

KINETICS AND MECHANISM OF VINYL CHLORIDE POLYMERIZATION

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CONTENTS

ABSTRACT

INTRODUCTION

1. CHAIN TRANSFER REACTION IN VINYL CHLORIDE POLYMERIZATION
 2. BULK AND SUSPENSION POLYMERIZATION
 - 2.1. Particle formation
 - 2.2. Kinetics of polymerization
 3. ORDINARY EMULSION POLYMERIZATION
 - 3.1. Particle formation
 - 3.1.1. Below CMC
 - 3.1.2. Above CMC
 - 3.2. Kinetics and mechanism
 - 3.3. Seed polymerization
 4. EMULSION POLYMERIZATION WITH INITIATION IN MONOMER DROPLETS. THERMODYNAMIC TREATMENT OF FORMATION AND STABILITY
 - 4.1. Polymerization of monomer emulsions formed by the diffusion process
 - 4.2. Polymerization of monomer emulsions formed by "spontaneous" emulsification with mixed emulsifier systems
 5. POLYMERIZATION AT SUB-SATURATION PRESSURES
- LIST OF SYMBOLS
- REFERENCES

Abstract - Kinetic models for formation of CH_2Cl branch units based on head to head addition and the first order interruption of the growing chain with formation of $\text{Cl}\cdot$ and $\text{H}\cdot$ radicals are discussed. Some features of the formation and stabilization of primary particles in bulk and suspension polymerization are reviewed. Different kinetic models for bulk and suspension polymerization are critically reviewed.

Particle formation in emulsion polymerization below and above CMC is treated, due consideration being given to the desorption and reabsorption of radicals.

The kinetics of emulsion polymerization is discussed in detail. Desorption and reabsorption of radicals are discussed as well as the possibility of termination in the aqueous phase. Steady and non steady state treatments in seed polymerization are discussed. Thermodynamic principles for the formation and stability of monomer emulsions are treated. Initiation in monomer droplets with direct formation of latex particles in the 0.2-1.5 μm range as well as monodisperse particles in the 2-5 μm range are described. Spontaneous emulsification with formation of relatively stable monomer emulsions with different mixed emulsifier systems and subsequent polymerization with initiation in the monomer droplets is discussed.

Polymerization under conditions corresponding to sub-saturation pressures can be achieved by addition of a low molecular weight, water insoluble compound to the monomer phase.

INTRODUCTION

The intention of the present paper is to review critically some of the more recent investigations which have been published on the kinetics and mechanism of vinyl chloride polymerization. Some earlier papers which have not previously been subject to a critical examination are also included. Recent methods and results of measurements of PVC structure have shed new light on a number of experimental results which have previously not been clearly understood or even misinterpreted.

Important contribution to new understanding of the kinetics and mechanism of vinyl chloride polymerization have come from the recognition of the dominating role of short chain branches, i.e. CH_2Cl groups in the PVC and that these groups probably stem from a head to head addition (1). The concept of head to head addition has also founded the basis for a new mechanism for the interruption of the polymer chain with a simultaneous formation of a small radical. This reaction was formerly ascribed to a normal chain transfer to monomer with the polymer radical acting as the acceptor of a chlorine or hydrogen atom given off by the monomer, transferring the monomer to a radical.

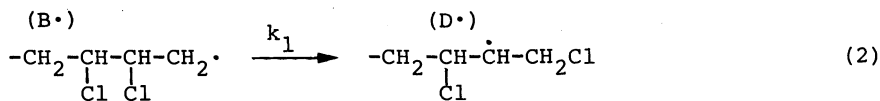
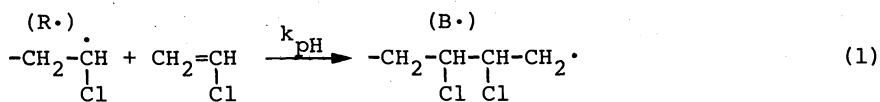
The present paper discusses the new explanation of "chain transfer to monomer" which involves head to head addition followed by a splitting off of Cl. or H. radicals and shows that this mechanism may be more in accordance with some of the previously published results on the kinetics of vinyl chloride polymerization.

The paper further deals with the mechanism and kinetics of particle formation in bulk, suspension, micro suspension and emulsion polymerization. In all cases the main features of the PVC, namely the insolubility of polymer in the monomer, the limited swelling of polymer by monomer and the interruption of the growing chain by a first order reaction with respect to the radical with a simultaneous formation of small active radicals play an important role in the processes and is responsible for the fact that in the case of VC there are so many similarities in the kinetics and mechanism of the different polymerization processes.

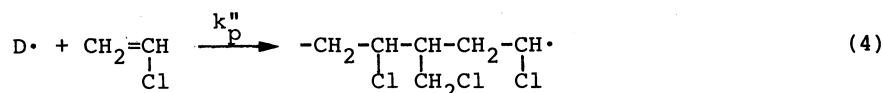
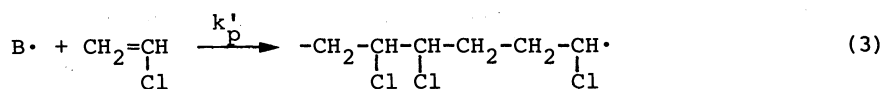
1. CHAIN TRANSFER REACTIONS IN VINYL CHLORIDE POLYMERIZATION

In the discussion of the mechanism of vinyl chloride polymerization it has generally been accepted that the main interruption reaction of the growing polymer chain is first order with respect to the growing chain. This was supposed to result from a chain transfer to monomer, the monomer acting as donator. While Ayrey *et al.* (2) considered only abstraction of a chlorine atom, Breitenbach *et al.* (3) took into consideration all three types of radicals which could result from the transfer reactions, resulting in the radicals $\cdot\text{CH}=\text{CHCl}$, $\text{CH}_2=\dot{\text{C}}\text{Cl}$ or $\text{CH}_2=\text{CH}\cdot$. Although it is recognised that the growing radical in VC polymerization, $-\text{CH}_2-\text{CHCl}$ is highly active and readily transfers to a number of substances, it has been questioned whether the reaction of polymer radicals with monomer creating the very reactive monomer radicals shown above, would be energetically feasible. Moreover NMR studies of PVC have not revealed any unsaturated end groups of the type $\text{CH}_2=\text{CCl}-\text{CH}_2-$, $-\text{CHCl}-$, $\text{CHCl}=\text{CH}-\text{CH}_2-\text{CHCl}-$, $\text{CHCl}=\text{CH}-\text{CHCl}-\text{CH}_2-$, or $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CHCl}-$ which would result from chains started from the radicals given above. The more recent assumption on the nature of the first order chain interruption stems from the recognition of the importance of the head to head addition in the radical polymerization of VC. The head to head addition was originally suggested by Rigo *et al.* (1) as an explanation of the presence of a relatively large number of CH_2Cl groups in PVC. Rigo and other authors did not originally combine this reaction with any polymer chain interruption process.

The scheme suggested by Rigo went as follows:

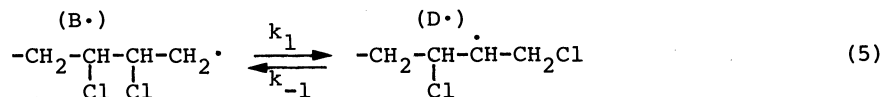


The radicals B· and D· may add monomer and continue the polymerization:



The experimental determination of CH₂Cl groups was carried out by reduction with LiAlH₄ followed by IR measurements of the -CH₃ content. The reorganization of radical B· into D· was found probable from an energetic point of view.

Rigo estimated that the value of an equilibrium constant for the reaction:



would be about 110 at 50 °C.

The authors consider the reaction scheme (1-4) together with the "equilibrium" (5) and derive an expression for the ratio of CH₂Cl branch units to the total monomer units in the polymer.

The final expression for the ratio of CH₂Cl groups to total monomer units is:

$$Z = (k_{pH}/k_p) / (1 + k'_p/k''_p K_{eq}) \quad (6)$$

where $K_{eq} = k_1/k_{-1} = [D\cdot]/[B\cdot]$. Introduction of K_{eq} , which necessitates that one has a rapid established equilibrium between [B·] and [D·] radicals, is obviously open to doubt. A necessary condition for this to be the case is that $k_{-1} \gg k''_p[M]$. Equation (6), which would seem to indicate that Z should be independent of conversion, is claimed to be in accordance with experimental evidence.

Quite recently Park et al. (4) have discussed several possible routes (1,5,6) for the formation of CH₂Cl branches and conclude that the kinetic evidence supports the route of reactions (1-4) given by Rigo. Park applies steady state equations for the different species involved, but contrary to Rigo he does not consider the reaction B· → D· to be reversible.

$$d[B\cdot]/dt = k_{pH}[R\cdot][M] - k_1[B\cdot] - k'_p[B\cdot][M] = 0 \quad (7)$$

$$d[D\cdot]/dt = k_1[B\cdot] - k''_p[D\cdot][M] = 0 \quad (8)$$

From (7) and (8) one obtains for the rate of CH₂Cl formation:

$$\begin{aligned} r_{(\text{CH}_2\text{Cl})} &= k''_p[D\cdot][M] = \frac{k_1 k_{pH}[R\cdot][M]}{k_1 + k'_p[M]} \\ &= k_{pH}[R\cdot] / (1/[M] + k'_p/k_1) \end{aligned} \quad (9)$$

The number of chloro methyl groups per monomer unit, Z, is given by:

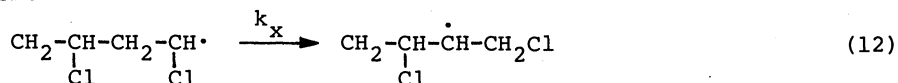
$$Z = r_{\text{CH}_2\text{Cl}}/r_p = (k_{pH}/k_p) / (1 + [M]k'_p/k_1) \quad (10)$$

and accordingly

$$1/Z = k_p/k_{pH} + [M]k'_p k_p / k_1 k_{pH} \quad (11)$$

Park finds that Z is independent of initiator concentration which is in accordance with Eq. (10). Park plotted $1/Z$ as a function of $[M]$. Although there is considerable scatter, the data appear to support the mechanism of Rigo (1). The regression line drawn through the points has an intercept of 75 and a slope of $19 \text{ dm}^3 \text{ mol}^{-1}$. From Eq. (11) these values would give: $k_p/k_{pH} = 75$ and $k'_p/k_1 = 0.25 \text{ dm}^3 \text{ mol}^{-1}$, which means that there should be about one head to head addition for every 75 propagation steps and that in a 4 molar monomer about half of the head to head additions would lead to chloromethyl side chains.

The mechanism suggested by Abbås *et al.* (5) involves a rearrangement by hydrogen transfer of an ordinary polymer radical formed by head to tail addition:



It follows that in this case the value of $1/Z$ would be:

$$1/Z = k_p[M]/k_x \quad (13)$$

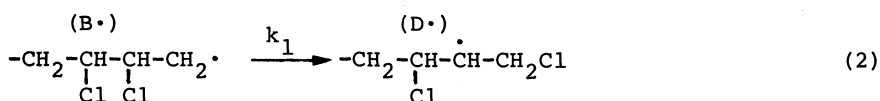
Park's treatment is based upon the assumption that radical $B\cdot$ may rearrange to radical $D\cdot$ and both radicals $B\cdot$ and $D\cdot$ add monomer in the usual polymerization reaction. No other possible reactions of the two radicals like splitting off of $\text{Cl}\cdot$ or $\text{H}\cdot$ radicals with formation of double bonds, are included. Park's assumption of values of k'_p and k_1 which are of the same order of magnitude would involve that there should also be present in the polymer a considerable number of $-\text{CHCl}-\text{CHCl}-$ structures. Detection of such groups by iodometry has been claimed (7), although as stated by Starnes *et al.* (8), this interpretation has not been supported by ^{13}C NMR spectra of numerous PVC samples (5,9,10). Also it is pointed out (8) that rearrangements of similar radicals as $B\cdot$ to structures of $D\cdot$ type are so fast that it would seem to preclude the addition of monomer to the $B\cdot$ radical. Assuming this to be the case the mechanism of Park would lead to:

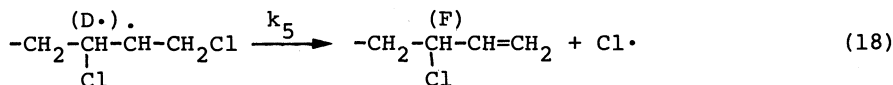
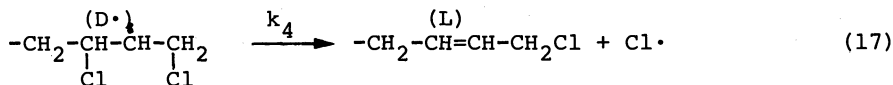
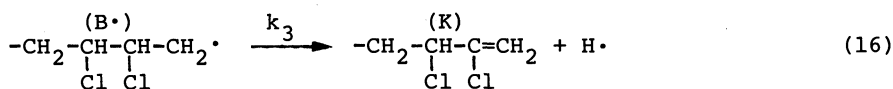
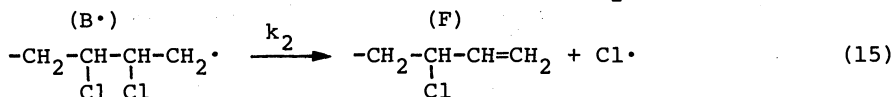
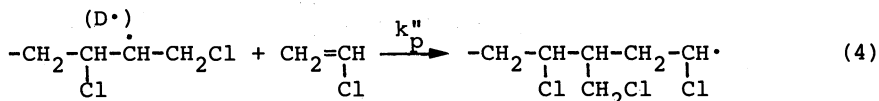
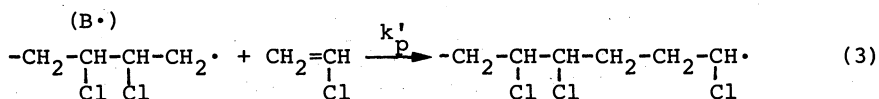
$$1/Z = k_p/k_{pH} \quad (14)$$

i.e. the degree of branching would be independent of the monomer concentration. Lyngås-Jørgensen (11) found 4 to 7×10^{-3} branches per monomer unit independent of conversion, Carrega (12) 4 to 6×10^{-3} branches per unit for the conversion range 0.08 to 0.86, which would indicate that the degree of branching was relatively independent of monomer concentration. It should be pointed out, however, that in bulk polymerization the monomer concentration at the reaction center, the swollen polymer particle, is approximately constant up to 77% conversion. Any noticeable contribution of splitting off of $\text{Cl}\cdot$ and/or $\text{H}\cdot$ radicals from $B\cdot$ and $D\cdot$ radicals would lead to modifications in the equation for $r_{\text{CH}_2\text{Cl}}$ and Z .

A number of papers have applied ^1H and ^{13}C NMR studies in the studies of the structure of PVC, especially for determination and characterization of branches and of double bonds (5,8-10,12-14). In order to be identified by NMR, however, the proposed structures must be present in sufficiently high concentration (above 2%). However, it is known that unsaturated structures in PVC are expected to be present in much lower concentrations. To overcome this the investigations have sometimes been carried out on fractionated samples containing an accumulated amount of low molecular weight material where the fraction of end double bonds necessarily will be higher. Also PFT-NMR techniques have proved to give clearly observable signals of unsaturated structures in PVC.

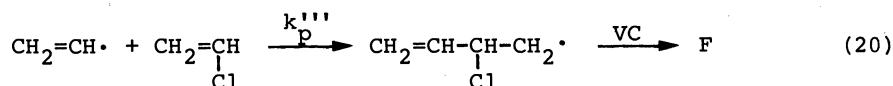
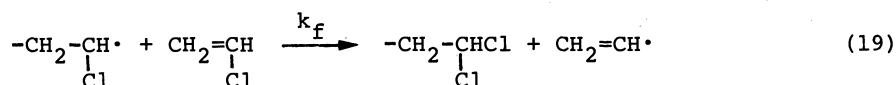
In some papers Caraculacu *et al.* (13,14) have described the determination of structures of different PVC samples. They consider the head to head addition to be the primary step in the scheme leading to the formation of double bonds with splitting off of $\text{Cl}\cdot$ or $\text{H}\cdot$ radicals. They consider the following possible schemes for the reaction of the very reactive radical stemming from a head to head addition:





Caraculacu et al. (13) claim to have provided evidence for structures F and K from PFT-NMR spectra, although they seem to make the reservation that the signals for F may be given by the $^{13}\text{CHCl}$ proton. Also they report the presence of a structure $-\text{CH}_2-\text{CH}=\text{CCl}-\text{CH}_2\text{Cl}$ which may have been formed by rearrangement of structure K. On energetic grounds Caraculacu finds it improbable that any chain transfer by reaction of $\text{R}\cdot$ with monomer will take place, the $\text{R}\cdot$ radical acting as an acceptor with formation of monomer radicals like $\text{CH}_2=\text{CH}\cdot$, $\text{CHCl}=\text{CH}\cdot$ and $\text{CH}_2=\text{CCl}\cdot$. This assumption is supported by the lack of presence of end groups with the structure $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CHCl}\cdot$, $\text{CHCl}=\text{CH}-\text{CH}_2-\text{CHCl}\cdot$ or $\text{CH}_2=\text{CCl}-\text{CH}_2-\text{CHCl}\cdot$.

