

## Emulsion polymerization of butadiene. 3. Kinetic effects of stirring conditions and monomer/water ratio

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## Emulsion polymerization of butadiene, 3<sup>a)</sup>

### Kinetic effects of stirring conditions and monomer/water ratio

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#### SUMMARY:

The stirring speed  $n$  influences the emulsion polymerization of butadiene, (1) by reducing the effective emulsifier concentration  $[E]_{\text{eff}}$  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  $[E]_{\text{eff}}$ , and thus the final particle number. At monomer volume fractions  $> 0,6$  mixed emulsions are likely to be formed initially, reducing  $[E]_{\text{eff}}$  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.

#### Introduction

In previous publications<sup>1–3)</sup> 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 (see *Results and discussion*). The physico-chemical properties of the monomer emulsion may markedly affect the course of the polymerization.

The effect of stirring on emulsion polymerization is a somewhat neglected aspect in this line of research; only a few studies have been reported<sup>4–6)</sup>. The main conclusions reached in these studies are: (1) the effective emulsifier concentration  $[E]_{\text{eff}}$  in the aqueous phase may be reduced by adsorption of emulsifier molecules onto the monomer droplets, especially with  $[E] \approx \text{CMC}$ ; (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.

<sup>a)</sup> Part 2: cf. 2).

## Experimental part

*Materials:* All materials used were of high purity quality, except *t*-dodecanethiol which was a crude mixture of C<sub>12</sub>-isomers, and Dresinate 214 which was a disproportionated aqueous dispersion of abietic acid-type of derivatives with dehydro-, dihydro- and tetrahydroabietic acid as main components, and less than 0,2% abietic acid. The standard recipes and reaction conditions are given in Tab. 1, while experimental details are described elsewhere<sup>1,2)</sup>.

Tab. 1. Standard polymerization recipes in parts by weight<sup>a)</sup>

Ingredient	Recipe 1	Recipe 2
Water	230	230
Butadiene	100	100
Dresinate 214	7,6	
Sodium dodecyl sulfate (SDS)		7,6
K <sup>+</sup> /Na <sup>+</sup> carbonate <sup>b)</sup>	4,4	2,0
K <sup>+</sup> /Na <sup>+</sup> persulfate <sup>b)</sup>	0,8	0,7
<i>t</i> -Dodecanethiol	0,7	0,7

a) [Initiator] = 13 mmol · L<sup>-1</sup>, temp. = 62 °C, pH 10,5–10,8.

b) In recipe 1 potassium salts and in recipe 2 sodium salts were used.

*Characterization:* Conversion data were based on the total solid content of samples collected with a high-pressure-proof syringe. The average particle diameter was measured by dynamic light scattering (DLS, Malvern Ilc) and transmission electron microscopy (TEM, Philips 420 and Jeol 2000 FX). The definitions of relevant particle size parameters were given previously<sup>2)</sup>.

The particle number density per unit volume of water ( $N$ ) was calculated according to

$$N = \frac{6c(M/W)}{(\rho_p/\rho_{aq})\pi\bar{d}^3} \quad (1)$$

where  $c$  is the fractional conversion, ( $M/W$ ) the monomer to water weight ratio,  $\rho_{aq}$  the density of aqueous phase,  $\rho_p$  the polymer density and  $\bar{d}$  the average particle diameter.

## Results and discussion

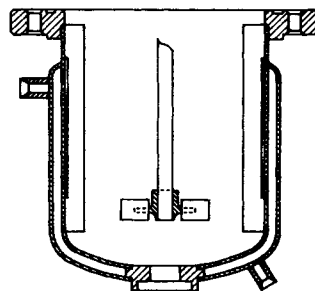
The course of an emulsion polymerization is conveniently divided into three distinct intervals. Interval I is the initial stage where particle formation takes place. Interval II is characterized by a constancy of particle number, while polymerization in the particles proceeds in the presence of a separate monomer phase. The beginning of interval II is sometimes taken as the conversion where the emulsifier concentration drops below the critical micelle concentration (CMC). Interval III begins with the disappearance of monomer droplets, after which the monomer concentration in the particles starts to decrease continuously.

### *Effects of 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 (Fig. 1). In two series

Fig. 1. Cross section of the polymerization reactor

Reactor dimensions in mm	
Impeller diameter	60
Reactor diameter	134
Baffle diameter	13,4
Blade diameter	18
Reactor height	175



of experiments, one with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 (using recipe 1) and another with  $16,2 \text{ g} \cdot \text{L}^{-1}$  SDS (using recipe 2), the stirring speed  $n$  was varied and the final particle number  $N$  determined (Fig. 2). In all cases the system was preemulsified by stirring a few minutes at 400 r.p.m., before adjusting  $n$  to the desired level. In both reaction systems, at sufficiently high  $n$  the particle number was found to be 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

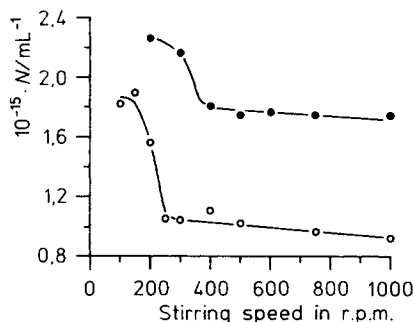


Fig. 2.

