Radiation-Induced Emulsion Ploymerization of Vinyl Acetate in a Pilot Plant Reactor II. Kinetics

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Synopsis

The recycle flow reactor pilot plant, described in Part I of this series, has been used to study some kinetic and other features of the emulsion polymerization of vinyl acetate. In particular, the dependence of the rate on the emulsifier concentration was determined and found to be 0.38 ± 0.09. Separate batch experiments were in reasonable agreement as 0.29 ± 0.10. The effects of temperature, dose rate, and agitation rate were also determined and were in agreement with most of the literature values.

Cationic emulsifiers were found to work well with the system, in contrast to most chemical initiators. The molecular weights of the polymers were measured before and after hydrolysis and reacetylation. They were consistent with chain transfer to monomer being the principal termination mechanism and with chain branching.

INTRODUCTION

Emulsion polymerization is known to be an effective technique for the synthesis of vinyl monomers due to the faster reaction rates and higher molecular weights that can often be obtained. In addition, vinyl acetate and its copolymers find extensive use in the latex form itself for paints, adhesives, and other applictions. The mechanism, kinetics, and other features of the emulsion polymerization of vinyl acetate have been studied extensively[1] but are still somewhat obscure. Most of the work, however, has been concerned with chemical initiation. The use of high-energy radiation for initiation was first reported in 1960.[2] However, there have been comparatively few studies published since that early date. Furthermore, there does not appear to be any practice on an industrial scale at present.

There are many advantages inherent in the use of high-energy gamma radiation for the initiation of vinyl monomers compared with chemical initiation. There is a constant rate of initiation that could, in principle, lead to less residual monomer. No electrolytes are introduced in the system, and there is no need to add buffers to keep the pH of the system reasonably constant. The rate of initiation can be easily controlled and varied by changing the dose rate. Most importantly, the radiation initiation process is temperature independent. Thus, the reaction temperature can be varied over any desired range, while still maintaining a constant rate of initiation. Furthermore, cationic emulsifiers can be employed without interfering with the initiation system.

There are some disadvantages associated with using radiation for initiation. Radiation can attack all components, including emulsifiers and the

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polymer, leading to grafting, branching, and some chemical changes. However, any economically viable industrial process would use low total doses and such effects should be negligible.

The radiation-induced emulsion polymerization of vinyl acetate has been investigated in several laboratories, including some pilot plant studies, and the results have been the subject of a recent review by the authors.[3]

In connection with the development of radiationnduced emulsion polymerization into a possible industrial process, a modified engineering recirculating flow reactor has been designed. The details and the feasibility of this type of reaction system have been discussed in the previous paper.[4] The present paper deals with the effects of physical-chemical variables on reaction rates and molecular weights using this recycle flow reactor. In addition, some comparative batch studies are described.

EXPERIMENTAL

The vinyl acetate was distilled through a vigreux column prior to use. Pure sodium lauryl sulfate and dioctyl sodium sulfosuccinate were the anionic surfactants used. The cationic surfactants used include cetyl pyridinium chloride, trimethyl dodecyl ammonium chloride, trimethyl octadecyl ammonium chloride, and methyl poly(oxyethylene) coco ammonium chloride. A nonionic surfactant, poly(oxyethylene) lauryl ether, was also used. The water used for all the experiments and analyses was deionized with a resistivity greater than 0.7 Ω-cm.

After each experimental run, the pilot plant was cleaned thoroughly by circulating emulsifier solution followed by methylene chloride. The helical coil reactor was cleaned by washing with concentrated caustic soda solution followed by passing steam through it at 14 psia.

