

On the Modeling of Bulk Poly(vinyl Chloride) Reactors

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Synopsis

A detailed mechanism and corresponding mathematical model is suggested for bulk PVC production. The model is more detailed and general than earlier models and is consistent with reported experimental data as well as new experimental evidence presented here. Equations are presented and computations performed showing the evolution of the particle size distribution of the polymer beads. The predicted particle size distributions are in reasonable agreement with the limited experimental data available.

INTRODUCTION

The polymerization of poly(vinyl chloride) (PVC) in emulsion, suspension, or bulk heterogeneous reactors is not a well-understood process. A fair amount of data on conversions, molecular weights, etc., has been reported but much of it appears to be in conflict. In addition, there have been proposed a number of mechanisms and models for these processes, many of which are also in conflict. It is our feeling that much of the disparity in the reported studies is due to an oversimplified view of the process. As in the case of blind men describing elephants, a large number of workers can have a good "local" view of the process, but if each is seeing a different effect predominate because of the operating conditions chosen, then none has an overall view of the process—and yet all may be correct in what they report.

In order to suggest a broader modeling framework for these processes, we shall discuss in this paper the behavior of *bulk* PVC reactors. First, we shall discuss the previous mechanisms and models suggested and review the reported experimental results. Then, we shall postulate a very general and detailed theory of bulk polymerization which can be supported by the experimental evidence. Finally, we shall perform calculations based on the proposed mechanism to demonstrate the quantitative predictions possible and to compare with available experimental data.

Before going further, let us describe in physical terms the observed behavior of PVC polymerized in bulk. If one begins the polymerization by adding a free radical-producing initiator, the monomer quickly becomes turbid due to the presence of PVC particles precipitating from the monomer. These particles will coalesce with frequency dependent on their size and the intensity of agita-

tion. As the polymerization progresses further, the mix assumes the consistency of a paste which slowly changes to a powder. Although this powder is dry in appearance, the monomer conversion at this point can be 30% to 70% (depending on reaction conditions) so that a large fraction of the monomer remains unconverted within this powder. Therefore, the last part of the polymerization occurs inside the polymer beads making up the powder.

REVIEW OF PREVIOUS MODELS

A number of mechanisms and mathematical models have been proposed for PVC bulk polymerization. In this section, we shall review and contrast the main features of these models.

Bengough and Norrish¹ formulated a model by proposing a kinetic scheme for heterogeneous bulk polymerization and then comparing the experimental results with the theoretical calculations based on the model. They observed a period of acceleration (over the first 40% of conversion) that was attributed to the co-catalytic effect of dead PVC and the initiator benzoyl peroxide. This co-catalytic effect was assumed due to chain transfer between growing polymer chains and molecules of dead polymer which produce free radicals in the surface of polymer and constitute stabilized centers of polymer growth. The reactivated polymer then continues to react with monomer until the chain is terminated by chain transfer with monomer, thus producing mobile free radicals. The mobile radicals reenter the liquid phase and terminate eventually by reaction with other radicals. The rate of polymerization was assumed proportional to the $2/3$ power of the weight of polymer because the catalytic effect would occur only at the external surface of the solid polymer. They also proposed that the rate of polymerization had an initiator dependence of $I^{1/2}$. They also differentiated between the autoacceleration effect which occurs at the beginning of the reaction and the gel effect which occurs at the later stages of the reaction and was assumed due to the increase in viscosity at that time.

Breitenbach and Schindler² proposed a model in which they postulate that precipitated polymer particles are swollen by the monomer and growing radicals arise inside them by both initiation in the particles as well as by entrance of chain radicals from the liquid monomeric phase. These trapped radicals do not change the propagation rate but reduce the overall termination rate giving rise to an autoacceleration effect. This reduction in termination rate is represented by the equation

$$(K_t)_{\text{overall}} = K_t/1 + ac \quad (1)$$

where c = degree of conversion and a = constant. By assuming (i) that the propagation rates in the liquid phase, in the polymer particles, and of monomeric radicals are the same, and (ii) that the velocity constants for chain transfer to monomer in the liquid phase and in the polymer particles are the same, they have arrived at an equation which shows that the degree of conversion is proportional to monomer concentration M and to the $1/2$ power of the initiator concentration in the initial stages, but to M^2 and I in later stages of the reaction. Thus, the degree of conversion consists of two terms, one of which is characteristic of homogeneous polymerization and gives rise to 0.5 order in initiator and the

second, which may be ascribed to the heterogeneous polymerization which depends on the initiator concentration to the power of 1. They conclude that the overall reaction order in the initiator should be between 0.5 and 1.0, depending on the relative importance of the two terms. These hypotheses are supported by data showing that the reaction rate experimentally determined at short reaction times depends on the initiator concentration to the power of 0.5.

Magat³ has made an attempt to apply the usual kinetic scheme (initiation, propagation, and mutual termination) to heterogeneous polymerization (bulk) by assuming that the quasi-steady state hypothesis cannot be applied in this case because of the strong decrease in termination rate. He also assumes that there are no chain transfer reactions to the monomer or polymer. Also, the termination constants are assumed to be low and equal in the liquid phase and in the polymer particles.

