Analytical Solutions of Emulsion Polymerization Models

James B. Rawlings
Department of Chemical Engineering
University of Texas
Austin, TX 78712

The objective of this paper is to develop a class of simplified emulsion polymerization models that retain essential features such as the distribution of particle sizes and radical numbers, but are still amenable to analytical solution. We take the detailed model of Rawlings and Ray (1988a) as the starting point. This model has been extensively compared to CSTR experimental data (Rawlings and Ray, 1988a,b) and is capable of simulating all of the reactor's interesting dynamic behavior including sustained oscillations and multiple steady states. Rawlings (1985) and Prindle (1989) have provided software for the numerical solution of this and other more complex models (see also Barandiaran et al., 1988; Prindle and Ray, 1987). Since numerical solutions of these models are well established, the thrust of this paper is to develop analytical solutions to simplified, limiting case models. The major justification for developing analytical solutions to simplified (and hence less realistic) models is to provide better insight and intuition about reactor behavior that is difficult to extract from numerical solutions of complex models.

In a companion paper (Rawlings and Ray, 1987), the simplifying assumptions that are made in this work are carefully listed and are justified by comparing simplified and complete model solutions. The interested reader is directed to this paper for the physical motivation and further details on the model derivation.

Model

We start with a population balance in the particles' birth time coordinate. Let $F(t', t)dt'$ denote the concentration of polymer particles at time t that were initiated in the reactor in the time interval t' to $t' + dt'$. Assuming no particles in the feed stream and no particle coalescence or breakage yields,

$$\frac{\partial[F(t', t)V_R]}{\partial t} = -QF \quad t \in (0, \infty), t' \in (-\infty, t) \tag{1}$$

in which Q is the volumetric flow rate from the reactor and V_R is the reactor volume. In general, the reactor volume changes because of the flow streams and the volume change upon polymerization since the monomer and polymer have different densities. For the purposes of arriving at an analytical solution to the model, the change in volume due to polymerization is neglected. We are concerned mainly with the well-mixed, batch reactor ($V_R = 1$, $Q_f = Q = 0$), but the analysis also applies to the well-mixed, continuous reactor ($V_R = 1$, $Q_f = Q = 1$) and can be applied to other choices of V_R and Q_f as well. The simplified population balance can then be written

$$\frac{\partial F(t', t)}{\partial t} = -Q_f F \quad t \in (0, \infty), t' \in (-\infty, t) \tag{2}$$

Particles are assumed to be initiated by aqueous-phase free radicals entering monomer swollen micelles. The initiation rate of these particles then provides the boundary condition for the population balance,

$$F(t', t) = k_f m(t) \quad t \in [0, \infty), t' = t \tag{3}$$

in which m is the concentration of micelles. The initial condition specifies the seed particle size distribution (PSD) in the reactor,

$$F(t', t) = F_0(t') \quad t = 0, t' \in (-\infty, 0) \tag{4}$$

In this paper, we mainly assume $F_0 = 0$, i.e. an unseeded reactor, but this assumption can be relaxed. The micelle concentration is described by a simple difference between the available emulsifier in the reactor and the amount required to stabilize the existing particles and saturate the aqueous phase,

$$m'(t) = C_7(S - S_{wc}) - \frac{C_8}{V_w}\int_{-\infty}^{t} F(t', t)r^2(t', t)\,dt' \tag{5}$$

If the total particle area becomes large enough, all of the emulsifier is required to stabilize the particle-aqueous interface, the micelles disappear as a separate phase, and new particle formation ceases. This is described by including the unit step or Heaviside function, H, to obtain the physical concentration of micelles, m,

$$m(t) = m'(t)H(m') \tag{6}$$

Following our previous paper, we examine a simple power law approximation for the average number of free radicals per particle,

$$\bar{i} = k_i r^w \quad 0 \leq w < 3 \tag{7}$$

Alternative model formulations that treat the distribution of radical numbers explicitly can be found in Lichti et al. (1982) and Giannetti (1989). The choice of k_i and w values to best fit different monomer systems is discussed by Rawlings and Ray (1987). Given Eq. 7 one can solve a growth rate expression for the particle radius, r, as a function of the time it has been in the reactor,

$$r(t', t) = k_r\,[t - t']^{1/(3-w)} \tag{8}$$

The overall rate of monomer conversion is described by integrating the reaction rate per particle over the PSD,

$$\frac{dx}{dt} = -Q_f x + C_2 C_3 g_{po} \phi_{\text{sat}} \int_{-\infty}^{t} F(t', t)\bar{i}(t', t)\, dt' \tag{9}$$

$$x(0) = 0 \tag{10}$$

Before proceeding to the solution of the model, first notice that the solution to Eqs. 2–4 is

$$F(t', t) = \begin{cases} k_f m(t') e^{-Q_f(t-t')} & t \in [0, \infty),\ t' \in [0, t] \\ F_0(t') e^{-Q_f t} & t \in [0, \infty),\ t' \in (-\infty, 0) \end{cases} \tag{11}$$

