Mechanism of Emulsion Polymerization of Vinylidene Chloride. I

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INTRODUCTION

The general theory of the mechanism of emulsion polymerization proposed by Harkins[1] envisions two stages. In the first, free radicals initiate polymerization in surfactant micelles swollen with imbibed monomer, but not all of the initially existing micelles become polymer particle loci. Many give up their monomer to growing particles and solubilize more monomer. They may then become sites of free radical initiation or repeat their function as transporters of monomer to already existing particles. As polymer particles grow, however, the polymer adsorbs a layer of surfactant, and micellar surfactant is gradually depleted. When the surface area of polymer increases until most of the available surfactant is adsorbed, the free surfactant concentration is reduced below the critical micelle concentration, and in the absence of micelles, no new polymer particles are formed.

The polymerization has now entered that period in which the growing polymer particles stabilized by surfactant absorb monomer from solution. Diffusion from the emulsified monomer droplets becomes the sole source of monomer for further polymerization. The monomer–polymer ratio in the particles changes at a rate which depends on the relative rates of diffusion and polymerization. According to Harkins, polymerization during the second stage is exclusively in the monomer–polymer particles and is found to follow a constant rate to high conversions, whereupon depletion of monomer results in a slower rate.

Smith and Ewart have proposed a theory of the kinetics of emulsion polymerization, based on the qualitative theory of Harkins, which agrees with the characteristics of styrene emulsion polymeriza-

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tion.[2] These authors expressed the steady state by a recursion formula and distinguished three cases: Case 1, in which the number of free radicals per polymer particle is much less than unity, Case 2 in which this number is ca. 0.5, and Case 3, in which the number is large. The authors showed that for Case 1 and Case 3 the rate of polymerization depends upon the volume of the polymer particles. For Case 2, which appeared to apply to the emulsion polymerization of styrene under usual conditions, the rate of polymerization per polymer particle was found to be independent of the particle size, since it is simply 0.5 times the rate for a single growing chain. The number of particles was shown to increase with the surfactant concentration to the 0.6-power and with the rate of formation of free radicals to the 0.4-power.

Recently, Roe and Brass[3] have demonstrated that the case of more than one growing chain per particle must be considered in order adequately to interpret the results of some styrene emulsion polymerizations. Stockmayer[4] has solved the recursion formula of Smith and Ewart.

The mechanism of emulsion polymerization of vinylidene chloride, which is not adequately explained by existing theories, has received little attention.

Kinetic studies of vinylidene chloride polymerization in bulk reactions[5-7] have revealed anomalously high propagation rates. An apparent complicating feature is the high degree of crystallinity of polyvinylidene chloride which makes it insoluble in and practically unswollen by the monomer.

Wiener,[8] investigating the emulsion polymerization of vinylidene chloride, recognized the inapplicability of theories which involve polymer particles swollen with monomer and proposed that the surface of the polymer particles may constitute the main locus of reaction. He found the solubility of monomer in a polymer latex (probably via adsorption) to be a function of polymer content and

surfactant concentration. Rates determined dilatometrically were constant up to 60% conversion. For low-surfactant experiments, rates were determined gravimetrically and found to be constant up to 40% conversion, and decreased thereafter. The rate of polymerization was dependent on the square root of the catalyst concentration and on approximately the 0.6-power of the surfactant concentration. The data were considered by Wiener to be in fair agreement with the predictions of Smith and Ewart but to provide no conclusive evidence as to the mechanism of the reaction.

Tkachenko and Khomikovskiĭ[9] studied the solubility of vinylidene chloride in surfactant solutions of different concentrations and the rate of polymerization in these solutions. Vinylidene chloride was supplied to the reaction mixture through the vapor phase. A rate of stirring was selected such that an increase in stirring did not affect the reaction rate. No kinetic data were presented, but it was proposed that the surface of the polymer particles was the main locus of reaction, owing to the insolubility of the polymer in monomer.

