

# Emulsion Polymerization of Vinyl Acetate Initiated by Intermittent $\gamma$ Radiation

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## Synopsis

The reaction kinetics of emulsion polymerization of vinyl acetate (VAc) monomer have been studied by using intermittent  $\gamma$  radiation. The purpose of this technique is to take advantage of the polymerization reaction which still continues after the radiation production has been stopped, as expected by the Smith-Ewart rate theory. Tween 20 (polyoxyethylene sorbitan monolaurate), was used as the emulsifier. The polymer conversion was determined by using the dilatometric method. The polymerization rate  $R_p$  decreased with increase in emulsifier content. The Smith-Ewart rate theory cannot explain the experimental evidence satisfactorily. The average polymerization rate  $\overline{R}_p$  between 20% and 80% conversion is a function of irradiation dose rate and can be written

$$\overline{R}_p = a_1 I^{a_2}$$

where  $a_1$  and  $a_2$  is a constant in which the value depends on the emulsifier content in the emulsion and  $I$  is the irradiation dose rate.

## INTRODUCTION

The mechanism of emulsion polymerization which is now generally accepted is based on the work done by Harkin<sup>1</sup> and his collaborators, published in 1947. The quantitative description was first given by Smith and Ewart and will be known as the Smith-Ewart rate theory.<sup>2</sup> A number of research workers<sup>3-6</sup> in a number of countries have studied the kinetics of  $\gamma$ -induced emulsion polymerization. It was found that the polymerization rate is much higher in the emulsion system than in bulk.

The purpose of this experiment is to study the kinetic aspect of radiation-induced emulsion polymerization of VAc monomer by using intermittent  $\gamma$  radiation.

The Smith-Ewart rate theory as well as the Ugelstad rate theory<sup>7</sup> were tried to explain the experimental results. According to the Smith-Ewart rate theory,<sup>2,8</sup> for ideal emulsion, it is found that the average number of radicals in each polymer particle,  $\bar{n}$ , is 0.5. Therefore the polymerization rate  $R_p$  can be written

$$R_p = k_p [M][N]/2N_A \quad (1)$$

where  $N$  is the number of polymer particles per liter of organic phase,  $k_p$  the propagation rate constant,  $M$  the monomer content in the polymer particles, and  $N_A$  the Avogadro number. Equation (1) predicts that the polymerization rate  $R_p$  for a given number of polymer particles is independent of initiator concentration or the rate of radical production. Even after the radical production has

been stopped, the polymerization reaction still continues at the same rate. However, this statement is true only if the polymer radicals in the polymer particles are perfectly trapped, hence mutual termination between two radicals in the different polymer particles is impossible.

Experimental evidence has concluded that for some monomers the reaction kinetics did not obey the Smith–Ewart rate theory. Chain transfer reaction may be the main factor which causes this deviation. Chain transfer reaction will produce low molecular weight polymer radicals with more chance to diffuse into the water phase. Hence, the average number of radicals in each polymer particle is much lower than 0.5 as expected by the Smith–Ewart rate theory. It must be noted that the VAc monomer is one of the monomers with a high transfer constant.<sup>9,10</sup>

This diffusion of polymer radicals into the water phase is the one responsible for the slowing down of the reaction rate after the radical production is stopped. Therefore, it is necessary to take a minor correction for the Smith–Ewart rate theory in which the average number of polymer radicals in each polymer particle is much less than 0.5. The Ugelstad rate theory, which is applicable for vinyl acetate emulsion, apparently gives better explanation concerning the role of the initiator concentration and the diffusion rate of the radicals.<sup>7</sup>

The Smith–Ewart rate theory was deduced by the assumption that the radicals enter one by one from the water phase into the micelles or polymer particles. This is only possible if the initiator used for this polymerization is a water-soluble initiator. The situation is quite different in the case of radiation emulsion polymerization. In this case, radicals can be produced in all phases although the rate of radical production is different in each phase. The rate of radical production can be written

$$\frac{d(R)}{d(t)} = 6.242 \times 10^{17} IG_R \quad (2)$$

where  $d(R)/d(t)$  is the rate of radical production (radicals/sec-g),  $I$  the irradiation dose rate (Mrads sec), and  $G_R$  the number of radicals produced by 100 eV of energy absorption (this value depends on the materials irradiated). In case the irradiation dose rate  $I = 60$  rads/sec and  $G_R = 1$ , the rate of radical production can be computed and is found to be  $3.75 \times 10^{19}$  radicals/sec-g.

