the acid is neutralised. Shoaf and Poehlein explained the decreased polymerisation rate of S, as observed in their batch seeded emulsion experiments, by a lower rate of capture of the partially neutralised oligomeric radicals. In our experiments, the influence of pH on the course of the reaction was not very pronounced. The kinetics is apparently dependent on the particle size only. Similar results are actually observed in Chapter 6, see Figure 6.7. In most cases, no or only a rather limited decrease in the polymerisation rate is observed at higher pH. The systems we studied, however, are different since we used a polystyrene seed latex containing no carboxylic groups. Carboxylated seed latexes have also been used by Coen *et al.* [1996] to study the influence of pH on the emulsion polymerisation of styrene. Poly(acrylic acid) as stabiliser proved to play a crucial role in the mechanism of the polymerisation, which is probably also the case in the work of Shoaf *et al.* [1991]. Our systems actually describe the carboxylation process of polystyrene latexes and in this context the limited effect of pH on the polymerisation rate is plausible.

$\bar{n}$ increases with the particle diameter which is in agreement with the emulsion polymerisation theory reported by Ugelstad *et al.* [1967], see Figure 2.2, since At constant initiator concentration and acid content Log α' can be replaced by Log d_p. In most cases when $\bar{n}$ was smaller than 0.5, there was no or only a limited dependence of the initiator concentration or the temperature on $\bar{n}$. This may indicate that termination of oligomeric radicals in the aqueous phase becomes dominant. The initiator efficiency decreases due to the production of more water-soluble dead oligomers. A similar results have been reported by Schoonbrood [1994] for the seeded emulsion copolymerisation styrene and methyl acrylate.

However, the final latexes produced under different conditions of pH are far from similar. The distribution of acid groups was completely different at pH 2.5 and pH 7 and was qualitatively in good agreement with the work of several authors [Greene, 1973; Emelie *et al.*, 1988; Dos Santos *et al.*, 1997]. All these authors reported that a high pH retains the dissociated carboxylic groups in the water phase whereas a lower pH increases the AA concentration in the organic phase. This can explain the difference in the amount of buried acid groups (assuming that the amount of buried groups is related to the partition coefficient) at different pH values. To the best of our knowledge it was not reported earlier that the amount of surface acid at low pH is sensitive to the initiator level and the temperature and that it depends strongly on the particle surface area per unit volume of the continuous phase. This indicates that the functional groups on the surface of the latex particles must originate from effective entry of oligomeric radicals. At higher pH values, the experimental conditions showed to have no influence on the incorporation of AA on the particle surface. The increased hydrophilicity of AA at pH > 6 together with the additional electrostatic effects impede the effective entry of AA-containing oligomeric radicals.

Establishing a relation between the amount of incorporated acid and the mechanism of the polymerisation is not straightforward. The following additional critical remark should be made: our observations about the kinetics are valid in interval II of the emulsion polymerisation only, whereas the distribution of acid groups is measured after complete reaction. If the interval IV hypothesis given by Shoaf *et al.* [1991] is retained, it means that a significant amount of acid reacts in the aqueous phase after almost complete depletion of S in the system. The question is then to know in which stage of the process the surface acid groups are built-in into the particles.

7.3. Incorporation of Acrylic Acid in latex products

In the previous section we described the influence of some reaction parameters on the progress of the seeded emulsion polymerisation of styrene in the presence of acrylic acid. These variables investigated included mainly the pH and temperature of the reaction mixture and the size of the seed latex particles. We investigated the effect of these parameters on the kinetics of the polymerisation and on the final distribution of the acid groups. The pH proved to have a moderate effect on the kinetics but to govern the amount of acid groups incorporated on the surface. In agreement with several authors [Greene, 1973; Emelie *et al.*, 1988; Dos Santos *et al.*, 1997], we observed that at pH 7 the very hydrophilic dissociated carboxylic monomer had the tendency to remain in the water phase. This behaviour together with the additional electrostatic effects preventing the effective entry of oligomer radicals in the particles resulted in a very poor incorporation of acid groups both on the surface and in the interior of the latex particles at pH 7. Generally less than 10% of the initial amount of AA was incorporated. At a pH value of 2.5 most of the AA was present as surface acid in the outer shell of the latex particles whereas a significant amount of AA was buried inside the particles.

The present Chapter aims at a better understanding of the mechanism of carboxylation process during the seeded emulsion polymerisation of styrene (S) in the presence of acrylic acid (AA). The parameters investigated include the pH of the reaction mixture and the ratio of the two monomers. Special attention was paid to the determination of the acid distribution during the course of the reaction. Attempts were made to determine the effect of a two-step process on the distribution of acid groups in the latex products. In the two-step process the functional monomer was added at different conversions.

7.3.1. Experimental

AA was supplied to the reactor before the equilibration period or at different overall conversions of the polymerisation process. All the seeded polymerisations were performed with a seed with a diameter of 97 nm at a temperature of 70°C, see recipes in Table 7.4.

In all the experiments the conversion was measured by gravimetry by withdrawing 5 ml of the reaction mixture. For the determination of the AA incorporation 50ml of the reaction mixture were withdrawn at regular time intervals. The cleaning steps preceding the characterisation procedure for the AA distribution in the latex products were always performed rapidly after sampling.

