

# A Kinetic Study of Vinyl Acetate Polymerization in Aqueous Media in the Absence of Emulsifier

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## Synopsis

In the absence of emulsifying agents, vinyl acetate polymerization in aqueous media was carried out at 50°C over a wide range of initial initiator and monomer concentrations to clarify the effect of reaction conditions on the kinetic behavior of the polymerization system. It was shown that the rate of polymerization was proportional to reaction time and initiator concentration and independent of the number of polymer particles present. The rate could also be successfully explained by the Smith and Ewart theory for emulsion polymerization when the dissolved monomer in water and the Trommsdorff effect were taken into consideration. A set of equations which could account for the effect of dissolved monomer in water on the rate of polymerization is proposed.

## INTRODUCTION

It is well known that highly water-soluble monomers such as vinyl acetate can be easily polymerized in aqueous media with the use of potassium persulfate as initiator even in the absence of emulsifying agents. In this case, a large number of polymer particles are generated in the early stage of the polymerization, though the number is considerably smaller than that observed in an usual emulsion polymerization system. To date, much work has been published on the polymerization of vinyl acetate in aqueous media.<sup>1-5</sup> Most of it deals only with polymerization systems with monomer concentrations lower than its solubility limit in water. However, the kinetics of vinyl acetate polymerization in aqueous media is not yet completely elucidated.

The purpose of this paper is first to make clear the kinetic behavior of vinyl acetate polymerization in aqueous media over a wide range of monomer and initiator concentrations and second, to propose a reaction model that explains the experimentally observed polymerization rate.

## EXPERIMENTAL

### Materials

Vinyl acetate monomer of commercial grade was distilled twice under reduced nitrogen pressure, stored at -20°C in a refrigerator, and redistilled just before use. Potassium persulfate of extra-pure grade was used as initiator without further purification. All water used in this experiment was purified by distillation in the presence of alkaline potassium permanganate.

### Apparatus and Procedure

A schematic diagram of the experimental apparatus and the dimensions of the reactor vessel and the impeller are shown in Figure 1. The reactor was a cylindrical glass vessel with a dished bottom equipped with a four-bladed paddle-type impeller and four baffle plates located on the vessel wall at 90° intervals. In the polymerization experiments, the reaction vessel was first charged with the desired amounts of purified monomer and water a small portion of which had been set aside for preparing an aqueous initiator solution. Dissolved oxygen was removed by bubbling purified nitrogen gas through the reaction mixture for about 20 min. The aqueous initiator solution previously prepared and deoxygenated with this pure nitrogen was quickly fed to the reactor and the polymerization started. In all cases, the reaction temperature was maintained at  $50^\circ \pm 0.5^\circ\text{C}$  by immersing the reaction vessel in a thermostatted water bath. In order for separate monomer droplets to be uniformly dispersed throughout the reaction vessel, the impeller speed was initially maintained at 400 rpm and then decreased to 250 rpm to avoid excess coagulation of the polymer particles present after the monomer droplets had disappeared. Monomer conversion was determined gravimetrically and the degree of polymerization, by the viscosity in benzene solution method employing Nakajima's equation<sup>6</sup>:

$$[\eta] = 5.36 \times 10^{-4} [M_\eta]^{0.62} \quad (1)$$

where  $M_\eta$  is the viscosity-average molecular weight. The number of polymer particles per unit volume of water,  $N_T$ , was calculated from the monomer conversion  $X_M$ , and the volume-average diameter of the polymer particles  $d_p$  was determined by the aid of an electron microscope, using the following equations:

$$d_p^3 = \Sigma n_i d_{pi}^3 / \Sigma n_i \quad (2)$$

$$N_T = 6M_0 X_M / \pi d_p^3 \rho_p \quad (3)$$

where  $\rho_p$  is the density of the polymer ( $\text{g}/\text{cm}^3$ ) and  $M_0$  is the initial monomer

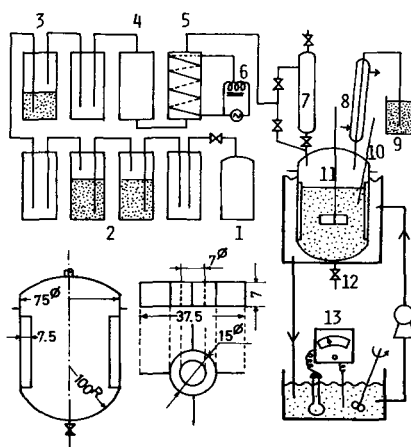


Fig. 1. Schematic diagram of experimental apparatus: (1)  $\text{N}_2$  gas cylinder; (2) alkaline pyrogallol solution; (3)  $\text{H}_2\text{SO}_4$ ; (4)  $\text{CaCl}_2$ ; (5) electric furnace containing copper gauze; (6) voltage regulator; (7) feeder for aqueous initiator solution; (8) reflux condenser; (9) pressure regulator; (10) thermometer; (11) paddle-type impeller; (12) sampling cock; initiator solution; (13) temperature regulator.

concentration (g/cc water). The monomer weight fraction in the monomer-swollen polymer particles,  $\psi$ , was determined by the use of the previous method.<sup>7</sup>

## RESULTS

### Effect of Initial Monomer Concentration on the Course of Polymerization and the Number of Polymer Particles Formed

Figure 2 shows the effect of initial monomer concentration on the course of polymerization at a fixed initiator concentration,  $I_0 = 1.25$  g/l. water, the monomer concentration being varied from 0.02 to 0.5 g/cc water. The variation of the number of polymer particles produced with progress of polymerization, corresponding to the experimental conditions shown in Figure 2, is presented in Figure 3. It is obvious from this figure that the number of polymer particles produced attains to a constant value at a very early stage of the polymerization process. In Figure 4 the constant value of  $N_T$  shown in Figure 3 is plotted against

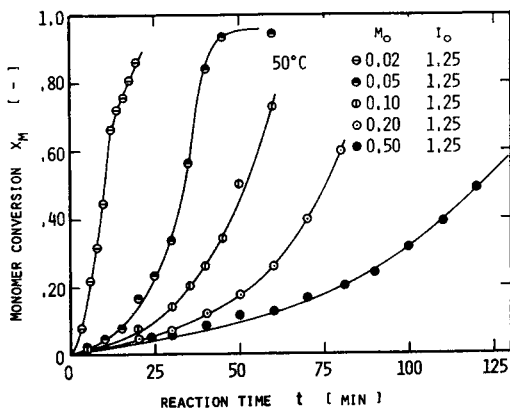


Fig. 2. Effect of initial monomer concentration on the course of polymerization.

