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Comparison between conventional emulsion and miniemulsion polymerization of vinyl acetate in a continuous stirred tank reactor

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Abstract

The conventional emulsion and miniemulsion polymerization of vinyl acetate in a continuous stirred tank reactor (CSTR) were studied in an attempt to demonstrate the feasibility of miniemulsion polymerization as a strategy to eliminate the oscillatory behaviour of CSTR reactors, even in very unfavourable conditions. Reactions were carried out under a wide range of operating conditions. No oscillations in the time evolution of the conversion and particle number were observed in any of the miniemulsion polymerizations, while the opposite was found in most of the conventional emulsion polymerizations. Different dependencies of the emulsifier and initiator concentrations on the reaction rate and particle number were obtained for both emulsion and miniemulsion polymerizations, as a consequence of the different nucleation mechanisms. Further, almost the same average molecular weight was obtained for the emulsions and miniemulsions carried out under similar experimental conditions. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion; Miniemulsion; Vinyl acetate

1. Introduction

In spite of the many advantages of continuous stirred tank reactors (CSTR), complex dynamics, essentially oscillation mechanisms and multiple steady states, have restricted their commercial use. The oscillations produce heterogeneous polymer and make production control difficult. An increase in the polymer concentration can cause an increase in the molecular weight and branching of the polymer, and create problems in the processing. Further, the sudden decrease in surfactant concentration can produce coagulation of the latex. In addition, the new nucleations create a large number of small particles increasing the viscosity of the system that can originate agitation and heat transfer problems.

The oscillatory behaviour arises as a result of the role of the surfactant in particle nucleation. At the beginning of the process, a large number of small polymer particles are formed, their number being controlled by the amount of emulsifier available in the system. As the polymer particles grow by polymerization, the free emulsifier concentration falls, depleting the aqueous phase of the emulsifier, as a result of additional surfactant being adsorbed onto the new polymer surface. Therefore, new particles are not formed and, as particles are continuously washed out from the reactor, the number of particles decreases. After some time, this process counteracts the increase in size of the particles and the amount of emulsifier increases, allowing nucleation of new particles. The cycle then repeats. This phenomenon is more acute for low emulsifier concentration and for polymerizing systems in which the volumetric growth rate of the polymer particle is strongly non-linear with particle diameter (usually systems with high radical desorption rates).

Most of the techniques for achieving steady state operation in a CSTR described in the literature proposed the elimination of the nucleation step in a CSTR. Berens [1] used a particle seed in the feed stream to a CSTR with PVC emulsion polymerization. Omi et al. [2,3] proposed the use of a tubular reactor upstream of the CSTR to eliminate the conversion instabilities. Further, the number of polymer particles produced could be maximized if the operating conditions were optimal [4]. Pollock et al. [5] suggested a newly designed reactor configuration in which a very small initial CSTR was added, where all the generation of particles were accomplished. These processes however, complicate the design and increase the cost.

The oscillatory behaviour could be avoided by modifying the nucleation mechanism. Miniemulsion and conventional emulsion polymerizations have different nucleation mechanisms. The main difference is that in miniemulsion

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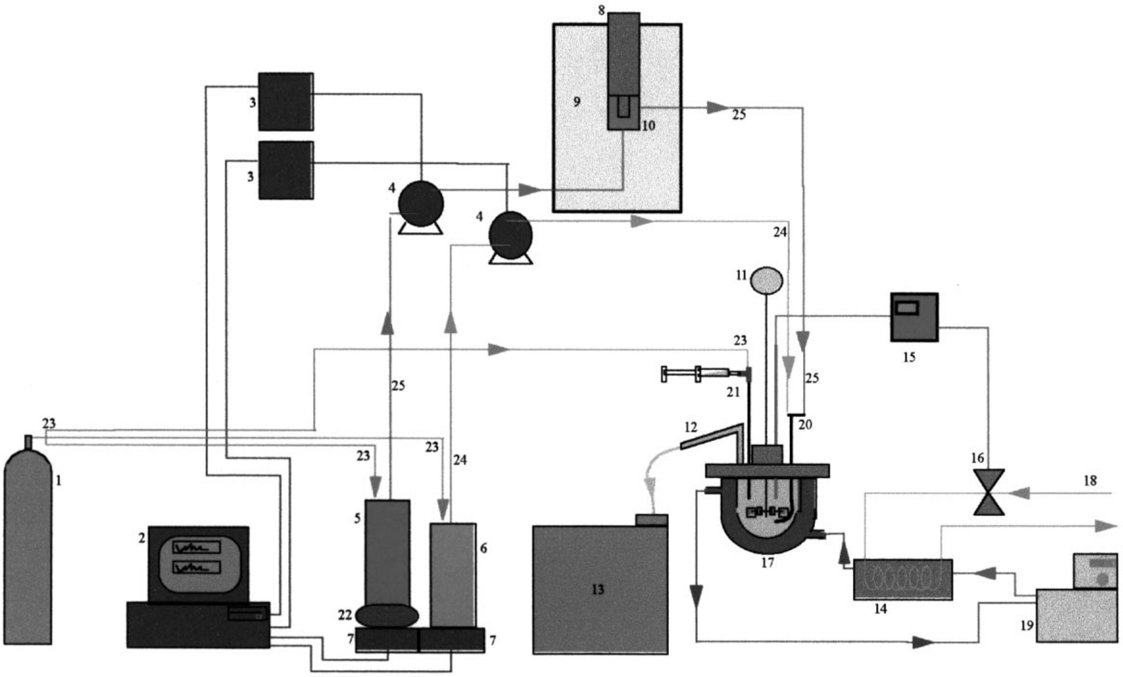