Apparently Caraculacu does not take into account the possibility that the reaction of the monomer radical may take place through attack on the $-\text{CHCl}$ end of the monomer. For instance, structure F may formally be formed by a mechanism starting out with transfer to monomer according to the scheme:



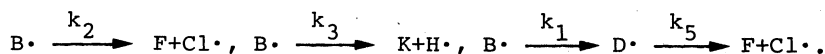
Schwenk et al. (15) investigated bulk PVC extracted with methanol. The molecular weight of the extracted polymer was 1500. They interpreted their results to show that the molecule contained 0.5 units of structure (L) and 0.25 units of the structure $-\text{CHCl}-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ (M). Contrary to the more accepted hypothesis for formation of double bonds accompanied by chain interruption, Schwenk assumes that the structures (L) and (M) result from a head to tail, respectively tail to head structure by rearrangement of ordinary radicals, followed by formation of double bonds by splitting off $\text{Cl}\cdot$, respectively $\text{H}\cdot$ radicals which then initiate new chains.

A comprehensive discussion of the PVC structure has recently been given by Starnes et al. (8). They accept the head to head addition as the primary step and discuss the rates of possible subsequent reactions of this compound by comparison with the rate of model reactions. They expect the reaction $\text{B}\cdot \rightarrow \text{D}\cdot$ to be so fast that it is improbable that there would be any noticeable polymerization of $\text{B}\cdot$ to give $-\text{CH}_2-\text{CHCl}-\text{CHCl}-\text{CH}_2-\text{CHCl}-$ structures in the polymer.

From considerations of the type of chain ends formed in the presence of

cyclohexane, which is an effective chain transfer agent, they conclude that $\text{Cl}\cdot$ radicals is formed by an intramolecular reaction during polymerization and consider this to be the reaction $\text{D}\cdot \rightarrow \text{L}$ given in Eq. (17). Also Starnes *et al.* abandon the previous mechanisms of chain transfer to monomer. Starnes and Caraculacu both consider the head to head addition to be the primary step in the route leading to termination of the chain. While Starnes limits the possibility of chain termination and double bond formation to the

reaction $\text{B}\cdot \xrightarrow{k_1} \text{D}\cdot \xrightarrow{k_4} \text{L} + \text{Cl}\cdot$, Caraculacu in addition includes a series of possible reactions leading to chain termination, i.e.



A complete set of steady state equations in accordance with the possible reactions discussed by Caraculacu would be as follows:

$$\begin{aligned} d[\text{B}\cdot]/dt &= k_{\text{pH}}[\text{R}\cdot][\text{M}] - k_{\text{p}}'[\text{B}\cdot][\text{M}] - k_1[\text{B}\cdot] - k_2[\text{B}\cdot] \\ &- k_3[\text{B}\cdot] = 0 \end{aligned} \quad (21)$$

$$d[\text{D}\cdot]/dt = k_1[\text{B}\cdot] - k_{\text{p}}''[\text{D}\cdot][\text{M}] - k_4[\text{D}\cdot] - k_5[\text{D}\cdot] = 0 \quad (22)$$

From (21) and (22) one obtains:

$$[\text{B}\cdot] = k_{\text{pH}}[\text{R}\cdot][\text{M}] / (k_1 + k_2 + k_3 + k_{\text{p}}'[\text{M}]) \quad (23)$$

$$[\text{D}\cdot] = \frac{k_1 k_{\text{pH}}[\text{R}\cdot][\text{M}]}{(k_1 + k_2 + k_3 + k_{\text{p}}'[\text{M}]) (k_4 + k_5 + k_{\text{p}}''[\text{M}])} \quad (24)$$

$$\text{and } r_{\text{CH}_2\text{Cl}} = \frac{k_{\text{p}}'' k_1 k_{\text{pH}}[\text{R}\cdot][\text{M}]}{(k_1 + k_2 + k_3 + k_{\text{p}}'[\text{M}]) (k_4 + k_5 + k_{\text{p}}''[\text{M}])} \quad (25)$$

In order to arrive at an expression for $r_{\text{CH}_2\text{Cl}}$ and $1/Z$ which is similar in form to the one obtained by Park, the condition

$$k_{\text{p}}''[\text{M}] > k_4 + k_5 \quad (26)$$

should be fulfilled. This leads to

$$r_{\text{CH}_2\text{Cl}} = \frac{k_1 k_{\text{pH}}[\text{R}\cdot][\text{M}]}{k_1 + k_2 + k_3 + k_{\text{p}}'[\text{M}]} \quad (27)$$

$$1/Z = \left(1 + \frac{k_2 + k_3}{k_1}\right) \frac{k_{\text{p}}}{k_{\text{pH}}} + \frac{k_{\text{p}}' k_{\text{p}}[\text{M}]}{k_1 k_{\text{pH}}} \quad (28)$$

The condition (26) may probably be approximately correct in view of the fact that there is a considerably higher number of CH_2Cl groups than there are double bonds in the polymer molecule.

The rate for formation of small radicals ($\text{Cl}\cdot + \text{H}\cdot$) is given by:

$$\begin{aligned} r_{(\text{Cl}\cdot + \text{H}\cdot)} &= (k_2 + k_3)[\text{B}\cdot] + (k_4 + k_5)[\text{D}\cdot] \\ &= \frac{k_{\text{pH}}[\text{R}\cdot][\text{M}]}{k_1 + k_2 + k_3 + k_{\text{p}}'[\text{M}]} \left(k_2 + k_3 + \frac{k_1 (k_4 + k_5)}{k_4 + k_5 + k_{\text{p}}''[\text{M}]} \right) \end{aligned} \quad (29)$$

According to the previous accepted mechanism for chain transfer to monomer, which assumed a reaction between $\text{R}\cdot$ and monomer to give a monomer radical,

the rate of small radicals is given by:

$$r_f = k_f [R\cdot] [M] \quad (30)$$

that is, a first order with respect to monomer concentration, while the new scheme for "chain transfer" (Eq. (29)) would tend to give an order less than unity. A first order reaction with respect to monomer may, however, be obtained from Eq. (29) if certain conditions are fulfilled. Before considering these, it may be convenient to establish some qualitative relations between various rate constants. As the formation of Cl· and H· radicals leads to interruption of the growing chains, one must obviously have that $k_1 > k_2 + k_3$ in order to obtain polymer chains with \bar{X}_n in the range of 1000, containing about 6 CH₂Cl branch units per chain. For the same reasons, $k_p'' [M] > k_4 + k_5$.

Introducing the conditions

$$a) \quad k_1 \gg k_p' [M] \quad \text{and} \quad b) \quad k_2 + k_3 \gg \frac{k_1 (k_4 + k_5)}{k_p'' [M]}$$

Eq. (29) reduces to

$$r_{(Cl\cdot + H\cdot)} = \frac{k_{pH} [R\cdot] [M]}{1 + k_1 / (k_2 + k_3)} \quad (31)$$

i.e. a first order reaction with respect to monomer concentration.

Formally, a first order may also be obtained if the condition $k_p'' [M] \ll k_4 + k_5$ is substituted for condition b) above. This would give the rate expression

$$r_{(Cl\cdot + H\cdot)} = k_{pH} [R\cdot] [M] \quad (32)$$

As discussed above, however, the fact that the number of CH₂Cl groups per molecules is considerably higher than the number of double bonds means that $k_p'' [M] > k_4 + k_5$. Thus the condition leading to Eq. (32) is not realistic.

Another limiting case arises if it is assumed that radical B· immediately isomerizes to give radical D·, other possible reactions of B· being completely negligible. This would seem to be consistent with the views of Starnes et al. (8). In this case one obtains from Eq. (29):

$$r_{(Cl\cdot)} = \frac{k_{pH} [R\cdot] [M]}{1 + k_p'' [M] / (k_4 + k_5)} \quad (33)$$

If now $k_p'' [M] \gg k_4 + k_5$, Eq. (33) reduces to

$$r_{(Cl\cdot)} = k_{pH} (k_4 + k_5) [R\cdot] / k_p'' \quad (34)$$

i.e. the rate of formation of Cl· radicals is independent of monomer concentration. This, however, is contradictory to experimental results which show that the "chain transfer" is approximately proportional to the monomer concentration.*

In conclusion, the experimental chain transfer constant should be determined by Eq. (31), that is

$$k_f = \frac{k_{pH}}{1 + \frac{k_1}{k_2 + k_3}} \quad (35)$$

* Starnes (95) has shown that his scheme may also lead to the conclusion that the rate of "chain transfer" is first order in monomer if the splitting off of Cl (Eq 17) is an equilibrium reaction with a cage effect.

2. BULK AND SUSPENSION POLYMERIZATION

2.1. Particle formation

Kuchanov and Bort (16) in a comprehensive discussion of bulk and suspension polymerization of vinyl chloride list about 60 papers that have been published on this subject prior to 1973. This large number reflects not only the great interest in, and extensive practical use of PVC, but also that the hetero-phase polymerization of VC is a very complex process. The authors list several characteristic features of the bulk polymerization of VC, some of which are referred below.

The process is considered to take place in three stages. During the first and third stage the reaction mixture consists of a single phase in which polymerization conforms to the conventional relations of homogeneous processes. During the second stage, two phases are present simultaneously. In the first stage globular polymer particles are formed by precipitation from the solution. This stage was considered completed at a conversion of about 0.5%. According to Cotman *et al.* (17) at least 25×10^{11} particles/g VC is formed during the very early stage of polymerization at 50 °C. At a conversion of a few tenths of a per cent this number drops to ca. 5×10^{11} /g VC, independent of the initiator concentration. During the second (hetero-phase) stage which lasts to about 77% conversion, a constant monomer concentration in the growing particles is upheld by diffusion of monomer from the liquid phase. Within the second stage, four typical ranges of conversion were distinguished, up to 1%, 1-10%, 10-20% and 20-77%. In the first range the polymer particles grow by aggregation of finer formations. Towards 1% conversion a certain concentration and morphology of particles are established which are then considered to remain unchanged during the process. According to Bort *et al.* (18) the number of particles increases from 5×10^{10} to 5×10^{11} per cm^3 when the average rate of polymerization in the initial range is increased from 2 to 200 mole/l sec. In the range of 1-10% conversion the globular particles are characterized by stability against aggregation. Between 10-20% conversion secondary structures form by coalescence. This secondary structure formation seems to be complete at about 20% conversion. The system now consists of a three-dimensional arrangement of loosely packed globules which has lost its fluidity. In the third stage, above 77% conversion, the monomer phase has disappeared and conventional homogeneous polymerization takes place in the monomer swollen polymer phase.

A number of papers on the mechanism of particle formation and the morphology of the polymer in dependence of various process parameters for both mass and suspension polymerization have appeared during the last decade. Boissel and Fischer (19) in a study of the nucleation phase of bulk polymerization found that PVC formed at the start of polymerization has a solubility in its monomer less than $10^{-3}\%$. This is significantly lower than the values obtained by other authors (16,20) for samples of "normal" PVC obtained after 70% conversion. The first particles (called granules) appear at a conversion of approximately $10^{-3}\%$ and their number remains constant up to a critical conversion τ_c which depends on agitation and decreases when the intensity of agitation increases. Hence under the experimental conditions employed, a value of $\tau_c \sim 0.12\%$ was observed with a peripheral agitation speed of 0.7 m/sec, whereas with a speed of 2 m/sec $\tau_c \leq 0.05\%$. Above the critical conversion a second nucleation seemed to take place. The authors suggest that this observation may explain the main differences between formerly published (16,17,20,21) data, which were obtained in non-agitated media, and their own results. In the absence of agitation the critical conversion is likely to be very high. The number of granules was also found to depend on the rate of formation of free radicals. In the region investigated ($\rho_1 \sim (0.2-200) \cdot 10^{-10}$ mol/dm³,sec), the following relationship was observed:

$$N = 2.7 \times 10^{13} (\rho_1 \times 10^{10})^\beta \text{ particles/dm}^3$$

where ρ_1 is the rate of radical formation and the exponent β varied as a function of temperature (θ) in accordance with the equation:

$$\log(1-\beta) = a+b\theta$$

It is seen that for any value of ρ_1 , the number of particles formed decreases with increasing temperature.

Behrens (22,23) found that the polymer chains formed in the early stages of polymerization aggregate to nuclei of about 10 nm diameter, each nucleus

consisting of from 5-10 macromolecules. He notes that this process is independent of whether polymerization is carried out in bulk or suspension. These nuclei grow uniformly to so called microglobules (primary particles) in the size range of 0.1 - 0.3 μm .

According to Bort et al. (16,18,24,25) the monomer swollen microglobules are the main loci of polymerization from between 6 to 10% conversion onwards. Macroglobules with diameters of 1-2 μm are formed from the microglobules, either by polymer growth or by aggregation. These macroglobules further agglomerate to form the final 100-150 μm particles.

In an investigation of the suspension polymerization of VC, Tregan and Bonnemayre (26) found that 0.1 μm microglobules existed at conversions below 1% and that macroglobules were formed above 5% conversion. They concluded that the phenomena observed by Bort et al. in bulk polymerization also take place inside the droplets in the suspension process.

Zichy (27) studied the morphology of a polymerizing vinyl chloride droplet suspended in water by means of a spinning drop apparatus. He observed that the nascent polymer appeared as spherical particles in various stages of aggregation and pointed out that in the absence of a repulsive force between the primary particles, each Brownian collision should lead to coagulation. Using Smoluchowsky's theory of diffusion controlled flocculation he calculated the expected average particle diameter at 2% conversion to be 10 μm , whereas the observed particle diameter was in the order of 0.1 μm . Zichy therefore concluded that some repulsive force must exist in order to account for the apparent lack of coagulation.

In some recent papers, Zichy and coworkers (28-30) studied the highly monodisperse and colloiddally stable primary particles (radius 0.15 μm) formed in the early stages of suspension polymerization. It was demonstrated that the particles carried a negative charge and electrophoretic measurements revealed zeta potentials of about -80 mV, corresponding to approximately 40 elementary charges per particle. The charges were attributed to ionized hydrogen chloride formed by decomposition of vinyl chloride peroxides. The presence of a negative charge on low conversion suspension PVC particles has recently been confirmed by Davidson and Witenhafer (31). Using dark field optical microscopy on an unagitated polymerizing vinyl chloride droplet at low conversion they found that the PVC grains (sub micron particles) inside the droplet appeared to form regular arrays suggesting a stabilizing force acting over long distances. The authors therefore assumed that the grains were electrically charged since particles stabilized by entropic or mechanical means would not be likely to exhibit this behaviour. The assumption was verified by studying the motion of the particles in an electric field. The authors also found that mass polymerized PVC particles precipitated in the monomer became negatively charged at low conversions. The charging species was assumed to be chloride ions producing by some unknown dehydrohalogenation reaction.

Davidson and Witenhafer also investigated the effect of agitation conditions on the morphology of the PVC inside the suspension droplets. At conversions below 2%, stable micro-size agglomerates of PVC grains were formed both in agitated and quiescent polymerizations. In the agitated system, these grains coagulated between 2 and 4% conversion to give an irregular structure in the interior of the droplet, while in quiescent systems they served as growth centers for further polymerization to give final particles possessing a uniform internal bead morphology. The authors note that the formation of these stable growth centers appear to be unique to PVC.

Davidson and Witenhafer also investigated the structure and formation of the pericellular membrane or skin which completely surrounds the polymerizing droplet after 1-2% conversion. They assumed that this membrane served as a barrier to the diffusion of the charging species out of the polymerizing droplet.

Summing up, it seems fairly well established that the unusual stability of the primary particles can be attributed to a negative surface charge, probably due to Cl^- ions. Although the surface charge density of the PVC particles is only about 1/100 th of that of a stable aqueous dispersion (30), the countercharges will be very diffusely distributed and extend far from the particle surface in a non-aqueous system. Therefore, as two equally charged particles approach each other, electrostatic repulsion due to double layer overlap will arise at far larger interparticle distances than in aqueous systems. Another feature of low permittivity solvents is that

minute surface charges are sufficient to produce appreciable potentials (32).

From the Gouy-Chapman theory (34) the characteristic thickness of the double layer is equal to $1/\kappa$ where

$\kappa = (2e^2 N_A cz^2 / \epsilon kT)^{1/2}$. Here e is the electron charge, N_A is Avogadro's number, c is the concentration of electrolyte, z is the charge of the electrolyte ions and ϵ is the permittivity (equal to dielectric constant times the permittivity of vacuum). In apolar solvents, only minute amounts of dissociated salts can be dissolved. Therefore, κ becomes very low and the double layer very thick. Rance and Zichy (30) estimate that in vinyl chloride, $1/\kappa > 10 \mu\text{m}$ as compared to $1/\kappa = 0.003 \mu\text{m}$ in a 10^{-2} molar 1:1 electrolyte solution.

