Emulsion Copolymerization of Vinyl Esters in Continuous Reactors: Comparison Between Loop and Continuous Stirred Tank Reactors

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SYNOPSIS

The high solids emulsion copolymerization of vinyl acetate and veova 10 was studied in a continuous loop reactor and in a continuous stirred tank reactor (CSTR) in an attempt to elucidate the similarities and differences between these reactors. Reactions were carried out under comparable conditions, namely, similar macromixing and the same feed composition and space time. The behavior of both reactors was almost the same when the heat generation rate was low; otherwise, thermal runaway occurred in the CSTR whereas the loop reactor temperature was easily controlled. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Continuous emulsion polymerization reactors are used when high production rates of a constant quality polymer are required. Different types of continuous emulsion polymerization reactors, including continuous stirred tank reactors (CSTRs),[1,2] loop reactors,[3,4] tubular reactors,[5,6] pulsed tubular reactors,[7,8] and Couette–Taylor flow reactors[9] have been developed. However, only CSTRs and, recently, loop reactors are used in industry. Continuous loop reactors are an attractive alternative in producing emulsion polymers because, due to their geometry, the heat of polymerization can easily be removed from the reactor, and hence the process can be conducted at high polymerization rates. This means that high conversions can be achieved in short residence times.

Tracer experiments showed[10] that the macromixing in the continuous loop reactor is determined by the recycle ratio, R, (the ratio between the reactor's internal flow rate and the feed flow rate). For large values of the recycle ratio ($R > 40$), the residence time distribution (RTD) of the continuous loop reactor was reported to be almost identical to that of a CSTR. These results were in conflict with those reported by Lee et al.,[11] who found that the RTD of a loop reactor working with a recycle ratio of 124 deviated significantly from the RTD of a CSTR. The main difference between these experiments is that in Abad et al.,[10] recycle was provided by a positive displacement pump, whereas Lee et al.[11] used a perhaps less efficient turbine stirrer. In addition, Lee et al.[12] reported that the dependences of the polymerization rate and the number concentration of polymer particles on emulsifier concentration observed in a continuous loop reactor were different from those expected in a CSTR. The authors attributed this difference to the different flow patterns in those reactors. However, no direct comparison of the performances of the loop reactor and the CSTR was carried out.

In the present paper, in an attempt to further elucidate the similarities and differences between the loop reactor and the CSTR, the redox-initiated emulsion copolymerization of vinyl acetate and veova 10 was studied in both types of reactors under comparable industrial-like conditions, namely: similar macromixing, same feed compositions and space time, and the use of high solids content (55 wt %) recipes.

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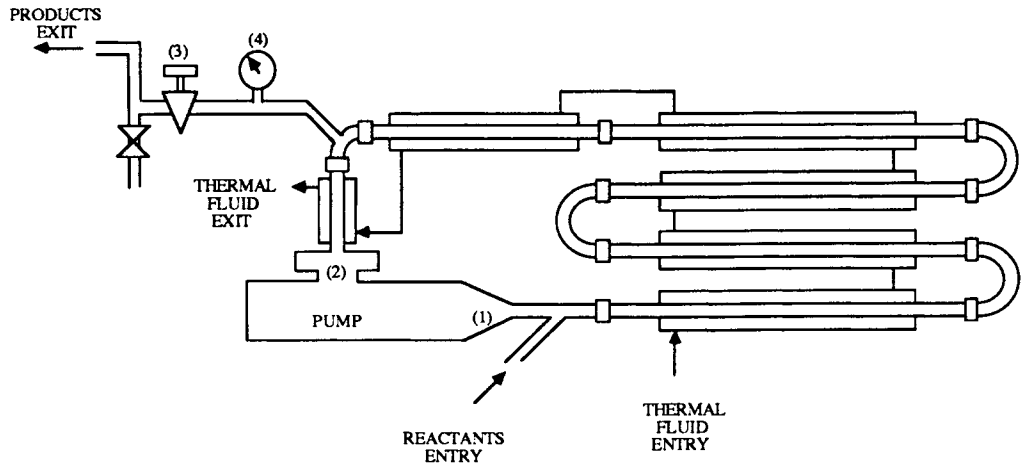

Figure 1 Continuous loop reactor.

