

Emulsion polymerization of butadiene. 2. Polymerizations with sodium dodecyl sulfate

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Emulsion polymerization of butadiene, 2^{a)}

Polymerizations with sodium dodecyl sulfate

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SUMMARY:

The emulsion polymerization of butadiene was investigated with sodium dodecyl sulfate as emulsifier, and the results were 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 dodecyl sulfate was found to be a better stabilizer than Dresinate 214. The average rate per particle in interval II (corresponding to the linear portion of the conversion vs. time curve) depends strongly on particle size, but not on recipe parameters used to vary the final particle diameter, such as the type and amount of emulsifier and ionic strength. The dependence of particle number per volume of water N on initiator ($[I]$) and emulsifier concentration ($[E]$) is usually expressed as the exponent in the empirical relationship $N \sim [I]^x \cdot [E]^y$. Promoting coagulation by increasing the ionic strength decreases x towards zero, while y increases sharply. Increasing $[I]$ at constant $[E]$ and constant ionic strength induces limited coagulation, presumably because the rate of emulsifier adsorption becomes insufficient.

Introduction

In a previous paper¹⁾ we described the kinetics of the emulsion polymerization of butadiene with the commercial emulsifier Dresinate 214, 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 an average number of radicals per particle \bar{n} of 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 dodecyl sulfate. The recipe employed closely resembles the one used previously.

Experimental part

Materials: Butadiene (from DSM Chemicals, Geleen, Holland) was purified by condensing the gas from a 27 litre storage vessel into a cooled steel recipient. Commercial grade "tertiary dodecanethiol" (from Pennwalt Chemicals, Rotterdam, Holland) is a mixture of dodecanethiol isomers and was used without further purification. Sodium dodecyl sulfate (SDS, purity > 99%,

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from Merck, Darmstadt, FRG), sodium peroxodisulfate (SPS, p. a., from Fluka AG, Buchs, Switzerland) and sodium carbonate (p. a., from Merck, Darmstadt, FRG) were used as received. Water was doubly distilled and purged with nitrogen. Dresinate 214 (from Hercules bv, Den Haag, Holland) constitutes a dispersion of abietic acid type derivatives in water, with dehydro-, dihydro- and tetrahydroabietic acid as main components, and less than 0,2 wt.-% of abietic acid.

Emulsion polymerization: The procedure for charging the reactor was described earlier¹⁾. Tab. 1 shows the standard polymerization recipes with Dresinate 214¹⁾ (recipe 1) and SDS (recipe 2). Differences between both standard recipes are not crucial and based on practical considerations. Potassium dodecyl sulfate was found to be insoluble in water at room temperature so that all potassium salts from recipe 1 were substituted by the same amounts (in mol) of sodium salts. The overall sodium ion concentration in recipe 2 is $0,3 \text{ mol} \cdot \text{L}^{-1}$, and kept constant unless stated otherwise.

Tab. 1. Standard polymerization recipes in parts by weight. Conditions for both recipes: conc. of initiator [I] = $13 \text{ mmol} \cdot \text{L}^{-1}$; temperature 62°C ; pH 10,5–10,8

Ingredient	Recipe 1	Recipe 2
Water	230	230
Butadiene	100	100
Dresinate 214	7,6	—
Sodium dodecyl sulfate	—	7,6
K ⁺ /Na ⁺ carbonate ^{a)}	4,4	2,0
K ⁺ /Na ⁺ peroxodisulfate ^{a)}	0,8	0,7
"tert-Dodecanethiol"	0,7	0,7

^{a)} In recipe 1 potassium salts and in recipe 2 sodium salts were used.

Characterization: Conversion data were based on gravimetric determinations of samples collected with a high-pressure-proof syringe. The polymerization rate R_{pol} (in $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$)* was taken as the slope of the linear portion of the conversion vs. time curve (i. e. interval II).

The average particle diameter was measured by dynamic light scattering (DLS, Malvern IIc) and transmission electron microscopy (TEM, JEOL 2000FX). For TEM the latex particles were hardened with OsO₄ and typically some 750–1000 particles were counted with a Zeiss TGA-10 particle analyzer. From DLS only the weight average diameter \bar{d}_w was used, while TEM gives complete information on average particle size and size distribution. The relevant definitions are given in Tab. 2. Comparison between both methods of particle sizing on the basis of \bar{d}_w gives excellent agreement as was shown previously¹⁾. However, the particle numbers calculated from this diameter are by definition systematically smaller than the more correct ones based on the mean-volume average diameter \bar{d}_v . In the present study this only affects numerical values by some 10–20% (e. g. Tab. 5), because the particle size distributions are relatively narrow (average polydispersity index $P = \bar{d}_w/\bar{d}_n = 1,08$; 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.

