

Kinetic Aspects of the Emulsion Polymerization of Butadiene

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

Introduction

Despite the enormous industrial importance of polybutadiene-containing polymers prepared by emulsion polymerization (e.g., synthetic rubbers, high-impact materials, coatings, adhesives), very little is known about the kinetic behavior of butadiene in emulsion polymerization systems. As early as the American synthetic rubber program in World War II, unusual effects were observed in the (co)polymerization of butadiene (75%)-styrene (25%) or butadiene alone, but no adequate explanations were provided. These effects included the observations that trace amounts of thiols of low water solubility seemed to be essential to bring about reaction in persulfate-initiated polymerizations,¹ while the rate of (co)polymerization was unaffected when changing the concentration of persulfate within wide limits.²

In previous publications³⁻⁵ we have reported on the *ab initio* emulsion polymerization of butadiene under conditions typically found in industrial practice, e.g., high ionic strength, large monomer/water ratios, using a commercial surfactant. Although these experiments were not especially designed to study the kinetics, they do contain a lot of useful information, which is now used to analyze the typical behavior of this monomer.

One of the principal problems encountered in interpreting the polymerization kinetics of butadiene is the chronic lack of reliable rate coefficients in open literature. The only values for the propagation rate coefficient stem from the early work by Morton et al.⁶ and at best represent an approximation of its true value since they were determined with *ab initio* polymerizations at low temperatures (0–30 °C), involving polydisperse latexes sized by the method of soap titration.

Within the limitations mentioned above, an analysis is given of the kinetics and mechanisms of the emulsion polymerization of butadiene.

Experimental Section

All materials used were of high purity, except the *tert*-dodecanethiol, which was a crude mixture of C₁₂ isomers, and dresinate 214, which was a disproportionated aqueous dispersion of abietic acid-type derivatives with dehydro-, dihydro-, and tetrahydroabietic acid as main components and less than 0.2% abi-

etic acid. The standard recipes and reaction conditions are given in Table I, while experimental details are described elsewhere.^{4,5}

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 IIc) and transmission electron microscopy (TEM, Philips 420 and Jeol 2000 FX). For TEM the latexes 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 d_w was used, while TEM gives complete information on average particle size and size distribution. The relevant definitions are given in Table II. The numerical values of d_w measured with TEM and DLS usually coincide within 5% as the particle size distributions are relatively narrow (average polydispersity index $P = 1.08 \pm 0.03$).

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

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

where c is the fractional conversion, m/w the monomer to water weight ratio, ρ_{aq} the density of aqueous phase, ρ_p the polymer density, and d the average particle diameter.

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 surfactant concentration drops below its 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.

Coagulation Phenomena. Performing a polymerization with dresinate 214 (recipe 1) as surfactant gave a characteristic behavior, as depicted in Figure 1. Obviously, limited coagulation is involved in the particle formation process, and following the definition for interval II (*viz.*, constancy of particle number in the presence of monomer droplets), this stage commences at ca. 40% conversion. Nevertheless, the polymerization rate (R_p) has already

Table I
Standard Polymerization Recipes in Parts by Weight

ingredient	recipe 1	recipe 2
water	230	230
butadiene	100	100
dresinate 214	7.6	
sodium dodecylsulfate		7.6
K ⁺ /Na ⁺ carbonate ^a	4.4	2.0
K ⁺ /Na ⁺ persulfate ^a	0.8	0.7
t-dodecanethiol	0.7	0.7
[initiator]	13 mmol·L ⁻¹	
temperature, °C	62	
pH	10.5–10.8	

^a In recipe 1 potassium salts were used, and in recipe 2 sodium salts were used.

Table II
Definitions of Relevant Particle Size Parameters, Where n_i Represents the Number of Particles with Diameter d_i ^a

d_n	d_v^3	d_w	P
$\sum n_i d_i / \sum n_i$	$\sum n_i d_i^3 / \sum n_i$	$\sum n_i d_i^4 / \sum n_i d_i^3$	d_w / d_n

^a Subscripts: n denotes number average, v volume average, and w weight average diameters.