The general expression for the repulsive energy, V_R , which results from the overlapping of the diffuse double layer, are very complex. Verwey and Overbeek (33) have given solutions for various limiting cases. For low potentials and low values of $\kappa \cdot a$, where a is the particle radius,

$$V_R = \frac{4\pi\epsilon a^2 \psi_0^2}{R} e^{-\kappa H}$$

where R is the distance between the centers of the spheres, ψ_0 is the surface potential and $H = R - 2a$.

In non-aqueous systems the surface potential is usually equated to the electrokinetic (zeta) potential (ζ) and the expression for V_R for very low values of κ may be written:

$$V_R = \frac{4\pi\epsilon a^2 \zeta^2}{R}$$

The Van der Waal's attraction at short distances of separation is given by:

$$V_A = - \frac{A}{12} \cdot \frac{a}{H}$$

where A is the Hamaker constant.

The total interaction energy is then given as

$$V_T = V_R + V_A$$

Rance and Zichy made an approximate calculation of the total potential energy as a function of interparticle distance for PVC particles in vinyl chloride and compared the result to a similar calculation for polystyrene particles in an aqueous solution of 10^{-2} molar 1:1 electrolyte. For both systems a zeta potential of -80 mV and a particle radius of $0.15 \mu\text{m}$ were used. The results are illustrated in Fig. 1. It is seen that the potential energy maximum for the PVC/VC system are much lower than for the PS/H₂O system, reflecting the much lower permittivity of VC as compared to H₂O. However, due to the far greater thickness of the electrical double layer in vinyl chloride, the potential energy decays much less rapidly with increasing interparticle distance than it does in aqueous solution. The rate of slow flocculation relative to fast (no electrostatic repulsion) is usually expressed by Fuchs' stability ratio W ,

$$W = 2a \int_{2a}^{\infty} \exp(V_T/kT) dR/R^2$$

Because of the slow decay of V_T with R , W may have a considerable value even in a non-aqueous system. An interesting feature with such a system is also that W may be decreased with increasing particle concentration because the particles already have surmounted a part of the energy barrier at their largest distance of separation (integration limit less than ∞).

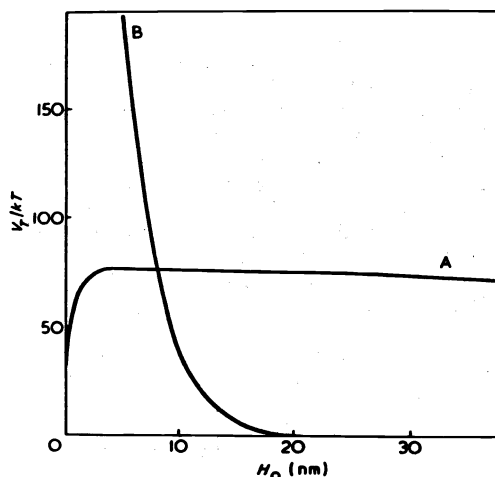


Fig. 1. Diagram of total potential energy (V_T) against distance of particle separation (H_0) for spherical particles of radius $0.15 \mu\text{m}$ and ζ potential -80 mV . (A) PVC particles in VCM, (B) polystyrene particles in 10^{-2} mol/dm^3 1:1 electrolyte solution. Reproduced from Rance, D.G. and Zichy, E.L., *Polymer* 20, 268 (1979) by permission of the publishers, IPC Business Press Ltd. (C).

2.2. Kinetics of polymerization

There has in the past been presented a vast number of papers on the kinetics of radical polymerization of vinyl chloride in bulk and suspension, and different mechanistic models have been advanced in order to describe the experimental results. These papers have been described in detail in previous review papers (16,35,36) and are only referred to in cases where they are relevant to the discussion of more recent models.

The models which more recently have most often been applied in the discussions of the bulk and suspension polymerization are the models of Talamini et al. (37,38), Ugelstad et al. (35,36,39), Kuchanov and Bort (16) and Olaj (40,41). The present paper gives a short summary of these models with reference to more recent applications and modifications. Also a model which involves a more drastic difference in view on the mechanism of the reaction is discussed. The main feature of the models presented by the above mentioned authors is the assumption that the reaction takes place in two phases, the liquid phase, consisting of practically pure monomer (denoted the L phase) and the polymer phase consisting of polymer particles swollen with monomer (denoted P phase). The P phase has a constant composition up to about 77% conversion where the L phase disappears as a separate phase. Kinetically we therefore have three main stages. Up to a conversion which is $< 1\%$ we have a homogeneous reaction. From the point where polymer precipitates and to about 77% conversion we have a heterogeneous system and from then on we have a homogeneous system of polymer particles swollen with monomer with a declining concentration of monomer as the reaction proceeds. The general expression for the rate of polymerization is:

$$-dM/dt = \frac{d(M_L + M_P)}{dt} = k_p ([M]_L [R]_L V_L + [M]_P [R]_P V_P) \quad (36)$$

where M_L and M_P , respectively R_L and R_P are the number of moles of monomer and radicals in the two phases, and V_L and V_P are the volumes of the two phases.

$$\rho_i = \rho_{iL} + \rho_{iP} = 2k_i [I]_L V_L + 2k_i [I]_P V_P = 2k_{tL} [R]_L^2 V_L + 2k_{tP} [R]_P^2 V_P \quad (37)$$

where ρ_i is the rate of radical formation, k_{tL} and k_{tP} are the termination constant in the two phases. It is assumed that the production of radicals may take place in both phases. For the sake of simplicity, the effectivity factor is set equal to unity.

The model which differs most from the others is the one given by Talamini *et al.* It states that the reaction takes place in the two phases but does not take into consideration any radical transfer between the two phases. Radicals are formed in the L phase and terminates there. In the same way, radicals formed in the P phase terminate there. Polymer is only transferred from the L phase to the P phase as dead molecules or aggregates of dead molecules. In the discussion of this model and the subsequent ones, one point should be made clear. When a molecule is formed in the L phase it will polymerize rapidly and at a certain stage precipitate as a coiled radical of say 20 monomer units. It is a question of terminology whether we will consider this single molecule as a particle or still consider it as a dissolved molecule. In the treatment of Talamini we still consider it as a single radical which may terminate in the L phase by reaction with a radical in a dissolved state or by collision with another single precipitated radical. This latter process will take place with a rate given by $16\pi Dr [R_{prec}]^2 N_A$. The term $16\pi Dr N_A$ is of the same order of magnitude as the bimolecular termination constant, k_{tL} . The important point is that radicals will be absorbed in the polymer phase, but only after having terminated in the L phase by a bimolecular process. Talamini furthermore assumes that the distribution coefficient for the initiator between the two phases is equal to unity. Accordingly we have that the ratio of radical concentrations in the two phases is given by:

$$[R]_P/[R]_L = (k_{tL}/k_{tP})^{1/2} = Q \quad (38)$$

and accordingly for the rate of reaction:

$$-dM/dt = k_p (k_i [I]_L / k_{tL})^{1/2} (M_L + QM_P) \quad (39)$$

In terms of conversion C:

$$dC/dt = (k_i [I]_L / k_{tL})^{1/2} k_p (1-C-AC+QAC) \quad (40)$$

where A is the weight ratio of monomer to polymer in the particle. Talamini finds that with a value of $Q \sim 15$, Eq. (40) describes well a series of bulk and suspension polymerization experiments up to quite high conversions.

The model of Talamini has been further developed and refined by Abdel-Alim and Hamielec (42,43). They take into account the change in volume:

$$V = V^0(1-BC) \quad (41)$$

where $B = (d_p - d_m)/d_p$

This relation was also used to calculate conversion from dilatometric measurements. It should be noted that Eq. (41) involves that there is no change in volume by mixing. Abdel-Alim also takes into account the decrease in initiator with time. Also the authors include in their model Interval III where one has a homogeneous reaction in the polymer particles. The value of k_{tP} is expected to decrease in this region and the value of $k_p (k_i/k_{tP})^{1/2}$ is set proportional to $(1-C)$ in this upper region, the proportionality factor is adjusted to fit the experimental results. The authors have found that their model most accurately describes the kinetics of bulk polymerization of vinyl chloride to high conversions with a number of different initiators.

The model given by Ugelstad *et al.* (36,39) also assumes production of radicals in both phases. However, quite contrary to the model by Talamini it is assumed that there is a rapid established equilibrium distribution of radicals between the L and P phase so that we have:

$$[R]_P/[R]_L = k_a/k_{dc} = Q \quad (42)$$

Combining Eqs. (36), (37) and (42) gives for the rate of reaction:

$$-dM/dt = [k_i I / (V_L k_{tL} + Q^2 V_P k_{tP})]^{1/2} k_p (M_L + Q M_P) \quad (43)$$

where

$$k_i I = k_i [I]_L V_L + k_i [I]_P V_P \quad (44)$$

In terms of conversion:

$$dC/dt = [k_i I / (V_L k_{tL} + Q^2 V_P k_{tP})]^{1/2} k_p (1 - C - AC + QAC) \quad (45)$$

Assuming that the volumes of the polymer phase is additive and expressing V_L and V_P by V^0 , one obtain:

$$dC/dt = \left[\frac{k_i I}{V^0 (1 - C - AC) k_{tL} + (A + (d_m/d_p) Q^2 C k_{tP})} \right]^{1/2} k_p (1 - C - AC + QAC) \quad (46)$$

Again it should be stressed that it is formally of no importance whether k_{tL} represents a bimolecular termination in the L phase between soluble radicals, between a soluble and a precipitated radical or a flocculation with rapid termination between two precipitated radicals in the L phase. One could also take into account that the absorption may involve dissolved and single precipitated radicals in the L phase.

The average absorption constant (k_a) in the absorption term $k_a [R]_L$ may then be written:

$$k_a = (k_{as} [R]_{Ls} + k_{aprec} [R]_{Lprec.}) / [R]_L \quad (47)$$

In the discussion of Eq. (46) Ugelstad applied a value of $k_{tL} = 5 \times 10^9 \text{ dm}^3/\text{mol sec}$ and a value of k_{tP} , based upon results of emulsion polymerization, of $10^8 \text{ dm}^3/\text{mol sec}$. The value of Q which gave the best fit to the experimental curves was found to be ca. 200, but the fit was rather insensitive to the value of Q if it was increased beyond this value. The conclusion drawn by Ugelstad was that even at low conversion the termination takes place mainly in the polymer particles: at 5% conversion, 98% of the total termination and 85% of the conversion takes place in the particles. The contribution of these reactions in the particles will increase with increasing value of Q . Ugelstad claimed that his model would explain the experimental fact that addition of a chain transfer agent like CBr_4 increases the initial rate but at the same time leads to disappearance of the auto acceleration. The addition of CBr_4 leads to a decrease in the ratio of $k_a/k_{dc} = Q$, and it is easily seen that this should have the above effects. Also the model may explain that precipitation leads to a decrease in rate, which has been observed experimentally in precipitating solvents (44,45). These experimental results, which have been obtained by dilatometric measurements, have been criticized by Bort (46) who suggests that the apparent drop in rate is caused by the precipitation process which is accompanied by a volume increase. Bort claims to have shown that such an increase takes place by comparing the volume of a diluted solution of PVC in THF with the volume of the same amount of PVC and THF before dissolution. Also he claims that if the reaction is followed thermometrically, there is no reduction in the rate at the point of phase separation. The desorption of radicals from the particles obviously will be restricted to small radicals stemming from the chain transfer process which will desorb at a steadily slower rate as they grow in size. Setting the rate of desorption equal to $k_{dc} [R\cdot]_p$ does not involve the assumption that all radicals in the particles may desorb, but rather that the number of such radicals is proportional to the total concentration of radicals, and further that an average value for k_{dc} may be applied for those radicals that are able to desorb. The low value of k_{dc} as compared to k_a reflects the fact that only a fraction of relatively small radicals formed by chain transfer to monomer may desorb. They will do so with decreasing rate as they grow. The criticism brought forward by Kuchanov and Bort, namely that Ugelstad's model should involve that all radicals may desorb, is incorrect. So is the criticism presented by Abdel-Alim and Hamielec who claim that the value of k_{dc} most certainly is too low to have any influence on the radical concentration. As stated in a previous paper (36), this calculation was based upon the assumption that the effective diffusion constant governing desorption of

radicals from the particles would be the same as that found in emulsion polymerization. Obviously it will be higher, because the solubility of the organic radicals in the L phase will be more favourable than is the case in emulsion polymerization with water as the continuous phase. It is probable that the value of Q will not be constant as the reaction proceeds. However, it will be obvious from Eq. (46) that already from low conversion on the absolute value of Q , if high, loses its significance. The reaction will take place completely in the P phase, the rate being:

$$dC/dt = \left[\frac{k_i I}{v^0 (A + (d_m/d_p)) k_{tP}} \right]^{1/2} A k_p C^{1/2} \quad (48)$$

A comprehensive study of the kinetics of bulk and suspension polymerization has been given by Kuchanov and Bort (16). In their discussion of the kinetics of the polymerization they are extremely careful in taking into account the changes in volume which take place when one goes from homogeneous to heterogeneous systems and claim that several authors using a dilatometric method for following the reaction have drawn wrong conclusions as to the apparent abrupt change in rate as precipitation takes place.

Kuchanov and Bort also consider that the reaction takes place in two phases. The volumes of the two phases are given by:

$$V_L = v_L^m M_L + v_L^p P_L, \quad V_P = v_P^m M_P + v_P^p P_P \quad (49)$$

where v_L^m and v_P^m are partial molare volumes of monomer in the L and P phase respectively, v_L^p and v_P^p are partial molar volume per monomer unit of reacted monomer in the two phases, M_L and M_P are number of moles of unreacted monomer, P_L and P_P number of moles of monomer already converted to polymer in the two phases. Up to 77% conversion the fraction of polymer U should remain constant in the two phases:

$$U_L = P_L / (M_L + P_L) \quad \text{and} \quad U_P = P_P / (M_P + P_P) \quad (50)$$

In the dilatometric formula which relates the volumetric variations of the polymerized product to conversion, the value $v = (U_P v_P - U_L v_L) / (U_P - U_L)$ should be substituted in place of the ratio of monomer and polymer density. v_L and v_P are the ratios of the partial molar volumes of polymer and monomer in the L phase and P phase, respectively.

The rate of reaction is given by:

$$-\frac{d(M_L + M_P)}{dt} = \frac{d(P_L + P_P)}{dt} = k_p ([M]_L R_L + [M]_P R_P) \quad (51)$$

$$[M]_L = \frac{1 - U_L}{1 + U_L (v_L - 1)} [M]^0, \quad [M]_P = \frac{1 - U_P}{1 + U_P (v_P - 1)} [M]^0 \quad (52)$$

Bearing in mind that $U_L \ll 1$ we get:

$$dC/dt = \frac{k_p}{v^0} (R_L + \frac{1 - U_P}{1 + U_P (v_P - 1)} R_P) \quad (53)$$

This equation is claimed to take care of the volume change accompanying the formation of a polymer phase in a correct way.

The main difference between the model of Kuchanov and Bort and that of Ugelstad lies in the derivation of R_L and R_P . Kuchanov does not accept any equilibrium distribution of radicals between the phases. He furthermore assumes that the desorption of radicals can be completely neglected and accordingly gets the steady state equations for the radicals in the two phases:

$$dR_L/dt = \rho_{iL} - 2k_{tL} R_L^2 / V_L - k_a R_L / V_L \quad (54)$$

$$dR_P/dt = \rho_{iP} - 2k_{tP}R_P^2/V_P + k_a R_L/V_L \quad (55)$$

where the absorption constant k_a is given by

$$k_a = 4\pi D_L r_P N \quad (56)$$

From Eqs. (54) and (55) one obtains:

$$R_L = (\rho_{iL}/k_{tL})^{1/2} \frac{V_L F}{1 + (1 + F^2 V_L)^{1/2}} \quad (57)$$

$$R_P = \frac{V_P}{k_{tP}} \left(\rho_{iP} + \frac{2\rho_{iL}}{1 + (1 + F^2 V_L)^{1/2}} \right)^{1/2} \quad (58)$$

where

$$F = (\rho_{iL} k_{tL})^{1/2} / 2\pi D_L r_P N \quad (59)$$

(The expressions for R_L and R_P given in the English translation of the paper is incorrect.)

On the basis of the Eqs. (49-59) Kuchanov calculates the rate of reaction and conversion as a function of time. The values of k_{tP} and D_L were found from comparison of the theoretical values of dC/dt with experimental results for a wide range of different polymerization conditions. Values of D_L of ca. 10^5 dm²/sec, and of k_{tL}/k_{tP} of about 250 is said to be in accordance with experimental results up to 10% conversion. The value of $k_{tL}/k_{tP} \sim 250$ corresponds to a value of $k_{tP} \sim 10^7$ dm³/mol sec, while Ugelstad found a value of $k_{tP} = \sim 10^8$ dm³/mol sec. From 20-77% conversion when the polymerized product is a continuous porous unit, the expression for interphase flow cannot be described by a simple equation. As is the case with the model of Ugelstad, however, this will only lead to a very slight error in the calculation as at such high conversions the whole reaction takes place in the polymer particles.