In the following report, we present results of a study of the effect of sodium lauryl sulfate concentration and initiator concentration on the emulsion polymerization of vinylidene chloride.

EXPERIMENTAL

Materials

Vinylidene chloride (Dow Chemical Co.) was washed with 10% aqueous sodium hydroxide to remove the inhibitor (phenol) and distilled in a nitrogen atmosphere from solid sodium hydroxide and calcium chloride immediately before use. The distilled monomer was transferred to the reaction flask by a procedure described below under "Special Precautions."

Ammonium persulfate, $(NH_4)_2S_2O_8$, Mallinckrodt analytical reagent grade, was used as received.

Sodium metabisulfite, $Na_2S_2O_5$, 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 polymerizations were performed in a 500-ml., round-bottomed, five-necked reaction flask immersed in a water bath which was held at $36 \pm 1°C$. The flask was equipped with a reflux condenser, stirring apparatus, a thermometer, and a sampling device shown in Figure 1. A few millimeters of nitrogen pressure was maintained through the top of the condenser to provide a nitrogen atmosphere and prevent loss of vinylidene chloride.

In one series of polymerizations, all factors were held constant except the amount of sodium lauryl sulfate. In the other series, all factors were held constant except the amounts of ammonium persulfate and sodium metabisulfite. The charge for the series of experiments to determine the rate dependence on sodium lauryl sulfate concentration was: 100.0 g. vinylidene chloride, x g. sodium lauryl sulfate, $(119.7 - x)$ g. deionized water, 0.15 g. ammonium persulfate, and 0.15 g. sodium metabisulfite, with x chosen as 10.0, 5.0, 4.0, 3.0,
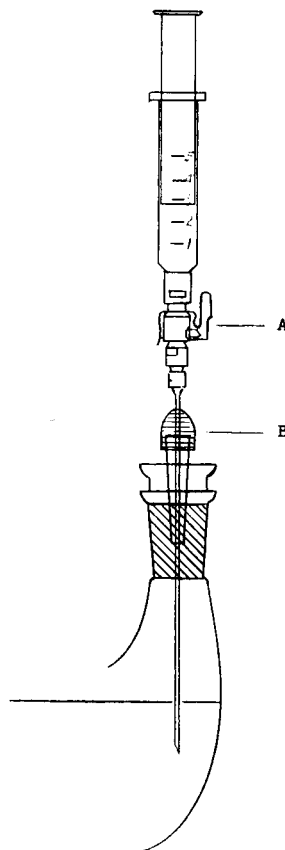

