

Mechanism of Emulsion Polymerization of Vinylidene Chloride. II. Effect of Coalescence of Polymer Particles on Kinetics

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INTRODUCTION

In a previous paper¹ we have reported that the emulsion polymerization of vinylidene chloride with the use of sodium lauryl sulfate as surfactant and ammonium persulfate and sodium metabisulfite as the redox catalyst system, when examined in detail, differs in several respects from the conventional course of such polymerizations. It is possible to divide a total polymerization kinetically into three stages. During approximately the first ten per cent of conversion to polymer in a given experiment, polymerization proceeds at a nearly constant rate, but then foaming rather quickly ceases, the rate of polymerization measurably decreases, and subsequently a phase consisting of unemulsified vinylidene chloride separates. This stage (called II) can be rather clearly delineated experimentally, and is followed by a third stage characterized by an increase in reaction rate, with a nearly constant polymerization rate up to high percentage conversion (85% or more).

These results are at variance with the general theory of Harkins,² which permits but two stages, and the theory of Smith and Ewart,^{3,4} which predicts a constant rate after a short initial reaction time. That vinylidene chloride should behave in emulsion polymerization somewhat unconventionally is not entirely unexpected, since it exemplifies a rare condition, in that the polymer is insoluble in the monomer and the monomer is, for practical purposes, insoluble in the polymer.⁵ Furthermore the solubility of vinylidene chloride in water is low; though not known with certainty, it is surely less than 10^{-3} moles/liter.⁶

Two different explanations have been adduced¹ to account for the three stages of vinylidene chloride polymerization which we have observed. It is possible that the decrease in rate in Stage II and the subsequent increase in Stage III can be

the result of coalescence of polymer particles or, alternatively, the result of marked changes in the mechanism of monomer transport and polymerization. The first of these theories has been reported briefly in a note.⁷ The purpose of the present paper is to discuss in detail the coalescence theory and to assess its importance in explaining the experimental results. A subsequent paper will discuss alternative explanations.⁸

DISCUSSION

We have assumed that the major locus of polymerization is in the surfactant micelles initially, and subsequently in the polymer particles. Smith and Ewart³ showed that the rate of polymerization will be constant if the number of growing particles remains constant, if the rate of termination of two free radicals in a particle is much greater than the rate of entry of free radicals into the polymer particle, if the average rate of polymerization per free radical is constant, and if the concentration of monomer in the polymer particle remains constant. The difference equation which they derived for the average number of free radicals per particle has been explicitly solved by Stockmayer.⁹ Experimental confirmation of the nonconstant rate of polymerization per particle has been given by Roe and Brass¹⁰ for polystyrene particles.

We have used Stockmayer's result and have introduced additional assumptions concerning the number of particles as a function of time. Apparent change in the number of particles has been noted by Smith,⁴ by Morton, Salatiello, and Landfeld,¹¹ and by Medvedev,¹² but only Medvedev has attached importance to the change or done extensive investigations of the phenomenon.

As mentioned above, the polymerization of vinylidene chloride passes through a period of drastic redistribution of surfactant. The surfactant performs at least three roles: the establishment of

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micelles wherein polymerization is begun, the formation of a protective layer about monomer droplets and a similar protective layer on the surface of polymer particles. Visually one sees the emulsified system separate into an emulsion and a separate vinylidene chloride layer in the reaction vessel after about 10% of the monomer has been polymerized, followed by reemulsification of the vinylidene chloride phase. It was quite reasonable to assume, therefore, that agglomeration of polymer particles might be occurring as the emulsification of vinylidene chloride consumed surfactant at the expense of the growing polymer particles.

In the theory presented here we make the following assumptions.

a. The average rate of polymerization per particle is proportional to the average number of free radicals per particle.

b. The number of free radicals per particle depends on the volume of the particle.⁹

c. The particles are formed from micelles, no new particles being formed after a short period of time. For mathematical simplicity we assume N_0 particles exist at time t_0 with initial volume V_0 . It is assumed that no particles are formed subsequently; i.e., t_0 is the time at which the micelles disappear, or shortly thereafter.

d. The number of particles may decrease through coalescence of particles. After coalescence of two particles, they are treated kinetically as one.

e. After coalescence the number of chains should decrease to the steady-state value in a time which is short compared with the time τ between entry of free radicals.

