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Model for Kinetics of Vinyl Chloride Polymerization

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ABSTRACT

This paper gives a critical review of recent models for the polymerization of vinyl chloride. In solution and bulk polymerization the effect of eventual degradative chain transfer to monomer, addition of chain transfer agents, and precipitation of polymer is discussed. A model for emulsion polymerization is described which includes particle formation and kinetics of polymerization where especially desorption and reabsorption of radicals in the particles are included.

SOLUTION AND BULK POLYMERIZATION

In treating polymerization of vinyl chloride, the reaction in solution is the most simple. Complications to simple kinetics arise from the degradative chain transfer to solvent and from termination by reaction with initiator radicals.

Degradative chain transfer to solvents has been discussed by a number of authors, and the mathematical treatment of this is treated in detail in an excellent paper by Atkinson, et al. [1]. The main point is that such a degradative chain transfer results in a sigmoidal curve when the rate is plotted as a function of the initiator concentration (Fig. 1). The order with respect to initiator concentration will be 0.5 at low initiator concentration, then increases to a

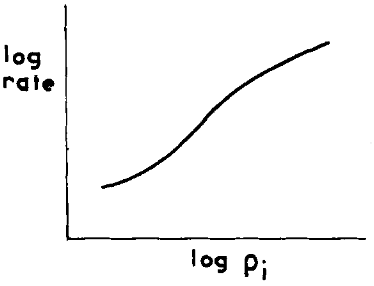

FIG. 1. Log-log plot of rate vs. initiator concentration.

value between 0.5 and 1 and finally at higher values of radical production ρ_i, the order is again 0.5.

A problem which is still very much discussed is the degradative chain transfer to monomer and the degree of degradation, i.e., the reinitiation constant for the monomer radical:

$$RM\cdot + M \xrightarrow{k_p'} R\cdot$$

The arguments for the degradative chain transfer to monomer are: (1) the order with respect to initiator is said to decrease from a value of 0.52-0.55 at low initiator concentrations to 0.5 at higher initiator concentrations; (2) addition of CBr_4 leads to an increase in rate. The effect of CBr_4 is to reinitiate polymerization by a rapid reaction between the monomer radical and CBr_4 to give much more active radicals. There are contradictory reports as to the effect of CBr_4 in the literature. Breitenbach et al. [2] report an increase in rate of 15-20% in diethylene chloride solution, while Crosato-Arnaldi et al. [3] reported that they did not find any effect of addition of CBr_4 in solution. The first argument, the slight increase in order with increasing initiator concentration is in my opinion somewhat doubtful. The equations to be considered are:

$$dR\cdot/dt = \rho_i - k_{fm}R\cdot[M] + k_p'RM\cdot[M] - k_t'[R\cdot][RM\cdot]V$$
$$- k_t[R\cdot]^2 V = 0 \tag{1}$$

$$dRM\cdot/dt = k_{fm}R\cdot[M] - k_p'RM\cdot[M] - k_t'[R\cdot][RM\cdot]V$$

$$- k_t''[RM\cdot]^2 V \tag{2}$$

If for simplification we accept the geometric mean rule:

$$k_t' = \sqrt{k_t k_t''}$$

we get, as shown by Breitenbach,

$$[R\cdot] = (\rho/Vk_t)^{\frac{1}{2}} \frac{(\rho/V)^{\frac{1}{2}} + k_p'[M]/k_t''^{\frac{1}{2}}}{(\rho/V)^{\frac{1}{2}} + k_p'[M]/k_t''^{\frac{1}{2}} + k_{fm}[M]/k_t^{\frac{1}{2}}} \tag{3}$$

An illustration of how $[R\cdot]$ will vary with ρ is shown in Fig. 2, with the following values for the constants: $V = 1$, $k_{fm} = 10$, $k_p' = 10$, $[M] = 5$, $k_t = k_t' = k_t'' = 2 \times 10^9$. The sigmoidal form of the curve is clearly shown. At low values of ρ we have a half order, with $[R\cdot]$ given by

$$[R\cdot] = (\rho/Vk_t)^{\frac{1}{2}}[k_p'/(k_p' + k_{fm})] \tag{4}$$

At high values of ρ we get:

$$[R\cdot] = (\rho/Vk_t)^{\frac{1}{2}} \tag{5}$$

With the chosen constants the rate at low values of ρ is only half of what it would be with no degradative chain transfer. With intermediate values of ρ, the order with respect to ρ is > 0.5.

It has recently been suggested that the value of $k_p' = 10\ k_{fm}$, which would give a decrease of 10% due to degradative chain transfer to monomer at low values of ρ. The question is, however, that most authors citing a decrease in the order with respect to ρ with increasing ρ most certainly work in the lower range of ρ values, so that in fact one would expect that the order with respect to ρ would increase

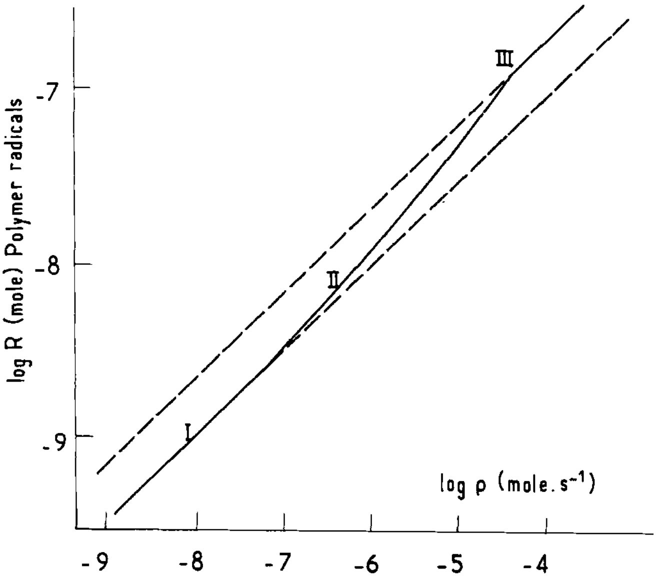

FIG. 2. Plots of log R· (polymer radicals) as a function of log ρ (rate of radical production) by solution polymerization. $k_p = k_{fm} = 10\ dm^3$/mole-sec; $k_t = k_t' = k_t'' = 2 \times 10^9$ dm/mole-sec; [M] = 5 mole/dm³; V = 1 dm³.

