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MODELING OF EMULSION POLYMERIZATION OF VINYL CHLORIDE

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ABSTRACT

A survey of the principles of emulsion polymerization modeling of vinyl chloride is presented. Experimental results and model equations for particle nucleation, particle coalescence, and particle growth are discussed. A mechanism for particle coalescence in the course of polymerization is proposed based on the assumption that radical desorption from a particle is the rate-determining step for coalescence. Equations for the coalescence rate and velocity constant are derived based on this assumption. The resulting population balance equations for describing the change of particle size distribution during emulsion polymerization of vinyl chloride can be applied to different polymerization procedures, e.g., discontinuous, continuous, and seeded polymerizations. Examples of model calculations are given for several polymerization procedures and compared with experimental data.

1. INTRODUCTION

In general terms, a mathematical model is a quantitative expression of inherent process regularities by mathematical equations. Sophisticated chemical or reaction engineering processes have usually been represented by a set of equations, e.g., differential, integro-differential, and partial differential equations. More complicated models can even consist of all types of these equations. Over the past 15 years, fast numerical methods with variable integration steps have been developed, thus drastically reducing computation times [1].

One topic in the area of polymerization reaction modeling which is of general interest is the emulsion polymerization process [2–4]. This is because on the great economic importance of this polymerization technique. Worldwide, emulsion polymerization is mainly employed for producing different kinds of acrylic-based latexes and butadiene rubbers. Especially in Europe, emulsion polymerization also plays an important role in the production of poly(vinyl chloride) (PVC) [5].

Emulsion polymerization is characterized by the fact that the polymerization reaction proceeds mainly within the individual monomer swollen polymer particles. Radical and monomer diffusion processes govern the polymerization kinetics. Therefore, the size distribution of the latex particles (psd) plays an important role in the mechanism of emulsion polymerization. Furthermore, psd has an influence on the application properties of latexes. So, for example, film formation of latex coatings is influenced by particle size.

In contrast to acrylic latexes, emulsion PVC is not applied as an aqueous dispersion. The PVC latex is spray-dried, and the powdered PVC is redispersed in a plasticizer. The viscosity of this organosol depends on the psd and several other factors. Moreover, an essential parameter for the application of plastisol-made PVC coatings is the emulsifier content which should be kept to a minimum. As the necessary emulsifier content rises with a broadening of the psd, reaction engineering can help to develop modified procedures leading to latexes with smaller psd. For all polymeric products produced by emulsion polymerization techniques, the psd determines the necessary emulsifier content in the latexes, thus influencing application properties. Emulsifiers without covalent bonding to the polymer can migrate through the polymer bulk to the surface. At the surface these hydrophilic molecules lead to an increase in water absorption and to the "blooming" ("blushing") phenomenon [6].

2. EXPERIMENTAL

Laboratory-scale emulsion polymerization experiments under saturated conditions regarding the monomer concentration were conducted at 50°C in a 2-dm^3 glass autoclave containing 700 mL water and 585 mL (500 g) vinyl chloride (VC) monomer. Subsaturation conditions regarding the monomer concentration were realized by continuously feeding the monomer to the reactor from a reservoir at a temperature lower than the polymerization temperature. By variation of the reservoir temperature, a variation of the monomer concentration in the reactor was achieved. The stirrer speed was 500 rpm. Potassium peroxidisulfate was chosen as the initiator and sodium dodecylsulfate as the emulsifier. The conversion/time curves were determined gravimetrically. Mean particle sizes were determined by turbidity measurements, and psd was determined by electron microscopy or fractional creaming.

The polymerization experiments [7] and analytical procedures [8] were described in detail earlier.

3. GENERAL REMARKS

The chain growth in emulsion polymerization occurs via a radical polymerization mechanism in most cases. Thus, classical radical polymerization theory can be applied to describe emulsion polymerization. With regard to each particular case, the well-known radical reaction steps have to be considered. Emulsion polymerization is more complicated than radical solution polymerization due to the heterogeneous composition of the reaction system. In this respect, several transfer processes between the organic phases and water, as well as the formation of new phases, play an important role. Hence, for modeling emulsion

TABLE 1. Summary of Chemical and Physical Reactions Influencing Emulsion Polymerization

Chemical reactions	Physical reactions
Initiator decomposition	Radical absorption by:
Initiation	Micelles
Propagation	Polymer particles
Chain transfer reactions to:	Monomer droplets
Monomer	Radical desorption
Polymer	Oligomer precipitation
Termination reactions	Particle interactions
	Monomer transport

polymerizations it is necessary to consider the chemical and physical reactions listed in Table 1.

The first kinetic theory of emulsion polymerization was developed by Smith and Ewart in 1948 [9]. Their model gives a mathematical description of Harkin's concept that monomer droplets, which are present in the reaction system during intervals I and II, supply monomer molecules via the water phase into micelles. Radicals of water-soluble initiators enter the micelles, thus starting the polymerization reaction and simultaneously generating the polymer particles. After all micelles have been converted into particles, the polymerization proceeds exclusively in the particles.

Smith and Ewart deduced that a steady-state recursion formula accounted for the distribution of free radicals between the water phase and the polymer particles. This model considers absorption, desorption, and mutual termination of the radicals within the particles.

Smith and Ewart solved the recursion formula concerning the radical balance for several limiting cases. Case I is characterized by a high transfer rate of free radicals out of the particles. The major locus of termination may be in the aqueous phase or in the polymer particles. The mean number of radicals in a particle (n) is much lower than unity. Case II is preferably used concerning the infinitely fast rate of mutual termination of free radicals within a polymer particle relative to the absorption of radicals. This case implies that a polymer particle can bear only zero or one free radical at a time. Hence, n is equal to 0.5.

Valuable contributions for modeling the emulsion polymerization of

TABLE 2. Velocity Constants of Chain Transfer to Monomer for Different Monomers

Monomer	Velocity constant k_{tr}, $dm^3 \cdot mol^{-1} \cdot s^{-1}$	Reference
Vinyl chloride	40.0000	12
	11.0000	13
	7.4000	14
	5.5000	15
Vinyl acetate	0.6880	16
Styrene	0.0106	17

vinyl chloride, in particular for calculating the mean number of radicals per particle, were made by Ugelstad and coworkers [10]. As a peculiarity of radically initiated polymerization of vinyl chloride, radical transfer processes to the monomer occur to a great extent. Some authors assume chlorine atoms act as the transfer agents instead of the monomer molecules [11]. In any case, low molecular weight radical species which may leave the monomer-swollen PVC particles are generated. Table 2 contains published data of chain transfer velocity constants for vinyl chloride, vinyl acetate, and styrene.