EXPERIMENTAL

Inhibited monomers, vinyl acetate (VAc), veova 10, and butyl acrylate (BuA) (hydroquinone in VAc and veova 10, and *p*-methoxyphenol in BuA) were used. Stability of the latex was provided by a mixture of emulsifiers, including Alipal CO430 (ammonium salt of sulfated nonylphenol poly[ethylenoxy] ethanol [4 ethylenoxy], Rhône Poulenc), Arkopal N230 (nonyl phenol poly[ethylenoxy] ethanol [23 ethylenoxy], Hoëchst), and hydroxyethyl cellulose. $K_2S_2O_8$ and $Na_2S_2O_5$ were used as redox pair. All materials were used as received. Deionized water was used throughout the work.

A scheme of the loop reactor used in this work is presented in Figure 1. A jacketed stainless steel tube (AISI 316) 6 m long and 1 cm internal diameter connects the discharge (1) and the suction (2) of a positive displacement pump (NETZCH Ne 240). This pump promotes the liquid movement due to the eccentric rotation of a stainless steel rotor in a PTFE stator. The fluid velocity in the reactor can be changed by varying the pump speed. The total volume of the reactor is 2.8 L (tube: 0.47 L; pump: 2.33 L). When considered isolated, both parts of the reactor are different from the point of view of macromixing; but connected in a recycling loop under the high recycle ratios used in this work, the macromixing of the whole system is that of a perfectly back-mixed reactor[10] of a volume equal to the total volume of the loop reactor (2.8 L). Reactants were fed into the reactor near the pump discharge, and the products exit was located before the pump inlet. To avoid cavitation in the pump, a pressure-sustaining valve (3) was placed in the products exit tube. The pressure in the reactor was measured by means of a diaphragm-type gauge (4). For a given feed-flow rate, the values of the reactor pressure are an indirect measurement of the viscosity of the latex. The reactants were fed in three different streams that were mixed just before the entrance to the reactor. Stream 1 contained the monomers; stream 2 was an aqueous solution of the emulsifiers, protective colloid, and $Na_2S_2O_5$; and stream 3 was an aqueous solution of $K_2S_2O_8$. The flow rates of streams 1 and 2 were controlled by mass flow controllers (KFlow PICO 2), and that of stream 3 was controlled by a Mettler Flow-pac flow controller. Temperature control was achieved through a cascade control system. The whole experimental setup was controlled by a personal computer.

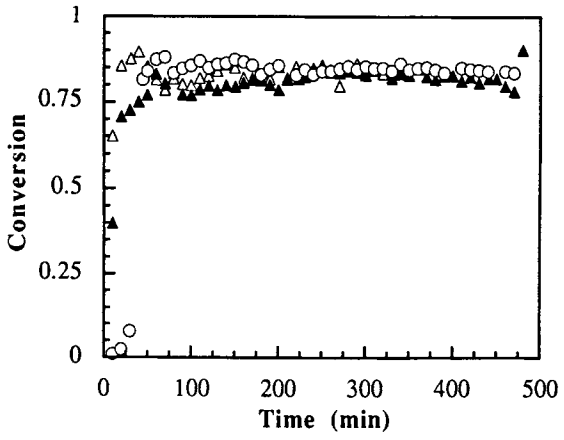

Figure 2 Time evolution of conversion when start-up was carried out using strategies A and B. Run L–A: △; C–A: ▲; L–B: ○.

