

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### A Study of Emulsion Polymerization Kinetics by the Method of Continuous Monomer Addition

R. A. Wessling<sup>a</sup>; D. S. Gibbs<sup>b</sup>

<sup>a</sup> Physical Research Laboratory, <sup>b</sup> Designed Products Research, The Dow Chemical Company, Midland, Michigan

**To cite this Article** Wessling, R. A. and Gibbs, D. S.(1973) 'A Study of Emulsion Polymerization Kinetics by the Method of Continuous Monomer Addition', *Journal of Macromolecular Science, Part A*, 7: 3, 647 – 676

**To link to this Article:** DOI: 10.1080/00222337308061163

**URL:** <http://dx.doi.org/10.1080/00222337308061163>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## A Study of Emulsion Polymerization Kinetics by the Method of Continuous Monomer Addition\*

R. A. WESSLING

Physical Research Laboratory

and

D. S. GIBBS

Designed Products Research  
The Dow Chemical Company  
Midland, Michigan 48640

### ABSTRACT

The differences in the kinetics of emulsion polymerization between nonswelling and swellable latex particles were explored in an attempt to define the locus of polymerization. The systems studied included vinylidene chloride, which forms a nonswelling particle, and mixtures of vinylidene chloride and butyl acrylate, which copolymerize to form a swellable particle. The basic experiment involved growing a seed latex by adding monomer at a constant rate. At low feed rates the rate of polymerization  $R_p$  was controlled by the rate of monomer addition  $R_a$ . The data fit

---

\*Presented at the symposium on "Emulsion Polymerization" at the 6th Great Lakes Regional Meeting of the American Chemical Society, Michigan Technological University, Houghton, Michigan, June 22-23, 1972.

the equation  $R_p = KR_a$  where the proportionality constant had an average value of 0.91.  $K$  was not dependent on monomer composition and appears to be a constant characteristic of the monomer addition process. In the range where this relationship holds, the reaction runs starved, i.e., monomer is consumed almost as fast as it enters the reactor. At higher rates of addition the reaction floods and excess monomer in the form of droplets can be detected. In this condition the rate starts out at a lower value but increases with conversion.  $R_p$  is not controlled by  $R_a$  but does depend on monomer composition.

No major differences were found between the behavior of swelling and nonswelling systems. Neither followed the kinetics expected if the Smith-Ewart theory were applicable. The results argue strongly that polymerization takes place at the particle-water interface or in a surface layer on the polymer particle.

## INTRODUCTION

Several aspects of the mechanism of emulsion polymerization have been investigated using vinylidene chloride (VDC) as a model system. Our primary objective was to show how the kinetics were influenced by the locus of reaction, whether in the particle or on its surface. The identification of the reaction site in emulsion polymerization is a problem of long standing that has received less attention than other features of the mechanism.

Part of the problem is that emulsion polymerization in its usual form, i.e., batch reaction of styrene at high temperatures and high rate, is a complicated process both experimentally and theoretically.

We have followed an experimental approach, the controlled monomer addition emulsion polymerization of VDC, which was designed both to simplify the process and to allow us to predetermine the locus of reaction. We do this by isolating the growth process from the seed formation step. A seed latex is first prepared and characterized. The seed is then grown to larger size by metering the reactants into the kettle at constant rate. In this way the concentration of monomer can be controlled throughout the reaction, whereas in the typical batch reaction all of the monomer is introduced in the initial charge.

The separate preparation of seed latex to facilitate growth studies has been well demonstrated in emulsion polymerization research [1-3]. But the use of controlled monomer addition techniques in the kinetic studies has not been widely explored, even though it is a common practice in the commercial preparation of latexes. The limited data

available indicate that even styrene does not follow the Smith-Ewart theory [4] under these conditions. Several possible explanations have been put forth. Gerrens [5] suggests that when the reaction is starved for monomer, the high particle viscosity may allow an increase in the number of radicals per particle. Krackler and Naidus [6] suggest that a concentration gradient is set up in the particle such that the experimentally derived average monomer concentration is less than that at the reaction site. This in turn leads to the postulate that polymerization takes place on the surface of the latex particle. Recent studies of latex particle morphology suggest that the latter mechanism may be true for emulsion polymerization in general [7].

The above results emphasize the value of being able to control the solubility of monomer in the polymer. Combinations of VDC and butyl acrylate (BA) are ideally suited for this purpose. VDC is insoluble in PVDC because of the latter's high crystallinity [8]. But incorporation of 10% or more of BA into the copolymer renders it amorphous and readily swellable by the monomer mixture [9]. The use of these monomers is further justified by the fact that they react nearly randomly,  $r_1 = 0.88$ ,  $r_2 = 0.83$ , and have about the same solubility in  $H_2O$  as styrene.

Unfortunately, even the kinetics of the batch emulsion polymerization of VDC are not well defined. The particle formation stage follows the pattern predicted by the Smith-Ewart theory, but there is some confusion over what takes place during the growth stage. Wiener [10] reported that conversion after the seed reaction increased linearly with time. He was able to analyze his results in terms of the Smith-Ewart theory even though the monomer in this case was insoluble in the polymer. He also reported a surprisingly high solubility of monomer in the latex that was very dependent on particle size.

Tkachenko and Khomikovskii [11] studied the growth stage in a system kept saturated with monomer. At low rates of polymerization they observed the same behavior as Wiener, but reactions with high initial rates stopped temporarily at low conversion and then accelerated to a constant but even higher final rate.

Hay et al. [12-14] in a more recent study observed the same pattern of behavior. They showed that the kinetics at high reaction rates were sensitive to stirring rate. The drop in rate correlated with the breaking of the monomer emulsion which suggested a sudden change in mechanism from normal to diffusion-controlled reaction. However, at low rates of polymerization with adequate stirring there was no region of constant rate as predicted by the Smith-Ewart limiting case.

## THEORY

Emulsion polymerization falls into the general class of heterogeneous reactions. The latter are defined as reactions involving two or

more phases which vary in proportion during the reaction. In the usual case the polymer is present as a dispersed phase which increases in volume during the reaction. Emulsion polymerization is a special case of heterogeneous polymerization in which the polymer phase is in the colloidal state. Therefore, particle size and charge can be expected to play an important role.

In general, reaction may occur in any phase or at the interface. Theories for emulsion polymerization are derived in part by assigning the reaction to a specific site. The basic models that can be used include the following:

1. Polymerization in a monomer swollen particle.
2. Polymerization in solution followed by precipitation of the polymer onto a particle surface.
3. Polymerization at the interface or on the surface of the particle.

Typically a batch emulsion polymerization can be subdivided into three stages: particle formation, particle growth, and finishing [15]. This is illustrated by means of a conversion-time curve in Fig. 1.

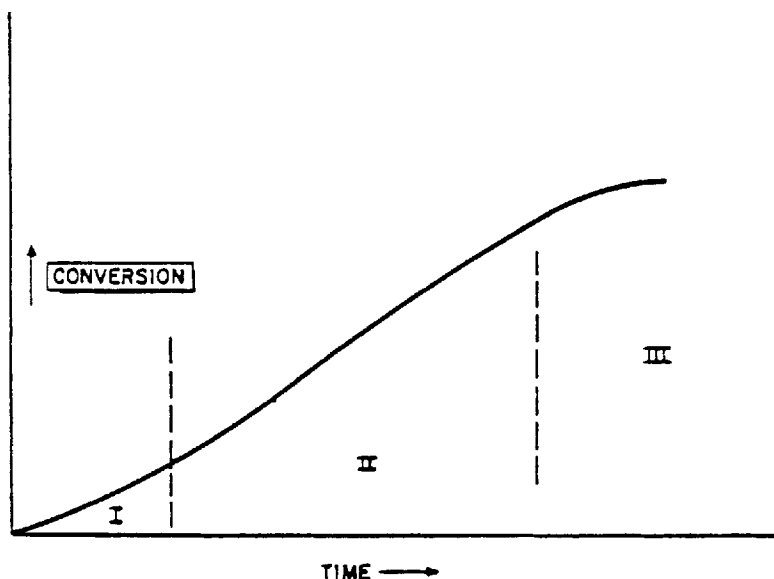


FIG. 1. Schematic illustration of the stages in emulsion polymerization.

Since we are dealing exclusively with seeded reactions, Stage I is of no concern. Stages II and III both involve further polymerization without change in the number of particles. The distinction between them lies in the fact that excess monomer in the form of droplets is present in Stage II. The droplets supply monomer to the particle as polymerization proceeds. The distinction between Stages II and III becomes vague in a monomer addition recipe. The level of monomer in the latter case is controlled externally by the feed rate.

The basic kinetics expressions for free radical polymerization can be applied to heterogeneous reactions provided the concentrations are properly specified. The governing equation for the rate of conversion in the growth stage in emulsion polymerization is

$$R_p = \frac{k_p}{M_0} \frac{MR}{V} \quad (1)$$

where  $R_p$  = the rate of conversion in units of  $t^{-1}$ ,  $M_0$  = moles of monomer added to the reaction,  $M$  = moles of monomer at the reaction site,  $R$  = moles of radicals at the reaction site, and  $V$  = volume of reaction site.

