Continuous Emulsion Polymerization. Modeling Oscillations in Vinyl Acetate Polymerization

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Synopsis

A theoretical investigation of the emulsion polymerization of vinyl acetate in a continuous stirred tank reactor operating under conditions of sustained oscillations is reported here. Models of two levels of sophistication are developed: a comprehensive model that solves for the age distribution function of polymer particles and a simplified model that assumes discrete nucleation periods. The latter model should find use in adaptive control of latex reactors. These models adequately simulate experimental data after Greene et al.[2] for the emulsion polymerization of vinyl acetate under conditions of sustained oscillations.

INTRODUCTION

In continuous emulsion polymerization the commercially important phenomena of sustained oscillations and steady-state multiplicity have been studied in carefully conducted laboratory experiments[1,2] for the monomers styrene, methyl methacrylate, and vinyl acetate. However, steady-state multiplicity has not been observed for vinyl acetate as it probably does not exist. Although there is no published literature on the subject, it is known that oscillations occur in the continuous emulsion polymerization of chloroprene and styrene–butadiene on a commercial scale. These oscillations can lead to emulsifier levels too small to adequately cover polymer particles with the result that excessive agglomeration and fouling can occur. Furthermore, for monomer systems where long-chain branching occurs, excursions to high polymer concentrations, due to the cycling behavior of conversion, can result in polymers with excessive branching and poor processability. In a recent review paper[3] Poehlein et al. present experimental data for the continuous emulsion polymerization of several monomers and summarize the prior state of the theoretical treatment of the problem.

One of the first theoretical attempts to explain sustained oscillations in continuous emulsion polymerization was done by Omi et al.[4] for styrene polymerization. Recently, Dickinson and Gall[5] simulated the experimental results of Gerrens[1] for styrene polymerization for the cases of both sustained and damped oscillations. In their model they considered a particle generation mechanism which depended on both the available free soap and the aqueous phase monomer concentration and corrected for diffusion-controlled termination in the polymer particles by letting the termination constant k_t fall with conversion.

The approach taken by Dickinson and Gall in developing their general model focuses on the residence time or age distribution of particles rather than on the size distribution. The latter approach, taken by Min and Ray,[7] can lead to some difficulties in modeling reactors where the growth rate of a particle is not only

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dependent upon its current size and the current conditions in the reactor but also on the conditions prevailing during its previous history. More recently, Jaisinghani and Ray[8] presented some dynamic models for the continuous bulk polymerization of both methyl methacrylate and styrene monomers. In fact, according to their models, operating conditions can be determined under which multiple steady states and limit cycles might be observed as coupled phenomena.

Our objective in this paper is to present simple but adequate models for continuous emulsion polymerization based on a minimum number of unknown parameters that can be easily calculated from experimental data. To illustrate the application of these models, we model sustained oscillations appearing in the continuous emulsion polymerization of vinyl acetate,[2] a monomer that conforms to case I kinetics.
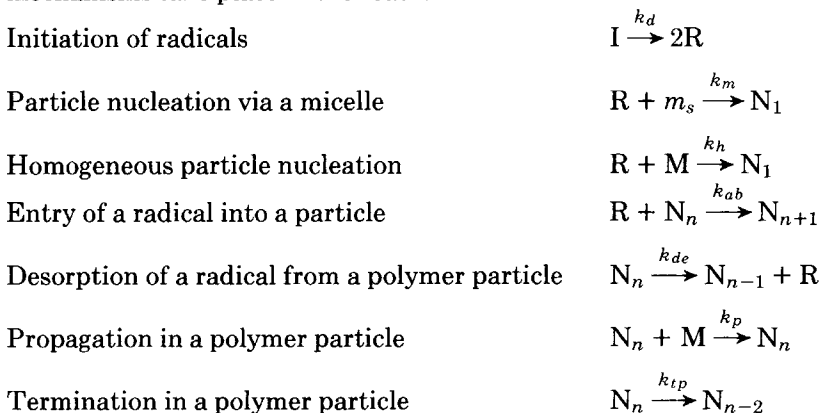
Experimental results reported by Greene et al.[2] are successfully simulated under sustained oscillation conditions. Latex properties such as particle size distribution, total particle surface area, total number of particles, and free soap concentration are accounted for in the present models. The unquestionable commercial importance of all the above properties for a latex makes such models useful for the design and control of latex reactors.

MODEL DEVELOPMENT

Particle Nucleation and Age Distribution Function

On the basis of the micellar nucleation mechanism, free radicals generated in the aqueous phase are captured by micelles or polymer particles. According to the homogeneous particle nucleation mechanism,[9] free radicals formed in the aqueous phase can either be captured by existing particles or they could react with dissolved (not solubilized) monomer. In the latter case, as the radicals grow to some size they precipitate out to form polymer particles which are stabilized by adsorbed emulsifier.

Consider the case where the following polymerization and particle nucleation mechanisms take place in the reactor:

Initiation of radicals $\qquad I \xrightarrow{k_d} 2R$

Particle nucleation via a micelle $\qquad R + m_s \xrightarrow{k_m} N_1$

Homogeneous particle nucleation $\qquad R + M \xrightarrow{k_h} N_1$

Entry of a radical into a particle $\qquad R + N_n \xrightarrow{k_{ab}} N_{n+1}$

Desorption of a radical from a polymer particle $\qquad N_n \xrightarrow{k_{de}} N_{n-1} + R$

Propagation in a polymer particle $\qquad N_n + M \xrightarrow{k_p} N_n$

Termination in a polymer particle $\qquad N_n \xrightarrow{k_{tp}} N_{n-2}$

where N_n denotes the number of particles having n radicals per particle.

The basic assumptions made in modeling this reaction in a continuous stirred tank reactor are (i) the reactor is uniformly mixed; (ii) the density change in the

reaction mixture is negligible; (iii) the extent of particle flocculation and breakup is negligible; (iv) in the proposed kinetic model particles are generated by micellar and homogeneous mechanisms; and (v) the monomer volume fraction in a particle, $\Phi(t)$, is assumed to be independent of particle size and age; in other words, monomer diffuses into particles independently of their size or age.

Therefore, for a constant monomer feed concentration we have

$$\Phi(t) = \Phi_{\text{sat}}; \qquad x \leq x_c$$

when monomer drops are present; otherwise,

$$\Phi(t) = \frac{1 - x(t)}{1 - x(t)(1 - d_m/d_p)}, \qquad x > x_c \tag{1}$$

in the monomer starved region. Φ_{sat} is given by eq. (1) by substituting for the total conversion $x(t)$ the conversion value x_c, above which the monomer drops disappear; d_m and d_p are the monomer and polymer densities, respectively.

Although we develop the model by considering a particular set of mechanisms taking place in the reactor, it is not difficult to add the effects of other mechanisms such as, for example, particle coalescence or particle breakage.

In deriving the differential equations, which describe the dynamic behavior of the important latex properties, the age distribution function is used, and this enables us to follow all variations in individual growth rates, due to past and present reaction conditions. Particle growth rate is generally considered a function of monomer concentration in the particle, particle size, and rates of radical adsorption and desorption.

