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Citation for published version (APA):

Weerts, P. A., Loos, van der, J. L. M., & German, A. L. (1989). Emulsion polymerization of butadiene. 1. The effects of initiator and emulsifier concentration. *Makromolekulare Chemie*, 190(4), 777-788.
<https://doi.org/10.1002/macp.1989.021900411>

DOI:

[10.1002/macp.1989.021900411](https://doi.org/10.1002/macp.1989.021900411)

Document status and date:

Published: 01/01/1989

Document Version:

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

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Emulsion polymerization of butadiene, 1

The effects of initiator and emulsifier concentration

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(Date of receipt: March 30, 1988)

SUMMARY:

The kinetics of the emulsion polymerization of butadiene was investigated using Dresinate 214 as emulsifier and three dissociative initiators, viz. potassium peroxodisulfate, 4,4'-azobis-(4-cyanopentanoic acid) and 2,2'-azoisobutyronitrile. All experiments were conducted in the presence of a thiol as chain transfer agent, as usual in diene-polymerizations. The polymerization rate in interval II, R_{pol} , was found to be highly insensitive to changes in the initiator concentration ($R_{pol} \propto [I]^{0.08}$). Primary radicals are generated in large abundance in interval I as compared with the final particle number, indicating that the initiator efficiency with regard to particle nucleation is very low. The development of particle number as a function of conversion at several emulsifier concentrations shows that limited coagulation is occurring in the present system. R_{pol} depends on the emulsifier concentration with an exponent of 0.61, while the final particle number after cessation of coagulation depends on the emulsifier concentration to the 1.6th power. As a consequence the average number of radicals per particle must be a function of particle size, because the monomer concentration in the latex particles is approximately 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.

Introduction

Despite the industrial importance of the emulsion (co)polymerization of butadiene, very little has been reported about its kinetic and mechanistic features.

A large review of the scientific spin-off of the U.S.-government sponsored synthetic rubber program during world war II became publicly available not until 1955⁽¹⁾.

In the early fifties Morton et al. published several articles about the cross-linking behaviour of polybutadiene (PB)⁽²⁾ and the emulsion polymerization of butadiene using several initiator systems^(3–5). The only value for the propagation rate constant of butadiene ever reported stems from that work.

More recently Wendler et al.^(6–9) 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⁽¹⁰⁾, indicating a strong deviation from Smith-Ewart case 2 behaviour.

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 article describes the influence of the initiator and

the emulsifier concentration, using disproportionated rosin acid^{a)} soap as emulsifier 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.

Experimental part

Materials: Butadiene (from DSM Chemicals, Geleen, Holland) was distilled directly from a 27-litre storage vessel into a cooled steel recipient. Dresinate 214 (from Hercules bv, Den Haag, Holland) was used as a 15 wt.-% dispersion of potassium salts of disproportionated rosin acid soap in water. Disproportionated rosin acid is a mixture of abietic acid-type of derivatives with dehydro-, dihydro- and tetrahydroabietic acid as main components, with less than 0,2 wt.-% abietic acid. Commercial grade "tertiary dodecanethiol" (from Pennwalt Chemicals, Rotterdam, Holland) is a mixture of isomers and was used without further purification. 4,4'-Azobis(4-cyanopentanoic acid) (ACPA, from Fluka AG, Buchs, Switzerland), potassium peroxodisulfate (PPS, p. a. from Merck, Darmstadt, FRG) and potassium carbonate (p. a. from Merck, Darmstadt, FRG) were used as received. 2,2'-Azoisobutyronitrile (AIBN, from Fluka AG, Buchs, Switzerland) was recrystallized from methanol and stored at 5°C. Water was doubly distilled and purged with nitrogen.

Emulsion polymerization: The emulsion polymerizations with butadiene were carried out in a stainless steel reactor (2,4 litre, from K. K. Juchheim, Bernkastel-Kues, FRG) fitted with four baffle plates located at 90° intervals and a twelve-bladed turbine-type impeller. The reactor was charged with all ingredients except the butadiene under N₂ using the recipe of Tab. 1. The system was freed from inert gases by flushing the gas cap with gaseous butadiene followed by evacuation. This procedure was repeated twice. The correct amount of freshly distilled liquid butadiene was added from a weighed steel vessel.