Further interpretation requires a description of the reaction zone. Smith and Ewart [16] adopted Model 1 and obtained the expression

$$R_p = k_p Q[M]N/M_0 \tilde{N} \quad (2)$$

where  $Q$  = the number of radicals per particle,  $[M]$  = monomer concentration in the particle,  $N$  = the number of particles, and  $\tilde{N}$  = Avogadro's number. In the limit of small particle size,  $Q = 1/2$ .

Assuming that  $[M]$  does not change significantly during a reaction, the Smith-Ewart theory predicts a constant rate in the growth stage if the particle size is small and  $N$  is constant. Monomers which are sparingly water soluble and compatible with their polymers exhibit such behavior. Under some circumstances, VDC apparently does likewise, but in this case the constant rate must result from factors other than those suggested by the Smith-Ewart model.

VDC is substantially insoluble both in the aqueous phase and in the polymer; yet growth of the polymer particles takes place. Therefore, the surface model is the only physically meaningful model.

The general application of the surface model to VDC polymerization has been described in a previous paper [17]. The same kinetic scheme applies to emulsion polymerization. In this model the layer of adsorbed monomer on the particle surface is the locus of polymerization. Since the latter is essentially pure monomer, Eq. (1) can be written as

$$R_p = k_p R \cdot / M_0 V_M \quad (3)$$

where  $V_M$  = molar volume of monomer.

If radicals on the particle surface are sufficiently mobile, the same considerations advanced by Smith and Ewart still apply; i.e., as the particle becomes sufficiently small, termination becomes almost instantaneous; therefore, the particle will have either zero or one radical at a time, and

$$R \cdot = N/2\tilde{N} \quad (4)$$

Substitution into Eq. (3) yields the following rate equation for the surface model:

$$R_p = k_p N/2\tilde{N} V_M M_0 \quad (5)$$

The form of this equation is the same as that derived by Smith and Ewart; they differ only in the interpretation of the monomer concentration term. This suggests that a kinetic study cannot be used to identify mechanisms unless the monomer concentration can be determined independently.

The assumption that radicals move freely on the particle surface is open to question. The polymeric radicals are probably immobilized in the rigid polymer phase with only the active ends at the surface [18]. Under these conditions the rate of termination may be slow and the number of radicals per particle could increase sharply with size.

The dependence of radical concentration on size has been calculated for the swollen particle model [19], and a similar analysis could undoubtedly be applied to the surface model. The major complication, however, is that  $k_t$  may not be constant.

Only the limiting case of large spherical PVDC particles with surface saturated with monomer has been analyzed [17]. For this calculation,  $k_t$  was assumed to be constant, and the radical concentration on the polymer surface was calculated by making the steady-state approximation. The exact form of the equation depends on the initiation process, but in general the analysis predicts that  $R_p$  should increase with conversion and be insensitive to the number of particles, i.e.,  $R_p \propto N^{1/2}$ .

The predicted low-order dependence on  $N$  seems to be characteristic of rate equations for heterogeneous reactions which are derived by

making a steady-state assumption. The validity of the latter in a colloidal system is questionable. Nonetheless, the analysis suggests that for a surface model,  $R_p$  should increase with polymer phase surface area but become less sensitive to the number of particles as they become larger.

The surface model assumes that the reaction is confined to a restricted zone at the particle surface. This could be a layer of adsorbed monomer as described above, or even a highly swollen surface. The latter may arise if the polymer forms initially in the amorphous state and then crystallizes. The thickness of the swollen layer in this case would depend on the difference between the rate of polymerization and the rate of crystallization. The monomer concentration in this case would not be  $V_M^{-1}$ . A similar situation could obtain where the rate of diffusion of the polymeric radicals was less than the rate of polymerization.

In the above discussion it has been assumed that monomer is available for reaction either because it is dissolved in the particle or can diffuse to the particle surface. The latter occurs as long as excess monomer is present in the reactor. But when all monomer is imbibed, the concentration at the reaction site must change. Under these conditions the level of monomer can be controlled by feeding in additional monomer. If the feed rate is higher than the polymerization rate, the reaction becomes flooded, i.e., excess monomer is now present; but if feed rate is less than the rate of polymerization, the latter becomes dependent on availability of monomer. The latter condition is commonly referred to as a "starved" reaction.

In the terminology of batch reaction kinetics, flooded reactions would fall in Region II and starved reactions in Region III. But in the latter case, as mentioned above, the monomer level in the particle is controlled independently by the rate of monomer addition.

The dependence of  $R_p$  on  $R_a$ , the rate of monomer addition, has been derived for the Smith-Ewart limiting case [4]. In a starved reaction

$$R_p = \frac{R_a R_p^*}{\phi_M^* R_a + R_p^*} \quad (6)$$

where  $R_p^*$  and  $\phi_M^*$  are the Smith-Ewart limiting case rate and monomer level, respectively. Since  $R_p$  is constant, conversion increases linearly with time with a slope dependent on addition rate. The monomer level in the reactor also increases linearly with time. In a flooded reaction the rate of polymerization equals the Smith-Ewart rate for a batch reaction and is independent of feed rate.



The excess monomer level in this case builds up in proportion to the difference between  $R_a$  and  $R_p^*$ . The maximum rate of addition that can be tolerated without flooding is

$$R_a = R_p^* / \phi_p^* \quad (7)$$

An analysis of the surface reaction model cannot be carried out completely as was done for the Smith-Ewart limiting case; but, in general,  $R_p$  will be a function of three time-dependent variables

$$R_p = f(Q, M, V)$$

Therefore, we need at least three independent equations specifying these quantities as functions of time in order to derive an equation for  $R_p(t)$ .  $M$  and  $V$  can both be derived from a material balance:

$$dM/dt = R_a - R_p \quad (8)$$

$$dV/dt \approx V_M R_a \quad (9)$$

The remaining variable,  $Q$ , is related to both  $M$  and  $V$ . Unfortunately, we do not have the capability of describing the relationship quantitatively. Hence, the analysis cannot be carried out further without introducing arbitrary assumptions or experimental facts.

## EXPERIMENTAL

Reactions were carried out in a 4-liter stirred glass flask at 25°C. The flask was equipped with reflux condenser and the entire system was blanketed with  $N_2$ . The reactions were stirred at 250 rpm during the seed reaction and while monomer was being pumped to the reactor. The reaction was initiated with the redox couple tert-butyl hydroperoxide and sodium formaldehyde sulfoxylate. The concentrations were adjusted to maintain a constant rate of initiation in all runs. The only recipe variations studied were rate of monomer addition and monomer composition. The seed recipe was

300 parts deionized water  
 3.2 parts 80% Aerosol MA  
 5 parts monomer (inhibitor free)  
 pH = 3.5  
 Reaction time = 2.5 hr

Seed latexes were made with both 5 and 10 parts monomer at the same soap level. The former recipe was found to be more reproducible; it yielded a dilute latex which contained on the average 1.54% polymer solids with particle size of 540 Å. This is very close to 100% conversion of the seed monomer. The larger seed produced particles of 600 Å on the average. In both cases the particle concentration averaged  $1.04 \times 10^{14}$  particles/cc of water.

At the end of the seed reaction the monomer feed was started. A total of 110 parts was normally added over an interval of 6 to 30 hr depending on the feed rate. Conversions are based, therefore, on the total of 115 parts monomer. Conversion was measured by sampling the reaction with a syringe. Particle size was obtained by light scattering using the dissymetry method. A typical run yielded a latex of 23% solids with particle size of 1500 Å.

The sample sizes were kept below 0.5% of the reactor contents to avoid producing significant changes in the total amount. The samples were freeze-dried and then dried in a vacuum oven at 40°C to constant weight. The residual was corrected for nonpolymeric nonvolatiles.

For each sample the net sample weight, net weight of dry residue (polymer, emulsifier, and initiator residues), time of sample withdrawal, and feed rates were known. The exact total weight of the reaction mixture at any time was then calculated. The total weight of polymer in the flask was obtained by multiplying the weight fraction of polymer in the sample by the total weight of the reaction mixture. Conversion to moles of monomer converted to polymer was accomplished using the average molecular weight of monomers if butyl acrylate was used, and the molecular weight of vinylidene chloride for the homopolymerization. Unreacted monomer levels were calculated from the difference between the amount of monomer loaded and the polymer recovered.

## RESULTS

### Latex Particle Morphology

The first concern was to establish that the PVDC latex particles were hard, crystalline, and unswollen, and in contrast that the copolymer particles were soft and swollen. In addition, we had to establish that the PVDC seed could be grown to a larger size without forming new particles or flocculating existing particles. In order to insure comparison would be made between highly crystalline and completely amorphous latexes, we studied a range of compositions from 100% VDC to 80% VDC/20% butyl acrylate (by weight).

The compatibility of monomer and polymer during polymerization

was studied independently in small batch reactions. Pure VDC, when irradiated with UV or initiated with 0.1% azobisisobutyronitrile, became turbid within minutes. The precipitate was identified as PVDC. Phase separation took place at < 0.1% conversion. A mixture of 80 g VDC and 20 g BA when treated similarly became viscous and eventually converted to a clear, rigid gel, but no polymer separated up to 45% conversion. A 90/10 mixture remained clear initially, but in time formed a swollen precipitate which converted finally to an opaque, rubbery gel.

