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Start-up procedures in the emulsion copolymerization of vinyl esters in a continuous loop reactor

Carlos Abad, José C. de la Cal and José M. Asua*
Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain
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Different start-up strategies for the 55 wt% solids content redox-initiated emulsion copolymerization of vinyl acetate and Veova 10 in a continuous loop reactor were studied to determine the optimal start-up procedure in terms of smoothness of the operation and minimum out-of-specification product. These strategies included different initial charges and temperature profiles. The evolutions of the monomer conversion, particle size, number of polymer particles and molecular weight distribution during the start-up were analysed and the effect of the start-up procedure on the steady-state values of these variables determined.

(Keywords: loop reactor; emulsion copolymerization; vinyl esters)

INTRODUCTION

Continuous loop reactors are an attractive alternative to produce emulsion polymers because, owing to their geometry, the polymerization heat can be easily removed from the reactor. This means that high conversions can be achieved in short residence times.

The first published information on the loop reactor process were patents[1,2] that describe a continuous recycling process for the polymerization of vinyl monomers. The history of this discovery as well as a discussion of the main characteristics of the loop process have been given by Geddes[3]. This author[4] studied the changes in physical properties during emulsion copolymerization in a continuous loop reactor, with particular reference to particle size distribution (*PSD*). Cycling of properties similar to that reported for CSTRs (continuous stirred tank reactors) was found. This behaviour was attributed to intermittent nucleation caused by changes in the surface area. Lee *et al.*[5–7] studied the low solids content emulsion polymerization of styrene in a continuous loop reactor. The effects of temperature, emulsifier concentration, initiator concentration, monomer concentration and mean residence time on the conversion, average particle diameter, number concentration of polymer particles and, in some cases, average molecular weights were investigated. Overshoots in both monomer conversion and number of polymer particles were reported, but neither oscillations nor multiple steady states were found.

Bataille and co-workers[8–10] studied the emulsion homopolymerization of styrene and vinyl acetate in a batch loop reactor. They found that a limiting conversion, lower than that obtained in a batch tank reactor, occurred for all cases. The value of the limiting conversion was maximum for the laminar–turbulent flow transition zone. Adams[11] claimed that the use of a tubular reactor after the loop reactor allows for a better control of the *PSD* as well as the production of core–shell particles. Geddes[12] proposed to increase the production rate of the continuous loop reactor by using a multi-passageway flow path operated at a shear rate above 800 s^{-1} whilst sustaining laminar flow in the flow path.

In this work, the effect of start-up strategy on the evolution of conversion, number of polymer particles and molecular weight distribution for the 55 wt% solids content redox-initiated emulsion copolymerization of vinyl acetate and Veova 10^{TM} (Shell) was investigated. The goal was to determine the optimal start-up strategy in terms of smoothness of the operation and minimum out-of-specification product.

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(ethyleneoxy) ethanol (4-ethyleneoxy), Rhône Poulenc), Arkopal N230 (nonylphenol poly (ethyleneoxy) ethanol (23 ethyleneoxy), Hoëctch) and hydroxyethyl cellulose. $K_2S_2O_8$ and $Na_2S_2O_5$ were used as a redox pair. All materials were used as received. Deionized water was used throughout the work.

Polymerizations were carried out in the reactor shown in *Figure 1*. A double–jacketed steel (AISI 316) tube, 6 m long and 1 cm i.d. connects the discharge (1) and the

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* To whom correspondence should be addressed