Tab. 1. Standard recipe for emulsion polymerization of butadiene. Concentration of initiator [I] = 13 mmol · L⁻¹; temperature 62°C; pH = 10,5–10,8

Ingredients	Amount in parts by weight
Water	230
Butadiene	100
Dresinate 214	7,6
Potassium carbonate	4,4
"tert-Dodecanethiol"	0,7
Initiator	variable

Characterization: Conversion data were based on the total solid content of samples collected using a high-pressure-proof syringe. The polymerization rate R_{pol} was taken as the slope of the linear portion (i.e. interval II) of the conversion versus time curve. Most reactions were performed in duplicate. The average particle diameter was measured using dynamic light scattering (DLS, Malvern IIc) and transmission electron microscopy (TEM, Philips 420). For TEM the latexes were hardened with OsO₄ and typically some 750–1 000 particles were counted with a Zeiss TGA-10 particle analyzer. Both techniques yield among other things a weight-average diameter $\bar{d}_w$, used to calculate the particle number N . Despite the difference in definition between $\bar{d}_w$ (TEM) and $\bar{d}_w$ (DLS) the numerical values usually coincide within 5% because the particle size distributions are relatively narrow (Tab. 2). The particle number per

^{a)} For rosin acid see *Exptl. part*.

Tab. 2. Comparison between average particle diameters $\bar{d}$ measured using transmission electron microscopy (TEM) and dynamic light scattering (DLS)

$\frac{\bar{d}_n(\text{TEM})}{\text{nm}} = \frac{\sum n_i d_i / \sum n_i}{\text{nm}}$	$\frac{\bar{d}_w(\text{TEM})}{\text{nm}} = \frac{\sum n_i d_i^4 / \sum n_i d_i^3}{\text{nm}}$	$\frac{\bar{d}_w(\text{DLS})}{\text{nm}} = \left(\frac{\sum n_i d_i^6}{\sum n_i d_i^3} \right)^{1/3} / \text{nm}$	Polydispersity $P = \frac{\bar{d}_w(\text{TEM})}{\bar{d}_n(\text{TEM})}$
33,7	37,5	37,9	1,11
46,1	53,8	55,8	1,17
63,5	68,2	69,5	1,07
79,8	88,3	89,3	1,11
100,1	113,0	115,9	1,13
130,2	139,0	138,6	1,07
151,5	161,4	161,6	1,07
182,9	189,8	191,3	1,04

gram of water N was calculated according to:

$$N = \frac{6 C (m/w)}{\pi \rho \bar{d}_w^3}$$

where C is the fractional conversion, (m/w) the monomer to water weight ratio, $\bar{d}_w$ the weight-average particle diameter and ρ the polymer density¹¹⁾ $\rho = 0,89 \text{ g} \cdot \text{mL}^{-1}$.

Results and discussion

Effect of initiator concentration

In earlier investigations of emulsion polymerization it was found that the rate of (co)polymerization of butadiene(75 parts by weight)-styrene(25 parts by weight) or butadiene alone remained unaffected when changing the concentration of persulfate within wide limits¹⁾.

In order to get more insight into this phenomenon polymerizations were performed with various types of dissociative initiators: potassium peroxodisulfate (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 ($\text{pH} = 10,5 - 10,8$), whereas AIBN is only sparingly soluble in water. The additional potassium-ion concentration was kept constant at $0,3 \text{ mol} \cdot \text{L}^{-1}$ by adjustment of the amount of potassium carbonate.

Fig. 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 $R = 2k_d [I] N_{\text{Av}}$, where k_d is the decomposition rate constant, $[I]$ the initiator concentration in moles per gram of emulsion and N_{Av} the Avogadro number. Values for k_d at the polymerization temperature (62°C) are calculated from data in Polymer Handbook¹²⁾: PPS $6,3 \cdot 10^{-6} \text{ s}^{-1}$, ACPA $6,6 \cdot 10^{-6} \text{ s}^{-1}$ and AIBN $1,3 \cdot 10^{-5} \text{ s}^{-1}$.

Fig. 1.

Fig. 2.