with increasing value of ρ. One might argue that the values of k_t, k_t', and k_t'' may not be equal, which might lead to a shift in the curve so that the upper limit would be reached at much lower values of ρ.

Numerical calculations show, however, that if we have to have a degradative chain transfer to monomer, we will in any case have to accept that to reach from region II where the order with respect to ρ is > 0.5 up to region III we will have to operate with values of ρ much higher than used in practice. Note that this argument does not exclude a degradative chain transfer to monomer; it merely questions whether the change in order with respect to ρ may be taken as evidence for this.

Several authors have found that the initial rate in bulk polymerization increases markedly with addition of CBr_4. Breitenbach found an increase of about 100%, which is taken as a proof of degradative chain transfer to monomer. Tavan et al. [4, 5] have recently argued against this interpretation on the following grounds. If, as is now considered probable, the reaction takes place in the precipitated particles already from very low conversion, the value of ρ/V_p, where V_p is the total volume of precipitated polymer particles, will be very high in the start; a consequence of this would be that we start in region III with a half order with respect to ρ. As the reaction proceeds, V_p increases, the value of ρ/V_p decreases, and the order with respect to ρ should increase. The experimental results show that the order with respect to ρ stays constant at 0.5 up to high conversion, although some authors, for instance Cotman [6], report an increase in order with increasing conversion.

Again I will postulate that, even at low conversions (say 1-2%), we hardly work in region III—most probably in region I, and possibly at very low conversion in region II, but in this last case the order should be > 0.5 at low conversion and decrease with increasing conversion. There is another point concerning the difference in the effect of CBr_4 in solution and in bulk polymerization which is of interest. The question is, if we accept a value of $k_p'/k_{fm} \sim 10$, which might be anticipated from the results of Breitenbach, this would lead to an increase in rate in solution of maximally only 10% on addition of CBr_4. Why is the effect so much greater in bulk polymerization? This should in fact be expected, because in the precipitated particles we would expect that the value of termination constants for the polymer radicals k_t would decrease while the values of k_t' and k_t'' change much less. This implies that the effect of degradative chain transfer to monomer becomes more important and that even if we accept $k_p'/k_{fm} = 10$, which in solution leads only to a minor effect of degradative chain transfer to monomer, in bulk polymerization we will find that with this value of k_p'/k_{fm} the effect of degradative chain transfer would be higher, and therefore that the effect of addition of CBr_4 is much higher. As an example, in Fig. 3 is shown the total number of radicals in the particles calculated for a case where one has the constants: $k_t = 10^7$, $k_t' = 5 \times 10^8$, $k_t'' = 10^9$, initial volume = 1 dm^3, total volume of particles = 0.02 dm^3; i.e., conversion is less than 2%. We see from Fig. 3 that in this case, even with $k_p'/k_{fm} = 10$, we have a marked effect of degradative chain transfer to monomer if we operate in region I. Even in this case with $V_p = 10^{-2}$ dm^3 this will be true for ρ values below $\sim 10^{-7}$

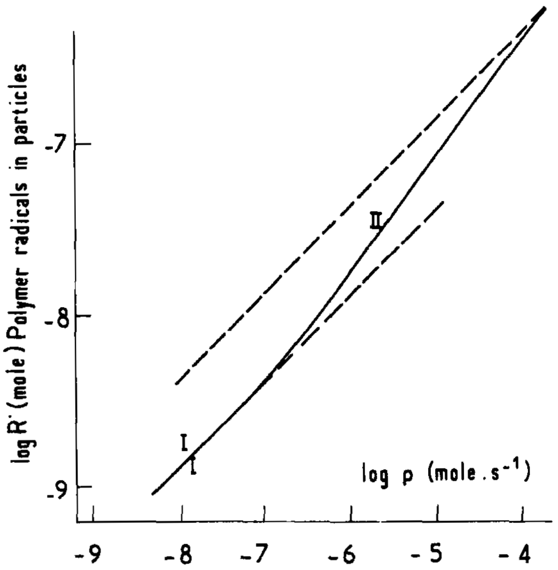

FIG. 3. Plots of log R· (polymer radicals in the particles) as a function of log ρ (rate of radical production) in bulk polymerization. $k_p' = 100$ dm³/mole-sec; $k_{fm} = 10$ dm³/mole-sec; $k_t = 10^7$, $k_t' = 5 \times 10^8$, $k_t'' = 10^9$ dm³/mole-sec; $[M]_p = 5$ mole/dm³; $V_p = 0.02$ dm³.

mole/sec, which has usually been applied. We see also that in this case the effect of addition of CBr_4 may, even with k_p'/k_{fm} as high as 10, lead to an increase in the rate a factor 2.5.

