Continuous Tubular Reactors for Latex Production: Conventional Emulsion and Miniemulsion Polymerizations

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ABSTRACT: An investigation of the use of continuous tubular reactors for the production of polymeric latices is presented. In an initial step, it is demonstrated that tubular reactors can be used to produce latices by conventional emulsion polymerization at solids contents of up to 30% by volume. Under these conditions, the kinetics are identical to those found in batch reactors (as expected), and stable operating conditions are obtained, usually after one to two residence times. The use of a miniemulsion in a tubular reactor was also investigated, and it is demonstrated that in this case, solids contents of at least 60% can be obtained under stable operating conditions. It is therefore proposed that difficulties in operating tubular reactors with conventional emulsion polymerization arise essentially from the presence of monomer droplets in the early stages of the reaction. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2195–2207, 2004

Key words: emulsion polymerization; miniemulsion polymerization; tubular reactor; stabilization; particle formation

INTRODUCTION

Given the highly exothermic nature of free-radical polymerizations, combined with the fact that almost all process development studies are done in batch reactors, it is very tempting to use tubular reactors for latex production. Also, as has been shown in the literature,[1] the high surface to volume ratio makes them ideal for heat removal or temperature control in the event that one would seek to use well-controlled temperature profiles. In addition, the kinetics (conversion–time) should be the same in both closed-loop reactors and continuous linear flow tubular reactors. This facilitates scale-up to the extent that we should obtain the same product in a loop reactor as we obtain in a batch system used for process development [with the obvious exception of a linear flow reactor with a recycle stream, which is similar to a constant stirred tank reactor (CSTR)]. For these reasons, such reactors have been investigated by a number of authors in the past.

For example, Rollin et al.[2] investigated the use of a closed-loop reactor for the emulsion polymerization of styrene stabilized with sodium dodecylsulfate (SDS) and potassium persulfate (KPS) at a solids content of approximately 25% by weight (solids content refers to the ratio of the organic to aqueous phases in the reactor) in a stainless-steel tube. These authors studied the influence of the Reynolds number (Re) on the conversion and the polymerization rate and found that higher conversion and reaction rate could be obtained when the flow rate was in the transition from laminar to turbulent. However, they observed that the final conversion obtained in the tube was always below the final conversion obtained in the batch reactor using the same recipe for the same time frame. The inefficiency in turbulent flow with respect to batch operation was attributed to a decrease in the micelle concentration. The authors proposed that at the higher shear rates studied, the monomer droplets were smaller, and were thus able to adsorb more surfactant, which meant that there were fewer micelles than at low shear rates, and thus fewer polymer particles were produced. This would lead to an increase in the reaction time, but did not explain the incomplete conversion obtained at steady state. It seems more likely that the emulsions remained more stable at higher shear because the monomer droplets present during the initiation stage were smaller and therefore led to less coagulation.

The emulsion polymerization of vinyl acetate (VAc) in a closed-loop glass reactor was also studied by Bataille et al.[3] Based on previous runs in a stirred batch reactor, they used SDS concentrations of 2.7 and 4.0 times the cmc (critical micelle concentration) at a solids content on the order of 38%. The experiments conducted in the transition zone between the laminar and turbulent flow (Re 2100–3000), and led to very low final conversions (≤20%) for the two surfactant concentrations. The final conversion began to increase as Re increased, and a maximum conversion of 60%

was reached at Re = 6800. For Re values higher than this, the final conversion was once again lower (probably attributable to shear induced coagulation). In this study the authors attributed the higher conversions at higher Re to the fact that different nucleation mechanisms were important for vinyl acetate compared to styrene. Although not discussed by the authors, it is likely that the poor results in terms of conversion were attributed to the presence of monomer droplets at the solids content investigated in their experiments.

In a slightly different vein, Abad et al.[4] investigated the start-up conditions in a stainless-steel continuous-loop reactor for the emulsion copolymerization of vinyl esters. Tracer experiments allowed the authors to conclude that their loop reactor had a residence time distribution similar to that of CSTR. They found that start-up was most efficient with the reactor was initially charged with latex from a previous run and heated to the reaction temperature before injection of fresh monomer began.

The first use of continuous linear (i.e., no recycle stream) tubular reactors was reported in patents,[5,6] and it was shown that fouling and plugging were the main obstacles. Some of the earlier publications in the scientific literature focused on the effect of flow regime during the polymerization. Feldon et al.[7] presented the emulsion copolymerization of styrene–butadiene (25 : 75) in a stainless-steel reactor at 33% wt solids content under isothermal conditions at 50°C. The reactor operated under laminar flow for 45 days without problems of plugging (Re < 1000). However, these authors did not report conversion and particle size data. Others authors (e.g., Ghosh and Forsyth[8]) reported reactor plugging at high temperature and low surfactant concentrations for polystyrene under laminar flow. It was observed that the plugging could be reduced by intensely mixing the feed emulsion. Rollin et al.[9] used the same recipe used in a batch-loop reactor and investigated the polymerization of styrene at a solids content of 25% using SDS as the stabilizer and KPS as the initiator in a fluoropolymer tube arranged in four helical coils.[10] The final steady-state conversion remained below the final conversion in batch at lower Re and no plugging occurred in any of the runs.

One patent showed that the material type of the continuous tubular reactor influenced the degree of plugging.[11] It was found that the use of a polyolefin or fluoropolymer tube, compared to stainless-steel tube, significantly lowered the risk of plugging. Shoap and Poehlein[12] showed that complete conversion could be achieved when the residence time, level of mixing, and the temperature were well adjusted. They investigated the emulsion copolymerization of ethyl acrylate and methacrylic acid in two tubes of different diameters (3.1 and 4.7 mm ID) and found that the best results were obtained in the narrower tube, and that the final number of particles was similar to that obtained in a batch reactor. However, phase separation and plugging occurred for some runs at low flow rates, but when they increased the flow rate and added a narrow tube (3.1 mm ID, high Re) in the early stage of reaction, the results were similar to these obtained in the batch reactor. Paquet and Ray[13] compared the performance of a batch reactor, a CSTR, and a tubular reactor for the emulsion polymerization of MMA at a solids content of 30%. Based on previous studies[14,15] they used pulsed flow to avoid fouling and plugging. It was shown that the pulsed tubular reactor offered effectively the same results in terms of conversion and particle size as those of a batch reactor. In addition, these conclusions were obtained for the reactions carried out at surfactant concentrations below the cmc. This is a promising result, given that other authors[16,17] reported plugging and limiting conversion at low surfactant concentration.