Fig. 1. The CSTR system. 1, Nitrogen; 2, Computer; 3, Control of the pumps; 4, Pumps; 5, Preemulsion; 6, Initiator solution; 7, Balances; 8, Sonicator; 9, Soundproofing chamber; 10, Sonication chamber; 11, Agitation motor; 12, Outlet tubes; 13, Products container; 14, Heat exchanger; 15, Temperature controller; 16, Electrovalve; 17, Reactor; 18, Tap water; 19, Thermostatic bath; 20, Reactants feed tube; 21, Sampling tube; 22, Magnetic stirrer; 23, Nitrogen stream; 24, Initiator feed stream; 25, Preemulsion feed stream.

polymerization particle nucleation occurs in submicron monomer droplets, unlike emulsion polymerization where most of the nucleation takes part in the micelles. Thus, Barnette et al. [6] reported a case in which the miniemulsion polymerization of MMA in a CSTR did not show oscillations whereas the conventional emulsion polymerization did present decaying oscillation transients. Surprisingly, the authors reported that the particle size distribution of the latex resulting from the miniemulsion was indistinguishable from the corresponding conventional emulsion latex.

The aim of the present work is to demonstrate the feasibility of miniemulsion polymerization as a strategy to eliminate the oscillatory behaviour of CSTR reactors for a wide range of operating conditions. In order to achieve this goal, a comparative study of the conventional emulsion and miniemulsion polymerization of vinyl acetate – a monomer with high radical desorption rate, which makes the oscillatory behaviour more acute – in a CSTR is presented in terms of conversion, particle number, particle size distribution and molecular weight distribution.

2. Experimental

2.1. Materials

Vinyl acetate was washed with 1% NaOH solution to remove the inhibitor. The treated monomer was further washed with deionized water and dried with $CaCl_2$. Potassium persulphate (Merk), sodium dodecyl sulphate (Merk) and hexadecane (Aldrich) were used as received. Deionized water was used throughout the work.

2.2. Procedure

Experiments were performed in a 0.47 l jacketed tank reactor equipped with a six-bladed turbine, a sampling device and inlet and outlet tubes (Fig. 1). The reactants were fed into the reactor through a 1/4 in. stainless steel tube located near the turbine. The reactants were fed in two streams. One was a preemulsion (mixture of monomer, surfactant, cosurfactant – when required – and most of the water) and the other an aqueous solution of initiator. In the miniemulsion preparation, the preemulsion was subjected to sonication (Branson Sonifier 450). The flow rates of the two streams were controlled by means of weight-based flow controllers. The products left the reactor through a 1/2 in. tube located at the top of the reactor. There was no headspace in the reactor, which ensured a constant volume. 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 the tap water through the heat exchanger was controlled by means of a PID controller and a control valve.

Because of the major influence of any external perturbation in the performance of the polymerization, the same procedure was used in all the experiments. The reactor was filled with the chosen solution for the start-up

Table 1
Summary and legend of the start-up procedures

Start-up procedure	Emulsion	Miniemulsion
Water	E-1	M-1
Water + initiator	E-2	M-2
All the ingredients	E-3	M-3

procedure. This solution was kept 30 min under a N_2 atmosphere at 60°C. The preemulsion and initiator solutions were continuously purged with N_2. When conventional emulsion polymerization was run, the two streams were continuously fed to the reactor. In the case of the miniemulsion polymerization, the preemulsion previously passed through the sonifier equipped with a continuous-flow cell cooled with a water jacket. In order to ensure a similar droplet size for all the miniemulsion reactions, a previous study of the influence of the sonication time, power and cosurfactant concentration in the droplet size was performed. The conditions selected for the continuous sonication, as will be explained in Section 3, were: sonication intensity: 7; duty cycle: 80%; residence time in the flow cell: 2 min.

