EMULSION POLYMERIZATION

OF BUTADIENE

A KINETIC STUDY

Dit proefschrift is goedgekeurd door

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Chapter 1   Introduction

1.1 Short historic overview

The first attempts to develop an emulsion-like process were undertaken in Germany prior to and during World War I, out of necessity to cope with the shortage of natural rubber. Nowadays the processes disclosed in several patents granted to Farbenfabriken Bayer A.G.[1,2,3,4] would be referred to as suspension polymerizations; diene-monomers were polymerized in aqueous dispersions with egg albumin, starch or gelatin as stabilizers.

The first reference to a process which can be regarded as a true emulsion polymerization appeared in 1927, a patent granted to Dinsmore[5] working for the Goodyear Tire & Rubber Company. It describes the thermal polymerization over a period of six months of aqueous emulsions of various diene-monomers, with oleate salts and egg albumin as stabilizers. Luther and Heuck[6] of I.G. Farbenindustrie A.G. in 1932 were the first to introduce initiators to facilitate rapid polymerization. Although these first emulsion polymerizations were certainly not commercially viable, they led to the development of a complete industry over the next two decades.

Under the impulses of World War II the Synthetic Rubber Program in the United States, under coordination of the 'Office of Rubber Reserve' (ORR), led to the successful production of butadiene(75)-styrene(25) copolymer (socalled GR-S rubber) as a general purpose rubber. At the end of 1945 the total GR-S production had already reached a level of $7.5 \cdot 10^5$ tons;[7] natural rubber would never regain its leading position.

Under the synthetic rubber program research was more of an applied than a theoretical nature, and focused on the development of copolymers of butadiene with styrene or acrylonitrile, as these had qualities superior to that of the polybutadiene homopolymer. Yet, much of the fundamental knowledge about the emulsion homopolymerization of butadiene stems from this early work. Excellent reviews[8] are available, although some of the work was only declassified in 1980. However, little attention has been paid to butadiene since those early days of research, eventhough the importance of polybutadiene containing polymers and resins has increased enormously (e.g. high impact materials, coatings, adhesives). A brief summary of relevant literature after 1950 will be given below.

In the early fifties Morton et al. published a series of articles about the cross-linking behaviour of polybutadiene,[9] and the use of several initiator systems in the emulsion polymerization of butadiene.[10,11,12] The only values reported for the propagation rate coefficient (k_p) stem from this work,[11] but at best represent an approximation of the true values since they were determined with *ab initio* polymerizations at low temperatures (0 - 30°C), involving poly-disperse latexes sized by the method of soap titration.

In 1964 a *Ph. D. Thesis* by Bhakuni[13] appeared on the "Kinetics of the Persulfate-Mercaptan Emulsion Polymerization of Butadiene". Several note-worthy conclusions were reached: the nature of the emulsifier influences reaction kinetics, network formation within the latex particles has no influence on the saturation monomer solubility in the particles, while the possibility of radical desorption was mentioned.

More recently Wendler et al.[14,15,16,17] reported about the emulsion polymerization of butadiene in the presence of excessive amounts of bis(alkyloxythiocarbonyl)disulfanes in order to prepare low molecular weight oligobutadienes. Results were compared with the Smith-Ewart theory, indicating a strong deviation from the 'ideal' case II behaviour. The average number of radicals per particle ($\bar{n}$) was supposed to be larger than 0.5.

Of some interest is the radiation-induced emulsion polymerization of butadiene.[18] Polymerizations were found to be much slower than anticipated

from the reported k_p value,[11] but comparable with the corresponding persulfate-initiated polymerizations. A profound effect of the mode of agitation was found, indicating a diffusion-controlled process.

Results from Russian workers have been reviewed by Eliseeva et al..[19] When increasing the initial butadiene/styrene ratio from zero to one in the emulsion copolymerization of butadiene and styrene, the final particle number increases, whereas the overall polymerization rate decreases. It is stated that this effect can only be partially explained by the difference in k_p, so that other yet undetermined factors must be operative. Similar results were found by others.[13]

Altogether, literature on butadiene emulsion polymerization is sparse. The chronic lack of reliable rate coefficients makes a thorough interpretation of kinetic data difficult. Despite the long history of emulsion (co)polymerization of butadiene, the process definitely merits further investigation.

1.2 Aim of this investigation

The investigation described in this thesis aims at a better understanding of the kinetics of the *ab initio* emulsion polymerization of butadiene. Any emulsion polymerization system is complex due to its heterogeneous and colloidal nature. In many studies attention is focused on the chemical parameters that influence the process (usually the initiator and emulsifier concentration). In this study a complete survey of all relevant parameters was intended. The following parameters were considered, classified according to their nature:

Chemical:	type and concentration of initiator
	amount of chain transfer agent
Physical:	monomer to water ratio
	intensity of agitation
Colloidal:	type and concentration of emulsifier
	overall cation concentration

As a starting point, a typical industrial recipe was chosen, using the frequently employed emulsifier dresinate 214. In order to establish whether the anomalous behaviour found was related to specific experimental conditions, polymerizations with the well-defined emulsifier sodium dodecylsulfate were performed under comparable conditions. No major recipe-related phenomena were found, so a generalized semi-quantitative description could be given, which in turn led to novel insights and a reinterpretation of results reported by others.

1.3 Survey of thesis

Major theoretical aspects of the mechanisms and kinetics of emulsion polymerization relevant to this investigation are briefly discussed in **Chapter 2**.

Chapter 3 deals with the experimental procedures and techniques used throughout this investigation, and typical aspects of various recipe ingredients (e.g. composition of emulsifier, initiator decomposition and gel analysis).

In **Chapter 4** the *ab initio* emulsion polymerization of butadiene with the industrial grade emulsifier dresinate 214 was investigated. Attention is focused on the kinetic effects of the initiator and emulsifier concentration. The main body of this chapter has already been published.[20]

In **Chapter 5** the well-defined research grade emulsifier sodium dodecyl-sulfate was used in studying the effects of initiator and emulsifier concentration. Since the performance of this emulsifier is virtually pH-independent, the ionic strength was varied by changing the amount of sodium carbonate in the recipe. A profound effect on colloidal stability was found; under the experimental conditions chosen particle nucleation is coagulative in nature.

As industrial batch processes are often performed at the highest monomer to water ratio feasible, the effect of this parameter was studied in **Chapter 6**. Furthermore, the effect of agitation was considered with regard to the emulsification of the monomer, and its impact on reaction kinetics.

The *ab initio* experiments described in the preceding chapters contain valuable information about the kinetics of butadiene in emulsion polymerization. A kinetic analysis of interval II and interval III is presented in **Chapter 7**, showing conclusively that the present system should be treated as a zero-one system, with $\bar{n} \ll 0.5$.

In **Chapter 8** the role of thiols with a low water solubility is evaluated. Primarily they are added to control the extent of branching and cross-linking, and thus the amount of insoluble gel formed. In this respect they behave as ideal chain transfer agents, as no gross effects on polymerization kinetics were found (except maybe at a high dresinate 214 to butadiene ratio). The socalled promoting effect of thiols has also been considered. A minor part of this chapter has been published in Polymer Communications.[21] The chapters 5,6 and 8,[22] as well as chapter 7[23] will be submitted for publication.

Parts of this work have been presented at the International Symposium on Free Radical Polymerization (Santa Margherita Ligure, May 1987), the 2nd International Symposium on Copolymerization and Copolymers prepared in disperse media (Lyon, April 1989), the Rolduc Polymer Meeting-4 (Kerkrade, April 1989) and the Polymer Latex III Conference (London, June 1989).

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Chapter 2   Emulsion Polymerization

2.1 Emulsion polymerization

In contrast to bulk and solution polymerization, emulsion polymerizations are heterogeneous reaction systems, initially consisting of a continuous aqueous phase and finely dispersed monomer droplets. Systems with a discontinuous aqueous phase also occur, referred to as inverse emulsion polymerizations. The product, a colloidal dispersion of submicron polymer particles, is called a latex.

Water-soluble radical initiators are mostly used in emulsion polymerizations, and reaction takes place mainly in the monomer-swollen latex particles; this in contrast to the related process of suspension polymerization where oil-soluble initiators are employed to initiate polymerization in the monomer droplets. Emulsifiers are often added to assist in the particle formation process, and to enhance colloidal stability of the latex particles. Optionally other ingredients may be included in the recipe, such as chain transfer agents to reduce the molecular weight of the polymer, or electrolytes to influence the colloidal and rheological properties of the latex.

The advantages of emulsion polymerization are well-known. (1) The heat generated during the exothermic polymerization is quite easily dissipated via the aqueous phase. (2) The rate of polymerization is greater than in the corresponding bulk process, (3) while at the same time the molecular weight of the polymer formed is considerably higher. (4) The latter can readily be controlled by addition of chain transfer agents. The resulting latex is water-

based, which is advantageous in certain applications (e.g. paints), but it also contains emulsifier and initiator residues which are hard to remove and may affect the polymer properties adversely.

It is convenient to divide the course of an emulsion polymerization into three distinct intervals. Interval I is the initial stage where particle formation takes place. Several mechanisms of particle nucleation have been proposed,[1] involving the emulsifier micelles,[2] the aqueous phase,[3] or the monomer droplets;[4] some mechanisms take account of the colloidal instability of the latex particles.[5,6,7] Interval II is characterized by a constancy of particle number, while polymerization in the particles proceeds in the presence of a separate monomer phase. The beginning of interval II is sometimes taken as the conversion where the emulsifier concentration drops below its critical micelle concentration. Interval III begins with the disappearance of monomer droplets, after which the monomer concentration in the particles starts to decrease continuously.

2.2 Emulsion polymerization kinetics

Emulsion polymerization is a particular case of free radical polymerization. The kinetics and mechanisms involved are highly complicated, since events occurring in several phases, and exchange of radicals between the phases need to be taken into account. Models and theories dealing with these aspects of emulsion polymerization are numerous, but excellent reviews are available.[e.g. 1,8,9] A brief discussion of emulsion polymerization kinetics in order to introduce a theoretical framework in the context of this investigation is thus considered sufficient. Details can be found in the references cited.

In general, the rate of free radical polymerization R_{pol} is given by:

$$R_{pol} = k_p [M] [R^\bullet] \tag{2.1}$$

where k_p is the propagation rate coefficient, [M] and [R$^\cdot$] the monomer and free radical concentrations, respectively. This equation is not convenient to use because of the unknown radical concentration [R$^\cdot$]. In emulsion polymerization the overall polymerization rate can be taken as a summation of those in each individual latex particle, leading to:

$$R_{pol} = k_p \, C_M \, (\bar{n}/N_{Av}) \, N \tag{2.2}$$

where C_M is the monomer concentration within the latex particles, $\bar{n}$ the average number of radicals per particle, N the particle number per unit volume of aqueous phase, and N_{Av} Avogadro's number. The parameters most difficult to predict are $\bar{n}$ and N.

2.2.1 Average number of radicals per particle. A set of population balance equations can be given for the the number of particles N_n containing n radicals:

$$\frac{dN_n}{dt} = \frac{\rho_a}{N} \, [N_{n-1} - N_n] + k \, [(n + 1)N_{n+1} - nN_n]$$

$$+ \frac{k_t}{v} \, [(n + 2)(n + 1)N_{n+2} - n(n - 1)N_n] \tag{2.3}$$

where ρ_a is the rate of entry of free radicals into the particles (absorption), k[a] the rate coefficient for exit of radicals from the particles ("desorption"), k_t the rate coefficient for bimolecular termination within the particles, and v the volume of a monomer-swollen particle, all in appropriate units. The rate of radical production in the aqueous phase ρ_i, which was sometimes used in earlier equations for N, is equal to ρ_a only when radical exit is negligible and the initiator efficiency 100 %.

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[a] Smith and Ewart[10] applied $k_o A/v$ instead of k, where A is the surface of a monomer-swollen particle, and k_o an exit rate coefficient.

The first terms on the right hand side of equation (2.3) account for changes in N_n due to radical entry, the second terms for radical exit, and the third ones for bimolecular termination.

Smith and Ewart[10] were the first to obtain some limited solutions for the system represented by equation (2.3), based on a steady-state analysis (i.e. taking $dN_n/dt = 0$) for monodisperse latexes. Three special cases were distinghuished.

Case 1, with $\bar{n} \ll 1$. This situation occurs if the exit rate is great as compared with the entry rate, i.e. $(\rho_a/N) \ll k$. Under these conditions only the first of the recurrence relationships of equation (2.3) needs to be considered, as particles containing two or more radicals may be neglected:

$$\frac{dN_0}{dt} = -N_0 \frac{\rho_a}{N} + N_1 k = 0$$

Since $N_0 \simeq N$, it follows that $N_1 \simeq (\rho_a/k) = \bar{n}.N$; thus the overall rate of polymerization R_{pol} can be written as:

$$R_{pol} = k_p C_M \frac{\rho_a}{k N_{Av}} \tag{2.4}$$

Case 2, with $\bar{n} = 0.5$. In this case, which is most generally known as the Smith-Ewart theory, the following conditions need to be satisfied simultaneously: (1) radical exit is negligible, (2) and bimolecular termination is instantaneous when a second radical enters a particle, i.e. $k \ll (\rho_a/N) \ll (k_t/v)$. It follows trivially that $N_0 = N_1$, so that $\bar{n} = N_1/(N_0 + N_1) = 0.5$. Only in this case is R_{pol} proportional to the particle number N:

$$R_{pol} = k_p C_M \frac{N}{2 N_{Av}} \tag{2.5}$$

Case 3, with $\bar{n} \gg 1$. This situation will occur when the entry rate is much greater than the rate of bimolecular termination, i.e. $(k_t/v) \ll (\rho_a/N)$. Smith and Ewart neglected radical exit in their treatment of this case. With a sufficiently

large $\bar{n}$, the steady-state condition is $\rho_a/N = 2k_t\bar{n}^2/v$. Since the total volume of polymer per unit volume of aqueous phase $V = N.v$, the rate R_{pol} becomes:

$$R_{pol} = k_p\, C_M\, (\rho_a V/2k_t)^{0.5} \qquad (2.6)$$

The Smith-Ewart case 1 and 2 situations are conveniently encompassed in the socalled zero-one system, where only zero or one free radical per particle need to be considered. The main condition for such a system is that the rate of bimolecular termination is considerably greater than those for radical entry or exit. Two radicals cannot coexist in a particle because they terminate virtually instantaneously, viz. $\bar{n} \leq 0.5$. For convenience, the pseudo-first-order entry rate coefficient ρ is introduced to replace ρ_a/N in equation (2.3). In the steady-state the population balance is:

$$\rho N_0 = (\rho + k)N_1$$

so that
$$\bar{n} = \frac{\rho}{2\rho + k} \qquad (2.7)$$

Smith-Ewart case I behaviour is characterized by $k \gg \rho$, thus $\bar{n} \simeq \rho/k$, while in case II $k \ll \rho$, inevitably leading to $\bar{n} = 0.5$.

Stockmayer[11] was the first to give a general solution for equation (2.3) involving Bessel functions, which was later modified by O'Toole[12] to give:

$$\bar{n} = \frac{a}{4}\; \frac{I_m(a)}{I_{m-1}(a)} \qquad (2.8)$$

where I represents Bessel functions of the first kind, and m and a dimensionless parameters defined as:

$$m = k.v/k_t$$
$$a = (8\alpha)^{0.5}$$
$$\alpha = \rho_a v/Nk_t$$

The parameter m is a measure of the exit rate relative to the rate of bimolecular termination (e.g. m = 0, no exit), while α represents the rate of radical entry vs. the rate of bimolecular termination. Utilization of equation (2.8) is not straightforward because ρ_a cannot be obtained unambiguously, as it is influenced by the rates of radical production in the aqueous phase, termination in the aqueous phase, and reentry of exited free radicals. Ugelstad et al.[13] derived a general method of calculating $\bar{n}$, taking the abovementioned aqueous phase events fully into account. The following equation was obtained:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \qquad (2.9)$$

where:
$$\alpha' = \rho_i v / N k_t$$
$$Y = 2 N k_t k_{taq} / k_a^2 v$$

with ρ_i the rate of radical production in the aqueous phase, k_{taq} the termination rate coefficient in the aqueous phase, and k_a the absorption rate coefficient.
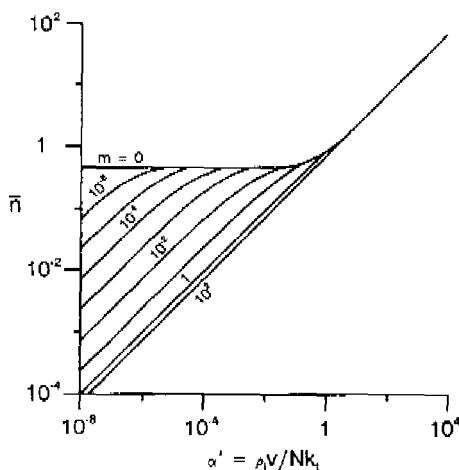
Figure 2.1.   Ugelstad plot for Y = 0.[13]

Numerical methods were used to obtain solutions for equations (2.8) and (2.9). Typical results are shown in Figure 2.1, for the case of negligible aqueous phase termination ($Y = 0$). The three special Smith-Ewart cases are fully encompassed in this figure; the straight horizontal line with $m = 0$ represents case 2 ($\bar{n} = 0.5$), the curves on the lower left side with $m > 0$ include case 1 ($\bar{n} \ll 0.5$), while the line in the upper right side gives case 3 ($\bar{n} \gg 0.5$).

2.2.2 Particle number. The Smith-Ewart model[10] for the prediction of the particle number is based on their case 2 growth kinetics (i.e. a constant volume growth rate), assuming a micellar particle nucleation mechanism as proposed by Harkins.[14,15] Particle nucleation supposedly stops when the total surface of the particles becomes sufficient to adsorb all the emulsifier added. The particle number N predicted by this nucleation model is given by:

$$N = K \left(\rho_i / \vartheta \right)^{0.4} \left(A_s [E] \right)^{0.6} \tag{2.10}$$

where K is a constant between 0.37 and 0.53, ϑ the volume growth rate of a particle, A_s the specific area per unit amount of emulsifier, and $[E]$ the emulsifier concentration, all in appropriate units. Usually, ρ_i can be taken proportional to the initiator concentration $[I]$, so that $N \simeq [I]^{0.4}.[E]^{0.6}$.

It was later shown by Roe[16] that this power law is also consistent with a homogeneous nucleation mechanism, where particles are nucleated by precipitation of oligomeric radicals in the aqueous phase. In fact, the two exponents are predicted by any model that takes cessation of complete surface coverage by emulsifier as the main criterion of the end of the particle nucleation period.

However, experimentally observed exponents cover a wide range of values,[17] while they do not always obey a simple power law when plotted over a large concentration range.[18] Nowadays it is realized that limited coagulation (or coalescence) of the latex particles should be taken into account; models based on this concept are extremely complex, but also show a good agreement with experimental findings.[6,7,19]

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Chapter 3   Experimental Procedures and Techniques

SUMMARY: The recipe ingredients, experimental set up, and reaction conditions used throughout this investigation are outlined in detail. Procedures for gel-analysis and particle sizing are discussed, and some kinetically relevant properties of polybutadiene (e.g. gel content, density, monomer solubility) were determined. The decomposition of persulfate in the presence of the emulsifier dresinate 214 is 1.5 - 2 times faster than in water, presumably due to oxidation of emulsifier components. The necessity to include a buffering substance in the recipe is illustrated; in its absence pH drops below 3 and polymerization is severely retarded.

3.1 Standard polymerization recipes

The two standard recipes used throughout this study are shown in Table 3.1, and were chosen in analogy with recipes found in industrial practice.[e.g. 1,2,3)] For comparison, the GR-S or mutual recipe (for a butadiene homopolymerization) developed during the synthetic rubber program in World War II for production of general purpose butadiene(75)-styrene(25) rubber is shown in the last column.

The similarity between recipe 1 and the mutual recipe is striking; the spin-off of the synthetic rubber program is still relevant to current commercial processes for the production of polybutadiene containing polymers and resins.

Recipe 1 is a typical industrial recipe with regard to the choice of the emulsifier dresinate 214, being a mixture of surface-active components of natural

origin (see section 3.3), with a quality and performance that may vary with source and time. The number of batches dresinate 214 used throughout this investigation was limited, while each series of experiments was always done with one batch over a short period of time.

In order to avoid these problems, the analogous recipe 2 was introduced, employing the well-defined research grade emulsifier sodium dodecylsulfate. Differences between both standard recipes are not crucial and based on practical considerations; potassium dodecylsulfate was found insoluble in water at room temperature, so that all potassium salts from recipe 1 were substituted by the subsequent sodium salts on a molar basis. The overall cation concentration (including the emulsifier contribution) in recipe 2 is $[Na^+] = 0.3$ mol.L^{-1}, while in the standard recipe 1 $[K^+] = 0.4$ mol.L^{-1}.

In the following sections the experimental procedures and relevant characteristics of the recipe ingredients will be discussed.

Table 3.1. Standard polymerization recipes in parts by weight.

Ingredient	Recipe 1	Recipe 2	Mutual recipe
water	230	230	180
butadiene	100	100	100
dresinate 214	7.6		5[a]
sodium dodecylsulfate		7.6	
K^+/Na^+ carbonate[b]	4.4	2.0	
K^+/Na^+ persulfate[b]	0.8	0.7	0.3
t-dodecanethiol	0.7	0.7	0.5
[initiator]	13 mmol.L^{-1}		6 mmol.L^{-1}
temperature	62°C		50°C
pH	10.5 - 10.8		

[a] Initially a commercial emulsifier of 'ORR quality' was used, with sodium palmitate, stearate and oleate as main components; later this was frequently substituted by dresinates (see section 3.3).
[b] In recipe 1 and the mutual recipe potassium salts, and in recipe 2 sodium salts were used.

3.2 Reactor design and experimental procedures

The butadiene (DSM Hydrocarbons, Geleen, Holland) was purified by condensing the vapour from a 27-litre storage vessel into a cooled steel recipient (Figure 3.1, page 19). The polymerizations were performed in a stainless steel reactor (from K. K. Juchheim, Bernkastel-Kues, FRG) fitted with four baffle plates located at 90° intervals and a twelve-bladed turbine impeller (Figure 3.2). The reactor was charged under N_2 with all ingredients except the butadiene. The system was freed from inert gases by flushing the gas cap with gaseous butadiene, followed by evacuation. This procedure was repeated twice. Lastly, the correct amount of freshly distilled liquid butadiene was added from a weighed steel vessel.

The polymerization temperature was kept constant within 0.1°C. During polymerization samples (ca. 8 mL) were taken with a high-pressure-proof syringe, and the conversion determined from the total solid content of the sample. The polymerization rate R_{pol}[a] was taken as the slope of the linear portion of the conversion-time curve (i.e. interval II).
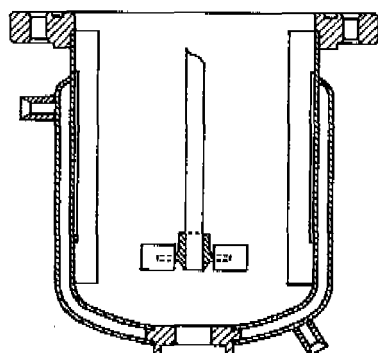
Reactor dimensions in mm	
impeller diameter	60
reactor diameter	134
baffle diameter	13.4
blade diameter	18
reactor height	175
initial liquid height[b]	162
final liquid height[b]	139

[b] Calculated for a standard recipe without sampling.

Figure 3.2.   Cross section of the polymerization reactor.

[a] The steady-state polymerization rate R_{pol} is expressed in grams (or moles) of polymer formed per unit volume of water per second.

The effective volume of the reactor shown in Figure 3.2 is 2.36 litre. After charging the reactor according to one of the standard recipes, the initial degree of filling is 92 %. As polymerization proceeds, the reaction volume decreases due to the large difference in density between butadiene and polybutadiene. Without any samples being taken, the final degree of filling becomes 78 %.

Under atmospheric circumstances butadiene is a gaseous monomer (boiling point - 4.4°C); thus in a polymerizing system the amount in the gas phase needs to be considered. Assuming ideal gas behaviour as a first order approximation, the amount of butadiene vapour at an initial degree of filling of 92 %, is 0.6 % of the total amount charged. This constitutes a small systematic error for gravimetric conversion data, as samples are taken from the emulsion. Nevertheless, its magnitude is comparable with statistical errors involved in the sampling procedure, as long as the gas space is minimized and excessive sampling avoided. The effect on R_{pol} is negligible, as R_{pol} represents the slope of the conversion-time curve.

3.3 Emulsifier

Two emulsifiers have been used routinely: dresinate 214 (Hercules bv, Den Haag, Holland) and sodium dodecylsulfate (SDS, purity > 99 %, Merck, Darmstadt, FRG). Other emulsifiers employed occasionally are potassium stearate and oleate, formed *in situ* from stearic acid (purity > 98 %, Merck, Schuchardt, FRG) and oleic acid (Merck, Darmstadt, FRG).

Dresinate 214[4,5] was used as a 15 weight % dispersion of potassium salts of disproportionated rosin acid soap in water. Rosin is a resinous substance obtained from pine trees by solvent extraction of wood stumps, or collecting the exudate from the living trees (wood and gum rosin). In chemical composition, it comprises some 90 % of socalled resin acids and ca. 10 % non-acidic material (e.g. esters of rosin and fatty acids, and various hydrocarbons). Rosin acid is a
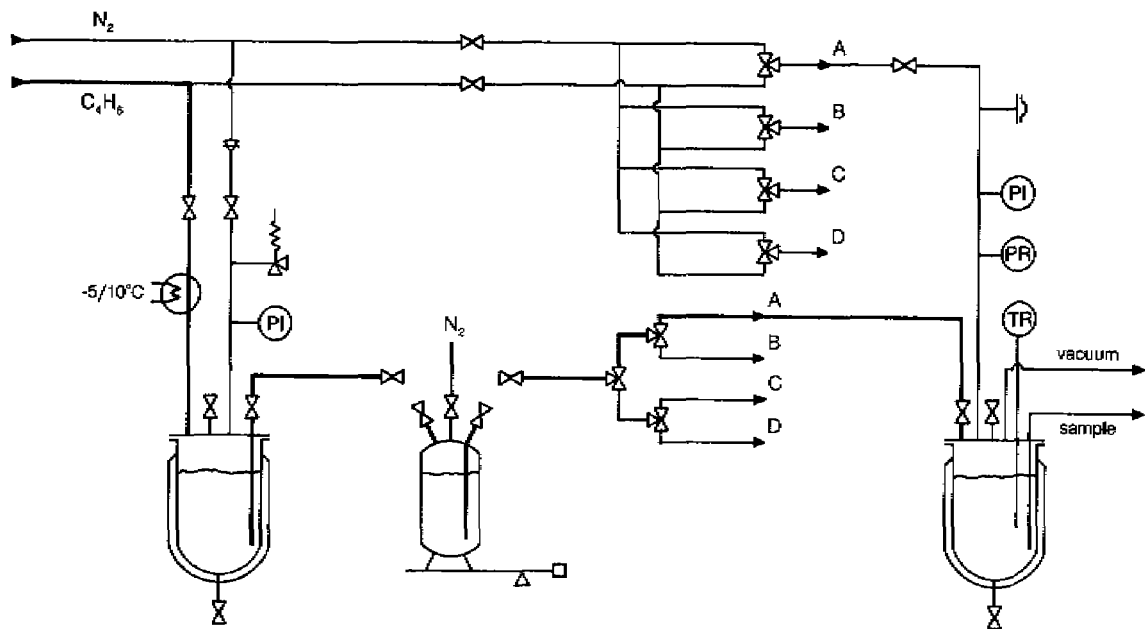
Figure 3.1. Butadiene flow scheme (thick line) for the distillation unit (left), dosage vessel (middle), and polymerization reactor (right). Appendages include pressure indicator (PI), pressure recorder (PR), and temperature recorder (TR).

complex mixture of monocarboxylic acids of alkylated hydrophenanthrene nuclei, the main components having the formula $C_{19}H_{29}CO_2H$ and containing two double bonds per molecule. It dissolves in strong alkaline solutions to give rosin-acid soaps. Rosin acid soaps by themselves are unsatisfactory for use in emulsion polymerizations, due to the presence of conjugated double bonds of the abietic-type acids, giving rise to severe retardation.[6,7,8] The double bonds can readily be eliminated by disproportionation, a process where the rosin is heated over a palladium catalyst giving simultaneous hydrogenation and dehydrogenation. The resulting mixture has dehydro-, dihydro- and tetrahydroabietic acid as main components, and contains less than 0.2 weight % abietic acid. Several qualities are commercially available under the tradename dresinate.

The performance of rosin acid soaps is strongly pH-dependent, with an optimum value of ca. 10 - 11. For this reason a moderate excess of potassium carbonate (pK = 10.2 at 25°C) is included in recipe 1, and for reasons of comparison maintained in recipe 2. This is not essential for SDS, as its solubility and performance depend only weakly on pH; minor effects arise from changes in micellar size.[9] Although the prime function of K^+/Na^+ carbonate is to maintain a constant pH, its presence gives rise to secondary effects, originating from the increase in ionic strength of the aqueous phase (chapter 5). It is further realized that micelles of SDS may be non-spherical in systems with a high ionic strength.[e.g. 10] However, no specific effects on reaction kinetics were found.

3.4 Initiator

An initiator serves as a source of radicals that initiate and maintain the free radical polymerization process. At elevated temperatures peroxodisulfate (as ammonium, sodium or potassium salt) is the most common initiator employed.