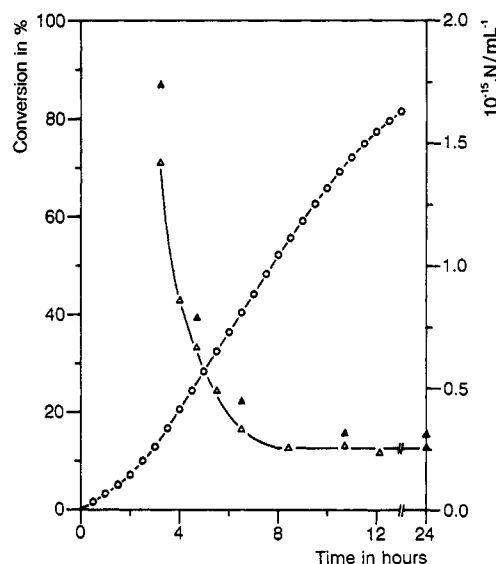


Figure 1. Conversion (O) and particle number N vs time curves for a polymerization with 16.2 g·L⁻¹ dresinate 214 (recipe 1). Particle number based on d_w obtained with light scattering (Δ) and d_v obtained with electron microscopy (\bullet).

become constant at about 25%, when particle number (N) is still decreasing. Obviously, R_p is not proportional to N , as is frequently assumed in emulsion polymerization. The same phenomenon was also observed when using sodium dodecylsulfate (recipe 2) as surfactant (Figure 2).

A similar behavior has been reported with more water-soluble monomers, such as methyl methacrylate,⁷ ethyl acrylate,⁸ and vinyl acetate.⁹ These systems are kinetically dominated by radical desorption, and the average number of radicals per particle (\bar{n}) can be much smaller than 0.5, suggesting the feasibility of an analogous situation in the present system.

Limited coagulation has also been observed in surfactant-free polymerizations,^{10,11} while the role of coagulation in the particle nucleation mechanism has been treated quantitatively by several workers.^{12–14} However, coagulation in the present system seems qualitatively different. Butadiene is only sparingly water-soluble ($C_{aq} = 37$ mmol·L⁻¹ at 50 °C),¹⁵ the surfactant concentrations are far above the cmc,^{4,5} and coagulation extends well beyond

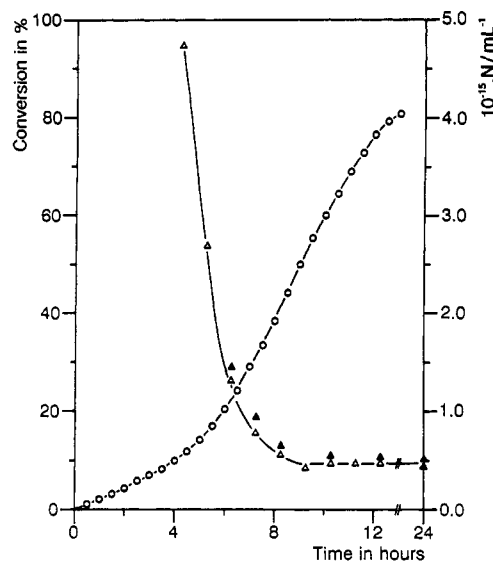


Figure 2. Conversion and particle number N vs time curves for a polymerization with 8.1 g·L⁻¹ sodium dodecylsulfate (recipe 2). For symbols see the caption to Figure 1.

the nucleation stage and involves particles of “normal” size. As shown previously,⁵ coagulation in this system is caused by the high ionic strength of the aqueous phase, in agreement with the general principles of electrostatic stabilization of colloidal particles outlined in DLVO theory.¹⁶ Although depending on the specific choice of reaction conditions, constancy of particle number after the disappearance of surfactant micelles seems more coincidental than characteristic.

Interval II Analysis. The overall rate of polymerization R_p is usually expressed as

$$R_p = \frac{dc}{dt} n_M^0 = k_p C_M (\bar{n} / N_{Av}) N \quad (2)$$

where c is the fractional conversion, n_M^0 the number of moles of monomer initially present per unit volume of water, k_p the propagation rate coefficient, C_M the monomer concentration within the particles, and N_{Av} Avogadro's number. Since k_p is not known with sufficient accuracy, it is better to use the average rate per particle (R_p/N) as a semiquantitative equivalent of \bar{n} , because k_p and C_M are both constant in interval II to within an excellent approximation (see below).