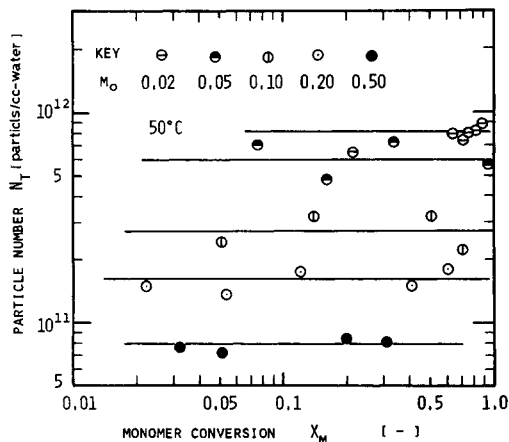


Fig. 3. Effect of initial monomer concentration on the variation of the number of polymer particles produced with progress of polymerization.

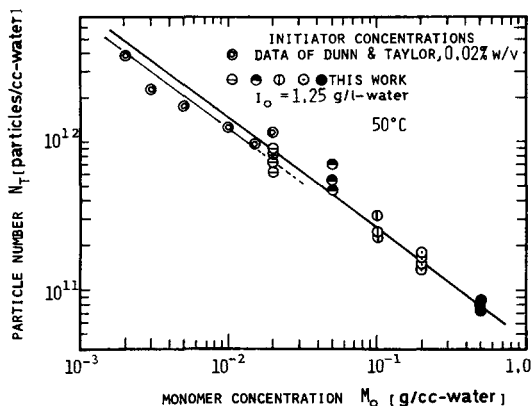


Fig. 4. Effect of initial monomer concentration on the number of polymer particles produced.

the initial monomer concentration, together with the experimental data reported by Dunn and Taylor.<sup>2</sup> It is seen that the slope of the best straight line through the data points obtained in this experiment is  $-0.75$  and equals the slope of a straight line through those of Dunn and Taylor. The reason why the number of polymer particles formed is proportional to the  $-0.75$  power of the initial monomer concentration is not clear at the present stage and stands further clarification.

#### Effect of Initial Initiator Concentration on the Course of Polymerization and the Number of Polymer Particles Formed

The conversion-versus-time curves obtained with five different initiator concentrations are illustrated in Figure 5. It is evident that the polymerization rate is gradually accelerated up to more than 80% conversion, followed by a region of decelerating rate. Therefore, there is no region of constant rate as observed in the emulsion polymerization of vinyl acetate.<sup>7,8</sup> In all the above experiments, the number of polymer particles formed was also constant from the early stage of the polymerization process. The constant number of polymer particles is plotted in Figure 6. It is concluded that the initiator concentration has little

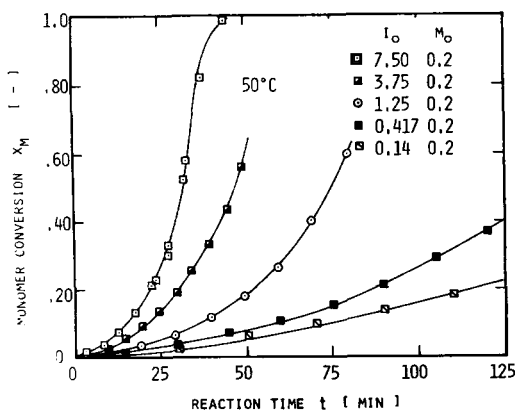


Fig. 5. Effect of initial initiator concentration on the course of polymerization.

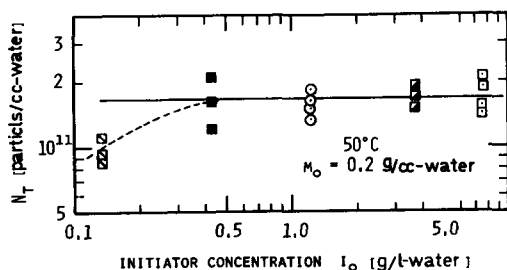


Fig. 6. Effect of initial initiator concentration on the number of polymer particles produced.

or no influence on the number of polymer particles produced in this system. The same result has also been found in the emulsion polymerization of vinyl acetate.<sup>8,14</sup> This result does not coincide with that reported by Dunn et al.<sup>2,5</sup> They have found that the number of polymer particles increased with increasing the initial initiator concentration. The initiator concentrations used in their investigations were very low and about one order of magnitude lower than those in this study. The same result as that found by Dunn et al.<sup>2,5</sup> has also been obtained by Litt et al.<sup>9</sup> in the emulsion polymerization of vinyl acetate when the polymerizations were conducted in lower initiator concentrations (0.054–0.54 g/l. water) which were comparable to those employed by Dunn et al.<sup>2,5</sup> This result may be due mainly to a small amount of impurity remaining in the reaction mixture. This would affect the number of polymer particles produced, the degree of its influence becoming more and more drastic as the initial initiator concentration decreases. The reason for this is not clear at the present stage and must be investigated in more detail.