In another experiment, molded sheets of polymers of the above composition were immersed in their respective monomer mixtures and the weight gain monitored. The 80/20 copolymer was soluble. The 90/10 copolymer, though crystallized, still swelled substantially in comparison to PVDC as indicated in Table 1.

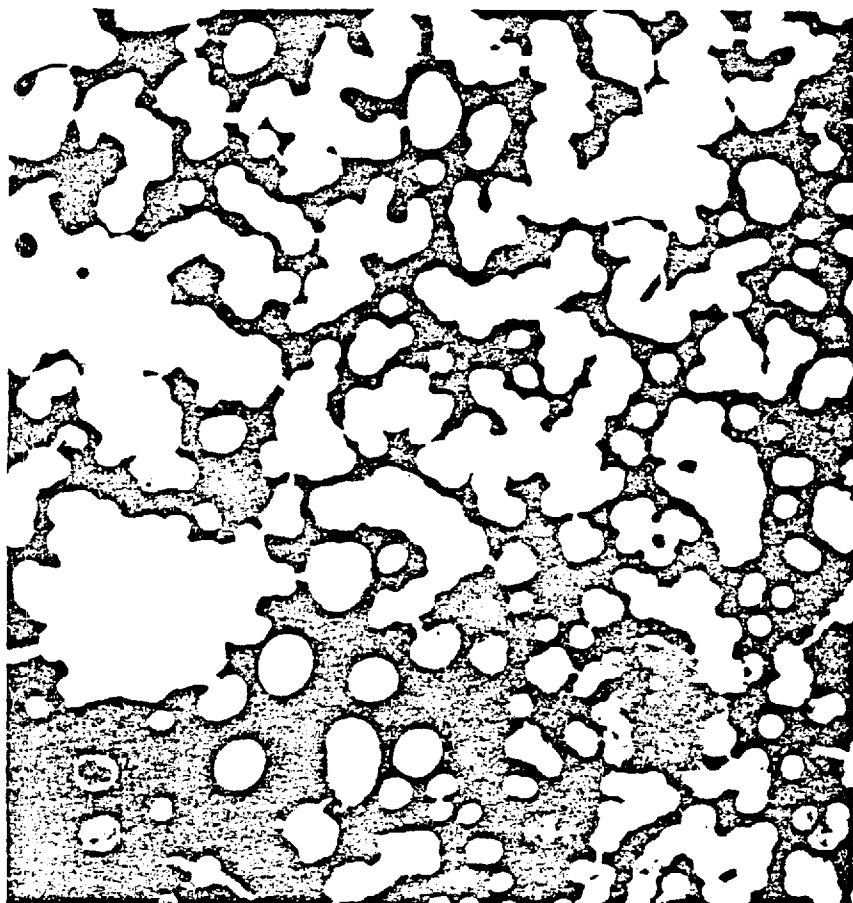
TABLE 1. Swelling Behavior of VDC/BA Copolymers

Polymer composition wt% VDC	Polymer state	$W_t^a/W_0$
100	Crystalline	1.04
90	Crystalline	1.20
80	Amorphous	Soluble

<sup>a</sup>Weight of swollen film after 3 weeks immersion in monomer.

The character of the polymers in latex form was established both by film casting and electron microscopy. Latexes with compositions from 100 to 80% VDC were explored. The latter is definitely amorphous. The particles deform and coalesce extensively on the electron microscope grid as shown in Fig. 2. Cast films remained clear and soft and showed no evidence of crystallinity over a period of several weeks. The 90 VDC/10 BA latex particles also appeared to be spherical and soft by electron microscopic examination. The latexes when cast on glass plates formed clear, well-coalesced, flexible films. This indicates that the latex particles were substantially amorphous in the dispersed state. However, this composition does tend to crystallize on aging.

The possibility exists that PVDC is actually produced as an amorphous polymer in the latex and crystallizes after polymerization. If this were the case, we would not really be comparing hard and soft particles. In order to establish whether this could be the case, both the PVDC seed



1  $\mu$

FIG. 2. Transmission electron micrograph of an 80 VDC/20 BA latex.

latex and grown particle latexes were examined by various techniques including electron microscopy, electron diffraction, and x-ray diffraction.

A micrograph of seed particles formed with the small seed shot is shown in Fig. 3. The particles are monodisperse and spherical, suggesting that the seed formation process is normal. This implies that the polymer remains amorphous during this process. However, the particles did not deform nor would the seed latex dry into a continuous film. Both observations suggest that the seed was crystalline after the reaction.

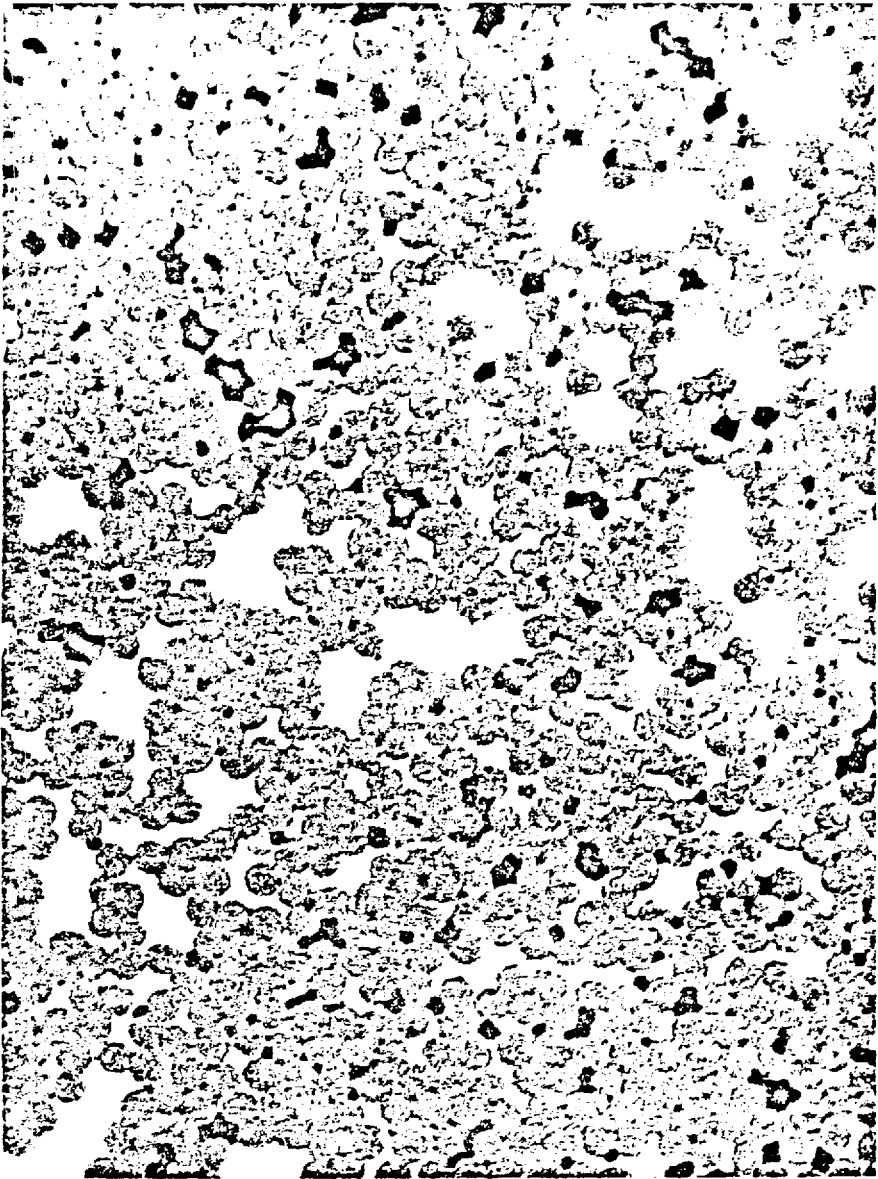
In order to determine if crystallization took place during or after seed preparation, a fresh seed was made and immediately cooled to 0°C. The cold diluted latex was sprayed on a cold grid and the ice sublimed away. The cold residue showed the same crystalline electron diffraction patterns as a control which received no special treatment. This implies that crystallization took place during the 2.5-hr interval used for the seed reaction.

PVDC latexes isolated at higher conversion levels were also characterized by electron microscopy. The larger particles were shown by transmission electron micrographs to be nonspherical (Fig. 4). The larger the particle, the more pronounced was the irregularity in shape. All specimens showed crystalline diffraction patterns both in the latex form and when dried on grids. They were all nonfilm forming at room temperature regardless of age or thermal history.

As a further check, the density of the homopolymer in the latex suspension was measured. A value of 1.92 g/cc was obtained. This falls in the range usually observed for highly crystalline PVDC (1.37-1.94 g/cc) [9] and indicates that the latex particles in the colloidal state have a high level of crystallinity—around 75% assuming  $d = 1.96$  for crystalline PVDC and 1.77 for amorphous PVDC. Such particles should be virtually insoluble in monomer.