The decomposition of peroxodisulfate (hereafter persulfate) in aqueous media has been studied extensively. An excellent review of literature up to 1980 has been given by Behrmann and Edwards.[11]

In weak basic and neutral solutions decomposition occurs through a thermal homolytic scission of the O-O bond, often considered a unimolecular reaction:

$$S_2O_8^{2-} \quad \rightarrow \quad 2\ SO_4^{\bullet-} \tag{3.1}$$

although there are strong indications that the homolytic scission may also occur through a bimolecular reaction involving a water molecule:

$$S_2O_8^{2-} + H2O \quad \rightarrow \quad SO_4^{\bullet-} + HSO_4^- + HO^\bullet \tag{3.2}$$
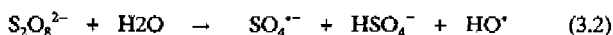
Steps after the radical formation include:

$$SO_4^{\bullet-} + H_2O \quad \rightarrow \quad HSO_4^- + HO^\bullet \tag{3.3}$$

$$2\ HO^\bullet \quad \rightarrow \quad H_2O_2 \tag{3.4}$$
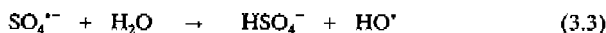
Hydrogen peroxyde decomposes to form oxygen. In the presence of monomer the radical intermediates are capable of initiating polymerization.

At pH < 3, the following process contributes increasingly to the decomposition of persulfate, without producing radicals:

$$HS_2O_8^- + H_2O \quad \rightarrow \quad HSO_5^- + HSO_4^- + H^\bullet \tag{3.5}$$
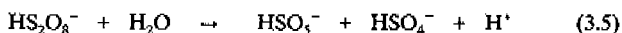
Although such acidic solutions are of little significance to emulsion polymerization, it emphasizes the necessity to include a buffering substance in the recipe to maintain pH > 3, as HSO_4^- is formed in steps (3.2) and (3.3). This is illustrated for the butadiene emulsion polymerization in section 3.5.

It has frequently been reported[e.g.12,13,14] that the presence of organic material (including emulsifiers and monomers) increases the rate of disappearance of persulfate, mainly due to oxidation of the material present in solution. Although this does not increase the effective rate of radical production, the phenomenon should not be ignored, as excessive consumption of persulfate leads to a premature exhaustion of the initiator and incomplete polymerization.

In order to check this in the present system, the decomposition of persulfate in the presence of dresinate 214 (recipe 1) was studied titrimetrically as a function of temperature and emulsifier concentration.

Procedure: the procedure followed is a modified version described by Kolthoff et al.[15] Latex samples collected at regular time intervals during polymerization were cooled in ice under N_2. The water content of the latex was determined by evaporating 10 mL of sample to complete dryness. About 20 - 30 mL (containing ca. 0.2 mmol persulfate) was weighed accurately in a centrifuge tube, coagulated with 5 mL H_2SO_4 (3 mol.L^{-1}), and centrifuged at 2500 rpm for several minutes. The clear serum was transferred to a titration vessel under N_2, and the polymer rinsed thoroughly with water. Potassium iodide (4.0 grams) was added, and after 30 minutes the iodine titrated with 0.01 mol.L^{-1} sodium thiosulfate; the end-point was determined with a starch solution. The potassium persulfate concentration per unit volume of water [I] follows readily from the stoichiometry of the titration.

Results: a plot of ln [I] vs. time gave linear curves, where the slope yields the first-order decomposition rate coefficient k_d (Table 3.2). The presence of dresinate 214 obviously increases the rate of disappearance of persulfate by a factor of 1.5 - 2, in agreement with results reported for other emulsifiers.[13,16] As the emulsifier concentration C_g is decreased, k_d also decreases towards the value found by Kolthoff and Miller[17] in a solution of 0.1 mol.L^{-1} NaOH, a strong indication of a direct chemical interaction between persulfate and the emulsifier or components therein. Yet, in this case such a side-reaction would hardly affect the rate of radical production R; consequently the value for k_d of Kolthoff and Miller (i.e. 6.3 10^{-6} s^{-1} at 62°C) was used to calculate R.

Polymerization times are of the order of the half life times of the initiator (Table 3.2). Nevertheless, the significant decrease in persulfate concentration does not appear to affect the steady-state kinetics, as interval II remains linear, indicating an 'ideal' Smith-Ewart case 2 situation where $\bar{n}$ is independent of [I], or, as will be shown later, an extremely low initiator efficiency.

Table 3.2. Decomposition rate coefficients k_d and half life times $t_{1/2}$ for $S_2O_8^{2-}$ at various temperatures θ and emulsifier concentrations C_E

θ °C	C_E g.L^{-1}	$10^6.k_d$ s^{-1}	$t_{1/2}$ hr	$10^6.k_d$[a] s^{-1}
57	32.4	6.9	28	3.1
62	32.4	12.5	15	6.3
62	16.2	10.8	18	6.3
62	8.1	8.3	23	6.3
67	32.4	22.5	9	13.1

[a] Data by Kolthoff and Miller[17] in a solution of 0.1 mol.L^{-1} NaOH.

Other dissociative initiators used were 4,4'-azobis(4-cyanopentanoic acid) (ACPA, Fluka AG, Buchs, Switzerland) and 2,2'-azoisobutyronitrile (AIBN, Fluka AG, Buchs, Switzerland). ACPA was used as received, whereas AIBN was recrystallized from methanol and stored at 5°C.

ACPA is completely water soluble at high pH, whereas AIBN will be partitioned between the aqueous and organic phases present. Although AIBN is often referred to as an oil soluble initiator, its water solubility is appreciable, about 13 mmol.L^{-1}.[18] In fact, in the present study AIBN behaved similar as the other, water-soluble initiators. The decomposition rate coefficients for ACPA and AIBN in water at $\theta = 62$°C were taken from literature: $1.2 \ 10^{-5}$ s^{-1} for ACPA,[19] and $6.3 \ 10^{-6}$ s^{-1} for AIBN.[18]

3.5 Buffer

In the preceding section 3.4 it was shown that when using persulfate as initiator, the pH tends to decrease due to the formation of HSO$_4^-$. At pH < 3, decomposition is predominantly via the acid-catalyzed pathway (equation 3.5), without producing radicals capable of initiating polymerization. It is thus essential to maintain the aqueous solution neutral or basic, especially when initiator efficiency with regard to the polymerization is low. As a result of the

long reaction times at relatively high polymerization temperatures, the emulsion polymerization of butadiene is particularly susceptible to this phenomenon. Figure 3.3 shows a polymerization with SDS as emulsifier (recipe 2), in the absence of sodium carbonate. As pH drops, polymerization becomes severely retarded. A similar effect for the emulsion polymerization of butadiene using sodium dodecyl benzenesulfonate as emulsifier was reported by Bhakuni.[20] In contrast, many other monomers (e.g. styrene,[21] vinyl acetate,[22] various acrylates and methacrylates[23]) can readily be polymerized via emulsion polymerization up to high conversions in the absence of a buffering substance.
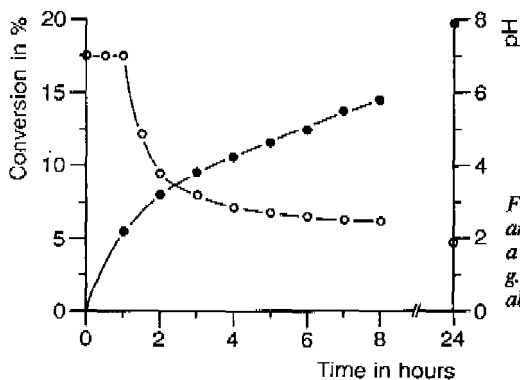
Figure 3.3. Conversion (●) and pH (○) versus time for a polymerization with 32.4 $g.L^{-1}$ SDS (recipe 2) in the absence of Na_2CO_3.

3.6 Chain transfer agent and gel analysis

Chain transfer agents are routinely used in emulsion polymerizations of diene-monomers, to control the extent of branching and cross-linking of the polymer. Thiols of low water solubility are mostly employed for this purpose.

In this study several types of dodecanethiol were used: (1) an industrial grade tertiary dodecanethiol (Pennwalt Chemicals, Rotterdam, Holland), which is a crude mixture of C_{12}-isomers, containing small amounts of other compounds

(e.g. higher and lower thiols, isomeric alkanes), and (2) a well-defined mixture of two isomeric tertiary dodecanethiols (Fluka AG, Buchs, Switzerland): $(CH_3)_3CCH_2C(CH_3)_2CH_2C(CH_3)_2SH$ and $(CH_3)_3CCH_2C(CH_3)(SH)CH_2C(CH_3)_3$. Unless stated otherwise, tertiary dodecanethiol (t-DT) refers to the commercial grade material supplied by Pennwalt. Furthermore, (3) n-Dodecanethiol (n-DT, 98 %, Merck, Darmstadt, FRG) was occasionally used in this study.

Although the gel content of a cross-linkable polymer is theoretically well defined as the fraction of material of "infinite" molecular weight, experimental criteria are usually more arbitrary, and strongly depend on the experimental procedure. The same holds for the gel point, i.e. the conversion at which the first insoluble polymer network makes its appearance. Therefore, the procedures followed to determine the gel content and gel point in this study will be described in some detail.

The first method is based on a <u>toluene extraction</u> of the soluble fraction of the polybutadiene (PB). The insoluble residue is by definition the gel fraction. The polybutadiene is isolated from the latex by precipitation in acidic methanol, followed by repeated washing with water and methanol. The polymer is dried under nitrogen at 50°C. Toluene (100 mL) is pipetted to 1 gram of an accurately weighed PB sample in a stoppered flask. After gentle shaking for at least 48 hours at room temperature, the contents is passed over a 100 mesh filter, and 50 mL of the filtrate evaporated to dryness in a weighed aluminium dish.

The gel content is simply calculated according to $(w_{PB} - 2w_P)/w_{PB}$, where w_{PB} is the weight of the PB sample and w_P is the weight of the dried filtrate. Linear extrapolation to zero of the gel content as a function of conversion, gives the experimental gel point. This can be markedly different from the theoretical gel point, since any possible gel structures of latex particle dimensions or smaller (i.e. microgel) that persist after coagulation, remain undetected by this method as they pass through the filter. It is assumed that during isolation of PB from the latex the microgel agglomerates completely.

The socalled vistex method is based on measurements of the intrinsic viscosity $[\eta]$ of diluted latex solutions. The procedure is a slightly modified version of the one described by Henderson and Legge.[24] One gram of latex is dissolved in 100 mL toluene-isopropanol (80 : 20 by volume), and diluted with pure toluene, successively. The viscosity was measured with an Ubbelohde viscometer at 25°C, and $[\eta]$ in pure toluene is obtained by extrapolation of the reduced or inherent viscosity to zero concentration. A plot of $[\eta]$ versus conversion has a pronounced maximum, taken as the gel point.

Initially $[\eta]$ increases with conversion as molecular weight increases through branching and cross-linking. Although the presence of toluene-swollen microgel may still raise $[\eta]$ somewhat, as the amount of microgel and the cross-link density therein increases, the contribution to $[\eta]$ inevitably decreases and a maximum in the $[\eta]$ vs. conversion curve occurs.

3.7 Particle size analysis

The average particle diameter was measured by dynamic light scattering (DLS, Malvern IIc) and transmission electron microscopy (TEM, Philips 420 and Jeol 2000 FX). For TEM the latexes were hardened with OsO_4 and typically some 750 - 1000 particles were counted with a Zeiss TGA-10 particle analyzer. From DLS only the weight-average diameter d_w (calculated from the measured z-average diameter) was used, while TEM gives complete information on particle size and size distribution. Relevant definitions are given in Table 3.3. The particle number density per unit volume of water (N) was calculated as:

$$N = \frac{6\ c\ (M/W)}{(\rho_p/\rho_{aq})\ \pi\ d^3} \tag{3.6}$$

where c is the fractional conversion, (M/W) the monomer to water weight ratio, ρ_{aq} the water density, ρ_p the polymer density, and d the particle diameter.

Table 3.3. Definitions of relevant particle size parameters,
were n_i represents the number of particles with diameter d_i

d_n	d_s^2	d_v^3	d_w	P
$\dfrac{\Sigma n_i.d_i}{\Sigma n_i}$	$\dfrac{\Sigma n_i.d_i^2}{\Sigma n_i}$	$\dfrac{\Sigma n_i.d_i^3}{\Sigma n_i}$	$\dfrac{\Sigma n_i.d_i^4}{\Sigma n_i.d_i^3}$	$\dfrac{d_w}{d_n}$

Subscripts: n denotes number-average, s surface-average,
v volume-average, and w weight-average diameters.

Comparison between both methods of particle sizing on the basis of d_w gives
excellent agreement; numerical values usually coincide within 5 % (Table 3.4).
However, the particle numbers calculated from these diameters are by definition
systematically smaller than the more correct ones based on the mean-volume
average diameter d_v. In the present study this only affects numerical values by
some 10 - 20 % (e.g. Table 4.2 and Table 5.3), because the particle size
distributions are relatively narrow (average polydispersity P = 1.08; standard
deviation = 0.03). The main conclusions are thus independent of the method of
particle sizing, which makes DLS, being faster and more convenient than TEM,
a very useful method.

Table 3.4. Comparison between average particle diameters obtained
with transmission electron microscopy and dynamic light scattering.

conversion (%)[a]	d_n/nm	d_w/nm TEM	d_w/nm DLS	P
15	34	38	38	1.11
26	46	54	56	1.17
99	64	68	70	1.07
98	80	88	89	1.11
27	100	113	116	1.13
41	130	139	139	1.07
57	152	161	162	1.07
96	183	190	191	1.04

[a] Latex samples taken from different polymerizations (recipe 1).

3.8 Polybutadiene

The microstructure of polybutadiene (PB) consisting of sequences of cis-1.4, trans-1.4, and vinyl-1.2 units has been studied extensively with various techniques.[25,26,27)] For PB prepared by emulsion polymerization the fractions of these microstructural units are statistically determined, and depend only on the polymerization temperature. A check by ^{13}C NMR with a randomly chosen PB-sample, using the triad determination method developed by Van der Velden et al.[28)] gave values in good agreement with other data (between brackets data from Hampton[29)] using IR): 18 % vinyl-1.2 (19 %), 20 % cis-1.4 (23 %) and 62 % trans-1.4 (58 %) units, at θ_{pol} = 62°C.

The microstructure (and the degree of cross-linking) may influence the density of polybutadiene. This was assessed experimentally by using butadiene-free latex samples taken at several conversions. The density of the latex was measured with a calibrated Anton Paar precision density meter equipped with a remote cell DMA 401, and the density of PB calculated assuming additivity of the specific volumes of the aqueous phase and the polymer phase:

$$\frac{1}{\rho_L} = \frac{w_{aq}}{\rho_{aq}} + \frac{w_p}{\rho_p} \qquad (3.7)$$

where w is the weight fraction and ρ the density, while the subsripts L, p and aq denote the latex, polymer and aqueous phase, respectively. The density ρ_{aq} was determined separately. From Table 3.5 ρ_p appears constant and independent of conversion, viz. 0.878 g.mL^{-1} at 62°C. This value is in good agreement with the one determined by Mandelkern et al.[30)] at 25°C, viz. 0.892 g.mL^{-1}.

Table 3.5. Polymer density ρ_p determined with a precision density meter, using latex samples taken at several conversions c (standard recipe 1).

c in %	14	27	39	52	65	77	82	99
ρ_p/g.mL^{-1}	0.884	0.876	0.880	0.880	0.878	0.878	0.874	0.876

In an attempt to determine the saturation solubility of butadiene in polybutadiene, the method outlined by Meehan[31] based on vapour pressure measurements was tried. In short, a latex with an accurately known PB content was equilibrated with liquid butadiene, while stirring constantly with a magnetic stirring bar. The pressure was measured with a manometer, keeping sample and manometer both immersed in a water bath at 25°C. This was done at various butadiene/PB ratios, while a correction was applied for the amount of butadiene in the gas phase. A typical example is shown in Figure 3.4. Interpolation might yield the saturation solubility of butadiene in PB, a situation equivalent to the beginning of interval III. However, interpolation is not straightforward as butadiene vapour does not obey Henry's law. The point where pressure reaches the plateau value was taken instead.[31]
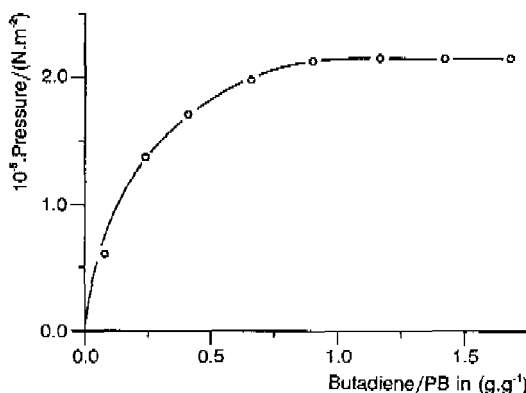
Figure 3.4. Vapour pressure at 25°C of latexes with varying butadiene/ PB ratios. The latex used stems from a polymerization with 32.4 g.L^{-1} dresinate 214 (recipe 1), having a conversion of 96 % (see Table 3.6).

Measurements were performed with samples taken at several conversions (Table 3.6) during a polymerization with 32.4 g.L^{-1} dresinate 214 (recipe 1). An average value of 0.95 gram butadiene per gram of polybutadiene was obtained,

in agreement with data from Meehan[31] (0.92 g.g^{-1}) and Morton et al.[32] (0.8 ± 0.05 g.g^{-1}).[b] A value of 0.95 g.g^{-1} would lead to a conversion value of 51 % for the beginning of interval III, when all the butadiene is absorbed by the maximum swollen latex particles.

Table 3.6. Solubility of butadiene in PB measured with latex samples taken at several conversions during a standard polymerization (recipe 1).

conversion (%)	26	35	45	54	66	76	96[a]
solubility (g.g^{-1})	0.98	1.09	0.87	0.98	0.86	0.94	0.92

[a] Shown in Figure 3.4.

Despite the relatively large experimental error, it appears that monomer solubility is independent of conversion. However, the determination of the point where pressure begins to drop (or alternatively a rough interpolation to yield this point), is not neccessarily equal to the beginning of interval III. In Chapter 7 an unambiguous and exact method will be presented to calculate this point, based on the polymerization kinetics in intervals II and III. According to this method, the beginning of interval III is at 60 % conversion, and was found independent of particle size.

[b] All data obtained by vapour pressure measurements.

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Chapter 4   Polymerizations with Rosin Acid Soap

SUMMARY: The kinetics of the emulsion polymerization of butadiene was investigated, using dresinate 214 as emulsifier in combination with three dissociative initiators, namely potassium persulfate, 4,4'-azobis(4-cyanopentanoic acid) and 2,2'-azoisobutyronitrile. The reaction rate R_{pol} in interval II was found to be highly insensitive to changes in the initiator concentration ($R_{pol} \propto [I]^{0.08}$), indicative of a low initiator efficiency. The development of particle number N as a function of conversion at several emulsifier concentrations [E], reveals a limited colloidal stability of the particles. R_{pol} depends on [E] with an exponent of 0.61, whereas N after cessation of coagulation has an exponential dependence of 1.6. As a consequence R_{pol}/N (and thus $\bar{n}$) must depend on particle size, since the monomer concentration within the particles is virtually constant in interval II. A certain analogy in behaviour between the emulsion polymerization of various polar monomers, kinetically dominated by radical desorption, and the emulsion polymerization of butadiene, suggests that similar events determine the kinetic course in the present system.

4.1 Introduction

Despite the industrial importance of the emulsion (co)polymerization of butadiene, very little has been reported about its kinetic and mechanistic features. The aim of this research is to investigate the effects of various reaction parameters on the kinetics of the emulsion polymerization of butadiene, deliberately starting from a typical industrial recipe. This chapter describes the influence of the initiator and emulsifier concentration, using disproportionated

rosin acid soap as emulsifier (recipe 1), and several dissociative initiators differing in structure and water solubility. All experiments were conducted in the presence of a thiol as chain transfer agent, in concordance with general practice.

4.2 Effect of the initiator concentration

In earlier investigations it was found that the rate of emulsion (co)polymerization of butadiene(75)-styrene(25) or butadiene alone (using the GR-S recipe) remained virtually constant even when the concentration of persulfate was changed 100-fold.[1] In order to get more insight into this phenomenon polymerizations were performed with various types of dissociative initiators: potassium persulfate (PPS), 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and 2,2'-azoisobutyronitrile (AIBN). The first two initiators are completely water-soluble under the experimental conditions (pH = 10.5 - 10.8), whereas AIBN is only sparingly soluble in water. The overall $[K^+]$ was kept constant at 0.4 mol.L^{-1} by appropriate adjustment of the amount of K_2CO_3.
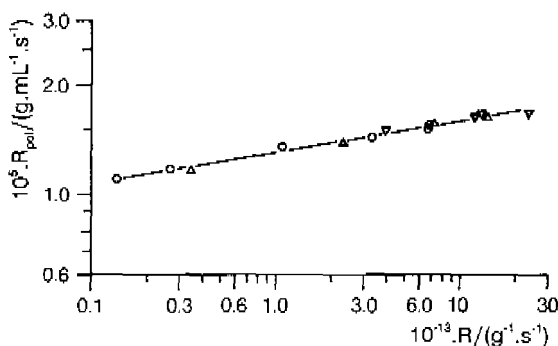
Figure 4.1.   Variation of the overall polymerization rate R_{pol} with the radical production rate per gram emulsion R for three different initiators: PPS (○), ACPA (△), and AIBN (▽), using dresinate 214 as emulsifier (recipe 1).

Figure 4.1 shows the effect of variation of initiator concentration on polymerization rate R_{pol}. The rate of radical production per gram emulsion R is calculated according to $R = 2 k_d [I] N_{Av}$, where k_d is the decomposition rate coefficient, [I] the initiator concentration in moles per gram of emulsion and N_{Av}, Avogadro's number. Values for k_d at polymerization temperature (62°C) were calculated from data in the literature: PPS[2] $6.3 \ 10^{-6} \ s^{-1}$, ACPA[3] $1.2 \ 10^{-5} \ s^{-1}$ and AIBN $1.3 \ 10^{-5} \ s^{-1}$ in toluene,[4] and $6.3 \ 10^{-6} \ s^{-1}$ in water.[5] As all values for k_d are of comparable magnitude, the net effect on R will be small.

It appears that the polymerization kinetics is highly insensitive to the initiator concentration, irrespective of the nature of the initiator ($R_{pol} \propto [I]^{0.08}$). Inspection of the conversion-time curves (Figure 4.2) indicates that particle formation is a slow process since the nucleation period (i.e. interval I) is unusually long, typically some two hours or more. The total number of primary radicals generated during this period is 10^{17} - 10^{18} per mL of water, while the particle number is of the order of 10^{15} per mL of water (see Table 4.2). This large discrepancy implies that all three initiators investigated are very inefficient in the particle nucleation process. Therefore, the relatively small variation of initiator concentrations in the studied region will hardly affect the kinetics.

Figure 4.2. Conversion-time curves of persulfate-initiated polymerizations at different initiator concentrations [I] = 13.0 mmol.L^{-1} (△); [I] = 2.6 mmol.L^{-1} (○); [I] = 0.52 mmol.L^{-1} (▽); and [I] = 0.26 mmol.L^{-1} (□).

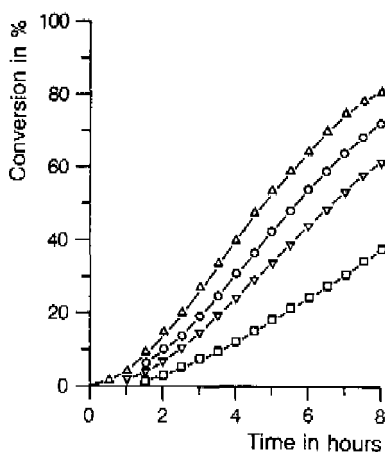The low initial rates and long duration of interval I cannot be attributed to the presence of any possible retarding components in the dresinate 214 (e.g. abietic acid-type of derivatives, section 3.3), as similar results were obtained with other emulsifiers, including sodium dodecylsulfate (see chapter 5).

A comparison between the experimental values for the particle number N and the critical time t_{cr} (the duration of interval I) on the one hand, and the predictions by the Gardon theory[6] (being an extension of the Smith-Ewart theory) in Table 4.1 shows that the present system deviates significantly from the 'ideal' emulsion polymerization as embodied in the Smith-Ewart assumptions.[7] It should be noted that Gardon's treatment is only applicable to cases with negligible radical desorption ($\bar{n} \geq 0.5$).

The nature and ionic charge of the primary radicals evidently have no effect on the reaction kinetics, indicating that the reactivity of the oligomeric radical species initiating polymerization in the loci is dominated by the hydrophobic moiety. Similar effects have been reported for the emulsion polymerization of styrene, using initiator systems generating anionic, neutral or cationic radicals.[8]

Table 4.1. Experimental and theoretical values for the particle number N, and critical time t_{cr} (see text) for polymerizations with different initiators.

Initiator	c in %	d_v/nm	$10^{-15}.N/mL^{-1}$		$10^{-3}.t_{cr}/s$	
			exp.	Gardon[a]	exp.[b]	Gardon[a]
PPS	95	83	1.5	10	9.5	0.18
PPS	98	87	1.4	10	9.5	0.18
ACPA	99	88	1.3	13	8.5	0.13
AIBN	94	84	1.5	10 - 14[c]	9.0	0.12 - 0.18[c]

[a] Calculated using a value of 100 $L.mol^{-1}.s^{-1}$ for the propagation rate coefficient at $62°C$,[9] and an initiator concentration [I] = 13 $mmol.l^{-1}$.

[b] Roughly estimated from the conversion-time curves as the elapsed time till polymerization rate becomes constant.

[c] Calculated with the values for k_d in toluene and water.

4.3 Effect of the emulsifier concentration

Figure 4.3 shows the conversion-time curves of polymerizations in which the emulsifier concentration was varied eightfold between 64.8 $g.L^{-1}$ and 8.1 $g.L^{-1}$. All experiments were conducted above the critical micelle concentration (CMC) of dresinate 214, determined tensiometrically with the *DuNouy* ring method to amount to 1.2 $g.L^{-1}$, i.e. about 3.5 10^{-3} $mol.L^{-1}$ (θ = 25°C and $[K_2CO_3]$ = 0.15 $mol.L^{-1}$). Agreement with values reported in literature is good if differences in electrolyte concentration are taken into account: 10.4 10^{-3} $mol.L^{-1}$ for dresinate 214[10] and < 10^{-3} $mol.L^{-1}$ for "sodium rosinate" (presumably dresinate 731),[1] both values determined at 50°C and without additional electrolyte.
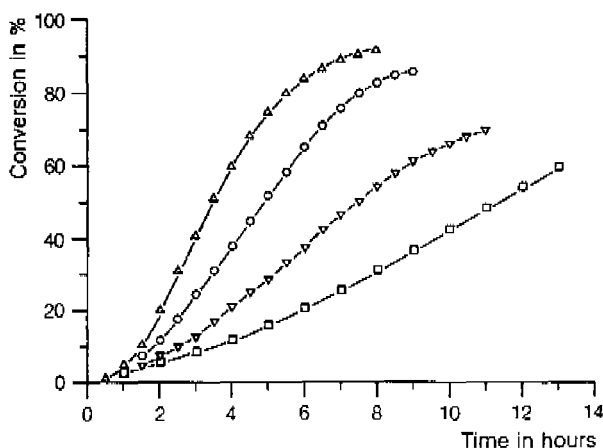
Figure 4.3. Conversion-time curves of persulfate-initiated polymerizations at different dresinate 214 concentrations C_E = 64.8 $g.L^{-1}$ ($\triangle$); C_E = 32.4 $g.L^{-1}$ ($\bigcirc$); C_E = 16.2 $g.L^{-1}$ ($\triangledown$); and C_E = 8.1 $g.L^{-1}$ ($\square$).

Plotting the polymerization rate in interval II against the emulsifier concentration on a log-log scale yields a value 0.61 for the emulsifier exponent (Figure 4.4). This is in excellent accordance with the Smith-Ewart case 2

behaviour, insofar as R_{pol} is proportional to N. However, in the present system this agreement is apparent, as will be explained in the following.

Data on particle size and number as a function of conversion are given in Table 4.2 and Figure 4.5 (see page 40). Agreement between TEM and DLS is excellent. Within each experiment the particle number reaches a constant value at conversions greater than ca. 40 %, however, the behaviour at lower conversions is of more interest. In the intermediate emulsifier concentration range studied, a steady decrease in particle number is clearly observable. This implies that beside particle nucleation (micellar or homogeneous) a second mechanism is operative which is coagulative in nature. This process is relatively slow since it could be detected using conventional sampling procedures.
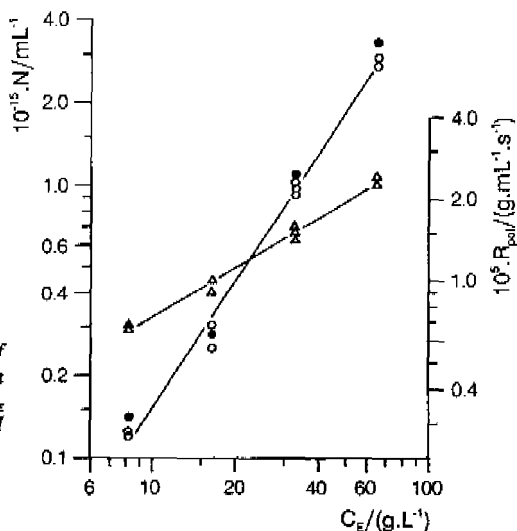
Figure 4.4. Dependence of R_{pol} ($\triangle$) and final N on emulsifier concentration C_E Particles sized with TEM ($\bullet$) and DLS ($\circ$).