An 0.47-L jacketed tank reactor equipped with a

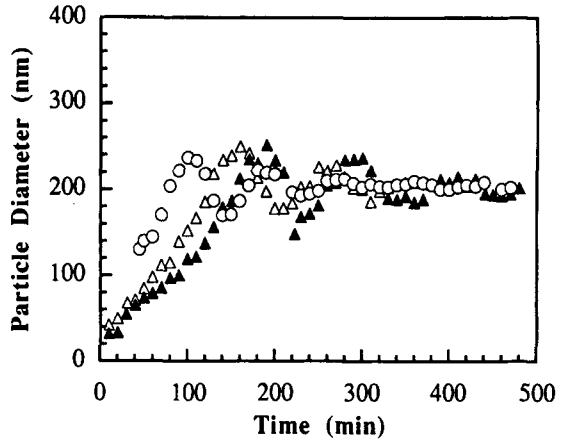

Figure 3 Time evolution of the particle diameter when start-up was carried out using strategies A and B. Run L–A: △; C–A: ▲; L–B: ○.

six-bladed turbine, a sampling device, and inlet and outlet tubes was used as CSTR. The reactants were fed into the reactor through a $\frac{1}{4}$" stainless steel tube located near the turbine. The reactants were fed in three different streams that were mixed just before the entrance of the reactor. The streams were the same as for the loop process. The flow rates of the three streams were controlled by means of weight-based flow controllers. The products left the reactor through a $\frac{1}{2}$" tube located at the top of the reactor. There was no head space in the reactor and this ensured that a constant volume was maintained. Reactor temperature was controlled by means of a thermostatic bath. Before entering the reactor jacket, the thermal fluid flowed through a heat exchanger that provided additional cooling capacity. The flow of tap water through the heat exchanger was controlled by means of a proportional-integral derivative (PID) controller and a control valve.

Samples were withdrawn from the reactor and the polymerization short-stopped with hydroquinone. Monomer conversion was measured by gravimetry. For the calculation of the conversion, the residence time distribution and the volume contraction due to polymerization were taken into account. Copolymer composition was not measured because the reactivity ratios of the main monomers (VAc and veova 10) are close to 1,[13] and hence copolymer composition drift was not expected. This point was checked in prior batch polymerizations. Polymer particle diameter was measured by dynamic light scattering. This value and that of the conversion were used to calculate the number of polymer particles. Molecular weight distributions were obtained by gel permeation chromatography (GPC) using 2 photoluminescent (PL) gel 20 μm Mixed A columns from Polymer Laboratories and a refractive index detector. The solvent was tetrahydrofuran, and the flow rate 1 cm^3/min. The columns were calibrated with nine standard polystyrene samples. Molecular weights were determined using the universal calibration with polystyrene and the Mark-Houwink constants for linear vinyl acetate.

Table I summarizes the polymerizations carried out using the recipe given in Table II. Three polymerizations were carried out in each reactor, varying the start-up procedure. The main differences were the composition of the initial charge and the temperature profiles. The strategies used were as follows:

Run A: Reactor initially filled with water, emulsifiers, protective colloid, and $Na_2S_2O_5$ and heated to the reaction temperature (60°C).

Run B: Reactor initially filled with a preemulsion of water, emulsifiers, protective colloid, $Na_2S_2O_5$, and the monomer mixture in the same proportions as in the overall recipe. The reactor was initially set at room temperature and then heated to reaction temperature (60°C) following a given temperature profile.

Run C: Reactor initially filled with a latex from a previous reaction and heated to the reaction temperature (60°C).

The total feed rates were Q_0 = 100 g/min (105.7 cm^3/min) for the continuous loop reactor, and Q_0 = 16.8 g/min (17.8 cm^3/min) for the CSTR process. The space time for both reactors was 26.5 min. The steady state reaction temperature was 60°C for all reactions. The pump speed in the loop reactor was