A further examination was carried out in order to bring out more details of the PVDC particle morphology. The external morphology of the particles was elucidated by metal shadowing techniques. A micrograph of shadowed particles is shown in Fig. 5. There is a recognizable fibrillar pattern on the surface. What appears to be a nucleation site is also evident in many particles. As can easily be seen from the picture, these sites are not centered in the particle. The particles are clam-shaped, about 1300 Å in diameter, and from the shadow length only about 600 Å thick.

An explanation that immediately arises on examining these pictures is that amorphous particles deposited on the grid, spread out slightly, and then crystallized in the usual mode from a single nucleus. In opposition to this explanation is the fact that latexes known to be crystalline also showed this morphology in the dried state. It is also



1/3 μ

FIG. 3. Transmission electron micrograph of a PVDC seed latex.

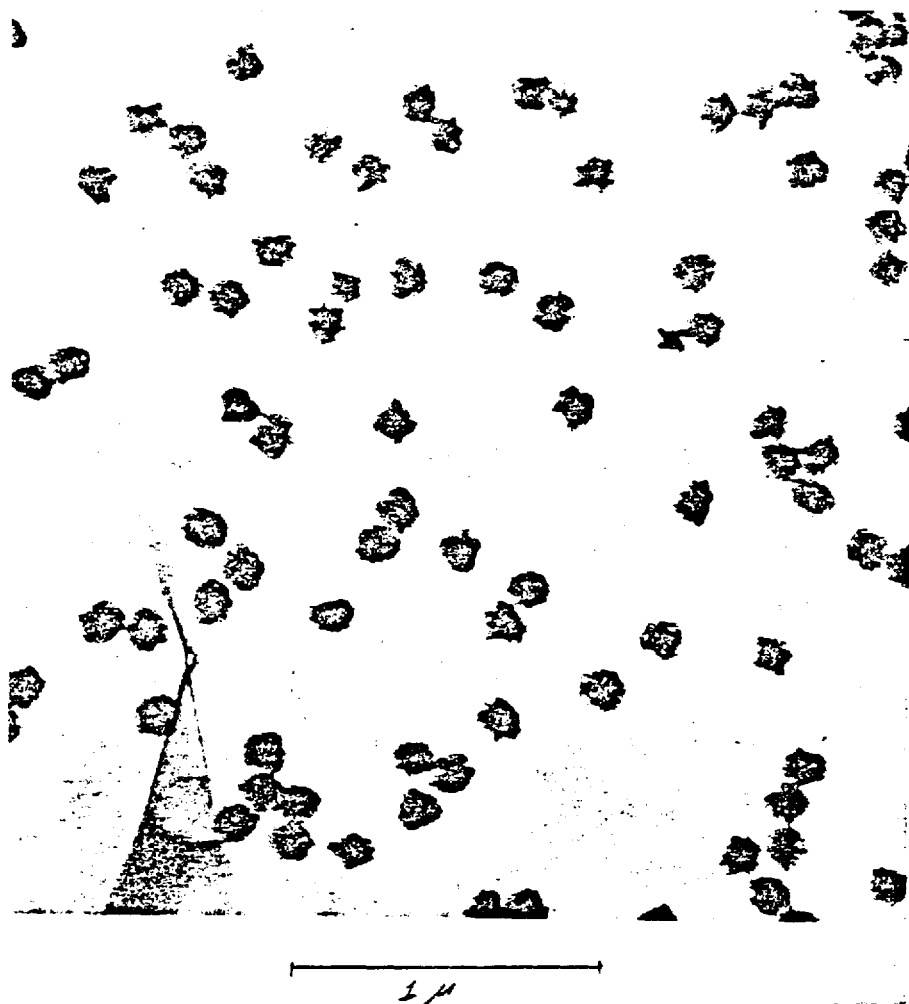


FIG. 4. Transmission electron micrograph of a PVDC latex.

possible that the PVDC particles were porous and collapsed on drying. However, no evidence for this could be found. Therefore, we are left with only one possible conclusion: this morphology must be developed in the colloidal state by crystallization during the polymerization process.



0.1  $\mu$

FIG. 5. High magnification view of shadowed PVDC latex particles.



In another series of experiments we tried to estimate how much BA was required in the feed to keep the polymer amorphous during the run. A series of latexes were prepared at the same feed rate using a 20-hr run time. The monomer composition was varied. The results are tabulated in Table 2. The run with 3% BA seemed to produce amorphous particles in the early stages, but crystallization took place

TABLE 2. Comparison of Particle Morphologies

BA (%)	Seed	Large particles	Crystallinity	Film formation
0	Spherical	Irregular	Yes	No
3	-	Irregular	Yes	No
7	-	Soft	No	Yes
10	Spherical	Soft	No	Yes
20	-	Soft	No	Yes

some time before the 10th hour, as judged from the appearance of the particles. This latex had definitely crystallized by the end of the run.

### Kinetic Studies

Homopolymerizations were carried out at feed rates ranging from 0.38 to 1.90 moles/hr. Two types of conversion-time curves were observed depending on feed rate: for  $R_a < 0.95$  moles/hr, the plots were linear indicating a constant rate of polymerization; for  $R_a \geq 0.95$  moles/hr,  $R_p$  increased with conversion.

The rate of polymerization is controlled by feed rate in the case where the plots are linear. This is illustrated by the conversion-time curves shown in Fig. 6. In every case, however,  $R_p$  is slightly less than  $R_a$ , indicating that the level of unreacted monomer in the kettle builds up during the run.

Though the total amount of monomer increases, the ratio of monomer to polymer falls continuously during the run. As the data plotted in Fig. 7 show, the initial values of  $M/m$  are quite high, greatly exceeding the level of solubility of monomer in polymer.

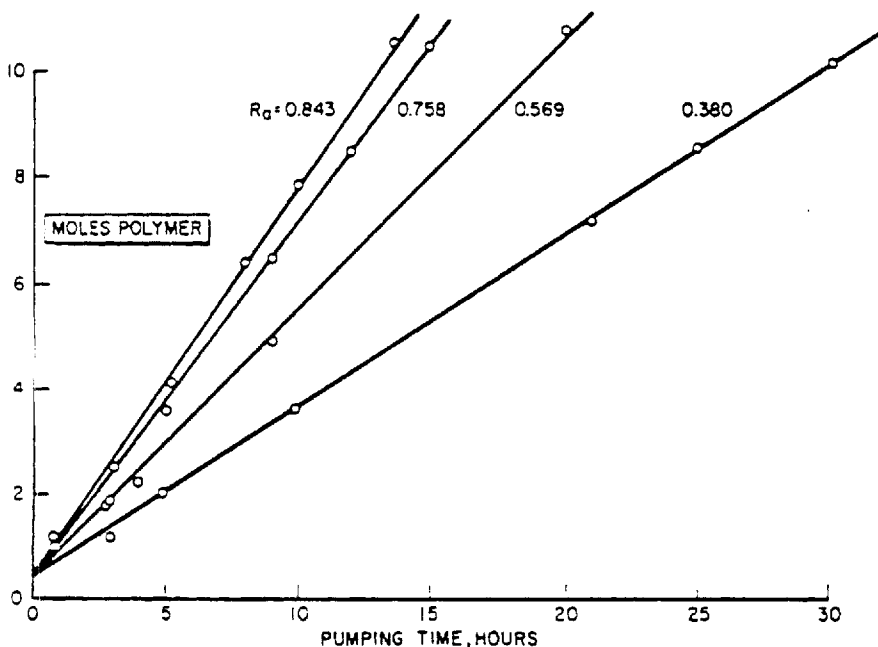


FIG. 6. Conversion-time curves for the continuous monomer addition emulsion polymerization of VDC.

However, the ratio falls with time, reaching a limiting value of  $\sim 0.1$ . These data also show that the level of excess monomer at constant conversion is independent of feed rate.

Though the level of unreacted monomer exceeds its solubility in the polymer, no excess could be detected. This indicates that the monomer is adsorbed onto the particles in some manner. Wiener [10] has shown by swelling studies that PVDC latex is capable of adsorbing substantial amounts of monomer but the amount is dependent on particle size. The ratios  $M/m$  calculated from his data span the same range, 0.5-0.1, as was observed in the present study. It therefore seems likely that all monomer in the reactor is adsorbed on the polymer particles. The solid curve in Fig. 7 is calculated by assuming the monomer is adsorbed in a layer 25 Å thick. The fit is reasonable considering that  $M/m$  cannot be measured very accurately.

