Loop Polymerization of Vinyl Acetate

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Synopsis

The emulsion polymerization of vinyl acetate was studied using a loop reactor. The results were compared with some earlier work done in a batch reactor. A parallel was drawn with the results obtained with a tubular loop reactor and with a continuous reactor using styrene as monomer. The same phenomena of the optimum conversion peak with styrene at the laminar turbulent flow transition zone also occurred for the vinyl acetate. The peak obtained in this case was, however, broader and in the lower turbulent zone. The effect of the surfactant concentration on the broadness of the peak is discussed.

INTRODUCTION

The advantages of emulsion polymerization are well known: high rates, good control of the various polymerization steps, relatively low polymerization temperature conditions, little or no agitation and heat transfer problems, and in certain cases direct use of the latex obtained.

The usual way of making these emulsions latexes is by batch process. Continuous process has also been used as it offers the possibility of better heat transfer, less raw material handling, lower investment, and more uniform products.

Different types of continuous systems exist; we have the continuous stirred tank reactor[1,2] (CSTR), the multireactor train,[3] and the tubular reactor.[4,5] Although continuous emulsion polymerization is an area of considerable industrial interest, very little has been published on it as compared to the batch process. Most of the work done so far dealt with monomers with low polarity and with low water solubility, styrene being the classical example. This allowed the comparison with the Harkins hypothesis[6] and the more quantitative model of Smith and Ewart.[7,8] But when dealing with more soluble monomers such as methyl acrylate, acrylonitrile, and vinyl acetate, one observes deviations from the so-called ideal case. Many authors have attempted to readjust or modify the Smith–Ewart–Harkins theory but without arriving at a general consensus. One of the reasons for this state of affairs is the number and the complexity of the variables.

The operating conditions, the monomer/water ratio, the type and quantity of surfactant as well as initiators varies from author to author. The main points on which the authors don't seem to agree on are the particle nucleation mode, the polymerization site, the effect of the different variables on the polymerization rate, and the number of particles. From this, one can understand quite easily that it will be difficult to be able to have strict coherence with the reference monomer taken as styrene.

It has been shown,[9] using a tubular reactor, that the optimum conversion is attained in a certain flow regime when using styrene as monomer, this flow regime being situated in the transition zone between the laminar and the turbulent flow.

In this work we would like to show that certain phenomena reported for the styrene polymerization in a tubular reactor occurs also for a much more soluble monomer such as vinyl acetate. To achieve this and to be able to follow more easily the reaction throughout, the reactor body was made of glass tubes. This also had the added advantage of being able to follow the progress of the emulsion formation or the possible coagulation and the eventual plugging.

Instead of using the normal flow through reactor, for raw material availability, waste disposal, and residence time reasons, a loop reactor was used.

EXPERIMENTAL

Reactor Design

As indicated earlier, the reactor is made of a series of glass tubes held vertically (see Fig. 1). The dimensions of the whole system are 1 m high and 3 m long for a total reactor length of 8 m. The inside diameter of the tubes is 1.9 cm. The emulsion is pumped through the tube by a variable speed Moyno type pump.

The material used for the rotor of the pump is stainless steel whereas the stator is made of EPDM, both materials are resistant to vinyl acetate at 60°C. The connections between the pump and reactor are made of Teflon and polyethylene flexible tubes. The two valves R_1 and R_2 situated on the top of the reactor and the one, R_4, situated at the bottom serve either as filling or compensating stations, pressure relief valve, sampling valve, or overflow valve. The fourth valve, R_3, is used as a draincock.

The emulsion temperature may be monitored through the thermocouples inserted in the system (T_1, T_2, and T_3). The temperature is held constant with the help of the controlled temperature bath. Before the actual emulsion polymerization is started, the mixture of water/monomer/surfactant is pre-
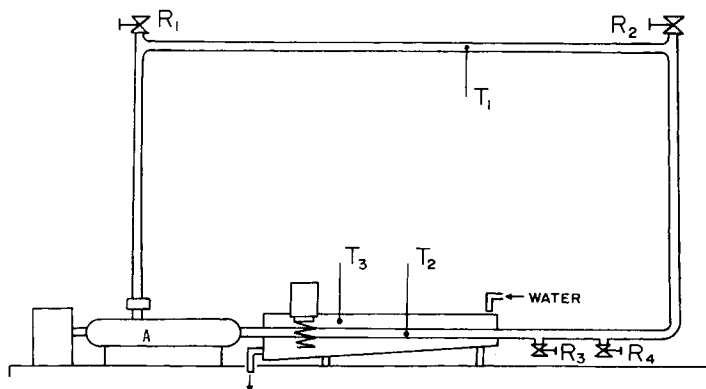

Fig. 1. Tubular reactor—closed loop: (A) pump; (R) valve; (T) thermocouple.