In a continuous stirred tank reactor particles can be generated continuously leading to distributions of particle size and age. Let $f(t)$ denote the net rate of particle generation in the reactor (Fig. 1). The function $n(t,\tau)d\tau$ is defined to be the number of particles in the reactor, at time t, that were born in the time interval $[\tau, \tau + d\tau]$. Following Dickinson's[6] approach, a particle population
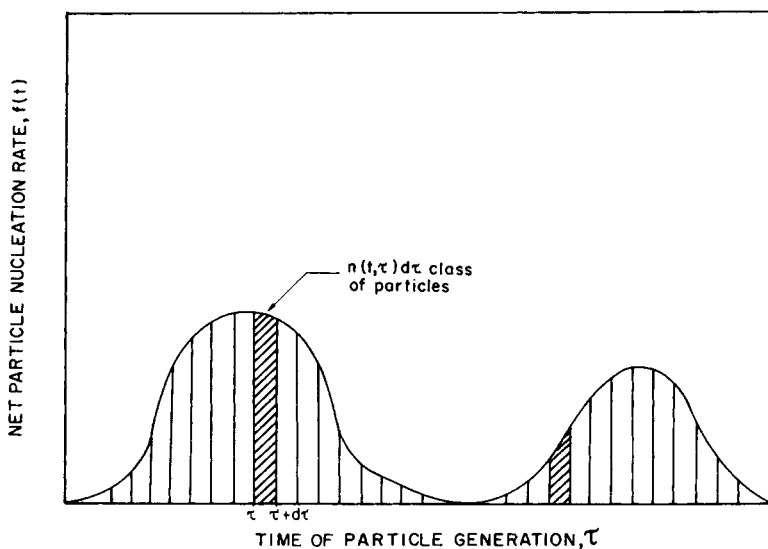

Fig. 1. Net particle nucleation rate $f(t)$ with respect to birth time τ.

balance about the reactor for the class of particles $n(t,\tau)d\tau$ is

$$\frac{\partial}{\partial t} n(t,\tau) \, d\tau = \frac{-n(t,\tau) \, d\tau}{\theta} + \delta(t - \tau)f(\tau) \, d\tau \qquad (2)$$

where the Dirac function $\delta(t - \tau)$ indicates the time of appearance of a particular class of particles and θ is the mean residence time. It may be easily shown by taking the Laplace transform of eq. (2) that

$$n(t,\tau) \, d\tau = f(\tau) \, d\tau e^{-(t-\tau)/\theta} \qquad (3)$$

is a solution of eq. (2), and $t - \tau$ denotes the age of all particles in the reactor which were generated at some previous time interval $[\tau, \tau + d\tau]$ at a rate $f(\tau)$. In deriving eq. (2), it is assumed that particle appearance in the reactor is due only to nucleation mechanisms.

We define now $p(t,\tau)$ to be some property of the latex associated with the class of particles $n(t,\tau) \, d\tau$. Then the total property for all particles in the reactor will be given by

$$P(t) = \int_0^t p(t,\tau)n(t,\tau)d\tau \qquad (4)$$

Differentiating eq. (4) with respect to t, we obtain

$$\frac{dP(t)}{dt} = \int_0^t \frac{\partial p}{\partial t} (t,\tau) \, n(t,\tau) \, d\tau + \int_0^t p(t,\tau) \left[\frac{\partial n(t,\tau)d\tau}{\partial t} \right] \qquad (5)$$

Replacing the term inside the square brackets with the expression in eq. (2), eq. (5) becomes finally

$$\frac{dP(t)}{dt} = - \frac{P(t)}{\theta} + f(t) \, p(t,t) + \int_0^t \frac{\partial p(t,\tau)}{\partial t} n(t,\tau) \, d\tau \qquad (6)$$

where the property $p(t,t)$ is taken to be negligible for newly generated particles except where $p(t,t)$ stands for number of particles.

The Total Property Balances

The differential equations, which describe the total properties of a latex in a continuous reactor, can be now derived directly from eq. (6). Therefore, total property balances for number of particles, polymer volume, area of particles, and conversion are written

$$\frac{dN(t)}{dt} = - \frac{N(t)}{\theta} + f(t) \qquad (7)$$

$$\frac{dV_p(t)}{dt} = - \frac{V_p(t)}{\theta} + \int_0^t \mu_p(t,\tau) \, \bar{q}(t,\tau) \, n(t,\tau) \, d\tau \qquad (8)$$

$$\frac{dA_p(t)}{dt} = - \frac{A_p(t)}{\theta} + \frac{2}{3} (36\pi)^{1/3} \int_0^t v(t,\tau)^{-1/3}\mu(t,\tau) \, \bar{q}(t,\tau) \, n(t,\tau) \, d\tau \qquad (9)$$

$$\frac{dx(t)}{dt} = - \frac{x(t)}{\theta} + \frac{d_p}{M_F M_w} \int_0^t \mu_p(t,\tau) \, \bar{q}(t,\tau) \, n(t,\tau) \, d\tau \qquad (10)$$

where $N(t) = \int_0^t n(t,\tau) \, d\tau$ is the total number of particles, $V_p(t) = \int_0^t v_p(t,\tau) n(t,\tau) \, d\tau$ is the total polymer volume, $A_p(t) = \int_0^t a_p(t,\tau) \, n(t,\tau) \, d\tau$ is the total particle area, and $x(t)$ is the total conversion in the reactor at time t.
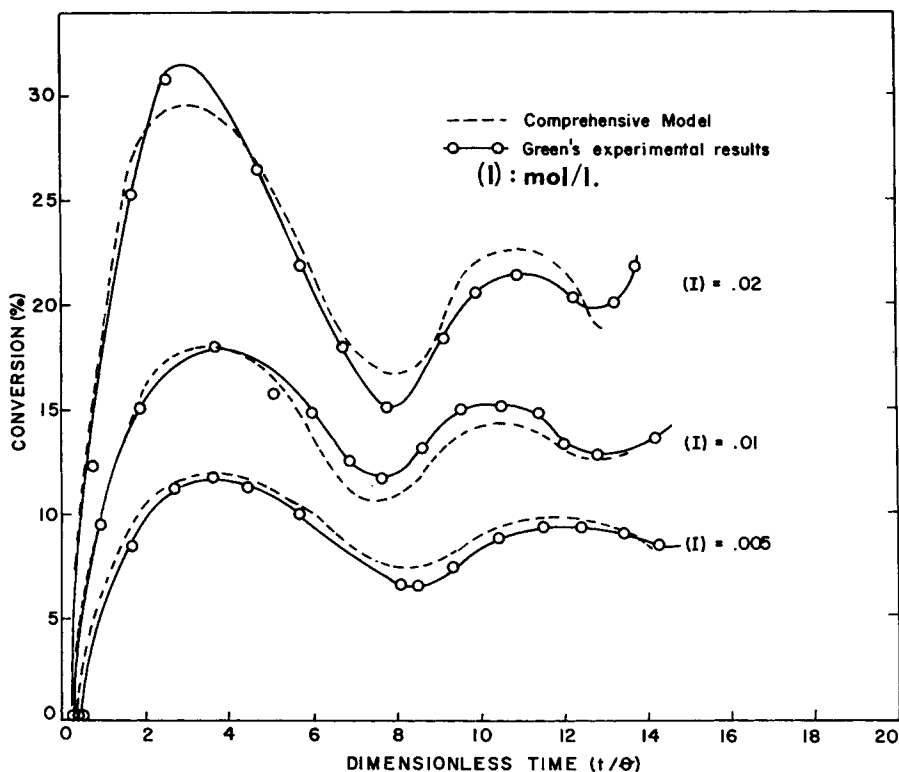
Fig. 2. CSTR conversion transients. Comparison between experimental[2] and predicted results (comprehensive model, vinyl acetate, θ = 30 min, T = 40°C, (S) = 0.01 mol/l, M/W = 0.43).