Kuchanov and Bort find that the P phase is the main locus for polymerization already at low conversion (< 10%), and that up to about 30% conversion, the chain growth in the particles takes place mainly on radicals which have entered the particles from the monomer phase. They also make an estimate of the rate of diffusion of radicals out of the particles compared to the rate of termination in the particles. For a particle number of 2.8×10^{14} per dm³ and with a rather arbitrarily chosen value of 10^{-11} dm²/sec for the effective diffusion constant, they conclude that the loss of radicals by transport out of the particles may be neglected compared to the loss by termination. It will appear that the treatment of Kuchanov and Bort is rather similar to the one suggested by Ugelstad. The assumption of a considerable effect of radical desorption in the Ugelstad model may well be true at start when there is a great number of particles. Also the Ugelstad model proclaims that the desorption of radicals loses its significance at conversions above $\sim 10\%$.

In some recent papers Olaj (40,41) has discussed the kinetics of bulk polymerization. Olaj definitely takes into account the formation of precipitated 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 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 radicals will absorb preferentially in these. Thus he neglects termination of dissolved radicals, which may be justified. He also neglects absorption of dissolved radicals and most important he neglects pairwise termination by flocculation of precipitated radicals with themselves, which seem to be doubtful in the start of reaction.

Olaj applies the following steady state expressions:

$$dR_{prec}/dt = \rho_{iL} - k_{aprec} R_{prec} = 0 \quad (60)$$

$$dR_p/dt = \rho_{iP} + k_{aprec} R_{prec} - k_{tP} [R]_P^2 V_P = 0 \quad (61)$$

and arrives at the following expression:

$$\frac{dC}{dt} = \frac{2k_i [I]}{k_{aprec}} k_p (\phi_m^* - C \frac{\phi_m d_m}{\phi_p d_p}) + k_p \left(\frac{k_i [I]}{k_{tP}} \cdot \frac{d_m}{d_p} \cdot \frac{\phi_m^2}{\phi_p} \cdot C \right)^{\frac{1}{2}} \quad (62)$$

where ϕ_m and ϕ_p are volume fractions of monomer and polymer in the P phase and ϕ_m^* is the volume fraction at the site of reaction in the L phase.

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 Ugelstad model from low conversion on. Olaj states that both models lead to expressions of the form: rate = $a + bC^{\frac{1}{2}}$. In the Ugelstad expression the term a is proportional to $I^{\frac{1}{2}}$ while in Olaj's model a should vary with I . Olaj finds that the intercept of dC/dt versus $bC^{\frac{1}{2}}$ is proportional to $[I]^{0.67}$, indicating that the truth lies somewhere between the two assumptions.

Boissel and Fischer (19) investigated the kinetics of bulk polymerization at very low conversion in stirred systems. They found that conversion could be expressed as:

$$C = K \cdot t^{1.5}$$

The finding of an order with respect to time that is larger than unity already at such low conversions ($\sim 0.1\%$) seems to indicate an autocatalytic reaction from very low conversions on (almost from start). Olaj's model, and even more so the models of Ugelstad and of Kuchanov would predict a linearity with time at such low conversions. The value of K varies with the critical concentration and with temperature. The latter variation corresponds to an activation energy of 30 kcal/mole. At a constant temperature, $\log K$ versus $\log \rho_i$ was found to give a straight line with a slope of unity, indicating a first order with respect to initiator. Thus the results seem to support the expression of Olaj for the low conversion case.

A number of recent papers have described experimental results of bulk and suspension polymerization. Most of them have applied one of the mechanisms discussed above for the discussion of the experimental results, although with some modifications, one has given a completely different mechanism.

Bulle *et al.* (47) investigated the kinetics of suspension polymerization of vinyl chloride with a number of initiators and mixtures of initiators. They compare their experimental results with kinetic models, one of which is similar to the one of Talamini, with no exchange of radicals between the particles, the other similar to the one by Bort, taking into account diffusion of radicals from the L phase to the P phase. They find that both models give a reasonable agreement with the experimental results, with a slight preference for the Bort model.

Modified models both assuming reaction in two phases and including transport of radicals between the phases have recently been suggested by Thiele *et al.* (48) and by Kafarov *et al.* (49). Ray *et al.* (50) have considered a different model. They claim that primary polymer particles of about $1 \mu m$, which are formed at low conversion, swell to such a low degree that one may neglect polymerization inside these particles. The reaction takes place in the monomer phase and, as the conversion increases, to an increasing degree in the monomer phase in the pores of the polymer bead formed by coalescence of the primary particles. It is claimed that the autocatalytic effect stems from a decrease in the value of the diffusion controlled termination constant in the pores. To the present authors the assumption of non-swelling primary particles seems doubtful. Also it seems unclear why the termination constant in the pores should decrease, as the reaction zone according to Ray is also in the second stage a pure monomer phase, although present in pores.

3. ORDINARY EMULSION POLYMERIZATION

3.1. Particle formation

3.1.1. Below CMC. Below CMC one will have so-called homogeneous particle formation which implies that the particle formation takes place by precipitation in the aqueous phase. In the case of VC, polymerization without emulsifier is easily carried out and leads to highly monodisperse latexes (51).

Fitch and Tsai (52) have suggested a general mechanism for homogeneous particle formation. In their model it is assumed that each growing radical initiated in the continuous phase forms a fresh polymer particle if it reaches some threshold degree of polymerization before being captured by preexisting polymer particles. The quantitative theory they have developed based upon this model has been criticized by a number of authors (53-55).

Hansen and Ugelstad (55-57) recently described in detail a model where one applies a steady state for all types of radicals up to the critical chain length and take into account the different factors which will influence the capture of each type of radical by the particles. A similar approach with steady state equations have also been applied by Barret (53).

In the previous model no desorption of radicals was included. If this is taken into account and one moreover distinguishes between active particles containing one radical (N_1), and particles with no radicals (N_0), the steady state equations for the different radicals in the aqueous phase may be written:

$$\begin{aligned} d[R_I]_w/dt &= \rho_i - k_{pI} [R_I]_w [M]_w - k_{twI} [R_I]_w [R]_w - k_{aI1} [R_I]_w N_1 \\ &- k_{aI0} [R_I]_w N_0 = 0 \end{aligned} \quad (63)$$

$$\begin{aligned} d[R_M]_w/dt &= k_{dN1} - k_{pM} [R_M]_w [M]_w - k_{twM} [R_M]_w [R]_w - k_{aM1} [R_M]_w N_1 \\ &- k_{aM0} [R_M]_w N_0 = 0 \end{aligned} \quad (64)$$

$$\begin{aligned} d[R_{M1}]_w/dt &= k_{pM} [R_M]_w [M]_w - k_p [R_{M1}]_w [M]_w - k_{tw} [R_{M1}]_w [R]_w \\ &- k_{aM11} [R_{M1}]_w N_1 - k_{aM10} [R_{M1}]_w N_0 = 0 \end{aligned} \quad (65)$$

$$\begin{aligned} d[R_{i1}]_w/dt &= k_{pI} [R_I]_w [M]_w - k_p [R_{i1}]_w [M]_w - k_{tw} [R_{i1}]_w [R]_w \\ &- k_{aI11} [R_{i1}]_w N_1 - k_{aI10} [R_{i1}]_w N_0 = 0 \end{aligned} \quad (66)$$

$$\begin{aligned} d[R_{ij}]_w/dt &= k_p [R_{i(j-1)}]_w [M]_w - [R_{ij}]_w (k_p [M]_w + k_{tw} [R]_w \\ &+ k_{aIj1} N_1 + k_{aIj0} N_0) = 0 \end{aligned} \quad (67)$$

$$\begin{aligned} d[R_{Mj}]_w/dt &= k_p [R_{M(j-1)}]_w [M]_w - [R_{Mj}]_w (k_p [M]_w + k_{tw} [R]_w \\ &+ k_{aMj1} N_1 + k_{aMj0} N_0) = 0 \end{aligned} \quad (68)$$

where R_I and R_M are the radicals produced from the initiator and by chain transfer respectively, R_{ij} and R_{Mj} radicals of chain length j originating from the initiator and the chain transfer reaction respectively, $[R]_w$ is the total concentration of radicals in the aqueous phase, k_{aIj1} and k_{aIj0} the absorption coefficient of radical of chain length j originating from an initiator radical in an active particle and in an unactive particle respectively, k_{aMj1} and k_{aMj0} are the corresponding values for the radicals stemming from the monomer radical formed by chain transfer (which in the case of VC possibly is a $Cl\cdot$ radical).

In the equations above we have made the simplification that all termination constants and propagation constants, except for the R_I and the R_M radicals, have the same value. Note that we have here explicitly expressed that the rate of radical absorption is proportional to N .

The rate of particle formation is given by:

$$dN/dt = k_p [M]_w ([R_{ij} j_{icr}^{-1}]_w + [R_{Mj} j_{Mcr}^{-1}]_w) \quad (69)$$

The rate of formation of N_1 particles is given by:

$$dN_1/dt = dN/dt + N_o \cdot \sum_{j=1}^{j_{icr}^{-1}} k_{aijd} [R_{ij}]_w + N_o \cdot \sum_{j=1}^{j_{Mcr}^{-1}} k_{aMjo} [R_{Mj}]_w - N_1 \cdot \sum_{j=1}^{j_{icr}^{-1}} k_{aijl} [R_{ij}]_w - N_1 \cdot \sum_{j=1}^{j_{Mcr}^{-1}} k_{aMjo} [R_{Mj}]_w - k_d N_1 \quad (70)$$

Rate of formation of N_o particles is obviously:

$$dN_o/dt = dN/dt - dN_1/dt$$

The total rate of particle growth, dV_p/dt , is given by:

$$dV_p/dt = (k_p/N_A) \phi_{mp} / (1 - \phi_{mp}) (d_m/d_p) N_1 + v' (dN/dt) \quad (71)$$

The last term in Eq. (71) gives the volume increase caused by the precipitation of particles. From V_p one gets r , needed for the value of k_a . In the expression for dV_p/dt we do not differentiate between N_o and N_1 particles as the particles rapidly change from being an active to inactive and vice versa.

By expressing R_j by R_{j-1} , Eqs. (64-69) give the following equation for the rate of particle formation:

$$dN/dt = \frac{\rho_i}{A} \cdot \frac{1}{\prod_{j=1}^{j_{icr}^{-1}} \{1 + \frac{k_{tw} [R]_w}{k_p [M]_w} + \frac{k_{aijl} N_1}{k_p [M]_w} + \frac{k_{aijo} N_o}{k_p [M]_w}\}} + \frac{k_d N_1}{B} \cdot \frac{1}{\prod_{j=1}^{j_{Mcr}^{-1}} \{1 + \frac{k_{tw} [R]_w}{k_p [M]_w} + \frac{k_{aMjl} N_1}{k_p [M]_w} + \frac{k_{aMjo} N_o}{k_p [M]_w}\}} \quad (72)$$

$$\text{where } A = 1 + k_{twI} [R]_w / k_{pI} [M]_w + k_{aiI} N_1 / k_{pI} [M]_w + k_{aIo} N_o / k_{pI} [M]_w \quad (73)$$

$$\text{and } B = 1 + k_{twM} [R]_w / k_{pM} [M]_w + k_{aMl} N_1 / k_{pM} [M]_w + k_{aMo} N_o / k_{pM} [M]_w$$

The expression given in Eq. (72) differs from the expression for particle formation in previous papers by the additional second term with particle formation due to desorbed radicals.

For the further discussion of Eq. (72) one will have to follow the same lines as in the previous paper by Hansen and Ugelstad (55). The value k_{aj} was set equal to $4\pi D_w r$ (which represents the case of irreversible absorption) multiplied with an effectivity factor which was made up of the electrostatic repulsion and the reversibility factor. The latter took into account that the radicals which were absorbed might desorb again, this would be more probable to happen the lower the value of j . In the discussion of the influence of the reversibility factor it was also taken into account that radicals of any chain length may be more readily trapped in particles containing a radical than in particles not containing a radical, i.e. $k_{ajl} \geq k_{ajo}$.

The reversibility factor (as well as the electrostatic repulsion) would be expected to have the largest influence on the absorption of the charged radicals. The uncharged radicals formed by chain transfer have a higher tendency to be irreversibly absorbed. This would tend to diminish the importance of the second term. On the other hand we would expect that j_{cr} might be considerably lower for these uncharged radicals. In any case the effect of chain transfer would be to increase the number of particles formed. One possibility of particle formation has been neglected in the above discussion, namely the one that may result from a termination by coupling of radicals, each of which has a chain length below j_{cr} but which by coupling reaches a sufficient chain length to precipitate. Such a particle formation mechanism has been included in a recent study by Arai et al. (54) in discussion of particle formation in the case of methyl methacrylate. Particle formation by this process might seem to be more likely to take place with this monomer than with VC.

Eq. (72) does not take into account any flocculation of particles which most certainly will be of importance if one work with no or very little emulsifier. This is evident from the fact that in the presence of emulsifier, one has a marked increase in the number of particles formed even below CMC. Especially with VC one often experiences that there is no drastic change in the slope of the curve of \log (particle number) as a function of \log (emulsifier concentration) at the CMC (58). The flocculation is clearly evident in experiments with VC without emulsifier from the effect of ionic strength on the number of particles formed (51).

3.1.2. Particle formation above CMC. The formation of particles above CMC may possibly be treated in the same way as done by Nomura et al. (59) for VAC. They applied a non steady treatment. Quite recently Hansen and Ugelstad (60) have applied a very simplified steady state treatment in order to reveal the most significant features of the effect of radical desorption on particle formation.

The rate of particle formation was expressed as:

$$dN/dt = \rho_A \frac{\delta N_M r_M^x}{\delta N_M r_M^x + N r_p^x} \quad (74)$$

where N_M and r_M are the number and radius of micelles, N and r_p as before the number and radius of particles, x is the order of absorption rate with respect to radius, which in the present very approximative treatment is assumed to be the same for particles and micelles. The efficiency factor for absorption in a micelle relative to a particle of the same size, δ , is assumed to be independent of the type of particle.

In Interval I where the particles are very small the rate of termination will usually be much faster than the initiation and desorption. The value of \bar{n} is in this case when $\bar{n} \leq 0.5$ given by (61,62):

$$\bar{n} \sim \{(\rho_i/2Nk_d)^2 + \rho_i/2Nk_d\}^{1/2} - \rho_i/2Nk_d \quad (75)$$

which in the case of VC where $\bar{n} \ll 0.5$ reduces to:

$$\bar{n} \sim (\rho_i/2Nk_d)^{1/2} \quad (76)$$

The total absorption rate of radicals is given by

$$\rho_A = \rho_i + k_d \bar{n} N \quad (77)$$

From Eqs. (74) and (77):

$$dN/dt = (\rho_i + k_d \bar{n} N) \left[1 + \frac{N}{\delta N_M} \cdot \left(\frac{r_p}{r_M} \right)^x \right]^{-1} \quad (78)$$

In the case of VC the value of k_d may probably be expressed as:

$$k_d = k_{dm} k_f / k_{PM} \quad (79)$$

where k_{dm} is the desorption constant for the monomer radicals, k_f the "transfer" constant and k_{PM} the propagation constant for the radical formed by the chain transfer.

The value of k_{dm} is given by:

$$k_{dm} = \frac{3D_p D_w}{(aD_p + D_w) r_p^2} = 3D_m / r_p^2 \quad (80)$$

where D_p and D_w are diffusion constants in the polymer particles and in the aqueous phase respectively, a is the distribution coefficient for the monomer radical between the particle and water, D_m may be defined as the effective dissociation constant for the monomer radical.

The increase in volume V_p is given by:

$$dV_p/dt = \frac{k_p \phi_m}{N_A (1 - \phi_m)} \left(\frac{d_m}{d_p} \right) \bar{n} N + v_M \frac{dN}{dt} \quad (81)$$

where v_M is the micelle volume. The last term will usually be negligible. The value of r_p calculated from the value of V_p and N at any instant is:

$$r_p = (3V_p/4\pi N)^{1/3} \quad (82)$$

The particle area A_p is obtained from r_p and N_p , and the number of micelles is then found from the equation:

$$N_M = N_{M0} (1 - A_p/a_s S_0) \quad (83)$$

where N_{M0} is number micelles, S_0 concentration of micellar emulsifier at start. Furthermore one has for the case that the specific area of the emulsifier a_s has the same value on a particle as in a micelle:

$$4\pi r_p^2 N_{M0} = a_s S_0 \quad (84)$$

Values for D_m for VC (63) and styrene (56) were calculated from experimental results of emulsion polymerization with the monomer. The details of the procedure of calculation of N and the value of the other parameters are given in the original paper.

The calculations show that the order with respect to ρ_i and S_0 for styrene is close to the ones predicted by the Smith-Ewart theory, namely 0.4 and 0.6, respectively.

In the case of VC, the calculated orders with respect to ρ_i and S_0 are zero and unity, respectively, which are in accordance with experimental results. Also the value of N is much higher in the case of VC than for styrene. This deviation from the Smith-Ewart theory in the case of VC is caused by the higher value of D_m . Desorbed radicals will take part in particle formation which will increase the particle number. At the same time this will lead to that the order with respect to ρ_i will decrease. The results indicated that the value for δ for VC is very low, in the order of 10^{-3} .