## DISCUSSION

### Presentation of Basic Rate Equations

Recently, it has been established by many investigators<sup>1,2,8,14</sup> that in heterogeneous polymerizations of vinyl acetate, such as emulsion polymerization or dispersion polymerization in aqueous media, the reaction proceeds exclusively in the monomer-swollen polymer particles. If the reaction in the polymer particles is dominant, it is quite reasonable to assume that the theory worked out for emulsion polymerization is also applicable to this heterogeneous polymerization system. The rate of polymerization should be given by the following well-known expression:

$$-\frac{d[M]}{dt} = \frac{k_p[M_p]M_g}{N_A} \bar{n}N_T \quad (4)$$

Rewriting eq. (4) in terms of monomer conversion  $X_M$ , we have

$$\frac{dX_M}{dt} = \frac{k_p M_g}{M_0 N_A} [M_p] \bar{n} N_T \quad (5)$$

where  $k_p$  is the rate constant of propagation (l./mole-sec),  $M_g$  is the molecular weight of monomer (g/mole),  $N_A$  is Avogadro's number,  $[M_p]$  is the monomer concentration in the polymer particles (mole/l.), and  $\bar{n}$  is the average number of radicals per particle (molecule/particle).

Ugelstad et al.<sup>10</sup> has derived an exact solution to the recursion formula proposed by Smith and Ewart<sup>11</sup> for the average number of radicals per particle  $\bar{n}$  under the steady-state assumption for the polymer particles with  $n$  radicals, taking account of radical balance in the water phase:

$$\bar{n} = \frac{\alpha}{4} \frac{I_m(\alpha)}{I_{m-1}(\alpha)} \quad \alpha^2 = 8\alpha \quad (6)$$

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2$$

where  $I_m$  is the modified Bessel function of the first kind and the other nondimensional parameters are defined as follows:

$$\alpha = \rho_A v_p / k_{tp} N_T, \quad \alpha' = r_i v_p / k_{tp} N_T,$$

$$m = k_f v_p / k_{tp} N_T, \quad Y = 2N_T k_{tw} / K_a^2 v_p \quad (6')$$

where  $\rho_A$  is the total rate of radical absorption in the particles (molecule/cc water-sec),  $v_p$  is the volume of a particle (cm<sup>3</sup>),  $k_{tp}$  is the rate constant of termination in the polymer particles (cm<sup>3</sup>/molecule-sec),  $r_i$  is the production rate of initiator radicals in the water phase (molecules/cc water-sec),  $k_f$  is the rate coefficient of radical desorption from the polymer particles (1./sec),  $k_{tw}$  is the rate constant of termination in the water phase (cm<sup>3</sup>/molecule-sec), and  $K_a$  is the rate constant of radical absorption into the polymer particles (1./sec).

Ugelstad et al.<sup>12</sup> and the present authors<sup>13</sup> have shown that eq. (6) is approximated by the following simple equations when  $\bar{n} < 0.1$ :

$$\bar{n} = \left[ \frac{r_i}{2k_f N_T} + \frac{r_i v_p}{2k_{tp} N_T} \right]^{0.5} \quad (7)$$

and when  $\bar{n} \gg 1$ ,

$$\bar{n} = \left[ \frac{r_i v_p}{2k_{tp} N_T} \right]^{0.5} \quad (8)$$

The validity of eq. (7) has been tested by Ugelstad et al.<sup>12</sup> and Friis et al.<sup>15</sup> in the emulsion polymerization of vinyl chloride and by the present authors<sup>7,8</sup> and Friis et al.<sup>14,15</sup> in the emulsion polymerization of vinyl acetate. It is obvious that eq. (8) is of the same form as case 3 in the Smith and Ewart theory.<sup>11</sup> Napper et al.<sup>1</sup> have already suggested the possibility of the Smith and Ewart case 3 kinetics in the polymerization of vinyl acetate in aqueous solution. However, the rate of vinyl acetate polymerization in aqueous media in the absence of emulsifying agents is still not completely explained.

### Monomer Concentrations in the Polymer Particles and in the Water Phase

As can be seen from eq. (4) or (5), the monomer concentration in the polymer particles is one of the principal factors affecting the rate of polymerization. Further, it has influence, as a matter of course, on the monomer weight fraction in the polymer particles and consequently on the rate constant of mutual termination of radicals in the polymer particles,  $k_{tp}$ . This is because the value of  $k_{tp}$  strongly depends on the polymer weight fraction in the particles.<sup>8,14,16</sup> Therefore, for estimating the rate of polymerization it is important that the exact values of the monomer concentration in the polymer particles be known.

The material balance equation for monomer in the reaction mixture is represented by

$$M_0 = M_w + M_p + P + M \quad (9)$$

where  $M_w$  is the quantity of monomer dissolved in the water phase,  $M_p$  is the quantity of monomer absorbed in the polymer particles,  $P$  is the weight of polymer in the polymer particles per unit volume of water and equal to  $M_0 X_M$ , and  $M$  is the quantity of monomer existing as monomer droplets in the water phase. These symbols are all expressed in g monomer/cc water. When the value of  $M_0$  is less than that of the solubility limit of the monomer in water,  $M_{wc}$ , the term  $M$  can be omitted from eq. (9).

The monomer concentration in the polymer particles,  $[M_p]$ , may be given by the following simple expression, provided the volumes of monomer and polymer in the monomer-swollen polymer particles are approximately additive:

$$[M_p] = \frac{M_p}{M_p/\rho_M + P/\rho_p} \frac{1000}{M_g} \text{ mole/l. particles} \quad (10)$$

Since the value of the densities of the monomer,  $\rho_M$ , and the polymer,  $\rho_p$ , are close to unity, eq. (10) may be approximated as

$$[M_p] = \frac{M_p}{M_p + P} \frac{1000}{M_g} = \frac{\gamma}{1 + \gamma} \frac{1000}{M_g} \quad (10')$$

where  $\gamma$  is the weight ratio of monomer to polymer in the polymer particles and is defined by

$$\gamma = M_p/P \quad (11)$$

Other properties concerning the polymer particles are the weight fractions of monomer,  $\psi$ , and of polymer,  $\omega$ , given by

$$\psi = \frac{M_p}{P + M_p} = \frac{\gamma}{1 + \gamma} \quad (12)$$

$$\omega = \frac{P}{P + M_p} = \frac{1}{1 + \gamma} \quad (13)$$

The relationship between  $[M_w]$ , the monomer concentration in the water phase, and  $M_w$  is expressed by

$$[M_w] = \frac{M_w}{1 + M_w/\rho_M} \frac{1000}{M_g} \text{ mole/l. water} \quad (14)$$