Fig. 1. Variation of butadiene polymerization rate R_{pol} with radical production rate per gram emulsion R for three different initiators: potassium peroxodisulfate ($\circ$), 4,4'-azobis(4-cyanopentanoic acid) (Δ) and 2,2'-azoisobutyronitrile (∇)

Fig. 2. Conversion versus time curves of $\text{K}_2\text{S}_2\text{O}_8$ -initiated polymerizations of butadiene at different initiator concentrations $[I] = 13,0 \text{ mmol} \cdot \text{L}^{-1}$ (Δ); $[I] = 2,6 \text{ mmol} \cdot \text{L}^{-1}$ ($\circ$); $[I] = 0,52 \text{ mmol} \cdot \text{L}^{-1}$ (∇); $[I] = 0,26 \text{ mmol} \cdot \text{L}^{-1}$ ($\square$)

It appears that the polymerization kinetics is highly insensitive to the initiator concentration, irrespective of the nature of the initiator used ($R_{\text{pol}} \propto [I]^{0.08}$). Inspection of the conversion versus time curves (Fig. 2) indicates that particle formation is a slow process since the nucleation period (i. e. interval I) is usually long, typically some two hours or more. The total number of primary radicals generated during this period is $10^{17} - 10^{18}$ per gram of water. The final particle number is about 10^{15} per gram of water. This large discrepancy implies that all three initiators investigated are very inefficient in the particle nucleation process. Therefore, the relatively small variation of initiator concentration in the region studied will hardly effect the polymerization kinetics.

The low initial rates are not due to the presence of any possible retarding components in the emulsifier¹³⁾. The Dresinate 214 has been disproportionated prior to use and similar results have been obtained with other emulsifiers, e. g. sodium dodecyl sulfate. This will be discussed in a subsequent paper.

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 Gardon¹⁴⁾ in Tab. 3 shows that the present system deviates significantly from the 'ideal' emulsion polymerization as embodied in the Smith-Ewart assumptions¹⁰⁾. It should be noted that Gardon's treatment is only applicable to cases with negligible radical desorption.

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 styrene¹⁵⁾.

Tab. 3. Experimental and theoretical values for particle number N , weight-average (cf. Tab. 2) particle diameter determined using transmission electron microscopy $\bar{d}_w$ (TEM) and critical time t_{cr} (see text) for emulsion polymerizations of butadiene using different initiators I ($[I] = 13 \text{ mmol} \cdot \text{L}^{-1}$)

I ^{a)}	Conver- sion in %	$\bar{d}_w$ (TEM) nm	$10^{-15} \cdot N/\text{g}^{-1}$		$10^{-3} \cdot t_{\text{cr}}/\text{s}$	
			exp.	Gardon ^{b)}	exp. ^{c)}	Gardon ^{b)}
PPS	95	90	1,2	8,5	9,5	0,15
PPS	98	93	1,1	8,4	9,5	0,15
ACPA	99	93	1,1	8,6	8,5	0,15
AIBN	94	89	1,2	10,8	9	0,11

^{a)} Abbreviations used for initiators: PPS = potassium peroxodisulfate $\text{K}_2\text{S}_2\text{O}_8$; ACPA = 4,4'-azobis(4-cyanopentanoic acid); AIBN = 2,2'-azoisobutyronitrile.

^{b)} Calculated using a value of $10^5 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for the propagation rate constant at polymerization temperature⁴⁾.

^{c)} Roughly estimated from the conversion vs. time curves as the elapsed time till polymerization rate becomes constant.

Effect of emulsifier concentration

Fig. 3 shows the conversion versus time curves of polymerizations in which the emulsifier concentration was varied eightfold between 64,8 and 8,1 $\text{g} \cdot \text{L}^{-1}$. All experiments were conducted above the critical micelle concentration (C.M.C.) of Dresinate 214, determined tensiometrically with the DuNouy ring method to amount

Fig. 3. Conversion vs. time curves of $\text{K}_2\text{S}_2\text{O}_8$ -initiated polymerizations of butadiene at different emulsifier concentrations $c_E = 64,8 \text{ g} \cdot \text{L}^{-1}$ (Δ); $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$ ($\circ$); $c_E = 16,2 \text{ g} \cdot \text{L}^{-1}$ (∇); $c_E = 8,1 \text{ g} \cdot \text{L}^{-1}$ ($\square$)

to $1,2 \text{ g} \cdot \text{L}^{-1}$, i.e. ca. $3,5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ($\theta = 25^\circ\text{C}$ and $[\text{K}_2\text{CO}_3] = 0,15 \text{ mol} \cdot \text{L}^{-1}$). Agreement with values reported in the literature is good if differences in electrolyte concentration are taken into account: $10,4 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ for Dresinate 214¹⁶⁾ and $< 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ for "sodium rosinate"¹⁾ (see *Exptl. part*), both values determined at 50°C and without additional electrolyte. Plotting the polymerization rate in interval II against the emulsifier concentration on a log-log scale yields a value of 0,61 for the emulsifier exponent (Fig. 4). This is in excellent accordance with

