Particle Size Dispersion during Latex Growth

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Synopsis

The evolution of the latex particle diameter distribution during batch emulsion polymerization is investigated, with emphasis on changes in the breadth of the size distribution. A model utilizing a surface area-dependent volumetric growth rate of a single particle results in a time-invariant standard deviation of the size distribution during periods of particle growth only. This behavior is reconciled with some experimental observations by considering the occurrence of particle nucleation during some part of the growth interval. Conclusions based on the results of the model suggest that higher inhibitor and low emulsifier concentrations favor narrow particle size distributions.

INTRODUCTION

It is well known that the polymer particles produced by emulsion polymerization are not of uniform size. The appearance of a distribution in particle sizes is primarily due to the fact that nucleation occurs over a period of time during which existing particles grow.[1] The particle size distribution, therefore, is coupled interdependently to the behavior of the polymerization system. Consequently, the particle size distribution can provide information about the colloid growth, e.g., particle nucleation, the size dependence of growth, or agglomeration of particles. The average growth rate can be related to the mean of the size distribution. The standard deviation, a measure of the breadth of the distribution, is indicative of the dependence of growth on particle size.

If the volumetric growth rate of an individual particle were written in a power law form,

$$\frac{dv}{dt} = kr^b \tag{1}$$

the kinetic order b would be important in dictating the dynamics of the particle size distribution. When $b > 2$, for example, the larger particles grow at a higher relative rate than the smaller particles and the size distribution broadens with time. When $b = 2$, the particles grow at a uniform relative rate, yielding in a distribution having a time-invariant standard deviation. If $b < 2$, the particle size distribution would exhibit self-sharpening behavior, that is, the size distribution would become narrower with time. By experimentally measuring the particle size distribution as it evolves during the course of a batch emulsion polymerization, the dependence of particle growth on particle size can be determined (in the absence of subsequent nucleation). Vanderhoff and co-workers[2-4] have reported on the values of b obtained from competitive growth experiments for several polymers grown in emulsion.

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The standard deviation is affected not only by the size dependence of growth, but by size (or growth) dispersion as well. Size dispersion accounts for the observation that two particles of the same size may grow at different rates, in spite of a growth law which would dictate that the particles should grow at the same rate. Size dispersion, therefore, accounts for random fluctuations in the growth rate of particles. This phenomenon has been discussed in the recent literature for crystallization systems.[5-7] In some situations, dispersion can be ignored. However, in the preparation of monodisperse latices, the effect of size dispersion may be important.

The present study of emulsion polymerization kinetics is directed toward the dynamics of the particle size distribution in a batch reactor. The reaction conditions which affect the monodispersity of the latex are investigated. The model developed here, based on previous work,[8-10] predicts a self-sustaining profile, remaining unchanged in shape as it moves along the size axis after the nucleation stage has terminated. The breadth of the distribution, therefore, is solely a function of the nucleation process. The accordance of this prediction with experimental observations is discussed. The motivation for the work stems from the fact that the model has been used to study the behavior of continuous emulsion polymer reactors,[8-10] and yet the ramifications of the model in batch reactor synthesis are not well understood.

BACKGROUND

The mechanistic concepts put forth by Harkins[11] form the basis for the majority of emulsion polymerization models. Smith and Ewart[12] presented a mathematical description of Harkins' mechanism. All polymer particles were assumed to be of equal size and growing at a constant and uniform rate. The Smith–Ewart model took the form of a recursion relation, which they solved for three limiting cases. The most important of these solutions was the case of instantaneous mutual termination of a free radical in a growing particle upon the arrival of a second radical. The significant consequence of the underlying assumptions of this case was that the average number of radicals per particle was 0.5. The Smith–Ewart model found acceptance because it adequately described styrene polymerization data for small particles and low initiation rates. Stockmayer[13] and O'Toole[14] extended the Smith–Ewart work by providing analytical solutions to the recursion formula.

Significant deviations from Smith–Ewart theory were noted in experimental studies by Ewart and Carr,[1] especially at large particle sizes and high rates of initiation. They were the first to recognize the effect of latex polydispersity on emulsion polymerization kinetics. The roles of surfactant, initiator, and reaction temperature as they relate to the distribution in polymer particle size brought about by the occurrence of nucleation and concurrent growth were investigated. Their major conclusion was that the particle volumetric growth rate was proportional to the particle surface area, that is, $b = 2$ in eq.(1). Unfortunately, by carrying out their experimental reactions to complete conversion, the changing nature of size-dependent growth during different intervals may have been masked.

Other exceptions to Smith–Ewart theory were found by Vanderhoff and co-workers.[2-4] Using a competitive growth technique whereby two monodisperse

seed latices were polymerized in the absence of nucleation, they demonstrated the dependence of particle growth rate on the 2.0–2.5 power of the particle diameter (i.e., $2.0 < b < 2.5$). Smith and Ewart had predicted a zeroth order dependence (i.e., $b = 0$). The discrepancy is indicative of the shortcomings of Smith–Ewart theory at larger particle sizes.

Brodnyan et al.[15] showed that the particle size distribution changed from normal to log-normal during the course of batch polymerization of methyl methacrylate. Their interpretation of this phenomenon was that the particle growth mechanism changes from one of surface area dependence (limited by diffusion of radicals) to one of volume dependence (proportional to the free radical concentration in the polymer particles). The predominant mechanism was determined by the surface to volume ratio of the particles.

O'Toole[16] related the stochastic nature of the number of radicals in a polymer particle to latex polydispersity for various kinetic models. O'Toole postulated that a competition between the propagation and termination steps leads to breadth in the particle size distribution. At high relative rates of termination, particles grow at a nearly uniform rate. At low termination rates, the active particles grow for substantially longer periods before termination occurs. The disparity in polymer particle growth rates results in a broader distribution at low termination rates.