Fig. 1. Latex sampling device as mounted on the flask. A 5-ml. hypodermic syringe, fitted with a 6-in. 14-gauge needle, and a brass stopcock (A), is passed through a self-sealing rubber bulb (B) and suitable ground-glass joints.
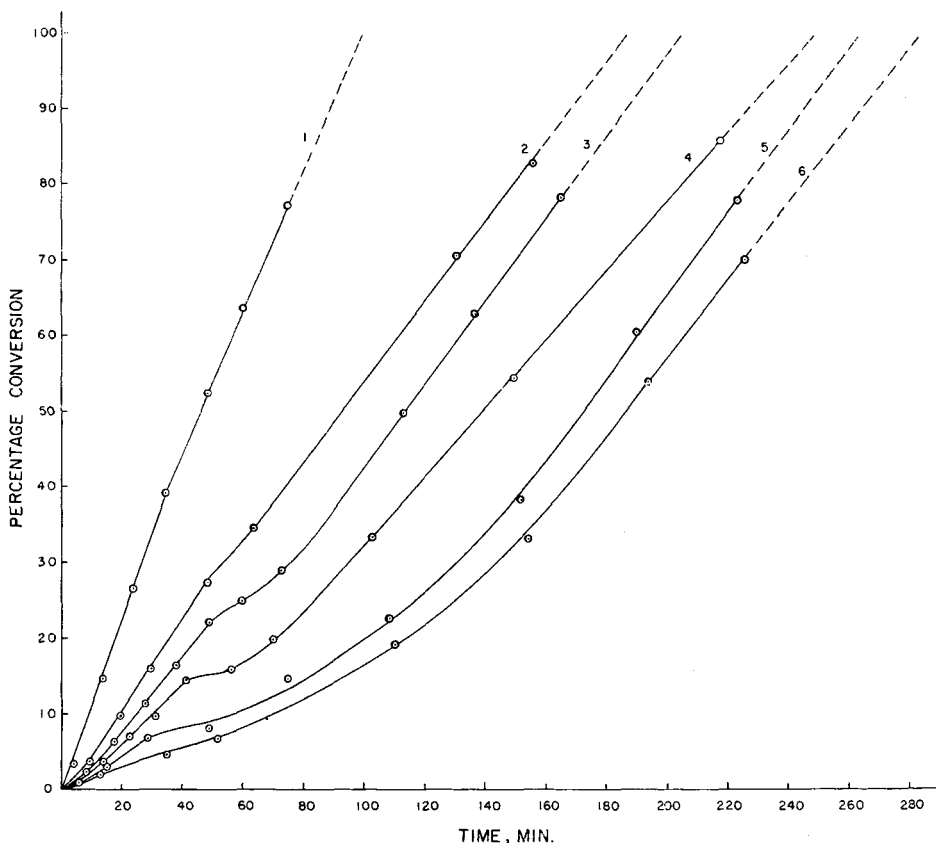
Fig. 2. Effect of surfactant concentration on emulsion polymerization of vinylidene chloride at 36.0°C. Initial catalyst charge: 0.15 g. $(NH_4)_2S_2O_8$, 0.15 g. $Na_2S_2O_5$/100 g. monomer. Sodium lauryl sulfate concentrations: (1) 10.0 g., (2) 5.0 g., (3) 3.0 g., (4) 2.0 g., (5) 1.0 g., (6) 0.50 g./100 g. monomer.

2.0, 1.0, and 0.5. A 10% stock solution of sodium lauryl sulfate was prepared for each series of experiments. The reaction charge for the series of experiments to determine rate dependence on catalyst concentration was 100.0 g. vinylidene chloride, 2.0 g. sodium lauryl sulfate, x g. ammonium persulfate, x g. sodium metabisulfite, and $(118 - 2x)$ g. deionized water, with x chosen as 0.60, 0.45, 0.30, 0.225, 0.15, 0.075, and 0.0375. In the activated persulfate catalyst system ammonium persulfate is the initiator; sodium metabisulfite, the activator. In these experiments they were used in a 1:1 weight ratio. The concentration of persulfate will be used when referring to catalyst concentration, it being understood that an equal amount of activator was also used. Solutions of persulfate and bisulfite were prepared immediately before use so that 5 ml. of solution contained the desired quantity of each.

Water and sodium lauryl sulfate solution were added to the flask and stirred at a standard rate under steady flow of nitrogen for approximately 30 min. The previously distilled vinylidene chloride was then added under nitrogen pressure. The stirring speed was maintained constant at 285 rpm (tachometer measurement) for all of the polymerization runs. A standard 3-in. Teflon stirring blade was used. Catalyst was added with a hypodermic syringe shortly after refluxing of vinylidene chloride had begun.

At appropriate intervals, samples of latex were drawn into a previously cooled hypodermic syringe. The latex was coagulated in cold methanol in tared aluminum weighing dishes. Sample weights were obtained by weighing the syringe before and after discharging the latex. The samples were dried in air overnight and then dried to constant weight in a vacuum oven at 50°C. and 10 mm. pressure (2 hr. in the vacuum oven was sufficient).

