

## Kinetics of Continuous Addition Emulsion Polymerization

RITCHIE A. WESSLING, *Plastics Department Research Laboratory,  
The Dow Chemical Company, Midland, Michigan 48640*

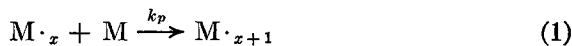
### Synopsis

An analysis of the kinetics of continuous addition emulsion polymerization is presented. For systems that follow the Smith-Ewart mechanism, this analysis predicts that the reaction will approach a steady-state condition if the rate of monomer addition  $R_a$  is constant. In the steady state, the rate of polymerization depends on  $R_a$  according to a reciprocal relationship,  $1/R_p = (1/K) + (1/R_a)$ , where  $K$  depends on the number of particles and the propagation rate constant. Above a critical value of  $R_a$ , the particles will become saturated with monomer and  $R_p$  will be constant and independent of  $R_a$ .

### Introduction

The rate equations normally used to describe free radical polymerizations are valid only for constant volume reactions. Some polymerizations, however, are conducted in open systems in which ingredients are added or removed and the volume does not remain constant. For example, the case of continuously adding monomer to an emulsion polymerization is an established technique.<sup>1</sup> This paper describes an extension of the theory to include such cases. The results of this analysis can be used not only to describe reaction behavior but also to evaluate competing theories of emulsion polymerization.

The classical theory<sup>2</sup> treats a reaction with the propagation step



where  $k_p$  is the propagation rate constant. An equation for the rate of polymerization at constant volume is easily deduced from this mechanism.

$$[R_p] = k_p[M][M \cdot]$$

where the brackets indicate molar concentrations and  $[R_p]$  is the rate of conversion in units of moles/l.-sec. If the volume is changing with time, the correct expression is:

$$[R_p] = d[m]/dt = k_p[M][M \cdot] - (m/V^2)(dV/dt) \quad (2)$$

where  $m$  is the moles of monomer converted to polymer.

This equation is rather awkward to use; the molar rate equation is preferable for reactions in open systems.\*

$$dm/dt = k_p(MM \cdot /V) \quad (3)$$

Equation (3) applies to any homogeneous reaction. This could be a solution or bulk polymerization or the polymerization within a particular phase in a heterogeneous reaction.

Equation (3) is independent of any reaction mechanism beyond the usual assumptions for a free-radical chain reaction. In the following sections, this rate law will be combined with an appropriate material balance to analyze three problems: the steady-state behavior of an emulsion polymerization in which monomer is added at a constant rate; the approach to steady state in a seeded continuous addition emulsion polymerization; and finally the case of a continuous addition polymerization with constant radical concentration.

The kinetics of polymerization within a latex particle follow eq. (3) but the macroscopic rate (total rate of conversion) is the measured variable. In order to deduce the total rate, further calculations must be based on a model for emulsion polymerization. The results which follow will, therefore, reflect the validity of the model in question, the Smith-Ewart theory.<sup>3</sup> The principal assumptions in this theory are: that the particles are swollen with monomer, polymerization takes place in the particle, and the average number of radicals per particle is  $\frac{1}{2}$  (for small particles).

It is generally agreed that batch emulsion polymerization is a two-stage process: a particle formation or seed step and a growth step. The second stage is the concern of this paper.

The two stages of reaction can be isolated experimentally.<sup>4,5</sup> Seed is prepared by a normal batch reaction and subsequently grown to larger size in a separate experiment. The emulsifier level is critical in this stage in order to prevent new particle formation.<sup>6</sup> Monomer may be added in one shot but is usually added continuously at a fixed rate. It should be noted also that both stages can be combined in a continuous addition process.

The growth stage in "con-add" emulsion polymerization has been studied from many points of view. Only one kinetic analysis has appeared, however. Gerrens<sup>7</sup> has reported an experimental study of the continuous polymerization of styrene in emulsion but did not analyze the kinetics rigorously.

### Steady-State Emulsion Polymerization with a Constant Rate of Monomer Feed

It has been observed experimentally that if the number of particles  $N$ , remains constant, the rate of polymerization takes on a constant value.

