

Influence of Disproportionated Rosin Acid Soap on the Emulsion Polymerization Kinetics of Styrene

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SYNOPSIS

The effect of disproportionated rosin acid soap (DRAS) on the emulsion polymerization kinetics of styrene has been studied. Batch experiments reveal a significant influence of chain transfer and limited particle coagulation on the polymerization process. For the recipes studied, the number of growing chains in the emulsion and consequently the polymerization rate were found to be independent of the particle number during the interval of coagulation. However, for relatively large particles ($d_p \approx 100$ nm), the polymerization rate was proportional to the particle number, indicating Smith–Ewart case II kinetics. These effects have been shown to be well predicted by model calculations using a radical population balance over the particles. Since DRAS is derived from naturally occurring constituents found in pine trees, its performance, and with that the properties of the product latex, may vary significantly. However, if the performance of DRAS is known, the recipe and process conditions can be optimized. For this reason a procedure has been developed to quantify the performance of DRAS from the simple batch experiments discussed in this paper, the polymerization kinetics, and the information obtained about the coagulation process. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the industrial production of rubbers and latexes, disproportionated rosin acid soap (DRAS) is often used as an emulsifier. An advantage of using DRAS instead of, for example, fatty acid soaps is that rubbers produced with DRAS show more branching.¹ Since DRAS is derived from naturally occurring constituents found in pine trees, its composition varies greatly.^{2,3} For this reason it is of industrial importance to have simple methods for the characterization of each batch of DRAS.

The performance of an emulsifier is, for a given polymerization system and shear rate in the reactor, usually expressed in two parameters:

1. The particle surface that can be covered by one emulsifier molecule (a_s).

2. The critical surface coverage of emulsifier on the particles below which the colloidal stability of the dispersion is lost and coagulation occurs (θ_{crit}).

Titov et al.⁴ have shown that phenanthrene-type cyclic compounds with an aliphatic or aromatic type double bond, which are present in DRAS, may act as chain transfer agents. Because of the significant influence of chain transfer on emulsion polymerization processes with DRAS as an emulsifier, it is necessary to quantify the effective chain transfer constant (k_{tr}), in addition to the parameters a_s and θ_{crit} .

The experimental determination of the parameter k_{tr} is hampered by limited coagulation of polymer particles during the polymerization reaction. Meuldijk et al.⁵ have demonstrated that this particle coagulation results from a loss of electrostatic stabilization and occurs when the surface coverage of emulsifier on the particles (θ) drops below a critical value (θ_{crit}). When the monomer droplets have disappeared, coagulation no longer proceeds. From that

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moment the particle growth by absorption of monomer stops; there is no decrease of the electrostatic repulsion force between the particles with conversion and the particle number remains constant.

This paper presents a study of the influence of DRAS on the emulsion polymerization kinetics. A simple procedure is described to determine the overall chain transfer constant (k_{tr}) and the value of θ_{crit} , using data from batch experiments.

Procedure for the Quantification of Chain Transfer

The chain transfer constant (k_{tr}) can be determined from a batch experiment by measuring the polymerization rate, the particle number, and the particle size distribution, and applying a solution of a radical population balance over the particles. Since coagulation stops when the monomer droplets have disappeared, the particle number at the beginning of interval III equals the particle number at complete conversion. For this reason the apparent chain transfer constant (k_{tr}) was determined using data from batch experiments obtained after the interval of coagulation.

For batch emulsion polymerization, the overall polymerization rate for a discrete particle size distribution with k particle size classes is given by:

$$R_p = C_{M0} \frac{dX}{dt} = \frac{k_p C_{Mp} \sum_{i=1}^k N_i \bar{n}_i}{N_{Av}} \quad (1)$$

where C_{M0} is the monomer content in the recipe, k_p is the propagation rate constant, C_{Mp} is the monomer concentration in the particles, N_i is the number of particles in particle size class i , and \bar{n}_i is the time averaged number of growing chains per particle in particle size class i .