Fig. 2. Final particle number  $N$  vs. stirring speed, for polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 (○) and  $16,2 \text{ g} \cdot \text{L}^{-1}$  SDS (●)

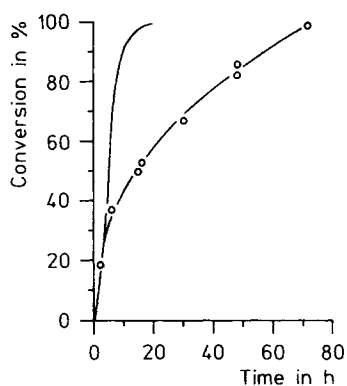


Fig. 3.

Fig. 3. Conversion vs. time curves for polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 (recipe 1), at a stirring speed  $n = 400$  r.p.m. (unbroken line; data points omitted) and  $n = 100$  r.p.m. (○)

always satisfactory, especially at low  $n$ , the change in  $N$  is considered significant. As pointed out earlier, the effective emulsifier concentration  $[E]_{\text{eff}}$  available for particle nucleation and stabilization is influenced by adsorption of emulsifier onto the monomer droplets. At high  $n$  the droplets will be finely dispersed and  $[E] > [E]_{\text{eff}}$ . Going to lower  $n$ , agitation ultimately becomes insufficient to counterbalance droplet

coalescence, so that  $[E]_{\text{eff}}$ , and thus  $N$ , increase. Since the change in  $N$  is discontinuous, the phenomenon must be related to the flow conditions.

The impeller Reynolds number  $Re$ , defined as the ratio of inertial forces vs. viscous forces in an agitated liquid system, can be used as an indicator of the overall conditions of flow. In the case of mechanical agitation,  $Re = D^2 n \rho / \mu$ , where  $D$  is the impeller diameter, and  $\rho$  and  $\mu$  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<sup>7,8)</sup>:

$$\rho = \varphi_C \rho_C + \varphi_D \rho_D \quad (2)$$

$$\mu = \frac{\mu_C}{\varphi_C} \left[ 1 + \frac{1,5 \mu_D \varphi_D}{\mu_D + \mu_C} \right] \quad (3)$$

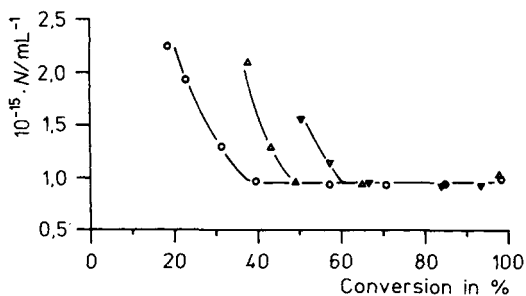
where  $\varphi$  is the volume fraction, while the subscripts C and D denote the continuous and the dispersed phase, respectively.

For the polymerizations depicted in Fig. 2 with  $\varphi_D = 0,43$ ,  $n \geq 230$  r.p.m. will provide sufficient turbulency (i.e.  $Re \geq 10^4$ ). Agreement with measured values for  $n$  above which  $N$  is constant is reasonable, 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 when  $[E]_{\text{eff}} \approx \text{CMC}$ , 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 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 Fig. 3, showing conversion vs. time curves for polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 at 100 r.p.m. and 400 r.p.m. The curve at  $n = 100$  r.p.m. is based on a small number of data points, as representative samples could not be taken due to the inhomogeneity of the system. Each data point at  $n = 100$  r.p.m. stems from a separate polymerization, as conversion was determined by raising  $n$  to 400 r.p.m. with samples taken a few minutes later.

For these polymerizations where the stirring speed  $n$  is raised from 100 to 400 r.p.m., the development of the particle number  $N$  after the increase in  $n$  is shown in Fig. 4. In all cases  $N$  decreases to a level corresponding to that for an experiment with  $n = 400$  r.p.m. from the start of the polymerization. Redispersion of the monomer by raising  $n$  creates new interface, whereupon emulsifier molecules adsorb. Emulsifier molecules

Fig. 4. Particle number  $N$  vs. conversion for polymerizations (recipe 1) where the stirring speed is raised from 100 to 400 r. p. m. at different conversions: 18% ( $\circ$ ); 37% ( $\Delta$ ); 50% ( $\nabla$ )



will desorb from the latex particles, introducing colloidal instability and thus a (limited) decrease in  $N$ .

