

Continuous Emulsion Polymerization of Vinyl Chloride

A. R. BERENS, *Corporate Research, The B. F. Goodrich Company,
Brecksville, Ohio 44141*

Synopsis

For batch emulsion polymerizations of vinyl chloride, the reaction rate can be well represented by the empirical expression $dx/dt = k(1 + ax)$, where x is the polymer concentration, and k and a are constants dependent upon initiator concentration and particle number. A simple mathematical model for continuous stirred-reactor polymerizations has been derived from this expression. The model predicts that at short residence times, a steady state of low PVC concentration is reached quickly; with longer residence time, the system more slowly approaches a higher steady-state polymer concentration. Above a critical residence time, equal to $1/ak$, the rate of monomer supply becomes the limiting factor. Experimental data on continuous polymerizations are in good qualitative accord with the predictions of the model using constants fitted to batch-charge data. Quantitative agreement is best when the particle number is large; discrepancies may be attributed to a broader particle size distribution in continuous runs. Particle size measurements show evidence of intermittent particle formation in unseeded continuous runs; continuous seeding narrows the particle size distribution, but it is still broader than in batch charges. The model seems sufficiently valid to yield a number of useful implications about practical aspects of continuous emulsion PVC polymerization.

INTRODUCTION

Continuous polymerization of vinyl chloride in aqueous emulsion systems has been in commercial use for over 30 years,^{1,2} yet the published information about this process consists largely of qualitative accounts of equipment and procedures in the patent literature. It would be very useful to have a method for predicting and correlating the reaction rate behavior of a continuous process in terms of such parameters as monomer, initiator, and emulsifier concentrations and residence time or feed and output rates. One likely reason for the long lack of such a method is that the emulsion polymerization of vinyl chloride does not follow the relatively simple Smith-Ewart Case 2 kinetics which are the basis for most published studies of continuous emulsion polymerizations.^{3,4} Only in the past few years, largely through the work of Ugelstad and co-workers,⁵⁻⁹ has the kinetic behavior of vinyl chloride emulsion polymerizations been thoroughly studied and largely explained. The kinetic relations developed by Ugelstad, particularly the dependence of rate upon particle number and con-

version, are sufficiently complex that their rigorous application to a continuous process will be difficult. In the present paper, we present a simple, empirical relation for predicting the behavior of a continuous system from rate data on batch polymerizations in corresponding recipes.

EXPERIMENTAL

Materials

Vinyl chloride monomer (B. F. Goodrich Chemical Co.) was redistilled and stored under nitrogen. Emulsifiers used were sodium dodecyl sulfate (NaLS; Matheson, U.S.P.) and sodium laurate (NaL; prepared from Eastman White Label lauric acid and analytical-grade NaOH). Potassium persulfate initiator and trisodium phosphate buffer were reagent grade. All aqueous solutions were prepared from oxygen-free distilled water (boiled under nitrogen) and stored and handled under nitrogen.

Apparatus and Procedure

Polymerizations were carried out in a single, stirred, glass autoclave (Ingenieurbureau S.F.S., Zurich) at 50°C. For batch runs, all ingredients except initiator were charged to the N₂-purged, evacuated reactor and preheated to reaction temperature, and then K₂S₂O₈ solution was injected by syringe at time zero. Conversion-versus-time data were obtained from the dried polymer content of weighed latex samples withdrawn by syringe throughout the polymerization.

For continuous runs, the procedure was as follows: Water, emulsifier, and buffer (and seed latex when used) were charged to the evacuated reactor followed by vinyl chloride; these were stirred and preheated to reaction temperature. At time zero, initiator solution was injected into the reactor, and feeding and withdrawal started at once. The feed stream contained water, initiator, emulsifier, buffer, and seed latex in the same proportions as the aqueous phase initially charged to the reactor; this stream was pumped in at a constant rate by a Milton-Roy Minipump from a graduated reservoir. The initial charge of monomer was periodically replenished from a heated reservoir as needed to maintain an excess of free liquid monomer phase throughout the run. The output stream was semi-continuously withdrawn through a valve in the bottom of the reactor and monitored by weight; feed and withdrawal rates were adjusted for PVC contents and so matched as to maintain a constant volume of water in the reactor. Agitation was sufficient that the output stream was representative of the reactor contents. Residence time was varied from run to run by changing either the pumping rate or the volume of water resident in the reactor. The course of the reaction was followed by periodically determining the dried polymer content of samples from the output stream. Particle size measurements were made by electron microscopy.