In eq. 1, the monomer concentration in the particles (C_{Mp}) is assumed to be independent of the particle diameter. Calculations with the Morton relation,⁶ which is based on the thermodynamic equilibrium between the particles and the waterphase, show that this assumption is correct for particle sizes studied in this paper.

The influence of chain transfer on the rate of polymerization (R_p) finds expression in the time averaged number of growing chains per particle (\bar{n}), which can be calculated through the solution of a radical population balance over the particles. Since radical entry, desorption, and termination events are very fast compared to the volume growth of the particles, a quasi-steady state on the population balance

for the radicals over the particles may be assumed, yielding to the Smith-Ewart⁷ recursion relation:

$$\begin{aligned} & \frac{\rho_{a,i} N_{Av}}{N_i} (N_{i,n-1} - N_{i,n}) + k_{des,i} [(n+1)N_{i,n+1} - nN_{i,n}] \\ & + \frac{k_t}{v_{p,i} N_{Av}} [(n+2)(n+1)N_{i,n+2} - n(n-1)N_{i,n}] \\ & = 0 \quad (2) \end{aligned}$$

in which, $N_{i,n}$ is the number of particles in particle size class i containing n growing radicals, $v_{p,i}$ is the volume of a particle in size class i , $\rho_{a,i}$ is the radical entry rate into the particles of size class i , $k_{des,i}$ is the radical desorption rate for particles in size class i , k_t is the termination rate constant, and N_{Av} is Avogadro's number.

Stockmayer⁸ and O'Toole⁹ derived the following equation for the time averaged number of growing chains per particle (\bar{n}_i) in size class i :

$$\bar{n}_i = \frac{a}{4} \frac{I_b(a)}{I_{b-1}(a)} \quad (3)$$

where $I_b(a)$ is a modified Bessel function of the first kind of order b and argument a . The values of a and b are respectively given by:

$$a = 2 \left(\frac{2v_{p,i} N_{Av}^2 \rho_{a,i}}{N_i k_t} \right)^{0.5} \quad (4)$$

$$b = \frac{v_{p,i} N_{Av} k_{des,i}}{k_t} \quad (5)$$

According to Ugelstad et al.,¹⁰ the rate of radical absorption (ρ_a) can be expressed in terms of radical formation by thermal dissociation of the initiator in the water phase (ρ_i), radical desorption from the particles, and termination of radicals in the water phase. For a latex with k particle size classes the radical absorption rate may be represented by:

$$\rho_a = \rho_i + \frac{\sum_{i=1}^k N_i k_{des,i} \bar{n}_i}{N_{Av}} - 2k_{tw} C_{rw}^2 \quad (6)$$

where C_{rw} is the radical concentration in the water phase. For the recipes investigated, termination of radicals in the water phase is negligible with respect to radical desorption and radical production in the

water phase. As a consequence, the third term on the right-hand side of eq. 6 may be neglected.

Friis and Nyhagen,¹¹ Nomura and Harada,¹² and Asua et al.¹³ derived expressions for the radical desorption rate from the particles to the water phase. For situations where the mass transfer rate of the (small) radicals from the particles to the water phase is much less than the propagation rate of the radicals, i.e., for sparingly water soluble monomers such as styrene, the following equation has been found for the desorption rate of particles in size class i :

$$k_{\text{des},i} = \frac{3D_m \frac{k_{\text{tr}}}{k_p}}{\left(\frac{d_{p,i}}{2}\right)^2} \quad (7)$$

in which D_m is the effective diffusivity of the (small) radical and k_{tr} is the effective chain transfer rate constant.