Mickley et al.⁴ studied the polymerization of PVC in the presence of a solvent as well as in bulk. For polymerization in the bulk, these authors give an expression similar to that given by Breitenbach and Schindler² for the rate of polymerization:

$$R_p = k M I^{1/2} + f(P) I^{1/2}. \quad (2)$$

They argue that the first term is the contribution of homogeneous polymerization taking place simultaneously with heterogeneous polymerization represented by the second term. They observe that $f(P)$ is proportional to P at low conversions and to $P^{2/3}$ at high conversions (this latter observation is in agreement with the work of Bengough and Norrish¹). According to these authors, the homogeneous component arises from the reaction of polymer radicals before they reach a critical size for coiling into primary polymer particles. Such particles will be very small and flocculate with others rapidly at a rate governed essentially by their rate of collision. By application of Von Smoluchowski's treatment of particle flocculation, it was postulated that virtually every particle was incorporated into a larger particle as soon as it is formed. Also, these small particles will sediment extremely slowly, and the frequency of collision between particles of very different sizes is much higher than that between aggregates of similar sizes. Large particle clusters thus tend to scavenge the primary particles as they are produced. The system may be regarded as a precipitation process in which the primary particles, as they are formed, deposit on the larger particles present, which remain constant in number but increase in size. These authors assume that radical activity is trapped within a primary particle when it is incorporated into a larger particle; or, if radical activity is transferred into particles from the liquid phase, a polymer concentration-dependent contribution to the polymerization rate can be expected. When the particles are small enough for the primary particles comprising them to be readily accessible to monomer or radicals actively present in solutions, a first-order rate dependence on polymer concentration is to be anticipated. However, when the agglomerates reach dimensions such that only the regions in the outer shell have effective access to the solution, a $2/3$ power dependence (because of proportionality to surface area) will be found.

Thus, the main features of the mechanism proposed by these authors⁴ include (a) normal liquid phase kinetics, (b) radical occlusion by coalescence, (c) shallow penetration of radical activity into particles, (d) negligible mutual termination in

particles, (e) escape of trapped radical activity by monomer transfer, and (f) limitation of short chain radical escape by propagation and transfer to polymer.

Cotman et al.⁵ studied bulk polymerization techniques as well as particle properties to ascertain what control the latter exercise on rates of polymerization. In their view, free radicals precipitate on or within agglomerates of partially swollen dead polymer. The nature of precipitated PVC changes with conversion. At the onset of polymerization, particles insoluble in monomer are produced. At very low conversions (<1%), particles grow into agglomerate units which grow further in size by deposition of polymer particles. The rate of agglomeration of particles, quite high at low conversions, proceeds throughout the latter parts of the polymerization at a less rapid rate. Polymerization on solid polymer is characterized by autoacceleration rates due to a progressive reduction in termination rate. This reduction is due to the fact that as the reaction progresses and more polymer accumulates, there is a decrease in the mobility of free radicals produced by chain transfer and thus a lower probability of termination of growing chains.

At very low conversion, a decrease in polymerization rate occurs before autoacceleration sets in. This is explained by rapid particle coalescence which reduces the surface area and increases the termination rate by confining particles to a limited volume in close proximity. The different kinetic steps which could take place in bulk polymerization, as proposed by these authors, are (a) initiation, propagation, and termination of mobile soluble radicals; (b) chain transfer to monomer (i) by mobile radicals or (ii) by surface-entrapped free radicals on polymer; (c) sticking of mobile free radicals on polymer (i.e., reactivation of dead polymer); (d) propagation of radicals on polymer; (e) termination by (i) reaction of mobile free radical with "stuck" free radical or (ii) mutual reaction of two "stuck" free radicals.

Due to a lower mobility of the stuck free radicals, these termination steps are slower as compared to the termination of mobile soluble radicals. Also, these authors⁵ indicate that the assumption of a "pseudo steady state" and use of single valued rate constants is not valid.

Talamini et al.⁶ have studied both bulk and suspension polymerization and report them to be kinetically equivalent. Their modeling equations derived for the polymerizing system are based on the assumption that the overall process is the sum of two reactions, both obeying the usual kinetic law valid for homogeneous free radical polymerization. In addition, they assume that the kinetic constants do not change during the whole polymerization process—quite parallel to the assumptions introduced by Magat³ in his model.

The modeling equation for monomer conversion developed by Talamini et al.⁶ takes the form of an infinite series and is quite similar to the one proposed by Breitenbach and Schindler² if we consider only the first two terms of the series. This expression may also fit an observed reaction order higher than 0.5 with respect to initiator, because the equation for degree of conversion is formed by a sum of terms with initiator concentrations raised to power 0.5, 1.0, 1.5, etc.

Abdel-Alim and Hamielec⁷ propose a model for bulk polymerization of vinyl chloride which accurately predicts conversion and MWD over a wide range. Their model is essentially an extension of Talamini's model⁶ described earlier, with a number of modifications. Among these are a correction due to the volume change with conversion and the assumption that initiator is being con-

sumed by a first-order rate law. Also, the concentration of polymer in the monomer-rich phase is assumed to be negligible. Initiator concentrations in the two phases are assumed equal. They have proposed different polymerization rates depending on the conversion. When the conversion is greater than X_f (conversion at which the monomer-rich phase disappears), they have introduced a change in the kinetic constants because at that stage, the termination rate and propagation rates will decrease due to a "gel effect."

These workers⁷ have also given formulas for calculating the MWD. They postulate that transfer to monomer plays an important part in controlling the molecular weight averages and that disproportionation is the dominant mode of termination. There are two sets of equations for the rate of conversion and MWD proposed, one for low conversion and one for high conversion.

Ugelstad et al.⁸ have recently presented a two-phase model similar to that of Talamini et al.⁶ and fit parameters to make the model agree with conversion data.

It is useful to contrast the models we have discussed. For example, we see that the models of Bengough and Norrish,¹ Breitenbach and Schindler,² Mickley et al.,⁴ and Cotman et al.⁵ consider that branching in the polymer is important, while Magat,³ Talamini et al.,⁶ and Abdel-Alim and Hamielec⁷ do not consider it significant. Also, in the models of Bengough and Norrish, Mickley et al., Abdel-Alim and Hamielec, and Ugelstad et al.,⁸ the polymerization rate depends on the initial initiator concentration to the power 0.5, whereas Schindler et al. and Talamini et al. have more complex relationships.

Similarly, most of the models consider chain transfer to monomer the most important means of molecular weight control, but Magat neglects chain transfer entirely.

From these varied approaches to modeling, one can see that there are a wide variety of opinions in the literature regarding a model for the bulk polymerization of PVC. In addition, many of the models appear to be "mechanical" in that they postulate "two phases" and discuss transfer between these while avoiding (for the most part) a discussion of the detailed physical nature of these two phases. In the discussion which follows, we shall try to be more specific in the model we propose.