First is shown the effect of coalescence, second the effect of increasing particle size, and finally the effect of the combination of the two upon the rate of polymerization.

Particle Coalescence

We shall apply the general method which Smoluchowski¹³ and Chandrasekhar¹⁴ developed for the theoretical treatment of recurrent processes, and which the former applied specifically to develop a theory of the kinetics of coagulation of colloidal mixtures.¹⁵

$$dN/dt = -B'N^2 \quad (1)$$

where $B' = 2kT/3\eta$, N is the number of particles per cubic centimeter, k is Boltzmann's constant, η is the viscosity of the fluid medium, and T is in degrees Kelvin.

In applying these results to emulsion polymerization, B' must be modified somewhat because of the presence of the emulsifier. Let $B = \alpha B'$ where α is the fraction of collisions resulting in coalescence and is a function of the amount of surfactant on the particles. In order to simplify the mathematics we shall take $\alpha = 0$ as long as micelles are present and equal to some constant β when micelles are no longer present. The former seems justified, since the surface energy per unit area of the particles should be approximately equal to that of the micelles when the micelles are present and the surface of the particles is covered with surfactant. Upon coalescence under these conditions, new micelles would have to form, and so the total energy of the system would not be reduced. After the micelles disappear, however, the total energy presumably can be reduced by reducing the surface area of the polymer-water interface, i.e., by coalescence of particles.

We may therefore write $dN/dt = 0$ as long as micelles are present ($t < t_0$), and for $t > t_0$,

$$dN/dt = -(2\beta kT/3\eta)N^2 = -BN^2 \quad (2)$$

Solving, with $N = N_0$ at $t = t_0$, gives

$$N = N_0/[1 + BN_0(t - t_0)] = N_0/y \quad (3)$$

For $t > t_0$, $y = 1 + BN_0(t - t_0)$.

If BN_0 is very small, the number of particles will remain approximately the same throughout the reaction as Smith and Ewart assumed. The constant, B , will be evaluated for the vinylidene chloride polymerization case in the last section below.

Rate of Growth of a Particle not Constant

Stockmayer has shown⁹ that if $\gamma = V/k_t\tau$ and $m = k_0S/k_t$, where V is the volume of the particle, k_t is the specific rate of termination of free radicals (assumed constant), τ is the average time between entries of free radicals, k_0 is the rate of transfer of radicals out of the particle per unit area, and S is the surface area of the particle, the average number of growing chains per particle, \bar{n} , is

$$\bar{n} = (\sqrt{2\gamma}/2) [I_{-m}(2\sqrt{2\gamma})/I_{1-m}(2\sqrt{2\gamma})] \quad (4)$$

($m \leq 1$ where $I_p(x) = i^{-p}J_p(ix)$ and J_p is a Bessel function of the first kind).

For small V , $\gamma < 1$, and $k_0 = 0$, eq. (4) becomes approximately

$$\bar{n} = 1/2 + (V/2k_t\tau) = (\rho/r)(dV/dt) \quad (5)$$

where ρ is the density of the polymer and r is the rate of polymerization per free radical (g./cc.).

Equation (5) assumes that the rate of growth per particle is proportional to the number of growing chains per particle. Solving this with the conditions, $V = 0$ at $t = 0$, gives

$$V = k_t \tau (\exp\{rt/2k_t \tau \rho\} - 1) \quad (6)$$

For large values of $k_t \tau$, corresponding to rapid termination within a particle compared with the rate of entry of free radicals, this reduces to $V = rt/2\rho$, case 2 of Smith and Ewart. In this treatment, τ , the time between entries of free radicals is assumed to be constant, though this is not strictly correct, since τ will depend to some extent on the size of the polymer particles, being smaller for the larger particles.

