

# RADICAL POLYMERIZATION OF VINYL CHLORIDE: KINETICS AND MECHANISM OF BULK AND EMULSION POLYMERIZATION

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## ABSTRACT

Bulk and emulsion polymerization have as a common feature that there are already formed, from the start, particles which are one-phase systems consisting of polymers swollen with monomer. The composition of the particles is the same in the two cases and is constant up to about 70 per cent conversion at 50°C. Bulk and emulsion polymerization differ in that in the former case the outer phase is practically pure monomer while in the latter it consists of a dilute aqueous solution of vinyl chloride ( $\sim 0.1$  mole/l. at 50°C).

Mechanisms of bulk and emulsion polymerization are discussed. A mechanism involving desorption and reabsorption of radicals into the particles is treated in more detail. The result of the calculations seems to indicate that the bulk and emulsion polymerization are similar in that already at low conversion the main reactions, both polymerization and termination, take place in the particles. Even for bulk polymerization the number of radicals in the outer phase is, under ordinary conditions, practically independent of the rate of radical termination in that phase. The present treatment does not involve any assumption of an established thermodynamically determined equilibrium distribution of radicals in the two phases. In both these respects the present theory differs from previously advanced theories for bulk polymerization. The subdivision of the reaction zone in discrete particles has a similar effect on the bulk polymerization as on emulsion polymerization. It increases the rate of polymerization compared to that which would be obtained if the particles formed a continuous phase. The present theory may readily explain the experimentally observed drop in rate at precipitation, as well as the autocatalytic course of the reaction. The increase in the initial rate of bulk polymerization by addition of chain transfer agents results from an increase in the effective rate constant for desorption. Bulk and emulsion polymerization will respond differently to a change in the rate of desorption and absorption of radicals in the particles. This is due to the difference in the concentration of monomer in the outer phase in the two cases. In the case of bulk polymerization an increase in the rate of desorption and a decrease in the rate of absorption of radicals into the particles will tend to increase the rate of reaction whereas the opposite is expected for emulsion polymerization.

New experimental evidence concerning emulsion polymerization with mixed emulsifiers consisting of sodium dodecylsulphate and different  $n$ -fatty alcohols is presented. A marked decrease in the rate is obtained by use of  $n$ -hexadecanol. The mixed emulsifier is compared with the pure anionic emulsifier at seed polymerization with a given amount of seed and number of particles. With the pure anionic emulsifier the rate of polymerization is independent of the degree

of coverage with emulsifier. A complete coverage of the particles with a mixture of sodium dodecylsulphate and *n*-hexadecanol in a certain ratio leads to a marked decrease in rate. It is suggested that these results may be due to the mixed emulsifier forming a condensed layer on the surface of the particles which reduces the effective absorption constant.

## INTRODUCTION

The following significant features of kinetics of radical polymerization of vinyl chloride are common for bulk-, suspension- and emulsion polymerization.

1. The reaction is autocatalytic from the onset of reaction.
2. The reaction order, with respect to the initiator, is close to 0.5.
3. Molecular weight does not depend upon the conversion or the initiator concentration. Molecular weight and molecular weight distribution are similar for bulk and emulsion polymerization.

This similarity in the kinetics of bulk and emulsion polymerization, which will be outlined in more detail, is typical for vinyl chloride.

Although several theories, which may account for some of the experimental results have been put forward, there still seems to exist great uncertainty as to the mechanism of the polymerization both in bulk and emulsion. Talamini and Peggion<sup>1</sup> have recently given an extensive review of the polymerization of vinyl chloride covering the literature up to 1965. Therefore in the present paper special attention has been paid to new experimental evidence and theoretical approaches to the problem of kinetics and mechanisms of the radical polymerization processes.

### A. BULK POLYMERIZATION

Vinyl chloride is a very poor solvent of its own polymer. Therefore the polymerization system, from the start, separates into two phases; a dilute phase with practically no polymer and a concentrated phase consisting of polymer particles swollen with monomer. The activity of the monomer in the dilute phase is approximately equal to unity and the Flory-Huggins equation for the partial free energy of the monomer in the particles at saturation pressure is given by:

$$\bar{\Delta}G_1 = RT \left( \ln \phi_1 + \left( 1 - \frac{1}{x} \right) \phi_2 + \phi_2^2 \lambda \right) + \frac{2V_1 \sigma}{r} = 0 \quad (1)$$

where  $V_1$  is the molar volume of the monomer,  $\sigma$  the interfacial tension,  $r$  the particle radius,  $\phi_1$  and  $\phi_2$  the volume fractions of monomer and polymer in the particles respectively, and  $\lambda$  the interaction constant. The value of the latter is 0.88 at 50°C<sup>2</sup> which corresponds to a concentration of monomer in the particles of 6 mole/l. Therefore in the bulk polymerization of vinyl chloride the system consists of two different phases each of them having a constant composition up to about 70 per cent conversion. The influence of

## RADICAL POLYMERIZATION OF VINYL CHLORIDE

the interfacial energy term in limiting the dilution of the particles with monomer is negligible compared to the effect of the interaction energy term.

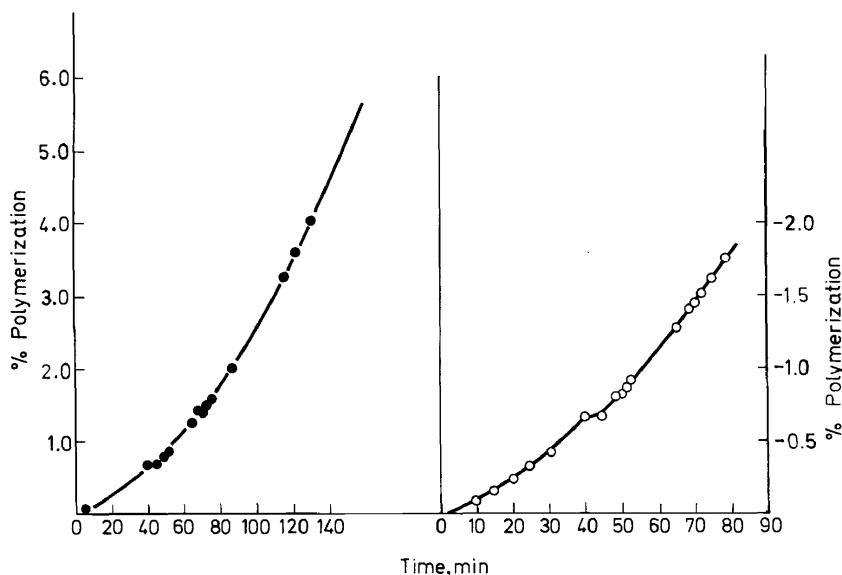
The concentrated phase in bulk polymerization and generally under

*Table 1.* Particle size and number as a function of conversion  $C$  in the bulk polymerization of vinyl chloride at  $50^\circ\text{C}^3$

$C$	Diameter $d \times 10^5$ (cm)	$N_p \times 10^{-11}$
0.0017	< 1.0	> 23.2
0.009	2.90	5.10
0.045	5.10	4.65
0.096	5.90	6.41
0.148	7.20	5.40
0.300	9.6	4.70

$N_p$  = number of particles per g of initial amount of vinyl chloride.

conditions which lead to precipitation of PVC, is subdivided into discrete particles. Results of Cotman *et al.*<sup>3</sup> are given in *Table 1*. Cotman found that the number of particles in bulk polymerization remained constant between



*Figure 1.* Bulk polymerization of VC at  $47^\circ\text{C}$ , AIBN initiator, 0.0175 mole/l. Right, low conversion data on an expanded scale. (Reprinted by permission of the *Journal of Polymer Science*)

1 and 30 per cent conversion and was independent of the initiator concentration. Between 0.2 and 1 per cent conversion there was a sudden decrease in the particle number. The reduction in the number of particles did have kinetic

consequences also. As indicated by the results given in *Figure 1*, a decrease in rate coincides with the sharp decrease in the particle number. Cotman concluded that the absence of secondary nucleation of particles indicated a predominant absorption of radicals in the particles in contact with monomer.

Bort *et al.*<sup>4,5</sup> reported that at relatively high rates of radical production single particles with a smooth surface were formed. The number of particles was about the same as that found by Cotman and corresponded to  $4.5 \times 10^{14}$  particles per l of the monomer at start. At low rates of radical production aggregates are formed consisting of a number of globular particles. An important observation made by Bort was that both number and morphology of the particles (single particles or aggregates) were determined by the initial conditions of polymerization, below 1 per cent conversion. A change in rate of polymerization after 1–2 per cent conversion did not bring about any change in either number or morphology of the particles. Bort, as well as Cotman, concludes that the polymerization mainly takes place in the particles already at a very low conversion.

Previous authors dealing with the kinetics of the bulk polymerization of vinyl chloride ascribed the autocatalytic behaviour of the polymerization to a trapping of chain radicals in the polymer particles. The high viscosity in the particles was not expected to influence the value of the propagation constant but was suggested to lead to a decrease or complete stop of the termination reaction. Schindler and Breitenbach<sup>6</sup> assumed the steady state condition for the radicals. Moreover they assumed that the value of the termination constant in the particles was lower than that in the monomer phase. In the calculation of an expression for the reaction rate they made use of an overall termination constant which was suggested to decrease with increasing conversion according to a purely empirical equation. Both Bengough and Norrish<sup>7</sup>, and Mickley, Michaels and Moore<sup>8</sup> assumed in their mechanisms that the termination in the particles was effectively stopped. The steady state condition for the radicals in the particles was maintained by chain transfer of radical activity to the monomer and desorption of monomer radicals from the particles. The termination took place in the monomer phase only. The complete stop of termination in the particles may seem unreasonable in view of the relatively high content of monomer in the particles. Monomer has been found to be a very effective plasticizer for PVC<sup>37</sup>.

An interesting new contribution to the theory of the bulk polymerization has recently been given by Talamini and coworkers. In a number of papers<sup>9–11</sup> they have underlined the fact that in bulk polymerization of vinyl chloride the reaction takes place in two phases from a very low conversion onwards. With increasing conversion the amount of the dilute phase decreases while that of the concentrated phase increases. The two phases have constant composition in the whole range of their coexistence. Therefore, although the values of the termination constants may be different in the two phases, the individual values will not be expected to vary up to about 70 per cent conversion.