The advantage of the use of  $\gamma$  radiation as an initiator for emulsion polymerization compared with an organic initiator is that the radical production can be stopped at any time easily, hence the reaction kinetics can be studied after the radical production has been stopped. Furthermore, there are no initiator residues compared to the emulsion polymerization initiated by chemical initiators.

## EXPERIMENTAL

### Materials

Vinyl acetate monomer (VAc) was purified by using vacuum distillation immediately before use. The emulsifier, Tween 20 (polyoxyethylene sorbitan monolaurate), was supplied by Merck Company and used without further purification. Bidistilled water was used for the emulsion preparation. The irra-

diation facility was a Gamma Cell 220, made in Canada, 2000 Ci. Irradiation dose rate was calculated by using a Fricke dosimeter.

### Polymerization

The VAc emulsion was prepared in an electric blender with 30 min of stirring. Tween 20 was used as the emulsifying agent.

The amount of Tween 20 in the emulsion is variable, between 0.5 and 3.0 parts per 100 parts VAc + water. However, the ratio between VAc and water is constant for all the experiments, that is, VAc:water = 30:70. The emulsion prepared by this method is quite stable for more than two weeks, especially the emulsion with the high emulsifier content.

The irradiation was carried out in a round flask with a long graduated neck, placed in the gamma cell container. Intermittent radiation was used in this experiment. Normally, the irradiation period was 5 min and the nonirradiation period was 5 min. The monomer conversion was determined by the dilatometric method, a well-known method for the determination of conversion and polymerization rate.<sup>11</sup> The shrinkage of volume was measured every 5 min of reaction time. The temperature of the emulsion was maintained at 28–29°C. The irradiation dose rate was variable between  $0.63 \times 10^5$  rad/hr and  $2.10 \times 10^5$  rads/hr. Polymer conversion at the end of the reaction was determined gravimetrically.

## RESULTS AND DISCUSSION

### Rate of Polymerization

The polymerization rate during the irradiation period and after irradiation was studied by the use of an emulsion with the following composition: VAc:H<sub>2</sub>O:Tween, 20 = 70:30:1.5. In the first experiment, the emulsion was irradiated at a dose rate of  $2.1 \times 10^5$  rads/hr, intermittent irradiation with 5 min of irradiation and 5 min of nonirradiation period.

In the second experiment, the sample was irradiated at a dose rate of  $2.1 \times 10^5$  rad/hr, intermittent irradiation with 5 min of irradiation and 15 min of nonirradiation period.

Figure 1 shows the results of these experiments. It is seen that the polymerization rate in the irradiation period is nearly the same as the polymerization rate in the nonirradiation period after 5 min of irradiation has been stopped. However, more than 5 min after the irradiation has been stopped, the polymerization rate decreases and reaches nearly a zero value after 15 min. This evidence means that there are some interactions between the polymer radicals in the different polymer particles, hence the average number of radical in each polymer particle decreases with time. Chain transfer to monomer or emulsifier maybe took place, and the results were the low molecular weight radicals with more chance to diffuse into the water phase. Termination between two radicals can take place easily in the water phase.

It can be calculated that the effective irradiation dose to obtain 90% of conversion was about  $1.50 \times 10^5$  rads.

