

# **Radiation-Induced Emulsion Polymerization of Vinyl Acetate in a Pilot Plant Reactor I. Recycle Flow Reactor**

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## **Synopsis**

A number of successful radiation polymerizations of vinyl acetate in emulsion have been carried out in a modular stainless steel flow pilot plant. In a recycle mode, the system was utilized for extremely accurate kinetic measurements and experimental verification of model restrictions such as plug flow, lack of post irradiation effects and differential reactor behavior. Experimental conditions were explored to minimize contaminant, primarily oxygen, inhibition, and the tendency for this formulation, essentially an adhesive, to build up on the reactor walls. Industrial scaleup of such a prototype system appears attractive.

## **INTRODUCTION**

Recycle flow reactor systems have broad application in experimental kinetic analysis<sup>1,2</sup> due primarily to advantages in control and sampling. Such systems have long been used in the system studies of gas phase heterogenous catalysis. In such systems, as the recirculation flow rate is increased, differential reactor conditions are achieved, and they behave as batch reactors. The purpose here is to verify experimentally the validity of the assumptions made in the development of the recycle flow reactor model. The further objective is to study the applicability of such model for the low flow rates regime used in this work. Also, experimental problems encountered using such a recycle flow scheme reactor are presented and discussed. Part II deals with the kinetic study of the emulsion polymerization of vinyl acetate using this recycle flow reactor in an engineering flow pilot plant system of broad versatility.

### **The Emulsion Polymerization Pilot Plant**

The flow system used in the present study was designed and built by Stahel and Stannett.<sup>3</sup> Figure 1 shows the flow diagram for the system. Emulsion is continuously recirculated from an agitated vessel, through a tubular reactor located in a high-intensity Co-60 irradiator and back to the vessel. A more detailed diagram for the equipment is shown in Figure 2. The system is flexible enough to be used for different monomers, comonomers as well as grafting, and can be easily modified for a number of different experimental conditions including pressure operation to 1000 psi. The latter make usable normally gaseous monomers.

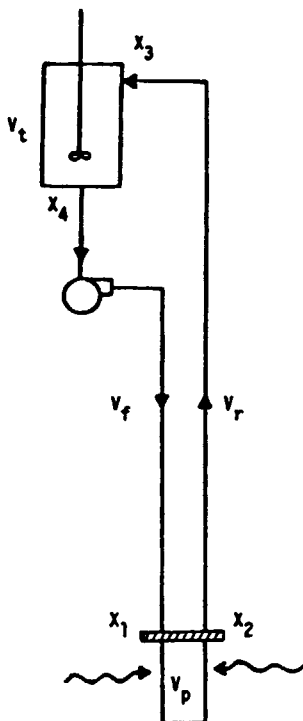


Fig. 1. Recycle flow reactor. Volumes:  $V_t$  of tank,  $V_f$  of feed line,  $V_p$  of reactor, and  $V_r$  of return. Conversions:  $X_1$  at reactor inlet,  $X_2$  at reactor outlet,  $X_3$  at tank inlet, and  $X_4$  at tank outlet.

The pilot plant was designed to obtain accurate kinetic data at high initiation rates. Although the rate of polymerization in the tubular reactor located within the source can be quite fast, as much as 15%/min, the rate of conversion of the contents of the stirred vessel can be rather slow due to the adjustable large total volume of emulsion. Thus, one can effectively slow down the polymerization process and obtain more accurate data than is otherwise possible, hampered as is often the case by heat transfer and sampling problems.

Osborne et al.<sup>4</sup> developed a model for this system. The assumptions involved in the development of the model are:

1. Ideal plug flow conditions in the tubular reactor, feed, and return lines.
2. Perfect mixing in the stirred vessel.
3. The rate of polymerization is the same at any point in the tubular reactor.
4. All the polymerization takes place within the tubular reactor.

With these assumptions, model equations and boundary conditions were developed and solved using Laplace transformation techniques.<sup>4</sup> According to the outcome of the model in the limit, the rate of polymerization is equal to the rate of polymerization within the tubular reactor multiplied by the ratio of the residence time in the reactor to the residence time in the whole system.