The volumetric growth rate of the polymer phase in a particle can be obtained from eq. (11):

$$\frac{\partial v_p(t,\tau)}{\partial t} = \mu_p(t,\tau)\,\overline{q}(t,\tau) = \frac{k_p d_m}{N a d_p}\,\Phi(t)\,\overline{q}(t,\tau) \tag{11}$$

and the total volume of a particle is given by

$$v(t,\tau) = \frac{v_p(t,\tau)}{1 - \Phi(t)} \tag{12}$$

Assuming spherical particles, the surface area of a single particle is given by

$$a_p(t,\tau) = (36\pi)^{1/3} v^{2/3}(t,\tau) \tag{13}$$

where $\overline{q}(t,\tau)$ denotes the average number of radicals per particle, k_p is the propagation rate constant, M_F is the feed monomer concentration, M_w is the molecular weight of monomer, and Na is Avogadro's number. The average number of radicals in a particle of volume $v(t,\tau)$ up to relatively high conversions for vinyl acetate monomer can be estimated by the following eq. (14) after Ugelstad[10]:

$$\overline{q}(t,\tau) = \frac{\rho_n}{k_{de}(t,\tau)\,n(t,\tau)\,d\tau} \tag{14}$$

where ρ_n is the radical entry rate to the $n(t,\tau)\,d\tau$ class of particles. Assuming
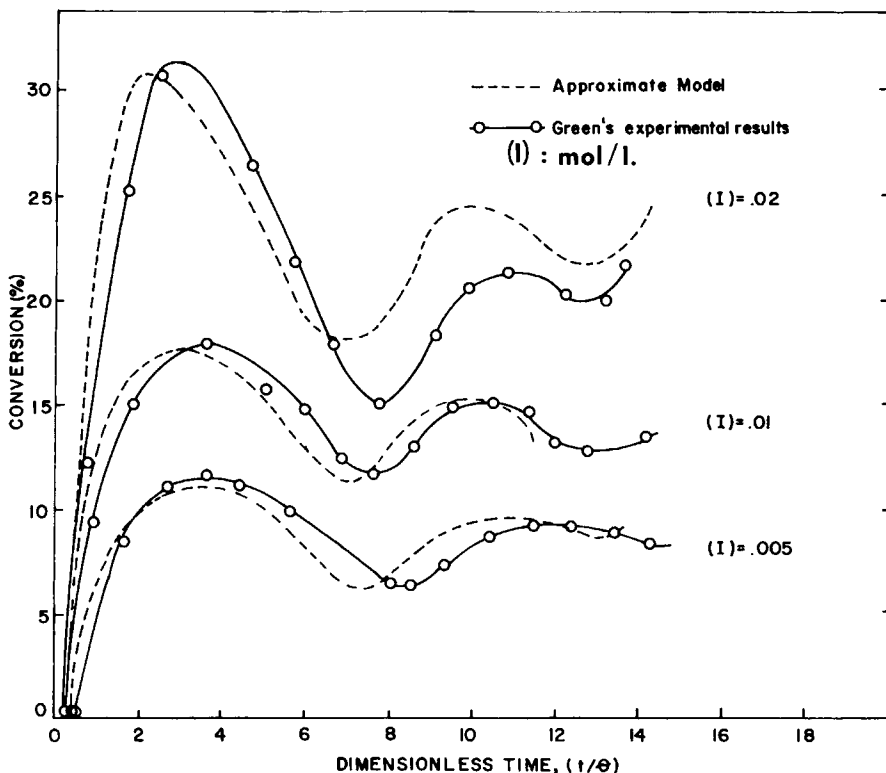
Fig. 3. CSTR conversion transients. Comparison between experimental and predicted results (approximate model, vinyl acetate, θ = 30 min, T = 40°C, (S) = 0.01 mol/l, M/W = 0.43).

that termination takes place exclusively in polymer particles,[10] a steady-state treatment gives

$$r(t,\tau) = 2\rho_n \bar{q}(t,\tau) \tag{15}$$

where $r(t,\tau)$ is the radical initiation rate corresponding to the $n(t,\tau)\,d\tau$ class of particles, and it is taken to be equal to $R_I[A_n(t,\tau)\,d\tau]/A_p(t)$, where $A_n(t,\tau)\,d\tau$ is the surface area of the $n(t,\tau)\,d\tau$ class of particles and R_I is the total initiation rate. Substituting eq. (15) into eq. (14) we obtain

$$\bar{q}(t,\tau) = \left(\frac{R_I}{2k_{de}(t,\tau)n(t,\tau)\,d\tau}\right)^{1/2} \left(\frac{A_n(t,\tau)\,d\tau}{A_p(t)}\right)^{1/2} \tag{16}$$

where k_{de} is a desorption coefficient of radicals from polymer particles given by[10]

$$k_{de}(t,\tau) = \left(\frac{12D_w\delta}{mD_p{}^2}\right)\left(\frac{k_{fm}}{k_p}\right) = k'_{de}\upsilon^{-2/3}(t,\tau) \tag{17}$$

where D_w is the diffusion coefficient of monomeric radicals in the water phase, D_p denotes the diameter of particle, m is a partition coefficient of monomeric radicals between water and particle phases, and k_{fm} is the rate coefficient of chain transfer to monomer. Combining eq. (16) with eqs. (3), (12), and (17) and substituting the new equation into eq. (11), the volumetric growth rate of the polymer phase in a particle can be written as

$$\frac{\partial \upsilon_p(t,\tau)}{\partial t} = \frac{K}{f(\tau)^{1/2}}\,e^{(t-\tau)/2\theta}(1 - e^{-t/\theta})\upsilon_p{}^{1/3}(t,\tau) \tag{18}$$
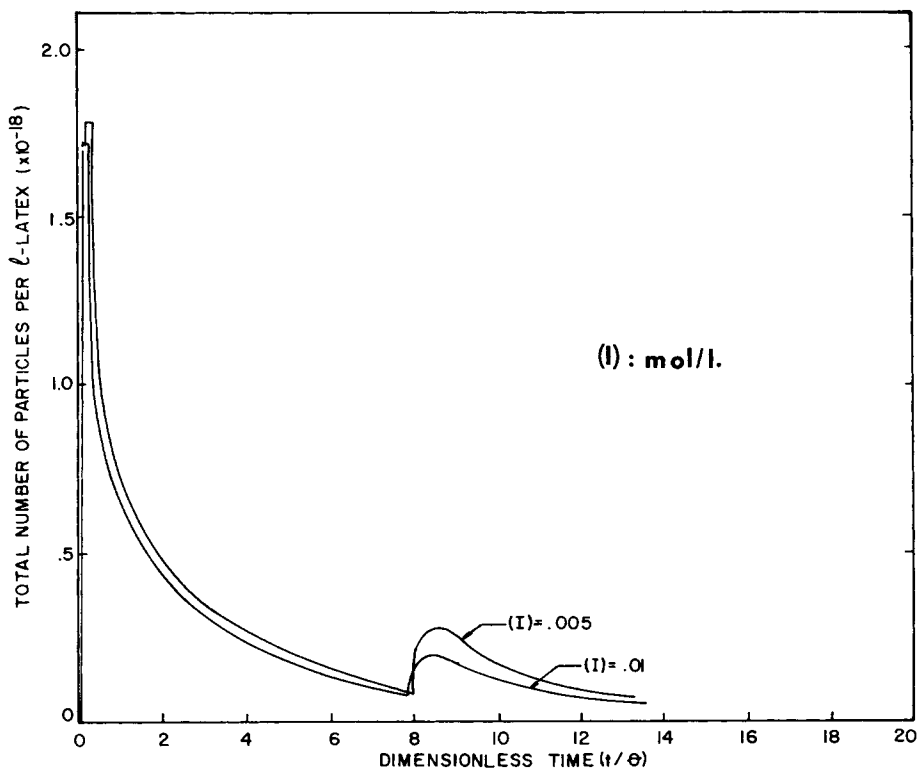
Fig. 4. Relationship between total number of polymer particles and dimensionless reaction time (t/θ) (comprehensive model, VA, $\theta = 30$ min, $T = 40°C$, $(S) = 0.01$ mol/l, $M/W = 0.43$).

