

Emulsion Polymerization of Vinyl Acetate in a Tubular Loop Reactor

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SYNOPSIS

A study was conducted on the emulsion polymerization of vinyl acetate using a loop reactor. Among the variables studied were the agitation, that is, the Reynold's number, and the effect of the presence of silver ions on the reaction rate. The molecular weight and molecular weight distribution of the polymer were determined as well as its particle size. The results are compared with earlier work done in a batch, a continuous tubular, and in a tubular loop reactor. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A continuous reactor system has many intriguing features: better heat transfer, reduction in down time, and the cooling capacity, less manipulations, etc., all leading to a lower investment cost. Few experimental studies were conducted on the polymerization in a tubular reactor. Many used a monomer, such as styrene, having a low polarity and a low solubility in water.¹⁻⁷ Generally the results obtained are in accord with the Harkins et al. theory.⁸⁻¹⁰ One of the problems encountered was the plugging of the reactor. This was attributed to the reaction conditions, the tube diameter, and the material in which the reactor is made.

A common feature of all these systems is that the optimum conversion occurred in the transition zone^{2,4,11,12} and that this optimum conversion is usually lower than the one obtained by the batch process.

It is generally accepted that for monomers such as vinyl acetate, the Harkins et al. theory is not satisfactory as the particle formation locus systems is from possibly a bimodal system: a solution polymerization-precipitation mechanism and a micellar polymerization. A great deal of this difference is attributed to the greater solubility of the vinyl acetate in water: the molecular interaction at the water-

monomer interface promotes the formation of particle in the water phase.^{13,14}

In this work we would like to present the results of the polymerization of vinyl acetate in a tubular loop reactor. In order to improve the conversion, silver ions were added to the formulation because this has been shown to improve both the yield and the conversion rate.¹⁶

EXPERIMENTAL

Materials and Characterization

Vinyl acetate was obtained from Aldrich Chemical. It was distilled and kept under refrigeration at -9.5°C until required. The potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$ was supplied by Anachemia as 99.5% pure. It was purified by recrystallization. Sodium lauryl sulfate (SLS) was used as supplied by Fischer Scientific. Its Critical Micelle Concentration (CMC) is 2.6 g/L. The source of silver ion, AgNO_3 , was provided by Anachemia and used as received with no further purification. Demineralized water was used throughout this work. The polymerization was short-stopped with hydroquinone. In order to reduce the amount of oxygen present, the reactor was kept under a constant blanket of nitrogen. This nitrogen was purified by molecular sieves.

The reaction yield was determined gravimetrically. After drying under an infrared lamp, this process is followed by vacuum drying until a constant weight was obtained. The molecular weight and mo-

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lecular weight distribution were determined by a Waters gel permeation chromatograph. A scanning microscope, Jeol 840, and an image analyzer, a Kontron I base, were used in order to obtain the average diameter as well as the distribution of the particles obtained.

Polymerization Reactor

A schematic diagram of the reactor is given in Figure 1. It is essentially a Teflon tube surrounded by stainless steel mesh. The inside diameter is 2.2 cm. In order to visualize the polymerization evolution a glass section was incorporated in the circuit. A variable speed pump having a progressive cavity was used to assure the circulation of the reaction mixture inside the tube. In order to avoid possible contamination, all the internal parts of the reactors were either made of Teflon or stainless steel.

For practical reasons the pumping system and the monomer preparation section were the only parts not immersed in the thermostated bath [Fig. 1(A)]. However, they were insulated by foam tubings. Three thermocouples were installed in order to be able to monitor the temperature throughout the run. Three sampling valves were also installed.