The percentage of solids and percentage conversion of each sample were calculated from sample weights and residue weights as follows (nonpolymer
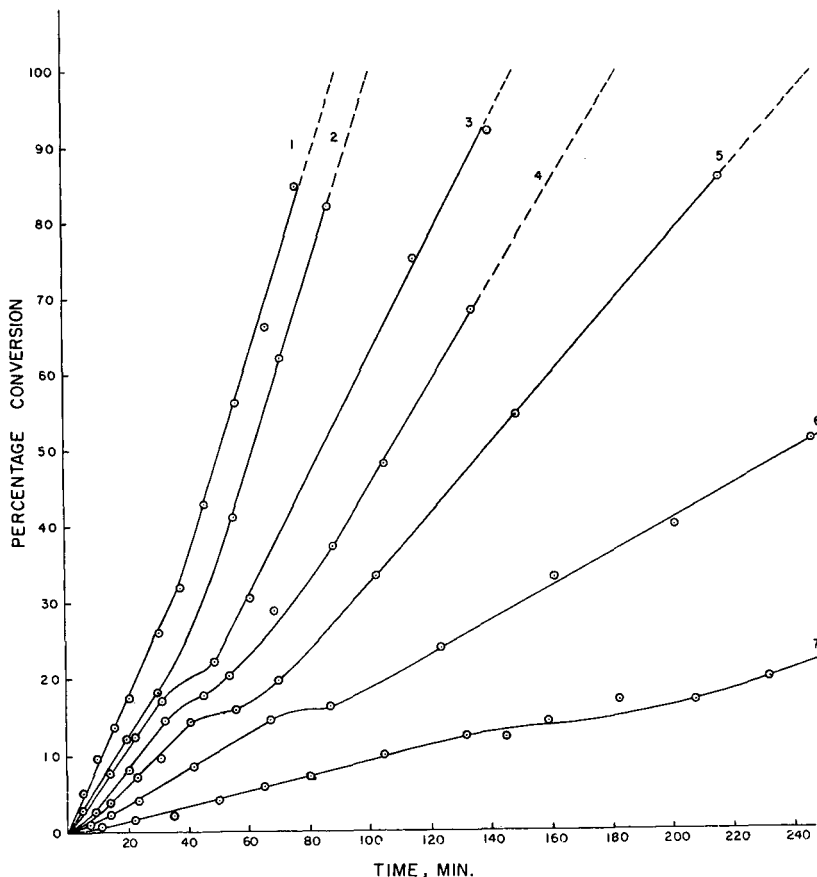
Fig. 3. Effect of catalyst concentration on emulsion polymerization of vinylidene chloride at 36.0°C. Initial sodium lauryl sulfate charge: 2.0 g./100 g. monomer. Catalyst concentrations: (1) 0.60 g., (2) 0.45 g., (3) 0.30 g., (4) 0.225 g., (5) 0.15 g., (6) 0.075 g., (7) 0.0375 g. each of ammonium persulfate and sodium metabisulfite/100 g. monomer.

solids refers to surfactant and catalyst initially).

$$\text{Percentage of solids} = \frac{\text{Residue weight} \times 100}{\text{Sample weight}}$$

Percentage conversion

$$= \frac{\begin{array}{c}\text{Percentage} \\ \text{of solids}\end{array} - \begin{array}{c}\text{Percentage of} \\ \text{nonpolymer solids}\end{array} \times 100}{\text{Theoretical percentage of polymer solids}}$$

Special Precautions

Vinylidene chloride readily forms peroxides on contact with air, and therefore special precautions were necessary in the transfer from the distillation receiving flask to the reaction flask. The transfer was made with a graduated dropping funnel with stopcocks at top and bottom, which was first evacuated and then attached to the distillation receiver. - The upper stopcock of the dropping funnel was opened, and the vinylidene chloride was drawn into the funnel through a fritted glass filter. The dropping funnel was then fitted to the reaction flask and emptied by nitrogen pressure. The weight of vinylidene chloride used was determined by weighing the dropping funnel before and after charging the reaction flask.

To insure efficient condensation of vinylidene chloride vapors in the system, a mixture of ethylene glycol and ethanol, maintained at 0–5°C., was circulated through the condenser. Samples for determination of reaction rate were removed by a hypodermic syringe and needle. One neck of the reaction flask was equipped with a self-sealing rubber bulb. It was necessary to cool the syringes with Dry Ice before removing samples to prevent loss of vinylidene chloride vapor.