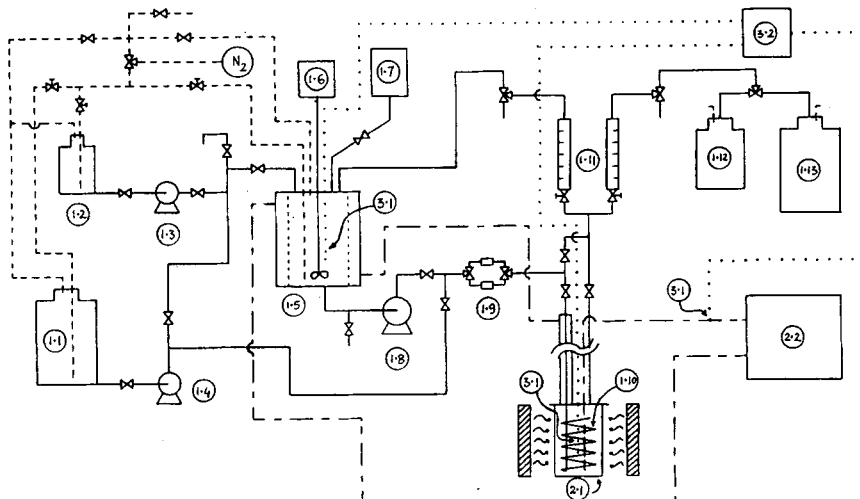


Fig. 2. North Carolina State University polymerization pilot plant: emulsion handling; nitrogen vent; temperature control; temperature measurement. Components: (1) Emulsion handling system: (1.1) emulsifier solution storage vessel; (1.2) monomer storage vessel; (1.3) monomer metering pump; (1.4) emulsifier solution metering; (1.5) stirred vessel; (1.6) variable speed stirrer; (1.7) transfer vessel; (1.8) diaphragm pump; (1.9) in-line filters; (1.10) helical coil reactor; (1.11) purgemeters; (1.12) product vessel; (1.13) off-product vessel. (2) Temperature control system: (2.1) reactor canister; (2.2) combination chiller/heater w/40 gal storage tank for controlled glycol solution. (3) Temperature measurement system: (3.1) copper-constantan thermocouples; (3.2) digital read-out transducer.

With this rather simple result for the limiting case, one can determine kinetic data on the rate of polymerization in the reactor by measuring the rate of change of composition within the stirred tank. One of the principle advantages of this recirculating system is the ability to adjust the total volume. The reaction time can thus be extended permitting numerous samples to be withdrawn during the polymerization. Since the system can involve over 4 L of emulsion, errors of sampling can also be minimized.

Figure 2 shows a detailed diagram of the pilot plant. The central part of the pilot plant is a 4-L jacketed stainless steel vessel fitted with a variable speed stirrer which forms and maintains the emulsion. During the run, the emulsion is pumped through a helical coil tubular reactor located in the radiation source and is returned to the top of the vessel. The radiation source consists of a circular array of 12 cobalt-60 rods located under 10 ft of water.

A nitrogen system is used to purge the starting materials prior to a run to remove dissolved oxygen and to maintain a nitrogen atmosphere in the stirred vessel during a run. High pressure capability exists up to 1000 psi. The nitrogen used in this study is an ultra high purity grade with less than 3 ppm oxygen.

During the polymerization isothermal conditions are maintained by heat exchange with a temperature controlled ethylene glycol/water mixture. Three heat exchangers are incorporated in the system. The stirred vessel is jacketed to allow the temperature control fluid to flow around the outside walls of the vessel. Second, a 10 ft long tube-in-tube counter-current flow

heat exchanger is provided through which the emulsion flows before entering the reactor. Third, the reactor is located within a cylindrical sealed vacuum jacketed cannister through which temperature control fluid is circulated. All components are stainless steel, modular, and standard industrial valves and fittings. Reaction temperatures can be maintained to 0.1°C, using this entry element heat exchanger. The system includes storage, transfer vessels (and additional pumps), and can be operated in several continuous modes.

## EXPERIMENTAL

The vinyl acetate was distilled through a Vigroux column prior to use. Sodium lauryl sulfate and dioctyl sodium sulfo succinate were the anionic surfactants used. The water used for all the experiments and analyses was deionized with resistivity greater than 0.7 M $\Omega$  cm.

After each experimental run the pilot plant was cleaned thoroughly by circulating emulsifier solution followed by methylene chloride. The reactor was cleaned by several techniques including burning it in a muffle furnace at 850°C for 5 min and stored under inert nitrogen atmosphere.

