

## Mechanism of Emulsion Polymerization of Vinylidene Chloride.

### III. Effects of Stirring Rate on Kinetics

CHARLES P. EVANS, PETER M. HAY,\* LEON MARKER, ROBERT W. MURRAY,† and ORVILLE J. SWEETING‡

*Film Division, Olin Mathieson Chemical Corporation, New Haven, Connecticut*

#### INTRODUCTION

In previous papers,<sup>1,2</sup> we have shown that the kinetics of the emulsion polymerization of vinylidene chloride, with sodium lauryl sulfate as surfactant and ammonium persulfate and sodium metabisulfite as redox catalyst system, do not follow the generally constant rate predicted by the theories of Harkins<sup>3</sup> and Smith and Ewart.<sup>4</sup> These authors predicted a constant rate after a short induction period until near the end of the reaction when the monomer supply becomes reduced. Actually, the S-shaped curve predicted by the existing theory has rarely been completely realized. Bakker<sup>5</sup> has indicated that it may be impossible to obtain a constant rate over an extended range of polymerization.

We have discussed the effect which agglomeration of polymer particles might be expected to have on the kinetics of polymerization and have shown that probably particle coalescence plays a part in the overall process, but is in itself insufficient to account for observations in the early stages of polymerization.<sup>2</sup> In the present work the three-stage nature of the reaction has been reconfirmed, and a careful study has been made of the effect of stirring on the reaction rate, particularly in Stage I, preceding the slowdown that characterizes Stage II.

#### EXPERIMENTAL PART

##### Materials

*Vinylidene chloride* (Dow Chemical Co.) was distilled once from 20% aqueous NaOH, and distilled again from solid NaOH, just before use, both times in an atmosphere of nitrogen (Linde HP dry).

\* Present address: Celanese Plastics Co., Newark, New Jersey.

† Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

‡ To whom inquiries may be directed.

*Ammonium persulfate*,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , Mallinckrodt analytical reagent grade, was used as received.

*Sodium metabisulfite*,  $\text{Na}_2\text{S}_2\text{O}_5$ , Baker and Adamson anhydrous powder, reagent grade, was used as received.

*Water* was distilled and deionized with Amberlite IRC-50 (H) resin (Rohm & Haas Co.).

*Sodium lauryl sulfate*, "Sipon WD" crystals (American Alcolac Co.), was used without further purification.

##### Procedure

The emulsion polymerization reactions were done in a 500-ml. round-bottomed four-necked flask immersed in a constant temperature water bath which was held at  $36.0 \pm 1^\circ\text{C}$ . The flask was equipped with a reflux condenser, a 3-in. Teflon stirring blade driven by a constant-speed stirring motor (catalog No. 25175, Will Corp.), a thermometer, and a self-sealing rubber serum stopper.

Special precautions were taken in the preparation of the reaction charge, since vinylidene chloride readily forms peroxides on contact with air. A special distillation receiver assembly was designed to allow an exact amount of vinylidene chloride to be transferred to the reaction flask without its coming in contact with air. Figure 1 is a sketch of the apparatus used. Before distillation of vinylidene chloride, the distillation apparatus and receiver assembly were flushed with nitrogen (Linde HP Dry). The lower stopcock of the distillation receiver assembly was then closed and the receiver filled to a calibrated mark. The receiver assembly had been previously calibrated to contain a known weight (101.1 g.) of vinylidene chloride at  $0^\circ\text{C}$ . To insure efficient condensation of the vinylidene chloride vapors the distillation condenser was maintained at approximately  $-20^\circ\text{C}$ . by a circulating mixture of ethanol and ethylene glycol. The receiver was maintained at  $0^\circ\text{C}$ . by circulating

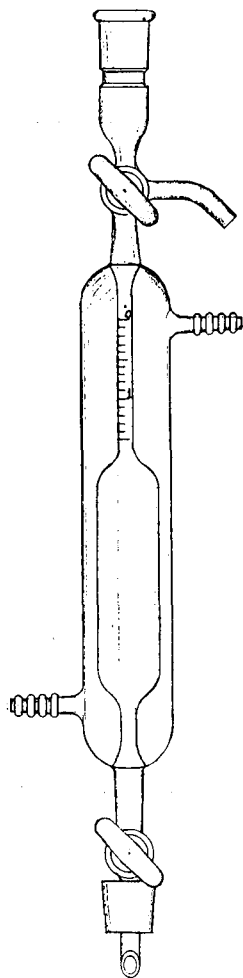


Fig. 1. Receiver and transfer vessel for vinylidene chloride.

ice water. The vinylidene chloride was transferred to the reaction flask from the calibrated receiver by nitrogen pressure.

Samples for conversion calculations were removed from the reaction flask by means of a special sampling device. This device (Fig. 2) was a dental syringe, equipped with a 6-in., 14-gauge needle, modified to hold small glass vials which were closed at both ends by means of self-sealing rubber caps. The vials were approximately 2 in. in length and were cut from 4-mm. glass tubing.

