

## A Kinetic Study of the Emulsion Polymerization of Vinyl Acetate

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### Synopsis

The emulsion polymerization of vinyl acetate was studied at 50°C. It was found that the rate of polymerization was proportional to the 0.5 power of the initiator concentration and the 0.25 power of the number of particles. The number of particles was proportional to the power  $0.5 \pm 0.05$  of the emulsifier concentration, but independent of the initiator concentration. The limiting viscosity number of the polymers produced was independent of the initiator concentration and number of polymer particles. It is suggested that the mechanism of vinyl acetate emulsion polymerization is similar to that of vinyl chloride. The linearity of the conversion-versus-time curve is explained as being due partly to a decrease in the desorption rate of radicals from the polymer particles and partly to a decrease in the termination rate constant.

### INTRODUCTION

In the literature it is generally concluded that the emulsion polymerization of vinyl acetate does not fall within the classic theories proposed by Smith and Ewart.<sup>1</sup> It is believed that this is due partly to the high transfer constant to monomer in vinyl acetate polymerization and partly to the relatively high solubility of vinyl acetate in water. In vinyl acetate emulsion polymerization, it is often observed that the rate of polymerization remains constant until 85% conversion, although the separate monomer phase has vanished already at or before 30%. This anomaly has caused much speculation concerning the mechanism of vinyl acetate emulsion polymerization, and during the past decade several investigations have been performed in order to explain this behavior.<sup>2-7</sup>

Some investigators<sup>4,6</sup> have proposed a mechanism in which most of the polymerization takes place in the water phase. The constant rate behavior is thus explained by assuming the monomer-polymer particles to act like reservoirs, keeping the monomer concentration in the water phase constant. However, the water phase hypothesis is not compatible with the high rates of polymerization usually found in emulsion systems. Thus, Gershberg<sup>6</sup> had to assume a termination rate constant in the water phase several orders of magnitude lower than that reported for vinyl acetate in bulk polymerization. Furthermore, in a study of the polymerization of vinyl acetate in aqueous media, Napper and Parts<sup>8</sup> have observed a marked increase in

polymerization rate as soon as the initially formed polymer precipitated. This suggests that the major locus of polymerization is the monomer-swollen polymer particles and not the water phase.

Recently, three different models have been proposed for vinyl acetate emulsion polymerization.<sup>5,7,9</sup> Common to these models is that they all involve a mechanism allowing radicals to escape the polymer particles. This mechanism was originally introduced by Smith and Ewart<sup>1</sup> and is necessary to explain the low concentration of radicals per particle usually observed in vinyl acetate emulsion polymerization. However, the implications of the three models are vastly different, and the experimental results on which the models are based are contradictory. We therefore decided to reexamine the emulsion polymerization of vinyl acetate.

## EXPERIMENTAL

### Materials

Vinyl acetate was distilled 24 hr prior to use on a 2-ft column filled with glass helices. The initiator used in the emulsion experiments was an analytical-grade potassium persulfate obtained from Merck, and in the bulk experiments an analytical-grade  $\alpha,\alpha'$ -azoisobutyronitrile obtained from Fluka AG. The emulsifier was a purified-grade sodium lauryl sulfate (Quolac ON WD), obtained from the American Alcolac Corporation.

### Polymerization Procedure

The polymerization was carried out in a 2-liter Pyrex vessel provided with stirrer, thermometer, and N<sub>2</sub> inlet. The emulsion was purged with nitrogen 30 min prior to the addition of initiator. The nitrogen was obtained from a standard cylinder and deprived of any oxygen by passing through a 5% solution of pyrogallol in 2*N* NaOH. The temperature was controlled within  $\pm 0.2^\circ\text{C}$ .

In all experiments the emulsion was composed of 550 ml vinyl acetate, 1150 ml redistilled water, and varying amounts of emulsifier and initiator.

The degree of conversion was determined from samples withdrawn at regular intervals. The emulsion was broken by freezing in liquid nitrogen. The precipitated polymer was washed thoroughly with distilled water and dried to constant weight at 50°C. Elemental analysis proved that the dried polymer contained less than 0.01% initiator and emulsifier.

The number of polymer particles was determined by light scattering and electron microscopy. High-quality micrographs were obtained by using the hardening technique developed by Vanzo.<sup>2</sup>

## RESULTS

### Disappearance of the Separate Monomer Phase

In order to establish the point of which the separate monomer phase disappears, latex samples were withdrawn at various conversions early in

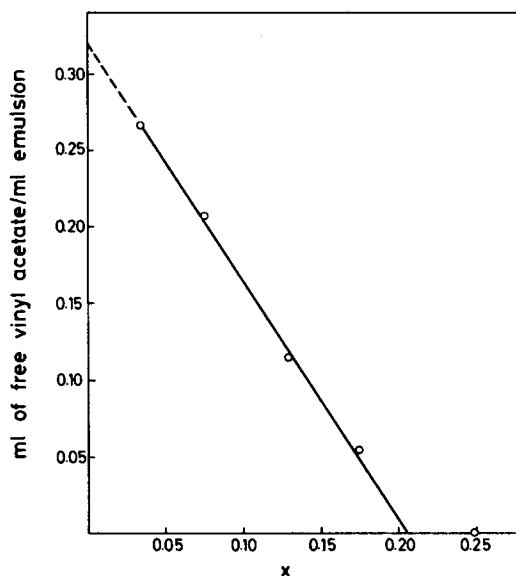


Fig. 1. Amount of vinyl acetate present as a separate monomer phase as function of conversion.

the polymerization. The samples were centrifuged for 15 min at 2000 rpm. The amount of vinyl acetate separated in this way was measured by a graduated scale and taken to equal the amount of vinyl acetate present as monomer droplets in the emulsion. Figure 1 shows a plot of this quantity, in ml vinyl acetate/ml emulsion, as a function of conversion. From this curve it appears that the separate monomer phase vanishes at 20% conversion.