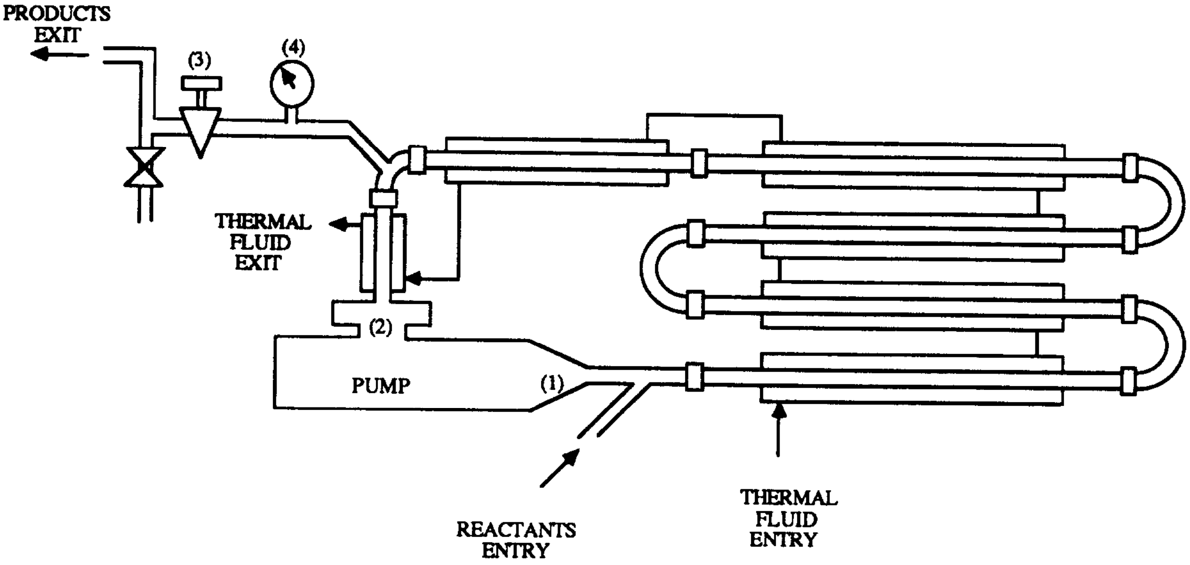

Figure 1 Experimental set-up

suction (2) of a positive displacement pump (Netzch Ne 240). This pump promotes liquid movement by 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 via a manual motor speed controller. The total volume of the reactor is 2.80 l (tube: 0.47 l; pump: 2.33 l). Reactants were fed into the reactor near the discharge of the pump and the products' exit was located before the suction of the pump. To avoid cavitation of 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 of 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 means of mass flow controllers (KFlow PICO 2), and that of stream 3 was controlled by means of a Mettler Flow-pac flow controller.

Temperature control was achieved through a cascade control system. Temperatures along the tube were measured, an average temperature obtained and used as the controlled variable of the primary PI controller. This primary controller determined the set point for the temperature of the thermal fluid. This set point was used by the secondary PID controller to manipulate the final control elements. The latter were a 2 kW resistance and a control valve that varied the flow of tap water through a heat exchanger through which the thermal fluid flowed. The whole experimental set-up was controlled by a personal computer.

Samples were collected from the exit tube and the polymerization short stopped with hydroquinone. Monomer conversion was measured by gravimetry. For 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) were close to 1 (ref 13), and hence copolymer composition drift was not expected.

This point was checked in previous 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 (g.p.c.) using two PL-gel 20 μ Mixed A columns from Polymer Laboratories and a refractive index detector. The solvent was tetrahydrofuran, and the flow rate 1 $cm^3 min^{-1}$. 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[14].

Different start-up strategies were used. The main differences between them are the composition of the initial charge and the temperature profiles. These strategies were as follows.

- Run A: reactor initially filled with water and heated to the reaction temperature (60°C).
- Run B: reactor initially filled with water, emulsifiers, protective colloid and $Na_2S_2O_5$, and heated to the reaction temperature (60°C).
- Run C: reactor initially filled with a pre-emulsion of water, emulsifiers, protective colloid, $Na_2S_2O_5$ and the monomer mixture in the same proportions as in the overall recipe. Two different temperature profiles were tried for this type of start-up (1) C-1: reactor initially heated to the reaction temperature (60°C) and (2) C-2, C-3: reactor initially at room temperature and then heated to reaction temperature (60°C) following a given temperature profile.
- Run D: reactor initially filled with a latex from a previous reaction, and heated to the reaction temperature (60°C).

Table 1 shows the recipe used for all the reactions. The total feed rate was 100 g min^{-1}, and the time in the reactor was 26.5 min. The reaction temperature was 60°C for all the reactions, except for runs C-2 and C-3, in which increasing temperature profiles starting from room temperature up to 60°C were used. For all

Table 1 Recipe used for all the reactions, based on 100 parts by weight of total monomer

	Stream 1 (parts by weight)	Stream 2 (parts by weight)	Stream 3 (parts by weight)
Vinyl acetate	75.0	–	–
Veova 10	25.0	–	–
Butyl acrylate	1.00	–	–
Water	–	72.0	9.81
Alipal (CO430)	–	1.50	–
Arkopal (N230)	–	2.00	–
Hydroxyethyl cellulose	–	0.10	–
$Na_2S_2O_5$	–	0.21	–
$K_2S_2O_8$	–	–	0.30
Flow rate (g min^{-1})	53.98	40.61	5.404

reactions, the pump speed was 100 rev min^{-1} which corresponds to an internal flow rate of 5500 cm^3 min^{-1}. For this velocity, the recycle ratio between the inside flow rate and the feed flow rate was 55. Previous tracer experiments showed that under these conditions the residence time distribution in the loop reactor is close to that of a CSTR.