The vials for sample collection were weighed on an analytical balance. The latex from the reaction flask was drawn into the weighed vials by the use of a standard 5-ml. hypodermic syringe fitted with a 3-in., 12-gauge needle. The vial was then removed from the sampling device and weighed. The vial contents was coagulated in cold methanol in an aluminum weighing cup.

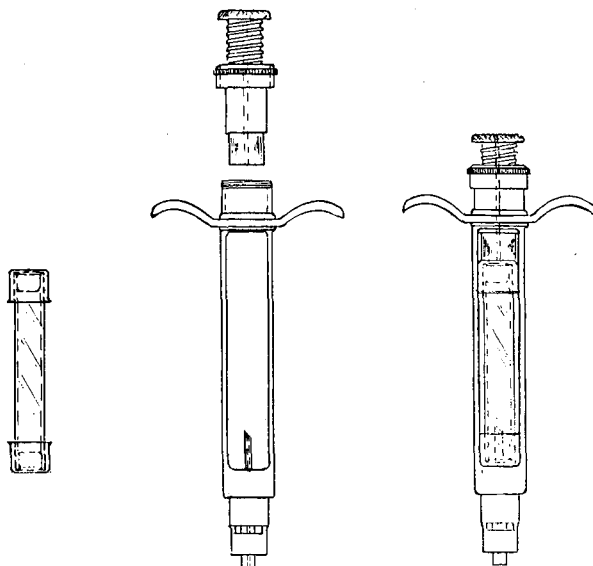


Fig. 2. Special sampling device: (left) vial with serum stoppers; (center) modified dental syringe; (right) syringe with vial in place.

Several series of experiments were conducted to determine the effect of stirring speeds on the vinylidene chloride emulsion polymerization.

The reaction charge for the experiments was 101.1 g. of vinylidene chloride, 2.02 g. of sodium lauryl sulfate, 0.1517 g. of ammonium persulfate, 0.1517 g. of sodium metabisulfite, and 89.80 g. of deionized water.

The solutions of persulfate and bisulfite were prepared immediately before use so that 5 ml. of the solution contained the desired quantity of each.

#### *a. Runs at Various Stirring Speeds*

Water and sodium lauryl sulfate solution were added to the flask and stirred under a steady flow of nitrogen for approximately 30 min. in order to remove oxygen. The vinylidene chloride was then added as previously described. The system was sealed under a constant pressure of nitrogen, maintained by a needle valve, and measured by a mercury manometer inclined as a draft gauge. For this series the system was under a pressure of 24 mm. of mercury above atmospheric. After the reaction system had been allowed to come to temperature and pressure equilibrium, the catalyst and activator were added by means of 5-ml. hypodermic syringes through the self-sealing rubber serum stopper on one neck of the flask. The stirring speed control on the constant speed motor was set prior to charging the flask and was checked

periodically throughout the reaction with a tachometer. These checks indicated that the speed remained constant. Each of the runs of the series was carried out at a different stirring speed: 0, 106, 131, 388, and 756 rpm. Samples of the latex were removed at 3- to 5-min. intervals for the first 15 min. of the reaction and then at 10- to 20-min. intervals for the remainder of the reaction. The samples were weighed and coagulated as described and dried in air overnight. They were then dried to constant weight in a vacuum oven at 40°C. and 10 mm. pressure.

One run was done in which the stirring motor was turned off 30 sec. after the catalyst had been introduced. The reaction flask was kept in the constant-temperature bath under the controlled reaction pressure for 240 min. Stirring was then resumed and a sample taken immediately.

The percentage of solids and percentage conversion of each sample were calculated from the sample weights and residue in the usual way.<sup>1</sup>

To estimate the degree of separation of the monomer phase as the reaction proceeded, 2-ml. samples were removed periodically from two of the runs mentioned above (388 and 756 rpm). These samples were placed in centrifuge tubes containing hydroquinone in order to stop the polymerization (for the first run, each of the centrifuge tubes contained about 10 mg. of hydroquinone and for the second run, 0.1 ml. of a saturated aqueous solution of hydroquinone). The centrifuge tubes were sealed with self-sealing rubber serum stoppers. The latex samples were injected into the tubes by means of a hypodermic syringe and needle. During injection of the samples the tubes were vented by means of a small hypodermic needle inserted through the serum stopper. After completion of sample injection, both hypodermic needles were removed. The samples were allowed to settle and both the total volume and the volume of the lower monomer phase were recorded. It was necessary to centrifuge the last three or four samples for a short time to permit reading of the volumes.