A model in which the assumption of a volume average growth rate, implicit in Smith–Ewart theory, was removed was given by Lichti et al.[17] The particle size distribution was accounted for directly. The model was in the form of coupled partial differential equations that were solved numerically using transformation techniques. The polymer particles were divided into classes based on the number of radicals in each. The model was theoretically capable of describing the growth rate of each species of particle, but the necessary growth rate information was not available. Consequently, the only practical approach was to class particles as either active or inactive, which introduced some averaging of growth rates. Simulations of this simple case demonstrated polydispersity in the particle size distribution due to the ordered variations in the growth rate. This result was not unexpected in light of O'Toole's study of stochastic contributions to the particle size distribution breadth.

The factors that lead to monodispersity of the particle size distribution were discussed by Fitch.[18] The conditions necessary were reported to be (a) the nucleation period must be short relative to the time for polymer growth, and (b) the volumetric growth rate must be proportional to some power of the particle diameter less than 3. If these two requirements are met, then the size distribution should narrow as polymerization proceeds. Fitch gave a brief description of the role of experimental parameters in achieving monodisperse polymer colloids.

The role of size dispersion in particle size distribution dynamics has not been studied in the context of polymer colloid growth. However, size dispersion has been investigated in crystallization systems. White and Wright[5] noticed that sucrose crystals of relatively uniform size grew to have a polydisperse distribution. The effect was believed to be the result of random fluctuations in the crystal growth rate. For the purpose of modeling batch and continuous crystallizers, Randolph and White[6] modified the population balance to include size dispersion in a fashion similar to Fickian diffusion superimposed on convective flow in a

tube. The batch crystallizer case demonstrated the effect of growth diffusivity to be a broadening of the size distribution. The effect of growth diffusivity was undiscernable in continuous crystallizers. Janse and DeLong[7] treated growth dispersion effects by considering a distribution of growth rates about a mean size-dependent growth rate. This treatment was shown to be equivalent to assuming a size-dependent growth rate, and the two effects could not be distinguished.

Very few experimental studies have addressed the relationships among the reaction conditions, the latex properties, and the particle size distribution. Gerrens[19] presented the most comprehensive account of the effect of temperature, emulsifier, initiator, and monomer levels on the particle size distribution. Increases in temperature and catalyst concentration resulted in narrower particle size distributions. Increases in the soap charge and the monomer-to-water ratio had the opposite effect. Gerrens did not consider the time evolution of the particle size distribution. The review by Gardon[20–23] contained experimental evidence which he concluded was supportive of Smith–Ewart theory. Gardon determined the influence of the ingredients on the size distribution for poly-(methyl methacrylate). His results are qualitatively consistent with Gerren's work with polystyrene. Measurements of the size distribution during the course of a batch polymerization were made. The distribution was found to increase in breadth slightly during Interval II. Berens[24] also presented data showing the evolution of the particle size distribution. He described the size distribution as shifting steadily to larger size with little broadening.

THEORETICAL DEVELOPMENT

The modeling of emulsion polymerization can be divided into two tasks: (a) determining the number of particles present, and (b) accounting for the growth of each individual particle. The present model considers the particle population to be distributed in particle age, specifically, the nucleation time, or "birthdate," This treatment, first suggested by Dickinson,[8] has the advantage of accounting for both age and size dependence. Kiparissides et al.[9] used the age distribution approach to study oscillations in continuous vinyl acetate polymerization. The model incorporates the free radical kinetic mechanisms of radical absorption, desorption, chain transfer, termination, propagation, and micellar and homogeneous nucleation. Chiang and Thompson[10] extended the model by converting Kiparissides' model equations from integro-differential to purely differential form. The present model is derived from the system of equations presented by Chiang and Thompson, rewritten for the case of a batch emulsion polymerization. Detailed derivations can be found elsewhere[10,25] and will not be repeated here. The model is given by the set of nonlinear ordinary differential equations found in Table I. The assumptions made in deriving the equations are as follows:

(1) The polymerization vessel is a uniformly mixed, isothermal, contant-volume batch reactor.

(2) Flocculation and particle breakage are negligible.

(3) Monomer diffuses to particles independently of their size and age and does not limit the process.

(4) Aqueous phase termination of the free radicals can be neglected.

TABLE I
Equations Describing the Behavior of a Batch Emulsion Polymerization

$$\frac{dN(t)}{dt} = f(t) \tag{2}$$

$$\frac{dD(t)}{dt} = 2\lambda\zeta(t)\,N(t) + d_0\,f(t) \tag{3}$$

$$\frac{dA(t)}{dt} = 4\pi\lambda\zeta(t)\,D(t) + a_0\,f(t) \tag{4}$$

$$\frac{dV(t)}{dt} = \lambda\zeta(t)\,A(t) + v_0\,f(t) \tag{5}$$

$$\rho(t) = 2f_i k_d N_a I_0\, e^{-k_d t} + \frac{f_i k_d I_0 k_p \rho_m \phi}{\rho_p(1-\phi)\lambda}\,\zeta(t)\,N(t) \tag{6}$$

$$A_m(t) = [S_0 - S_{cmc}]S_\alpha - A(t) \tag{7}$$

$$f(t) = \rho(t)\left\{\frac{k_v A_m(t) + \mu\left[1 - \dfrac{A(t)}{4}L\right]}{k_v A_m(t) + k_v A(t) + \mu\left[1 - \dfrac{A(t)}{4}L\right]}\right\} \tag{8}$$

$$k_v(t) = \frac{V(t)}{1 - V(t)} \tag{9}$$

$$\zeta(t) = \left[\frac{e^{-k_d t}}{A(t)}\right]^{1/2} \tag{10}$$

$$\lambda = \frac{\phi k_p \rho_m}{(1-\phi)N_a \rho_p}\left[\frac{k_p f_i k_d N_a I_0 M_0}{12\pi D_w \delta k_{fm}}\right]^{1/2} \tag{11}$$

Note that the restriction of constant monomer concentration in the particles limits consideration to Intervals I and II of the polymerization.