Evidence is accumulating that coagulation of latex particles cannot be neglected in emulsion polymerization.[11] It has been shown that limited coagulation determines the particle number in the emulsion polymerization of more water-soluble monomers (e.g. vinyl acetate,[12] ethyl acrylate,[13] methyl

methacrylate[14]), and of non-polar monomers in emulsifier-free systems.[15] Recently Feeney, Napper and Gilbert[16] proposed a coagulative nucleation mechanism combining Müller-Smoluchowski coagulation kinetics with the DLVO theory of colloidal stability,[e.g. 17] thus suggesting that limited coagulation is inherent in any emulsion polymerization.

Table 4.2. Particle diameter d and particle number N determined with TEM and DLS at different concentrations of dresinate 214 (recipe 1).

$C_E/g.L^{-1}$	c in %	d_v/nm	d_w/nm		$10^{-15}.N/mL^{-1}$ [a]	
			TEM	DLS	TEM	DLS
64.8	74	55	59	61	4.1	3.2
	99	65	68	69	3.3	2.9
32.4	15	35	37	38	3.2	2.6
	26	49	54	56	2.1	1.6
	41	65	71	73	1.4	1.1
	68	83	88	89	1.1	0.92
	98	87	93	97	1.4	1.1
16.2	14	42	43	45	1.7	1.6
	26	67	72	71	0.79	0.65
	40	94	100	104	0.45	0.37
	70	126	132	134	0.32	0.28
	99	143	149	153	0.31	0.28
8.1	13	78	90	90	0.25	0.17
	27	104	113	116	0.22	0.17
	41	134	139	139	0.15	0.14
	57	155	161	162	0.14	0.13
	97	185	190	191	0.14	0.13

[a] N based on d_v when using TEM.

It is obvious that coagulation will influence the initiator efficiency toward particle nucleation, the duration of interval I, and the final particle number. Deducing the emulsifier exponent from a linear log-log plot of final particle number versus emulsifier concentration (Figure 4.4), gives a value of 1.6. The corresponding exponent toward polymerization rate R_{pol} was found to be 0.61. Since the butadiene concentration in the latex particles was found to be practically constant in interval II and independent of emulsifier concentration

(chapter 7 and references therein), the average rate per particle R_{pol}/N must be a function of particle size to account for the observed behaviour.

Similar but unexplained results for the homopolymerization of butadiene have been reported by Morton et al.[18] and Wendler et al..[19] The latter found a distinct effect of the amount of bis(isopropoxythiocarbonyl)disulfane on particle size, as a result of changing the colloidal properties of the system.[20] Experimental results are summarized in Figure 4.6 were d_{90} represents the particle diameter at 90 % conversion, calculated from the experimental data assuming a constant particle number: $d_{90} = (0.9 \ d^3/c)^{1/3}$.
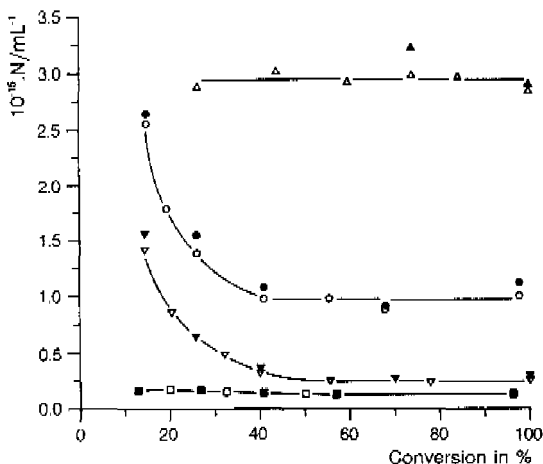
Figure 4.5. Variation of particle number N with conversion for polymerizations with different dresinate 214 concentrations C_c (symbols see legend of Figure 4.3). Full symbols indicate TEM data, and open symbols DLS data (both using d_w).

Using R_{pol}/N as a semi-quantitative equivalent of the average number of radicals per particle $\bar{n}$, it becomes obvious that the larger particles will have higher values for $\bar{n}$ and thus will grow more rapidly. For polydisperse latexes this means that the polydispersity increases upon polymerization, an effect that is enhanced by the coagulation of particles. Figure 4.7 shows cumulative particle
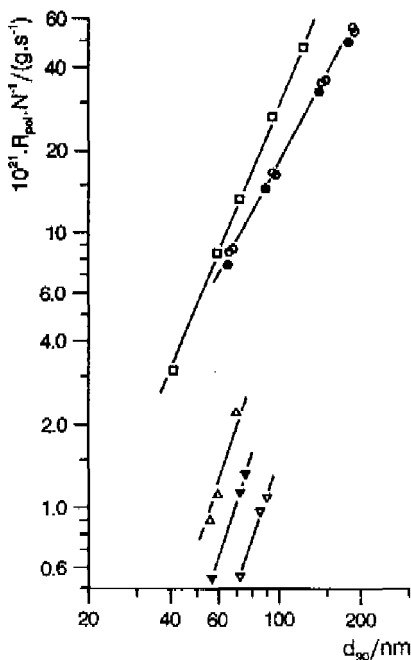
Figure 4.6. Average rate per particle (R_{pol}/N) vs. particle diameter at 90 % conversion (d_{90}) for different butadiene emulsion polymerizations: experimental results at 62°C, using TEM (●) and DLS (○) for particle size analysis. Data of ref.[19] at θ_{pol} = 70°C using d_v obtained with TEM (□); data of ref.[18] based on surface-average diameters d_s (determined by soap titration) at 40°C (▽), 50°C (▼) and 60°C (△).

size distributions for a single experiment at various degrees of conversion as a function of particle size and volume. A positive skewness develops at low conversion which becomes more pronounced as polymerization proceeds.

Surprisingly, the mechanistic complexity is not reflected in the conversion-time curves, which are simply S-shaped with a linear interval II. A constancy of rate is usually taken to imply that the particle number is also constant, which is definitely not true for the present system (Figure 4.8). In this particular case a decrease in particle number through coagulation will practically be compensated by an increase in $\bar{n}$ of the resulting particles, since $R_{pol}/N \propto d^{1.8}$ as calculated from the data in Figure 4.6. Other factors cannot be completely ruled out. For example, the cross-linking behaviour of the polymer and its effect on monomer

concentration and rate coefficients may play a role. If present, their net effect on polymerization rate is very small and remained undetected, because R_{pol} was found constant within experimental error.

An analogous behaviour is known to occur if more water-soluble monomers are used:[12,13,14] a decreasing particle number while the rate of polymerization is constant. Radical desorption is relatively facile with such monomers and $\bar{n}$ may be much less than 0.5. A Smith-Ewart case 1 situation arises and R_{pol} will only depend weakly on particle number. This type of behaviour may also be found with styrene at certain emulsifier concentrations.[21] Dunn and Chong[12] showed that the variation of particle number in the emulsion polymerization of vinyl acetate is in accord with expectations on the basis of DLVO theory.
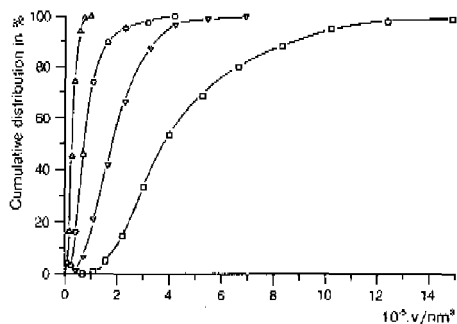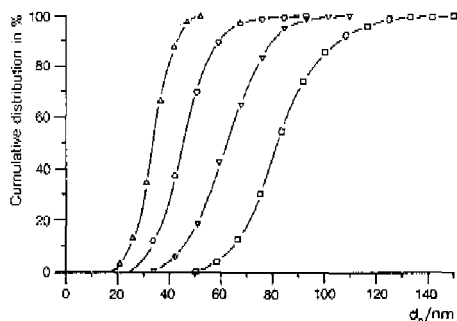
Figure 4.7. Cumulative particle size distribution vs. particle diameter d_n (top) and particle volume v (bottom) for a $S_2O_8^{2-}$ initiated polymerization ([I] = 13 mmol.L^{-1}, C_E = 32.4 g.L^{-1}, recipe 1) at various degrees of conversion: 15 % ($\triangle$), 26 % (O), 41 % (∇) and 98 % ($\square$).

Figure 4.8. Conversion (○) and particle number vs. time curves for a polymerization with 16.2 g.L^{-1} dresinate 214. Particle number N based on d_v (▲), and on d_w (△).
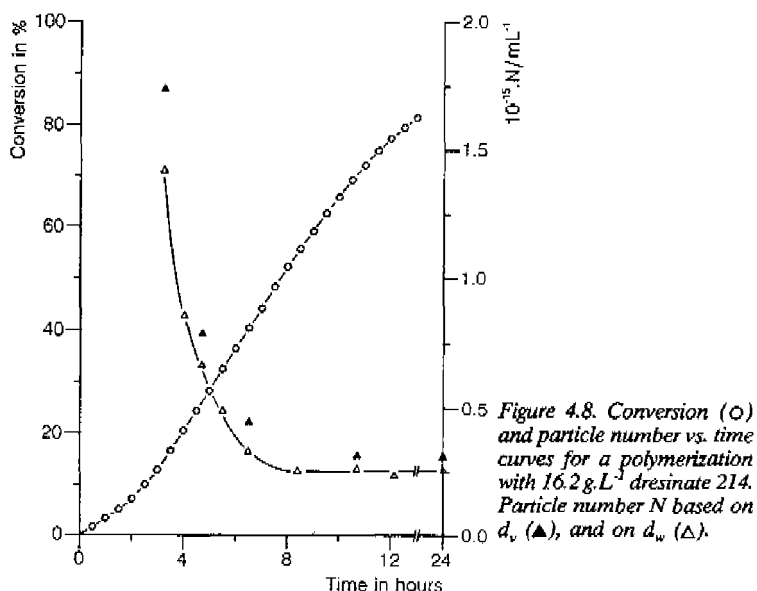
It is common practice in diene-polymerizations to use chain transfer agents such as thiols and bis(alkyloxythiocarbonyl)disulfanes to control the extent of cross-linking of the polymer. Chain transfer agents were also found[22,23] to promote desorption of radicals from the latex particles and as a consequence to lower $\bar{n}$. However, Nomura[22] showed that n-dodecanethiol did not affect either the rate of polymerization or the particle number in the emulsion polymerization of styrene. He concluded that the $CH_3(CH_2)_{11}S^{\cdot}$ radicals cannot desorb because of their extremely low water solubility. It is not yet clear if desorption of tert-dodecanethiol radicals is significant in the present system.

Furthermore, small amounts of thiols of low water solubility seemed to be essential to bring about reaction at acceptable rates in the persulfate-initiated polymerizations of butadiene(75)-styrene(25) or butadiene.[24] These important effects of thiols in the emulsion polymerization of butadiene were investigated, and will be discussed in chapter 8.

Accurate calculation of the absolute value of $\bar{n}$ is not yet possible due to the large uncertainty in the value for the propagation rate coefficient k_p cited in literature,[9] and the unknown distribution of $\bar{n}$ among particles of different sizes. Based on the present experimental data no conclusive evidence can be provided as to which mechanisms determine the reaction kinetics. Either radical exit or first-order termination (e.g. by radical trapping) may suppress $\bar{n}$. Moreover, slow termination of radicals in the particles, which would raise $\bar{n}$ significantly, cannot be ruled out. The observed similarity in behaviour between the emulsion polymerizations of certain polar monomers and butadiene, suggests a Smith-Ewart case 1 situation for the latter monomer as well. Nonetheless, it is surprising that the observed anomalies are so pronounced for such a sparingly water-soluble monomer in the size range studied (d_{50} = 50 - 150 nm), while emulsifier concentrations are well above the critical micelle concentration.

This initial work raised many new questions: the low initiator efficiency, the ease of limited coagulation of PB-latexes, the size-dependence of $\bar{n}$ and many others. Nevertheless, it became obvious that regardless of apparent simplicity of the conversion-time history and partial agreement of experimental data with Smith-Ewart theory, the mechanism and kinetics of this polymerization are more complicated than is usually assumed.

4.4 Conclusions

The concentration of three dissociative initiators differing in structure and water solubility described in this chapter hardly affects the reaction kinetics of the emulsion polymerization of butadiene. The number of primary radicals necessary for nucleation exceeds the final particle number by at least two orders of magnitude, so that the kinetics will become almost independent of the rate of initiator decomposition. The nature and ionic charge of the primary radicals also have no influence on the polymerization, indicating that the hydrophobic moiety of the oligomeric radicals originating in the aqueous phase governs the initiation kinetics of polymerization in the loci.

The particle number is partially determined by limited coagulation of colloidally unstable particles. Experimental results may not be compared with theories (e.g. Smith-Ewart and Gardon) that neglect this phenomenon. The particle number after cessation of coagulation (conversion > 40 %) varies with the emulsifier concentration C_e to the 1.6th power, and the polymerization rate in interval II with C_e to the 0.61st power. This implies that the average number of radicals per particle $\bar{n}$ is a function of particle size, since the monomer concentration within the latex particles is approximately constant in interval II.

Larger particles have higher values for $\bar{n}$ and will grow more rapidly. Data on particle size distributions are in agreement with this observation: a positive skewness develops at low conversion, and becomes more pronounced as the polymerization proceeds.

The kinetic similarity of the emulsion polymerization of butadiene with those of certain more water-soluble monomers (e.g. vinyl acetate, various acrylates) reported in literature is striking: the rate of polymerization is constant whereas the particle number is decreasing. It has been shown that for the latter emulsion polymerizations radical desorption is dominating the reaction kinetics, leading to $\bar{n} \ll 0.5$, suggesting a similar situation for butadiene.

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Chapter 5   Polymerizations with Sodium Dodecylsulfate

SUMMARY: The emulsion polymerization of butadiene was investigated with sodium dodecylsulfate as emulsifier, and results compared with those obtained with the industrial grade emulsifier dresinate 214. Limited coagulation was observed in both cases, caused by the high ionic strength of the aqueous phase. Sodium dodecylsulfate was found a better stabilizer than dresinate 214. The average rate per particle in interval II depends strongly on particle size, but not on recipe parameters used to vary the final particle diameter. The dependence of particle number N on initiator ([I]) and emulsifier concentration ([E]) is usually expressed as the exponent in the empirical relationship $N \propto [I]^x.[E]^y$. Promoting coagulation by increasing the ionic strength, decreases x toward zero, while y increases sharply. Increasing [I] at a constant [E] and ionic strength induces limited coagulation, presumably because the rate of emulsifier adsorption becomes insufficient.

5.1 Introduction

In the previous chapter the kinetics of the emulsion polymerization of butadiene with the commercial emulsifier dresinate 214 was discussed, using a thiol as chain transfer agent as customary in diene-polymerizations. Several remarkable results were obtained with this 'industrial' recipe: the initiator efficiency with regard to particle formation is low and independent of the type of initiator, limited coagulation is involved in the particle formation process, and no Smith-Ewart case 2 regime with $\bar{n} = 0.5$ was observed. At that point it was unclear if these phenomena resulted from specific reaction conditions, such as

the choice of emulsifier and the presence of a chain transfer agent. In order to answer these questions, additional experiments were performed with the well-defined emulsifier sodium dodecylsulfate, under comparable conditions.

5.2 Effect of the emulsifier concentration

The concentration of sodium dodecylsulfate (SDS) was varied between 64.8 and 4.0 $g.L^{-1}$ (224 and 14 $mmol.L^{-1}$), all concentrations well above the CMC, which was determined with the *Wilhelmy* plate method to amount to 0.17 $g.L^{-1}$, i.e. 0.6 $mmol.L^{-1}$ (θ = 25°C and $[Na_2CO_3]$ = 0.15 $mol.L^{-1}$). The overall $[Na^+]$ is 0.3 $mol.L^{-1}$, and kept constant by adjustment of the concentration of Na_2CO_3. The small variation in pH that may result is unimportant, since the performance of SDS is virtually pH-independent at pH > 7, this in contrast to dresinate 214. The $[Na^+]$ is thus an additional adjustable parameter in recipe 2 (section 5.3).
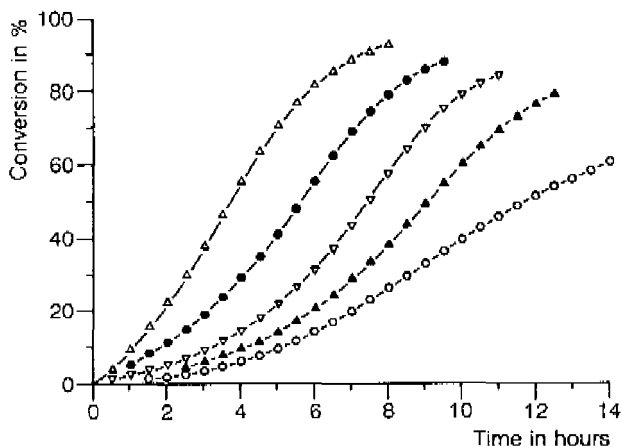
Figure 5.1. Conversion vs. time curves for polymerizations (recipe 2) with different sodium dodecylsulfate concentrations C_E = 64.8 $g.L^{-1}$ ($\triangle$); C_E = 32.4 $g.L^{-1}$ ($\bullet$); C_E = 16.2 $g.L^{-1}$ ($\triangledown$); C_E = 8.1 $g.L^{-1}$ ($\blacktriangle$); C_E = 4.0 $g.L^{-1}$ (o).
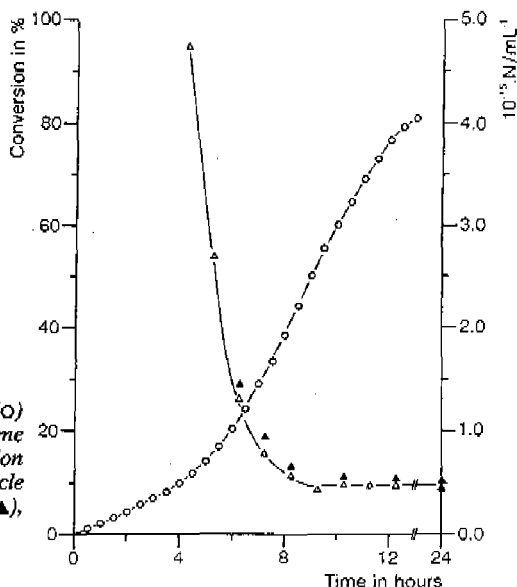
Figure 5.2. Conversion (O) and particle number vs. time curves for a polymerization with 8.1 g.L^{-1} SDS. Particle number N based on d_v (▲), and on d_w (△).

All conversion-time curves (Figure 5.1) are convex toward the time axis up to about 40 % conversion, this in contrast to similar polymerizations with dresinate 214 (Figure 4.3), where linearity already was attained at about 25 % conversion. Interval III begins at 60 % conversion (see chapter 7), so that interval II appears rather short in the present system.

Figure 5.2 gives the particle number and conversion vs. time curves for the polymerization with 8.1 g.L^{-1} SDS. Evidently, as in polymerizations with dresinate 214 (Figure 4.8), limited coagulation is occurring with SDS as emulsifier. Also in concordance with previous observations, the decrease of N by coagulation is not showing up in the conversion-time curve, i.e. R_{pol} is not proportional to N, so that $\bar{n}$ cannot be constant at 0.5 (Smith-Ewart case 2). Indeed, N decreases while R_{pol} still increases. R_{pol} is usually expressed as:

$$R_{pol} \;=\; k_p \, C_M \, (\bar{n}/N_{Av}) \, N \qquad (2.2)$$

where k_p is the propagation rate coefficient, $\bar{n}$ the average number of radicals per particle, and C_M the monomer concentration within the latex particles.

The average rate per particle in interval II (R_{pol}/N) can be used as an equivalent for $\bar{n}$, since the other parameters (i.e. k_p and C_M) are constant in interval II to within a good approximation (see chapter 7). Obviously, $\bar{n}$ must depend on particle size to account for the observed behaviour (Figure 5.3). This effect becomes strongly pronounced by the coagulation process, causing an enhanced variation in particle diameter within one single experiment.
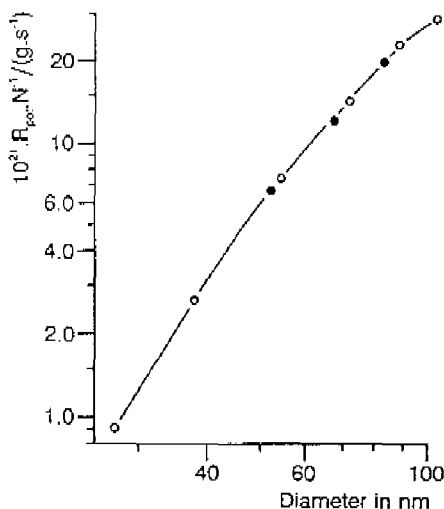
Figure 5.3. Average rate per particle R_{pol}/N vs. particle diameter d_v (●) and d_w (○), for the polymerization with 8.1 g.L^{-1} SDS from Figure 5.2.

The dependence of particle number (or rate) on emulsifier ([E]) and initiator concentration ([I]) is usually expressed as the exponent in the empirical relationship $N \propto [I]^x.[E]^y$. The theoretical values $x_{th} = 0.40$ and $y_{th} = 0.60$ are obtained with any nucleation mechanism (homogeneous[1] or micellar[2]) that ignores coagulation. Experimentally obtained values for y (and y') in the emulsion polymerization of butadiene are given in Table 5.1.

Table 5.1.   Emulsifier exponents with regard to N and R_{pol}

Emulsifier	y in $N \propto [E]^y$	y' in $R_{pol} \propto [E]^{y'}$	Ref.
SDS	2.1	0.24	ch. 5
Dres. 214	1.6	0.61	ch. 4
Dresinate	1.0	0.62	3)

Given the non-ideal kinetic behaviour of the present system (i.e. $R_{pol} \neq N$), the different exponents for R_{pol} and N are not surprising, while the significantly higher values with regard to N as compared with theory (y_{th} = 0.60), clearly result from the coagulation process. The purity and structure of the emulsifier can only be partially responsible for this; other parameters are also involved.

5.3 Effect of the sodium ion concentration

The general principles of electrostatic stabilization of colloidal particles are well established in DLVO theory.[e.g. 4)] In short, electrostatic repulsion between particles results from the presence of charged surface groups (from initiator fragments or functional (co)monomers), or adsorbed ionic surface active agents. As a consequence, the surface acquires a surface potential ψ_o, giving rise to a Boltzmann distribution of counter ions and co-ions in a region close to the surface. According to a simplified model for a spherical particle of diameter d, the potential at a distance r from the centre of the particle ψ_r is (ψ_o < 25 mV):

$$\psi_r = \psi_o \frac{d}{2r} \exp[\kappa(0.5d - r)] \tag{5.1}$$

The parameter κ is related to the ionic strength σ by:

$$\kappa^2 = \frac{2 N_{Av} e^2 \sigma}{\varepsilon_o \varepsilon_r kT} \tag{5.2}$$

where N_A is Avogadro's number, e the fundamental electronic charge, ε_r the relative permittivity of the aqueous phase and ε_0 that of free space, **k** the Boltzmann constant and T the absolute temperature. It is κ that mainly determines the fall off of the electrostatic potential with distance from the surface, and consequently the range of electrostatic interaction between particles. From this simplified description, it already becomes obvious that the ionic strength is an important parameter in achieving colloidal stability.

The significance of ionic strength on colloidal stability of polystyrene particles prepared by emulsifier-free emulsion polymerization has been demonstrated by Goodwin et al..[5,6] Limited coagulation is well established in the emulsion polymerization of more water-soluble monomers,[7,8,9] caused by slow and/or weak adsorption of emulsifier on the polar polymer-water interface as suggested by Yeliseyeva.[9] Dunn[7] showed for vinyl acetate that the coagulation observed experimentally can be described satisfactorily with DLVO theory. Furthermore, the role of coagulation in the particle nucleation mechanism has been treated quantitatively by several workers.[e.g. 10,11,12]

However, butadiene is only sparingly water-soluble (37 mmol.L^{-1} at 50°C),[13] the emulsifier concentrations are far above the CMC, while coagulation extends well beyond the nucleation stage and involves particles of 'normal' size.

As pointed out earlier, the [Na^+] in recipe 2 is an extra adjustable parameter, which can be varied by changing the amount of sodium carbonate, present in reasonable excess. In this way we can separate the effects of ionic strength on particle nucleation and growth phenomena, from those associated with the emulsifier and initiator, compounds that beside their prime function in emulsion polymerization systems, also act as inert electrolytes that contribute to the ionic strength σ. However, the anion concentration (and thus σ) changes continuously during polymerization, owing to the decomposition of the initiator and adsorption of surface active ions on newly formed surfaces. Therefore we have chosen the overall cation concentration as the equivalent of σ (although not exactly identical, since 1 : 2 electrolytes were used).

The overall $[Na^+]$ was varied at two emulsifier concentrations, viz. $C_E = 32.4$ g.L^{-1} and $C_E = 8.1$ g.L^{-1}, while $[I]$ was kept constant at 13.0 mmol.L^{-1}. The final particle diameter at an arbitrarily chosen conversion, viz. 90 %, increases markedly with $[Na^+]$ (Figure 5.4). The minimum $[Na^+]$ indicated in Figure 5.4 by the dotted vertical lines would represent polymerizations in the absence of sodium carbonate. Higher values for $[Na^+]$ than the ones shown render latexes with a poor shelf stability. The range of $[Na^+]$ in these experiments corresponds to a variation in ionic strength roughly between 0.1 mol.L^{-1} and 1 mol.L^{-1}, about 1 - 2 orders of magnitude larger than in the study of Goodwin et al.[5,6] on the emulsifier-free emulsion polymerization of styrene.

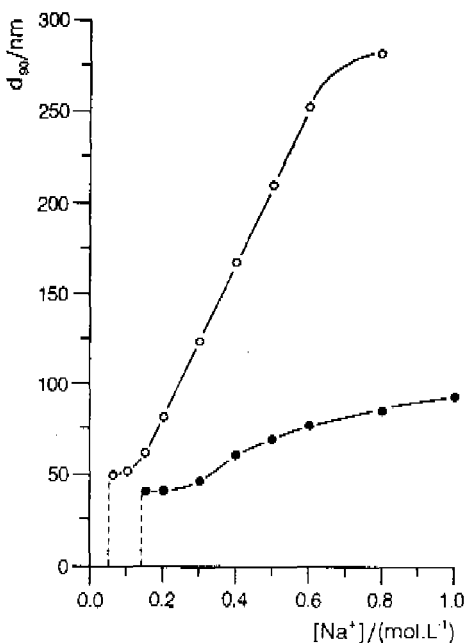*Figure 5.4. Particle diameter d_w at 90 % conversion (d_{90}) vs. the overall $[Na^+]$, at two SDS concentrations $C_E = 32.4$ g.L^{-1} (●); $C_E = 8.1$ g.L^{-1} (○).*

At $C_E = 8.1$ g.L^{-1} the observed 5-fold increase in diameter corresponds to a decrease in N by some 2 orders of magnitude. Realizing that in the standard

recipe 2 the $[Na^+] = 0.3$ mol.L^{-1} (in analogy with recipe 1), it is obvious that limited coagulation must play a dominant role in the particle formation process. The reason for the presence of a moderate excess of potassium carbonate in recipe 1, and for comparison maintained in recipe 2, is threefold:

- Performance and solubility of dresinate 214 is strongly pH-dependent;[14] pH must be kept constant between 10 and 11 throughout the polymerization.
- In industrial practice the polymer content is usually high, between 30 and 60 % by weight. Inert electrolytes are often added to reduce latex viscosity and thus maintain a reasonable fluidity.[15]
- In certain applications large sized spherical particles are desired, e.g. as impact modifiers in materials exhibiting crazing and/or yielding (ABS, HIPS, toughened PVC). Since the electrolyte induced coagulation is confined to microscale and does not result in reactor fouling, this phenomenon can be used advantageously in the one-step preparation of large PB-particles.[16,17]

The data from Figure 5.4 can be presented alternatively by plotting the particle number (calculated from d_{90}) on a log-log scale versus C_E (Figure 5.5). The slopes of these apparently linear (owing to the limited range of C_E) curves at a fixed $[Na^+]$ thus represent the emulsifier exponent y toward N (Table 5.2).

Table 5.2. Variation of the emulsifier exponent y toward N with $[Na^+]$.