Conversion analysis was carried out gravimetrically. Large gram samples are possible with the engineering pilot plant system making reproducible data possible of an order of magnitude greater precision when compared to laboratory reactors normally utilized for these liquid reactions. The latex sample was diluted with an equal volume of water and saturated NaCl solution was added to coagulate the polymer. The dose rate of the cobalt-60 gamma radiation source was determined by the use of a modified Fricke dosimeter as described by Weiss.<sup>5</sup>

## RESULTS AND DISCUSSION

At the beginning of this study, the dose rate for the system with 12 cobalt-60 rods in place was determined as 0.28 Mrad/m. The effect of naturally decaying dose rate was undetectable due to the relatively long half life of cobalt-60 (5.2 years). All errors reported represent 95% confidence limits as determined from Students' *t*-distribution.

Samples were taken at the outlet of the stirred vessel during all the runs following a procedure shown to be reproducible. The system was highly reproducible as shown in Figure 3. For the standard runs the rate of polymerization was constant between 10 and 85% conversion, as expected. The rate of polymerization within the helical coil reactor was determined by applying the model developed previously.

### Recycle Flow Reactor and Its Importance

Recycle reactors have a broad application in experimental kinetic analysis. The importance of a recycle reactor in examining fast reactions can be seen in the following illustration. Figure 3 shows the conversion-time history of a run which was carried out for more than 90% conversion. Figure 4 shows the conversion-time history of the same run which describes the polymerization that occurs in the helical coil reactor. Line A was drawn

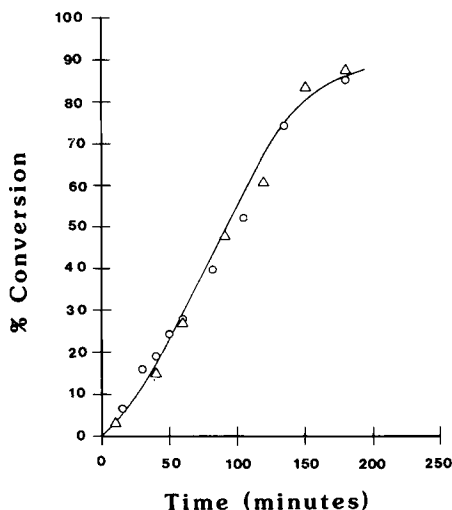


Fig. 3. Check of reproducibility: (○) run 43; (△) run 48.

from the data by applying the model to adjust the time frame of polymerization. Line A can be interpreted as the conversion–time history that would be obtained with a batch system exposed to the same dose rate.

One can see that polymerization would reach 90% conversion in less than 10 min time. For this reason, sampling such a polymerization would be difficult and inaccurate. Figure 4 shows the conversion–time history of a recycle reactor in which the polymerization took about 120 min to reach 90% conversion. Errors due to sampling and analysis would be, effectively, 12 times less than with a batch system. Fast polymerizations, such as vinyl acetate emulsion polymerization with high dose rates, can thus be monitored accurately using a recycle reactor.

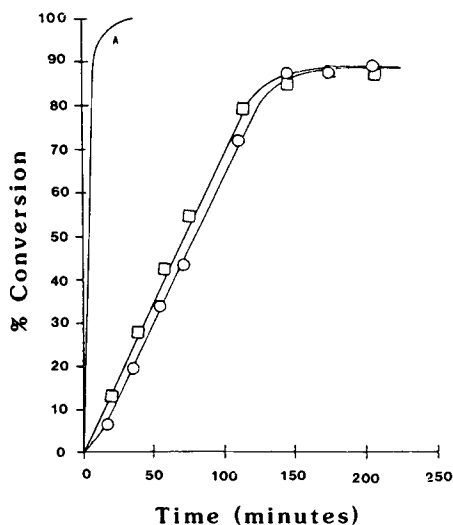


Fig. 4. Conversion history of polymerization, run 14: (○) feed; (□) return. Line A is theoretical conversion curve for the corresponding batch system at same dose rate.

Further, exothermic (or even endothermic) reactions, occurring at high rates even with reasonable activation energies, often present insurmountable experimental problems in large volumes.

### Validity of the Recycle Flow Reactor Model

The several assumptions made in the development of the model for this recycle flow reactor were discussed in previous paragraphs. The present data<sup>6</sup> could be utilized to test the validity of some of these assumptions.