Further evidence of the validity of the results obtained by this technique is the fact that extrapolation of the straight line gives a value of 0.32 ml vinyl acetate/ml emulsion, which is the initial composition of the emulsion.

It should be mentioned that results from similar investigations reported in the literature are somewhat scattered. Thus, French<sup>10</sup> has found that the separate monomer phase disappeared at 13.5% conversion, while Vanzo<sup>2</sup> on the basis of vapor pressure measurements has found a value of 32%. Recently, Nomura et al.<sup>7</sup> have reported a value of 0.23.

The disappearance of the separate monomer phase should be reflected in the conversion-versus-time curve. The data obtained in the present work show that the curves become linear between 15% and 20% conversion, and a value of 20% is therefore not unreasonable.

### Shape of the Polymerization Curve

Figure 2 shows typical conversion-versus-time plots obtained at different initiation rates. It appears that the rate of polymerization is constant in the interval 20–90% conversion and that the shape of the curves is independent of the initiation rate.

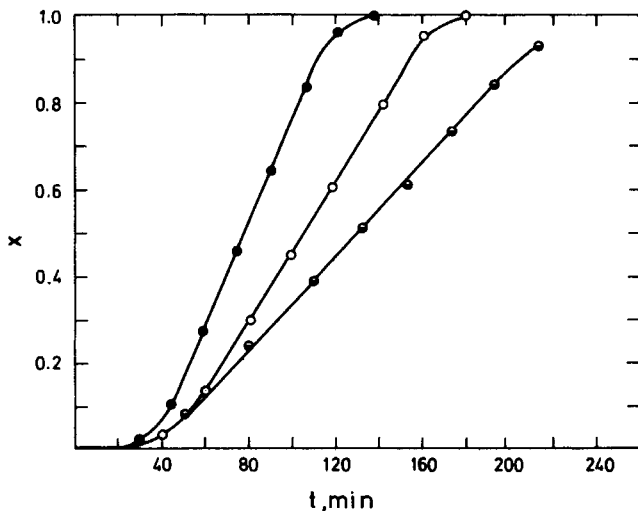


Fig. 2. Conversion-vs.-time curves at different initiation rates: (●)  $4 \times 10^{-3}$ ; (○)  $2 \times 10^{-3}$ ; (●)  $10^{-3}$  moles  $K_2S_2O_8/l.$   $H_2O$ , 9.5 g sodium lauryl sulfate/ $l.$   $H_2O$ .

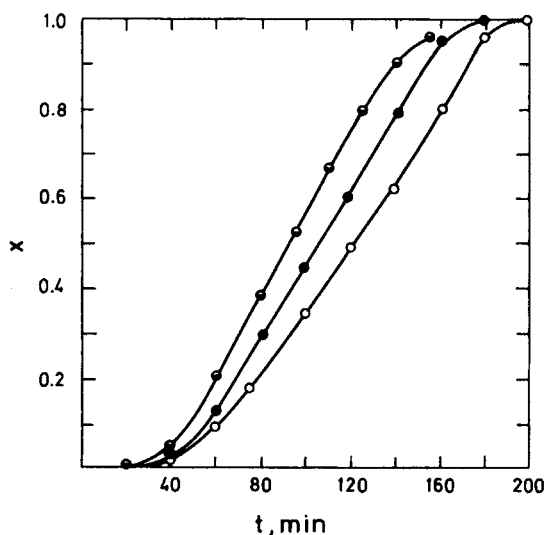


Fig. 3. Conversion-vs.-time curves at different emulsifier concentrations: (●) 24.0; (●) 9.5; (○) 2.4 g sodium lauryl sulfate/ $l.$   $H_2O$ .  $2 \times 10^{-3}$  moles  $K_2S_2O_8/l.$   $H_2O$ .

In a study of the effect of emulsifier concentration on the polymerization rate, we observed that the emulsifier concentration exerts a certain effect on the shape of the polymerization curve. At high emulsifier concentrations, the rate of polymerization begins to decrease from 80% conversion. At low concentrations, i.e., when the particles are relatively large, we observed a slight acceleration in polymerization rate, beginning at 70% conversion. This effect, which we reproduced several times, is shown in Figure 3.