Now in this treatment we have accepted that, with and without chain transfer, the reaction takes place completely in the particles, and that the effect of addition of CBr_4 is to increase the rate of reaction in the particles. This leads to some difficulties as regards the loss of autoacceleration by addition of CBr_4, however. With the constants used in Fig. 3, the termination reaction would be dominated by reaction between a monomer radical and a polymer radical. If this is so, the equation for determining R· and thereby the rate will be very much simplified. Assuming that all reactions take place in the particles, we have, for the case without CBr_4:

$$\rho_i = 2k_t'[R\cdot][RM\cdot]\, V_p = 0 \qquad (6)$$

$$dRM\cdot/dt = k_{fm}[R\cdot]_p[M_p]V_p - k_p'[RM\cdot][M]_pV_p - k_t'[R\cdot][RM\cdot]V_p = 0 \qquad (7)$$

which gives

$$[R\cdot] = \frac{\rho_i}{4V_pk_{fm}[M]_p} + \left[\frac{\rho_ik_p'}{V_p2k_t'k_{fm}} + \left(\frac{\rho_i}{4V_pk_{fm}[M]_p}\right)^2\right]^{1/2} \qquad (8)$$

and accordingly for the rate of polymerization $= k_p[M]_p[R\cdot]V_p$

$$\text{rate} = \frac{\rho_ik_p}{4k_{fm}} + k_p[M]_p\left[\frac{\rho_iV_pk_p'}{2k_t'k_{fm}} + \left(\frac{\rho_i}{4k_{fm}[M]_p}\right)^2\right]^{1/2} \qquad (9)$$

As we accepted that we operate in region I we have:

$$\text{rate} = k_p[M]_p(\rho_iV_pk_p'/2k_t'k_{fm})^{1/2} \qquad (10)$$

This expression is in accordance with experimental results.

If we have added a chain transfer agent and we accept that this will react rapidly with the monomer radicals to form radicals of equal reactivity as the polymer radical, we do not divide between radicals formed from reaction with chain transfer agents and polymer radicals, and we may write the following steady-state equation:

$$\rho - 2k_t'[R\cdot][RM\cdot]\ V_p = 0 \qquad (11)$$

$$dRM\cdot/dt = k_{fm}[R\cdot][M]_pV_p - k_{pT}[RM\cdot][T]V_p - k_t'[RM\cdot][R\cdot]\ V_p = 0 \qquad (12)$$

which gives for the rate in region I,

$$\text{rate} = k_p[M]_p\,(\rho_i V_p k_{pT}[T]/2k_t' k_{fm}[M]_p) \qquad (13)$$

Again we should find that even if the rate increases because $k_{pT}[T] > k_p'[M]_p$, we should have the rate proportional to $V_p^{\frac{1}{2}}$, i.e., we should have the same autoacceleration.

Another explanation may be given for the effect of addition of CBr_4 which is based upon an increase in the desorption of radicals from the particles. However, there seems to be considerable evidence for that k_p' is considerably lower than the value of k_p, the propagation constant for polymer radicals. Additional evidence for this is brought from results of emulsion polymerization to be discussed below.

A series of papers have treated the kinetics of bulk polymerization and different models have been suggested to explain the kinetics. Three of the most recent models will be discussed here.

The first one to be discussed is the one suggested by Talamini and co-workers [7] which has recently been restated by Hamielec et al. [8] in a somewhat refined form. It states that the reaction takes place in two phases, the monomer-rich phase and the polymer particles. In discussion of this model and the subsequent ones, one point should be made clear. When a radical is formed in the monomer-rich phase it will polymerize rapidly and probably reach a state where it "precipitates" as a "primary particle," say consisting of a coiled radical at a degree of polymerization which is about 25. It is a question of terminology whether we will call this coiled radical consisting of one molecule a precipitated primary particle or still consider it a dissolved radical. In the treatment of Talamini we still consider this as being a dissolved radical belonging to the monomer-rich phase. This primary radical may terminate in the monomer phase by flocculation of two primary radicals. This will take place with a rate given by $16\pi Dr[R_{prim}]^2 N_A$. The constant $16\pi DrN_A$ is of the same order of magnitude as the bimolecular termination constant which is denoted k_{tL}. Therefore, formally it makes no difference in the model of Talamini whether the termination in the monomer phase takes place between really dissolved radicals or primary "precipitated" radicals. The important point in Talamini's model is that there is no interchange of radicals between the two phases. Radicals are formed in the monomer phase and terminate there, either as dissolved radicals or as precipitated radicals. In the latter case they will be absorbed in the polymer-rich phase only as dead particles. In the same way, radicals are formed in the polymer-rich phase and terminate there. No desorption of radicals from the polymer-rich phase is taken into account.

If we accept that this is the case and furthermore that the distribution coefficient for the initiator between the monomer-rich and polymer-rich phases is unity, we have:

$$dR_L\cdot/dt = (\rho_i V_L/V_t) - 2k_{tL}[R\cdot]_L^{\,2} V_L = 0 \tag{14}$$

$$dR_p\cdot/dt = (\rho_i V_p/V_t - 2k_{tp}[R\cdot]_L^{\,2} V_p = 0 \tag{15}$$

$$[R\cdot]_L = (k_i[I]/k_{tL})^{1/2} \tag{16}$$

$$[R\cdot]_p = (k_i[I]/k_{tp})^{1/2} \tag{17}$$

$$[R\cdot]_p = (k_{tL}/k_{tp})^{1/2}\ [R\cdot]_L = Q[R\cdot]_L \tag{18}$$

$$\text{Rate} = -\ dM/dt = k_p(k_i[I]/k_{tL})^{1/2}(M_L + QM_p)$$

In conversion

$$\text{Rate} = dC/dt = (k_i[I]/k_{tL})^{1/2}\ k_p(1 - C - AC + QAC) \tag{19}$$

where A is the weight ratio of monomer to polymer in the particles. Equation (19) may also be written as

$$dC/dt = k_i[I]^{1/2}\ k_p\ \{[(1 - C - AC)/k_{tL}^{\ 1/2}] + (AC/k_{tp}^{\ 1/2})\} \tag{20}$$