REVIEW OF EXPERIMENTAL RESULTS

Most of the authors whose models we have discussed have also performed experiments for interpreting their respective kinetic models. Nevertheless, there has not been a single model which could actually fit all the experimental data for the complete range of conversions. Generally speaking, a particular model is valid for a certain range of conversions. Only the most recent mechanical models proposed by Talamini,⁶ Abdel-Alim and Hamielec,⁷ and Ugelstad⁸ have been found to fit experimental data over a wide range of conversions (up to about 70%). However, these models involve empirical curve fitting and thus should be expected to fit the data reasonably well.

Bengough and Norrish¹ in their experiments studied the autoacceleration in the rate of polymerization over the first 30–40% of reaction over a whole range of temperatures from 33° to 75°C and for varying initiator concentration. They found an acceleration in rate due to the addition of dead PVC beads, and from their results they conclude that the catalytic effect of polymer is propor-

tional to the power of $2/3$, as their model predicts. They also found that degree of polymerization is independent of conversion and decreases with increasing temperature.

Arlman and Wagner⁹ found that the autocatalytic behavior also depends on the type of initiator. With benzoyl peroxide, the autocatalytic effect was seen up to 20% conversion; but with 2,2'-azoisobutyronitrile, it was observed up to 80% conversion. Bengough and Norrish¹ had observed that the catalytic effect of polymer is proportional to the $2/3$ power of its concentration; Mickley et al.⁴ have found that the autocatalytic effect depends on polymer concentration to the first power in the first stages of the conversion and to $2/3$ power at higher conversions. Cotman's experimental data fitted the Bengough-Norrish equation from 0.5% to 10% conversion and failed at higher conversions. A similar failure of Bengough and Norrish's model has also been reported by Arlman and Wagner⁹ and Mickley et al.⁴ The Breitenbach and Schindler model² only agreed to a limited extent with the experimental observations of Cotman, while Magat's model³ correlates the data at higher conversions but it does not fit the low conversion data.

The reaction order with respect to initiator has been proposed as a value between 0.5 and 1.0 by the various authors. Bengough and Norrish¹ found a value of 0.5 in polymerization carried out at 40°C with benzoyl peroxide as initiator. Breitenbach and Schindler² found an order of 0.58 at 30° to 60°C using the same initiator. Danusso¹⁰ observed different reaction orders for initiator with changing conversion; i.e., he found reaction orders of 0.46 to 0.52 from 2–8% conversion, while at 30% conversion the reaction orders had values between 0.50 and 0.54. Mickley et al.⁴ found that the order was approximately 0.5. Hamielec assumed a dependence of 0.5 on initiator concentration and was able to fit his data. However, as mentioned, the general consensus is that the initiator order is between 0.5 and 1.0, the exact dependence depending on the reaction conditions, the model chosen, and the relative importance of the homogeneous and heterogeneous terms comprising the polymerization rate equations.

The molecular weight as a function of temperature has been studied by various authors. The molecular weight of polymer increases with decreasing temperature, reaching a maximal value at about -30°C , according to Talamini et al.¹¹ However, recent results by Abdel-Alim and Hamielec¹² suggest that this MWD maximum may be spurious due to failure to account for molecular aggregation.

Another controversial feature in the mechanism of heterogeneous polymerization is with regard to chain branching. The Bengough and Norrish mechanism¹ assumes chain transfer to polymer and therefore postulates that long branches must be formed in the polymer. Cotman¹³ found that the extent of branching in commercial PVC is about one branch per 50 monomer units. George et al.¹⁴ found that branching was dependent on temperature and showed specifically that at -40°C there was almost no branching. Boccato et al.¹⁵ also studied the branching of PVC. They found that PVC samples prepared at 50°C have approximately one side chain for every 60 carbon atoms, whereas samples prepared at temperatures below -60°C are practically linear. Other authors^{16–20} have also reported similar results on degree of branching. However, it is not clear whether the branching is of a long chain type (due to transfer between growing radicals and dead polymer, or due to addition of terminal double bonds

of preformed molecules to a growing radical) or of a short chain type (due to intramolecular chain transfer through intermediate formation of a five- or six-membered ring, or by head-to-head addition followed by radical isomerization to produce pendent $-\text{CH}_2\text{Cl}$ groups²¹).

Therefore, the conclusion which we can draw from this is that, although chain branching seems to be present, the evidence^{13-21,39} seems to indicate that the short chain type predominates. Therefore, the chain transfer to polymer mechanism proposed by Bengough and Norrish,⁷ Mickley et al.,⁴ and Cotman et al.⁵ is not confirmed. As noted earlier, the models proposed by Magat,³ Talamini et al.,⁶ Abdel-Alim and Hamielec,⁷ and Ugelstad et al.⁸ do not consider long-chain branching as important and yet are as successful in fitting the data as the other models.

From the experimental results quoted above, it is clear that none of the available models is entirely successful in representing the data over the entire range of experimental conditions, and none of them can predict the influence of the reactor operating conditions on the particle size distribution and particle structure, and indeed the influence of the particle morphology on the rate of conversion and MWD of the polymer.

A DETAILED MODEL FOR BULK PVC

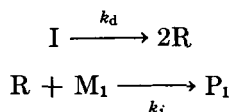
In this section, we shall make use of the experimental data discussed earlier together with new, as yet unpublished results to suggest a detailed mechanistic model for the bulk polymerization of vinyl chloride. In subsequent sections of the paper, we shall derive modeling equations based on the postulated mechanism and begin quantitative testing of the model predictions with the available experimental data.

