

## High-conversion emulsion polymerization

***Citation for published version (APA):***

Maxwell, I. A., Verdurmen, E. M. F. J., & German, A. L. (1992). High-conversion emulsion polymerization. *Makromolekulare Chemie*, 193(10), 2677-2695. <https://doi.org/10.1002/macp.1992.021931016>

***DOI:***

[10.1002/macp.1992.021931016](https://doi.org/10.1002/macp.1992.021931016)

***Document status and date:***

Published: 01/01/1992

***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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## High-conversion emulsion polymerization

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(Date of receipt: January 13, 1992)

### SUMMARY:

The four important factors that determine the rate of emulsion polymerization are the propagation rate coefficient, the latex-particle concentration, the monomer concentration in the latex particles, and the free-radical concentration in the latex particles. Both theoretical considerations and experimental evidence suggest that the important factors that may reduce the rate of emulsion polymerization at high conversion are the propagation rate coefficient and the monomer concentration in the latex particles, and not the free-radical concentration in the latex particle, if the initiator is not depleted. Various approaches for increasing the rate of emulsion polymerization at high conversion are suggested.

### 1. Introduction

One of the important considerations in any industrial application of the emulsion polymerization process is residual monomer in the final emulsion latex product. Often it is very difficult to remove the last few percent of monomer during the polymerization reaction, since the rate of an emulsion polymerization can become relatively slow at high weight fractions of polymer in the latex particles. It should be noted that the problem of slow rates of emulsion polymerization at high conversions apply for both continuous and batch processes, since in continuous and semi-continuous reactors residual monomer is normally removed by reaction in a post (batch) reactor.

In this paper theories of emulsion polymerization are considered in an attempt to show the causes of the often slow rate of emulsion polymerization at high conversions of monomer. Case studies are presented for the emulsion polymerizations of methyl methacrylate and butadiene. The aim of this paper is to distinguish the effect of high conversion upon those factors that determine the rate of an emulsion polymerization. Specifically, we wish to determine why the rate of emulsion polymerization of a specific system may become (uneconomically) slow at high conversion. Having isolated some of the major difficulties, some techniques for circumventing the slow rates of emulsion polymerization at high conversion are suggested.

### 2. Theory

In the following discussions we consider, for simplicity, emulsion homo-polymerization, i.e. the emulsion polymerization of one monomer. However, most of the theoretical description can be easily extended to account for two or more monomers.

The rate of any free-radical polymerization can be written as:

$$\text{rate} = -\frac{d[M]}{dt} \propto k_p [M][R^*] \quad (1)$$

where  $[M]$  is the average monomer concentration in the system,  $k_p$  is the propagation rate coefficient for the monomer-polymer system, and  $[R^*]$  is the average free-radical concentration in the system.

An emulsion polymerization is a heterogeneous polymerization, wherein most of the polymerization occurs in the latex particles, except at very unusual circumstances (e. g. the emulsion polymerization of 2-hydroxyethyl methacrylate or acrylonitrile where the term emulsion polymerization is used only in a generic sense). Considering the isolation of a polymerization within latex particles, the average radical concentration can be written as a product of the concentration of latex particles in the system ( $[P]$ ) and the average number of free radicals per particle ( $\bar{n}$ ). The emulsion polymerization rate equation is written as:

$$\text{rate} = -\frac{d[M]}{dt} = k_p \cdot C_{mo} \cdot [P] \bar{n} \quad (2)$$

where the concentration of monomer in the latex particles,  $C_{mo}$ , replaces the average concentration in the whole latex. Eq. (2) is often written in terms of the fractional conversion of monomer ( $x$ ):

$$\text{rate} = -\frac{dx}{dt} = \frac{k_p \cdot C_{mo} \cdot [P] \bar{n}}{n_{mo}} \quad (3)$$

where  $n_{mo}$  is the initial average concentration of monomer in the latex system.

We now consider those factors which may affect the rate of emulsion polymerization at high conversions. In this paper high conversion always applies to the so-called interval III of an emulsion polymerization, where there are no monomer droplets in the system and all the monomer is contained in the latex particle and aqueous phases. Note that we are specifically interested in the latter part of interval III. There are four variables in the rate equation (Eqs. (2) or (3)) that can vary during the course of polymerization in interval III: (1) the propagation rate coefficient, (2) the latex particle concentration, (3) the monomer concentration in the latex particles, and (4) the average number of free radicals per latex particle. The effect of each of these factors upon the rate of emulsion polymerization during interval III are discussed below.

### 2.1. Propagation rate coefficient

The propagation rate coefficient represents the rate of reaction between a particular polymeric radical and monomer. The rate-determining step for the propagation reaction is usually the chemical rate of reaction. For this reason, for a particular system at a particular temperature and pressure, a propagation rate coefficient measured from independent techniques, say rotating sector in solution polymerization, may be used in emulsion polymerization. However, at high conversions the rate of diffusion of monomer to the polymeric radical may become slower than the rate of chemical reaction between these two species<sup>1,2</sup>. At these conditions the propagation rate

coefficient is said to be diffusion-controlled. The overall propagation rate coefficient ( $k_p$ ) can be expressed as the minimum value of the chemically controlled propagation rate coefficient ( $k_{pc}$ ) and the diffusion-controlled propagation rate coefficient ( $k_{pd}$ )<sup>1)</sup>:

$$\frac{1}{k_p} = \frac{1}{k_{pc}} + \frac{1}{k_{pd}} \quad (4)$$

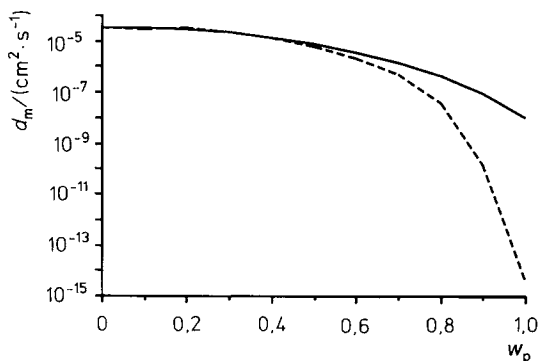
The value of  $k_{pc}$  can only be determined by experimental techniques<sup>3)</sup>, while the value of  $k_{pd}$  can be estimated from Smoluchowski's equation<sup>2)</sup>:

$$k_{pd} = 4\pi d_m \cdot RN_A \quad (5)$$

where  $d_m$  is the diffusion coefficient of the monomer in the polymer,  $N_A$  is Avogadro's number, and  $R$  represents the mutual radii of the reacting species, which is well estimated by the Lennard-Jones diameter of the monomer<sup>2)</sup>. In emulsion polymerization the value of the diffusion coefficient of the monomer in the polymer depends critically upon the temperature, monomer type, polymer type and the weight fraction of polymer in the latex particles. For systems polymerized below the glass transition temperature of the polymer the diffusion coefficient of the monomer through the polymer is normally rapid while the particles are saturated with monomer. However, at high conversions the monomer is depleted and the diffusion coefficient may become negligible (Fig. 1), and hence also the rate of polymerization (Fig. 2). If a system is polymerized well above its glass transition temperature then it is often the case that propagation never becomes diffusion-controlled, simply because the rate of diffusion through a rubbery polymer may be sufficiently rapid (Fig. 1) to ensure that propagation never becomes diffusion-controlled. In this case the rate of polymerization is unaffected by the diminishing monomer content with respect to any effect upon the propagation rate coefficient at high conversions (Fig. 3).

From the above discussion it can be seen that the rate of polymerization is dramatically slowed down by the changing value of the propagation rate coefficient only when the propagation rate coefficient becomes diffusion-controlled. The weight

Fig. 1. Typical diffusion coefficients of small penetrants in polymer ( $d_m$ ) versus weight fraction of polymer ( $w_p$ ) both below (solid line) and above (dashed line) the glass transition temperature of the polymer<sup>4)</sup>



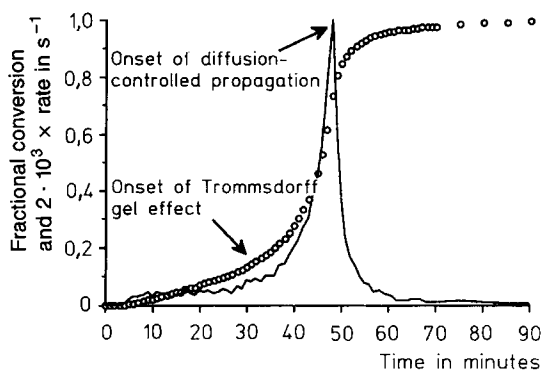


Fig. 2. The interval III conversion-time (circles) and rate (solid line) curves for the seeded emulsion polymerization of methyl methacrylate at  $60^{\circ}\text{C}$ . Seed diameter = 200 nm, latex particle concentration,  $[\text{P}] = 1 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ , peroxodisulfate initiator concentration,  $[\text{I}] = 3 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

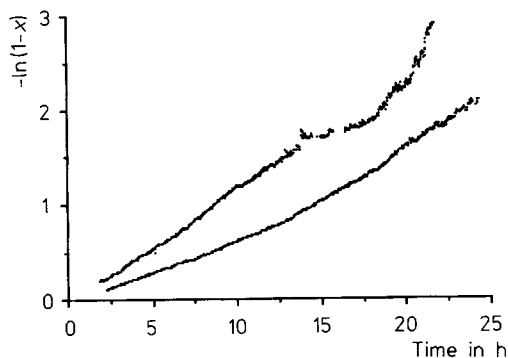


Fig. 3. The interval III:  $-\ln(1-x)$  versus time ( $x$  is fractional conversion of monomer) for the seeded emulsion polymerization of 1,3-butadiene at  $60^{\circ}\text{C}$  with initial initiator concentration  $[\text{I}] = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ , for two different latex particle seed diameters: (top line) seed diameter = 150 nm, (bottom line) seed diameter = 215 nm. Final conversions are  $x = 0,97$  (150 nm) and  $x = 0,87$  (215 nm)

fraction of polymer in the latex particles, at which propagation becomes diffusion-controlled, if indeed it does so, depends upon the values of the chemically controlled propagation rate coefficient and the diffusion coefficient of the monomer through the polymer. Propagation will normally become diffusion-controlled for monomers polymerized below the glass transition temperature of their corresponding polymer. The onset of diffusion-controlled propagation may be avoided, or the value of the diffusion-controlled propagation rate coefficient may be increased by the following techniques:

- 1) The addition of an inert diluent which increases the diffusion coefficient of the monomer, and therefore the propagation rate coefficient. This diluent may be a gas at room pressure but added under pressure as a liquid, and can therefore be removed after reaction by simply reducing the pressure. It should be noted that a diluent may also slow the rate of polymerization, since it reduces the concentration of monomer in the particle. However, at high conversions in interval III this should be a minor effect, well compensated for by the increase in the diffusion coefficient of monomer and hence the propagation rate coefficient.

2) Changing the conditions of the reaction, e.g. the temperature, at high fractions of polymer so that the diffusion coefficient of monomer in the polymer is increased.

## 2.2. Latex particle concentration

In interval III of an emulsion polymerization the rate of latex particle formation is usually negligible. If this is the case the latex particle concentration is constant, unless particle coagulation is occurring. Obviously the rate of polymerization depends directly upon the particle concentration, so to ensure an observable rate of polymerization at high conversions, sufficient latex particles must be created during the earlier periods of the polymerization. This is often a problem for (added) surfactant-free emulsion polymerizations, in which the particle concentrations are usually considerably lower than for conventional emulsion polymerizations<sup>6)</sup>.

It should be noted that, say, a higher latex particle concentration will not directly aid in the removal of residual monomer, since the kinetics that determine the rate of conversion per particle during reaction in interval III are probably insensitive to the latex particle concentration. This is not to suggest that the latex particle concentration does not affect the kinetics (which it almost certainly does), rather to emphasize that, say, low diffusion coefficients of monomer in the latex particles are not affected by the latex particle concentration.