$[Na^+]$/mol.L^{-1}	0.1	0.15	0.2	0.3	0.4	0.5	0.6
exponent y	0.5	0.8	1.4	2.1	2.2	2.4	2.6

The minimum value y = 0.5 is quite close to y_{th} = 0.60, obtained when coagulation is fully neglected. Promoting coagulation by raising $[Na^+]$ clearly increases the dependence of N on [E]. Values for the emulsifier exponent as high as 3 have been reported in literature for other systems.[18] The coagulative nucleation model developed by the Sydney-group[11] predicts a range of exponential values ($0.4 \leq y_{th} \leq 1.2$), while raising the coagulation rate coefficient in the nucleation model of Song and Poehlein[12] also leads to higher values for y_{th}.
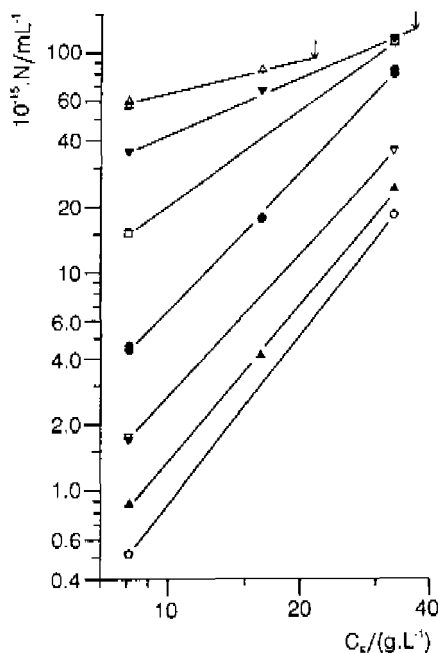
Figure 5.5. Particle number N (calculated using d_w) vs. SDS concentration C_E as a function of the overall $[Na^+] = 0.1$ mol. L^{-1} ($\triangle$); 0.15 mol.L^{-1} ($\blacktriangledown$); 0.2 mol.L^{-1} ($\square$); 0.3 mol.L^{-1} ($\bullet$); 0.4 mol.L^{-1} ($\triangledown$); 0.5 mol.L^{-1} ($\blacktriangle$); 0.6 mol.L^{-1} ($\circ$). Arrows indicate the maximum C_E at that particular $[Na^+]$. Data points at $C_E = 32.4$ g.L^{-1}, $C_E = 16.2$ g.L^{-1}, and $C_E = 8.1$ g.L^{-1}.

Table 5.3. Influence of the overall $[Na^+]$ on the polymerization with $C_E = 8.1$ g.L^{-1} SDS and $[I] = 13.0$ mmol.L^{-1} (recipe 2).

$[Na^+]$ mol.L^{-1}	$10^5.R_{pol}$ g.mL^{-1}.s^{-1}	10^{-14}.N/mL^{-1} [a]		d_v at 90 % nm	P
		DLS	TEM		
0.1	1.55	60	68	52	1.06
0.3	1.34	4.7	5.2	121	1.06
0.5	0.53	0.96	0.92	215	1.06

[a] The particle numbers N determined with DLS are based on d_w, and those with TEM on d_v.

The effect of limited coagulation on conversion-time history (Figure 5.6) is rather complicated: increasing $[Na^+]$ gives higher initial rates in interval I, but the steady state rate R_{pol} decreases significantly (Table 5.3). Similar results were found with dresinate 214. This will be discussed somewhat further in chapter 6.
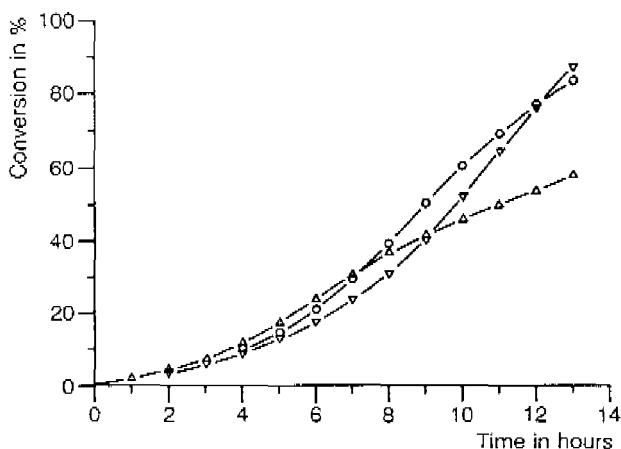
Figure 5.6. Conversion-time curves for polymerizations (recipe 2) with $C_{tr} = 8.1$ g.L^{-1} SDS, as a function of the overall $[Na^+] = 0.1$ mol.L^{-1} (∇); $[Na^+] = 0.3$ mol.L^{-1} (O); $[Na^+] = 0.5$ mol.L^{-1} ($\triangle$).

The average rate per particle for these and previous experiments with dresinate 214 (chapter 4), can be calculated from the steady state R_{pol} and the final particle number N after cessation of coagulation. These values for R_{pol}/N are in fact upper limits for the individual experiments involved, since at lower conversions R_{pol}/N is smaller because of the smaller particle size (Figure 5.3). Making a log-log plot of R_{pol}/N versus d_{90} (Figure 5.7), clearly shows that the particle growth kinetics in interval II is internally consistent, and depends solely on particle size. A similar plot with varying dresinate 214 concentrations (Figure 4.6) gave an apparent linear relationship (owing to the limited data range); this behaviour is seen to be encompassed by the generalized curve in Figure 5.7.

The graphs in Figure 4.6, Figure 5.3 and 5.7 are analogous to the well-known Ugelstad-plots of log $\bar{n}$ vs. log α'.[19] Obviously R_{pol}/N is equivalent to $\bar{n}$. Combining $\alpha' = \rho_i v/Nk_t$ and $N = V/v$ (for definitions see chapter 2), it is easily seen that $\alpha' \propto v^2 \propto d^6$. At constant [I] (implying a constant ρ_i), log α' can thus be replaced by log d_{90} or log d. A more rigorous treatment of particle growth kinetics in intervals II and III will be given in chapter 7.
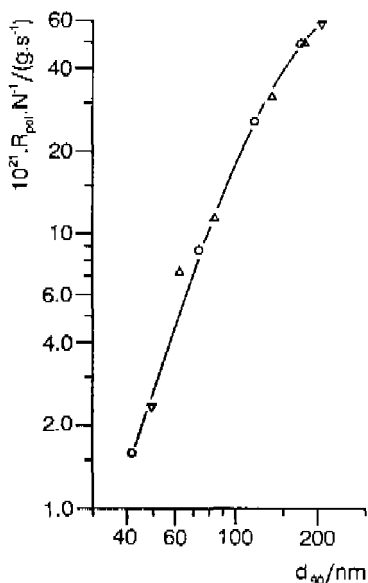
Figure 5.7. Average rate per particle R_{pol}/N vs. mean-volume diameter d_v at 90 % conversion (d_{90}). Final particle diameter was varied by changing the concentration of dresinate 214 ($\triangle$), SDS ($\circ$) or the overall $[Na^+]$ ($\triangledown$).

5.4 Effect of the initiator concentration

The sodium persulfate (SPS) concentration was varied 100-fold between 26.0 and 0.26 mmol.L^{-1}, at two emulsifier concentrations, viz. $C_E = 32.4$ g.L^{-1} and $C_E = 16.2$ g.L^{-1}. The $[Na^+] = 0.3$ mol.L^{-1} and kept constant, so coagulation phenomena may be considered a constant factor. The experimentally determined initiator exponents are given in Table 5.4. The small effect of $[I]$ on R_{pol} is rather typical of a Smith-Ewart case 1 system with $\bar{n} \ll 0.5$ (see chapter 7).

As limited coagulation is promoted (by lowering C_E or raising [cation]), the effect of $[I]$ on N diminishes, since the particle number becomes predominantly determined by coagulation. This effect appears to be relatively small in the first series of experiments from Table 5.4, since the exponent for N ($x = 0.46$), is quite close to the theoretical one ($x_{th} = 0.40$), when coagulation is ignored.

Table 5.4. Initiator exponents with regard to N and R_{pol} at different emulsifier concentrations C_E and overall cation concentrations [cation].

Recipe	C_E g.L^{-1}	[cation] mol.L^{-1}	x in N $\propto$ [I]^x	x' in $R_{pol} \propto$ [I]$^{x'}$
2	32.4	0.3	0.46	0.04
2	16.2	0.3	0.16	0.09
1	32.4	0.4	0.02	0.08[a]

[a] Taken from chapter 4.

The insensitivity of R_{pol} to the 100-fold variation of [I] is remarkable; its effect on conversion-time history is even more striking (Figure 5.8, with C_E = 32.4 g.L^{-1} SDS). Increasing [I], especially at [I] > 1.0 mmol.L^{-1}, appears to be slowing down the polymerization in interval I, eventhough the steady state polymerization rate in interval II steadily keeps increasing with [I] (Table 5.5). Results at C_E = 16.2 g.L^{-1} SDS are similar.

Table 5.5. The periods of time required to reach 25 % (t_{25}) and 50 % conversion (t_{50}), and R_{pol} as a function of [I] at C_E = 32.4 g.L^{-1} SDS.

[I] mmol.L^{-1}	t_{25} hours	t_{50} hours	$10^5.R_{pol}$ g.mL^{-1}.s^{-1}
0.26	2.55	4.40	1.61
0.52	2.50	4.35	1.64
1.30	2.60	4.40	1.75
2.60	2.90	4.75	1.69
6.50	3.30	5.20	1.79
13.0	3.65	5.60	1.82
26.0	3.90	5.85	1.92

Polymerizations with dresinate 214 (Figure 4.2) behave 'normally' in that the duration of interval I increases with decreasing [I]. The discrepancy may be caused by possible impurities in the emulsifier. Eventhough dresinate 214 has been disproportionated to eliminate abietic acid-type of derivatives, small amounts are still present and can affect the kinetics, especially at lower [I].
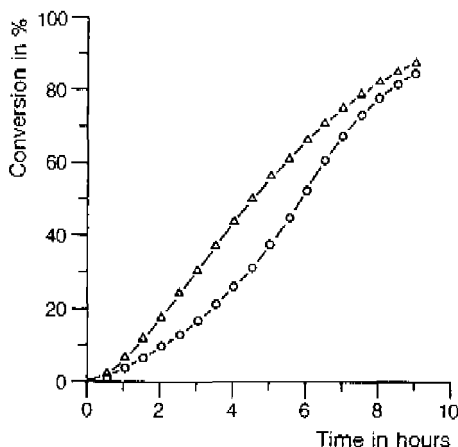
Figure 5.8. Conversion-time curves for polymerizations (recipe 2) with C_E = 32.4 g.L^{-1} and different [I] = 26.0 mmol.L^{-1} (○); [I] = 0.26 mmol.L^{-1} (△). Initiator I is sodium persulfate.

The absence of retarders in SDS makes the observed behaviour even more surprising. On the one hand, increasing [I] sufficiently, may possibly lead to substantial termination of oligomeric radicals in the aqueous phase, thereby reducing the radical entry rate into the particles. However, the initiator concentrations are not excessively high, so this effect appears unlikely. On the other hand, the behaviour in interval I may simply arise from differences in initial particle size. This was observed previously, when promoting coagulation by raising [Na$^+$] at a fixed C_E gave higher initial rates (Figure 5.6).

This is further illustrated in Figure 5.9, showing particle number and conversion-time curves for two polymerizations with a different [I] and [E], but with the same steady state R_{pol} and final N. The initial behaviour in interval I was found markedly different, apparently as a result of a difference in colloidal stability. The data in Table 5.5 suggest an analogous behaviour; increasing [I] above 1.0 mmol.L^{-1} clearly prolongs interval I. At [I] = 13 mmol.L^{-1} the particle number was indeed found to decrease initially, whereas the polymerization depicted in Figure 5.9 at [I] = 0.52 mmol.L^{-1} shows no limited coagulation. So colloidal stability is not only determined by the emulsifier concentration and ionic strength, but also by the radical production rate (or alternatively [I]).
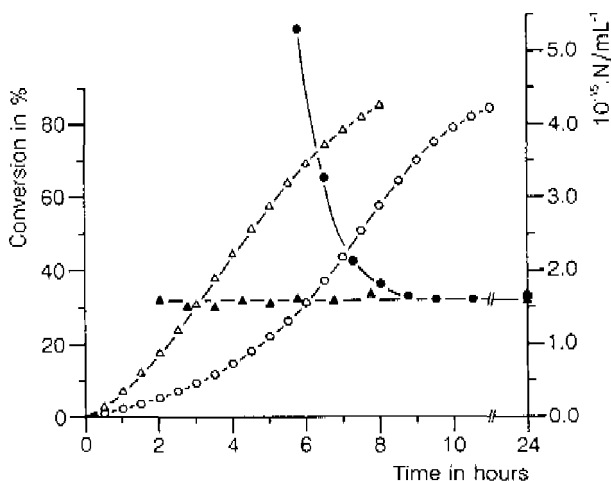
Figure 5.9. Conversion (open symbols) and particle number N (full symbols) vs. time curves for two polymerizations (recipe 2) with the same R_{pol} and final N: $C_E = 32.4$ g.L^{-1} and $[I] = 0.52$ mmol.L^{-1} (triangles); $C_E = 16.2$ g.L^{-1} and $[I] = 13.0$ mmol.L^{-1} (circles).

If the total polymer-water interface increases faster than it adsorbs emulsifier molecules, the surface charge density decreases and particles may become colloidally unstable. A rapid reduction of surface charge density by incorporating a high molecular chain into a small nucleus (i.e. rapid polymerization) was theoretically deduced by Goodall et al..[20]

At a sufficiently high initiator concentration colloidal instability is apparently induced, presumably because the emulsifier adsorption cannot keep up with the rapid increase in particle surface as a result of the high particle nucleation rate. Limited coagulation is observed experimentally, and consequently the reaction slows down in interval I.

This behaviour is also reflected in the apparent dependence of N on C_E. For polymerizations with $[I] = 13.0$ mmol.L^{-1} and $[Na^+] = 0.3$ mol.L^{-1} a value of 2.1 was found for the emulsifier exponent y (Table 5.1). However, decreasing $[I]$ at constant $[Na^+]$ in the same range of $[E]$ will give lower values for this exponent,

since the initiator exponent x at C_E = 32.4 g.L^{-1} and C_E = 16.2 g.L^{-1} is different, x = 0.46 and x = 0.16, respectively (Table 5.4). Values for the exponent y between 2.2 (for [I] = 26.0 mmol.L^{-1}) and 0.8 (for [I] = 0.26 mmol.L^{-1}) were calculated. Although these values for y are based on only two data points per [I], the trend is considered significant.

5.5 Comparison between dresinate 214 and sodium dodecylsulfate

The two emulsifiers used in this investigation differ in almost every relevant aspect: chemical structure, composition and purity, nature of the ionic group etc., Yet, this does not affect the reaction kinetics in interval II (and III), as is evident from Figure 5.7, which unambiguously shows that R_{pol}/N is independent of the choice of emulsifier. The prime function of the emulsifier in the present system is thus the stabilization of latex particles formed in interval I.

The emulsifier exponents for SDS and dresinate 214 were found to be 2.1 and 1.6, respectively (Table 5.1). However, in the experiments with dresinate 214 (section 4.3) the contribution of the emulsifier to the cation concentration had not been taken into account; the overall [K$^+$] thus varied with [E] between 0.3 and 0.4 mol.L^{-1}. Additional experiments with a varying concentration of dresinate 214 at a fixed overall [K$^+$] = 0.3 mol.L^{-1} were performed and compared with similar experiments with SDS at [Na$^+$] = 0.3 mol.L^{-1} (Figure 5.10).

The emulsifier exponents as deduced from the linear portions[a] of the log N vs. log C_E curves are identical within experimental error, viz. y = 2.0 for dresinate 214 and y = 2.1 for SDS. This indicates that the magnitude of limited coagulation must be comparable, since a higher value for the emulsifier exponent was earlier shown to correspond to a larger extent of coagulation.

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[a] It is generally recognized that over a wide range of C_E the log N vs. log C_E curves are S-shaped for sparingly water-soluble monomers; this is beginning to manifest itself in Figure 5.10.
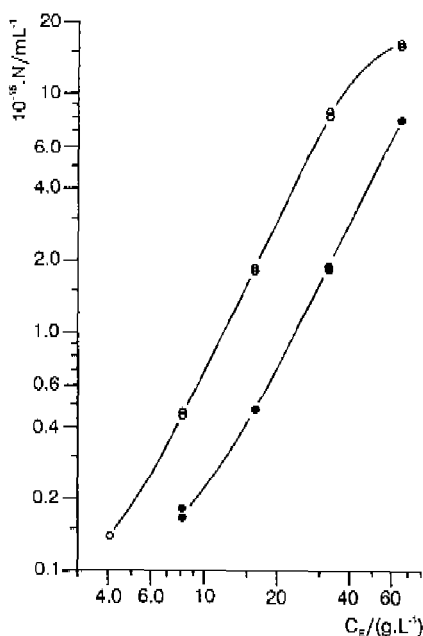
Figure 5.10. Particle number N versus emulsifier concentration C_E for polymerizations with SDS (○) and dresinate 214 (●), at a persulfate concentration [I] = 13 mmol.L⁻¹ and an overall cation concentration of 0.3 mol.L⁻¹.

Table 5.6. Kinetic data for polymerizations with 16.2 g.L⁻¹ SDS (recipe 2) and 32.4 g.L⁻¹ dresinate 214 (recipe 1), under otherwise comparable conditions.[a]

Emulsifier	t_{20}[b] hours	t_{40} hours	t_{60} hours	$10^5.R_{pol}$ g.mL⁻¹.s⁻¹	d_v (nm) at 90 %	$10^{-15}.N$ mL⁻¹
dresinate 214	2.85	4.45	5.85	1.70	73	2.1
SDS	4.75	6.75	8.20	1.68	74	2.1

[a] Experimental conditions: [cation] = 0.3 mol.L⁻¹ and [I] = 13 mmol.L⁻¹.
[b] t_{xx} Represents the time required to reach xx % conversion.

For a further analysis of the stabilizing potential of both emulsifiers the polymerizations with 32.4 g.L⁻¹ dresinate 214 (ca. 95 mmol.L⁻¹) and 16.2 g.L⁻¹ SDS (56 mmol.L⁻¹) were chosen, as the final particle numbers were fortituously found identical (Table 5.6). Again interval II kinetics are independent of the type of emulsifier. The difference in the initial rates may be caused by

differences in rate of emulsifier adsorption, or in the number of micelles initially present. The conversion-time curve of the polymerization with 16.2 g.L^{-1} SDS was already shown in Figure 5.9.

The specific area per emulsifier molecule A_E was determined by the method of soap titration described by Maron et al.[21] In short, the latex is titrated with the corresponding emulsifier solution (including K$^+$/Na$^+$ carbonate; [CO$_3^{2-}$] = 0.15 mol.L^{-1}), until the CMC is attained. Surface tension measurements with the *Wilhelmy* plate method were used to determine the end point, which, in contrast to Maron's findings,[22] could be obtained accurately in this way. In fact, conductance measurements as suggested for rosin soap solutions[22] are useless, because of the high electrolyte concentration in the present system. Assuming that at the end point the particles are completely covered with a monolayer of emulsifier molecules, A_E was calculated as:

$$A_E = \frac{6 \; MW \; (d_s^2/d_v^3) \; P}{(E - CMC) \; \rho_p \; N_{Av}} \tag{5.3}$$

where P and E are the polymer and emulsifier content at the end point, respectively, both in grams per unit volume of water, d_s the mean-surface diameter, d_v the mean-volume diameter (both obtained with TEM), ρ_p the polymer density, and MW the molecular weight of the emulsifier. The main components of dresinate 214 have the formula $C_{19}H_{29}CO_2K$, giving MW = 340. The CMC for dresinate 214 was found to be 1.2 g.L^{-1} (with [K$_2$CO$_3$] = 0.15 mol.L^{-1}, see section 4.3), and for SDS 0.17 g.L^{-1} ([Na$_2$CO$_3$] = 0.15 mol.L^{-1}).

The value for A_E of dresinate 214 (Table 5.7) is in excellent agreement with the one of 43.7 10^{-20} m^2 determined by Maron et al.[22] for dresinate 214 and dresinate 731, the latter being the sodium salt analogue. The surface coverage of both latexes at 100 % conversion is readily calculated as [E]$A_E N_{Av}/\pi d_s^2 N$. Since the emulsifier concentration [E] is far above the CMC, a correction for the amount dissolved in the aqueous phase is marginal. This also makes a knowledge of the full adsorption isotherms superfluous, so that the less cumbersome soap titration method was considered sufficient for these systems.

Table 5.7.   Characteristics of SDS, dresinate 214, and latexes
prepared with 16.2 g.L⁻¹ SDS and 32.4 g.L⁻¹ dresinate 214 (see text).

Emulsifier	$10^{20}.A_E$ m^2	Surface coverage final latex in %	Zeta-potential[a] mV
dresinate 214	45	68	- 80
SDS	42	38	- 86

[a]   Determined at 25°C with a Malvern Zetasizer 3, with $\kappa d < 0.01$
(see section 5.3); dilution with Na_2CO_3 solution (0.15 M).

The large difference in surface coverage at the same final N, clearly shows
that SDS is more effective in stabilizing PB-particles than dresinate 214. This is
further substantiated by the close identity of the zeta-potentials (ζ) of both
latexes. The ζ potential represents the electrostatic potential at the 'slipping
plane' of the particle when it is in motion, and is readily obtained from electro-
kinetic experiments (in this case with laser Doppler spectroscopy of the particles
in an applied electric field). It is comparable in magnitude to the potential in
the socalled Stern plane (using a model for the double layer more sophisticated
than the one described in section 5.3), and is therefore a good indication of the
electrostability of the particles. Apparently, the surface charge density per unit
amount of emulsifier adsorbed on (equally sized) particles is significantly larger
for SDS. Although experimentally unambiguous, this effect is not readily
explained. Dresinate 214 contains ca. 10 % of non-surface active material. This
not only decreases the effective amount of surface active material, but it may
also interfere directly with the adsorption characteristics. The hydrophobic tail
of the main components of dresinate 214 consists of a rigid tricyclic ring system,
which definitely will affect the mode of adsorption, as compared with SDS with
its flexible linear tail. Altogether, the dresinate 214 emulsifier system is too
complicated to describe its colloidal behaviour in the present context.

5.6 Conclusions

Electrolyte induced limited coagulation is observed in polymerizations with sodium dodecylsulfate and dresinate 214, two emulsifiers differing widely in chemical structure and composition. Sodium dodecylsulfate (SDS) was found a more effective stabilizer than dresinate 214, because the surface charge density per unit of amount emulsifier is appparently larger for SDS.

Coagulation is well established in polymerizations of polar monomers and emulsifier-free systems; in contrast butadiene is only sparingly water-soluble, while [E] » CMC. It is obvious that the experimental observations are not specific for butadiene, suggesting that limited coagulation can be induced in any emulsion polymerization system by electrolyte addition. Constancy of particle number after the disappearance of emulsifier micelles seems more coincidental than characteristic, strongly depending on the choice of reaction conditions.

The average rate per particle in interval II was found to depend solely on particle size, and not on recipe parameters utilised to manipulate the final particle diameter, such as the amount and type of emulsifier and the cation concentration. No constancy of $\bar{n}$ was found in the particle size range covered.

Promoting coagulation by raising $[Na^+]$ leads to a marked decrease in N, while the exponent y in the empirical relationship $N \propto [I]^x.[E]^y$ increases. Experimental values for y between 0.5 and 2.6 were found.

The dependence of N on initiator concentration [I] is also strongly determined by the colloidal properties of the system. Increasing coagulation reduces the exponent x toward zero, since the final particle number becomes independent of the nucleation rate of (colloidally unstable) primary particles.

Raising [I] at a constant ionic strength increases the exponent y over a narrow range of C_E. Apparently, adsorption of emulsifier on newly formed particles may become rate-determining, resulting in a limited colloidal stability.

Kinetic relationships between particle number, [I] and [E] appear to be extremely complicated in systems with a limited colloidal stability. Nevertheless, electrolyte addition is common practice in industry (e.g. for freezing point depression, or to decrease latex viscosity), so that a better understanding of its effects on reaction kinetics and mechanisms may prove extremely useful.

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Chapter 6   **Physico-Chemical Aspects**

SUMMARY: The stirring speed n affects the emulsion polymerization of butadiene, (1) by reducing the effective emulsifier concentration $[E]_{eff}$ available for particle nucleation and stabilization at high n, and (2) by limiting diffusion of monomer to the latex particles at low n. The large density difference between butadiene and water promotes the breaking up of droplets at high n, while the same condition constitutes a large driving force for (partial) phase separation at low n. Increasing the monomer/water ratio at constant [E] decreases $[E]_{eff}$, and thus the final particle number. At monomer volume fractions > 0.6 mixed emulsions are likely to be formed initially, reducing $[E]_{eff}$ even further. In the presence of mixed emulsions, polymerization in the monomer phase may no longer be neglected, giving rise to a complex kinetic behaviour.

6.1 Introduction

In previous chapters the role of various chemical and colloidal parameters in the emulsion polymerization of butadiene was discussed. However, systems using monomers at concentrations above their saturation water solubility are necessarily heterogeneous in appearance, due to the presence of a separate monomer phase in intervals I and II. The physico-chemical properties of the monomer emulsion may markedly affect the course of the polymerization.

The effects of stirring on emulsion polymerization is a somewhat neglected aspect in this line of research; only a few studies have been reported.[1,2,3)

The main conclusions reached in these studies include: (1) the effective

emulsifier concentration $[E]_{eff}$ in the aqueous phase may be reduced by adsorption of emulsifier molecules onto the monomer droplets, especially with $[E] \simeq CMC$; (2) at low stirring speeds transport of monomer from the droplets to the aqueous phase may become rate-determining due to (partial) phase separation; (3) at high stirring speeds particles may coagulate and coalesce.

The influence of stirring in the present study, together with the effect of the monomer/water ratio, will be discussed in the following. It will be shown that the atypical physical properties of butadiene, being a liquified gas under the prevailing experimental conditions, accentuates the significance of the physical state of the polymerization system.

6.2 Agitation

Polymerizations were performed in a 2.3 litre reactor fitted with four baffle plates located at 90° intervals and a twelve flat-bladed turbine impeller (see Figure 3.2). In two series of experiments, one with 32.4 g.L^{-1} dresinate 214 (recipe 1) and another with 16.2 g.L^{-1} SDS (recipe 2), the stirring speed n was varied and the final particle number N determined (Figure 6.1). In all cases the system was preemulsified by stirring a few minutes at 400 rpm, before adjusting n to the desired level. In both reaction systems, at sufficiently high n the particle number was found constant within experimental error, while a discontinuous increase in N became apparent when going to lower values for n. Although reproducibility of *ab initio* polymerizations is not always satisfactory, especially at low n, the change in N is considered significant. As pointed out earlier, the effective emulsifier concentration $[E]_{eff}$ available for particle nucleation and stabilization is influenced by adsorption of emulsifier onto the monomer droplets. At high n the droplets will be more finely dispersed and $[E] > [E]_{eff}$. Going to lower n, agitation ultimately becomes insufficient to counterbalance droplet coalescence, so that $[E]_{eff}$ and thus N, increase. Since the change in N is discontinuous, the phenomenon must be related to the flow conditions.
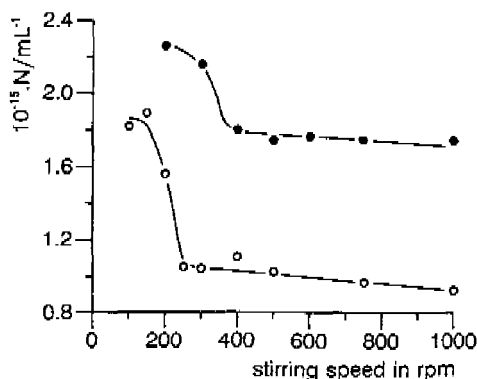
Figure 6.1. Final particle number N vs. stirring speed, for polymerizations with 32.4 g.L^{-1} dresinate 214 (○) and 16.2 g.L^{-1} SDS (●).

The impeller Reynolds number Re, defined as the ratio of inertial forces versus viscous forces, can be used as an indicator of the overall conditions of flow. In the case of a mechanically agitated system, Re = $D^2n\rho/\mu$, where D is the impeller diameter, and ρ and μ the density and dynamic viscosity of the liquid, respectively. At Re > 10^4 flow is usually highly turbulent, which in the case of a liquid-liquid system of two poorly miscible liquids will result in a homogeneously distributed dispersion. If the two liquids have different densities and viscosities, the volume ratio of the two phases also needs to be considered. The average density and viscosity can be calculated according to:[4,5)]

$$\rho = \varphi_C\rho_C + \varphi_D\rho_D \tag{6.1}$$

$$\mu = \frac{\mu_C}{\varphi_C}\left[1 + \frac{1.5\mu_D\varphi_D}{\mu_D + \mu_C}\right] \tag{6.2}$$

where φ is the volume fraction, while the subscripts C and D denote the continuous and the dispersed phase, respectively.

For the polymerizations depicted in Figure 6.1 with φ_D = 0.43, n ≥ 230 rpm was calculated to provide sufficient turbulency. Agreement with measured values for n above which N is constant is reasonably good, taking into account the unsatisfactory reproducibility of these *ab initio* polymerizations at low n.

Using the impeller Re to characterize the flow field in an emulsion polymerization system is of course of limited value, since the presence of the emulsifier and its ability to suppress coalescence of monomer droplets is ignored. However, as polymerization proceeds emulsifier molecules become adsorbed on the latex particles and less is available for stabilizing the monomer droplets. At the end of interval I the monomer emulsion thus tends to become unstable and mechanical agitation is essential to keep the monomer sufficiently dispersed. Inadequate stirring at that stage inevitably leads to a reduction of the total surface area of the monomer emulsion; even creaming-up and (partial) demixing might occur. This will inevitably affect the polymerization rate as diffusion of monomer from the droplets into the aqueous phase becomes rate-determining and the monomer concentration within the latex particles decreases below its saturation value. This is evident from Figure 6.2, showing conversion-time curves for polymerizations with 32.4 g.L^{-1} dresinate 214 at 100 rpm and 400 rpm. The curve at n = 100 rpm is based on a limited number of data points, as representative samples could not be taken due to the inhomogeneity of the system. Each data point at n = 100 rpm stems from a separate polymerization; the conversion was determined by raising n to 400 rpm, followed by sampling.
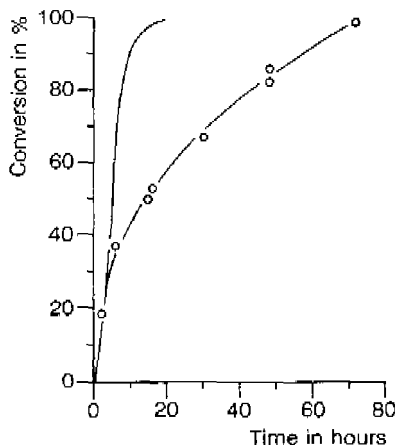

Figure 6.2. Conversion-time curves for polymerizations with 32.4 g.L^{-1} dresinate 214 (recipe 1), at a stirring speed n = 400 rpm (unbroken line; data points omitted), and n = 100 rpm (○) .