Table 7.4: Standard recipe for seeded emulsion polymerisation of styrene and acrylic acid

Seed	10 g of solid polymer
Styrene	85 g
Acrylic acid	0 / 2 / **5** / 10 g
DI water	900 g
Sodium persulfate ($Na_2S_2O_8$)	10.10^{-3} mol dm^{-3}
Sodium dodecyl sulfate (SDS)	$5.5.10^{-3}$ mol dm^{-3}
Sodium carbonate (Na_2CO_3)	0 / 50.10^{-3} mol dm^{-3}
Sodium chloride (NaCl)	100.10^{-3} / 0 mol dm^{-3}
$C_{M,0}$	0.91 / 0.940 / **0.985** / 1.06 mol dm^{-3}
$f_{AA}^{ov,initial}$	0 / 0.03 / **0.08** / 0.15
$C_{AAtot.}$ ($\mu_{eq}\ g_{pol}^{-1}$)	0 / 277 / **694** / 1388

7.3.2 Overall polymerisation rate

The parameters that are varied in the seeded emulsion copolymerisation of S and AA are the pH of the reaction mixture and $f_{AA}^{ov,initial}$ the overall AA mole fraction in the monomer feed, see Table 7.4. Each experiment is checked for secondary nucleation with Transmission Electron Microscopy. The particle growth in seeded systems must indeed occur in the absence of particle formation, which would impede any mechanistic study. The results obtained by TEM showed in most cases a final particle size diameter and polydispersity in good agreement with the initial seed latex.

Table 7.5: Results from all runs

	pH	**$f_{AA}^{ov,initial}$**	**Np (dm^{-3})**	**R_p/N_p (10^{-21}mol s^{-1})**	**$\bar{n}$**	**D.S.I. (%)**	**Buried AA $^{b)}$**	**Free AA $^{b)}$**
			AA introduced at 0 min					
PS-0L	2.5	0	2.1 10^{16}	3.90	0.9	-	-	-
PS-0H	7.0	0	2.1 10^{16}	4.70	1.1	-	-	-
PSAA-5L	2.5	0.08	2.3 10^{16}	3.50	0.8	37	25	38
PSAA-5H	7.0	0.08	2.3 10^{16}	4.40	1.0	6	6	88
PSAA-5Lbis$^{a)}$	2.5	0.08	2.3 10^{16}	3.90	0.9	40	-	-
PSAA-5Hbis$^{a)}$	7.0	0.08	2.3 10^{16}	3.90	0.9	5	-	-
PSAA-2L	2.5	0.03	2.1 10^{16}	4.30	1.0	65	27	8
PSAA-10L	2.5	0.15	R_p=1.28 10^{-4} mol dm^{-3} s^{-1}, Secondary nucleation			70	30	10
			AA introduced at 80 min					
S80-PSAA-L	2.5	0.08	2.1 10^{16}	4.30	1.0	45	10	45
S80-PSAA-H	7.0	0.08	2.1 10^{16}	4.50	1.0	10	8	82
			AA introduced at 100 min					
S120-PSAAL	2.5	0.08	2.1 10^{16}	4.10	0.9	50	5	45
S120-PSAAH	7.0	0.08	2.1 10^{16}	4.70	1.1	10	1	89

a) with sampling for the determination of AA incorporation at different conversions
b) expressed in % of the initial amount of acid groups

In our study, N_p was constant throughout the polymerisation and R_p was calculated from the conversion-time histories in the conversion region between 0 and 0.4. The average number of growing chains per particle $\bar{n}$ was calculated with Equation 7.1. As already discussed $\overline{k_p}$ in the particle phase was approximated by the propagation rate constant for the homopolymerisation of S, see Table 6.8. The results collected in Figures 7.5 and 7.6 and in Table 7.5 show that all the polymerisations can be roughly approximated with Smith-Ewart

Case 2 kinetics with $\bar{n}=0.5$ or more probably with a transition to Case 3 kinetics with $\bar{n}>1$. The increase in the polymerisation rate observed for conversions higher than 0.6 should be attributed to a gel effect, see conversion time histories in Figures 7.5 and 7.6.

For $f_{AA}^{ov,initial}=0$ and $f_{AA}^{ov,initial}=0.08$, the pH of the reaction mixture had no influence on the polymerisation rate and therefore on $\bar{n}$. This behaviour is the result of the entry rate coefficient being independent of the pH, see section 7.2.4.

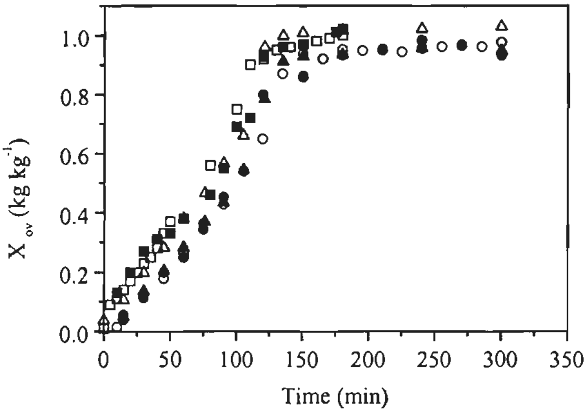


Figure 7.5: Overall conversion as a function of time for the batch seeded emulsion polymerisation of Styrene at 70°C at pH2.5 (solid symbols) and pH7 (open symbols).
■ no AA; ▲ 0.92/0.08 S/AA mole ratio; ● 0.92/0.08 S/AA mole ratio, continuous sampling.