## 2.3. Monomer concentration in the latex particles

The rate of emulsion polymerization depends directly upon the monomer concentration in the latex particles. Therefore, as monomer is consumed, the rate decreases. In interval III, if it is assumed that all monomer is contained within the latex particles, the fractional conversion of monomer is given by:

$$x = \frac{C_{s,mo} - C_{mo}}{C_{s,mo}} \quad (6)$$

where  $C_{s,mo}$  is the saturation concentration of monomer in the latex particles (or that at the beginning of reaction in interval III). Therefore, the emulsion polymerization rate equation (Eq. (3)) can be written as<sup>7)</sup>:

$$\frac{-d \ln(1 - x)}{dt} = \frac{k_p \cdot C_{s,mo} \cdot [P] \bar{n}}{n_{mo}} \quad (7)$$

Since in Eq. (7)  $C_{s,mo}$  is a constant, it is obvious that the consumption of monomer results in an exponentially decreasing rate of polymerization during interval III. This is only true, if monomer is contained mainly within the latex particles, a situation that arises only for relatively water-insoluble monomers (e.g. styrene). Obviously for more water-soluble monomers the effect of the monomer concentration upon the rate of polymerization is complicated by monomer partitioning between the latex particle and aqueous phases<sup>8)</sup>. The manner in which monomer partitions between the two phases

has been the subject of some discussion<sup>9-11)</sup> and a simple empirical equation, which well describes experimental monomer partitioning results, has recently been developed<sup>11)</sup>:

$$\ln(1 - v_p) + v_p + \text{corr} = \ln\left(\frac{[M]_{\text{aq}}}{[M]_{\text{aq, sat}}}\right) \quad (8)$$

where  $v_p$  is the volume fraction of polymer in the latex particles,  $[M]_{\text{aq}}$  the concentration of monomer in the aqueous phase at that volume fraction of polymer,  $[M]_{\text{aq, sat}}$  the concentration of monomer in the aqueous phase as saturation swelling of the latex particles by monomer, and corr a correction factor given by<sup>11)</sup>:

$$\text{corr} = -[v_{p, \text{sat}} + \ln(1 - v_{p, \text{sat}})] \quad (9)$$

where  $v_{p, \text{sat}}$  is the volume fraction of polymer in the latex particles at saturation swelling of the latex particles by the monomer. The overall monomer concentration in the system is given by:

$$[M] = xn_{\text{mo}} = C_{\text{mo}} \cdot v_{\text{part}} + [M]_{\text{aq}} \cdot v_{\text{aq}} \quad (10)$$

where  $v_{\text{part}}$  is the volume fraction of the particle phase and  $v_{\text{aq}}$  is the volume fraction of the aqueous phase. If we know the volume fraction of the latex particle phase at a particular conversion of monomer, then the concentration of monomer can be calculated by solving Eqs. (8)–(10) (numerically, as no algebraic solution is available).

The effects of conversion (total monomer concentration) upon the concentration of monomer in the latex particle and aqueous phases for emulsion polymerizations with various monomers of differing aqueous-phase saturation solubilities are displayed in Fig. 4. In essence, the partitioning of all partially water-soluble monomers display a

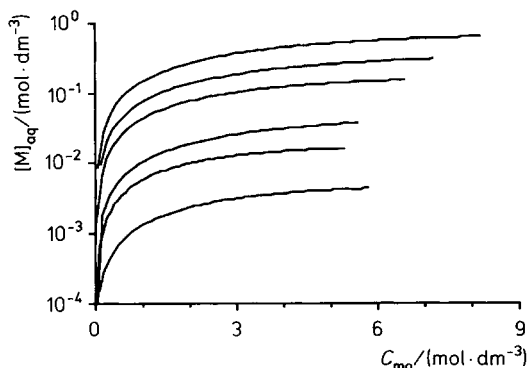


Fig. 4. The concentration of monomer in the latex particles ( $C_{\text{mo}}$ ) versus the concentration in the aqueous phase ( $[M]_{\text{aq}}$ ) calculated from Eqs. (8), (9) for various monomers at 50 °C. In increasing saturation water solubilities the monomers are styrene, butyl acrylate, butadiene (saturation pressure), methyl methacrylate, vinyl acetate and methyl acrylate. All parameters utilized in these calculations listed in Tab. 1

similar behaviour. That is, in terms of phase saturation by monomer the aqueous phase is favoured. The similarity in monomer partitioning behaviour arises because the configurational free energy associated with the entropy of mixing of monomer and polymer within the latex particles dominates the in-particle thermodynamics<sup>11)</sup>. The effect of this partitioning behaviour upon the rate of emulsion polymerization depends upon the saturation concentration of the monomer in the aqueous phase. If it is relatively high, then a significant proportion of the monomer may reside in the aqueous phase, thus reducing both the concentration of monomer and the rate of polymerization in the latex particles. This effect is counterbalanced by the fact that the more water-soluble monomers tend to have higher saturation concentrations of monomer in the latex particles (Fig. 4) resulting from lower latex-particle/water interfacial tensions<sup>10)</sup>.

The decreasing rate of the polymerization with decreasing monomer concentration is an effect which cannot be avoided, simply because the rate of polymerization is proportional to the concentration of monomer in the particles. However, the rate of polymerization can be enhanced if the monomer partitioning favours the latex particle phase over the aqueous phase. The following points need to be considered:

1) Latex-particle/water interfacial tension: For small latex particles the degree of swelling by monomer is enhanced by lower interfacial tensions, which may be affected by the choice of surfactant<sup>12)</sup>. Generally, the more water-soluble the monomer and the more hydrophilic the polymer, the lower the interfacial tension (in fact it seems that for a particular surfactant a monomer droplet has the same interfacial tension as a latex particle composed of the polymer of that monomer)<sup>13)</sup>.

2) The addition of water-soluble organic agents, e. g. methanol, may lower the latex-particle/water interfacial tension, but would simultaneously increase the solubility of the monomer in water<sup>14)</sup>.

3) A temperature change may shift the monomer partitioning in favour of the latex-particle phase, simply by affecting the saturation solubility of the monomer in the latex particle and aqueous phases<sup>11)</sup>.