Samples were withdrawn at regular intervals and the polymerization was short-stopped with hydroquinone. The conversion was determined gravimetrically. The particle size was measured by Quasi Elastic Light Scattering (QELS)(Malvern 4700) and TEM (Hitachi H-7000 FA) and the particle size distribution was determined from the TEM photographs by means of a graphics tablet (Summasketch Plus). Molecular weight distribution was obtained by gel permeation chromatography (Waters 510) using 2 photoluminescent 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. Miniemulsion samples taken from some of the experiments were diluted in saturated monomer aqueous solution and monomer droplet size was measured by QELS.

Two series of experiments were carried out. In the first series, the feasibility of miniemulsion polymerization for eliminating the oscillatory behaviour was studied for different start-up procedures. Table 1 summarizes the strategies employed, which differ from the composition of the initial charge in the reactor. In the second series of experiments, conventional emulsion and miniemulsion polymerizations for different surfactant and initiator concentrations were compared. Low surfactant concentrations were used to enhance the oscillatory mechanism of the conventional emulsion. The reactions carried out are given in Table 2. In these reactions, the reactor was initially filled with aqueous initiator solution.

Table 2
Summary and legend of reactions carried out at different initiator and surfactant concentrations

Initiator (mM)	Emulsifier 5 mM	10 mM	40 mM
Emulsion/miniemulsion			
5	E-S1H1/M-S1H1	E-S2H1/M-S2H1	–
7.5	E-S1H2/M-S1H2	E-S2H2/M-S2H2	E-S3H2/M-S3H2
10	E-S1H3/M-S1H3	E-S2H3/M-S2H3	E-S3H3/M-S3H3

All the experiments were carried out at 60°C. The concentration of monomer was 24.9 wt.% (based on water) and 2 wt.% hexadecane (based on the monomer) was used as cosurfactant in the miniemulsion runs. The mean residence time (θ) was 20 min.

3. Results and discussion

3.1. Influence of the sonication conditions on the miniemulsion mean droplet size

Fig. 2 shows the influence of the sonication time on the miniemulsion mean droplet size. In spite of the data dispersion because of the difficulty of measuring the droplet size precisely, the figure shows a clear trend: as the sonication time increases the mean droplet size decreases until a time (around 60 s) from which there is almost no change. The residence time of the preemulsion in the sonication chamber is about 2 min. Therefore, from these results it can be concluded that any small perturbation on the residence time will not influence the mean droplet size.

The influence of the sonication intensity (from 1 (45 W) to 10 (450 W)) is shown in Fig. 3. Again, a big data scatter is found. However, the trend of the curve clearly shows that at intensity values higher than 6 (270 W) the size of the droplets remains almost constant. In this work, an intensity of 7 (315 W) was chosen.

Table 3 shows the influence of the hexadecane concentration in the droplet size, at two different sonication intensities. The results indicate that the droplet size is not influenced by the surfactant concentration at these levels. The difference shown is less than the measurement error of such equipment, for polydisperse samples. Therefore, 2 wt.% hexadecane (based on monomer) was used throughout this work.

3.2. Influence of the start-up procedure

Figs. 4 and 5 present the time evolution of the conversion (a), and particle number (b), for the different start-up procedures given in Table 1, when the polymerization is carried out by conventional emulsion and miniemulsion, respectively. It can be seen that the start-up procedure has a pronounced effect on the conventional emulsion dynamics, however, there is almost no effect on the miniemulsion.

In the case of the emulsion polymerization, when the reactor is filled with all the ingredients, the system initially

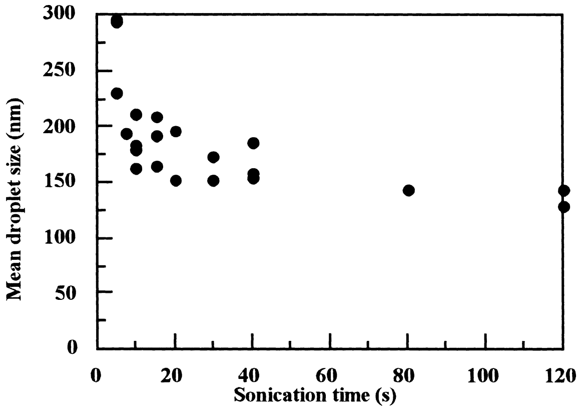

Fig. 2. Effect of the sonication time on the mean droplet size.