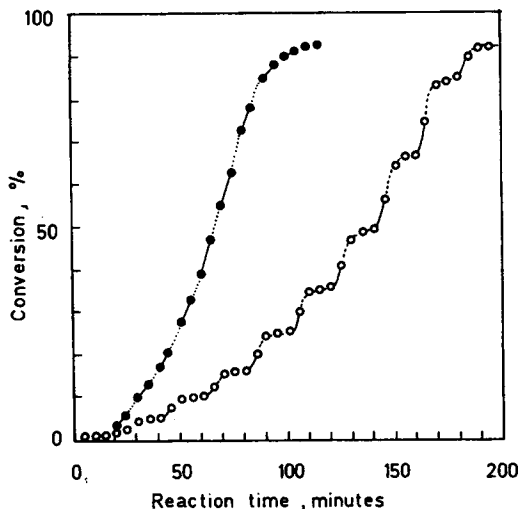


Fig. 1. Conversion of VAc vs reaction time. Irradiation dose rate  $2.1 \times 10^5$  rads/hr. Tween 20 content is 1.5 part/100 VAc and water: (●—●) irradiation period 5 min; (●- - -●) nonirradiation period 5 min; (○—○) irradiation period 5 min; (○- - -○) nonirradiation period 15 min.

### Influence of Emulsifier Content

Figure 2 shows the relation between the reaction time and the monomer conversion for the emulsion of different emulsifier content. Irradiation dose rate was  $2.10 \times 10^5$  rads/hr intermittent irradiation. It is seen that the polymerization rate decreases with the increase of the emulsifier content in the emulsion sample. The region of 20%–80% of conversion can be regarded as the region of constant polymerization rate. According to the Smith–Ewart rate theory, this region can be assumed as the region between the disappearance of micelles and droplets.

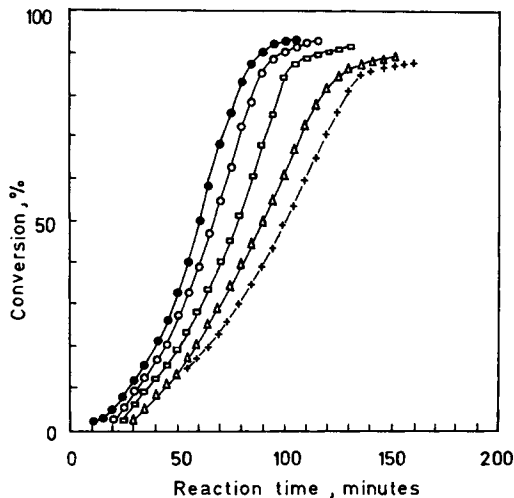


Fig. 2. Conversion of VAc vs reaction time. Influence of emulsifier content. Intermittent  $\gamma$  radiation, with 5 min irradiation and 5 min nonirradiation. Irradiation dose rate is  $2.1 \times 10^5$  rads/hr. Influence of Tween 20 content in the emulsion. Tween 20 content: (●—●) 1.0 part/100 VAc + water; (○—○) 1.5 part/100 VAc + water; (□—□) 2.0 parts/100 VAc + water; ( $\Delta$ — $\Delta$ ) 2.5 parts/100 VAc + water; (+—+) 3.0 parts/100 VAc + water.

However, in the case of decrease of the polymerization rate with increase in emulsifier content it cannot be explained by the Smith-Ewart theory. It can be assumed that the average number of radicals, in each polymer particle,  $\bar{n}$ , is much less than 0.5, as expected by the Smith-Ewart and depends on total surface area of the polymer particles. The total surface area of the polymer particles depends on the emulsifier content, according to the Smith-Ewart rate theory. There is more chance of radical diffusion into the water phase with increase of the polymer particle surface area, hence the average number of radicals in each particle decreases with increase in emulsifier content. It must be noted that the VAc monomer is the one monomer with the highest value of transfer constant.

Figure 3 shows the relationship between the average polymerization rate  $\bar{R}_p$  in the constant region and the emulsifier content  $C$ . This semilog plot shows a straight line, and hence it can be written

$$\bar{R}_p = 2.171 \exp(-0.272C) \quad (3)$$

where  $C$  is the emulsifier content in the emulsion, expressed in parts emulsifier/100 VAc + water;  $\bar{R}_p$  is the polymerization rate, expressed in % conversion/min. It is found that the polymerization rate decreases with increase in emulsifier content. However, the stability of the emulsion is reduced with decrease in emulsifier content. It is clear that both the Smith-Ewart and Ugelstad rate theories cannot explain these experimental results satisfactory.