The system of equations in Table I can be solved with a suitable set of initial conditions. These are, for the case of a seeded batch polymerization, as follows:

$$N(0) = N_0$$
$$D(0) = D_0$$
$$A(0) = A_0 \tag{12}$$
$$V(0) = V_0$$

These constants can be evaluated from measurements on the seed latex. For unseeded polymerizations, it can be shown that the constants are equal to zero.

The model equations were solved numerically. The computations were carried out using a predictor-corrector technique programmed on a DEC-PDP10 digital computer. Core requirements and cpu times for a single simulation were modest.

DISCUSSION

Comparison with Literature Results

The model was compared to experimental results to demonstrate its capabilities. Results of the model were applied to data by Gardon[21,23] for the batchwise emulsion polymerization of methyl methacrylate, using sodium lauryl sulfate emulsifier, potassium persulfate initiator, and aqueous solvent. The reader is referred to the article by Gardon[23] for a detailed description of the exerimental procedures. Values of the parameters used are given in Table II. The values of the constants were obtained from Gardon's work.[23] Only the values of L, μ, and ϵ were uncertain and were estimated from the work by Kiparissides et al.[9]

A simulation of the conversion profile is given in Figure 1. Some deviation from experimental measurement is noted at higher conversion, in the range where monomer droplets disappear. At high conversions, the polymer particles no longer maintain the saturation concentration of monomer, and the conversion rate decreases. Since the model assumes a constant monomer concentration, the conversion in the later stages of the polymerization is overestimated.

Figure 2 compares the predicted average particle radius with experimental measurements. Initially, the rate of increase in particle radius is relatively steep, because nearly all particles contain one growing chain. Arrival of a second terminating radical is not likely to occur early in the nucleation stage. As nucleation ends and particles only grow, at about 10% conversion in this case, the slope of the average particle radius–conversion profile decreases. At this point, the termination and desorption mechanisms become important, and the rate of particle growth decreases. It should be noted that the behavior of the average particle size with time is due to the size dependence of the volumetric growth law.

Figure 2 also shows the prediction of the standard deviation of the particle radius distribution. The standard deviation increases sharply initially due to the temporal distribution of the nucleation events. Once nucleation has ended

TABLE II
Values for Constants for Gardon's Data[21,23] (Used in Simulations Shown in Figures 1 and 2)

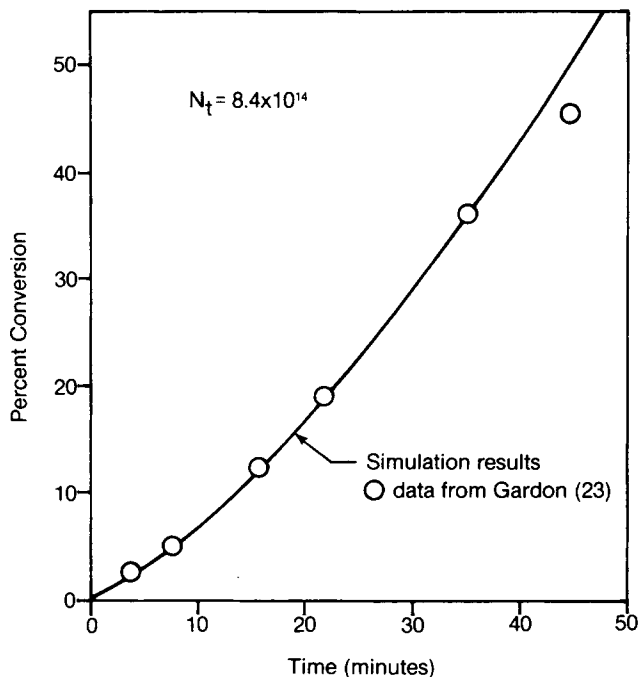| Constant	Units
$d_0 = 1.6 \times 10^{-6}$	cm
$I_0 = 6.032 \times 10^{-6}$	mol/cm^3
$k_d = 1.358 \times 10^{-4}$	min^{-1}
$k_{fm} = 1.874 \times 10^{-2}$	cm^3/mol min
$k_p = 1.874 \times 10^{7}$	cm^3/mol min
$L = 1.796 \times 10^{-2}$	cm
$S_{cmc} = 2.0 \times 10^{-6}$	mol/cm^3
$S_0 = 8.362 \times 10^{-6}$	mol/cm^3
$S_\alpha = 3.67 \times 10^{9}$	cm^2/mol
$\rho_m = 0.939$	g/cm^3
$\rho_p = 1.19$	g/cm^3
$\mu = 1.0$	cm^{-1}
$f_i = 1.0$	
$M_0 = 45.70$	
$\epsilon = 150.$	
$\phi = 0.73$	

Fig. 1. Simulation of the conversion–time profile for batch emulsion polymerization of methyl methacrylate.

entirely, the distribution profile progresses along the size axis while maintaining its shape. This result differs from experimental results reported by Gardon[23] and Berens,[24] who indicate a slight broadening of the diameter distribution as polymerization proceeds through the growth stage. This apparent inconsistency is worth further discussion.