\* The difficulty in using molar rates is that the magnitude depends on the reaction volume. It might be desirable to use "reduced" variables by dividing by the initial or final volume. However, this may lead to confusion with constant volume rates because of the similarity in units. The practice in this paper is simply to use molar rates; if necessary, reaction volumes will be specified.

The value of  $R_p$  depends on the rate of addition  $R_a$  in a starved reaction but is independent of  $R_a$  when the system contains excess monomer.

If these observations are accepted as correct, the steady-state behavior can be derived from a material balance and the rate law [eq. (3)]. Equation (3) can be rewritten according to the Smith-Ewart model.

$$R_p = (k_p N / 2\tilde{N}) \cdot (M/V) \quad (4)$$

where  $M$  is the average molar concentration of monomer in the particles and  $\tilde{N}$  is Avogadro's number. If  $R_p$  is constant, it follows that

$$dM/dt = (M/V)(dV/dt) \quad (5)$$

The derivatives in eq. (5) can be evaluated from a material balance. If the reaction is starved,

$$dM/dt = R_a - R_p \quad (6)$$

and

$$\frac{dV}{dt} = V_M R_a - (V_M - V_p) R_p \quad (7)$$

where  $V_M$  and  $V_p$  are the molar volumes of monomer and polymer, respectively. (It was assumed that the volume change due to mixing monomer and polymer is negligible.) The equations can be combined to eliminate  $(M/V)$  and rearranged to give eq. (8):

$$\frac{1}{R_p} = \frac{1}{K} + \frac{1}{R_a} \left[ 1 + \frac{R_p}{K} \left( 1 - \frac{V_p}{V_M} \right) \right] \quad (8)$$

According to eq. (8), a plot of  $1/R_p$  versus  $1/R_a$  will be virtually linear with a slope of unity and intercept  $K$ , where

$$K = k_p N / 2\tilde{N} V_M \quad (9)$$

The quantity in brackets in eq. (8) is limited to the range

$$1 \leq \left[ 1 + \frac{R_p}{K} \left( 1 - \frac{V_p}{V_M} \right) \right] < 1 + \delta$$

where  $\delta$  is of the order of 0.1. The upper limit depends on the maximum swelling of the polymer particles.

Beyond the point of maximum swelling, the monomer begins to form droplets, and eq. (6) is no longer valid. The rate of polymerization reaches a maximum value

$$\overline{R_{p_{\max}}} = K v_{\text{eq}} \quad (10)$$

where  $v_{\text{eq}}$  is the equilibrium volume fraction of monomer in the latex particles.

The maximum rate of addition which can be tolerated without flooding

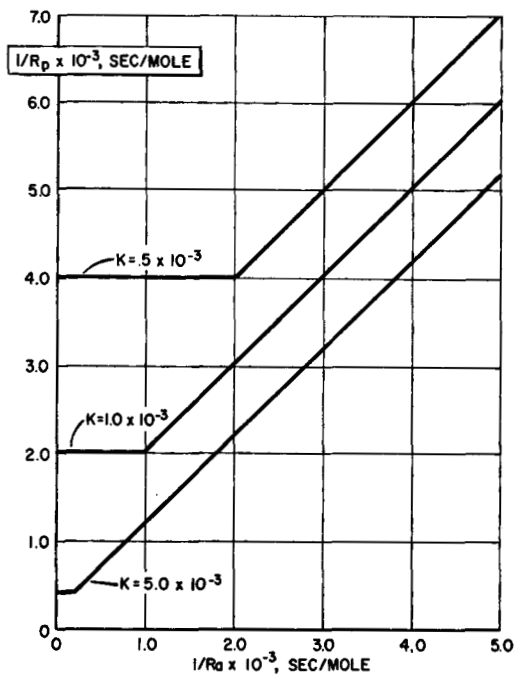


Fig. 1. Effect of increasing the number of particles on the rate of steady-state continuous addition emulsion polymerization;  $v = 0.5$ .

the system can be deduced from a new material balance. If the amount of excess monomer in the system is to remain constant (or zero if desired) then

$$R_a - R_{p\max} = (R_{p\max}/K) \{R_a - R_{p\max} [1 - (V_p/V_M)]\} \quad (11)$$

A little manipulation will show that

$$R_a = R_{p\max}/W_p \quad (11')$$

where  $W_p$  is the weight fraction of polymer in the latex particles.