The detailed mechanism is postulated to be as follows:

Homogeneous Polymerization

The initiator decomposes to form free radicals and polymerization begins in the homogeneous monomer by the following free-radical kinetic mechanism:

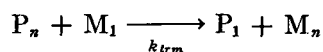
Initiation



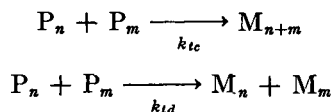
Propagation



Chain transfer to monomer



Termination



Although a much more complex kinetic mechanism involving chain branching, chain transfer agents, etc., has been considered by one of us,²² it is our feeling that the present simplified kinetics is adequate for most purposes. It is true that chain branching has been reported,¹³⁻²⁰ but the data suggest that the reactivity of these branches may be small and they remain very short so that they have a negligible influence on polymer properties, MWD, and conversion.

We postulate that the polymer chains grow according to mechanism (3) and will become insoluble in the monomer. If the temperature is sufficiently high, most of the chains will coil and precipitate as individual polymer chains or small aggregates. For lower temperatures, the polymer chains will aggregate and precipitate as aggregates of perhaps 10-25 chains.^{12,24,25} The work of Abdel-Alim and Hamielec^{12,23} and Salovey and Gebauer²⁴ suggests that these precipitating aggregates will be 0.25-0.5 μ in diameter and that the fraction of polymer precipitating as aggregates decreases sharply above 30-40°C. Other reported work^{5,26} on PVC particle sizes also suggests that the primary PVC particles are approximately 0.5 μ in diameter soon after precipitation.

So long as there is free monomer and initiator available, polymer chains continue to be formed by homogeneous reaction, coil and possibly aggregate, and then precipitate out as primary polymer particles.

Development of the Polymer Particle Structure

The formation of primary polymer particles has been observed to occur at below 1% conversion so that two phases are present almost from the beginning. The primary polymer particles formed are very unstable even under high agitation and coalesce readily to form larger particles which are agglomerates of these coalesced primary particles. The rate of coalescence depends strongly on the particle sizes, the degree of agitation, and the surface properties of the particles. (We shall come back to a more detailed discussion of these points in a later section.)

It appears that there is low solubility of vinyl chloride monomer in PVC (no data on this point seem to have been published). Thus, we assume that these polymer particles are for practical purposes only slightly swollen by monomer, and thus there is very slight growth of the particles due to polymerization.²² Indeed the most significant mechanism affecting particle growth would seem to be particle-particle coalescence. The experimental evidence supporting this conclusion arises both from studies showing that surface active agents and rate of agitation have very strong effects on the particle size distribution²⁷ and from electron microscope photographs of polymer beads showing that they are agglomerates composed entirely of coalesced $\sim 1 \mu$ primary polymer particles.

One such photograph, displayed in Figure 1, shows a PVC bead produced in a two-stage commercial process. It is clear that the microstructure of this bead consists entirely of primary particles (with a diameter of $\sim 1 \mu$) which have coalesced to form the polymer bead. Ancillary measurements of the pore size distribution (by mercury porosimetry [28]) of the photographed beads shows a sharp peak at a pore size of $\sim 0.45 \mu$, which is consistent with the interstices between these $\sim 1 \mu$ primary particles.

The polymer particles continue to be formed by precipitation and disappear by coalescence so long as free monomer is available. Somewhere between 20-70% monomer conversion, depending on reactor conditions, the polymerization

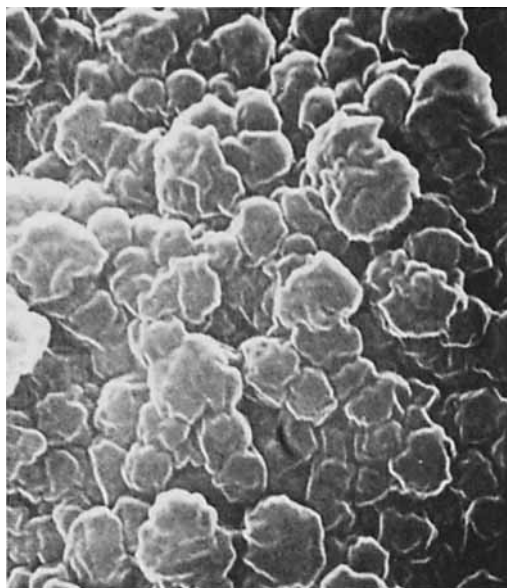


Fig. 1. Scanning electron micrograph showing structure of PVC band²⁸; 12 mm = 1 μ .

medium changes from a slurry to a paste and then to a powder which is dry in appearance. After this powder forms and no monomer is present as free liquid, a large fraction of the monomer still remains *in the pores* of the polymer beads. From the mercury porosimetry data²⁸ on the polymer bead which shows that the smallest pores measured are $\sim 0.45 \mu$, it appears that the interstices between the primary particles are the smallest pores and the primary particles themselves are largely nonporous. This conclusion is supported by internal surface area measurements²⁸ showing less than 1 m²/g of internal surface area, a value much too low for porous primary polymer particles.

The exact mechanism by which the $\sim 1 \mu$ primary polymer particles are created is not entirely clear. One plausible possibility is that the larger aggregates (which appear initially to be¹² $\sim 0.5 \mu$), serve as collection points for the single polymer chain coils, growing polymer chains, and smaller aggregates. Through coalescence of these smaller particles (with a size range¹² of 0.01–0.1 μ) with the larger aggregates formed, one quickly produces primary particles in the 1 μ size range. This hypothesis is supported by the data of Cotman et al.⁵ which show a very large number of these small particles at extremely low conversions (<1%); yet for conversion above 1%, there is a sharp decrease in the number of particles and the mean particle size has increased to 0.5–1 μ . Further evidence in support of this mechanism comes from the papers and patent of Thomas^{29–31} which indicate that a conversion of $\sim 7\%$ is required before the polymer particles are structurally stable.

If one accepts this mechanism, then it is possible that the evolution of primary particles at very low temperatures ($\sim -50^\circ\text{C}$) will occur quite differently from the evolution at high temperatures ($\sim +50^\circ\text{C}$). This will happen because a much larger fraction of polymer precipitates as aggregates at lower temperatures than at the higher temperatures¹²; thus, there will be many more large collector particles to sweep up the smaller aggregates and single chain coils.