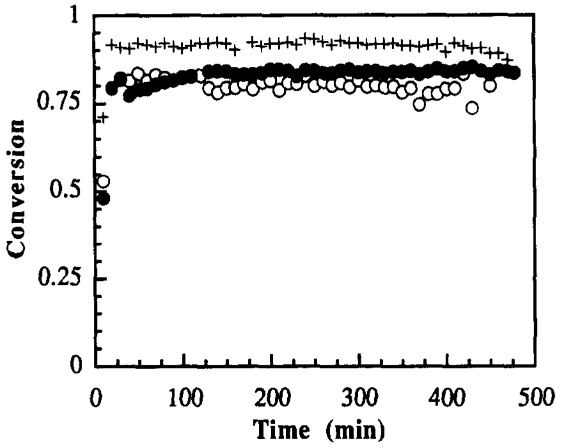

Figure 2 Time evolution of the gravimetric conversion for three replicate experiments carried out following the start-up procedure A: +, run A-1; ○, run A-2; ●, run A-3

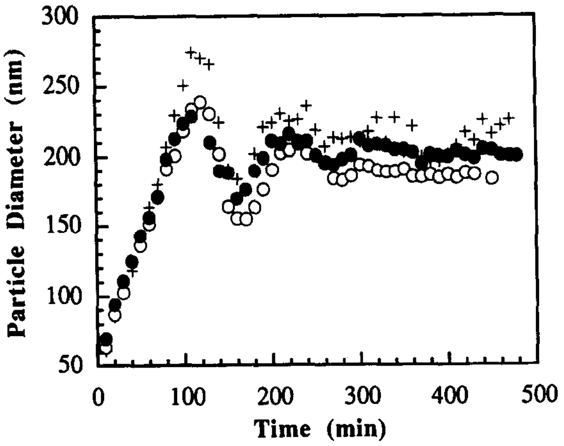

Figure 3 Time evolution of the particle diameter for three replicate experiments carried out following the start-up procedure A: +, run A-1; ○, run A-2; ●, run A-3

RESULTS AND DISCUSSION

Figure 2 presents the time evolution of the gravimetric conversion for three replicate experiments following the start-up procedure A (runs A-1, A-2 and A-3), namely starting the polymerization with the reactor filled with water at the reaction temperature (60°C). It can be seen that the conversion obtained in run A-1 was significantly higher than those obtained in runs A-2 and A-3. *Figures 3* and *4* present the evolutions of the average particle diameter (d_p) and number of polymer particles (N_p), respectively, for runs A-1, A-2 and A-3. The oscillatory behaviour of these variables can be explained as follows. At the beginning of the process, a large number of small polymer particles was formed, the maximum number of these particles being controlled by the amount of emulsifier available in the system. These polymer particles grew by polymerization, and hence their surface area increased, depleting the aqueous phase of emulsifier. Therefore, new particles were not formed and the number of polymer particles in the reactor decreased. After some time, this process counteracted the increase in size of the polymer particles and the amount of free emulsifier increased, allowing nucleation of new polymer particles. The second nucleation occurred in the presence of polymer particles and the number of particles formed was smaller than for the case of the first nucleation. This led to damped oscillations. The oscillations of the conversion were almost imperceptible. Calculations showed that $\bar{n}$ was >0.5, namely close to the Smith–Ewart case 3 kinetics[15] where the conversion is not sensitive to the number of polymer particles. In addition, *Figure 4* shows that the number of polymer particles was the same in three replicate experiments. Therefore, a different number of particles was not the reason for the differences in conversion reported in *Figure 2*. However, it can be argued that the dynamic light scattering measurements are not sensitive enough to small-size polymer particles and this type of particle can be the origin of the differences in conversion. Another possibility is that there would be multiple steady states. This point will be checked later.

On the other hand, runs A-1, A-2 and A-3 proceeded smoothly with an easy control of the reactor temperature and a small increase in the viscosity of the latex. A