where

$$K = \frac{k_p d_m}{N a d_p} \left(\frac{m k_p}{12 D_w \delta k_{fm}} f k_d [I]_{\text{feed}} \frac{A_n(t,\tau)}{A_p(t)} \right)^{1/2} \left(\frac{6}{\pi} \right)^{1/3} \Phi(t)(1 - \Phi(t))^{-1/3} \quad (19)$$

$$\delta = (1 + D_w/D_p m)^{-1} \quad (20)$$

$$[I]_w = [I]_{\text{feed}}(1 - e^{-t/\theta})/(1 + k_d \theta) \quad (21)$$

To derive eq. (18) we used the fact that the start-up procedure, to be considered later, consists of filling the reactor with degassed water prior to introducing any feed streams.[2]

The extension of the above developed equations to more than one reactor is straightforward. However, the complexity of the resulting equations can lead to some numerical difficulties during solution.

Initiator, Oligomeric Radicals, and Emulsifier Balances

The aqueous phase initiator and oligomeric radicals balances can be written

$$\frac{d[I]_w}{dt} = \frac{1}{\theta} ([I]_{\text{feed}} - [I]_w) - k_d [I]_w \quad (22)$$

$$\frac{d[R]_w}{dt} = \frac{1}{\theta} ([R]_{\text{feed}} - [R]_w) + 2 f k_d [I]_w - k_{ab} A_p [R]_w k_v$$
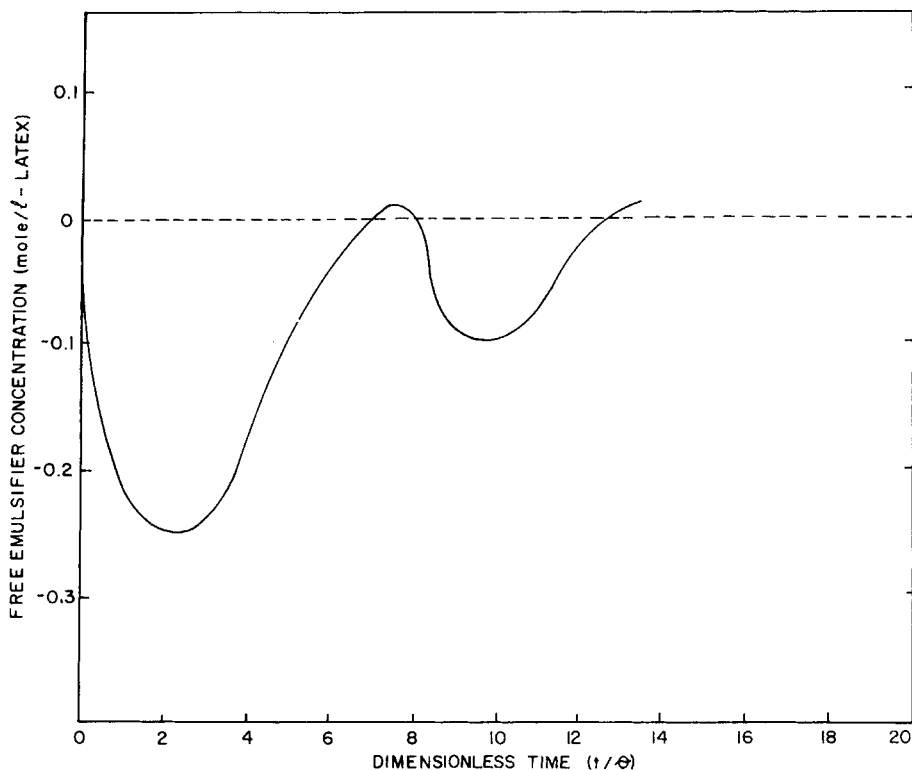
Fig. 5. Relationship between free emulsifier concentration and dimensionless reaction time (t/θ) (comprehensive model, VA, $\theta = 30$ min, $T = 40°C$, $(S) = 0.01$ mol/l, $(I) = 0.01$ mol/l, $M/W = 0.43$).

$$- k_m A_m [R]_w k_v - k_h [R]_w - k_{tw} [R]_w^2 + \int_0^t k_{de} n(t,\tau)\, \overline{q}(t,\tau)\, d\tau \quad (23)$$

In deriving eq. (23) it was assumed that the rate of radical capture is proportional to the total surface available for radical capture (Smith-Ewart, Gardon,[11] and Fitch and Tsai[9]). However, a mass balance equation in which the radical capture would be proportional to the radius[10] of particles or micelles could equally be used. In eq. (23), $[I]_{feed}$, $[R]_{feed}$ are the initiator and radical concentrations in the aqueous phase in the reactor. The third term on the right of eq. (23) represents the rate at which radicals are captured by polymer particles, and it is proportional to the total particle area A_p and the radical concentration $[R]_w$; k_{ab} is an overall transport coefficient for radical transfer from the aqueous phase into polymer particles.

The next term in eq. (23) represents the rate at which polymer particles are generated by the micellar mechanism. A_m is the free coverage area of micelles given by

$$A_m = S_T - S_{CMC} - A_p \quad (24)$$

where S_{CMC} is the critical micelle concentration converted in dm^2/l. emulsion and S_T is the total emulsifier concentration in dm^2/l. emulsion given by

$$dS_T/dt = (S_F - S_T)/\theta \quad (25)$$

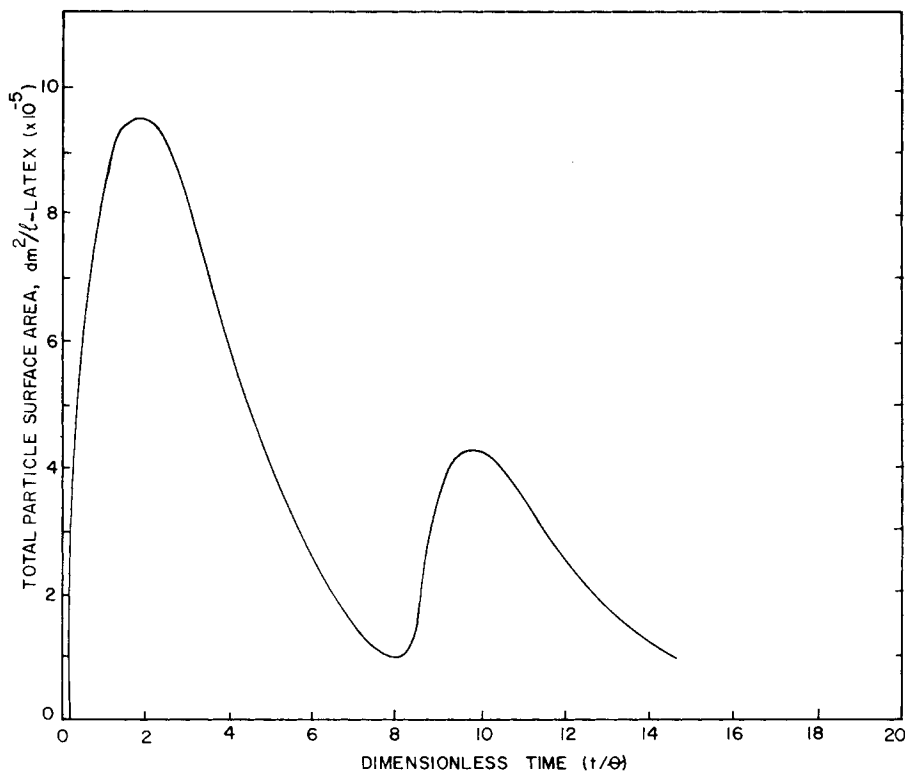where S_F is the emulsifier concentration in the feed.