EXPERIMENTAL RESULTS

Graphs of percentage conversion as a function of time for two series of polymerizations are shown in Figures 2 and 3.
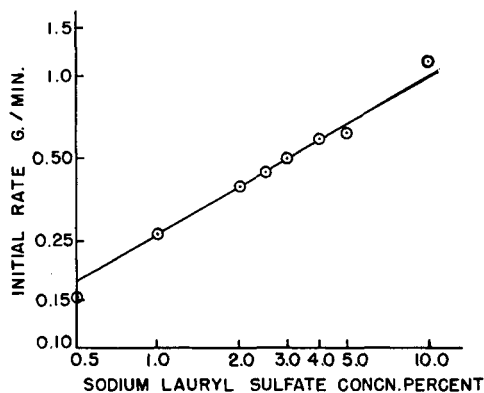
Fig. 4. Logarithm of initial polymerization rate as a function of logarithm of surfactant concentration. Slope = 0.60.
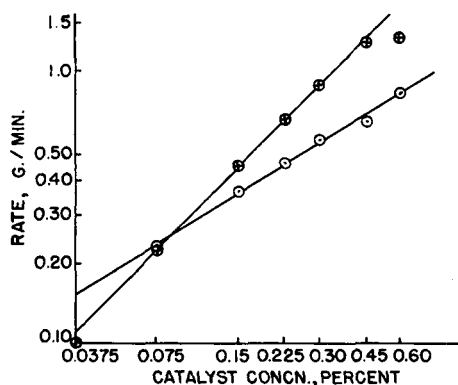

Fig. 5. Logarithm of polymerization rate as a function of the logarithm of catalyst concentration: (⊙) initial rate, slope = 0.60; (⊕) final rate, slope = 1.0.

In the first series, catalyst concentration was held constant, while the emulsifier concentration was varied from 0.5 to 10.0%, based on monomer used. Inspection of the curves shows that the rate of the initial stage increased as the sodium lauryl sulfate concentration was increased, and that the rate achieved in the final stage did not appear to be dependent on the sodium lauryl sulfate concentration. (Constant rates for the first and final stages are assumed.)

In the second series, the emulsifier concentration was held constant and the catalyst concentration was varied from 0.0375 to 0.60% of persulfate, based on monomer, with an equal quantity of metabisulfite. The rate of the initial stage increased with increasing catalyst concentration. The rate of the final stage was also dependent on the initial catalyst concentration. The dependence of rate on emulsifier and catalyst concentration was determined graphically.

Log–log plots of rate as a function of sodium lauryl sulfate concentration (Fig. 4) and rate as a function of catalyst concentration (Fig. 5) gave straight lines, the slopes of which define the values of x and y in the rate equations,

$$\text{rate} = k \, [\text{sodium lauryl sulfate}]^x$$

and

$$\text{rate} = k' \, [\text{catalyst}]^y$$

The dependence of initial rate on sodium lauryl sulfate concentration was found to be 0.60. The dependence of initial rate on catalyst was also 0.60. Final rate dependence on catalyst concentration was 1.0.

The most unusual result of the two series of polymerizations was the shape of the conversion–time curves representing polymerization in the
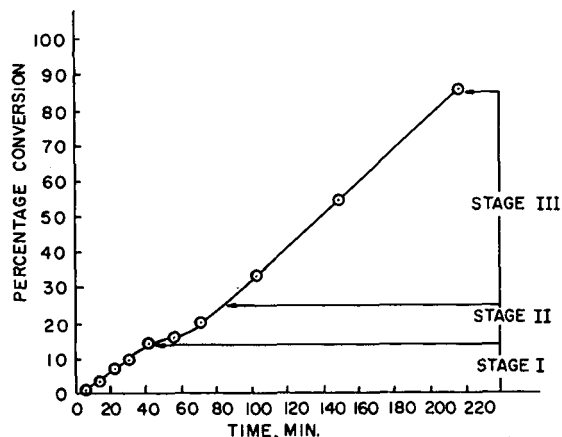