BATCH POLYMERIZATIONS

Our experimental results in batch-charged emulsion polymerizations are quite consistent with those reported by Ugelstad.^{6,8,9} The polymerization rate accelerates continuously with conversion as long as free liquid monomer is present, although the number of particles per liter of water, N , remains constant after a very early stage. When compared at equal particle number and equal polymer concentration (g PVC per liter H_2O), polymerization rates are proportional to the square root of initiator concentration. For given initiator and polymer concentrations, the reaction rate is increased by an increase in N (smaller particle size), but the effect is much smaller than the first power dependence of the Smith-Ewart Case 2. Polymer concentration-versus-time data for several typical batch runs are shown in Figures 1 and 2 to illustrate the effects of initiator concentration and particle number, the two principal variables controlling the rate of polymerization.

In seeking a mathematical expression of the experimental data, we found that plots of polymerization rate versus polymer concentration (conversion)

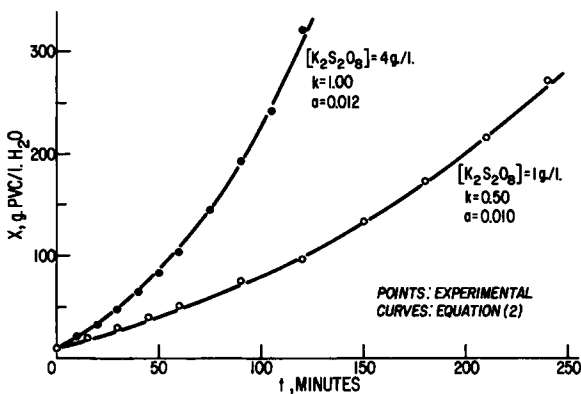


Fig. 1. Yield vs. time, batch polymerizations; $[K_2S_2O_8]$ varied, $N = 5.5 \times 10^{16}/l$.

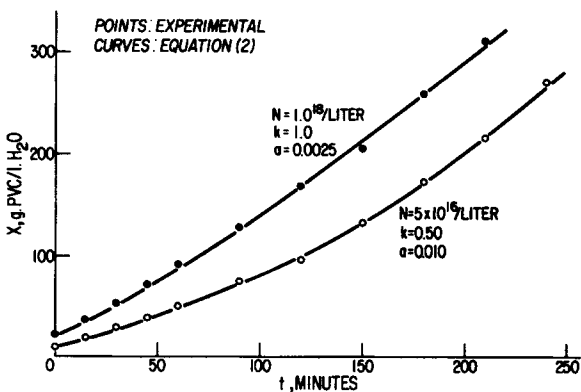


Fig. 2. Yield vs. time, batch polymerizations; N varied, $[K_2S_2O_8] = 1.0 \text{ g/l}$.

for each run are approximately linear, and that both the slope and intercept are proportional to $[\text{K}_2\text{S}_2\text{O}_8]^{1/2}$. Thus, the rate of polymerization may be expressed as

$$\frac{dx}{dt} = k(1 + ax) \quad (1)$$

where x is the PVC concentration (g/l. H_2O), k is the initial polymerization rate, and a is a constant expressing the degree of rate acceleration with conversion. Integration of eq. (1) gives the yield-versus-time expression

$$x = \frac{1}{a} (e^{akt} - 1). \quad (2)$$

We find that this equation, with suitably chosen constants, satisfactorily represents our data, as illustrated in Figures 1 and 2. The constants were evaluated either from the slope and intercept of dx/dt -versus- x plots or by trial fitting directly to x -versus- t data.

For runs at a given N , the change in yield-versus-time curves with initiator concentration is largely expressed by the proportionality of k to $[\text{K}_2\text{S}_2\text{O}_8]^{1/2}$; a changes very little (Fig. 1). For runs at constant $[\text{K}_2\text{S}_2\text{O}_8]$, k increases and a decreases with increasing N (Fig. 2). The exact form of the dependence of a and k upon N is not apparent from our data, but the trends are in qualitative agreement with the results of Ugelstad's studies.^{6,9}