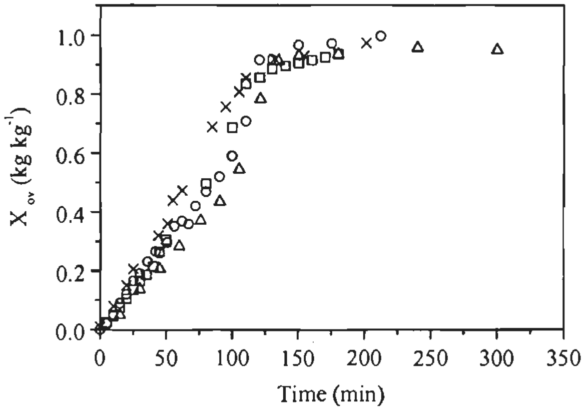


Figure 7.6: Overall conversion as a function of time for the batch seeded emulsion polymerisation of Styrene at 70°C at pH2.5.
S/AA mole ratios: □=0, ○=0.97/0.03, △=0.92/0.08, x=0.965/0.035.

At pH 2.5, the AA content did not have any influence on the polymerisation rate for $f_{AA}^{ov,initial}=0$, 0.03 or 0.08. However, an increase in the polymerisation rate was observed for $f_{AA}^{ov,initial}=0.15$, see Figure 7.6 and Table 7.5. The analysis of the particle size of the final latex with TEM showed a bimodal distribution. Secondary nucleation not be avoided. In these conditions, no conclusion could be drawn concerning the kinetics of particle growth and the process of AA incorporation.

7.3.3. Incorporation of acrylic acid

Table 7.5 gives the amount of surface and buried acid groups in all the latex products after complete conversion. For $f_{AA}^{ov,initial}$ =0.15, all the acid was incorporated in the latex products. Because of the occurrence of secondary nucleation during the corresponding polymerisation, more AA was eventually buried in the latex particles since the precursor particles of the newly formed population originate from AA-rich oligomers. Moreover, some of those acid groups were likely to migrate to the surface of the particles, stretch out into the aqueous phase and contribute to the amount of surface acid. In addition, the latex particles offered a much larger total surface area for entry than when secondary nucleation was avoided. This eventually resulted in an increased amount of surface acid groups as well. For both $f_{AA}^{ov,initial}$ =0.03 and 0.08 no secondary nucleation occurred and about 25% of the initial AA was buried inside the particles. The absolute amount of surface acid groups increased with $f_{AA}^{ov,initial}$. The absolute amount of acid groups present in the serum at the end of the polymerisation also increased with $f_{AA}^{ov,initial}$. The incorporation of AA in or onto the latex particles was therefore more efficient at lower $f_{AA}^{ov,initial}$.

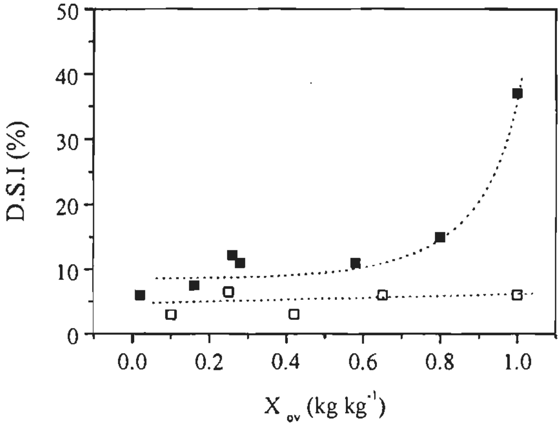


Figure 7.7: Surface incorporation of Acrylic Acid as a function of the conversion for the batch seeded emulsion polymerisation of Styrene at 70°C at pH2.5 (solid symbols) and pH7 (open symbols).

In order to get more insight into the mechanism of incorporation of AA in latex products, the distribution of acid groups between the interior and the surface of the particles was determined throughout the whole emulsion polymerisation process. Figure 7.7 shows the fraction of AA present as surface acid as a function of the overall conversion for polymerisations performed with $f_{AA}^{ov,initial}=0.08$ at pH values of 2.5 and 7.

As expected from the distribution in the final products, hardly any surface acid was found at intermediate conversions at pH 7. At pH 2.5 the amount of surface acid groups remained low up to $x_{ov}=0.6$. Until the last stage of the emulsion polymerisation process, only about 10% of the total acid groups consisted of surface acid. No clear trend could be observed in the region $0<x_{ov}<0.6$ mainly because of the very low incorporation figures. Most of the surface acid groups were actually incorporated in the last 20% conversion of the polymerisation process.

7.3.4. Two-step emulsion polymerisations

Some experiments were performed in two steps. In the first step all the reagents except AA were supplied to the reaction mixture. The second step started with the addition of AA to the reaction mixture. The initial AA mole fraction in the overall monomer feed was kept at $f_{AA}^{ov,initial}=0.08$. The moments at which AA was introduced into the reaction mixture were evaluated from experiments performed without AA and corresponded to the expected beginning of Interval III (80minutes) and to an overall conversion of about 0.8 (100 minutes). For reactions performed at pH 7 some sodium carbonate was used in the first step.

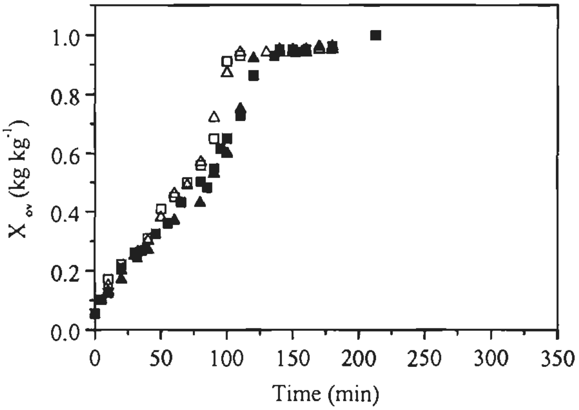


Figure 7.8: Overall conversion as a function of time for the seeded batch emulsion polymerisation of Styrene and Acrylic Acid at 70°C at pH 2.5 (solid symbols) and pH7 (open symbols) with a shot of 5g of Acrylic Acid acid at 80min (■) and at 100min(▲).