Calculating R_p/N using R_p in interval II and the final particle number after cessation of coagulation gives an upper limit of this quantity, since at lower conversions R_p/N is evidently smaller due to the smaller particle size (Figure 3). Besides type and concentration of surfactant, other recipe parameters such as monomer/water ratio, ionic strength, and initiator concentration were utilized to vary the final particle size. Plotting the average rate per particle on a log-log scale as a function of final particle diameter at an arbitrarily chosen conversion, viz., 90% (Figure 4; 90% was chosen for the sake of experimental convenience, as the majority of polymerizations was stopped between 85 and 95%) clearly shows that R_p/N (and thus \bar{n}) depends solely on particle size. Polymerization kinetics is internally consistent and otherwise uninfluenced by variables such as surfactant concentration and ionic strength, except in regard to how these affect final particle size.

Figure 4 also contains data points taken from the work of Wendler et al.¹⁷ for butadiene emulsion polymerizations at 70 °C, where particle size was varied by changing the amount of diisopropylxanthogen disulfide, a chain-transfer

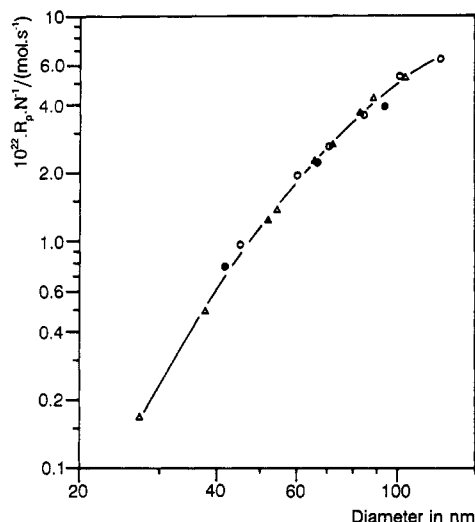


Figure 3. Average rate per particle R_p/N vs particle diameter, d_w (open symbols) and d_v (full symbols), for the polymerizations of Figure 1 (circles) and Figure 2 (triangles).

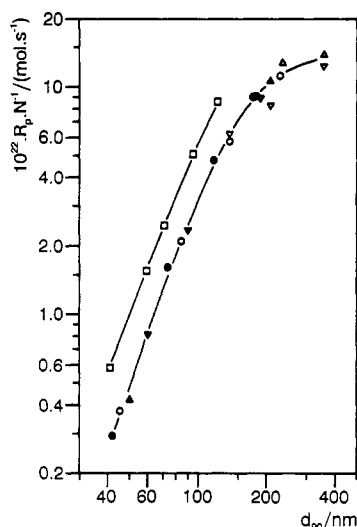


Figure 4. Average rate per particle R_p/N vs particle diameter d_v at 90% conversion (d_{90}), for polymerizations with dresinate 214 (open symbols) and sodium dodecylsulfate (full symbols). The final particle size was varied by changing the surfactant concentration (O), monomer/water ratio (V), or cation concentration (A) in the standard recipes. Data of Wendler et al.¹⁷ (□) for polymerizations at 70 °C.

agent that decreases colloidal stability by introducing polar end groups that reduce surfactant adsorption.¹⁸ Agreement with our results is good, given the temperature difference of 8 °C.

Figures 3 and 4 are analogous to the well-known Ugelstad plots of $\log \bar{n}$ vs $\log \alpha'$,¹⁹ where $\alpha' = \rho_i v / N k_t$, ρ_i the rate of radical production in the aqueous phase, v the volume of a monomer-swollen particle, and k_t the rate coefficient for bimolecular termination within the particles. Obviously R_p/N is proportional to \bar{n} . Since $N = V/v$, with V the total volume of polymer per unit volume of the aqueous phase, it is easily seen that $\alpha' \propto v^2 \propto d^6$. At constant [I] (implying a constant ρ_i), $\log \alpha'$ can thus be replaced by $\log d_{90}$ or $\log d$.