CONTINUOUS POLYMERIZATIONS

Mathematical Model

Let us consider a single stirred vessel operated in continuous manner under the following conditions: (1) The volume of water in the reactor is kept constant at v . (2) An excess free liquid phase of VCl monomer is maintained; i.e., the aqueous, vapor, and polymer phases remain saturated with monomer, and the monomer supply rate is not considered to be a limiting factor. (3) The feed to the reactor consists of water containing dissolved initiator, emulsifier, and buffer, and may contain seed PVC particles at a concentration of x_0 g PVC/l. H_2O . (4) The rates of water feed to, and withdrawal from, the reactor are constant at r l./min. (5) The concentrations of initiator, emulsifier, and buffer are equal in the reactor, feed, and output stream, and are constant during the experiment; only the PVC concentration changes. (6) Mixing is "ideal" in that the concentrations of PVC in the output stream and in the reactor are equal at x g PVC/l. H_2O . We define average residence time $t_r = v/r$.

Under these conditions, if eq. (1) describes the polymerization rate, then the total rate of change in PVC concentration in the reactor is given by

$$\frac{dx}{dt} = \frac{(x_0 - x)}{t_r} + k(1 + ax). \quad (3)$$

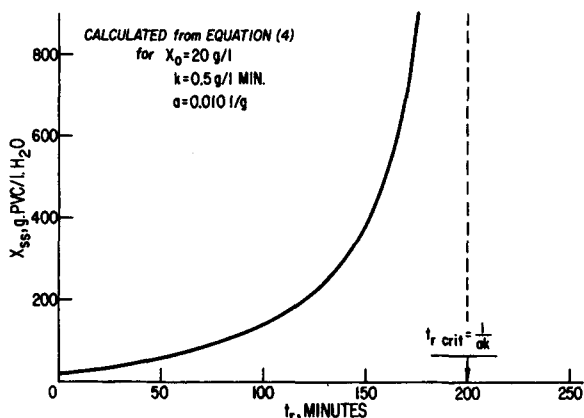


Fig. 3. Effect of residence time t_r on steady-state PVC concentration x_{ss} .

By setting $dx/dt = 0$ and solving for x , an expression is obtained for the steady-state PVC concentration, x_{ss} :

$$x_{ss} = \frac{kt_r + x_0}{1 - akt_r} \quad (4)$$

Rearrangement and integration of eq. (3) yields an equation for the PVC concentration as a function of time:

$$x = \frac{1}{B} [(A + Bx_0)e^{Bt} - A] \quad (5)$$

where

$$A = \frac{x_0}{t_r} + k \quad B = \left(ak - \frac{1}{t_r} \right)$$

Equations (3)–(5) represent a model which should allow the essential characteristics of a continuous emulsion polymerization, under the conditions assumed, to be predicted from the residence time and two constants obtained from a single batch run at the same N and $[K_2S_2O_8]$. The principal features predicted by this model may be illustrated by numerical calculations using values of k and a from a typical batch polymerization. In Figure 3 is shown the relationship between residence time t_r and steady-state PVC concentration x_{ss} , calculated through eq. (4). The model predicts a critical residence time,

$$t_{r \text{ crit}} = \frac{1}{ak} \quad (6)$$

at which x_{ss} becomes infinite. In reality, this means that monomer would polymerize as fast as it was fed; the assumptions of the model could not be met, and the monomer feed rate would control the polymerization rate for $t_r > 1/ak$. Figure 4 shows a series of x -versus- t curves for varied t_r 's cal-

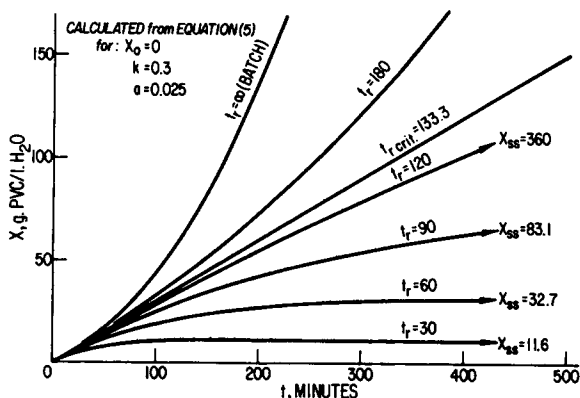


Fig. 4. Effect of residence time on yield-vs.-time curves.

culated from eq. (5). At t_r much below $t_{r, \text{crit}}$, the system rather quickly reaches a steady state of low PVC content, but as t_r approaches $t_{r, \text{crit}}$, the time required to reach the steady state becomes much longer.