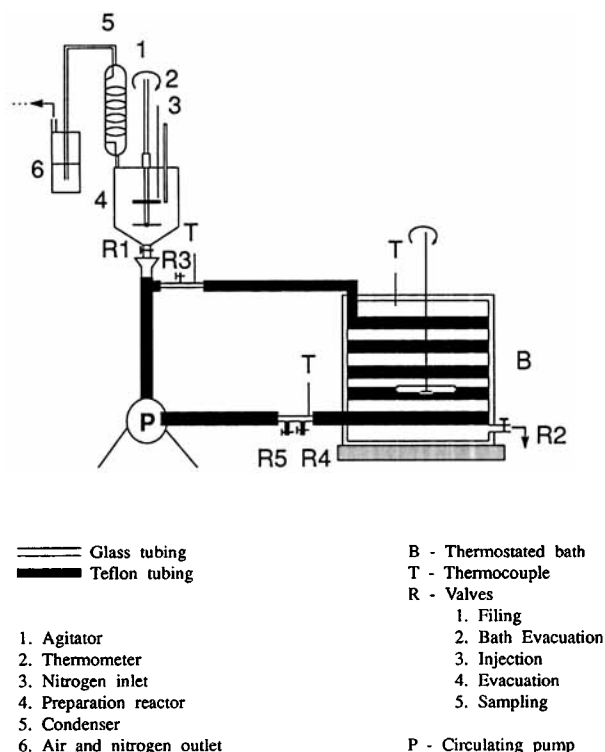


Figure 1 Reactor design.

Table I General Formulation

Material	Reference (g)	This Work (g)
Demineralized water	2175.00	2294.00
Vinyl acetate, monomer	825.00	800.00
Sodium lauryl sulfate, surfactant	15.76	16.11
Potassium persulfate initiator	0.50	0.55
Nopco, antifoaming agent	—	1.20
Silver nitrate	—	0.0071
Total amount (g)	3015.76	3111.80

Polymerization Procedure

The actual formulation used is given in Table I. Except for the potassium persulfate, all the ingredients were added to the 4 L mixing reservoir and mixed at room temperature for 1 h [Fig. 1(B)]. In order to eliminate the oxygen during the mixing, nitrogen was bubbled through the emulsion, after which the emulsion is heated to 60°C and then transferred to the reactor. The catalyst solution, also raised at 60°C, was injected in the reactor through the R₄ valve.

RESULTS AND DISCUSSION

Analysis of Conversion—Effect of AgNO₃

The initial trials were done using a batch reactor. A stable emulsion with a 92% monomer conversion was obtained when a 160 revolution/min agitation was used. The results are very similar to the ones found by Nomura et al.¹⁵ The variation of the molecular weight and the polydispersity after 50 min of reaction, as function of agitation are given in Table II. One can notice that there is an increase in conversion with the increase in molecular weight. The polydispersity results are also interesting as it decreases with a better agitation due to the higher number average molecular weight.

Some preliminary trials with the loop reactor indicated that although the conversion rates were higher using a tubular reactor in this case, as compared to some previous work, it was still below the conversion rate obtained with a batch reactor. It was felt that the addition of silver ions might improve this situation. In some earlier work it was found that the addition of silver nitrate increased the conversion by 50% after 10 min of reaction with styrene.¹⁶ This phenomena was later confirmed with

Table II Effect of Agitation on Molecular Weight and Polydispersity after 50 min in Batch Reactor

Agitation Revolution/Min	Conversion (%)	$\bar{M}_w \times 10^{-6}$	$\bar{M}_n \times 10^{-6}$	Polydispersity
70	51.74	1.90	0.317	5.97
160	78.11	2.78	0.910	3.04
250	63.14	2.61	0.635	4.11

vinyl acetate.¹⁷ All these reactions were done in a batch type reactor and it was never tried in this type of reactor. As can be seen in Figure 2, the phenomena is reproduced in the tubular reactor. Although the optimal conversion is not affected, the initiation time is reduced giving about a 11% conversion advantage when the AgNO_3 is present. This translates into a reduction for the time to reach a maximum conversion from 100 to 80 min. The addition of silver ions as silver nitrate was thus adopted as part of the standard recipe. The effect of the flow rate expressed as the Reynolds number (N_{Re}) on the conversion is shown in Figure 3. Here again an increase of the conversion occurred in the 5500–8500 N_{Re} with an optimum at around 7500 N_{Re} . This compares well with the 5000–7000 obtained by some previous workers^{11,12} with vinyl acetate and to a much wider range of 2800–7800 N_{Re} with styrene.^{2,4}