Using the uncertain value for $k_p = 100 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ reported by Morton et al.⁶ at 62 °C, and $C_M = 5.6 \text{ mol} \cdot \text{L}^{-1}$ (see the Appendix), a value of $4.7 \times 10^{-22} \text{ mol} \cdot \text{s}^{-1}$ for R_p/N would result if $\bar{n} = 0.5$. Given this rough estimate of a Smith-Ewart case 2 situation (see below) and again emphasizing that the calculated values for R_p/N are upper

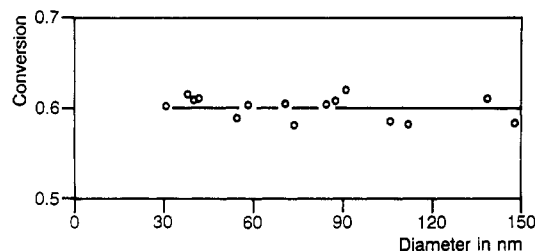


Figure 5. Fractional conversion where interval III begins (x') vs particle diameter d_w at x' . Average value for $x' = 0.60$.

limits for the experiments involved, it is evident from Figures 3 and 4 that values for $\bar{n} < 0.5$ are realistic.

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

Interval III Analysis. The complications associated with particle nucleation and coagulation can be avoided by using the kinetic information in interval III, where particle number is truly constant, as shown in Figures 1 and 2. Since monomer concentration in the particles is decreasing continuously, it is convenient to remove C_M from the right side of eq 2 and write the expression in terms of the fractional conversion in interval III, x , with $x = (C_M^0 - C_M)/C_M^0$ and C_M^0 the initial monomer concentration in the particles²⁰

$$-\frac{d \ln(1-x)}{dt} = \frac{k_p \bar{n} C_M^0 N}{N_{Av} n_M} \quad (3)$$

where n_M is the number of moles of monomer per unit volume of water present at the beginning of interval III.

Since $n_M = (1-x')n_M^0$, with x' the conversion where interval III begins, we can calculate x' from the experimental values of interval II (R_p) and interval III rate ($-d \ln(1-x)/dt$). The conversion x' is found to be 0.60 (standard deviation = 2.3%, using 25 data points) and independent of particle size (Figure 5). This latter observation further substantiates the common assumption of constancy of C_M in interval II. The value of x' is somewhat higher than those reported in the literature based on vapor pressure measurements, viz., 0.52²¹ and 0.56.⁶ These latter values are considered more inaccurate because the nonideal gas behavior of butadiene vapor complicates an accurate determination of the conversion at the point where pressure begins to drop.

For the simple zero-one system (i.e., only particles with zero or one free radical need to be considered) where bimolecular termination is not rate-determining, it is easily shown that²²

$$\bar{n} = \frac{\rho}{2\rho + k} \quad (4)$$

where ρ is the pseudo-first-order rate coefficient for entry of radicals into particles and k the rate coefficient for radical exit ("desorption"). During interval III ρ may be considered unchanging to within a good approximation, since the swollen particle diameter is almost constant. On the other hand, k may depend on factors other than the particle volume (e.g., C_M). A reasonable starting point is

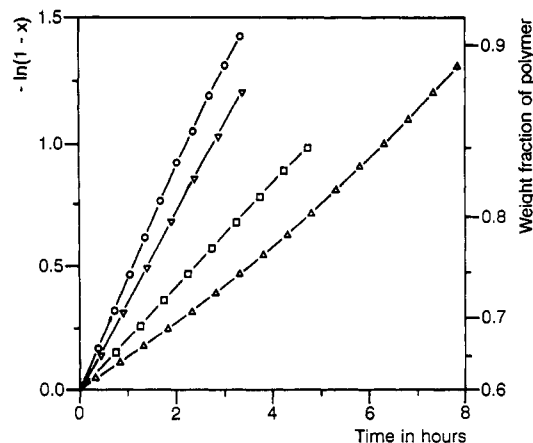


Figure 6. $-\ln(1-x)$ vs reaction time in interval III, for polymerizations at different dresinate 214 concentrations: 64.8 g·L⁻¹ (○); 32.4 g·L⁻¹ (▽); 16.2 g·L⁻¹ (□); 8.1 g·L⁻¹ (Δ). On the right axis is indicated the weight fraction of polymer w_p .