### *b. Interrupted Stirring*

A second series of experiments was conducted in which stirring was discontinued during a portion of the total reaction time. The reaction charge used for these experiments was the same as that taken for the previous series. In the first of these experiments the stirring speed used was 485 rpm. After the reaction had run for 57 min., the stirrer

was turned off and restarted after 57 min. Samples for conversion were taken every 5 min. during the first 57 min. of the reaction. While the stirrer was off no samples were taken, and when the stirrer was turned on again, sampling was resumed. A similar experiment was conducted wherein the stirring speed used was 242 rpm. In this case the polymerization was allowed to proceed for 75 min. before the stirrer was turned off. The stirrer remained off for 88 min., whereupon the run was continued as before.

### *c. Stirring Speed Changed after Stage I*

In a final series of experiments a stirring speed of 82 rpm was maintained for 20 min. during Stage I of all runs. The speed for the remainder of the polymerization was different for each run: 0, 106, 291, and 390 rpm, respectively. The equipment and procedures were the same as described previously.

## RESULTS

The conversion-time curves for the first series of experiments are presented in Figures 3 and 4. These curves show that the average rate in Stage I, as well as the rate thereafter are affected by stirring speed. This is shown more clearly for Stage I in Figure 11, in which conversion is plotted as a function of time-squared. In general, a faster stirring speed gave a slower rate in the first stage.

In two of the runs, samples were removed by syringe and used to determine monomer separation as a function of conversion (separation was defined as the volume percentage of the monomer layer). The results of these runs are given in Figures 5 and 6. The curves show that monomer separation began early in the reaction, beginning at about 7% conversion, regardless of stirring speed. Maximum separation occurred at about 20% conversion for both runs. The percentage separation of the maximum was greater for the run at lower speed. Separation was found to disappear between 64 and 67% conversion.

The results for the runs in which the stirring motor was turned off for a period after the reaction had recovered from the slowdown are shown in Figures 7 and 8. These curves show that it is possible to reintroduce the slowdown by stopping stirring. The final rate achieved again is always the same regardless of the length of the slowdown period.

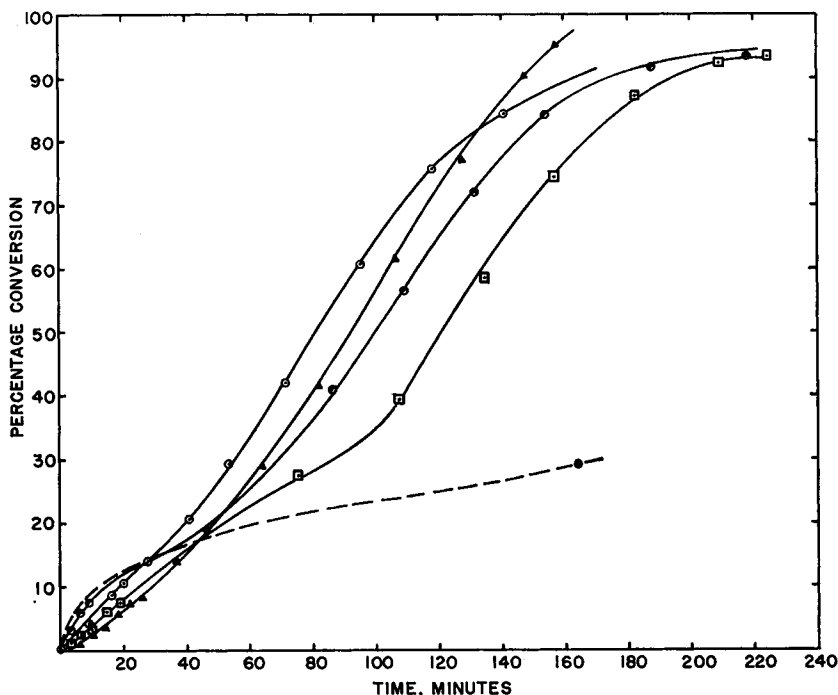


Fig. 3. Polymerizations at various stirring speeds: (●) no stirring; (◻) 106 rpm; (○) 131 rpm; (◊) 388 rpm; (▲) 756 rpm. See also Fig. 4.

In the final series of experiments, the effect of stirring rate on the second stage was compared directly by maintaining the same stirring rate during the first stage in all experiments. The results of these experiments are shown in Figures 9 and 10. Here the rate was found to be the same

for Stage I in all runs. The duration of Stage II decreased as the stirring rate increased. Stage III was not affected by stirring rate.

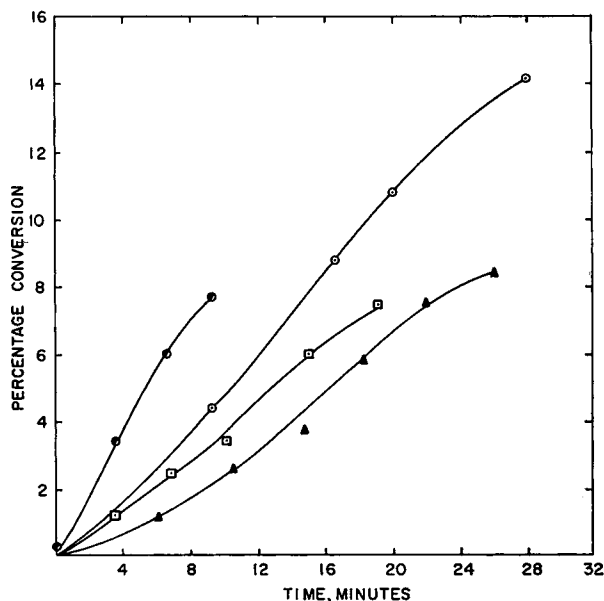


Fig. 4. Plot of the data of Fig. 3 for the initial 30 min. on an expanded scale. Symbols as for Fig. 3.