The basic statement of Ugelstad for modeling the VC emulsion polymerization is that the reabsorption of these radicals enhances the probability of termination reactions in the particles. Hence, in contradiction to the classical theory, a considerably lower number of radicals per particle (about 10^{-3}) has been found for VC systems with particle sizes lower than 100 nm. Reexamination in our laboratory confirmed that the Hansen–Ugelstad model corresponds to batch experiments on a laboratory scale for conversions ranging from 10% to nearly 60%. Figure 1 shows a comparison between the mean number of radicals per particle calculated according to the Ugelstad/Hansen equation (1), $\bar{n}_U$, using experimental data for particle size and particle concentration, and $\bar{n}_{exp}$ calculated from reaction rates and particle concentrations according to Eq. (2).

$$\bar{n}_U = N^{-0.5}(k_1 D^3 + k_2 D^2)^{0.5} \tag{1}$$

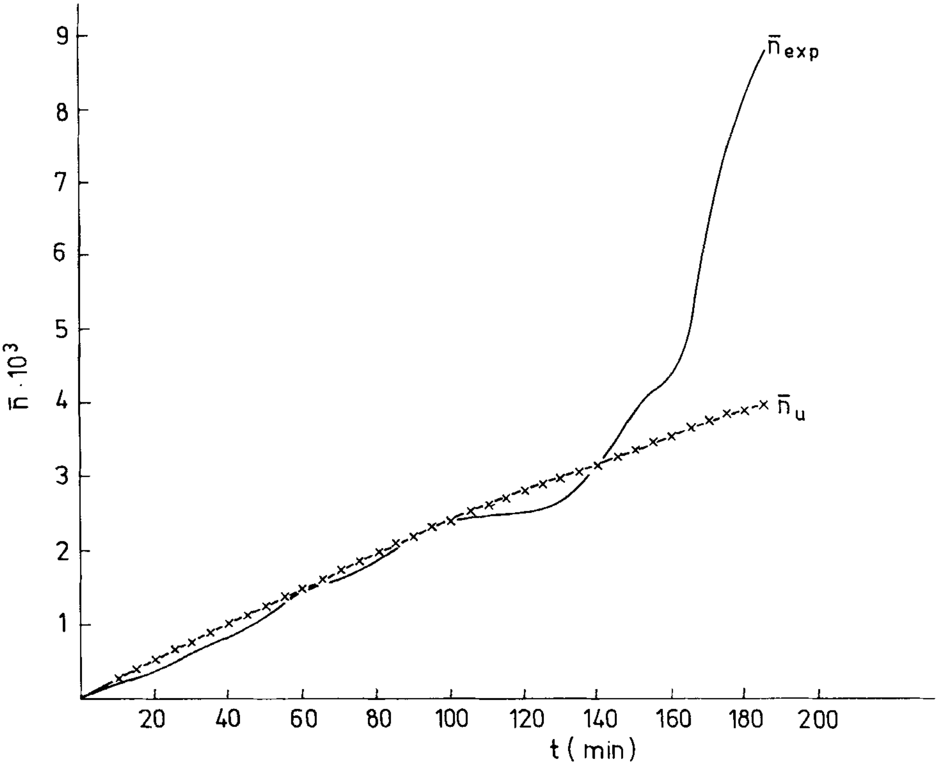

FIG. 1. Comparison between the mean number of radicals per particle calculated according to Eq. (1), $\bar{n}_U$, and Eq. (2), $\bar{n}_{exp}$, for the batch emulsion polymerization of vinyl chloride under standard conditions.

where N = number of particles per liter, cm^{-3}
D = mean particle diameter, cm
$k_1 = (6/\pi)(\rho_i/2k_t)$, cm^{-6}
$k_2 = (6/\pi)^{2/3}(\rho_i/2k_d)$, cm^{-5}
k_t = termination rate constant, cm^3/s
k_d = diffusion rate constant for chain transfer radicals (desorption of radicals), cm^2/s
ρ_i = initiation rate (radical absorption rate by the particles), cm^{-3}/s

$$n_{exp} = r_p/(k_p C_M N) \qquad (2)$$

where r_p = rate of polymerization, $\mathrm{mol \cdot cm^{-3} \cdot s^{-1}}$
k_p = propagation rate constant, $\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}}$
C_M = monomer concentration within the particle, $\mathrm{mol/cm^3}$
N = Particle concentration, $\mathrm{mol/cm^3}$

Another important consideration regarding the mechanism of emulsion polymerizations was introduced by Fitch and coworkers [18]. They developed the idea of homogeneous nucleation as a second fundamental possibility in addition to the micellar nucleation. According to this concept, monomers with enhanced solubility in water should polymerize in the water phase outside the micelles, even at an excess of the surfactant in the dispersion. Furthermore, they considered the possibility of water-soluble oligomers being caught by existing particles. This leads to a limitation of particle formation and explains particle generation in the presence of preformed polymer particles.

A basic equation for the calculation of any growth process in a continuously stirred vessel was derived by Behnken, Horowitz, and Katz in 1963 [19]. In 1974, Min and Ray presented a general framework for modeling emulsion polymerizations [1, 20]. Based on population balances, they derived a comprehensive model for calculating nearly all latex and polymer properties, e.g., particle size distribution, molecular weight distribution, and radical distribution during the polymerization time. Using the approach of Min and Ray, we developed a comprehensive model system for the calculation of latex psd [21]. We considered individual reactions influencing the psd, which were different from those by Min and Ray. Min and Gostin applied this general framework to the semicontinuous emulsion polymerization of vinyl chloride [22]. They showed that, by using their model, even bimodal psd can be simulated. However, the calculated size of the small particles remains below the experimental value. The authors suggest that this is due to a higher rate of agglomeration between small particles than predicted by the model. The sizes of large particles are in good agreement with the experimental data.

4. KINETICS AND MODELING

The determination of kinetic constants of the polymerization reaction should be discussed in this paper, too. Obviously, kinetic constants hitherto derived from experiments in solution or in bulk have been used as parameters in the emulsion polymerization models. Whereas the rate constants of propagation, termination, and transfer to the monomer may be somewhat influenced by the environment of the active species, the initiation rate constant is very sensitive to solvent interactions and surface-based forces.

Thus, we have investigated the influence of the conditions of emulsion polymerization upon the rate constants of different important individual reactions of the emulsion polymerization.

Initiation Rate Constant

The initiation rate coefficient was derived from inhibition experiments by applying 2,2′,6,6′-tetramethyl-piperidine-*N*-oxide as the radical scavenger. Independently, k_i values were estimated from end-group analyses using a tracer technique with ^{35}S tagged peroxidisulfate as the initiator [23]. Radical-induced decomposition of the initiator has been assumed to precede the initiation reaction. In the presence of an inhibitor, the induced decay is suppressed. Hence, the real initiation conditions can be represented preferably by the tracer experiments. The initiation rate constant slightly depends on the emulsifier concentration (Fig. 2).

Particle Formation

At the beginning of an emulsion polymerization, the conditions for particle formation differ from the conditions in the course of the polymerization when particles are present. Technologically, it is important that particle formation in the presence of preformed particles be controlled. For example, during continuous emulsion polymerization at steady state, the permanent formation of new particles on a limited level is necessary for maintaining a constant polymerization rate and constant product properties. On the other hand, during a seeded emulsion polymerization, additional particle formation may strongly disturb the polymerization, leading to a broadening of particle size distribution. Independent of the concrete conditions for particle formation, the reactions in the water phase play an important role due to the use of water-soluble initiators. The composition of the water phase before starting a discontinuous emulsion polymerization of vinyl chloride is shown in Table 3.