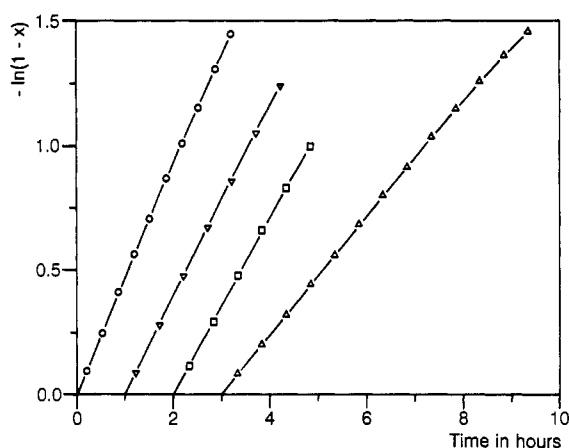


Figure 7. $-\ln(1-x)$ vs reaction time in interval III, for polymerizations at different sodium dodecylsulfate concentrations: 64.8 g·L⁻¹ (○); 32.4 g·L⁻¹ (▽); 16.2 g·L⁻¹ (□); 8.1 g·L⁻¹ (Δ). For convenience the zero-point is shifted 1 h along the x-axis for each experiment.

to assume k to be constant and then to check if this is consistent with the data. Several limiting cases can be distinguished:

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

Smith-Ewart case 1, with $k \gg \rho$: $\bar{n} \approx \rho/k$

Plotting $-\ln(1-x)$ vs reaction time (Figures 6 and 7) gives straight lines up to a weight fraction of polymer in the particles w_p (equivalent to the ab initio fractional conversion c) of 0.85 or higher, for all polymerizations with $d_{90} < 175$ nm.

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

Furthermore, Figures 6 and 7 show that the product of $k_p \bar{n}$ is constant within each experiment; it would be highly fortuitous if k_p and \bar{n} would counterbalance under all experimental conditions tried, so it is apparent that k_p and \bar{n} are both constant in interval III. This further implies that k_p is not diffusion controlled, at least for $w_p < 0.85$; this is to be expected given the low glass transition temperature of polybutadiene prepared by emulsion polymerization ($T_g = -86$ °C).²³

Table III
Initiator Exponents for the Particle Number ($N \propto [I]^x$) and Polymerization Rates in Interval II ($R_p \propto [I]^y$) and Interval III ($-d \ln(1-x)/dt \propto [I]^z$), at Different Surfactant Concentrations [S] and Overall Cation Concentrations [cation]

recipe	[S], g·L ⁻¹	[cation], mol·L ⁻¹	n^a	x	y	z	$d_{90},^b$ nm
2	32.4	0.3	9	0.46	0.04	0.04	46
2	16.2	0.3	7	0.16	0.09	0.09	80
1	32.4	0.4	7	0.02	0.08		94

^a n = number of experiments. ^b d_w at $[I] = 13.0$ mmol·L⁻¹.

The pseudo-first-order termination rate coefficient may start to become sufficiently small for very large particles as to become rate-determining, consistent with the non-linearity of $-\ln(1-x)$ observed for polymerizations with $d_{90} > 175$ nm (e.g., the polymerization with 8.1 g·L⁻¹ dresinate 214 in Figure 6, with $d_w = 180$ nm at 90% conversion). At a relatively low w_p of ca. 0.7, the interval III rate $-d \ln(1-x)/dt$, and thus \bar{n} , begins to increase. Termination is no longer instantaneous, yet the initial steady state suggests a zero-one behavior at lower w_p . If we assume the initial $\bar{n} = 0.5$, an estimation for $k_p = 180$ –200 L·mol⁻¹·s⁻¹ is obtained. Although intuitively not unreasonable, this assumption is not necessarily correct, since the initial \bar{n} can still be < 0.5 . The particle size distributions of these latexes are narrow, yet not monodisperse, which further complicates a proper interpretation. Therefore, this estimate of k_p should be regarded as a lower limit of its true value.

Effect of the Initiator Concentration. Having established that the studied system shows zero-one behavior over a wide range of experimental conditions, we can further explain the effect of initiator concentration $[I]$ on polymerization kinetics (Table III). The initiator concentration was varied 100-fold between 0.26 and 26.0 mmol·L⁻¹, while every change of $[I]$ was accompanied by an appropriate adjustment of the amount of sodium or potassium carbonate to keep the overall cation concentration [cation] constant. Under all conditions tried and in agreement with previously reported results,² both R_p and $-d \ln(1-x)/dt$ are only weakly dependent on $[I]$.