Model Solution and Discussion

Figure 1 displays typical micelle concentrations for batch and CSTR reactors. The key question addressed in our previous paper is whether the CSTR's steady state is stable for a given set of operating conditions. This paper therefore focuses mainly on the batch reactor. For the batch reactor, the questions of interest are how many particles are produced before particle initiation ceases and how the PSD and the monomer conversion evolve in time. Considerable analytical progress can be made since Eq. 5 is linear in F until $t = t_1$, at which time the micelles are consumed to stabilize the particles. Substituting Eq. 11 into Eq. 5 gives

$$m'(t) = s(t) - \frac{\alpha}{\Gamma(c)} \int_0^t e^{-Q_f(t-t')}(t - t')^{c-1} m'(t')\, dt' \qquad t \leq t_1 \tag{12}$$

in which

$$\alpha = \frac{C_8}{V_w} k_f k_r^2 \Gamma(c) \tag{13}$$

$$c = \frac{5 - w}{3 - w} \tag{14}$$

$$s(t) = C_7(S(t) - S_{wc}) - \frac{C_8}{V_w} e^{-Q_f t} \int_{-\infty}^{0} F_0(t') r^2(t', t)\, dt' \tag{15}$$

Equation 12 is a Volterra integral equation of the second kind and can be solved using the contraction method discussed by Rawlings and Ray (1987) yielding,

$$m'(t) = s(t) + \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{\Gamma(nc)} \cdot \int_0^t s(t - p) e^{-Q_f p} p^{nc-1}\, dp \qquad t \leq t_1 \tag{16}$$

If the function $s(t)$ is an exponential or an exponential times a polynomial, then one can perform the integrals in Eq. 16 to achieve a closed form solution for m'. One can also approximate an arbitrary function $s(t)$ as a linear combination of exponentials times polynomials (orthonormal Laguerre polynomial basis functions, for example) and obtain a closed form evaluation of Eq. 16. Of these $s(t)$, $s = 1$ is of great practical importance. This describes the case of no initial seed particles and a constant total emulsifier concentration. This case is subsequently discussed in some detail. Substituting $s = 1$ into Eq. 16 gives

$$m'(t) = 1 + \sum_{n=1}^{\infty} \frac{(-\alpha)^n}{Q_f^{nc}} \frac{\gamma(nc, Q_f t)}{\Gamma(nc)} \qquad t \leq t_1 \tag{17}$$

The variety of other reactor properties of interest can be computed from Eq. 17. We first note that the moments of the PSD can be computed by substituting Eqs. 8 and 17 into Eq. 11 and performing the integration. The μth moment of F is computed as,

$$F^{\mu}(t) \equiv \int_{-\infty}^{t} F(t', t) r^{\mu}(t', t)\, dt' \tag{18}$$

$$= c_{\mu} \sum_{n=0}^{\infty} \frac{(-\alpha)^n \gamma\left[nc + 1 + \frac{\mu(c-1)}{2}, Q_f t\right]}{Q_f^{nc+1+\mu(c-1)/2}\, \Gamma\left[nc + 1 + \frac{\mu(c-1)}{2}\right]} \qquad t \leq t_1 \tag{19}$$

Integration and limit formulae that are useful in deriving the results of this section are collected in the Appendix. The