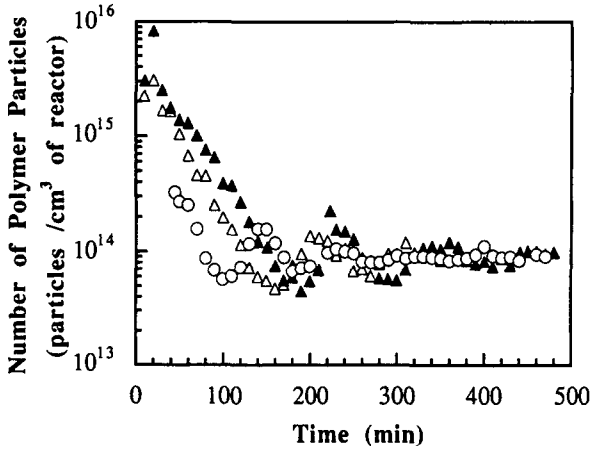

Figure 4 Time evolution of the number of polymer particles when start-up was carried out using strategies A and B. Run L–A: △; C–A: ▲; L–B: ○.

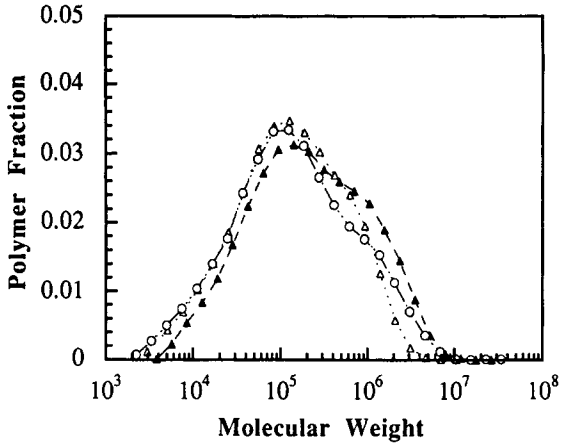

Figure 5 Steady state molecular weight distributions obtained when start-up was carried out using strategies A and B. Run L–A: △; C–A: ▲; L–B: ○.

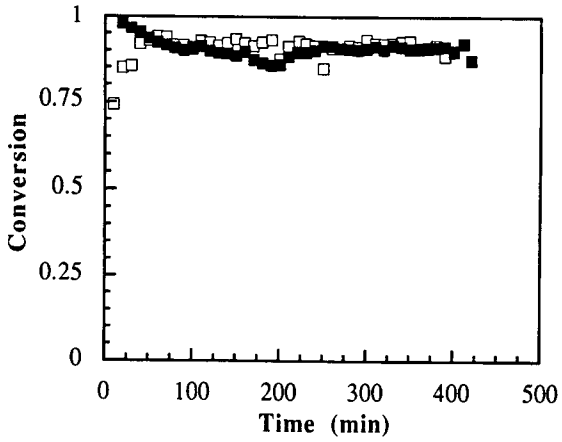

Figure 7 Time evolution of conversion in runs L–C (□) and C–C (■).

100 rpm, which corresponds to an internal flow rate of 5500 cm^3/min. For this flow rate, the recycle ratio was 55. The speed of the stirrer in the CSTR was fixed at 200 rpm.

The flow pattern in the reactor was characterized by means of tracer experiments. The reaction mixture was replaced by an aqueous solution of hydroxyethyl cellulose. The viscosity of the solution was adjusted to a value similar to that of the steady state latex by varying the concentration of hydroxyethyl cellulose. An automatic injection valve was used to inject the tracer (NaCl). Conductivity sensors were placed at the entrance and exit of both reactors. Under the conditions in which the reactions were carried out, both reactors were found to behave like an ideal CSTR.