Considering that normally  $M_w/\rho_M \ll 1$ , eq. (14) is approximated as

$$[M_w] = M_w (1000/M_g) \quad (15)$$

On the other hand, we assume here that  $[M_p]$  may be approximately connected to  $[M_w]$  by the following linear relationship:

$$[M_p] = m[M_w] \quad (16)$$

where  $m$  is the partition coefficient of monomer between the water and particle phases. The validity of eq. (16) will be shown later.

Figure 7 illustrates the results of measurement of the weight fraction of monomer in the polymer particles,  $\psi$ , together with the experimental data obtained

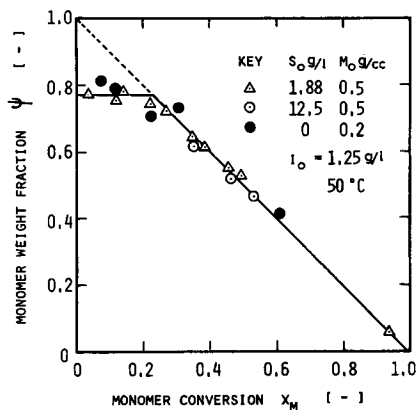


Fig. 7. Monomer weight fraction in the polymer particles,  $\psi$ , vs monomer conversion,  $X_M$ .

in the emulsion polymerization of vinyl acetate.<sup>8</sup> It is concluded from this figure that in the region where monomer droplets exist in the water phase, the monomer concentration in the polymer particles is constant and equal to 8.95 mole/l. particles, this has also been reported for an emulsion polymerization system.<sup>8</sup> Napper et al.<sup>1</sup> have reported that the saturation concentration of vinyl acetate in water,  $[M_w]_c$ , is 0.33 mole/l. water. The value of  $m$ , therefore, can be calculated to be 27.1 from eq. (16) if the constant values of  $[M_p]_c = 8.95$  mole/l. particles and  $[M_w]_c = 0.33$  mole/l. water are employed.

In the region where monomer droplets disappear in the water phase, that is, where  $M = 0$ , one can obtain the following formula using eqs. (9) to (16):

$$X_M = \frac{(1 - mM_w)(M_0 - M_w)}{M_0} \quad (17)$$

Hence, the critical conversion  $X_{Mc}$  at which the monomer droplets phase disappear in the reaction mixture is, from eq. (17),

$$X_{Mc} = \frac{(1 - mM_{wc})(M_0 - M_{wc})}{M_0} \quad (18)$$

where  $M_{wc}$  is the critical solubility of the monomer in water (g/cc water). Table I shows the values of  $X_{Mc}$  calculated by eq. (18) at various initial monomer concentrations using the values of  $m = 27.1$  and  $M_{wc} = 0.028$  g/cc water.

On the other hand,  $\gamma$  can be written in terms of  $M_w$  and  $[M_w]$  by the use of eqs. (10'), (15), and (16):

$$\gamma = \frac{mM_w}{1 - mM_w} = \frac{(mM_g/1000)[M_w]}{1 - (mM_g/1000)[M_w]} \quad (19)$$

TABLE I  
Theoretical Relationship Between  $X_{Mc}$  and  $M_0$

$M_0$ , g/cc water	$X_{Mc}$
0.50	0.22
0.20	0.20
0.10	0.16
0.05	0.10
0.04	0.07



Introducing values of  $M_g = 86.06$  and  $m = 27.1$  into eq. (19) yields

$$\gamma = \frac{2.33[M_w]}{1 - 2.33[M_w]} \quad (20)$$

A comparison of the experimental and calculated values of  $\gamma$  is illustrated in Figure 8. The solid line shows the values calculated by eq. (20) and is in fairly good agreement with the experimental data obtained by Napper et al.<sup>1</sup> This result is indirect but is strong evidence that eq. (16) is reasonable and, therefore, may be used to correlate  $[M_p]$  to  $[M_w]$ .

One can now evaluate the monomer concentrations in the polymer particle and water phases by the equations summarized below.

(1) In the region where monomer droplets exist in the water phase ( $X_M < X_{Mc}$ ),

$$[M_p] = [M_p]_c = 8.95 \text{ mole/l. particles} \quad (21)$$

$$[M_w] = [M_w]_c = 0.33 \text{ mole/l. water} \quad (22)$$

$$\gamma = \gamma_c = 3.35 \quad (23)$$

$$\omega = \omega_c = 0.23 \quad (24)$$

(2) In the region where monomer droplets disappear in the water phase ( $X_M \geq X_{Mc}$ ), we get, from eq. (17),

$$M_w = \frac{(1 + mM_0) - [(1 + mM_0)^2 - 4mM_0(1 - X_M)]^{0.5}}{2m} \quad (25)$$

From eqs. (15), (16), and (25), we have

$$[M_p] = m[M_w] = (1000/M_g)mM_w = (500/M_g) \{ (1 + mM_0) - [(1 + mM_0)^2 - 4mM_0(1 - X_M)]^{0.5} \} \quad (26)$$

Introducing eq. (25) into eq. (19) yields

$$\gamma = \frac{(1 + mM_0) - [(1 + mM_0)^2 - 4mM_0(1 - X_M)]^{0.5}}{(1 - mM_0) + [(1 + mM_0)^2 - 4mM_0(1 - X_M)]^{0.5}} \quad (27)$$

Hence,

$$\omega = \frac{(1 - mM_0) + [(1 - mM_0)^2 - 4mM_0(1 - X_M)]^{0.5}}{2} \quad (28)$$

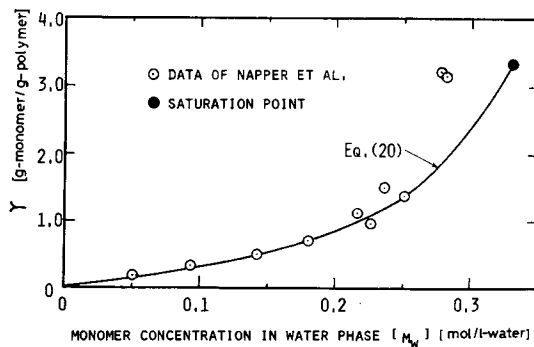


Fig. 8. Comparison between experimental and theoretical  $\gamma$  vs  $[M_w]$ .