It is interesting to note that the above simplified steady state treatment leads to that the sum of the orders of N with respect to ρ_i and S_0 is always equal to one, so that

$$N \propto S_0^z \rho_i^{1-z} \quad (85)$$

where $0.6 \leq z \leq 1$

The value of z increases with increasing desorption. Eq. (85) was first obtained by Nomura *et al.* (59) from a steady state treatment of the particle formation process.

3.2. Kinetics and mechanism

In the present paper, attention will be focused on some specific points in the kinetics of emulsion polymerization which are essential in connection with the emulsion polymerization of VC. In the case of VC under ordinary polymerization conditions the average number of radicals per particle, \bar{n} , is usually less than 0.5 due to desorption and reabsorption of radicals formed by "chain transfer". Considering only particles with zero (N_0), one (N_1) and two (N_2) radicals and assuming that $N_0 \gg N_1 \gg N_2$, that the water phase termination might be neglected and that $\bar{n} \sim N_1/N$, the following expression for \bar{n} was derived (58,64):

$$\bar{n} = \frac{1}{N} \rho_i^{\frac{1}{2}} \left(\frac{V_p}{2k_{tp}} + \frac{N}{2k_d} \right)^{\frac{1}{2}} \quad (86)$$

where ρ_i is the rate of radical production in the aqueous phase, V_p the total volume of the particles and N the number of particles per unit volume of water, k_{tp} is the termination constant in the particles and k_d the desorption constant. Molecular units are applied in Eq. (86) and subsequent equations in this chapter. The rate of desorption of radicals from a particle with n radicals was set equal to nk_d .

Assuming that only monomer radicals formed by chain transfer are able to desorb, it was shown that one had to distinguish between two cases (60). If the monomer radicals which are desorbed become reabsorbed in another particle before adding any monomer in the aqueous phase, k_d may be expressed by:

$$k_d = k_{dm} \frac{k_f [M]_p}{k_{pM} [M]_w + \bar{n} k_d} \quad (87)$$

This expression was also derived by Harada et al. (62) and Nomura et al. (65). In case the monomer radicals add at least one monomer unit in the aqueous phase before reentering another particle,

$$k_d = k_{dm} \frac{k_f [M]_p}{k_{pM} [M]_w + k_{dm}} \quad (88)$$

Experimental results obtained with VC seem to indicate that the value of k_d is given by (58):

$$k_d = k_{dm} \frac{k_f}{k_{pM}} \quad (89)$$

In the above expression k_{dm} is the desorption constant for monomer radicals, k_f is the rate constant for chain transfer to monomer, k_{pM} the propagation rate constant for the monomer radical. It should be kept in mind that in case of vinyl chloride the monomer radical may be a $Cl\cdot$ radical and the chain transfer constant a constant given by Eq. (35). This does not change the mathematical treatment.

From Eq. (80) the value of k_{dm} is given by:

$$k_{dm} = \frac{3D_p D_w}{(aD_p + D_w) r_p^2}$$

where D_p and D_w are the diffusion coefficients for the monomer radical in the polymer particles and the aqueous phase respectively, r_p is the particle radius and a is the distribution coefficient for the monomer radical between the particle and the aqueous phase.

From Eqs. (80), (86) and (89) one obtains:

$$\bar{n} = \frac{1}{N} \rho_i^{\frac{1}{2}} \left(\frac{V_p}{2k_{tp}} + \frac{N^{1/3} V_p^{2/3}}{2k'_d} \right)^{\frac{1}{2}} \quad (90)$$

where k'_d is a constant given by:

$$k'_d = k_f \{ 3(4\pi/3) \}^{2/3} \frac{D_w D_p}{k_{pM} (aD_p + D_w)} \quad (91)$$

where k_{PM} is the propagation constant for the radical formed by the transfer reaction.

The rate of reaction in mol monomer reacted per unit volume of water is accordingly:

$$-dM/dt = k_p [M]_p \bar{n} \bar{n} / N_A = \frac{k_p [M]_p \rho_i^{1/2}}{N_A} \left(\frac{v_p}{2k_{tp}} + \frac{N^{1/3} v_p^{2/3}}{2k_d'} \right) \quad (92)$$

Eq. (92) has been found to describe the emulsion polymerization of VC over a wide range of initiator and emulsifier concentrations.

Friis and Hamielec applied Eq. (92) for the discussion of experimental results obtained with both VC and vinyl acetate (VAc). They pointed out (66) that at the same conversion there seemed to be a discrepancy in the value of k_d' obtained for VC and VAc. The value of k_d' was 120 times higher for VC than for VAc. If we accept that k_{PM} is equal to k_p for both vinyl chloride and vinyl acetate, we should from Eq. (80) expect a value of 6 for the ratio of k_d' between VC and VAc. In this calculation we accepted a value of "a" in Eq. (80) of 35 for VC and 28 for VAc as estimated by Nomura and Harada (62,65) on the assumption that in both cases one had to deal with a monomer radical, that is a monomer molecule from which is abstracted a H· or Cl· radical. The new evidence pointing to that the chain transfer reaction in the case of VC leads to a Cl· radical obviously will imply that the value of "a" in Eq. (80) should have a much lower value for VC, which in turn will lead to a higher rate of desorption. Thus it seems that the results from emulsion polymerization may support the suggestion that the "chain transfer" reaction in the case of VC leads to formation of Cl· radicals. It should be pointed out that the propagation constant for the Cl· radical may have a lower value than that of the growing chain. Also, this would tend to increase the value of k_d' for vinyl chloride.

A general problem in the discussion of the kinetics of emulsion polymerization with water soluble initiators like persulphate is that the radicals originating from the initiator are charged and therefore will be expected to have to add a certain number of monomer units before they are absorbed by the already formed polymer particles, due to an unfavourable equilibrium distribution for small charged radicals between particles and aqueous phase. This point was discussed in the chapter on particle formation.

A reduced rate of capture of radicals by the particles will generally tend to increase the chance of radical termination in the aqueous phase.

The situation is, however, more complex in cases where one has chain transfer processes with formation of small uncharged radicals. In principle one would then have to take into account two different steady state equations, one for the charged radicals originating from the initiator (denoted R_i), and one for those originating from the chain transfer reaction (R_f). Note that R_i and R_f here include all radicals stemming from the initiator and the chain transfer reaction respectively, also those that have added some monomer. The two steady state equations for the reactions in the aqueous phase are as follows:

$$d[R_i]_w/dt = \rho_i - k_{ai} [R_i]_w - 2k_{tw} [R_i]_w - k_{twi} [R_i]_w [R_f]_w = 0 \quad (93)$$

$$d[R_f]_w/dt = \Sigma n k_d' N_n - k_{af} [R_f]_w - 2k_{twf} [R_f]_w^2 - k_{twi} [R_i]_w [R_f]_w = 0 \quad (94)$$

where k_{ai} and k_{af} are the two different absorption constants.

It is expected that the value of k_{aj} will increase with increasing chain length (j) and likewise that uncharged radicals are more readily captured than charged radicals of the same chain length, so that $k_{afj} > k_{aij}$.

To make it complete, the possibility that the termination constants may differ is also included, although this point is probably not essential for the difference in the net rate of absorption of the two types of radicals.

In the discussion below we will first consider the original treatment by Ugelstad and Hansen (61), namely the case that one does not distinguish between various types of radicals. Then is discussed in more detail a recent and probably much more correct treatment first presented by Ugelstad *et al.* (67), where the difference in capture of the two types of radicals is taken into account.

By not distinguishing between the radicals we get:

$$d[R]_w/dt = \rho_i + \Sigma nk_d N_n - k_a [R]_w - 2k_{tw} [R]_w^2 = 0 \quad (95)$$

The rate of adsorption, ρ_A , is given by:

$$\rho_A = k_a [R]_w \quad (96)$$

O'Toole's solution (68) of Smith-Ewart's (69) recursion formulae gives \bar{n} as a function of $\alpha = \rho_a V_p / N^2 k_{tp}$ and $m = k_d V_p / N k_{tp}$.

Ugelstad and Mørk (64) combined these expressions with the equation

$$\rho_A = \rho_i + \Sigma nk_d N_n - 2k_{tw} [R]_w^2 \quad (97)$$

and obtained a solution for \bar{n} as a function of the independent variables

$$\alpha' = \rho_i V_p / N^2 k_{tp}, \quad m = k_d V_p / N k_{tp} \quad \text{and} \quad Y = 2N^2 k_{tp} k_{tw} / (k_a^2 V_p) \quad (98)$$

A comprehensive discussion of the contribution of aqueous phase termination as a function of α' , m and Y , and the effect of these variables on \bar{n} , the average number of radicals per particle, has recently been published (61). In the case that $\bar{n} \ll 0.5$ the value of \bar{n} is given by:

$$\bar{n} = \left[\frac{\rho_i k_a^2 (N k_{tp} + V_p k_d)}{2N^2 (k_a^2 k_d k_{tp} + k_d^2 k_{tw} (N k_{tp} + V_p k_d))} \right]^{\frac{1}{2}} = \left[\alpha' (1+1/m) / (2+Ym(1+m)) \right]^{\frac{1}{2}} \quad (99)$$

Note that in the case that $\bar{n} \ll 0.5$, the order of \bar{n} with respect to α' and thereby ρ_i will always be 0.5 independent of the value of m and Y . In this case the condition for neglecting the aqueous phase termination is $Ym(1+m) \ll 2$, i.e.

$$k_{tw} k_d (1 + k_d V_p / N k_{tp}) \ll k_a^2 / N \quad (100)$$

and Eq. (99) reduces to

$$\bar{n} = \{ (\alpha'/2) (1+1/m) \}^{\frac{1}{2}} = \frac{1}{N} \rho_i^{\frac{1}{2}} \left(\frac{V_p}{2k_{tp}} + \frac{N}{2k_d} \right)^{\frac{1}{2}}$$

which is identical to Eq. (86). The excellent correlation of Eq. (86) with experimental results seems to justify the neglect of aqueous phase termination.

A more general expression for the case that water phase termination is neglected, which is valid for $\bar{n} \leq 0.5$, was also derived (61):

$$\bar{n} = (\alpha'/2) (\frac{1}{2} - 1/m) + \{ (\alpha'/2) (1+1/m) + (\alpha'/2) (\frac{1}{2} + 1/m) \}^{\frac{1}{2}} \quad (101)$$

In some recent papers it has been found that under certain conditions and with some monomers, one may have a reduced rate of absorption of radicals into the particles. This may result from some sort of hindered absorption caused by special emulsifier systems. Such effects have been discussed for the case of VAc by Napper and coworkers (70-73) and for VC by Ugelstad et al. (63) in seed polymerizations. One point should be made clear before the discussion of the effect of a possible reduced rate of capture of radicals by the particles. Napper and coworkers assume that in any case the maximum rate of capture is given by:

$$\rho_{A(\max)} = \rho_i \quad \text{so that} \quad \rho_A \leq \rho_i \quad (102)$$

Consequently they do not take into consideration any reabsorption of radicals which have desorbed from the particles. They do not give any reason for this surprising assumption. Accordingly, they look upon ρ_A as an independent parameter.

Contrary to this Ugelstad *et al.* apply the expression:

$$\rho_A = \rho_i + \Sigma n_k N_n - 2k_{tw} [R]_w^2 \quad (103)$$

This involves that ρ_A may be larger or smaller than ρ_i depending upon the rate of termination in the aqueous phase and the rate of desorption of radicals from the particles, the latter also being dependent upon the rate of termination in the particles. Therefore ρ_A is not generally an independent variable.

As pointed out by Ugelstad *et al.* (61,67) there is one special case where ρ_A is an independent variable, namely in the case that the termination in the aqueous phase is the dominating one. In this case one gets:

$$\rho_A = k_a [R]_w = k_a (\rho_i / 2k_{tw})^{1/2} \quad (104)$$

Note again that in this first treatment we do not distinguish between the two types of radicals.

As long as this condition is fulfilled, the treatment of O'Toole giving \bar{n} as a function of α and m gives a complete description of the system at any value of \bar{n} , giving \bar{n} as a function of the independent variables:

$$\alpha = \rho_A V_p / N^2 k_{tp} = (\rho_i / 2k_{tw})^{1/2} V_p / N^2 k_{tp} \quad \text{and} \quad m = k_d V_p / N k_{tp} \quad (105)$$

As is always the case when $\bar{n} \ll 0.5$ and no distinction is made between various types of radicals, the order of \bar{n} with respect to ρ_i is also in this case equal to 0.5. (As \bar{n} increases above 0.5, the order will approach 0.25. This value is reached at lower values of ρ_i the lower the value of m .) With $\bar{n} \ll 0.5$ and the water phase termination dominating, \bar{n} would be given by:

$$\bar{n} = \frac{1}{N} (\rho_i / 2k_{tw})^{1/2} k_a / k_d \quad (106)$$

As discussed previously (61), this would seem to imply that the rate of polymerization is independent of N . Therefore Eq. (106), which is the other extreme case derived from the general equation (99), is as distinct from Eq. (86) not at all in accordance with experimental results. It is clear that situations where termination in the aqueous phase is dominating will be more likely to be observed the lower the value of k_a and the higher the value of m . Also, an increase in ρ_i will tend to increase the importance of aqueous phase termination.

Quite recently Ugelstad *et al.* (67) pointed out that the above treatment, where the two types of radicals, the charged and uncharged, are considered equal with respect to their chance of absorption, is unlikely to be true. Ugelstad also suggested a kinetic model where the difference in the type of radical was taken into account. One may assume that uncharged radicals will travel forth and back between the particles with a certain chance of being terminated, but that they will not at all terminate in the aqueous phase. This is quite likely to be true as the uncharged radicals stemming from the chain transfer reaction will be much more likely to be absorbed in the particles without having to add monomer in the aqueous phase. VC may be an exceptional case because the radical formed by the chain transfer process may possibly be a $Cl\cdot$ radical with a relatively high water solubility. Also in this case, however, addition of only one monomer unit will suffice to make the particle a much more favourable residence for the radical. The charged radicals originating from the initiator will be hindered in being absorbed by the particles until they have grown to a certain chain length in the aqueous phase. They may therefore to a certain degree terminate in the aqueous phase but do so only by reaction with themselves.

Restricting ourselves to systems consisting of particles with zero, one and two radicals, we have the steady state situations:

$$dN_1/dt = \rho_{Ai} N_0/N - 2k_d N_1^2/N + 4k_d N_2 N_0/N = 0 \quad (107)$$

$$dN_2/dt = \rho_{Ai} N_1/N + k_d N_1^2/N - 2k_d N_2 N_0/N - 2(k_{tp}/v)N_2 = 0 \quad (108)$$

where ρ_{Ai} is the rate of absorption of radicals originating from the initiator. The second term on the right side of Eq. (107) states that if a radical which desorbs from a particle with one radical is reabsorbed in another particle with one radical, 2 N_1 particles are lost. When the radical is reabsorbed in a N_0 particle, the number of N_1 particles is unchanged. The third term states that if a radical is desorbed from a N_2 particle and is reabsorbed in a N_0 particle, 2 N_1 particles are formed. The rate of the process is $2k_d N_2$, therefore the factor 4. If the radical desorbed from a N_2 particle is reabsorbed into a N_1 particle there is obviously no change in the number of N_1 particles. The second term on the right side of Eq. (108) says that a N_2 particle is formed if the radical desorbed from a N_1 particle is reabsorbed in a N_1 particle. The third term states that N_2 particles are only lost when the radical desorbed from a N_2 particle is reabsorbed in a N_0 particle. By reabsorption in a N_1 particle there is no change in the number of N_2 particles. Setting: $\bar{n} = N_0 - N_1 - N_2$ we obtain:

$$dN_1/dt = \rho_{Ai} (1 - 2N_1/N - N_2/N) - 2k_d N_1^2/N + 4k_d N_2 - 4k_d N_1 N_2/N - 4k_d N_2^2/N = 0 \quad (109)$$

$$dN_2/dt = \rho_{Ai} N_1/N + k_d N_1^2/N - 2k_d N_2 + 2k_d N_1 N_2/N + 2k_d N_2^2/N - 2(k_{tp}/v)N_2 = 0 \quad (110)$$

If we look at the case of $\bar{n} \ll 0,5$ which involves that $N_0 \gg N_1 \gg N_2$, Eqs. (109) and (110) may be simplified and it is easily derived that

$$\bar{n} \sim N_1/N = \frac{1}{N} \rho_{Ai}^{\frac{1}{2}} \left(\frac{V_p}{2k_{tp}} + \frac{N}{2k_d} \right)^{\frac{1}{2}} \quad (111)$$

Applying a steady state for radicals R_i in the aqueous phase we have:

$$d[R_i]_w/dt = \rho_i - k_{ai} [R_i]_w - 2k_{twi} [R_i]_w^2 = 0 \quad (112)$$

giving

$$[R_i]_w = \frac{2\rho_i}{(8\rho_i k_{twi} + k_{ai}^2)^{\frac{1}{2}} + k_{ai}} \quad (113)$$

As $\rho_{Ai} = k_{ai} [R_i]_w$ we obtain from Eqs. (111) and (113) when $\bar{n} \ll 0,5$:

$$\bar{n} = \frac{1}{N} \cdot k_{ai}^{\frac{1}{2}} \left(\frac{2\rho_i}{(8\rho_i k_{twi} + k_{ai}^2)^{\frac{1}{2}} + k_{ai}} \right)^{\frac{1}{2}} \left(\frac{V_p}{2k_{tp}} + \frac{N}{2k_d} \right)^{\frac{1}{2}} \quad (114)$$

Eq. (114) may be looked upon as a general equation for the case that $\bar{n} \ll 0,5$ provided the above assumption regarding absorption of the two types of radicals is accepted. The following special case may occur:

If $k_{ai} \ll (8\rho_i k_{twi})^{\frac{1}{2}}$

$$\bar{n} = \frac{1}{N} k_{ai}^{\frac{1}{2}} (\rho_i / 2k_{twi})^{1/4} \left(\frac{V_p}{2k_{tp}} + \frac{N}{2k_d} \right)^{\frac{1}{2}} \quad (115)$$

which represents the lower limit with a strong reduction in the rate of capture of R_i radicals. The order with respect to initiator is in this case 0.25.