Number of Particles Varying and Interval τ Not Constant

In this case we may not assume that τ is a constant, but that it is a function of the number of particles, and therefore of time. If the rate of production of free radicals is p , and if all these radicals enter the particles, then $\tau = N/p$. By considering the change in rate when two particles collide, we may derive an expression for the overall rate of polymerization.

Suppose two particles of volumes V_1 and V_2 coalesce. Before they coalesce, the rate of polymerization of the two is

$$dP_{12}/dt = r[1 + (V_1 + V_2)p/2k_t N] \quad (7)$$

After coalescence the rate of polymerization is

$$\begin{aligned} \frac{dP_{12}}{dt} &= \frac{r}{2} \left[1 + \frac{(V_1 + V_2)p}{k_t(N-1)} \right] \\ &\doteq \frac{r}{2} \left[1 + \frac{(V_1 + V_2)p}{k_t N} \right] \quad \text{for } N \gg 1 \end{aligned} \quad (8)$$

Therefore the average change in rate upon coalescence of two particles is

$$-\Delta dP/dt = r/2 \quad (9)$$

and this change is independent of the size of the particles for a system containing many small particles (i.e., $V/k_t \tau < 1$).

We may write the rate of polymerization of a system containing N_0 particles originally as

$$\begin{aligned} dP/dt &= N_0 \cdot (\text{rate for a single particle which has not coalesced}) \\ &\quad - (r/2) \cdot (\text{number of coalescences}) \end{aligned} \quad (10)$$

or as eq. (11):

$$dP/dt = N_0 \rho (dV/dt) - rN_c/2 \quad (11)$$

Here

$$\begin{aligned} N_c &= N_0 - N = N_0 - N_0/y \\ &= N_0(y - 1)/y = BN_0^2(t - t_0)/y \end{aligned}$$

Before any coalescence ($t < t_0$), we have the result

$$\begin{aligned} dP/dt &= (N_0 r/2)(1 + V/k_t \tau) \\ &= \rho dV/dt \\ &= (N_0 r/2)(\exp\{rpt/2k_t \tau N_0 \rho\}) \end{aligned} \quad (12)$$

To solve for the rate of polymerization when $t > t_0$, we must use eq. (5) and replace τ by N_0/py , since τ now varies with time. Therefore,

$$\begin{aligned} dV/dt &= (r/2\rho)(1 + pVy/k_t N_0) \\ &= BN_0(dV/dy) \end{aligned} \quad (13)$$

At $t = t_0$, $V = V_{t_0}$, and, setting $A^2 = pr/4k_t B\rho$,

$$\begin{aligned} V &= (r/2BA\rho) \exp\{A^2 y^2/N_0^2\} \\ &\quad \int_{A/N_0}^{Ay/N_0} \exp\{-u^2\} du \\ &\quad + V_{t_0} \exp\{A^2(y^2 - 1)/N_0^2\} \end{aligned} \quad (14)$$

Therefore, the overall rate of polymerization for a system with coalescence and an increasing number of free radicals per particle is

$$\begin{aligned} dP/dt &= rN_0/2y + rAy \exp\{A^2 y^2/N_0^2\} \\ &\quad \int_{A/N_0}^{Ay/N_0} \exp\{-u^2\} du \\ &\quad + 2A^2 B\rho V_{t_0} y \exp\{A^2(y^2 - 1)/N_0^2\} \end{aligned} \quad (15)$$

Validity of Equation (15)

Assumptions made in deriving the equation for the rate of polymerization above, of course limit the range over which it may be applied. In the application of the Smith-Ewart theory, four assumptions have been made: the rate of polymerization per free radical is constant, the rate of transfer of free radicals out of particles is zero, the time between entry of free radicals is constant, and the rate of production of free radicals is constant.

Two other approximations have been introduced, here which warrant further analysis. We have assumed that B , the coagulation rate constant, is zero before the micelles disappear, and is some positive constant later. There seems to be no *a priori* reason for B to remain constant after t_0 , however, and it is probably affected by the concentration of surfactant on the surface of the particles and changes with the degree of polymerization. Thus for a hard polymer, B probably decreases to zero by the time fraction is over.