The model also suggests that there may be a critical initiator concentration, which would operate in much the same way as $t_{r, \text{crit}}$. For a fixed value of t_r , eq. (4) indicates that x_{ss} would become infinite as k is increased to a critical value,

$$k_{\text{crit}} = \frac{1}{at_r} \quad (7)$$

Since k is proportional to $[\text{K}_2\text{S}_2\text{O}_8]^{1/2}$, the critical initiator concentration for any t_r could be estimated from one batch run to evaluate a and k at a given $[\text{K}_2\text{S}_2\text{O}_8]$ and N . Calculation of x versus t for various values of k at fixed t_r , through eq. (5), gives a set of curves similar to Figure 4. Again, there is a slower approach to higher x_{ss} as the initiator concentration is increased, and above k_{crit} no steady state is reached until the monomer feed rate becomes the limiting factor.

Experimental Results

In Figures 5 and 6 are shown some typical results of continuous polymerization experiments in which the same recipe was run at several different residence times. The similarity to Figure 4 clearly shows that the results agree qualitatively with the behavior predicted by the model.

Good quantitative agreement between experimental results and predictions of the model was also obtained in polymerizations carried out at the high end of the particle number range covered in this work. Figure 7 shows a batch charge and two continuous runs in which an N of approximately 10^{18} particles/l. H_2O was achieved by seeding with 20 g/l. of PVC of about 300 Å number-average particle size. The continuous run x -versus- t curves calculated using k and a fitted to the batch charge agree very well with the observed data.

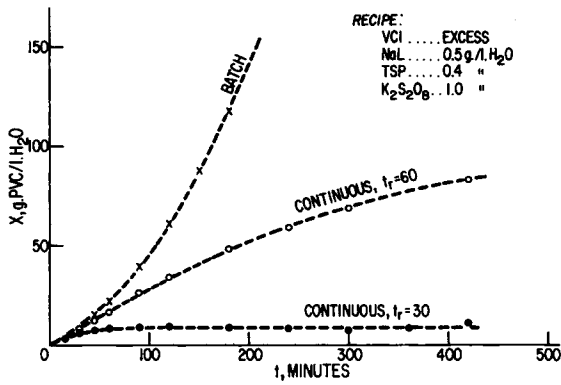


Fig. 5. Experimental yield-vs.-time data, batch and continuous runs, unseeded.

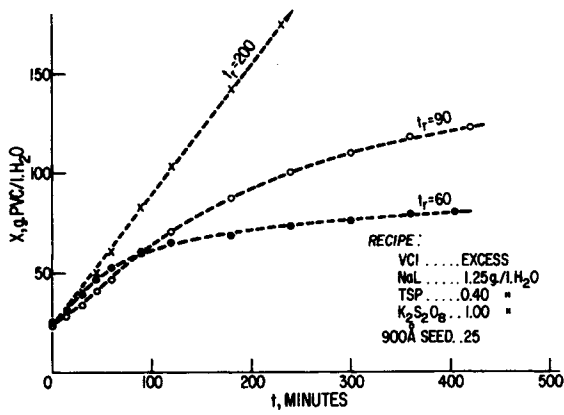


Fig. 6. Experimental yield-vs.-time data, seeded continuous runs.

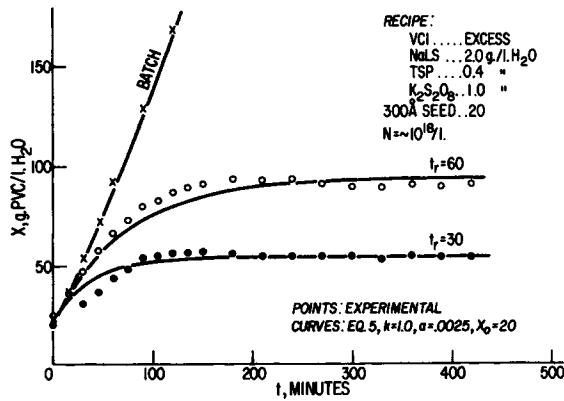


Fig. 7. Comparison of experimental results with model for continuous runs; constants *a* and *k* fitted to batch run.