Although the reactor material used is closer to the styrene case, the results obtained are much more comparable to the ones obtained by the other workers using vinyl acetate. These results are given in

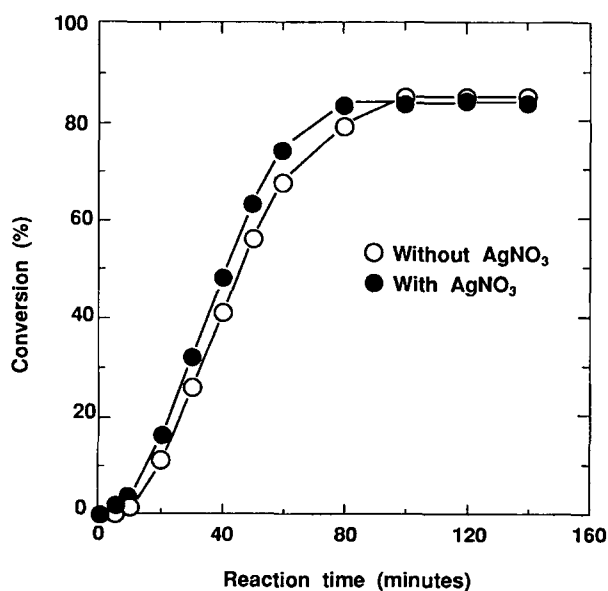
**Figure 2** Effect of silver ions on the reaction rate in the tubular reactor: (○) without AgNO_3 ; (●) with AgNO_3 .

Table III. It is interesting to compare this work results with the previous results. One can notice that a higher conversion was obtained. This is attributed to a better elimination of air in the emulsion and to the presence of AgNO_3 .

A direct comparison between the best conditions of conversion for a batch and a loop reactor are given in Figure 4; as indicated previously the loop conversion although improved were still not up to par to the batch reactor results with a conversion of 83 versus 92%.

Effect of Flow Rate on Particle Size

The analysis of the particles were done on the emulsion after 40 and 100 min reaction time and at the different flow rates. The results are given in Figures 5 and 6. The average size particle is affected by the flow rate: after 40 min of reaction the particle size varies from 0.07 to 0.22 μm with the optimum at 5500 N_{Re} . At 100 min of reaction again an optimum is obtained at the same N_{Re} of 5500 if one excludes the results of N_{Re} of 10500. The particles of every

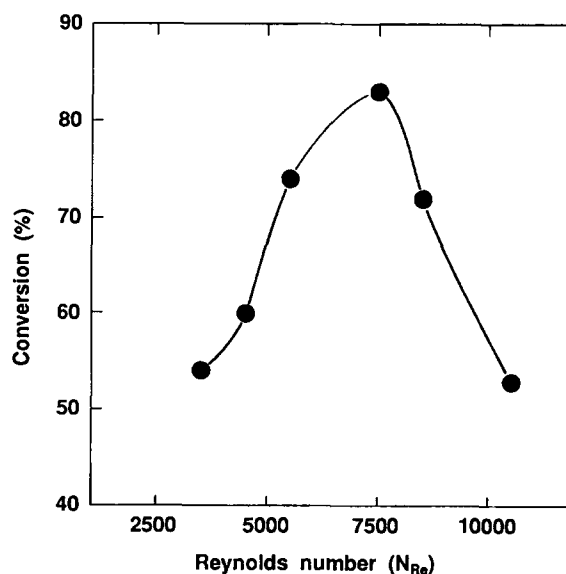
**Figure 3** Conversion versus flow rate (N_{Re}).

Table III Comparison Results

	Current Work	Dalpé ¹²	Rollin et al. ¹
Conversion plateau	83% after 80 min	65% after 60 min	65% after 60 min
Reactor type	Tubular loop	Tubular loop	Continuous tubular reactor
Monomer	Vinyl acetate	Vinyl acetate	Styrene

size varies from 0.17 to 1.96 μm . At high agitation, N_{Re} of 10500, particles are much larger, $\approx 4.25 \mu\text{m}$. This may be explained by the coagulation of the unstable particles¹⁸ due to the lack of surfactant required to stabilize a much higher surface. As expected, the particles are larger toward the end of the reaction.