We see, therefore, that B probably varies, reaching a maximum at some time during the reaction. Since it seems impossible to treat this analytically, we hope a suitable average value of B can be found.

The approximation that $\bar{n} = (1/2)(1 + V/k_i\tau)$ sets more definite limits on the validity of the equation. This is the limiting form of Stockmayer's equation for $(V/k_i\tau)$ approaching zero. By the time $(V/k_i\tau) = 3$, this limiting form is about 45% too high. The approximation $\bar{n} = 1/8 + aV^{1/2}$ fits over a much larger range of \bar{n} , but was not used since the change in rate upon coagulation would then depend on the size of the particles coagulating, and this makes the equations insoluble for a polydisperse system. By using the first approximation to Stockmayer's equation, the effect of coagulation does not depend on the particle size. We know, however, that the calculated values of the rate must become too high as $V/k_i\tau$ increases above about 1, since eq. (4) gives $\bar{n} = 0.89$ and eq. (5) gives $\bar{n} = 1.0$ at this point.

In the derivation of eq. (9) it was assumed that only the change in rate of the two coalescing particles need be considered. That this is not strictly true can be easily shown.

The rate of polymerization before a coalescence occurs is given by the expression,

$$\begin{aligned} (dP/dt)_1 &= r \sum_{i=1}^N n_i \\ &= (r/2) \sum_{i=1}^N [1 + (V_i/k_i\tau_i)] \quad (7') \end{aligned}$$

in which n_i is the average number of growing chains in the i th particle, V_i the volume of the i th particle and τ_i the average interval between radical collisions with the i th particle.

The rate of polymerization after coalescence is given by the expression,

$$\left(\frac{dP}{dt}\right)_2 = \frac{r}{2} \sum_{i=3}^N \left(1 + \frac{V_1}{k_i\tau'_i}\right) + \frac{r}{2} \left(1 + \frac{V_1 + V_2}{k_i\tau'}\right) \quad (8')$$

in which τ'_i is the value of τ_i after coalescence and τ' is the value of τ_i for the coalesced particle.

The average change in polymerization rate caused by a coalescence is then

$$\begin{aligned} \Delta dP/dt &= -(r/2) + (r/2) \sum_{i=3}^N (V_i/k_i) \\ &\quad [(1/\tau'_i) - (1/\tau_i)] \quad (9') \end{aligned}$$

If $1/\tau_i = p/N$ and $1/\tau'_i = p/(N-1)$,

$$\begin{aligned} \Delta dP/dt &= -(r/2) + (r/2) \left[\frac{p}{k_i N(N-1)} \right] \sum_{i=1}^N V_i \\ &= -(r/2) + (r/N) \sum_{i=1}^{N-1} (\bar{n}_i - 1/2) \end{aligned}$$

$$\text{And } \Delta dP/dt = -(r/2) + r(\bar{n} - 1/2) \quad (9'')$$

It is likely that the probability of radical capture increases with particle radius as predicted by Smith and Ewart.³

In this case,

$$1/\tau_i = p(V_i^{1/2}/\sum_1^N V_i^{1/2})$$

If all particles were the same size before coalescence,

$$\begin{aligned} \Delta dP/dt &= -(r/2) + (2^{1/3} - 2^{2/3})(r/2)(\bar{n} - 1/2) \\ &= -(r/2) + 1.26(r/2)(\bar{n} - 1/2) \quad (9''') \end{aligned}$$

This means that eq. (9) predicts a rate which is too low at all values of n greater than $1/2$. Since the approximation, $\bar{n} = 1/2[1 + (V/k_i\tau)]$, predicts a rate which is too large with an error which increases with \bar{n} , the two effects tend to offset each other and to increase the range of validity of eq. (15).

Equation (15) also assumes that the monomer-polymer particle is homogeneous, i.e., that the reaction can take place throughout the particle, and not merely in a surface layer. For vinylidene chloride polymers, this is almost surely not true,⁶ but the assumption seems necessary to get a general solution for the rate.