*¹⁾ In our previous publication¹⁾ both R_{pol} (in $\text{g} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) and N (in g^{-1}) were expressed per gram of water. However, the density of the aqueous phase was found to be 1,00–1,01 $\text{g} \cdot \text{mL}^{-1}$, and hardly varied with the amount of water-soluble additives. The volumetric unit is preferred in the present investigation.

Tab. 2. Definitions of relevant particle size parameters, where n_i represents the number of particles with diameter d_i

\bar{d}_n	\bar{d}_s^2	\bar{d}_v^3	\bar{d}_w	P
$\frac{\sum n_i \cdot d_i}{\sum n_i}$	$\frac{\sum n_i \cdot d_i^2}{\sum n_i}$	$\frac{\sum n_i \cdot d_i^3}{\sum n_i}$	$\frac{\sum n_i \cdot d_i^4}{\sum n_i \cdot d_i^3}$	$\frac{\bar{d}_w}{\bar{d}_n}$

The particle number per volume of water (N) was calculated as:

$$N = \frac{6 C \cdot (m/w)}{\pi \cdot (\rho_p/\rho_{aq}) \cdot \bar{d}^3} \quad (1)$$

where C is the fractional conversion, (m/w) the monomer-water weight ratio, \bar{d} the average particle diameter, ρ_p the polymer density ($0,89 \text{ g} \cdot \text{mL}^{-1}$ at 25°C) and ρ_{aq} the density of the aqueous phase.

Results and discussion

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. 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.

Effect of emulsifier concentration

The concentration of sodium dodecyl sulfate (SDS) was varied between 64,8 and $4,0 \text{ g} \cdot \text{L}^{-1}$ (224 and $14 \text{ mmol} \cdot \text{L}^{-1}$), all concentrations well above the CMC, which was determined with the Wilhelmy plate method to amount to $0,17 \text{ g} \cdot \text{L}^{-1}$, i.e. $0,6 \text{ mmol} \cdot \text{L}^{-1}$ ($\theta = 25^\circ\text{C}$ and $[\text{Na}_2\text{CO}_3] = 0,15 \text{ mol} \cdot \text{L}^{-1}$). The overall Na^+ concentration, $[\text{Na}^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$, was always kept constant by adjustment with sodium carbonate. The small variation in pH that may result is unimportant, since the performance of SDS is virtually pH-independent at $\text{pH} > 7$, in contrast to the carboxylate emulsifier Dresinate 214. The Na^+ concentration is thus an additional adjustable parameter in recipe 2 which will be discussed in detail below.

All conversion vs. time curves (Fig. 1) are convex toward the time axis up to about 40% conversion, in sharp contrast to similar polymerizations with Dresinate 214¹⁾, where linearity was attained at about 25% conversion. Interval III begins at ca. 60% conversion²⁾ so that interval II appears to be rather short in the present system.

Fig. 2 gives the particle number and conversion vs. time curves for the polymerization with $8,1 \text{ g} \cdot \text{L}^{-1}$ SDS. Evidently, as in polymerizations with Dresinate 214, limited coagulation is occurring with SDS as emulsifier. Also in concordance with previous

observations, the decrease of the particle number per volume of water, N , by coagulation is not showing up in the conversion vs. time curve, i.e. the rate of polymerization, R_{pol} , is not proportional to N , so that the average number of radicals per particle, \bar{n} , cannot be constant at 0,5 (Smith-Ewart case 2)³. Indeed, N decreases while R_{pol} still increases. R_{pol} is usually expressed as:

$$R_{\text{pol}} = k_p \cdot c_M \cdot (\bar{n}/N_A) \cdot N \quad (2)$$

where k_p is the propagation rate coefficient, c_M the monomer concentration within the particles, and N_A Avogadro's number.

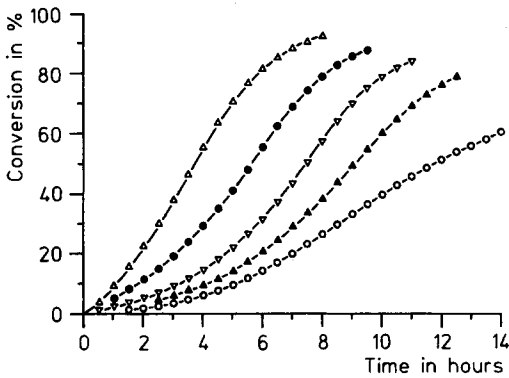


Fig. 1. Conversion vs. time curves for polymerizations with different sodium dodecyl sulfate concentrations: $c_E = 64,8 \text{ g} \cdot \text{L}^{-1}$ (Δ); $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ (\bullet); $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$ (∇); $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$ (\blacktriangle); $c_E = 4,0 \text{ g} \cdot \text{L}^{-1}$ (\circ)