The influence of emulsifier content on the intrinsic viscosity  $[\eta]$  in acetone solution can be seen in Figure 4. It is a straight line which can be written with the equation:

$$[\eta] = -0.579C + 3.20 \quad (4)$$

where  $C$  is the emulsifier content, parts/100 VAc + water, and  $[\eta]$  the intrinsic viscosity in acetone solution, dl/g. It is found that the intrinsic viscosity decreases with increase in emulsifier content. It is known that there is a relationship between the intrinsic viscosity and the average molecular weight. Hence, it can be computed that the average molecular weight decreases with increase in emulsifier content.

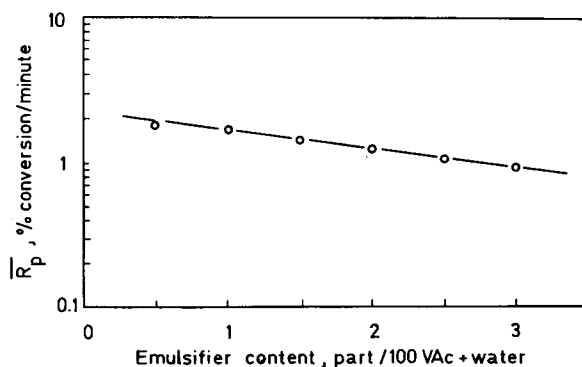


Fig. 3. Semilog plot of polymerization rate of VAc emulsion vs Tween 20 content. Influence of emulsifier content on  $\bar{R}_p$ . Irradiation dose rate  $2.1 \times 10^5$  rads/hr. Intermittent  $\gamma$  irradiation.

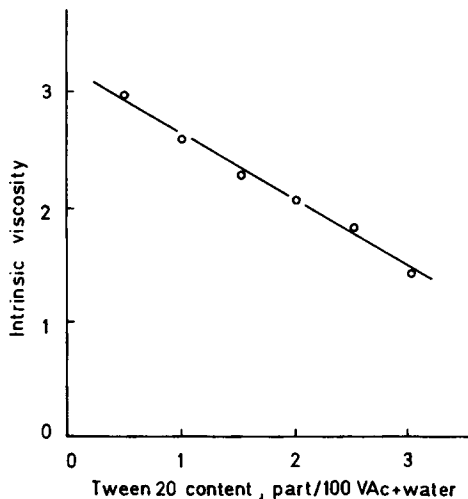


Fig. 4. Influence of emulsifier content on intrinsic viscosity. Irradiation dose rate  $2.1 \times 10^5$  rads/hr.

### Influence of Irradiation Dose Rate

The influence of irradiation dose rate on the polymerization rate can be seen in Figure 5. The emulsifier content of Tween 20 used in this experiment was 1.5 part per 100 VAc + water. It is seen that the polymerization rate is much influenced by irradiation dose rate.

The influence of irradiation dose rate on the average polymerization rate, between 20% and 80% of conversion,  $\bar{R}_p$ , can be seen in Figure 6. This log-log plot shows a straight line and therefore can be written

$$\bar{R}_p = a_1 I^{a_2} \quad (5)$$

where  $a_1$  and  $a_2$  are constants in which the value depends on the emulsifier