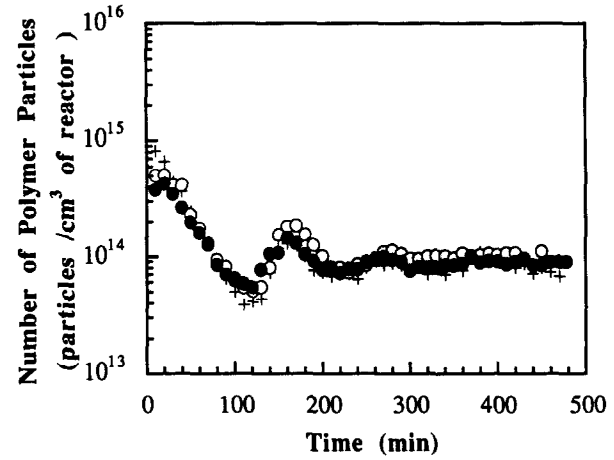

Figure 4 Time evolution of the number of polymer particles per unit volume of reactor for three replicate experiments carried out following the start-up procedure A: +, run A-1; ○, run A-2; ●, run A-3

negligible amount of coagulum (< 0.1%) was found at the end of the experiments (18 residence times).

Figure 5 presents the evolution of the molecular weight distribution (*MWD*) during run A-2. It can be seen that all *MWD*s present a shoulder, showing that two different mechanisms controlled the *MWD*. It is proposed that the small molecular weight peak resulted from the chain transfer reaction to monomer, and the high molecular weight shoulder from chain transfer to polymer and propagation to terminal double bonds. *Figure 5* also shows that the *MWD* remained almost unchanged during the process.

Figure 6 presents the evolution of the gravimetric conversion for two replicate experiments carried out using the start-up procedure B, runs B-1 and B-2. In this start-up strategy, the reactor was initially charged with an aqueous solution of the emulsifiers, protective colloid and $Na_2S_2O_5$, and heated to 60°C before starting the feeding. It can be seen that good reproducibility was obtained and that the conversion oscillated at the beginning of the process. These oscillations also appeared in the evolutions of the particle diameter and number of polymer particles (*Figures 7* and *8*, respectively). However, there was some time delay between the oscillations of the conversion and that of the number of polymer particles.

Figure 9 presents the time evolution of the molecular weight distribution in run B-1. It can be seen that the first

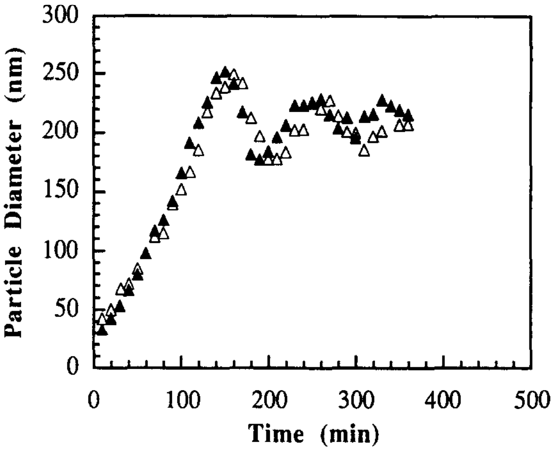

Figure 7 Time evolution of particle diameter for the replicate experiments carried out following the start-up procedure B: △, run B-1; ▲, run B-2

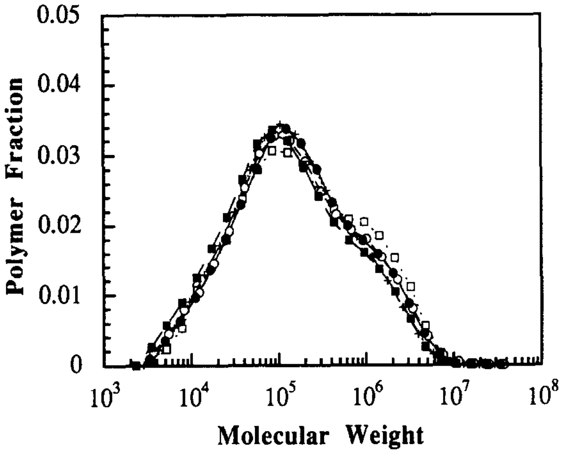

Figure 5 Time evolution of molecular weight distribution in the experiment A-2: □, $t = 30$ min; ○, $t = 60$ min; +, $t = 110$ min; ●, $t = 240$ min; ■, $t = 340$ min

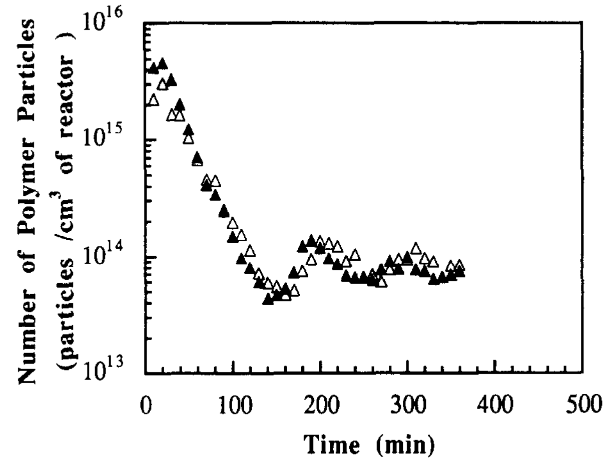

Figure 8 Time evolution of the number of polymer particles per unit volume of reactor for the replicate experiments carried out following the start-up procedure B: △, run B-1; ▲, run B-2