One might first ask if the slight broadening of the diameter distribution during Interval II is a real effect. Central to the conclusion that the distribution spreads during Interval II is the questionable assumption that the number of particles remains constant during this period, i.e., nucleation ends after a few percent conversion. Alexander and Napper[26] argue against the premise of a constant number of particles. Figure 3 shows polystyrene data by van der Hoff[27] typical of that used to show the time variation of the total number of particles. Smith–Ewart theory suggests that the experimental measurements can be described by a linear increase in N up to about 20% conversion, after which N remains constant. The simulation, using the present model, shows the nucleation occurs up to about 35% conversion. Based on a comparison with the data, either account is viable. The point to be made is that slight increases in the standard deviation through Interval II may be explained by the occurrence of nucleation during this time.

From a physical viewpoint, it is reasonable to suspect that some nucleation takes place during the "growth period," that is, Interval II. Homogeneous nucleation may occur if insufficient particle area is present to capture growing aqueous phase oligomers before they reach the critical size for nucleation. Micellar nucleation may occur once the emulsifier which initially stabilized
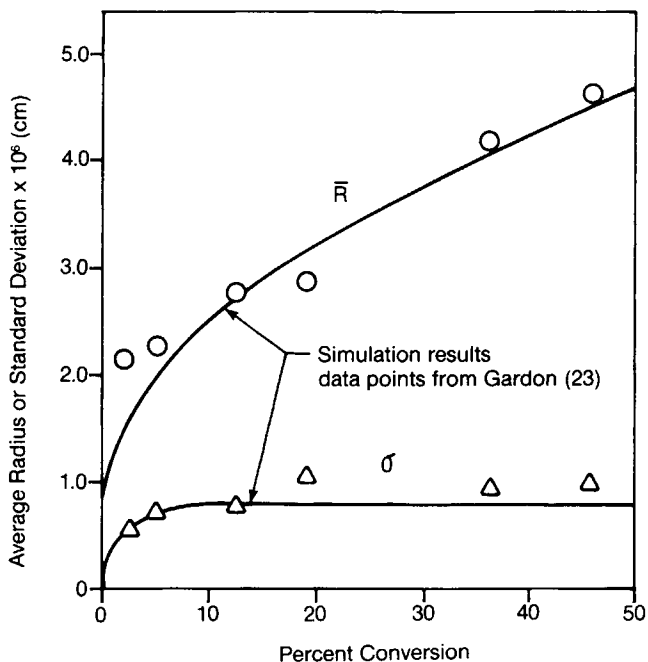
Fig. 2. Simulation of average particle radius and standard deviation histories for batch emulsion polymerization of methyl methacrylate.

monomer droplets "enters" the water phase. The conclusion that the number of particles is constant during Interval II is debatable.

It is also instructive to point out that the notion of a batch emulsion polymerization consisting of three intervals embodies the ideal separation of nucleation, growth, and growth without monomer droplets. Interval I is typically assumed to be a nucleation period during which new particles are formed and existing particles grow at constant rates. These assumptions led to the early predictions for the total number of particles formed.[12] We are suggesting here that these assumptions are not valid, specifically that the nucleation rate slows down gradually troughout Interval I, even the extent of overlapping with Interval II.
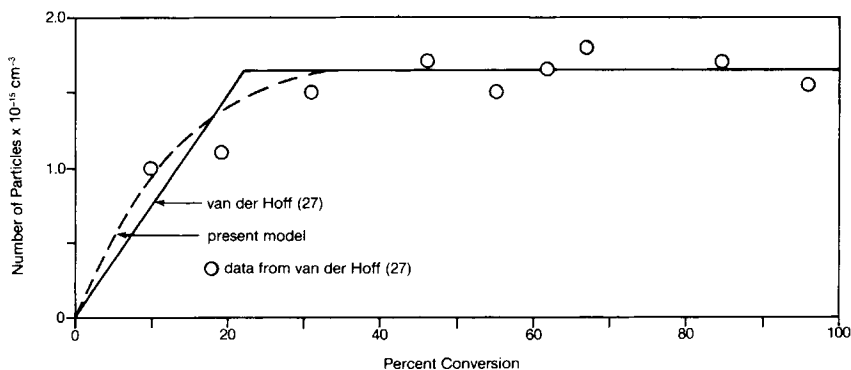

Fig. 3. Variation of the number of particles with conversion for batch emulsion polymerization of styrene. Adapted from Alexander and Napper.[26]

No reliable means of directly measuring the number concentration of particles exists as yet. Only careful experimentation will eliminate the uncertainty to whether or not the particle size distribution broadens during Interval II. While we are not questioning the validity of the experimental results cited, we are suggesting that the transition from Interval I to Interval II is not abrupt. In fact, in some cases an apparent zero order growth stage (Interval II) may not exist at all. If the effect of size broadening during particle growth is real, then the explanation of the present model's inability to track the change in the distribution breadth is in order.