Although not exhaustive, this discussion reveals two points about tubular reactors. First of all, when the tubes are ungarnished, or strictly constant flow rates are used, phase separation at low Re number can be a problem. This seemed to be more important at very low flow rates, or with solids contents above 30%. It is therefore difficult to conclude whether tubular reactors are interesting alternative batch processes. On the one hand, we have these problems of latex stability; on the other hand, it seems that linear reactors, especially under pulsed flow and/or garnished conditions, are promising alternatives for batch and semibatch process.

Miniemulsions differ from conventional emulsions in that the mechanism of particle formation is completely different. In this type of system, the particles are directly formed by polymerizing in the monomer droplets. These droplets are typically generated by adding a hydrophobic agent to the formulation, and intensely mixing the unreacted mixture of monomer, stabilizer, and hydrophobe. Recent reviews on this subject discuss particle formation and means of generating miniemulsions.[18,19]

In the area of miniemulsion polymerization in continuous tubular reactors, virtually no work seems to have been done. Samer and Schork[20] have begun to model miniemulsion polymerization in a CSTR based on some limited experimental data, but to the best of our knowledge, no systematic experimental study on the use of miniemulsions in a tubular reactor exists.

In this article we propose to investigate the feasibility of producing latices with moderate to high solids contents in a continuous tubular reactor. We will look at the results of different operating conditions, notably MMA homopolymerization and its copolymerization with BuA, stabilized with anionic and/or nonionic surfactants. We also briefly investigated the feasibility of making core–shell particles or at least making par-

TABLE I
Experimental Runs for Conventional Emulsion Polymerization[a]

Run	MMA (wt %/total mass)	Q (mL min^{-1})	MMA/BuA (50/50) (wt %/total mass)	SDS ($\times$ cmc)[b]	Triton X-405 ($\times$ cmc)[b]
B1	30	—	—	3.8	—
B2	—	—	20	3.8	—
B3	—	—	20	—	0.5
T1	30	6	—	3.8	—
T2	30	12	—	3.8	—
T3	30	15	—	3.8	—
T4	30	25	—	3.8	—
T5	30	28	—	3.8	—
T6	30	33	—	3.8	—
T7	—	6	20	3.8	—
T8	—	25	20	3.8	—
T9	—	5	20	—	0.5
T10	—	10	20	—	0.5
T11	—	12	20	—	0.5
T12	—	22	20	—	0.5

[a] Experimental conditions: in batch reactor stirring rate = 250 rpm, T = 70°C; in continuous tubular reactor the flow rate Q is varied, and T = 70°C.
[b] cmc, critical micelle concentration.

ticles with controlled morphology in such continuous process. Finally, we also look at the polymerization of a miniemulsion in the tubular reactor at high solids contents to propose alternatives to conventional emulsions.

EXPERIMENTAL

Experiments were performed in both tubular and batch reactors under similar conditions to compare the operability of the different experiments under similar operating conditions. The runs that we will present in the first section are summarized in Table I. Different types of stabilization were tested; we began with an anionic surfactant (SDS) at high concentration for MMA homopolymerization and MMA/BuA copolymerization. Afterward, a nonionic emulsifier (Triton X-405) was used at low concentration, to test the stability limits of the continuous reactor. All the runs were carried out at different flow rates to determine the influence of mixing on the conversion, average particle diameter (d_p), the width of the particle size distribution (PSD), and the number of particles per liter of latex (N_p). Particle sizes were measured using quasi-elastic light scattering at a fixed angle of 90° (Malvern Lo-C; Malvern Instruments, Lyon, France).

The experiments in the batch reactor were carried out in a 2-L glass vessel with an external jacket for heating and cooling. The emulsion was mixed with an anchor agitator at 250 rpm and water was passed through the external jacket at a constant temperature to maintain the reactor at 70°C. The monomers employed (MMA, BuA) were used as received; the surfactant SDS and Triton X-405 (70% in water solution)

were used without further purification. Potassium persulfate was used as initiator for all the following runs (0.1% wt/monomer). Deionized water was used throughout the work.

Before starting the reaction, water and surfactant were added to the reactor under low agitation, and the mixture was bubbled with nitrogen for 30 min, after which the monomer was added and the agitation rate increased. After the homogenization of the initial charge, the reactor was heated to the desired temperature. The reaction started with the initiator injection. A sampling valve located at the bottom of the reactor allowed us to take samples to follow the evolution of the conversion and particle size. Monomer conversion was determined by gravimetric measurements and particle size by quasi-elastic light scattering (QELS; Malvern Lo-C).

The tubular reactor used in this study is composed of a number of sections (1–3) of variable lengths made of Teflon tubes with an ID of 0.4 cm. Each reactor section was rolled into a helical coil of 16–24 cm in diameter, and each coil was submerged in a constant temperature bath. In the event that more than one coil was used, a sampling valve located between the two baths allowed us to withdraw samples at intermediate point. Samples were always collected at the outlet of the tube. A membrane pump ensured the circulation of fluid in the reactor and an electronic balance situated at the reactor outlet was used to verify the flow rate. One or two sections were used for the conventional emulsion study of homo- and copolymerization in the continuous tubular reactor (length depends on the residence time we need). Two sections were used for the sequential polymerization, and for the mini-

TABLE II
Recipe Used for the Miniemulsion Polymerization of Styrene in the CTR[a]

Run	Sty (wt %/total)	SMA (wt %/sty)	SDS (× cmc)	Triton (× cmc)	KPS (wt %/total)
TB1	35	2	0.4	2.3	0.26
TB2	45	2	0.7	4.4	0.26
TB3	60	2	1.4	4.4	0.43

[a] $T = 70°C$. SMA, stearyl methacrylate.

emulsion runs, the reactor was made up of three sections with a total length of 84 m (19.6 + 44.8 + 19.6 m) and a total volume of 1 L.

The continuous tubular reactor (CTR) was fed from a tank containing water, emulsifier, and monomer stirred with a magnetic stirrer at the ambient temperature. Dissolved oxygen was removed from the initial emulsion by bubbling nitrogen through it for 0.5 h before each run. The initial charge was maintained under nitrogen pressure throughout the reaction. The initiator solution, also previously stored under bubbling nitrogen, was added to the reservoir tank a few minutes before the reaction started. Gravimetric measurements on the remaining emulsion confirmed that no reaction occurred in the reservoir tank. The initial time of the reaction was taken when the initial emulsion passed at the entrance of the coil heated at 70°C. A 2-L polyethylene receptacle was used as the reservoir for the mixture at the outlet. Previous investigations in a batch reactor allowed us to select operating conditions that should be favorable for the CTR.[21] Note that no significant temperature gradients are expected in our system because of the small tube diameters used.[22] No temperature measurements were made inside the reactor, but it is reasonable to expect that the reactor remains isothermal under the isoperibolic conditions used here.