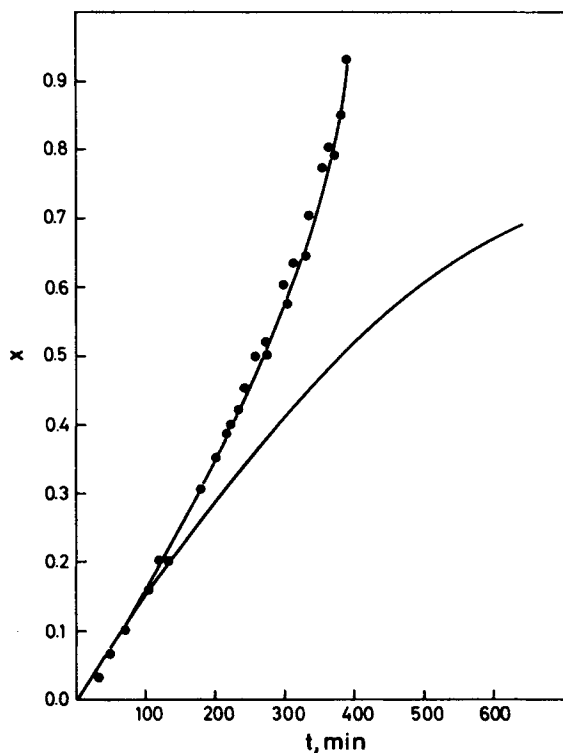


Fig. 4. Bulk polymerization of vinyl acetate at 50°C. [AIBN] =  $4 \times 10^{-3}$  moles/l. H<sub>2</sub>O: (●) experimental; (—) theoretical.

In emulsion polymerization a single polymer particle can be regarded as a locus of bulk polymerization with intermittent initiation. A decrease in the termination rate which is observed in bulk polymerization should therefore also occur in a single polymer particle. For the sake of comparison vinyl acetate was polymerized in bulk at 50°C with  $\alpha, \alpha'$ -azoisobutyronitrile as initiator, and Figure 4 shows a conversion-versus-time plot obtained from such an experiment. Together with the experimental curve is shown the theoretical curve obtained by integration of the rate expression given in eq. (1), assuming that the initiation rate is constant:

$$-d[M]/dt = k_p[M] (k_{rf}[I]/k_{tp})^{1/2} \quad (1)$$

where  $k_p = 3500$  l./mole-sec,<sup>11</sup>  $k_{tp} = 10^8$  l./mole-sec,<sup>11</sup> and  $k_{rf} = 1.7 \times 10^{-6}$ /sec.<sup>12</sup> It appears that there is an appreciable autoacceleration, beginning at approximately 10% conversion. On the assumption that  $k_p$  remains constant,  $k_{tp}$  can be obtained as a function of conversion from the experimental curve in Figure 4. Equation (2) gives the relation between  $k_{tp}$  and conversion  $x$  thus obtained, and Figure 5 shows the corresponding plot of  $k_{tp}$  versus conversion:

$$k_{tp} = 2 \exp(A + A_1x + A_2x^2 + A_3x^3) \text{ l./mole-sec} \quad (2)$$

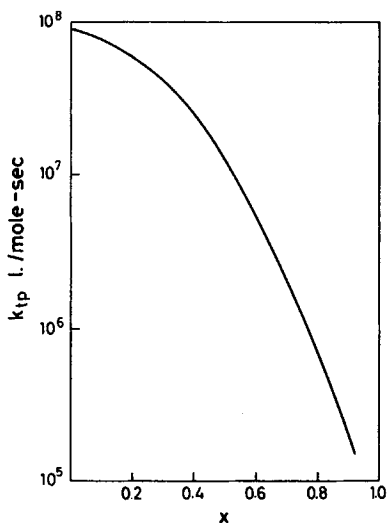


Fig. 5. Termination rate constant vs. conversion in bulk polymerization of vinyl acetate at 50°C.

where  $A = 17.6620$ ,  $A_1 = -0.4407$ ,  $A_2 = -6.7530$ , and  $A_3 = -0.3495$ . The application of eq. (2) to emulsion polymerization will be discussed in a later section.

### Effect of Emulsifier Concentration

The effect of emulsifier concentration on the polymerization rate was investigated at three different initiation rates. Figure 6 shows log-log plots of  $R_p$  versus emulsifier concentration.  $R_p$  is calculated from the slope of the linear portion of the conversion-versus-time plot. It appears that the effect of emulsifier concentration is independent of the initiation rate. From the slope of the straight lines, the emulsifier dependence exponent is calculated to be 0.12. Although this exponent is much smaller than the 0.6 power predicted in the classical theory of styrene emulsion polymerization, there is, nevertheless, good agreement in the literature that the emulsifier concentration does not affect the rate of polymerization to the same extent in vinyl acetate as in styrene emulsion polymerization.

The effect of the emulsifier concentration on the number of polymer particles was investigated at a persulfate concentration of  $10^{-3}$  moles/l.  $H_2O$ . From the log-log plot shown in Figure 7, it appears that the number of polymer particles increases with increasing emulsifier concentration; and from the slope of the straight line the emulsifier dependence exponent is calculated to be  $0.5 \pm 0.05$ , a value not far from the 0.6 power predicted by the theory of Smith and Ewart.<sup>1</sup> The value of 0.5 is also in good agreement with the data recently reported by Nomura et al.<sup>7</sup> From the relationship between emulsifier concentration and number of polymer particles and polymerization rate, respectively, it can be deduced that the poly-

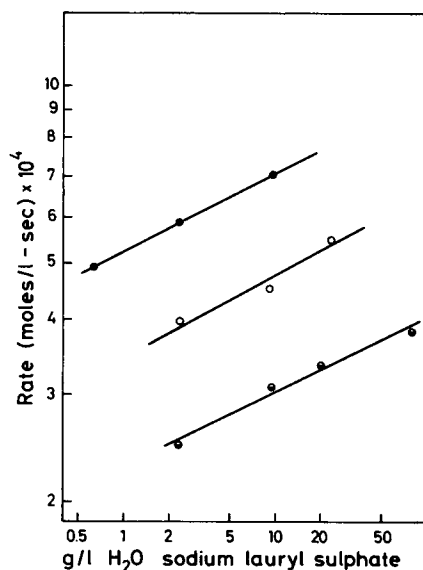


Fig. 6. Effect of emulsifier concentration on polymerization rate at different rates of initiation: (●)  $4 \times 10^{-3}$ ; (○)  $2 \times 10^{-3}$ ; (◐)  $10^{-3}$  moles  $K_2S_2O_8/l$ .  $H_2O$ .