The effective chain transfer rate constant is defined as:

$$k_{\text{tr}} = k_{\text{trm}} \left(1 + \frac{k_{\text{trt}} C_{\text{tr}}}{k_{\text{trm}} C_{\text{Mp}}} \right) \quad (8)$$

where, k_{trm} is the chain transfer to monomer constant, k_{trt} is the constant for chain transfer to chain transfer agents, and C_{tr} is the concentration of chain transfer agents. Note that the effective chain transfer constant (k_{tr}) depends on the concentration of the chain transfer agents, e.g., the concentration of DRAS in the recipe and the monomer concentration in the particles. An increase in the chain transfer constant leads to an increase in the overall radical desorption rate (eq. 7) and a decrease in the average number of growing chains per particle. If each of the parameters k_p , ρ_i , k_t , D_m , C_{Mp} , and k_{tr} and the particle size distribution are known, the polymerization rate of a latex with any particle size distribution are known, the polymerization rate of a latex with any particle size distribution can be calculated using eqs. 1–8.

In this study the effective chain transfer coefficient (k_{tr}) has been determined by adjusting the value of k_{tr} until the observed conversion-time history matched the calculated conversion-time history.

Procedure for the Determination of θ_{crit}

Coagulation occurs as soon as the fractional surface coverage of emulsifier on the particles drops below a critical value (θ_{crit}). In consequence of this, the

value of θ is equal to θ_{crit} during the complete interval of coagulation. The parameter θ_{crit} depends on the performance of the emulsifier, the cation concentration, and the shear rate.

In a batch process, the particle size distribution changes only slightly after the interval of coagulation because of the different densities of polystyrene and styrene. With the assumption that the relative volume concentration of monomer in the particles does not depend on the particle size, the value of θ_{crit} can easily be calculated from the particle size distribution at complete conversion:

$$\theta_{\text{crit}} = \frac{\text{surface that can be covered by emulsifier}}{\text{particle surface at the end of the coagulation interval}} \quad (9a)$$

$$\theta_{\text{crit}} = \frac{a_s N_{\text{Av}} (C_E - C_{\text{CMC}})}{A_p^{\text{tot}} (X = 1) \left(X_m + (1 - X_m) \frac{\rho_p}{\rho_m} \right)^{2/3}} \quad (9b)$$

where $A_p^{\text{tot}} (X = 1)$ is the overall particle surface at complete conversion, X_m is the conversion at which monomer droplets disappear, C_E is the overall amount of emulsifier in the recipe, and C_{CMC} is the critical micelle concentration.

EXPERIMENTAL

The chemicals used in this study were distilled water, distilled commercial-grade styrene, dresinate 214 supplied by Abieta Chemie GmbH (90% resin acids or salts and 10% non-ionogenic materials, $a_s = 4.17 \times 10^{-19} \text{ m}^2/\text{molecule}$,¹⁴ $C_{\text{CMC}} = 1.04 \times 10^{-2} \text{ kmol/m}^3$ ¹⁵), $\text{K}_2\text{S}_2\text{O}_8$ (initiator), and K_2CO_3 (pH buffer), all laboratory grade.

The emulsifier concentrations were based only on resin acids or salts. Unless stated otherwise the following concentrations were used, all expressed in kmol per $\text{m}^3_{\text{water}}$: emulsifier 0.07, initiator 0.0125, and monomer 4.04. The pH was 10.5. The batch reactor was a stainless-steel tank equipped with an eight-bladed Rushton turbine impeller and four baffles. The volume of the batch reactor was 1.2 dm^3 . The impeller speed applied was 500 rpm. During the polymerization, samples were taken to determine the conversion by gravimetry, the particle number and particle size distribution by transmission electron microscopy, and the molecular weight distribution of the polymer by gel permeation chromatography (2 shodex KF80M columns in series, $T = 40^\circ\text{C}$, eluent tetrahydrofuran).

RESULTS

Figure 1 shows a typical observed course of both the conversion and the particle number as a function of time for the batch emulsion polymerization of styrene with DRAS as an emulsifier.