If $k_{ai} \gg (8\rho_i k_{twi})^{\frac{1}{2}}$:

$$\bar{n} = \frac{1}{N} \rho_i^{\frac{1}{2}} \left(\frac{V_p}{2k_{tp}} + \frac{N}{2k_d} \right)^{\frac{1}{2}}$$

which is identical to Eq. (86). The above treatment may be looked upon as an alternative and more general method for deriving \bar{n} at low values of the same.

A reduction in the rate of capture of R_1 radicals to the extent that termination of these radicals in the aqueous phase become noticeable would lead to an order with respect to ρ_i lower than 0.5. The good correlation of Eq. (86) with experimental data therefore seems to bring strong support for the mechanism previously outlined. With "ordinary" emulsion systems that do not form a surface layer which reduces k_{a1} considerably, even charged radicals will be almost completely captured by the particles.

The rate of capture of radicals in the particles has been outlined in the chapter on particle formation. The method involves formulation of steady state equations for the aqueous phase concentration of every type of radical, taking into account formation by addition of monomer to a radical one unit smaller, disappearance of the radical by addition of a monomer unit, the rate of capture of the radical and the rate of termination. In the present discussion it is assumed that only radicals originating from the initiator may have a chance of terminating in the aqueous phase.

$$d[R_I]_w/dt = \rho_i - k_{pI}[R_I]_w[M]_w - k_{twI}[R_I]_w[R]_w - k_{aI}[R_I]_w N = 0 \quad (116)$$

$$d[R_1]_w/dt = k_{pI}[R]_w[M]_w - k_p[R_1]_w[M]_w - k_{tw}[R_1]_w[R]_w - k_{a1}[R_1]_w N = 0 \quad (117)$$

$$d[R_j]_w/dt = k_p[R_{j-1}]_w[M]_w - k_p[R_j]_w[M]_w - k_{tw}[R_j]_w[R]_w - k_{aj}[R_j]_w N = 0 \quad (118)$$

where R_I denotes the primary radicals formed by decomposition of the initiator, and R_j is the radicals of chain length j . $[R]_w$ is the total concentration of radicals in the aqueous phase.

By successively expressing $[R_j]$ by $[R_{j-1}]$ one obtains:

$$[R_j]_w = \frac{\rho_i}{A} \cdot \frac{1}{\prod_{j=1}^{j-1} (1 + k_{tw} \frac{[R]_w}{k_p [M]_w} + \frac{k_{aj} N}{k_p [M]_w})} \quad (119)$$

where R_j is the radical produced from the initiator after addition of j monomer units. A is defined by Eq. (73). No distinction between N_0 and N_1 . The total rate of absorption would be given by:

$$\text{rate of absorption} = \sum k_{aj} [R_j] N \quad (120)$$

It is obvious that it is very difficult even to estimate the total rate of absorption relative to the rate of radical production from Eqs. (119) and (120).

Several attempts have been made to simplify the expressions. One method is to state that all radicals below a critical chain length will not be absorbed at all (96). Radicals with a critical chain length j_{cr} will spontaneously be absorbed. Assuming for sake of simplicity that k_{pI} and k_{twI} is equal to k_{tw} , this assumption would lead to:

$$\text{rate of absorption} = \frac{\rho_i}{(1 + (k_{tw}[R]_w/k_p[M]_w)^{j_{cr}})} \quad (121)$$

which means that the fraction of radicals formed that will become absorbed is given by

$$\frac{1}{(1 + k_{tw}[R]_w/k_p[M]_w)^{j_{cr}}} \quad (122)$$

where $[R]_w$ is the concentration of radicals that will not become absorbed but

will terminate in the aqueous phase.

It will be obvious from Eq. (122) that the highest ratio would be encountered in the case that one had a low ratio $k_{tw}/k_p[M]_w$ and moreover had a low value of j_{cr} . Also we will expect that the ratio would be higher the lower the rate of production of radicals, which would mean a lower value of $[R]_w$. One may estimate that in the case of VC with a relatively high value of $k_p[M]_w$ there will usually be a relatively small degree of termination in the aqueous phase in case one does not have any specific hindrance of absorption at the surface of the particles.

It will appear, however, from the above discussion that one should bear in mind that a high initiator concentration will increase the chance of termination in the aqueous phase. If one want to prevent the formation of the small molecules resulting from termination in the aqueous phase, it might be preferable to use initiators which even if they are water soluble, give radicals which are not charged or, if they are charged, in themselves are of a nature (so large) that they will be absorbed as such or after addition of a small number of monomer molecules.

3.3. Seed polymerization

Seed processes are very often applied in PVC latex production, especially when preparing relatively large particles. Also it has proved a useful tool in the study of the kinetics and mechanism of the polymerization. This has not been restricted to VC emulsion polymerization but applies to emulsion polymerization in general. Problems which are studied by seeded polymerizations include attempts to study the effective rate of absorption of radicals into the particles, the effect of specific emulsifier systems on the absorption rate and studies of competitive growth of seed particles of different size.

Attempts on measurement of the rate of absorption of radicals into the particles have been connected with investigations on the approach to the steady state value of \bar{n} .

It is in itself obvious that in seeded polymerizations, the time needed to establish a steady state value of \bar{n} may be increased almost at will by applying a large number of seed particles and/or a sufficiently low concentration of initiator. It is important to note that this form of non steady state is a different problem from that discussed by Gardon (74,75) which involved the possibility that one during an ordinary polymerization possibly would not be able to establish the steady state value of \bar{n} corresponding to the steadily growing value of the particle volume.

Also, in the non steady state treatment of seed polymerization one might preferably distinguish between two different models, one with no distinction between the radicals and one where R_{ij} radicals and R_{fj} radicals are treated separately and where R_{ij} radicals are subject to hindered absorption.

As discussed by Ugelstad and Hansen (61) one may in the first case express N_1 and N_2 as a function of time and the parameters ρ_A , k_d and k_{tp} at low values of $\bar{n} < 0.5$ from the non steady state equations:

$$dN_1/dt = \rho_A(N-N_1)/N - \rho_A N_1/N - k_d N_1 \quad (123)$$

$$dN_2/dt = \rho_A N_1/N - 2k_d N_2 - 2(k_{tp}/v)N_2 \quad (124)$$

which gives:

$$N_1 = [\rho_A/(k_d+2\rho_A/N)] \{1 - \exp[-(k_d+2\rho_A/N)t]\} \quad (125)$$

$$N_2 = K_1(K_2+K_3) \quad (126)$$

$$\text{where } K_1 = \rho_A^2 / [N(k_d+2\rho_A/N)(2k_d+2k_{tp}/v)]$$

$$K_2 = 1 - [(2k_d+2k_{tp}/v)/(k_d+2k_{tp}/v-2\rho_A/N)] \exp(-k_d+2\rho_A/N)t$$

$$K_3 = [(k_d+2\rho_A/N)/(k_d+2k_{tp}/v-2\rho_A/N)] \exp(-2k_d+2k_{tp}/v)t$$

In case that $N_1 \ll N$ the term $2\rho_A N_1/N$ in Eq. (123) may be neglected. It follows that the term $2\rho_A/N$ will then disappear from Eqs. (125) and (126). It will appear that the establishment of the steady state values of N_1 and N_2 will be faster the higher the value of k_d . As pointed out by Ugelstad and Hansen the above equations are only unambiguously applicable in the case that

ρ_A is an independent variable. This will as stated earlier be the case if the termination in the aqueous phase is dominating, in which case $\rho_A = k_a \cdot (\rho_i/2k_{tw})^{1/2}$. As discussed above, in the case of VC such a situation is only likely to be observed in cases with special hindrance of radical absorption by the surface layer. It should be pointed out that the above treatment differs from the treatment of Napper and coworkers on seed polymerization of VAc with hindered absorption. They do a priori accept that ρ_A is an independent variable and also assume that radicals which are desorbed from a particle do not under any circumstances reenter the particles. As stated in previous papers it is the opinion of the present authors that the treatment of Napper is not a general treatment of a case with radical desorption but a mathematical model for a case where k_d represents a first order loss of radicals from the system.

One may also apply a non steady state treatment for the other extreme case of hindered absorption discussed above, namely that the charged radicals R_1 , originating from the initiator, may be noticeably hindered in the absorption and may partly terminate in the aqueous phase, but then only with themselves, while radicals stemming from the chain transfer reaction travel forth and back between the particles without termination in the aqueous phase. In this case we would have to consider the non steady state form of Eqs. (109) and (110). Simplifying these equations by assuming $N_0 \gg N_1 \gg N_2$ we have:

$$dN_1/dt = \rho_{Ai} - 2k_d N_1^2/N + 4k_d N_2 \quad (127)$$

$$dN_2/dt = \rho_{Ai} N_1/N + k_d N_1^2/N - 2k_d N_2 - 2(k_{tp}/v)N_2 \quad (128)$$

which can be integrated numerically.

In case one operates under conditions where the termination in the particles may be considered to take place spontaneously, Eq. (127) reduces to:

$$dN_1/dt = \rho_{Ai} - 2k_d N_1^2/N \quad (129)$$

which gives:

$$\bar{n} = \frac{N_1}{N} = (\rho_{Ai}/2Nk_d)^{1/2} \frac{\exp\{(8\rho_{Ai}k_d/N)^{1/2}t\}-1}{\exp\{(8\rho_{Ai}k_d/N)^{1/2}t\}+1} \quad (130)$$

The value of ρ_{Ai} is generally given by:

$$\rho_{Ai} = \frac{2k_{ai}\rho_i}{(8\rho_i k_{twi} + k_{ai}^2)^{1/2} + k_{ai}} \quad (131)$$

Also in this case the system is unambiguously determined at a given value of k_{ai} as ρ_{Ai} is given by the independent variable ρ_i , the rate of radical production. It will appear from Eq. (130) that the steady state value of \bar{n} should be established faster the higher the value of k_d , and it will appear that we in the case of vinyl acetate and vinyl chloride would expect a very rapid establishment of the steady state value of \bar{n} under ordinary conditions. The reduced rate observed with special types of emulsifiers (70-73) is most likely due to a decrease in the value of ρ_{Ai} . However, it should be pointed out that a reduced rate with a special emulsifier system does not in itself imply non steady state conditions. A lowering of the value of k_a for the first case or k_{ai} for the second case may lead to a drop in the steady state value of \bar{n} even if this value is rapidly established.

It will be seen from Eqs. (130) and (131) that at conditions of strongly hindered radical absorption, so that $\rho_{Ai} = (\rho_i/2k_{twi})^{1/2}$, the steady state value of $\bar{n} = N_1/N$ is given by:

$$\bar{n} = (\rho_i/2k_{twi})^{1/4}/(2Nk_d)^{1/2} \quad (132)$$

i.e. a 0.25 order with respect to ρ_i .

A very much applied method in latex production make use of seeds of different sizes. In this case one has a competitive growth, a problem which was first

studied for styrene (76). A comprehensive theoretical study of competitive seed polymerization for the case of VC has been given by Ugelstad et al. (63). Denoting the two different particle sizes "a" and "b", we may write for the ratio of the differential volume growth (76):

$$\frac{dv_a}{dv_b} = \left(\frac{d_a}{d_b}\right)^X \quad (133)$$

where d_a and d_b are the diameters of the particles. Also the ratio of differential growth in the two particles is simply given by the ratio of the mean number of radicals and monomer concentration in the particles.

$$\frac{dv_a}{dv_b} = \frac{[M]_a \bar{n}_a}{[M]_b \bar{n}_b} \quad (134)$$

In the case of vinyl chloride the monomer concentration is independent of particle size and Eqs. (133) and (134) give:

$$X = \log\left(\frac{\bar{n}_a/\bar{n}_b}{d_a/d_b}\right) \quad (135)$$

The special situation with VC is of course that \bar{n} is dependent not only upon ρ_i and k_{tp}/v , but also upon the rate of desorption. The reader is referred to the original literature for the rather complicated evaluation of this system. It turns out that the value of X for VC experimentally lies between 2 and 3 as is expected from a mechanism involving desorption and reabsorption of radicals. Also it was found that the value of X decreased with increasing initiator concentration as expected from the theoretical calculation. It is interesting to note that in the case of PVC it was found that addition of a given number of large particles to a seed with very small particles lead to a decrease in the rate of polymerization. Calculations show that this is what would be expected in cases where the radicals desorb from the particles, and what is important in relation to the discussion above, are again reabsorbed in the particles.

Desorption and reabsorption of radicals in the particles are also clearly shown in a recent patent (77) where one starts out with seed particles containing a completely water insoluble organic initiator and then add another seed containing no initiator. When monomer is added and polymerization carried out, it turns out that not only do the seed particles with initiator grow, but also the seed particles without initiator grow considerably during the run. This of course strongly supports the assumption that the desorbed radicals are again reabsorbed.

4. EMULSION POLYMERIZATION WITH INITIATION IN MONOMER DROPLETS. THERMODYNAMIC TREATMENT OF FORMATION AND STABILITY

Latexes with relatively large particles may be obtained by initiation in monomer droplets. A common method to achieve this is the so-called micro suspension method where one homogenize the monomer with water and emulsifier, using an oil soluble initiator. Other methods where one do not at all homogenize the monomer but prepare fine dispersions of the monomer by other means have been described in a series of papers by Ugelstad et al. The micro suspension method as well as the other methods have certain thermodynamic principles in common. These principles, which concern mixtures of monomer, low molecular weight water insoluble compounds and polymer and transport between phases have been treated in several papers by the present authors (67,78-80). A review of these papers have recently been published (81).

In the authors' opinion these principles are of great and general interest in the field of VC polymerization in emulsion, micro suspension and suspension polymerization. Therefore a relatively detailed description of these principles are given below.

Consider a system of three compounds "1", "2" and "3" which exist in a phase x consisting of emulsion droplets of radius r_x . If one chooses pure "1" in a bulk state as the reference state one has for the partial molar free energy of mixing for compound 1 $= \Delta \bar{G}_{1x}^P = (\delta \Delta G_x / \delta N_1)_{TPN_1} = \Delta \bar{G}_{1x}^P + 2\bar{V}_{1M} \gamma / r_x$ where $\Delta \bar{G}_{1x}^P$ refers to a phase x with $r_x = \infty$ (plane surface).

$$\Delta\bar{G}_{1x} = RT(\ln\phi_{1x} + (1-j_1/j_2)\phi_{2x} + (1-j_1/j_3)\phi_{3x} + \phi_{2x}^2\chi_{12} + \phi_{3x}^2\chi_{13} + \phi_{2x}\phi_{3x}[\chi_{12} + \chi_{13} - (j_1/j_2)\chi_{23}]) + 2\bar{V}_{1M}\gamma/r_x RT \quad (136)$$

where ϕ are volume fractions, j_1 , j_2 and j_3 the number of segments in the three components, χ_{12} and χ_{13} are interaction energy per mol of "1" with compound 2 and 3 respectively, χ_{23} the interaction energy per mol of 2 with compound 3, \bar{V}_{1M} the partial molar volume of "1" and γ the interfacial energy. Note that j_1/j_2 are equal to the ratios of molar volumes, $j_1/j_2 = \bar{V}_{1M}/\bar{V}_{2M}$, $j_1/j_3 = \bar{V}_{1M}/\bar{V}_{3M}$. Eq. (136) may be applied in calculation of transport of "1" between phases and of possible semi equilibrium distribution between phases in various cases of interest in emulsions and suspensions. The driving free energy for transport of compound 1 from phase b to phase a is $\Delta\bar{G}_{1b} - \Delta\bar{G}_{1a}$. With equal composition of the phases one will initially have:

$$\Delta\bar{G}_{1b} - \Delta\bar{G}_{1a} = [2\bar{V}_{1M}\gamma(\frac{1}{r_b} - \frac{1}{r_a})] \quad (137)$$

As a first case one may look upon a bidisperse system of droplets of pure "1" with droplet radii r_a and r_b , $r_b < r_a$. In this case the composition of the droplets will not change with time. If the solubility of "1" in the continuous phase, say water is low and one may set the activity in water proportional to concentration, one obtains from Eq. (136) the Kelvin equation $C_{1x} = C_{1\infty} \times \exp(2\bar{V}_{1M}\gamma/r_x RT)$ where $C_{1\infty}$ and C_{1x} are concentrations of "1" in water in equilibrium with pure 1 in bulk (plane surface) and in droplets of radius r_x respectively.