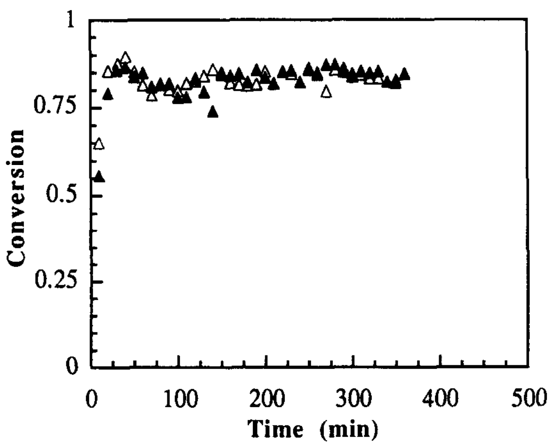

Figure 6 Time evolution of the gravimetric conversion for the replicate experiments carried out following the start-up procedure B: △, run B-1; ▲, run B-2

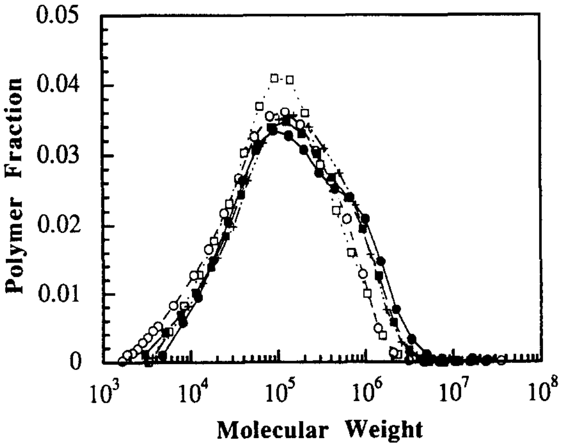

Figure 9 Time evolution of molecular weight distribution in the experiment B-1: □, $t = 20$ min; ○, $t = 100$ min; +, $t = 150$ min; ●, $t = 210$ min; ■, $t = 280$ min

sample shows a single peak whereas the *MWD*s of the other samples show extensive long branching. This difference might be due to the relative low conversion of the first sample, which reduced the extent of the long-chain branching reactions.

Runs B-1 and B-2 did not proceed smoothly, with a substantial increase of the reactor pressure being observed. This increase caused some problems in the stability of the feed flow rates. After some disturbances the reactor pressure could be kept at the desired value. The sudden increase of reactor pressure was due to an increase of the latex viscosity that resulted from the high number of polymer particles formed at the beginning of the process. The number of polymer particles in runs B-1 and B-2 was much higher than in the case of runs A, because of the large amounts of emulsifiers in the initial charge. Later, as the number of polymer particles in the reactor decreased, the viscosity of the latex decreased towards the steady-state value. On the other hand, except for a small overshoot of less than 2°C occurring during the first 30 min of the reaction, temperature could be controlled at the set point value (60°C).

Three experiments were carried out using the start-up strategy C, namely using an initial charge made of a pre-emulsion of the monomers in an aqueous solution of emulsifiers, protective colloid and $Na_2S_2O_5$. Different temperature profiles during the start-up were used. In run C-1, the reactor was initially heated to 60°C. This reaction could not be completed because after about one residence time, the viscosity of the latex increased sharply leading to a dangerous increase of the reactor pressure and a thermal runaway. In run C-2, the reactor was initially at room temperature and the thermal fluid was not circulating through the jacket. When the feed was started, a short inhibition period was observed. Later the polymerization started and the reaction temperature increased slowly until a stable temperature of 65°C was obtained. It has to be stressed that during this process thermal fluid was not circulated through the jacket. This is an autothermic behaviour similar to that found by Geddes[3]. After nine residence times the temperature control system was turned on and the reactor temperature was set to 60°C. In run C-3, a temperature profile starting at room temperature and reaching 60°C in 90 min was used.

Figure 10 presents the evolution of the gravimetric conversion in runs C-2 and C-3. The lower conversion showed at the beginning of the process by run C-2 compared with run C-3 was due to the slower temperature increase that occurred in run C-2. Nevertheless, the same steady-state conversion was reached in both runs.