As has been discussed earlier, these primary particles (which quickly assume a size of $\sim 1 \mu$) themselves coalesce to produce the final polymer bead whose diameter is $\sim 50\text{--}150 \mu$. This macrocoalescence occurs so long as there is free monomer liquid present. After the disappearance of the free monomer phase, we postulate that the polymerization continues *in the pores* of the polymer bead. Because the density of the monomer (0.85 g/cc) is roughly 60% that of the polymer (1.4 g/cc), shrinkage on polymerization means that these pores are not rapidly filled by the newly formed polymer. In fact, the porosity and internal surface area of the polymer beads can be significantly decreased by altering polymerization conditions²⁸ in support of our theory of in-pore polymerization.

Monomer Conversion

It has been observed experimentally that there is a definite autoacceleration in the rate of polymerization both early in the polymerization if dead polymer is added¹ and later in the polymerization after much of the free monomer has disappeared.^{4,5,7,8,9} Both of these phenomena can be explained by assuming that the termination step is diffusion limited when polymerization occurs in the pores of the polymer bead. This "gel" effect⁷ causes the marked rate acceleration at high conversions when the bead porosity is decreasing with conversion. This effect can also account for the observed acceleration at lower conversions with reacted polymer. In this case, only a smaller fraction of the polymerization occurs in the bead pores, and thus the acceleration is not so striking. However, as the free liquid-phase volume decreases, and the beads become less and less porous, the gel effect becomes more and more pronounced.

The changing dependence of the rate of polymerization on the initiator concentration can also be explained by polymerization within the pores. As has been observed experimentally,¹⁰ early in the polymerization R_p should be proportional to $I^{1/2}$ because mostly homogeneous polymerization is occurring. However, as the fraction of the monomer in the liquid phase, ϕ , decreases, more and more polymerization is occurring in the pores where the gel effect is important. When this happens, the rate of polymerization will appear to depend more strongly on I . However, in actuality it is the rate constant k_t which is decreasing, producing the same effect as a stronger dependence on I . As can be seen in section III, all the reported rate data are consistent with this theory.

Molecular Weight Distribution

The most comprehensive experimental studies of the MWD produced in bulk PVC^{7,37} show that the degree of polymerization is largely determined by chain transfer to monomer and the MWD is very narrow, with a polydispersity of close to 2.0. These results are consistent with the modeling assumptions chosen by several earlier workers.^{1,4,6,7} If chain transfer to monomer controls the formation of dead polymer, then at constant temperature the instantaneous molecular weight distributions produced at each instant are the same even with gross changes in monomer concentration and diffusion limited termination. This causes the MWD to have a polydispersity of 2.0 and take the form of the "most probable distribution". Thus, the MWD produced in the pores of a polymer bead will be approximately the same as that produced in the free liquid monomer.

THE MODELING EQUATIONS

Very general modeling equations showing the detailed interactions among the particle size distribution, molecular weight distribution in the homogeneous phase, molecular weight distribution in the particles, conversion in the homogeneous phase, conversion in the particle, etc., have been developed by one of us.²² This modeling framework is quite general and similar to a modeling structure developed for emulsion polymerization reactors.³² Rather than presenting these rigorous modeling equations in their full complexity here, we shall discuss modeling equations for the rate of polymerization and molecular weight distribution, and then present a model and calculations for the total particle size distribution.

Conversion and MWD Prediction

The mechanism presented here for PVC bulk polymerization is not in fundamental conflict with the *mechanical models* of some of the earlier workers.⁶⁻⁸ If we interpret the *monomer-rich phase* to be the free liquid monomer, the *polymer-rich phase* to be the monomer polymerizing in the pores as well as inside the polymer beads, and the "gel effect" to be mainly caused by diffusion limitations of growing chains in the polymer pores, then the fundamental form of these earlier models are consistent but simplified versions of the more complex modeling equations given in references 22 and 32. Thus, it is not surprising that these earlier models have been quite successful in predicting the MWD and conversions over a wide range of operating conditions. However with the present detailed physical theory it is possible to relate the undetermined parameters in these earlier models to independently determined particle parameters. For example, the distribution of monomer between the monomer-rich phase and polymer-rich phase can be related to the total pore volume of the polymer beads as measured by mercury porosimetry. Similarly, the gel effect can be related to the fundamental rate of diffusion of growing chains in a porous particle structure.

Total Particle Size Distribution

The modeling equation for the total particle size distribution²² takes the form

$$\frac{\partial F(V,t)}{\partial t} + \frac{\partial(\bar{c}F(V,t))}{\partial V} = \int_0^V k_c(V-v)vF(V-v,t)F(v,t)dv - F(V,t) \int_0^\infty k_c(V,v)F(v,t)dv + \delta(V-v_c)r_{\text{prec}}(v_c) \quad (4)$$

where $F(V,t)dV$ is the concentration of polymer particles having volume V to $V + dV$ at time t . The first term on the left-hand side of eq. (4) represents the accumulation of F with time, while the second term represents the rate at which particles enter and leave the size range V to $V + dV$ owing to growth by polymerization. The parameter \bar{c} represents the average rate of growth of the polymer particles due to polymerization; however, because we assume the polymer is only *slightly* swollen by the monomer, we shall neglect the effect of polymerization on particle growth and assume $\bar{c} = 0$. (This assumption is made in the absence of experimental data on PVC-VC solubility. The effect of particle swelling on growth can easily be incorporated if the solubility parameters are known.

Nevertheless, the available data still indicates that particle-coalescence is the dominant mechanism of particle growth.)²² The first two terms on the right-hand side of eq. (4) represent the rate at which particles enter and leave the size range V to $V + dV$ due to particle-particle coalescence. The parameter k_c is a kinetic constant for coalescence which depends strongly on the particle size, the degree of agitation, and the surface properties of the particles. Although several functional forms have been suggested,³³⁻³⁶ we have selected the expression

$$k_c(V, v) = \alpha(Vv)^{-1/2} \quad (5)$$

for the preliminary calculations to be shown here. The parameter α depends on the agitation rate and the particle surface properties. This functional form suggests that the probability of coalescence is proportional to the surface area per unit volume of the particles colliding. This expression has theoretical appeal and also is consistent with the reported experimental observations^{4,5,27} showing very small particles coalescing rapidly while very large ones remain stable for long periods of time.