The prediction of a constant standard deviation is a consequence of the area dependent volumetric growth rate used. Specifically, the volumetric growth rate for a polymer particle at time t having birthdate τ is given by

$$\frac{\partial v(t,\tau)}{\partial t} = \frac{k_p \rho_m \phi}{N_a \rho_p (1 - \phi)} \overline{q}(t,\tau) \tag{13}$$

and the value of $\overline{q}(t,\tau)$ has been shown[9,10,25] to be equal to

$$\overline{q}(t,\tau) = \left[\frac{f_i k_d I_0\, e^{-k_d t} k_p M_0}{12 \pi D_w \delta k_{fm} A(t)} \right]^{1/2} a_p(t,\tau) \tag{14}$$

This area dependence indicates that diffusion of radicals to particles is the limiting factor of the polymerization process. The area dependence seems appropriate in systems of small particle size and low radical concentration because rapid interparticle termination limits the number of radicals that particles can accommodate. The arrival of radicals controls the state of the particle, that is, whether it is growing or inactive. Growth in systems with large particles may be described better by a volumetric growth rate which is proportional to particle volume, because larger particles can accommodate several growing chains simultaneously. A volume-dependent volumetric growth rate exhibits spreading in the size distribution through periods of only growth, that is, $b = 3$ in eq. (1). While this choice may be more appropriate for larger particle sizes, the current investigation is focused on low conversion levels where monomer is present for which the surface area growth rate dependence should be valid.

Parameter Study

It is of interest to investigate the operating conditions which affect the monodispersity of the latex. It is especially instructive to examine the predictions of this model related to batchwise emulsion polymerization, because this has not been done before and the model has recently been used to evaluate continuous emulsion polymerization reactor behavior. The controllable system parameters are the emulsifierlevel, the initiator concentration, the monomer to-water ratio, and the reaction temperature. Other variables are dictated by the physical properties of the system and cannot be adjusted.

The appearance of certain groups of parameters in the equations suggests combining each group into fewer lumped constants. Investigating the effects of lumped parameters minimizes the total effort required because the effect of several parameters can be found from a single group. For the sake of convenience, the following parameters are defined:

$$\alpha = f_i k_d I_0 N_a \tag{15}$$

$$\beta = \frac{\phi \rho_m}{(1 - \phi) \rho_p} \tag{16}$$

TABLE III
Values for Constants for van der Hoff's Data[27] (Used in Simulation shown in Figure 3)

Constant	Units
$d_0 = 5 \times 10^{-7}$	cm
$I_0 = 9.87 \times 10^{-6}$	g-mol/cm^3
$k_d = 6.0 \times 10^{-4}$	min^{-1}
$k_{fm} = 59.8$	cm^3/g-mol min
$k_p = 4.98 \times 10^6$	cm^3/g-mol min
$L = 4 \times 10^{-4}$	cm
$S_{cmc} = 6.00 \times 10^{-5}$	g-mol/cm^3
$S_0 = 3.61 \times 10^{-5}$	g-mol/cm^3
$S_\alpha = 3.30 \times 10^9$	cm^2/g-mol
$\rho_m = 0.905$	g/cm^3
$\rho_p = 1.06$	g/cm^3
$\mu = 10.$	cm^{-1}
$f_i = 1.00$	
$M_0 = 4.80 \times 10^{-6}$	g-mol/cm^3
$\epsilon = 500.$	
$\phi = 0.60$	

$$\gamma = \left[\frac{M_0}{12\pi D_w \delta k_{fm}} \right]^{1/2} \tag{17}$$

$$S = [S_0 - S_{cmc}]S_\alpha \tag{18}$$

Some physical significance can be attached to these groups. Specifically, α is related to the dissociation of initiator, β represents the mass ratio of monomer to polymer within a particle, γ accounts for the initial monomer-to-water ratio in the batch reactor, and S is the surface area of soap at the aqueous-organic interface. Values of the parameters used are shown in Table IV.

Figure 4 shows solutions of the model for the conversion, average particle size, and standard deviation histories for several values of α. The model predicts a greater number of polymer particles of smaller average radius at a given conversion level for higher values of α. This behavior has been noted in previous simulation studies.[18,28] The polymerization rate is shown here to increase with α, qualitatively consistent with experimental observations.[15,29] The standard deviation rises at an increased rate with larger values of α but reaches a slightly lower final value. The scale chosen suggests that the final values are essentially equal, however, larger variations in α would accentuate the differences. The behavior of the standard deviation is in agreement with the results of other au-

TABLE IV
Values of Parameters Used in Simulations (Used in Figures 4–7, Except Where Noted Otherwise)

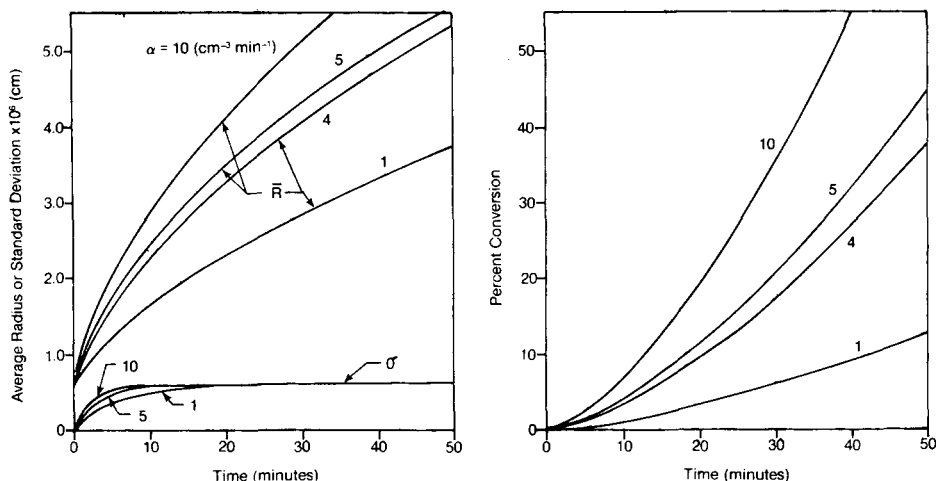| Parameter	Units
$\alpha = 5.0 \times 10^{13}$	cm^{-3} min^{-1}
$\beta = 2.0$	
$\gamma = 10.0$	min mol$^{1/2}$ cm$^{5/2}$
$d_0 = 1.0 \times 10^{-6}$	cm
$\epsilon = 100.0$	
$k_p = 2.0 \times 10^7$	cm^3/mol min
$L = 2.0 \times 10^{-2}$	cm
$S = 3.0 \times 10^4$	cm^{-1}