The other important point is the distribution of the particle size. At 40 min the distribution is narrower for the two outside limits of our flow range, that is, N_{Re} 3500 and 10500. At low agitation over half of the particles measured have a diameter between 0 and 0.1 μm . For high agitation, over 80% of the particles have a diameter of 1–2 μm . This is probably due at low agitation to more diffusion control of both the radical from the aqueous to particle phase and the monomer from the droplet to the aqueous phase. At high agitation (N_{Re} 10500) the particle size distribution shrinks due to the agglomeration already observed. For the other conditions the particle distributions are very broad.

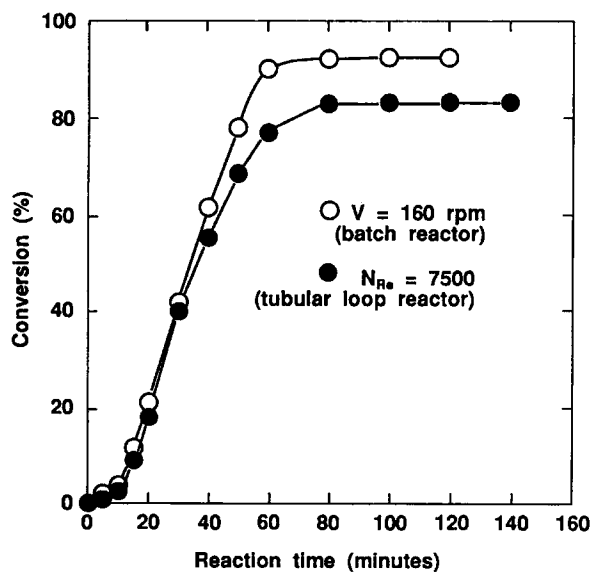


Figure 4 Comparison between the conversion in a batch and a loop reactor: (○) batch reactor at 160 rpm; (●) tubular loop reactor at $N_{\text{Re}} = 7500$.

Thus while keeping the reactant concentration constant, it is possible to preselect the final particle size by varying the reaction time and on the flow rate. A few examples are given in Table IV. A similar relation exists here with published data^{1,2} for the size of the particle with time. In their case however the average particle diameter was about 0.08 μm with styrene.

Effect of Reaction Time on Molecular Weight and Polydispersity

The analysis was limited to the results obtained from the best run as far as conversion is concerned, that is, N_{Re} 7500 and SLS concentration of $2.7 \times \text{CMC}$. The results are shown in Table V. The molecular weights (\overline{M}_w and \overline{M}_n) increase regularly from 4.5×10^5 to 9.5×10^5 and from 2.4×10^5 to 3.2×10^5 , respectively, for the first 60 min of reaction to reach a plateau. These results are in agreement with results obtained in a batch reactor by other workers. However, our conversion was limited to 83%, which precluded the full impact of chain ramification leading to the increase in molecular weight as observed previously.¹⁶ According to Friis and Hamielec¹⁹ the increase in \overline{M}_n and \overline{M}_w with the conversion is due to transfer and termination by dismutation reaction. The polydispersity also follows the same path with a gradual increase throughout the reaction. It is felt that ramification in vinyl acetate is getting to be more important throughout the reaction; it will offer more \overline{M}_w than \overline{M}_n value thus leading to a higher polydispersity. Also of interest is the two peaks obtained by GPC, confirming the bimodal mechanism of polymerization in the aqueous phase and in the micelles^{11,16} (see Fig. 7).

Effect of Flow Rate on Molecular Weight and Polydispersity

The results are given in Tables VI and VII of the average molecular weight after 40 and 100 min of reaction.