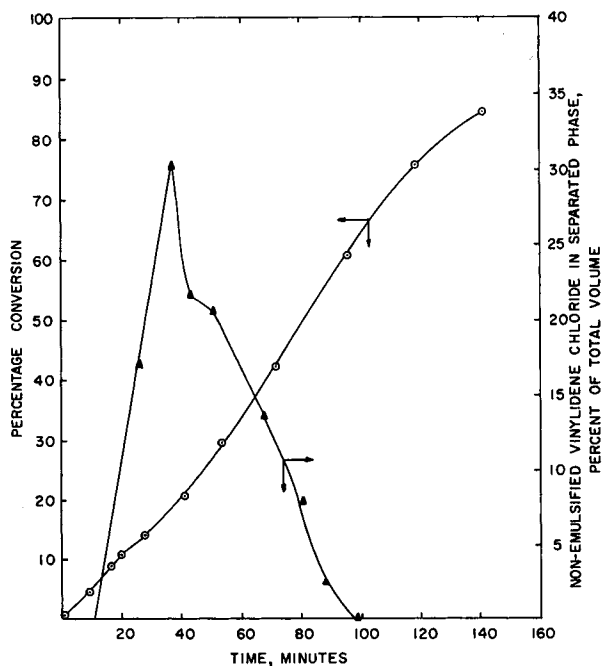


Fig. 5. Percentage conversion and separation of monomer as a function of time; stirring speed 338 rpm; (○) percentage conversion; (▲) percentage phase separation.

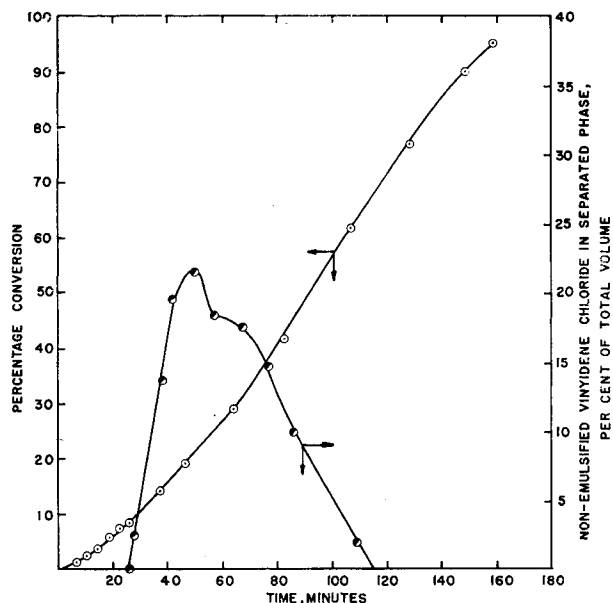


Fig. 6. Percentage conversion and separation of monomer as a function of time, stirring speed 756 rpm; (○) percentage conversion; (●) percentage phase separation.

The single experiment which was not stirred at all following initial mixing of ingredients and emulsification of monomer was found to proceed at a

very slow rate, as indicated by its curve. (This curve was of necessity drawn from two points. Sampling during the run was impractical because of the inhomogeneity of the mixture. The second point was obtained by turning on the stirrer and withdrawing a sample immediately. This run never attained Stage III.)

Stage I can be divided into two parts. During the first, a linear relationship is found between the percentage of conversion to polymer and the square of the reaction time. This linear relationship confirms the assumption that most of the free radicals produced early lead to the formation of new polymer particles. The dependence on time-squared became more evident in the present work because a larger number of samples was taken during the early part of the reaction than had been done previously. Figure 11 shows the time-squared relationship in four polymerizations at stirring speeds of 131, 388, 485, and 756 rpm which shows a decrease in slope with increasing stirring speed. The second part of the initial stage corresponds to the linear portion usually reported for emulsion polymerizations. Trommsdorf<sup>6</sup> also has observed a decrease in reaction rate with faster rates of stirring