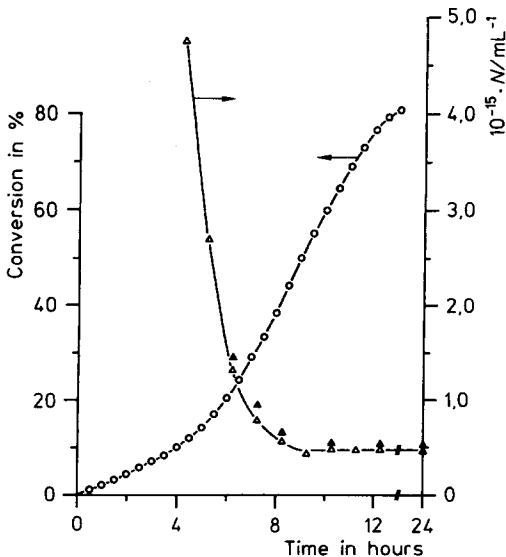


Fig. 2. Conversion (\circ) and particle number per volume of water N vs. time curves for a polymerization with $8,1 \text{ g} \cdot \text{L}^{-1}$ sodium dodecyl sulfate. Particle number based on \bar{d}_v obtained with transmission electron microscopy (\blacktriangle), and \bar{d}_w obtained with dynamic light scattering (Δ). (Definitions of \bar{d}_v and \bar{d}_w see Tab. 2)

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 a good approximation²). Obviously, \bar{n} must depend on particle size to account for the observed behaviour (Fig. 3). This effect becomes strongly pronounced by the coagulation process, causing an enhanced variation in particle diameter within one single experiment.

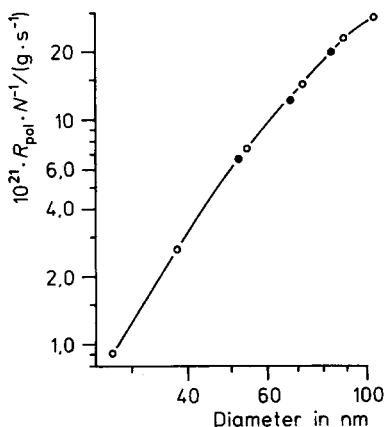


Fig. 3. Average rate of polymerization per particle, $R_{\text{pol}} \cdot N^{-1}$, as a function of particle diameter, \bar{d}_v (●) and \bar{d}_w (○), for the polymerization with 8,1 g · L⁻¹ of sodium dodecyl sulfate (from Fig. 2) (Definitions of \bar{d}_v and \bar{d}_w see Tab. 2)

The dependence of particle number (or rate) on emulsifier ([E]) and initiator concentration ([I]) is usually expressed as the exponent in the empirical relationship $N \sim [I]^x \cdot [E]^y$. Theoretical values of $x_{\text{th}} = 0,40$ and $y_{\text{th}} = 0,60$ are obtained with any nucleation mechanism (micellar³) or homogeneous⁴) that ignores coagulation. Experimentally obtained values for y in the emulsion polymerization of butadiene are given in Tab. 3.

Tab. 3. Emulsifier exponents with regard to particle number N and polymerization rate R_{pol}

Emulsifier	y (in $N \sim [E]^y$)	y' (in $R_{\text{pol}} \sim [E]^{y'}$)	Reference
SDS	2,1	0,24	this paper
Dresinate 214	1,6	0,61	1)
Dresinate	1,0	0,62	5)

Given the non-ideal kinetic behaviour in the present system (i. e. R_{pol} is not proportional to N), the different exponents for R_{pol} and N are not surprising, while the significantly higher exponents of N as compared with theory ($y_{\text{th}} = 0,60$), 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.

Effect of sodium ion concentration

The general principles of electrostatic stabilization of colloidal particles are well established in DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, see e. g. ref.⁶). 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_0 , giving rise to a Boltzmann distribution of counter ions and co-ions in a region close to the surface. According to this simple model for a spherical particle of diameter d , the potential in the aqueous phase at a distance r from the centre of the particle, $\psi(r)$ is given (for $\psi_0 < 25$ mV) by:

$$\psi(r) = \psi_0 \frac{d}{2r} \exp [\kappa (0,5d - r)] \quad (3)$$

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

$$\kappa^2 = \frac{2 N_A \cdot e^2 \cdot \mu}{\epsilon_0 \cdot \epsilon_r \cdot kT} \quad (4)$$

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 is 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. ^{7,8}. Limited coagulation is well established in the emulsion polymerization of more water-soluble monomers⁹⁻¹¹, caused by slow and/or weak adsorption of emulsifier on the polar polymer-water interface as suggested by Yeliseyeva¹¹. Dunn and Chong⁹ showed for vinyl acetate that the coagulation observed experimentally can be described satisfactorily with the DLVO theory. Furthermore, the role of coagulation in the particle nucleation mechanism has been treated quantitatively by several workers, see e. g. refs. ¹²⁻¹⁴. However, butadiene is only sparingly water-soluble (37 mmol · L⁻¹ at 50 °C)¹⁵, 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, $[Na^+]$ 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 μ . However, the anion concentration (and thus μ) 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 μ (although not exactly identical).