Tab. 1. Values of saturation concentration of monomer in the latex particles  $C_{s,mo}$ , concentration of monomer in the aqueous phase at saturation swelling of the latex particles by monomer  $[M]_{aq,sat}$ ,  $\rho_m$  the density of monomer,  $\rho_p$  the density of polymer, and molar mass  $M$ , utilized to calculate monomer partitioning between aqueous phase and the latex-particle phase at 50 °C (Fig. 4). In each case the latex particle is composed of homopolymer of that monomer

Monomer	$C_{s,mo}$ mol · dm <sup>-3</sup>	$[M]_{aq,sat}$ mol · dm <sup>-3</sup>	$\rho_m$ g · cm <sup>-3</sup>	$\rho_p$ g · cm <sup>-3</sup>	$M$ g · mol <sup>-1</sup>
styrene	5,8	$4,3 \cdot 10^{-3}$	0,878	1,044	104,15
butyl acrylate	5,3	$1,6 \cdot 10^{-2}$	0,579	0,875	54,09
1,3-butadiene	5,6	$3,7 \cdot 10^{-2}$	0,869	1,026	128,17
methyl methacrylate	6,6	0,15	0,909	1,178	100,12
vinyl acetate	7,0	0,30	0,940	1,170	86,09
methyl acrylate	8,2	0,62	0,950	1,100	86,09



#### 2.4. Free-radical concentration in the latex particles

The time dependence of the concentration of latex particles containing  $i$  free radicals ( $N_i$ ) is commonly thought to be fully described by the Smith-Ewart equations<sup>15)</sup>:

$$\frac{dN_i}{dt} = \rho (N_{i-1} - N_i) + k[(i+1)N_{i+1} - iN_i] + c[(i+2)(i+1)N_{i+2} - i(i-1)N_i] \quad (11)$$

where  $\rho$  is a first-order entry rate coefficient for the entry of free radicals into latex particles,  $k$  is a first-order rate coefficient for the exit of free radicals from latex particles, and  $c$  is the first-order termination rate coefficient between two free radicals in the latex particles. The Smith-Ewart equations by themselves are not very useful for the present work (i. e. estimating the concentration of free radicals in the latex particles) for the following reasons:

1) The possible variation in latex-particle size within a system is not implicitly taken into account in these equations. That is, the rate coefficients may be particle-size dependent, and since different particle sizes may accommodate different numbers of free radicals, the rate coefficients may be dependent upon  $N_i$ .

2) The rate coefficients are all assumed to be first-order and independent of the number of radicals in each particle, an assumption that has been shown to be incorrect for at least two of these rate coefficients, viz. those for exit<sup>7)</sup> and bimolecular termination<sup>16)</sup>.

In order to overcome the difficulties presented above, in what follows current theories for the individual rate coefficients in the Smith-Ewart equations will be assessed independently, especially with regard to the qualitative effect of high conversion of monomer upon these rate coefficients, and the concomitant effect upon the rate of polymerization. It should be noted that most of the rate coefficients are not simple numbers reflecting a chemical process, but coefficients representing a plethora of reaction and diffusion events. For this reason the various rate coefficients can be dependent upon all or some of the other variables discussed in this paper, i. e. monomer concentration in the latex particles and water phase, the propagation rate coefficient, the latex particle concentration, and the free-radical concentration in the latex particles.

##### 2.4a. Entry-rate coefficient

The most successful model<sup>17)</sup> for the entry of free radicals into latex particles proposes that an aqueous-phase free radical formed from peroxodisulfate decomposition in the aqueous phase, a sulfate anion radical, must add on a specific number of monomeric units, thereby becoming a surface-active oligomeric free radical. The diffusion of these surface-active free radicals to the latex-particle surfaces and subsequent propagation into the particles (entry) is not rate-determining in the presence of any appreciable concentration of latex particles, since these processes are relatively rapid compared to the rate of growth of these free radicals to the size that distinguishes the

species as surface-active. Note that termination of free radicals in the aqueous phase is a relatively rapid process, hence the initiator efficiency can often be very low in emulsion polymerization. The entry rate coefficient,  $\rho$ , is given by<sup>17)</sup>:

$$\rho = \left( \frac{2k_d \cdot [S_2O_8^{2-}]}{[P]} \right) f \quad (12)$$

where  $k_d$  is the initiator decomposition rate coefficient, and the fractional initiator efficiency,  $f$ , is given by<sup>17)</sup>:

$$f = \left( 1 + \frac{2k_{ta} \cdot [T^*]}{k_p \cdot [M]_{aq}} \right)^{1-z} \quad (13)$$

where  $k_{ta}$  is the diffusion-controlled aqueous-phase termination rate coefficient between two oligomeric radicals in the aqueous phase, and  $z$  the number of monomeric units that must add to a sulfate anion radical to form a surface-active species. The total aqueous phase radical concentration ( $[T^*]$ ) is given by<sup>17)</sup>:

$$[T^*] = \left( \frac{k_d \cdot [S_2O_8^{2-}]}{k_{ta}} \right)^{1/2} \quad (14)$$

Utilizing Eqs. (13)–(15) we can calculate the effect of the changes in the rate parameters and variables that determine the entry-rate coefficient at high conversions in emulsion polymerization. In Fig. 5 the effect of the decreasing monomer concentration in the aqueous phase (displayed as a function of the concomitant increase in the weight fraction of polymer in the latex particles with increasing conversion) upon the entry-rate coefficient throughout interval III of a styrene emulsion polymerization is displayed along with experimental data<sup>17)</sup>. It can be seen that at moderate conversions theory and experiment show excellent agreement. At higher conversions theory predicts that the rate of free-radical entry into latex particles decreases as the monomer

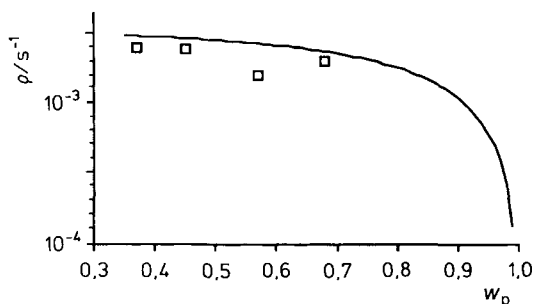


Fig. 5. Calculated (line) and experimental<sup>17)</sup> entry-rate coefficients ( $\rho$ ) versus weight fraction of polymer  $w_p$  in the latex particles for the emulsion polymerization of styrene at 50°C with initial initiator concentration  $[I] = 5 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ . Entry rate coefficients calculated from Eqs. (12)–(14) with aqueous-phase monomer concentration calculated from Eqs. (8)–(10). All other parameters as listed in Tab. 2

Tab. 2. Values of the number of monomeric units that must add to a sulfate anion radical ( $z$ ), rate coefficients of propagation, termination and initiator decomposition ( $k_p$ ,  $k_t$  and  $k_d$ ), concentration of latex particles in the system  $[P]$ , and concentration of monomer in the aqueous phase at saturation swelling of the latex particles by monomer  $[M]_{\text{aq, sat}}$  from ref. <sup>17)</sup> utilized in the calculation of entry-rate coefficients for the emulsion polymerization of styrene (Fig. 5 and Fig. 6). The saturated monomer concentrations in the aqueous phase apply only to Fig. 6