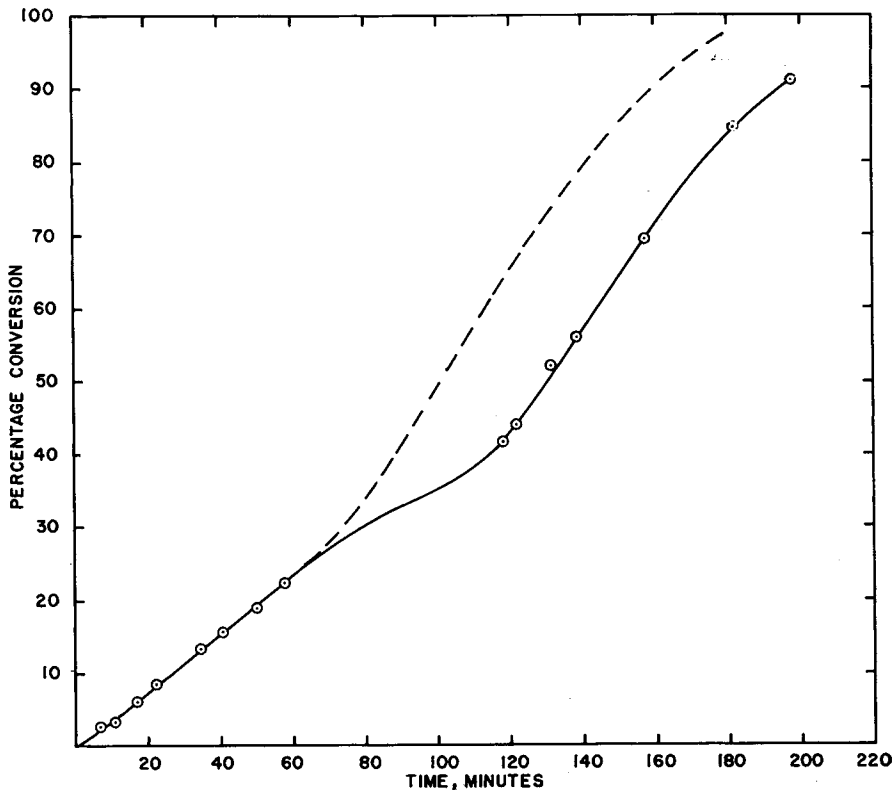


Fig. 7. Effect of interrupted stirring, stirring speed 485 rpm; (- -) denotes expected course for steady stirring. Stirring was stopped between 57 and 114 min.

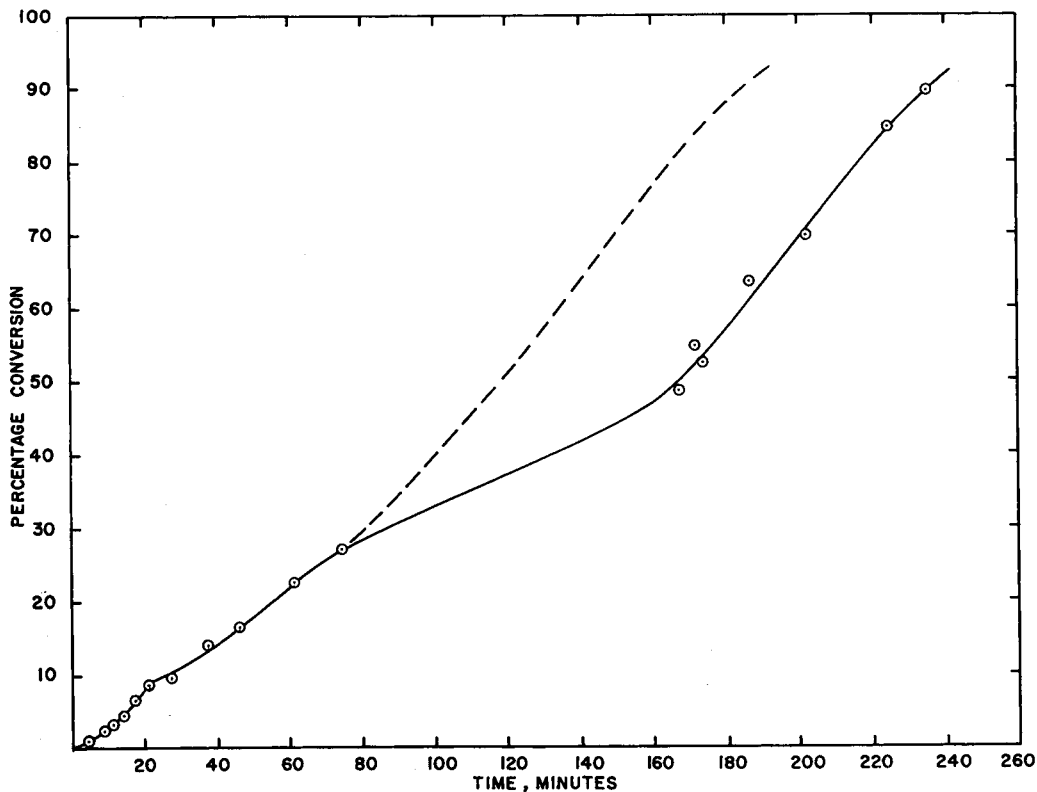


Fig. 8. Effect of interrupted stirring, stirring speed 242 rpm: (--) denotes expected course for steady stirring. Stirring was stopped between 75 and 163 min.