Talamini finds that with a value of Q ~ 15, Eq. (20) describes very well a series of results of bulk and suspension polymerization with a number of initiators. In our opinion, some points in this model are open to doubt. The main point is that there should be no interchange of radicals between the monomer phase and particles. As stated, the model is formally correct, even if one accepts that the termination in the monomer-rich phase takes place chiefly by flocculation of two precipitated radicals which are absorbed by the particles only as dead particles. From consideration of flocculation kinetics, it is highly improbable that when after a short time a relatively large number of particles are formed, the primary precipitated radicals should solely flocculate with each other. More probably, after a short time the radicals formed in the monomer-rich phase will be absorbed by the already formed particles, either as soluble radicals or as "precipitated" radicals. Also we should, in our opinion, take into account the desorption of radicals from the particles which at low conversion may be expected to play a role in the distribution of radicals between the two phases.

Ugelstad [9] suggested a model where the interchange of radicals play a dominant role at low conversion. The steady-state equations (21) and (22) were applied.

$$\rho_{iL} - k_a[R\cdot]_L + k_d[R\cdot]_p - 2k_{tL}[R\cdot]_L^2 V_L = 0 \tag{21}$$

$$\rho_{ip} + k_a[R\cdot]_L - k_d[R\cdot]_p - 2k_{tp}[R\cdot]_p^2 V_p = 0 \tag{22}$$

With the terms $k_a[R\cdot]_L$ and $k_d[R\cdot]_p$ dominating, we get approximately:

$$[R\cdot]_p/[R\cdot]_L = k_a/k_d = Q \tag{23}$$

Note that Q also in this case is equal to $[R\cdot]_p/[R\cdot]_L$, as was the case discussed by Talamini. However, this ratio is now given by k_a/k_d, while by Talamini it was given by $(k_{tL}/k_{tp})^{1/2}$. Inserting Eq. (23) in Eqs. (21) and (22) gives:

$$[R\cdot]_L = [k_i I/(V_L k_{tL} + Q^2 V_p k_{tp})]^{1/2} \tag{24}$$

$$[R\cdot]_p = [k_i I/(V_L k_{tL} + Q^2 V_p k_{tp})]^{1/2}\, Q \tag{25}$$

Note that I is the total number of moles of initiator. Accordingly, for the rate

$$-\,dM/dt = [k_i I/(V_L k_{tL} + Q^2 V_p k_{tp})]^{1/2} k_p(M_L + QM_p) \tag{26}$$

In conversion C:

$$dC/dt = [k_i I/(V_L k_{tL} + Q^2 V_p k_{tp})]^{1/2} k_p(1 - C - AC + QAC) \qquad (27)$$

Expressing V_L and V_p by V_0 yields:

$$dC/dt = \{k_i[I]_0/[(1 - 1.47C)k_{tL} + 1.07Ck_{tp}Q^2]\}^{1/2}$$

$$k_p(1 - 1.47C + 0.47CQ) \qquad (28)$$

Again it should be stressed that it is formally of no importance whether k_{tL} represents a termination between soluble radicals in the monomer-rich phase or a flocculation with rapid termination between two precipitated radicals in the monomer-rich phase. In the discussion of this equation we accepted a value of 5×10^9 dm^3/mole-sec for k_{tL} and a value of k_{tp} based upon results of emulsion polymerization of 10^8. The value of Q which gave the best fit to the experimental curves was found to be ~200, but the fit was rather insensitive to the value of Q if we increased it beyond this value. Especially it should be noted that if we decrease the value of k_{tL} somewhat, which might be anticipated if it should represent the case of termination between two precipitated radicals, a higher value of Q should be used. The important point is that even at low conversion the termination takes place mainly in the polymer particles; at 5% conversion 98% of the total termination and 84% of the conversion takes place in the particles. The contribution of these reactions in the particles would be even higher if the value of Q is higher, which as stated above may be the case. This last model explains the fact that precipitation leads to a decrease in rate which has been experienced in experiments with precipitative solvents. Moreover it may explain the effect of addition of CBr_4. Addition of CBr_4 leads to a decrease in the ratio k_a/k_d, that is of Q, and it is easily seen that at low conversion this would lead to an increase in the rate.

$$dC/dt = \{k_i[I]_0/(k_{tL} + 1.07\, CQ^2 k_{tp})\}^{1/2} k_p \qquad (29)$$

Also this model explains why the addition of CBr_4 leads to that the autoacceleration disappears.

From Eq. (28) it furthermore follows that with Q = 200 and the given value of k_{tL}, beyond 10% conversion we will have:

$$dC/dt = (k_i[I]_0/k_{tp})^{1/2}\ 0.45\, k_p\, C^{1/2} \tag{30}$$

From the slope of the curve we can accordingly get the value of k_{tp}. The calculated value of k_{tp} from bulk experiments is $\sim 10^8$ dm^3/mole-sec at 50°C, in very good agreement with the value obtained from emulsion polymerization which is discussed later on.