When feed rates are increased to 0.95 mole/hr, the behavior of

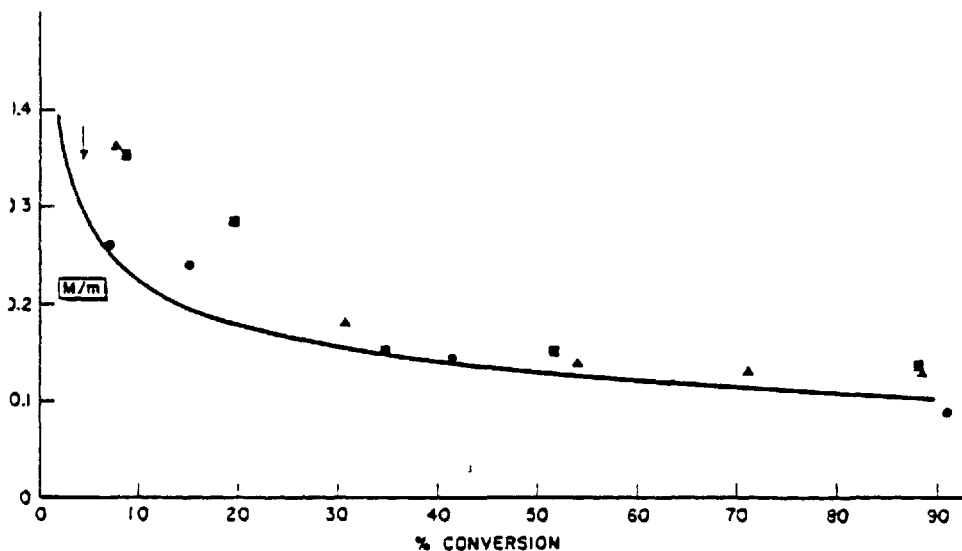


FIG. 7. Change in unreacted VDC level as a function of conversion: (■) 0.843 moles/hr, (▲) 0.758 moles/hr, and (●) 0.569 moles/hr. The arrow indicates seed conversion.

the system changes abruptly. As shown by the plot in Fig. 8,  $R_p$  is initially only about 1/2 the expected value (obtained from the slope of the dashed line). But, because the conversion-time curves were nonlinear,  $R_p$  was observed to increase with time, eventually reaching values in excess of  $R_a$  at high conversion.

The polymerization rates with feed rates between 0.948 and 1.14 moles/hr were not controlled but were not completely flooded either. Flooding was noted qualitatively by the appearance of macroscopic monomer droplets in the reaction. The excess monomer level actually increases initially, reaches a maximum value, and then begins to fall as the polymerization rate rises and finally exceeds the feed rate. In the example shown in Fig. 9, the run is beginning to approach a controlled condition at the end. The excess monomer level to be expected for a controlled reaction is indicated by the dashed line.

At still higher feed rates the conversion-time curves remained nonlinear, but became independent of feed rate as shown in Fig. 10. The level of excess monomer continues to build up during the run because  $R_p$ , though increasing, does not exceed  $R_a$  in the region

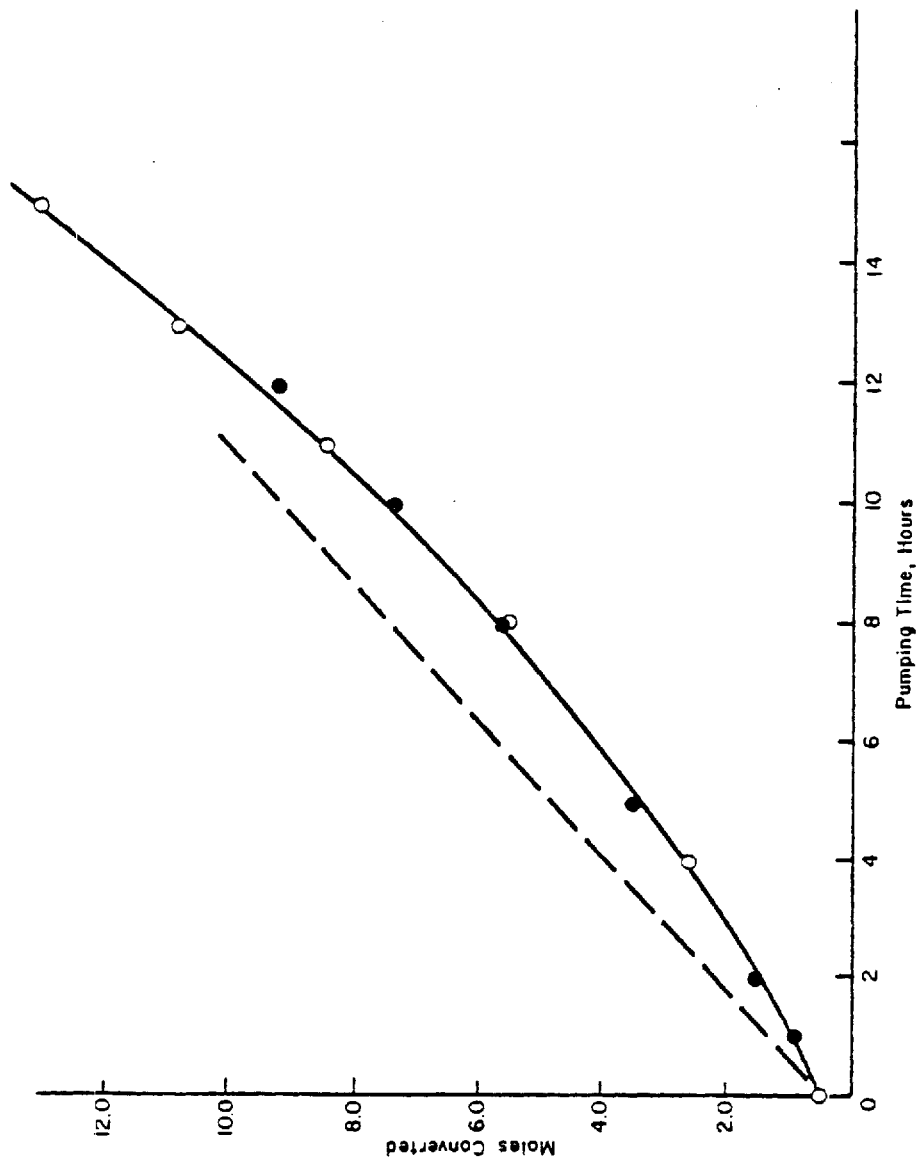


FIG. 8. Conversion-time curve for VDC in a partially flooded reaction; (o, ●) duplicate runs.

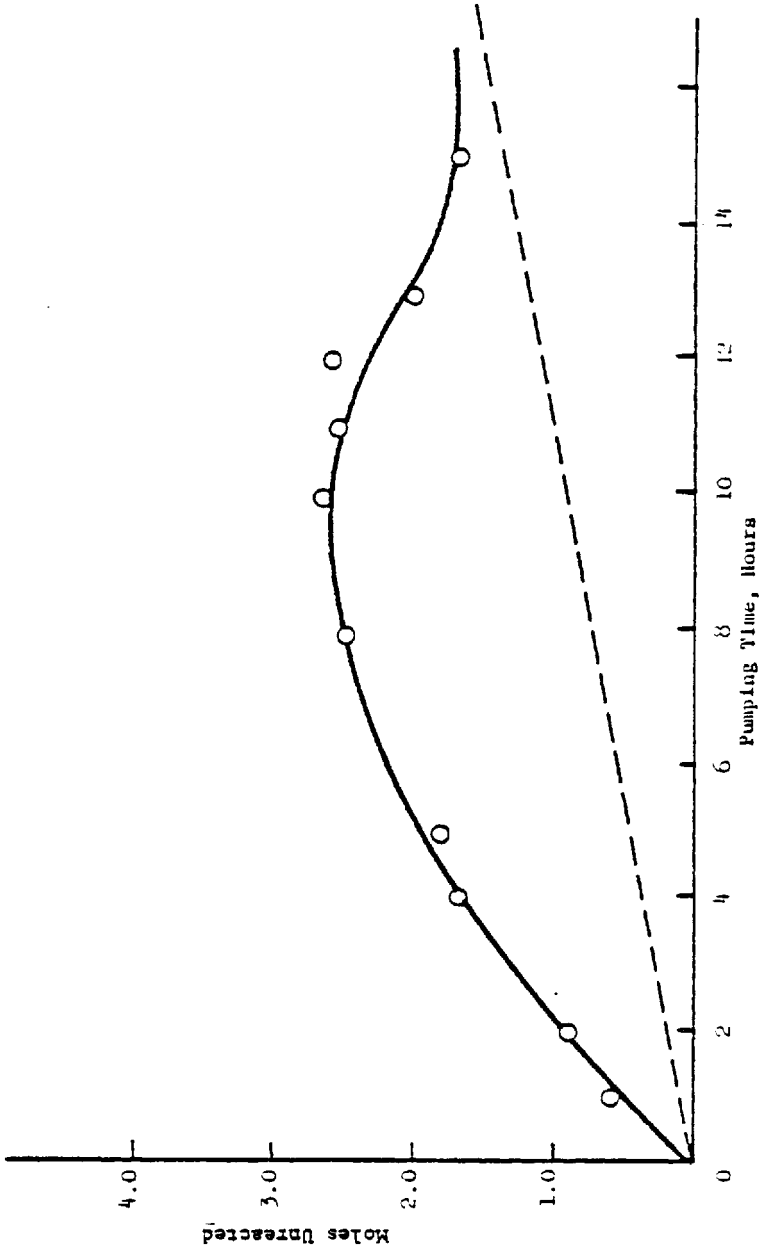


FIG. 9. Change in unreacted VDC level with reaction time in a partially flooded reaction.