For polymerizations where n is raised from 100 to 400 rpm, the development of the particle number after the increase in n is shown in Figure 6.3. In all cases N decreases to a level corresponding to a polymerization with n = 400 rpm from the start of the reaction. Redispersion of the monomer by raising n creates new interface, whereupon emulsifier molecules adsorb. Thus emulsifier desorbs from the latex particles, introducing colloidal instability and a decrease in N.
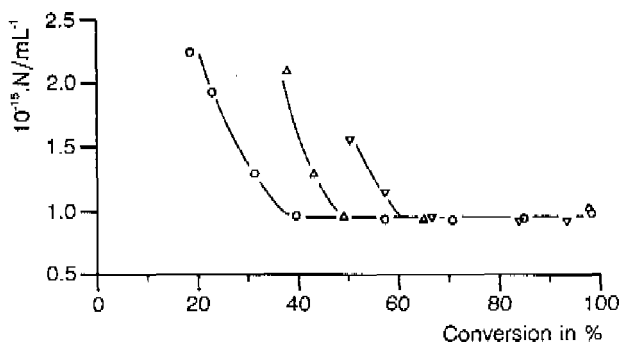
Figure 6.3. Particle number N vs. conversion for polymerizations (recipe I) where the stirring speed is raised from 100 to 400 rpm at different conversions: 18 % (○), 37 % (△) and 50 % (▽).

The pressure as sensed with a pressure transducer can serve as a qualitative indicator of the state of mixing. In a properly mixed system the pressure is equal to the saturation pressure of butadiene vapour, and will remain virtually constant until the beginning of interval III (Figure 6.4a). At n = 100 rpm a different behaviour is observed; pressure drops below the butadiene saturation pressure well before the end of interval II, remains more or less constant thereafter, and drops off sharply at the end of the polymerization (Figure 6.4c). Upon raising n from 100 to 400 rpm somewhere in 'interval II', the pressure rises immediately to saturation pressure and behaves normally after that (Figure 6.4b).

When stirring is insufficient, mass and heat transfer into the gas phase is not optimal, while at the same time butadiene vapour is continuously condensing

against the (non jacketed) top of the reactor. Consequently, the temperature in
the gas phase will decrease somewhat, and pressure cannot be maintained at
saturation level.

*Figure 6.4. Recordings of temperature and pressure (<u>read from right to left</u>) for
polymerizations with 32.4 g.L⁻¹ dresinate 214, at a stirring speed n = 400 rpm (a);
n raised from 100 rpm to 400 rpm, indicated by the arrows (b); n = 100 rpm (c).*

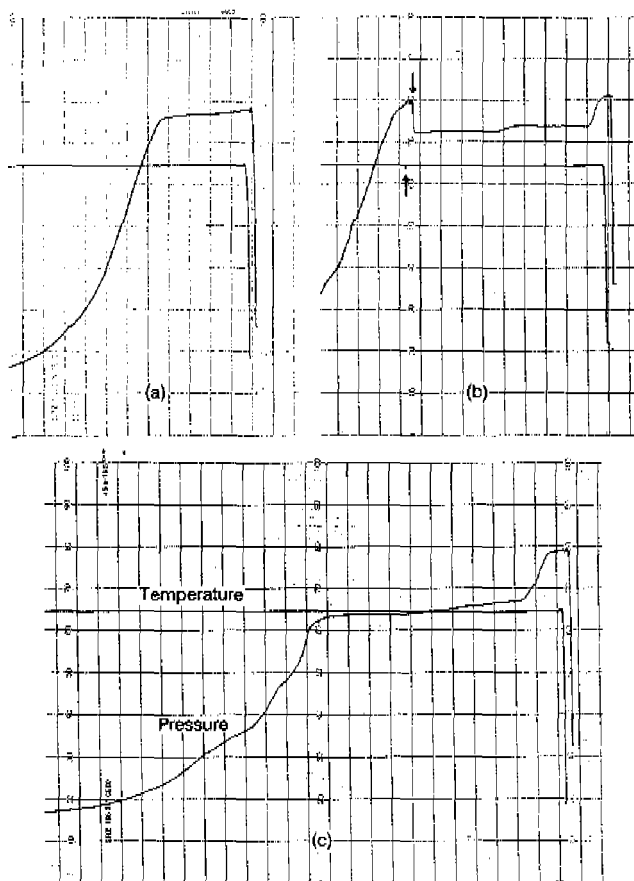For dispersions of two poorly miscible pure liquids an empirical correlation for the total interfacial area per unit volume of dispersed phase A_o, was obtained by Rodger et al.:[6]

$$A_o = \frac{K}{D} \left(\frac{D^3 n^2 \rho_c}{\gamma} \right)^{0.36} \left(\frac{D}{D_r} \right)^K \left(\frac{\nu_D}{\nu_C} \right)^{1/5} \left(\frac{t}{t_o} \right)^{1/6} \exp \left[3.6 \ \frac{\Delta \rho}{\rho_c} \right] \Phi \quad (6.3)$$

where K and κ are constants, D the impeller diameter, D_r the reactor diameter, t the settling time of the dispersion, t_o the reference settling time, γ the interfacial tension, $\Delta\rho$ the density difference, ν the kinematic viscosity ($= \mu/\rho$), and Φ a scale-up function. This relation is in accordance with the model for agitated dispersions proposed by Shinnar and Church,[7] based on Kolmogoroff's theory of local isotropy in turbulent flow fields.

A correlation for the minimum stirring speed n_{min} for complete dispersion of two virtually immiscible liquids has been given by Skelland et al.:[8]

$$n_{min} = K' \left(\frac{D_r}{D} \right)^{\kappa'} \ \frac{g^{0.42} \ \Delta\rho^{0.42} \ \mu^{0.08} \ \gamma^{0.04} \ \varphi_D^{0.05}}{D^{0.71} \ \rho^{0.54}} \quad (6.4)$$

where K' and κ are constants, and g the gravitational constant.

Stricktly speaking these correlations are only valid for emulsions of pure liquids, and cannot be used to describe an emulsifier-stabilized monomer emulsion. Yet, they do imply that $\Delta\rho$, and to a much lesser extent ν, also need to be considered with emulsifier-stabilized emulsions, since both parameters are macroscopic properties. The emulsifier will exert its effect on A_D mainly by reducing the interfacial tension γ and increasing the settling time t. The unique physical properties of liquid butadiene (b.p. $= -4.4°C$) tend to increase n_{min} and A_D (i.e. reduce the average droplet diameter), relative to other monomers (e.g. styrene; b.p. $= 145°C$) under otherwise identical conditions (Table 6.1).

It is evident that a large relative density difference $\Delta\rho/\rho_c$ promotes the breaking up of droplets in a turbulent flow field. Furthermore, in the presence of emulsifier coalescence is greatly suppressed, consequently a rather small average diameter of the monomer droplets is expected in the present system.

Table 6.1. *Physical properties of butadiene, styrene and water at 62°C.*

pure liquid	$10^4.\mu$ $kg.m^{-1}.s^{-1}$	$10^7.\nu$ $m^2.s^{-1}$	ρ $kg.m^{-3}$	$\Delta\rho/\rho_c$ [a]
butadiene	0.93 [9]	1.65	565	0.42
styrene	4.58	5.28	868	0.12
water	4.53	4.61	982	----

[a] For monomer emulsions in water.

The average droplet diameter of a monomer emulsion d_M can take values between 5.10^{-5} m and 1.10^{-6} m, depending on the method of emulsification.[10] Based on the previous discussion d_M of a butadiene emulsion in a turbulent field is expected to be found at the lower end of this scale. This was experimentally verified by an OsO_4-staining of a butadiene emulsion prepared at 400 rpm with 16.2 $g.L^{-1}$ SDS. The procedure is a modified version of the technique described by Yang.[11] In short, a sample of the initial emulsion was taken with a 10^{-4} dm^3 GLC sampling valve, and immediately (< 5 sec) contacted with OsO_4 by pushing a 2 % OsO_4-solution from one high-pressure-proof syringe to another via the GLC sample loop. The solution turned black within seconds. The resulting stained particles are ready for electron microscopy analysis with SEM and TEM (Figure 6.5). Particle counting gave an average diameter $d_n = 8.10^{-7}$ m. Although the uptake of OsO_4 will certainly affect density, the order of magnitude is considered typical of the initial droplet diameter in all recipes, as [E] » CMC, while the breaking up of droplets is mainly determined by the macroscopic property $\Delta\rho/\rho_c$.

Using $A_E = 42\ 10^{-20}$ m^2 for the specific area per molecule SDS (section 5.5), the effective emulsifier concentration in the aqueous phase, for the recipe with 16.2 $g.L^{-1}$ SDS varies with d_M as shown in Figure 6.6. With $d_M \simeq 10^{-6}$ m, it follows that ca. 30 % SDS is initially adsorbed onto the droplets, despite the fact that [E] » CMC (= 0.17 $g.L^{-1}$, section 5.2). In contrast, Nomura et al.[3] concluded for the emulsion polymerization of styrene with SDS as emulsifier, that emulsifier adsorption on monomer droplets and the effect of stirring thereupon were both insignificant for recipes with [E] $\geq$ 12 CMC.
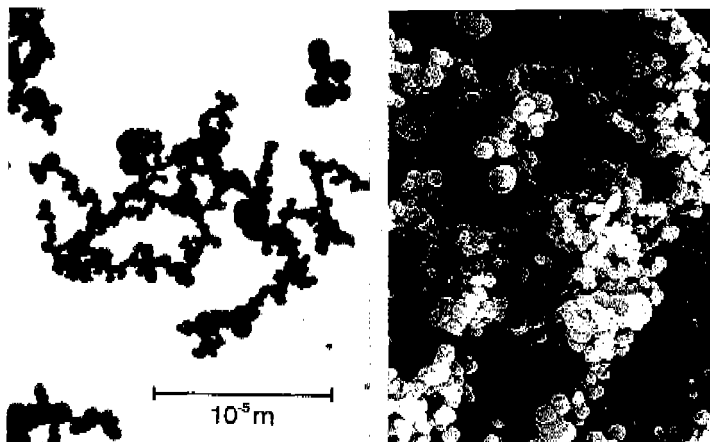
Figure 6.5. Transmission electron micrograph (left) and scanning electron micrograph (right) of an OsO₄-stained butadiene emulsion, prepared at a stirring speed n = 400 rpm, in the presence of 16.2 g.L⁻¹ SDS (recipe 2).
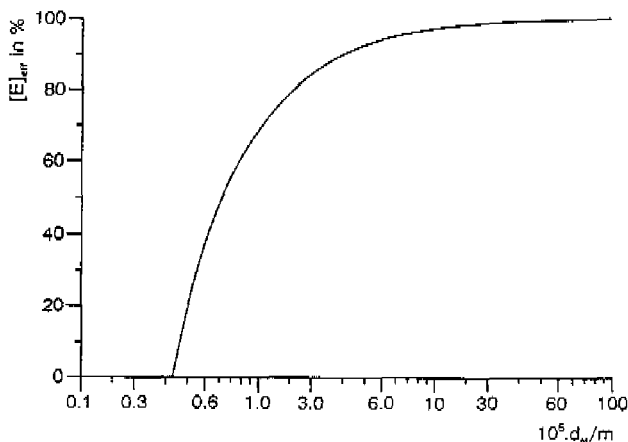
Figure 6.6. Effective emulsifier concentration $[E]_{eff}$ vs. droplet diameter d_M for a butadiene emulsion with 16.2 g.L⁻¹ SDS ($[E]$ = 56 10⁻³ mol.L⁻¹) and a monomer/water ratio M/W = 3/7 g.g⁻¹ (recipe 2), with $[E]_{eff}$ calculated according to $[1 - 6(M/W)/([E] - CMC) A_E N_{Av} d_M \rho_M]$ 100 %.

It should be noted that such finely dispersed butadiene emulsions are unavoidable, as the relatively high stirring speeds are necessary to obtain homogeneous emulsions, allowing reproducible sampling. Yet, the effect on reaction kinetics in the present system is propably small, as particle formation is coagulative in nature, and stops at 40 - 45 % conversion, when most of the emulsifier has already become adsorbed onto the particle surface.

If the total surface area of the monomer droplets is sufficiently large, polymerization in the droplets might no longer be negligible. Smith and Ewart[12] conveniently ignored radical entry into monomer droplets, as emulsification normally gives values for d_M in the size range of $2 - 5 \ 10^{-6}$ m; droplets of this size cannot compete effectively with the smaller and more numerous micelles in capturing radicals. A similar argument can be made for homogeneous nucleation mechanisms. However, this argument might no longer hold in the present system. Yet, the fraction of particles $> 5.10^{-7}$ m (supposedly polymerized droplets) normally found in the particle size distribution of the final latex is insignificant as compared with that of the true latex particles.

Several reasons can be given for this negligible droplet polymerization, despite the large overall surface area of the initial monomer emulsion:

- The value for d_M is the result of a dynamic equilibrium between the breaking up of droplets by shear and viscous forces, and droplet coalescence. The latter process is mainly determined by diffusional thinning of the films surrounding adhering droplets. The high stability of emulsions in the presence of surface active agents mainly results from an increased stability of this protective film. The experimentally determined droplet diameter is that of the initial emulsion, when [E] » CMC. As polymerization proceeds, [E] drops below the CMC and A_o must decrease due to a higher rate of droplet coalescence. The number of droplets (and thus A_o) further decreases quickly by diffusion of monomer from the droplets to the latex particles.

- As droplets continuously coalesce there is a constant exchange of material between them; the polymerization kinetics in the droplets is essentially that of a bulk process, which is considerably slower than the corresponding emulsion

process. Only when the latter is extremely slow (usually at high monomer to water ratios or at low N), polymerization in the droplets becomes competitive. This shows up in the particle size distribution (PSD) of the final latex, which begins to show an extreme positive skewness, with particles sometimes as large as 10^{-6} m; these particles evidently stem from polymerized droplets. An illustrative example is shown in Figure 6.7, giving PSD's of final latexes prepared with 8.1 $g.L^{-1}$ dresinate 214 (recipe 1) at different $[K^+]$ (Table 6.2).

Table 6.2. Data on polymerization kinetics and particle size distributions for experiments with 8.1 $g.L^{-1}$ dresinate 214 (recipe 1) at different overall $[K^+]$.

$[K^+]$ mol.L^{-1}	time hrs	conv. %	$10^6.R_{pol}$ g.mL^{-1}.s^{-1}	d_v at 90 % nm	P	$f(d_v) >$ 5.10^{-7} m [a)]
0.32^5	25	96	6.9	181	1.04	---
0.35	30	90	4.3	236	1.05	---
0.37^5	72	94	1.4	358	1.14	14
0.40	120	93	0.88	375	1.49	35

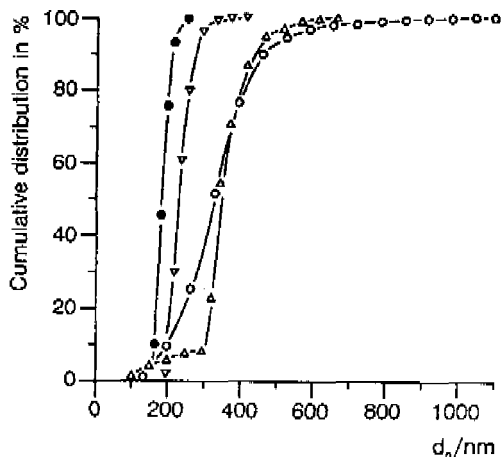[a)] $f(d_v)$ = the fraction of particles with diameter d_v.

Figure 6.7. Cumulative particle size distributions for polymerizations with 8.1 $g.L^{-1}$ dresinate 214 at different overall $[K^+]$ = 0.40 mol.L^{-1} (o); $[K^+]$ = 0.37^5 mol.L^{-1} (△); $[K^+]$ = 0.35 mol.L^{-1} (▽);$[K^+]$ = 0.32^5 mol.L^{-1} (●). M/W = 3/7 g.g^{-1} (recipe 1).

Similar results were reported for styrene emulsions prepared with ultra-sonification, with $d_M \simeq 10^{-6}$ m.[10] After polymerization, the weight ratio of large particles/small particles in the final latex was found negligible, despite the fact that initially 25 - 30 % of the emulsifier was adsorbed on the monomer droplets (estimation of the present author using $A_s = 45 \cdot 10^{-20}$ m^2 for Aerosol MA[13]).

Under turbulent flow conditions (Re $> 10^4$), butadiene emulsions with a small d_M can be prepared relatively easily, even with customary equipment, as a result of the unique physical properties of this monomer. Paradoxically, at Re $< 10^4$ the large $\Delta\rho$ also promotes the settling out of the two phases, especially in interval II when the droplet surface is slowly being depleted of emulsifier. The duration of interval II for butadiene polymerizations is of the order of several hours; besides a large driving force for phase separation, the opportunity to do so is also overwhelming. Once started, the process of creaming and demixing is irreversible at constant n, ultimately leading to a diffusion-controlled polymerization. This is in agreement with experimental results (Figure 6.2).

An illustrative example of ineffective mixing found in literature, is the radiation-induced emulsion polymerization of butadiene reported by Ishigure et al..[14] Glass ampoules filled with butadiene emulsions were placed on a rotating wheel.[a] In view of the foregoing discussion, this experimental set-up appears inadequate for dispersing butadiene properly. Indeed, a pronounced effect of the agitation conditions was found when stirring was improved by using a magnetic stirring bar; in contrast similar polymerizations with styrene were claimed to behave normally using the rotating wheel. This is consistent with our observation that at Re $< 10^4$ phase separation is relatively facile for butadiene emulsions, while emulsions of styrene under identical conditions can remain adequately dispersed. Styrene, being more reactive than butadiene, will have passed through the critical stages in interval II before extensive demixing could have occurred.

Similar comments apply to results on butadiene emulsion polymerizations reported by Morton et al..[15] The socalled bottle polymerization technique was

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[a] The degree of filling of the ampoules and the gravitational orientation of the wheel (believed to be vertical) were not specified.

used, where bottles were rotated vertically end-over-end at 35 rpm. The initial degree of filling of the bottles was extremely high, about 90 %.[16] Experimental results thus obtained, together with data from Wendler et al.[17] (using a 2 litre reactor with n = 360 rpm) and the present investigation, are shown in Figure 6.8 as a log-log plot of R_{pol}/N vs. d_{90}. The values for R_{pol}/N from Morton et al.[15] are significantly lower than those in the other studies where stirring was adequate, and can only be partially attributed to the difference in temperature (only 2°C with the present study) and the particle sizing method (soap titration in ref.[15]). Again, ineffective mixing appears responsible for this behaviour. It may be noted that the value for k_p reported by Morton et al. (100 L.mol^{-1}.s^{-1} at 62°C),[18] is significantly smaller than our estimate, $k_p \geq$ 180 L.mol^{-1}.s^{-1} (see chapter 7). This is to be expected with a diffusion-controlled polymerization; a lower value for R_{pol} inevitably results in a lower value for k_p.
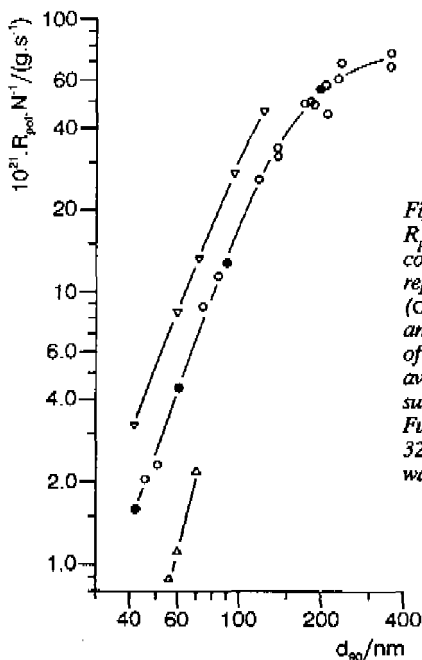
Figure 6.8. Average rate per particle R_{pol}/N vs. particle diameter at 90 % conversion (d_{90}), for polymerizations reported in this investigation at 62°C (O), from Wendler et al.[17] at 70°C ($\triangledown$), and Morton et al.[15] at 60°C ($\triangle$). Data of first two references based on volume-average diameters d_v, and of ref.[15] on surface-average diameters d_s.
Full circles indicate experiments with 32.4 g.L^{-1} SDS at different monomer/water ratios M/W (see section 6.3).

6.3 Monomer to water ratio

Commercial emulsion polymerization processes in batch-operation are for obvious economical reasons performed at the highest polymer content feasible. For industrial butadiene emulsion polymerizations monomer to water weight ratios (M/W) up to 1.5 are employed.[19] As is obvious from the previous discussion, the agitation conditions at such high M/W must be considered for an optimal performance of the process. Table 6.3 shows the final particle number as a function of the stirring speed n at M/W = 1 with 32.4 g.L^{-1} dresinate 214. Emulsions appear adequately stabilized by turbulence at n > 400 rpm; with φ_D = 0.64, an impeller Re of 10^4 is obtained with n = 450 rpm.

Table 6.3. Effect of the stirring speed n on particle number N for polymerizations at M/W = 1 with dresinate 214 (recipe 1).

n in rpm	200	300	400	500	750
10^{-15}.N/mL.$^{-1}$	0.38	0.42	0.22	0.21	0.20

Going to yet higher M/W it was realized that a turbine impeller might no longer provide sufficient agitation, as it is typically designed for low-viscosity systems ($\mu \leq 50$ kg.m^{-1}s^{-1}). This was indeed experienced at M/W = 1.5, where power consumption increased drastically and temperature control was poor. For these polymerizations a low pitch helical ribbon agitator was chosen at n = 300 rpm. The ribbon agitator and the turbine impeller at M/W $\leq$ 1 were found equivalent in performance with regard to conversion-time history and final N.

The monomer to water weight ratio M/W was varied between 0.25 and 1.5, with both dresinate 214 and sodium dodecylsulfate (SDS) as emulsifiers. All other recipe ingredients were kept constant on water basis. Conversion-time curves for polymerizations with SDS at varying M/W are given in Figure 6.9, and those of polymerizations with dresinate 214 at M/W = 1.5 in Figure 6.10. The dependence of final particle number on M/W for polymerizations with both emulsifiers is shown in Figure 6.11.
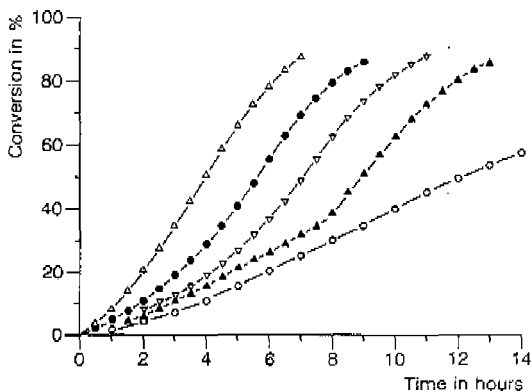
Figure 6.9. Conversion-time curves for polymerizations with 32.4 g.L⁻¹
SDS (recipe 2), at different monomer/water ratios M/W = 0.25 (△);
M/W = 3/7 (●); M/W = 2/3 (▽); M/W = 1 (▲); M/W = 1.5 (○).
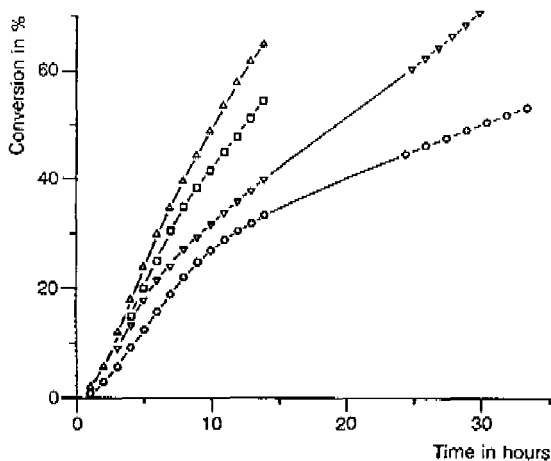
Figure 6.10. Conversion-time curves for polymerizations with a monomer/
water ratio M/W = 1.5, at different dresinate 214 concentrations C_E = 61.6
g.L⁻¹ (△); C_E = 51.8 g.L⁻¹ (□); C_E = 42.1 g.L⁻¹ (▽); C_E = 32.4 g.L⁻¹ (○).
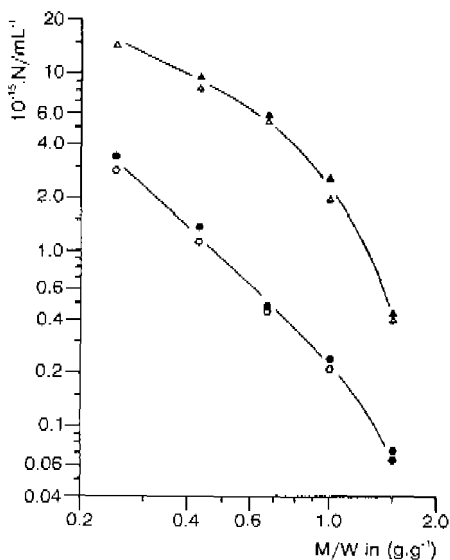
Figure 6.11. Particle number N vs. monomer/water ratio M/W, for polymerizations with 32.4 g.L^{-1} dresinate 214 (○) and 32.4 g.L^{-1} SDS (△). Particle sizing by DLS (open symbols) and TEM (full symbols).

It should be noted that the volume fraction φ of butadiene is considerably larger than the corresponding weight fraction. For example, for M/W = 1, the initial $\varphi = 0.64$, and for M/W = 1.5 even $\varphi = 0.73$, both at 62°C. At such high volume fractions the type of emulsion may differ significantly from the normally encountered oil-in-water type (o/w). Rodger et al.[6] noted in their investigation with pure liquids[b] that many o/w emulsions could be inverted to the water-in-oil type (w/o) by increasing the energy input, this being more facile with larger values for $\Delta\rho/\rho_c$. In fact, systems with $\Delta\rho/\rho_c$ values of the order of 0.6 could not be made to produce o/w-type emulsions without changing the position of the impeller. For butadiene $\Delta\rho/\rho_c = 0.42$ (Table 6.1). However, the use of anionic, water-soluble emulsifiers will favour emulsions with a continuous aqueous phase.

Although a thorough knowledge of the behaviour of butadiene emulsions seems crucial, a microscopic study is virtually impossible due to the low boiling

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[b] Volume fraction of the organic phase believed to be 0.5.

point of butadiene (- 4.4°C). In order to get some insight in the emulsification behaviour at high M/W, styrene emulsions prepared with dresinate 214 at different phase ratios were studied instead (Figure 6.12). This experiment showed that the (handshaken) emulsions get coarser with increasing M/W, while at styrene volume fractions $\geq$ 0.60 mixed w/o/w emulsions were being formed.

Obviously, increasing φ at a constant emulsifier concentration, must lead to a decrease in $[E]_{eff}$, and thus in final N. At M/W $\geq$ 1 (i.e. $\varphi \geq$ 0.63), when mixed emulsions are formed, $[E]_{eff}$ and N will decrease even further. This is clearly observable in the experiments with SDS as emulsifier (Figure 6.11).

The type of emulsion may also affect the course of polymerization. As interval II ends at 60 % conversion (see chapter 7 and Table 6.4), it is obvious that many conversion-time curves at high M/W have two kinetic regimes in interval II. In the presence of a mixed emulsion, polymerization in the monomer phase may no longer be negligible. As polymerization proceeds, the monomer volume fraction φ decreases, so that a transition from a mixed emulsion to a normal o/w emulsion is likely to occur, as the latter is preferred at lower φ. This change in type of emulsion, which is expected to be abrupt, will reduce radical entry into the monomer phase significantly. Based on this concept, polymerization before the rate inflection occurs simultaneously in the latex particles and monomer droplets, while after the inflection the latter locus is strongly reduced or eliminated. Unfortunately, this hypothesis is extremely hard to test, as butadiene emulsions cannot be studied in a direct way.

However, the kinetics of the experiments with 32.4 g.L^{-1} SDS at different M/W (Figure 6.9) provide some useful indications (Table 6.4). The average rate per particle R_{pol}/N for these polymerizations is indicated in Figure 6.8 by the full circles. The polymerization with M/W = 1 is of special interest, as it clearly shows two kinetic regimes. The rate R_{pol} used to calculate R_{pol}/N is the one after the inflection point. As can be seen in Figure 6.8, the experiment with M/W = 1 (having d_{90} = 90 nm) fits in perfectly with the rest; the second regime appears to be that of a true emulsion polymerization (for the first regime R_{pol}/N = 5.6 10^{-21} g.s^{-1}). On the other hand, polymerization in the first regime is indeed faster than anticipated on the basis of the experiments at lower M/W.