RESULTS AND DISCUSSION

Figures 2, 3 and 4 present the time evolution of conversion, particle diameter, and number of polymer particles for both types of reactor when the start-up was carried out using strategy A. It can be seen that the same conversion was reached in both reactors. In addition, slight oscillations in conversion were observed. Figures 3 and 4 show that these oscillations were due to damped oscillations of the size and number of polymer particles. The amplitude and frequency of the oscillations of both particle size and particle diameter were almost the same for both reactors, although a small time delay was observed for the CSTR process. This time delay has its origin in a short inhibition period during start-up. The presence of random inhibition periods is quite common in emulsion polymerization systems using

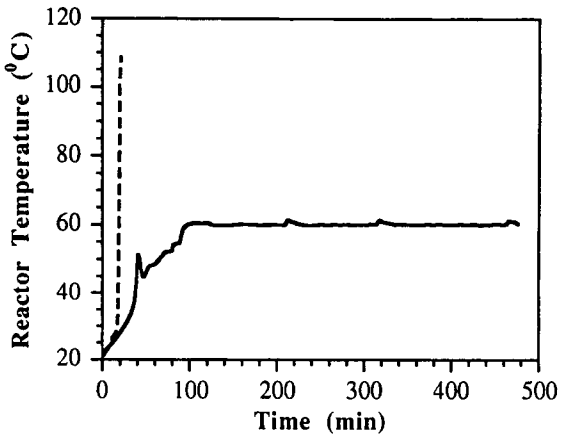

Figure 6 Temperature profile control in runs L–B (——) and C–B (- - -).

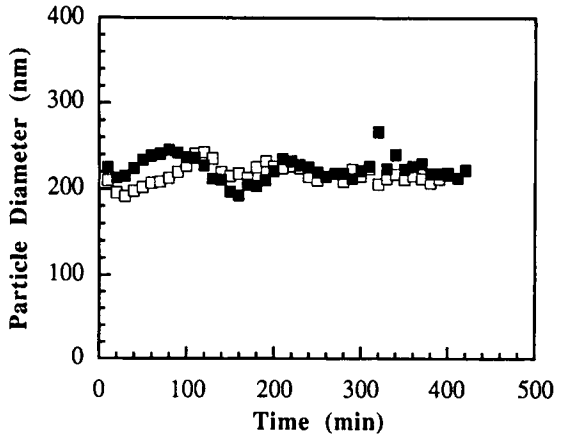

Figure 8 Time evolution of particle diameter in runs L–C (□) and C–C (■).

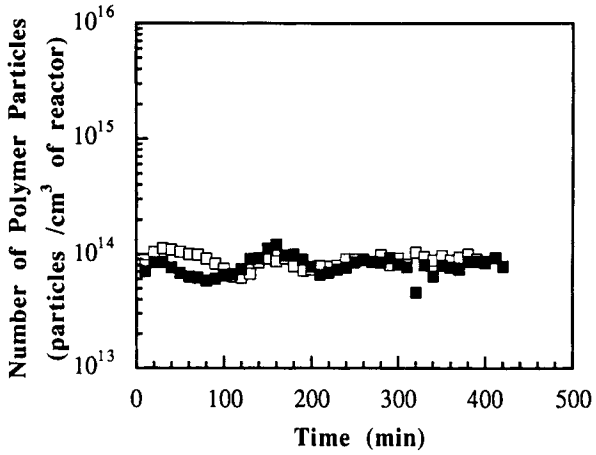

Figure 9 Time evolution of the number of polymer particles in runs L–C (□) and C–C (■).

technical monomers; hence the time lag in the particle size and number evolutions cannot be attributed to the type of reactor. Figure 5 presents the molecular weight distribution (MWD) of the last samples collected in each process. It can be seen that the molecular weight of the polymer produced in the CSTR was significantly higher than that obtained in the loop reactor. Admittedly, no explanations can be provided for the different MWD in two systems that have the same conversion and the same particle size and number.