Figure 1 shows that the number of particles decreases as a function of conversion after the interval of particle nucleation, indicating limited particle coagulation. For conversion values above 0.45, when the monomer droplets have disappeared and particle growth by monomer absorption stops, no further coagulation was observed. The constant number of particles for conversions above 0.45 also implies that the time scale of coagulation is small as compared to the time scale of particle growth by absorption. These results are in accordance with experiments of Hoedemakers¹⁶ and Meuldijk et al.⁵

For the batch process presented in Figure 1, Figure 2 shows the particle size distribution at complete conversion, determined with transmission electron microscopy.

Substitution of the total particle surface at complete conversion A_p^{tot} ($X = 1$) into eq. (9) gives $\theta_{\text{crit}} = 0.51$.

In Figure 3 the course of conversion as a function of time for the experiment presented in figure 1 is given in the time interval where the monomer droplets have disappeared and therefore no coagulation occurs. Figure 3 also shows the conversion versus time for a seed latex which is stabilized with sodium lauryl sulphate instead of DRAS but which has a particle size distribution similar to that shown in Figure 2.

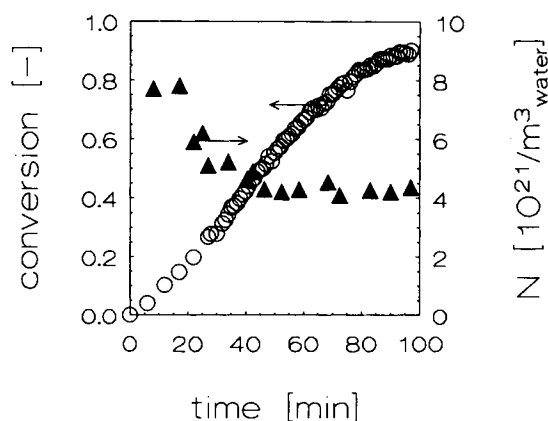


Figure 1 Batch emulsion polymerization of styrene with DRAS as emulsifier at 50°C. $C_{K^+} = 0.14 \text{ kmol/m}^3_{\text{water}}$, $C_{M0} = 4.04 \text{ kmol/m}^3_{\text{water}}$, $C_{E0} = 0.095 \text{ kmol/m}^3_{\text{water}}$, $C_{I0} = 0.013 \text{ kmol/m}^3_{\text{water}}$; O conversion time history, ▲ particle number as a function of time.

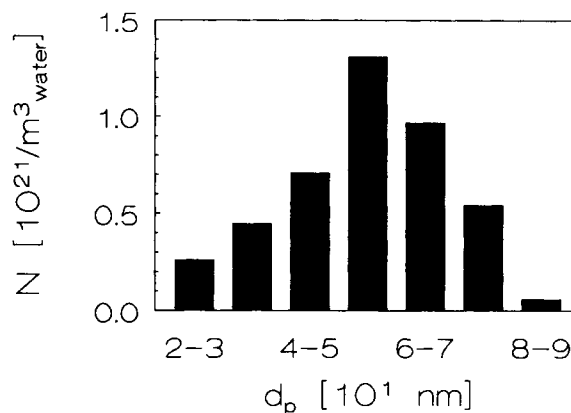


Figure 2 The particle size distribution at complete conversion for the batch process presented in Figure 1. $d_{p,\text{vol}} = 57 \text{ nm}$, $d_{p,\text{surface}} = 55 \text{ nm}$, $N_{\text{product}} = 4.3 \times 10^{21} \text{ 1/m}^3_{\text{water}}$.

The solid lines in Figure 3 represent model calculations with eq. (1). \bar{n}_i has been calculated from the solutions of the radical population balance using eq. 3–8 and the physical and kinetic parameters summarized in Table I.