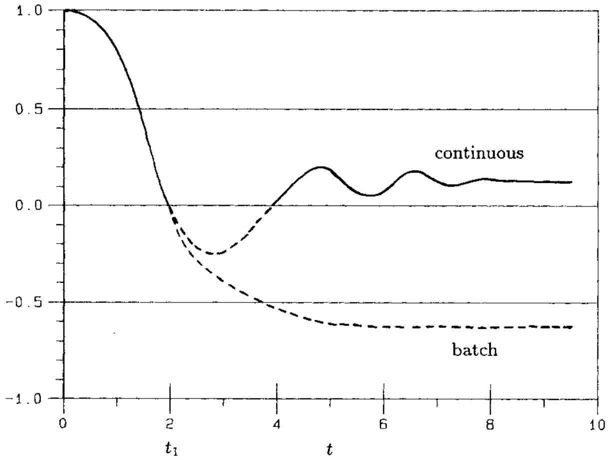

Figure 1. Micelle concentration vs. time.

monomer conversion can be computed by solving Eq. 9 and substituting F^w from Eq. 18,

$$x(t) = k_x \sum_{n=0}^{\infty} \frac{(-\alpha)^n \gamma\left(nc + \frac{3c-1}{2}, Q_f t\right)}{Q_f^{nc+(3c-1)/2}\Gamma\left(nc + \frac{3c-1}{2}\right)} \quad t \le t_1 \tag{20}$$

Substituting $Q_f = 1$ into Eqs. 17–20 recovers the CSTR solution of our previous paper, and taking the limit as $Q_f \rightarrow 0$ yields the new batch solution,

$$m'(t) = 1 - \sum_{n=1}^{\infty} \frac{(-\alpha)^n t^{nc}}{\Gamma(nc+1)} \quad t \le t_1 \tag{21}$$

$$F^{\mu}(t) = c_{\mu} \sum_{n=0}^{\infty} \frac{(-\alpha)^n t^{[nc+1+\mu(c-1)/2]}}{\Gamma\left[nc + 2 + \frac{\mu(c-1)}{2}\right]} \quad t \le t_1 \tag{22}$$

$$x(t) = k_x \sum_{n=0}^{\infty} \frac{(-\alpha)^n t^{(nc+(3c-1)/2)}}{\Gamma\left[nc + \frac{3c+1}{2}\right]} \quad t \le t_1 \tag{23}$$

Equation 21 governs the time at which particle initiation ceases as the micellar phase is consumed to stabilize the particles. Solving for t_1, the time at which the micelles disappear,

$$0 = 1 + \sum_{n=1}^{\infty} \frac{(-\alpha)^n t_1^{nc}}{\Gamma(nc+1)} \tag{24}$$

Equation 24 is similar in form to that developed by Smith and Ewart (1948). In fact, their classic result is a special case of this solution as discussed subsequently. Defining $b_0 = \alpha t_1^c$ allows one to write Eq. 24 as

$$0 = 1 + \sum_{n=1}^{\infty} \frac{(-b_0)^n}{\Gamma(nc+1)} \tag{25}$$

The numerical solution of Eq. 25 for $b_0(c)$ [scaled by $\Gamma(c+1)$] is plotted in Figure 2. Unless one includes additional sources of particle stabilization as in Min and Ray (1974), no new particles are generated after $t = t_1$ in the batch reactor. One can substitute b_0 into Eq. 22 for the total number of particles (zeroth moment) to obtain,

$$F^0(t) = c_0 t_1 \sum_{n=0}^{\infty} \frac{(-b_0)^n}{\Gamma(nc+2)} \quad t \ge t_1 \tag{26}$$

The expression,

$$b_1(c) = \sum_{n=0}^{\infty} \frac{(-b_0)^n}{\Gamma(nc+2)} \tag{27}$$

is also evaluated numerically and plotted in Figure 2. One can then compactly summarize the number of particles generated in a batch reactor by,

$$F^0(t) = c_0 \left(\frac{b_0}{\alpha}\right)^{1/c} b_1 \quad t \ge t_1 \tag{28}$$

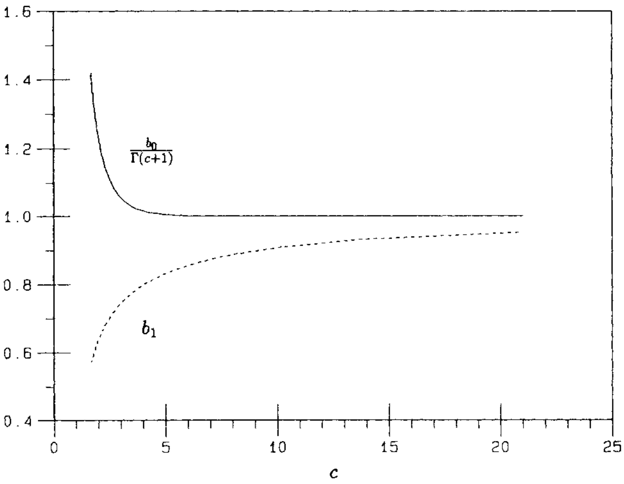

Figure 2. $b_0/\Gamma(c+1)$ and b_1 vs. c.