The total rate expressed in moles of monomer reacted per unit time is given by

$$r_p = -\frac{dM}{dt} = k_p[R\cdot]_L[M]_L V_L + k_p[R\cdot]_P[M]_P V_P \quad (2)$$

## RADICAL POLYMERIZATION OF VINYL CHLORIDE

where  $[R\cdot]_L$  and  $[M]_L$  are the radical and monomer concentration in the dilute phase respectively, and  $V_L$  is the volume of the dilute phase.  $[R\cdot]_P$ ,  $[M]_P$  and  $V_P$  refer to the concentrated phase. Introducing the degree of conversion  $C$  into equation 2 gives:

$$\frac{dC}{dt} = k_p[R\cdot]_L \frac{M_L}{M_0} + k_p[R\cdot]_P \frac{M_P}{M_0} \quad (3)$$

where  $M_0$  is the number of moles of monomer at the start. Talamini introduces the specific rates  $r_L$  and  $r_P$  in the two phases, defined as degree of conversion per unit time:

$$\frac{dC}{dt} = r_L \frac{M_L}{M_0} + r_P \frac{M_P}{M_0} \quad (4)$$

If  $C_0$  is the degree of conversion at which phase separation occurs and  $A$  the monomer to polymer weight ratio in the particles, one obtains:

$$\frac{dC}{dt} = r_L[1 - C - A(C - C_0)] + r_P A(C - C_0) \quad (5)$$

The conversion at which separation occurs is very low, hence with a good approximation equation 5 can be rewritten:

$$\frac{dC}{dt} = r_L(1 - C - AC) + ACr_P \quad (6)$$

Talamini states that because of the constant composition of the two phases the ratio of the corresponding specific rates will stay constant:

$$r_P = Q \times r_L \quad (7)$$

From equations 3 and 4 this is equivalent to a constant ratio of radical concentrations in the two phases

$$[R\cdot]_P = Q[R\cdot]_L \quad (8)$$

Talamini proceeds as follows: from equations 6 and 7:

$$\frac{dC}{dt} = r_L - (1 + A - AQ)Cr_L \quad (9)$$

Substitution of  $-(1 + A - AQ) = q$  gives:

$$\frac{dC}{dt} = r_L + qr_L C \quad (10)$$

Upon integration:

$$C = \frac{1}{q} [\exp(qr_L t) - 1] \quad (11)$$

By expanding the exponential term in series it results in:

$$C = \frac{1}{q} \sum_{n=1}^{\infty} \frac{(qr_L t)^n}{n!} \quad (12)$$

Talamini furthermore assumes that  $r_L$  may be expressed as:

$$r_L = k[I]^{\frac{1}{2}} = \frac{k_p(k_i)^{\frac{1}{2}}}{k_{tL}^{\frac{1}{2}}} [I]^{\frac{1}{2}} \quad (13)$$

where  $[I]$  apparently stands for the overall concentration of initiator in the system and  $k_{tL}$  is the termination constant in the dilute phase. Inserting for  $r_L = k[I]^{\frac{1}{2}}$  into equation 12 gives:

$$C = \frac{1}{q} \sum_{n=1}^{\infty} \frac{(qk)^n}{n!} [I]^{n/2} t^n \quad (14)$$

This equation is found to agree well with experimental results both from bulk and suspension polymerization over a wide range of conversion, initiator type and concentration. Examples are shown in *Figures 2 and 3*<sup>11</sup>. By limiting to the second term in the series one obtains from equation 14 an equation of the form:

$$C = \alpha_1 [I]^{\frac{1}{2}} t + \alpha_2 [I] \times t^2 \quad (15)$$

where  $\alpha_1$  and  $\alpha_2$  are constants.

This should, according to Talamini, lead to a reaction order, with respect to the initiator, which varied with conversion. The order would be 0.5 at time zero and may increase with time as the second term becomes more important. However, if the differential rates with different initiator concentration are compared at the same conversion, which is obviously correct, equation 15 predicts a constant order of 0.5, independent of conversion. Solving for  $t$  from equation 15 and inserting in the rate expression

$$\frac{dC}{dt} = \alpha_1 [I]^{\frac{1}{2}} + 2\alpha_2 [I] t \quad (16)$$

gives:

$$\frac{dC}{dt} = [I]^{\frac{1}{2}} (4\alpha_2 C + \alpha_1^2)^{\frac{1}{2}} \quad (17)$$

It seems to the present authors that the main assumptions made by Talamini in the evaluation of equation 14 may be open to some doubt. These are the assumptions of a constant ratio of polymerization rates in the two phases (equation 7) and moreover the assumption that the concentration of radicals in the dilute phase at a constant rate of radical production is determined solely by the rate of termination in the dilute phase. The argument against this is as follows: one may, in accordance with many authors, assume a quasi steady state for the number of moles of radicals in the two phases:

$$\frac{dR_{\cdot L}}{dt} = 2k_i [I]_L V_L - k_a [R_{\cdot}]_L + k_{dC} [R_{\cdot}]_P - 2k_{tL} [R_{\cdot}]_L^2 V_L = 0 \quad (18)$$

$$\frac{dR_{\cdot P}}{dt} = 2k_i [I]_P V_P + k_a [R_{\cdot}]_L - k_{dC} [R_{\cdot}]_P - 2k_{tP} [R_{\cdot}]_P^2 V_P = 0 \quad (19)$$

# RADICAL POLYMERIZATION OF VINYL CHLORIDE

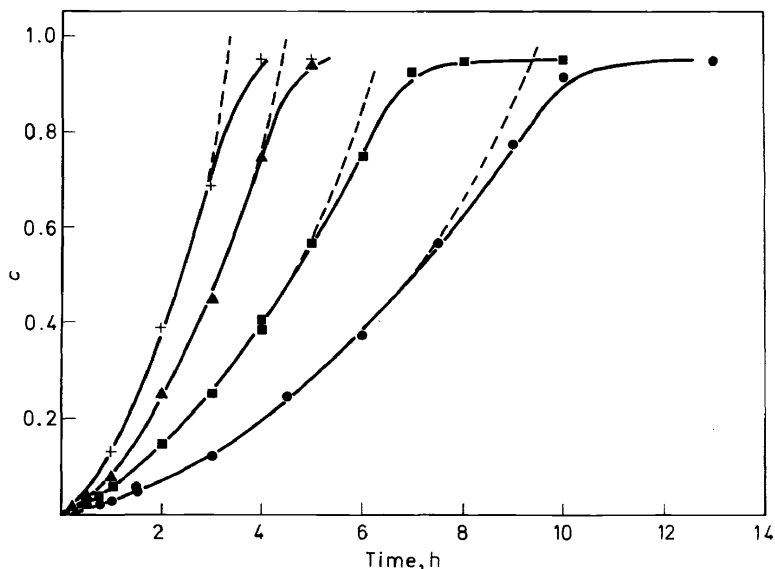


Figure 2. Bulk polymerization of VC at 50°C, initiated by lauroyl peroxide. Dotted lines: theoretical curves obtained from equation 14.  $C$  = degree of conversion:  $[I]_0$  mole/l 14 = ●  $1.06 \times 10^{-2}$ ; ■  $2.14 \times 10^{-2}$ ; ▲  $4.60 \times 10^{-2}$ ; +  $7.48 \times 10^{-2}$ . (Reprinted by permission of *Makromolekulare Chemie*)

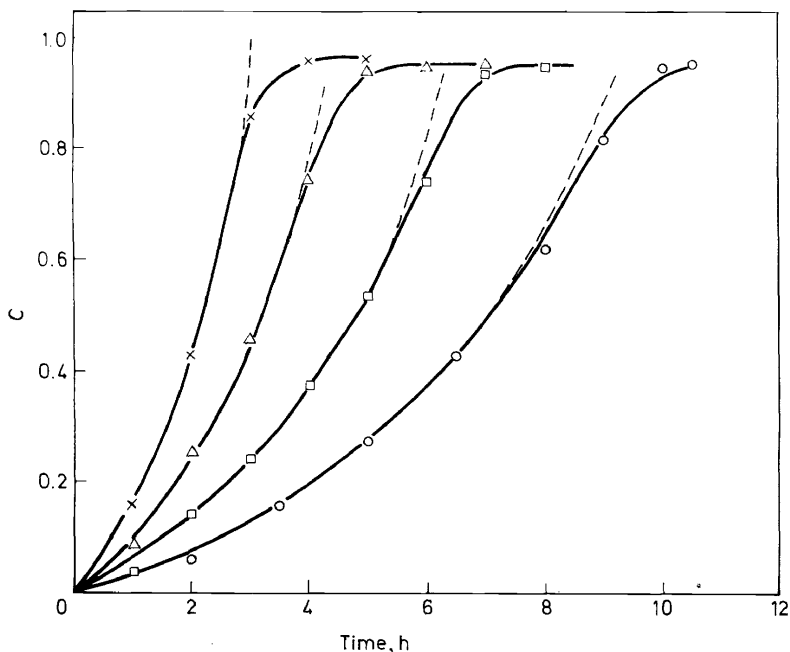


Figure 3. Suspension polymerization of VC at 50°C, initiated by lauroyl peroxide. Dotted lines: theoretical curves obtained from equation 14.  $[I]_0$  mole/l VC: ○  $1.13 \times 10^{-2}$ ; □  $2.14 \times 10^{-2}$ ; △  $4.60 \times 10^{-2}$ ; ×  $8.98 \times 10^{-2}$ . (Reprinted by permission of *Makromolekulare Chemie*)

Here are included the terms describing transport of radicals from one phase to the other in addition to those giving the formation and destruction of radicals by termination in the two phases. It is assumed that the rate of absorption of radicals from the dilute phase into the particles is proportional to the concentration of radicals in the dilute phase and vice versa for the desorption of radicals from the concentrated phase. The values of  $k_a$  and  $k_{dC}$  are of course expected to be constant at a given conversion and particle number only. Addition of equations 18 and 19 gives:

$$k_i I = k_{tL} [R\cdot]_L^2 V_L + k_{tP} [R\cdot]_P^2 V_P \quad (20)$$

which is a completely general equation. It gives the connection between the total rate of radical production  $k_i I$ , which may be considered to be constant, and the total rate of radical destruction. For sake of simplicity the efficiency factor is throughout this discussion assumed to be equal to 1. Generally, the concentration of radicals in one of the phases will also depend upon the rate of radical destruction in the other phase. It is furthermore obvious that in such cases, where the radical concentrations are determined by quasi steady state conditions, the ratio of the concentration of radicals in the two phases will not generally be governed by an established, thermodynamically determined equilibrium. For this to hold, the value of  $k_a$  and  $k_{dC}$  must be so high that the terms describing the absorption and desorption of radicals are the dominating ones in one or both phases. Under these conditions one has:

$$[R\cdot]_P / [R\cdot]_L = k_a / k_{dC} = Q \quad (21)$$

Inserting from equation 21 into equation 20 gives:

$$[R\cdot]_L = [k_i I / (k_{tL} V_L + Q^2 k_{tP} V_P)]^{\frac{1}{2}} \quad (22)$$

Even in this case the radical concentration in the liquid phase will generally also depend upon the termination in the concentrated phase and vice versa. Two limiting cases may be considered:

A:  $Q^2 k_{tP} V_P \ll k_{tL} V_L \quad (23)$

$$[R\cdot]_L = (k_i I / k_{tL} V_L)^{\frac{1}{2}} \quad (24)$$

$$[R\cdot]_P = Q (k_i I / k_{tL} V_L)^{\frac{1}{2}} \quad (25)$$

B:  $Q^2 k_{tP} V_P \gg k_{tL} V_L \quad (26)$

$$[R\cdot]_L = \frac{1}{Q} (k_i I / k_{tP} V_P)^{\frac{1}{2}} \quad (27)$$

$$[R\cdot]_P = (k_i I / k_{tP} V_P)^{\frac{1}{2}} \quad (28)$$

In case A the termination in the particles is negligible. The rate is:

$$-\frac{dM}{dt} = \left( \frac{k_i I}{k_{tL} V_L} \right)^{\frac{1}{2}} k_p (M_L + Q M_P) \quad (29)$$

or expressed in degree of conversion:

$$\frac{dC}{dt} = \left( \frac{k_i I}{k_{tL} V_L} \right)^{\frac{1}{2}} k_p (1 - C - AC + ACQ) \quad (30)$$



## RADICAL POLYMERIZATION OF VINYL CHLORIDE

These rate expressions are in principle similar to that obtained by Mickley *et al.* Also at low conversion where  $k_t I / V_L$  is approximately constant, equation 30 is identical to that obtained by Talamini (equation 9). As discussed below both the assumption of a thermodynamically determined equilibrium distribution of radicals in the two phases and the assumption of a negligible termination in the particles may be questioned from a theoretical point of view. The latter also seems to be contradicted by experimental evidence. According to equation 24 the formation of the particles should not influence the number of moles of radicals in the dilute phase at low conversion where  $V_L$  is approximately constant, and therefore not even the rate of polymerization in the dilute phase. As discussed below the experimental fact is that the formation of polymer particles leads to a marked decrease in rate. A more detailed treatment of the kinetics of bulk polymerization is given below, after presentation of new experimental evidence on the effect of the precipitation and the effect of addition of chain transfer agents.