Parameter at	25 °C	50 °C	75 °C
$z$	2	2	2
$k_p/(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	110	258	646
$k_t/(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	$3,7 \cdot 10^9$	$3,7 \cdot 10^9$	$3,7 \cdot 10^9$
$k_d/(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	$2 \cdot 10^{-8}$	$1 \cdot 10^{-6}$	$9 \cdot 10^{-5}$
$[P]/(\text{mol} \cdot \text{dm}^{-3})$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$
$[M]_{\text{aq, sat}}/(\text{mol} \cdot \text{dm}^{-3})$	$2,7 \cdot 10^{-4}$	$4,3 \cdot 10^{-4}$	$7,0 \cdot 10^{-4}$

concentration decreases. If all other kinetic events were unaffected by high conversion then this result would predict that both the concentration of free radicals in the latex particles and the rate of polymerization should become relatively small at high conversions. However, as will be seen in the next two sections, similar reductions in the radical loss mechanisms at high conversions may counterbalance the effect upon the rate of polymerization predicted by the theory for entry alone. For example, at steady state the number of free radicals per latex particle in a Smith-Ewart case-1 system is given by  $\bar{n} \approx \rho/k$ . If both the entry- and exit-rate coefficients decrease at the same rate then no effect upon the radical concentration per particle will be observed.

In Fig. 6 the effect of decreasing initiator ( $S_2O_8^{2-}$ ) concentration upon the entry-rate coefficient calculated from Eqs. (12)–(14) for the emulsion polymerization of styrene is displayed at various temperatures, all other parameters being constant. It can be seen that at 80 °C the entry-rate coefficient decreases dramatically over a period of time as a result of initiator depletion. This trivial problem can obviously be overcome by the addition of further initiator, or the use of initiator with the appropriate decomposition rate coefficient at the reaction temperature.

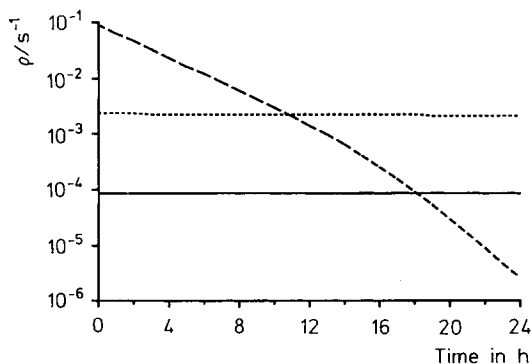


Fig. 6. Entry-rate coefficient ( $\rho$ ) versus time calculated from Eqs. (12)–(14) for the emulsion polymerization of styrene at 20 °C (solid line), 50 °C (dotted line) and 80 °C (dashed line). Initial initiator concentration,  $[I] = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ . All other parameters as listed in Tab. 2

If the concentration of latex particles is low in a particular emulsion polymerization then aqueous-phase free radicals may react in the aqueous phase before they encounter a latex particle. Specifically, free-radical termination in the aqueous phase reduces the number of free radicals that enter the latex particle phase. However, during interval III of an emulsion polymerization the concentration of latex particles is usually sufficient to ensure that all surface-active free radicals are captured.

At moderately high conversions or weight fraction of polymer it can be shown<sup>18)</sup> that the simple arguments used to derive Eqs. (12)–(14) are still valid despite the lower monomer concentrations in the latex particles, since diffusion to, and reaction within latex particles of surface-active radicals is so much more rapid than reaction of a surface-active radical in the aqueous phase. However, for very glassy polymers with little monomer content (at very high conversions) it is easy to imagine that a surface-active free radical in the aqueous phase may terminate before it propagates with monomer at the surface of a latex particle. For peroxodisulfate the presence of a charged group on the oligomeric entering free radicals most likely prevents diffusion of the entering radical into the interior of the particle. This particular problem may be overcome by using a less water-soluble (unchanged) initiator (e. g. azo-initiators). This possibility will be discussed below.

The theory for entry described by Eqs. (12)–(14) was developed specifically for the peroxodisulfate initiator. Other initiators, e. g. azo-initiators, do not have such clear-cut behaviour, since they can be both water-soluble and oil-soluble. For azo-initiators it is thought<sup>19)</sup> that much of the free-radical polymerization is initiated by radicals formed by initiator decomposition in the aqueous phase or by free radicals formed by initiator decomposition in the latex-particle phase followed by desorption of one free radical. At high conversions the often small diffusion coefficients in the latex particles ensure geminate recombination of any pair of free radicals formed in the latex particles<sup>3)</sup> (i. e. the two radicals formed from initiator decomposition combine to form a species that cannot undergo further decomposition to give free radicals). This so-called cage effect is the cause of the slow rates of high-conversion bulk polymerization<sup>2)</sup>.

Despite the problems described above free radicals formed in the organic phase have one advantage over, say peroxodisulfate-generated free radicals, in that they may penetrate the latex particles. One possible route to aid in the removal of residual monomer is the development of an organic (latex particle) phase free-radical generating species which avoided the problem of geminate recombination. Possibilities include initiators that: 1) create free radicals one at a time in the latex-particle phase, 2) create two free radicals that may undergo non-geminate recombination in the latex-particle phase, or 3) create two free radicals that may not undergo combination for steric reasons, or since one of the radicals is very stable.

#### 2.4b. Free-radical exit

The exit of free radicals from latex particles has been the subject of many theoretical considerations and few experimental studies. Currently, a limit of the theory for the exit of free radicals from latex particles developed<sup>20)</sup> for a Smith-Ewart case 1 and 2 system

is most widely accepted. A small free-radical species is created by transfer of polymeric free-radical activity to monomer or chain transfer agent. This small free-radical species can either propagate within the latex particles or exit to the aqueous phase. Assuming that all exited free radicals are destroyed in the aqueous phase, the latex-particle-size dependent exit-rate coefficient for monomeric radicals is given by<sup>20)</sup>:

$$k = k_{tr} \cdot C_{mo} \frac{k_{es}}{k_{es} + k_{p0} \cdot C_{mo}} \quad (15)$$

where  $k_{tr}$  is the transfer rate coefficient,  $k_{p0}$  the propagation rate coefficient of the small free radical, and  $k_{es}$  is the rate coefficient for diffusion of the small free radicals out of the latex particles, given by<sup>20,21)</sup>:

$$k_{es} = \frac{3d_w}{qR_s^2} \quad (16)$$

where  $d_w$  is the diffusion coefficient of the small radical in the aqueous phase,  $R_s$  is the swollen radius of the latex particles, and  $q$  the ratio of the chemical potential of the exiting radical in the particle and aqueous phases, given, in the case of a monomeric radical, by the ratio of saturation concentrations of the monomer in the latex-particle and aqueous phases. Note that this theory is not valid for systems with more than one radical per particle.