From these data it can be concluded that the reaction of an initiator radical with a monomer molecule dissolved in water is much more likely than its reaction with a micelle or even with a monomer droplet. Further-

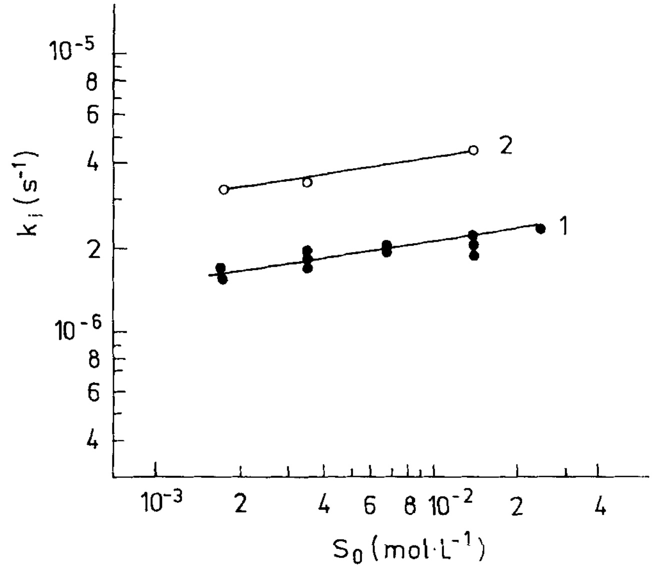

FIG. 2. Dependence of the initiation rate constant (k_i) on the sodium dodecylsulfate concentration for the batch emulsion polymerization of vinyl chloride: (1) k_i determined by inhibition experiments; (2) k_i determined by tracer technique.

more, the data in Table 3 show that particle formation is most likely via homogeneous nucleation rather than via micelles. Homogeneous particle formation also corresponds to the experimental facts that particles are formed in the absence of micelles and an emulsifier-free emulsion polymerization of vinyl chloride is feasible during continuous polymerization. The first stage of a vinyl chloride emulsion polymerization can therefore be characterized as a solution polymerization in water.

The reactions in the water phase lead to the formation of oligomers as a result of disproportionation termination having the following idealized structure:

$$CH_2{=}CH{-}(CH_2{-}CHCl)_nSO_4^-$$

$$CHCl_2{-}CH_2{-}({-}CH_2{-}CHCl)_nSO_4^-$$

Nucleation of these water-borne oligomers may take place in the following steps. First, the degree of oligomerization (n) reaches values so high

TABLE 3. Composition of the Water Phase before Starting a Discontinuous Emulsion Polymerization of Vinyl Chloride[a]

Component	Concentration, mol/dm^3	Remarks
Vinyl chloride	1.90×10^{-1}	Saturation concentration at 50°C
Na-dodecylsulfate	1.39×10^{-2}	Overall concentration
Micelles	$(2.78-1.39) \times 10^{-4}$	Corresponds to an aggregation number of 50–100 per micelle
K-peroxidisulfate	5.93×10^{-3}	
VC droplets	6.23×10^{-8}	Estimated by OsO_4 fixation

[a] Recipe: 695 mL of water; 500 g vinyl chloride; 1.107 g K-peroxidisulfate as initiator 2.78 g Na-dodecylsulfate as emulsifier; 0.695 g *tert*-Na-phosphate as buffer.

that the chains are no longer soluble in water. Second, the oligomer concentration increases so that supersaturation for precipitation is reached. By GPC investigations of these water-soluble products, the degree of oligomerization was found to be between 2 and 10 with the maximum in the distribution curves corresponding to the value of $n = 5$. Since oligomers of the above-mentioned structure with $n = 5$ should still be soluble in water, the second possibility of nucleation has been assumed to be valid. Therefore, the rate of particle formation via oligomer precipitation can be described by

$$r_{op} = k_{op}n(D_{n,w} + P_{n,w}) \tag{3}$$

where r_{op} = rate of particle formation, mol/cm^3
k_{op} = velocity constant of particle formation, s^{-1}
n = degree of oligomerization
$D_{n,w}$ = concentration of dead oligomers in water, mol/cm^3
$P_{n,w}$ = concentration of living oligomers in water, mol/cm^3

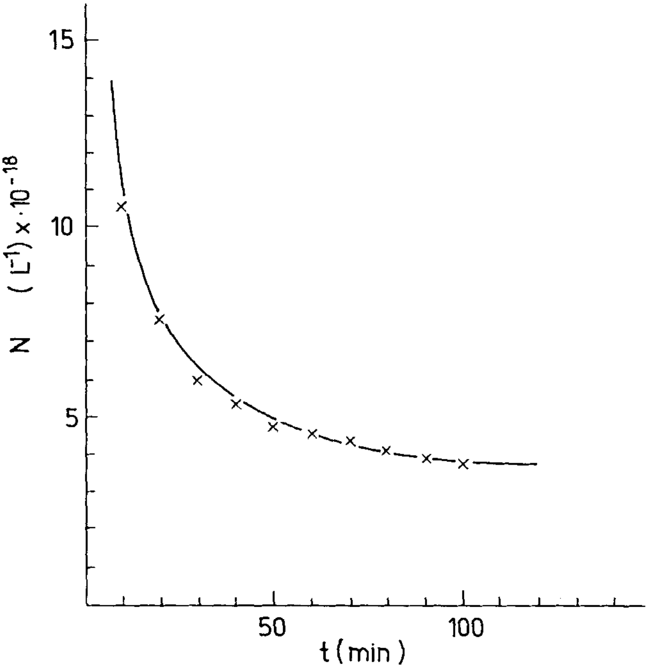

FIG. 3. Particle number/time curve for the discontinuous emulsion polymerization of vinyl chloride under standard conditions.

Particle Coalescence Phenomena

After the particles have been formed, their fate depends on polymerization conditions. The classical case that, after particle formation, their number remains unchanged during further polymerization does not apply in general. In order to prove the validity of the Hansen-Ugelstad model for the very first stage of vinyl chloride emulsion polymerization, experimental investigations have been performed. Unexpectedly, we observed a rapid decrease in the number of particles from the very beginning of the reaction in batch reactors on a laboratory scale [7]. Figure 3 shows a particle number/time curve for polymerization measured under our standard condition, e.g., at an initial emulsifier concentration sufficiently above the critical micelle concentration. Although we investigated a wide variety of polymerization conditions, a particle number maximum has never been observed. It could only be detected by combining experimental data for the rate of polymerization and the increasing particle diameter with model assumptions [24]. The decrease in the number of particles in experiments was observed both below and above the critical micelle concentration. Furthermore, the experimental results [7] clearly show that the drop in the particle number only takes place in a polymerizing (living) system. If the polymerization stops, the decrease in the particle number also stops. In view of the possible importance of these findings, a quantitative treatment together with a theoretical explanation will be attempted. We interpret the observed decreases in the particle concentration as a coalescence process. This means that two particles flow together to form a new spherical particle. A quantitative treatment of the experimental data is possible in the following manner.