As limited coagulation is promoted (by lowering the surfactant concentration [S] or raising [cation]), the effect of $[I]$ 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 Table III, since the initiator exponent for N , viz., 0.46, is close to the theoretical value of 0.40 predicted by simple micellar²⁴ and homogeneous nucleation theories²⁵ that ignore coagulation.

The average rates per particle as a function of particle size for the first two series of experiments (recipe 2) from Table III are shown in Figure 8, where the solid line represents the best fit of data points from Figure 4. Again the kinetics is internally consistent, yet the 100-fold variation of $[I]$ has an almost negligible effect. This implies that α' (and thus ρ) is independent of $[I]$ in the present system; i.e., initiator efficiency must be extremely low. Furthermore, for latexes with a narrow particle size distribution, ρ can be taken to be inversely proportional to N , as is proven in a new model for radical entry proposed by Maxwell et al.,²⁶ a model that has been found to give agreement with all extant data for ρ , including variation with N .

Substituting this into eqs 2 and 3 and assuming a low value for \bar{n} , viz., $\bar{n} \approx \rho/k$, render both R_p and $-d \ln(1-x)/dt$ independent of $[I]$ and N . This is in good agreement

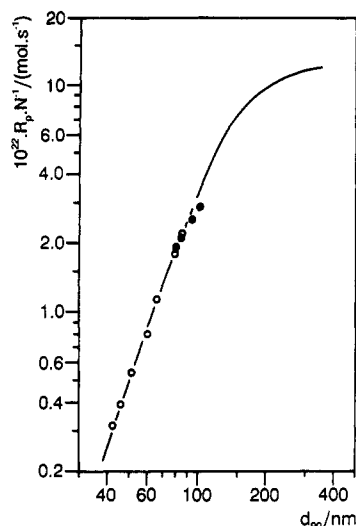


Figure 8. Average rate per particle R_p/N vs particle diameter d_w at 90% conversion (d_{90}), for polymerizations with a 100-fold variation in persulfate concentration (see Table III) at two sodium dodecylsulfate concentrations (recipe 2): 32.4 g·L⁻¹ (○) and 16.2 g·L⁻¹ (●). The solid line represents the empirical relationship from Figure 4.

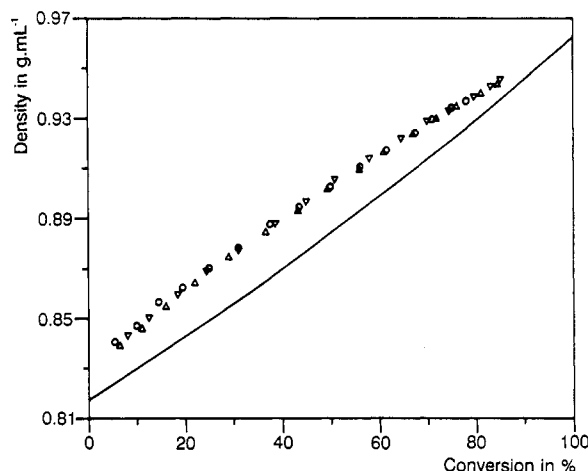


Figure 9. Density of the reaction mixture vs gravimetric conversion. Symbols represent experimental points from three polymerizations using recipe 1, and the solid line, the theoretical relationship, assuming ideal mixing of monomer and polymer.

with the data summarized in Table III, especially for the first series of experiments, since the above assumption of $\bar{n} \ll 0.5$ is most valid for small particles. The reason for the very weak dependence of ρ on $[I]$ is as yet uncertain and is the subject of current theoretical and experimental investigation.

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

1. First-order termination by monomer occlusion is highly unlikely, since monomer and polymer are completely miscible (or highly swellable if the polymer is cross-linked), while the glass transition temperature ($T_g = -86^\circ\text{C}$)²³ is well below the reaction temperature of 62°C .

2. Radical trapping by transfer to polybutadiene, as proposed by Hagiopol et al.²⁷ for the emulsion copolymerization of styrene and acrylonitrile in the presence of polybutadiene, is not important, since $-d \ln(1-x)/dt$ (and thus \bar{n}) is constant over a period of several hours, whereas w_p changes significantly during this time.