The overall $[\text{Na}^+]$ was varied at two emulsifier concentrations, viz. $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ and $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$, while $[\text{I}]$ was kept constant at $13,0 \text{ mmol} \cdot \text{L}^{-1}$. The final particle diameter at an arbitrarily chosen conversion, viz. 90%, increases markedly with $[\text{Na}^+]$ (Fig. 4). The minimum $[\text{Na}^+]$ indicated in Fig. 4 by the dashed vertical lines represent polymerizations in the absence of sodium carbonate. Higher values for $[\text{Na}^+]$ than those shown render latexes with a poor shelf stability. The range of $[\text{Na}^+]$ in these experiments corresponds to a variation in ionic strength roughly between $0,1 \text{ mol} \cdot \text{L}^{-1}$ and $1 \text{ mol} \cdot \text{L}^{-1}$, about 1–2 orders of magnitude larger than in the study of Goodwin et al.^{7,8)} on the emulsifier-free emulsion polymerization of styrene.

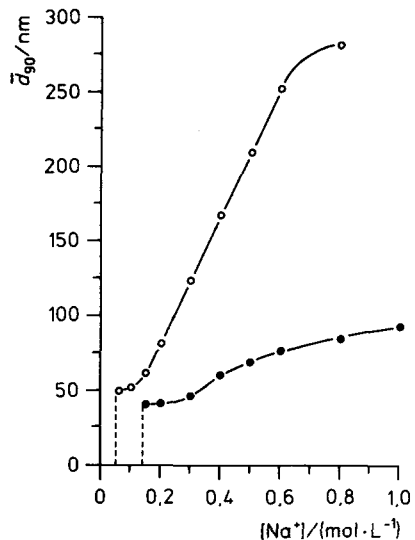


Fig. 4. Particle diameter \bar{d}_w at 90% conversion (\bar{d}_{90}) as a function of the overall sodium ion concentration $[\text{Na}^+]$ at two sodium dodecyl sulfate concentrations $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ (\bullet); $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$ (\circ); for dashed vertical lines see text

At $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$ the observed 5-fold increase in diameter corresponds to a decrease in N by about 2 orders of magnitude. Realizing that in the standard recipe 2 $[\text{Na}^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ (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:

— The performance and solubility of Dresinate 214 is strongly pH-dependent¹⁶⁾; 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 wt.-%. Inert electrolytes are often added to reduce latex viscosity and thus maintain a reasonable fluidity¹⁷⁾.

— In certain applications large-sized spherical particles are desired, e.g. as impact modifiers in materials exhibiting crazing and/or yielding (ABS (acrylonitrile-butadiene-styrene) resins, high-impact polystyrene, 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 polybutadiene particles^{18,19}.

The data from Fig. 4 can be presented alternatively by plotting the particle number (calculated from \bar{d}_{90}) on a double-logarithmic scale vs. c_E (Fig. 5). The slopes of these apparently linear (owing to the limited range of c_E) curves at fixed $[\text{Na}^+]$ thus represent the emulsifier exponent y (Tab. 4).

Tab. 4. Variation of the emulsifier exponent y towards particle number ($N \sim [E]^y$) with the sodium ion concentration $[\text{Na}^+]$

$[\text{Na}^+]/(\text{mol} \cdot \text{L}^{-1})$	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

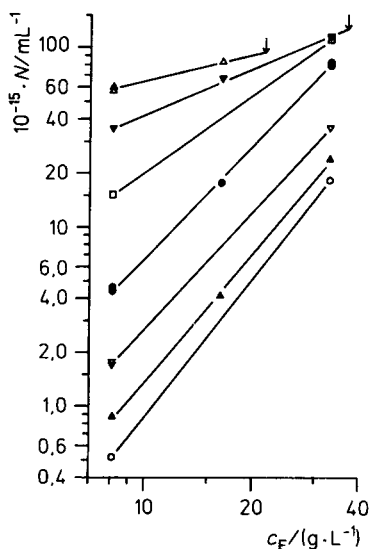


Fig. 5. Particle number N based on \bar{d}_w vs. sodium dodecyl sulfate concentration c_E as a function of the overall sodium ion concentration $[\text{Na}^+] = 0,1 \text{ mol} \cdot \text{L}^{-1}$ (Δ); $[\text{Na}^+] = 0,15 \text{ mol} \cdot \text{L}^{-1}$ (∇); $[\text{Na}^+] = 0,2 \text{ mol} \cdot \text{L}^{-1}$ (\square); $[\text{Na}^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ (\bullet); $[\text{Na}^+] = 0,4 \text{ mol} \cdot \text{L}^{-1}$ (∇); $[\text{Na}^+] = 0,5 \text{ mol} \cdot \text{L}^{-1}$ (\blacktriangle); $[\text{Na}^+] = 0,6 \text{ mol} \cdot \text{L}^{-1}$ (\circ). Arrows indicate the maximum c_E at that particular $[\text{Na}^+]$. Data points at $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$, $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$ and $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$