This analysis predicts that the steady-state behavior of a continuous addition emulsion polymerization should show these relationships:

$$1/R_p \approx (1/K) + (1/R_a) \quad R_p < R_{p\max} \quad (12)$$

$$R_{a\max} = R_{p\max}/W_p \quad (13)$$

$$v_m \approx R_a/(K + R_a) \quad v_m < v_{eq} \quad (14)$$

Therefore, a plot of  $1/R_p$  versus  $1/R_a$  should be linear over a certain range with a slope of unity. At some critical point given by eq. (13), the slope will change to zero.

Figure 1 shows how the number of growing particles (reflected by an increase in  $K$ ) affects steady-state behavior. The reciprocal plots show that as  $N$  increases, the range where  $R_p$  is controlled by  $R_a$  increases. An increase in the rate of propagation would show a similar effect.

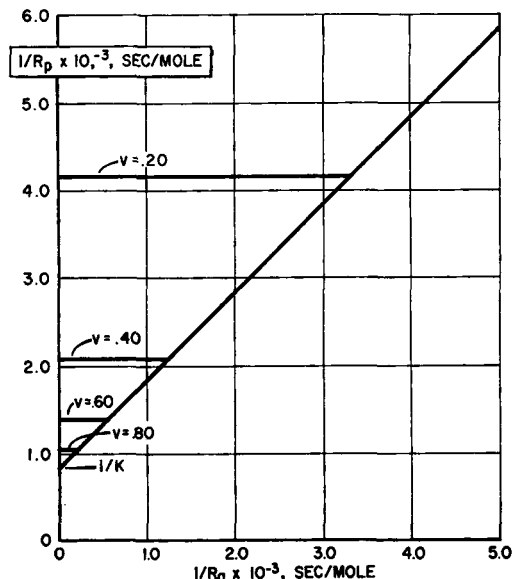


Fig. 2. Effect of equilibrium particle swelling on steady-state polymerization;  $K = 1.2 \times 10^{-3}$  mole/sec.

Figure 2 shows the effect of changing equilibrium swelling of a latex particle when  $K$  is fixed. In this case, the behavior at low rates of addition is unaffected, but the range of control is broadened by increased equilibrium swelling.

#### Approach to Steady State in a Seeded Reaction

In many cases, monomer is pumped into a seed latex which contains only polymer. The rate of polymerization is initially zero. Consequently, there will be a time lag before the system reaches steady-state conditions. During this period,  $M/V$  is not constant as with constant monomer feed. The same material balance, however, can be used to evaluate the time dependence of  $M/V$ . This gives the equation below:

$$R_p = \frac{k_p N}{2\bar{N} V_M} \left[ \frac{R_a t - m}{m_0 + R_a t} \right] \quad (15)$$

where  $m$  is the amount of polymer in the system at any time and  $m_0$  is the amount in the original seed. Since in the previous section consideration of the difference in molar volume between polymer and monomer was an unnecessary refinement, it was neglected in deriving eq. (12). Equation (12) can be solved by the usual methods to give:

$$R_p(t) = \frac{K R_a}{K + R_a} \left[ 1 - \left( \frac{m_0}{m_0 + R_a t} \right)^{\frac{K + R_a}{K}} \right] \quad (16)$$

and

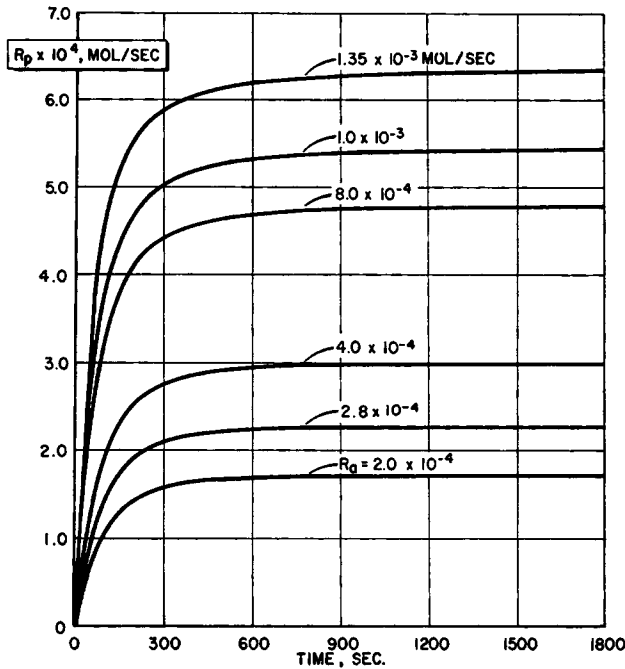


Fig. 3. Effect of addition rate on the approach to steady state;  $K = 1.2 \times 10^{-3}$  mole/sec.