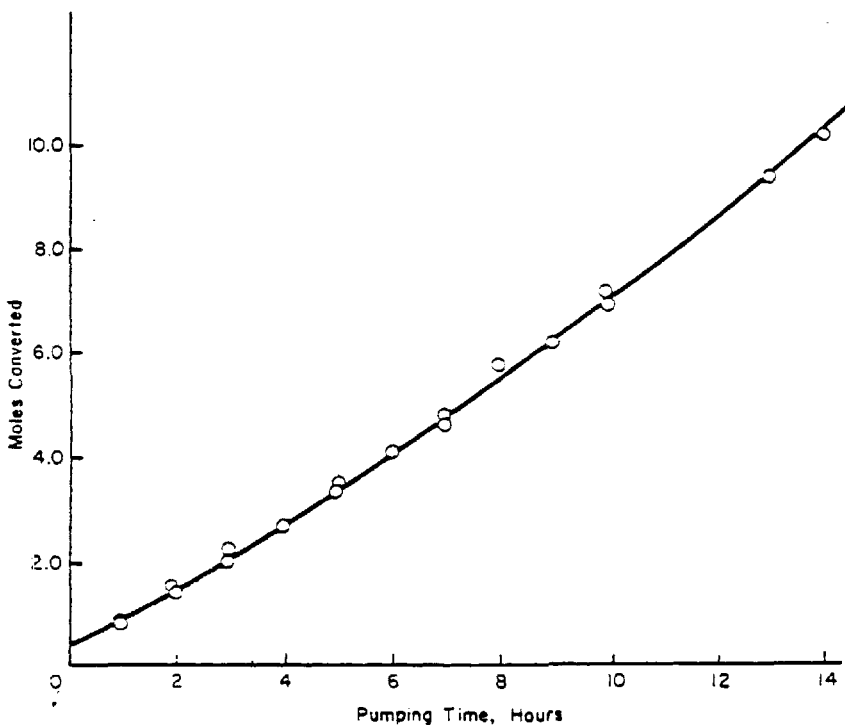


FIG. 10. Conversion-time curve for VDC in a flooded reaction.

investigated. Under these conditions the reaction is essentially equivalent to Region II in a batch emulsion polymerization.

As pointed out above, the transition from controlled to flooded reaction occurs rather abruptly. The change is manifested by a sharp drop in the initial rate of polymerization and a sharp rise in the level of excess monomer in the kettle.

The transition from controlled to flooded reaction apparently takes place when  $R_a$  is greater than the inherent ability of the seed latex to consume monomer.

A similar series of experiments was carried out with various levels of BA in the feed. Linear conversion-time curves were again obtained at low feed rates, as shown in Figs. 11 and 12. The behavior in this region was essentially independent of monomer composition.  $R_p$  was again slightly lower than  $R_a$ , but the ratio was independent of monomer composition as shown in Fig. 13.

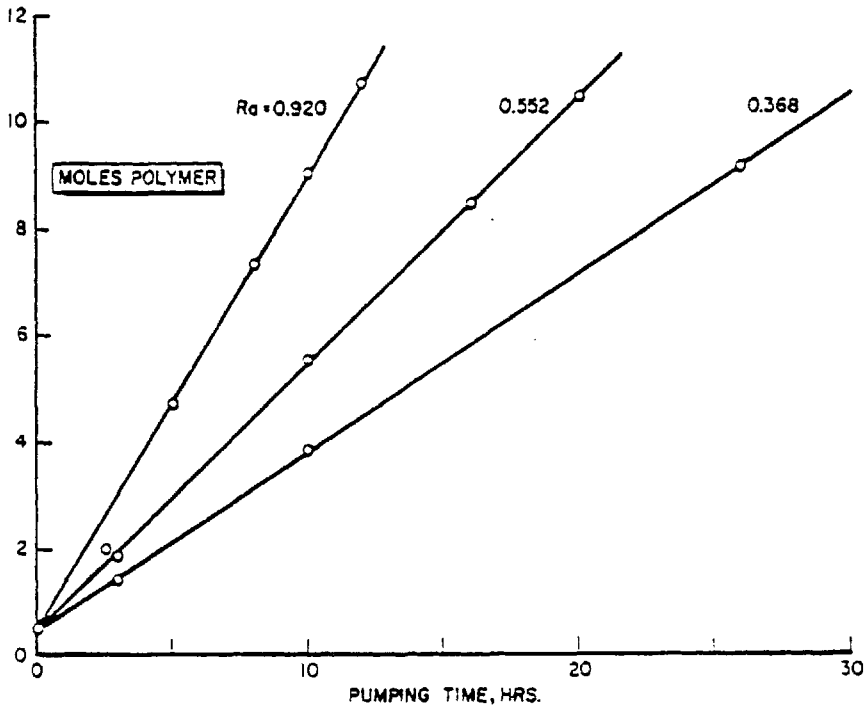


FIG. 11. Conversion-time curves for the continuous monomer addition emulsion polymerization of a 90/10 VDC/BA mixture.

The level of unreacted monomer in the kettle showed the same increase with time as for VDC polymerizations. This indicates that the monomer level is not related to the ability of the monomer to swell the particle.

At higher feed rates there was again an abrupt change in behavior. The feed rate at which flooding began increased from 0.95 to  $\sim 1.05$  moles/hr as the level of BA was increased to 20%. Other features of the transition were similar to what was observed with VDC. The initial rate dropped to a lower value; the conversion-time curves became nonlinear, and at sufficiently high feed rates,  $R_p$  was independent of  $R_a$ . A conversion-time curve for the latter condition is shown in Fig. 14.

The nonlinearity of the conversion-time curves in the flooded reactions does not fit the prediction of the Smith-Ewart theory even

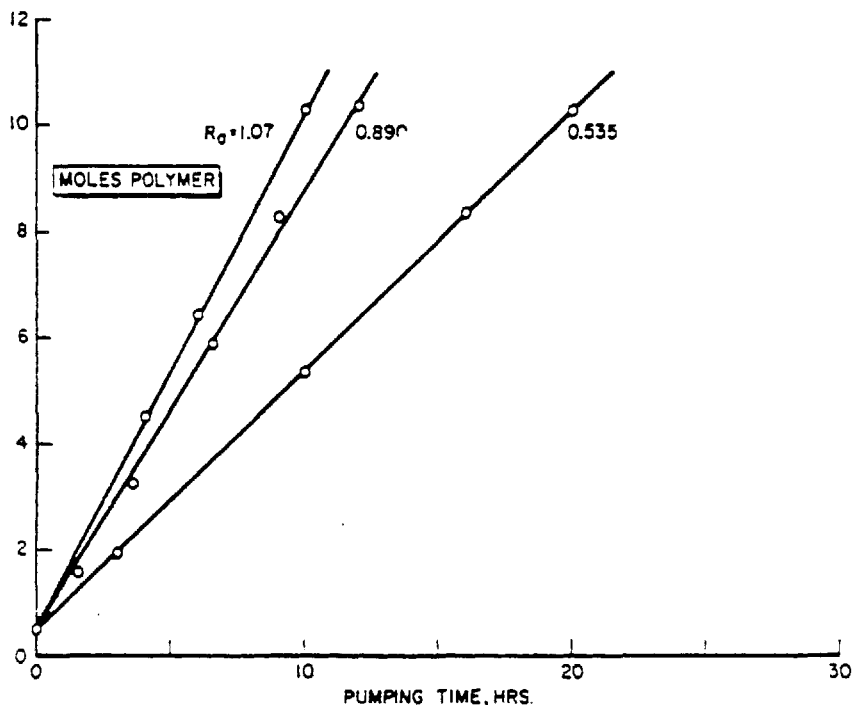


FIG. 12. Conversion-time curves for the continuous monomer addition emulsion polymerization of an 80/20 VDC/BA mixture.

for the compatible system. This is further demonstrated by an analysis of the results in terms of the monomer addition theory discussed earlier. The latter predicts a specific relationship between  $M/m$ ,  $R_p$ , and  $R_a$  for cases where the swollen particle model is valid.

The dependence of  $R_p$  on  $R_a$  is shown by the plot in Fig. 15. The curve is linear in the controlled region with a slope of 0.91.  $R_p$  reaches a maximum for  $R_a \approx 1.0$  and then falls as the reaction floods. Finally  $R_p$  becomes independent of  $R_a$ . Clearly, the VDC system does not follow the predicted pattern even where monomer and polymer are compatible.