The pressure in the system 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 (Fig. 5a). At  $n = 100$  r. p. m. a different behaviour is observed experimentally; the pressure drops below the butadiene saturation pressure roughly at the end of interval I, and decreases gradually with time, to drop off sharply at the end of the polymerization (Fig. 5c). Upon raising  $n$  from 100 to 400 r. p. m. somewhere in 'interval II', the pressure rises immediately to saturation pressure and behaves normally after that (Fig. 5b). 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,

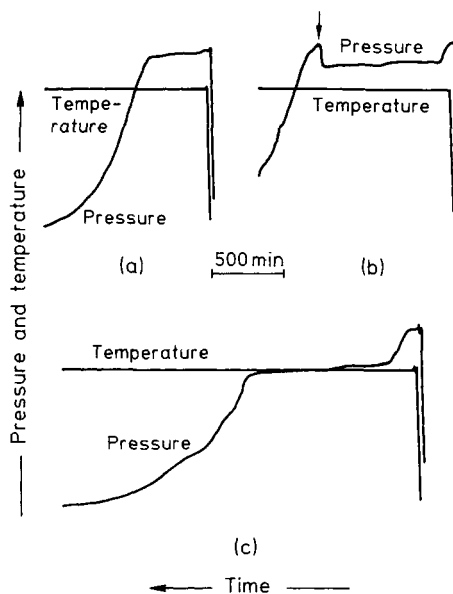


Fig. 5. Recordings of temperature and pressure for polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214, at a stirring speed  $n = 400$  r. p. m. (a);  $n$  raised from 100 r. p. m. to 400 r. p. m., indicated by the arrow (b);  $n = 100$  r. p. m. (c)

the temperature in the gas phase will decrease somewhat, and pressure can no longer be maintained at saturation level.

For dispersions of two poorly miscible pure liquids, an empirical correlation for the total interfacial area per unit volume of dispersed phase,  $A_D$ , was obtained by Rodger et al.<sup>9)</sup>:

$$A_D = \frac{K}{D} \left( \frac{D^3 n^2 \rho_C}{\gamma} \right)^{0,36} \left( \frac{D}{D_r} \right)^{K_a} \left( \frac{v_D}{v_C} \right)^{1/5} \left( \frac{t}{t_0} \right)^{1/6} \exp \left[ 3,6 \frac{\Delta \rho}{\rho_C} \right] \Phi \quad (4)$$

where  $K$  and  $K_a$  are constants,  $D$  the impeller diameter,  $D_r$  the reactor diameter,  $t$  the settling time of the dispersion,  $t_0$  the reference settling time,  $\gamma$  the interfacial tension,  $\Delta \rho$  the density difference,  $\nu$  the kinematic viscosity ( $= \mu/\rho$ ), and  $\Phi$  a scale-up function. This relation is in accordance with the model for agitated dispersions proposed by Shinnar and Church<sup>10)</sup>, 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.<sup>11)</sup>:

$$n_{\min} = K' \left( \frac{D_r}{D} \right)^{K'_a} \frac{g^{0,42} \Delta \rho^{0,42} \mu^{0,08} \gamma^{0,04} \varphi_D^{0,05}}{D^{0,71} \rho^{0,54}} \quad (5)$$

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

Strictly 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  $\nu$ , 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  $\gamma$  and increasing the settling time  $t$ . The unique physical properties of liquid butadiene (b. p. =  $-4,4^\circ\text{C}$ ) tend to increase  $n_{\min}$  and  $A_D$  (i. e., reduce the average droplet diameter), relative to other monomers (e. g., styrene; b. p. =  $145^\circ\text{C}$ ) under otherwise identical conditions (Tab. 2). It is evident that the 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, so that a small average diameter of the monomer droplets is expected in the present system.

Tab. 2. Physical properties<sup>a)</sup> of butadiene, styrene and water at  $62^\circ\text{C}$

Pure liquid	$\frac{10^4 \cdot \mu}{\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}}$	$\frac{10^7 \cdot \nu}{\text{m}^2 \cdot \text{s}^{-1}}$	$\frac{\rho}{\text{kg} \cdot \text{m}^{-3}}$	$\Delta \rho/\rho_C$ <sup>b)</sup>
Butadiene	0,93	1,65	565	0,42
Styrene	4,58	5,28	868	0,12
Water	4,53	4,61	982	—

a)  $\mu$ : dynamic viscosity,  $\nu$ : kinematic viscosity,  $\rho$ : density.

b) For monomer emulsions in water;  $\rho_C$ : density of continuous phase.

The average droplet diameter of a monomer emulsion  $\bar{d}_M$  can be found anywhere between  $5 \cdot 10^{-5}$  m and  $1 \cdot 10^{-6}$  m, depending on the method of emulsification<sup>12)</sup>. Based on the previous discussion,  $\bar{d}_M$  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  $\text{OsO}_4$ -staining of a butadiene emulsion prepared at 400 r.p.m. with  $16,2 \text{ g} \cdot \text{L}^{-1}$  SDS. The procedure is a modified version of the technique described by Yang<sup>13)</sup>. In short, a sample of the initial emulsion was taken with a  $10^{-4} \text{ dm}^3$  GLC sampling valve (modified for the purpose), and immediately contacted with a surplus  $\text{OsO}_4$  by pushing 10 mL of a 2 wt.-%  $\text{OsO}_4$ -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 measurements with SEM and TEM (Fig. 6). Particle counting gave an average diameter of  $8 \cdot 10^{-7}$  m; although not exact (the uptake of  $\text{OsO}_4$  will affect density somewhat), the order of magnitude is considered typical for these systems, especially since in all recipes  $[\text{E}] \gg \text{CMC}$ .