Fig. 6. Relationship between total particle surface area and dimensionless reaction time (t/θ) (comprehensive model, VA, $\theta = 30$ min, $T = 40°C$, $(S) = 0.01$ mol/l, $(I) = 0.01$ mol/l, $M/W = 0.43$).

The term $k_h[R]_w$ stands for the rate of homogeneous nucleation of particles. This means that polymer particles can be generated even though micelles do not exist. However, according to Fitch,[9] the rate of homogeneous generation of particles should be allowed to tend toward zero when the rate of radical capture by the existing polymer particles becomes greater than the rate of initiation of radicals. Therefore, the rate constant k_h can be equated with the term $k_{ho}[1 - (A_p/4)L]$, where L is now defined, after Fitch, as the distance which a growing radical will diffuse before it precipitates out to form a primary particle, and it is obtained from Einstein's diffusion law as

$$L = (2D_w DP_{max}/k_p M_{wc})^{1/2} \tag{26}$$

where DP_{max} is the maximum degree of polymerization before radical precipitation and M_{wc} is the saturation concentration of monomer in the water phase. Gardon[11] and Gatta[12] have presented expressions similar to Fitch's equation.

Finally, the last term in eq. (23) denotes the total desorption rate of radicals from the polymer particles. Thus, according to our proposed kinetic model the total rate of particle nucleation may be written as

$$f(t) = k_m A_m [R]_w k_v + k_{ho}[1 - (A_p/4)L][R]_w \tag{27}$$

where k_m and k_{ho} are rate coefficients of particle nucleation by micellar and homogeneous mechanism, respectively, and the constant k_v represents the volume of emulsion phase over the volume of aqueous phase, in l. emulsion/l.
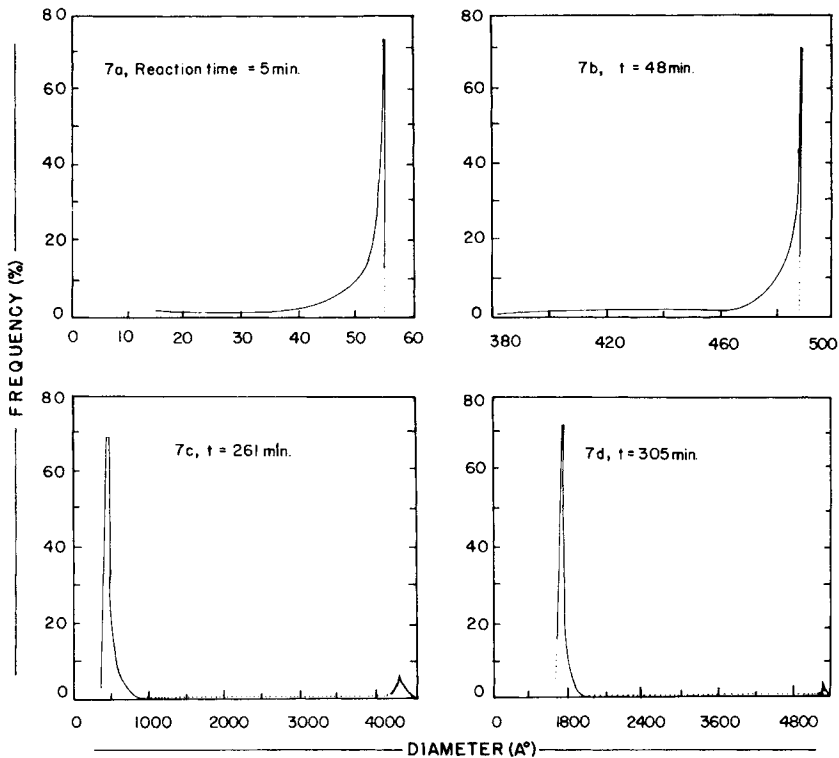
Fig. 7. Total particle size distribution at different reaction times (comprehensive model, VA, θ = 30 min, T = 40°C, (S) = 0.01 mol/l, (I) = 0.01 mol/l, M/W = 0.43).

It is interesting to note that according to eq. (27) particles will be generated even though micelles are not present, and homogeneous nucleation of particles will cease only when the term $[1 - (A_p/4)L]$ becomes less than or equal to zero.

Equation (23) may be simplified by applying a stationary-state hypothesis to the monomeric and oligomeric radicals:

$$[R]_w = \rho/(k_{ab}A_p k_v + k_m A_m k_v + k_h)$$

where ρ is equal to $R_I + \int_0^t k_{de} n(t,\tau)\, \bar{q}(t,\tau)\, d\tau$.

Therefore, the net particle generation rate, eq. (27), is now written

$$f(t) = \cfrac{\rho}{1 + \epsilon\cfrac{A_p}{A_m} + \cfrac{\mu(1 - A_p L/4)}{k_v A_m}}$$
$$+ \cfrac{\rho}{1 + k_v\cfrac{\epsilon A_p}{\mu(1 - A_p L/4)} + \cfrac{k_v A_m}{\mu(1 - A_p L/4)}} \tag{28}$$

where ϵ is defined to be the ratio k_{ab}/k_m and μ is the ratio k_{ho}/k_m. These parameters ϵ and μ can be estimated from conversion and particle size distribution data collected from the reactor.

Equations (3), (7)–(10), (18)–(23), and (28) represent a general enough model
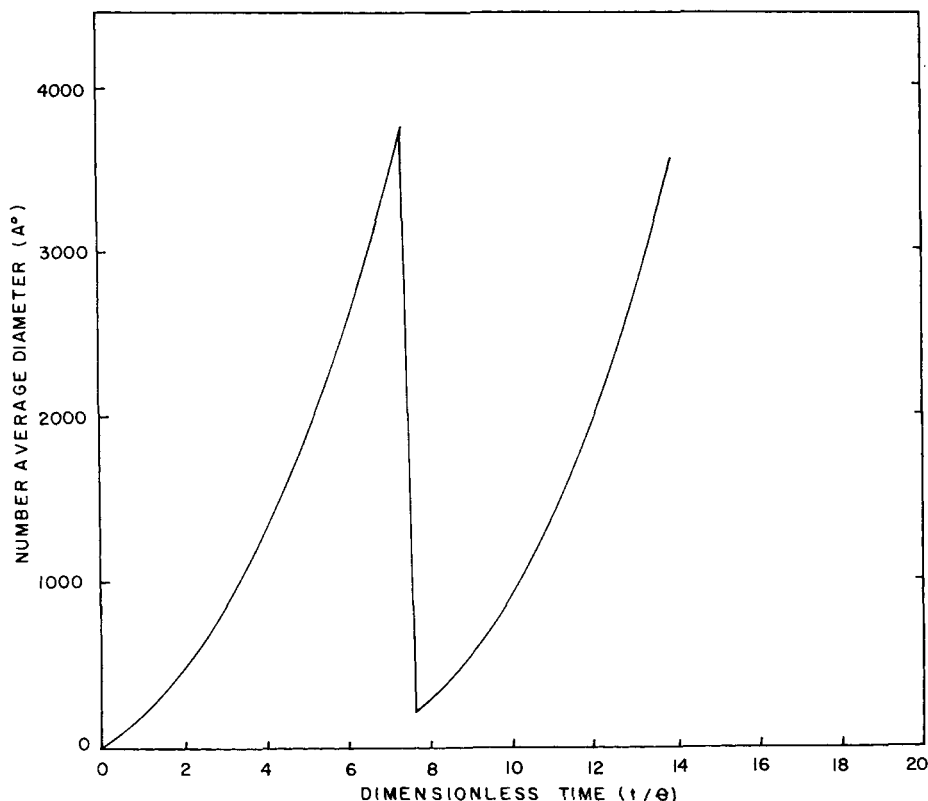
Fig. 8. Number-average diameter with respect to dimensionless reaction time (t/θ) (comprehensive model, VA, $\theta = 30$ min, $T = 40°C$, $(S) = 0.01$ mol/l, $(I) = 0.01$ mol/l, $M/W = 0.43$).