The theory predicts further that  $M/m$  should be constant during a run, and should be proportional to  $R_a$ . A plot of  $M/m$  vs  $R_a$  at constant



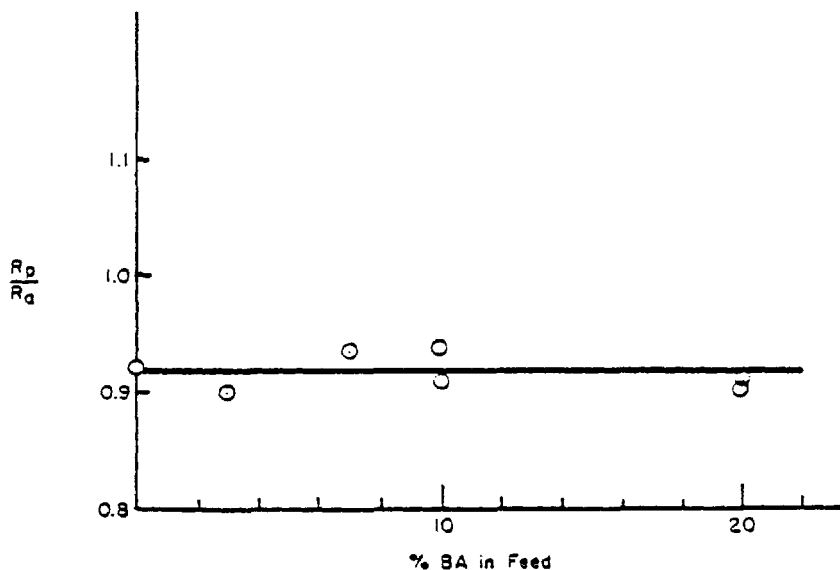


FIG. 13. Effect of BA content on the relationship between  $R_p$  and  $R_a$ .

conversion is shown in Fig. 16. The monomer level is low and constant in the controlled region and not proportional to  $R_a$ . Beyond the transition zone, however, it does appear to increase approximately linearly with  $R_a$ , but this is because  $R_p$  is small and changing relatively slowly.

A plot of  $M/m$  vs per cent conversion for several monomer mixtures at the same feed rate is shown in Fig. 17. The theoretical line is the same as that shown earlier in Fig. 7 (assuming an adsorbed layer 25 Å thick).  $M/m$  for the comonomer mixtures changes less with conversion than does VDC itself, but the data are not accurate enough to draw further conclusions.

## DISCUSSION

This study shows that the kinetics of emulsion polymerization of VDC are not dependent on the ability of the monomer to swell the polymer. The results do not follow the predictions of an analysis based on the small swollen particle model. This was anticipated to be the case for VDC but also holds for the monomer mixtures as well.

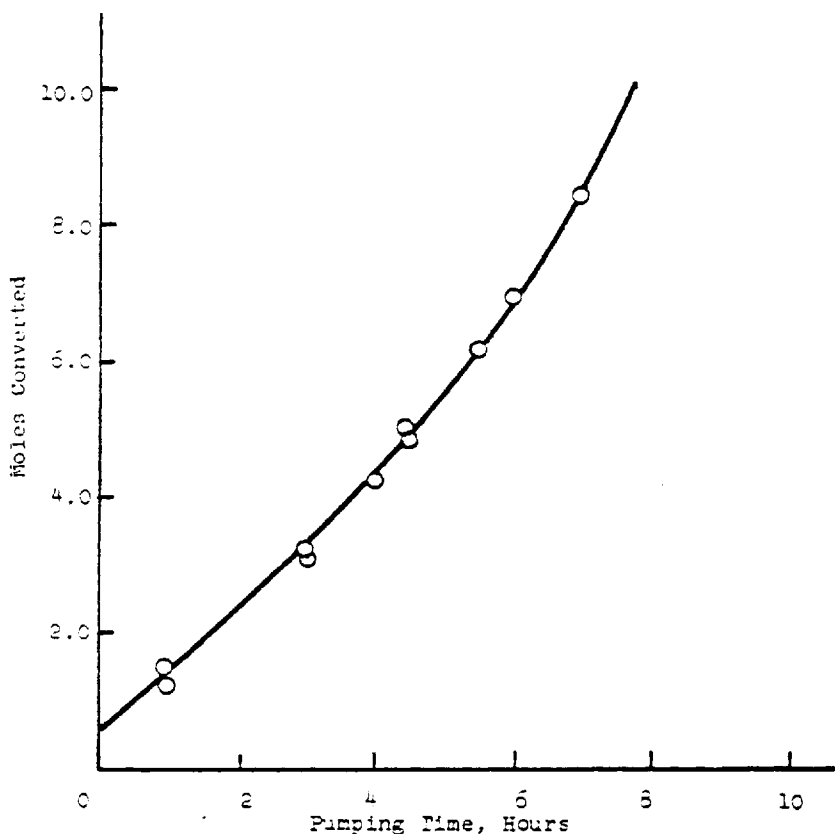


FIG. 14. Conversion-time curve for 80/20 VDC/BA mixture in a flooded reaction.

The important observations are that  $R_p$  does not increase with  $R_a$  to a limiting value characteristic of the batch reaction, and  $M/m$  when measured at the same conversion (or particle size) is independent of  $R_a$ . Both observations are difficult to rationalize within the framework of established theories.

Another significant point that emerges from the present study is that  $R_p$  is proportional to but not equal to  $R_a$  in controlled reactions. A proportionality constant of  $0.91 \pm 0.02$  fits the data obtained both with VDC and VDC/BA mixtures. It also gives a reasonable fit to the monomer

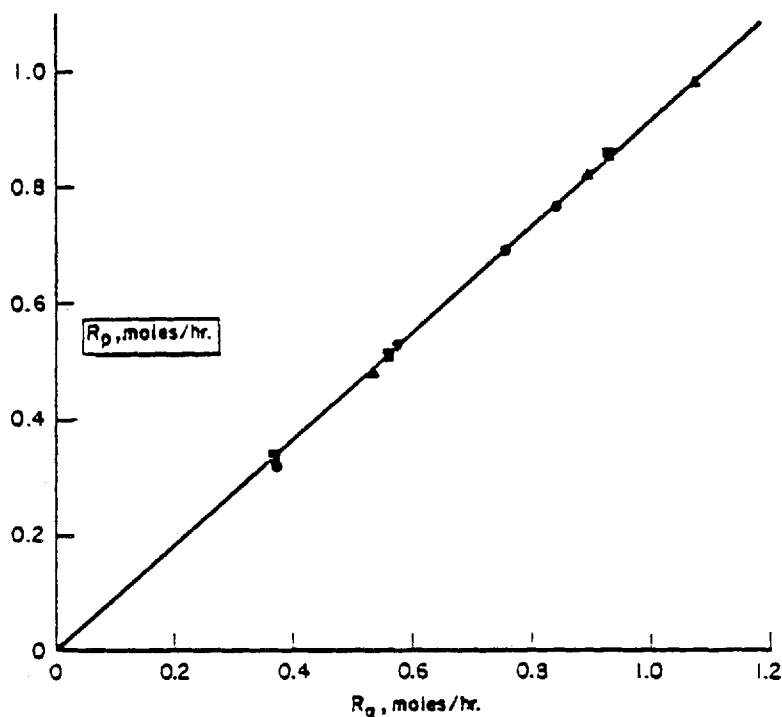


FIG. 15. Dependence of  $R_p$  on  $R_a$  in controlled reactions. (●) VDC, (■) 90/10 VDC/BA, and (▲) 80/20 VDC/BA.

addition kinetic data on styrene reported by Gerrens [5] and Krackler and Naidus [6]. Thus it may be a constant characteristic of the monomer addition process.

A particularly perplexing observation is the sudden drop in rate which occurs when the system becomes flooded. Initially, it appeared that the high rate in the starved reactions was due to a gel effect; and flooding simply caused the polymer particles to swell and the kinetics to revert to the simple Smith-Ewart case. However, the same phenomenon was observed in homopolymerization where the particle does not swell under either condition.

Vanderhoff [20] suggested that flooding may reduce the rate of initiation since the decomposition of tert-butyl hydroperoxide is affected by the medium. Another possibility is that the monomer droplets deplete the surfactant supply either on the surface of the polymer