The pH of the buffered reaction mixture did not change when AA was added in the second step. A pH of 2.5 during the second step was obtained by performing the first step without acid or buffer system. The pH dropped to the value of 2.5 upon the addition of AA and remained constant.

Figure 7.8 shows the conversion time histories of the two-step polymerisations processes. As expected from previous results, neither the pH nor the delayed introduction of AA had an effect on $\bar{n}$ always estimated before the addition of AA, see Table 7.5. The progress of the polymerisations after the addition of AA was hardly affected by the shot of functional monomer, see Figure 7.8. Secondary nucleation could be avoided in all four experiments.

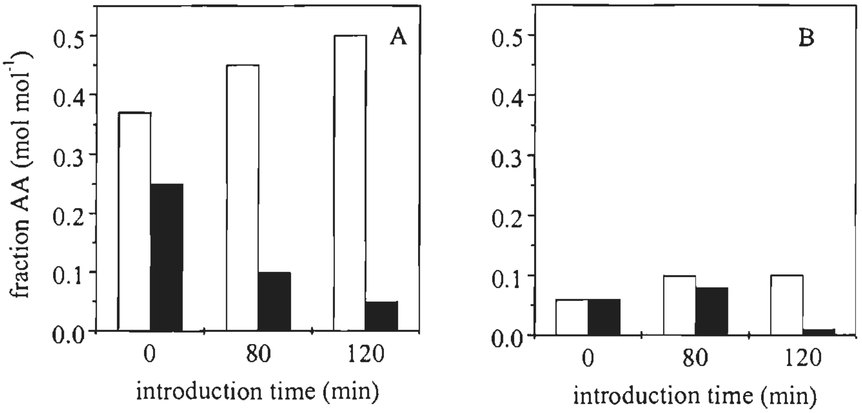


Figure 7.9: Incorporation of Acrylic Acid in the final latex products as a function of the introduction time for the two-step seeded emulsion polymerisation of Styrene at 70°C. ■ buried acid, □ surface acid. Reactions at pH 2.5 (A) and pH 7 (B).

The results collected in Table 7.5 and Figure 7.9 show the distribution of AA between the surface and the interior of the final latex particles at different pH as a function of the AA introduction time. The pH had a strong influence on the distribution. At pH 7 the amounts of surface and buried acid groups were very low. More than 80% of the total AA remained in the aqueous phase whenever AA was supplied to the reaction mixture. The incorporation was increased at pH 2.5 as already observed for the single step process. Retarding the introduction of AA into the reaction mixture resulted in a significant increase in the amount of surface acid groups and a decrease in the amount of buried groups in comparison with the single step process. The decrease in the amount of buried acid groups can be explained by the absence of an equilibration period when AA was introduced during the polymerisation process. The partitioning of monomer AA between the different phases of the reaction mixture could not occur and had to compete with the reactions taking place in the aqueous phase upon the addition of the water-soluble monomer. The introduction of AA monomer during the polymerisation therefore resulted in a decreasing fraction of the acid groups in the particle phase. Supplying AA to the system for $x_{ov}>0.5$ also means that the acid groups eventually incorporated on the surface during the polymerisation cannot be buried by further growth of the latex particles since in Interval 3 of emulsion polymerisation the particle diameter does not increase any more.

7.3.5. Discussion

The present study confirms the influence of pH on the distribution of acid groups in the final latex products. In agreement with the previous report, the lowest pH resulted in the highest acid group incorporation in and onto the latex particles. The determination of the acid group distribution in the latex products during the course of the reaction shows that AA was mainly incorporated after the S monomer phase has disappeared. Shoaf *et al.* [1991] studied the S/AA system and developed a model for predicting batch copolymerisation rates in seeded emulsion polymerisations. These authors reported that the primary locus of polymerisation probably shifts from the particle phase to the aqueous phase after S has been consumed and they defined an interval IV in the emulsion polymerisation process accounting for this typical behaviour. Yuan [1996] studied the emulsion copolymerisation of styrene and butadiene in the presence of AA and reported a shift in the main polymerisation locus as well in the last stage of the process with most of the functional monomer being still present in the aqueous phase. Nomura *et al* [1997] studied the seeded emulsion polymerisation of S and AA and reported that when the number of seed particles was higher than a certain critical value, AA did not polymerise until the S conversion exceeded 75%. Guillaume *et al.* [1988] studied the emulsifier-free emulsion copolymerisation of styrene and butyl acrylate in the presence of methacrylic acid and investigated the location of the functional monomer in the latex as a function of conversion. These authors reported the presence of a significant amount of unreacted methacrylic acid in the last stage of the process together with an increase in the amount of acid groups incorporated on the surface of the latex particles in the last 20% conversion. Although their experiments were carried out at pH values between 5 and 7, the results are in good agreement with our study. Our results are in good agreement with all the studies mentioned here above and suggest that during the last stage of the process, AA monomer units are still present in the aqueous phase and contribute to a great extent to the carboxylation process. This behaviour is remarkable at a pH value of 2.5. At the beginning of the process, the AA monomer units participate to the aqueous phase polymerisation and to the mass transfer processes between the aqueous phase and the particle phase but the main locus of polymerisation remains the particle phase with much higher monomer and radical concentrations. Increasing $f_{AA}^{ov,initial}$, *i.e.* the amount of AA monomer initially supplied to the reaction mixture, has hardly any influence on the average copolymerisation rate constant in the aqueous phase, see section 5.3.3.2 and Figure 5.20 but results in a higher fraction of AA units built in the copolymer chains formed in water, see Figure 5.22 and Table 5.9. This has plausibly no influence on the entry rate of oligomer radicals in the particle phase and therefore no influence on initiator efficiency and on the overall polymerisation rate as it has been observed experimentally. Only the absolute amount of acid groups incorporated on the surface via radical entry might then be affected and increased when $f_{AA}^{ov,initial}$ increases. We found indeed some evidence for this behaviour in our experiments. The amount of surface acid groups can apparently be increased by using larger amounts of AA in the recipe but is however limited by the occurrence of secondary nucleation. Further, the incorporation of the functional monomer is the most efficient at low $f_{AA}^{ov,initial}$ since the amount of residual acid groups in the serum of the final latex is very low. The last stage of the process seems to correspond to an enhanced capture of oligomer radicals. During that stage the concentration of S in the aqueous phase decreases and the oligomer radicals may contain more AA units, see Figure 5.22. Our results show that these species are however likely to enter the latex particles and actually constitute the main carboxylation process. These mass transfer events have however to compete with termination. Not all the functional monomer can be incorporated and a significant amount of acid groups remain in the aqueous phase. The use of smaller amounts of AA can actually cause the relative importance of capture to be enhanced compare to termination and may explain the limited formation of water soluble acid rich polymer and the high incorporation yield. The determination of the total amount of acid groups incorporated on the surface of the particles is however not sufficient to elucidate the complex carboxylation process unless it is combined with the determination of the number of oligomer radicals that effectively entered the latex particles.