The other PSD moments and monomer conversion can also be computed, but they change with time after t_1 since the particles continue to grow until the monomer is consumed. Smith and Ewart's case II ($\bar{i} = 1/2$) analysis can be extracted by setting $k_i = 1/2$ and $w = 0$ in Eq. 7. The computations leading to Figure 2 for $w = 0$ ($c = 5/3$) give $b_0 = 2.134$ and $b_1 = 0.5691$ in good agreement with Smith and Ewart's (1948, p. 598) values of 2.13 and 0.569.

During the last 40 years there has been considerable discussion of why certain monomer systems obey the predictions of Smith-Ewart kinetics and others do not. Additional light can be shed on this topic by examining the effect of the operating parameters, such as initiator and emulsifier concentration, on the total number of particles generated. Substituting the various dimensionless constants into Eq. 28 yields (in *dimensional* variables),

$$F^0 \propto \frac{1}{k_i} S^{1/c} I^{1-1/c} \tag{29}$$

Since $c = 5/3$ for the Smith-Ewart case II kinetics, Eq. 29 yields the classic result that the total particle number generated in a batch reactor is proportional to emulsifier to the 3/5's power and initiator to the 2/5's power. Experimental data displaying deviations from these powers are often cited as proof that Smith-Ewart case II kinetics or even the micellar initiation theory is invalid. Since the only physical restriction on w in Eq. 7 is $0 \le w < 3$, it follows that

$$0 \le \frac{1}{c} \le \frac{3}{5} \tag{30}$$

$$\frac{2}{5} \le 1 - \frac{1}{c} \le 1 \tag{31}$$

Table 1. Particle Number Dependence on Emulsifier and Initiator Concentration

Case	Model	w	c	Dependence k_i	Dependence F^0
A	S-E case II	0	5/3	none	$S^{3/5}I^{2/5}$
B	Large r diffusion	2	3	$(I/S)^{1/2}$	$S^{2/3}I^{1/3}$
C	Large r collision	5/2	5	$(I/S)^{1/2}$	$S^{3/5}I^{2/5}$
D	Small r diffusion	1	2	(I/S)	$S^1 I^0$
E	Small r collision	2	3	(I/S)	$S^1 I^0$

Thus it is in principle possible to find monomer systems, in which the total particle number is completely independent of emulsifier concentration. The existence of such data does not *by itself* invalidate the micellar initiation mechanism. It only invalidates the assumption that $\bar{i} = 1/2$.

A more complete understanding of the limitations of micellar initiation theory can be achieved by considering Rawlings and Ray's (1987) method for choosing appropriate values of k_i and w. Their scheme is based on using asymptotic fits to the full Stockmayer (1957) and O'Toole (1965) relation for $\bar{i}$. In this approach, k_i may also depend on the emulsifier and initiator concentrations. Using their notation, Table 1 lists five choices of parameters k_i and w. Note that these models predict a range of exponents for the dependence of particle number on emulsifier and initiator concentrations. In addition, any kinetic mechanism, which causes the slope of the log $\bar{i}$ vs. log r line to change, also changes the exponents in the total particle number relation. Examples of such mechanisms are radical desorption through high rates of chain transfer to monomer, chain transfer agents, and certain types of impurities.