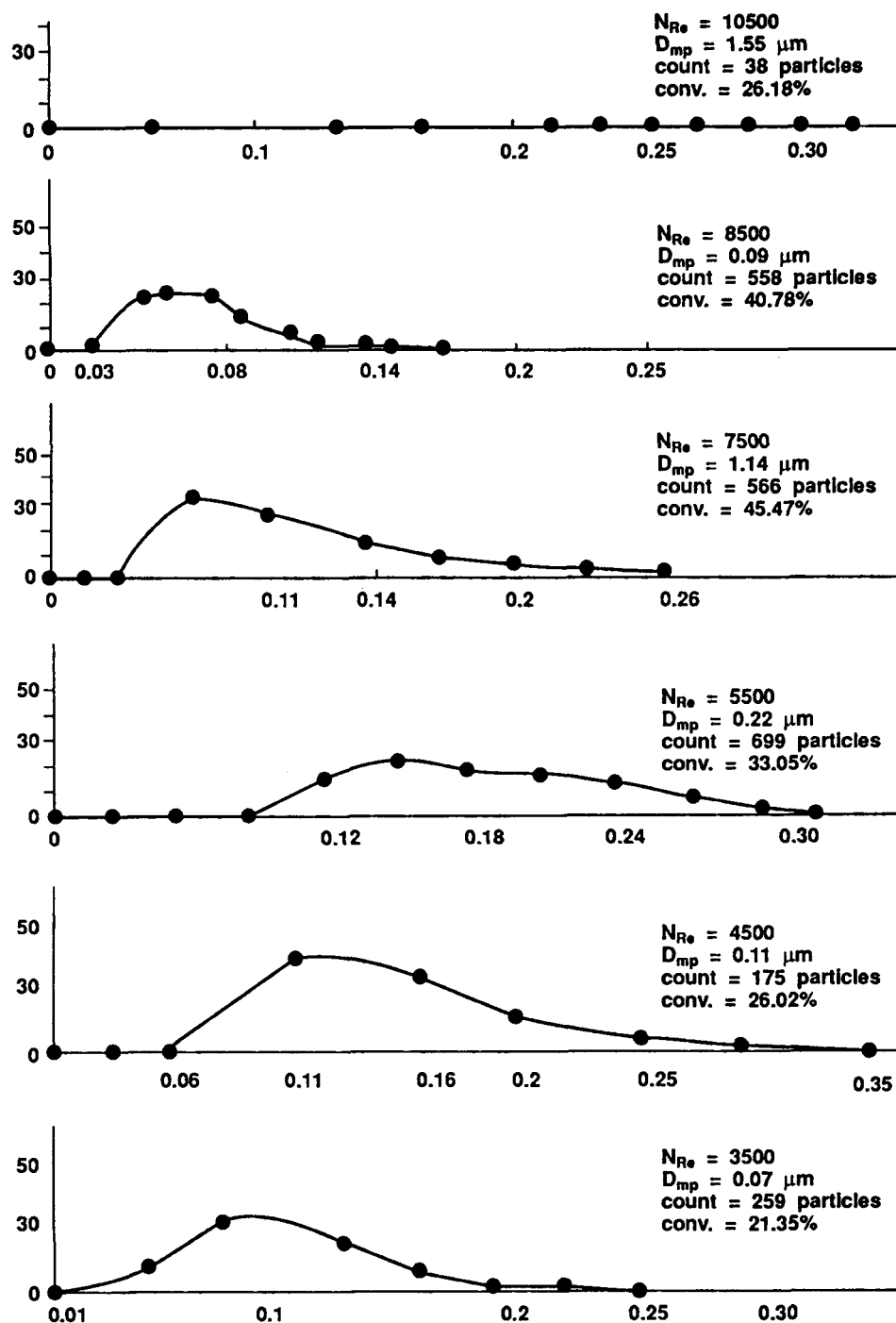


Figure 5 Normalized distribution of PVA particles after 40 min of reaction. Number of measured particles versus diameter of particles (microns).