Start-up strategy B was carried out by initially filling the reactor with a preemulsion of water, emulsifiers, protective colloid, $Na_2S_2O_5$, and the monomer mixture, and starting the polymerization at room temperature. The aim of starting at low temperature was to minimize the exotherm due to

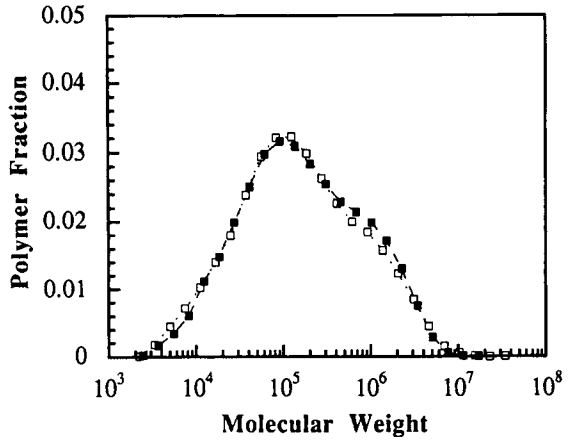

Figure 10 Steady state molecular weight distributions in runs L–C (□) and C–C (■).

Table I Summary of the Polymerizations

RUN Number	Residence Time (min)	Reactor Type	Start-up Procedure
L–A	26.5	Loop	A
C–A	26.5	CSTR	A
L–B	26.5	Loop	B
C–B	26.5	CSTR	B
L–C	26.5	Loop	C
C–C	26.5	CSTR	C

the polymerization of the highly concentrated monomers. Figure 6 presents the evolution of the reactor temperature for runs L–B and C–B. It can be seen that whereas the temperature of the loop reactor could be controlled, the heat transfer area/reactor volume ratio of the CSTR was not enough to remove the polymerization heat and a thermal runaway occurred, even though the volume of CSTR was less than one-fifth that of the loop reactor. Consequently, run C–B could not be completed. The results obtained in run L–B are presented in Figures 2–5 together with those of experiments L–A and C–A. It can be seen that because of the initial reactor temperature profile, the approach to the steady state is different than in the case of runs L–A and C–A,

Table II Recipe Used for All Reactions, Based on 100 Parts by Weight of Total Monomer

	STREAM 1	STREAM 2	STREAM 3
Vinyl acetate	75.0	—	—
Veova 10	25.0	—	—
Butyl acrylate	1.0	—	—
Water	—	72.0	9.81
Alipal (CO 430)	—	1.50	—
Arkopal (N-230)	—	2.00	—
Hydroxyethyl cellulose	—	0.10	—
$Na_2S_2O_5$	—	0.21	—
$K_2S_2O_8$	—	—	0.3
Flow rate (loop) (g/min)	40.61	5.404	53.98
Flow rate (CSTR) (g/min)	6.82	0.907	9.06

but the steady state values of conversion, particle size and particle number are the same in the three experiments. In addition, Figure 5 shows that the MWD obtained in run L–B was similar to that obtained in run C–A.

Figures 7–9 present the time evolution of conversion, particle size and particle number for the experiments carried out using start-up strategy C. These figures show that the steady state conditions were reached quickly and no oscillations were observed. In addition, a perfect agreement between the results obtained in the loop reactor and in the CSTR was found. Figure 10 presents a comparison between the MWDs of the last samples collected in runs L–C and C–C. It can be seen that a perfect coincidence was obtained. Comparison between the results presented in Figures 7–10 with those in Figures 2–5 shows that, provided that the reactor has enough heat-removal capacity, the steady state values of the variables were not influenced by the type of reactor used. The steady state results were also independent of the start-up procedure.

CONCLUSIONS

The redox-initiated high solids emulsion copolymerization of vinyl acetate and veova 10 was carried out in a continuous loop reactor and a CSTR in an attempt to elucidate the similarities and differences between the two kind of reactors. Several start-up strategies were tried in both reactors under comparable conditions, namely, similar macromixing and using the same feed composition and space time. It was found that for operation conditions in which the heat-removal capacity of the reactor exceeded the heat generation rate, there are no differences between the loop reactor and the CSTR in terms of conversion, particle size and number, and molecular weight distributions. However, under conditions in which the heat generation rate is high, a thermal runaway occurred in the CSTR whereas the loop reactor temperature was easily controlled. This difference is due to the different geometry of the reactors and is critical from the point of view of production rate. In addition, it was found that the steady state results were independent of the start-up procedure.

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