form. Solution of these equations with the proper initial conditions will give information for the most important latex properties (e.g., conversion, total particle area, free emulsifier concentration, etc.) as well as the particle size distribution at any time t.

Application of Model Equations

To simulate Greene's[2] data, the complex system of integro-differential eqs. (7)–(10) must be solved according to Greene's start-up procedure which consisted of filling the reactor with degassed water prior to introducing any feed streams. To simplify the numerical calculations, the integral terms in eqs. (7)–(10) are replaced by equivalent summation terms over a finite number of time intervals $\Delta\tau_i, i = 1, 2, \ldots, r_t$ (see Fig. 1), yielding

$$\frac{dN(t)}{dt} = -\frac{N(t)}{\theta} + f(t) \tag{29}$$

$$\frac{dV_p(t)}{dt} = -\frac{V_p(t)}{\theta} + \sum_{i=1}^{r_t} K v_p^{1/3}(t,\tau_i) n^{1/2}(t,\tau_i)\Delta\tau_i \tag{30}$$

$$\frac{dA_p(t)}{dt} = -\frac{A_p(t)}{\theta} + \frac{2}{3}(36\pi)^{1/3}(1 - \phi(t))^{-2/3} \sum_{i=1}^{r_t} K n^{1/2}(t,\tau_i)\Delta\tau_i \tag{31}$$

$$\frac{dx(t)}{dt} = -\frac{x(t)}{\theta} + \frac{d_p}{M_T M_w} \sum_{i=1}^{r_t} K v_p^{1/3}(t,\tau_i)\, n^{1/2}(t,\tau_i)\, \Delta\tau_i \tag{32}$$
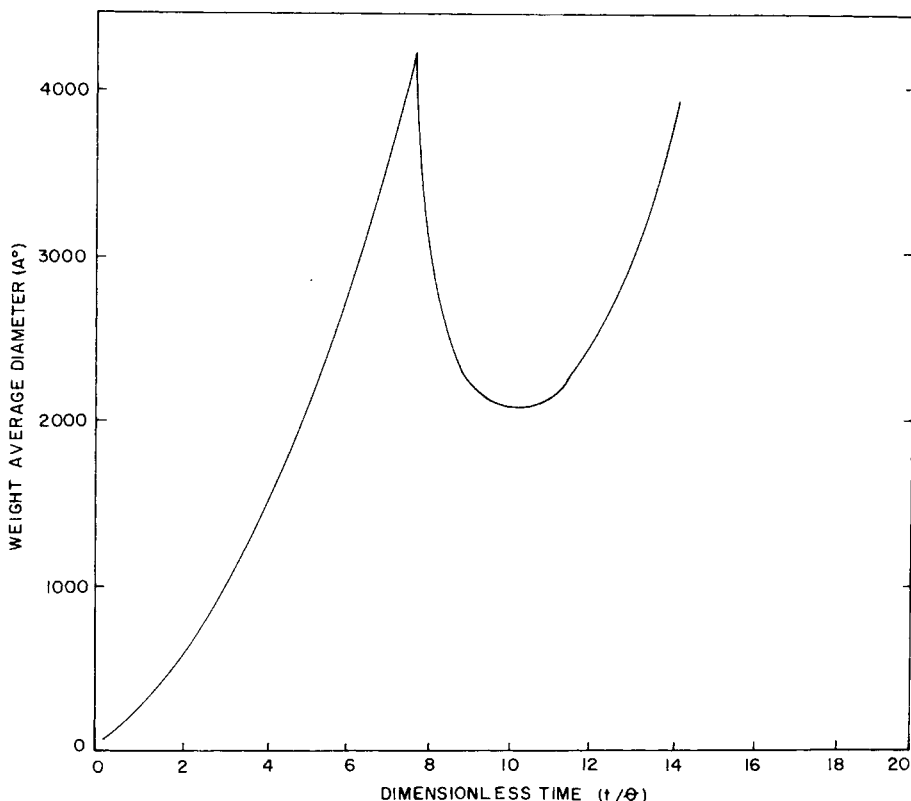
Fig. 9. Weight-average diameter with respect to dimensionless reaction time (t/θ) (comprehensive model, VA, θ = 30 min, T = 40°C, (S) = 0.01 mol/l, (I) = 0.01 mol/l, M/W = 0.43).

with the number of particles in the ith class of particles $(\tau_i, \tau_i + \Delta\tau_i)$ given by

$$n(t,\tau_i)\Delta\tau_i = f(\tau_i)\,\Delta\tau_i e^{-(t-\tau_i)/\theta} \qquad (33)$$

The particle volume $v_p(t,\tau_i)$ in eqs. (30) and (32) associated with the ith class of particles over a short time interval (t_{j-1}, t_j) is given by integrating eq. (18) over that interval to give

$$v_p(t_j,\tau_i) = \left[v_p^{2/3}(t_{j-1},\tau_i) + \frac{2}{3}\frac{K}{f(\tau_i)^{1/2}} \int_{t_{j-1}}^{t_j} e^{(t-\tau_i)/2\theta}(1 - e^{-t/\theta})\,dt \right]^{3/2} \quad (34)$$