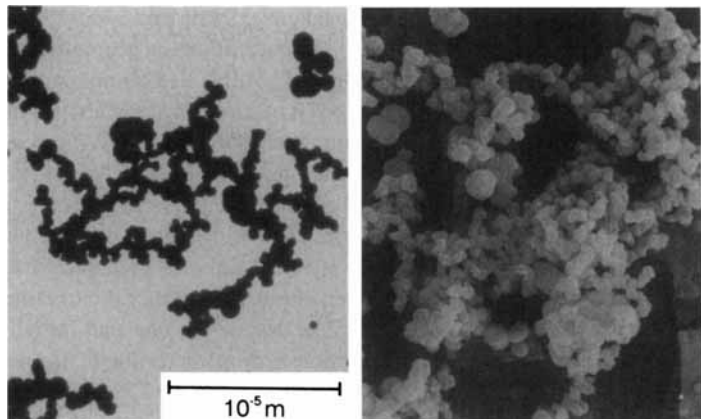


Fig. 6. Transmission electron micrograph (a) and scanning electron micrograph (b) of an  $\text{OsO}_4$ -stained butadiene emulsion, prepared at a stirring speed  $n = 400$  r.p.m., in the presence of  $16,2 \text{ g} \cdot \text{L}^{-2}$  SDS (recipe 2)

Using  $A_E = 42 \cdot 10^{-20} \text{ m}^2$  for the specific area per molecule SDS<sup>2)</sup>, the effective emulsifier concentration in the aqueous phase, for the recipe with  $16,2 \text{ g} \cdot \text{L}^{-1}$  SDS, varies with  $\bar{d}_M$  as shown in Fig. 7. With  $\bar{d}_M \approx 10^{-6}$  m, it follows that ca. 30% SDS is initially adsorbed onto the droplets, despite the fact that  $[\text{E}] \gg \text{CMC}$  ( $= 0,17 \text{ g} \cdot \text{L}^{-1}$ )<sup>2)</sup>. In contrast, Nomura et al.<sup>6)</sup> concluded for the emulsion polymerization of styrene using SDS as emulsifier, that emulsifier adsorption on monomer droplets and the effect of stirring thereupon were both insignificant for recipes with  $[\text{E}] \geq 12 \text{ CMC}$ .

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 probably small, as particle formation is coagulative in nature, and stops at



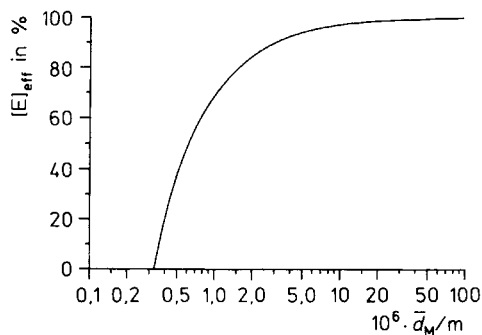


Fig. 7. Effective emulsifier concentration  $[E]_{\text{eff}}$  vs. average droplet diameter  $\bar{d}_M$  for a butadiene emulsion with 16,2  $\text{g} \cdot \text{L}^{-1}$  SDS and a monomer/water ratio  $M/W = 3/7$  (recipe 2), with  $[E]_{\text{eff}}$  calculated according to  $\{1 - 6(M/W)/([E] - \text{CMC}) A_E N_{\text{Av}} \bar{d}_M \rho_M\} \cdot 100$  (for symbols see text)

40–45% conversion<sup>1,2)</sup>, 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<sup>14)</sup> conveniently ignored radical entry into monomer droplets, as emulsification normally gives values for  $\bar{d}_M$  in the size range of  $2 - 5 \cdot 10^{-6}$  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  $> 5 \cdot 10^{-7}$  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.

Similar results were reported for styrene emulsions prepared with ultrasonification, with  $\bar{d}_M \approx 10^{-6}$  m<sup>12)</sup>. After polymerization, the weight ratio of large to 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 (estimate of present authors using  $A_E = 45 \cdot 10^{-20}$  m<sup>2</sup> for Aerosol MA<sup>15)</sup>).

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

— The value for  $\bar{d}_M$  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  $[E] \gg \text{CMC}$ . As polymerization proceeds,  $[E]$  drops below the CMC and  $\bar{d}_M$  must increase due to a higher rate of droplet coalescence. The number of droplets decreases further 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 (pseudo-)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 Fig. 8, giving the PSDs of the final latexes prepared with  $8,1 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 (recipe 1) at different  $[\text{K}^+]$  (Tab. 3).