Figure 3 shows that the polymerization rate of the emulsion stabilized with sodium lauryl sulphate is significantly higher than the polymerization rate of the emulsion stabilized with DRAS. This result can be explained by the presence of substances in DRAS acting as chain transfer agents. These chain transfer agents increase the radical desorption rate (see eqs. [7] and [8]). As a consequence the value of \bar{n}_i , and therefore the overall polymerization rate R_p ,

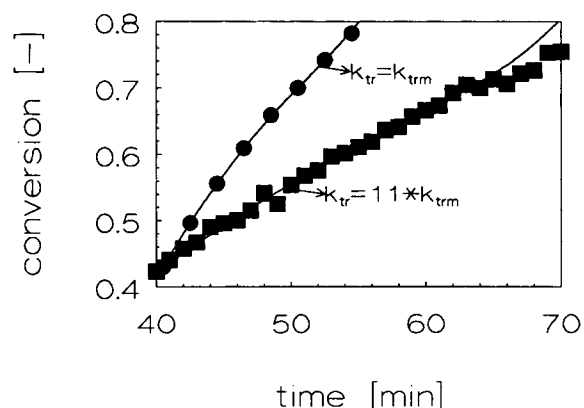


Figure 3 Conversion as a function of time for two latexes with a similar particle size distribution (see Fig. 2) for the batch emulsion polymerization of styrene at 50°C. The solid lines represent calculations with equations 3–8. ■ latex stabilized with DRAS; ● latex stabilized with sodium lauryl sulphate.

Table I Physical and Kinetic Parameters for the Emulsion Polymerization of Styrene with Sodium Persulphate as Initiator and Sodium Lauryl Sulphate as Emulsifier at 50°C

ρ_m [kg/m ³]	878	Weast ¹⁷
ρ_p [kg/m ³]	1053	DeGraff et al. ¹⁸
C_{Mp} [kmol/m ³]	5.2	Harada et al. ¹⁹
k_p [m ³ /(kmol × s)]	258	Rawlings and Ray ²⁰
k_t [m ³ /(kmol × s)]	$6.8 \times 10^7 \times \exp(-19 \times X^{2.1})$	Hawkett et al. ²¹
ρ_i [kmol/(m ³ × s)]	$2 \times f \times k_i \times C_I$	Rawlings and Ray ²⁰
f [-]	0.5	Rawlings and Ray ²⁰
k_i [1/s] (50°C)	1.6×10^{-6}	Rawlings and Ray ²⁰
$3 \times D_m \times k_{tr}/k_p$ [m ² /s]	6×10^{-18}	Hawkett et al. ²²

is lower than for the recipe with sodium lauryl sulphate.

Figure 3 also shows that the conversion rate of styrene in the latex stabilized with sodium lauryl sulphate can be predicted by eqs. (1)–(8) and the parameters in Table I. Variation of the chain transfer coefficient k_{tr} (see eqs. [7] and [8]) until the predicted conversion-versus-time plot matches the observed course of the conversion for the latex with DRAS as emulsifier implies that the rate coefficient for radical desorption for recipes with DRAS is about one order of magnitude larger than for recipes with sodium lauryl sulphate.

Figure 4 shows the influence of the cation concentration on the particle number in the product latex and the value of θ_{crit} , calculated with eq. (9b) for the batch emulsion polymerization of styrene with DRAS as emulsifier.

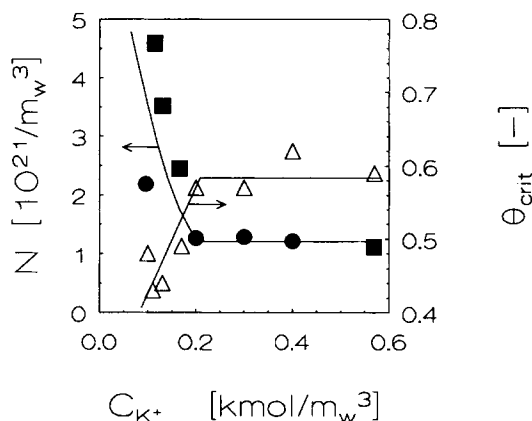


Figure 4 The particle number in the product latex and the value of θ_{crit} as a function of the cation concentration for the batch emulsion polymerization of styrene with DRAS as emulsifier at 50°C. $C_{M0} = 4.0$ kmol/m³_{water}, $C_{E0} = 0.07$ kmol/m³_{water}, $C_{I0} = 0.0125$ kmol/m³_{water}. ● ■ Particle number. Δ θ_{crit} . For the experiments marked with ■, the conversion-versus-time plots are shown in Figure 6.