The batch polymerization arrangement is shown in Figure 1. Very pure nitrogen (<1 ppm oxygen) was used, not only for eliminating oxygen but also as a source of agitation. Polymerizations were conducted utilizing a U.S. Nuclear Corporation GR9 Gamma irradiator. A typical batch of reactants consisted of 45 g of water, 15 ml of vinyl acetate, and a range of sodium lauryl sulfate concentrations from 0.225 to 2.25 g. The reactor temperature was maintained at 4.5°C.
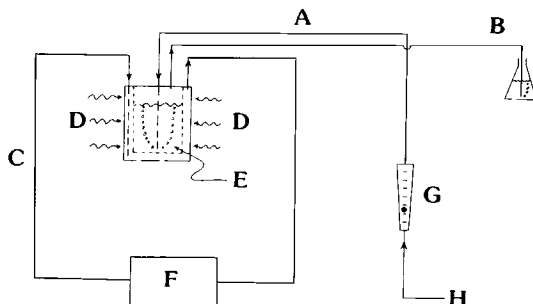

Fig. 1.   Batch polymerization equipment: (A) nitrogen inlet, (B) nitrogen outlet, (C) 50:50 ethylene glycol-water mixture (D) gamma radiatin, (E) reactants, (F) temperature controller, (G) gas rotameter, and (H) nitrogen, $\sim$ 3 ppm O_2.

The conversion analysis was carried out gravimetrically. When using an anionic emulsifier, the sample was diluted with an equal volume of water and saturated NaC1 solution was aded to coagulate the polymer. When a nonionic emulsifier was used, the latex was coagulated by pouring the sample into methanol. With cationic emulsifier, the polymer was coagulated by freezing in liquid nitrogen.

The dose rate of the cobalt-60 gamma radiation source was determined by the use of a modified Fricke dosimeter as described by Weiss.[5] Viscosity-average molecular weights were obtained by measuring the intrinsic viscosity of the polymer solution in acetone with an Ostwald-Fenske Viscometer at $25 \pm 0.1°C.$[6]

EXPERIMENTAL RESULTS

All the experiments except one group were carried out in the recirculating flow system described above and in Part I of this series. The exception involved a number of simple batch experiments conducted to determine the dependence of the rate of polymerization on the emulsifier concentration.

All errors reported represent 95% confidence limits as determined from the Student's T distribution. Samples were taken at the outlet of the stirred vessel. For most runs, the rate of polymerization was constant between 10 and 85% conversion. The rate of polymerization within the helical coil reactor was determined by applying the model developed previously.

$$R_{reactor} = R_{stirred\ tank} \times \frac{total\ system\ volume}{coil\ reactor\ volume}$$

Effect of Emulsifier Concentration on Polymerization Rate

The results of the studies in the flow system are shown in Figure 2. Included in the same figure are those obtained in the batch system described in the experimental section (see also Fig. 3). The order of reaction, both
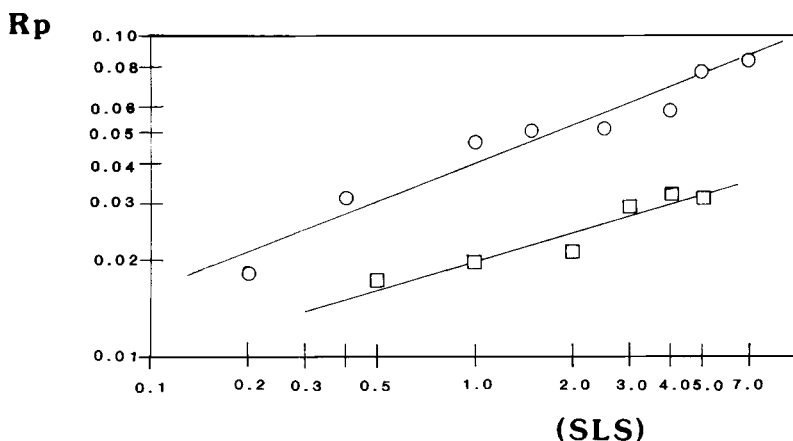
Fig. 2. Effect of emulsifier concentration on rate of polymerizatin R_p. (○) Flow system at 20°C. Slope $= 0.38 \pm 0.09.$ (□) Batch system at 4.5°C. Slope $= 0.29 \pm 0.10.$ R_p in moles per 100 ml of H_2O per minute. SLS concentration as percentage in aqueous phase.
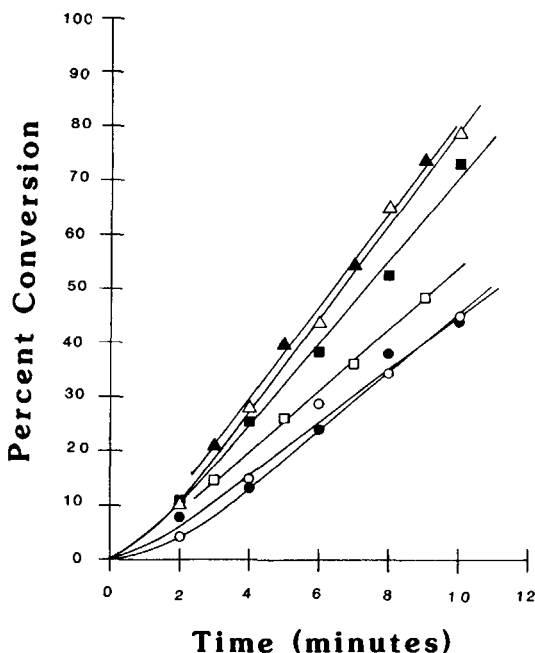
Fig. 3.   Effect of SLS concentration on the rate of polymerization, batch system, 4.5°C.