During the course of interval III the concentration of monomer in the latex particle decreases (as was shown in section 2.3.). An example of the effect of the decreasing monomer concentration in the latex particles on the exit-rate coefficient for the emulsion polymerization of styrene with different-size latex particles is given in Fig. 7. Clearly, the rate coefficient for free-radical loss by exit decreases as the monomer concentration in the particles decreases. This fact would act to enhance the rate of emulsion polymerization.

Recently, a more complex theory for the free-radical exit has been developed which can be applied at high weight fractions of polymer in the latex particles<sup>22)</sup> in which

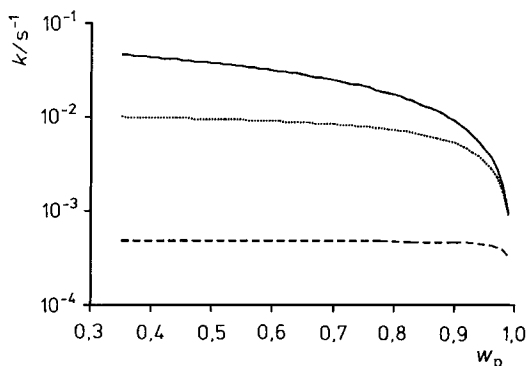


Fig. 7. Exit-rate coefficient ( $k$ ) versus weight fraction of polymer  $w_p$  calculated from Eqs. (15), (16) for the emulsion polymerization of styrene at 50 °C with latex particle radii,  $R_s = 20$  nm (full line), 100 nm (dotted line), and 500 nm (dashed line)

reaction and diffusion are coupled within the latex particles. This theory takes into account slow diffusion within the latex particles at high weight fractions of polymer, and the effect this has upon the escape rate coefficient. Unfortunately, this theory does not properly take into account the fate of the exited free radical nor has it been tested with experimental data. However, the theoretical considerations suggest that, at very high weight fractions of polymer in the latex particles, the rate of free-radical exit is reduced, and hence the rate of polymerization is increased.

#### 2.4c. Bimolecular termination

In emulsion polymerization bimolecular termination between two free radicals is probably achieved in two major ways, termination between polymeric free radicals and termination between a polymeric free radical and a short free radical created via transfer of free-radical activity from a polymeric radical<sup>16</sup>.

The rate of termination between two polymeric free radicals in a latex particle has been shown to be controlled by 'reaction-diffusion'<sup>23</sup>: Since the weight fraction of polymer within the latex particles is always high, the polymeric species are always entangled and the polymeric radical ends can only diffuse to each other via propagational growth. Considering this the second-order termination rate coefficient,  $k_t$ , is given by the Smoluchowski relationship<sup>23</sup>:

$$k_t = 16\pi R_{\text{int}} \cdot d_{\text{end}} \cdot N_A \quad (17)$$

where the diffusion coefficient of the radical end is given<sup>23</sup>) by the rate of propagation,  $d_{\text{end}} = k_p \cdot C_{\text{mo}} \cdot a^2/6$  where  $a$  is the root-mean-square end-to-end distance per square root of the number of monomeric units in the polymer chain. The radius of interaction of two radicals,  $R_{\text{int}}$  is given<sup>23</sup>) by considerations of chain-end displacements. Note that the first-order termination rate coefficient is given by  $c = k_t/(N_A \cdot V_S)$ , where  $N_A$  is Avagadro's constant and  $V_S$  the swollen volume of a latex particle.

As the weight fraction of polymer in the latex particles increases with increasing conversion, two important parameters cause the termination rate coefficient described by Eq. (17) to decrease. First, the decreasing concentration of monomer will reduce the rate of propagational growth of two free radicals towards each other. Secondly, the increasing fraction of polymer in the latex particles will limit the mobility of the free-radical end of the polymer chain, and hence reduce the value of  $R_{\text{int}}$ .

Recently, it has been recognized<sup>16,24</sup>) that small free radicals, created by the transfer of radical activity to monomer and chain transfer agent, can diffuse very rapidly throughout the latex particles, and hence terminate much quicker than long free radicals. The theory developed for this, the so-called 'short-long' termination process is, not surprisingly, quite complex, since the concentration of all small radical species must be considered individually, because each small-size radical has its own diffusion coefficient and concentration. Despite these complexities the important points for a consideration of high-conversion emulsion polymerization are that higher weight fractions of polymer result in: 1) lower diffusion coefficients of all species through the

polymer<sup>16</sup>), and hence lower rate of short-long termination, and 2) lower degrees of polymerization at which small free radicals become entangled in the polymer matrix, whereupon they do not participate in short-long bimolecular termination<sup>16</sup>). Hence, the rate of free-radical loss by bimolecular termination through both the mechanisms discussed above is reduced at high conversions of monomer to polymer. This is often reflected by the observation of the Trommsdorff gel effect where the rate of emulsion polymerization is most rapid<sup>16</sup>).

#### 2.4d. Free-radical concentration in the latex particles: summary

At high conversions in emulsion polymerization both the radical-loss and radical-gain mechanisms are retarded. In the case of free-radical entry into latex particles, current theory suggests that the entry-rate coefficient is reduced, since radical growth in the aqueous phase is slowed down by the decreasing monomer concentration in that phase. Both radical-loss mechanisms, free-radical exit and bimolecular termination, are retarded by, amongst other things, the decreasing monomer concentration within the latex particles and the concomitant lowering of the diffusion coefficient of the monomer in the particles. The rate of polymerization at high conversion is therefore slowed down due to the decreasing rate of entry of free radicals into latex particles, but enhanced considerably by the decrease in the rate of free-radical loss by exit and bimolecular termination. It should be noted that the conclusions reached above are dependent upon the values of the rate parameters utilized in the kinetic models for entry, exit and termination. Differing values of these parameters for different systems may alter the quantitative results, but the qualitative trends should remain unchanged.