The velocity of a two-particle contact is calculated according to the equation of Smoluchowski [25]:

$$r_C = k_C N^2 \tag{4}$$

where r_C = velocity of particle contact, $\mathrm{mol \cdot cm^{-3} \cdot s^{-1}}$
k_C = velocity constant, $\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}}$
N = particle concentration, $\mathrm{mol/cm^3}$

From this equation, the kinetic time law for a second-order reaction is derived:

$$N^{-1} = k_C t + N_0^{-1} \tag{5}$$

where N_0 = maximum particle concentration, $\mathrm{mol/cm^3}$.

According to Eq. (5), it is therefore possible to obtain the velocity constant k_C directly by differentiating experimental reciprocal particle number/time curves. Figure 4 shows the result of differentiation for our standard recipe. It can be clearly seen that the value for k_C is not constant from the beginning. For reaction times longer than 100 min, nearly constant values have been obtained. This result shows that the mere number of particle contacts alone is not sufficient for a description of the particle decreases. It is obvious that in addition to the closest possible distance between the particles under reaction conditions, there must be another process initiating the coalescence. In agreement with the experimental results that the decrease in the particle number only occurs in a polymerizing system, we assume that the radical desorption from a parti-

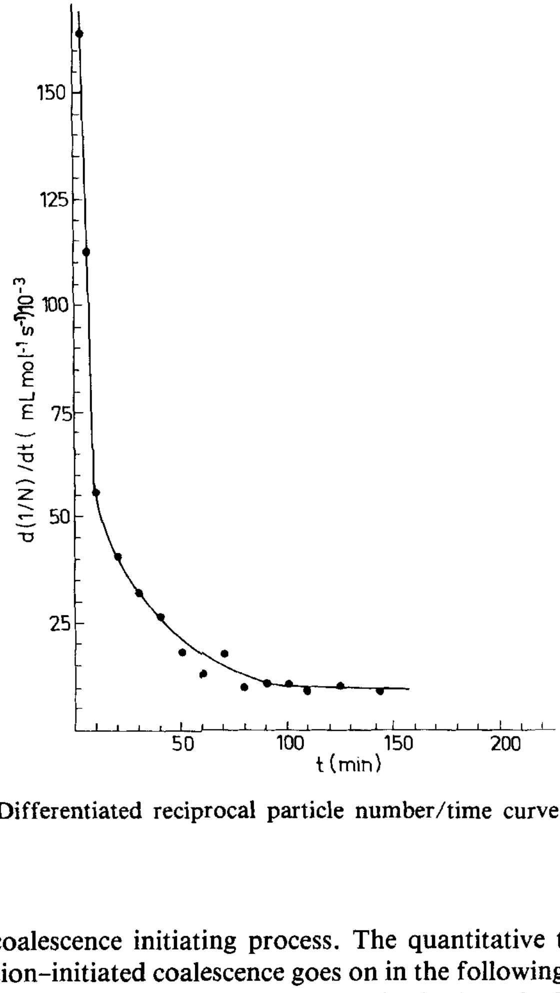

FIG. 4. Differentiated reciprocal particle number/time curve according to Fig. 3.

cle is the coalescence initiating process. The quantitative treatment of the desorption-initiated coalescence goes on in the following manner.

The mean number of radicals at the very beginning of a VC emulsion polymerization can be expressed by a reduced Ugelstad formula (Eq. 6), where *n* is mainly determined by the radical desorption from the small particles.

$$\bar{n} = N^{-0.5}(k_2D^2)^{0.5} \qquad (6)$$

The maximum number of particles detectable in the above-mentioned manner depends on the concentration of the stabilizing agent in such a way that Eq. (7) can be used as an approximation. By using Eq. (7), the contribution of the initiator end groups (mainly sulfate groups) to the stabilization of particles is neglected.

$$N^0 = (a_S S_M)/(D_0^2) \tag{7}$$

where N_0 = maximum particle concentration, mol/cm^3
D_0 = particle diameter after nucleation (nucleation diameter), cm
a_S = surface area for the stabilizing agent, cm^2
S_M = concentration of the stabilizing agent, mol/cm^3

The velocity of radical desorption, which has the highest value after particle nucleation, can be expressed by

$$r_{des} = k_{des}\bar{n}_0 N_0 \tag{8}$$

where r_{des} = desorption rate, mol·cm^{-3}·s^{-1}
k_{des} = desorption rate constant, s^{-1}
$\bar{n}_0$ = mean number of radicals per particle after nucleation

The drop in desorption velocity according to our model assumption is caused by the increasing particle diameter, which brings about a decrease in radical desorption. Thus, the velocity constant of radical desorption for a particle is described by

$$k_{des} = (6/\pi)^{2/3} D_R D^{-2} \tag{9}$$

where D_R = diffusion constant of a desorbing radical within the particle, cm^2/s.

By combining Eqs. (8) and (9), Eq. (10) gives the radical desorption velocity for a particle with a given diameter.

$$r_D = (6/\pi)^{2/3} D_R \bar{n}_0 N_0 D^{-2} \tag{10}$$

If there is no change in the reaction conditions, such as emulsifier and initiator concentration, the change of desorption velocity is mainly caused by the change of particle diameter. Assuming that the desorption of a radical is the rate-determining step of particle coalescence, the combination of Eqs. (4), (8), and (10) leads to Eq. (11) for the calculation of the coalescence rate constant.

$$k_C = k_{C1}D^{-2} \tag{11}$$

The real coalescence rate constant under the conditions of emulsion polymerization of VC can be calculated according to the above assumptions by using

$$k_{C1} = (6/\pi)^{2/3}D_R\bar{n}_0N_0^{-1} \tag{12}$$

Substituting $\bar{n}_0$ and N_0 in Eq. (12) by Expressions (6) and (7) yields Eq. (13), which makes it possible to calculate k_{C1} from initial polymerization parameters.

$$k_{C1} = 1.729((D_R\rho_{i0}D_0^8)/(a_SS_M)^3)^{0.5} \tag{13}$$

where ρ_{i0} = initial initiation rate, $\text{cm}^{-3}\cdot\text{s}^{-1}$. Hence, Eq. (14) results for the coalescence rate:

$$r_C = k_{C1}D^{-2}N^2 \tag{14}$$

The rate of the particle coalescence during emulsion polymerization of VC is thus determined by the change of particle diameter and particle concentration.

The value of the coalescence velocity constant k_{C1} can be calculated from the experimentally determined particle number/time curves by

$$k_{C1} = (d(1/N)/dt)D^2 \tag{15}$$

where k_{C1} = coalescence velocity constant, $\text{cm}^5\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
N = particle concentration, experimental values, mol/cm^3
D = mean particle diameter, experimental values, cm
t = time, s

Table 4 shows a comparison between the experimental values of k_{C1} and the values calculated according to Eq. (13) for discontinuous emulsion polymerizations of VC with different emulsifier and monomer concentrations.