with sodium lauryl sulfate as the emulsifier, were found to be 0.38 ± 0.09 for the flow system and 0.29 ± 0.10 with the batch experiments. Results reported in the literature vary considerably. With radiation initiation and sodium lauryl sulfate as the emulsifier, Friis[7] found, with a flow system, only a 0.1 dependence; O'Neill et al.[8] on the other hand, found 0.32 ± 0.06 and 0.27 ± 0.05 for batch studies at two different dose rates and 0.24 ± 0.10 for a flow system. The latter results are all in reasonable agreement with present study, as are the early results of Okamura et al.[2] However, Stannett et al.[9] found a dependency of 1.0, also with sodium lauryl sulfate. With the same emulsifier and potassium persulfate, initiation results between 0 and 0.25 have been reported.[10]

Effect of Various Types of Emulsifiers on Polymerization Rate

One of the advantages of radiation initiation is that cationic emulsifiers can be used without interfering with the initiation system. The rate of polymerization with several different emulsifiers was determined. The results in Table I indicate that some of the cationic emulsifiers gave fairly high rates of polymerization. Direct comparison between emulsifiers must be made cautiously as the monomer concentration was varied. Evidence exists, however, that indicates varying the monomer concentration does not greatly affect the polymerization rate.[3,9] Cetyl pyridinium chloride gave practically no polymerization. the pyridinium group is a scavenger for vinyl acetate radicals and probably inhibits the initiation process. Nonionic and anionic emulsifiers all gave somewhat similar polymeriation rates.

TABLE 1
Effect of Different Emulsifiers on the Rate of Polymerization Emulsion
Concentration 2.5% at 20°C

Emulsifier	Emulsifier type	Rate in reactor mol (100 mL . H_2O . min)$^{-1}$
1. Cetyl pyridinium chloride	Cationic	0.001 ± 0.003
2. Poly(oxyethylene) lauryl ether	Nonionic	0.040 ± 0.019
3. Dioctyl sodium sulfosuccinate	Anionic	0.033 ± 0.034
4. Sodium lauryl sulfate	Anionic	0.057 ± 0.015
5. Trimethyl octadecyl ammonium chloridge	Cationic	0.015 ± 0.002
6. Trimethyl dodecyl ammonium chloride	Cationic	0.014 ± 0.001
7. Methyl poly(oxyethylene) coco ammonium chloride	Cationic	0.005 ± 0.001