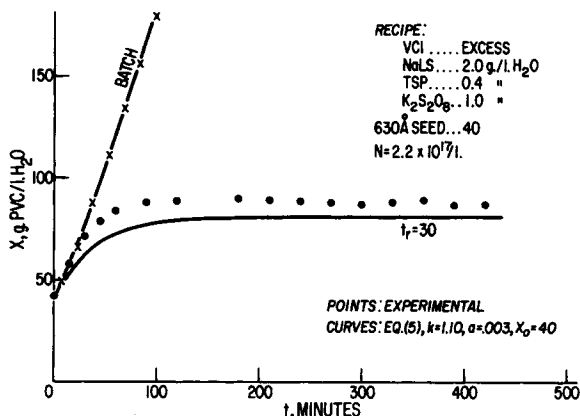


Fig. 8. Comparison of experimental results with model for continuous run; constants a and k fitted to batch run.

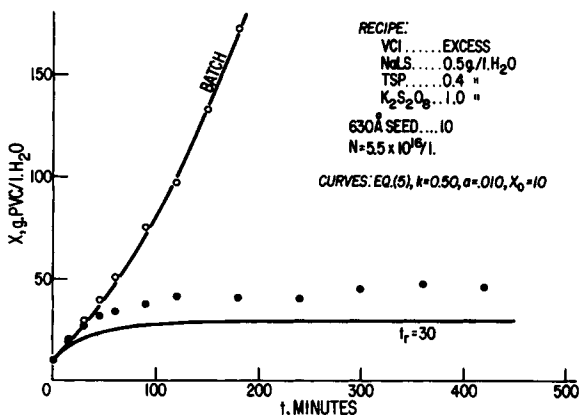


Fig. 9. Comparison of experimental results with model for continuous run; constants a and k fitted to batch run.

In continuous runs at lower N (larger particle-size seed), the observed x_{ss} was generally higher than calculated from k and a fitted to a corresponding batch run. Figures 8 and 9 illustrate such results. The shapes of the observed x -versus- t curves are similar to those calculated, but the PVC concentrations reach higher levels; i.e., the polymerization rate is higher than expected from the batch charge data. The discrepancy appears to become more pronounced at lower N and at longer residence times. A possible explanation is discussed below.

Particle Size Distribution

The results of particle size counts from electron photomicrographs of samples taken at various times from a batch charge and an unseeded and a seeded continuous run are shown in Figures 10, 11, and 12, respectively.

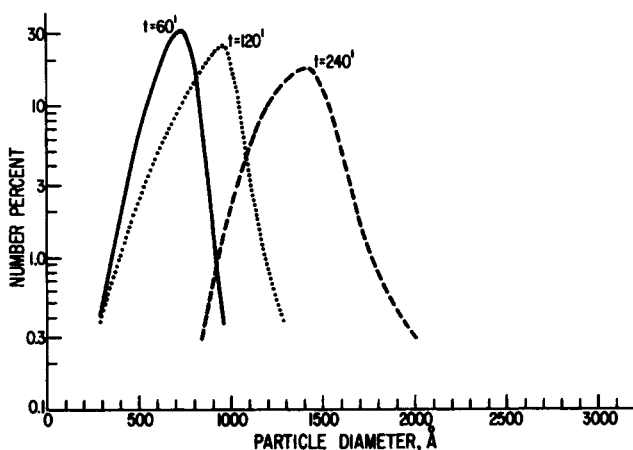


Fig. 10. Particle size distributions at various times in batch run; H_2O , 1 liter; VCl , 400 g; NaL , 0.5 g; TSP , 0.4 g; $\text{K}_2\text{S}_2\text{O}_8$, 1.0 g, no seed.

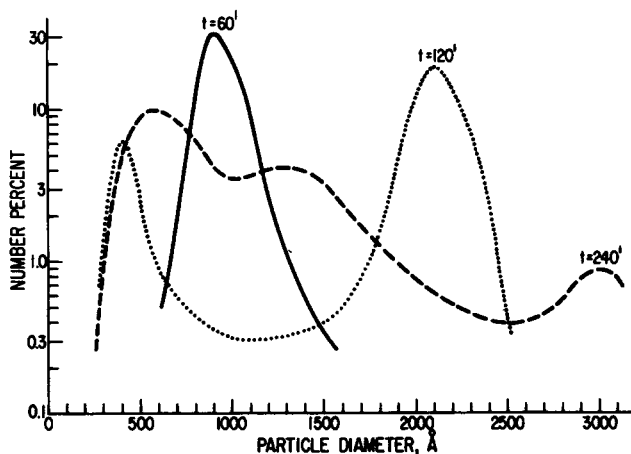


Fig. 11. Particle size distributions at various times in unseeded continuous run; recipe as in Fig. 10; $t_r = 30$ min.