Figure 6.12. Optical micrographs of styrene emulsions (handshaken) in the presence of 32.4 g.L^{-1} dresinate 214, at different styrene volume fractions $\varphi = 0.20$ (a); $\varphi = 0.30$ (b); $\varphi = 0.40$ (c); $\varphi = 0.50$ (d); $\varphi = 0.60$ (e-f); $\varphi = 0.70$ (g); and $\varphi = 0.80$ (h). Light areas represent styrene domains.
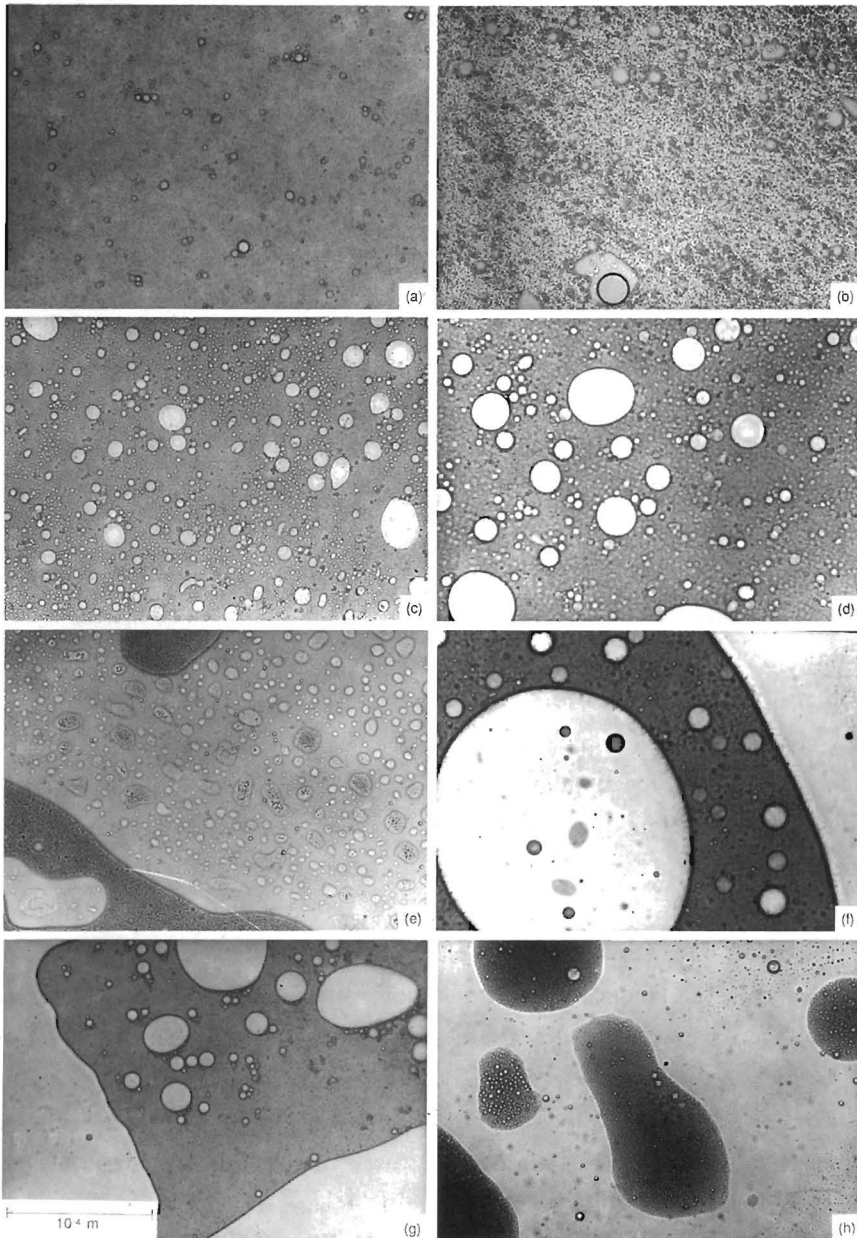
Table 6.4.   Kinetic data of polymerizations with 32.4 g.L⁻¹
SDS (recipe 2) and different monomer/water ratios M/W.

M/W g.g⁻¹	$10^5.R_{pol}$ g.mL⁻¹.s⁻¹	d_v at 90 % nm	P	x' [a]
0.25	1.1	---	-----	0.593
0.43	1.8	44	1.06	0.598
0.67	2.6	60	1.07	0.588
1.00	1.5 [b]			
	3.4	90	1.06	0.607
1.50	2.1	197	1.30	-------

[a]   Conversion where interval III begins (see section 7.3).
[b]   Rate before the inflection point.

Beside the latex particles, an additional locus for polymerization, viz. the monomer phase, must be kinetically significant in these systems.

The number of large off-sized particles found in the latex with M/W = 1.5 was significant; the PSD showed a profound positive skewness, with particles as large as 6.10^{-7} m. This was not observed in the final PSD's at M/W < 1.

The polymerizations at M/W = 1.5 with 61.6 g.L⁻¹ dresinate 214 (d_v = 174 nm at 90 % conversion) and 32.4 g.L⁻¹ SDS both lack a clear inflection point; both final particle sizes are comparable. Decreasing the concentration of dresinate 214 obviously leads to smaller particle numbers, while at the same time a negative inflection in the conversion-time curves becomes apparent (Figure 6.10). A decrease in interval II rate was observed earlier in an experiment with M/W = 3/7, where the particle number was reduced substantially by electrolyte addition (Figure 5.6, with 8.1 g.L⁻¹ SDS and $[K^+]$ = 0.5 M). Polymerization in the monomer phase again appears competitive in the initial stage of polymerization, this time caused by the extremely low particle number.

The leveling off at $d_{90} > 200$ nm of R_{pol}/N in Figure 6.8 thus is likely to be caused by competitive polymerization in the monomer phase; at high M/W due to the presence of a mixed emulsion, and at low M/W resulting from a low particle number. Yet, an additional factor may be that for these large particles $\bar{n}$ is possibly close to 0.5 (see chapter 7). Seeded experiments with monodisperse latexes in this size range are intended to clarify this behaviour.

6.4 Conclusions

Agitation needs to be sufficiently intense to prepare homogeneous emulsifier-stabilized emulsions of butadiene, which is a prerequisite for reproducible, gravimetric sampling (e.g. for conversion). An unavoidable side-effect is the significant decrease in $[E]_{eff}$, as a result of the small average droplet diameter obtained under these conditions.

The large density difference $\Delta\rho$ between butadiene and water promotes the breaking of droplets in a turbulent flow field. Paradoxically, if turbulence is insufficient $\Delta\rho$ stimulates (partial) phase separation, leading to a diffusion-controlled polymerization, whereas other monomers may still behave normally.

Increasing M/W at constant $[E]$ leads to a decrease in the final N as $[E]_{eff}$ decreases. An additional reduction of N was found at M/W $\geq$ 1, presumably because mixed emulsions are formed which reduce $[E]_{eff}$ even further. The presence of mixed emulsions in a polymerizing system is likely to affect the kinetics, as polymerization in the monomer phase may no longer be negligible. In fact, it was frequently observed that polymerizations at high M/W had two kinetic regimes in interval II. There are strong indications that the (change in) type of emulsion is responsible for the anomalous kinetic behaviour at high monomer/water ratios.

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Chapter 7   Kinetics of the Emulsion Polymerization of Butadiene

SUMMARY: Kinetic information on particle growth is obtained for the *ab initio* emulsion polymerization of butadiene. It is shown that the decrease in particle number by coagulation (induced by the high ionic strength) hardly affects polymerization rate, since the average number of radicals per particle ($\bar{n}$) increases with particle size. From a rate-analysis of intervals II and III it follows that the system is 'zero-one' ($\bar{n}$ < 0.5), i.e. termination is not rate-determining. Zero-one kinetics, in combination with a low initiator efficiency, explains the small effect of initiator concentration on polymerization rate. The radical loss mechanism responsible for the zero-one kinetics could not be established unambiguously, but chain transfer/desorption processes involving polybutadiene, thiol, emulsifier, and the Diels-Alder dimer 4-vinyl-1-cyclohexene, were all refuted on experimental grounds. Desorption of monomeric species seems a reasonable explanation, given the rather low estimate of the propagation rate coefficient.

7.1 Introduction

Despite the enormous industrial importance of polybutadiene-containing polymers prepared by emulsion polymerization (e.g. synthetic rubbers, high impact materials, coatings, adhesives), very little is known about the kinetic behaviour of butadiene in emulsion polymerization systems.

As early as the synthetic rubber program unusual effects were observed in the (co)polymerization of butadiene(75)-styrene(25) or butadiene alone, but no adequate explanations were provided. These effects included the observations

that trace amounts of thiols of low water solubility seemed to be essential to bring about reaction in persulfate-initiated polymerizations,[1] while the rate of (co)polymerization was unaffected when changing the concentration of persulfate within wide limits.[2]

In the previous chapters was discussed the *ab initio* emulsion polymerization of butadiene under conditions typically found in industrial practice, e.g. high ionic strength, large monomer to water ratios, and the use of a commercial emulsifier. Although these experiments were not especially designed to study the kinetics, they do contain a lot of useful information, which is now used to analyse the typical behaviour of this monomer.

One of the principal problems encountered in interpreting the kinetics of butadiene is the chronic lack of reliable rate coefficients in open literature. The only values for the propagation rate coefficient k_p stem from the early work of Morton et al.,[3] and at best represent an approximation of its true value since they were determined under dubious experimental conditions (see chapter 6).

Within the limitations mentioned above an analysis is given of the kinetics and mechanisms of the emulsion polymerization of butadiene, based on experimental evidence discussed in the preceding chapters.

7.2 Interval II analysis

The overall rate of polymerization R_{pol} ($L.mol^{-1}.s^{-1}$) is usually expressed as

$$R_{pol} = \frac{dc}{dt} \, n_M^\circ = k_p \, C_M \, (\bar{n}/N_{Av}) \, N \tag{7.1}$$

where n_M° is the number of moles of monomer initially present per unit volume of water, $\bar{n}$ the average number of radicals per particle, N_{Av} Avogadro's number, C_M the monomer concentration within the particles, and N the particle number.

Since k_p is not known with sufficient accuracy, it is better to use the average rate per particle (R_{pol}/N) as a semi-quantitative equivalent of $\bar{n}$, because k_p and

C_M are constant in interval II to within an excellent approximation (see below). Data can be conveniently presented as log-log plots of R_{pol}/N vs. particle diameter d, in analogy with the well-known Ugelstad plots of log $\bar{n}$ vs. log α'.[4] Figure 7.1 shows R_{pol}/N vs. diameter for two polymerizations discussed earlier: one with 16.2 g.L^{-1} dresinate 214 depicted in Figure 4.8, and with 8.1 g.L^{-1} SDS shown in Figure 5.2. Obviously, the observed decrease in particle number by coagulation is compensated by an increase of $\bar{n}$ of the resulting particles, so that R_{pol} remains virtually unchanged during the polymerization.
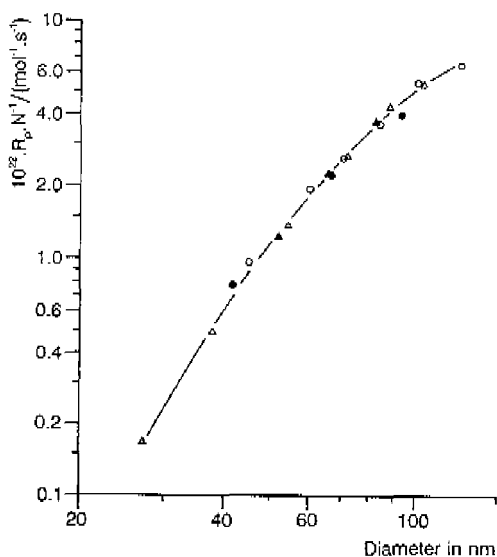
Figure 7.1. Average rate per particle R_{pol}/N vs. diameter, d_w (open symbols) and d_v (full symbols), for reactions with 16.2 g.L^{-1} dresinate 214 (O), and 8.1 g.L^{-1} SDS (△).

Calculation of R_{pol}/N using R_{pol} in interval II and the final particle number after cessation of coagulation gives an upper limit of this quantity, since at lower conversions R_{pol}/N is evidently smaller due to the smaller particle size. Besides type and concentration of emulsifier, other recipe parameters such as monomer/ water ratio, ionic strength and initiator concentration were utilised to vary the final particle size. Plotting the average rate per particle on a log-log scale as a

function of final particle diameter at an arbitrarily chosen final conversion, viz. 90 %[a] (Figure 7.2 and 7.3), clearly shows that R_{pol}/N depends solely on particle size. Polymerization kinetics is internally consistent, and otherwise unaffected by variables such as emulsifier concentration and ionic strength, except in regard to how these affect the final particle size. Furthermore, the general trend is not affected by the method of particle sizing. Figure 7.3 also contains data points taken from the work of Wendler et al.[5] for butadiene emulsion polymerizations at 70°C, where particle size was varied by changing the amount of bis(iso-propoxythiocarbonyl)disulfane, a chain transfer agent which decreases colloidal stability by introducing polar end-groups that reduce emulsifier adsorption.[6] Agreement with our results is excellent, given the temperature difference of 8°C.
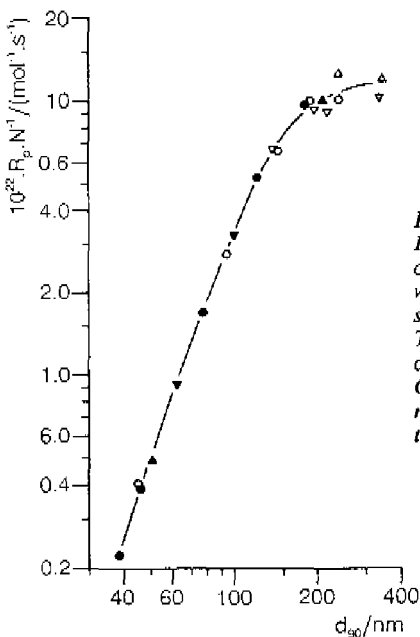
Figure 7.2. Average rate per particle R_{pol}/N vs. the diameter d_w at 90 % conversion (d_{90}), for polymerizations with dresinate 214 (open symbols) and sodium dodecylsulfate (full symbols). The final particle size was varied by changing the emulsifier concentration C_E (○), cation concentration (△), or monomer/water ratio M/W (▽) in the standard recipes.

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[a] 90 % Conversion was chosen for the sake of experimental convenience, as the majority of polymerizations was stopped between 85 and 95 %.
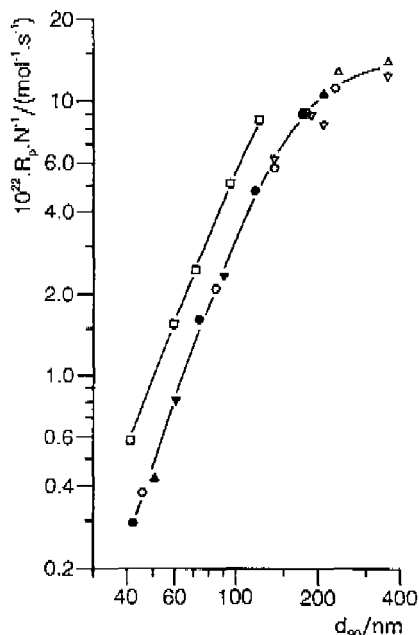
Figure 7.3. Average rate per particle R_{pol}/N vs. the diameter d_v at 90 % conversion (d_{90}). Data of Wendler et al.[5] for polymerizations at 70°C ($\square$). For other symbols see Figure 7.2.

Using the uncertain value for $k_p = 100$ L.mol^{-1}.s^{-1} reported by Morton[3] at 62°C, and $C_M = 5.6$ mol.L^{-1} (see **Appendix**), a value of 4.7 10^{-22} mol.s^{-1} for R_{pol}/N would result if $\bar{n} = 0.5$. Given this rough estimate of a Smith-Ewart case 2 situation, and again emphasizing that the calculated values for R_{pol}/N are upper limits for the experiments involved, it is evident from Figures 7.1 - 7.3 that values for $\bar{n} < 0.5$ are realistic.

Importantly, no constancy of R_{pol}/N associated with $\bar{n} = 0.5$ is observed in the particle size range covered. The apparent leveling off at $d_{90} > 200$ nm may be artificial, because the polymerizations involved are extremely slow, sometimes taking 2 to 3 days to complete conversion. On such a time scale bulk polymerization in the monomer droplets can no longer be neglected as is usually done. This behaviour clearly shows up in the particle size distribution of the final latexes, which are extremely positively skewed (see Figure 6.7). Therefore these experiments are ignored in the following discussion.

7.3 Interval III analysis

The complications associated with particle nucleation and coagulation can be avoided by using the kinetic information in interval III, where the particle number is truly constant (see Figures 4.8 and 5.2). Since monomer concentration in the particles is decreasing continuously, it is convenient to remove C_M from the right-hand side of equation (7.1) and write the expression in terms of the fractional conversion in interval III, x, with $x = (C_M^\circ - C_M)/C_M^\circ$ and C_M° the initial monomer concentration in the particles:[7)]

$$ - \frac{d\ln(1-x)}{dt} = \frac{k_p \, \bar{n} \, C_M^\circ \, N}{N_{Av} \, n_M} \tag{7.2} $$

where n_M is the number of moles of monomer per unit volume of water present at the beginning of interval III. Since $n_M = (1 - x')n_M^\circ$, with x' the conversion where interval III begins, we can calculate x' from the experimental values of the rates in interval II (R_{pol}) and interval III ($-d\ln(1 - x)/dt$). The conversion x' is found to be 0.60 (standard deviation = 2.3 %, using 25 data points), and independent of particle size (Figure 7.4). This latter observation further substantiates the common assumption of constancy of C_M in interval II.
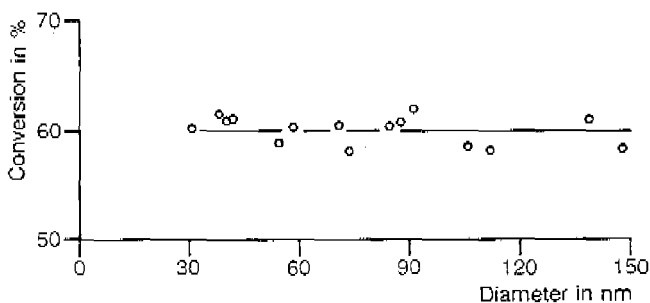
Figure 7.4. The fractional conversion where interval III begins (x') vs. particle diameter d_w at x'. An average value x' = 0.60 was obtained.

The value of x' is somewhat higher than those reported in literature based on vapour pressure measurements, viz. 0.52[8] and 0.56.[3] These latter values are considered more inaccurate because the non-ideal gas behaviour of butadiene vapour complicates an accurate determination of the conversion at the point where pressure begins to drop.

For the simple zero-one system (i.e. only particles with zero or one free radical per particle need to be considered) where bimolecular termination is not rate determining, it is easily shown that (see section 2.2):[9]

$$\bar{n} = \frac{\rho}{2\rho + k} \tag{2.7}$$

where ρ is the rate coefficient for radical entry and k the rate coefficient for exit (desorption). During interval III, ρ may be considered unchanging to within a good approximation, since the swollen particle diameter is almost constant. On the other hand, k may depend on factors other than the particle volume, e.g. the monomer concentration C_M. However, a reasonable starting point is to assume k to be constant, and then to check if this is consistent with the data. Several limiting cases can be distinguished:

Smith-Ewart case 2, with $k \ll \rho$: $\bar{n} = 0.5$
Smith-Ewart case 1, with $k \gg \rho$: $\bar{n} \simeq \rho/k$

Plotting $-\ln(1 - x)$ vs. reaction time (Figures 7.5 and 7.6) gives straight lines up to a weight fraction of polymer w_p (equivalent to the *ab initio* conversion c) of 0.85 or higher, for all polymerizations with $d_{90} < 175$ nm.

Since the bimolecular termination rate coefficient varies significantly with w_p, termination cannot be rate-determining because $-d\ln(1 - x)/dt$ is constant for $0.60 < w_p < 0.85$ under all conditions investigated. The approximation of instantaneous termination is thus valid, and $\bar{n} \leq 0.5$.

Figure 7.5 (top). -ln(1 - x) vs. Reaction time in interval III, for polymerizations with different SDS concentrations $C_E = 64.8$ g.L^{-1} (O); $C_E = 32.4$ g.L^{-1} ($\bigtriangledown$); $C_E = 16.2$ g.L^{-1} ($\square$); $C_E = 8.1$ g.L^{-1} ($\triangle$). For convenience the zero-point is shifted one hour along the x-axis.

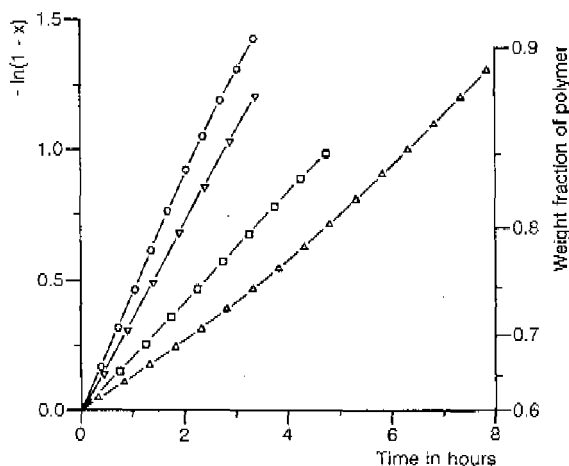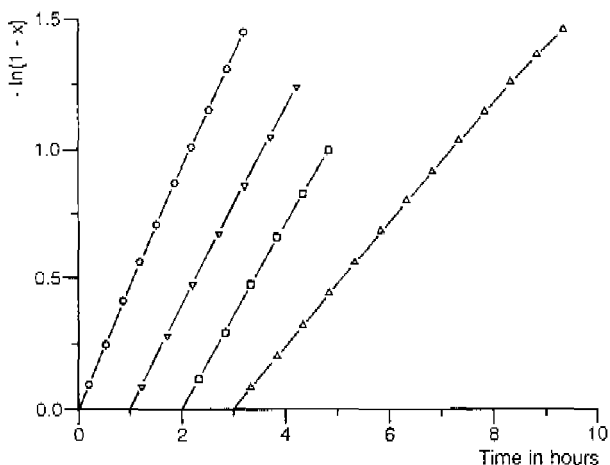*Figure 7.6 (bottom). -ln(1 - x) vs. Reaction time in interval III, for polymerizations with different dresinate 214 concentrations $C_E = 64.8$ g.L^{-1} (O); $C_E = 32.4$ g.L^{-1} ($\bigtriangledown$); $C_E = 16.2$ g.L^{-1} ($\square$); $C_E = 8.1$ g.L^{-1} ($\triangle$). On the right axis is indicated the weight fraction of polymer w_p*

Furthermore, Figures 7.5 and 7.6 show that the product of $k_p.\bar{n}$ is constant within each experiment; it would be highly fortituous if k_p and $\bar{n}$ would counterbalance under all experimental conditions, so it is apparent that k_p and $\bar{n}$ are both constant in interval III. This further implies that k_p is not diffusion controlled, at least for $w_p < 0.85$; this is to be expected given the low glass transition temperature of (emulsion) polybutadiene ($T_g = -86°C$).[10]

The termination rate coefficient may start to become sufficiently small for very large particles as to become rate-determining, consistent with the non-linearity of $-\ln(1-x)$ observed for polymerizations with $d_{90} > 175$ nm (e.g. the polymerization with 8.1 g.L^{-1} dresinate 214 in Figure 7.6, with $d_v = 180$ nm at 90 % conversion). At a relatively low w_p the interval III rate $-d\ln(1-x)/dt$, and thus $\bar{n}$, begin to increase. Termination is no longer instantaneous, yet the initial steady state suggests a zero-one behaviour at lower w_p. If we assume the initial $\bar{n} = 0.5$, an estimation for $k_p = 180 - 200$ L.mol^{-1}.s^{-1} is obtained. Although intuitively not unreasonable this assumption is not necessarily correct, since the initial $\bar{n}$ can still be < 0.5. The particle size distributions (PSD) of these latexes are quite narrow, but not monodisperse, which further complicates a proper interpretation. Therefore this estimate of k_p should be regarded as a lower limit of its true value.

7.4 Effect of the initiator concentration

Having established that the studied system shows zero-one behaviour over a wide range of experimental conditions, we can further explain the effect of initiator concentration [I] on polymerization kinetics (Table 7.1). The initiator concentration was varied 100-fold between 26.0 and 0.26 mmol.L^{-1}, while every change of [I] was accompanied by an appropriate adjustment of the amount of K^+/Na^+ carbonate to keep the overall cation concentration constant. Coagulation phenomena are thus a constant factor in these experiments.

Under all conditions tried, and in agreement with previously reported results,[2] both R_{pol} and $-d\ln(1-x)/dt$ are only weakly dependent on [I].

Table 7.1. Initiator exponents with regard to particle number ($N \propto [I]^x$) and polymerization rates in intervals II ($R_{pol} \propto [I]^y$) and III ($-dln(1 - x)/dt \propto [I]^z$), at different emulsifier concentrations C_E and cation concentrations [cation].

Recipe	C_E g.L^{-1}	[cation] mol.L^{-1}	$\beta^{a)}$	x	y	z	$d_{90}^{b)}$ nm
2	32.4	0.3	9	0.46	0.04	0.04	46
2	16.2	0.3	7	0.16	0.09	0.09	80
1	32.4	0.4	7	0.02	0.08	-----	94

a) β = number of experiments.   b) d_w at $[I]$ = 13.0 mmol.L^{-1}.
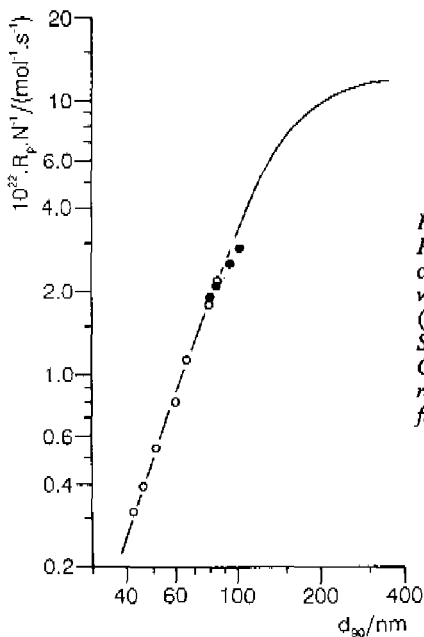
Figure 7.7. Average rate per particle R_{pol}/N vs. the diameter d_w at 90 % conversion (d_{90}), for polymerizations with a 100-fold variation in $[S_2O_8^{2-}]$ (see Table 7.1) at two concentrations SDS (recipe 2) C_E = 32.4 g.L^{-1} (○); C_E = 16.2 g.L^{-1} (●). The solid line represents the empirical relationship from Figure 7.2.

The average rate per particle as a function of particle size for the first two series of experiments (recipe 2) from Table 7.1 are shown in Figure 7.7, where the solid line represents the best fit of data points from Figure 7.2. Again the

kinetics is internally consistent, yet the 100-fold variation of [I] has an almost neglible effect on kinetics. This implies that ρ is independent of [I] in the present system, i.e. the initiator efficiency must be extremely low. Furthermore, for latexes with a narrow PSD, ρ can be taken inversely proportional to N. Substituting this into equations (7.1) and (7.2) and assuming a low value for $\bar{n}$, viz. $\bar{n} \simeq \rho/k$, render both R_{pol} and $-d\ln(1 - x)/dt$ independent of [I] and N. This is in good agreement with the data in Table 7.1, especially for the first series of experiments, since the assumption of $\bar{n} \ll 0.5$ is most valid for small particles.

7.5 Radical loss mechanisms

It is obvious that a first-order radical loss process is kinetically dominant in this system, whose nature is as yet uncertain. Several possibilities may arise:

(1) First-order termination by monomer occlusion is highly unlikely, since monomer and polymer are completely miscible (or highly swellable if the polymer is cross-linked), while the glass transition temperature ($T_g = -86°C$) is well below the reaction temperature of 62°C.

(2) Radical trapping by transfer to polybutadiene, as proposed by Hagiopol et al.[11] for the emulsion copolymerization of styrene and acrylonitrile in the presence of PB, is not important, since $-d\ln(1 - x)/dt$ (and thus $\bar{n}$) is constant over a period of several hours, whereas w_p changes significantly during this time.

(3) Chain transfer to thiol and subsequent desorption of thiol radicals can also be ruled out, since Nomura et al.[12] showed that n-dodecanethiol radicals do not desorb because of their extremely low water solubility. Furthermore, omitting the thiol from the recipes used in this investigation never increased R_{pol}/N (see chapter 8), as would be expected in case of desorption of thiol radicals. Instead, a marked decrease of R_{pol}/N was sometimes observed.

(4) It is well-known that butadiene easily undergoes Diels-Alder cyclizations at elevated temperatures, giving products such as 4-vinyl-1-cyclohexene (VCH). Although it is described as a mild retarder in the copolymerization of butadiene(75)-styrene(25),[13] addition of 1 wt.-% VCH to a butadiene emulsion polymerization using SDS (recipe 2) had no effect whatsoever, either on the conversion-time history or on the final particle number. Furthermore, addition up to 4 wt.-% VCH to a styrene emulsion polymerization (using recipe 2 without thiol at 50°C) did not affect the molecular weight significantly (Table 7.2). Although inherently present during polymerization, this Diels-Alder dimer does not seem to facilitate the extensive radical desorption observed experimentally.