Fig. 6. Typical three-stage curve. 2.0% sodium lauryl sulfate, 0.15% catalyst.
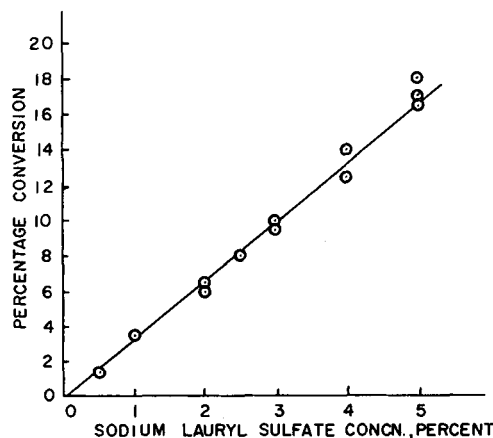

Fig. 7. Plot of percentage conversion at which foaming ceased as a function of initial sodium lauryl sulfate concentration.

intermediate ranges of sodium lauryl sulfate concentration (1.0–5.0%) and catalyst concentration (0.075–0.30%). The detailed aspects of these curves were related to several experimental observations and will be discussed in terms of a typical reaction with 2% sodium lauryl sulfate and 0.15% catalyst (Fig. 6).

As described above, the catalyst was added to the flask after the reaction mixture has reached equilibrium temperature. This temperature was established by vinylidene chloride reflux at about 32°C. Sufficient emulsifier was present initially in all runs to stabilize bubbles of boiling vinylidene chloride and thereby allow considerable foaming. The foam persisted during the early part of the reaction and then rather suddenly subsided. In 2.0% sodium lauryl sulfate runs this always occurred at 6–7% conversion. When the percentage conversion at which foaming stopped was plotted against surfactant concentration, a direct dependence was found, as seen in Figure 7. These data agree with a 1.2-power dependence on surfactant concentration, a relationship derived from the basic Smith-Ewart theory, if it is assumed that the time at which foaming stops is coincident with the disappearance of micelles.

At first the refluxing rate was slow and steady, and the emulsion showed no separation. After foaming had stopped, the refluxing rate became gradually faster. The development of an oily flow on the wall of the flask was also observed. Each successive sample of latex removed from the flask revealed a greater degree of coalescence of monomer droplets. This process of coalescence and increasing refluxing rate continued at an ac-
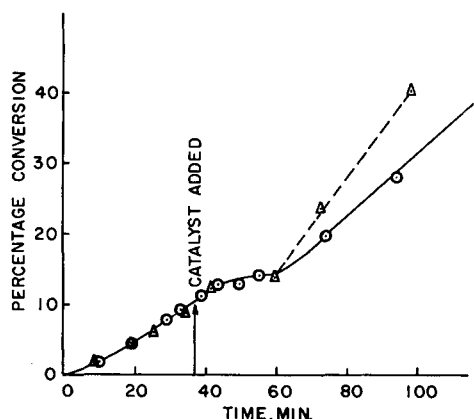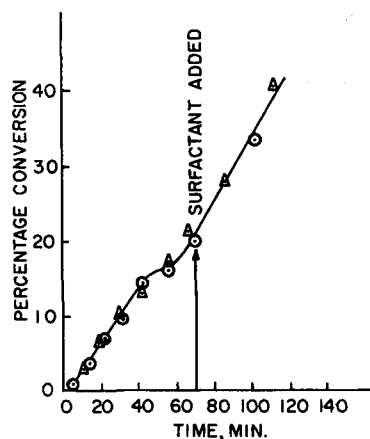

Fig. 9. Effect of addition of a small amount of sodium lauryl sulfate during stage III. Initial charge: 2.0% sodium lauryl sulfate, 0.15% catalyst; (⊙) no extra sodium lauryl sulfate added; (△) 0.5 g. sodium lauryl sulfate added after 70 min.

celerating pace until a time was reached when there seemed to be a sudden and complete instability of the monomer phase and a sharp increase in refluxing rate. As shown in Figure 6, up to this point (about 15% conversion for 2.0% sodium lauryl sulfate) the rate of conversion was apparently constant. In the discussion which follows, this part of the polymerization preceding a decrease in rate will be referred to as Stage I. (A more thorough study of Stage I has shown that the percentage conversion in the beginning is proportional to the second power of time.[10] This is to be expected if the number of particles is increasing linearly while the conversion rate per particle remains constant.)