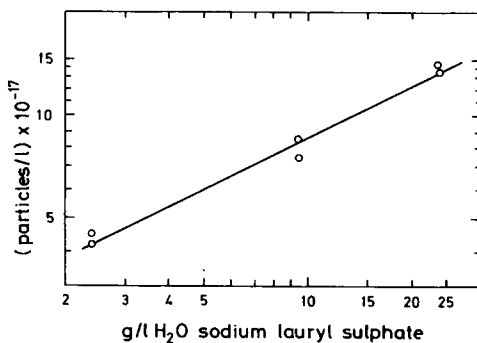


Fig. 7. Effect of emulsifier concentration on number of polymer particles.

merization rate is proportional to the 0.25 power of the number of particles. This exponent is in good agreement with the value 0.20 reported by Pat-siga.<sup>3</sup>

The small effect of the number of particles is not unique for vinyl acetate emulsion polymerization. Thus, Ugelstad<sup>13</sup> has reported that the order of reaction with respect to the number of particles was 0.05 to 0.15 in vinyl chloride emulsion polymerization.

Figure 8 shows a plot of limiting viscosity number  $[\eta]$  against conversion at two different emulsifier concentrations. It appears that there is no significant change in  $[\eta]$  as the emulsifier concentration and the number of particles are changed. This was also concluded by O'Neill<sup>14</sup> in a study of the radiation-induced emulsion polymerization of vinyl acetate. GPC

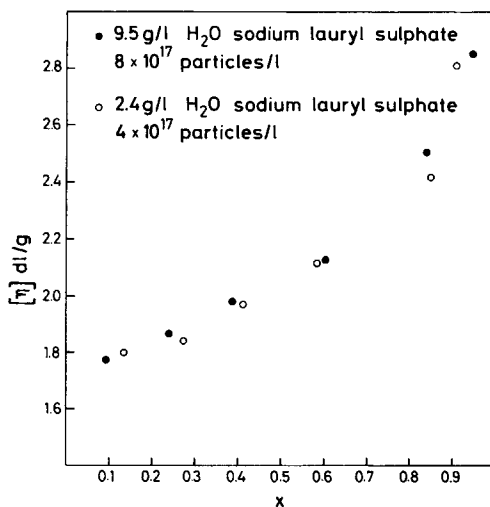


Fig. 8. Limiting viscosity number of poly(vinyl acetate) as function of conversion:  $10^{-3}$  moles  $K_2S_2O_8/l$ .  $H_2O$ .

measurements are now in progress in order to investigate if the MWD of the polymers is also unaffected by the number of particles. This will be the subject of a future publication.

#### Effect of Initiator Concentration

The influence of initiator concentration was investigated at two different emulsifier concentrations. Figure 9 shows a log-log plot of polymerization rate versus initiator concentration. From the slope of the lines it is found that the initiator dependence exponent is 0.5. This is in good agreement with the findings of Dunn and Taylor and Gershberg<sup>6</sup> but contradictory to the results reported by Stannett<sup>5</sup> and Vanzo,<sup>2</sup> where the rate was found to

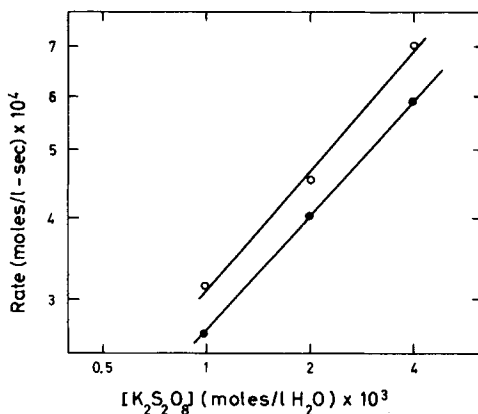


Fig. 9. Effect of initiator concentration on polymerization rate at two different emulsifier concentrations: (○) 9.5; (●) 2.4 g sodium lauryl sulfate /l.  $H_2O$ .



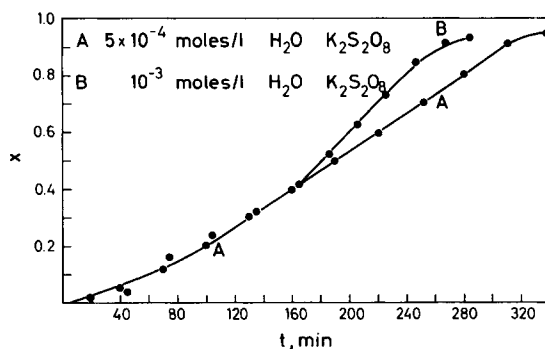


Fig. 10. Effect of addition on extra amount of initiator.