Figures 11 and *12* present the time evolution of the particle diameter and number of polymer particles, respectively, for runs C-2 and C-3. Both reactions present similar evolutions of d_p and N_p, with a time lag due to the inhibition period observed in run C-2. *Figure 13* presents the evolution of the *MWD* in run C-3. It can be seen that the peak of high molecular weights was higher than that of the low molecular weights for the first sample, whereas the reverse was found for the other samples. The reason for this behaviour is that, owing to the temperature profile used, the reactor temperature when the first sample was collected was significantly lower than for the other samples.

Runs C-2 and C-3 were very difficult to control because of the sharp increase of the latex viscosity that led to a substantial increase of the reactor pressure and temperature. In these cases, the increase of the latex viscosity was not due to the large number of polymer particles but to the high volume fraction of the dispersed phase.

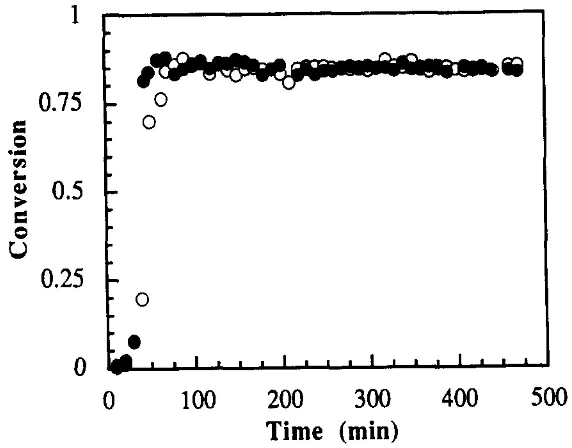

Figure 10 Time evolution of gravimetric conversion for the experiments carried out following strategy C: ○, run C-2; ●, run C-3

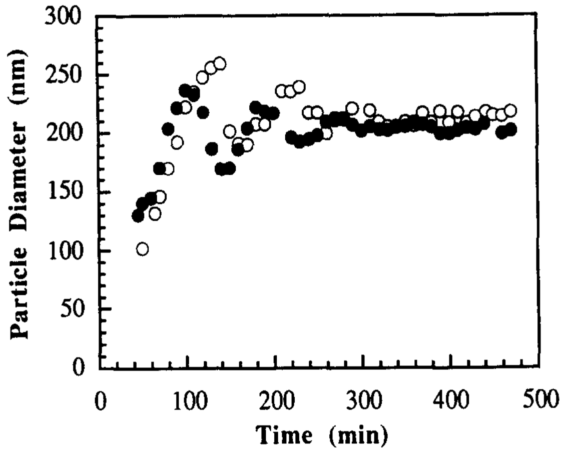

Figure 11 Time evolution of particle diameter for the experiments carried out following strategy C: ○, run C-2; ●, run C-3

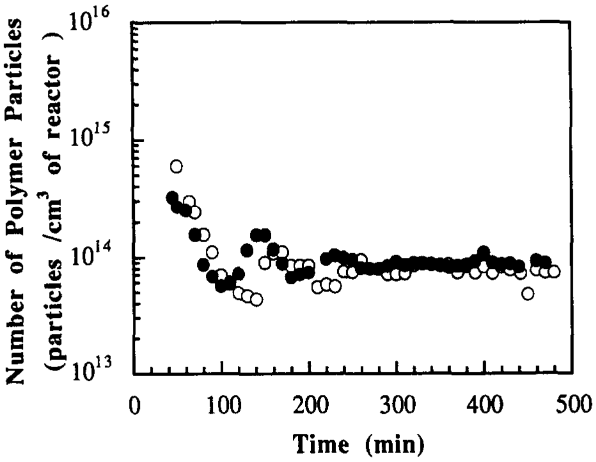

Figure 12 Time evolution of the number of polymer particles per unit volume of reactor for the experiments carried out following strategy C: ○, run C-2; ●, run C-3