TABLE I
Emulsion Formulation

Constant parameters	
Demineralized water (total charge)	2175 mL
Vinyl acetate (monomer)	825 mL
Initiator solution $K_2S_2O_8$	0.5 g
Variable parameter	(in 115 mL of water)
Surfactant—sodium lauryl sulfate (SLS)	15 g and 23 g
Volume ratio monomer/water	0.38

emulsified in a batch reactor, the same way as described previously.[10] It is only when the preemulsion has reached the required operating temperature of 60°C that the initiator is introduced in the system. The actual formulation used is given in Table I.

As the Reynolds number (N_{Re}) is one of the key parameters on which is based the design of the loop reactor, and in order to be able to study the transition zone, one had to use a pump with progressive cavity and a variable speed. Knowing the initial properties of the emulsion, it is possible to define the $N_{Re, em}$ as function of the flow rate,[11, 12]

$$N_{Re, em\ init} = \frac{\rho_{em\ 60°C} D_{int} \langle V \rangle}{\mu_{cm\ 60°C}} \tag{1}$$

where $N_{Re, em\ init} = N_{Re}$ at the initial emulsion condition, $\rho_{em\ 60°C}$ = density of the emulsion at 60°C (0.96 g/cm^3), D_{int} = interior diameter of the glass tube (cm), $\langle V \rangle$ = average flow rate (cm/s), and $\mu_{cm\ 60°C}$ = viscosity of the emulsion at 60°C (g/cm s (0.5 cP). This gave an eq. (1) having the final form of

$$N_{Re, em\ init} = 365 \langle V \rangle \tag{2}$$

This permitted selection of the proper pump covering the desired flow rate range.

Reactants Preparation

Vinyl acetate was distilled under vacuum in order to eliminate the inhibitor. Demineralized and distilled water was used in order to reduce the effect of ions[13, 14] and of air. The sodium lauryl sulfate (SLS) and the $K_2S_2O_8$ are used as provided by the suppliers.

Sample Analysis

Samples were taken from the reactor at 5 min intervals and analyzed for the reaction conversion, molecular weight, and distribution of molecular weight of the polymer as well as for particle size. The determination of the molecular weight and the distribution of the molecular were obtained by GPC using a Waters HPLC Model-150-C THF was used as solvent. For the micrographs, a JEOL Model JFM-840 was used.

TABLE II
Results of Tubular Reactor

Experience no.	Operating conditions		Maximum conversion (%)	Polymerization rate (% min^{-1})
	[SLS]	$N_{Re, em}$		
T-1	2.7 ×	4300	20	0.3
T-11	CMC	4900	28	0.5
T-9		5300	57	1.5
T-10		5900	59	2.1
T-5		6400	58	2.1
T-8		6800	61	2.4
T-3		7400	53	2.7
T-6		8100	48	3.1
T-4		8600	37	3.2
T-19	4.0 ×	4900	55	2.3
T-20	CMC	5900	61	2.75
T-16		6800	63	2.8
T-18		8100	62	4.5

RESULTS AND DISCUSSION

Preliminary experiments have shown that one could have prepared the preemulsion inside the reactor instead of in a batch reactor. This was done for reference sake, in order to be able to compare the results with the one obtained by batch. Experiments were also conducted in the transition zone for a straight tube (2100–3000) but the conversion was so low (20%) that it was decided to work at a more satisfactory flow rate. The results are given in Table II. It can be noted that two levels of concentration of surfactant has been used. These two concentrations were selected on the basis of preliminary experiments run on a batch reactor.[10] The concentrations of the surfactant are expressed relatively to the critical micelle concentration (CMC) of SLS in water.