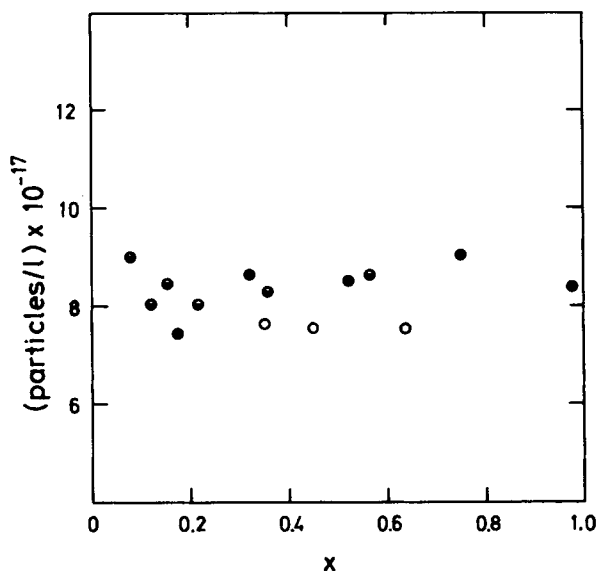


Fig. 11. Number of particles vs. conversion at three different initiator concentrations: (●)  $2 \times 10^{-3}$ ; (◐)  $10^{-3}$ ; (○)  $5 \times 10^{-4}$  moles  $K_2S_2O_8$ /l.  $H_2O$ .  $9.5$  g sodium lauryl sulfate/l.  $H_2O$ .

be of first order with respect to initiator concentration. For vinyl chloride, Ugelstad<sup>13</sup> has reported an order of 0.5 with respect to initiator concentration.

The effect of the addition of an extra amount of initiator at different conversions was also investigated. Figure 10 shows that the polymerization rate increases when more initiator is added. From the slopes of the curves it is found that the ratio between the rates before and after the addition is approximately proportional to the square root of the ratio between the respective initiator concentrations. This effect is also observed in vinyl chloride emulsion polymerization,<sup>16</sup> but not in styrene polymerization.

Figure 11 shows the number of polymer particles as a function of conversion at three different initiator concentrations. Although the points are somewhat scattered, it is reasonable to conclude that the initiator concentration does not affect the number of particles. Also at this point the emulsion polymerization of vinyl acetate resembles that of vinyl chloride<sup>16</sup> but is different from styrene, where the number of particles depends on the initiator concentration to the 0.4 power. Figure 11 also shows that the

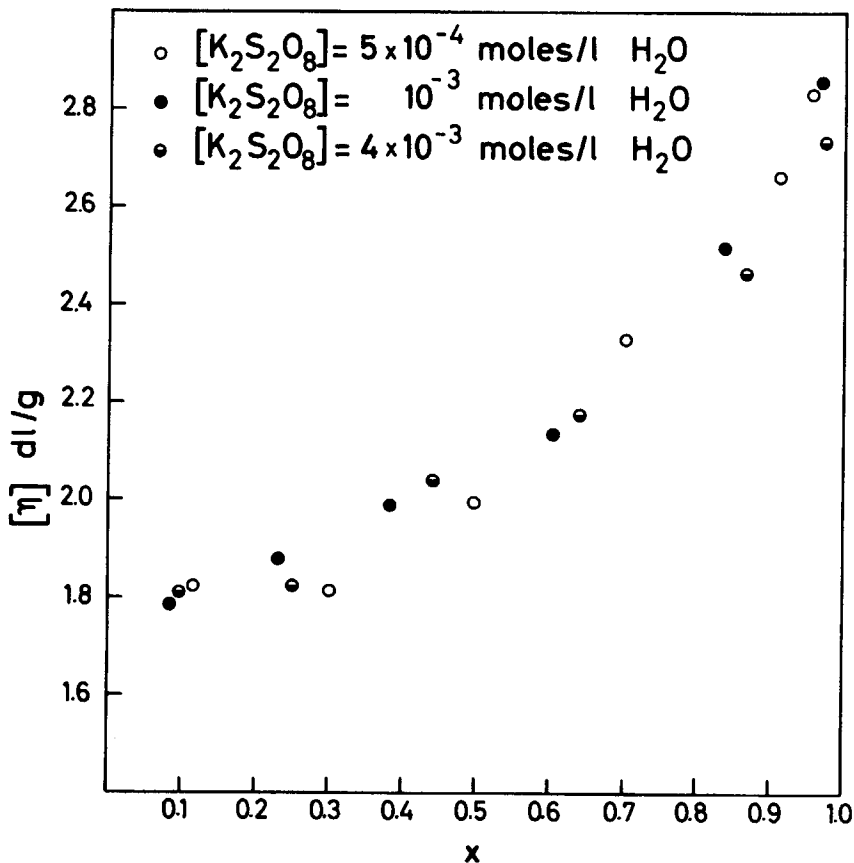


Fig. 12. Limiting viscosity number of poly(vinyl acetate) as function of conversion: 9.5 g sodium lauryl sulfate/l. H<sub>2</sub>O.

number of polymer particles remains constant between 10% and 100%. A similar result has been reported by Napper and Parts.<sup>9</sup>

In Figure 12 is plotted the limiting viscosity number  $[\eta]$  as a function of conversion at three different initiator concentrations, and it appears that  $[\eta]$  is independent of the initiator concentration. The independence of  $[\eta]$  on initiator concentration and number of polymer particles suggests that the molecular weight is controlled primarily by transfer to monomer and polymer. GPC measurements will confirm whether this is the case.