In Figure 4, two regions can be distinguished: one where the particle number in the product latex decreases as a function of the cation concentration in the recipe, and one where the particle number is independent of the cation concentration. In the first region an increase of the cation concentration decreases the electrostatic repulsion between the latex particles. As a result the fractional surface coverage of emulsifier on the particles below which coagulation occurs (θ_{crit}) increases, leading to a decrease of the particle number in the product latex.

In the second region, electrostatic repulsion between the particles no longer contributes to the colloidal stability of the latex. In this situation the colloidal stability of the latex is completely determined by steric stabilization of the particles.

Figures 5(a) and 5(b), respectively, show the particle size distribution at complete conversion for a batch emulsion polymerization at a relatively low and a batch experiment at a relatively high potassium ion concentration. The final particle numbers of these experiments have been given in Figure 4.

In Figure 5 it can be seen that an increase of C_{K^+} from 0.13 to 0.57 kmol/m³_{water} enhances the degree of particle coagulation and shifts the particle size distribution to large diameters.

Figure 6 shows the influence of the recipe's cation concentration on the conversion-time history for those batch experiments marked with a black square in Figure 4.

From Figures 4 and 6 it can be concluded that for $0.11 < C_{K^+}$ kmol/m³_{water} < 0.17 , the polymerization rate is not significantly influenced by the number of particles in the latex. Apparently the effect of the decrease in the particle number on the polymerization rate is compensated by the increase in the average number of growing chains per particle. This compensation means that the overall number of growing chains in the reaction mixture ($\sum \bar{n}_i \times N_i$) is independent of the particle number for the

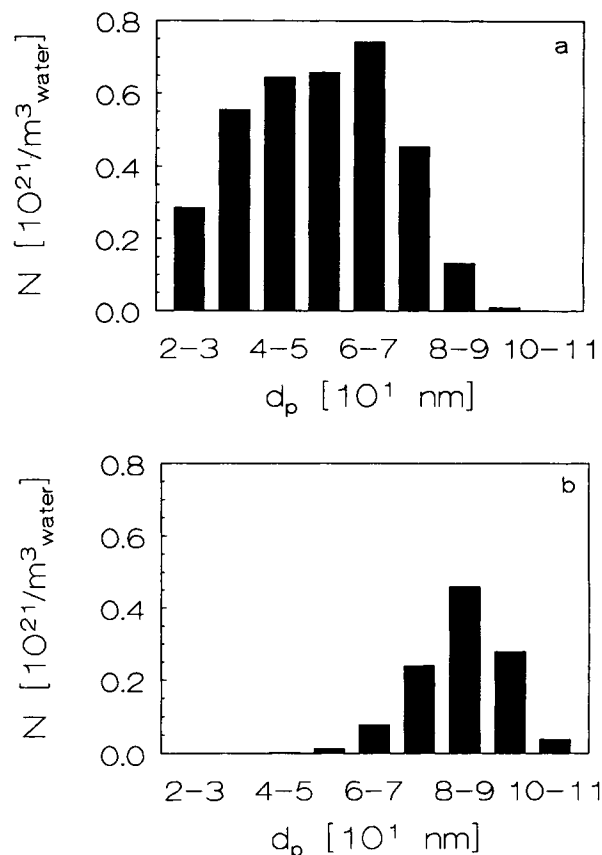


Figure 5 The particle size distribution in the product latex for the batch experiments in Figure 4 with $C_{K^+} = 0.13 \text{ kmol/m}^3_{\text{water}}$ (Fig. 5[a]) and $C_{K^+} = 0.57 \text{ kmol/m}^3_{\text{water}}$ (Fig. 5[b]) determined with TEM.

recipe in Figure 4 and $0.11 < C_{K^+} < 0.17$. For batch emulsion polymerization of vinyl acetate it has also been observed that $(\sum \bar{n}_i \times N_i)$ is independent of the particle number.²³ Calculations of the conversion-time history with eqs. (1)–(8) confirm the experimental result that $\sum \bar{n}_i \times N_i$ is independent of the particle number and that Smith–Ewart case I kinetics occur in analogy with vinyl acetate emulsion polymerization. The transfer coefficients used in the calculations on polymerizations with DRAS are determined from Figure 3, accounting for the different emulsifier concentrations used in the experiments in Figures 3 and 6 (see eq. [8]).