To solve this system of eqs. (29)–(32) over the time period (t_{j-1}, t_j), all summation terms were originally evaluated at time t_{j-1}, and then the system of four differential equations was solved from t_{j-1} to t_j (iteration one). With the new values of variables obtained from iteration one, the summation terms were computed again and the solution of differential equations was repeated. Under this iterative scheme, convergence of the solution was achieved relatively fast (two or three iterations). The particle size distribution at any time t was found by plotting the frequency ratio $n(t,\tau)\,d\tau/N(t)$ for each class of particles against the particle size of that class given by eq. (34).
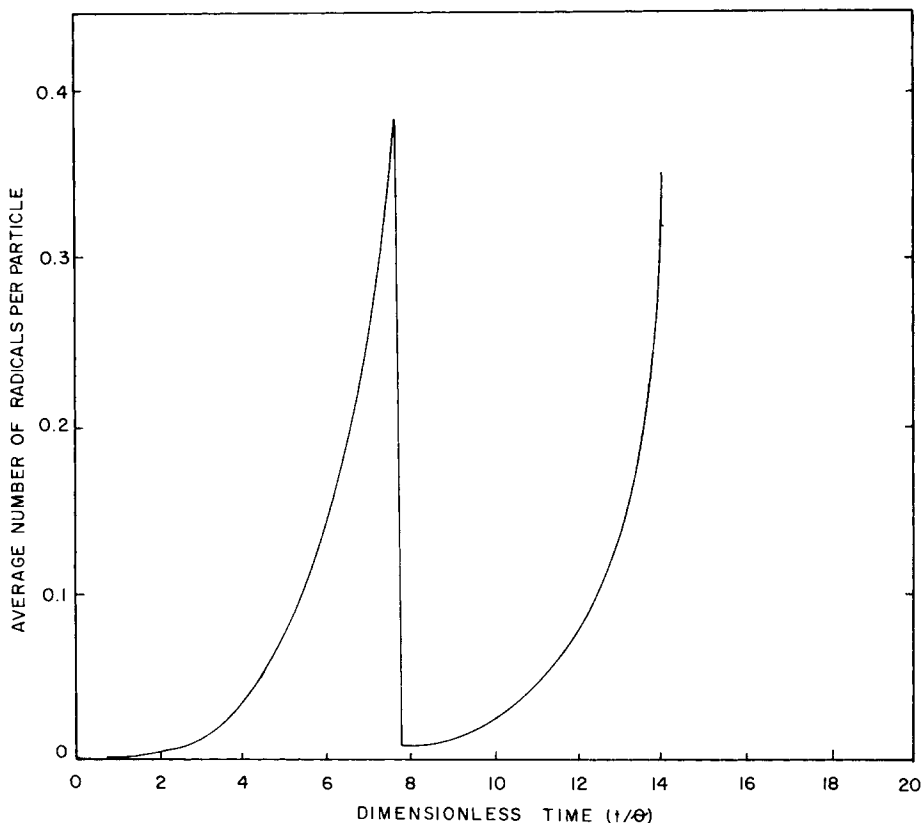
Fig. 10. Relationship between number of radicals per particle and dimensionless reaction time (t/θ) (comprehensive model, VA, $\theta = 30$ min, $T = 40°C$, $(S) = 0.01$ mol/l, $(I) = 0.01$ mol/l, $M/W = 0.43$).

Model Approximation

When particle generation occurs only during certain periods of time and these periods of particle generation are sufficiently short, as in the case for an emulsion system under sustained oscillation conditions, one can make the assumption that only one class of particles $n(t,\tau)\,d\tau$ is generated for each discrete period of particle nucleation. By lumping all the particles in each generation into a single class, the summation terms in eqs. (29)–(32) can be replaced by equivalent average values for that class. For example, the average volume of the ith particle generation may be approximated by the average value

$$v_p(t,\tau_i) = \bar{v}_{pi}(t) = V_{pi}(t)/N_i(t) \tag{35}$$

Therefore, the dynamic eqs. (29)–(32) can be approximated by a set of differential equations describing the development of each particle generation "i" in the reactor (where the summations have been replaced by the single average values for that generation)

$$\frac{dN_i(t)}{dt} = -\frac{N_i(t)}{\theta} + f(t) \tag{36}$$

$$\frac{dV_{pi}(t)}{dt} = -\frac{V_{pi}(t)}{\theta} + \frac{k_p d_m}{N a d_p}\,\Phi(t)\bar{q}_i(t)N_i(t) \tag{37}$$

$$\frac{dx_i(t)}{dt} = - \frac{x_i(t)}{\theta} + \frac{k_p d_m}{M_T M_w} \Phi(t) \bar{q}_i(t) N_i(t) \tag{38}$$

$$A_{pi}(t) = (36\pi)^{1/3} [\bar{v}_{pi}(t)]^{2/3} N_i(t) \tag{39}$$

where N_i, V_{pi}, x_i, A_i, and $\bar{q}_i$ denote respectively the total number of particles, total polymer volume, total conversion, total particle area, and average number of radicals per particle of the ith generation of particles. When two or more particle generations have been formed in the reactor, the total properties of the latex product at the exit of the reactor will be given by

$$x(t) = \sum_{i=1}^{q_t} x_i(t), V_p(t) = \sum_{i=1}^{q_t} V_{pi}(t), N(t) = \sum_{i=1}^{q_t} N_i(t), A_p(t) = \sum_{i=1}^{q_t} A_{pi}(t) \tag{40}$$

where q_t denotes the number of discrete particle generations which have appeared in the reactor until time t.

This simpler model was also numerically solved, and the results obtained were found to agree quite well with those of the more comprehensive model. Due to the simple form of this approximate model, numerical calculations are shorter. In addition, eqs. (36)–(39) can be recast to the usual state space form

$$\dot{\mathbf{x}}(t) = A\mathbf{x}(t) + B\mathbf{u}(t) \tag{41}$$

when dealing with the control problem.

DISCUSSION AND RESULTS

Greene et al.[2] have experimentally demonstrated that conversion shows a significant cyclic behavior in the continuous emulsion polymerization of vinyl acetate for certain emulsifier and initiator concentrations.

According to the present model, sustained oscillations are mainly caused by the particle formation mechanisms. Thus, in periods where either of the terms A_m or k_h are greater than zero, then by eq. (27) rapid generation of particles occurs leading to the formation of a large surface area. This new surface area is then covered with emulsifier at a rate which exceeds the feed rate of fresh emulsifier to the reactor. The reactor is thus depleted of free emulsifier and consequently of micelles. Furthermore, as the number of particles increases, the rate of radical capture into polymer particles increases, and at some time (k_h < 0) homogeneous nucleation ceases. This leads to a long period where particles are not generated. The duration of this period depends on the feed rate of emulsifier and the residence time of polymer particles. Because of a continuous washout of existing particles, emulsifier concentration starts to build up in the reactor and also the term $(A_p/4)L$ starts to decrease. When $(A_p/4)L$ becomes smaller than 1 in eq. (27), homogeneous nucleation of particles starts; and as soon as the free emulsifier concentration exceeds the CMC, formation of particles by micellar mechanism begins. Particles are then formed by both mechanisms until both terms A_m and k_h become again less than zero. This periodic nucleation leads to the formation of discrete particle populations with concomitant oscillations in polymerization rate and conversion.

Figure 2 shows conversion time data for a number of vinyl acetate runs[2] for a single CSTR. The dashed lines represent conversion values calculated using the present comprehensive model, eqs. (29)–(32). The same values of parameters ϵ and μ were used for all three simulated runs, and it can be seen that the model's predicted values are in very good agreement with the experimental results.

Figure 3 shows experimental and predicted sustained oscillations by the approximate model, eqs. (36)–(39). Although in this case the computed values are somewhat less accurate, it is clear that this approximate model has adequate predictive power to be useful for reactor control purposes.

Figure 4 shows how the total number of polymer particles changes with time. Periodic nucleation of particles occurs almost every seven residence times, and formation of particles takes place in time periods of about 0.2 to 0.4 residence times. In Figure 5 it is shown that under sustained oscillation conditions the reactor is substantially depleted of free emulsifier for long periods of time. Therefore, polymer particles are not adequately covered by emulsifier, which could result in particle flocculation and reactor fouling. From the plot of total particle area versus time in Figure 6, it can be easily seen that the total particle area follows a similar limit cycle.

The particle size distribution at different reaction times is given in Figure 7. The single narrow peak in the distribution in Figure 7(a) indicates that particle formation occurred during a brief interval early in the run and then stopped. By $t = 48$ min, Figure 7(b), this peak has been shifted to a larger particle size. In Figure 7(c), a new narrow peak at small particle size shows that a second generation of particles has been formed over a short time interval. Such cyclic particle formation has also been reported for continuous emulsion polymerization of styrene[1,3,13] and PVC[14] where the development of multipeaked polymer particle size distributions has also been observed.