(3) In the case where monomer droplets do not exist in the water phase from the start of polymerization, that is, when  $M_0 < M_{wc}$ , eqs. (25) to (28) are also applicable to the prediction of the values of  $[M_p]$ ,  $[M_w]$ ,  $\gamma$ , and  $\omega$ .

The effect of dissolved monomer in water on the monomer concentration in the polymer particles was taken into consideration. In the conventional treatment,<sup>8,14</sup> however, the critical conversion  $X_{Mc}$  at which the monomer droplets disappeared in the water phase was regarded as a constant value of 0.23 or 0.21 independent of the initial monomer concentration  $M_0$ .<sup>8,14</sup> The following simple equations were used to calculate the monomer concentration in the polymer particles.<sup>8</sup>

(a) In the region where monomer droplets exist in the water phase ( $X_M < X_{Mc} = 0.23$ ),

$$[M_p] = [M_p]_c = 8.95 \text{ mole/l. particles} \quad (21)$$

$$\gamma = \gamma_c = 3.35 \quad (23)$$

$$\omega = \omega_c = 0.23 \quad (24)$$

(b) In the region where monomer droplets disappear in the water phase ( $X_M > X_{Mc} = 0.23$ ),

$$[M_p] = [M_p]_c \left( \frac{1 - X_M}{1 - X_{Mc}} \right) \quad (29)$$

$$\gamma = \frac{1 - X_M}{X_M} \quad (30)$$

$$\omega = X_M \quad (30')$$

Figure 9 represents the effect of the initial monomer concentration  $M_0$  on the variation of the monomer concentration in the polymer particles. The solid line shows the values predicted by the conventional method, that is, by using eqs. (21) and (29). It is concluded from this result that the conventional method is approximately valid only when the initial monomer concentration is in the higher range.

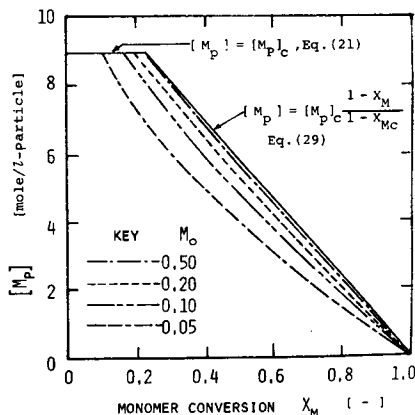


Fig. 9. Effect of initial monomer concentration on the variation of monomer concentration in the polymer particles.

## Derivation of Polymerization Rate Equations

Choice among eqs. (6) to (8) depends upon the actual average number of radicals per particle in this emulsion polymerization system. Figure 10 shows the observed values of  $(k_p \bar{n})_{\text{obs}}$  calculated from the instantaneous polymerization rate obtained by graphic differentiation of the monomer conversion-versus-time curves given in Figures 2 and 5 using eqs. (5), (21), and (26) and the observed values of  $N_T$ . It is clear from this figure that the actual value of  $\bar{n}$  is much greater than unity in most runs shown here because the value of  $k_p$  at 50°C is generally expected to be in the range  $10^3$ – $10^4$  l./mole-sec. It is concluded, therefore, that eq. (8) is applicable to this polymerization system. In using eq. (8), however, it is necessary to know correct values of  $r_i$  and  $k_{tp}$ . The rate of radical production in the water phase  $r_i$  will be given by

$$r_i = 2k_d f I_0 N_A / 1000 M_I \quad \text{molecules/cc water} \cdot \text{sec} \quad (31)$$

where  $k_d$  is the rate constant of initiator decomposition (l./sec),  $f$  is the initiator efficiency (—),  $I_0$  is the initial initiator concentration (g/l. water), and  $M_I$  is the molecular weight of the initiator. It is reasonable to assume that the value of  $r_i$  is constant regardless of the progress of polymerization, because the half-life of the decomposition of potassium persulfate initiator is sufficiently long compared with the whole reaction time.

It is not yet fully understood how  $k_{tp}$ , the rate constant of termination of radicals in the polymer particles, varies as the polymerization progresses and what factors affect its value, although it is widely known that  $k_{tp}$  decreases with the progress of polymerization due to the Trommsdorff effect. The present

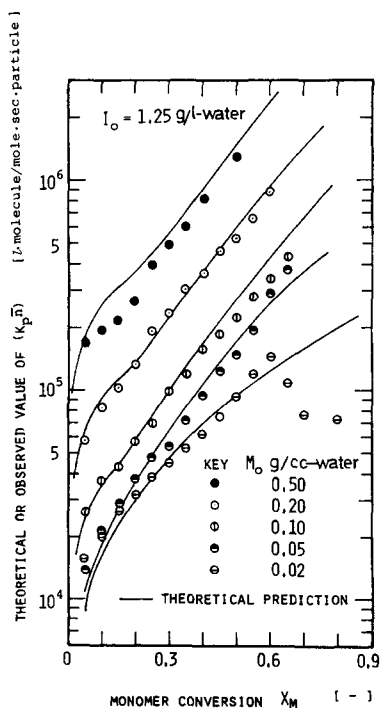


Fig. 10. Plot of experimental  $(k_p \bar{n})_{\text{obs}}$  vs  $X_M$  at various initial monomer and initiator concentrations; (—) theoretical prediction referred to later.

authors have shown that in the emulsion polymerization of vinyl acetate,  $k_{tp}$  may be expressed as a function of the weight fraction of polymer in the polymer particles  $\omega$ , as given below<sup>8</sup>:

$$k_{tp} = 7.8 \times 10^{-13} \exp[-8.3\omega] \quad \text{cm}^3/\text{molecule} \cdot \text{sec} \quad (32)$$

However, it is not adequate to use eq. (32) in this system, because eq. (32) was obtained without considering the effect of dissolved monomer in water on the monomer concentration in the polymer particles.