### Effect of precipitation

Most interesting contributions to the problem of the mechanism of the polymerization have recently come from experiments where the conditions have been gradually changed from homogeneous to heterogeneous conditions. Ryska *et al.*<sup>12</sup> have investigated the polymerization in the presence of diethyl oxalate. Figure 4 shows the course of the kinetic curves at concentrations of monomer higher than 10 mole/l. Contrary to concentrations lower than 10 mole/l where the course of the polymerization is nearly linear, in this region of monomer concentration the following anomalies are observed: The initial rate decreases with concentration. The course of polymerization is slightly accelerated and after a certain period of time the polymerization rate suddenly decreases. However, the subsequent course shows a marked acceleration. The higher the concentration of the monomer the sooner a break is observed. In the polymerization of the pure monomer the initial

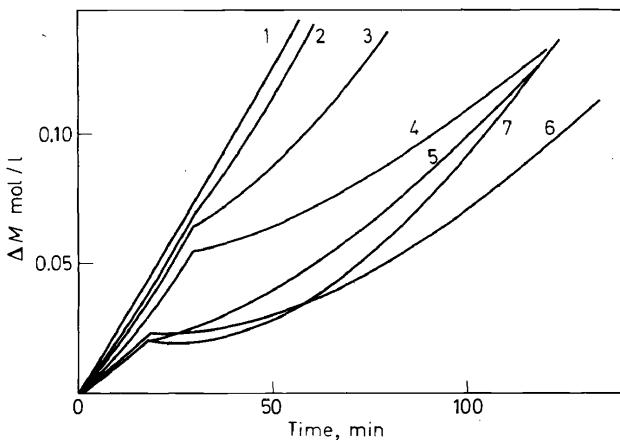


Figure 4. Polymerization of VC in diethyl oxalate at 25°C; Initiator: 2,2' azobis (2,4-dimethyl-4-methoxy) valeronitril  $3.3 \times 10^{-4}$  mole/l;  $[M]$  (mole/l.): (1) 9.81; (2) 10.65; (3) 11.22; (4) 11.63; (5) 12.12; (6) 12.59; (7) 13.05. (Reprinted by permission of *The Journal of Polymer Science*)

almost linear course was not observed. As mentioned earlier, however, Cotman observed a similar break in the curve at very low conversion, also with pure monomer, at the point where the number of particles suddenly decreased, although the effect was less pronounced than that shown in Figure 4.

Figure 5 gives the initial rates of polymerization as a function of the monomer concentration at different initiator concentrations. The initial rate passes through a maximum at about 10 mole/l. of monomer. At the monomer concentration of about 7.5 mole/l. a marked increase in the intensity of scattered light was observed during the polymerization but the precipitation of polymer did not take place until monomer concentrations were higher than 10 mole/l. Ryska concludes that the value of  $k_p^2/k_t$  in the initial course of the heterogeneous polymerization may be considerably lower than the corresponding value for the homogeneous polymerization and suggests that the propagation constant must have been more changed than the termination constant. The accelerated course shows that at increasing polymer concentration the termination constant drops more rapidly than the propagation constant. The authors mean to find a support for the reduction of the propagation constant by precipitation from measurements of the effect of carbon tetrabromide on the degree of polymerization. At a given concentration of  $\text{CBr}_4$  the degree of polymerization decreases with increasing monomer concentration, which is taken to indicate that the ratio between the propagation constant and the transfer constant decreases with increasing heterogeneity of the system. However, as discussed below, the decrease in rate caused by precipitation may possibly be explained without the assumption of a decrease in the value of  $k_p$ .

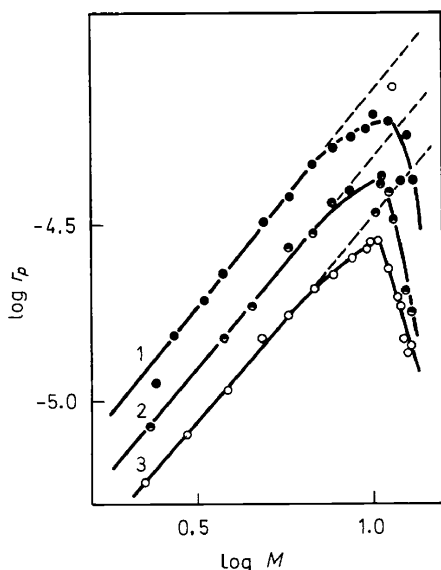


Figure 5. Dependence of initial rate of polymerization of VC in diethyl oxalate on the monomer concentration at 25°C.  $[I]_0$  (mole/l.): (1)  $1.1 \times 10^{-3}$ ; (2)  $3.3 \times 10^{-4}$ ; (3)  $1.1 \times 10^{-4}$   
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## RADICAL POLYMERIZATION OF VINYL CHLORIDE

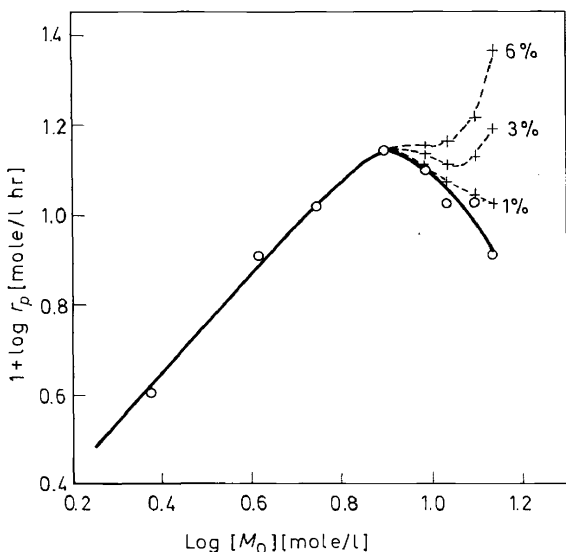


Figure 6. Rate of polymerization of VC in 1,2-dichloroethane at 50°C as a function of the monomer concentration. —○— initial polymerization rates; —+ +— polymerization rates at indicated degrees of conversion. Initiator = lauroyl peroxide,  $4.64 \times 10^{-2}$  mole/l. (Reprinted by permission of *Makromolekulare Chemie*)

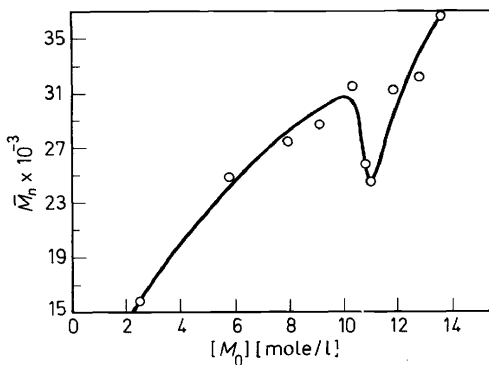


Figure 7. Molecular weight as a function of the monomer concentration for the polymerization of VC in 1,2-dichloroethane at 50°C.  $[I] = 4.64 \times 10^{-2}$  mole/l. (Reprinted by permission of *Makromolekulare Chemie*)

Crosato-Arnaldi *et al.*<sup>13</sup> investigated the kinetics of polymerization in the presence of different solvents. Figure 6 gives results of polymerization in 1,2 dichloroethane. In the region of homogeneity ( $[M]_0 < 7.9$  mole) the reaction rate increases with the monomer concentration, the reaction order with respect to monomer is 1. For  $[M]_0 > 8$  mole/l. the initial polymerization rate begins to decrease as the initial monomer concentration increases. The form of the curves for the differential rate versus initial monomer concentration will depend upon the conversion because of the autocatalytic

effect in the heterogeneous region. Molecular weight of polymer formed up to 6 per cent conversion shows a similar behaviour (*Figure 7*). Obviously, the decrease in rate caused by precipitation is accompanied by a decrease in the degree of polymerization. The decrease in rate caused by precipitation is explained by Crosato-Arnaldi *et al.* in the following way: the polymerization starts and proceeds in solution (homogeneous conditions) until the polymer concentration reaches the value at which the polymerization system separates into two phases, one concentrated and the other very dilute in polymer. If  $V$  is the volume of the system and  $\rho_i$  the number of moles of radicals produced in unit time, the steady state number of moles of radicals under homogeneous conditions is:

$$R_{st} = \left( \frac{\rho_i V}{2k_t} \right)^{\frac{1}{2}} \quad (31)$$

When the polymerization system separates into two phases it is assumed that the volume does not vary and the radical production rate is unaffected. Indicating with  $V_L$  the volume of the dilute phase and with  $\alpha_L$  the number of moles of radicals, produced per unit of time, which remain in this phase, the number of radicals at steady state,  $R_{\cdot L}$  is given by:

$$R_{\cdot L} = \left( \frac{\alpha_L V_L}{2k_{tL}} \right)^{\frac{1}{2}} \quad (32)$$

Analogously, if  $V_P$  is the volume of the concentrated phase and  $\alpha_P$  the number of radicals produced per unit of time in this phase, the number of radicals at steady state condition  $R_{\cdot P}$  is:

$$R_{\cdot P} = \left( \frac{\alpha_P V_P}{2k_{tP}} \right)^{\frac{1}{2}} \quad (33)$$

The overall steady state radical concentration  $[R_{\cdot}]$  in the polymerization system is given by:

$$[R_{\cdot}] = \frac{R_{\cdot L} + R_{\cdot P}}{V} \quad (34)$$

Denoting by  $\phi_L$  and  $\phi_P$  the volume fraction of the dilute and concentrated phase respectively, the relation 34 can be rewritten in the form:

$$[R_{\cdot}] = \left( \frac{\alpha_L \phi_L}{2k_{tL} V} \right)^{\frac{1}{2}} + \left( \frac{\alpha_P \phi_P}{2k_{tP} V} \right)^{\frac{1}{2}} \quad (35)$$

With the assumption that  $k_{tL} = k_t$  and indicating with  $f_L = \alpha_L/\rho_i$  and  $f_P = \alpha_P/\rho_i$ , the fractions of the radicals going in the dilute and concentrated phase respectively, the ratio  $y = ([R_{\cdot}]/R_{st}/V)$  of the overall radical steady state concentration in the polymerization system constituted of the two phases, to that in the system before phase separation, is given by the following equation:

$$y = f_L^{\frac{1}{2}} \phi_L^{\frac{1}{2}} + \left( \frac{k_{tL}}{k_{tP}} \right)^{\frac{1}{2}} (1 - f_L)^{\frac{1}{2}} (1 - \phi_L)^{\frac{1}{2}} \quad (36)$$

If it is assumed that the growing radicals, are more soluble in the concentrated phase,  $f_L$  is always lower than  $\phi_L$ . Numerical solution of equation 36 yields that if  $k_{tP} = k_{tL}$  phase separation will lead to a sharp decrease in rate and successively to an autocatalytic effect. If  $k_{tL}/k_{tP} > 1$ , the decrease in rate due to phase separation is reduced and the successive autocatalytic effect increased.