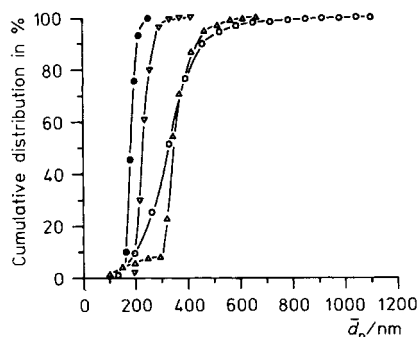


Fig. 8.

Fig. 8. Cumulative particle size distributions for polymerizations with  $8,1 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 at different overall  $[\text{K}^+] = 0,40 \text{ mol} \cdot \text{L}^{-1}$  ( $\circ$ );  $[\text{K}^+] = 0,375 \text{ mol} \cdot \text{L}^{-1}$  ( $\triangle$ );  $[\text{K}^+] = 0,35 \text{ mol} \cdot \text{L}^{-1}$  ( $\nabla$ );  $[\text{K}^+] = 0,325 \text{ mol} \cdot \text{L}^{-1}$  ( $\bullet$ ).  $M/W = 3/7$  (recipe 1)

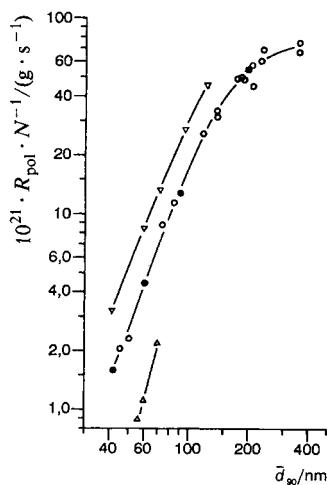


Fig. 9.

Fig. 9. Average rate per particle  $R_{\text{pol}}/N$  vs. particle diameter at 90% conversion ( $\bar{d}_{90}$ ), for polymerizations reported in this investigation at  $62^\circ\text{C}$  ( $\circ$ ), from Wendler et al.<sup>19)</sup> at  $70^\circ\text{C}$  ( $\nabla$ ), and Morton et al.<sup>17)</sup> at  $60^\circ\text{C}$  ( $\triangle$ ). Data of first two investigations based on volume-average diameters  $\bar{d}_v$ , and of ref.<sup>17)</sup> on surface-average diameters  $\bar{d}_s$ . Full circles indicate experiments with  $32,4 \text{ g} \cdot \text{L}^{-1}$  SDS at different monomer/water ratios  $M/W$  (see text)

Tab. 3. Data on polymerization kinetics and particle size distributions for experiments with  $8,1 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 (recipe 1) at different overall  $[\text{K}^+]$

$[\text{K}^+]$ $\text{mol} \cdot \text{L}^{-1}$	Time in h	Conv. in %	$10^6 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$	$\bar{d}_v^{\text{a}}$ at 90% in nm	$P^{\text{b}}$	$f(\bar{d}_w) >$ $5 \cdot 10^{-7} \text{ m}^{\text{c}}$
0,325	25	96	6,9	181	1,04	—
0,35	30	90	4,3	236	1,05	—
0,375	72	94	1,4	358	1,14	0,14
0,40	120	93	0,88	375	1,49	0,35

<sup>a</sup>  $\bar{d}_v$  = volume-average diameter ( $= \{\sum n_i \cdot d_i^3 / \sum n_i\}^{1/3}$ ).

<sup>b</sup>  $P$  = polydispersity index, defined as  $P = \bar{d}_w / \bar{d}_n$ , with  $\bar{d}_w$  the weight-average ( $= \sum n_i \cdot d_i^4 / \sum n_i \cdot d_i^3$ ) and  $\bar{d}_n$  the number-average diameter ( $= \sum n_i \cdot d_i / \sum n_i$ ).

<sup>c</sup>  $f(\bar{d}_w)$  = fraction of particles with diameter  $\bar{d}_w$ .

Under turbulent flow conditions ( $Re > 10^4$ ), butadiene emulsions with a small  $\bar{d}_M$  can be prepared relatively facile, even with customary equipment, partly because 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 emulsion 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 (low)  $n$ , ultimately leading to a diffusion-controlled polymerization. This is in agreement with experimental results (Fig. 3).