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Notation

$b_0 = \alpha t_1^c$, Eq. 25
$b_1 =$ constant, Eq. 27
$c = (5 - w)/(3 - w)$
$c_i = k_f k_r^i \Gamma(1 + i(c - 1)/2)$
$C_2 - C_9 =$ dimensionless constants, Rawlings and Ray (1987)
$f =$ initiator efficiency factor
$F(t', t) =$ number of particles at time t with birth time t'
$F_0(t') =$ initial seed distribution
$F^i =$ ith moment of F, Eq. 18
$g_{po} =$ gel effect in the propagation rate
$H =$ Heaviside or unit step function
$\bar{i} =$ average number of radicals per polymer particle
$k_f = C_5 R_f V_{wf}$, Rawlings and Ray (1987)
$k_i =$ constant, Eq. 7
$k_r = [(3 - w)/3 \; C_6 g_{po}\phi_{sat}/(1 - \phi_{sat})k_i \;]^{1/(3-w)}$, Rawlings and Ray (1987)
$k_x = C_2 C_3 g_{po}\phi_{sat} k_f k_i k_r^w (3 - w)/3$, Rawlings and Ray (1987)
$m =$ micelle concentration
$m' =$ available free emulsifier to form micelles
$Q =$ volumetric product flow rate
$Q_f =$ volumetric feed flow rate
$r(t', t) =$ radius of particle with birth time t' at time t
$R_f =$ aqueous phase free radical concentration, $R_f = 2 f C_4/C_9$
$s =$ Eq. 15
$S =$ total emulsifier concentration
$S_{wc} =$ critical micelle concentration
$t =$ time
$t' =$ birth time
$t_1 =$ time at which micelles disappear as a separate phase
$V_R =$ reactor volume
$V_w =$ aqueous phase volume fraction
$w =$ power law exponent, Eq. 7
$x =$ monomer conversion

Greek letters

$\alpha =$ parameter, Eq. 13
$\gamma =$ incomplete gamma function
$\Gamma =$ complete gamma function
$\phi_{sat} =$ saturated monomer volume fraction in particles

Literatured Cited

Barandiaran, M. J., J. C. Prindle, and W. H. Ray, "Effect of Chain Transfer Agents on the Stability of Continuous Emulsion Polmerization Reactors," AIChE Meeting, Washington, DC (1988).

Giannetti, E., "Emulsion Polmerization: Comprehensive Theory for Particle Size Distributions in the Smith-Ewart Interval II," *Polym. Reaction Eng.* K.-H. Reichert and W. Geiseler, eds., 343, VCH (1989).

Lichti, G., R. G. Gilbert, and D. H. Napper, "Theoretical Predictions of the Particle Size Distrubitions in Emulsion Polymerizations," I. Piirma, ed., *Emulsion Polymerization,* 93, Academic Press, New York (1982).

Min, K. W., and W. H. Ray, "On the Mathematical Modelling of Emulsion Polymerization Reactors," *J. Macro. Sci. Revs.,* **C11**(2), 177 (1974).

O'toole, J. T., "Kinetics of Emulsion Polymerization," *J. Appl. Poly. Sci.,* **9,** 1291 (1965).

Prindle, J. P., "Dynamics and Stability of Emulsion Polymerization Reactors," PhD Thesis, Univ. Wisconsin-Madison (1989).

Prindle, J. C., and W. H. Ray, "Emulsion Polymerization Model Development for Operation Below the CMC," AIChE Meeting, New York (1987).

Rawlings, J. B., "Simulation and Stability of Continuous Emulsion Polymerization Reactors," PhD Thesis, Univ. Wisconsin-Madison (1985).

Rawlings, J. B., and W. H. Ray, "Emulsion Polymerization Reactor Stability: Simplified Model Analysis," *AIChE J.,* **33**(10), 1663 (1987).

———, "The Modelling of Batch and Continuous Emulsion Polymerization Reactors. Part I: Model Formulation and Sensitivity to Parameters," *Polym. Engr. Sci.,* **28**(5), 237–256 (1988a).

———, "The Modelling of Batch and Continuous Emulsion Polymerization Reactors: Part II. Comparison With Experimental Data From Continuous Stirred Tank Reactors," *Polym. Engr. Sci.,* **28**(5), 257 (1988b).

Smith, W. V., and R. H. Ewart, "Kinetics of Emulsion Polymerization," *J. Chem. Phys.,* **16,** 592 (1948).

Stockmayer, W. H., "Note on the Kinetics of Emulsion Polymerization," *J. Polym. Sci.,* **XXIV**(106), 314 (1957).

Appendix

The following formulae are useful in deriving Eqs. 16–23.

$$\int_0^t e^{-Q(t-t')}(t - t')^{c-1}\, dt' = \frac{\gamma(c, Qt)}{Q^c}$$

$$\int_0^t \gamma(a, Qt')e^{-Q(t-t')}(t - t')^{c-1}\, dt' = \frac{\Gamma(a)\Gamma(c)}{\Gamma(a + c)} \frac{\gamma(a + c, Qt)}{Q^c}$$

$$\lim_{Q \to 0} \frac{\gamma(a, Qt)}{Q^a} = \frac{t^a}{a}$$

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