Effect of Dose Rate on Polymerization Rate

The results of these flow experiments are presented in Figure 4. The dose rate was varied by changing the number of cobalt-60 rods in the source leading to 0.24, 0.17, and 0.12 Mrad/hr for the three experiments conducted. The scatter in Figure 4 appears small; however, because of the small number of points the rate dependency was 1.03 ± 0.49. The pressure of time, as the source was to be dismantled, prevented any further measurements. Literature values with the same emulsifier and radiation vary from 0.50 to 0.79 and for potassium persulfate from 0.5 to 1.0, so the pressent values are within the reported range. See Table II, for example.
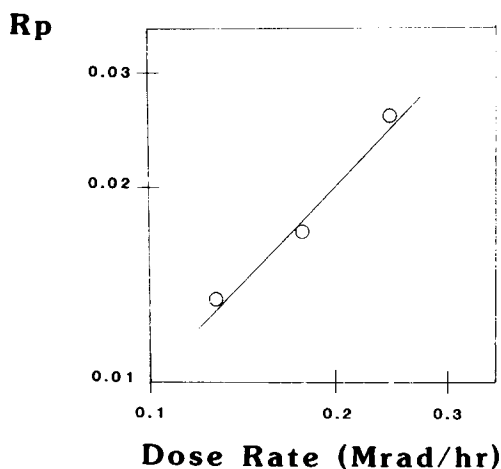

Fig. 4.   Effect of dose rate on rate of polymerization. R_p in moles per 100 ml H_2O per minute. Temperature at 20°C.

TABLE II
Dependence of Rate of Polymerization on Dose Rate

Source	Conditions	Range of dose rate (Mrad/h)	Exponential dependence
Stannett et al.[9]	30°C, SLS	0.003–0.02	0.79
Friis[7]	20°C, SLS	0.062–0.301	0.50
Present study	20°C, SLS	0.124–0.239	1.03

Effect of Agitation Rate on Polymerization Rate

Previous studies showed that rate of polymerization of styrene increased as the agitation rate in the stirred tank was decreased.[11] Presumably, at lower agitation rates there were larger monomer droplets and more emulsifier was available in the system to form micelles and polymer particles. Shunmukham et al.[12] found a similar effect in the batch polymerizartion of styrene.

Because of the possibly significant amount of aqueous-phase polymerization, the rate of polymerization of vinyl acetate should be less affected by the agitation rate than styrene. Havewala[11] found a dependence of -0.51 for the emulsion polymerization of styrene using a similar flow system as used in the present study. The results of vinyl acetate emulsion polymerization are shown in Figure 5. The order of dependence is -0.37 ± 0.08, somewhat less than that for styrene, as expected.

Effect of Temperature on Polymerization Rate

Figure 6 shows the effect of temperature on the rate of polymerization with sodium lauryl sulfate and poly(oxyethylene) lauryl ether as emulsifiers. From these Arrehenius plots, the activation energy for polymerization was calculated to be 5.1 ± 1.9 and 5.5 ± 2.1 kcal/mol for sodium lauryl sulfate and poly(oxyethylene) lauryl ether, respectively. These values are
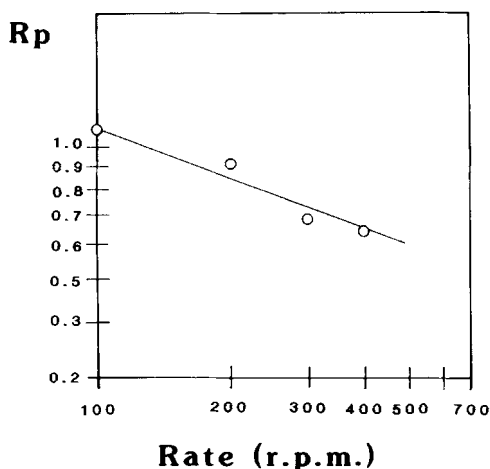

Fig. 5. Effect of agitation rate R_p on rate of polymerization R_p in percent per minute. Temperature at 20°C.
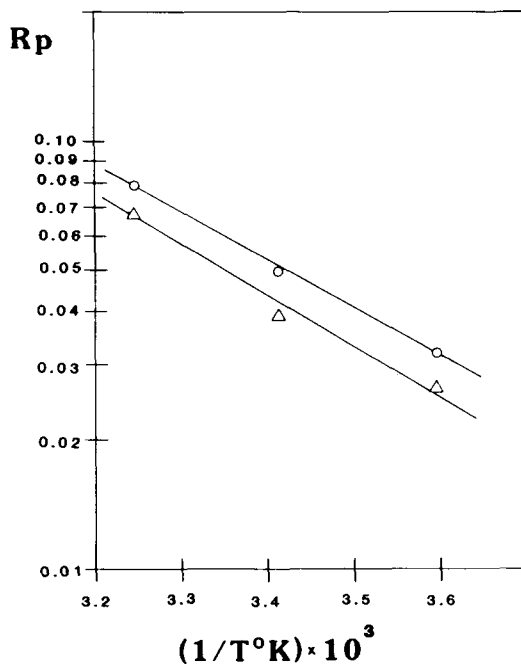
Rp