Two reactions were carried out starting with the

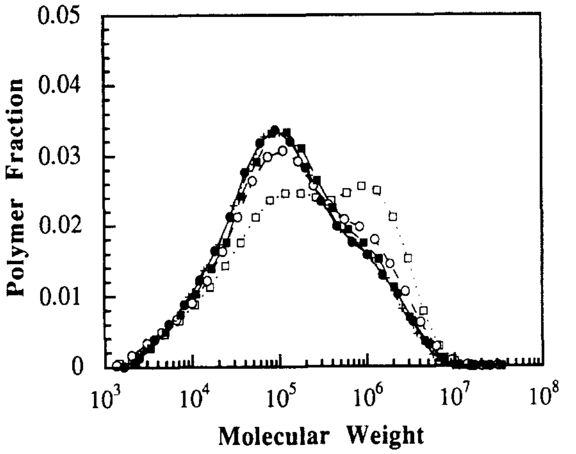

Figure 13 Time evolution of molecular weight distribution in the experiment C-3: □, $t = 30$ min, ○, $t = 70$ min; +, $= 100$ min; ●, $t = 180$ min; ■, $t = 300$ min

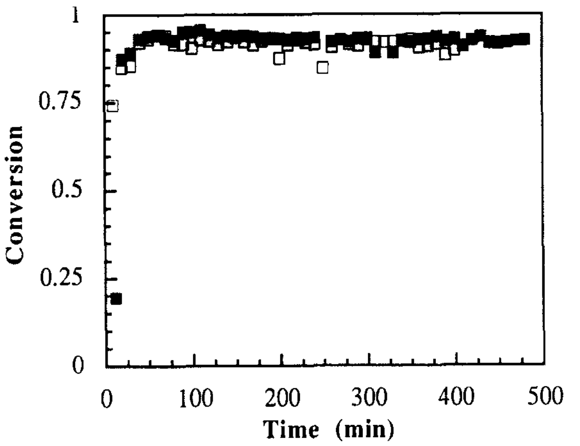

Figure 14 Time evolution of gravimetric conversion for the experiments carried out following strategy D: □, run D-1; ■, run D-2

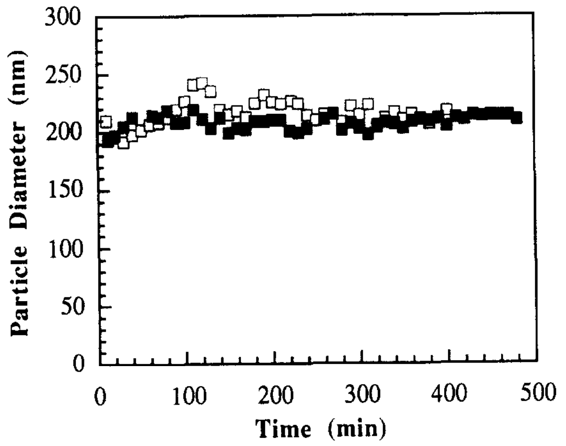

Figure 15 Time evolution of particle diameter for the experiments carried out following strategy D: □, run D-1; ■, run D-2

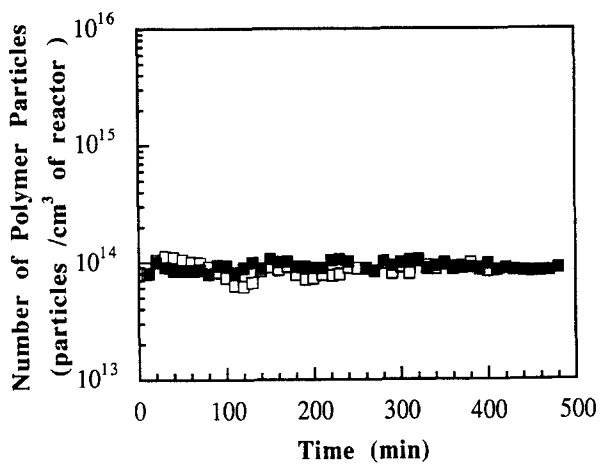

Figure 16 Time evolution of the number of polymer particles per unit volume of reactor for the experiments carried out following strategy D: □, run D-1; ■, run D-2

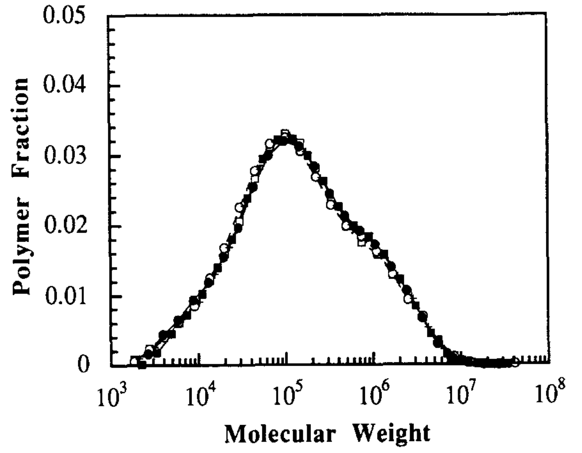

Figure 17 Time evolution of molecular weight distribution in the experiment D-1: □, $t = 30$ min; ○, $t = 110$ min; +, $t = 190$ min; ●, $t = 240$ min; ■, $t = 310$ min