There exists a similarity between the effects of the flow rate and the conversion on the molecular weight. As is the case of the conversion, the highest molecular weight was obtained at a N_{Re} of 5500. However, the largest polydispersity was obtained at a N_{Re} of 3500. This level of agitation is in the laminar

flow zone that is insufficient to obtain a good mixing leading to a highly polydispersed polymer. Also to be noted is that the polydispersities are higher at both extremes of our agitation spectrum, N_{Re} of 3500 and 10500, and that the molecular weight is independent of the particle size confirming previous

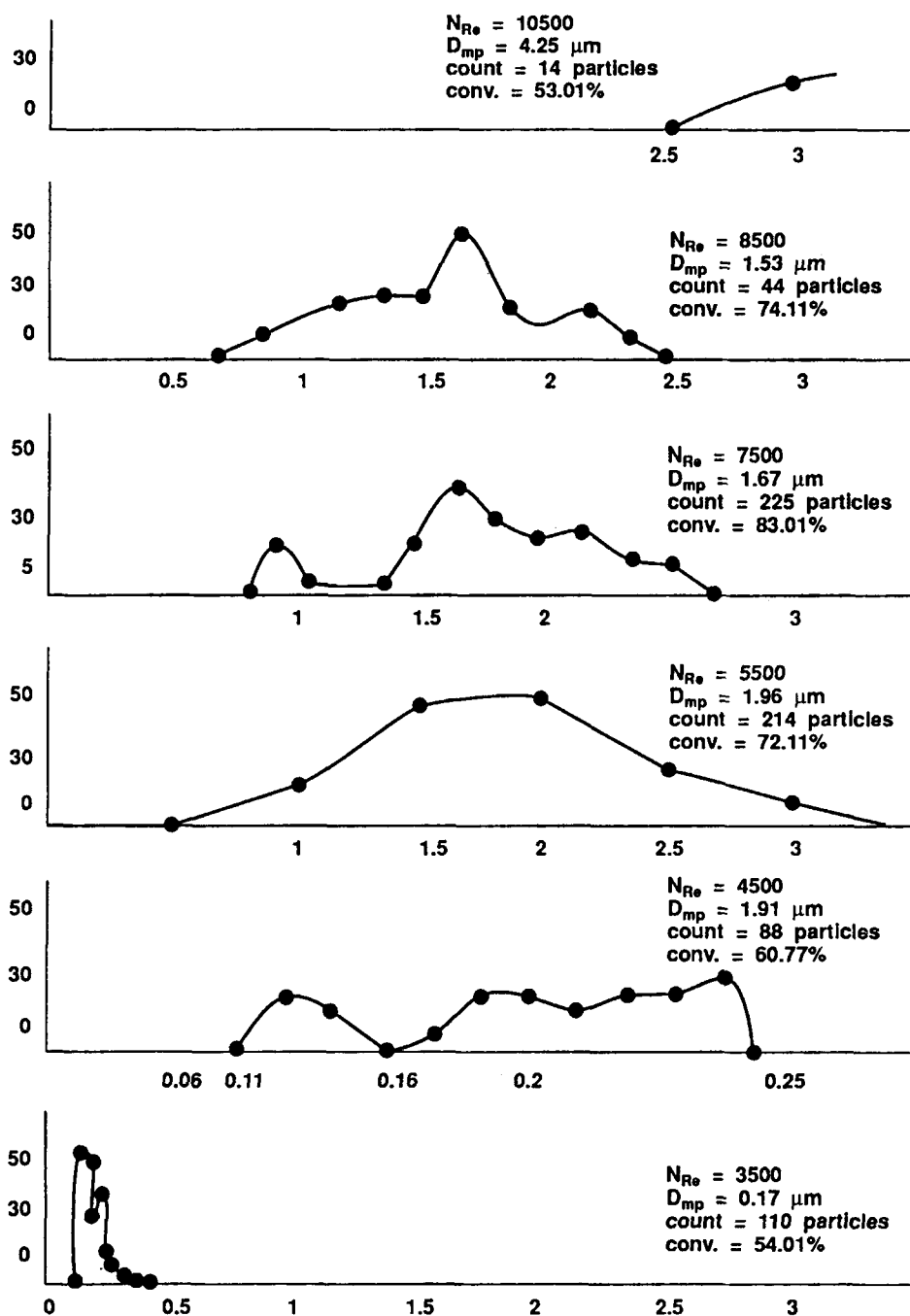


Figure 6 Normalized distribution of PVA particles after 100 min of reaction. Number of measured particles versus diameter of particles (microns).