The miniemulsions were prepared following the same procedure as described by Ouzineb et al.[23] The sonification time was fixed at 6 min/L of miniemulsion, and the latices remained stable overnight (no change in d_p). Different solids contents for the styrene miniemulsion polymerization were carried out; therefore the surfactant concentrations were adapted to stabilize the higher number of droplets. The recipes employed are summarized in Table II . In the case of BMA miniemulsion polymerization with LPO as the initiator and costabilizer, respectively, the recipe employed was similar to that used for the run BO4. All the runs were carried under laminar flow regime, at $T = 70°C$. The tube was initially filled with water; the reactor was fed from a tank containing the monomer miniemulsion stirred with a magnetic stirrer at the ambient temperature. Dissolved oxygen was removed from the initial miniemulsion by bubbling nitrogen through it 0.5 h before each run. A 1- or 2-L polyeth-

ylene flask tank was used to hold the initial charge and was maintained under nitrogen pressure throughout the reaction. In the case of styrene miniemulsion, the initiator solution previously stored under bubbling nitrogen was added in the reservoir tank a few minutes before the reaction started. Gravimetric measurements on the remaining monomer miniemulsion confirmed that no reaction occurred in the reservoir tank for all the runs. The initial time of the reaction was taken when the initial miniemulsion passed at the entrance of the coil heated at 70°C. For the styrene miniemulsion polymerization the three helical coils were used (i.e., 84 m), whereas only the first two coils (i.e., 64.4 m) were used for the BMA miniemulsion polymerization.

Before performing reactions in the tubular reactor, we sought to characterize the flow regime in the tube by measuring residence time distribution.[24] The residence time distribution studied was performed using pulse inputs of 1 wt % KCl solution. The tube was initially filled with distilled water at $T = 25°C$ and a conductivity meters were placed at the entrance and the exit of the reactor. It was assumed that there was no time delay between the exit of the tube and the meter. For each flow rate the measurements were repeated twice at the inlet and outlet of the tube.

RESULTS AND DISCUSSION

Hydrodynamic conditions

Considering the range flow rates possible with our pump and the ID of the tube (0–33 mL min^{-1}) all the runs were carried out under laminar conditions (Re $\leq$ 200). Most previous studies in tubular reactors were done in the laminar flow regime, or in the transition between the laminar and the turbulent regimes[7,9,10,13] to avoid problems of plugging arising from shear-induced coagulation under turbulent conditions. On the other hand, in laminar flow, one of the main obstacles to good process operation is the lack of radial mixing, which can lead to droplet coalescence and phase separation. The importance of this will depend on the reaction rate and rate of particle nucleation. If high rates are used, it might be that the time required for droplets to coalesce is greater than the time that
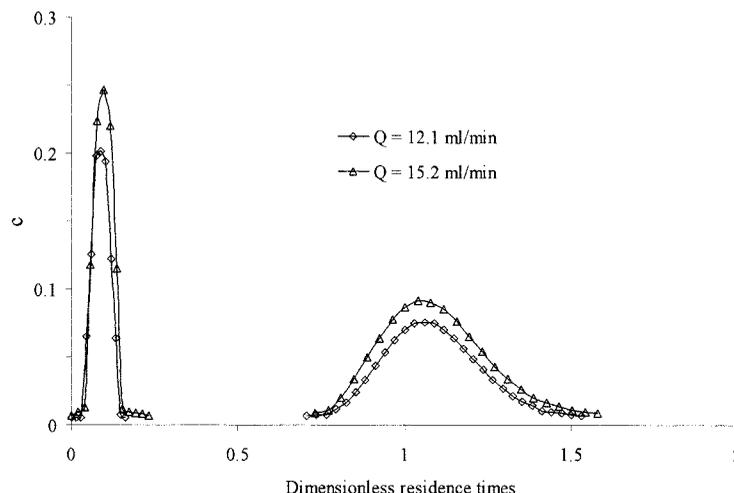
Figure 1 Responses to KCl injection (0.1 kmol m^{-3}) at two different flow rates, $T = 298$ K. The tube is initially filled with distilled water. c is the normalized concentration as a function of the dimensionless residence time (time divided by the residence time of a pure plug flow reactor).

droplets are actually present, whereas for lower rates, the opposite might be true.

Figure 1 shows typical experimental measurements obtained at both the entrance and the exit of the first coil of the reactor (total coil length = 19 m; injection port located at $Z_1 = 1.42$ m; total effective reactor length $Z_2 = 17.58$ m; total reactor volume = 220 mL). If we consider an isothermal tubular reactor with a Newtonian fluid (strictly speaking this is not the case because a latex is a non-Newtonian fluid; nevertheless, this approach allows us to demonstrate the approximate flow conditions more simply), the concentration profile of the inert species can be described by the dispersion model[24]:

$$\frac{\partial c}{\partial \theta} + \frac{\partial c}{\partial z} = \frac{1}{Pe} \frac{\partial^2 c}{\partial z^2} \qquad (1)$$

where c is the normalized tracer response to an ideal pulse input, here taken to be the measured conductivity at the outlet divided by the area under the conductivity versus time curve; $z = (ut + Z)/L$, where Z is the axial direction, L is the tube length, and u is the average axial velocity.

The Peclet number [Pe can be calculated from Pe = uL/D, where D is the axial dispersion coefficient] and effective average residence time τ ($\tau = L/u$ is the mean residence time and the dimensionless time $\theta = ut/L = t/\tau$) were calculated from the variance and mean of the experimental RTD curves for different flow rates using the method reported in Levenspiel.[24] According to this same reference, the analytical solution to eq. (1) is

$$c_\theta = \frac{1}{2\sqrt{\pi\theta(D/uL)}} \exp\left[-\frac{(1-\theta)^2}{4\theta(D/uL)}\right] \qquad (2)$$

The experimental data were used to fit the solution to eq. (2) by minimizing the function

$$E = \sum |C(\theta) - C_{exp}(\theta)|^2 \qquad (3)$$

The results of the data fitting are also summarized in Table III. These results show that we can reasonably conclude that there is axial dispersion for the entire range of flow rates used here. As the flow rate increases the axial dispersion increases.

Homopolymerization of mma with anionic surfactant

The results of a typical batch experiment for the homopolymerization of MMA are shown in Figure 2. The very short reaction time of 10 min needed to reach complete conversion suggests that such a reaction is a suitable candidate for a tubular reactor. A flow rate in the tube corresponding to a residence time of 8 to 10 min (20–30 mL min^{-1}) should therefore be sufficient to attain complete conversion.