One of the most stringent was that all the polymerization took place in the helical coil reactor. This assumption was tested by measuring the rate of polymerization in the reactor directly and comparing it with the rate calculated from the model. If a significant amount of polymerization occurred outside the reactor, the rate calculated by the model could be expected to be greater than the measured rate. The run of Figure 4 was used for this purpose.

The conversion per single pass was obtained by sampling at both stirred tank outlet and the return line. The difference between these two curves gave the conversion per pass. By dividing by the actual residence time, an estimated actual rate of polymerization within the helical coil reactor was obtained:

$$\text{rate in the stirred} = 0.897 \pm 0.124\%/\text{min}$$

$$\text{conversion per pass} = 6.35 \pm 2.22\%$$

The model with the experimental lumped parameters predicts:

rate in reactor

$$\begin{aligned} &= \frac{0.897 \pm 0.124\%}{\text{min}} \frac{3000 \text{ mL}}{210 \text{ mL}} \frac{0.932 \text{ g } V_{AC}}{\text{mL } V_{AC}} \frac{\text{mL } V_{AC}}{3 \text{ mL H}_2\text{O}} \frac{\text{mol } V_{AC}}{86.09 \text{ g } V_{AC}} \\ &= 0.046 \pm 0.0064 \text{ mol}/(100 \text{ mL H}_2\text{O min}) \end{aligned}$$

The rate of polymerization can be determined in the reactor as:

$$\text{rate in reactor} = \text{conversion per pass}/\text{residence time}$$

$$\begin{aligned} &= \frac{0.635 \pm 222\%}{0.467 \text{ min}} \frac{0.932 \text{ g } V_{AC}}{\text{mL } V_{AC}} \frac{\text{mL } V_{AC}}{3 \text{ mL H}_2\text{O}} \frac{\text{mol } V_{AC}}{86.09 \text{ g } V_{AC}} \\ &= 0.049 \pm 0.0172 \text{ mol}/(100 \text{ mL H}_2\text{O min}) \end{aligned}$$

The rate of polymerization in the reactor, determined from the rate in the stirred tank was the same within the experimental error, as that determined from the conversion per pass. This indicates that all the polymerization occurred in the helical coil reactor and that no post-polymerization occurred in the transfer lines or stirred tank. This is in good agreement with the results of Stannett's<sup>7</sup> batch system and O'Neill's<sup>8</sup> flow system.

It is interesting, however, that the work of Allen et al.<sup>9,10</sup> shows that some further polymerization was obtained after stopping the radiation at 70% conversion compared with styrene, the lack of the post-effect during most of the polymerization of vinyl acetate is probably due to the ease of chain

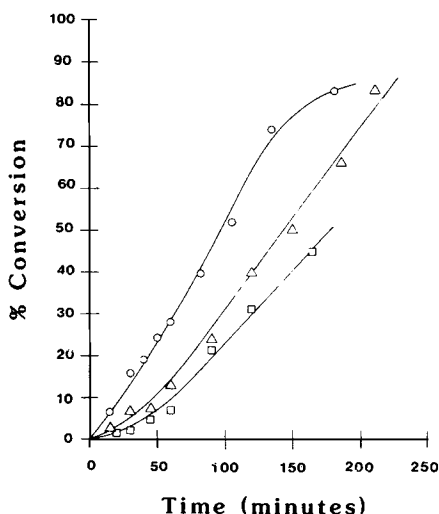


Fig. 5. Effect of flow rate on the rate of polymerization: (○) 200 mL/min; (□) 535 mL/min; (△) 345 mL/min.

transfer to the monomer, plus the larger propagation rate constant of vinyl acetate. It has been calculated that, compared with styrene, vinyl acetate transfers many times during the kinetic chain length. The resulting radicals can easily diffuse out of the particles and eventually lead to termination. However, it is suggested as conversion increases, more and more macroradicals are produced, and these remain in the particles, hindered in diffusion. Thus, the post-reactor effects commonly seen with most monomers are absent with vinyl acetate, except at high conversions.

Another assumption made in the development of the model was that in the limit rate of polymerization is constant throughout the reactor. If such is the case, a change in reactor volume would not change the rate of polymerization on a unit volume basis. This assumption was verified using two different helical coil reactors with volumes of 95 and 210 mL, respectively. If the rate is not constant throughout the reactor and there is a significant period of time during which the rate within a fluid element is increasing after it has entered the reactor, then one would expect that increasing the residence time would increase the average rate in the reactor. That is each fluid element would spend a relatively longer period of time at the constant rate in the larger reactor than in the smaller reactor. Table I shows the rates of polymerization that were found when the reactors of different volumes were employed. The same experimental conditions were used, and it was found that the rates were equal within the experimental error, thus supporting the validity of the assumption.