In sum, the expression presented should approximate the rate of emulsion polymerizations, with the qualifications mentioned. It reduces to the proper constant rate of Smith and Ewart when A and B are zero. It contains two constants, A and B , which may be determined experimentally by electron micrography, photocatalysis, or in other ways; but when once fixed, they should permit calculation of the rate over wide variations of surfactant and catalyst concentrations. The other quantities in the final equation, r , N_0 , time, and amount of polymer at the critical micelle concentration, can be determined more easily. In the following section the polymerization data previously obtained¹ are examined for a few cases and compared with curves constructed from the calculated values.

TABLE I
Summary of Data for Polymerization of Vinylidene Chloride
 $r = 4.95 \times 10^{-18}$ (g./min.); $B = 1.4 \times 10^{-19}$ (120 ml./min.)

Run	[C], g./120 ml.	[Sf], g./120 ml.	$N_0, \times 10^{-16}/$ 120 ml.	$A, \times 10^{-16}/$ 120 ml.	$P_0,$ g./120 ml.	$t_0,$ min.	$(P_{\max.} - P_0),$ g./120 ml. ^a	From ref. 1
1 ^b	0.075	2.0	9.60	2.16	8.0 ^c	38	35	Fig. 3, Curve 6
2	0.15	2.0	14.6	3.64	7.5 ^c	28	42.5	5
3	0.225	2.0	18.6	5.04	4.4	15	36	4
4	0.15	0.500	5.84	3.64	2	10	12	Fig. 2, Curve 6
5	0.15	1.0	9.31	3.64	3.5	17	21	5
6	0.15	3.0	19.0	3.64	15.0 ^c	34	57.5	3

^a Approximate limit of validity of theoretical curves (where $V/k_t\tau \doteq 1$).

^b Number of particles measured by electron photomicrography.

^c Increased over 6.2, 6.0, and 10, respectively, to obtain better fit. Also, t_0 was increased correspondingly.

CORRELATION WITH EXPERIMENTAL RESULTS

It has already been shown experimentally¹ that the average rate in Stage I (i.e., before micelles disappear) is given by the expression

$$\text{Initial rate} = a[\text{Sf}]^{0.60}[\text{C}]^{0.60} \quad (16)$$

where a is a constant and [Sf] and [C] are the concentrations of surfactant and catalyst, respectively. We then assumed that the initial rate is proportional to the number of particles at time, t_0 , or

$$N_0 = b[\text{Sf}]^{0.60}[\text{C}]^{0.60} \quad (17)$$

Electron photomicrographs were made of samples taken during one run, thus providing a direct means of determining N . The times were observed carefully at which the unreacted monomer began to form large droplets; by surface tension measurements these times were found to coincide with the disappearance of micelles from the reaction mixtures. From the observed values of N in a single experiment for a given surfactant and catalyst concentration, a rough estimate of B was made, and from the value of N_0 , the constant b in eq. (17) was computed. And from this constant the N_0 's for other runs were calculated.

If the rate of production of free radicals is taken proportional to the catalyst concentration to the 3/2 power,

$$p = c[\text{C}]^{3/2} \quad (18)$$

as has been suggested¹⁶ to explain the persulfate-catalyzed polymerization of vinyl acetate, eq. (17) is brought into accord with the Smith-Ewart estimates of N_0 .

The constants A and B were determined by the best fit of the theoretical curve to the experimental run number 5. Since the constants cannot be

TABLE II
Sample Calculation for Run 4^a

$t - t_0$	y	Term 1 ^b	Term 2 ^b	Term 3 ^b	dP/dt	$P - P_0$
0	1	0.144	0	0.0127	0.157	0
20	1.164	0.124	0.013	0.017	0.154	3.11
60	1.491	0.097	0.060	0.032	0.189	9.97
100	1.818	0.080	0.158	0.056	0.294	19.63
140	2.143	0.067	0.368	0.105	0.540	36.31
180	2.47	0.058	0.840	0.227	1.125	69.61

^a $N_0 = 5.84 \times 10^{-16}$; $\rho V t_0 = 3.43 \times 10^{-17}$ g.; $A^2/N_0^2 = 0.388$; $P_{\max} - P_0 = 12.0$ g.