### Effect of Electrolytes

Stannett et al.<sup>5</sup> have investigated the effect of adding electrolytes. They have found that both phosphate buffer and potassium sulfate increased the rate of polymerization. Furthermore, they have found that in the presence of electrolytes the dependence of rate on initiator was decreased. An attempt to reproduce these effects failed. In our experiments, the presence of electrolytes in concentrations of 0.05 moles/l. H<sub>2</sub>O did not affect the rate of polymerization, nor the dependence on initiator concentration.

### Discussion

From the data presented here, the following points can be established concerning vinyl acetate emulsion polymerization:

1. The average concentration of radicals per particle increases with increasing initiator concentration.
2. The rate of polymerization is approximately proportional to the square root of the initiator concentration.
3. The rate of polymerization is proportional to the 0.25 power of the number of particles.
4. The number of polymer particles remains constant in the interval 10% to 100% conversion.
5. The number of polymer particles is independent of the initiator concentration.
6. The number of polymer particles is proportional to the 0.5 power of the emulsifier concentration.
7. The limiting viscosity number is independent of the initiator concentration, emulsifier concentration, and number of polymer particles.

This picture does not resemble that of styrene emulsion polymerization, but rather that of vinyl chloride emulsion polymerization. Ugelstad<sup>13</sup> has recently presented a model for vinyl chloride emulsion polymerization, and it is suggested that the same model could be applied to the vinyl acetate system.

### Presentation of the Model

For vinyl chloride, Ugelstad<sup>13</sup> has deduced the rate expression

$$R_p = \frac{k_p[M_p]}{N_A} (2k_i f[I])^{1/2} \left[ \frac{N_A^2 V_p}{2k_{tp}} + \frac{N_t}{2k_d} \right]^{1/2} \quad (3)$$

where  $k_p$  = propagation rate constant,  $[M_p]$  = monomer concentration in the polymer particles,  $N_A$  = Avogadro's number,  $k_i$  = decomposition rate constant of initiator,  $f$  = initiator efficiency factor,  $[I]$  = initiator concentration,  $V_p$  = total volume of the monomer-swollen polymer particles,  $k_{tp}$  = termination rate constant,  $N_t$  = total number of polymer particles, and  $k_d$  = desorption rate constant.

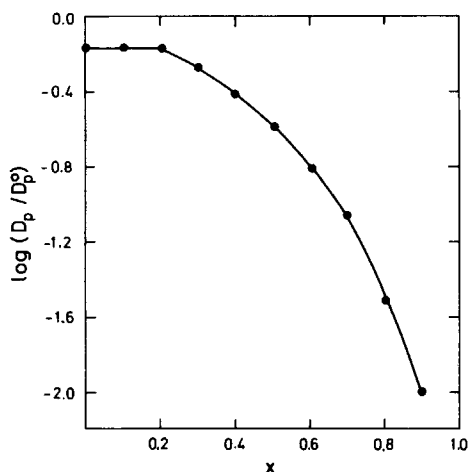


Fig. 13. Plot of  $\log(D_p/D_p^0)$  vs. conversion. Computed from experimental data with aid of eqs. (3) and (5).

To fit the rate expression given in eq. (3) to experimental data, Ugelstad defined the desorption rate constant  $k_d$  as

$$k_d = KD_p(N_i/V_p)^{2/3}k_{fm}/k_p \quad (4)$$

where  $k_{fm}$  is the transfer constant to monomer,  $D_p$  is the self-diffusion constant of a monomer radical in a polymer particle, and  $K$  is a numerical constant. Equation (4) expresses that only radicals formed by transfer to monomer can escape the particles.

In this paper,  $k_d$  will be defined in a different manner. Suppose a monomer radical is formed by transfer to a monomer molecule. This radical can either escape the particle, or it can add a monomer molecule to form a dimeric radical. The probability for the radical to escape is given as

$$\Phi = \frac{2D_p}{r^2} / \left( \frac{2D_p}{r^2} + k_p[M_p] \right) \quad (5)$$

where the diffusion term is obtained from Einstein's diffusion equation<sup>17</sup> and the radius of the particle  $r$  is chosen as the mean displacement necessary for the radical to escape the particle. If desorption of dimeric and larger radicals is neglected owing to a rapid decrease in  $D_p$ , the desorption rate constant is given as the product of  $\Phi$  and the frequency at which monomer radicals are being formed:

$$k_d = \Phi k_{fm}[M_p]/N_A. \quad (6)$$

A certain fraction of the radicals entering the particles from the water phase will escape the particles before adding a monomer molecule. This is accounted for in the absorption rate constant, which, however, drops out in the final rate expression when termination in the water phase is neglected.