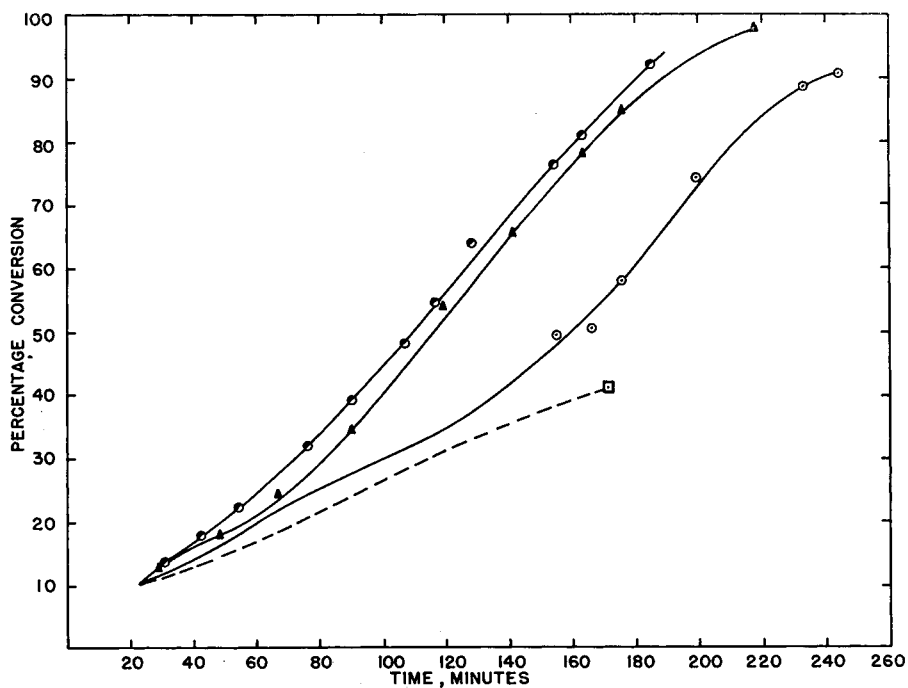


Fig. 9. Stirring speed changed after Stage I, initial stirring speed on all, 82 rpm: ( $\square$ ) no stirring after 20 min.; ( $\odot$ ) 106 rpm after 20 min.; ( $\blacktriangle$ ) 291 rpm after 20 min.; ( $\bullet$ ) 390 rpm after 20 min. See also Fig. 10.

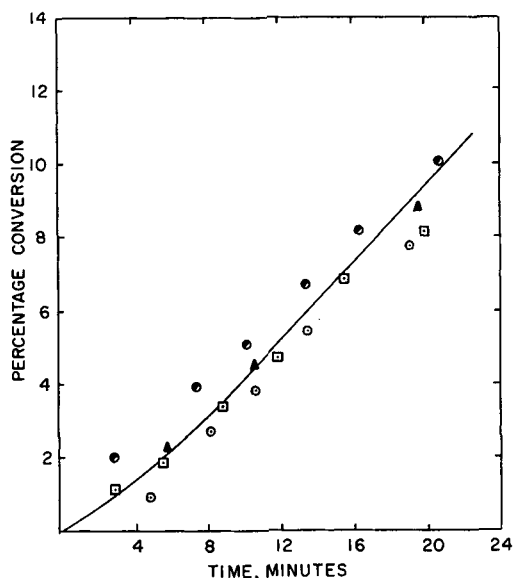


Fig. 10. Plots of the points obtained up to 20 min. (Fig. 9) shown on an expanded scale. Symbols as for Fig. 9.

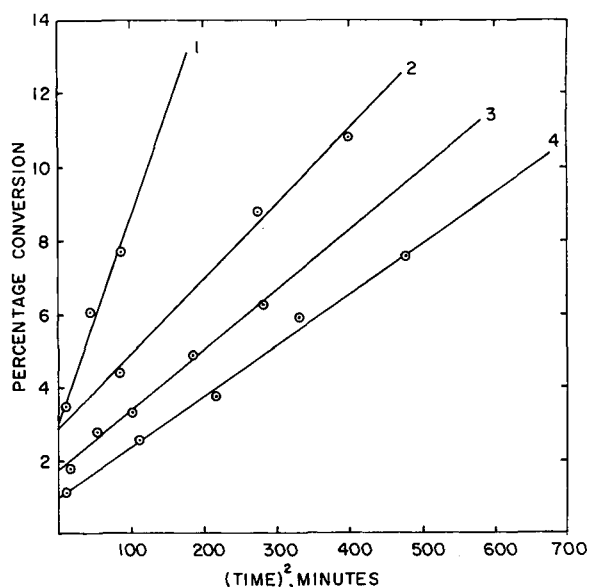


Fig. 11. Relation of conversion to time-squared in Stage I: (1) 131 rpm; (2) 388 rpm; (3) 485 rpm; (4) 756 rpm.

in the emulsion polymerization of methyl methacrylate. (We are currently engaged in a study of this phenomenon.)