Fig. 4. Effect of the parameter α on model predictions.

thors whose predictions indicate that σ should decrease as initiator levels increase.[18,28]

Systems of higher initiator concentration yield narrower size distributions for several reasons. First, the nucleation period is shortened, so the sizes of the particles at the end of the nucleation period are more uniform in size. Secondly, the time interval between arrival of radicals is shortened at higher free radical concentrations. Growth then occurs at a more uniform rate, and size dispersion due to the on–off behavior of growth is minimized. This effect is important in systems of low initiator concentrations.

Physically, an increase in α corresponds to an increase in the free radical production rate and free radical concentration in solution. The number of particles formed would be expected to increase with α, since the likelihood would be greater that a micelle would absorb a radical and form a new particle before the micelle would be adsorbed as a stabilizer on the surface of an existing particle. The overall polymerization rate also would be increased by the presence of additional reaction loci. The average particle size is smaller for smaller values of α (low initiator values) because of the increased duration of the nucleation period. The longer that small particles are added to a collection of growing particles, the slower will be the rate of increase in the average size of those particles. The presence of the younger, smaller particles reduces the average particle size.

Figure 5 shows the variation of N_t with initiator level for two values of k_p. The value of k_p can be thought of as the rate of growth of a single particle away from the size of a nucleus. At low values of k_p and at the extremes of initiator concentration, the number of particles formed is independent of I_0. For high values of k_p, N_t exhibits a 0.40 power dependence on I_0 at intermediate initiator levels. These results can be understood by considering the competition for free radicals between polymer particles and micelles during the nucleation interval.

At high initiator levels, the nucleation process is limited by the supply of micelles. The system is so flooded with free radicals that most of the micelles are stung with one radical to initiator polymer growth. Arrival of subsequent radicals into the small particles results in the Smith–Ewart limit of Q of 0.5. In this range of initiator concentrations, the total number of particles formed is inde-
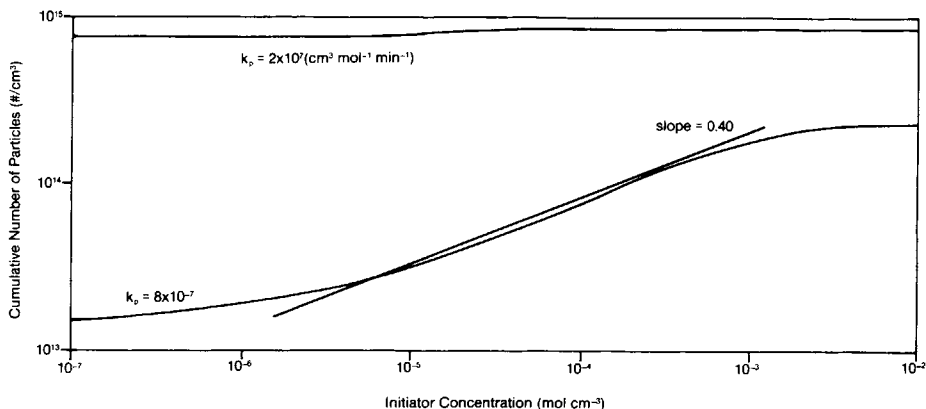
Fig. 5. Variation of the number of particles with initial initiator level.

pendent of I_0 and the radicals resulting from free radical desorption make a negligible contribution.

At very low initiator concentrations, the total number of particles formed is independent of I_0 because the process is limited by the rate of formation (and, therefore, absorption) of free radicals. Once a certain number of particles has been formed (governed by S_0) and these particles have grown away from the nucleus size, the available soap will have been consumed by the growing particles. Thus, the rate of particle growth relative to the rate of particle nucleation is critical in establishing the total particle concentration, and not simply I_0.

The difference in the two profiles having different values of k_p results from the growth rates of the polymer particles. The faster the particles grow (i.e., the larger k_p), the faster polymer particle surface area is generated, which requires soap for stabilization. As $A(t)$ increases, the value of $A_m(t)$ decreases [see eq. (7)] and $f(t)$ decreases because of the increase of the denominator in eq. (8). Therefore, higher growth rates of particles result in the formation of fewer total particles, because of the competition for the fixed amount of soap present.

The dependence of the cumulative number of particles on initiator level for methyl methacrylate has been shown to be 0.4 order by Gardon[21] and zero order by Brodnyan et al.[15] The present model appears to be capable of describing both sets of data for an appropriate set of parameters.

Figures 6 and 7 illustrate the effect of the emulsifier concentration on the emulsion polymerization. An increase in S causes an increase in the total number of particles formed, the conversion rate, and the breadth of the distribution. Large values of S result in small average particle sizes due to the longer particle nucleation period. Note, for example, that at a very high level of emulsifier, nucleation occurs over a lengthy time span, e.g., up to 40% conversion for $S = 3 \times 10^5$. Practically speaking, this situation might be undesirable because a very broad particle size distribution would result.