At a pH value of 7, hardly any AA is incorporated in the final latex products in both the single-step and the two-step processes. The deprotonated AA units have the tendency to remain in the aqueous phase for hydrophilicity reasons and the entry of oligomer radicals in the latex particles is moreover impeded by electrostatic repulsion. The amount of acid groups incorporated in the first stage on the polymerisation, until about 70% conversion, is hardly different at pH 2.5 and pH 7 which is consistent with the similar polymerisation rates observed. This may indicate that in both cases the phase transfer events in the first stage of the polymerisation concern mainly S rich species.

Adding AA at the end of polymerisation proved to be the most efficient method for the carboxylation of the latex particles at low pH. However the shot process hardly increased the amount of surface acid at pH 7 probably for electrostatic reasons. As already mentioned, although the S concentration decreases in the aqueous phase in the last stage of the process the AA rich oligomer radicals are still likely to enter the latex particles at pH 2.5 since they do incorporate hydrophobic monomer units, see Figure 5.22. This result is in good agreement with the work of Emelie *et al.* [1988] who also investigated a two-step process for the emulsion copolymerisation of methyl methacrylate and butyl acrylate in the presence of AA. These authors reported that the addition of the functional monomer at 90% conversion had hardly any effect on the distribution of acid groups in the final latex products unless a small amount of butyl acrylate was added together with AA. The amount of surface acid then increased while the amount of buried groups decreased. The addition of AA in the last stage of the emulsion polymerisation process results in a higher concentration of AA monomer available in the aqueous phase compared to the single-step process. Indeed, in the latter case, AA partitions better in the particle phase during the equilibration period and some functional monomer is likely to be consumed in the first stage of the process by aqueous phase polymerisation.

7.4. Conclusions

Seeded emulsion copolymerisation experiments give valuable information about the process of incorporation of carboxylic groups in latex particles. Provided the number of latex particles is kept constant throughout the reaction, the average number of growing chains per particle can be estimated from the experimental conversion-time histories.

Additional mechanistic information can be obtained from a good and detailed knowledge of the distribution of the carboxylic groups over the entire latex system. The amount of surface acid groups is a valuable information to compare latex products.

The pH had generally a minor influence on the polymerisation rate in the seeded systems but had a strong influence on the characteristics of the end latex products. No evidence was found that the pH affects the rate of free radical generation in emulsion polymerisations initiated with persulfate. The incorporation of acid groups on the surface of final latex particles was more efficient at lower pH. This behaviour can partially be explained by the more hydrophilic nature of the carboxylic species in their ionised form.

The AA was mainly incorporated in the last stage on the emulsion polymerisation process at conversions higher than 70%. At the beginning of the process hardly any AA was incorporated at both pH 2.5 and pH 7. This might indicate that only S rich oligomer radicals give entry.

The use of smaller amounts of AA in the recipes resulted in the presence of a minimum amount of acid in the aqueous phase of the final latexes. The consumption of AA through aqueous phase polymerisation and termination is minimised and the incorporation efficiency optimised.

The use of a two-step process in which the AA was introduced in the last stage of the emulsion polymerisation was a good method to increase the amount of surface acid groups in comparison with the single step process. In addition, the amount of buried acid groups was decreased for partitioning reasons.

The present study indicates that the AA incorporation process is mainly governed by the aqueous phase polymerisation. A better knowledge of the main kinetic parameters in the aqueous phase and the influence of pH on these parameters is a crucial point for the better understanding of the carboxylation process.