In the view of the present authors some of the basic assumptions of this treatment may be open to doubt. As in the previously cited paper by Talamini *et al.*<sup>10</sup>, it is assumed that the steady state concentration of the radicals in one phase is governed solely by the rate of radical production and the rate of radical destruction by termination in that phase. By comparison with equations 18 and 19 it is seen that equations 32 and 33 involve that

$$\alpha_L = \rho_L - k_a \frac{R_{\cdot L}}{V_L} + k_{ac} \frac{R_{\cdot P}}{V_P} = 2k_{tL} \frac{R_{\cdot L}^2}{V_L} \quad (37)$$

$$\alpha_P = \rho_P + k_a \frac{R_{\cdot L}}{V_L} - k_{ac} \frac{R_{\cdot P}}{V_P} = 2k_{tP} \frac{R_{\cdot P}^2}{V_P} \quad (38)$$

where  $\rho_L$  and  $\rho_P$  are the rates of radical production from the initiator in the dilute and concentrated phase respectively. The relationship between the number of radicals in the two phases is obviously more complex than assumed by Crosato-Arnaldi. The number of radicals in one phase may depend upon the rate of termination in the other phase. Moreover, the number of radicals in each phase is not generally proportional to the square root of the radical production in this phase.

### Effect of chain transfer agents

Another type of experiment which has been used in the discussion of mechanisms is measurement of the effect of chain transfer agents. Breitenbach and Schindler<sup>14</sup> found that addition of small amounts of chain transfer agents such as  $\text{CBr}_4$  and dodecyl mercaptane lead to a very marked increase in the initial rate of reaction (*Figure 8*) and at the same time caused a reduction or complete removal of the autocatalytic effect. These results have recently been confirmed by several authors<sup>12,15</sup>. *Figure 9* gives results obtained by Vidotto *et al.*<sup>15</sup> which illustrate the reduction of the autocatalytic effect caused by  $\text{CBr}_4$ .

This most interesting effect of an increase in rate with the addition of chain transfer agents has been given different explanations in the literature. As discussed above, Talamini assumes an established, thermodynamically determined equilibrium distribution of radicals between the two phases. In accordance with wellknown principles the decrease in polymer weight, caused by the chain transfer agent, will be expected to increase the preference for polymeric species and thus for the growing radicals in the liquid phase and lead to an increase in the rate. Cotman<sup>3</sup> suggests that the lower average degree of polymerization leads to an increasing fraction of soluble radicals and, moreover, that the insoluble fraction, by virtue of the lower molecular weight, may coalesce more slowly. Finally Breitenbach suggests that the effect may be ascribed to a transfer of rather unreactive monomer radicals to active radicals by the chain transfer agents.

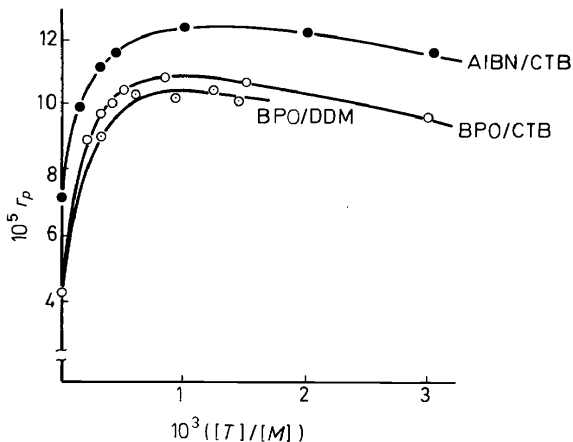


Figure 8. Dependence of rate of polymerization ( $r_p$ , in mole/l sec) on the concentration of chain transfer agents (in moles per mole of monomer) in the bulk polymerization of vinyl chloride at 50°C. ● chain transfer agent carbon tetrabromide (CTB),  $6.85 \times 10^{-3}$  mole/l azo-isobutyronitrile (AIBN); ○ transfer agent CTB,  $13.6 \times 10^{-3}$  mole/l. benzoylperoxide (BPO); ⊙ transfer agent dodecyl mercaptane (DDM),  $13.6 \times 10^{-3}$  mole/l. BPO. (Reprinted by permission of *Makromolekulare Chemie*)

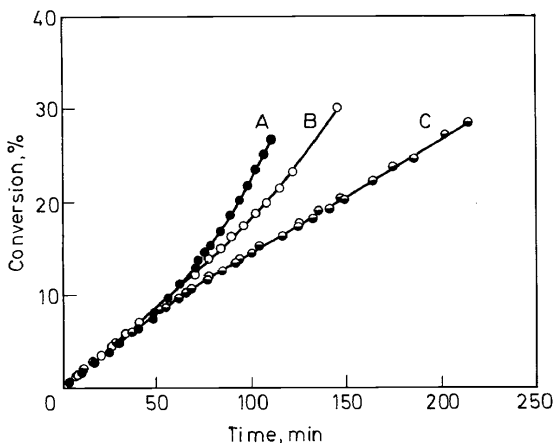


Figure 9. Polymerization kinetics of bulk at 50°C with various concentrations of carbon tetrabromide. Initiator is lauroyl peroxide.  $[CBr_4] = 5 \times 10^{-3}$  mole/l. (Curve A);  $5 \times 10^{-2}$  mole/l. (Curve B);  $5 \times 10^{-1}$  mole/l. (Curve C). (Reprinted by permission of *Makromolekulare Chemie*)

### Derivation of kinetic expressions for the reaction rate in bulk polymerization

The main feature of the kinetics of the radical polymerization in bulk polymerization may be summarized to be:

A marked decrease in rate as well as in degree of polymerization accompanies the formation of precipitated polymer particles. The subsequent

course is characterized by a marked autocatalytic effect. There is a significant influence of particle number on the reaction rate at low conversion.

Addition of certain chain transfer agents leads to a marked increase of the initial rate of bulk polymerization and at the same time the autocatalytic effect disappears.

In order to derive an expression for the rate of reaction, equation 2 is conveniently rewritten in the form

$$-\frac{dM}{dt} = k_p[M]_L R\cdot_L + k_p[M]_P R\cdot_P \quad (39)$$

or in degree of conversion:

$$\frac{dC}{dt} = \frac{1}{M_0} (k_p[M]_L R\cdot_L + k_p[M]_P R\cdot_P) \quad (40)$$

The concentrations of monomer in the dilute phase,  $[M]_L$  and concentrated phase  $[M]_P$  are constant up to  $\sim 70$  per cent conversion and equal to 13.6 and 6 mole/l respectively, at  $50^\circ\text{C}$ . The number of moles of radicals in the dilute phase,  $R\cdot_L$ , and in the particles,  $R\cdot_P$ , are calculated from equations 18 and 19 without applying any *a priori* assumption on the distribution of radicals between the two phases. In accordance with Mickley *et al.*<sup>8</sup> it is assumed that the rates of radical absorption and desorption are determined and may be expressed as diffusion processes.

$$k_a = 4\pi D_L N r \quad (41)$$

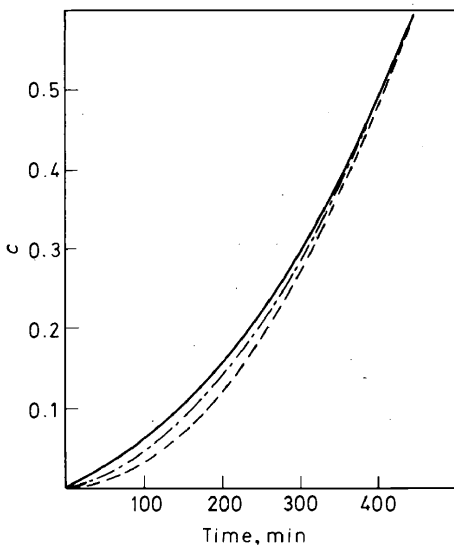
$$k_{dc} = 4\pi D_P N r \quad (42)$$

where  $N$  is the number of particles,  $r$  is the particle radius and  $D_L$  and  $D_P$  are the diffusion coefficients in the dilute phase and in the particles, respectively.

The values  $3.6 \times 10^8$  l/mole sec and  $2 \times 10^{-11}$  dm<sup>2</sup>/sec are used for  $k_{iP}$  and  $D_P$  respectively. These values and the form of  $k_{dc}$ , being determined by a diffusion process within the particles, are based upon experimental results with emulsion polymerization, as described later. The experimentally determined quantities are in fact  $k_p/k_{iP}^{\frac{1}{2}}$  and  $k_p/k_{dc}^{\frac{1}{2}}$ . The absolute values given for  $k_{iP}$  and  $D_L$  are based upon Burnett and Wright's value of  $k_p = 1.1 \times 10^4$  l/mole sec, at  $50^\circ\text{C}$ <sup>16</sup>. The value of absorption of radicals is not known. If it is determined by the diffusion of the radicals in the dilute phase, the value of  $D_L$  is probably of the order of magnitude of  $10^{-8}$  to  $10^{-7}$  dm<sup>2</sup>/sec. The comparatively low value of  $D_P$  is possibly due to the fact that the desorption of a radical from a particle has to be preceded by a chain transfer to monomer<sup>3,3</sup>. The distribution of the initiator between the two phases is also unknown. If this distribution is solely determined by entropy factors, a value of  $[I]_P/[I]_L = 0.5$  is estimated. The value of  $k_{iL}$  is uncertain. Burnett and Wright give a value of  $k_{iL} = 2 \times 10^9$  l/mole sec, at  $50^\circ\text{C}$  which gives a value of  $k_p/k_{iL}^{\frac{1}{2}} = 0.24$ . Several authors have reported that this value may be too high<sup>12,13,17-19</sup>. Because of the uncertainty as to the value of  $k_{iL}$ , the calculations have been carried out for  $k_{iL}/k_{iP} = 5$  (as obtained by use of the Burnett and Wright values), 20 and 40. The last value is obtained by use of the

value of  $k_p$  as given by Burnett and Wright =  $1.1 \times 10^4$  l./mole sec and the value of  $k_p/k_{tL}^{\frac{1}{2}} = 0.089$  ( $l^{\frac{1}{2}}$  mole $^{-\frac{1}{2}}$  sec $^{-\frac{1}{2}}$ ) given by Tkachenko *et al.*<sup>18</sup>. The definition of the  $k_{tL}$  applied in the calculation of  $k_p/k_{tL}^{\frac{1}{2}}$  is uncertain. In most papers it is apparently, by definition, twice the value applied in this paper. In this case a value  $k_{tL}/k_{tP} = 20$  would be more correct. It should be pointed out that the value of  $k_{tL}$  will affect the value for the number of moles of radicals in the particles and in the dilute phase only in conditions where the termination in the dilute phase has a significant influence on the total rate of termination†.

In *Figure 10* calculated curves with  $k_{tL}/k_{tP} = 20$  and  $D_L = 10^{-7}$  and  $10^{-8}$  dm<sup>2</sup>/sec are compared with an experimental curve from *Figure 2* at a given rate of radical production. In this calculation a value of  $k_i = 1.15 \times 10^{-6}$  sec $^{-1}$  for the decomposition of LPO at 50°C and an efficiency factor<sup>11</sup> of 1 has been assumed. It appears from *Figure 10* that while the shape of the theoretical curves at conversions above  $\sim 2$  per cent is similar to the experimental curve, the calculated curves predict a considerably lower rate at low conversion. It does not seem possible by this simple treatment to explain the high rate at low conversion without accepting a rather unreasonable low rate of radical absorption into the particles. Calculations carried out with  $k_{tL}/k_{tP} = 5$  and 40 showed that the value of  $k_{tL}$  hardly had any effect on the number of radicals in the particles and in the dilute phase even at very low conversion under the given conditions.



*Figure 10.* Bulk polymerization at 50°C of VC. Solid curve: experimental curve taken from *Figure 2* with  $[I]_0 = 1.06 \times 10^{-2}$  mole/l.; dotted curves calculated by help of equations 10, 18 and 19; ····  $D_L = 10^{-8}$ ; ----  $D_L = 10^{-7}$  dm<sup>2</sup>/sec.