### Model Flow Rate Limitation

The runs that were used to discuss the validity of the assumptions made in the development of the model were conducted at a flow rate of 450 mL/min. Throughout the study of kinetics, presented in the following paper, a flow rate of 450 mL/min was maintained to ensure the validity of the model, which facilitated an easier interpretation of the data obtained from ana-

TABLE I  
Comparison of Rates of Polymerization in Two Helical Coil Reactors  
with Different Volumes

Run no.	Reactor volume (mL)	Rate of polymerization in reactor (mol/100 mL H <sub>2</sub> O min)
Avg. of 6,7,8	95	0.0456 ± 0.0383
14	210	0.0463 ± 0.0064

lyzing the samples from the outlet of the stirred tank as explained below.

If the flow rate is increased in the limit, the whole system approaches a single batch reactor. That is, there is only a differential volume in the radiation zone, and all regions are approximately the same composition. At the other extreme, of a diminishingly small flow rate, the integral reactor behavior is observed, and the system approaches a continuous flow reactor wherein each flow element must be analyzed as to RTD and conversion as well as combined under a mixing rule.

### Effect of Flow Rate on the Rate of Polymerization

The present study includes the effect of three different flow rates, 200, 345, and 535 mL/min, on the rate of polymerization. The conversion time histories for these runs are shown in Figure 5. But the question arises whether the linear portion of the curves represent a single rate of polymerization within the reactor at a low flow rate of 200 mL/min, as the reactor ceases to behave like a differential reactor at low flow rates. In such a case a single rate of polymerization may not represent the whole kinetics as the rate varies at different points in the reactor due to significant conversion per pass, invalidating the assumption made in the development of Osborne and Stahel's model.<sup>4</sup>

A kinetic analysis was made on the system accounting for the deviations from the plug flow condition both in transfer lines and reactor. The detailed analysis is shown elsewhere.<sup>11</sup> Considering a parabolic velocity profile in the transfer lines, the deviation from the plug flow conditions was derived to be equal to

$$\frac{R_c \tau_p (\tau_f + \tau_p + \tau_r)}{(\tau_f + \tau_p + \tau_r + \tau_t) 2t}$$

where  $R_c$  = rate of polymerization,  $\tau_p$  = residence time in the reactor,  $\tau_t$  = residence time in the tank,  $\tau_f$  and  $\tau_r$  = residence time in forward and return lines, and  $t$  = sampling time. For a flow rate of 200 mL/min and a sampling time of 30 min, the above deviation was shown to be equal to 0.004  $R_c$ , which may be neglected.

For the case of deviation from the plug flow conditions in the reactor itself, a parabolic flow with a pseudo-first-order reaction was assumed. For



a condition when radial diffusivity  $D \rightarrow \infty$ , it gave the familiar plug flow reactor equation:

$$X_{\text{out}} = 1 - e^{-k\tau_p}$$

when the radial diffusion was neglected ( $D \rightarrow 0$ ):

$$X_{\text{out}} = 1 - \left[ (e^{k\tau_p/2} / (1 - k\tau_p/2)) + \frac{k\tau_p^2}{2} \text{Ei}\left(\frac{-k\tau_p}{2}\right) \right]$$

$k$  = pseudo-first-order rate constant

The results of a typical run and a literature value of the propagation rate constant at 20°C gave the pseudo-first-order rate constant  $k$ , which, when used in the above two equations together with a  $\tau_p$  obtained for a flow rate of 200 mL/min, resulted in a deviation of 0.1% from the plug flow condition. This may be neglected.

Following the analysis, it can be assumed that differential reactor conditions were achieved at all the flow rates used. Tables II shows the rates of polymerization at different flow rates. The results show that an increase in the flow rate causes a decrease in rate of polymerization within the reactor. O'Neill et al.<sup>8</sup> observed a similar behavior. This effect could be attributed to traces of oxygen present in emulsion. At high flow rates the residence time in the reactor could become too short for the oxygen to be consumed leading to the retardation in the rate. Friis,<sup>12</sup> in his similar studies, in the absence of any gas phase, found that increasing the flow rate increased the rate of polymerization lending credence to the explanation of O'Neill et al.<sup>8</sup> that traces of oxygen are responsible for the opposite effect of flow rate.