The results of these runs are shown in Figure 3 and in Table IV. It may be observed that complete conversion was obtained for all flow rates except for the run T5 with a flow rate of 28 mL min^{-1}. In this case, the

TABLE III
The Peclet (Pe) Number at Different Flow Rates

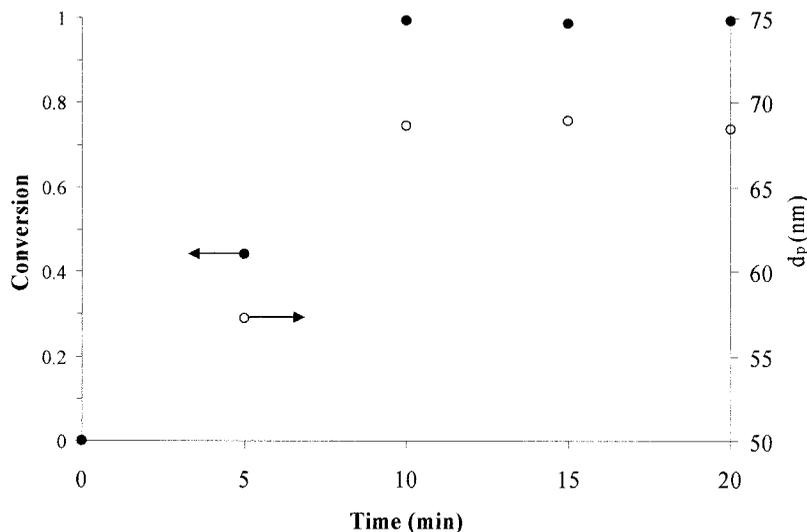| Q (mL/min^{-1})	Pe$_{theoretical}$	Pe$_{experimental}$	D (m^2 s^{-1})
7.8	100	80	2.2×10^{-3}
12.1	97	79	3.6×10^{-3}
15.2	80	69	5.7×10^{-3}

Figure 2 Evolution of the conversion (●) and average particle diameter (○) for the homopolymerization of MMA in a batch reactor with an SDS concentration of 3 times the critical micelle concentration (cmc), $T = 70°C$, $\omega = 250$ rpm.

final conversion was limited to about 50%, most likely because of a problem of mixing that was observed in the reservoir tank halfway through the experiment. All of the residence times used in this series of runs here are long enough that complete conversion should be observed at the outlet; with the exception of run T5, this occurs after a certain time. It is important to note that the tube is initially filled with water, which means that only water passes through the tube outlet for at least one residence time. It is interesting to note that the number of residence times necessary to reach steady state increased with the flow rate, as did the level of dispersion (see Table III). The reason for this is

not entirely clear, but it is possible that because the absolute time needed to achieve steady is more or less constant, then there is perhaps a phenomenon related to the development of flow in the tube, or to the time needed to start nucleating particles at a steady rate in the tube inlet. It might be possible to improve on this by modifying the start-up conditions. Araujo et al.[25] and Abad et al.[1] studied different start-up strategies for emulsion copolymerization in a continuous-loop reactor, and investigated (among other points) the optimal procedure in terms of smoothness of the operation and minimum production of off-specification materials. They found that the best procedure was to
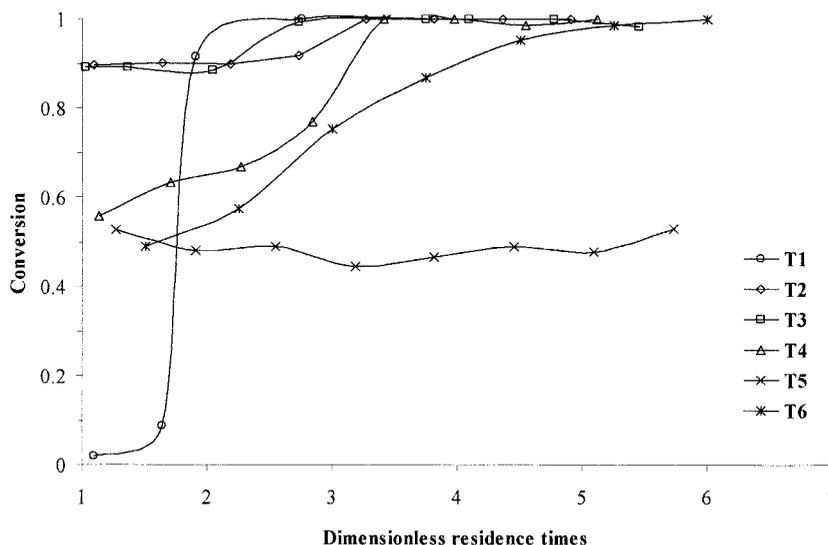

Figure 3 Evolution of conversion versus the number of residence time for the MMA homopolymerization at 3.8 × cmc in SDS, $T = 70°C$. The reactor is initially filled with distilled water at 70°C. Flow rate (mL min^{-1}): ○ 6 (T1); ◇ 12 (T2); □ 15 (T3); △ 22 (T4); × 25 (T5); ✳ 33 (T6).

TABLE IV
Average Residence Time (t_0), Final Particle Size at Steady State, and Polydispersity Coefficient (PI) of the Final Latices Obtained in Continuous Tubular Reactor and in the Batch Reactor at Complete Conversion ($X = 1$) for MMA Homopolymerization

Run	$t_{X=1}$ (min)	$d_{p\,X=1}$ (nm)	$PI_{X=1}$	t_0 (min)	$d_{p\,\text{steady state}}$ (nm)	$PI_{\text{steady state}}$
B1	8	72	0.03	—	—	—
T1	—	—	—	37	112	0.113
T2	—	—	—	18	71	0.09
T3	—	—	—	15	76	0.05
T4	—	—	—	9	69	0.08
T5	—	—	—	8	65	0.04
T6	—	—	—	7	67	0.03

start with the reactor filled with latex from a previous run heated to the polymerization temperature. This strategy was not used in the current study because the major point of interest was to see whether we could obtain steady-state conditions, rather than trying to optimize them.

It may also be observed that average final particle diameter and polydispersity coefficient are essentially the same in the batch reactor and in the CTR (once steady state is attained). Note that this in not true for run T1; however, the average residence time of 37 min is significantly higher than the time needed for complete conversion in batch, and it is entirely possible that limited amounts of coalescence occurred in the tube once the reaction was complete. It is also possible that at such low flow rates (and Re), the mixing was so poor that particle nucleation in the early stages of the tube was adversely affected by large droplet size and/or slight destabilization of the latex because of the presence of large droplets. However, it is important to note that no problems of plugging or fouling

were observed during any of these six runs in the CTR. This suggests that because no coagulum formation was observed in T1, it is more likely that the difference between the PSD obtained in that run, and those obtained in the others is attributable to mass transfer limitations in the nucleation stage because the surface area available from monomer transfer from the droplets will be very low. Thus despite the fact the MMA is easily transferred through the aqueous phase, it is possible that the mass transfer exchange area is too low in T1.