^b These are the terms of the right side of eq. (15).

found algebraically from eq. (15), however, the values given here are merely the best values which could be found by an iterative procedure. Once fixed by this calibration curve, B was kept constant, and A was varied with catalyst concentration only through the relationship (18) and the definition in eq. (13) in calculating the other five theoretical curves.

Table I presents a summary of the data for six experiments, and Table II summarizes a sample calculation (for Run 4) of the sort on which the figures are based.

In Figure 1 are plotted for six runs (Table I) the experimental points relating polymer conversion to time after t_0 , and the corresponding values calculated from eq. (15). Also shown is the corresponding curve from Smith-Ewart values. The approximate limit of validity of the application of eq. (15) is indicated by an arrow on each figure ($Vpy/k_t N_0$ equals approximately unity).

DISCUSSION

The calculated and experimental points fit a single curve quite well. Agreement is better in all

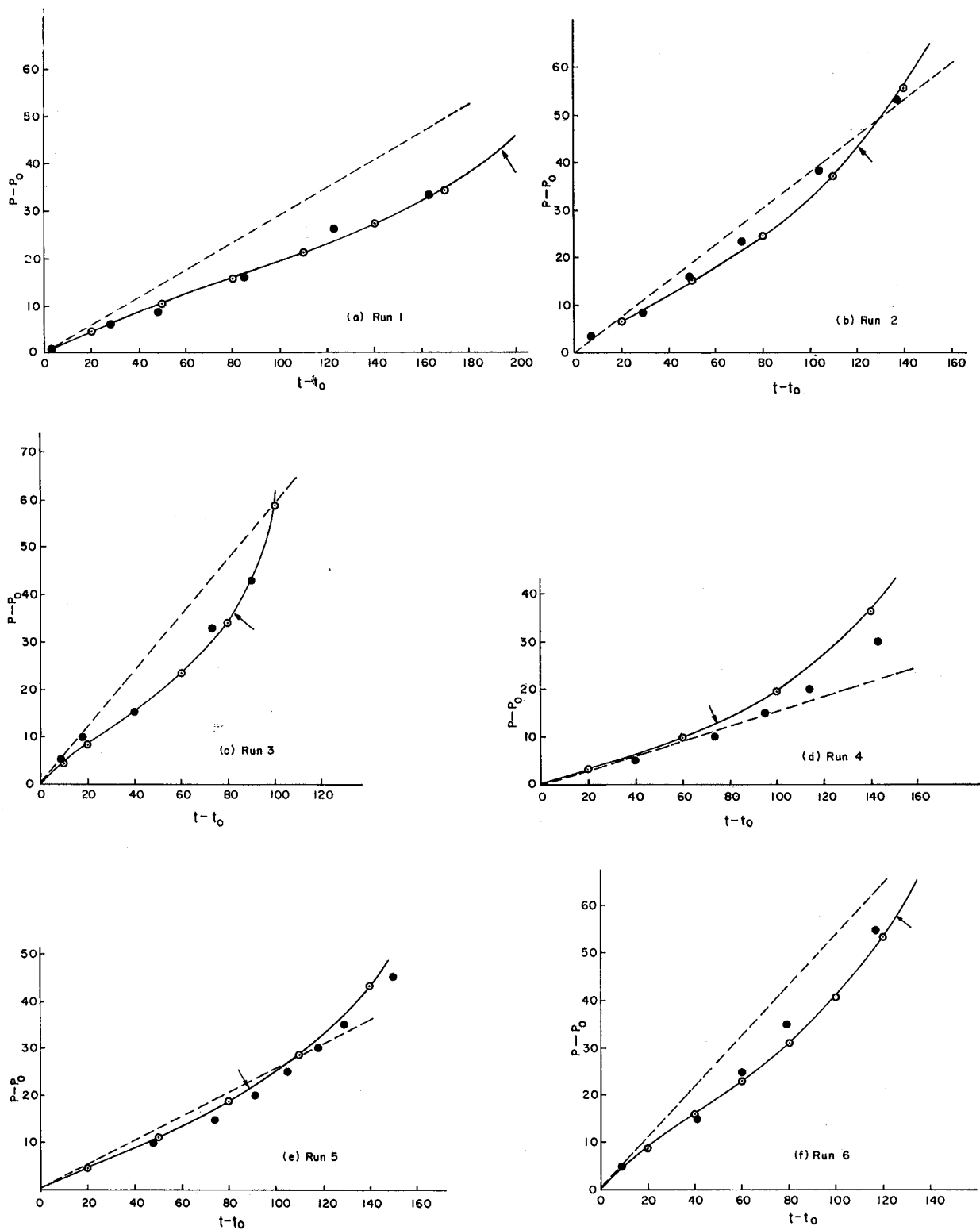


Fig. 1. (a)-(f). Rate of formation of polymer as a function of time (measured from the apparent disappearance of micelles): (●) experimental values; (○) values calculated by theory presented in this paper. The broken curve is the result predicted by Smith-Ewart theory. The arrow indicates the approximate limit of validity which our theory permits.

cases with the present hypothesis than with Smith-Ewart theory applied to the vinylidene chloride case.

In the present treatment it has been assumed that coalescence of polymer particles begins when the surfactant micelles disappear, and that this time coincides experimentally with the cessation of foaming. This is probably not true, and as noted in Table I, the values of P_0 and t_0 were increased in three instances to secure better agreement between the curves and experiment. It should be noted that experimentally it is not simple to say unequivocally at what precise minute foaming ceases.