findings.^{11,12} These results also confirm those obtained by other workers using either a batch or a loop reactor.^{11,12,19,20}

The polydispersity, however, was lowered to 2.5 as compared to 4 obtained in a previous work with loop reactor. This may be explained by a better control of the temperature in this system and in part

to an improvement in the reactor design. Ngo,²¹ working in the laminar flow zone, obtained a very heterogeneous polymer similar to the ones obtained with our low flow rate of N_{Re} 3500.

Finally the work with styrene in a tubular reactor gave a highly dispersed polymer of 3–9 with a \overline{M}_w of 1.5 to 5×10^6 . These differences completes our

Table IV Variation of Average Diameter of Latex Particles as Function of Flow Rate and Reaction Time

Particles Diameter	Size Distribution of Particles (%)	N_{Re}	Average Diameter	Reaction Time (min)	Conversion (%)
0.04-0.10	70	3500	0.0886	40	21.3
0.10-0.15	28				
0.00-0.10	50	3500	0.1673	100	54.0
0.10-0.20	34				
Sup.-0.20	16				
0.80-1.40	15	7500	1.67	100	83.0
1.40-2.00	50				
2.00-2.40	24				
Sup.-2.40	11				
0.00-0.10	65	7500	≈ 0.10	40	45.4
0.10-0.20	25				
0.20-0.30	10				

observations of the comparative behavior between styrene and vinyl acetate.

Effect of Emulsifier on Conversion and Particle Size

The variation of the conversion of vinyl acetate as a function of time at different emulsifier concentrations is shown in Figure 8. After a gradual increase in the conversion with the increase in emulsifier concentration it reaches a plateau at 2.7 times CMC after which it falls back. The other interesting feature is that for the first 10 min of induction the conversion is essentially nil for all emulsifier concentrations. The reaction rate also goes through a maximum at about 2-2.7 times the CMC. This disagrees with results obtained by other workers²² and may be attributed to the different agitation system. Also of interest is the variation of the mean diameter of the particle as a function of the CMC (see Table

VIII). Again an optimum is noted at about 2.7 times CMC.

According to the homogeneous nucleation theory¹⁸ the polymerization is initiated in the aqueous phase and then precipitate onto themselves to form particles. These particles may grow further as they capture more monomer and more surfactant. This does not preclude the formation of micelles containing monomer. If the concentration of the surfactant is high, more micelles will be present and the surface will be larger between the micelles and water. This will lead to a decrease in the possibility of the penetration of the activated oligomers into the micelles, thus leading to the possibility of having "unattended" micelles by the activated oligomers. This could explain the lower conversion rate as well as the lower average particle size at a high concentration of surfactant.

At low concentration of surfactant, that is, near the CMC, we have unstable system that will prevent

Table V Effect of Reaction Time on Weight Average Molecular Weight and Polydispersity of PVA Latex Particles

Sample Number	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	Polydispersity	Time (min)	Conversion (%)
1	4.94	2.42	2.04	5	3.9
2	4.54	2.65	1.71	10	7.1
3	4.51	2.41	1.87	20	16.1
4	6.08	2.73	2.23	40	45.4
5	9.44	3.27	2.89	60	73.1
6	9.58	3.24	2.97	80	82.0

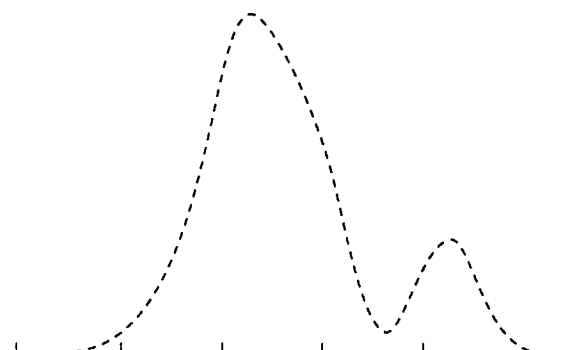


Figure 7 Typical GPC distribution curve.

the particles from accepting more monomer, leading to a lower conversion and a smaller particle size. Because these particles are more solubility-controlled, it should give a more uniform particle size distribution.