Table 7.2. Number-average (M_n) and weight-average (M_w) molecular weight determined by GPC of polystyrene samples, prepared according to recipe 2[b] at 50°C, without t-dodecanethiol (t-DT) and different amounts of VCH.

VCH[a]	0 %	0.25 %	1 %	2 %	4 %	1 % t-DT[a]
$10^{-5}.M_n$	4.1	4.3	3.9	3.8	3.9	0.49
$10^{-6}.M_w$	2.1	2.5	2.3	1.8	1.7	0.21

[a] weight percentage of VCH and t-DT on monomer basis.
[b] $[I] = 13.0$ mmol.L^{-1} and $C_E = 16.2$ g.L^{-1} SDS.

(5) Many common emulsifiers (including sodium dodecylsulfate) can act as chain transfer agents.[14] However, this phenomenon cannot be of major importance in the present system, since polymerizations yielding the same final particle size have the same value for R_{pol}/N, regardless of the type of emulsifier.

(6) Lastly, transfer to monomer (or dead oligomeric material), followed by exit of the monomeric radical seems reasonable given the rather low estimate of k_p. In the transfer/diffusion model developed by Nomura and Harada[15,16] a propagating polymer chain transfers its free-radical activity to a monomer molecule (or to a chain transfer agent), which then diffuses to the particle surface where it desorbs. The process is completed when the radical diffuses away from the surface into the bulk aqueous phase. When all of these three

sequential events are significant, the exit rate coefficient k is given by:

$$k = \frac{12\,z\,D_{aq}}{(q + 2D_{aq}/D_p)d_{sw}^2}\,\frac{k_{tr}}{k_p} \tag{7.3}$$

where D_{aq} and D_p are the diffusion coefficients of the exiting species in the aqueous phase and in the particle, respectively, z is roughly equal to the maximum degree of polymerization of the exiting radical,[b] d_{sw} the swollen particle diameter, and k_{tr} and k_p the rate coefficients for transfer to monomer and for propagation, respectively. The parameter q is the partition coefficient of the exiting species between the particles and the aqueous phase, and is roughly equal to the ratio of saturated monomer solubilities in the particles and aqueous phase (C_M/C_{aq}). A similar expression was derived by Hansen and Ugelstad.[17]

If in the transfer/diffusion mechanism for radical exit transfer to monomer is the rate-determining step, equation (7.3) can be replaced by:[18]

$$k \simeq k_{tr}\,C_M \tag{7.4}$$

Obviously, this is not the case in the present system, since $\bar{n}$, and thus k, were found constant far into interval III, whereas C_M decreases continuously. However, the constancy of k is consistent with the general equation (7.3), since d_{sw} and q are not expected to vary significantly in interval III.

For a sparingly water-soluble monomer $q \gg 2D_{aq}/D_p$, so that equation (7.3) can be approximated by:[18]

$$k \simeq \frac{12\,z\,D_{aq}}{d_{sw}^2}\,\frac{k_{tr}}{k_p}\,\frac{C_{aq}}{C_M} \tag{7.5}$$

---

[b] The parameter $z = \Sigma[k_p C_M/(k\bar{n} + k_p C_M)]^j$, where k is a desorption rate coefficient, and j the degree of polymerization of the exiting species, with $1 \leq j \leq j_{max}$. When $k_p C_M \gg k\bar{n}$, this gives $z \simeq j_{max}$.

Table 7.3. Kinetic data for butadiene and styrene at 50°C.

Parameter	Butadiene	Ref.	Styrene	Ref.
$k_{tr}/L.mol^{-1}.s^{-1}$			7.10^{-3}	19)
$k_p/L.mol^{-1}.s^{-1}$	60	3)	258	20)
$C_{aq}/mmol.L^{-1}$	6	21)	3.7	22)
	37	23)		
$C_M/mol.L^{-1}$	$5.7^{a)}$		5.8	9)

[a] Estimated from C_M determined at 62°C in the present study.

On the basis of equation (7.5) an estimate can be made of the order of magnitude of k for butadiene, relative to the one for styrene at the same d_{sw}. Values for C_M, C_{aq} and k_p for both monomers are given in Table 7.3.

According to the Wilke-Chang correlation[24] the diffusion coefficient D_{aq} is related to the molar volume of the solute at its boiling temperature under atmospheric pressure, V_M, according to $D_{aq} \propto V_M^{-0.6}$. It follows that D_{aq} for butadiene is about 1.3 times larger than the one for styrene.

Based on chemical structure, the maximum degree of polymerization of the exiting species z is expected to be roughly two times larger for butadiene (C_4H_6) as compared with styrene (C_8H_8).

Unfortunately, no value for k_{tr} has been reported for butadiene. However, values for k_{tr} and k_p are known for 2-chloro-1,3-butadiene at 50°C, determined from low conversion solution polymerizations, viz. $k_{tr} = 0.18$ L.mol^{-1}.s^{-1} and k_p = 792 L.mol^{-1}.s^{-1}.[25] Initiator efficiency was found to be 0.4 and the average degrees of polymerization between 2000 and 3000; both quite normal values for solution experiments, indicating a good stability of the chlorine atom towards chain transfer. For styrene k_{tr}/k_p between 0.35 and 0.78 10^{-4} have been reported, while for o-chlorostyrene a similar value is found, viz. 0.27 10^{-4}, all at 50°C.[26] Apparently, the presence of a chlorine atom hardly affects k_{tr}; thus for butadiene $k_{tr} \simeq 0.1$ L.mol^{-1}.s^{-1} at 50°C seems quite reasonable.

There appears to be some confusion about C_M for butadiene. Most values reported (and referred to thereafter) were determined at 25°C and 1 atmosphere (C_M = 14 - 15 mmol.L^{-1}),[2,27,28] while polymerizations are normally performed at saturation pressure. This markedly increases C_M, as is obvious from Figure 7.8.
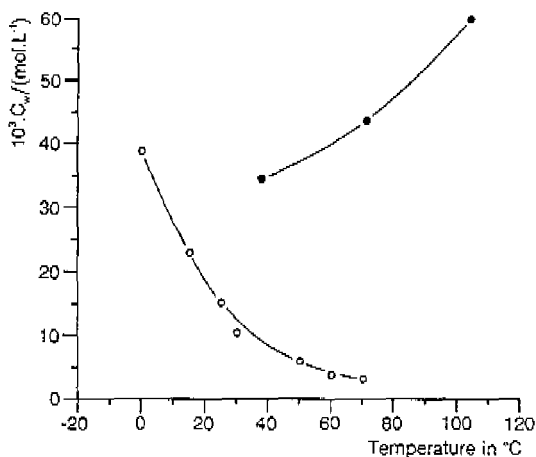
Figure 7.8. Solubility of butadiene in water C_{aq} as a function of temperature at 1 atmosphere ($\circ$),[21] and at butadiene saturation pressure ($\bullet$).[23]

Based on the above estimates for the parameters in equation (7.5), and using C_{aq} = 37 mmol.L^{-1} at 50°C, the exit rate coefficient for butadiene is expected to be at least one, and possibly two orders of magnitude larger than the one for styrene. Altogether, radical desorption by monomeric species in the emulsion polymerization of butadiene appears reasonable, but experimental evidence is as yet insufficient to substantiate this possibility. The similarity between the emulsion polymerization of more water-soluble monomers (e.g. vinyl acetate, methyl acrylate), kinetically dominated by desorption of monomeric radicals, and the butadiene emulsion polymerization, suggests that similar events determine the kinetic course in the present system.

Further research is necessary to elucidate the exact kinetic scheme, but the new results presented here certainly provide a much better understanding of the behaviour of this widely used monomer in emulsion polymerization systems.

7.6 Conclusions

The average rate per particle in interval II was found to depend strongly on particle size, indicating that $\bar{n}$ is either smaller or larger than 0.5. No constancy of R_{pol}/N associated with $\bar{n} = 0.5$ was found in the particle size range covered.

An analysis of interval III rates showed unambiguously that the present system follows zero-one kinetics with $\bar{n} < 0.5$, so that second-order termination cannot be rate-determining (except perhaps for very large particles).

By combining interval II and interval III rates of a single experiment, the conversion where interval III begins could be calculated. After correction for the non-ideal mixing of monomer and polymer, the saturation solubility of butadiene in polybutadiene was obtained, and found constant in interval II and independent of particle size.

Over the range of particle number N and initiator concentration [I] studied, R_{pol}/N (and thus ρ) was found only weakly dependent on [I], indicating a low initiator efficiency. This, in combination with the established zero-one kinetics of the system, makes R_{pol} virtually independent of [I] and N, in concordance with experimental findings.

Loss of free-radical activity within the particles is a first-order process, which is likely to be transfer to monomer followed by exit. The desorption rate coefficient of butadiene is expected to be significantly larger than the one of styrene, where $\bar{n}$ is often found close to 0.5 within fairly wide experimental limits. This also, at least qualitatively explains the observation that upon increasing the initial butadiene/styrene ratio from zero to one in the emulsion copolymerization of these monomers, the particle number increases, while the polymerization rate decreases (see section 1.1).[29,30] Beside a decrease in apparent k_p as the fraction of butadiene increases, $\bar{n}$ is also expected to drop off significantly, as a result of an increased exit rate.

Appendix   **Calculation of the saturation monomer concentration**

The beginning of interval III at conversion x' corresponds to a situation were the unreacted monomer is almost completely imbibed in the latex particles. For butadiene the small amount dissolved in the aqueous phase can be ignored.

Taking conversion x' at 0.60 (see section 7.3) and using ρ_p = 0.88 g.mL^{-1} and ρ_M = 0.565 g.mL^{-1} at 62°C, a value for C_M = 5.32 mol.L^{-1} is obtained, assuming ideal mixing of monomer and polymer. However, systems like these rarely behave ideally, which is revealed by measurements of the density of the polymerization system as a function of conversion. For this purpose an Anton Paar density meter with a remote cell (DMA 401, max. pressure 10 atm.) was employed. Samples were taken at regular time intervals, in between which the cell was flushed with distilled water. Conversions were determined gravimetrically as described previously (see section 3.2).
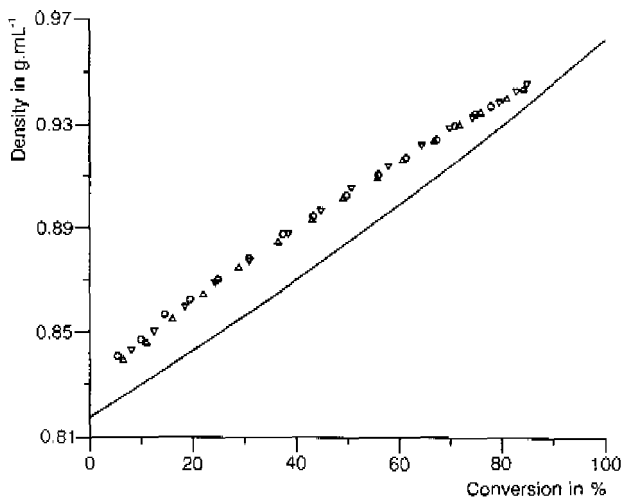
Figure 7.9. Density of the reaction mixture vs. gravimetric conversion. Symbols represent experimental points from three polymerizations (recipe 1), and the solid line the theoretical relationship, assuming ideal mixing of monomer and polymer.

The experimentally determined density-conversion relationship (Figure 7.9) differs markedly from that calculated assuming ideal mixing of monomer and polymer and additivity of specific volumes of the separate phases. Mutual solubility of butadiene and water is low enough to be ignored.

At conversions < 50 % the discrepancy between ideality and experiment may be partly caused by the instability of the monomer emulsion. Demixing started seconds after the cell was filled with a fresh latex sample. In the absence of a steady signal the minimum value for the density was taken, which may introduce a serious systematic error. It should be noted though that this minimum value was quite reproducible. In contrast, at conversions > 50 % measurements were free of this artifact and can be used without reservations.

At conversion $x' = 0.60$ only the aqueous phase and the monomer-swollen latex particles have to be considered. Additivity of the specific volumes of both phases is justified, since mutual solubility is negligible. From the experimentally determined density at 60 % conversion, the density of the swollen particles can be calculated. A volume contraction factor then can be defined as the ratio of 'ideal' to measured density of the swollen particles, which was found to be 0.95. The saturation monomer concentration C_M corrected for non-ideal mixing of monomer and polymer thus becomes 5.6 $mol.L^{-1}$, and was found independent of (unswollen) particle diameters between 30 and 150 nm (Figure 7.4).

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Chapter 8   Effects of Thiols

SUMMARY: The role of thiols of low water solubility, commonly used in the emulsion polymerization of butadiene, has been investigated. The following effects have become apparent: (1) these thiols act as efficient chain transfer agents in limiting the formation of heavily cross-linked polymer networks; (2) the monomer concentration within the particles is not affected by the thiol; (3) thiol radicals do not desorb because of their extremely low water solubility. The socalled 'promoting effect' of thiols in emulsion polymerizations of diene-hydrocarbons in fact appears to be related to impurities present in the emulsifier; this effect is completely absent in emulsifier-free polymerizations.

8.1 Introduction

In earlier chapters the *ab initio* emulsion polymerizations of butadiene with dresinate 214 and sodium dodecylsulfate as emulsifiers, both in the presence of tertiary dodecanethiol as chain transfer agent, were discussed. Chain transfer agents are routinally used in diene-polymerizations to limit the extent of branching and cross-linking of the polymer, and thus the amount of heavily cross-linked insoluble gel. A limited gel content greatly facilitates processability of the crude polymer, such as in the compounding of synthetic rubbers.

However, chain transfer agents also exert other, sometimes less desirable effects in emulsion polymerization systems. It is well known they can promote radical desorption,[1,2] thus lowering the rate of polymerization. Furthermore,

slightly water-soluble thiols were found to be essential to bring about reaction at acceptable rates in many persulfate-initiated polymerizations of butadiene(75)-styrene(25)[3] or butadiene,[4] a phenomenon referred to as the 'promoting effect'.

This chapter describes the various effects of the chain transfer agent tertiary dodecanethiol (t-DT) in the *ab initio* emulsion polymerization of butadiene, with regard to the process of gel formation as well as to the reaction kinetics.

8.2 Thiol as chain transfer agent

The gel point (i.e. the conversion at which the first insoluble polymer network makes its appearance) was determined with the vistex and extraction procedures described in section 3.6, for polymerizations with dresinate 214 (recipe 1) as emulsifier (Figure 8.1). Agreement between these techniques is good, as in both cases the same solvent/diluent was used. Results with varying amounts of t-DT are summarized in Table 8.1.
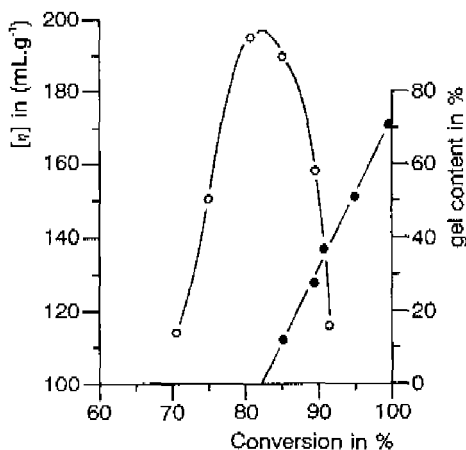
Figure 8.1. Determination of the gel point and gel content with the vistex (○) and toluene extraction procedure (●).

Table 8.1.   The gel points for polymerizations with dresinate
214 (recipe 1) and different amounts of t-dodecanethiol (t-DT).[a]

$10^3.C_{t\text{-}DT}$[b]	gelpoint in %		% conversion after				$10^5.R_{pol}$
$g.g^{-1}$	vistex	extraction	2hr	4hr	6hr	8hr	$g.mL^{-1}.s^{-1}$
0.0	25, 26	28	16	42	69	85	1.6
3.5	68, 73	72	18	42	68	87	1.6
7.0	83, 84	83, 84	15	43	71	89	1.7

[a]   Particle number is 1.0 ($\pm$ 0.05) 10^{15} mL^{-1} in all experiments.
[b] $C_{t\text{-}DT}$ expressed in grams t-DT per gram of butadiene.

As expected, the gel point goes to higher conversions with increasing amounts of thiol. However, there appears to be no significant effect on the polymerization kinetics; both R_{pol} and N are identical within experimental error.

Cross-linking and network formation may possibly affect the monomer solubility within the latex particles (and thus the kinetics). Even when monomer and polymer are completely miscible, the swelling of a particle is limited, because the free energy of mixing, which favours swelling, is counterbalanced by the resulting increase in interfacial energy. The monomer concentration C_M at saturation swelling is described by the Morton-Kaizerman-Altier equation:[5]

$$- H_v - H_v^2 \ln(1 - 1/H_v) = \chi + \frac{4\,V_M\,\gamma}{d\,RT}\,H_v^{5/3} \tag{8.1}$$

where H_v is the volume swelling ratio, V_M the molar volume of the monomer, d the unswollen particle diameter, χ the Flory-Huggins interaction parameter, γ the interfacial tension, **R** the gas constant and T the absolute temperature. H_v is related to the monomer volume fraction ϕ_M by: $H_v = 1/(1 - \phi_M)$.

For densely cross-linked latex particles the contribution of the elastic energy in limiting the swelling capacity is given by the Flory-Rehner theory,[6] and is expressed in equation (8.1) by an extra term on the left-hand side:

$$- (V_M\,\rho_p/M_c)(H_v^{5/3} - H_v/2) \tag{8.2}$$

where ρ_p is the polymer density and M_c the average molecular weight of the segments between two cross-links.

Given the large variation in gel point in the experiments described above, and consequently the large variation in cross-link density, the effect on C_M appears negligible. Apparently, even in the absence of t-DT the cross-link density is still too low (or alternatively M_c too large) to further restrict monomer solubility within the particles under the prevailing experimental conditions.

In section 7.3 an average value of x' = 0.60 (standard deviation 2.3 %) was determined for the conversion x' where interval III begins, and this value was found to be independent of particle size between 30 and 150 nm. The values of x' at different levels of t-DT for polymerizations with SDS (Table 8.2) and dresinate 214 were also found identical within experimental error, and in perfect agreement with those previous results. Consequently, the monomer concentration C_M must be constant and independent of the amount of t-DT.

Table 8.2.   The conversion x' where interval III begins, for
polymerizations with 32.4 g.L^{-1} SDS and varying amounts of t-DT.

$10^2.C_{t\text{-}DT}/g.g^{-1}$	0.0	0.0	0.7	1.4	2.8
conversion x'	0.616	0.609	0.598	0.610	0.625

8.3 Promoting effect of thiols

Another important effect of slightly water-soluble thiols is the socalled 'promoting effect'. At the time of the synthetic rubber program during World War II it was already known that the persulfate-initiated emulsion polymerization of butadiene or butadiene(75)-styrene(25) was extremely slow in the absence of an appropriate thiol. In the presence of such thiols, R_{pol} is virtually independent of the persulfate concentration within wide limits,[7] and above a

certain minimum level also independent of the amount of thiol.[3] Similar results were found for the emulsion polymerization of isoprene.[8] This rate-enhancing effect was commonly explained as being caused by a redox reaction between persulfate and thiol. Hydrogen abstraction by sulfate radical-anions would give uncharged, lyophilic thiol radicals, which supposedly are more efficient in entering a latex particle. Indeed, thiols containing 8 to 12 C-atoms solubilized in emulsifier solutions are being oxidized by persulfate to disulfides.[9] The latter compound is easily envisaged as being formed by combination of thiol radicals.

The promoting effect is reconsidered here qualitatively, using as emulsifiers dresinate 214, SDS, potassium stearate and potassium oleate, and as initiators sodium (SPS) or potassium persulfate (PPS), 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and 2,2'-azoisobutyronitrile (AIBN). In a preliminary communication[4] (Table 8.3) it was shown that the promoting effect was specific of persulfate-initiated polymerizations, with dresinate 214 as emulsifier. However, at lower concentrations of ACPA, the polymerizations in the absence of t-DT also become markedly slower (Figure 8.2, extension of Figure 4.1). The type and amount of initiator clearly plays an important role.
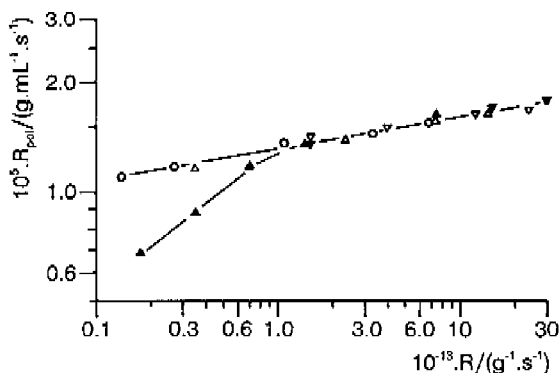

Figure 8.2. Variation of polymerization rate R_{pol} with radical production rate per gram emulsion R for three initiators in the presence (open symbols) and absence (full symbols) of t-dodecanethiol (recipe 1): PPS (○), ACPA (△) and AIBN (▽). For details on R see section 4.2.

The type of emulsifier also appears to be crucial in the promoting effect of t-DT, as Table 8.4 reveals large differences between the emulsifiers employed. It may be noted that Ishigure et al.[10] found a similar increase in R_{pol} of about 30 % with SDS in the radiation-induced emulsion polymerization of butadiene.

As pointed out by other investigators[3] reproducibility of the experiments without thiol is greatly affected by traces of impurities. Bhakuni[11] showed that with peroxide-containing emulsifiers some polymerization occurs in the absence of thiol, whereas with peroxide-free emulsifiers no polymerization was found. The results in Table 8.4 confirm the suggestion that impurities in the emulsifier need to be considered in relation to the poorly understood promoting effect.

Altogether, the experimental data presented here qualitatively confirm the observations from early literature, but also gross quantitative differences become apparent, related to the nature and concentration of emulsifier and initiator. This certainly is not helpful in clarifying the mechanistic role of thiols of low water solubility in the emulsion polymerization of butadiene. In an attempt to eliminate artifacts introduced by the emulsifier, *ab initio* emulsifier-free emulsion polymerizations with potassium persulfate as initiator were planned.

8.4 Emulsifier-free polymerizations

Emulsifier-free polymerizations in the presence and absence of t-DT were performed; the monomer/water ratio was chosen low (i.e. 1/9 by weight), to reduce the polymerization time to an acceptable level (after 25 hours a conversion of 90 % was reached).

The kinetics in interval II of both emulsifier-free polymerizations, and of similar polymerizations with emulsifier and t-DT, were all found identical within experimental error, taking into account the variation of R_{pol}/N with particle size. These data are consistent with the observation that R_{pol}/N is solely determined by particle size, and not by the parameters utilised to manipulate the final particle diameter (see section 7.2). This behaviour strongly suggests that the promoting effect is indeed related to impurities present in the emulsifier.

Table 8.3. Effect of the type and concentration of initiator on reaction kinetics, both in the presence and absence of t-DT. First part with dresinate 214 as emulsifier, and second part with SDS (C_E = 32.4 g.L^{-1}).

Initiator	10^3.[I] mol.L^{-1}	Polymerization with t-DT					Polymerization without t-DT				
		conversion in % after				10^5.R$_{pol}$ g.mL^{-1}.s^{-1}	conversion in % after				10^5.R$_{pol}$ g.mL^{-1}.s^{-1}
		2hr	4hr	6hr	8hr		2hr	4hr	6hr	8hr	
PPS	13.0	15	39	63	80	1.5	3	6	7	7	----
ACPA	13.0	14	38	67	84	1.6	14	39	65	82	1.6
AIBN	13.0	14	37	62	80	1.6	13	40	63	79	1.6
SPS	13.0	11	29	55	79	1.82	11	25	43	66	1.38
ACPA	13.0	--	--	--	--	-----	14	32	60	82	1.77
SPS	0.52	19	45	69	83	1.64	13	29	46	61	0.99
ACPA	0.52	--	--	--	--	-----	13	33	55	73	1.31

Table 8.4. Effect of the type of emulsifier on reaction kinetics, both in the presence and absence of t-DT.[a]

Emulsifier	[cation] mol.L^{-1}	Polymerization with t-DT						Polymerization without t-DT					
		conversion in % after					10^5.R$_{pol}$ g.mL^{-1}.s^{-1}	conversion in % after					10^5.R$_{pol}$ g.mL^{-1}.s^{-1}
		2hr	4hr	6hr	8hr	24hr		2hr	4hr	6hr	8hr	24hr	
Dresinate	0.4	15	39	63	80	99	1.52	3	6	7	7	10	-----
K-stearate	0.16	21	46	75	89	100	1.85	3	6	8	9	20	-----
K-oleate	0.16	15	37	65	82	100	1.71	2	3	4	6	20	0.21[b]
SDS	0.3	11	29	55	79	99	1.82	11	25	43	66	98	1.38

[a] Initiator is persulfate; [I] = 13.10^3 mol.L^{-1}.   [b] R$_{pol}$ determined between 20 to 35 % conversion.

Table 8.5.   Emulsifier-free emulsion polymerizations of butadiene.

C_s	$10^3.C_{t-DT}$	$10^5.R_{pol}$	$10^{20}.R_{pol}/N$	d_v at 90 %	P
$g.L^{-1}$	$g.g^{-1}$	$g.mL^{-1}.s^{-1}$	$g.s^{-1}$	nm	
0.0	0.0	0.19	4.7	173	1.26
0.0	7.0	0.18	3.9	167	1.16
4.0[a)]	7.0	0.79	4.9	173	1.03

Experimental details emulsifier-free runs : M/W = 1/9 (w/w),
[PPS] = 10 mmol.L^{-1}, [K$_2$CO$_3$] = 10 mmol.L^{-1}, n = 500 rpm.
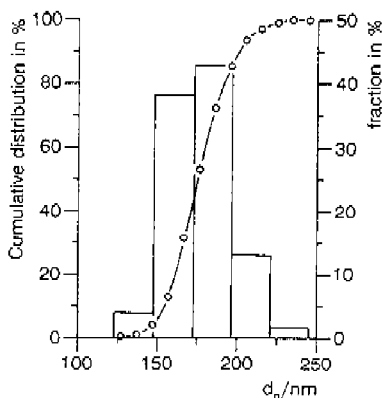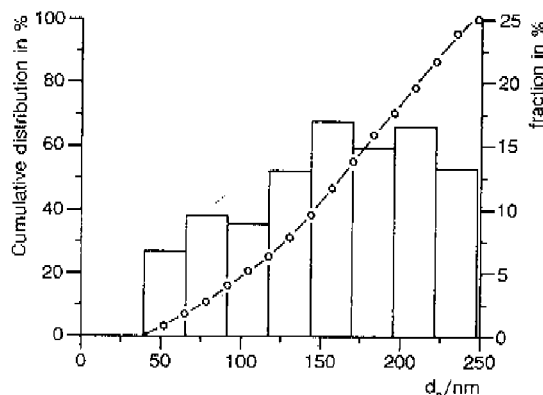[a)] Polymerization described in section 5.2.

Figure 8.3.   The cumulative (○) and fractional particle size distributions versus number average diameter d_n for the emulsifier-free polymerization without t-dodecanethiol (top), and the polymerization with 4.0 g.L^{-1} SDS and t-DT (bottom). For details see text.

The particle size and size distribution of the final latexes of these emulsifier-free polymerizations (Figure 8.3), reveal some other marked peculiarities.

For the emulsifier-free emulsion polymerization of styrene Goodwin et al.[12] have derived an empirical correlation between the particle diameter, initiator and monomer concentration, ionic strength, and temperature. From this relationship it follows that under the experimental conditions specified in Table 8.5, a monodisperse polystyrene (PS) latex with a diameter of 700 nm would be obtained. In contrast, the polybutadiene (PB) latexes are highly polydisperse, and of a significantly smaller diameter. The large polydispersity strongly suggests that (homogeneous) particle nucleation is not restricted to the very beginning of the polymerization (i.e. interval I), and that once formed, the PB-particles are highly stable toward coagulation. Consequently, the number of stabilizing SO_4^--groups (introduced by the initiator) on PB-particles must be significantly larger than on PS-particles prepared under identical conditions. This is consistent with the observation that the rate of volume growth, being proportional to k_p and $\bar{n}$, for a PB-particle is significantly smaller than for an equally sized PS-particle.

Although the socalled promoting effect is still not completely understood, some aspects have become clearer, such as:
- The structure and purity of the emulsifier, as well as concentration and type of initiator, all play a crucial role.
- There is no apparent reason why sulfate radical anions (or oligomers thereof) should not initiate butadiene, as is shown in the persulfate initiated emulsifier-free polymerizations in the absence of thiol.
- Although this does not disprove the involvement of thiol radicals in the initiation mechanism in polymerizations with emulsifier, a simple redox reaction between thiol and persulfate would oversimplify the actual situation.

The most puzzling aspect yet remains to be solved: why is the promoting effect specific of diene-hydrocarbons, such as butadiene and isoprene, and not showing up when using other monomers. Styrene can readily be polymerized without a chain transfer agent, using any type of initiator or emulsifier (including dresinate 214), both at widely varying concentrations.

8.5 Radical desorption

Regardless of the complexity of the data presented above, one common characteristic is the observation that addition of t-DT never decreases the steady state R_{pol}, nor the average rate per particle R_{pol}/N. If a chain transfer agent were facilitating radical desorption, a decrease in R_{pol}/N is expected, whereas all experimental data indicate the reverse.

Nomura et al.[1] investigated the effect of radical desorption by chain transfer agents in the emulsion polymerization of styrene. Carbon tetrachloride and tetrabromide, ethanethiol, and n-butanethiol were found to give extensive radical desorption; in contrast, n-dodecanethiol (n-DT) did not affect the polymerization rate nor the particle number. The fact that n-DT radicals apparently do not desorb was attributed to their extremely low water solubility. The concentration of n-DT was varied between $2.7 \ 10^{-5}$ and $1.1 \ 10^{-4}$ mol.g^{-1} styrene, comparable with that in the present system, viz. $3.5 \ 10^{-5}$ mol t-DT per gram butadiene.