On examination of Table II, one notices that the conversion begins to be significant only above a $N_{Re, em}$ of 5000. Trials at 5300 and 5900 show an
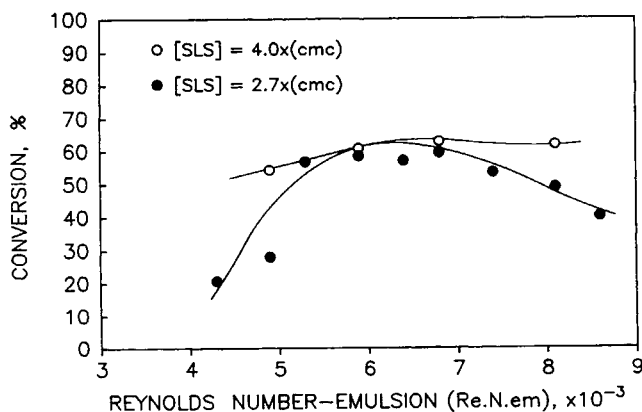
Fig. 2.   Maximum conversion vs. $N_{Re, em}$.

acceptable conversion and a peak at 60% conversion seems to be reached for a $N_{Re, em}$ of about 6800 after which a drop is noted. This phenomena may be observed in Figure 2.

This peak does not correspond to the peak obtained by other workers[9] in the transition zone for the styrene system. In this case, we are in the turbulent zone which implies that a different mechanism must be at play for vinyl acetate. In order to elucidate this mechanism, runs with a higher level of surfactant were performed—see Table II. With the surfactant level at four times the CMC, the flow regime has effectively little effect on the optimum conversion, the polymerization rates are, however, higher than at 2.7 times the CMC and almost constant.

For an $N_{Re, em}$ of 6000–7000, the conversion is constant whatever the level of surfactant. In order to explain this, one must remember that the proposed kinetic models for vinyl acetate polymerization does not follow the classical Smith–Ewart–Harkins model and the modes of nucleation—micellar and homogeneous—might both come into play.

At low $N_{Re, em}$ (see Fig. 2), the level of shear is not high enough to permit a satisfactory level of conversion. For both mechanisms of nucleation, the probability of a radical meeting a monomer molecule in solution or in the micelle is low; although at 2.7 times the CMC, there is already present some micelles, when the level of the surfactant is increased to four times the CMC, one obtains a more acceptable conversion level with a higher polymerization rate. This can be seen in experiment T-11 as compared to experiment T-19. This suggests that the micellar nucleation would be the accelerating factor here as it would be logical to think that the number of micelles would increase as one would increase the level of surfactant, thus increasing at the same time the probability of a radical meeting a micelle.

It seems that the best conditions of shear are met for $N_{Re, em}$ of 5900–6800 and favor both nucleations mechanisms. Both the conversion and the reaction rate are higher for an SLS concentration of four times the CMC, suggesting here again the effect of the micelle. For a higher level of agitation, 7400–8600, and at 2.7 times the CMC for the SLS, the polymerization rate is increased but the maximum conversion is lowered.

With a level of four times the CMC, the conversion drops slightly but the polymerization rate increases also in this case. The drop of the conversion, in the case for 2.7 × CMC, is probably due to the fact that at this level of shear, the particle have a tendency to be unstable and flocculate. This phenomenon is less significant at higher surfactant concentration. These observations, which were valid for styrene, seems to apply also to vinyl acetate when it is polymerized with a surfactant at a concentration a little higher than the CMC.

Effect on the Molecular Weight M_w

In Table III are given the results of weight average molecular weight as well as the polydispersity of the polymer. For each flow rate one can notice an increase in both the M_w and the polydispersity with conversion, confirming what other workers have found in a batch system.[13,15] For the lowest flow rates (4300 and 4900) corresponded the lowest M_w and this for all levels of