The observed behavior can be explained by considering the role of the soap in forming particles. Micellar nucleation continues as long as there are micelles present to act as nuclei. A greater supply of micelles results in the formation of a greater number of particles. In a system flooded with soap, polymer particles are formed over a longer period of time, because the process is limited by free radical production and absorption. Thus, the observed higher conversion rate
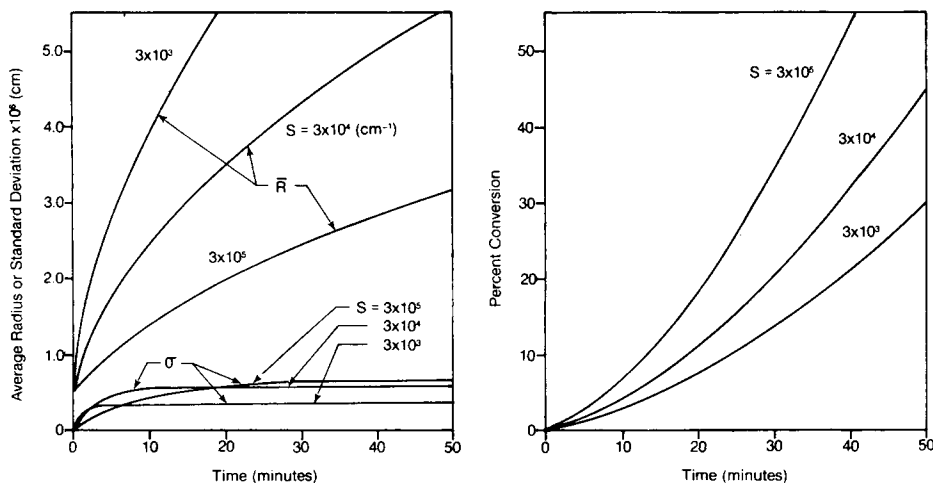
Fig. 6. Effect of initial soap level on model predictions.

at high values of S shown in Figure 6 is due to the greater number of reaction loci. The broader size distribution at high values of S is caused by the longer nucleation period. The smaller average particle size as S increases is a result of particles being formed over a longer nucleation period. The contribution of the small particles, formed near the end of the nucleation period, is significant when computing these average particle sizes (number averages).

The dependence of the total number of particles on the initial emulsifier concentration is shown in Figure 7. At levels below the critical micelle concentration, the number of particles does not depend on the emulsifier concentration because homogeneous nucleation is the dominant mechanism of particle formation. At greater soap charges, the number of particles becomes proportional to the soap cocentration. This region should not be of great concern, as the high soap concentration is outside the range of practical interest. Smith–Ewart theory predicts a dependence of particle number on the emulsifier level to the 0.6 power. This conclusion is based on the assumption that at the end of nucleation, the
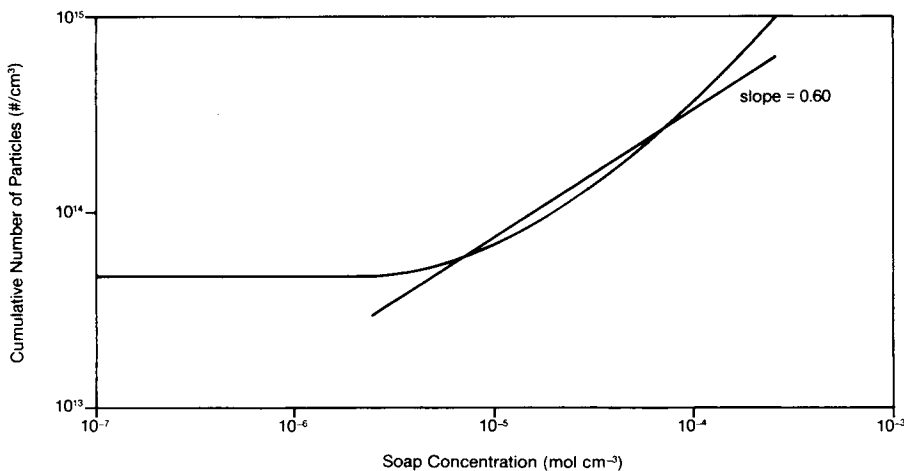

Fig. 7. Variation of the number of particles with initial soap level.

surface area of the particles is equal to the surface area coverage of the emulsifier charge, neglecting soap lost to stabilize monomer droplets and the critical micelle concentration. The volumetric growth rate and radical entry rate to micelles were assumed constant in the Smith–Ewart development. By dividing the soap coverage area by the total particle area, the number of particles can be calculated. Experimental measurements for poly(methyl methacrylate) over the range 10^{-5}–10^{-4} mol/cm^3 support the Smith–Ewart theory.[21] This data is in the transition region of the present model, where a line of slope 0.6–0.7 could approximate the model solution. Thus, the model agrees with some experimental observations.

The initial monomer-to-water ratio, M_0, is involved in the parameter γ and is easily varied in the batch reactor recipe. The effect of variations in γ (or the monomer-to-water ratio) is shown in Figure 8. Note that the length of the nucleation period is not affected by variations in the value of γ; however, the particle polydispersity increases as γ increases. The conversion rate is seen to increase as the relative amount of monomer increases, principally a result of the larger average particle size which evolves as γ increases. Once again the polydispersity (i.e., σ) is seen to remain constant after nucleation has ceased. These results are consistent with those cited earlier from Gerrens work.[19]

Higher reaction temperatures increase both the polymerization and catalyst decomposition rates. During the nucleation period, the increased initiator dissociation rate due to increased temperature is favorable to latex monodispersity. The concurrent increase in polymerization rate is not, because it leads to greater disparity in the particle sizes. At a greater rate of polymerization, existing particles grow more rapidly away from nucleus size. A balance between the two effects must be found. In periods of growth only, higher temperatures increase the reaction rate without adversely affecting dispersity of particle size. This result suggests that a reactor with a schedule of lower temperature in the nucleation stage followed by a higher temperature during the growth stage might most effectively produce a monodisperse latex.