Furthermore it can be shown that when micelles disappear only approximately half of the surfactant forms a protective layer on monomer droplets and the balance is available for stabilization of polymer particles. At any degree of conversion x the total surface area of polymer particles A_p , is equal to $3V_p/l_p$, where V_p and l_p are the volume and radius, respectively, of a polymer particle, provided all particles have the same size. Similarly for the monomer droplets, $A_m = 3V_m/l_m$. Hence, the ratio of surface areas of monomer and polymer in the dispersion is given by the following expression (where ρ_p and ρ_m are the respective densities).

$$A_m/A_p = (\rho_p/\rho_m)[(1-x)/x](l_p/l_m) \quad (19)$$

For polymerization runs with 2% sodium lauryl sulfate present, foaming ceased at about 6% conversion.¹ Taking this fact and the ratio of densities of polymer to monomer as 1.3, $A_m/A_p = 20l_p/l_m$. From the known total volume of monomer present at 6% conversion and the density, and for a value of N_0 from Run 1 of Table I (9.60×10^{16}) the average radius of a polymer particle is found to be 230 Å. If the Flory value¹⁷ for monomer droplets is used (diameter = 10^4 Å.), $A_m/A_p \doteq 1$, i.e., when micelles disappear the surfactant is about equally distributed between monomer droplets and polymer particles. Coalescence should begin only when the polymer particles become starved for stabilizer, and this appears not to occur until some time after foaming stops, possibly at the end of Stage II.

The value of B used is about five times larger than the minimum estimated from the electron photomicrographs. This seems to indicate that some other factor than coalescence is operating to cause the decrease in rate which has been ob-

served in Stage II. A full discussion of other factors will be given later.⁸

The extent of agreement between experiment and theory over a rather wide range of surfactant and catalyst concentrations argues that coalescence of polymer particles and increased rate of polymerization per particle influence the overall rate of polymerization, though they are not alone sufficient to explain the slowdown observed in Stage II. These phenomena may, however, explain the dependence on surfactant and catalyst concentration observed in Stage III.