#### DISCUSSION OF RESULTS

We have confirmed our earlier observations that the emulsion polymerization of vinylidene chloride is a three-stage process.<sup>1</sup>

For Stage I the average rate varies as the 0.6-power of the catalyst concentration and as the 0.6-power of the surfactant concentration. During the early part of this stage polymer particles are formed, but after the excess surfactant has been consumed in coating the growing polymer particles, foaming stops, and no new particles are formed. The rate data for this stage are in agreement with the prediction of the Smith-Ewart theory, if it is assumed that radical formation proceeds as a reaction of 3/2 order, as has been suggested to explain the kinetics of the persulfate-catalyzed polymerization of vinyl acetate.<sup>7</sup>

After foaming stops we have observed a gradual separation of an unemulsified monomer phase, caused, no doubt, by a lack of sufficient surfactant to form a complete monolayer at the surface of both monomer droplets and polymer particles. The former, which are more easily deformable, tend to coalesce in such a manner as to conserve the total surface area of particles and droplets. The consequent decrease in the number of monomer droplets leads to a decrease in the amount of monomer diffusing from the droplets into the solution.

It is assumed that the principal mode of transfer of monomer to the reaction site is by diffusion of monomer from the monomer droplet into the aqueous phase and from the aqueous phase to the polymer particles. Under steady-state conditions the rate of diffusion of monomer from the monomer droplets equals the rate of diffusion to the polymer particle. Assuming the concentration of monomer at the surface of the monomer droplet is the aqueous saturation value,  $C_0$ , and that the concentration at the surface of the polymer particles is zero, then the total rate of diffusion,  $Q$ , is given by the expression,

$$Q = 4\pi\bar{r}_m N_m D(C_0 - C_1) = 4\pi\bar{r}_p N_p D C_1 \quad (1)$$

$$Q = 4\pi\bar{r}_m N_m [(1 + (\bar{r}_m N_m / \bar{r}_p N_p))^{-1}] C_0 \quad (2)$$

wherein  $\bar{r}_m$  and  $\bar{r}_p$  are the average radii of the monomer droplet and polymer particle, respectively,  $N_m$  and  $N_p$  are the respective number of monomer droplets and polymer particles,  $D$  is the diffusion coefficient for monomer in the aqueous phase, and  $C_1$  is the concentration of monomer in the aqueous phase.

Since, in general,  $\bar{r}_m N_m / \bar{r}_p N_p$  is much less than unity, the diffusion rate is governed by the rate of diffusion from the monomer droplets.

The rate at the end of the first stage of a typical run [Ref. 2, Table I, Run 5] was calculated to be

$3.95 \times 10^{-5}$  moles/sec. In the absence of an experimental value,<sup>8</sup> we make the reasonable assumption that the solubility of vinylidene chloride in water is  $10^{-3}M$ . Using these values and a diffusion constant of  $10^{-5}$  cm.<sup>2</sup>/sec. we find that the diffusion rate would become less than the polymerization rate when the radius of the droplet exceeds  $8 \times 10^{-3}$  cm. Microscopic observations of a latex indicates that unstabilized droplets do in fact exceed this size. It thus seems reasonable to assume that the slowdown in the second stage is the result of a diffusion-controlled process. Because the polymer particles can hold only a small reserve of monomer (vinylidene chloride is nearly insoluble in its polymer), the concentration of monomer in the particles decreases rapidly until the polymerization rate equals the diffusion rate. During this diffusion-controlled stage, the size of the monomer droplets and hence the rate of polymerization are determined by the stirring speed.

During the first stage and at the beginning of the second stage, both polymer particles and monomer droplets are almost completely covered by surfactant. The resultant double layer causes a large repulsive force between them.<sup>9</sup> This repulsive force has been confirmed by both theoretical and experimental studies.<sup>9,10</sup> Pethica and Few<sup>11</sup> have studied the change in surface potential with decreasing surfactant coverage in a system where sodium octadecyl sulfate was at a water-air interface. They found that the surface potential falls rapidly to a low value as the surfactant coverage is reduced from the close-packed monolayer.

In the course of the second stage the polymer particles continue to grow and require more surfactant for stabilization. When these polymer particles become sufficiently large, there is no longer enough surfactant to form a complete monolayer. When incompletely stabilized particles approach each other, the charge on their surfaces can be redistributed in such a manner as to minimize the repulsive force. This effect will be greater for larger particles, and it is therefore expected that these will have the greater probability of collision.

It is not surprising then, that monomer droplets should start to coalesce soon after micelles disappear. Lawrence and Mills<sup>12</sup> have demonstrated that the rate of coalescence of unstabilized oil droplets is faster by several orders of magnitude than the rate for surfactant-stabilized droplets. This process, as noted above, will tend to maintain a constant total surface area for monomer droplets and polymer particles. Ultimately, the monomer

droplet size will be governed by a balance between the stabilizing effect of the surfactant and the shearing effect of agitation.