EPILOGUE

In this thesis emulsion copolymerisation in the presence of acrylic acid was investigated from a mechanistic point of view. The objective and challenge were to obtain a better understanding of the mechanisms involved in the incorporation of carboxylic groups into latex products. Attention was focused on oligomer radical entry into the latex particles, on kinetics of polymerisation with acrylic acid, and on analysis of the latex product in terms of acid distribution and intermolecular copolymer chemical composition.

Polymerisation strategy

Ab-initio and seeded emulsion polymerisations were performed and provided valuable information about the process of incorporation of carboxylic groups into latex products. Ab-initio experiments showed that a significant amount of carboxylic monomer participates in the nucleation of latex particles.

The particle growth process could be studied without any disturbing effect of nucleation by performing seeded emulsion polymerisations. The advantages of the seeded process were of major interest in this particular case of carboxylated systems. First, the polymerisation rate in the seeded systems could be directly related to the average number of radicals per particle which in turn was related to the influence of the reaction parameters like pH, ionic strength and particle diameter on radical entry. Information about the polymerisation process with respect to the classical Harkins' theory could hereby be obtained. It was also possible to study the incorporation of carboxylic groups into seed latex particles initially bearing no functional group. Note that the work can be extended to seed latexes with well-defined surface characteristics for a further investigation on surface effects.

Influence of pH

The pH of the reaction mixture plays a crucial role in the polymerisation of carboxylic monomers in water. The influence of pH on the propagation rate constant for methacrylic acid homopolymerisation was investigated using Pulsed Laser Polymerisation. A decrease of the propagation rate constant from 3150 $dm^3\ mol^{-1}\ s^{-1}$ at pH 2 to 918 $dm^3\ mol^{-1}\ s^{-1}$ at pH was observed with PLP experiments performed at 25°C. The results point out that the dissociation equilibria of carboxylic groups involved in the polymerisation scheme play a dominant role in the polymerisation process.

In future investigations, the experimental procedures should be improved to obtain a non-selective and reliable isolation of the polymerisation products over a wide range of experimental conditions expressed in terms of pH and ionic strength. The dissociation behaviour of the propagating free radicals and the ionic associations between the species bearing carboxylic groups should be considered.

It was shown that the pH plays a crucial role in emulsion polymerisation as well. Emulsion polymerisation experiments were performed at two different pH values. pH values of 2.5 and 7 were chosen on the basis of the trend observed for the pH-dependent homopropagation rate constant and corresponded to the presence of fully protonated or dissociated carboxylic acid groups. It was concluded from partitioning considerations that low acrylic acid fractions in the recipe did not have a significant influence on the propagation rate constant in the particle phase at both pH values. However, the influence of pH and acrylic acid concentration on the propagation rate constant in the aqueous phase and the chemical composition of the corresponding copolymerisation products was demonstrated. The calculated chemical composition of the initiator-derived growing oligomer radicals revealed that a significant amount of sparsely water soluble monomer units are incorporated during the emulsion polymerisation process so that entry of those species becomes probable.

Accurate measurements of reactivity ratios involving dissociated carboxylic monomer are necessary for further investigations of the polymerisation reactions in the aqueous phase. Additionally, relations between the chemical composition and the surface activity of the species formed in water should also be determined to obtain a better insight into the probability of oligomeric radical entry.

Incorporation of carboxylic groups

Valuable and reliable information was obtained from the distribution of the carboxylic groups between the different phases of the latexes by means of acid-base titrations. The participation of acrylic acid in the radical entry was demonstrated since the efficient entry of acid rich oligomeric radicals resulted in carboxylic groups chemically bound to the particle surface. The influence of pH on the acid incorporation was significant. The pH-dependent surface incorporation yield was explained in terms of different water solubilities of the oligomeric radicals in the aqueous phase.

The determination of the amount of carboxylic groups incorporated into latex particles during the investigated emulsion polymerisation processes revealed that most of the functional groups were incorporated during the last stage of the reaction. Additionally, no significant influence of pH on the polymerisation rate during Interval II i.e. particle growth in the presence of monomer droplets, could be observed. It was therefore suggested that the species participating in mass transfer phenomena during Interval II did not involve significant amounts of acrylic acid. Furthermore, the limited incorporation efficiency was attributed to the loss of carboxylic groups via termination of growing acid rich polymer chains in the water phase during Interval II. Incorporation of acrylic acid during the final stage of the reaction was confirmed by experiments in which the acrylic acid was supplied to the reaction mixture at almost complete conversion. Addition of acrylic acid at almost complete conversion resulted in the maximum absolute amount of acid groups incorporated onto the surface of the particles observed in the study.

The work presented in this thesis provides improved insights into the role played by the different parameters involved in emulsion polymerisation processes for the production of carboxylated latexes. It was demonstrated that the acid incorporation efficiency is strongly related to the events taking place in the aqueous phase. This thesis shows that the control and the optimisation of the amount of carboxylic groups incorporated in latex products is possible. Therefore, future investigation concerning the production of latexes with well-defined characteristics should focus on the kinetic and physico-chemical aspects of aqueous phase events.