TABLE III
Weight Average Molecular Weight (M_w), Tubular Reactor

Operating conditions	Sample no.	Conversion (%)	M_w ($\times 10^5$)	PD
T-1	8	5.3	1.05	1.91
	10	11.6	1.75	2.47
[SLS] = 2.7 × CMC	11	15.8	1.75	2.35
	12	18.2	2.17	2.59
$N_{Re, em}$ = 4300	14	20.7	2.49	2.67
T-11	7	11.6	2.19	2.72
	9	20.3	2.82	3.02
[SLS] = 2.7 × CMC	10	27.5	3.10	2.98
	11	28.1	4.23	3.30
$N_{Re, em}$ = 4900	13	25.2	3.53	3.05
T-9	3	12.0	3.22	3.03
	4	26.7	4.60	3.33
[SLS] = 2.7 × CMC	5	33.8	5.22	3.84
	7	45.4	6.90	4.14
$N_{Re, em}$ = 5300	10	56.8	6.25	4.04
T-10	4	9.8	2.22	2.59
	6	27.8	4.99	3.53
[SLS] = 2.7 × CMC	7	43.2	5.51	3.60
	8	48.4	5.71	3.90
$N_{Re, em}$ = 5900	11	58.5	5.79	3.22
T-5	6	24.9	6.17	4.24
	7	47.8	8.40	4.08
[SLS] = 2.7 × CMC	10	49.5	8.69	4.04
	11	50.5	9.18	3.72
$N_{Re, em}$ = 6400	15	57.1	8.20	4.58
T-8	4	6.1	4.72	3.40
	5	21.3	6.52	3.85
[SLS] = 2.7 × CMC	6	35.1	6.90	3.92
	7	44.2	8.14	4.64
$N_{Re, em}$ = 6800	11	59.5	8.35	5.12
T-4	5	4.8	1.80	2.97
	7	34.6	6.30	4.12
[SLS] = 2.7 × CMC	8	37.1	7.10	4.10
	10	36.5	6.08	3.78
$N_{Re, em}$ = 8600	15	40.2	9.70	3.66
T-15	2	16.2	5.20	4.10
	4	48.1	6.18	3.62
[SLS] = 2.7 × CMC	8	61.9	6.53	4.10
	11	64.5	8.25	4.28
$N_{Re, em}$ = 6800	13	63.9	7.28	4.34
T-19	2	12.1	3.36	3.13
	3	18.7	3.60	3.65
[SLS] = 4.0 × CMC	4	27.5	5.34	4.30
	6	47.6	5.49	4.54
$N_{Re, em}$ = 4900	8	54.3	4.54	3.92
T-20	2	11.4	2.97	2.97
	3	21.5	3.98	3.15
[SLS] = 4.0 × CMC	4	34.4	4.71	3.05
	5	48.0	6.35	4.24
$N_{Re, em}$ = 5900	10	60.8	6.61	3.91
T-16	2	12.5	4.81	3.47
	3	37.4	5.68	3.53

TABLE III (*Continued from the previous page.*)

Operating conditions	Sample no.	Conversion (%)	M_w ($\times 10^5$)	PD
[SLS] = 4.0 × CMC	4	44.9	5.67	3.55
	6	57.9	6.64	3.83
$N_{Re, em}$ = 6800	9	62.6	7.92	3.81
T-18	1	20.6	5.43	3.75
	2	46.2	5.33	4.27
[SLS] = 4.0 × CMC	4	54.1	5.75	4.33
	6	59.0	6.08	4.37
$N_{Re, em}$ = 8100	9	61.9	4.98	4.65
T-17	2	23.4	6.24	3.60
	4	38.6	7.43	3.81
[SLS] = 4.0 × CMC	10	62.5	9.02	4.08
REINJECT · $K_2S_2O_8$	12	61.3	8.55	4.93
$N_{Re, em}$ = 6800	13	62.9	8.57	4.51

conversion. For higher $N_{Re, em}$ of 5300–5900, the evolution of M_w is the same, stabilizing at an M_w of 650,000, the polydispersity situated between 1.8 and 4.2. For an even higher flow regime, while keeping the SLS concentration constant (CMC × 2.7), there is an increase in M_w with conversion.

If one analyzes the evolution of the parameters as compared to the level of surfactant, one notices that when the level of surfactant is 2.7 × CMC, the increase of M_w is regular and tends, to a certain value of M_w of about 1×10^6 whereas when the surfactant concentration is four times the CMC, the rate of increase of M_w is not as regular and gives very different values at high conversions.

In most experiments performed, it was around 20–30% conversion that a second peak developed. Going back to Table III, one notices that for low conversions and for a surfactant concentration of 4 × CMC the M_w's are higher than for the case of 2.7 × CMC, suggesting that the first peak is from the micellar nucleation. With the increase of conversion and the gradual disappearance of the micelle, one should observe a greater part of the polymerization in the aqueous phase (appearance of a second peak) with longer chains, confirming the work of other authors.[2]

CONCLUSION

It was found, just like the styrene case, that there exists, a zone of optimum conversion at a precise flow rate in the tubular reactor. This zone is not situated in the transition zone between the laminar and the turbulent flow, as was the case for the styrene, but situated at about a $N_{Re\ em}$ of 6200. The maximum conversion attained during these experiments are in great part, due to the reactor design.

The concentration of the surfactant is not as critical as in the case of styrene, the increase in the amount of surfactant, much above the CMC, broaden the optimal conversion zone. It thus decreases the importance of the flow rate but increases the resulting emulsion impurity. Two peaks were noted

in the molecular weight distribution analysis curve, confirming two modes of particuiate nucleation.

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