Crosato-Arnaldi's<sup>11</sup>, as well as Mickley's<sup>8</sup> expressions seems to fit better the experimental results at low conversion, as their treatment assumes

† It is of course possible that the value of  $k_p$  given by Burnett *et al.* is too high and their  $k_{tL}$  is correct. Calculations show that this leads to the same general conclusions as presented below.



contribution to the rate from a practically constant rate of polymerization in the dilute phase at low conversion. As discussed earlier, this assumption may be open to doubt. The question is whether it is possible to explain the relatively high rate at low conversion as found experimentally even if it is accepted that the absorption of radicals into the particles and termination of radicals in the particles, already at very low conversion, plays a dominant role in determining the total number of radicals in the system. This is what the experiments with precipitation polymerization would suggest, as well as the observations of Cotman<sup>3</sup> and Bort<sup>5</sup> on particle formation. The subdivision of the reaction zone in discrete particles may possibly account for the relatively high rate at low conversions. For the calculation of this effect one may use the Stockmayer<sup>20</sup> and O'Toole<sup>21</sup> treatment, as modified by Ugelstad *et al.*<sup>22</sup> to take into account the reabsorption of desorbed radicals into the particles. The effect of the subdivision may only be expected to be of importance at low conversion. In that case the formation of radicals from initiator decomposition inside the particles may be neglected and one may make use of the recursion formula, which applies for the case when the radicals are liberated in the outer phase:

$$(\rho_A/N)P_n = [k_d + nk_{tP}/v](n+1)P_{n+1} + (k_{tP}/v)(n+1)(n+2)P_{n+2} \quad (43)$$

$\rho_A$  is the rate of radical absorption into the particles,  $N$  is the number of particles per l of initial volume and  $k_d$  is the rate constant for desorption of radicals from a particle. (The rate of desorption from a particle containing  $n$  radicals is now expressed as  $r_d = n \times k_d \times N_n$ . Therefore  $k_d = k_{dc}/V_p$ ). Also  $P_n$  is the probability of an  $n$  fold occupancy in a particle and  $v$  is the volume of one particle. The solution of this equation as given by O'Toole for the average number of radicals per particle is:

$$\bar{n} = \frac{a}{4} I_m(a)/I_{m-1}(a) \quad (44)$$

where  $I_m$  and  $I_{m-1}$  are modified Bessel functions.

$$a = (8\alpha)^{\frac{1}{2}} = (8\rho_A v/Nk_{tP})^{\frac{1}{2}} \quad (45)$$

$$m = k_d v/k_{tP} \quad (46)$$

The rate of absorption of radicals into the particles may be expressed as:

$$\rho_A = \rho^L + k_d \sum_{n=1}^{\infty} nN_n - 2k_{tL} \frac{n_L^2}{V_L} \quad (47)$$

where  $\rho^L$  is the rate of formation of radicals in the dilute phase,  $n_L$  the number of radicals in the dilute phase. The rate of absorption is assumed to be proportional to the concentration of radicals in the liquid phase, i.e.  $\rho_A = k_d(n_L/V_L)$ . By insertion of  $(n_L/V_L) = \rho_A/k_d$  into equation 47 and multiplying each term by  $v/k_{tP}N$  one obtains:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \quad (48)$$

where

$$\alpha' = \rho^L V_p/N^2 k_{tP} \quad (49)$$

$$Y = 2N^2 k_{tP} k_{tL} V_L / k_a^2 V_P \quad (50)$$

By means of equations 44 and 48  $\bar{n}$  may be calculated as a function of  $\alpha'$ ,  $m$  and  $Y$  as described in a previous paper<sup>22</sup>. The total number of radicals in the particles,  $n_p$  is obtained as  $N \times \bar{n}$  and the number of radicals in the dilute phase is given by:

$$n_L = Y \times \alpha \times \frac{k_a}{2k_{tL}} \quad (51)$$

The values of  $\rho_A$ ,  $\rho^L$ ,  $k_{tL}$ , and  $k_{tP}$  in equations 43–51 are expressed in units of molecules.  $m$  is a measure of the relative chance of radical escape from the particle,  $Y$  is a measure of the chance of reabsorption. The higher the value of  $Y$  at a given particle number, the lower is the chance for reabsorption. High values of  $m$  and  $Y$  will at a given particle number tend to decrease the overall number of radicals in the particles and to increase the number of radicals in the liquid phase.

Results of calculations based upon the above treatment, which takes into account the subdivision of the concentrated phase are given in *Tables 2*

*Table 2.* Effect of subdivision of the concentrated phase on the number of moles of radicals in the dilute,  $R_L$ , and the concentrated phase,  $R_p$ , and the total rate of polymerization. The calculations are based upon 1l. monomer at the start. Rate of radical production =  $\rho = 2.4 \times 10^{-8}$  mole/sec;  $k_{tP} = 3.6 \times 10^8$  l/mole sec;  $D_p = 2 \times 10^{-11}$  dm<sup>2</sup>/sec;  $N = 4.5 \times 10^{14}$  particles;  $k_{tL}/k_{tP} = 20$  and  $40^*$

$C$	$R_L \times 10^{10}$ (mole)	$R_p \times 10^{10}$ (mole)	$dC/dt \times 10^6$ (sec <sup>-1</sup> )
0.001	1.05 (0.871)	2.82 (1.87)	2.52 (1.87)
0.002	0.761 (0.660)	3.62 (2.65)	2.59 (2.01)
0.005	0.497 (0.458)	5.12 (4.19)	3.03 (2.54)
0.01	0.362 (0.346)	6.79 (5.93)	3.69 (3.26)
0.02	0.274 (0.260)	9.4 (8.39)	4.86 (4.36)
0.05	0.180 (0.173)	14.1 (13.3)	7.04 (6.63)
0.1	0.126 (0.120)	19.2 (18.8)	9.45 (9.24)

\*  $k_{tL}/k_{tP} = 20$  and  $40$  give the same values. Initial rate without precipitation:  $k_{tL}/k_{tP} = 20$ :  $(dC/dt) = 1.4 \times 10^{-5}$  sec<sup>-1</sup>.  $k_{tL}/k_{tP} = 40$ :  $(dC/dt) = 1 \times 10^{-5}$  sec<sup>-1</sup>.

and 3. The rate of radical production is the same as in *Figure 10* and the value of  $D_L$  is  $10^{-7}$ . The values given in the brackets are those obtained when the effect of subdivision on the termination reaction in the particles is not taken into account. The effect of the subdivision of the concentrated phase is to decrease the chance of termination in the particles at low conversion. As seen from *Table 2* the result is a marked increase in the number of moles of radicals in the particles, and also a small increase in the dilute phase, at low conversion. The effect decreases with increasing conversion. Therefore the effect of the subdivision will be to increase the rate of polymerization at low conversion, and thus bring the theory more into accordance with the experimental result. If one uses the values given in *Table 2* to compare the rate of termination in the two phases, it is easily calculated that the termination in the particles is already quite dominating at low conversion. Therefore not only the number of moles of radicals in the particles, but also in the dilute phase is practically completely determined by the rate of termination in the

## RADICAL POLYMERIZATION OF VINYL CHLORIDE

particles. The value of  $k_{tL}$  will not be expected to influence the value of the number of radicals in either of the two phases over quite a wide range of  $k_{tL}$ . Thus calculation with  $k_{tL}$  values corresponding to  $k_{tL}/k_{tP} = 5$  and  $k_{tL}/k_{tP} = 40$  have only negligible influence on the radical number in the two phases. In this respect the present theory is completely different from the one of Mickley *et al.* and Crosato-Arnaldi *et al.* where the number of radicals in the dilute phase is considered to be determined by the termination in that phase.

The rate which would be obtained in the absence of precipitation is given at the bottom of *Table 2*, and therefore this treatment may also directly explain the decrease in rate by precipitation. The decrease in the molecular weight accompanying the decrease in rate due to precipitation follows naturally from the high concentration of radicals in the precipitated phase at low conversion.

It is noteworthy that even at  $k_{tL}/k_{tP}$  values of 40 the precipitation will be expected to lead to a marked decrease in rate. Absorption of radicals into the particles leads to a decrease in the effective volume and thereby to an increase in the total rate of the second order termination reaction. The effect is partly counteracted by the effect of subdivision of the reaction zone and by desorption of radicals from the particles. Furthermore the values given in *Table 2* predict that the particles are the dominating reaction zone for the polymerization reaction already at very low conversion.

*Table 3.* Influence of particle number on the total rate of polymerization. The calculations are based upon 11. monomer at the start

C	dC/dt $\times 10^6$ (sec <sup>-1</sup> )		
	N = $4.5 \times 10^{14}$ (particles)	N = $4.5 \times 10^{15}$ (particles)	N = $4.5 \times 10^{16}$ (particles)
0.001	2.52	3.59	4.91
0.002	2.59	3.90	5.31
0.005	3.03	4.77	6.53
0.01	3.69	5.79	8.00

*Table 3* illustrates the calculated effect of an increase in the number of particles on the rate of reaction. The increase in subdivision caused by a higher particle number is expected to decrease further the overall rate of termination in the particles. As seen from *Table 3* this leads to a further increase in the rate of polymerization. The experimental evidence is that the number of particles at low conversion, below 1 per cent, is considerably higher than  $4.5 \times 10^{14}$ . It seems that when this is taken into account, the agreement between the theoretical and experimental results is improved. It should be pointed out that the calculations in *Tables 2* and *3* are based upon a rather high value of  $D_L$ . A lower value of  $D_L$  will lead to an increase in the rate at low conversion.

The presence of a chain transfer agent is, by the present theory, expected to increase the value of  $m$  by increasing the effective diffusion coefficient. If the experimental value of the diffusion coefficient is given by  $D_{P,k_{fM}}/k_p$ <sup>33</sup>

Table 4. Influence of the desorption constant on moles of radicals in the dilute and the concentrated phase and on the total rate of reaction. The calculations are based upon 1l. monomer at the start

C	$D_p = 2 \times 10^{-11} \text{ dm}^2/\text{sec}$			$D_p = 1 \times 10^{-9} \text{ dm}^2/\text{sec}$			$D_p = 2 \times 10^{-9} \text{ dm}^2/\text{sec}$		
	$R_L \times 10^{10}$ (mole)	$R_P \times 10^{10}$ (mole)	$dC/dt \times 10^6$ (sec <sup>-1</sup> )	$R_L \times 10^{10}$ (mole)	$R_P \times 10^{10}$ (mole)	$dC/dt \times 10^6$ (sec <sup>-1</sup> )	$R_L \times 10^{10}$ (mole)	$R_P \times 10^{10}$ (mole)	$dC/dt \times 10^6$ (sec <sup>-1</sup> )
0.001	1.05	2.82	2.52	11.0	1.13	12.6	12.2	0.631	13.8
0.002	0.761	3.62	2.59	9.06	1.84	10.9	11.7	1.21	13.5
0.005	0.497	5.12	3.03	6.90	3.48	9.28	10.0	2.65	12.3
0.01	0.362	6.79	3.69	5.29	5.48	8.48	8.44	4.35	11.4
0.02	0.274	9.41	4.86	3.87	8.09	8.18	6.96	7.25	11.2
0.05	0.180	14.1	7.04	2.51	13.3	9.21	4.53	12.3	11.0
0.1	0.126	19.2	9.45	1.66	18.9	11.0	3.02	17.7	11.9

(where  $D_p$  is the diffusion coefficient for monomer and transfer agent radicals and  $k_{fM}$  is the transfer constant to monomer) the ratio of the values of  $m$  with and without chain transfer agents,  $T$ , is given by:  $k_{fT}[T]/k_{fM}[M]$  where  $k_{fT}$  is the chain transfer constant to  $T$  and  $[M]$ , and  $[T]$  refers to the concentration in the particles.