It has recently been argued by Abdel-Alim and Hamielec [10], who apply the Talamini model, that it is very unlikely that there will be any interchange of radicals between the two phases. That there should be an absorption of radicals from the monomer-rich phase either as soluble radicals or as precipitated radicals is, from what is said above, very likely to be the case. Their argument must be based upon the fact that they do not accept the occurrence of any desorption of radicals from the polymer-rich phase. From a calculation they mean to prove that in the very start, the term involving desorption may be of the same order as the termination term, while at higher conversion, when the porosity decreases, the term involving desorption disappears. We would like to make two comments to this statement. In the calculation of the desorption term, Abdel-Alim and Hamielec apply an effective diffusion coefficient for desorption of radicals from the particles of 10^{-12} dm^2/sec, which is cited as taken from our papers. Now this is the value estimated for emulsion polymerization. For emulsion polymerization we showed that the value of k_d given by expressing the rate of desorption of radicals from particles containing n radical is given by $k_d N_n n$ as:

$$k_d = (k_{fm}/k_p')k_{dm} = (k_{fm}/k_p')[3D_L D_p/(aD_p + D_w)r^2] \tag{31}$$

The value k_{dC} applied in the present treatment is given by $k_{dC} = k_d Nv$. If, as assumed in emulsion polymerization where the outer phase is water, only monomer radicals can desorb, we get:

$$k_{dC} = (k_{fm}/k_p')4\pi Nr[D_p D_L/(aD_p + D_L)] \tag{32}$$

where k_{fm} is the transfer constant to monomer, k_p' the reaction constant for reaction between a monomer radical and a monomer (which may be different from the value of k_p), D_p is the diffusion coefficient in the particles, D_L is the diffusion coefficient in the water phase, and a is the distribution coefficient for monomer radicals between the particles and the outer phase. For the effective diffusion constant

$$D = (k_{fm}/k_p' [D_p D_L/aD_p + D_L)] \tag{33}$$

we found a value of $\sim 10^{-12}$ dm^2/sec, but that was in the case of emulsion polymerization, where the volume of a is very high ($\sim$35) and where most probably only monomer radicals may desorb.

In the case of bulk polymerization, not only do we expect a value of a below unity, but we also have to take into account that radicals larger than the monomer radicals may desorb. It is therefore probable that in the bulk phase the value of D should be about two magnitudes of order higher than was found for emulsion polymerization, i.e., $D > 10^{-10}$ dm^2/sec. In that case, the desorption of radicals from the particles most certainly will play a dominant role in the start of the reaction. It is true, as stated by Hamielec, that the contribution of this term will decrease with increasing conversion with increasing agglomeration of particles, but this is of minor importance. We see from the expression that already at 5% conversion the term Q no longer has any influence. The model states that already at low conversion everything happens within the particles, and the rate is given by Eq. (30). Even if, as is probably the case, the value of Q changes, probable increases beyond a relative low conversion do not affect the model. The important point is that we have to take into account desorption of radicals at low conversion.

It is seen that Eq. (28) predicts that the initial rate will be given by

$$dC/dt = k_p(k_i[I]_0/k_{tL})^{1/2} \tag{34}$$

It may well be that k_{tL} should be replaced by the flocculation constant for precipitated radicals. Also, this reaction will be second-order, and the initial rate expression, half-order with respect to the initiator, will hold also in this case.

Quite recently, Olaj [11] presented a model for bulk polymerization in which he definitely takes into account the formation of precipitated primary radicals. Radicals are formed in both phases. Radicals formed in the monomer-rich phase will add monomer and form precipitated radicals before any noticeable termination takes place. At the start, these precipitated radicals will flocculate to form particles. However, Olaj considers only the case where so many particles have been formed that the precipitated radical will absorb preferentially in these already formed particles. Thus he neglects termination of soluble radicals, which is possibly correct; also he neglects termination by flocculation of precipitated radicals with themselves, which is obviously doubtful in the start of the reaction. Thus Olaj applies the following steady-state equations:

$$dR_{pr}/dt = \rho_{iL} - k_a R_{pr}\cdot = 0 \qquad (35)$$

$$dR\cdot/dt = \rho_{ip} + k_a R_{pr}\cdot - k_{tp}[R_p\cdot]^2 V_p = 0 \qquad (36)$$

and arrives at a rate expression which is the sum of the reaction of primary radicals precipitated in the monomer-rich phase and the radicals in the polymer-rich phase:

$$\frac{dC}{dt} = \frac{2k_i[I]}{k_a} k_p(\phi_M - rC\frac{\phi_M}{\phi_p}) + k_p\left(\frac{k_i[I]}{k_t} rC\frac{\phi_M{}^2}{\phi_p}\right)^{1/2} \qquad (37)$$

where ϕ_M and ϕ_p are the volume fractions of monomer and polymer respectively in the polymer rich phase, and r is the ratio between the density of monomer and polymer.

Olaj concludes that even at low conversion the last term will be the dominant one. This term is the same as the expression which results from the one derived by Ugelstad et al. from low conversions on. It is possible that Eq. (37) correctly describes the situation from the conversion on when the first term becomes insignificant. It is also probably correct that the growing radical will precipitate as a primary particle before any termination takes place. However, at very low conversions when the first term will be significant, it may be doubted if the Eq. (37) describes the situation. At low conversion, desorption of radicals from the particles should be taken into account. Moreover, even if termination of soluble radicals between each other may be neglected, the primary precipitated particles will initially begin to flocculate with each other, a process which is second-order with respect to the precipitated radicals. We believe that our model, which gives the rate at very low conversion as

$$dC/dt = k_p(k_i[I]_0/k_{tL})^{1/2}$$

may be more correct; possibly it is improved if k_{tL} is replaced by the rate constant for flocculation of primary precipitated radicals with each other.