The minimum value of $y = 0,5$ is quite close to the theoretical value $y_{\text{th}} = 0,6$, obtained when coagulation is fully neglected. Promoting coagulation by raising $[\text{Na}^+]$ clearly increases the dependence of N on $[E]$. Values for the emulsifier exponent as high as 3 have been reported in literature for other systems²⁰. The coagulative nucleation model proposed by the Sydney-group¹³ predicts a range of exponential values ($0,4 \leq y_{\text{th}} \leq 1,2$), while raising the coagulation rate coefficient in the nucleation model of Song and Poehlein¹⁴ also leads to higher values for y_{th} .

The effect of limited coagulation on conversion vs. time history (Fig. 6) is rather complicated: increasing $[\text{Na}^+]$ gives higher initial rates in interval I, but the steady state rate R_{pol} decreases significantly (Tab. 5). Similar results have been found with Dresinate 214.

The average rate per particle for these and previous experiments with Dresinate 214¹⁾, 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 (see Fig. 3).

Making a double-logarithmic plot of R_{pol}/N vs. \bar{d}_{90} (Fig. 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 (Fig. 6 in ref. ¹⁾) gave an apparent linear relationship (owing to the limited data range). This behaviour is seen to be encompassed by the generalized curve in Fig. 7. A more rigorous treatment of particle growth kinetics in intervals II and III is given elsewhere²⁾.

Fig. 6. Conversion vs. time curves for polymerizations with $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$ sodium dodecyl sulfate, as a function of the overall sodium ion concentration
 $[\text{Na}^+] = 0,1 \text{ mol} \cdot \text{L}^{-1}$ (∇);
 $[\text{Na}^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ (\circ);
 $[\text{Na}^+] = 0,5 \text{ mol} \cdot \text{L}^{-1}$ (Δ)

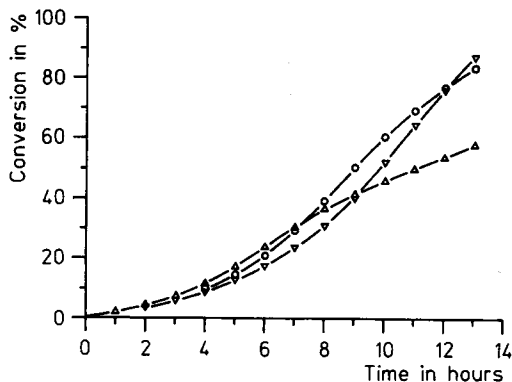
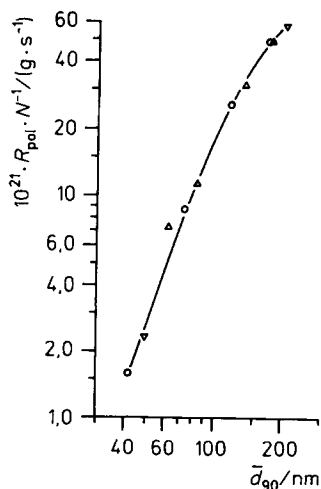


Fig. 7. Average rate per particle $R_{\text{pol}} \cdot N^{-1}$ vs. the mean-volume average diameter \bar{d}_v at 90% conversion (\bar{d}_{90}). Final particle diameters were varied by changing the Dresinate 214 concentration¹⁾ (Δ), sodium dodecyl sulfate concentration (\circ) or overall sodium ion concentration (∇)



Tab. 5. Influence of overall $[\text{Na}^+]$ on the rate of polymerization, R_{pol} , with emulsifier concentration $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$ (SDS) and $[\text{I}] = 13,0 \text{ mmol} \cdot \text{L}^{-1}$ (sodium peroxodisulfate)

$[\text{Na}^+]$ $\text{mol} \cdot \text{L}^{-1}$	$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$	$10^{-14} \cdot N / (\text{mL}^{-1})^{\text{a}}$		\bar{d}_v at 90% in nm	P (see Tab. 2)
		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 per volume of water, N , determined with DLS (dynamic light scattering) are based on \bar{d}_w , and those with TEM (transmission electron microscopy) on \bar{d}_v (see Tab. 2).

Effect of initiator concentration

The sodium peroxodisulfate (SPS) concentration was varied 100-fold between 26,0 and $0,26 \text{ mmol} \cdot \text{L}^{-1}$ at two emulsifier concentrations, viz. $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ and $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$. $[\text{Na}^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ was kept constant, so coagulation phenomena may be considered to be a constant factor. The experimentally determined initiator exponents are given in Tab. 6. The small effect of $[\text{I}]$ on R_{pol} is rather typical of a Smith-Ewart case 1 behaviour with ²⁾ $\bar{n} \ll 0,5$.