Therefore, we have reanalyzed<sup>17</sup> the rate data taking account of this effect and obtained the result shown by the symbol ( $\blacktriangle$ ) in Figure 11, the other symbols showing the results determined in this system by the following procedure. From eqs. (5) and (8), we get

$$\frac{dX_M}{dt} = \frac{k_p[M_p]}{M_0 N_A} \left( \frac{r_i v_p N_T}{2k_{tp}} \right)^{0.5} \quad (33)$$

Introducing eq. (31) and the relation  $v_p N_T = M_0 X_M (1 + \gamma) = M_0 X_M / \omega$  into eq. (33) yields

$$\frac{dX_M}{dt} = [M_p] M_g \left( \frac{k_p^2 k_{df}}{10^3 M_I N_A} \right)^{0.5} \left( \frac{I_0}{M_0} \right)^{0.5} \left( \frac{X_M}{k_{tp} \omega} \right)^{0.5} \quad (34)$$

Rewriting eq. (34) leads to

$$k_{tp} = ([M_p] M_g)^2 \left( \frac{k_p^2 k_{df}}{10^3 M_I N_A} \right) \left( \frac{I_0}{M_0} \right) \left[ \frac{X_M}{(dX_M/dt)^2 \omega} \right] \quad (35)$$

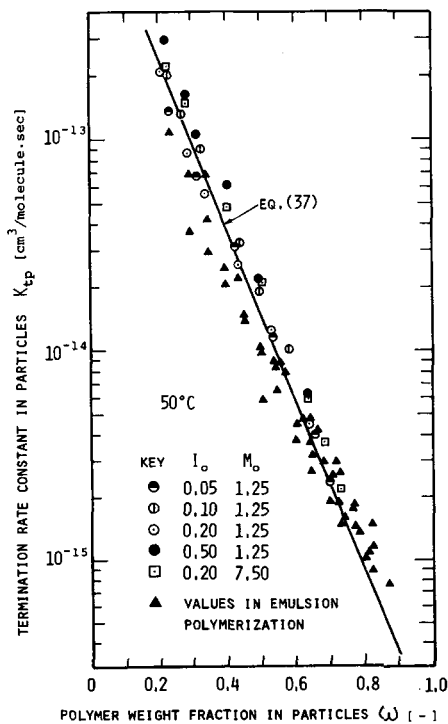


Fig. 11. Experimental correlation of  $k_{tp}$  with  $\omega$ .

It is evident that the right-hand side of eq. (35) is only a function of the monomer conversion  $X_M$  at fixed initial initiator and monomer concentrations, since  $\omega$  is also a function of  $X_M$ , as given by eqs. (24) and (28). In the previous paper dealing with the emulsion polymerization of vinyl acetate,<sup>8</sup> we have found the following value:

$$k_p k_{df} = 1.63 \times 10^2 \text{ l.}^2/\text{mole}^2 \cdot \text{sec}^3 \quad (36)$$

Applying this value to eq. (35) and analyzing the experimental conversion-versus-time data given in Figures 2 and 5 in accordance with eq. (35), we get the values of  $k_{tp}$  as a function of  $\omega$ , as shown in Figure 11. It is seen that the values of  $k_{tp}$  observed in this polymerization system are in good agreement with those determined in the emulsion polymerization. This result also indicates that eq. (8) is applicable to this polymerization system. These experimentally determined values of  $k_{tp}$  are approximately correlated by a single straight line expressed by the following formula:

$$k_{tp} = 16.6 \times 10^{-13} \exp[-9.4\omega] \text{ cm}^3/\text{molecule} \cdot \text{sec} \quad (37)$$

From the discussion and the equations given above, we can get the following rate expressions for vinyl acetate polymerization in aqueous media.

(1) In the region where monomer droplets exist in the water phase ( $X_M < X_{Mc}$ ),

$$\frac{dx_M}{dt} = [M_p]_c M_g \left( \frac{k_p^2 k_{df}}{10^3 M_I N_A} \right)^{0.5} \left( \frac{I_0}{M_0} \right)^{0.5} \left[ \frac{X_M}{(k_{tp})_c \omega_c} \right]^{0.5} \quad (38)$$

Integration of eq.(38) yields

$$X_M = \frac{([M_p]_c M_g)^2 k_p^2 k_{df} I_0}{4(k_{tp})_c \omega_c 10^3 M_I N_A M_0} t^2 \quad (39)$$

where  $(k_{tp})_c$  is the constant value of  $k_{tp}$  at  $\omega = \omega_c = 0.23$ . Equation (39) predicts that the monomer conversion should vary proportionally with the square of the reaction time at fixed initial initiator and monomer concentrations.

(2) In the region where monomer droplets disappear in the water phase ( $X_M \geq X_{Mc}$ ), eq. (34) is valid. Unfortunately, eq. (34) cannot be integrated analytically because  $[M_p]$  and  $\omega$  are complicated functions of  $X_M$ . However, the reaction time  $t$  can be known as a function of  $X_M$  by numerical integration of eq. (34).