A complete treatment of the situation at low conversion is obviously very complicated. One has to take into account flocculation of primary precipitated radicals with each other to form dead particles consisting of two primary particles. This will be important in the start. As these dead particles become sufficiently high in number, flocculation of primary precipitated radicals with these will take part to form a living particle consisting of three primary particles and so on. The particles built up of several primary particles will themselves flocculate with each other and so on. Only the first reaction which involves flocculation of two primary precipitated radicals will be second-order, and further on the rate constant for flocculation will vary depending upon the size. It may possibly not be possible to reach a correct description of the kinetics at the very start, including the flocculation kinetics, except by a nonsteady-state treatment.

EMULSION POLYMERIZATION

Important contributions to the kinetics of emulsion polymerization of vinyl chloride have recently come from Peggion and Talamini [12] and Stannett et al. [13]. A model which recently has been cited stems from the present author [14-16]. The important point in emulsion polymerization is that the average number of radicals in the particles is much lower than 0.5 and decreases with increasing particle number. The value of $\bar{n}$ varies in the range 10^{-3} to 10^{-1}. The order with respect to particles is very low: it increases from ~0 to a maximum of ~ 1/6. The rate increases from the start with increasing conversion; the order is $\frac{1}{2}$ with low particle number and decreases with increasing number to 1/3.

The model derived by Ugelstad and co-workers was based upon the assumption that the reason for the low value of $\bar{n}$ was that monomer radicals formed by chain transfer to monomer might desorb from the particles and again reabsorb into other particles. This increases the chance of termination and explains the low value of $\bar{n}$. The model was derived by taking into account particles without radicals, with one monomer radical, with one polymer radical, with one polymer and one monomer radical, and with two polymer radicals, and writing steady-state equations for those particles and for the total number of radicals in the system.

$$dN_m/dt = \rho_A(N_0/N) + k_{fm}N_p[M]_p - k_p{}'N_m[M]_p - k_dN_m = 0 \quad (38)$$

$$dN_p/dt = -\rho_A(N_p/N) - k_{fm}N_p[M]_p + k_p{}'N_m[M]_p + k_dN_{pm} = 0 \quad (39)$$

$$dN_{pm}/dt = \rho_A(N_p/N) + 2k_{fm}N_{2p}[M]_p - k_{dm}N_{pm}$$

$$- (k_t{}'^*/v)N_{pm} = 0 \quad (40)$$

$$dN_{2p}/dt = k_p{}'\,N_{pm}[M]_p - 2k_fN_{2p}[M]_p - (2k_t{}^*/v)N_{2p} = 0 \quad (41)$$

$$\rho^w = (2k_t{}'^*/v)N_{pm} + (4k_t{}^*/v)N_{2p} \quad (42)$$

ρ_A is the rate of absorption of radicals, ρ^w rate of radical production, $k_p{}'$ the rate constant for reaction between a monomer radical and a monomer, $k_t{}^*$ is the termination constant for reaction between two polymer radicals, $k_t{}'^*$ for reaction between a polymer and a monomer radical (dm³/molecules-sec). The above equation led to that in case termination between polymer radicals were dominating, the rate was given by:

$$-\frac{dM}{dt} = \frac{k_p[M]_p\rho^{w\frac{1}{2}}}{N_A}\left[\frac{V_p}{2k_t{}^*} + \frac{N}{2k_f[M]_pk_{dm}/(k_p{}'[M]_p + k_{dm})}\right]^{\frac{1}{2}} \quad (43)$$

with termination between polymer and monomer radicals dominating

$$-\frac{dM}{dt} = \frac{k_p[M]_p\rho^{w\frac{1}{2}}}{N_A}\left[\frac{V_p}{2k_t{}'^*(k_{fm}/k_p{}')} + \frac{N}{2k_{dm}(k_{fm}/k_p{}')}\right] \quad (44)$$

In this derivation it was assumed that the desorbed monomer radical was reabsorbed without adding any monomer in the aqueous phase. If one assumed that the latter is the case, the equation for termination between polymer radicals dominating is the same, while the latter changes to

$$-\frac{dM}{dt} = \frac{k_p[M]_p}{N_A}\rho^{w\frac{1}{2}}\left\{\frac{V_p(k_p'[M]_p + k_{dm})}{2k_t'^*k_{fm}[M]_p} + \frac{N(k_p'[M]_p + k_{dm})}{2k_{dm}k_{fm}[M]_p}\right\}^{\frac{1}{2}} \tag{45}$$

With low particle number, termination between polymer radicals will be favored, and probably $k_p'[M]_p > k_{dm}$. At high particle number the chance that the monomer radical will be reabsorbed without addition of any monomer in the aqueous phase increases. Therefore the expression

$$-\frac{dM}{dt} = \frac{k_p[M]_p}{N_A}\rho^{w\frac{1}{2}}\left(\frac{V_p}{2k_T} + \frac{N}{2k_{dm}k_{fm}/k_p'}\right)^{\frac{1}{2}} \tag{46}$$

where k_T stands for the termination term, was found to be reasonable and in fact describes the kinetics very well.

In the further description of the process we showed, in accordance with Nomura [17], that the value of k_{dm} should be given by

$$k_{dm} = 3D_wD_p/(aD_p + D_w)r^2$$

which, inserted in Eq. (46) gives the final expression

$$-\,dM/dt = (k_p[M]_p/N_A)\rho^{w\frac{1}{2}}\left[(V_p/k_T) + (N^{1/3}V_p^{2/3}/k_d')\right]^{\frac{1}{2}} \tag{47}$$

where k_d' is a constant.

Nomura et al. [17] and Friis and Hamielec [18] found that a similar expression could be applied for vinyl acetate.

There is one important point we have repeatedly stressed, but which apparently has often been overlooked. The value of k_p' defined above is not necessarily the same at k_p. As discussed above, it may be considerably lower, and evidence of this is indeed indicated from emulsion polymerization.