As limited coagulation is promoted (by lowering c_E or raising [cation]), the effect of $[\text{I}]$ on N diminishes, since the final particle number becomes predominantly determined by coagulation. This effect appears to be relatively small in the first series of experiments from Tab. 6, since the exponent for N ($x = 0,46$), is quite close to the theoretical one ($x_{\text{th}} = 0,40$) when coagulation is ignored.

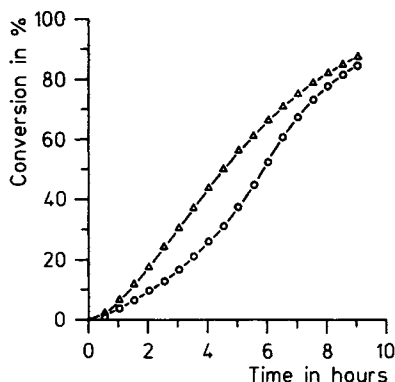
Tab. 6. Initiator exponents with regard to the particle number per volume of water, N , and polymerization rate R_{pol} , at different emulsifier concentrations c_E and overall cation concentrations, [cation]

Recipe	c_E $\text{g} \cdot \text{L}^{-1}$	[cation] $\text{mol} \cdot \text{L}^{-1}$	x ($N \sim [\text{I}]^x$)	x' ($R_{\text{pol}} \sim [\text{I}]^{x'}$)
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 ref. ¹⁾.

The insensitivity of R_{pol} to the 100-fold variation of $[\text{I}]$ is remarkable; its effect on conversion vs. time history is even more striking (Fig. 8, with $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$). Increasing $[\text{I}]$, especially at $[\text{I}] > 1,0 \text{ mmol} \cdot \text{L}^{-1}$, appears to slow down the polymerization in interval I, even though the steady-state polymerization rate in interval II steadily keeps increasing with $[\text{I}]$ (Tab. 7). Results at $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$ are similar.

Fig. 8. Conversion vs. time curves for polymerizations with emulsifier concentration $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ (sodium dodecyl sulfate) and different sodium peroxodisulfate concentrations $[I] = 26,0 \text{ mmol} \cdot \text{L}^{-1}$ (\circ) and $[I] = 0,26 \text{ mmol} \cdot \text{L}^{-1}$ (Δ)



Tab. 7. Periods of time required to reach 25% (t_{25}) or 50% conversion (t_{50}) and rate of polymerization R_{pol} for different with initiator concentrations $[I]$ at emulsifier concentration $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ (sodium dodecyl sulfate)

$[I]$ $\text{mmol} \cdot \text{L}^{-1}$	t_{25}/h	t_{50}/h	$10^5 \cdot R_{pol}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$
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

Analogous polymerizations with Dresinate 214 (Fig. 2 from ref. ¹) behave 'normal' in that the duration of interval I decreases with increasing $[I]$. The discrepancy may be caused by possible impurities in the emulsifier. Even though Dresinate 214 has been disproportionated to eliminate abietic acid-derivatives, small amounts are still present and can affect the kinetics, especially at lower $[I]$.

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 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 $[\text{Na}^+]$ at fixed c_E gave higher initial rates (Fig. 6).

This is further illustrated in Fig. 9, showing particle number and conversion vs. time curves for two polymerizations with different $[I]$ and $[E]$, but with the same steady state R_{pol} and final N . The initial behaviour in interval I was found to be markedly

different, as a result of a difference in colloidal stability. The data in Tab. 7 suggest an analogous behaviour; increasing $[I]$ above $1,0 \text{ mmol} \cdot \text{L}^{-1}$ clearly prolongs interval I. At $[I] = 13,0 \text{ mmol} \cdot \text{L}^{-1}$ the particle number was indeed found to decrease initially, whereas the polymerization depicted in Fig. 9 at $[I] = 0,52 \text{ mmol} \cdot \text{L}^{-1}$ 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 $[I]$).

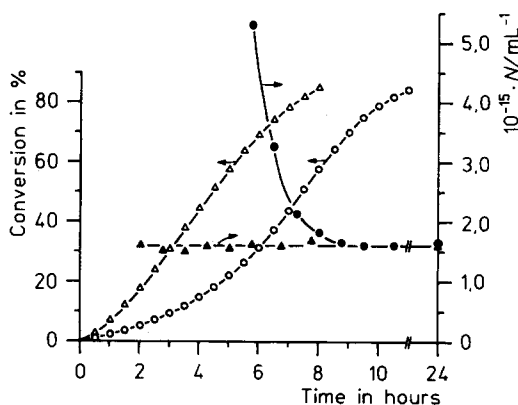


Fig. 9. Conversion (empty symbols) and particle number N (full symbols) vs. time curves for two polymerizations with the same steady state rate of polymerizations, R_{pol} , and final N : $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ and $[I] = 0,52 \text{ mmol} \cdot \text{L}^{-1}$ (triangles), $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$ and $[I] = 13,0 \text{ mmol} \cdot \text{L}^{-1}$ (circles) ($I =$ sodium peroxodisulfate, $E =$ SDS)

If the total polymer-water interface increases faster than it adsorbs emulsifier molecules, the surface charge density decreases and particles may become colloidal unstable. A rapid reduction of surface charge density by incorporating a high-molecular-weight chain into a small nucleus (i.e. rapid polymerization) was theoretically deduced by Goddall et al.²¹⁾

At a sufficiently high initiator concentration colloidal instability is apparently induced, presumably because 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 and the reaction slows down in interval I.