Table 4 shows the results of calculations of an increase in  $m$  by factors of 50 and 100. An increase in  $m$  leads to a higher number of moles of radicals in the liquid phase and a lower number of radicals in the particles. The overall rate at low conversion is increased, the autocatalytic effect is absent. At sufficiently high values of  $m$  the theory predicts that the rate at low conversion should be independent of the value of  $m$ . This seems to be in accordance with the experimental results (Figure 9). It should be pointed out again that this treatment does not involve any *a priori* assumption of a thermodynamically established equilibrium distribution of radicals between the two phases.

## B. EMULSION POLYMERIZATION

All authors who have studied the emulsion polymerization of vinyl chloride agree that the reaction does not follow case 2 of the Smith-Ewart theory. The main deviations from this theory are:

1. The number of latex particles varies strongly with the emulsifier concentration while the polymerization rate changes relatively very little.
2. The number of particles is independent of the initiator concentration.
3. The rate of reaction increases with increasing initiator concentration at a constant number of particles. (The reaction order found by the different authors varies between  $0.5^{23}$  and  $0.8^2$ .)
4. The conversion versus time curves show an autocatalytic behaviour up to high conversion.

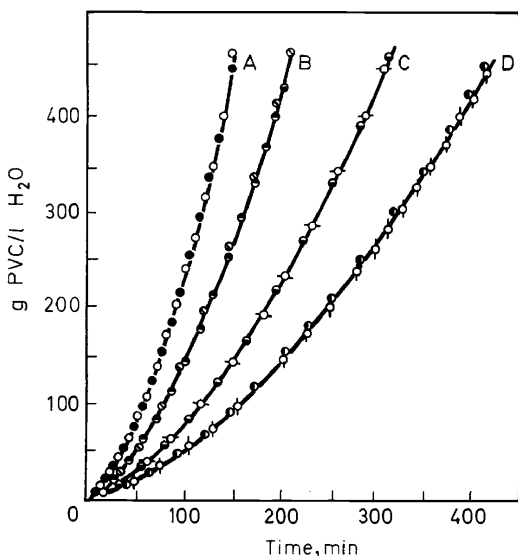
In order to explain the small effect of particle number on the rate of reaction, Giskehaug<sup>24</sup> suggested a considerable contribution from polymerization in the water phase. He then had to assume a value of  $k_p/k_{tw}^{\frac{1}{2}}$  of about 5 ( $1^{\frac{1}{2}}$  moles<sup>-1/2</sup> sec<sup>-1/2</sup>), which may seem unreasonably high compared to the value obtained by other authors. Gerrens *et al.*<sup>2</sup> found that the experimental values of rate and particle number when inserted in the rate expression

$$r_p = \frac{k_p C_M}{N_A} \times N \times \bar{n}$$

leads to a value of  $\bar{n}$  considerably below 0.5, which indicated that at a given moment only a small fraction of particles contained a radical. In order to explain the low value of  $\bar{n}$ , Gerrens suggested a degradative chain transfer reaction to polymer. He found a reaction order of 0.8 with respect to initiator. This was taken in support of the assumption of a degradative chain transfer reaction. This high order with respect to initiator has not been confirmed by other authors<sup>23, 24</sup>. Peggion *et al.*<sup>25</sup> suggest that the deviation from the Smith-Ewart theory may be due both to the relatively high solubility of monomer in water and to the low solubility of polymer in monomer. The concentration of monomer in the particles at equilibrium is given by equation

1. In cases when the monomer is a good solvent for its polymer, the restricted swelling of the particles, which is obtained in emulsion polymerization, is determined by a balance between the swelling force and the interfacial energy<sup>26</sup>. In the case of vinyl chloride, however, the interfacial energy term will even in emulsion polymerization be of minor importance, compared to the term containing the interaction energy, in limiting the swelling of the particles with monomer<sup>27</sup>. It is not easy to see why this difference should lead to any deviation from the Smith-Ewart theory. Also in the case of vinyl chloride the reaction zones, the particles, are one-phase systems of a constant composition. The composition of the particles is the same as in bulk polymerization, i.e. they contain a considerable amount of monomer.

The situation with emulsion polymerization is in fact somewhat simpler than in bulk polymerization because the particles are certainly the sole reaction zones and moreover the initiator is present in the outer sphere only, during the whole reaction. However, it has been suggested that for bulk polymerization also the polymer particles are under ordinary conditions the most dominating reaction zone and, as they have the same composition as the latex particles in the emulsion polymerization, one would expect the kinetics of bulk and emulsion polymerization to be rather similar. Therefore one might anticipate that if the particle number and rate of radical production were the same in the two cases, the rate of polymerization, compared at the same amount of polymer formed, should be very close. *Figure 11* gives some experimental results from emulsion polymerization with an emulsifier which gives a relatively low number of particles. It appears that the curves are similar in shape to those for bulk polymerization (*Figure 2*). In order to make a completely quantitative comparison of the rates at a given amount of



*Figure 11.* Emulsion polymerization of VC with 2.0 g sodium di-*n*-butylsulphosuccinate (Aerosol DBM)/l H<sub>2</sub>O: (A) 6.4 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/l H<sub>2</sub>O; (B) 3.2 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/l H<sub>2</sub>O; (C) 1.6 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/l H<sub>2</sub>O; (D) 0.8 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/l H<sub>2</sub>O. (Reprinted by permission of *The Journal of Polymer Science*).

## RADICAL POLYMERIZATION OF VINYL CHLORIDE

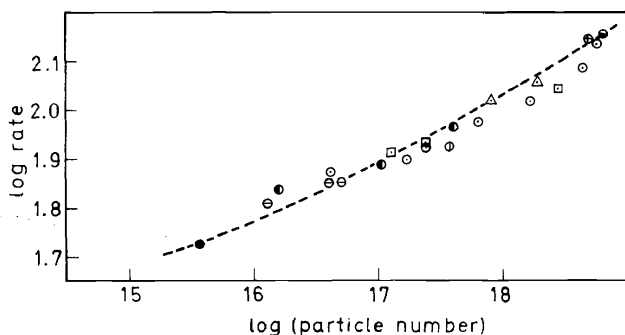


Figure 12. Log differential rate (g PVC/l. H<sub>2</sub>O h) versus log (number of particles per l H<sub>2</sub>O) at a conversion of 100 g PVC/l. H<sub>2</sub>O. Concentration of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 1.6 g/l. H<sub>2</sub>O. ● No emulsifier; ⊖ sodium octylsulphate; ⊙ sodium decylsulphate; ⊕ sodium dodecylsulphate (Empicol-8043); ⊗ sodium tetradecylsulphate; ⊚ sodium hexadecylsulphate; ⊛ sodium di-*n*-butylsulphosuccinate; □ K-30, C<sub>12</sub>; Δ K-30, C<sub>15</sub>; K-30 is a mixture of various paraffinsulphonates with average chain length of 12 and 15 C-atoms respectively

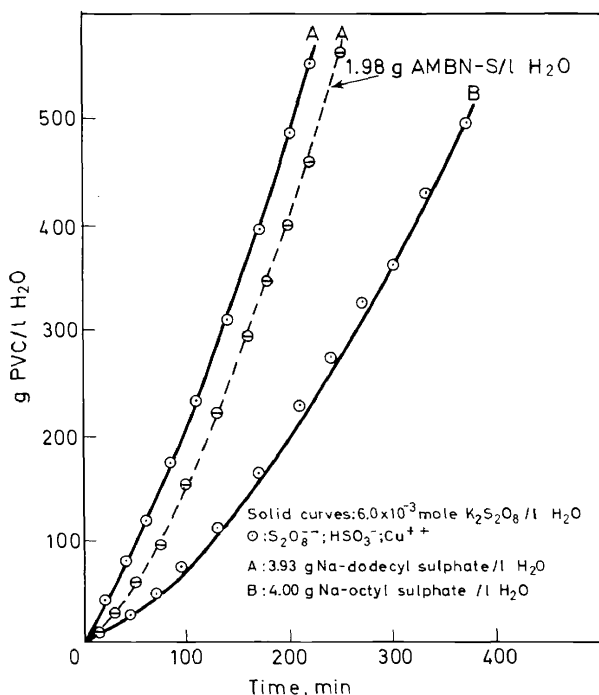


Figure 13. Comparison of g PVC formed as a function of time with different initiator systems. Solid curves: [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 6 × 10<sup>-3</sup> mole/l. H<sub>2</sub>O; ⊙ [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 2 × 10<sup>-4</sup> mole/l. H<sub>2</sub>O; [HSO<sub>3</sub><sup>-</sup>] = 1.2 × 10<sup>-3</sup> mole/l. H<sub>2</sub>O, [CuSO<sub>4</sub>] = 7.9 × 10<sup>-4</sup> mole/l. H<sub>2</sub>O; ⊖ α,α'-azobis (methylbutyronitrile-γ-N<sub>4</sub>-sulphonate (AMBN-S) = 5.4 × 10<sup>-3</sup> mole/l. H<sub>2</sub>O.

polymer formed, one would have to compare experiments where both the rate of radical production and particle number were the same. Such data are not available. However, one may from the experimental effect of the particle number on the rate (*Figure 12*) extrapolate the result of emulsion polymerization to the corresponding conditions for bulk polymerization. Such an extrapolation does indicate that the rates are nearly the same.

*Figure 12* gives log differential rate at 100 g PVC formed as a function of log particle number with different types and amounts of emulsifiers. This figure includes results with a larger number of emulsifiers than in a previous paper<sup>23</sup>. It appears that the rate of emulsion polymerization is determined, not by the type of emulsifier, but by the number of particles formed. The reaction order with respect to the number of particles is very low. It increases with increasing number of particles up to the value of about 0.15.

In view of the fact that the rate of decomposition of persulphate is very sensitive to the presence of any foreign agents in the water<sup>28</sup>, it might have been suggested that the effect shown in *Figure 12* was due to an effect on the rate of radical production from persulphate. To clarify this question, the rates obtained with different emulsifiers and persulphate as initiator were compared with the same emulsifier systems using a redox system composed of persulphate, bisulphite and copper ions<sup>29</sup> as the initiator system. Any effect on the rate of radical production from persulphate, caused by the particles, emulsifiers or other agents present, may be expected to be completely outbalanced by the effect of the bisulphite-copper system. The results of this investigation are shown in *Figure 13*. The redox system was adjusted to give the same rate as  $6 \times 10^{-3}$  moles of pure persulphate per l H<sub>2</sub>O at a given amount of sodium lauryl sulphate. Exactly the same initiator systems were then applied with a given amount of sodium octylsulphate. The ratio of particle number obtained with lauryl sulphate to that obtained with octylsulphate is about 50. Octylsulphate gives a considerably lower rate and again the kinetic curves with the two initiator systems practically overlap. This result confirms the previously assumed effect of particle number on the polymerization rate, at a constant rate of radical production. *Figure 13* includes the result of a run with a water soluble azo compound also. The decomposition rate constant for this compound is  $3.35 \times 10^{-6} \text{ sec}^{-1}$  at 50°C and is reported to be quite unaffected by the presence of any foreign substances<sup>30</sup>. It may be anticipated from a comparison of the rates in the two cases that the rate of radical production from persulphate in the presence of vinyl chloride is 3.4 times higher than that which would be expected from the rate constant for decomposition in pure water<sup>31</sup>. Breitenbach *et al.*<sup>32</sup> found that the rate of radical production from persulphate was increased by a factor of 10 when the solution was saturated with vinyl acetate.