The batch charge shows the normal behavior expected in an emulsion polymerization when particle formation is completed at an early stage. The distribution consists of a single narrow peak, which shifts steadily toward larger size with little broadening as conversion proceeds.

In the unseeded continuous run (Fig. 11), the single narrow peak in the distribution at $t = 60$ min indicates that particle formation occurred during a brief interval early in the run and then stopped. By $t = 120$ min, this peak has shifted to a larger particle size than the corresponding batch-charge sample, reflecting a decrease in N (due to dilution) and greater growth per particle in the continuous case. At the same time, a new narrow peak at small particle size shows that a second generation of par-

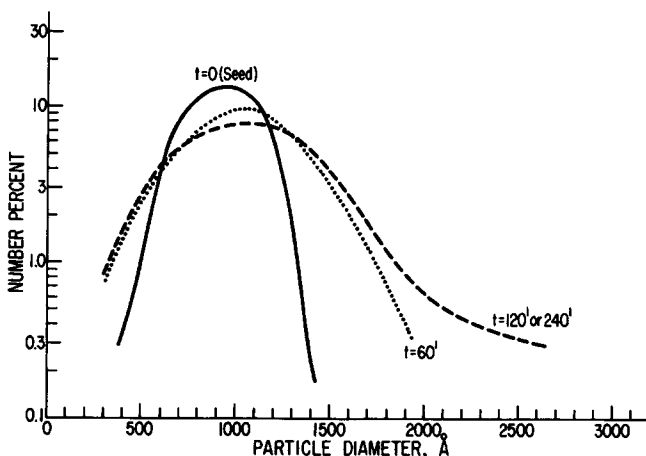


Fig. 12. Particle size distributions at various times in seeded continuous run; recipe as in Fig. 10 plus 25 g 900-Å PVC seed per liter H_2O ; $t_r = 30$ min.

ticles has formed over a short time interval. In the 240-min sample, there are at least three distinct peaks in the distribution, indicating further intermittent formation of new particles. Such cyclic particle formation has also been reported for continuous emulsion polymerization of styrene.¹⁰ It should be noted that the PVC concentration remained essentially constant over the period covered by Figure 11; i.e., the system appeared to be at a steady state, although the particle size distribution fluctuated widely.

In the seeded continuous run (Fig. 12), the particle size distribution shows a single peak throughout. The continuous addition of seed particles prevents new particle formation. The distribution simply broadens, compared to that of the seed, as might be expected due to a distribution of residence times among different particles. The particle size distributions of the 120- and 240-min samples were virtually identical; the steady state here involves consistency of size distribution and number of particles, as well as PVC concentration. The size distribution, however, is clearly broader than in a batch charge.

DISCUSSION

Model Versus Experimental Results

In applying our batch polymerization model, eq. (1), to the continuous system, we make the implicit assumption that the rate of polymerization (at a given initiator concentration) depends only on the number of particles and the PVC concentration. We suggest that the principal reason that continuous polymerization rates are higher than predicted is that the particle size distribution also affects the rate. There is clear evidence in Ugelstad's competitive growth experiments⁹ that larger PVC particles grow more rapidly in weight than smaller ones under otherwise equal

conditions. And our finding that the "acceleration factor" a increases with decreasing N indicates that the rate increase with particle weight is greater at larger particle sizes. Thus, when particle size distribution is broadened (as by changing from batch to continuous mode), we might expect the additional particles at the large end of the size distribution to contribute a rate increase which exceeds the rate decrease from the additional smaller particles; the net result would be an increase in rate with wider distribution. The increasing discrepancy between model and experiment at larger average particle size also seems in accord with this explanation. The good agreement at large N suggests there may be a range of small particle sizes over which rate is relatively insensitive to particle size.