TABLE 4. Comparison between Experimental (e) and Calculated (c) Values of k_{C1}

S_M, mol/ cm^3	M	D_0, cm $\times 10^7$	$k_{C1,c}$, cm^5 $\cdot$mol$^{-1}\cdot$s^{-1}	$k_{C1,e}$, cm^5 $\cdot$mol$^{-1}\cdot$s^{-1}
1.17×10^{-5}	0.35	3.5	1.62×10^{-7}	2.53×10^{-7}
1.17×10^{-5}	0.30	2.3	1.10×10^{-8}	4.72×10^{-8}
1.17×10^{-5}	0.27	1.8	2.66×10^{-9}	1.77×10^{-8}
2.56×10^{-5}	0.30	1.8	1.91×10^{-9}	5.47×10^{-9}
1.17×10^{-5}	0.30	2.3	1.10×10^{-9}	4.72×10^{-8}
8.23×10^{-6}	0.30	2.3	1.85×10^{-8}	8.00×10^{-8}

For the calculation of $k_{C1,c}$ according to Eq. (13), the following values were used: $D_R = 7 \times 10^{-10}$ cm^2/s, $\rho_{i0} = 2.722 \times 10^{-11}$ mol$\cdot$cm$^{-3}\cdot$s^{-1} and $a_S = 5 \times 10^{-10}$ cm^2.

The values compared in Table 4 show surprisingly good agreement. However, we have to realize that values for D_0 and D_R are affected by a relatively high uncertainty. In particular, k_{C1} changes with the fourth power of D_0.

Particle Growth

After nucleation, the particles have a diameter in the range of 2–5 nm. In the final latexes the mean particle diameter ranges between 100 and 1000 nm, depending on the recipe and the polymerization conditions. Particle growth is controlled by the monomer concentration within the latex particles (C_M) and the mean number of radicals per particle. By the mean number of radicals, the volume growth rate of the particles is connected with particle number, particle size, initiation reaction, termination, and radical desorption. The monomer concentration in the particles depends on the interfacial tension of particle/water and on the particle size. Monomer concentration within the particles, expressed as the monomer volume content for the period of monomer saturation, can be expressed by the equation of Morton, Kaizerman, and Altier [26]. To calculate the decreasing monomer concentration during the classical third stage of an emulsion polymerization, empirical relations can be used [27, 28]. For practical application, the volume growth rate can be expressed by

$$dv/dt = (\pi/2)D^2 dD/dt = k\bar{n}C_M \tag{16}$$

where v = particle volume, cm^3
t = time, s
D = particle diameter, cm
k = constant, $\text{cm}^6 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
$\bar{n}$ = mean number of radicals per particle
C_M = monomer concentration within the particles, mol/cm^3

For estimation of the volume growth rate parameters, Eq. (17) is advantageous.

$$\bar{n} = k''D^x \tag{17}$$

where k'' = constant, cm^{-x}
x = particle diameter exponent of $\bar{n}$

Table 5 shows values determined for the particle size exponent of the mean number of radicals in a particle size range beyond the validity of the Ugelstad formula, e.g., for particle diameters larger than 100 nm.

These results clearly reveal that the value of x depends on the polymerization procedure and on the formation, or the lack of formation, of

TABLE 5. Estimated Values for the Particle Size Exponent of the Mean Number of Radicals per Particle for Particle Diameters Larger than 100 nm

Polymerization procedure	x
Continuous polymerization (CSTR)	2.0
Continuous seeded polymerization (CSTR) without additional particle nucleation	1.5
Continuous seeded polymerization (CSTR) with additional particle nucleation	2.0
Discontinuous seeded polymerization with and without additional particle formation	2.0

new particles during polymerization. In the case of continuous polymerization with or without seeding, x equals 2 if new particles are formed. The exclusive growth of seeded particles during continuous polymerization leads to a value of x equal to 1.5. In the case of discontinuous seeded polymerization, the value of x does not depend on the formation of new particles.

Models for Polymerization and Particle Growth Including Coalescence

Hansen and Ugelstad [29] developed a model for describing the course of a discontinuous emulsion polymerization of VC with regard to conversion, mean number of particles, and mean particle size. This model mainly considers radical transfer, radical desorption, and particle formation for recipes with emulsifier concentrations equal to or above the CMC. A micellar nucleation is assumed. The change of the particle number with polymerization time is expressed by

$$dN/dt = (\rho_i + k_{des}\bar{n}N)[1 + N/(\delta N_M)(r_P/r_M)^x]^{-1} - k_{C1}N^2D^{-2} \qquad (18)$$

where ρ_i = rate of initiation, $\text{mol}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$
k_{des} = desorption rate constant, s^{-1}
= $3D_R/r_P^2$
r_P = mean particle radius, cm
r_M = micelle radius, cm
N_M = micelle concentration, mol/cm^3
= $N_{M0}(1 - A_P/(a_S S_M N_A))$
A_P = total polymer surface, cm^2/cm^3
N_{M0} = initial micelle concentration, mol/cm^3
N_A = Avogadro number, mol^{-1}
δ, x = parameters

The last term on the right-hand side of Eq. (18) describes particle coalescence according to our model assumptions.

The change of total polymer volume with polymerization time (rate of polymerization) is expressed by

$$dV_P/dt = k_P(\phi_M/(1 - \phi_M))(d_M/d_P)\bar{n}N + v_M N_A(dN/dt) \qquad (19)$$

where k_P = propagation constant, $cm^3 \cdot mol^{-1} \cdot s^{-1}$
ϕ_M = monomer volume fraction in particles
d_M = density monomer, g/cm^3
d_P = density polymer, g/cm^3
v_M = micelle volume, cm^3
$= (\pi/6)D_M^3$
D_M = micelle diameter, cm

The mean number of radicals per particle is calculated according to Eq. (1).

To provide the model calculations, we have chosen the parameters and values listed in Table 6 [30]. These model parameters correspond to the following polymerization recipe: 500 g VC monomer, 695 g water, 4 g/dm^3 Na-dodecylsulfate, 1.6 g/dm^3 $K_2S_2O_8$, and 1.0 g/dm^3 $Na_3PO_4 \cdot 12H_2O$ as buffer. The polymerization temperature was 50°C.

The results of the model computation (Figs. 5–7) show that a sufficient description of the polymerization process is only possible if the

TABLE 6. Parameters and Velocity Constant for Calculations

Parameter/velocity constant	Numerical value	Unit
i	2.722×10^{-11}	$mol \cdot cm^{-3} \cdot s^{-1}$
D_R	7.000×10^{-10}	cm^2/s
S_M	1.170×10^{-5}	mol/cm^3
a_s	5.000×10^{-15}	cm^2
D_M	3.340×10^{-7}	cm
N_{M0}	1.669×10^{-7}	mol/cm^3
k_{Cl}	2.066×10^{-7}	$cm^5 \cdot mol^{-1} \cdot s^{-1}$
k_p	1.000×10^{7}	$cm^3 \cdot mol^{-1} \cdot s^{-1}$
k_1	4.120×10^{25}	cm^{-6}
k_2	1.370×10^{21}	cm^{-5}
d_M	0.8534	g/cm^3
d_P	1.400	g/cm^3
M	0.340	
	1.000	
x	1.000	