NOTATION

Small letters

d_p	particle diameter [nm]
d_{pswol}	monomer swollen particle diameter
f_i	molar fraction of monomer i at the locus of polymerisation
k	exit rate coefficient [s^{-1}]
k_a	radical absorption rate coefficient [s^{-1}]
k_p	homopropagation rate coefficient [dm^3 mol^{-1} s^{-1}]
$\bar{k}_p$	average propagation rate coefficient [dm^3 mol^{-1} s^{-1}]
k_{pij}	ultimate propagation rate coefficient of radical species with endgroup of type j with monomer i [dm^3 mol^{-1} s^{-1}]
k_t	bimolecular termination rate coefficient in the continuous phase [dm^3 mol^{-1} s^{-1}]
k_{tp}	bimolecular termination rate coefficient in the particle phase [dm^3 mol^{-1} s^{-1}]
m	dimensionless parameter defined as $m = k \, v / k_t$
$\bar{n}$	average number of radicals per particle [-]
n_A^{org}	amount of acid in the organic phase [mol]
r_i	reactivity ratio of monomer i
v	volume of a (monomer swollen) particle [dm^{-3}]
x_A^{org}	acid fraction in the organic phase [mol mol^{-1}]
z	degree of polymerisation [-]

Capitals

A_p	particle specific surface area (per unit volume continuous phase) [m^2 dm^{-3}]
C	concentration [mol dm^{-3}]
C_{AAaq}	concentration of acid groups in the aqueous phase [mol $gpol^{-1}$]
C_{AAint}	concentration of acid groups in the particle interior [mol $gpol^{-1}$]
C_{AApart}	concentration of acid groups in the particle phase [mol $gpol^{-1}$]
C_{AAsurf}	concentration of acid groups on the surface of latex particles [mol $gpol^{-1}$]
C_{AAtot}	total acid group concentration [mol $gpol^{-1}$]
C_i	concentration in ion I [mol dm^{-3}]
$C_{M,0}$	initial monomer concentration (per unit volume continuous phase) [mol dm^{-3}]
C_{Mp}	monomer concentration in the particle phase [mol dm^{-3}]
D_f	diffusion coefficient [m^2 s^{-1}]
DP_{max}	critical degree of polymerisation resulting in precipitation [-]
E_A	activation energy [J mol^{-1}]
F_i	molar fraction of monomer i in copolymer [mol mol^{-1}]
K	acid-base equilibrium constant
K_a	dissociation constant
L	distance that an oligomeric radical travels before precipitation [m]
L_i	length of a polymer chain terminated after I pulses in a PLP experiment [-]
M	molecular weight [g mol^{-1}]
M/W	monomer to water ratio [kg kg^{-1}]
Mw	molecular weight [g mol^{-1}]

N_{av}	Avogadro's number [mol^{-1}]
N_p	number of particles (per unit volume of continuous phase) [dm^{-3}]
P/W	polymer to water ratio [$kg\ kg^{-1}$]
R_p	polymerisation rate [$mol\ dm^{-3}\ s^{-1}$]
SC	solid contents [$kg\ kg^{-1}$]
T	temperature [°C]
T	time [s]
V	volume [dm^3]
X_{ov}	overall conversion [$kg\ kg^{-1}$]
Y	dimensionless parameter, defined as $Y = 2\ N_p\ k_{tp}\ k_t / k_a^2\ v$

Greek symbols

α	dissociation degree [$mol\ mol^{-1}$]
α'	dimensionless parameter, defined as $\alpha' = \rho_i\ v / N_p\ k_t$
κ	conductivity [$S\ m^{-1}$]
Φ_i	parameter in Mandel's equation
λ_i	molar conductivity of ion I [$S\ m^2\ mol^{-1}$]
ρ	density [$kg\ m^{-3}$]
ρ_i	rate of radical production in the aqueous phase [$dm^{-3}\ s^{-1}$]
τ	time interval between two laser pulses [s]

Subscripts and superscripts

app	apparent
aq	aqueous phase
org	organic phase
ov	overall
p	particle
sat	saturation conditions
W	water

Acronyms

AA	acrylic acid
A-	dissociated acid form
AH	protonated acid form
B	butadiene
CCD	chemical composition distribution
CPC	cloud point composition
D.S.I.	degree of surface incorporation
ELSD	evaporative light scattering detector
GPEC	gradient polymer elution chromatography
I	initiator
M	monomer
MWD	molecular weight distribution
NS	non-solvent

P	polymer
P	polymer chain
PAA	polyacrylic acid
PB	polybutadiene
PC	partition coefficient
PLP	pulsed laser polymerisation
PMAA	polymethacrylic acid
PS	polystyrene
PSB	poly(styrene-butadiene)
PSD	particle size distribution
R	radical species
S	solvent
S	styrene
S	surfactant
SC	sodium carbonate
SDS	sodium dodecyl sulfate
SEC	size exclusion chromatography
SPS	sodium persulfate
T	chain transfer agent
TEM	transmission electron microscopy

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Acknowledgements

J'aimerais remercier toutes les personnes qui m'ont aidée à réaliser ce travail et qui m'ont supportée dans tous les sens du terme durant ces cinq dernières années (ou bien plus). Tout d'abord, je pense plus particulièrement à toute ma petite famille: c'est bon de vous savoir toujours là, votre amour et votre confiance sont sans prix pour moi. Une petite pensée pour tous ceux qui sont partis trop vite et n'ont pas pu voir ce travail achevé. Greg, merci pour ton support, ta patience et tout le reste...et la liste est longue!

I would like to thank Prof. Ton German for the five years I spent working in his group and Prof. Gerard Riess, for accepting to be part of my examination committee as second promoter. The rest of the committee is gratefully acknowledged as well. Special thanks to Jan Meuldijk for reading and correcting my manuscript and for the discussions. Jan, your enthousiasm was always so motivating! I wish to thank all the students who made a contribution to this work: Marieke van Rens, Marcel Dinghs, Patrick de Man, Jacques-Francois Hanssen, Mike Schellekens (ben je moe ???), Martijn Munnik, Gijs Hermans and Sébastien Stawicki. From the polymer chemistry or the coatings technology group I would also like to thank the numerous people I worked with or that assisted me in any way. Special thanks to Alex van Herk, my first roommate, for the discussions and the "women nights" and to Helly for helping me with many things.