An illustrative example of ineffective mixing found in literature is the radiation-induced emulsion polymerization of butadiene reported by Ishigure et al.<sup>16)</sup> Glass ampoules filled with butadiene emulsions were placed on a rotating wheel\*). 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 normal using the rotating wheel device. This is consistent with our observations that at  $Re < 10^4$  phase separation is relatively facile for butadiene emulsions, while emulsions of styrene under identical conditions may remain adequately dispersed. Also, styrene, being more reactive than butadiene, will probably 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.<sup>17)</sup> The so-called bottle polymerization technique was used, where bottles were rotated vertically end-over-end at 35 r. p. m. The initial degree of filling of the bottles was extremely high, about 90%<sup>18)</sup>. Experimental results thus obtained, together with data from Wendler et al.<sup>19)</sup> (using a 2-litre reactor with  $n = 360$  r. p. m.) and the present investigation, are shown in Fig. 9 as a log-log plot of the average rate per particle  $R_{pol}/N$  vs. particle diameter at 90% conversion  $\bar{d}_{90}$ . The values for  $R_{pol}/N$  from Morton et al.<sup>17)</sup> 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 (i. e., soap titration in ref.<sup>17)</sup>). Again, ineffective mixing appears responsible for this behaviour. It should be noted that the value for  $k_p$  determined by Morton et al.<sup>20)</sup> ( $k_p = 100$  L · mol<sup>-1</sup> · s<sup>-1</sup> at 62 °C) is significantly smaller than our lower limit estimate, viz.,  $k_p \geq 180$  L · mol<sup>-1</sup> · s<sup>-1</sup><sup>3)</sup>. This is to be expected when the polymerization is diffusion controlled; a lower value for  $R_{pol}$  inevitably results in a lower value for  $k_p$ .

### *Effects of the monomer/water ratio*

Commercial emulsion polymerization processes in batch-operation are, for obvious economical reasons, performed at the highest polymer content feasible. For industrial

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

butadiene emulsion polymerizations monomer to water weight ratios ( $M/W$ ) up to  $3/2$  are employed<sup>21</sup>). 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. Tab. 4 shows the final particle number as a function of the stirring speed  $n$  at  $M/W = 1$  with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214. Emulsions appear adequately stabilized by turbulence at  $n > 400$  r. p. m.; using  $\varphi_D = 0,64$ , the condition  $Re = 10^4$  is satisfied when  $n = 450$  r. p. m.

Tab. 4. Effect of the stirring speed  $n$  on final particle number  $N$  for polymerizations at  $M/W = 1$  with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 (recipe 1)

	200	300	$n$ in r. p. m. 400	500	750
$10^{-15} \cdot N/\text{mL}^{-1}$	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-viscous systems ( $\mu \leq 50 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ ). This was indeed experienced at  $M/W = 3/2$ , where power consumption increased drastically and temperature control was poor. For these polymerizations, a low pitch helical ribbon agitator was chosen at  $n = 300$  r. p. m. 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 particle number. The monomer to water weight ratio  $M/W$  was varied between  $1/4$  and  $3/2$ , with both Dresinate 214 and sodium dodecylsulfate (SDS) as emulsifiers. All other recipe ingredients were kept constant on water basis. Conversion vs. time curves for polymerizations with SDS at varying  $M/W$  are given in Fig. 10, and those of polymerizations with Dresinate 214 at  $M/W = 3/2$  and different emulsifier concentrations in Fig. 11. The dependence of final particle number on  $M/W$  for polymerizations with both emulsifiers is shown in Fig. 12.

It should be noted that the volume fraction  $\varphi$  of butadiene is considerably larger than the corresponding weight fraction. For example, for  $M/W = 1$ , the initial  $\varphi$  is 0,64, and

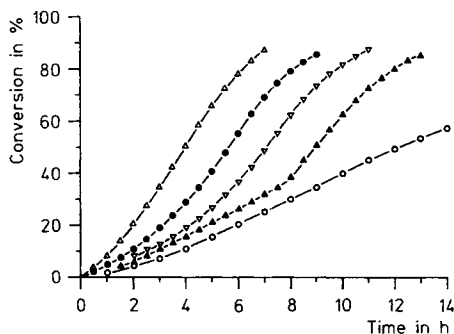


Fig. 10. Conversion vs. time curves for polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  SDS (recipe 2), at different monomer/water ratios:  $M/W = 1/4$  ( $\Delta$ );  $M/W = 3/7$  ( $\bullet$ );  $M/W = 2/3$  ( $\nabla$ );  $M/W = 1$  ( $\blacktriangle$ );  $M/W = 3/2$  ( $\circ$ )

for  $M/W$  3/2 even 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.<sup>9)</sup> noted in their investigation with pure liquids\*) 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 positions of the impeller. For butadiene  $\Delta\rho/\rho_C = 0,42$  (Tab. 2). Nevertheless, the use of anionic water-soluble emulsifiers will strongly favour o/w emulsions.

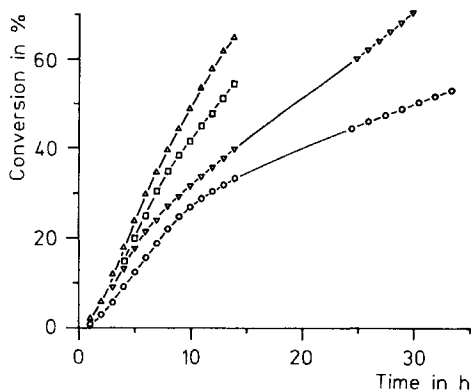


Fig. 11.