As the polymer particles grow and their surfactant deficiency increases, the probability of collision with monomer droplets increases. It is expected that on each collision, monomer will be transferred from monomer droplets to polymer particles. We suggest this transfer process by collision will lead to a sufficient monomer supply to remove the diffusion restriction and allow recovery from the slowdown of the reaction rate in the second stage. The hypothesis proposed here to explain the shape of the conversion-time curves is being tested and will be subsequently reported.

In the third stage, the reaction rate seems to depend on the first power of the catalyst concentration and to be independent of the surfactant concentration. It is further found that addition of more catalyst during the second stage causes an increase of the third-stage reaction rate. This suggests that the rate per particle in the final stage is dependent on the catalyst concentration. A tentative explanation of this behavior can be found in the suggestion of Stockmayer<sup>13</sup> that in viscous polymer-monomer systems, the termination step may be inhibited and that more than one growing chain can exist in a polymer particle of sufficient size. Recent work<sup>14-16</sup> has confirmed that this effect occurs at rather small particle sizes for polymethyl methacrylate and at larger sizes for polystyrene.

It should be pointed out, however, that the data apparently lead to an anomaly. The surfactant independence of the final rate suggests that this rate does not depend on the number of polymer particles but only on the concentration of catalyst. As mentioned above, addition of catalyst in the second stage increases the rate in the third stage of the reaction. This rate is, however, less than the rate that would be obtained had the additional catalyst been added initially. This suggests a rate which depends on the number of particles in the final stage. Resolution of this anomaly must await further experimental work.

Though particle coalescence doubtless occurs and influences the shape of the conversion-time curve, we believe that coalescence cannot account for the magnitude of the rate decrease in the second stage. It may, however, explain the surfactant and catalyst dependence of the final stage. The general shape of the curves seems to result largely from a slowdown caused by decreased diffusion from mono-



mer droplets as these coalesce and recovery by collision transfer of monomer.

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### Synopsis

The effect of stirring speed on the rate of the persulfate-catalyzed polymerization of vinylidene chloride has been determined. It was found that the first-stage rate decreases with increasing stirring speed, that the second-stage rate increases with increasing stirring speed, and that the rate of the third stage is independent of stirring speed. These results, as well as those of an earlier paper, may be

explained in the following manner. The second stage slow-down results from monomer starvation, caused by slow diffusion from coalesced droplets. Recovery is caused by transfer of monomer at the time of collision between a polymer particle and a monomer droplet. These collisions are allowed when the repulsive forces between monomer droplet and polymer particle are reduced because of surfactant deficiency.

### Résumé

On a déterminé l'influence de la vitesse d'agitation sur la vitesse de polymérisation du chlorure de vinylidène catalysée par le persulfate. On a trouvé que la première étape de vitesse décroît avec une augmentation de la vitesse d'agitation, que la seconde étape de vitesse augmente avec une augmentation de la vitesse d'agitation et que la troisième étape est indépendante de la vitesse d'agitation. Ces résultats ainsi que ceux d'une publication antérieure peuvent être expliqués de la manière suivante. La deuxième étape de ralentissement provient du manque de monomère dû à sa lente diffusion au départ des gouttelettes agglomérées. La réinitiation est causé par le transfert du monomère à l'instant d'une collision entre une particule polymérique et une gouttelette de monomère. Ces collisions peuvent avoir lieu lorsque les forces répulsives entre la gouttelette de monomère et la particule polymérique sont réduites par suite d'un défaut de surface.

### Zusammenfassung

Der Einfluss der Rührgeschwindigkeit auf die Geschwindigkeit der persulfat-katalysierten Polymerisation von Vinylidenchlorid wurde bestimmt. Es wurde gefunden, dass die Geschwindigkeit in der ersten Stufe mit wachsender Rührgeschwindigkeit abnimmt, dass die Geschwindigkeit in der zweiten Stufe mit wachsender Rührgeschwindigkeit zunimmt und dass die Geschwindigkeit in der dritten Stufe von der Rührgeschwindigkeit unabhängig ist. Diese Ergebnisse und auch diejenigen einer früheren Arbeit können in folgender Weise erklärt werden. Die Verlangsamung in der zweiten Stufe ist eine Folge der Verarmung an Monomerem, die durch langsame Diffusion aus den koagulierten Tröpfchen verursacht wird. Die Erhöhung kommt durch den Übergang von Monomerem im Moment des Zusammenstoßes zwischen einem Polymerteilchen und einem Monomertröpfchen zustande. Diese Zusammenstöße sind möglich, sobald die Abstossungskräfte zwischen Monomertröpfchen und Polymerteilchen wegen des Fehlens von Emulgator herabgesetzt werden.

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