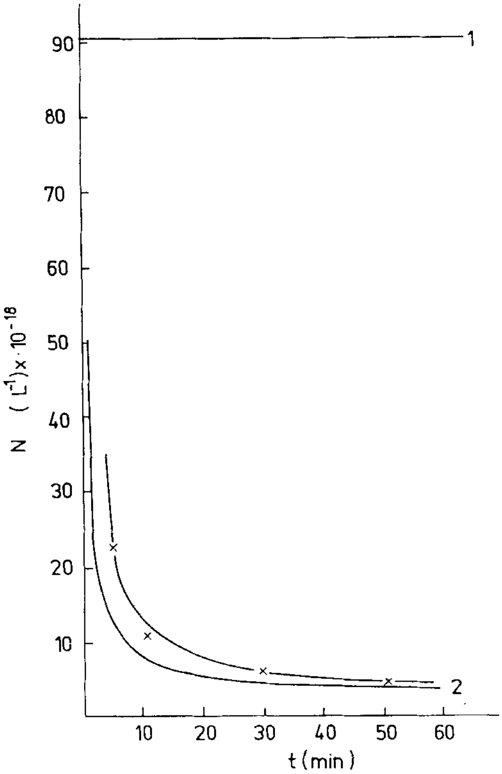

FIG. 5. Modeling of particle number/time curves using Eqs. (18) and (19) for the discontinuous emulsion polymerization of vinyl chloride under standard conditions: (1) modeling without particle coalescence; (2) modeling with particle coalescence; (×) experimental values.

particle coalescence is taken into account. If the coalescence is neglected, large discrepancies occur not only between the calculated and measured particle number/time curves but also in the conversion/time curves and particle diameter/time curves.

5. MODELING THE PARTICLE SIZE DISTRIBUTION

Population balance models permit a mathematical approach to the calculation of psd as a function of reaction time for different chemical reactions such as the precipitation of inorganic salts and emulsion poly-

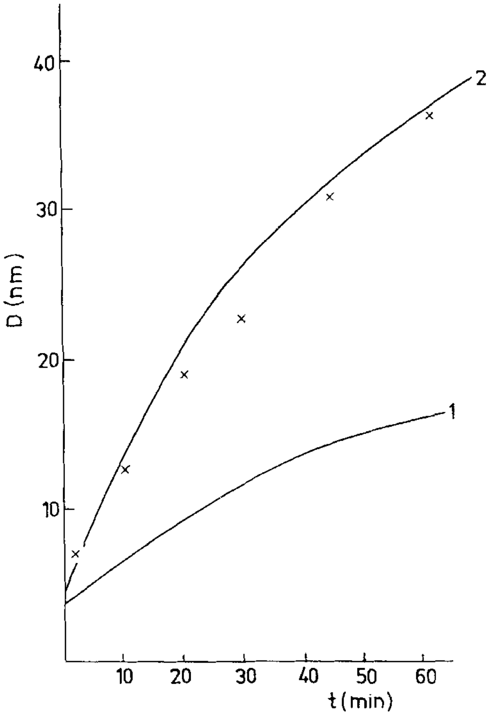

FIG. 6. Modeling of mean particle diameter/time curves using Eqs. (18) and (19) for the discontinuous emulsion polymerization of vinyl chloride under standard conditions: (1) modeling without particle coalescence; (2) modeling with particle coalescence; (×) experimental values.

merizations. The fundamental work was published by Behnken, Horowitz, and Katz in 1963 [19]. In 1972, models of this type were introduced by Stevens and Funderburk [31] for emulsion polymerizations and further developed by Thomson and Stevens [32]. As mentioned in the Introduction, Min and Ray formulated a population balance model for emulsion polymerization reactors. It was successfully applied to semibatch VC polymerization reactors by Min and Gostin [22]. We used a similar model approach based on population balances for the polymerization reaction in order to simulate discontinuous, continuous, and seeded continuous processes. Particle formation is described by a homogeneous nucleation mechanism. For particle sizes smaller than 100 nm, it is neces-

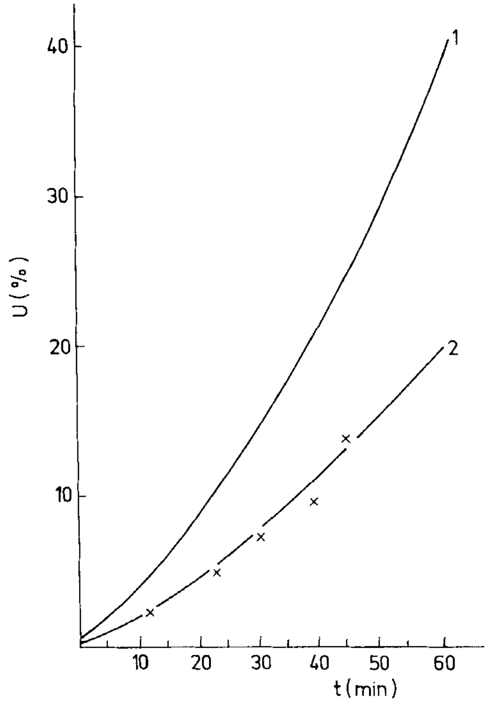

FIG. 7. Modeling of the conversion-time curve using Eqs. (18) and (19) for the discontinuous emulsion polymerization of vinyl chloride under standard conditions: (1) modeling without particle coalescence; (2) modeling with particle coalescence; (×) experimental values.

sary to consider the particle coalescence which largely contributes to the volume growth of particles in this size range. For comparison with the experiments, psd was analytically determined by fractional creaming. This efficient and simple method, originally developed for rubber particles in the range of 50 to 1000 nm by Schmidt and Biddison in 1960 [33], was applied to PVC latexes by Tauer and Jaeger [34]. As compared with the photosedimentation method, preparative fractionation exhibited excellent agreement [35].

Continuous emulsion polymerization of VC on a technical scale is usually carried out in a continuously stirred tank reactor (CSTR). The conversion is maintained at about 90%. The population balance equa-

$$\frac{\partial \bar{F}(\bar{v})}{\partial \bar{t}} + C_P \frac{\partial}{\partial \bar{v}} \left(\bar{n} \frac{\Phi_M}{1-\Phi_M} \bar{F}(\bar{v}) \right) =$$

Propagation

$$C_C \left(\frac{1}{2} \int_0^{\bar{w}} \bar{F}(\bar{v}-\bar{w})\, F(\bar{w})\, (\bar{v}-\bar{w})^{-1/3}\, \bar{w}^{-1/3}\, d\bar{w} - \int_0^{\infty} \bar{F}(\bar{v})\, F(\bar{w})\, (\bar{v}\,\bar{w})^{-1/3}\, d\bar{w} \right) +$$

Coalescence

$$C_N [\bar{P}]_w \cdot \bar{V}_w \cdot \delta(\bar{v}-\bar{v}_m) - C_F [\bar{G}(\bar{v})] - \bar{F}(\bar{v})]$$

Nucleation Flow term

$$C_P = \frac{k_p}{k_{po}} \cdot \frac{d_m}{d_{mo}} \quad ; \quad C_C = \frac{k_{C1}}{k_{po}} \cdot \frac{d_m}{d_{mo}} \cdot N_{mo} \cdot N_a \cdot v_m{}^{1/3}$$

$$C_N = \frac{k_{op}}{k_{po}} \cdot \frac{d_p}{d_{mo}} \cdot [I]_0 \cdot N_a \quad ; \quad C_F = \frac{N_a \cdot d_p \cdot v_m}{k_{po} \cdot d_{mo} \cdot t_m}$$

FIG. 8. Population balance equation for modeling the particle size distribution for the emulsion polymerization of vinyl chloride in dimensionless form: $F(v)$ = particle concentration of particles with a volume of v to $v + dv$; $G(v)$ = seed particle concentration of particles with a volume of v to v + dv; v, w = particle volume; $[P]_w$ = total concentration of oligomers in the water phase; v_w = water fraction in the latex; v_m = nucleation volume of particles; C_P, C_C, C_N, C_F = model constants.

tion for modeling the psd in a CSTR is shown in Fig. 8. Depending on the polymerization conditions, particle coalescence must be considered.