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Synopsis

In seeking an explanation for the unusual kinetics observed in the persulfate-catalyzed emulsion polymerization of vinylidene chloride, the role of particle coalescence has been examined. A theory has been proposed and the predicted results have been compared with experiment. Development of the theory assumes that after excess surfactant (sodium lauryl sulfate) has been removed from the solution

by adsorption on the surface of growing polymer particles, coalescence commences as a second-order process with an invariant specific rate constant, and that the rate of polymerization per particle increases linearly with particle volume (it is assumed that more than one growing chain can exist in a particle). The equations derived involve two adjustable parameters: B , a measure of the coalescence rate which is fixed from best fit of one experimental resin, and A , a function of the catalyst concentration. The equations predict a minimum in the conversion rate at some time after the coalescence starts. Data for the third stage of the persulfate-catalyzed polymerization of vinylidene chloride can be explained by this theory. It is shown that particle coalescence alone cannot completely explain all of the observations which have been made on this system, however; in particular, the extent of slowdown in Stage II greatly exceeds that predicted by theory.

Résumé

En cherchant une explication pour la cinétique irrégulière observée au cours de la polymérisation en émulsion du chlorure de vinylidène catalysée par le persulfate, on a examiné le rôle de la coalescence des particules. On a proposé une théorie dont les résultats prévus ont été comparés à l'expérience. Le développement de la théorie nous a montré qu'après disparition de l'excès de l'émulsifiant (laurylsulfate de soude) par adsorption à la surface des particules polymériques croissantes, la coalescence commence comme un processus du second ordre, avec une vitesse invariante, spécifique et constante. A ce point la vitesse de polymérisation augmente linéairement avec le volume de la particule (on peut admettre qu'il peut y avoir plus d'une chaîne en croissance dans une particule). L'équation dérivée comprend deux paramètres ajustables: B est une mesure de la vitesse de coalescence qu'on a fixé en choisissant une valeur qui s'accordait le mieux aux résultats expérimentaux d'une résine, A est une fonction de la concentration en catalyseur. Les équations prévoient un minimum pour la vitesse de conversion peu après le début de la coalescence. Les données expérimentales pour la

troisième étape de la polymérisation du chlorure de vinylidène catalysée par le persulfate peuvent être expliqués par cette théorie. On a démontré que l'effet de la coalescence de la particule seule n'explique pas complètement toutes les observations faites sur ce système. Néanmoins l'importance de la diminution de vitesse dans l'étape II surpasse fortement celle prévue par la théorie.

Zusammenfassung

Um eine Erklärung für die ungewöhnliche, bei der persulfatkatalysierten Emulsionspolymerisation von Vinylidenchlorid beobachteten Kinetik zu finden, wurde die Rolle der Partikelkoaleszenz untersucht. Eine Theorie wurde aufgestellt und die theoretischen und experimentellen Ergebnisse verglichen. Bei der Entwicklung der Theorie wurde angenommen, dass nach Entfernung des überflüssigen Emulgators (Natriumlaurylsulfat) aus der Lösung durch Adsorption an der Oberfläche der wachsenden Partikeln die Koaleszenz als ein Prozess zweiter Ordnung mit einer invarianten, spezifischen Geschwindigkeitskonstanten einsetzt und dass die Polymerisationsgeschwindigkeit per Partikel mit dem Teilchenvolumen linear zunimmt (es wird angenommen dass mehr als eine wachsende Kette in einem Teilchen vorhanden sein kann). Die abgeleiteten Gleichungen enthalten zwei variierbare Parameter: B , ein Mass für die Geschwindigkeit der Koaleszenz, das durch beste Angleichung eines experimentellen Polymeren festgelegt wird und A , eine Funktion der Katalysatorkonzentration. Die Gleichungen lassen ein Minimum der Umsatzgeschwindigkeit nach einer gewissen Zeit nach Beginn der Koaleszenz erwarten. Die Theorie kann die Ergebnisse für die dritte Stufe der persulfat-katalysierten Polymerisation von Vinylidenchlorid erklären. Es wird jedoch gezeigt, dass die Partikelkoaleszenz allein nicht alle Beobachtungen an diesem System völlig erklären kann; besonders das Ausmass der Verlangsamung in Stufe II übertrifft das nach der Theorie zu erwartende bei weitem.

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