The constant α in eq. (5) must be determined experimentally and perhaps correlated with agitation rate and surface free energies of the polymer particles.³²

The last term on the right-hand side of eq. (4) is the rate at which particles enter the size range v_c to $v_c + dV$ due to precipitation from the liquid phase. Note that we represent the appearance of particles of only size v_c through the use of the Dirac delta function $\delta(V - v_c)$. The rate of precipitation of the various particle sizes is a distribution which requires determination. Detailed experimental studies of particle size distribution versus time at low conversions should provide useful information here.

In the initial calculations which follow, it was assumed that the polymer precipitates as quickly as it was formed so that the rate of precipitation is proportional to the rate of polymerization. In addition, we were primarily concerned with the distribution of sizes of the final product bead; thus we assumed the $\sim 1 \mu$ primary particles were formed instantaneously according to the expression

$$F(v_c) = \frac{\delta(V - v_c)r_{\text{prec}}}{\alpha \int_0^{\infty} F(v)(v_c v)^{-1/2} dv} \quad (6)$$

This expression arises if one neglects the dynamic terms in eq. (4) and will be a good approximation when the primary particle development proceeds on a time scale very much faster than that required for bead growth through coalescence of primary particles.

It should also be noted that a more precise expression for the rate of precipitation would account for the fact that early in the polymerization, essentially all of the polymer formed would go to produce primary particles. However, as the polymerization progresses, more and more of the polymer would be formed in the pores of the polymer beads, would attach to the pore walls, and would not contribute to the particle population. This would produce an expression for the rate of formation of new primary particles of the following form:

$$r_{\text{prec}} = \phi r_p \quad (7)$$

where ϕ is the fraction of monomer present as free monomer liquid outside the pores.

TABLE I

Temperature = 50°C
$k_p = 1.013 \times 10^4$ l./mole-sec
$k_t = 1.8702 \times 10^9$ l./mole-sec
$k_{tr} = 10.02$ l./mole-sec
$k_d = 1.15 \times 10^{-6}$ sec ⁻¹
$M = 6$ moles/l.
$I = 1.75 \times 10^{-3}$ moles/l.

* Data from references 8 and 38.

With the assumptions we have made, and using eqs. (4) and (5), the modeling equation takes the form

$$\frac{\partial F(V,t)}{\partial t} = \int_{v_c}^V \alpha[(V-v)v]^{-1/2} F(V-v,t) F(v,t) dv - F(V,t) \int_{v_c}^{\infty} \alpha(Vv)^{-1/2} F(v,t) dv \quad (8)$$

for $V > v_c$, and eq. (6) is used to determine $F(v_c)$. We choose as an initial condition $F(V,0) = 0$ (unseeded polymerization). In physical terms, eq. (6) is a quasi-steady-state balance between primary particles of size v_c formed from precipitation and removed by coalescence. Similarly, eq. (8) represents the rate at which the population of a certain size range increases (first term on the right-hand side) and disappears (second term on the right-hand side) because of coalescence.

Simulation studies were carried out with this equation, both to determine the effects of the model parameters and to afford a direct comparison with experimentally determined particle size distributions. The numerical algorithm is described in great detail in reference 22, so that we will only note its essential features here.

A finite difference scheme was used to solve this integro-partial differential equation. The particle size interval $0 < V < \infty$ is, of course, too general, so we chose the practical size range corresponding to particle diameters from 1μ to 100μ . Because even this range is two orders of magnitude, it was decided to use a finite difference scheme with unequal step size chosen according to a logarithmic scale. Some experimentation showed that this gave reliable solutions with a relatively small number of steps.

Simulations were done with a number of values of α and with a number of initiation rates; however, we shall only display a few of these here. Figures 2-4 show the particle size distribution produced after 20 min in a batch reactor with the conditions^{8,38} given in Table I. The values of α range from 0.333×10^{14} to 3.0×10^{14} . As the figures show, the higher the coalescence rate, the larger the average particle size and the smaller the total number of particles of all sizes, N_T , which is defined as

$$N_T(t) = \int_0^{\infty} F(V,t) dV. \quad (9)$$

As an indication of the consistency of our model, we can see that the values of N_T calculated compare favorably with the total particle populations reported by Cotman.⁵

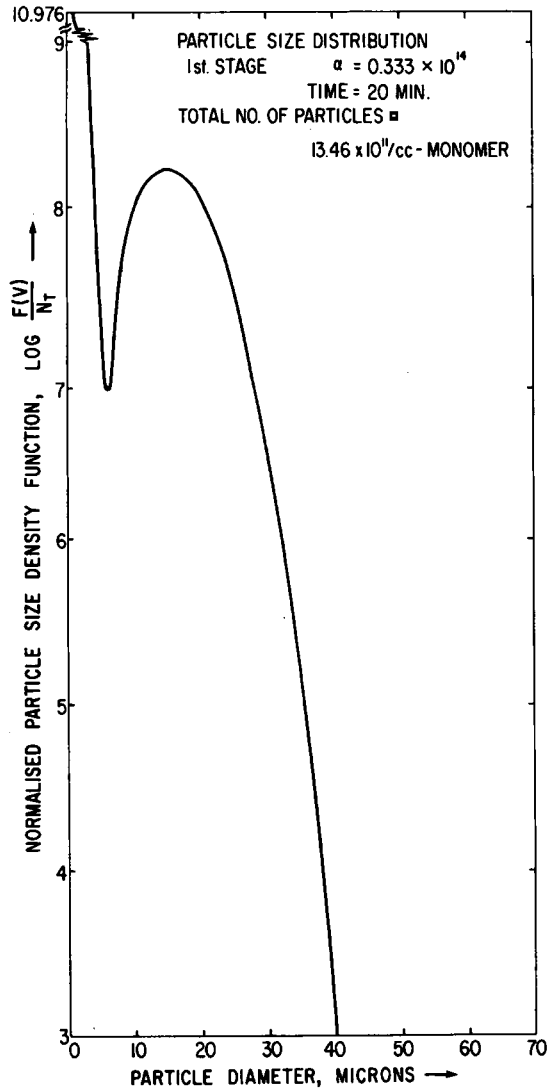


Fig. 2. Calculated total particle size density function ($\alpha = 0.333 \times 10^{14}$) after 20 min.