The effect of high conversion upon free-radical concentration in the latex particles, and hence the rate of polymerization, depends critically upon the number of free radicals in the latex particles. For example, if there is always less than one free radical per latex particle, then the decreasing rate of termination does not affect the rate of polymerization. The number of free radicals per latex particle itself depends upon the value of the rate coefficients for entry, exit and termination for the particular system of interest at the particular reaction conditions. Hence it is often difficult to estimate how the rate of polymerization of a particular system will change with increasing conversion of monomer to polymer, especially considering the number of unknown parameters that are needed to estimate the values of the relevant rate parameters by theoretical considerations alone. Often, complete studies of the system of interest will allow the determination of, say, the average number of radicals per particle and hence allow some scope for improving the rate of emulsion polymerization at higher conversions by utilizing the knowledge of how the relevant rate parameters vary at high conversions.

In section 4 of this paper new experimental evidence is presented which suggests that the total radical concentration in the latex particles is not greatly affected by low monomer concentrations in the latex particles at high conversions, suggesting that the retardation of the entry process at high conversions is counterbalanced by the slowing down in the rates of the free-radical loss mechanisms. This is the major result of this

work, since it suggests that the effect of changing radical concentrations in the latex particles at very high conversions may be ignored with respect to developing methods that may overcome slow rates of polymerization.

### 3. Experimental part

3.1. *Materials*: 1,3-Butadiene (DSM Chemical, The Netherlands) was distilled directly from a 27 litre storage vessel into a cooled steel recipient. A two-isomer mixture of "tertiary dodecylthiol" (mixture of  $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{SH}$  and  $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)(\text{SH})\text{CH}_2\text{C}(\text{CH}_3)_3$ ), sodium peroxydisulfate (Fluka AG, Switzerland) and sodium carbonate (p. a. Merck, Germany) were all used without further purification. Water was doubly distilled and purged with nitrogen to remove oxygen. The polybutadiene seed latices were prepared by techniques described elsewhere<sup>25</sup>.

3.2. *Emulsion polymerizations of 1,3-butadiene*: A complete overview of the experimental conditions used in the seeded interval III emulsion polymerization of 1,3-butadiene will be given elsewhere<sup>25</sup>. The recipe for reaction is as follows: water (84 wt.-%), polybutadiene seed with various diameters (9,3 wt.-%), butadiene (6,2 wt.-%), sodium carbonate ( $10^{-2}$  mol · dm<sup>-3</sup>), sodium peroxydisulfate ( $10^{-2}$  mol · dm<sup>-3</sup>), and *tert*-dodecylthiol (1 wt.-% of monomer). The seeded emulsion polymerizations were carried out in a stainless steel reactor (1 180 cm<sup>3</sup>) at 60 °C. The reactor was connected with a density meter (Anton Paar DMA 401, Austria), a registry unit (Anton Paar DMA 60, Austria) and a computer. The reaction mixture was pumped in a continuous loop through the density meter to determine the on-line density of the reaction mixture. These density measurements were calibrated with gravimetric conversion data, thus allowing the on-line measurement of fractional monomer conversion ( $x$ ). The final products of all reactions were checked for secondary latex particle nucleation by electron microscopy. Secondary nucleation was not observed.

### 4. Case studies — results and discussion

In this section the results of both previous and new experimental studies of emulsion polymerization at high conversions are discussed. All experiments are seeded, i. e. are performed within the presence of added latex with the proviso that no new latex particles are formed during the reaction. All reactions are performed in interval III at 60 °C.

#### 4.1. *The emulsion polymerization of methyl methacrylate at 60 °C*

The emulsion polymerization of methyl methacrylate is one of the most studied systems in the field<sup>1, 5, 8, 26</sup>. It is known that the interval II and III kinetics are well characterized by 'pseudo-bulk' kinetics<sup>1, 8</sup>. That is, bimolecular termination is rate-determining and there are many radicals in each particle. In interval III the number of radicals per latex particle increases, because the diffusion-controlled termination rate coefficient decreases. This behaviour is well displayed in Fig. 2. The increase in the radical concentration due to decreased termination is seen as the Trommsdorff gel effect. The point at which propagation becomes diffusion-controlled is well characterized in Fig. 2, and has been measured directly elsewhere<sup>1, 27</sup>. Since the reaction rate is dramatically reduced at high conversions, it is difficult to determine the values of the rate parameters that determine the free-radical concentrations in this regime, although attempts have been made<sup>26</sup>. These will be discussed below.



#### 4.2. The emulsion polymerization of 1,3-butadiene at 60 °C

Recently, much work has been performed on the seeded peroxodisulfate-initiated emulsion polymerization of 1,3-butadiene. It was found<sup>25</sup> that 1,3-butadiene obeys a Smith-Ewart case 1 and 2 system, i. e. there is at most one free radical in each latex particle, and bimolecular termination is not rate-determining. It was thought that this system would provide a good indication of the effect of low monomer concentrations associated with high conversions upon those rate parameters that determine the free-radical concentration in the latex particle. This is because the low glass transition temperature of polybutadiene ( $T_g = -86^\circ\text{C}$ ) ensures that the polymerization never becomes diffusion-controlled. This fact is supported by the absence of the Trommsdorff gel effect in the experimental polymerization rate curves (Fig. 3): for styrene (also a Smith-Ewart case 1 and 2 system during interval II) the slow-down of the diffusion coefficient is first indicated by a decrease in the rate of termination and hence the observation of the Trommsdorff gel effect<sup>7</sup>). The saturation water solubility of butadiene at the reactions conditions ( $[M]_{\text{aq}} = 0,037 \text{ mol} \cdot \text{dm}^{-3}$ ) is low enough to allow the use of Eq. (7)<sup>25</sup>). Hence, the experimental plot of  $\ln(1 - x)$  versus time should give a good indication of the changes in the free-radical concentration in the latex particles at high conversion, since all other variables in the rate equation (i. e. the propagation rate coefficient and the latex particle concentration) are constants throughout interval III.