Figure 6 also shows that for the recipe with the highest cation concentration, the decrease of the particle number N is not compensated by the increase of \bar{n} . In this situation the mean particle size (Fig. 5[b]) is large enough to suppress the influence of chain transfer and radical desorption on \bar{n} and therefore on the polymerization kinetics. Model calculations with eqs. (1)–(8) show that, for the particle

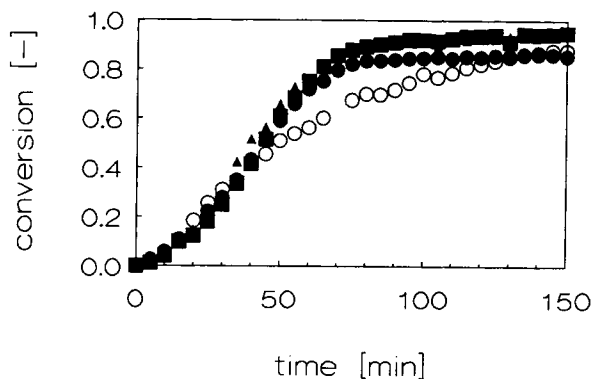


Figure 6 Conversion-time history for the batch experiments in Figure 4 marked with a black square. ● $C_{K^+} = 0.11 \text{ kmol/m}^3_{\text{water}}$; ■ $C_{K^+} = 0.13 \text{ kmol/m}^3_{\text{water}}$; ▲ $C_{K^+} = 0.17 \text{ kmol/m}^3_{\text{water}}$; ○ $C_{K^+} = 0.57 \text{ kmol/m}^3_{\text{water}}$.

size distribution in Figure 5(b), the polymerization rate is almost proportional to the particle number, indicating Smith–Ewart case II kinetics.

Figure 7 shows the number mean M_n and the weight mean M_w as functions of conversion for the batch experiment in Figure 1.

It can be seen that both M_n and M_w were practically constant during the batch experiment where coagulation occurs, and that the overall amount of growing chains in the reaction mixture $\bar{n} \times N$ does not change with conversion. This can be explained as follows: The chemical events determining the chain length distribution are bimolecular termination when a second radical enters a particle and chain transfer. The chain transfer rate dominates the polymerization process and depends neither on

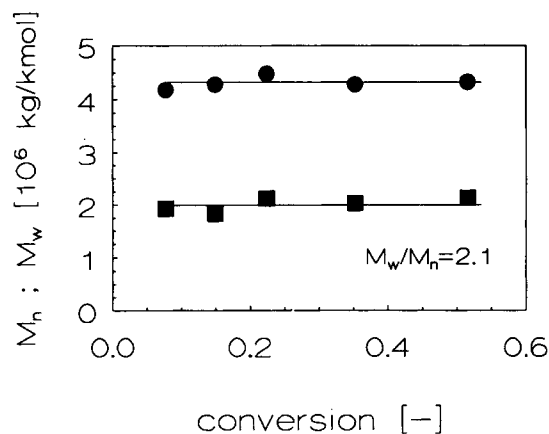


Figure 7 The number mean molecular weight M_n and the weight mean molecular weight M_w determined with gel permeation chromatography as a function of conversion for the batch experiment in Figure 1.