The results of emulsion polymerization of vinyl chloride have led to the conclusion that the mean number of radicals per particle is very low,  $10^{-3} - 10^{-1}$ , dependent upon the particle number<sup>2, 23</sup>. Ugelstad *et al.*<sup>22, 23, 33</sup> have shown that the low value of  $\bar{n}$  may be explained by interparticle termination brought about by a rapid desorption and reabsorption of radicals. Such a mechanism may be especially favourable in the case of vinyl chloride because of the chain transfer to monomer. Approximate expressions for the rate of polymerization, valid at low values of  $\bar{n}$  ( $\ll 0.5$ ),



## RADICAL POLYMERIZATION OF VINYL CHLORIDE

were evaluated. This was done by assuming that at low values of  $\bar{n}$  only particles with 0, 1, and 2 radicals need to be considered, which led to the following simplified expression for the rate of reaction<sup>23</sup>:

$$r_p = \frac{k_p C_M}{N_n} \rho^{w\frac{1}{2}} \left( \frac{V_p}{2k_{tP}} + \frac{N^w}{2k_d} \right)^{\frac{1}{2}} \quad (52)$$

$\rho^w$  and  $k_{tP}$  are expressed in units of molecules,  $r_p$  is the rate of reaction in moles of monomer,  $\rho^w$  is the rate of radical production in the water phase,  $V_p$  is the total volume of the particles and  $N^w$  is the number of particles, all values defined per 1 H<sub>2</sub>O.  $C_M$  is the concentration of monomer in the particles,  $k_d$  is the rate 'constant' of desorption of radicals.

If the desorption is determined by a diffusion process within the particles ( $k_d = 4\pi D_p r/v$ ), equation 52 takes the form:

$$r_p = \frac{k_p C_M}{N_A} \rho^{w\frac{1}{2}} \left( \frac{V_p}{2k_{tP}} + \frac{N^w \frac{1}{2} V_p^{\frac{1}{2}}}{2k'_d} \right)^{\frac{1}{2}} \quad (53)$$

Equation 53 was found to describe the experimental results of emulsion polymerization over a wide range of particle number and conversion. The value of  $k_{tP}$  and  $D_p$  applied in the treatment of bulk polymerization has been obtained from the experimental data for emulsion polymerization (Figure 12 and equation 53). The values given for  $k_{tP}$  and  $D_p$  in the present case are higher than those previously reported<sup>23</sup>. This is due to the higher value of the radical production from persulphate, which the results given in Figure 13 indicated, that has been applied in the present calculation.

The evidence for the low values of  $\bar{n}$  was based upon calculations from the familiar rate equation for emulsion polymerization,  $r_p = k_p C_M \bar{n} \times N/N_A$ , by application of experimental values for  $C_M$  and  $N$ , and with Burnett and Wright's value of  $k_p$ . As discussed above the value of  $k_p$  is somewhat uncertain. Independent evidence for the low value of  $\bar{n}$  in emulsion polymerization of vinyl chloride has recently been obtained by experiments where the rate of radical production was changed during the run<sup>33</sup>. Figure 14 gives results obtained with post addition of initiator. With the type and amount of emulsifier applied, the number of particles was  $8 \times 10^{18}$  per 1 H<sub>2</sub>O. In the experiments with post addition of initiator the reaction was initiated with the same amount of initiator as in the reference run. After three different conversions the concentration of initiator was increased 4 and 16 times respectively. It appears that the differential rate of reaction at a given conversion is independent of the time at which post addition took place. A fourfold increase in the initiator concentration led to a doubling of the rate in accordance with a half order with respect to initiator. The important fact concerning the question of the value of  $\bar{n}$  is that the 'new' rate after post addition of initiator was established very rapidly, in less than one minute. After addition of initiator, and establishment of a rate twice that of the reference run, the total number of radicals in the system must accordingly be twice that before addition, i.e.  $16 \times 10^{18} \times \bar{n}$ . The establishment of the

new rate therefore requires the production of at least  $8 \times 10^{18} \times \bar{n}$  radicals. The time  $t$  required to produce this number of radicals is:

$$t = 8 \times 10^{18} \bar{n} / \rho \quad (54)$$

where  $\rho$  is the rate of radical production from persulphate after a fourfold increase in the persulphate concentration. Inserting into equation 54,  $t = 1$  min, and the experimental value for  $\rho$ , gives a value of  $\bar{n} < 0.05$ . *Figure 15* gives results where the rate of radical production has been reduced after a certain conversion. In these experiments the redox system of persulphate, bisulphite and copper ions has been applied and the rate of radical production has been reduced by an increase in the amount of citrate in the system. Again the 'new' rates corresponding to the new rate of radical production are established very rapidly.

Although these effects of change in rate of radical production refer to emulsion polymerization, the similarity of emulsion and bulk polymerization of vinyl chloride may possibly allow general conclusions to be drawn. In the authors' opinion the rapid establishment of the 'new' rate corresponding to a given conversion and rate of radical production argues strongly for the justification of the application of the quasi steady state treatment and speaks against the non-steady state treatment suggested by Magat<sup>34</sup>.

In comparison of emulsion polymerization with bulk polymerization it should be brought to mind that in bulk polymerization an increase in the rate of desorption of radicals from the particles leads to an increase in rate at low conversions. In the same way a decrease in the rate of absorption was shown theoretically to be expected to increase the rate. In the case of emulsion polymerization the opposite is true. The concentration of monomer in the water phase is so low that an increase in desorption or a decrease in absorption is expected to lead to a decrease in rate, due to a decrease in the number of radicals in the particles. The effect of a decrease in  $k_a$  is to increase the parameter  $Y$ . *Figures 16* and *17* illustrate the calculated effect of an increase in  $Y$ . Comparing at the same values of  $\alpha'$  and  $m$ , an increase in  $Y$  leads to a decrease in the number of radicals in the particles, which in the case of emulsion polymerization leads to a decrease in rate. Possibly, such a decrease in rate of radical absorption is responsible for the effects with mixed emulsifiers<sup>35</sup>.

*Figure 18* gives results with Na-laurylsulphate and mixtures of Na-laurylsulphate with fatty alcohols of different chain length as emulsifiers. It appears that hexadecyl alcohol leads to a strong decrease in the rate of reaction and number of particles, while the lower alcohols have hardly any effect in either respect.

*Figure 19* gives the result of experiments where the amount of hexadecyl alcohol has been varied. An increase in the amount of the fatty alcohol leads to a steady reduction in the particle number. The initial rate is strongly reduced and rather surprisingly is the same in all cases, independent of the amount of fatty alcohol. An increase in the amount of fatty alcohol does, however, lead to a delay in the upswing of the curve. One might, at first sight, think that this would mean that in all cases where fatty alcohol was applied, the particle number at low conversion was the same and very low. This did not appear to be the case. There is only a small change in the particle number

# RADICAL POLYMERIZATION OF VINYL CHLORIDE

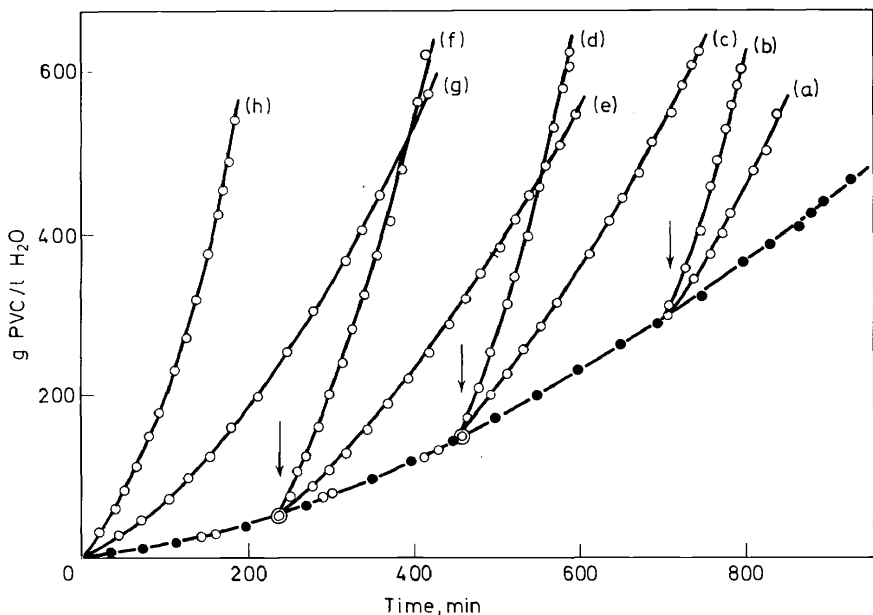


Figure 14. Post-addition of  $K_2S_2O_8$  at various conversions. ● Reference run with  $3.75 \times 10^{-4}$  mole  $K_2S_2O_8$ /l.  $H_2O$ . The initial recipes in runs (a), (b), (c), (d), (e) and (f) are equal to that of reference curve. The following amounts of  $K_2S_2O_8$  (mole/l.  $H_2O$ ) were post-added at the conversions indicated by arrows:  $11.25 \times 10^{-4}$  in runs (a), (c) and (e);  $56.25 \times 10^{-4}$  in runs (b), (d) and (f). Runs (g) and (h) were initiated by  $15 \times 10^{-4}$  and  $60 \times 10^{-4}$  mole  $K_2S_2O_8$ /l.  $H_2O$  respectively. All runs with 3.93 g Empicol/l.  $H_2O$  at  $50^\circ C$

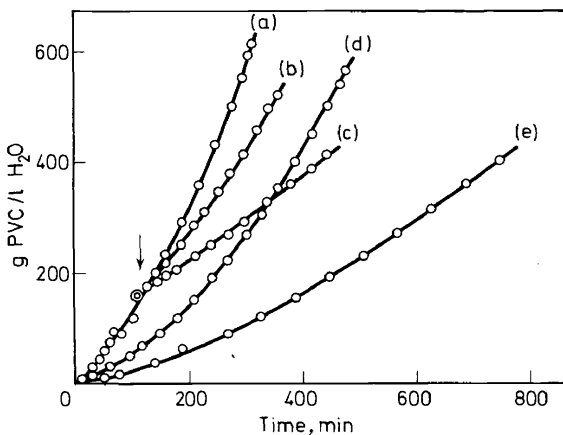


Figure 15. Comparison of runs with post-added citrate and runs with the same total amount of citrate added initially. All runs with 3.93 g sodium dodecyl sulphate (Empicol 8043)/l.  $H_2O$ ,  $2.0 \times 10^{-4}$  mole  $K_2S_2O_8$ /l.  $H_2O$ ,  $10^{-3}$  mole  $NaHSO_3$ /l.  $H_2O$ ,  $7.9 \times 10^{-6}$  mole  $CuSO_4$ /l.  $H_2O$ ,  $1.3 \times 10^{-3}$  mole Borax/l.  $H_2O$ .  $t = 50^\circ C$ . Initially added amounts of citrate (mole/l.  $H_2O$ ): (a), (b) and (c)  $2.8 \times 10^{-5}$ , (d)  $7 \times 10^{-5}$  and (e)  $3.08 \times 10^{-4}$ . Amounts of citrate (mole/l.  $H_2O$ ) added at a conversion of 160 g PVC/l.  $H_2O$ : (b)  $4.2 \times 10^{-5}$  and (c)  $2.8 \times 10^{-4}$  (Reprinted by permission of *The British Polymer Journal*)