If the latex contains a perceptible amount of particles with a diameter smaller than 100 nm, particle coalescence should be taken into account. Figure 9 shows that the experimental psd is in good agreement with the calculations. Figure 10 demonstrates that the model can also be applied for discontinuous emulsion polymerization on a laboratory scale. In this case, the flow terms are not valid and particle coalescence has to be taken into account. If the coalescence is neglected, the calculated polymerization behavior (conversion, psd, etc.) does not correspond with the experiments. Figure 11 exhibits the dependence of the psd on polymerization time. The influence of particle coalescence is clearly illustrated.

Both examples of the model application reveal that, for the calculation of psd, population balances can be applied to rather different ranges of particle sizes. Reactor models generally allow the simulation of the conceived reactor types. Thus, we have modeled a continuous tube reac-

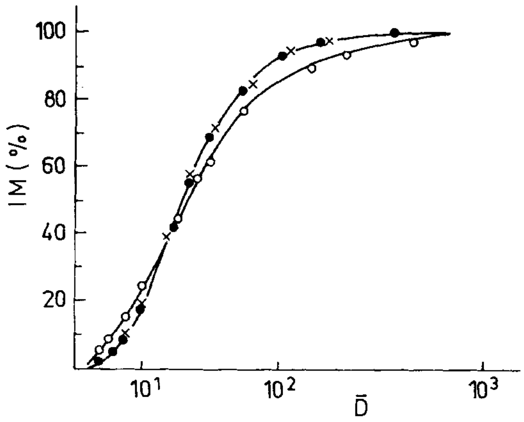

FIG. 9. Modeling the particle size distribution for the steady state of the continuous emulsion polymerization of vinyl chloride: D = dimensionless particle diameter; IM = cumulative mass fraction of latex particles; (●) experimental values; calculations corresponding to polymerization times of 20 (○) and 170 h (×).

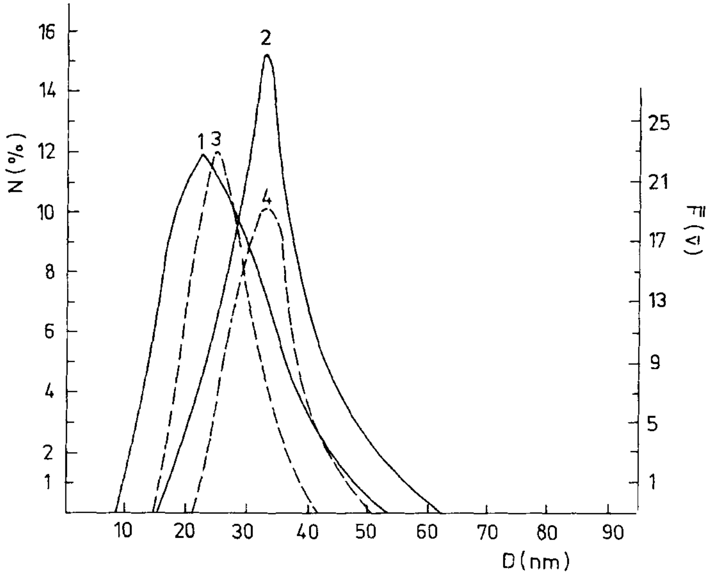

FIG. 10. Modeling of particle size distribution for discontinuous emulsion polymerization under standard conditions: (1, 2) left y-axis; (3, 4) right y-axis; (1) experimental values for a conversion of 14%; (2) experimental values for a conversion of 20%; (3) calculation for a conversion of 13%; (4) calculation for a conversion of 21%.

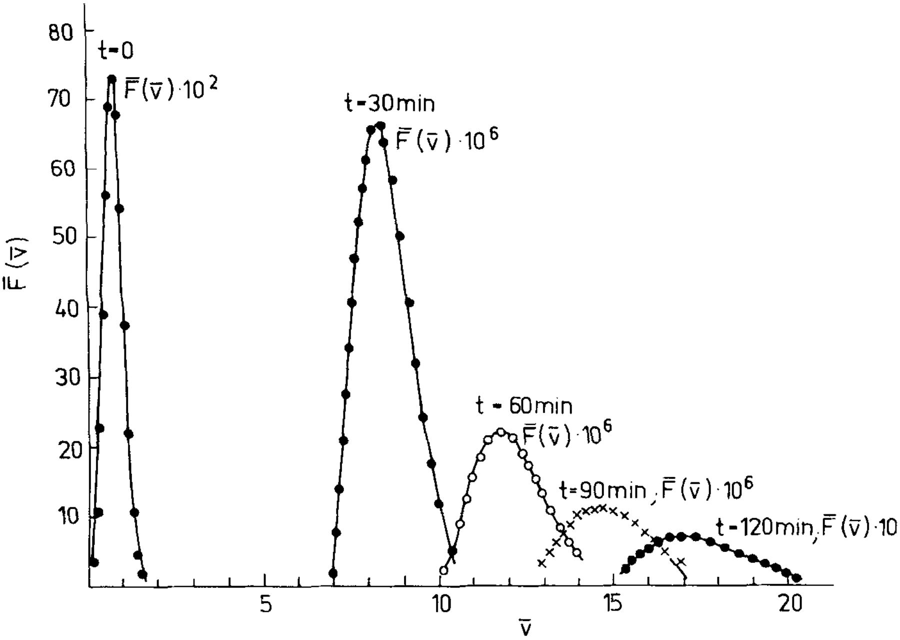

FIG. 11. Model calculations regarding the influence of particle coalescence on particle size distribution for a discontinuous emulsion polymerization.

tor assuming an unperturbed plug flow. Figure 12 demonstrates that, in this case, a narrowing of the psd can be observed with increasing residence time in the reactor. Real seeded polymerizations were performed in a CSTR on a semitechnical scale. The seed latex with a narrow psd is synthesized in a separate process. Figure 13 represents the psd for different filling states and the continuous development of the psd in the filled reactor until steady state is reached.

Modeling technical processes is mainly aimed at calculating the course of process variables with respect to the desired product property. In Fig. 14, the calculated continuous metering parameters for emulsifier and water are shown which maintain the emulsifier concentration required for adjusting a desired psd. The curves of the calculated and experimentally determined psd in Fig. 15 demonstrate the predictive power of the model concerning engineering parameters and psd to be satisfactory.