Another important point to discuss here is the solids content (i.e., ratio of organic to aqueous phases) used in this study. The results presented above are for solids contents of 30% by mass (or volume). Other runs were carried solids contents between 30 and 50% with the same concentration of surfactant; however, the results of these runs are not reported here because none of them was successful. Extremely low conversions were obtained after several residence times in some cases, whereas in others the loss of stability of
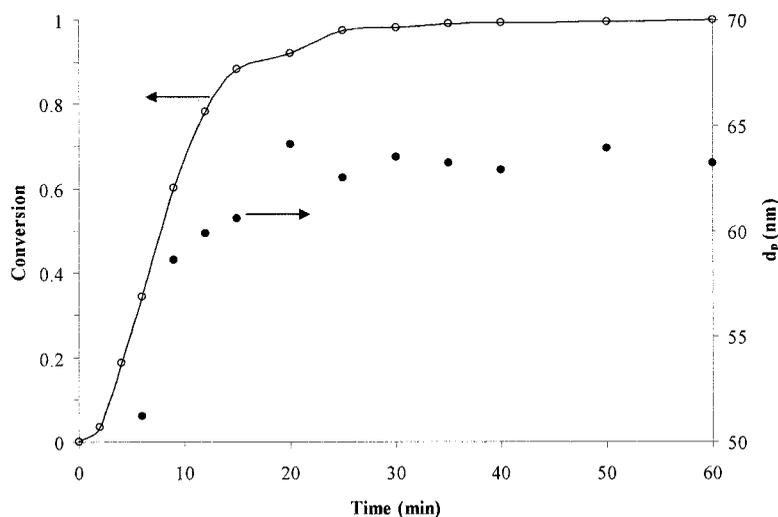

Figure 4 Evolution of the conversion and average particle diameter obtained for the batch copolymerization BuA/MMA (50/50) at 3.8 $\times$ cmc in SDS, $T = 70°C$, $\omega = 250$ rpm.
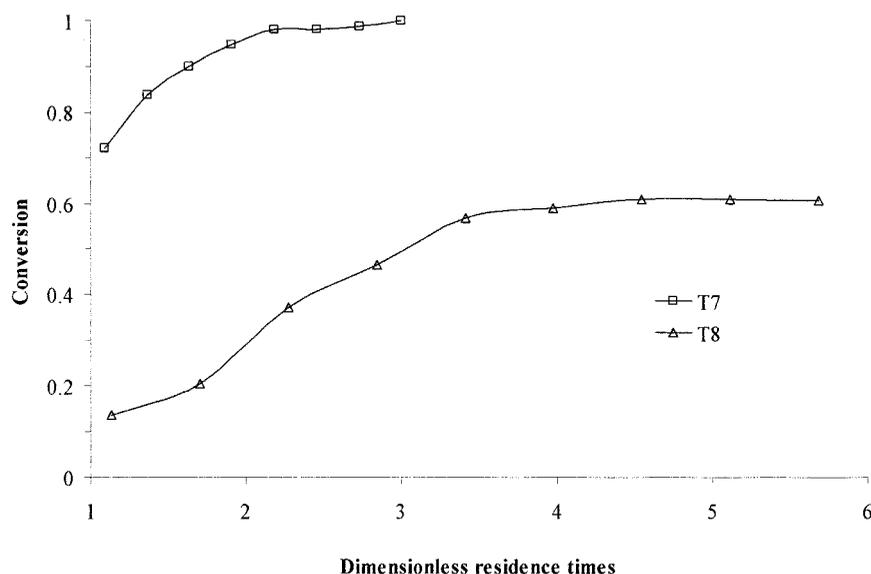
Figure 5 Evolution of conversion versus the number of residence time for the MMA/BuA copolymerization at 3.8 × cmc in SDS, $T = 70°C$. The reactor is initially filled with distilled water at 70°C. Flow rate (mL min^{-1}): □ 6 (T7); ○ 25 (T8).

the latex was so significant that the tube became plugged after only a short while. For this reason, the remainder of the runs presented for conventional emulsion polymerization were limited to solids contents of 20–30%.

Copolymerizations of MMA and BuA

Mixtures of MMA and BuA (50 : 50 w/w), stabilized with SDS or with Triton X-405, were polymerized in conventional emulsion in batch and tubular reactors. The experiments where SDS was used were run at 3.8 times the cmc, whereas the experiments with Triton X-405 were run under the cmc to investigate the influence of the rate of nucleation on the final results.

As we can see from Figure 4, the final conversion and particle size are reached in less than 30 min in a batch reactor. Once again, an average residence of the same order should allow us to obtain complete conversion at the outlet of the tube. As shown in Figure 5 and Table V, steady states are obtained after two to three residence times for a flow rate of 6 mL min^{-1}, whereas at 25 mL min^{-1} it appears that a steady state has been reached by six residence times. As was the case with MMA homopolymerizations, the number of residence times necessary to reach steady state increases with the flow rate. A flow rate of 6 mL min^{-1} corresponds to an average residence time of 37 min, which should be enough to attain complete conversion in the CTR, whereas at 25 mL min^{-1}, which corresponds to an average residence time of 9 min, a maximum conversion of 80% is obtained under steady conditions. This corresponds well enough with the results obtained in the batch reactor after approxi-

mately the same reaction time. Furthermore, in both cases (T7 and T8), the average particle sizes measured in the outlet streams are the same as those found in batch for similar reaction times. These results suggest that, under the conditions investigated here, tubular reactors can yield the same results as in batch, and that reaction time measured in batch is an excellent indication of the order of magnitude of the average residence time necessary to reach complete conversion in the CTR. Finally, as we mentioned above for the MMA homopolymerizations, increasing the solids content to above 30% (w/w) resulted in fatal phase separation problems, loss of stability, and plugging of the reactor.