Fig. 6. Temperature dependence of the rate of polymerization R_p. (moles per 100 ml of H_2O per minute). (◯) Sodium lauryl sulfate (SLS). (△) Poly(oxyethylene) lauryl ether.

in good agreement with the activation energy of 5.7 kcal/mol found by Okamura et al.[2] in a batch system. Friis[7] obtained an activation energy of 23.0 kcal/mol for the chemically initiated emulsion polymerization of vinyl acetate in a batch system.

The difference in activation energies of chemically and radiation-initiated systems is approximately equal to one-half of the activation energy for the chemical initiation process, as expected from the simplified kinetics. It is apparent that the radiation initiation process has practically no activation energy. This means that one can conduct polymerizations at any temperature and initiation rate. In principle, the same thing could be accomplished with chemical initiation. However, low-temperature initiation, such as redox systems, are difficult to achieve and control, particularly with such polar monomers as vinyl acetate. Such monomers as vinyl acetate, whose degree of polymerization is governed by chain transfer to monomer, have a negative dependence of molecular weight on temperature. To achieve high molecular weights, low-temperature polymerizations are necessary. These can be successfully carried out utilizing radiation as the initiation method.

Molecular Weight Measurements

Drew[13] measured the intrinsic viscosity of poly(vinyl acetate) using the "single point method" similar to that described by Schulz and Sing.[14] Initially, the flow times at several concentrations of the products of five runs

in acetone were measured. The results were used to develop the equation

$$[n] = \frac{n_s/c}{(1 + 0.34 n_s)} \qquad @ \ 0.3 \ g/dL$$

where n_s is the specific viscosity. The above equation was then used to determine $[n]$, the intrinsic viscosity for the products of each of the runs from a simgle-point measurement at 0.3 g/dL. Viscosity-average molecular weights were calculated using Wagner's equation[6]:

$$[n] = 1.76 \times 10^{-4} M_v \ 0.68$$

Table III shows the viscosity-average molecular weight obtained for some of the runs, together with the run conditions and percentage conversion. From the results it appears that the product that has the highest molecular weight was the one that has the highest percentage conversion. This is consistent with the findings of O'Neill et al.[8] and is usually ascribed to branching. Also, the two lowest molecular weight products resulted from the polymerizations with the two highest emulsifier concentrations. O'Neill et al.[8] observed a slight diminution in the molecular weights at higher sodium lauryl sulfate concentrations.

Strictly speaking, general comparisons could not be made with the results of Table III as the conditions vary with the runs. Branching is known to occur as the conversion increases. In these results there could be overlapping of the effect of branching with those of other variables on the molecular weight. For this reason, this study included the hydrolysis and reacetylation of poly(vinyl acetate), which essentially separates the branches on the main chain and makes it a linear polymer. The procedure for hydrolysis and reacetylation is described elsewhere.[15]

Figure 7 shows the intrinsic viscosity of the polymer samples both before and after hydrolysis and reacetylation as a function of percentage conversion. Extrapolation of both the curves to zero percent conversion gives the

TABLE III
Molecular Weights of the Products (at 20°C)