3. Chain transfer to thiol and subsequent desorption of thiol radicals can also be ruled out, since Nomura et

Table IV
Number-Average (M_n) and Weight-Average (M_w) Molecular Weights Determined by GPC of Polystyrene Samples, Prepared According to Recipe 2^b at 50°C , without *tert*-Dodecanethiol (TDT) and Different Amounts of 4-Vinyl-1-cyclohexene (VCH)

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

^a Weight percentage of VCH (and TDT) on monomer basis.

^b $[I] = 13.0 \text{ mmol}\cdot\text{L}^{-1}$ and $[S] = 16.2 \text{ g}\cdot\text{L}^{-1}$. ^c 1% TDT added.

al.²⁸ showed that *n*-dodecanethiol radicals do not desorb because of their extremely low water solubility. Furthermore, omitting the thiol from the recipes used in this investigation never increased R_p/N , as would be expected in the case of desorption of thiol radicals. Instead, a marked decrease of R_p/N was sometimes observed.³

4. It is well-known that butadiene easily undergoes Diels–Alder cyclizations at elevated temperatures, giving products such as 4-vinyl-1-cyclohexene (VCH). Although it is described as a mild retarder in the copolymerization of butadiene (75%)–styrene (25%),²⁹ addition of 1% VCH to a butadiene emulsion polymerization using sodium dodecylsulfate (recipe 2) had no effect whatsoever either on the conversion–time history or on the final particle number. Furthermore, addition up to 4% VCH to a styrene emulsion polymerization (using recipe 2 without thiol at 50°C) did not affect the molecular weight significantly (Table IV). Although inherently present during polymerization, this Diels–Alder dimer does not seem to facilitate the extensive radical desorption observed experimentally.

5. Many common surfactants (including sodium dodecylsulfate) can act as chain-transfer agents.³⁰ However, this phenomenon cannot be of major importance in the present system, since polymerizations yielding the same final particle size have the same value for R_p/N , regardless of the type of surfactant.

6. Last, transfer to monomer (or dead oligomeric material) followed by exit of the monomeric radical seems reasonable, given the rather low estimate of k_p and the moderate water solubility of butadiene.

In the transfer/diffusion model developed by Nomura and Harada,^{31,32} a propagating polymer chain transfers its free-radical activity to a monomer molecule (or to a chain-transfer agent), which then diffuses to the particle surface where it desorbs. The process is completed when the radical diffuses away from the surface into the bulk aqueous phase. When all of these three sequential events are significant, the exit rate coefficient k is given by

$$k = \frac{12zD_{aq}}{(q + 2D_{aq}/D_p)d_{sw}^2} \frac{k_{tr}}{k_p} \quad (5)$$

where D_{aq} and D_p are the diffusion coefficients of the exiting species in the aqueous phase and in the particle, respectively, z is roughly equal to the maximum degree of polymerization of the exiting radical (The parameter $z = \sum [k_p C_M / (k\bar{n} + k_p C_M)]^j$, where k is a desorption rate coefficient and j the degree of polymerization of the exiting species, with $1 \leq j \leq j_{max}$. When $k_p C_M \gg k\bar{n}$, this gives $z \approx j_{max}$), d_{sw} is the swollen particle diameter, and k_{tr} and k_p are the rate coefficients for transfer to monomer and for propagation, respectively. The parameter q is the partition coefficient of the exiting species between the particles and the aqueous phase and is roughly equal to the ratio of saturated monomer solubilities in the particles

and the aqueous phase C_M/C_{aq} . A similar expression was derived by Hansen and Ugelstad.³³

If in the transfer/diffusion mechanism for radical exit transfer to monomer is the rate-determining step, eq 5 can be replaced by³⁴

$$k \simeq k_{tr} C_M \quad (6)$$

Obviously, this is not the case in the present system, since \bar{n} , and thus k , was found constant far into interval III, whereas C_M decreases continuously. However, the constancy of k is consistent with the general eq 5, since d_{sw} and q are not expected to vary significantly in interval III.