The extrapolation of information from unseeded systems provides insight into the monodispersity of seeded polymerzations. This can be done by viewing a

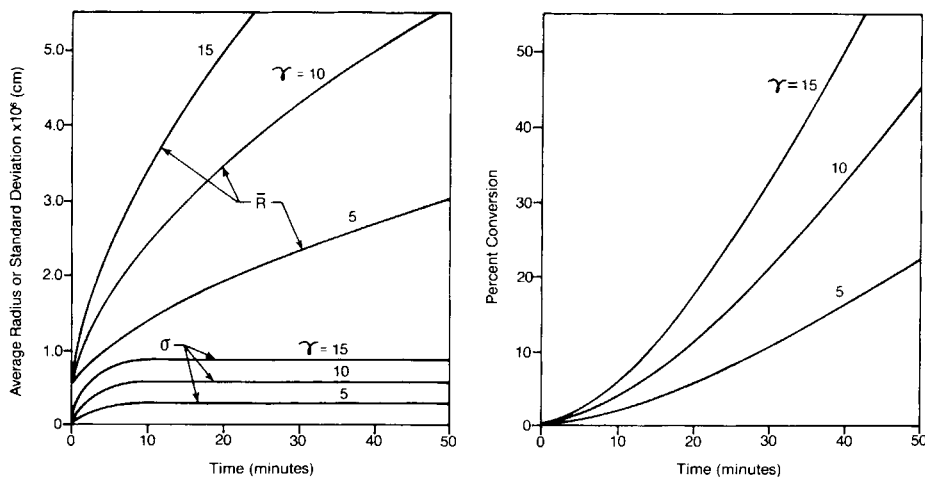
Fig. 8. Dependence of model predictions on the parameter γ.

seeded polymerization as equivalent to an unseeded polymerization under conditions of only growth (during Interval II). Nucleation must be prevented if the goal is to maintain a narrow particle size distribution. In this regard, the proper amount of emulsifier is important. Adequate soap must be added to insure the stability of the latex because agglomeration is likely to occur, which can increase the breadth of the distribution. The total surface area of the seed latex should be sufficiently large to capture essentially all oligomeric radicals which form in the aqueous phase before they precipitate to nucleate new particles. The number and size of seed particles determine whether or not homogeneous nucleation is suppressed.

Other factors such as initiator concentration, initial monomer-to-water ratio, and reaction temperature do not affect the dispersity of the particle size distribution for seeded polymerization, according to model predictions during periods of only particle growth. These parameters may be chosen to maximize the growth rate of particles without adversely affecting the breadth of the size distribution.

CONCLUSIONS

Simulations with the model presented herein demonstrated that the dispersity of the particle diameter distribution was solely a function of events occurring in the nucleation stage of the emulsion polymerization. The rate of particle growth away from the nucleus size relative to the rate of particle formation dictates the breadth of the size distribution. Once nucleation ends, the distribution was shown to progress along the size axis with no further spreading.

The controllable factors which lead to a monodisperse latex were investigated. High initiator concentrations were shown to lead to narrow size distributions, because the rate of nucleation increased with catalyst level. Low emulsifier concentrations were favorable to monodisperse distributions, because they shortened the time period for nucleation. The initial monomer-to-water ratio was shown to increase the breadth of the size distribution based on the predictions of this model, but the duration of the nucleation period was not affected. The reaction temperature was found to increase both the polymerization and nucleation rates. Consequently, the temperature effect of the particle size distribution will be dependent on the nature of the two rate constants involved in each particular case.

Predictions from the model were shown to be in agreement with experimental observations of conversion history, average particle diameter profile, and particle number dependence on emulsifier and initiator concentration. Discrepancy in the aspect of the standard deviation of particle diameters was noted, in that experimental measurements have shown a slight increase in standard deviation during the growth period where the model predicted none. It was suggested that the apparent inconsistency was a result of nucleation occurring during the growth interval.

Nomenclature

$A_m(t)$ total micelle surface area
$A(t)$ total particle surface area

a_0	surface area of nucleus
$a_p(t,\tau)$	surface area of particle at time t having birth date τ
b	kinetic order for volumetric growth
$D(t)$	total particle diameter
D_w	diffusion coefficient for radicals in water
d_0	diameter of nucleus
$f(t)$	particle nucleation rate
f_i	initiator decomposition efficiency
I_0	initial charge of initiator
k	rate constant for volumetric growth
k_d	initiator dissociation rate constant
k_{fm}	chain transfer rate constant
k_p	polymerization rate constant
$k_v(t)$	volume ratio of polymer phase to aqueous phase
L	critical diffusion length
M_0	initial monomer/water concentration ratio
$N(t)$	total number of particles
N_a	Avogadro's number
N_t	total number of particles per cm^3 of reactor volume
Q	average number of radicals per particle
$\overline{R}$	average particle radius
r	particle radius
S	soap coverage area per cm^3 of reactor volume
S_{cmc}	critical micelle concentration
S_0	initial soap concentration
S_α	soap coverage per mole of soap
t	time
$V(t)$	total particle volume
v	particle volume
v_0	volume of nucleus

Greek

α	initiator dissociation parameter
β	monomer volume fraction parameter
γ	lumped desorption parameter
δ	lumped radical diffusion coefficient
ϵ	ratio of absorption to micellar nucleation rate constants
ϕ	saturation volume fraction of monomer in poymer
λ	constant given in Table I
μ	ratio of homogeneus to micellar nucleation rate constants
$\rho(t)$	free radical production rate
ρ_m	monomer density
ρ_p	polymer density
σ	standard deviation
$\zeta(t)$	function given in Table I

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