During the polymerization, both  $D_p$  and  $k_{tp}$  decrease. The decrease in  $k_{tp}$  is given as function of conversion in eq. (2). It is therefore possible to calculate the decrease in  $D_p$  necessary for eq. (3) to fit the experimental results. Figure 13 shows the relative decrease in  $D_p$  thus obtained. It appears that the diffusion coefficient of monomer radicals should decrease by a factor 100 in the interval 0% to 90% conversion. This is not unreasonable. In an investigation of the diffusion of water through swollen polymer membranes, Peterlin et al.<sup>18</sup> have found a similar decrease in the diffusion coefficient in going from a highly swollen to a dry membrane. Peterlin et al.<sup>18</sup> deduced the following expression for the self-diffusion coefficient of low molecular weight compounds in polymers:

$$D_p = D_p^0 \exp(-\beta x_v(1 - \alpha)/(1 + \alpha x_v)) \quad (7)$$

where  $D_p^0$  is the self-diffusing coefficient of the diffusing compound in its own medium,  $\beta = V^*/V_{fm}$ ,  $\alpha = V_{fp}/V_{fm}$ , and  $x_v = (1 - H)/H$ .  $V^*$  is a critical free volume fraction necessary for diffusion to take place,  $V_{fm}$  and  $V_{fp}$  are free volume fractions of monomer and polymer, respectively, and  $H$  is the volume fraction of the low molecular weight compound. Since

$$x_v = \frac{x \cdot d_m}{(1 - x)d_p}$$

where  $x$  is conversion,  $d_m$  and  $d_p$  are densities of monomer and polymer, respectively, the following relationship between the self-diffusing coefficient and conversion is obtained:

$$D_p = D_p^0 \exp \frac{-\beta x d_m (1 - \alpha)}{(1 - x)d_p + \alpha x d_m} \quad (8)$$

Substituting eq. (8) into eq. (5) and eq. (5) into eq. (3), the values of  $\alpha$  and  $\beta$  necessary to describe the obtained data are found to be  $\alpha = 0.3$  and  $\beta = 3.2$ . In this computation, the following values of the constants were used:  $k_p = 3500$  l./mole-sec,  $2k_{if} = 10^{-6}$ /sec,  $k_{fm} = 0.75$  l./mole-sec,  $d_p = 1150$  g/l.,  $d_m = 900$  g/l., and  $D_p^0 = 10^{-8}$  dm<sup>2</sup>/sec.  $[M_p]$  was calculated from eqs. (9) and (10):

$$[M_p] = \frac{(1 - x_c)d_m}{(1 - x_c + x_c d_m/d_p)86} \quad x \leq x_c \quad (9)$$

$$[M_p] = \frac{(1 - x)d_m}{(1 - x + x d_m/d_p)86} \quad x > x_c \quad (10)$$

where  $x_c$  is the conversion at which the separate monomer phase disappears;  $k_{tp}$  was calculated from eq. (2).

The  $\alpha$  and  $\beta$  values cannot be calculated theoretically with great accuracy. However, comparison with data from the literature<sup>18</sup> shows that the

values computed here are not unreasonable. One should expect the value of  $\alpha$  to lie within 0.15 and 0.40.

With the values of  $\alpha$  and  $\beta$  obtained by fitting eq. (3) to a single experimental curve, we were able to simulate all our experimental data (more than 40 experiments) in the range of conversion from 0% to 100%. Figure 14

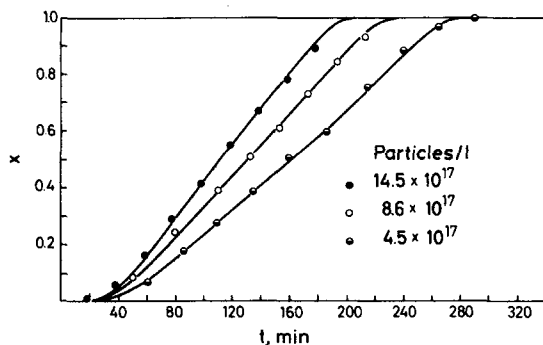


Fig. 14. Comparison between calculated and experimental conversion-versus-time plots. The solid line represents values calculated from eq. (3).

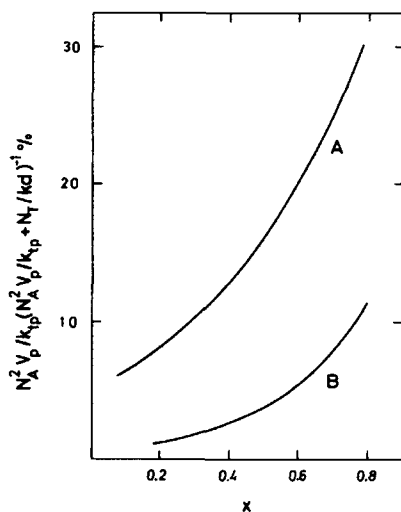


Fig. 15. Contribution of the term  $N_A^2 V_p / k_t p$  to polymerization rate as function of conversion: (A)  $5 \times 10^{18}$  particles./l.; (B)  $10^{18}$  particles/l.

shows a comparison between experimental and calculated conversion-versus-time plots. It is seen that the acceleration observed at high conversions in experiments with large polymer particles is reflected by the mathematical model. Furthermore, the model correctly reflects the effect of number of particles.

Although the termination constant decreases rapidly during the polymerization, the term  $N_A^2 V_p / k_{tp}$  only plays a secondary role for the rate of polymerization. This is illustrated in Figure 15, where the contribution of this term is calculated in per cent of the total polymerization rate as function of conversion at different concentrations of polymer particles.

Thus, it can be concluded that the constant rate behavior in vinyl acetate emulsion polymerization is mainly due to a decrease in the desorption rate constant.

### Comparison with Literature

Stannett et al.<sup>5</sup> have performed a very comprehensive study of the emulsion polymerization of vinyl acetate. Although the recipe used by these investigators is very similar to that used in the present work, a comparison of the results shows large deviations. Therefore, an attempt to apply their model to our data failed. The model deduced by Stannett et al. predicts that the polymerization rate decreases approximately with the fourth root of monomer concentration from the point of disappearance of the separate monomer phase. This is not in agreement with the constant rate behavior observed in this work. Also, the dependence of polymerization rate on initiator and emulsifier concentration is different.