$$m(t) - m_0 = \left[ \frac{KR_a}{K + R_a} \right] t + \left[ \frac{m_0 R_a}{K + R_a} \right] \left[ 1 - \left( \frac{m_0}{m_0 + R_a t} \right)^{K/R_a} \right] \quad (17)$$

As  $t$  increases, both equations yield the results presented above.

$$\lim_{t \rightarrow \infty} R_p = KR_a / (K + R_a) \quad (18)$$

and

$$\lim_{t \rightarrow \infty} (m - m_0) = [R_a m_0 / (K + R_a)] + R_p(\infty) t \quad (19)$$

Equation (18) can be arranged to the reciprocal relationship

$$1/R_p = (1/K) + (1/R_a) \quad (20)$$

and eq. (19) confirms the experimental fact that in the steady state, conversion increases linearly with time.

Equation (16) shows that the time required to reach steady state for a given monomer depends on the rate of addition and the number of particles. Some theoretical curves are shown in Figures 3 and 4.

Figure 3 shows how  $R_a$  affects approach to steady state for  $K = 1.2 \times 10^{-3}$  mole/sec. As might be anticipated, increasing  $R_a$  extends the time it takes to get to a steady state. Figure 4 shows the results of varying  $N$  (as reflected in  $K$ ). The system with the largest number of particles reaches

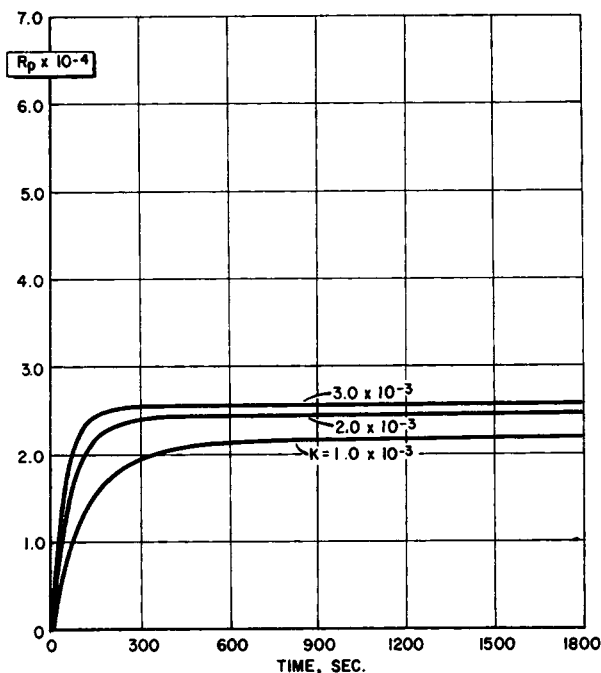


Fig. 4. Effect of increasing number of particles on the approach to steady state;  $R_a = 2.8 \times 10^{-4}$  mole/sec.

steady state the fastest. For a given number of particles, an increase in monomer reactivity produces a similar effect.

The time lag actually observed in a seeded reaction may involve other factors. Swelling of seed particles was assumed to occur instantaneously, being controlled only by availability of monomer. This seems reasonable. A more serious limitation is that the initial rate of addition must be less than the rate of diffusion. Otherwise, excess monomer will build up in the system, and eq. (15) will not apply.

#### Fixed Radical Concentration

In the preceding cases, the number of radicals was fixed by the number of particles. As particle size increases, the radical concentration must decrease. Eventually, a point is reached, however, where more than one radical is present per particle. The number increases with size until finally each particle behaves as a small bulk reaction.