In the preceding runs, high anionic emulsifier concentrations were employed. In the flow conditions chosen and emulsifier concentrations used, SDS offered adequate levels of stabilization and allowed us to produce particles with diameters that were, for the most part, independent of the flow rate. In this section

TABLE V
Total Reaction Times to Reach Steady State (t'_0) with the Corresponding Conversion (X), Particle Size (d_p), and Polydispersity Index (PI) at Different Re Number for Runs Performed in the Tube and Those Obtained in Batch, for the MMA/BuA Copolymerization at 3.8 × cmc in SDS, $T = 70°C$

Run	Residence time (min)	Final conversion (%)	$d_{p\,final}$ (nm)	PI
B2	30	100	70	0.05
T7	37	100	66	0.05
T8	9	70	60	0.07

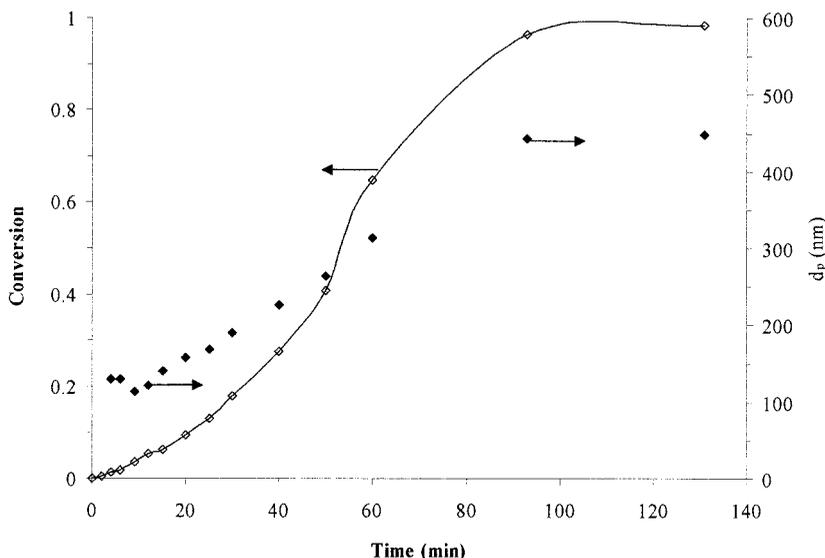**Figure 6** Time evolution of conversion and particle size for the MMA/BuA batch comopolymerization at 0.5 × cmc in Triton X-405, $T = 70°C$, $\omega = 250$ rpm.

we will change the surfactant type replacing SDS with Triton X-405, a nonionic surfactant. Ouzineb et al.[21] showed that for this system, nonionic surfactants produce significantly fewer particles for the same level of surfactant concentrations. In addition, it was shown that the stabilization and nucleation mechanisms are quite different. For these reasons, it was decided to use Triton X-405 at levels below the cmc to induce very different nucleation conditions to investigate whether the tubular reactor will function well when the nucleation conditions were different.

In this section, copolymerizations of MMA/BuA (50/50) were carried out in the tubular reactor at different flow rates with Triton X-405 as the emulsifier (cf. Table I). With a concentration well below the cmc, the reaction time in the batch reactor is substantially increased, which is why we decided to add a second coil for the tubular reactor to obtain acceptable conversion in the laminar flow regime. The total reactive volume is then 440 mL, and the residence times are therefore longer at similar flow rates.

As shown in Figure 6, the batch reaction is complete after 90 min, and a final particle size of 450 nm is obtained under these conditions. In this reaction, the process of particle formation is very slow, and the particle size increases throughout the entire reaction.
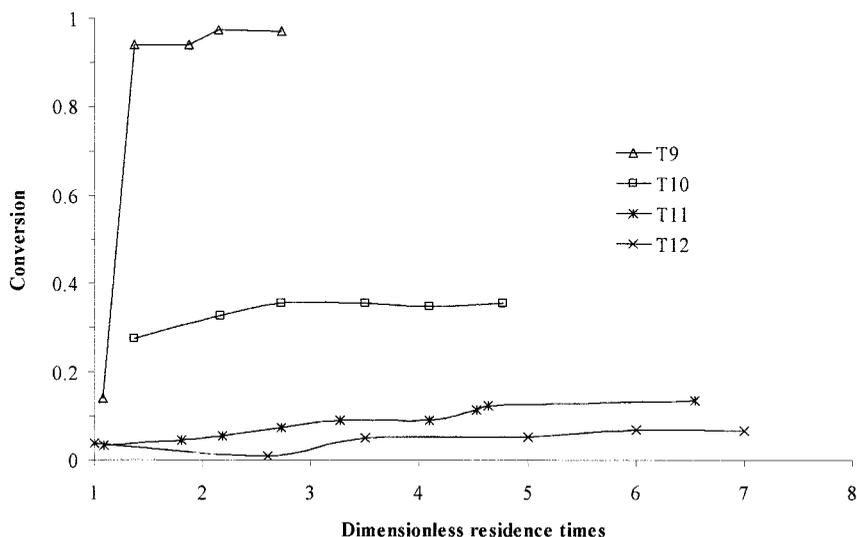

Figure 7 Evolution of conversion versus the number of residence time for the MMA/BuA copolymerization at 0.5 × cmc in Triton X-405, $T = 70°C$. The reactor is initially filled with distilled water at 70°C. Flow rate (mL min^{-1}): △ 5 (T9); □ 10 (T10); * 12 (T11); × 22 (T12).

TABLE VI
Total Reaction Times or Residence Times with the Corresponding Conversion,
Particle Size, and Polydispersity Index at Different Residence Times for Runs
Performed in the Tube and Those Obtained in Batch at the Corresponding Reaction
Time for MMA/BuA Copolymerization at 0.5 × cmc in Triton, $T = 70°C$

Run	Residence time (min)	$X_{\text{steady state}}$	$X_{\text{final batch}}$	$d_{p\ \text{steady state}}$ (nm)	$d_{p\ \text{final batch}}$ (nm)	PI
T9	88	0.97	—	445	—	0.05
T10	44	0.35	—	268	—	0.05
T11	37	0.13	—	220	—	0.06
T12	20	0.06	—	182	—	0.04
B3 ($t = 88$ min)	—	—	1	—	449	0.03
B3 ($t = 44$ min)	—	—	0.37	—	258	0.05
B3 ($t = 37$ min)	—	—	0.26	—	208	0.06
B3 ($t = 20$ min)	—	—	0.09	—	158	0.06

Once again, different flow rates were investigated for the CTR. As shown in Figure 7, complete conversion was obtained only at the lowest flow rate, which corresponds to an average residence time of 88 min. As expected from an analysis of the batch results, incomplete conversions are obtained at higher flow rates. However, as shown in Table VI, the steady state results obtained at shorter residence times correspond well with the results in batch at similar reaction times. Not only is the conversion very close in all cases, but the average particle size and the polydispersity coefficient are also in good agreement in all runs.