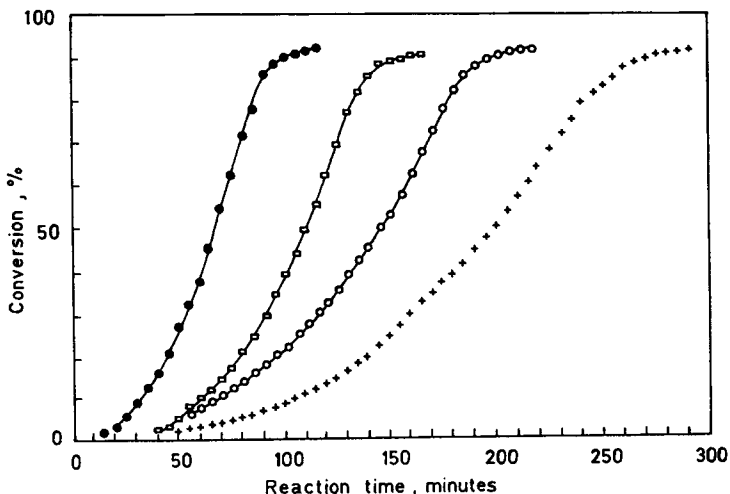


Fig. 5. VAc conversion vs reaction time. Influence of irradiation dose rate on  $R_p$ . Intermittent  $\gamma$  irradiation. Tween 20 content 1.5 part/100 VAc + water: (●—●)  $I = 2.1 \times 10^5$  rads/hr; (□—□)  $I = 1.57 \times 10^5$  rads/hr; (○—○)  $I = 1.05 \times 10^5$  rads/hr; (+—+)  $I = 0.63 \times 10^5$  rads/hr.

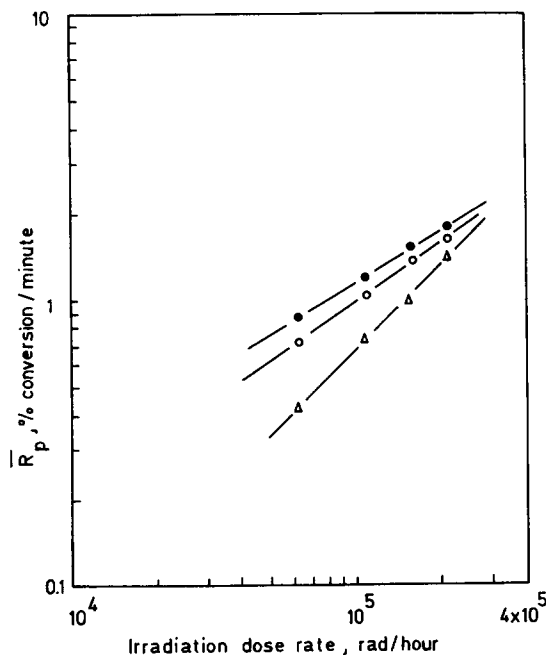


Fig. 6. Log-log plot of average polymerization rate of VAc emulsion  $\bar{R}_p$ , vs irradiation dose rate  $I$ . Influence of irradiation dose rate on  $R_p$ . Intermittent  $\gamma$  irradiation. Tween 20 content: (●—●) 0.5 part/100 VAc + water; (○—○) 1.0 part/100 VAc + water; ( $\Delta$ — $\Delta$ ) 1.5 part/100 VAc + water.

TABLE I  
Constant  $a_1$  and  $a_2$  as a Function of Emulsifier Content

Tween 20 content <sup>a</sup>	$a_1$	$a_2$
0.5	$1.974 \times 10^{-5}$	0.597
0.0	$0.581 \times 10^{-5}$	0.691
1.5	$0.114 \times 10^{-6}$	1.00

<sup>a</sup> Tween 20 content, expressed in parts/100 VAc + water.

content and  $I$  is expressed in rads/hr. However, Figures 5 and 6 cannot explain satisfactorily the role of the irradiation dose rate on the polymerization rate in the constant region or in the region where the formation of polymer particles has stopped, or the influence of the irradiation dose rate on the average number of radicals in each particle,  $\bar{n}$ .

## CONCLUSIONS

The polymerization rate of VAc emulsion decreases with increase in emulsifier content. The Smith-Ewart rate theory cannot explain this experimental results satisfactorily. Chain transfer reaction to monomer or emulsifier may take place with the results that the average number of radicals in each polymer particle is much less than 0.5. It can be computed that the average molecular weight decreases with increase in the emulsifier content.

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