Fig. 11. Conversion vs. time curves for polymerizations with a monomer/water ratio  $M/W = 3/2$ , at different Dresinate 214 concentrations:  $C_E = 61,6 \text{ g} \cdot \text{L}^{-1}$  ( $\Delta$ );  $C_E = 51,8 \text{ g} \cdot \text{L}^{-1}$  ( $\square$ );  $C_E = 42,1 \text{ g} \cdot \text{L}^{-1}$  ( $\nabla$ );  $C_E = 32,4 \text{ g} \cdot \text{L}^{-1}$  ( $\circ$ )

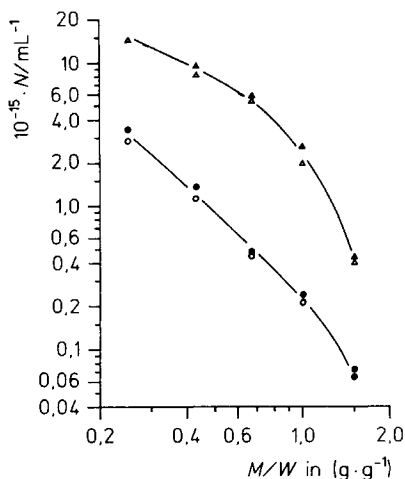


Fig. 12.

Fig. 12. Final particle number  $N$  vs. monomer/water ratio  $M/W$ , for polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 ( $\circ$ ) and  $32,4 \text{ g} \cdot \text{L}^{-1}$  SDS ( $\Delta$ ). Particle sizing by dynamic light scattering (open symbols) and transmission electron microscopy (full symbols)

Although a thorough knowledge of the behaviour of butadiene emulsions seems crucial, a microscopic study is virtually impossible due to the low boiling point of butadiene (b. p. =  $-4,4^\circ\text{C}$ ). 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 (Fig. 13). These experiments 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 observed.

\*) Volume fraction of the organic phase believed to be 0,5.

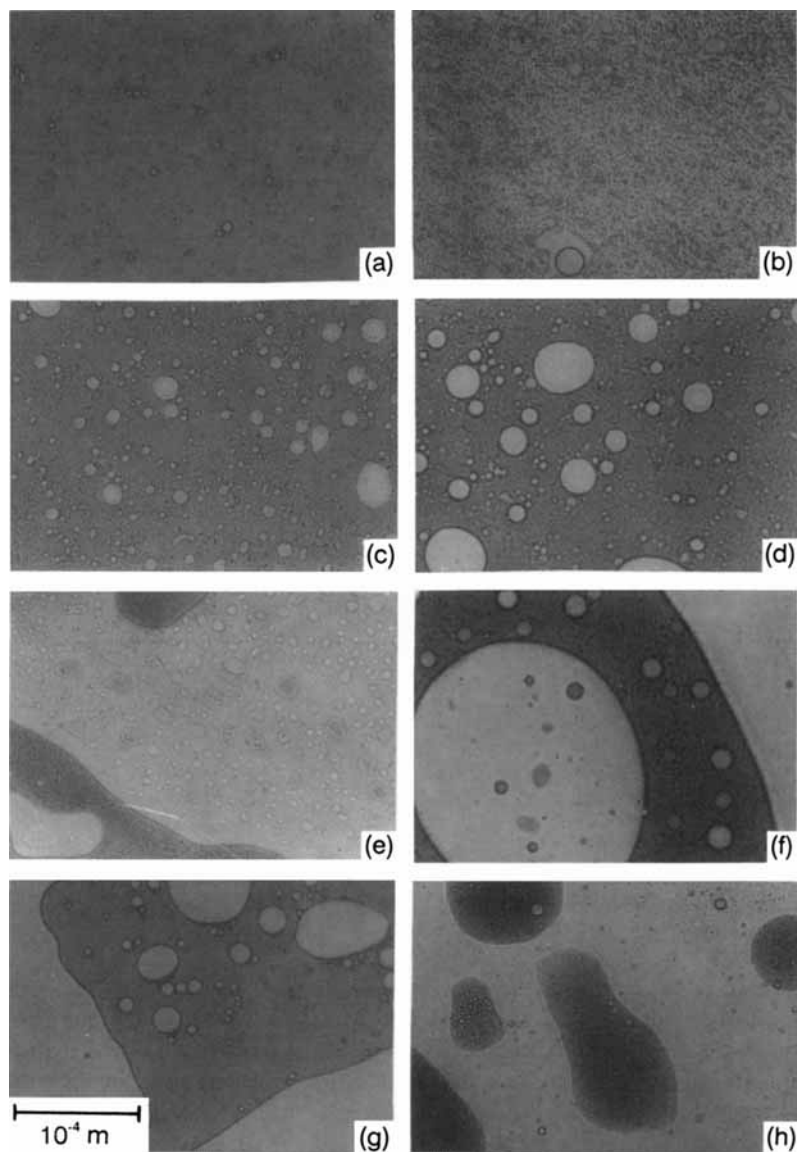


Fig. 13. Optical micrographs of (handshaken) styrene emulsions in the presence of  $32,4 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214, at different styrene volume fractions  $\varphi = 0,20$  (a);  $\varphi = 0,30$  (b);  $\varphi = 0,40$  (c);  $\varphi = 0,50$  (d);  $\varphi = 0,60$  (e–f);  $\varphi = 0,70$  (g); and  $\varphi = 0,80$  (h). Light areas represent styrene domains

Obviously, increasing  $\varphi$  at a constant emulsifier concentration, must lead to a decrease in  $[E]_{\text{eff}}$ , and thus in final  $N$ . At  $M/W \geq 1$  (i.e.  $\varphi \geq 0,63$ ), when mixed

emulsions are formed,  $[E]_{\text{eff}}$  and  $N$  will decrease even further. This is clearly observable in the experiments with SDS as emulsifier (Fig. 12).