Figure 5 shows how the particle size distribution is predicted to evolve with time. For short times, there are very few large beads and a relatively large number of very small particles. However, as the polymerization proceeds, more and more primary particles are formed and are quickly swept up by the larger beads.

In order to test more quantitatively the predictions from our particle size distribution model, we have compared it with experimentally determined particle size distributions. The only data available were for commercially produced beads formed in a two stage process.²⁹⁻³¹ The cumulative particle size distribution is shown in Figure 6, where the dots denote the experimental values determined by Coulter counter measurements,^{27,28} and the solid line denotes the model simulation.

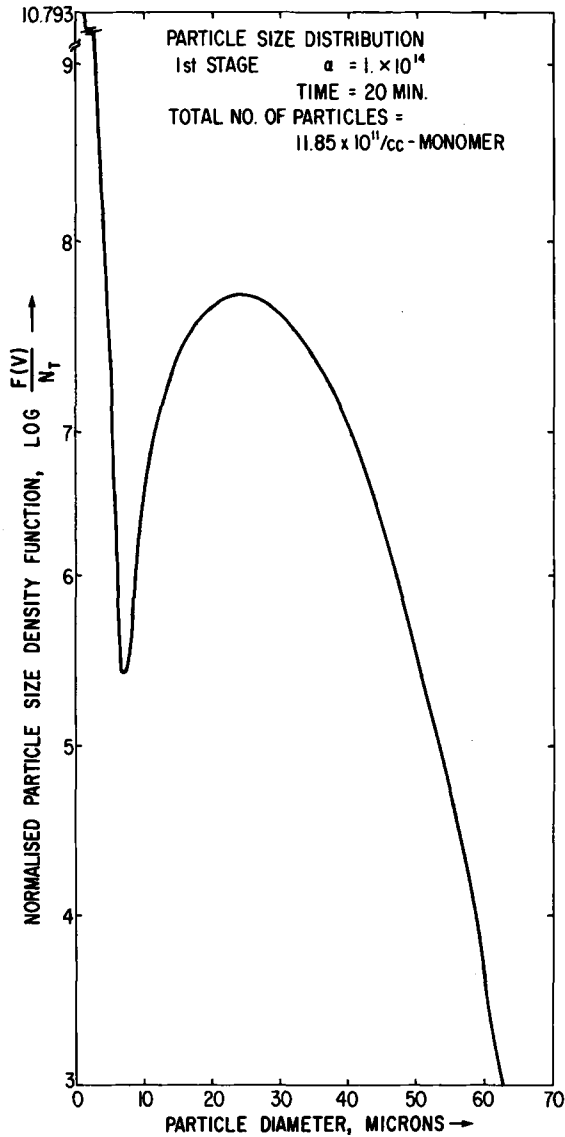


Fig. 3. Calculated total particle size density function ($\alpha = 1.0 \times 10^{14}$) after 20 min.

The model simulation was carried out in two parts: (i) polymerization for 20 min in the first stage with high agitation ($\alpha = 0.333 \times 10^{14}$), followed by (ii) addition of fresh monomer and polymerization for a further 50 min with slow agitation ($\alpha = 0.666 \times 10^{14}$). In the second stage, it was assumed that precipitation stopped after 10 min and coalescence ended after 50 min. These assumed polymerization conditions correspond quite closely to the actual experimental ones. However, the values of α had to be chosen rather arbitrarily because detailed correlations of α with agitation tip speed, slurry viscosity, etc., have not yet been carried out.

As can be seen, the model is able to predict the experimental particle size distribution reasonably well, indicating that the model structure is sound.

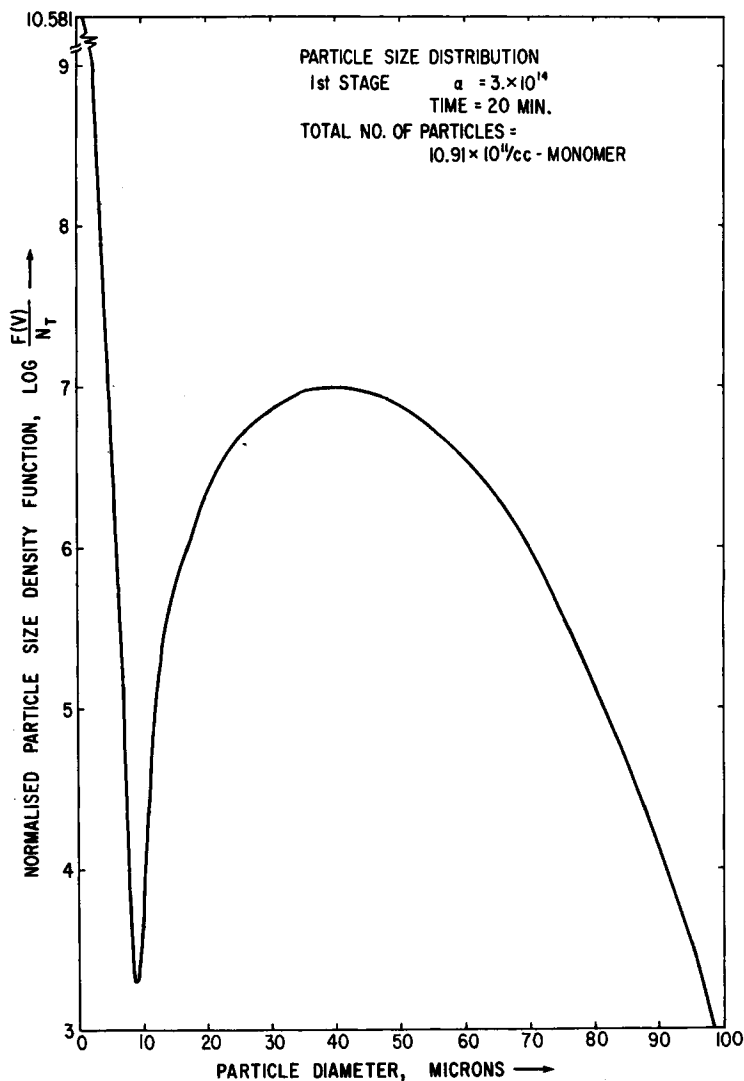


Fig. 4. Calculated total particle size density function ($\alpha = 3.0 \times 10^{14}$) after 20 min.