(3) In the case where monomer droplets do not exist in the water phase from the start of polymerization, that is, when  $M_0 \leq M_{wc}$ , eq. (34) is also used over the whole range of monomer conversion. According to the result of numerical integration of eq. (34), it is seen, as shown below, that  $X_M$  varies in proportion to the square of the reaction time up to considerably higher degree of the monomer conversion:

$$X_M = K(M_0) I_0 t^2 \quad (40)$$

where  $K(M_0)$  is a function of  $M_0$  and has found by numerical calculation to be inversely proportional to  $M_0^2$  in the vicinity of  $M_{wc}$ .

### Comparison Between Experimental and Theoretical Conversion-Versus-Time Relationship

To check the validity of eqs. (39) and (40), the monomer conversions experimentally observed under the condition  $M_0 > M_{wc}$  shown in Figures 2 and 5 are plotted against  $(I_0/M_0)t^2$ . It can be seen from this figure that these experimental data show good agreement with the theoretical prediction by eq. (39). From the slope of the best straight line through the data points less than the critical conversion  $X_{Mc}$ , the value of  $k_p^2 k_{df}$  can be found by calculation to be

$$k_p^2 k_{df} = 1.66 \times 10^2 \text{ l.}^2/\text{mole}^2 \cdot \text{sec}^3. \quad (41)$$

This value is almost the same as that obtained in emulsion polymerization as given by eq. (36). In Figure 12(B) are plotted the conversion-versus-time data obtained at  $M_0 = 0.020 \text{ g/cc water}$  (i.e.,  $M_0 < M_{wc}$ ) and shown in Figure 2, in accordance with eq. (40). This plot demonstrates that the monomer conversion varies in proportion to the square of the reaction time, as shown by eq. (40), even when monomer droplets do not exist in the water phase from the start of polymerization. Napper et al.<sup>1</sup> have also shown experimentally that the monomer conversion is linear with the square of the reaction time over a wide range of the monomer conversion and that the slope of the linear region of the conversion-versus-time curve is proportional to the initiator concentration. Their result is also good evidence supporting the validity of eq. (40).

The experimental and theoretical conversion-versus-time curves are compared in Figures 13 and 14, where the solid lines represent the theoretical curves predicted using the equations developed here and the rate constants given by eqs. (37) and (41). The dotted lines are the curves calculated using the same equations and rate constants except that eqs. (29) and (30') are used in place of eqs. (26) and (28). The solid lines show excellent agreement with the experimental values, whereas the dotted lines deviate gradually from the observed values as  $M_0$  decreases to  $M_{wc}$  (below  $M_{wc}$ , theoretical prediction cannot be made because eq. (29) is valid only for the region  $M_0 > M_{wc}$ ). Furthermore, it can be seen that theoretical values of  $k_p \bar{n}$  predicted by eqs. (8), (31), (36), and (37) also agree well with those observed, as shown in Figure 10. Therefore, it is concluded from these comparisons that the course of vinyl acetate polymerization in aqueous media

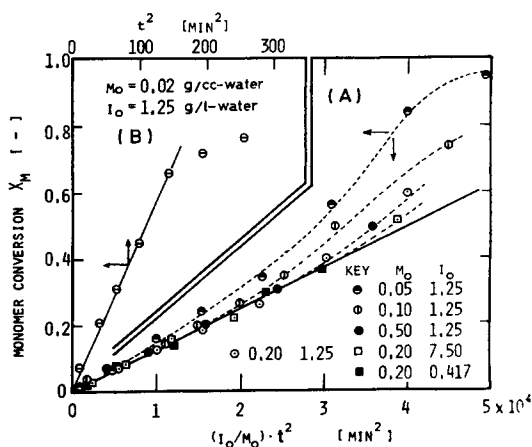


Fig. 12. Plot of experimental monomer conversion  $X_M$  vs  $(I_0/M_0)t^2$  or  $t^2$ .

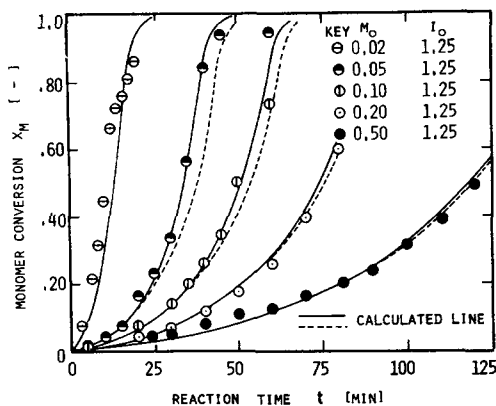


Fig. 13. Comparison between theoretical and experimental conversion-vs-time curves at various initial monomer concentrations.

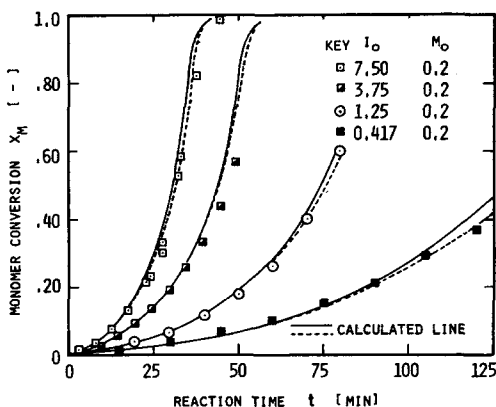


Fig. 14. Comparison between theoretical and experimental conversion-vs-time curves at various initial initiator concentrations.

can be well predicted by the reaction model developed in this study over a wide range of the initial initiator and monomer concentrations. It is very convenient that no knowledge of the number of polymer particles is needed to follow the progress of polymerization, because at present it is still impossible to estimate theoretically the number of polymer particles produced in the absence of emulsifying agents.