In this situation, the radical concentration is more likely to be constant. Then the rate of polymerization per particle will depend on the amount of unreacted monomer present. The total rate then is simply the sum of the particle rates. The system will, therefore, behave exactly like a continuous addition bulk or solution polymerization with constant radical concentration.

From eq. (3), the rate for this case is:

$$R_p(t) = K'M(t) \quad (21)$$

where the quantities refer to total moles in the system and  $K' = k_p [M]$ . If monomer is added at a constant rate and no products are removed, a material balance shows that

$$dM(t)/dt = R_a - R_p \quad (22)$$

The derivative of eq. (21) can be combined with eq. (22) to yield a first-order differential equation showing the time dependence of  $R_p$ :

$$(dR_p/dt) + K'R_p = K'R_a \quad (23)$$

The solution is

$$R_p = R_a + (R_p^0 - R_a)e^{-K't} \quad (24)$$

The conversion is obtained by integrating eq. (21)

$$m = R_a t + [(R_p^0 - R_a)/K](1 - e^{-K't}) \quad (25)$$

In this case, the steady-state rate of polymerization is equal to the rate of addition since the limiting value of eq. (24) is

$$\lim_{t \rightarrow \infty} R_p = R_a \quad (26)$$

### Comparison to Experimental Data

The steady-state behavior predicted by this analysis can be tested against Gerrens' data on styrene. This monomer is known to follow Smith-Ewart kinetics. Gerrens reported two sets of  $R_p$  versus  $R_a$  data. In each case part of the monomer was fed into the reactor initially and polymerized to make a seed. Then the remaining monomer was added at a constant rate.

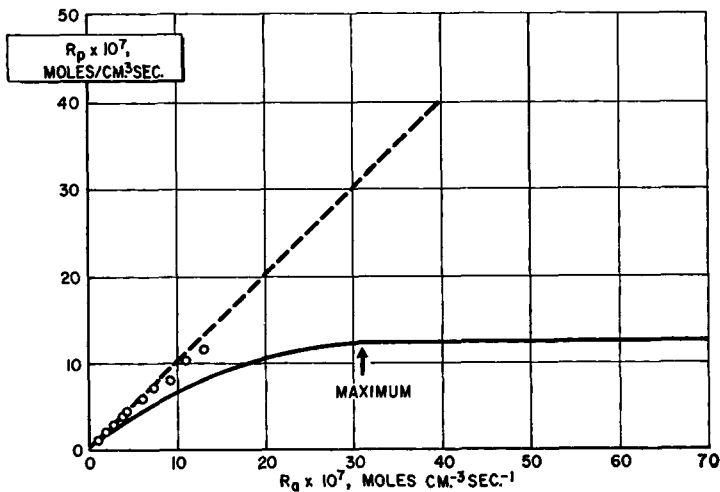


Fig. 5. The comparison of theory to Gerrens' data (monomer feed): the arrow denotes predicted saturation point; (---) theoretical; (O) experimental points.



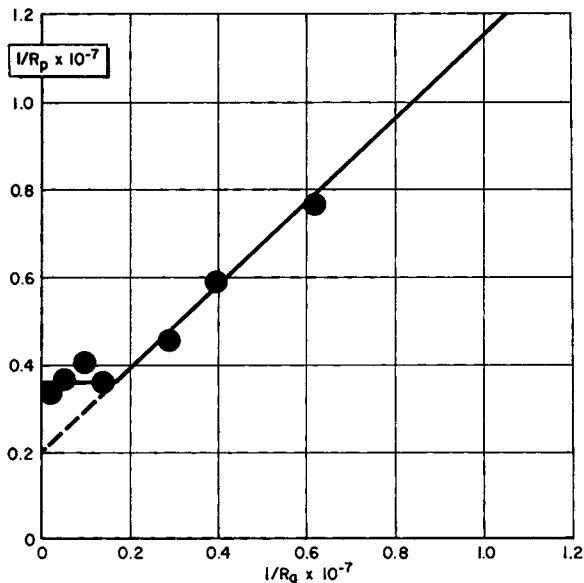


Fig. 6. Analysis of data from emulsion feed experiments.