The experimental rate data for seed latices of two different sizes are presented in Fig. 3. It is apparent in both cases that the rate of polymerization increases at high conversions (indicated by an upturn in the  $-\ln(1 - x)$  versus time curve), reflecting an increase in the free-radical concentration at high conversions (up to fractional monomer conversion  $x = 0,97$ ). This result suggests that the rate of exit decreases more rapidly than does the rate of free-radical entry. This is the most important result of this paper, because if it is a general result that the concentration of free radicals in the latex particles (for a peroxodisulfate-initiated system) is not greatly affected, or even enhanced, by the low monomer concentration in the latex particles at high conversions, then it can be stated that those factors that drastically affect the rate of emulsion polymerization at high conversion are the propagation rate coefficient and the monomer concentration, and not the free-radical concentration.

It may be argued that for glassy polymers the (much) lower diffusion coefficients of the monomer within the latex particles may cause the entry of free radicals to be much slower at high conversion. However, the radical concentration of a glassy emulsion polymer system at high weight fraction of polymer (methyl methacrylate in poly(methyl methacrylate)) has been measured directly by electron spin resonance<sup>1, 5, 26</sup> and it appears that the concentration of radicals continues to increase even up to a weight fraction of polymer in the latex particles,  $w_p = 0,97$ . Previously, the interpretation of this result has been confused by the fact that in these glassy emulsion polymer systems it is thought that both free-radical and monomer concentration gradients occur in the latex particles at high weight fractions of polymer<sup>27, 28</sup>). This makes the interpretation of the experimental results subject to artifact. The problem should not occur for the 1,3-butadiene system, since the much higher diffusion

coefficients in the latex particles, even at  $w_p = 1$ , would ensure rapid diffusion of both monomer and small free radicals within the latex particles.

## 5. Conclusions

The rate of an emulsion polymerization depends upon four major variables: the propagation rate coefficient, the latex particle concentration, the monomer concentration in the latex particles, and the free-radical concentration within the latex particles. Experimental data and theoretical models exist which purport to describe the changes of all these variables at high conversions. At high conversions the monomer concentration in both the latex particle and aqueous phase decreases, so causing other variables such as the diffusion coefficient of monomer in the latex particles to decrease. The aim of this paper was to determine the effect of high conversion upon the rate of emulsion polymerization, utilizing both current theory and new experimental results. In so doing it was hoped that techniques for overcoming the problem of slow rates of emulsion polymerization could be described.

There are two limiting kinds of behaviour of the propagation rate coefficient: the chemically controlled and the diffusion-controlled limit. The chemically controlled limit is independent of the weight fraction of polymer in the latex particles, and dependent upon the monomer-polymer system and the reaction conditions. The diffusion-controlled propagation rate coefficient occurs, when the diffusion of monomer to the polymeric radical is slower than the chemical reaction of these two species. The diffusion coefficient depends critically upon the weight fraction of polymer in the latex particles, the monomer-polymer system and the reaction conditions. Higher weight fractions of polymer (or higher conversions) may cause the diffusion-controlled propagation rate coefficient to decrease by orders of magnitude, thus causing very slow rates of polymerization. Diffusion-controlled propagation normally occurs for systems polymerized below the glass transition temperature of the polymer, but not for systems polymerized above the glass transition temperature of the polymer. If slow diffusion-controlled propagation is to be overcome, the reaction conditions must be changed to favour faster diffusion. This may be achieved by increasing the temperature or reducing the weight fraction of polymer by the addition of inert diluent (which itself must be removed — if it is gaseous at room pressure then this is easily achieved).

The latex particle concentration does not normally change at high conversions simply because latex particle nucleation is normally negligible in interval III (by definition). However, latex particle coagulation and low concentrations of latex particles (e. g. in (added) surfactant-free emulsion polymerizations) may cause unduly slow rates of polymerization.

If most of the monomer in an emulsion polymerization is contained within the latex particles, then the effect of polymerizing this monomer is an exponentially decreasing rate of polymerization. This is an effect that cannot be altered in a batch emulsion polymerization. For more water-soluble monomers the rate is further reduced by the effect of monomer partitioning between the latex particle and aqueous phase, but concomitantly the concentration of monomer within the particles is enhanced since the

higher water solubility of the monomer reduces the latex particle/water interfacial tension. The monomer partitioning can be easily calculated and its effect on the rate of polymerization deduced. The partitioning of monomer may be altered to favour the latex particle phase by altering the conditions of the reaction (e. g. the temperature), hence enhancing the rate of polymerization.

The final variable that affects the rate of polymerization is the free-radical concentration in the latex particles. It is thought that there are three kinetic events that may alter the concentration of radicals within latex particles: entry, exit and bimolecular termination. Both free-radical exit and termination are free-radical loss mechanisms, and have been shown to be diffusion-controlled. As the weight fraction of polymer in latex particles increases at high conversions, all models predict that the rate of free-radical loss via the mechanisms of exit and termination should be decreased, hence the rate of polymerization increased. The remaining question was whether the rate of free-radical entry changed with high conversion, in which manner and to what degree? Previously it had been shown that the free-radical concentration within the latex particles increased at high conversions of the methyl methacrylate system<sup>1)</sup>. However, this result was possibly affected by artifacts arising from concentration gradients of both monomer and free radicals within the latex particles<sup>27, 28)</sup>. New experimental studies of the peroxydisulfate-initiated emulsion polymerization of butadiene in a polybutadiene seed (a system for which propagation never becomes diffusion-controlled) show that the free-radical concentration does indeed increase at high weight fractions of polymer, which strongly suggests that free-radical loss is reduced more than free-radical entry. For these reasons the effect of free-radical concentration upon the slow rate of emulsion polymerization at high conversions can probably be ignored. It may be argued that this result is only valid for rubbery polymers (i. e. systems polymerized above the glass transition temperature of the polymer) and that for glassy polymers the entry-rate coefficient may be decreased. Even if this were the case, the problem of slow propagation in these systems would dominate, and any solution to this problem of slow diffusion would also enhance the rate of entry, since slow diffusion within the particles is perceived as the factor that may reduce the rate of entry of free radicals.

In summary, the important result of this paper is that the free-radical concentration within the latex particles does not appear to be the primary factor which causes the slow rate of emulsion polymerization at high conversions. The major factors are the concentration of monomer within the particles and the (sometimes) diffusion-controlled propagation rate coefficient. For monomers, polymerized below the glass transition temperature of the polymer, the rate of reaction may be enhanced by an inert diluent. The other variables that may enhance the rate of emulsion polymerization at high conversion are the initiator concentration and type, and the reaction conditions, namely temperature and pressure.

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