Practical Implications

Granting that our model needs refinement to take care of the effect of particle size distribution, it nonetheless seems sufficiently valid to provide some useful implications about the practical aspects of continuous emulsion PVC polymerization. Perhaps the most significant are those related to the critical residence time. As illustrated by Figure 3, a single stirred reactor would require operation at t_r quite close to the critical value in order to reach a practical steady-state output of several hundred grams PVC per liter H_2O . But in this operating range, x_{ss} is highly sensitive to small variations in t_r ; hence, very close control of feed and withdrawal rates would be required to prevent substantial changes in PVC output. Another problem of operation close to $t_{r,crit}$ is the long time required to reach steady-state conditions; the engineer's rule of thumb that a steady state is reached in $t = 3 t_r$ does not hold true in this case. Similar comments apply to operation with k close to k_{crit} .

Operation of a continuous reactor at $t_r > t_{r,crit}$, or $k > k_{crit}$, so that the monomer feed controls the polymerization rate, would avoid the control problem of operating just below critical conditions, but another practical problem then would be likely. Under this condition, the concentration of monomer in the PVC particles would be reduced below the level found in the presence of excess liquid monomer—the particles would be "monomer starved," i.e., the monomer concentration would continually be similar to that found only at high conversion in a batch charge. It has been recognized for some time that high conversion leads to decreased thermal stability of PVC.¹¹ We have recently suggested¹² that this effect may be due to an increase in tertiary-chlorine branch points, with increasing polymer/monomer ratio, resulting from copolymerization between VCl and unsaturated chain ends of PVC. Thermal instability from this source might then be introduced throughout a continuous polymerization run under "monomer starved" conditions. That these conditions may occur in commercial operations is suggested by the observation² that continuous-process emulsion PVC is less heat stable than batch process products.

Some other practical inferences may be drawn by applying our model to the comparison of batch and continuous systems, or different configurations of continuous systems. For example, it can be shown that, for a given N , $[K_2S_2O_8]$, and final x , the steady-state PVC output of a single continuous stirred reactor would exceed the average production rate of a batch reactor of the same size, even without allowing for the down time between batches. The behavior of a number of continuous reactors operated in series can be modeled by eqs. (3)–(5) with the output x for one reactor becoming x_0 for the next. The model then indicates that the polymerization rate would increase in each succeeding reactor in the series if the residence time were the same in each. It also can be shown that for a given total reactor volume and total residence time, with other factors equal, the productivity of a single continuous stirred reactor would be greater than that of a multiple-reactor series. The series of reactors might have some advantages, however: Control might be less critical, since each reactor could be operated well below the critical residence time; particle size distribution would be narrower, due to the narrower distribution of particle residence times compared to a single reactor. Hence, the quantitative predictions of the model might be more closely approached.

Further experimental work directed toward refinement of this model and verification of its consequences would be of great interest.

The author wishes to express his appreciation to Mr. S. A. Oxenrider for skilled experimental assistance, and to The B. F. Goodrich Company for permission to publish this work.

References

1. R. D. Dunlop and F. E. Reese, *Ind. Eng. Chem.*, **40**, 654 (1948).
2. N. Platzer, *Ind. Eng. Chem.*, **62**, 6 (1970).
3. A. A. J. Feast, *Rep. Progr. Appl. Chem.*, **56**, 45 (1971).
4. A. W. DeGraff and G. W. Poehlein, *J. Polym. Sci. A-2*, **9**, 1955 (1971).
5. J. Ugelstad, P. C. Mork, and J. O. Aasen, *J. Polym. Sci. A-1*, **5**, 2281 (1967).
6. J. Ugelstad, P. C. Mork, P. Dahl, and P. Rangnes, *J. Polym. Sci. C*, **27**, 49 (1969).
7. J. Ugelstad and P. C. Mork, *Brit. Polym. J.*, **2**, 31 (1970).
8. J. Ugelstad, H. Lervik, B. Gardinovacki, and E. Sund, *Pure Appl. Chem.*, **26**, 121 (1971).
9. J. Ugelstad, H. Flogstad, F. K. Hansen, and T. Ellingson, Preprints IUPAC Symposium on Macromolecules, Vol. I, Helsinki, 1972, pp. 273–278.
10. S. Omi, T. Ueda, and H. Kubota, *J. Chem. Eng. Japan*, **2**, 193 (1969).
11. W. I. Bengough and H. M. Sharpe, *Makromol. Chem.*, **66**, 31 (1963).
12. A. R. Berens, *Polym. Preprints*, **14** (2), 671 (1973), ACS National Meeting, Chicago, Aug. 27–31, 1973; *Polym. Eng. Sci.*, in press.

Received January 24, 1974

Revised February 4, 1974