### Polymer Buildup in the Reactor during Experimental Runs

The major problem encountered with the experimental runs was the buildup of polymer on the walls of the helical coil reactor tube. Some of the runs were invalid due to "early time" reactor buildup attributed to improper cleaning, and many of them had to be prematurely terminated because of the pressure buildup following the constriction of the reactor tube which indicated plugging and an unknown diameter.

TABLE II  
The Effect of Flow Rate on Rate of Polymerization

Run no.	Flow rate (mL/min)	Reynolds number	Rate of polymerization in reactor (mol/100 mL H <sub>2</sub> O min)
43	200	637.44	0.036 ± 0.004
37	345	1099.52	0.027 ± 0.005
42	450	1434.15	0.025 ± 0.010
38	535	1705.05	0.016 ± 0.006

In some runs, curvature appeared in the conversion-time history prior to terminating the reaction, even though the conversion was less than 55%. Such a curvature was due to rapid reduction in the available reactor volume prior to run termination.

It is believed in this study, increased polymer buildup was observed with a decrease in emulsifier concentration. In Table III the percentage decrease in reactor from the beginning to the end of the run is compared with the run conditions for several runs. One can see from this table that excessive polymer buildup is associated with lower emulsifier concentration. Of course, this general phenomenon is not unexpected as poly(vinyl acetate) is one of the most favored industrial adhesives, known for its extreme "stickiness."

Two reasons could be hypothesized for such behavior. At the lower emulsifier concentrations used, the lattices produced were colloiddally unstable. This resulted in polymer precipitation as high conversions were reached in the reactor. It is also believed that severe conditions of the reactor cleaning procedure, i.e., heating the reactor to 800°C to burn out the polymer, might have contributed to the polymer buildup, perhaps providing an active surface to which polymer could readily adhere. Also, it was observed that the polymer buildup obtained from the walls of the reactor swelled in acetone, indicating that it could have been crosslinked due to long dwell times. An alternate and better reactor cleaning method was adopted. The reactor was filled with a concentrated solution of sodium hydroxide and was left for 48 h. The reactor was then washed several times with water to remove the sodium hydroxide. It was then filled with fresh sodium hydroxide solution and was heated in water for 8 h. Later, the reactor was flushed out through a hole provided at the bottom of the reactor.

After this procedure was adopted, the decrease in reactor volume was always less than 5% and considered negligible.

It is interesting to note that at the low flow rates of 200 and 345 mL/mn used in this study, there was no pressure buildup in the system even after 3 h of reaction and above 90% conversion whereas at flow rates of 450 mL/min and above, the pressure buildup in the system was often observed. It is believed that, at the higher flow rates, polymer coagulation occurs more readily from the emulsion, causing the system plugup.

TABLE III  
The Effect of Emulsifier Concentration on Polymer Buildup in the Helical Coil Reactor

Run no.	Conditions	Decrease in reactor volume %
15A	1 h, 0.2% SLS	
B	1 h, 0.6% SLS	
C	10 min, 1.5% SLS	76
16A	1 h, 4.0% SLS	
B	1 h, 1.5% SLS	
C	1 h, 0.4% SLS	43
14	3 h, 1.0% SLS	10
13	3 h, 1.0% SLS	3
12	4 h, 1.0% SLS	3

## CONCLUSIONS

The system could be successfully utilized to obtain extremely accurate kinetic data for radiation-induced emulsion polymerization of vinyl acetate. The recycle reactor model proposed previously by the authors is experimentally verified to be valid at a flow rate of 450 mL/min.

Kinetic analysis of the system for the deviations from the plug flow conditions shows that deviation for the lowest flow rate used in the present study (200 mL/min) is negligible. The studies on the effect of flow rate indicates that oxygen is probably the principle agent inhibiting the polymerization.

The major problem encountered during the polymerization is polymer buildup in the helical coil tubular reactor. High emulsifier concentrations, low recirculation flow rates, and a change in reactor cleaning seems to help overcome the plugup problem. This limited data appears to suggest that a flow type system offers an attractive possibility for the manufacture of certain emulsion polymers by means of radiation initiation.

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