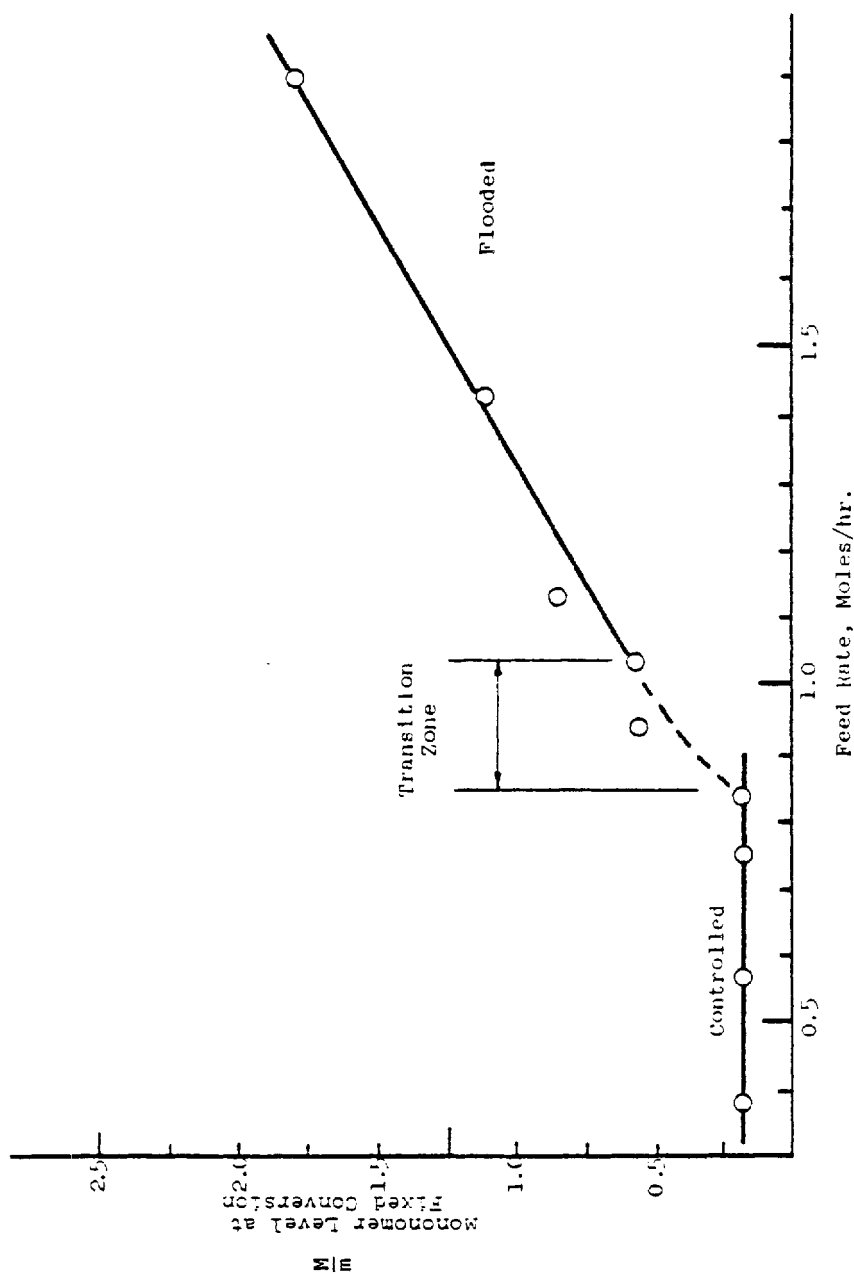


FIG. 16. Dependence of unreacted monomer level at fixed conversion on  $R_p$  showing the transition from controlled to flooded reactions;  $m = 4$  moles.

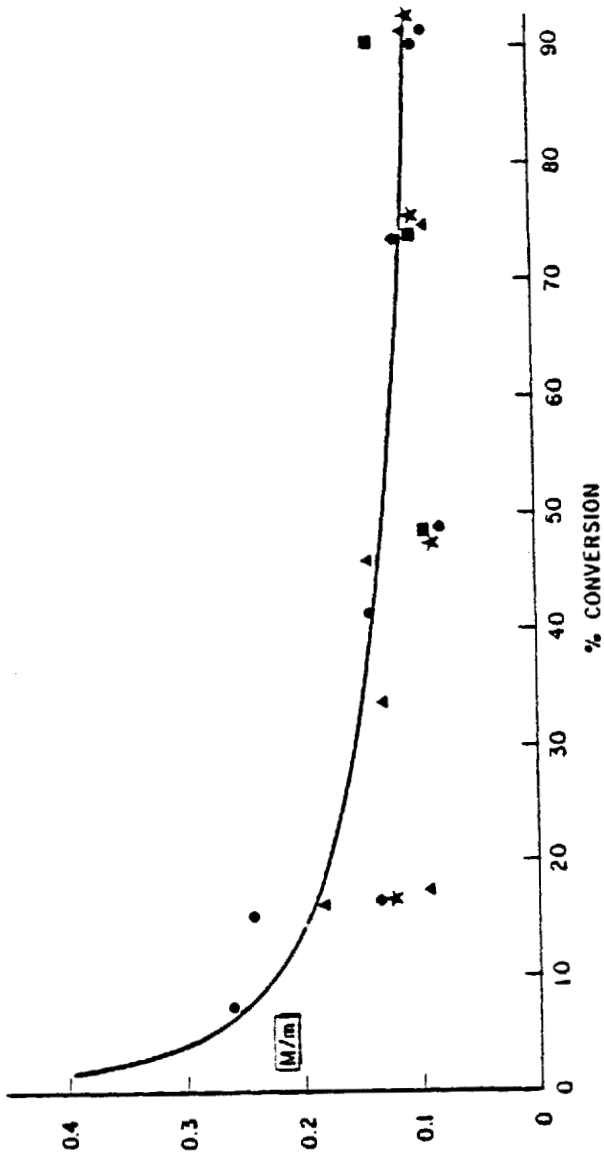


FIG. 17. Effect of monomer composition on unreacted monomer level; feed rate, 55.2 g/hr. (●) VDC, (■) 97/3 VDC/BA, (+) 93/7 VDC/BA, (×) 90/10 VDC/BA, and (▲) 80/20 VDC/BA.

or in solution. This could potentially produce a drop in rate; a similar situation has been reported for the batch reaction [12].

Another result that has been difficult to interpret is the lack of dependence of the unreacted monomer level on the feed rate. Intuitively, one would expect that the faster monomer is added to the reactor, the higher the steady-state level and, therefore, the higher the rate of polymerization. This is the situation predicted by the swollen particle model. However, in the present case  $M/m$  depends only on particle size even though  $R_p$  is dependent on  $R_a$ .

This may be related to the observation that the steady-state monomer level can be accommodated in a 25-Å thick layer on the particle surface. Data in the papers cited above indicate that this is also true for styrene. If this is the case, then the adsorbed monomer must be relatively unreactive. In the steady-state, another monomer unit must enter the layer before one can add to a growing radical. The rate of entry is, of course, determined by the rate of monomer addition in the controlled region.

The low reactivity of the adsorbed layer may result from a loss in reactant mobility as the layer becomes thinner than 25 Å. This leads to the further conclusion that the locus of polymerization is a mobile layer of chain ends, monomer, and emulsifier. The radicals are likely to be embedded in the polymer phase and have low mobility under all conditions. Therefore, one would expect the number of radicals per particle to increase with surface area. The latter would then be the rate-determining factor.

The above considerations are certainly consistent with the requirements of VDC polymerization. The fact that they also agree with the behavior of compatible systems such as VDC/BA and styrene argues that the surface reaction model is of general validity in emulsion polymerization.

#### ACKNOWLEDGMENTS

The authors were assisted in the experimental work by C. W. Fisher, N. Hyde and M. E. Kelly. Latex micrographs were supplied by the Dow Microscopy Laboratory. D. R. Carter and D. L. Ahr assisted in the elucidation of PVDC latex morphology. The authors also enjoyed many fruitful discussions about this work with Dr. T. Alfrey, Jr., and Professors J. W. Vanderhoff and H. Morawetz.

#### REFERENCES

- [1] W. V. Smith, *J. Amer. Chem. Soc.*, **70**, 3695 (1948).
- [2] J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford and T. Alfrey, Jr., *J. Polym. Sci.*, **20**, 225 (1956).

- [ 3 ] J. E. Vandegaer, J. Appl. Polym. Sci., 9, 2929 (1964).
- [ 4 ] R. A. Wessling, J. Appl. Polym. Sci., 12, 309 (1968).
- [ 5 ] H. Gerrens, J. Polym. Sci., Part C, 27, 77 (1969).
- [ 6 ] J. J. Krackler and H. Naidus, J. Polym. Sci., Part C, 27, 207 (1969).
- [ 7 ] M. R. Grancio and D. J. Williams, J. Polym. Sci., Part A-1, 8, 2617 (1970).
- [ 8 ] R. A. Wessling, J. Appl. Polym. Sci., 14, 1531 (1970).
- [ 9 ] R. A. Wessling and F. G. Edwards, in Encyclopedia of Polymer Science and Technology, Vol. 14, Wiley (Interscience), New York, 1971, p. 540.
- [ 10 ] H. Wiener, J. Polym. Sci., 7, 1 (1951).
- [ 11 ] G. V. Tkachenko and P. M. Khomikovskii, Dokl. Akad. Nauk SSSR, 72, 543 (1950).
- [ 12 ] P. M. Hay, J. C. Light, L. Marker, R. W. Murray, A. T. Santonicola, O. J. Sweeting, and J. G. Wepsic, J. Appl. Polym. Sci., 5, 23 (1961).
- [ 13 ] J. C. Light et al., J. Appl. Polym. Sci., 5, 31 (1961).
- [ 14 ] C. P. Evans et al., J. Appl. Polym. Sci., 5, 39 (1961).
- [ 15 ] B. M. E. VanDerHoff, Advan. Chem. Ser., 34, 1 (1962).
- [ 16 ] W. V. Smith and R. H. Ewart, J. Chem. Phys., 16, 592 (1948).
- [ 17 ] R. A. Wessling and L. R. Harrison, J. Polym. Sci., Part A-1, 9, 3471 (1971).
- [ 18 ] R. A. Wessling, J. H. Oswald, and L. R. Harrison, To Be Published in J. Polym. Sci.
- [ 19 ] W. H. Stockmayer, J. Polym. Sci., 24, 314 (1957).
- [ 20 ] J. W. Vanderhoff, Private Communication.

Received for publication October 10, 1972