Table 8.6. Effect of various grades of dodecanethiol in polymerizations with 32.4 $g.L^{-1}$ sodium dodecylsulfate (recipe 2).

thiol	conversion in % after				$10^5.R_{pol}$	d_{90}[c]	x'
	2hr	4hr	6hr	8hr	$g.mL^{-1}s^{-1}$	nm	
t-DT[a]	11	29	55	79	1.82	46	0.598
t-DT[b]	11	29	56	79	1.82	44	0.613
n-DT	13	32	62	83	1.88	51	0.608

[a] t-DT supplied by Pennwalt.   [c] d_w at 90 % conversion.
[b] t-DT supplied by Fluka.

A final check was made in relation to the quality of the commercial grade t-DT (supplied by Pennwalt), a crude mixture of C_{12}-isomers which may contain small amounts of lower and higher thiols. Additional polymerizations were performed (Table 8.6), using a mixture of only two tertiary C_{12}-isomers (supplied by Fluka; for structures see section 3.6) and pure n-DT. Both polymerizations with t-DT were found identical, while the one with n-DT was only slightly faster.

This latter observation is in accord with results reported by Kolthoff.[3] However, allowing for the difference in particle size and the dependence of $\bar{n}$ on particle size, the average rates per particle are equivalent for all three C_{12}-thiols used. Radical desorption of dodecanethiol radicals is obviously negligible, regardless of the structure and composition of the dodecanethiol employed.

8.6 Conclusions

From a kinetic standpoint, t-dodecanethiol appears to behave as an 'ideal' chain transfer agent in the emulsion polymerization of butadiene; it regulates cross-linking efficiently, but otherwise does not affect the reaction kinetics:

- Eventhough the gel point varies widely with the initial amount of thiol, C_M and x' were both found constant within experimental error. Even in the absence of a chain transfer agent, the extent of cross-linking is still to low to restrict the monomer swelling of latex particles.

- Dodecanethiol radicals do not desorb, regardless of their structure and composition, as a result of an extremely low water solubility.

The promoting effect of slightly water-soluble thiols appears specific of diene-hydrocarbon monomers, but the phenomenon is still poorly understood. Nevertheless, some aspect can now be placed in a better perspective:

- Sulfate radical-anions (or oligomers thereof) are capable of initiating the emulsion polymerization of butadiene, as was shown in the emulsifier-free experiments, which show polymerization with an R_{pol}/N identical to that of reactions with emulsifier and thiol leading to the same final particle size.

- Despite this observation, many authors (including the present one) have reported on the retardation of butadiene emulsion polymerizations in the absence of an appropriate thiol, using different types of emulsifiers.

- The extent of retardation in the absence of thiol depends on the structure, concentration and chemical purity of the emulsifier and initiator employed.

- It has become clear that a simple redox reaction between a sulfate radical anion and thiol is inadequate to provide a satisfactory explanation.

Appendix   **Anomalous effects with dresinate 214 as emulsifier**

A strange phenomenon was encountered when particle numbers were compared of polymerizations with dresinate 214 in the presence (initiator PPS) and absence (initiator ACPA) of t-DT (Figure 8.4, extension of Figure 4.5). On the basis of the previous discussion the choice of the initiator at $[I] = 13.10^{-3}$ mol.L^{-1} and the absence of t-DT is not expected to cause any disparity in the final particle number. This is indeed found for all polymerizations with $C_{B} \leq 32.4$ g.L^{-1}. However, the polymerization with $C_{B} = 64.8$ g.L^{-1} is markedly different with regard to the final N; without t-DT the particle number is significantly larger ($N = 9.10^{15}$ mL^{-1}) than in its presence ($N = 3.10^{15}$ mL^{-1}; see Figure 8.4)). The same phenomenon was encountered again (although less pronounced), when lowering the monomer/water weight ratio in recipe 1 from 3/7 to 2/8, keeping all other ingredients constant on water basis.
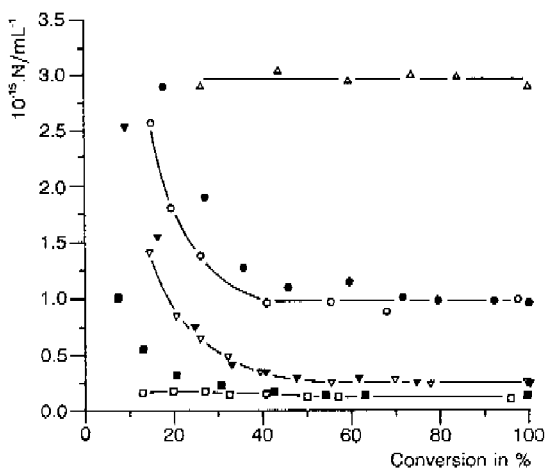

Figure 8.4. Development of particle number N with conversion for polymerizations in the presence (open symbols) and absence of t-DT (full symbols) at different dresinate 214 concentrations $C_{E} = 64.8$ g.L^{-1} *(△);* $C_{B} = 32.4$ g.L^{-1} *(○);* $C_{E} = 16.2$ g.L^{-1} *(▽);* $C_{E} = 8.1$ g.L^{-1} *(□).*

This effect was studied more systematically by varying the amount of t-DT using ACPA as initiator ($[I] = 13.10^{-3}$ mol.L^{-1}), and determining the final particle diameter at 90 % conversion (Figure 8.5). A steady increase in particle diameter d_w is observed. Figure 8.5 also contains data points for both standard recipes with dresinate 214 and sodium dodecylsulfate. For the polymerizations with 64.8 g.L^{-1} dresinate 214, the conversion-time curves (Figure 8.6) and the particle size distributions (PSD) of the final latexes (Table 8.7) were also determined.
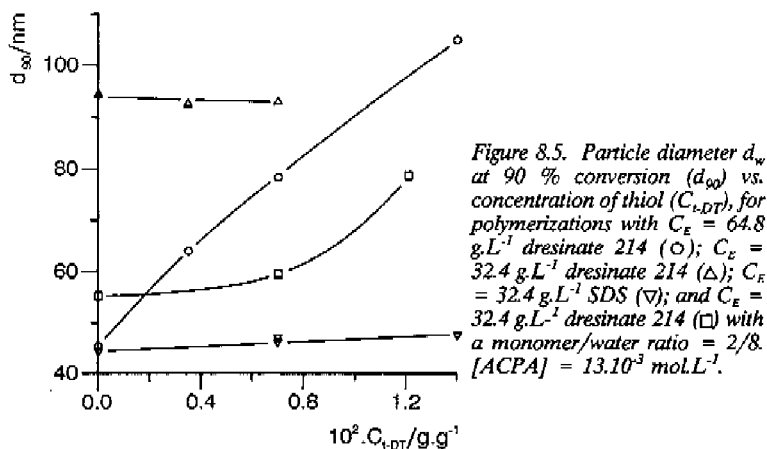
Figure 8.5. Particle diameter d_w at 90 % conversion (d_{90}) vs. concentration of thiol (C_{t-DT}), for polymerizations with $C_E = 64.8$ g.L^{-1} dresinate 214 (○); $C_E = 32.4$ g.L^{-1} dresinate 214 (△); $C_F = 32.4$ g.L^{-1} SDS (▽); and $C_E = 32.4$ g.L^{-1} dresinate 214 (□) with a monomer/water ratio = 2/8. [ACPA] = 13.10^{-3} mol.L^{-1}.

Table 8.7. Data on particle size distributions of latexes prepared with 64.8 g.L^{-1} dresinate 214 and varying amounts of t-dodecanethiol t-DT.

$10^2.C_{t-DT}$ g.g^{-1}	c in %	d_n nm	d_w nm	d_{min} nm	d_{max} nm	sd nm	P
0.0	99.7	45	50	25	69	8	1.1
0.7	99.0	63	76	21	104	20	1.2
1.4[a)]	99.2	88	112	32	140	29	1.3
2.8	99.4	64	103	25	170	30	1.6

Abbreviations: d_{min} and d_{max} are the minimum and maximum particle diameter d_n, respectively, and sd the standard deviation.
[a)] Particle size distribution slightly bimodal.
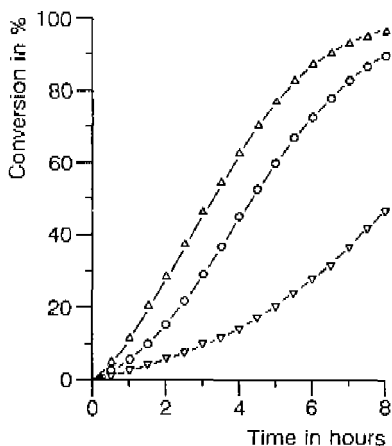
Figure 8.6. Conversion vs. time curves for polymerizations with C_E = 64.8 g.L^{-1} dresinate 214 and [I] = 13.0 mmol.L^{-1} ACPA, with varying amounts of t-DT $C_{t\text{-}DT}$ = 0.0 g.g^{-1} (Δ); $C_{t\text{-}DT}$ = 1.4 10^{-2} g.g^{-1} ($\circ$); and $C_{t\text{-}DT}$ = 2.8 10^{-2} g.g^{-1} ($\triangledown$).

Increasing the amount of t-DT clearly prolongs the particle nucleation period, resulting in a broadening of the PSD. Obviously, we are dealing with an exceptional behaviour, since this phenomenon was only encountered at a relatively high dresinate 214 to butadiene ratio, and not at all with SDS at comparable particle sizes. Radical desorption or cross-linking cannot provide a plausible explanation, as is evident from the discussion in the preceding sections. It may very well be that, as in the case of the promoting effect, impurities present in dresinate 214, interact with t-DT and/or persulfate, thereby influencing the radical entry rate and thus the particle nucleation rate in these *ab initio* experiments. Further research is necessary to unravel the exact role of thiols of low water solubility in the mechanism of radical entry, especially in emulsion polymerizations of diene-hydrocarbons.

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Summary

Emulsion polymerization is an extremely complex process, as it comprises a heterogeneous reaction system, consisting of three distinct phases: the aqueous phase, a colloidal dispersion of polymer particles, and a monomer emulsion. Radical polymerization may commence simultaneously in any of these phases, while exchange of material between the phases always needs to be considered.

This thesis attempts to provide a consistent overview of the effects of all relevant chemical, colloidal and physical parameters on the emulsion polymerization of butadiene. The reason for selecting butadiene is twofold: (1) although it was one of the first monomers to be studied systematically, very little is known about its kinetic behaviour in the context of recent models and theories; (2) polybutadiene containing polymers are of significant commercial importance.

As a starting point was chosen a typical industrial recipe, including the commercial emulsifier dresinate 214 (chapter 4). A study of the effects of initiator ([I]) and emulsifier concentration ([E]) led to the following preliminary conclusions: (1) initiator efficiency appears to be low; (2) particle formation is coagulative in nature; (3) the average number of radicals per particle $\bar{n} \neq 0.5$.

These observations were further tested by performing analogous reactions with sodium dodecylsulfate as emulsifier (chapter 5). It was shown that the coagulation was caused by the high ionic strength of the aqueous phase. Kinetic relationships between particle number, and [I] and [E], take a complex form when coagulation is involved. The dependence of average rate per particle (equivalent to $\bar{n}$) on particle size was found identical for both emulsifiers used, despite the enormous differences in composition, purity and performance.

Being a heterogenous system, emulsion polymerization is susceptible to the agitation conditions (chapter 6). The following effects were established: (1) at high stirring speeds (equivalent to impeller Reynolds number $Re > 10^4$) the effective emulsifier concentration, and consequently the final particle number, decrease significantly due to emulsifier adsorption onto the monomer droplets; (2) at low stirring speeds the polymerization becomes diffusion-controlled, as a result of a (partial) phase separation of the monomer emulsion. Simultaneously the particle number increases as less emulsifier is adsorbed onto the droplets. At monomer volume fractions > 0.6, additional effects occur as mixed monomer emulsions are formed, affecting both particle number and polymerization rate.

The combined kinetic information of intervals II and III of the *ab initio* experiments discussed above, unambiguously showed (chapter 7) that $\bar{n} < 0.5$ (except perhaps for very large particles). This implies that bimolecular termination within the particles is not rate-determining, and that radical exit from the particles is significant. The latter is most likely to be facilitated by oligomeric butadiene radicals. The low $\bar{n}$ behaviour, in combination with a low initiator efficiency, explains the small effect [I] has on polymerization rate.

Lastly, the role of C_{12}-thiols was considered. Apart from being effective chain transfer agents, no additional effects were found: (1) monomer solubility within the particles was found independent of the amount of thiol, and (2) the corresponding thiol radicals do not exit due to their low water solubility. With regard to the rate-enhancing promoting effect, it was found that impurities present in other recipe ingredients strongly determine its magnitude. In persulfate-initiated emulsifier-free polymerizations the promoting effect was found to be completely absent.

Based on this work, further research may be focused on the following items: (1) a full kinetic investigation of the emulsion polymerization of butadiene, preferably using monodisperse seed latexes, in order to obtain reliable values for the rate coefficients of propagation, exit, and possibly termination; (2) a mechanistic interpretation of the first-order radical loss process; (3) to provide an adequate explanation for the puzzling promoting effect of thiols in diene-hydrocarbon polymerizations.

Samenvatting

Emulsiepolymerisatie is een uitermate complex proces, daar het een heterogeen reactiesysteem vertegenwoordigt, bestaande uit drie verschillende fasen: de waterige fase, een colloidale dispersie van polymeerdeeltjes en een monomeeremulsie. Radicaalpolymerisatie kan gelijktijdig in elk van deze fasen plaatsvinden, evenals een continue uitwisseling van materiaal tussen de fasen.

Dit proefschrift beoogt een min of meer compleet overzicht te geven van de invloed van alle relevante chemische, colloidale en fysische parameters op de emulsiepolymerisatie van butadieen. Hierbij is voor butadieen gekozen, omdat: (1) ondanks het feit dat butadieen een van de eerste monomeren is dat systematisch is bestudeerd, is van het kinetische gedrag nog steeds weinig bekend; (2) polybutadieen bevattende polymeren van groot commercieel belang zijn. Als uitgangspunt werd een typisch industriële receptuur gekozen, met de commerciele emulgator dresinaat 214 (hoofdstuk 4). Uit de invloed van de initiator- ([I]) en emulgatorconcentratie ([E]) konden de volgende voorlopige conclusies worden getrokken: (1) de initiator efficiency is laag; (2) deeltjes-vorming is coagulatief; (3) het gemiddeld aantal radicalen per deeltje $\bar{n} \neq 0,5$.

Deze waarnemingen werden geverifieerd door analoge experimenten uit te voeren met natrium dodecylsulfaat als emulgator (hoofdstuk 5). Hierbij is aangetoond dat de coagulatie veroorzaakt wordt door de hoge ionensterkte. Kinetische relaties tussen het aantal deeltjes, [I] en [E], nemen hierdoor een complexe vorm aan. De afhankelijkheid van de gemiddelde snelheid per deeltje (equivalent met $\bar{n}$) van de deeltjesgrootte was identiek voor beide emulgatoren, ondanks hun grote verschil in samenstelling, zuiverheid en performance.

Vanwege het heterogene karakter zijn emulsiepolymerisaties gevoelig voor de roercondities (hoofdstuk 6). De volgende effecten zijn waargenomen: (1) bij hoge roersnelheden (met een Reynoldsgetal $Re > 10^4$) nemen de effectieve emulgatorconcentratie en het aantal deeltjes significant af, tengevolge van adsorptie van emulgator op de monomeerdruppels; (2) bij lage roersnelheden is de polymerisatie diffusiegelimiteerd, vanwege een (gedeeltelijke) fasenscheiding van de monomeeremulsie. Bij monomeer volumefracties > 0.6 treden additionele effecten op, doordat gemengde monomeeremulsies worden gevormd, hetgeen zowel het aantal deeltjes als de polymerisatiesnelheid beïnvloedt.

De gecombineerde kinetische informatie uit de intervallen II en III van de hierboven beschreven *ab initio* experimenten (hoofdstuk 7) toont onomstotelijk aan dat $\bar{n} < 0,5$ (behalve misschien voor grote deeltjes). Dit betekent dat bimoleculaire terminatie in de latexdeeltjes niet snelheidsbepalend is, terwijl radicaaldesorptie aanzienlijk moet zijn. Het laatste gebeurt vermoedelijk door oligomere butadieenradicalen. Het lage $\bar{n}$-gedrag, in combinatie met een lage initiator efficiency, verklaart het geringe effect van [I] op de reactiesnelheid.

Als laatste is de rol van C_{12}-thiolen bekeken. Naast de functie van effectief chain transfer agent, zijn hierbij geen additionele effecten waargenomen: (1) de monomeeroplosbaarheid in de latexdeeltjes is onafhankelijk van de hoeveelheid thiol, en (2) thiol radicalen desorberen niet vanwege hun geringe water oplosbaarheid. Met betrekking tot het snelheidsverhogende 'promoting effect' van thiolen is gevonden dat dit medebepaald wordt door verontreinigingen aanwezig in de andere ingrediënten. In persulfaat-geïnitieerde emulgatorvrije polymerisaties bleek het promoting effect volledig afwezig.

Gebaseerd op dit werk, zou toekomstig onderzoek zich op de volgende gebieden kunnen richten: (1) een volledig kinetisch onderzoek van de emulsiepolymerisatie van butadieen, bij voorkeur met monodisperse seedlatexen, gericht op het bepalen van nauwkeurige waarden voor de snelheidsconstanten van propagatie, desorptie en terminatie; (2) een mechanistische interpretatie van het eerste-orde radicaal verlies proces; (3) een verklaring van het promoting effect van thiolen bij de emulsiepolymerisatie van dieen-koolwaterstoffen.

Glossary of Symbols

Symbol		SI-units
a	dimensionless parameter, defined by a $= (8\alpha)^{0.5}$	-----
A	surface of a monomer-swollen particle	m^2
A_p	total interfacial area per unit volume of dispersed phase	m^{-1}
A_e	specific area per emulsifier molecule	m^2
c	(fractional) conversion	-----
C_E	emulsifier concentration on weight basis	$kg.m^{-3}$
C_M	monomer concentration within a particle	$mol.m^{-3}$
C_M^o	initial monomer concentration within a particle	$mol.m^{-3}$
C_{aq}	monomer concentration in the aqueous phase	$mol.m^{-3}$
d	average particle diameter	m
d_M	average monomer droplet diameter	m
d_{sw}	swollen particle diameter	m
d_{xx}	diameter at xx % conversion	m
D	impeller diameter	m
D_r	reactor diameter	m
D_p	diffusion coefficient in a particle	$m^2.s^{-1}$
D_{aq}	diffusion coefficient in the aqueous phase	$m^2.s^{-1}$
e	fundamental electronic charge	A.s
g	gravitational constant	$m.s^{-2}$
H_v	volume swelling ratio	-----
I	Bessel function of the first kind	-----
k	(first-order) rate coefficient for radical exit	s^{-1}

k_a	rate coefficient for radical absorption	s^{-1}
k_d	rate coefficient for initiator decomposition	s^{-1}
k_p	propagation rate coefficient	$m^3.mol^{-1}.s^{-1}$
k_t	rate coefficient for bimolecular termination	$m^3(.mol^{-1}).s^{-1}$
k_{tr}	rate coefficient for transfer to monomer	$m^3.mol^{-1}.s^{-1}$
k_{taq}	termination rate coefficient in the aqueous phase	$m^3.mol^{-1}.s^{-1}$
k	Boltzmann constant	$kg.m^2.K^{-1}.s^{-2}$
m	dimensionless parameter, defined by $m = k.v/k_t$	-----
M_c	average molecular weight of segments between two cross-links	-----
M_n	number-average molecular weight	-----
M_w	weight-average molecular weight	-----
M/W	monomer to water weight ratio	-----
n	stirring speed	s^{-1}
$\bar{n}$	average number of radicals per particle	-----
n_i	number of particles with diameter d_i	-----
n_M	amount of monomer present at the beginning of interval III, per unit volume of aqueous phase	$mol.m^{-3}$
$n_M{}^\circ$	amount of monomer initially present per unit volume of aqueous phase	$mol.m^{-3}$
N	particle number per unit volume of aqueous phase	m^{-3}
N_n	number of particles containing n free radicals	-----
N_{Av}	Avogadro's number	mol^{-1}
P	polydispersity index, defined by $P = d_w/d_n$	-----
q	partition coefficient of exiting species between particles and the aqueous phase	-----
R	rate of radical production (per unit amount of emulsion), assuming 100 % initiator efficiency	$kg^{-1}.s^{-1}$
R	gas constant	$kg.m^2.K^{-1}.mol^{-1}.s^{-2}$
R_{pol}	rate of free radical polymerization	$kg(or\ mol).m^{-3}.s^{-1}$
R_{pol}/N	average rate per particle	$kg(or\ mol).s^{-1}$
Re	Reynolds impeller number, defined by $Re = D^2 n \rho / \mu$	-----

t	settling time of a dispersion	s
t_o	reference settling time	s
t_{cr}	critical time, duration of interval I	s
$t_{1/2}$	half life time	s
t_{xx}	period of time required to reach xx % conversion	s
T	absolute temperature	K
v	volume of a (monomer-swollen) particle	m^3
V	total volume of polymer per unit volume of aqueous phase	-----
V_M	monomer molar volume	$m^3.mol^{-1}$
w_p	weight fraction of polymer (on a monomer-polymer basis)	-----
x	fractional conversion in interval III	-----
x'	(fractional) conversion where interval III begins	-----
Y	dimensionless parameter, defined by $Y = 2Nk_t k_{taq}/k_a^2 v$	-----
z	parameter in the Nomura transfer/diffusion model	-----
α	dimensionless parameter, defined by $\alpha = \rho_a v/Nk_t$	-----
α'	dimensionless parameter, defined by $\alpha' = \rho_i v/Nk_t$	-----
γ	interfacial tension	$kg.s^{-2}$
ε_o	permittivity of free space	$kg.m.A^{-2}.s^{-2}$
ε_r	relative permittivity	-----
ς	Zeta potential	$kg.m^2.A^{-1}.s^{-3}$
θ	temperature in degrees Celsius	K
ϑ	particle volume growth rate in the Smith-Ewart theory	$m^3.s^{-1}$
κ	parameter in the Debye-Hückel theory	m^{-1}
μ	(average) dynamic viscosity	$kg.m^{-1}.s^{-1}$
ν	kinematic viscosity, defined by $\nu = \mu/\rho$	$m^2.s^{-1}$
ρ	(pseudo-first-order) rate coefficient for radical entry	s^{-1}
ρ_x	(average) density of substance or phase x	$kg.m^{-3}$
$\Delta\rho$	density difference	$kg.m^{-3}$
ρ_a	rate of radical entry	$m^{-3}.s^{-1}$

ρ_i	rate of radical production in the aqueous phase	$m^{-3}.s^{-1}$
σ	ionic strength	$mol.m^{-3}$
φ	volume fraction	-----
ϕ_M	monomer volume fraction within a particle	-----
χ	Flory-Huggins interaction parameter	----
ψ_o	surface potential of a particle	$kg.m^2.A^{-1}.s^{-3}$
ψ_r	potential at a distance r from the centre of a particle	$kg.m^2.A^{-1}.s^{-3}$
[E]	emulsifier concentration	$mol.m^{-3}$
$[E]_{eff}$	effective emulsifier concentration	$mol.m^{-3}$
[I]	initiator concentration	$mol.m^{-3}$
[M]	monomer concentration	$mol.m^{-3}$
$[R^*]$	free radical concentration	$mol.m^{-3}$
$[\eta]$	intrinsic viscosity	$m^3.kg^{-1}$

Subscripts and abbreviations:

aq	aqueous phase		n	number-average
c	continuous phase		p	polymer, propagation
D	dispersed phase		s	surface-average
E	emulsifier		v	volume-average
L	latex		w	weight-average
M	monomer			

Curriculum Vitae

De schrijver van dit proefschrift werd op 23 augustus 1959 in Breda geboren. Hij behaalde in 1976 het havo diploma en in 1978 het atheneum-B diploma, beide aan de Newman-Ypelaar scholengemeenschap in Breda.

In 1978 begon hij aan de studie Scheikundige Technologie aan de Technische Universiteit Eindhoven, alwaar het kandidaatsexamen met lof werd afgelegd in februari 1982. Het doctoraalexamen met lof, tesamen met de onderwijsbevoegdheid voor scheikunde, werden behaald in september 1985, na een afstudeerwerk op het gebied van de synthetisch organische chemie onder leiding van prof. dr. E.F. Godefroi.

In oktober 1985 werd een aanvang gemaakt met het promotieonderzoek naar de emulsiepolymerisatie van butadieen in de vakgroep Polymeerchemie en Kunststoftechnologie (TUE), onder leiding van prof. dr. ir. A.L. German. In het kader hiervan verbleef hij drie maanden aan de School of Chemistry, Sydney University, in de groep van prof. dr. R.G. Gilbert en prof. dr. D.H. Napper.

Per 1 januari 1990 trad hij in dienst bij DSM Research in Geleen, als researchmedewerker op de afdeling CP-harsen.

Dankwoord

Bij deze wil ik iedereen bedanken voor de getoonde belangstelling, de wetenschappelijke bijdragen, de ondersteuning op technisch en administratief gebied en niet in de laatste plaats voor de warme collegialiteit, waardoor ik met veel plezier en enthousiasme aan mijn promotie heb kunnen werken.

Stellingen

(behorende bij het proefschrift van P.A. Weerts)

Het bepalen van de oplosbaarheid van butadiëen in water bij drukken kleiner dan 1 atmosfeer gaat volledig voorbij aan het feit dat met dit gasvormige monomeer altijd onder verhoogde druk wordt gewerkt.

J.W. McBain, J.J. O'Connor, *J. Am. Chem. Soc.* **63**, 875 (1941)

Eenmaal gepubliceerd kunnen data hardnekkig blijven circuleren, ongeacht hun betrouwbaarheid of relevantie. Dit blijkt ondermeer uit recente literatuur-waarden voor de wateroplosbaarheid van butadiëen, welke allen teruggaan op het werk van McBain en O'Connor, echter zonder specificatie van de originele experimentele condities.

F.A. Bovey, I.M. Kolthoff, A.I. Medalia, E.J. Meehan, in *"Emulsion Polymerization"*, Interscience, New York 1955, p.156
W.M. Saltman, in *"Encyclopedia of Polymer Science and Technology"*, Interscience, New York 1965, 1st ed., vol. 2, p. 682
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D.C. Blackley, *"Emulsion Polymerisation - Theory and Practice"*, Applied Publishers, London 1975, p.441
G.W. Poehlein, in *"Emulsion Polymerization"*, edited by I. Piirma, Academic Press, New York 1982, p.372
J.W. Vanderhoff, *J. Polym. Sci., Polym. Symp.* **72**, 161 (1985)

Het gebruik van de zogenaamde 'bottle polymerizer' voor kinetisch onderzoek aan heterogene systemen is ten sterkste af te raden, dit in verband met de zeer inefficiënte menging.

Hoofdstuk 6 uit dit proefschrift.

Inconsequent gebruik van de eenheden gram en mol in een en hetzelfde artikel kan leiden tot grote verwarring en komt derhalve de wetenschappelijke betrouw-baarheid niet ten goede.

M. Nomura, Y. Minamino, K. Fujita, M. Harada, *J. Polym. Sci., Polym. Chem. Ed.* **20**, 1261 (1982)

De beschrijving van de copolymerisatiekinetiek van styreen en acrylonitril in aanwezigheid van polybutadiëen door Hagiopol et al., gaat volledig voorbij aan het heterogene karakter van de gevormde ABS-resin.

C. Hagiopol, T. Deleanu, T. Memetea, *J. Appl. Polym. Sci.* **37**, 947 (1989)

De modellering van de emulsiepolymerisatie van butadiëen zoals beschreven door Morbidelli et al. laat overtuigend zien dat een goede data-fit nog niet betekent dat het gebruikte model ook correct is.

M. Morbidelli, G. Storti, S. Carrà, *J. Appl. Polym. Sci.* **28**, 901 (1983)

"Onbekend maakt onbemind". De grootschalige industriële toepassing en lang-durige historische ontwikkeling van butadiëen in emulsiepolymerisatieprocessen, suggereert, geheel ten onrechte, een grote bekendheid met de kinetiek van dit monomeer.

Hoofdstukken 1 t/m 8 uit dit proefschrift.

Terugdringen van het autogebruik middels financiële maatregelen zal weinig effect sorteren, omdat de automobilist bereid is een (te) hoge prijs voor zijn individuele vrijheid te betalen.

Herstel van de Oostduitse economie lijkt het meeste gebaat bij teruggave van alle onteigende goederen aan de voormalige eigenaren (vooropgesteld dat ze die rotzooi uberhaupt nog terug willen).

N.a.v. claim Solvay op zes Oostduitse chemische installaties, *Chemisch Weekblad* d.d. 22 maart 1990.

Afschaffing van de wettelijke bescherming van alle universitaire titels met uitzondering van de doctorstitel, zoals voorgesteld door de minister van onderwijs, is wellicht een probaat middel om het promoveren wat aantrekkelijker te maken.

Uitspraak minister Ritzen, *NRC Handelsblad* d.d. 13 april 1990.

Tijdens congressen en symposia overtreft het aantal doctoren altijd het aantal gepromoveerden.