the particle size nor on the particle number. Therefore the molecular weight distribution does not change significantly with the monomer conversion in spite of the decreasing particle number and the increasing particle diameter during the polymerization process. This result confirms the expected dominant influence of chain transfer on the polymerization kinetics. Figure 7 also shows that the value of M_w/M_n approximately equals 2, which is characteristic for processes dominated by chain transfer to monomer.²⁴

CONCLUSIONS

- (i) During the batch emulsion polymerization of styrene with DRAS as emulsifier, limited particle coagulation may occur. This coagulation results from a partial loss of electrostatic stabilization when the surface coverage of emulsifier on the particle drops below a critical value.
- (ii) The time scale for limited particle coagulation is small as compared to the time scale for particle growth.
- (iii) Batch experiments and molecular weight measurements show that chain transfer agents present in DRAS significantly influence the polymerization rate. This was confirmed by model calculations with a radical population balance over the particles.
- (iv) For the recipes investigated, the number of growing chains in the emulsion and consequently the polymerization rate were found to be independent of the particle number during intervals of coagulation, indicating Smith-Ewart case I kinetics. For recipes leading to large particle diameters, however, Smith-Ewart case II kinetics were observed.
- (v) The performance of DRAS is determined not only by the particle surface that can be covered by one emulsifier molecule (a_s) and the critical surface coverage of emulsifier on the particles below which coagulation occurs (θ_{crit}) but also by the concentration of chain transfer agents present in DRAS.
- (vi) The performance of DRAS in terms of the critical surface coverage of emulsifier on the particles below which coagulation occurs (θ_{crit}) and the overall chain transfer constant (k_{tr}) can easily be quantified from batch experiments, a radical population balance, and the procedure described in this paper.

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NOMENCLATURE

A_p^{tot}	overall particle surface at complete conversion [m^2/m_w^3]
a_s	surface that can be covered by one emulsifier molecule [$m^2/\text{molecule}$]
C_{CMC}	critical micelle concentration [kmol/m_w^3]
C_{EO}	overall amount of emulsifier in the recipe [kmol/m_w^3]
C_{I0}	overall amount of initiator in the recipe [kmol/m_w^3]
C_{M0}	overall amount of monomer in the recipe [kmol/m_w^3]
C_{Mp}	monomer concentration in the particles [kmol/m^3]
C_{rw}	radical concentration in the water phase [kmol/m_w^3]
C_{tr}	concentration of chain transfer agents [kmol/m^3]
D_m	effective diffusivity of the small radicals [m^2/s]
$d_{p,i}$	particle diameter of size class i [m]
$k_{des,i}$	desorption rate coefficient for particles in size class i [1/s]
k_p	propagation rate constant [$m^3/(\text{kmol s})$]
k_t	termination rate constant [$m^3/(\text{kmol s})$]
k_{tr}	effective chain transfer rate constant [$m^3/(\text{kmol s})$]
k_{trm}	chain transfer to monomer constant [$m^3/(\text{kmol s})$]
k_{trt}	chain transfer to transfer agent constant [$m^3/(\text{kmol s})$]
k_{tw}	termination rate constant for radicals in the water phase [$m^3/(\text{kmol s})$]
N_{Av}	Avogadro's constant [1/kmol]
N_i	number of particles in size class i [$1/m_w^3$]
\bar{n}_i	average number of growing chains of particles in size class i [-]
R_p	overall polymerization rate [$\text{kmol}/(m_w^3 \text{ s})$]
t	reaction time [s]
$v_{p,i}$	volume of a particle in size class i [m^3]
X	conversion [-]

Greek

ρ_a	rate of radical absorption [$\text{kmol}/(m_w^3 \text{ s})$]
ρ_i	rate of radical formation by initiator decomposition [$\text{kmol}/(m_w^3 \text{ s})$]

- ρ_m density of the monomer [kg/m³]
 ρ_p density of the polymer [kg/m³]
 θ fractional surface coverage of emulsifier on the particles [-]
 θ_{crit} fractional surface coverage of emulsifier on the particles below which colloidal stability is lost and limited particle coagulation occurs [-]

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