This behaviour is also reflected in the apparent dependence of N on c_E . For polymerizations with $[I] = 13,0 \text{ mmol} \cdot \text{L}^{-1}$ and $[\text{Na}^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ a value of 2,1 was found for the emulsifier exponent y (Tab. 3). However, decreasing $[I]$ should give lower values for this exponent, since the initiator exponent x at $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ and $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$ is different, $x = 0,46$ and $x = 0,16$, respectively (Tab. 6). Values for the exponent y between 2,2 (for $[I] = 26,0 \text{ mmol} \cdot \text{L}^{-1}$) and 0,8 (for $[I] = 0,26 \text{ mmol} \cdot \text{L}^{-1}$) were calculated. Although these values for y are based on only two data points per $[I]$, the trend is considered significant.

Comparison between Dresinate 214 and sodium dodecyl sulfate

The two emulsifiers used in this investigation differ in almost every relevant aspect: chemical structure, composition and purity, nature of the ionic group, etc. (for details on Dresinate 214 see ref.¹⁶⁾). Yet, this does not affect the reaction kinetics in interval II, as is evident from Fig. 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 (Tab. 3). However, in the experiments with Dresinate 214¹⁾ the contribution of the emulsifier to the cation concentration had not been taken into account; the overall $[K^+]$ thus varied with $[E]$ between $0,3 \text{ mol} \cdot \text{L}^{-1}$ and $0,4 \text{ mol} \cdot \text{L}^{-1}$. Additional experiments with a varying concentration of Dresinate 214 at a fixed overall $[K^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ were performed and compared with similar experiments with SDS at $[Na^+] = 0,3 \text{ mol} \cdot \text{L}^{-1}$ (Fig. 10).

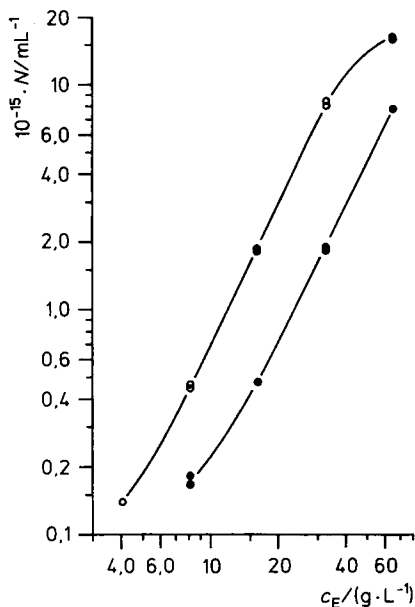


Fig. 10. Particle number N vs. emulsifier concentration c_E for polymerizations with sodium dodecyl sulfate (○) and Dresinate 214 (●), at a peroxydisulfate concentration $[I] = 13 \text{ mmol} \cdot \text{L}^{-1}$ and an overall cation concentration of $0,3 \text{ mol} \cdot \text{L}^{-1}$

The emulsifier exponents as deduced from the linear portions^{*)} 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.

For a further analysis of the stabilizing potential of both emulsifiers the polymerizations with $32,4 \text{ g} \cdot \text{L}^{-1}$ Dresinate 214 (ca. $95 \text{ mmol} \cdot \text{L}^{-1}$) and $16,2 \text{ g} \cdot \text{L}^{-1}$ SDS ($56 \text{ mmol} \cdot \text{L}^{-1}$) were chosen, as the final particle numbers were fortuitously found identical (Tab. 8). Again, interval II kinetics are independent of the type of emulsifier. The difference in the initial rates may be caused by differences in the rate of emulsifier adsorption or in the number of micelles initially present. The conversion vs. time curve of the polymerization with $16,2 \text{ g} \cdot \text{L}^{-1}$ SDS was already shown in Fig. 9.

^{*)} 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 can be seen in Fig. 9.