This bimodal polymerization mechanism is also suggested by the experimental results of other workers.^{17,23}

CONCLUSIONS

It has been shown that the agitation or flow has an important effect on the polymerization of vinyl ac-

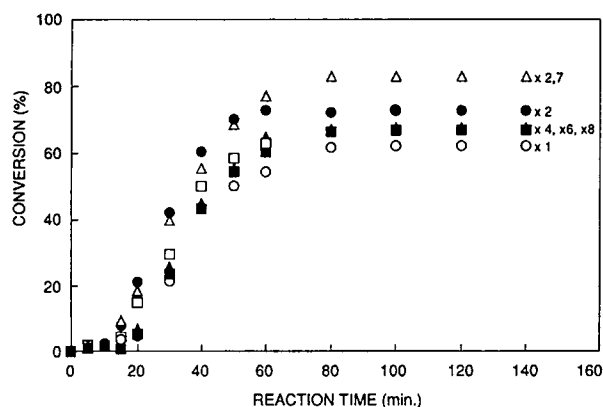


Figure 8 Effect of emulsifier concentration on the conversion rate of the vinyl acetate. (O) [SLS] = 1 × (CMC); (●) [SLS] = 2 × (CMC); (Δ) [SLS] = 2.7 × (CMC); (▲) [SLS] = 4 × (CMC); (□) [SLS] = 6 × (CMC); (■) [SLS] = 8 × (CMC).

etate in a tubular loop reactor. The optimum conversion occurred at a relatively narrow transition zone at N_{Re} of 7500. Depending on the final use of the emulsion the particle size may be preselected by varying the flow rate and reaction time. It was noted that a large particle size distribution corresponded to a relatively high polydispersity. The presence of

Table VI Effect of Flow Rate on Weight Average Molecular Weight and Polydispersity of PVA After 40 min Reaction

Trial Number	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	Polydispersity	N_{Re}	Conversion (%)
A2.10	2.91	0.82	3.51	3500	21.3
A2.11	3.24	1.59	2.04	4500	26.0
A2.12	4.04	2.12	1.91	5500	33.0
A2.13	5.70	3.13	1.82	7500	45.4
A3.14	5.48	3.08	1.78	8500	40.7
A4.15	4.30	2.21	1.94	10500	26.1

Table VII Effect of Flow Rate on Weight Average Molecular Weight and Polydispersity of PVA after 100 min Reaction

Trial Number	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	Polydispersity	N_{Re}	Conversion (%)
A2.10	5.58	1.42	3.93	3500	50.7
A2.11	5.82	1.90	3.05	4500	57.3
A2.12	6.63	2.06	3.21	5500	66.9
A2.13	9.00	4.00	2.25	7500	83.0
A2.14	8.40	3.10	2.71	8500	70.1
A2.15	6.00	1.94	3.08	10500	49.8

Table VIII Effect of Emulsifier Concentration on Size of Polymer Particles

[SLS] (×CMC)	Time (min)	Conversion (%)	Average Diameter (μm)
1.00	50	49.9	0.2216
2.00	50	70.3	0.2451
2.70	50	68.4	0.2489
4.00	50	56.3	0.2363
6.00	50	58.5	0.1567
8.00	50	54.5	0.1753

AgNO₃ shifts the conversion curve that translates into a reduction in the time to reach the maximum conversion. Contrary to styrene, the formation of small particles was not observed at high conversions. The emulsifier concentration has an affect on the conversion as well as on the particle size. A bimodal molecular distribution was observed confirming that two different mechanisms are also at play and it is independent of the reactor design. A bimodal polymerization mechanism is suggested.

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