Higuchi and Misra (82) discussed the kinetics of transport of "1" from b to a for such systems. The rate was expressed by the change in the radius of droplets b with time and was derived to be:

$$-dr_b/dt = \frac{DC_{1\infty}K}{d_1 r_b^2} \frac{N_a(r_a - r_b)}{N_a r_a + N_b r_b} \quad (138)$$

where $K = 2\bar{V}_{1M}\gamma/RT$, d_1 is the density of "1", D is the diffusion constant of "1" in the continuous phase and N_a and N_b are the number of droplets with radius a and b respectively. It will appear that the rate of degradation is directly proportional to the solubility of "1" in the aqueous phase. The rate of change in the radius of the small droplets expressed as $-dr_b/r_b$ is inversely proportional to the cube of r_b when $r_a \gg r_b$.

Hallworth *et al.* (83) and Davies *et al.* (84) compared the stability of emulsions of a number of different compounds and found that the stability increased with decreasing water solubility in accordance with Eq. (138). The system would kinetically be "completely" stable in case "1" was "completely" insoluble in water. Note that we in the present discussion of stability of emulsions assume that the droplets are stabilized towards degradation by flocculation and coalescence.

Vinyl chloride has a solubility in water of about 6 g per dm³. From Eq. (138) it is easily calculated that a heterodisperse emulsion of vinyl chloride with droplets in the micron and submicron range will rapidly degrade by diffusion.

Higuchi and Misra also suggested that addition of even small quantities of a highly water insoluble compound to a slightly water soluble compound before the preparation of the aqueous emulsion of the mixture would result in a stabilization of the emulsion, as the rate of degradation will be determined by the diffusion rate of the compound with the lowest water solubility. This prediction has been verified experimentally by Hallworth *et al.* (83), Davies *et al.* (84) and Azad *et al.* (85). A thermodynamic treatment of this stabilizing effect was first given by Ugelstad *et al.* (67, 79).

Consider an aqueous emulsion made up by emulsification of a mixture of "1" and "2" forming droplets of radii r_b and r_a where $r_b < r_a$. Obviously, as the composition of all droplets is the same, the presence of "2" will not initially change the driving free energy for transport of "1" from b to a droplets, $\Delta\bar{G}_{1b} - \Delta\bar{G}_{1a}$, which at start will be given by Eq. (137). If the solubility of "2" is comparable to that of "1", one would not experience any

stabilizing effect. If compound "2" has a very low solubility in water, much lower than "1", so that one in the time scale of the experiment may neglect any transport of "2", the transport of "1" from b to a droplets caused by the term $2\bar{V}_{1M}\gamma(1/r_b - 1/r_a)$ in Eq. (139) below will create a counteracting concentration potential as ϕ_{2b} increases and ϕ_{2a} decreases. One will soon reach a semi equilibrium state where $\Delta G_{1b} = \Delta G_{1a}$. From Eq. (136) the semi equilibrium state is determined by:

$$\ln(\phi_{1b}/\phi_{1a}) + (1-j_1/j_2)(\phi_{1b} - \phi_{1a}) + (\phi_{2b}^2 - \phi_{2a}^2)\chi_{12} + 2\bar{V}_{1M}\gamma(1/r_b - 1/r_a)/RT = 0 \quad (139)$$

where ϕ , r and γ are the volume fractions, radii and interfacial tension at equilibrium. Knowing the values of the droplet radii at start, one may from Eq. (139) combined with a material balance calculate the changes taking place in the system until the semi equilibrium state is established. Such calculations verify the experimental results, namely that even small amounts of "2" will lead to that the amount of "1" which will be transported from b to a will be very small.

Two points should be kept in mind when applying Eq. (139). First of all that it represents a semi equilibrium state. The emulsion is in principle thermodynamically unstable. When compound 2 is absolutely insoluble in the continuous phase, the emulsion will be completely kinetically stable after the semi equilibrium state is established. Again it should be stressed that we do not take into account any other processes that may lead to destruction of the emulsion. Even with relatively water insoluble compounds 2 the emulsion will in the course of time degrade by diffusion with a rate which is determined by the diffusion of "2". The necessity of having a highly water insoluble compound 2 for stabilization of vinyl chloride emulsions is an important factor when considering micro suspension polymerization. It is a well known experimental observation that micro suspension processes do not work satisfactorily with relatively water soluble initiators like azo-isobutyronitrile and benzoyl peroxide while for instance the highly water insoluble initiator lauroyl peroxide gives good results. The latter functions both as an initiator and as a water insoluble stabilizer while the other initiators mentioned are to water soluble to have any stabilizing effect.

The second necessary property for a compound 2 to be an effective stabilizer is that it has a relatively low molecular weight. This point is perhaps not so easily visualized from Eq. (139). It is an experimental fact that with a low molecular weight, water insoluble compound 2 like hexadecane, one can prepare stable emulsions of low molecular weight compounds in the micron and submicron range containing 100-500 times more of compound 1 than of "2". This means that the compound 2 due to its low molecular weight behaves quite different from a polymer which, when present as micron sized particles in water, is only capable of absorbing 1-5 times its own volume of low molecular weight compounds. This observation has led to the methods of preparation of emulsions by diffusion and subsequent polymerization by initiation in monomer droplets which is described below.

4.1. Polymerization of monomer emulsions formed by the diffusion process.

If one starts out with an emulsion of pure "2", which is water insoluble, and add to this emulsion a slightly water soluble compound, "1", the latter will diffuse through the water phase and become absorbed in the droplets of "2". The semi equilibrium state between the phases that one has to consider in this case is the one between a phase of droplets containing "2" and "1", and that of the reference state, pure "1" in the bulk state. In accordance with Eq. (136) the equilibrium will be described by (78,81):

$$\ln\phi_1 + (1-j_1/j_2)\phi_2 + \phi_2^2\chi_{12} + 2\bar{V}_{1M}\gamma/rRT = 0 \quad (140)$$

where the terms on the left side represent values for the droplets at equilibrium swelling.

Fig 2 gives the results of calculations based upon Eq. (140) for swelling of droplets of pure "2" with "1". The total volume of "1", V_1 , absorbed per unit volume of "2", V_2 , is plotted as a function of γ/r_0 where $r_0 = r(V_2/V_1 + V_2)^{1/3}$ is the initial radius of the droplets of "2".

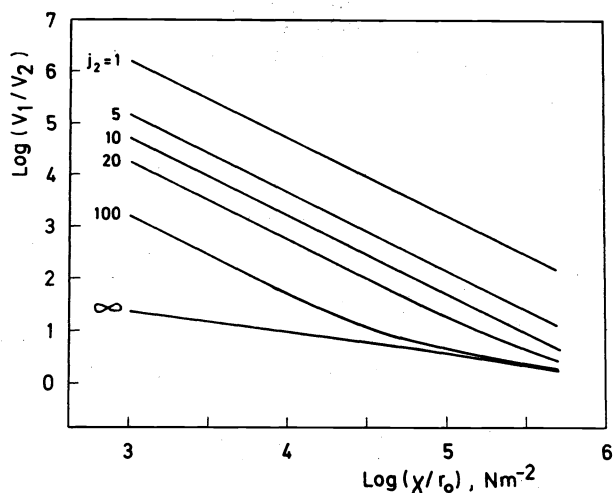


Fig. 2. Swelling capacity as a function of γ/r_0 for various values of $j_2 = \bar{V}_{2M}/\bar{V}_{1M}$ as calculated from Eq. (140). r_0 is the initial radius of the droplets of compound 2, γ = interfacial tension, $\chi = 0.5$, $\bar{V}_{1M} = 10^{-4} \text{ m}^3$, $T = 323 \text{ K}$.

For the sake of simplicity, j_1 is set equal to unity so that $j_2 = \bar{V}_{2M}/\bar{V}_{1M}$. The arbitrarily chosen values for χ_{12} , γ and T are given in the figure. It will appear that Eq. (140) predicts that the swelling capacity of a compound 2 with say $j_2 = 5$ will be enormously much higher than that of a polymer particle with the same value of γ/r_0 , and that the ratio of swelling increases with decreasing values of j_2 and of γ/r_0 . The influence of the value of χ_{12} on the swelling becomes smaller the lower the value of γ/r_0 and the lower the value of j_2 . When j_2 is equal to 5, there is no difference in swelling with $\chi_{12} = 0.5$ and 1.0 before the value of γ/r_0 increases beyond $\sim 10^5 \text{ Nm}^{-2}$.

In applying this method to practical processes, one may use an oil soluble initiator which may be added together with compound 2 in the first homogenizing step. One may, however, also apply water soluble initiators. The fact that one produces large monomer droplets involves that a major part of the emulsifier becomes absorbed on the droplets, leaving little emulsifier in the aqueous phase to facilitate initiation there. All the emulsifier may be added at once with little danger of formation of new particles. Also the droplet size and size distribution may be varied considerably by variation in the conditions of homogenization of compound 2 in the first step.

An interesting question arises when considering the processes taking place inside the droplets of vinyl chloride as the polymerization proceeds. Obviously one will inside the separate droplets have a situation similar to that in suspension and bulk systems.

Separation of small microglobules swollen with monomer and a minor part of compound 2 takes place inside the droplets. The liquid phase within the droplet consists of monomer with a small amount of compound 2 and with negligible amounts of polymer. Note that this situation is different from that which has previously been discussed by the authors (78-81), namely the swelling of polymer particles containing compound 2 with compound 1 with formation of homogeneous particles of the three compounds "1", "2" and polymer "3". The latter case represents a rather simple system as one has a phase of pure "1" which also serves as reference state.

In the present case we start out with a homogeneous mixture of "1" and "2" and obtain droplets consisting of two phases, both of which contain all three components. An adequate thermodynamic discussion of this system would require the use of equations for the partial free energy of mixing for both compound 1 and compound 2. For each compound the reference state is the pure compound in bulk (plane surface). One has for compound 1 at equilibrium between the two phases:

$$\ln\phi_{1L} + (1 - \frac{j_1}{j_2})\phi_{2L} + \phi_{2L}^2\chi_{12} = \ln\phi_{1p} + (1 - \frac{j_1}{j_2})\phi_{2p} + (1 - \frac{j_1}{j_3})\phi_{3p} + \phi_{2p}^2\chi_{12} + \phi_{3p}^2\chi_{13} + \phi_{2p}\phi_{3p}(\chi_{12} + \chi_{13} - \frac{j_1}{j_2}\chi_{23}) + 2\bar{v}_{1M}\gamma/rRT \quad (141)$$

where subscript L refers to the liquid phase and p to the particles (microglobules) within the droplets. Note that the interfacial tension in this equation is that between the particles and the liquid phase inside the droplets, not the interfacial tension between the droplets and the aqueous phase. Also, radius r refers to the microglobules formed inside the droplets. The expression for the equilibrium distribution of compound 2 between the phases will be:

$$\ln\phi_{2L} + (1 - \frac{j_2}{j_1})\phi_{1L} + (\frac{j_2}{j_1})\phi_{1L}^2\chi_{12} = \ln\phi_{2p} + (1 - \frac{j_2}{j_1})\phi_{1p} + (1 - \frac{j_2}{j_3})\phi_{3p} + (\frac{j_2}{j_1})\chi_{12}(\phi_{1p}^2 + \phi_{1p}\phi_{3p}) + \chi_{23}(\phi_{3p}^2 + \phi_{1p}\phi_{3p}) - (\frac{j_2}{j_1})\chi_{13}\phi_{1p}\phi_{3p} + 2\bar{v}_{2M}\gamma/rRT \quad (142)$$

It is assumed that no polymer is present in the liquid phase and Eqs. (141) and (142) together with a material balance allow the calculation of the composition of the two phases. In cases where one applies a compound 2 which is very little soluble in the polymer phase the equation will be very much simplified as one will then have to consider only the partial free energy of "1" and may neglect any content of "2" in the particles:

$$\ln\phi_{1L} + (1 - \frac{j_1}{j_2})\phi_{2L} + \phi_{2L}^2\chi_{12} = \ln\phi_{1p} + (1 - \frac{j_1}{j_3})\phi_{3p} + \phi_{3p}^2\chi_{13} + 2\bar{v}_{1M}\gamma/rRT \quad (143)$$

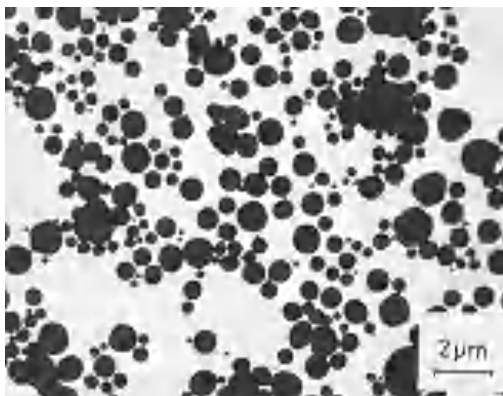


Fig. 3. PVC latex prepared by initiation in monomer droplets. The diffusion process.

In Fig. 3 is given an example of a latex prepared by the method described above. In this special case, 1 part of hexadecane, 5 parts of water and 0.05 parts of emulsifier was homogenized to give a stable emulsion of hexadecane. One hundred parts of water containing 0.5 parts of emulsifier and 100 parts of vinyl chloride were then added. After ordinary stirring for 30 minutes, potassium persulphate was added and the polymerization carried out in 8 hrs at 50 °C to give a latex with 48% solids and with particle diameters in the range 0.3 to 1.2 μm.

Recently Ugelstad et al. (80-81) developed the so-called two step method for preparation of latexes with large particles including monodisperse particles. The method is also applicable for PVC. One starts out with a polymer latex which may or may not be a PVC latex. In the first step there is introduced into the particles a low molecular weight highly water insoluble compound 2 in an amount corresponding to a v:v ratio of 1:1 to 5:1. The particles prepared in the first step contain both "2" and polymer. Because of their high content of "2" these particles have a capacity of absorption of monomer ("1") which is comparable to that of pure compound 2. In case a homogeneous

mixture is formed by the swelling with monomer, the swelling equilibrium will be determined by:

$$\ln\phi_1 + 1 - \frac{j_1}{j_2}\phi_2 + \left(1 - \frac{j_1}{j_3}\right)\phi_3 + \phi_2^2\chi_{12} + \phi_3^2\chi_{13} + \phi_2\phi_3(\chi_{12} + \chi_{13} - \left(\frac{j_1}{j_2}\right)\chi_{23}) + 2\bar{v}_{1M}\gamma/rRT = 0 \quad (144)$$

Calculations based upon Eq. (144) lead to similar curves as those shown in Fig. 2.

Vinyl chloride is added in the next step in a v:v ratio to the particles made in the first step of ca. 100:1 and is rapidly absorbed into the particles. Polymerization is carried out with an oil soluble initiator. It is an essential point in this process that the compound 2 is introduced into the particles in a first step. The reader is referred to recent papers by Ugelstad *et al.* (80,81) for a more detailed discussion of the theory and practice of the two step process.

In Fig. 4 are shown pictures of relatively monodisperse particles prepared by this method.

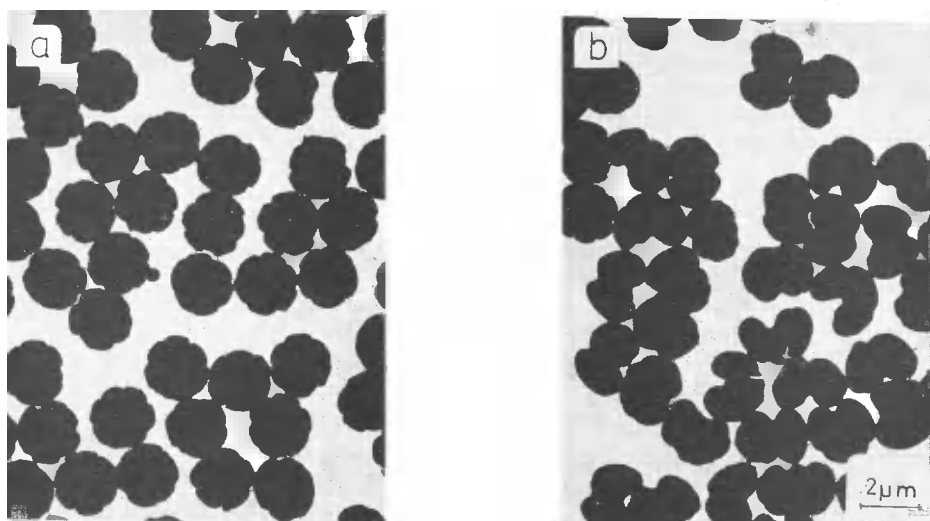


Fig. 4. PVC latex prepared by the two step method.

In these experiments polystyrene is the mother seed which in the first step has swollen with compound 2 and then with VC in an amount 100 times the original volume of polystyrene. The difference in particle shape is brought about by application of different emulsifiers.