Friis and Hamielec [18] used Eq. (47) for the discussion of the polymerization of vinyl acetate and vinyl chloride. They pointed out that at the same conversion the value of k_d' was ~ 120 times higher for vinyl chloride than for vinyl acetate. It seems to the author that this is a miscalculation, the factor is in fact 3-4 times higher, about 400. If we accept that the value of k_p' was the same as k_p for both vinyl chloride and vinyl acetate, we should find a ratio of k_d' between vinyl chloride and vinyl acetate of about 6. So apparently the ratio k_{fm}/k_p' is higher for vinyl chloride than for vinyl acetate. If we accept that for vinyl acetate $k_p' = k_p$, for vinyl chloride the value of k_p' would be ~ 1/70 of that of k_p. No quantitative derivation of the ratio k_{fm}/k_p' can be derived, as we do not know the ratio k_{fm}/k_p' for vinyl acetate, but the results strongly indicate nevertheless that k_p' is considerably lower than k_p for vinyl chloride.

PARTICLE FORMATION

It has been a tendency in the recent literature to abandon the theory of Smith-Ewart which involves particle formation by absorption of radicals from the aqueous phase into the micelles. This is especially so for more water-soluble monomers, of which VC is an example. Nucleation takes place outside the micelles, and the role of the emulsifier is only to stabilize the primary particles formed. Also for more water-insoluble monomers like styrene, such a nucleation process has been suggested. Even if the micelles act as a center for nucleation, Nomura et al. [19] found that the absorption efficiency of micelles should be taken to be much smaller than for the polymer particles.

The theory which has been much applied recently is the theory of Fitch and co-workers [20], which was developed on the basis of experiments with methyl methacrylate and claimed to describe the particle formation in this case. Fitch proceeds as follows. It is assumed that a radical formed in the aqueous phase will form a particle if it reaches a threshold degree of polymerization j before it is captured by an existing particle. The time to grow to this size is $t_j = j/k_p[M]_w$, which is also said to be the time elapsing before the first particle is formed. The average distance the oligomer can diffuse in this time is

$$L = (2t_jD)^{1/2}$$

$$= (2jD/k_p[M]_p)^{1/2} \quad (48)$$

where D is the mean diffusion coefficient. Fitch et al. derived for the rate of capture of oligomers which have travelled less than the critical distance L by a single particle of radius r the relation:

$$\rho_C = \pi r^2 L \rho_i \quad (49)$$

For N particles, then,

$$\rho_C = \pi r^2 L \rho_i N \quad (50)$$

The rate of nucleation is accordingly

$$dN/dt = \rho_i - \rho_C$$

$$= \rho_i(1 - \pi r^2 LN) \quad (51)$$

Substituting for r, this yields

$$dN/dt = \rho_i[1 - L(\pi N)^{1/3} (3V/4)^{2/3}] \quad (52)$$

For V which increases with time, Fitch found:

$$V = (k_p\bar{v}[M]/k_t) \ln[\cosh (\rho_i/k_t)^{1/2} t] \quad (53)$$

which, when inserted in Eq. (52) gives the particle number as a function of time by numerical integration. It increases at first rapidly, but then levels out. Fitch et al. claim a good correlation between the theory and number of particles formed with methyl methacrylate, although they have to accept a low efficiency for the initiator.

The time for formation of the first particle is not, as stated by Fitch, given by $j/k_p[M]$. This is the average time for getting a degree of polymerization of j. Some of the radicals will have a much shorter residence time. The point is that the rate of formation of a radical R_n from R_{n-1} is given by $1/k_p[M][R_{n-1}]$, which is much lower than $1/k_p[M]$ when R_{n-1} is high. The important criticism of the Fitch theory, which is discussed by Barrett [21], is that Fitch sets the rate of capture to be given by $\rho_C = \pi r^2 L \rho_i N$. The basic assumption in deriving this equation, namely, that the probability of an oligomer colliding with a particle is given by the fractional solid angle subtended at its point of origin, is really equivalent to saying that the oligomer travels in straight lines like rays of light. This greatly underestimates the probability of collision, because many oligomers which by this assumption are not captured because they move in other directions will in fact have passed through the region occupied by the particles at some time or other.

A treatment similar to the one given by Fitch was also suggested by Gardon. If the particles act as a sink for the oligomers, i.e., there is irreversible absorption, the rate of capture of an oligomer R_j would be given by $\rho_{Aj} = 4\pi D_{wj} Nr[R_j]$; this means that the rate of capture should be proportional to the radius of the particle, not to the surface. In this connection it should be noted that in seed experiments with varying Nr_s, Fitch for methyl methacrylate and Gatta and Talamini for vinyl chloride [23], found that the stop of nucleation of new particles was determined by $N_s r_s$, i.e., corresponding to that derived from ordinary diffusion theory for irreversible absorption.

Barrett derived an expression for the rate of nucleation of particles which was later somewhat extended by Hansen and Ugelstad [24, 25]. If we write for all radicals up to $j_{cr} - 1$ steady-state equations:

$$dR_j = k_p R_{j-1}[M] - k_p R_j[M] - k_{Cj} N R_j = 0 \tag{54}$$

and moreover if formation of particles is assumed equal to the rate of formation of R_{jer} radicals, we get:

$$\frac{dN}{dt} = \frac{dR_{jcr}}{dt} = \frac{\rho_i}{\prod_{1}^{jcr-1} 1 + (k_{Cj} N/k_p[M]) + (k_{tw}{*}[R\cdot]^2/k_p[M])} \tag{55}$$

The problem is that if we accept that $k_{Cj} = 4\pi D_j r$, we find that the number of particles formed is much too low compared to the experimental results. A possible explanation was recently given by Hansen and Ugelstad, where they took into account the reversibility of the absorption. As pointed out by Napper and Alexander [26], by Nomura and Harada and by Barrett, it is not probable that small oligomer radicals will be irreversibly absorbed in the micelles, not even in small particles.