Tab. 8. Kinetic data for the polymerization of butadiene with $16,2 \text{ g} \cdot \text{L}^{-1}$ of sodium dodecyl sulfate (SDS; recipe 2) and $32,4 \text{ g} \cdot \text{L}^{-1}$ Dresinate 214 (recipe 1) under comparable conditions^{a)}

Emulsifier	$t_{20}^{\text{b)}$ h	$t_{40}^{\text{b)}$ h	$t_{60}^{\text{b)}$ h	$10^5 \cdot R_{\text{pol}}$ $\text{g} \cdot \text{mL}^{-1} \cdot \text{s}^{-1}$	\bar{d}_v at 90% conversion in nm	$10^{-15} \cdot N^{\text{c)}$ 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: $[\text{cation}] = 0,3 \text{ mol} \cdot \text{L}^{-1}$; initiator concentration $[\text{I}] = 13 \text{ mmol} \cdot \text{L}^{-1}$.

b) t_{xx} represents the time required to reach $xx\%$ conversion.

c) Particle number per volume of water.

The specific area per emulsifier molecule A_E was determined by the method of soap titration described by Maron et al.²²⁾ In short, the latex is titrated with the corresponding emulsifier solution (including K_2CO_3 or Na_2CO_3 ; $[\text{CO}_3^{2-}] = 0,15 \text{ mol} \cdot \text{L}^{-1}$), 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 findings²³⁾, could be obtained accurately in this way. In fact, conductance measurements as suggested for Dresinates²³⁾ 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:

$$A_E = \frac{6 M (\bar{d}_s^2 / \bar{d}_v^3) c_p}{(c_E - \text{CMC}) \rho_p \cdot N_A} \quad (5)$$

where c_p and c_E are the polymer and emulsifier content at the end point, respectively, both in gram per unit volume of water, \bar{d}_s^2 and \bar{d}_v^3 see Tab. 2 (both obtained with TEM), ρ_p the polymer density, and M the molecular weight of the emulsifier. The main components of Dresinate 214 have the formula $\text{C}_{19}\text{H}_{29}\text{CO}_2\text{K}$, giving $M = 340$. The CMC for Dresinate 214 was found to be $1,2 \text{ g} \cdot \text{L}^{-1}$ (with $[\text{K}_2\text{CO}_3] = 0,15 \text{ mol} \cdot \text{L}^{-1}$)¹⁾, and for SDS $0,17 \text{ g} \cdot \text{L}^{-1}$ ($[\text{Na}_2\text{CO}_3] = 0,15 \text{ mol} \cdot \text{L}^{-1}$).

The value for A_E of Dresinate 214 (Tab. 9) is in excellent agreement with the one of $43,7 \cdot 10^{-20} \text{ m}^2$ determined by Maron et al.²³⁾ 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

$$[\text{E}] \cdot A_E \cdot N_A / (\pi \bar{d}_s^2 \cdot N) \quad (6)$$

Since the emulsifier concentration $[\text{E}]$ 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.

The large difference in surface coverage at the same final N clearly shows that SDS is more efficient in stabilizing polybutadiene particles than Dresinate 214. This is

Tab. 9. The area per molecule, A_E , of sodium dodecyl sulfate (SDS) and Dresinate 214, and characteristics of latexes prepared with $16,2 \text{ g} \cdot \text{L}^{-1}$ SDS and $32,4 \text{ g} \cdot \text{L}^{-1}$ Dresinate 214 (see text)

Emulsifier	$10^{20} \cdot A_E^{\text{a}}$ m ²	Surface coverage ^{b)} of final latex in %	Zeta-potential ^{c)} in mV
Dresinate 214	45	68	-80
SDS	42	38	-86

a) Calculated with Eq. (5).

b) Calculated with Eq. (6).

c) Determined at 25 °C with a Malvern Zetasizer 3; dilution with $0,15 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{CO}_3$.

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 electrokinetic experiments (in this case with laser Doppler spectroscopy on particles in an applied electric field). It is comparable in magnitude to the potential in the so-called Stern plane (using a more sophisticated model for the double layer than the one described previously), and is therefore a good indication of the electrostability of the particles. Apparently, the surface charge density per 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 material¹⁶⁾. 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 system¹⁶⁾, which definitely will affect the mode of adsorption, as compared with SDS with its linear hydrophobic tail. Altogether, the Dresinate 214 emulsifier system is too complicated to describe its colloidal behaviour in the present context.

Conclusions

Electrolyte-induced limited coagulation is observed in polymerizations with sodium dodecyl sulfate and Dresinate 214, two emulsifiers differing widely in chemical structure and composition. Sodium dodecyl sulfate (SDS) was found to be a more effective stabilizer than Dresinate 214, because the surface charge density per amount of emulsifier is apparently larger for SDS.

Although coagulation is well established in emulsifier-free systems and for polymerizations of polar monomers, butadiene is only sparingly water-soluble, while $[E] \gg \text{CMC}$. 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 thus 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 $N \sim [I]^x \cdot [E]^y$ increases. Experimental values for y between 0,5 and 2,6 were found.

The dependence of N on initiator concentration is also strongly determined by the colloidal stability of the system. Increasing coagulation reduces the exponent x towards 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 becomes rate-determining, resulting in a limited colloidal stability.

Kinetic relationships between particle number N , $[I]$ 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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