The type of emulsion may also affect the course of polymerization. As interval II ends at 60% conversion<sup>3)</sup> (Tab. 5), it is obvious that many conversion vs. times curves at high  $M/W$  have two kinetic regimes in interval II. In the presence of a mixed emulsion, the monomer phase as a locus for polymerization might no longer be neglected. As polymerization proceeds, the monomer volume fraction  $\phi$  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  $\phi$ . Any change in type of emulsion, which is usually abrupt, will then 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). Yet, an experimental testing of this hypothesis is extremely difficult, since butadiene emulsions cannot be studied directly.

Tab. 5. Kinetic data of polymerizations with  $32,4 \text{ g} \cdot \text{L}^{-1}$  SDS (recipe 2) and different monomer/water ratios  $M/W$

$M/W$ $\text{g} \cdot \text{g}^{-1}$	$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$	$\bar{d}_v^{\text{a)}$ at 90% in nm	$P^{\text{a)}$	$x'^{\text{b)}$
1/4	1,1	—	—	0,593
3/7	1,8	44	1,06	0,598
2/3	2,6	60	1,07	0,588
1	1,5 <sup>c)</sup>	—	—	—
	3,4	90	1,06	0,607
3/2	2,1	197	1,30	—

a) See Tab. 3.

b)  $x'$  = Conversion where interval III begins<sup>3)</sup>.

c) Rate before the inflection point.

However, the kinetics of the experiments with  $32,4 \text{ g} \cdot \text{L}^{-1}$  SDS at different  $M/W$  (Fig. 10) provide some useful indications (Tab. 5). The average rate per particle  $R_{\text{pol}}/N$  for these polymerizations is indicated in Fig. 9 by the full circles. The polymerization with  $M/W = 1$  is of special interest, as it shows a clear positive rate inflection. The rate  $R_{\text{pol}}$  used to calculate  $R_{\text{pol}}/N$  is the one after the inflection point. As can be seen in Fig. 9, the experiment with  $M/W = 1$  (with  $\bar{d}_{90} = 90 \text{ nm}$ ) fits in perfectly with the rest; the second regime appears to be that of a 'true' emulsion polymerization (for the first  $R_{\text{pol}}/N = 5,6 \cdot 10^{-21} \text{ g} \cdot \text{s}^{-1}$ ). On the other hand, polymerization in the first regime is faster than anticipated on the basis of the experiments at lower  $M/W$ . Besides 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  $M/W = 3/2$  was significant; the PSD showed a profound positive skewness, with particles as large as  $6 \cdot 10^{-7} \text{ m}$ . This was not observed in the final PSDs at  $M/W < 1$ .

The polymerizations at  $M/W = 3/2$  with  $61,6 \text{ g} \cdot \text{L}^{-1}$  Dresinate 214 ( $\bar{d}_v = 174 \text{ nm}$  at 90%) and  $32,4 \text{ g} \cdot \text{L}^{-1}$  SDS both lack a clear inflection point; both final particle sizes are comparable. Decreasing the concentration of Dresinate 214 at  $M/W = 3/2$  led to smaller particle numbers, but at the same time a negative inflection in the conversion vs. time curves became apparent (Fig. 11). Such 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 (Fig. 6 in ref.<sup>2)</sup>, with  $8,1 \text{ g} \cdot \text{L}^{-1}$  SDS and  $[\text{K}^+] = 0,5 \text{ mol} \cdot \text{L}^{-1}$ ). Polymerization in the monomer phase again appears competitive in the initial stage of polymerization, this time because of the extremely low particle number.

The leveling off at  $\bar{d}_{90} > 200 \text{ nm}$  of  $R_{\text{pol}}/N$  in Fig. 9 thus appears 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.

## 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  $[\text{E}]_{\text{eff}}$ , as a result of the relatively 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, easily leading to a diffusion-controlled polymerization, whereas other monomer systems may still behave normal.

Increasing  $M/W$  at constant  $[\text{E}]$  leads to a decrease in the final  $N$ , as  $[\text{E}]_{\text{eff}}$  decreases. An additional reduction of  $N$  was found at  $M/W \geq 1$ , presumably because mixed emulsions are formed which reduce  $[\text{E}]_{\text{eff}}$  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 reasonable indications that the (change in) type of emulsion is responsible for the observed anomalous kinetic behaviour at high monomer/water ratios.

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