For a sparingly water-soluble monomer, $q \gg 2D_{aq}/D_p$, so that eq 5 can be approximated by³⁴

$$k \simeq \frac{12zD_{aq}}{d_{sw}^2} \frac{k_{tr}}{k_p} \frac{C_{aq}}{C_M} \quad (7)$$

On the basis of eq 7 the exit rate coefficient k for butadiene is expected to be at least 1 order of magnitude larger than the one for styrene, where \bar{n} is often found close to 0.5 within fairly wide experimental limits:

(a) k_p for butadiene (ca. $200 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) is significantly smaller than the one for styrene ($380 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 62°C).³⁵

(b) $C_{aq} = 37 \text{ mmol} \cdot \text{L}^{-1}$ for butadiene,¹⁵ and $C_{aq} = 3.7 \text{ mmol} \cdot \text{L}^{-1}$ for styrene,³⁶ both at 50°C .

(c) On the basis of chemical structure, the maximum degree of polymerization of the exiting species z is expected to be roughly 2 times larger for butadiene (C_4H_6) as compared with styrene (C_8H_8).

Experimental evidence is as yet insufficient to further substantiate this possibility, although as mentioned previously the similarity with emulsion polymerizations of more water-soluble monomers, kinetically dominated by desorption of monomeric radicals, is suggestive of an analogous behavior for butadiene.

Further research (seeded experiments with monodisperse latexes are currently underway) is necessary to elucidate the exact kinetic scheme, but the results presented here give a better understanding of the behavior of this widely used monomer in emulsion polymerization systems.

The basic conclusions of this kinetic study are as follows:

1. In these typical butadiene emulsion homopolymerizations, termination is not rate-determining (except perhaps for very large particles), so that $\bar{n} \leq 0.5$.
2. Over the range of particle number and initiator concentrations studied, the entry rate coefficient is only very weakly dependent on initiator concentration.
3. Loss of free-radical activity within the particles is a first-order process, which may be transfer to monomer followed by exit.

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Appendix. Calculation of the Saturation Monomer Concentration

The beginning of interval III at conversion x' corresponds to a situation where the unreacted monomer is almost completely imbibed in the latex particles. Mutual solubility of butadiene and water is low enough to be ignored.

Taking conversion $x' = 0.60$ (see Results and Discussion) and using $\rho_p = 0.88 \text{ g} \cdot \text{mL}^{-1}$ and $\rho_M = 0.565 \text{ g} \cdot \text{mL}^{-1}$ at 62°C , a value for $C_M = 5.32 \text{ mol} \cdot \text{L}^{-1}$ is obtained, assuming

ideal mixing of monomer and polymer. However, systems like these rarely behave ideally, which is revealed by measurements of the density of the polymerization system as a function of conversion. For this purpose an Anton Paar density meter with a remote cell (DMA 401; maximum pressure 10 atm.) was employed. Samples were taken at regular time intervals, in between which the cell was flushed with distilled water. Conversions were determined gravimetrically as described previously (see the Experimental Section).

The experimentally determined density-conversion relationship (Figure 9) differs markedly from that calculated assuming ideal mixing of monomer and polymer and additivity of specific volumes of the separate phases. At conversions $< 50\%$ the discrepancy between ideality and experiment is partly caused by the instability of the monomer emulsion. Demixing started seconds after the cell was filled with a fresh latex sample. In the absence of a steady signal the minimum value for the density was taken, which can introduce a serious systematic error. It should be noted that this minimum value was quite reproducible. In contrast, at conversions $> 50\%$ measurements were free of this artifact and can be used without reservations.

At conversion $x' = 0.60$ only the aqueous phase and the monomer-swollen latex particles have to be considered. Additivity of the specific volumes of both phases is justified, since mutual solubility is negligible. From the experimentally determined density at 60% conversion, the density of the swollen particles can be calculated. A volume contraction factor can be defined as the ratio of "ideal" to experimental density of the swollen particles, which was found to be 0.95. The saturation monomer concentration C_M corrected for nonideal mixing of monomer and polymer thus becomes $5.6 \text{ mol} \cdot \text{L}^{-1}$ and was found independent of (unswollen) particle diameters between 30 and 150 nm (Figure 5).

References and Notes

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Registry No. VCH, 100-40-3; butadiene, 106-99-0; dresinate 214, 39389-48-5; sodium dodecylsulfate, 151-21-3.