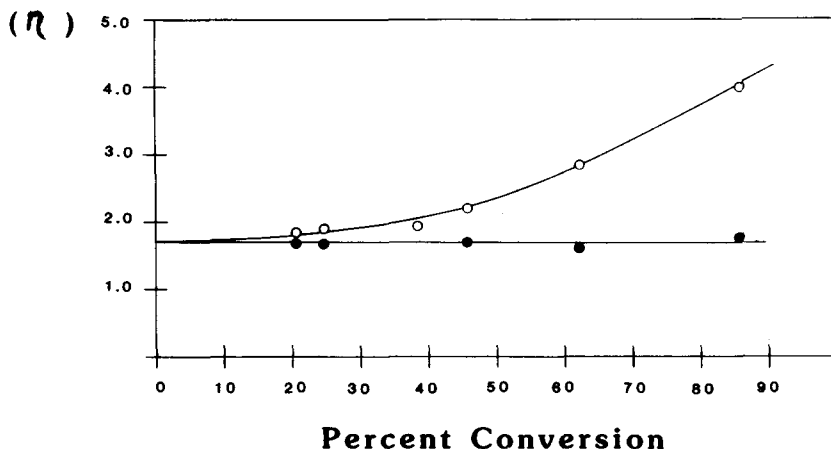| Emulsifier concentration (wt%)	Percentage conversion	Viscosity-average molecular weight $(M_v \times 10^{-5})$
1.0	40.4	11.35
1.0	36.5	12.90
1.0	31.7	10.82
1.0	45.5	13.05
5.0	35.6	8.63
0.5	43.5	11.15
1.0	92.5	16.16
0.2	22.8	12.77
0.6	24.0	13.63
4.0	40.6	10.73
1.5	43.4	14.80
0.4	28.6	14.23

Percent Conversion

Fig. 7. Variation of the intrinsic viscosity of poly(vinyl acetate) with conversion at 20°C. (○) Original sample. (●) After hydrolysis and reacetylation.

same intercept: $[n] = 173$ and 1.68 dL/g, respectively. This intercept corresponds to $DP_n = 8.4$ .ts 10^3, which is the value expected if the termination occurs via transfer to monomer with $C_m = 1.2 \times 10^{-4}$. This is in reasonable agreement with the published values.[16,17] Figure 7 also shows that the greater the conversion, the more marked is the decrease in intrinsic viscosity due to hydrolysis and reacetylation. The intrinsic viscosity extrapolated to zero conversion appeared to be unchanged by hydrolysis and reacetylation, showing that short-chain branching through the acetate group is absent and that internal acetate units formed by reactions of backbiting type do not occur. Similar ideas were put forth by the researchers working with chemical initiation.[18-21]

Table IV shows the viscosity-averge molecular weights of the hydrolyzed and reacetylated samples of several runs in which different emulsifiers were used. Table V shows the molecular weights of the products obtained with different emulsifier concentrations. From Tables IV and V, it appears that the type and concentration of the emulsifier used does not have a significant effect on the viscosity-average molecular weight. Table VI lists the viscosity-

TABLE IV
Effect of Type of Emulsifier on the Viscosity-Average Molecular Weight (After Hydrolysis and Reacetylation)

Emulsifier	Intrinsic viscosity η (dL/g)	Viscosity-average molecular weight $(M_v \times 10^{-5})$
1. Sodium lauryl sulfate (anionic)	1.63	6.80
2. Poly(oxyethylene) lauryl ether (nonionic)	1.54	6.26
3. Trimethyl octadecyl ammonium chloride (cationic)	1.61	6.72
4. Trimethyl dodecyl, ammonium chloride (cationic)	1.42	5.57

TABLE V
Effect of Emulsion Concentration on the Viscosity-Average Molecular Weight (After Hydrolysis and Reacetylation at 20°C)

Emulsifier concentration	Viscosity-average molecular weight ($M_v \times 10^{-5}$)
0.2% SLS	7.49
0.4% SLS	7.20
2.5% SLS	7.45
5.0% SLS	7.02

average molecular weights of the hydrolyzed and reacetylated samples of poly(vinyl acetate) abtained at different dose rates. A slight decrease in molecular weight with dose rate implies a small contribution of the second-order radical-radical termination to the total termination mechanism.

The relative insensitivity of molecular weights to changes in the emulsifier concentration, dose rate, and the observed molecular weight values themselves suggest that termination by chain transfer is dominant. Similar ideas were put forward by many workers in the field and are generally accepted.