However, excellent agreement is obtained by comparing the data reported by Nomura et al.<sup>7</sup> to our data. In a study of the effect of polymer particles in emulsion polymerization, these investigators have deduced a general rate expression for emulsion polymerization.<sup>19</sup> Application of this expression to vinyl acetate<sup>7</sup> leads to an expression similar to that deduced by Ugelstad for vinyl chloride polymerization.<sup>13</sup>

### CONCLUSIONS

In conclusion, we may say that the emulsion polymerization of vinyl acetate is similar to that of vinyl chloride. In both systems, transfer to monomer seems to play an important role in comparison with styrene emulsion polymerization.

However, one important problem still remains to be solved in the emulsion polymerization of vinyl acetate and vinyl chloride, namely, the mechanism by which the particles are formed. In styrene emulsion polymerization, the number of particles is proportional to the 0.4 power of initiator concentration. In the vinyl acetate system, there is no effect of initiator concentration on the final number of particles.

In accordance with the classic theory for styrene emulsion polymerization, the polymer particles are generated solely by the primary initiator radicals. In the vinyl acetate system the ability of radicals to escape the particles must give rise to formation of particles by such radicals in addition to the particles being generated by the primary initiator radicals. This difference might be contributory to the different effect of initiator concentration on particle formation in the two systems.

### Nomenclature

$d_m$	density of monomer
$d_p$	density of polymer
$D_p^0$	self-diffusion coefficient of monomer radicals in pure monomer
$D_p$	self-diffusion coefficient of monomer radicals in monomer-swollen polymer
$f$	initiator efficiency factor
$H$	volume fraction of monomer in monomer-swollen polymer
[I]	initiator concentration
$k_d$	desorption rate constant
$k_{fm}$	transfer rate constant to monomer
$k_i$	decomposition rate constant of potassium persulfate
$k_p$	propagation rate constant
$k_r$	decomposition rate constant of $\alpha, \alpha'$ -azoisobutyronitrile
$k_{tp}$	termination rate constant in monomer-swollen polymer
[M]	monomer concentration in bulk polymerization
[M <sub>p</sub> ]	monomer concentration in polymer particles
$N_A$	Avogadro's number
$N_T$	total number of polymer particles
$r$	average radius of polymer particles
$R_p$	rate of polymerization
$t$	reaction time
$V_p$	volume of the polymer phase
$V^*$	critical free volume fraction
$V_{fm}$	free volume fraction of monomer
$V_{fp}$	free volume fraction of polymer
$x$	degree of conversion
$x_v$	ratio between volume fraction of polymer and monomer in monomer-swollen polymer
$x_c$	degree of conversion when the separate monomer phase disappears

#### Greek Symbols

$\alpha$	$V_{fp}/V_{fm}$
$\beta$	$V^*/V_{fm}$
[ $\eta$ ]	limiting viscosity number

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### References

1. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
2. E. Vanzo, Ph.D. Thesis, State University College of Forestry at Syracuse University, Syracuse, N.Y., 1962.
3. R. A. Patsiga, Ph.D. Thesis, State University College of Forestry at Syracuse University, Syracuse, N.Y., 1962.
4. V. Stannett, M. Litt, and R. Patsiga, *J. Phys. Chem.*, **64**, 801 (1960).
5. V. Stannett, M. Litt, and R. Patsiga, *J. Polym. Sci. A-1*, **8**, 3607 (1970).



6. D. Gershberg, paper presented at Joint Meeting of A.I.Ch.E. and I.Ch.E. (England), London, June 14, 1965.
7. M. Nomura, M. Harada, K. Nakagawara, W. Eguchi, and S. Nagata, *J. Chem. Eng. (Japan)* **4** (No. 2), 160 (1971).
8. D. H. Napper and A. G. Parts, *J. Polym. Sci.*, **61**, 113 (1962).
9. P. Harriott, *J. Polym. Sci. A-1*, **9**, 1153 (1971).
10. D. M. French, *J. Polym. Sci.*, **32**, 395 (1958).
11. G. E. Ham, *Vinyl Polymerization*, Vol. 1, Part I, Marcel Dekker, New York, 1967, pp. 208-329.
12. F. Danusso, G. Pajaro, and D. Sianesi, *Chim. Ind. (Milan)*, **41**, 1170 (1959).
13. J. Ugelstad, P. C. Mork, P. Dahl, and P. Ragnes, *J. Polym. Sci. C*, **27**, 49 (1959).
14. T. O'Neill, J. Pinkava, and J. Hoigné, paper presented at the 3rd Symposium on Radiation Chemistry, Tihany, Hungary, May 10-15, 1971.
15. A. S. Dunn and P. A. Taylor, *Makromol. Chem.*, **83**, 207 (1965).
16. J. Ugelstad and P. C. Mork, *Br. Polym. J.*, **2**, 31 (1971).
17. A. Sheludko, *Colloid Chemistry*, Elsevier, Amsterdam, 1966, pp. 47-55.
18. A. Peterlin, H. Yasuda, and C. E. Lamaze, *J. Polym. Sci. A-2*, **9**, 1117 (1971).
19. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *J. Chem. Eng. (Japan)*, **4** (No. 1), 54 (1971).

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