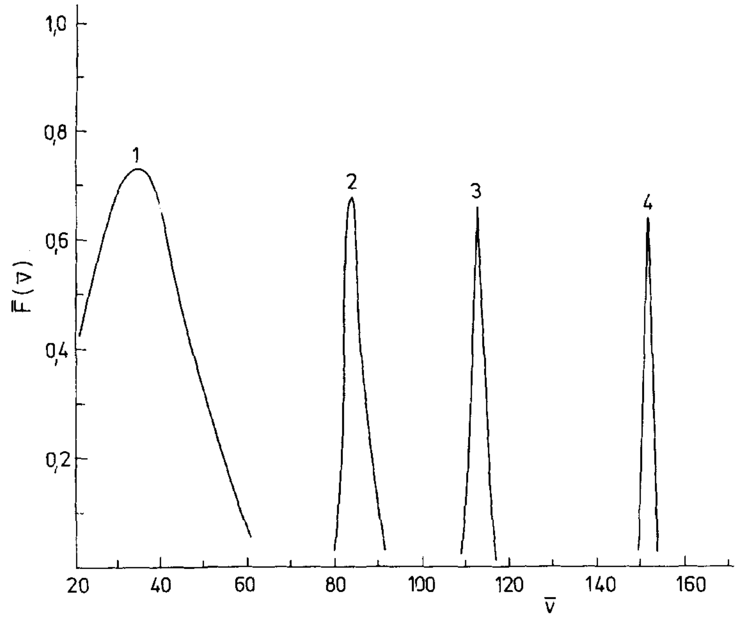

FIG. 12. Modeling the change of particle size distribution for an assumed seeded emulsion polymerization of vinyl chloride in a tube reactor with an unperturbed plug flow as related to the polymerization time: (1) seed particle size distribution; (2) particle size distribution after a polymerization time of 2.5 h; (3) particle size distribution after a polymerization time of 5 h; (4) particle size distribution after a polymerization time of 10 h.

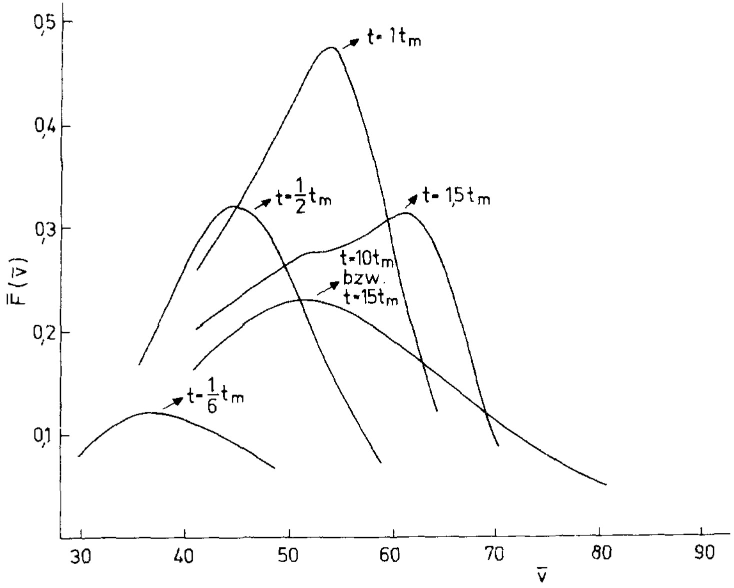

FIG. 13. Modeling the particle size distribution for different filling states and polymerization times for the seeded continuous emulsion polymerization of vinyl chloride in a CSTR: t_m = *mean residence time.*

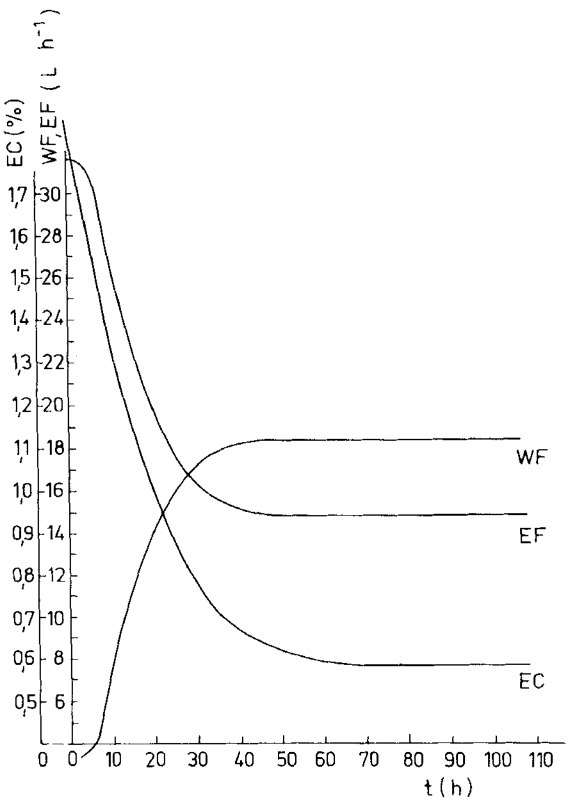

FIG. 14. Calculated metering parameters for the seeded continuous emulsion polymerization of vinyl chloride in a CSTR to achieve a desired emulsifier content in the final polymer: EC = emulsifier content in the final polymer; WF = water feed during polymerization; EF = emulsifier feed during polymerization.

6. CONCLUSIONS

Various strategies for modeling the course, special aspects, and special properties of the emulsion polymerization of vinyl chloride are available today. Particle nucleation, particle growth, and particle coalescence are important steps in the reactions, and they depend on reaction conditions and polymerization technology. For modeling particle nucleation and particle growth, well-established concepts are available and applicable. The proposed mechanism for modeling particle coalescence based on

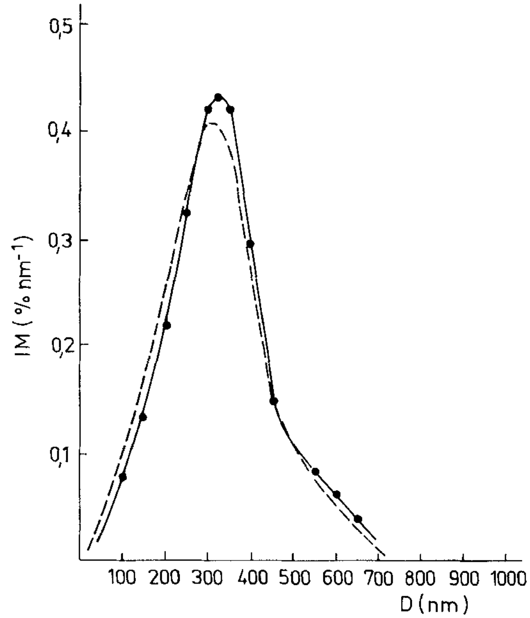

FIG. 15. Modeling the particle size distribution for the seeded continuous emulsion polymerization of vinyl chloride in the steady state: (●) experimental values; (— —) calculated values.

the hypothesis that radical desorption from a particle determines the coalescence velocity seems to be applicable as well.

Comparisons of experimental data and model calculations show that the particle coalescence has to be taken into account for modeling the course of an emulsion polymerization of vinyl chloride, especially in cases where particle diameters are smaller than 100 nm. Furthermore, the results show that models based on population balance equations can be applied for modeling very different technological procedures of the emulsion polymerization of vinyl chloride.

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