4.2. Polymerization of monomer emulsions formed by "spontaneous" emulsification with mixed emulsifier systems.

Ugelstad *et al.* (67,85-88) have in a series of papers described methods whereby a finely dispersed emulsion of monomer could be prepared by moderate stirring. The process involves that one in a first step mix fatty alcohol and ionic emulsifier with water at about 70 °C. A system containing mixed micelles, liquid crystals and also larger crystal structures is then formed. When monomer is added to this water-emulsifier-fatty alcohol system under mild stirring, a monomer emulsion with droplets in the size range 0.2 to 1.5 µm is "spontaneously" formed. The amount of ingredients is about 0.5 parts emulsifier, 1 part fatty alcohol, 100 parts of water in the first step and 90 g of VC in the second step. It is essential for the process that the procedure described above for the formation of the emulsion is followed. The process will not work in case the fatty alcohol is mixed with the monomer on beforehand. It is tempting to ascribe the mechanism of this process to some sort of diffusion process like the one described above. There are, however, certain distinct differences. Most important, the mixed micelles

are certainly much smaller than the droplets of hexadecane formed in the first step in the method described above. Still, the size of the final droplets of monomer are practically the same in both cases. If therefore a diffusion process is involved one must imagine a mechanism where the monomer diffuses to the neighbouring micelles and swell these to a limited degree. These swollen micelles may absorb unswollen micelles from the surroundings and thereby be supplied not only with emulsifier but also with fatty alcohol which in the present case also plays the role as "compound 2". A mechanism following these lines has been suggested by Ugelstad and Fitch (89). Chou et al. (90) discussed several mechanisms for the process which also involved some kind of diffusion of monomer. Another suggested mechanism involves that one in the course of the transfer of fatty alcohol from the micelles to the large droplets of the organic compound intermediately will get a high fatty alcohol concentration in the outer layer of the droplet, leading to a spontaneous emulsification. It seems that a number of questions regarding this process are still unexplained.

It is essential for the process that the fatty alcohol is of a certain minimum chain length, and the process does not work satisfactorily with fatty alcohols of shorter chain length than that of cetyl alcohol, indicating that the fatty alcohol after the emulsification also functions as a "compound 2". As with the diffusion method it is an essential point in the process that one after the preparation of the monomer emulsion has a system where the droplets, because of their large surface, have bound sufficient emulsifier to prevent initiation in the aqueous phase. In judging what type of emulsifier is the best one in the fatty alcohol process one has to take into account two factors which will be illustrated by comparing Na-dodecyl sulphate and Na-hexadecyl sulphate. Na-dodecyl sulphate has the highest CMC, ca. $2 \text{ g/dm}^3 \text{ H}_2\text{O}$ and a little less than this emulsifier concentration may be tolerated in the aqueous phase. However, adsorption of this emulsifier on the droplets is not especially high, and what is important, the adsorption is not effected by the fatty alcohol. Na-hexadecyl sulphate has a much lower CMC, ca. $0.2 \text{ g/dm}^3 \text{ H}_2\text{O}$. However, as shown by Hallworth and Careless (83), and as is also easily verified in experiments on preparation of emulsions of the type described above, the fatty alcohol has a marked effect on the efficiency of the adsorption of this emulsifier, increasing the amount of emulsifier adsorbed per unit surface of the droplets. Therefore, better results are usually obtained with Na-hexadecyl sulphate than with Na-dodecyl sulphate.

In Fig. 5 are shown latexes prepared by fatty alcohol emulsifier systems.

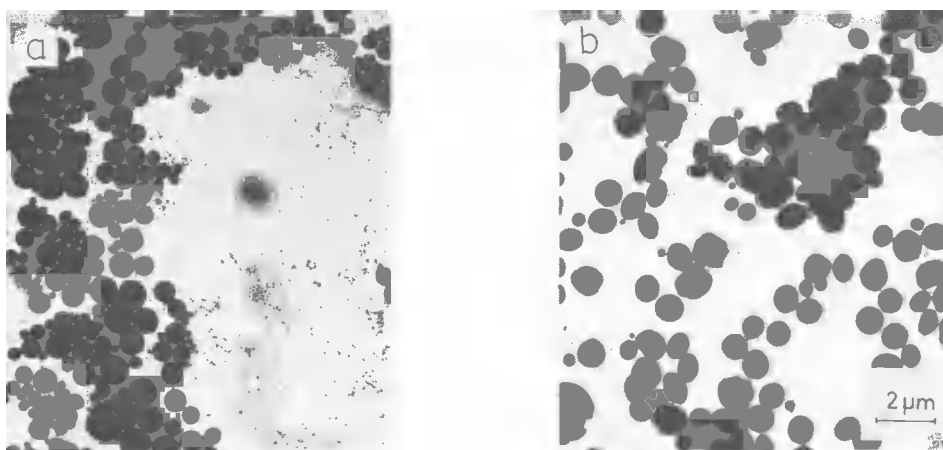


Fig. 5. PVC latex made by initiation in monomer droplets. Monomer emulsion made by spontaneous emulsification with fatty alcohol - anion, i.e. emulsifier mixtures.
 a) Cetyl alcohol - sodium lauryl sulphate
 b) Cetyl alcohol - sodium cetyl sulphate

In 5a one has in addition to the large particles got a considerable formation of new particles initiated in the aqueous phase, leading to latex instability. Fig. 5b shows a latex with Na-hexadecyl sulphate and cetyl alcohol. The latex is free from new particles and much more stable. In both cases potassium persulphate has been used as initiator.

5. POLYMERIZATION AT SUB SATURATION PRESSURE

Polymerization at sub saturation pressures was used by Ugelstad *et al.* (58) as a method of studying the gel effect in VC emulsion polymerization. After a certain conversion, the VC pressure was dropped below the saturation pressure and the polymerization continued, keeping the pressure constant by supplying VC from a second vessel kept at a temperature below that of the reaction vessel. The rate went through a maximum as the pressure decreased. The increased rate was supposed to be due to a reduction in the value of k_{tp} and possibly also in k_d . Liegois (91) came to similar conclusions in his study of kinetic models for emulsion polymerization of VC. He found that the molecular weight decreased with decreasing pressure. Allsopp (92) noted that when suspension polymerization of VC was continued at sub saturation pressures, the porosity of the material decreased and a more dense material was formed.

Sørvik *et al.* (93,94) made a comprehensive study of polymerization at sub saturation pressures in aqueous dispersions. They applied PVC particles prepared by suspension and emulsion polymerization as seed. Both monomer soluble and water soluble initiators were used. The monomer soluble initiator was added in the form of an aqueous dispersion stabilized with emulsifier. It is interesting to note that all the initiator apparently was captured by the seed, no new particles were formed and the reaction took place solely in the seed particles, comprised its total structure and reduced the porosity. At pressures near saturation, the rate and the molecular weight increased with conversion. As the pressure was further reduced the polymerization rate decreased, the amount of low molecular weight polymer increased and considerable long chain branching occurred. With emulsion PVC as seed, application of oil soluble initiator led to crust formation. Water soluble initiator worked much better in the latter case but they did not experience any maximum in rate at reduced pressures.

In accordance with the theory of swelling outlined above, one might also reduce the concentration of monomer in seed particles by addition of a water insoluble compound 2 to the monomer. Compound 2, if highly water insoluble, will not diffuse through the water phase to become absorbed by the particles as the reaction proceeds, but will remain as a separate phase containing monomer. The resulting decrease in the concentration of monomer in the particles will be more pronounced the higher the concentration of compound 2. Therefore one may with a given amount of monomer and compound 2 expect that the degree of reduction in the concentration in the particles will increase as the reaction proceeds, as long as one operates in Interval II.

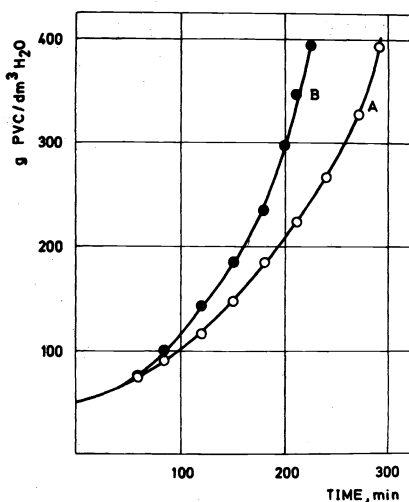


Fig. 6. Effect of hexadecane (HD) added to the monomer on the rate of seeded emulsion polymerization of VC.

$|K_2S_2O_8| = 2.7 \times 10^{-3}$ mole dm^{-3} H_2O .

Seed: 3.6×10^{16} part. dm^{-3} H_2O .

A: Without HD. B: 20% HD.

In Fig. 6 is shown an example of the effect of addition of "2", in this case hexadecane, to the monomer in a seed polymerization. The predicted increase in rate which, as explained above, is most probably ascribed to a decrease in the concentration of monomer in the particles, is clearly observed. The equilibrium swelling of the polymer particles will in this case be given by: Eg. (143) as we here have an equilibrium between a phase of monomer 1 and "2" and a phase of polymer 3 and "1".

LIST OF SYMBOLS

- a - particle radius
- a - distribution coefficient for radicals between particles and water
- a_s - specific surface area per molecule of emulsifier
- A - Hamaker constant
- A - weight ratio of monomer to polymer in particles
- A_p - total particle surface area
- c - concentration of electrolyte
- $C_{1\infty}$ - concentration of component 1 in the aqueous phase in equilibrium with a plane surface of pure "1"
- d_a - diameter of "a" particles
- d_b - diameter of "b" particles
- d_m - density of monomer
- d_p - density of polymer
- D_L - diffusion constant for radicals in the liquid phase
- D_m^p - effective diffusion constant for desorption of monomer radicals
- D_p^p - diffusion constant for radicals in particles
- D_w - diffusion constant for radicals in water
- e - electron charge
- $\Delta \bar{G}_{ix}$ - Partial molar free energy of mixing for component i in phase x

$$= (\delta \Delta G_x / \delta N_i)_{PTN_j} = \Delta \bar{G}_{ix}^p + 2\bar{v}_{iM} \gamma / r_x$$
- $\Delta \bar{G}_{ix}^p$ - partial molar free energy of mixing of compound i in a phase x where $r_x = \infty$ (plane surface)
- H - distance between particles
- I - total number of moles of initiator
- $[I]_L$ - concentration of initiator in the liquid phase
- $[I]_p$ - concentration of initiator in the polymer phase
- j - chain length
- j_{cr} - critical chain length where precipitation of particles take place
- j_{cr} - critical chain length where radical becomes irreversibly absorbed
- j_{icr} - critical chain length of a radical originating from the initiator
- j_{Mcr} - the same for a radical originating from the chain transfer reaction
- j_1 - number of segments in component 1
- j_2 - number of segments in component 2
- j_3 - number of segments in component 3 (polymer)
- k_a - absorption constant for radicals. Note that in some equations it includes the particle number, in others not.
- k_{af} - absorption constant for radicals originating from chain transfer
- k_{ai} - absorption constant for radicals originating from initiator
- k_{aijo} - absorption constant in an unactive particle for the radicals of chain length j, originating from initiator
- k_{aijl} - absorption constant in an active particle for radicals of chain length j, originating from initiator
- k_{ai} - absorption constant for primary initiator radicals
- k_{aiO} - absorption constant for primary initiator radicals in an unactive particle
- k_{aiI} - absorption constant for primary initiator radicals in an active particle
- k_{aMO} - absorption constant in an unactive particle for the radical formed by chain transfer
- k_{aMI} - absorption constant in an active particle for radical formed by chain transfer
- k_{aMjo} - absorption constant in an unactive particle for radicals of chain length j originating from the radical formed by chain transfer
- k_{aMjl} - absorption constant in an active particle for radical of chain length j, originating from radical formed by chain transfer
- k_{aprec} - absorption constant of single precipitated radicals in the liquid phase
- k_{as} - absorption constant of radicals dissolved in the liquid phase
- k_d - desorption constant

k_{dc}	- desorption constant = $k_d \cdot V_D$
k_{dm}	- desorption constant for monomer radicals
k_f	- experimental chain transfer constant
k_i	- rate constant for decomposition of initiator
k_p	- propagation constant
k_p^1	- propagation constant defined by Eq. (3)
k_p^2	- propagation constant defined by Eq. (4)
k_{pH}	- propagation constant for the head to head addition
k_{pI}	- propagation constant for primary initiator radicals
k_{pM}	- propagation constant for the radical formed by chain transfer
k_{tL}	- termination constant in the liquid phase
k_{tP}	- termination constant in the polymer phase
k_{tw}	- termination constant in the aqueous phase
k_{twf}	- termination constant in the aqueous phase of radicals originating from chain transfer
k_{twi}	- termination constant in the aqueous phase of radicals originating from the initiator
k_{twI}	- termination constant in the aqueous phase of a primary initiator radical with other radicals
k_{twM}	- termination constant in the aqueous phase of a radical formed by the chain transfer with other radicals
m	- $k_d V_D / N k_{tp}$
M	- total number of moles of monomer
M_L	- number of moles of monomer in the liquid phase
M_p	- number of moles of monomer in the polymer phase
$[M]$	- concentration of monomer
$[M]^0$	- initial concentration of monomer
$[M]_L$	- concentration of monomer in the liquid phase
$[M]_P$	- concentration of monomer in the polymer phase
$[M]_w$	- concentration of monomer in the aqueous phase
n	- average number of radicals per particle
N	- total number of particles
N_a	- number of "a" droplets
N_A	- Avogadro's number
N_b	- number of "b" droplets
N_M	- number of micelles
N_{M0}	- number of micelles at start
N_n	- number of particles containing n radicals
P_L	- number of moles of monomer converted to polymer in the liquid phase
P_p	- number of moles of monomer converted to polymer in the polymer phase
Q	- parameter defined by $Q = [R]_p / [R]_L$
r_a	- radius of "a" droplets
r_b	- radius of "b" droplets
r_M	- radius of micelles
r_p	- radius of polymer particles
$[R]$	- concentration of radicals
$[R]_L$	- concentration of radicals in the liquid phase
$[R]_{Lprec}$	- concentration of single precipitated radicals in the liquid phase
$[R]_{LS}$	- concentration of radicals dissolved in the liquid phase
$[R]_P$	- concentration of radicals in the polymer phase
$[R]_w$	- concentration of radicals in the aqueous phase
$[R]_{fw}$	- the aqueous phase concentration of radicals originating from chain transfer reaction
$[R]_{iw}$	- the aqueous phase concentration of radicals originating from the initiator
$[R]_{ij}w$	- the aqueous phase concentration of radicals of chain length j originating from the initiator
$[R]_{Iw}$	- the aqueous phase concentration of primary initiator radicals
$[R]_{jw}$	- the aqueous phase concentration of radicals with chain length j
$[R]_{Mw}$	- the aqueous phase concentration of the radical formed by the chain transfer
$[R]_{Mj}w$	- the aqueous phase concentration of the radicals of chain length j originating from the chain transfer reaction
R	- distance between particle centers
S_0	- initial amount of emulsifier present as micelles

U_L	- fraction of polymer in the liquid phase
U_P	- fraction of polymer in the polymer phase
v	- particle volume
v'	- initial volume of primary particles
v_L^m	- partial molar volume of monomer in the liquid phase
v_L^p	- particle molar volume per monomer unit of reacted monomer in the liquid phase
v_P^m	- partial molar volume of monomer in the polymer phase
v_P^p	- partial molar volume per monomer unit of reacted monomer in the polymer phase
v^0	- volume at start
V_1	- total volume of component 1
V_2	- total volume of component 2
\bar{V}_{1M}	- partial molar volume of component 1
\bar{V}_{2M}	- partial molar volume of component 2
\bar{V}_{3M}	- partial molar volume of component 3
V_A	- Van der Waal's energy of attraction
V_L	- volume of the liquid phase
V_P	- volume of the polymer phase
V_R	- repulsive energy
V_T	- total interaction energy
Y	- $2N^2k_{tp}k_{tw}/(k_a^2 v_p)$
z	- charge of the electrolyte ions
z	- order of particle number with respect to S_0
Z	- number of chloro methyl groups per monomer unit
α	- $\rho_A v_p / N^2 k_{tp}$
α'	- $\rho_i v_p / N^2 k_{tp}$
γ	- interfacial tension
δ	- efficiency factor for absorption in a micelle relative to a particle of the same size
ϵ	- permittivity
ζ	- zeta potential
κ	- the Debye-Hückel constant
v_L	- ratio of the partial molar volume of polymer and monomer in the liquid phase
v_P	- ratio of the molar volume of polymer and monomer in the polymer phase
ρ_A	- total rate of absorption of radicals
ρ_{Ai}	- rate of absorption of radicals originating from the initiator
ρ_i	- rate of radical formation from initiator
ρ_{iL}	- rate of radical formation in the liquid phase
ρ_{iP}	- rate of radical formation in the polymer phase
τ_c	- critical conversion
ϕ_{jx}	- volume fraction of component j in phase x
ϕ_m	- volume fraction of monomer in the polymer phase
ϕ_m^*	- volume fraction at the site of reaction in the liquid phase
ϕ_{mp}	- volume fraction of monomer in primary particles
ϕ_p	- volume fraction of polymer in the polymer phase
χ_{12}	- interaction energy per mole of compound 1 with compound 2
χ_{13}	- interaction energy per mole of compound 1 with compound 3
χ_{23}	- interaction energy per mol of compound 2 with compound 3
ψ_0	- surface potential

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