The number-average diameter, $D_n = \Sigma D_i n_i / \Sigma n_i$, and weight-average diameter, $D_w = \Sigma D_i^4 n_i / \Sigma D_i^3 n_i$, of the PSD are plotted in Figures 8 and 9 with respect to reaction time. The polydispersity ratio D_w/D_n for the first particle generation is very close to 1. It increases considerably after the appearance of the second particle generation because a lot of small particles are formed, but it decreases again as the particle washout of the first generation continues and the particles of second generation start growing. Gerrens[13] reported similar experimental results for the polydispersity ratio for styrene under limit cycles conditions.

Finally, in Figure 10, the average number of radicals per polymer particle, $\bar{q}$, is plotted with respect to time. It is interesting to note that early at the beginning of the reaction, $\bar{q}$ takes very small values, which is explained by the fact that a large number of particles is generated (Fig. 4) by homogeneous nucleation with no contribution from micellar mechanism. This is confirmed in Figure 5, where it is shown that the system is under starved emulsifier conditions from very early reaction times. In this case, as the oligomers in the aqueous phase grow to some size, they precipitate out to form dead polymer particles by simultaneous transfer of radicals to monomer.

SUMMARY

We have tried to present here two levels of models: a comprehensive one, which uses the age distribution of particles, and an approximate model, which accounts for discrete nucleation periods. In both models it is considered that polymer particles are generated by both micellar and homogeneous mechanisms. Formulating the net particle generation rate, we introduce two parameters which can be estimated from experimental data. The ability of the general model to provide reactor simulations by specifying reactor operating conditions has been demonstrated through the simulation of the experimental results of Greene et

al. for the continuous emulsion polymerization of vinyl acetate. However, studying the problem of controlling a CSTR and finding an optimal start-up policy, the approximate model developed should be very useful.

Currently, experiments are being conducted in our laboratory on the emulsion polymerization of vinyl acetate in a CSTR, with an ultimate objective of controlling the production rate and latex quality.

Nomenclature

A	matrix of constant parameters in eq. (41)
A_m	total surface area of micelles, dm^2/l emulsion
$A_n(t,\tau) \, d\tau$	surface area of $n(t,\tau) \, d\tau$ class of polymer particles, dm^2/l emulsion
A_p	total surface area of polymer particles, dm^2/l emulsion
a_p	interfacial area of a particle, $dm^2/molecule$
B	matrix of constant parameters in eq. (41)
d_m	density of monomer, 930 g/l
d_p	density of polymer, 1150 g/l
D_p	particle diameter, dm
D_w	diffusion coefficient of monomeric radicals in the water phase, 10^{-7} dm^2/sec
DP_{max}	maximum degree of polymerization,[11] 53
f	efficiency of initiator decomposition
fk_d	effective rate coefficient of initiator decomposition, $2.5 \times 10^{-7} \, sec^{-1}$ $[(NH_3)_2S_2O_8 \text{ at } 40°C]$
$f(t)$	net rate of particle nucleation at time t, 1/sec-l emulsion
I	initiator
$[I]_w$	initiator concentration
$[I]_{feed}$	initiator concentration in the feed, molecules/l emulsion
K	parameter in eqs. (18 and 19), $dm^2/l^{1/2}$ emulsion-sec
k_{ab}	overall transport coefficient for radical transfer from the aqueous phase into polymer particles, dm/sec
k_d	rate coefficient of initiator decomposition, sec^{-1}
k_{de}	rate coefficient of radical escape from the polymer particles, sec^{-1}
k_{fm}	rate coefficient of chain transfer to monomer, 0.75 l/mol-sec
k_{ho}	rate coefficient of homogeneous nucleation, sec^{-1}
k_m	rate coefficient of micellar nucleation, dm/sec
k_p	rate coefficient of polymer propagation, 3003 l/mol-sec
k_v	volume of emulsion phase over the volume of aqueous phase, l emulsion/l
k_{tw}	rate coefficient of termination in aqueous phase (it is assumed equal to zero)
L	critical diffusion length, 1.04×10^{-4} dm (comprehensive model)
M	monomer
M_F	monomer concentration in the feed, mol/l emulsion
M_T	total monomer concentration in the reactant, mol/l emulsion
M_w	molecular weight of monomer, 86 g/mol
M_{wc}	saturation concentration of monomer in the water phase,[15] 0.33 mol/l

m partition coefficient of monomeric radicals between water and particle phase[15]

m_s micelle

Na Avogadro's number

$N(t)$ total number of particles at time t, 1/l emulsion

$n(t,\tau)$ number of particles at time t which were born in the time interval $[\tau, \tau$
$d\tau$ $+ d\tau]$, 1/l emulsion

$n(t,\tau_i)$ number of particles at t that were born at time τ_i

$P(t)$ total polymer property at time t

$p(t,\tau)$ a polymer property associated with a particle of the class $n(t,\tau)\,d\tau$

$\overline{q}(t,\tau)$ average number of radicals per particle of the class $n(t,\tau)\,d\tau$

$\overline{q}_i$ average number of radicals per particle of the ith generation

q_t denotes the number of discrete particle generations

R free radical

R_I radical initiation rate, molecules/l emulsion-sec

$[R]_{\text{feed}}$ free-radical concentration in the feed stream, molecules/l emulsion

$[R]_w$ free-radical concentration in the aqueous phase, molecules/l emulsion

r_t total number of all particle $n(t,\tau)\,d\tau$ classes

$r(t,\tau)$ radical initiation rate corresponding to $n(t,\tau)\,d\tau$ class of particles

s_α area covered by one mole of emulsifier, dm^2/mol

S_F total emulsifier concentration in inflow, dm^2/l emulsion

S_T total emulsifier concentration in outflow, dm^2/l emulsion

S_{CMC} critical micelle concentration (4×10^{-3} mol/l) converted to corresponding surface area, dm^2/l emulsion

t time, sec

$\mathbf{u}(t)$ a control vector

$\upsilon(t,\tau)$ volume of a particle associated with the class $n(t,\tau)\,d\tau$, l

$\upsilon_p(t,\tau)$ polymer volume of a particle associated with the class $n(t,\tau)\,d\tau$, l

$\upsilon_p(t,\tau_i)$ volume of particles at t that were born at time τ_i, l

$\overline{\upsilon}_{pi}$ average polymer volume for a particle of ith generation, l

x_c monomer conversion at which monomer droplets disappear, 20%

$x(t)$ total monomer conversion

$x_i(t)$ monomer conversion in the ith generation of particles

$\mathbf{x}(t)$ state vector

Greek Symbols

$\Delta\tau_i$ time interval, sec

δ $= (1 + D_w/D_p m)^{-1}$, where D_p is diffusion coefficient of monomeric radicals in the polymer particles[15]

ϵ $= k_{ab}/k_m$, 1.0×10^2 dimensionless (comprehensive model)

θ mean residence time, sec

μ $= k_{ho}/k_m$, 1.6 (comprehensive model)

$\mu(t,\tau)$ rate of particle volume growth associated with a particle of the class $n(t,\tau)\,d\tau$, l/molecule-sec

$\mu_p(t,\tau)$ rate of polymer volume growth associated with a particle of the class $n(t,\tau)\,d\tau$, l/molecule-sec

ρ rate of radical production in the aqueous phase, molecules/l emulsion-sec

ρ_n radical rate entry to the $n(t,\tau)\,d\tau$ class of particles, molecules/l emulsion-sec

$\Phi(t)$ monomer volume fraction in a particle
Φ_{sat} saturation swelling volume fraction in a particle

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