Applying the theory of Dankwerts [27] for absorption with reaction, Hansen and Ugelstad derived that the rate of absorption should be given by:

$$\rho_{Aj} = 4\pi rND_{wj}[R_j]_w \frac{a_j D_{pj}(X_j \coth X_j - 1)}{D_{wj} + W_j a_j D_{pj}(X_j \coth X_j - 1)} \tag{56}$$

where

$$X_j = r(k/D_{pj})^{\frac{1}{2}} \tag{57}$$

D_{pj} and D_{wj} are the diffusion coefficients in particles and micelles of radicals with chain length R_j, a_j is the equilibrium distribution coefficient for the radical between particles/micelles and water, W_j is the electrostatic repulsion factor, and k is the first-order rate constant for the disappearance of radicals in the particles/micelles. The value of k in a micelle and in a particle which does not contain a radical is:

$$k = k_p[M]_p \tag{58}$$

and in a particle containing a radical is:

$$k = k_p[M]_p + k_t^*/v \tag{59}$$

[The radical with a chain length of j is by reaction transformed into a radical with a chain length j + 1, which may of course also desorb from a particle. This is taken into account in the numerical treatment of Eq. (56).] The capture constant k_{Cj} is in accordance with Eq. (56), given by:

$$k_{Cj} = 4\pi r D_j [R_j] U_j / W_j \tag{60}$$

where U_j is the reversibility factor and W_j is the electrostatic repulsion factor.

$$U_j = \frac{W_j a_j D_{pj}(X_j \coth X_j - 1)}{D_{wj} + W_j a_j D_{pj}(X_j \coth X_j - 1)} \tag{61}$$

A complete discussion of Eq. (61) is given by Hansen and Ugelstad in a recent paper. At low values of a, k, and r, the rate of absorption * will be given by:

$$\rho_{A_j} = V_p k a_j [R\cdot_j]_w \tag{62}$$

i.e., we have an equilibrium distribution with a very low rate of absorption. For micelles this will be the case even for relatively large oligomers. At higher values of a_j, k, and r we will get:

$$\rho_{Aj} = A_p (D_{pj} k)^{1/2} a_j [R\cdot_j]_w \tag{63}$$

i.e., the rate of absorption is higher and proportional to the total surface of the particles. Finally, at sufficient high values:

$$\rho_{Aj} = 4\pi N r D_{wj} [R\cdot_j]_w / W_j \tag{64}$$

which indicates an irreversible absorption.

This is the case for particles containing a radical where k is large, and also for relatively large particles when r is large. This theory explains the fact that in seed-experiments the new formation of radicals is dependent upon $N_s r_s$. Furthermore it explains the recent results given by Ugelstad et al. [16] on competitive growth where it was shown that the rate of absorption was proportional to Nr. Also, if we take into account the reversibility factor we find that the number of particles formed increases markedly from what is found based upon irreversible absorption.

Note that we do not say a priori that micelles do not absorb radicals; they do, but at a much slower rate than do larger particles and particles containing a radical. This new theory has been shown to give a good description of particle formation in the case of styrene, both with and without emulsifier. It has not yet been worked out in detail for vinyl chloride. A complicating factor arises here, namely, the desorption of monomer radicals formed by chain transfer. We hope to present a model in which this is taken into account within soon.

That the micelles should be of no importance for relatively water-soluble monomers has been questioned. Quite recently Nomura et al. [19] developed a model for particle formation for monomers with a high tendency to chain transfer, where they assumed that particles were formed by radical absorption in the micelles, but where they took into account that the effectivity of absorption of radicals into the micelles was much less because of the reversible absorption, than in the particles. They also took into account the effect of desorption of monomer radicals from the particles.

For initiator and monomer radicals in the water phase, we have for R*:

$$dR^*/dt = \rho_i + k_d N_1 + 2k_d N_2 - k_{a_s} m_s R^* - k_{a_p} N_T R^* \tag{65}$$

Applying a steady-state method to R* yields

$$R^* = (\rho_i + k_d N_1 + 2k_d N_2)/(k_{a_s} m_s + k_{a_p} N_T) \tag{66}$$

Introducing ϵ:

$$\epsilon = (k_{a_p}/k_{a_s}) M_m \tag{67}$$

where M_m is the aggregation number of micelles and S_m the number of emulsifier molecules forming micelles per unit volume of water, we obtain

$$\begin{aligned} dN_T/dt &= k_{a_s} m_s R^* \\ &= (\rho_i + k_d N_1 + 2k_d N_2)/(1 + \epsilon N_T/S_m) \end{aligned} \tag{68}$$

Equations for dN_1/dt and dN_2/dt were derived as shown above, only the expression for dN_1/dt in the region of particle formation contains a term $+ k a_s m_s R^*$. Numerical solution of the equations gives the following relationship:

$$N_T \propto S_0^{0.94} I_0^{0.04} \tag{69}$$

This equation is claimed to predict the number of particles well for the case of vinyl acetate at emulsifier concentrations higher than the critical micelle concentration. The similarity between vinyl acetate and vinyl chloride might mean that the derivation is valid also for vinyl chloride. It has been found that the order with respect to emulsifier for vinyl chloride is ~1 at sufficient high emulsifier concentrations beyond the critical micelle concentration. Below the critical micelle concentration the theory does not fit the experimental results, probably because of homogeneous nucleation.

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