### Comparison Between Experimental and Theoretical $\bar{P}_N$ , the Number-Average Degree of Polymerization

The viscosity-average degree of polymerization  $\bar{P}_\eta$  is defined by:

$$\bar{P}_\eta^a = \frac{\sum_{j=1}^{\infty} j^{1+a} p_j}{\sum_{j=1}^{\infty} j p_j} \tag{42}$$

where  $p_j$  represents a polymer molecule containing  $j$  monomer units and  $a$  denotes the power number in the Mark-Houwink equation shown by eq. (1) and

is equal to 0.62 in this case. If the mathematical form of molecular weight distribution of the polymer formed can be assumed to coincide with that of the "most probable distribution,"  $\bar{P}_\eta$  is related to  $\bar{P}_N$  by

$$\bar{P}_\eta = \Gamma(a + 2)^{1/a} \bar{P}_N = 1.82 \bar{P}_N \quad (43)$$

The relationship between the instantaneous and cumulative values of the viscosity-average degree of polymerization can be derived from eq. (42) as

$$\bar{P}_\eta(X_M)^a + X_M d\bar{P}_\eta(X_M)^a/dX_M = (\bar{P}_{\eta X})^a \quad (44)$$

where  $\bar{P}_\eta(X_M)$  is the cumulative or experimentally measured  $\bar{P}_\eta$  at the monomer conversion  $X_M$  and  $\bar{P}_{\eta X}$  is the instantaneous  $\bar{P}_\eta$  for the polymer formed at the monomer conversion  $X_M$ .

Provided that the relationship shown by eq. (43) is applicable to both  $\bar{P}_\eta(X_M)$  and  $\bar{P}_{\eta X}$ , then eq. (44) is rewritten as

$$\bar{P}_N(X_M)^a + X_M d\bar{P}_N(X_M)^a/dX_M = (\bar{P}_{NX})^a \quad (45)$$

The exact termination mechanism of vinyl acetate polymerization is still subject to uncertainty, and both termination by combination and disproportionation probably proceed competitively.<sup>18</sup> One recent study by Funt and Pasika<sup>19</sup> indicated that at 60°C disproportionation was the predominant termination for vinyl acetate polymerization. Therefore, if we assume as a limiting case that the termination by disproportionation is predominant in this system, we can calculate the value of  $\bar{P}_{NX}$  by the following equation:

$$\bar{P}_{NX} = k_p[M_p]\bar{n}N_T/(r_i + k_{mf}[M_p]\bar{n}N_T) \quad (46)$$

The variation of  $\bar{P}_N(X_M)$  with monomer conversion  $X_M$  can be followed by solving eq. (45) numerically with the use of eq. (46) and  $k_{mf}/k_p = 1.98 \times 10^{-4}$ .<sup>20</sup> A comparison between the experimental and theoretical values of  $\bar{P}_N(X_M)$  is illustrated in Figure 15. The solid lines show the theoretical  $\bar{P}_N(X_M)$  versus  $X_M$  curves predicted by calculation using, for example, such values of  $k_p = 3300$  l./mole-sec and  $k_{df} = 15.0 \times 10^{-6}$  1/sec as employed in the previous paper.<sup>8</sup>

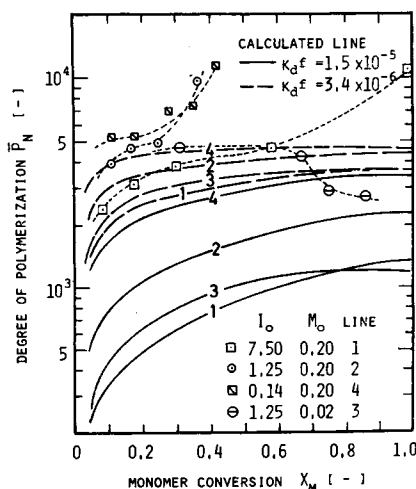


Fig. 15. Comparison between theoretical and experimental  $\bar{P}_N$ , the number-average degree of polymerization.



However, the calculated values are, in most cases, smaller than the experimentally observed values by a factor of about 3 to 10 even in the lower range of monomer conversion, where the transfer reaction to polymer is not dominating and hence need not be taken into account. Though this treatment is merely an approximation, it appears that the magnitude of this discrepancy is a little too large. The principal reason for this may be due to the fact that the values of the rate constants of propagation and decomposition of initiator used in the above calculations are not reasonable. If we adopt the value of  $k_p = 6990$  l./mole-sec given by Dixon-Lewis<sup>18</sup> (calculated from  $k_p = 4600$  l./mole-sec at 25°C and activation energy for propagation,  $E_p = 3.2$  kcal/mole), which is not unreasonable since Matsumoto and Maeda<sup>18</sup> obtained the value  $k_p = 7730$  l./mole-sec at 60°C, and Schulz and Stein obtained  $k_p = 19000$  l./mole-sec at 60°C, the value of  $k_{df}$  can be determined from eq. (41) to be  $3.39 \times 10^{-6}$  1/sec. This value is about two times that of Kolthoff and Miller<sup>21</sup> ( $k_d = 1.5 \times 10^{-6}$  1/sec at 50°C), but it is rather reasonable considering that the decomposition of potassium persulfate initiator is accelerated in the presence of ester monomers such as vinyl acetate. When these rate constants are used to calculate the theoretical  $\bar{P}_N(X_M)$ -versus- $X_M$  curves, more reasonable agreement can be seen between the experimental and theoretical values, as shown in Figure 15 by the broken lines. However, further detailed examinations are needed to draw any definite conclusions about this discrepancy along with exact values of the rate constants of propagation and initiator decomposition.

## CONCLUSIONS

In this study we have clarified that the dissolved monomer in the water phase affects not only the monomer concentration in the polymer particles but also the rate constant of termination in the polymer particles through the change in the weight ratio of monomer to polymer in the polymer particles. The polymerization rate in this system can be explained by the case 3 kinetics in the Smith and Ewart theory worked out for emulsion polymerization when the effect of dissolved monomer in water was taken into consideration. The conclusions obtained in this study will be expected to apply to emulsion polymerization and polymerization of other water-soluble monomers in aqueous media.

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