In general, the percentage conversion corresponding to the end of Stage I was dependent on sodium lauryl sulfate concentration and relatively independent of catalyst concentration (Figs. 2 and 3). In reactions with 10.0% sodium lauryl sulfate, the monomer never formed a separate unstable phase. At low concentrations of sodium lauryl sulfate, separation of vinylidene chloride occurred at very low conversions.

After the end of Stage I, visual observations were less significant. Refluxing continued at a rapid rate through Stages II and III, whereupon it slowly diminished and stopped. The rate of conversion showed a sharp decrease immediately after Stage I for a period of short duration (Fig. 6, Stage II). The rate gradually increased again to a constant rate (Stage III) which persisted to approximately 85% conversion.

Fig. 8. Effect of addition of catalyst during final part of stage I. Initial charge: 2.0% sodium lauryl sulfate, 0.15% catalyst; (⊙) no extra catalyst added; (△) 0.15% catalyst added after 37 min.

An experiment was performed to determine the effect of addition of more catalyst to a reaction which had proceeded beyond the end of foaming, but which had not yet reached Stage II. There was no apparent effect on the rates of Stage I and Stage II, but the rate of Stage III was increased (Fig. 8).

Another experiment was performed to determine the effect of the addition of more sodium lauryl sulfate during the early part of Stage III. The amount added, 0.5 g., probably not enough to form micelles, did not significantly change the rate of the reaction (Fig. 9).

DISCUSSION

The observations indicate that the mechanism of the emulsion polymerization of vinylidene chloride is not completely explained on the basis of existing theories. An essential condition in the mechanism proposed by Harkins[1] and extended by Smith and Ewart[2] is the formation of monomer-polymer particles. These particles consist of polymer swollen with absorbed monomer. In the polymerization of styrene, for example, the polystyrene formed is soluble in monomeric styrene and all of the monomer appears to be absorbed by polymer at less than 50% conversion.[1,3]

Polyvinylidene chloride, on the other hand, is a polymer which is insoluble in its own monomer and practically not swollen by it.[5] Therefore, the amount of monomer in monomer–polymer particles in a vinylidene chloride polymerization is limited to the amount which can be adsorbed at the surface.[8,9]

Smith and Ewart showed[2] that a constant rate of polymerization in the general case results only if (a) the number of growing particles remains constant, (b) the rate of combination of two free radicals in a single particle is much greater than the rate of entrance of radicals into the polymer particle, (c) the average rate of polymerization per free radical is constant, and (d) the concentration of monomer in the polymer particle remains constant.

Two alternative explanations may be adduced to explain the unusual results which have been described above. The simplest hypothesis is that coagulation of particles may follow Stage I and disturb the steady state which has been established for the transport of vinylidene chloride from emulsified monomer droplets through the aqueous phase to the micelles in which polymerization is taking place. This possibility has been investi-

gated experimentally by electron microscopy. A preliminary report has appeared,[11] and a subsequent paper discusses the theory and experiments in detail.[12] There is a little doubt that agglomeration of polymer particles plays a part in explaining the observed kinetics, but the magnitude of the effect appears to be insufficient to permit a full explanation solely from this cause.

A second explanation, to be discussed in detail subsequently,[10] involves a change in the transport mechanics of monomer following Stage I, at which time it is quite clear from experiment that a fundamental redistribution of surfactant takes place. It is likely that collision of polymer particles with droplets of vinylidene chloride may occur and that more than one free-radical chain may be growing simultaneously in or on some of the larger polymer particles.