These results show that even reactions with long nucleation periods can be carried out successfully in the continuous tubular reactor under laminar flow conditions when sufficient residence times are used and when the solids content remains below 20–30 wt %. From the three preceding examples (MMA homopolymerization, and MMA–BuA copolymerization with different stabilization systems), it can be seen that by varying the surfactant type and the concentration, the particle size can be varied between 60 and 450 nm, and that results from the batch reactor can be directly transposed to a CTR. Problems with solids content remain, at least under the laminar flow conditions used here. However, given the results of the previously cited studies, run on different monomers and with different stabilization systems, it does not seem likely that significant improvements can be obtained by increasing the flow rates. It thus appears that the real problem is linked to the presence of monomer droplets in the dispersion. These droplets are typically much bigger than the polymer particles, on the order of several microns, or even tens of microns if the flow conditions are not too severe. On the other hand, Schneider et al.[26] showed that the distance between particles is typically on the order of tens or hundreds of nanometers once the solids content is much above 10%. Thus it is clear that as the solids content increases, the distance between objects decreases, and the interaction between particles and monomer droplets will be important.

Different ways of overcoming this problem can be proposed. It might be possible to perform the nucleation stage in a stirred tank prepolymerization reactor, and then use the tube as a finishing reactor. One could also propose performing particle nucleation in the early sections of the tube, and then concentrating the latex downstream. Either solution would require that side feeds be used to add monomer at different positions in the reactor at levels low enough to avoid droplet formation. A third way to avoid this problem would be to begin the polymerization with a miniemulsion. In this manner the only "droplets" present in the reactor would be the small structures of a size to be polymerized (<500 nm).

Before going on to explore the last solution, we will demonstrate the feasibility of using side feeds in the tubular reactor to control particle structure and to increase the solids content in conventional emulsion polymerization. The previous experiments provided us enough information about the hydrodynamic conditions in the reactor used here to attain complete conversion at the outlet of the tubular reactor. Using the results obtained in the previous sections, we attempted to continuously produce a layered, or inverse core–shell BuA–MMA copolymer in a reactor containing two coils. The first coil was used to produce the PMMA homopolymer particles that will form the basis for the core–shell, and BuA was injected through

TABLE VII
Particle Size, Polydispersity Index (PI), Number of
Particles per Liter of Emulsion, and Final Surface
Coverage (SC) Obtained at Steady State at Outlet of the
First Coil and at Outlet of the Second Coil After the
BuA Addition

Steady state	d_p (nm)	PI	N_p (L^{-1})	SC (%)
Outlet of the first coil (PMMA)	73.3	0.04	1.10^{18}	15
Outlet of the second coil (copolymer of BuA/MMA)	102.3	0.04	7.10^{17}	9

TABLE VIII
Glass-Transition Temperatures Obtained at Steady State at Outlet of the First Coil and at Outlet of the Second Coil after the BuA Addition

	T_{g1} (°C)	T_{g2} (°C)
Outlet of the first coil steady state	—	102
Outlet of the second coil steady state	-25	105
Literature PMMA[27]	—	100
Literature PBuA[13]	-50	—

the sample valve located between the two (equivolumetric) coils. The final latex was analyzed by DSC and transmission electron microscopy (TEM) to elucidate the resulting particle morphology.

The goal here is therefore to nucleate a fixed number of particles in the first part of the tube, and then to avoid changing the number of particles when the second monomer is added. The experiments were carried out in a tubular reactor made of two coils, each with a volume of 220 mL. The flow rates were chosen in such a way that the residence time remained sufficiently long in each section to attain close to total conversion. The same feed conditions as used in run T4 (Table I) were used in the first coil (i.e., a solids content of 30%). Once the PMMA reaction was at steady state, pure BuA was fed through the sample valve at a flow rate of 8 mL min^{-1}, which means that the solids content was brought to a fraction over 45% at this point. The reaction was then followed by collecting samples at the end of the second coil. Under these conditions, we had an average residence time in the second coil of 7 min and a total average residence of 15 min. The conversion and particle size evolution versus the average number of residence time (t/t_0) at the outlet of

the reactor shows that steady state was obtained after three residence times. It is important to note that at the point where BuA was added at the entrance to the second coil, the conversion out of the first coil was greater than 96%.

As shown in Table VII, the average particle diameter increased between the end of the first coil and at the end of the reactor. Although the number of particles decreased slightly [the ratio N_p(outlet)/N_p(first-coil) = 0.7], a narrow PSD was nevertheless obtained, and no problems of flocculation, fouling, or plugging were observed. These results indicate that negligible renucleation occurred, and that some particles, probably the smaller ones, underwent controlled flocculation onto the larger ones. This is not an unreasonable conclusion because, as shown in the same table, the fractional surface coverage of the latex was fairly low at the end of the first section (15% of the surface covered by surfactant) and slightly lower at the end of the reactor (9%).

The DSC measurements of the final latex are summarized in Table VIII, and show two distinct glass-transition temperatures (T_g) at the outlet of the CTR. The lower T_g clearly corresponds to a copolymer extremely rich in PBuA. Consider the well-known Fox equation

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (4)$$

where w_1 and w_2 are the weight fractions of polymers 1 and 2, respectively; and T_{g1} and T_{g2} are the glass-transition temperatures of the same polymers. Fitting the data in Table VIII with this equation leads us to the conclusion that the composition of the copolymer with the T_g of -25°C contains approximately 95% (w/w)
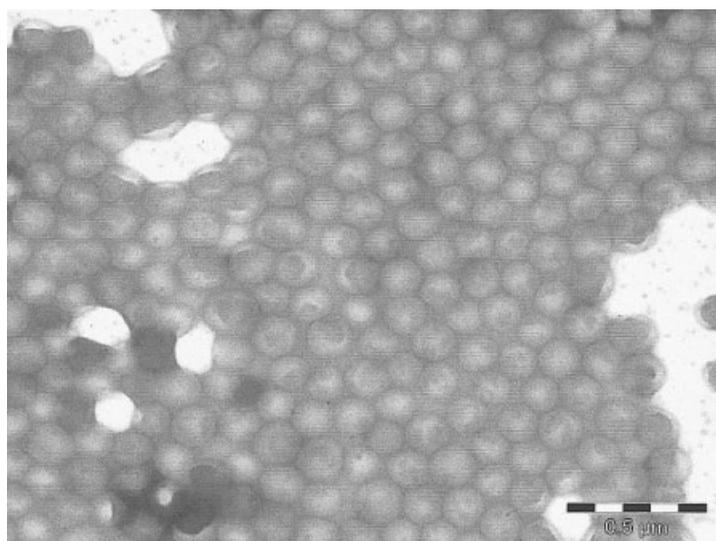

Figure 8 Microscopy image of the final core–shell latex obtained by TEM.

BuA. The high-temperature peak clearly corresponds to a PMMA homopolymer. Although it is clear that the Fox equation is not exact, this analysis corresponds well to what we expect to find in the absence of particle renucleation. The low-temperature peak corresponds to the product formed in the second coil, where there is a trace of MMA left in the original seed (4–5% under steady-state conditions).