DISCUSSION

The recycle flow reactor system has been shown previously[11,22,23] to be an effective system for obtaining accurate kinetic data. This is due to the multiplying factor of the ratio of volume of the total system to the helical reactor itself and to the possibilities of measuring the differential yields in and out of the reactor. With such polymers as polyvinyl acetate, which are "sticky" and have low glass transitions, there can be complications due to polymer buildup on the tubular reactor. This can be minimized by correcting for the change in diameter with conversion or by using wider tubing. Both methods were used in the present study.

The results obtained were all well within the range of kinetic orders found by previous workers. There was an exception with respect to the order of the emulsifier dependence of the rate of polymerization. Both the flow system and the independent batch measurements were in good agreement in the present work and also with those of O'Neill et al.[8] and Okamura et al.,[2] the order being approximately 0.3. On the other hand, Friis[7] with a flow system and Stannett et al.[9] with a batch system found dependencies

TABLE VI
Effect of Dose Rate on Viscosity-Average Molecular Weight (After Hydrolysis and Reacetylation at 20°C)

Dose rate (Mrad/h)	Viscosity-average molecular weight ($M_v \times 10^5$)
0.12	7.92
0.17	7.69
0.24	7.45

of 0.1 and 1.0, respectively. There is a tendency of the particles to coagulate with polyvinyl acetate and also a comparatively high dependency of the rate on the number of particles in the case of radiation.[3,9] These features combine to give a system that would be rather sensitive to the degree of agitation and the flow rate and also to the emulsifier type and concentration. It is probable that this provides an adequate explanation for the discrepancies found in the literature. Such discrepancies are also found with potassium persulfate-initiated polymerizations. The dose-rate experiments were too few in number and too scattered to do more than indicate that they were in the range of results previously reported.

The temperature dependence and molecular weight data are in good agreement with both radiation and chemically initiated systems in the literature.

The emulsion polymerization of vinyl acetate is highly complex, and various theories have been presented. These have been summarized through 1974 by Stannett et al.[10] However, the most comprehensive and acceptable theory appears to be that of Chang et al.[24] Their carefully controlled experiments with potassium persulfate as the initiator tend to confirm their theoretical findings. However, the sensitivity of the system both with persulfate and radiation initiation to the reaction conditions will always lead to discrepancies between theory and experiment, as in the present study.

The differences between persulfate and radiation initiation from the point of view of kinetics and mechanism include the temperature range. Except for the temperature dependence measurements, the entire study was conducted at 20°C, except for the batch studies at 4.5°C, in contrast to the 60°C usually employed with persulfate initiation. This leads to considerably less chain transfer to monomer and lower monomer solubility. Both these factors would tend to drive the kinetics more toward the standard case II Smith-Ewart model. To some extent this is true, as shown in Table VII. Other differences are that, with radiation, the initiating species are predominantly neutral highly reactive hydroxyl radicals and hydrogen atoms as opposed to the negatively charged sulfate radicals. The ionic strength is also lower in the cae of radiation since no inorganic salts are added. The possible consequences of these differences have been discussed by Barriac et al.[25] for the emulsion polymerization of vinyl chloride.

TABLE VII
Orders of Reaction for the Rate of Emulsion Polymerization of Vinyl Acetate Compared
with the Smith-Ewart Case II Kinetics[a]

Dependence of rate of polymerization on	Chemical initiation	Smith-Ewart case II	Radiation initiation
1. Initiatior	0.5–1.0	0.4	0.5–1.0
2. Emulsifier concentration	0–0.25	0.6	Mainly 0.3
3. Number of particles	0.2	1.0	0.7
4. Monomer-water ratio	0.35	0	Close to zero
5. Initiator with fixed number of particles	0.8	0	0.26

[a] All with SLS, taken from various sources; see Refs. 3 and 10, for example.

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1. See, for example, *Emulsion Polymerization of Vinyl Acetate*, ed. M. S. El. Asser and J. W. Vanderhoff. Applied Science Publishers, (Elsevier), London, 1981, and the references contained therein.

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