Fig. 4. Dependence of butadiene polymerization rate R_{pol} (Δ) and final particle number N determined with transmission electron microscopy ($\bullet$) and dynamic light scattering ($\circ$) on total emulsifier concentration c_E

Smith-Ewart case 2 behaviour, insofar as reaction rate is proportional to particle number. 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 Tab. 4 and Fig. 5. 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 observed. This implies that beside particle nucleation (micellar or homogeneous) a second mechanism is operative which is coagulative in nature. This process is relatively slow, because it could be detected using conventional sampling procedures.

Tab. 4. Weight-average (see Tab. 2) particle diameter $\bar{d}_w$ and particle number N determined using transmission electron microscopy (TEM) and dynamic light scattering (DLS) of potassium peroxodisulfate-initiated polymerizations of butadiene at different emulsifier concentrations c_E

$c_E / (\text{g} \cdot \text{L}^{-1})$	Conversion in %	$\bar{d}_w / \text{nm}$		$10^{-15} \cdot N / \text{g}^{-1}$	
		TEM	DLS	TEM	DLS
64,8	74	59	61	3,2	3,0
	99	68	69	2,9	2,8
32,4	15	37	38	2,6	2,6
	26	54	56	1,5	1,4
	41	71	73	1,1	1,0
	68	88	89	0,9	0,9
	98	93	97	1,1	1,0
16,2	14	43	45	1,6	1,4
	26	72	71	0,65	0,67
	40	100	104	0,37	0,33
	70	132	134	0,28	0,26
	99	149	153	0,28	0,25
8,1	13	90	90	0,17	0,16
	27	113	116	0,17	0,16
	41	139	139	0,14	0,14
	57	161	162	0,13	0,12
	97	190	191	0,13	0,13

Evidence is accumulating that coagulation of latex particles cannot be neglected in emulsion polymerization¹⁷⁾. It has been shown that limited coagulation determines the particle number in the emulsion polymerization of more water-soluble monomers (e.g. vinyl acetate¹⁸⁾, ethyl acrylate¹⁹⁾, methyl methacrylate²⁰⁾) and of non-polar monomers in emulsifier-free systems²¹⁾. Recently Feeney, Napper and Gilbert²²⁾ proposed a coagulative nucleation mechanism combining Müller-Smoluchowski kinetics with the D.L.V.O. theory²³⁾ of colloidal stability, thus suggesting that limited coagulation is inherent in any emulsion polymerization.

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

Fig. 5. Variation of particle number N with conversion for butadiene emulsion polymerizations with different emulsifier concentrations c_E (symbols see legend of Fig. 3). Full symbols indicate transmission electron microscopy data and empty symbols dynamic light scattering data

emulsifier exponent from a linear log-log plot of final particle number versus emulsifier concentration (Fig. 4), gives a value of 1,6. The corresponding exponent toward reaction 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 II¹⁾ and independent of emulsifier concentration²⁴⁾, the average rate per particle R_{pol}/N is therefore a function of particle size. Similar but unexplained results for the homopolymerization of butadiene have been reported by Morton et al.³⁾ and Wendler et al.⁶⁾. 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 system⁹⁾. Results are summarized in Fig. 6 where $\bar{d}_{90}$ represents the particle diameter at 90%

Fig. 6. Average rate per particle (R_{pol}/N) vs. particle diameter at 90% conversion ($\bar{d}_{90}$) for different emulsion polymerizations of butadiene: Experimental results at polymerization temperature $\theta_{pol} = 62^\circ\text{C}$, using transmission electron microscopy ($\bullet$) and dynamic light scattering ($\circ$) for particle size analysis. $R_{pol}/N \propto \bar{d}_{90}^x$, with $x = 1,8$. Data of ref.⁶⁾ at $\theta_{pol} = 70^\circ\text{C}$ using mean-volume diameters ($\square$); data of ref.³⁾ based on mean-surface diameters (determined by soap titration) at $\theta_{pol} = 40^\circ\text{C}$ (∇), 50°C ($\blacktriangledown$) and 60°C ($\triangle$)

conversion, calculated from the experimental data (conversion > 40%) assuming a constant particle number: $\bar{d}_{90} = (\bar{d}^3 \cdot 0,9/C)^{1/3}$.