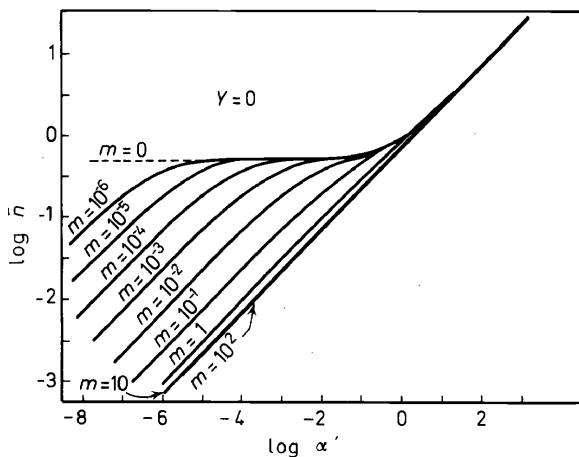


Figure 16. Illustration of the effect of the parameter  $Y$  on the mean number of radicals per particle (Reprinted by permission of *The Journal of Polymer Science*)

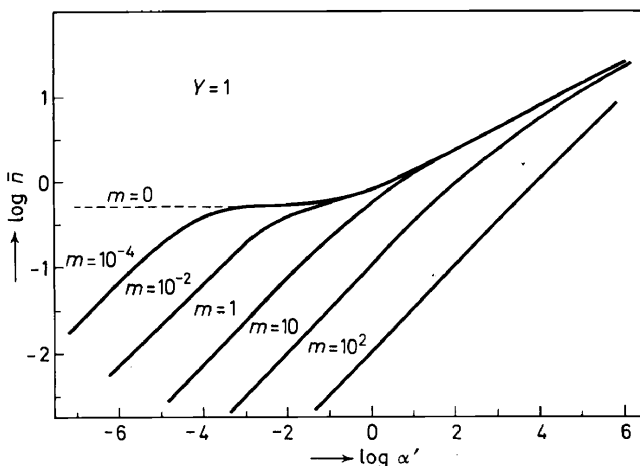


Figure 17. Illustration of the effect of the parameter  $Y$  on the mean number of radicals per particle (Reprinted by permission of *The Journal of Polymer Science*)

during the run. However, the upswing in the conversion versus time curves appears to be connected with the degree of coverage of the particles. The fact that a smaller number of particles is formed with increasing amount of fatty alcohol does of course mean that the particles are fully covered with emulsifier up to higher conversion.

Figure 20 gives measurements of the surface tension as a function of time for the same systems as shown in Figure 19. Indeed, the upswing in the rate of polymerization in the different systems seems to be connected with a marked increase in surface tension for the same systems, which is expected to occur at the points where there is no longer a full coverage of the particles.

RADICAL POLYMERIZATION OF VINYL CHLORIDE

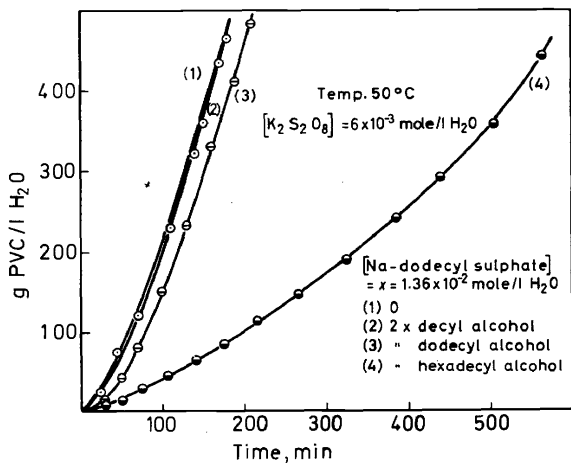


Figure 18. Effect of *n*-fatty alcohols of different chain length. Molar ratio of fatty alcohol and sodium dodecylsulphate = 2. All experiments with  $1.36 \times 10^{-2}$  mole/l.  $H_2O$  of sodium dodecylsulphate

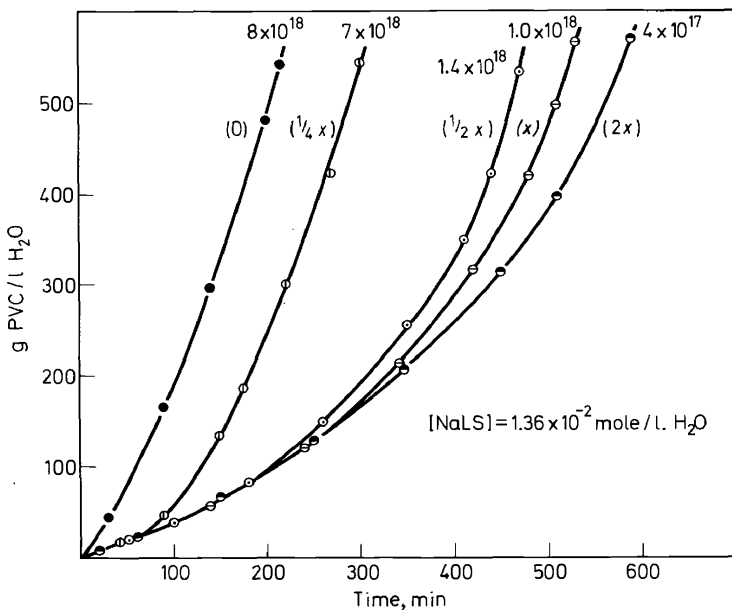


Figure 19. Effect of variation of the amount of hexadecyl alcohol. Sodium dodecylsulphate =  $1.36 \times 10^{-2}$  mole/l.  $H_2O$ .  $x$  = molar ratio of fatty alcohol and the anionic emulsifier.  $[K_2S_2O_8] = 6 \times 10^{-3}$  mole/l.  $H_2O$ .  $t = 50^\circ C$

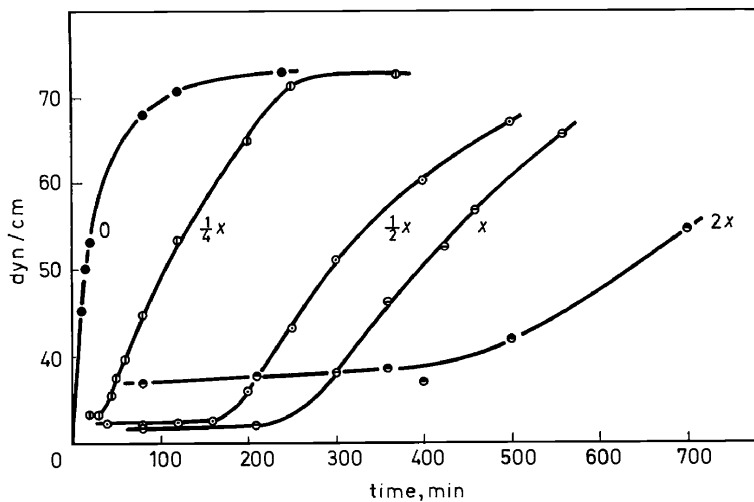


Figure 20. Surface tension as a function of time for the runs given in Figure 19

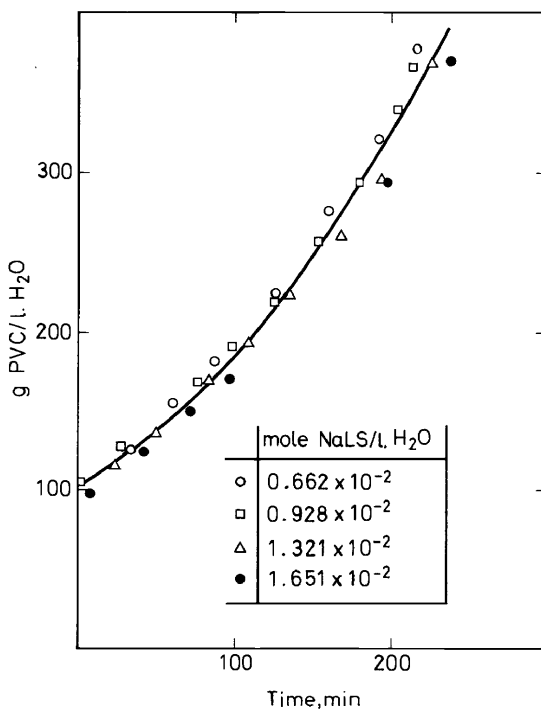


Figure 21. Effect of degree of coverage with sodium dodecylsulphate on the seed polymerization. Seed: 100 g/l. H<sub>2</sub>O. Particle diameter of seed = 100 μ; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] =  $3 \times 10^{-3}$  mole/l. H<sub>2</sub>O; t = 50°C

## RADICAL POLYMERIZATION OF VINYL CHLORIDE

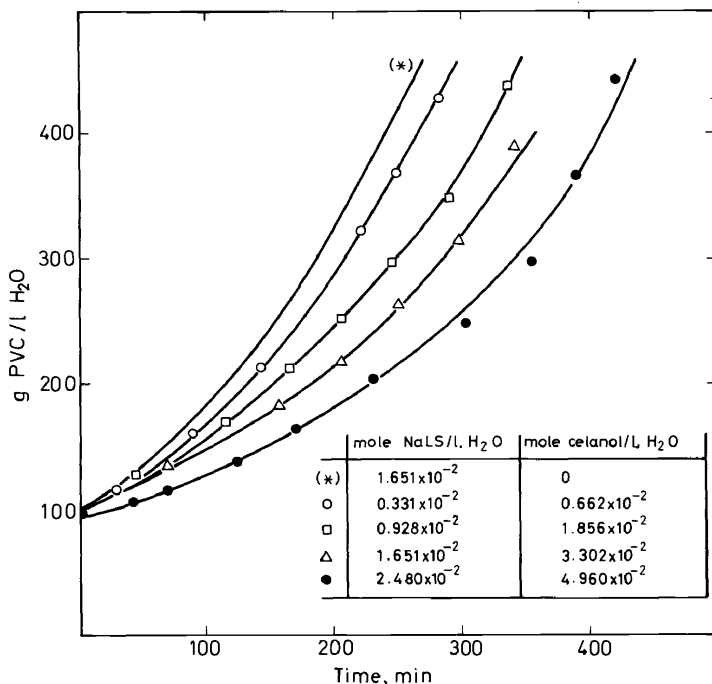


Figure 22. Effect of mixed emulsifier on seed polymerization. Experimental conditions the same as in Figure 21. NaLS = sodium dodecylsulphate

Experiments with seed polymerization also revealed the same effect of mixed emulsifiers on the rate of polymerization. Results of these experiments are shown in Figures 21 and 22. Addition of pure anionic emulsifier up to 100 per cent coverage does not influence the rate of polymerization (Figure 21). A mixture of Na-laurylsulphate and fatty alcohol leads, at full coverage, to a very marked reduction in rate (Figure 22). These phenomena may possibly be explained in terms of the Schulman-Cocbain theory<sup>36</sup> of mixed emulsifiers. The pure anionic emulsifiers will form a loose structure, behaving as a two-dimensional gas at the particle surface and will not prevent the absorption of radicals. Complex formation with fatty alcohol leads to a condensed layer and apparently to a decrease in the rate of absorption. According to the general Smith-Ewart theory this would not influence the rate of reaction. In the present treatment a decrease in the value of  $k_p$  (the radical absorption rate constant), leads to an increase in  $Y$  and thereby, as discussed above to a decrease in the rate of emulsion polymerization.

In conclusion one may therefore suggest that under normal conditions there exists a great similarity between emulsion, bulk and suspension polymerization of vinyl chloride. The reaction zones are in each case polymer particles swollen with monomer. Already at very low conversion the termination and subsequently the polymerization reaction in the dilute phase is negligible.

Bulk and emulsion polymerization will respond differently to a change in

the rate of radical desorption or absorption due to the difference in the monomer concentration in the liquid phase, in the two cases. A general theory based upon desorption and reabsorption of radicals in the particles is able to explain the experimental results both for bulk and emulsion polymerization.

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