During those five years I enjoyed the good times with them during coffee breaks, ski holidays, a visit to Eurodisney, a prolonged congress in Italy or in Switzerland, mountain bike trips, camping, squash ...and work, I name: Alfons Franken (a lot of thanks as well for the help in the crucial moments....), Amaia Montoya-Goni, Bart Manders, Bas Pierik, Camiel and Inga Peerlings, Christianne Göttgens, Dominique Hubert, Eelco van Hamersveld, Frank Bergman, Fréderic Vidal, John Verstegen, Mark van den Brink, Mike Schellekens (nog een keer?!), Stefan Bon, Tonnie Willems (thank you for your help with GPEC as well), my Quatsh team and coaches. John, thank you for reading and commenting my manuscript, for your support and your friendship. Grand merci à mon fiston Sébastien à l'origine de ce projet...

Curriculum Vitae

Martine was born on June 4th 1970 in Somain (France). She graduated from secondary school in 1988. She attented a two year preparatory education program in Valenciennes after which she started her academic studies in Nancy. During three years she studied chemistry, chemical and process engineering and graduated in 1993 from both the Ecole Nationale Supérieure des Industries Chimiques and the University of Nancy II.

In 1994 she started her Ph.D at the University of Technology in Eindhoven in the group of Prof. A.L. German. Since August 1999 she has been working for Totalfina at its Research Center in Feluy (Belgium) in the group Development PolyOlefines.

Stellingen

behorende bij het proefschrift

Strategic Aspects of the Incorporation of Acrylic Acid in Emulsion Polymers

van Martine Slawinski

1. The incorporation of carboxylic groups in emulsion polymers can be improved by lowering the pH of the reaction mixture and by introducing the corresponding monomers in the last stage of a batch polymerisation process. This behaviour correlates well with the relatively slow partial conversion of the carboxylic monomers compared to the scarcely water-soluble monomers.

   Chapters 6 and 7 of this Thesis.
   Shoaf G. L. and Poehlein G. W., J. Appl. Pol. Sci., 42, 1239 (1991)
   Guillaume J. L., Pichot C., Guillot J., J. Polym. Sci., Part A, 26, 1937 (1988)

2. The influence of pH in persulfate initiated emulsion polymerisations should be studied in reference to the effective rate of radical production and not the global decomposition rate.

   Chapter 7 of this Thesis.
   Dos Santos et al., J. Pol. Sci., Part B, 591 (1996)
   Henton et al., J. Polym., Sci., Part A, 34, 1271 (1996)

3. The isolation of water-soluble polymer chains in latex systems, and therefore their analysis, is technically difficult and selective. The mechanistic conclusions often drawn from the results are therefore questionable.

   Chapter 6 of this Thesis.
   Wang et al., J. Appl. Polym. Sci., 51, 593 (1994).

4. The polymerisation of carboxylic monomers in water is better described in terms of degree of dissociation and ionic strength than simply in terms of pH.

   Chapter 5 of this Thesis.

5. Le vieillissement, s'il est affaire de chimie, n'est pas particulièrement l'affaire des chimistes.

6. The observation of “confetti-like”, “raspberry-like”, “void”, “snowman-like”, “octopus ocellatus”, “hairy”, “golf ball-like”, “multi-hollow” latex particles shows that chemists must have both an extensive vocabulary and some imagination. The general term “anomalously shaped polymer particles” shows how “synthetic” their minds are.

   M. Okubo: Kobunshi Ronbunshu, 33, 575 (1976) and 33, 565, (1979); J. Polym. Sci. Polym. Chem. Ed., 18, 481 (1981); J. Polym. Sci. Polym. Lett. Ed., 19, 143 (1981); Chemistry Express, 1, 243 (1987); Colloid and Polym. Sci., 265, 876 (1987); Colloid Polym. Sci., 274, 520 (1996); Colloid Polym. Sci., 275, 634 (1997).

7. Predictions are difficult when they concern the future.

   Nostradamus, “Les Centuries”, 1555.
   Paco Rabane, “1999, Le feu du ciel”, 1999.
   Elisabeth Teissier, “Le passage de tous les dangers”, 1999.

8. **SI** les Pays-Bas avaient gagné le match contre le Brésil, la finale aurait pu opposer la France aux Pays-Bas. **SI** les Pays-Bas avaient alors battu la France, ils seraient sans aucun doute champions du monde. Avec des **SI**, on pourrait aussi mettre Paris dans un ballon de foot.

   Etat d’âme d’un mois de Juillet 1998 aux Pays-Bas.

9. L’observation de la nature est devenue une qualité rare, cela prend du temps et c’est fatalement moins rentable sur le plan de la publication scientifique que de faire des modèles sur ordinateur.

   Jean-Pierre Henry, La Recherche, n° 313, 1998

10. A sensible man should be able to estimate the number of piano tuners in the city of New York.

    Pierre Gilles de Gennes, “Les objets Fragiles”, 1994

11. The “relative” size of a room is strongly dependent on the amount of ornaments. A painting on the wall not only over-emphasizes the painting itself, but also the wall behind it.

12. It is always good to listen to somebody else’s experience. The French Army recently designed a nice boat according to the French “Direction des Constructions Navales” (Shipbuilding Head Office). Without any external consulting but with 3 billion Euros, they managed to build the aircraft carrier “Charles de Gaulle” which is 4.4 meters too short.