It is interesting to consider the TEM image shown in Figure 8. This image clearly shows distinct particles that have not formed a film. It can therefore be concluded that the BuA does not remain on the surface of the particles, but rather that it migrates (or at the PBuA migrates) toward the interior of the particle, leaving behind a PMMA-rich shell. Given the relatively high hydrophobicity of BuA and its homopolymer with respect to MMA and its homopolymer, this scenario seems likely to occur. It is possible that these results (two T_g values) could be explained by the presence of PMMA particles and a distinct population of BuA/MMA copolymer particles. However, this situation seems quite unlikely because the PMMA particles would have to be nucleated in the absence of BuA, which could happen only at the end of the second coil, and there is no reason for this to happen. In addition the particle size increased between the end of the first coil and the outlet of the tube and the number of particles decreased slightly, which indicates that particles coalesced rather than nucleated.

The main challenge in such a process is to adjust the flow rate of BuA to avoid the accumulation of BuA in the water phase and the formation of monomer droplets in the tube. The total flow rate (i.e., flow rate of PMMA emulsion plus the flow rate of BuA) must also be well adjusted to ensure that it is not added to the reactor faster than it can be transported through the aqueous phase to the growing particles.

Miniemulsion polymerization in the tubular reactor

As mentioned above, most studies with tubular reactors seem to have been done on conventional emulsion polymerizations. As we just saw, the main difficulties in doing this reaction in the tubular reactor are the related problems of fouling and demixing, most likely associated with the presence of monomer droplets in concentrated systems. However, to the best of our knowledge no studies on miniemulsions have been performed in tubular reactors. The objective of the last section of this article is to demonstrate that tubular reactors can be used to generate moderately high solids content latices by miniemulsion polymerization, and that it is possible to obtain good control over the size and the number of particles in the reactor.

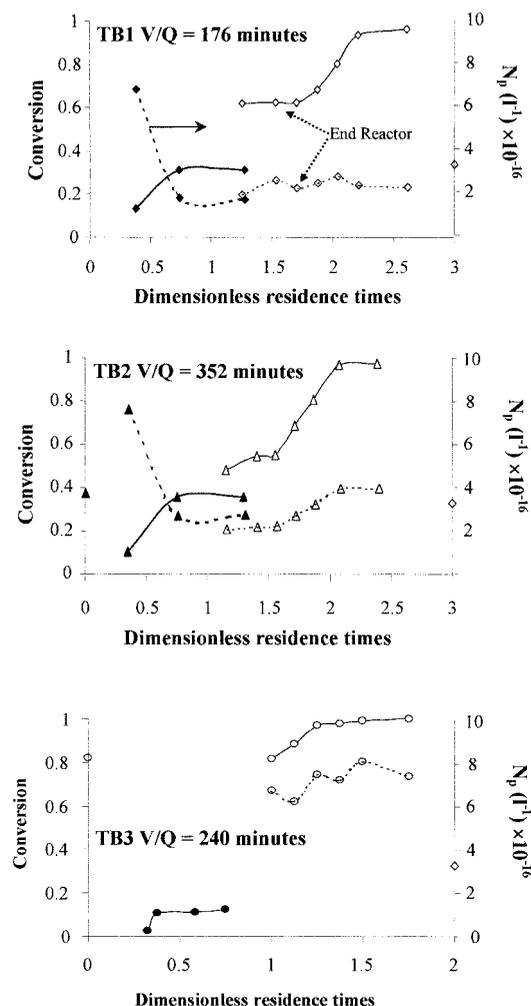As we can see in Figure 9, stable and complete conversion was obtained at the outlet of the tube after

Figure 9 Time evolution of conversion and particle number at the end of the first coil and at the outlet of the tube for the miniemulsion experiments. Dashed lines correspond to the number of particles per liter, and solid curves to the conversion. Filled symbols are measurements taken at the outlet of the first section, and open symbols for values measured at the outlet of the entire reactor (both sections).

two residence times. The laminar flow regime produced a sufficient level of mixing to allow droplet nucleation, polymerization all along the tube, and prevention of coalescence. The conversions measured at the outlet of the first section were less than 100%, as expected, but also reached constant values, showing that steady-state conditions were obtained throughout the reactor. By adjusting the average residence time, these stable conditions were obtained at different solids content (35–60 wt %). In addition, as may be seen in Table IX, the ratio between the initial number of droplets and the final number of particles is close to 1. A constant number of particles was obtained at the outlet of the tube.

It should be noted that in run TB3, where the solids content was on the order of 60% by weight, a significant increase in viscosity (>700 mPa s^{-1} at 20 s^{-1}) was

TABLE IX
Some Results for the Miniemulsion Polymerization of Styrene in the Continuous Tubular Reactor

Run	$N_{m,i}/N_{p,f}$	d_m (nm)	$PI_{initial}$	$d_{p\,final}$	PI_{final}
TB1	1.1	273	0.12	275	0.09
TB2	0.9	284	0.15	277	0.09
TB3	1.2	209	0.20	235	0.08

observed during the polymerization, and it was no longer possible to overcome the pressure drop induced by this change with the pump available for the study. Note that this viscosity is not particularly high; however, it was high enough to pose operability problems with the pump at hand. Finally, it is interesting to note that one does not need to significantly alter the residence time if the solids content increases.

CONCLUSIONS

MMA homopolymers and copolymers of BuA and MMA were made in a continuous tubular reactor under different operating conditions. Preliminary experiments in a batch reactor made it possible to select the adequate average residence time for the continuous process and to compare these two processes.

In the experiments in the CTR, no limiting conversion were obtained when the average residence time was greater than or equal to the total reaction time required in batch to achieve complete conversion. No problems of plugging occurred, even at low surfactant concentration for the copolymerization of BuA/MMA with Triton as emulsifier and when the solids content remained below 30%. Steady state was achieved within two to four residence times. No oscillatory behavior was observed, and once established, the exit conversion remained constant. In all cases the steady-state conversions were similar to the equivalent batch conversions, and conversions less than 100% could be obtained by reducing the average residence time.

Problems of solids contents over 30% were overcome by using a side feed to add monomer at high conversions. This technique was also used to control the final structure of the copolymer particles. This was demonstrated by making BuA/MMA core–shell co-

polymers that contained PMMA homopolymer and a copolymer containing more than 95% of PBuA. Finally, it was demonstrated that it is possible to make latices with a solids content of at least 60% in the continuous tubular reactor, and that under a laminar flow regime no problems of plugging or phase separation occurred.

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