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Synopsis

The rate of emulsion polymerization of vinylidene chloride has been measured as a function of catalyst and surfactant concentration in the system consisting of vinylidene chloride, water, ammonium persulfate, sodium metabisulfite, and sodium lauryl sulfate. The polymerization may be divided into three rather well-demarcated stages. In the first, a normal emulsion polymerization occurs at a rate which depends on the 0.6-power of the catalyst concentration and the 0.6-power of the surfactant concentration. In the second stage, the rate drops to less than half that of Stage I. The percentage conversion at which Stage II begins increases with increasing surfactant concentration. Stage II is absent at very high surfactant concentrations

(10 g./100 g. monomer). In the third stage, the rate increases and may exceed the rate of Stage I; it depends on the first power of the catalyst concentration and is independent of surfactant concentration. Addition of catalyst at the end of the first stage does not affect the rate of Stage II but increases the rate of Stage III. These results are discussed in relation to the theories of Harkins, Smith, and Ewart.

Résumé

La vitesse de polymérisation en émulsion du chlorure de vinylidène a été mesurée an fonction de la concentration en catalyseur et en agent tensioactif dans le système chlorure de vinylidène, eau, persulfate d'ammonium, métabisulfite de sodium et le sulfate de sodiumauryle. Les polymérisations peut être divisée en trois étapes, assez bien marquées. Dans la première étape une polymérisation en émulsion normale se produit à une vitesse, qui dépend de la puissance 0,6 de la concentration en catalyseur et de la puissance 0,6 de la concentration en agent tensioactif. Dans la seconde étape, la vitesse tombe à moins de la moitié de celle de la première étape. Le pourcentage de conversion, auquel la seconde étape commence, augmente avec l'augmentation de la concentration en agent tensioactif. La seconde étape est absente à des concentrations en agent tensioactif très élevées (10 gr/100 gr monomère). Dans la troisième étape la vitesse augmente et peut excéder la vitesse de l'étape I; elle dépend de la première puissance de la concentration en catalyseur et est indépendante de la concentration an agent tensioactif. L'addition de catalyseur à la fin de la première étape n'a pas d'influence sur la vitesse de la seconde étape, mais augmente la vitesse de l'étape III. Ces résultats sont discutés en relation avec les théories de Harkins et de Smith et Ewart.

Zusammenfassung

Die Geschwindigkeit der Emulsionspolymerisation von Vinylidenchlorid wurde als Funktion der Katalysator- und Emulgatorkonzentration in einem aus Vinylidenchlorid, Wasser, Ammoniumpersulfat, Natriummetabisulfit und Natriumlaurylsulfat bestehenden System gemessen. Die Polymerisation kann in drei ziemlich klar unterscheidbaren Stufen geteilt werden. In der ersten findet eine normale Emulsionspolymerisation statt, deren Geschwindigkeit von der Potenz 0,6 der Katalysatorkonzentration und def Potenz 0,6 der Emulgatorkonzentration abhängt. In der zweiten Stufe nimmt die Geschwindigkeit auf weniger als die Hälfte der Geschwindigkeit der ersten Stufe ab. Der prozentuelle Umsatz, bei welchem die Stufe II beginnt, nimmt mit steigender Emulgatorkonzentration zu. Stufe II fehlt bei sehr hoher Emulgatorkonzentration (10 g/100 g Monomeres). In der dritten Stufe nimmt die Geschwindigkeit zu und kann die der Stufe I übertreffen; sie hängt von der ersten Potenz der Katalysatorkon zentration ab und ist von der Emulgatorkonzentration unabhängig. Zusatz von Katalysator am Ende der ersten Stufe beeinflusst die Geschwindigkeit von Stufe II nicht, erhöht aber die Geschwindigkeit von Stufe III. Die Ergebnisse werden unter Bezugnahme auf die Theorien von Harkins und Smith und Ewart diskutiert.