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 coagulation of the latex particles. Fig. 7 shows the cumulative particle 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 and more pronounced as polymerization proceeds. This is in accordance with the kinetic results described above.

Fig. 7. Cumulative particle size distribution versus weight-average particle diameter $\bar{d}_w$ (TEM) (a) and particle volume V (b) for a $K_2S_2O_8$ -initiated polymerization of butadiene. (Concentrations of initiator $[I] = 13 \text{ mmol} \cdot \text{L}^{-1}$ and emulsifier $c_E = 32,4 \text{ g} \cdot \text{L}^{-1}$) at various degrees of conversion: 15% (Δ), 26% ($\circ$), 41% (∇) and 98% ($\square$)

Surprisingly, the mechanistic complexity is not reflected in the conversion versus time curves, these are simply S-shaped with a linear interval II. This constancy of rate in interval II is usually taken to imply that the particle number is also constant, which is definitely not true for the present system. 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 $R_{\text{pol}}/N \propto d^{1,8}$ (Fig. 6). Other factors cannot be completely ruled out. For example, the cross-linking behaviour of the polymer and its

effect on monomer concentration and reaction constants may play a role. If present, their net effect on polymerization rate is very small and remains undetected, because R_{pol} has been found constant within experimental error.

An analogous behaviour is known to occur if more water-soluble monomers are used¹⁸⁻²⁰: a decreasing particle number while the rate of polymerization is constant. Radical desorption is relatively facile with such monomers and $\bar{n}$ may become much less than 0.5. A Smith-Ewart case 1 situation then arises and R_{pol} will only depend weakly on particle number. This type of behaviour may also be found with styrene at certain emulsifier concentrations²⁵. Dunn and Chong¹⁸ showed that the variation of the particle number in the emulsifier polymerization of vinyl acetate is in accord with expectations on the basis of D.L.V.O. theory²³.

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^{26,27} to promote the desorption of radicals from the latex particles and as a consequence to lower $\bar{n}$. However, Nomura²⁶ showed that dodecanethiol did not affect the rate of polymerization nor the particle number in the emulsion polymerization of styrene. He concluded that the $\text{CH}_3(\text{CH}_2)_{11}\text{S}^\bullet$ 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 thiol seem to be essential to bring about reaction at acceptable rates in the persulfate-initiated polymerizations of butadiene(75 parts by weight)-styrene(25 parts by weight) or butadiene²⁸. These important effects of thiols in the emulsion polymerization of butadiene are being investigated and will be reported on in a separate publication.

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 constant cited in literature⁴ 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 desorption or first-order termination 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 ($\bar{d}_{50} = 50 - 150$ nm).

This work has 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 has become obvious that regardless of apparent simplicity of the conversion versus time history and partial agreement of experimental data with Smith-Ewart theory, the mechanism and kinetics of this polymerization are extremely complicated and will require much additional research.

Conclusions

The concentration of three dissociative initiators differing in structure and water solubility described in this article 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.

Furthermore, the particle number is also determined by limited coagulation of colloiddally unstable particles. Experimental results may not be compared with theories (e. g. Smith-Ewart and Gardon) neglecting this phenomenon.

The nature and ionic charge of the primary radicals 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 the polymerization in the loci. 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 in the latex particles is approximately constant in interval II. Larger particles have higher values for $\bar{n}$ and will grow more rapidly, thus enlarging polydispersity as conversion increases. Data on particle size distributions are in agreement with this observation: a positive skewness develops at low conversion that becomes more pronounced as 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 kinetics with $\bar{n} \ll 0,5$.

Research is continued by studying the effects of other relevant reaction parameters, such as the kind of emulsifier, the monomer to water ratio and the amount of thiol. The results will be reported in separate publications.

The authors are indebted to Mr. *T. Pijpers* and Mr. *W. Busing* for preparing the electron micrographs, and to *DSM Research and Patents*, Geleen, the Netherlands, for financially supporting this work.

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