Nevertheless, the experimental results seem to indicate a slightly narrower particle size distribution than the model predicts, and thus it appears that more data on particle size distributions at intermediate times and detailed studies of the effects of operating conditions on α would be desirable so that more rigorous testing of the model can be carried out.

CONCLUSIONS

In this paper we have proposed a detailed mechanism for the polymerization of PVC in bulk and have shown that the theory is consistent with the data cited from many sources. Detailed modeling equations are described and calculations performed which show the theory in reasonable agreement with experiments on the particle size distribution. In addition, the model is consistent with the

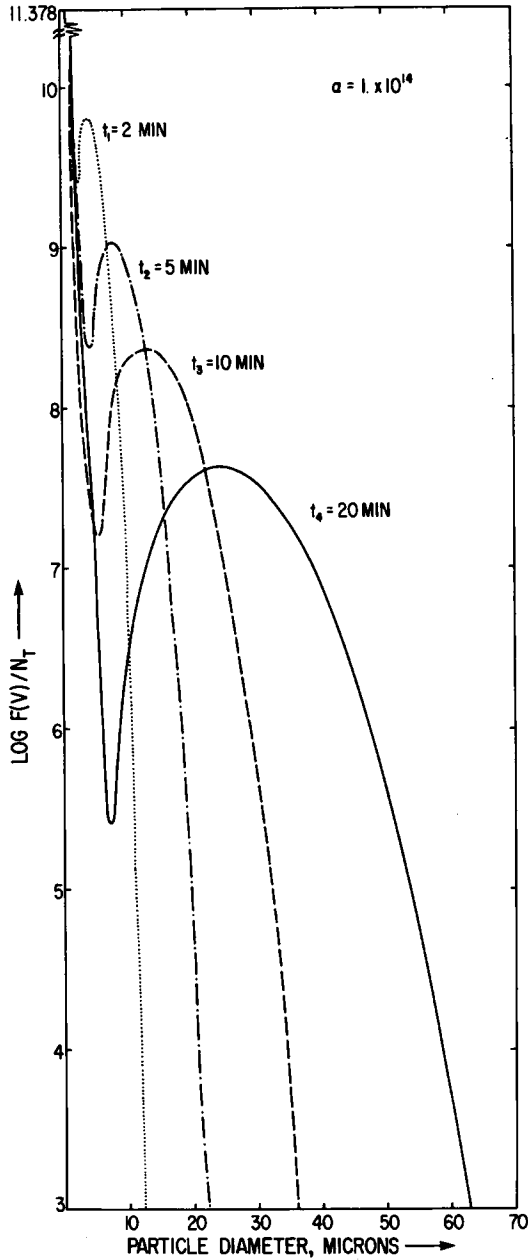


Fig. 5. Transient evolution of particle size density function.

reported experimentally observed rates of polymerization and molecular weight distribution.

It should be noted that this is the first reported mathematical model for the particle size distribution in PVC reactors, and the most detailed general theory proposed to date. Nevertheless, in order to take full advantage of the predictive capabilities of the model presented, further experimental work is required. For example, work is needed (i) to determine more precisely the influence of agita-

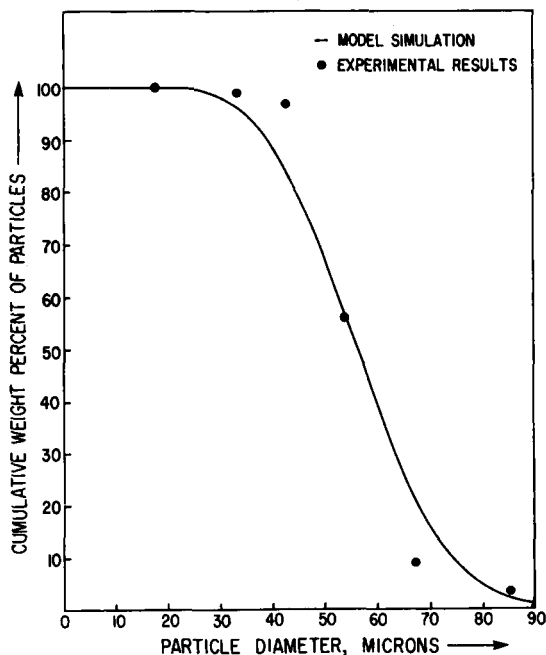


Fig. 6. Comparison of model predictions with experimental data for polymer beads produced in a two-stage process.

tion, slurry viscosity, and particle size on the rate of coalescence, and (ii) to get more detailed electron microscope photographs, pore size distribution, internal surface area measurements, and particle size distributions at a wider range of monomer conversions and polymerization temperatures so that a more precise experimental picture of the evolution of both the primary particles and the macroscale polymer beads can be determined. If this were done, then the model would be a very useful tool for predicting the effect of reactor operating conditions on the porosity, bead size, conversion, and molecular weight of the polymer product.

Because suspension, emulsion, and bulk polymerization of PVC have been found kinetically similar by earlier workers,^{6,7} it is thought that, with only minor, straightforward modifications, the model postulated here could also be used to predict the data for suspension and emulsion polymerizations.

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