reactor filled with a latex from a previous run. In the first (run D-1), the reactor was initially filled with a completely converted latex from run C-3. Run D-2 was carried out using an initial charge including a completely converted latex from a previous run (65 wt% of the reactor content) and a pre-emulsion of the monomers in an aqueous solution of emulsifiers, protective colloid and $Na_2S_2O_5$. This experiment was designed in an attempt to elucidate if the results obtained in series A were due to multiple steady states. *Figure 14* presents the evolution of the gravimetric conversion for runs D-1 and D-2. It can be seen that in both experiments the same steady-state conversion was reached. However, comparison of this value with those presented in *Figures 2, 6* and *10* shows that the steady-state conversion for runs D-1 and D-2 were significantly higher than for most of the other experiments, with the exception of run A-1. *Figures 15* and *16* present the evolution of the particle diameter and the number of polymer particles for runs D-1 and D-2. It can be seen that almost constant values of these variables were obtained throughout the process. The absence of oscillations can be explained by the fact that the initial conditions for d_p and N_p in this series were close to the steady-state conditions. In addition, the steady-state particle diameter and number of polymer particles were almost the same as in the other series. Therefore, there were no apparent reasons for the differences in conversion.

Figure 17 presents the evolution of the *MWD* in run

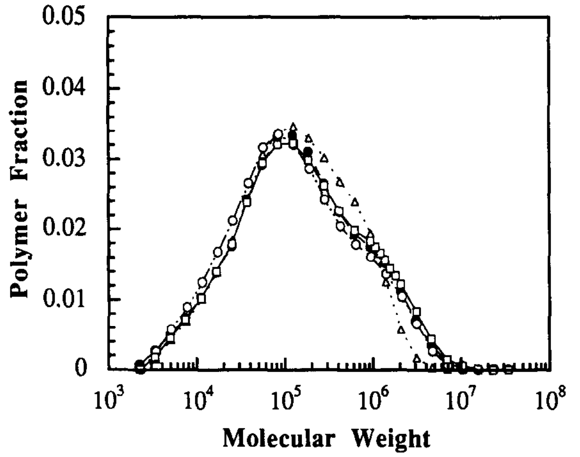

Figure 18 Comparison between the steady-state *MWD*s obtained by means of the different start-up methods. ○, method A (run A-2); △, method B (run B-1); ●, method C (run C-3); □, method D (run D-1)

Table 2 Steady-state results

Start-up method	Run	X	d_p (nm)	N_p (particles/cm^3 of reactor)
	A-1	0.92	220	10×10^{-13}
	A-2	0.80	185	11×10^{-13}
A	A-3	0.83	205	9×10^{-13}
	B-1	0.83	210	9×10^{-13}
B	B-2	0.84	220	8×10^{-13}
	C-1	–	–	–
	C-2	0.84	215	9×10^{-13}
C	C-3	0.85	205	9×10^{-13}
	D-1	0.92	215	9×10^{-13}
D	D-2	0.93	210	9×10^{-13}

D-1. It can be seen that the *MWD* remained almost constant during the whole process. Runs D-1 and D-2 proceeded smoothly without any significant variation in the process variables, namely the amount of out-of-specification product particularly in run D-1 was negligible.

Table 2 and *Figure 18* present a comparison between the steady-state values of the conversion, particle size, number of polymer particles and *MWD* obtained by means of the different start-up procedures. It can be seen that the steady-state results are independent of the start-up procedure.

CONCLUSIONS

In the foregoing, several start-up strategies for the 55 wt% solids content redox-initiated emulsion copolymerization of vinyl acetate and Veova 10 in a continuous loop reactor were considered. These strategies included different charges and temperature profiles. It was found that the best start-up procedure in terms of smoothness of the operation and amount of out-of-specification product was to start with the reactor filled with a latex from a previous run heated to the polymerization temperature (strategy D). A smooth operation was also obtained when the reactor was initially charged with water, strategy A, but the amount of out-of-specification product was larger than for strategy D. When the initial charge contained emulsifiers, protective colloid and $Na_2S_2O_5$ (strategy B), a sharp increase of the viscosity was observed that made it difficult to control the process. This viscosity increase was even higher when the initial charge also contained the monomers (strategy C). In this case, control of the process was very difficult and in one case impossible. The steady-state values of the conversion, particle size, number of polymer particles and molecular weight distributions were independent of the start-up procedure.

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