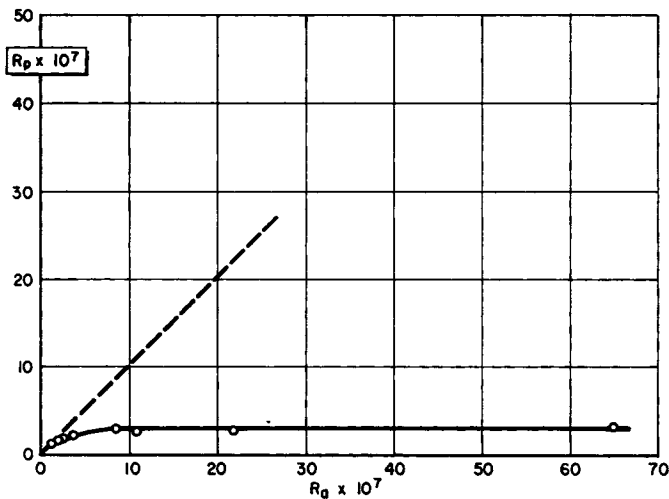


Fig. 7. Comparison of theory to emulsion feed data: (---) theoretical; (O) experimental points.

In the first case all of the soap was charged to the reactor initially while in the second case, soap was added with monomer in the form of an emulsion.

For Case 1, Gerrens reported the following data:

$$\bar{N}_n = 14.0 \times 10^{14} \text{ particles/cm.}^3$$

$$k_p = 2.06 \times 10^5 \text{ cm.}^3/\text{mole-sec. (50}^\circ\text{C.)}$$

$$v_{\text{eq}} = 0.60(50^\circ\text{C.)}$$

Both  $K$  and  $R_{p\max}$  can be calculated from these data.

$$K = 2.07 \times 10^{-6} \text{ mole/cm.}^3\text{-sec.}$$

$$R_{p\max} = 1.24 \times 10^{-6} \text{ mole/cm.}^3\text{-sec.}$$

(Note that these values are normalized by dividing by the final latex volume, 2000 cm.<sup>3</sup>.)

Figure 5 shows the predicted behavior of a plot of  $R_p$  versus  $R_a$  for this system. The experimental points are taken from Figure 1 in Gerrens' paper. The fit is not good in the range of addition rates investigated. Unfortunately, the rates were not extended to the saturation point.

In the case where a monomer emulsion was fed into the reactor, the range is adequate but the author did not report the particle concentration which may not have been constant. Figure 6, however, shows how these data can be analyzed by using eq. (12). (The data points were calculated from Fig. 1 in Gerrens' paper.) The intercept gives a value of  $K$  and with the propagation constant given above, a value for particle concentration can be calculated.

$$K = 5.0 \times 10^{-7} \text{ mole/cm.}^3\text{-sec.}$$

$$N = 4.4 \times 10^{14} \text{ particles/cm.}^3$$

This is quite reasonable. The ratio of  $R_p$  at the saturation point to  $K$  can be used to calculate  $v_{eq}$ :

$$v_{eq} = 0.56$$

This value is somewhat lower than the measured value but may simply reflect the lower soap concentration in this system. The slope is 0.95, which is reasonably close to theoretical.

A theoretical curve is calculated by using the  $K$  obtained from the reciprocal plot. In Figure 7 this is compared to the data points from Gerrens' paper (taken from his Figure 3). In this case, the fit is excellent.

### Discussion

The preceding analysis shows that steady-state polymerization can be achieved if the following conditions are met: monomer is added at a constant rate and at least one of the reactant concentrations is held constant. These conditions can be met in an emulsion polymerization which follows the Smith-Ewart mechanism. The monomer concentration is constant in this case provided no new particles are generated.

The approach to steady state and the saturation point may both depend on a variety of factors not accounted for in this simplified analysis. Clearly, the particle size and number, the water solubility and diffusion rate of the monomer, and the emulsifier level will affect the time required to reach equilibrium. It is known also that particle size and emulsifier affect the maximum rate of polymerization. Where these factors are held constant,

however, the behavior should follow the predicted dependence on rate of addition.

A test of the theory against Gerrens' data was somewhat ambiguous. Further experimental studies specifically designed to test both the steady-state behavior and the approach to steady state are required.

The author is indebted to Dr. T. Alfrey, Jr. for many valuable discussions concerning this analysis. Computer calculations were programmed by Dr. G. E. Molau.

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