behaves almost as a batch reactor. There is a lot of free emulsifier and many particles are formed. These particles grow consuming surfactant. Finally, the surfactant is depleted and the nucleation stops. After a period of time, there is again free emulsifier and a new nucleation appears. When the polymerization starts with the reactor filled with water, the small concentration of initiator is not able to start the polymerization, probably because of the presence of oxygen, and there is an accumulation of monomer. After one residence time, the conditions of the reactor are quite similar to the former run and there is a strong nucleation. The conversion increases until no more particles are nucleated. When the reactor is initially filled with an aqueous solution of initiator, the polymerization starts as soon as the preemulsion stream begin to enter the reactor, because of the presence of radicals, which consume the oxygen present in the reactor before starting the feeding. The concentration of the surfactant is too low, so fewer particles are formed, avoiding the initial strong overshoot, although oscillations are found during the polymerization.

In the case of miniemulsion, however, whichever the start-up procedure is, there are no oscillations and the same steady-state is reached in the three cases, as a result of the continuous nucleation in the monomer droplets, which are present at all times.

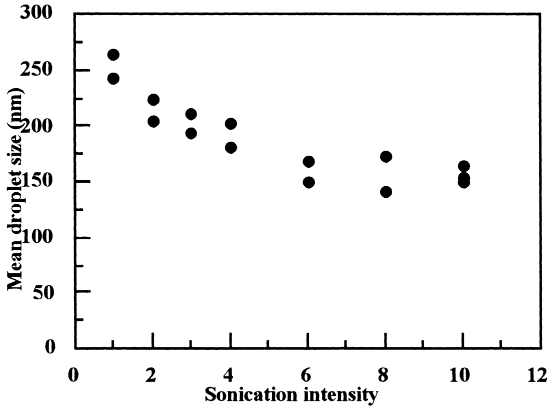

Fig. 3. Influence of the sonication intensity on the mean droplet size.

Table 3
Influence of the hexadecane concentration on the mean droplet size. Sonication time: 2 min

Hexadecane %wt (based on monomer)	Mean droplet size	
	Sonication intensity: 180 W	Sonication intensity: 315 W
2%	200 nm	165 nm
4%	206 nm	174 nm

3.3. Influence of surfactant and initiator concentrations

Fig. 6 shows the conversion-versus-time profiles for conventional emulsion and miniemulsion polymerizations carried out at different surfactant and initiator concentrations, when the reactor was filled initially with an aqueous

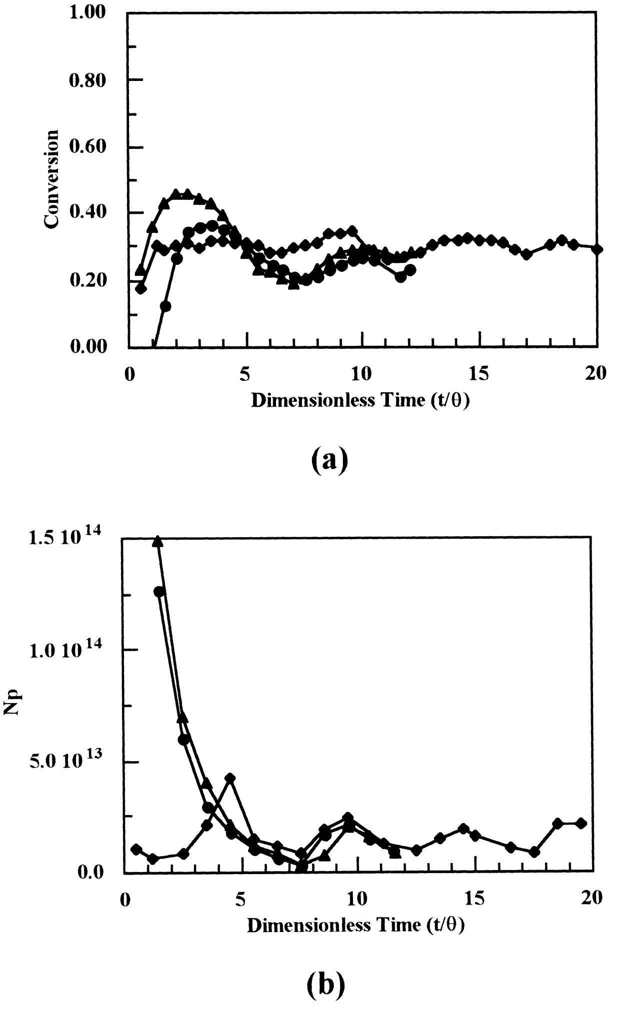

Fig. 4. Effect of the start-up procedure in the emulsion process. Time evolution of the conversion (a) and number of particles (b). Legend: (●) E–A, water; (◆) E–B, water and initiator; (▲) E–C, all the ingredients.

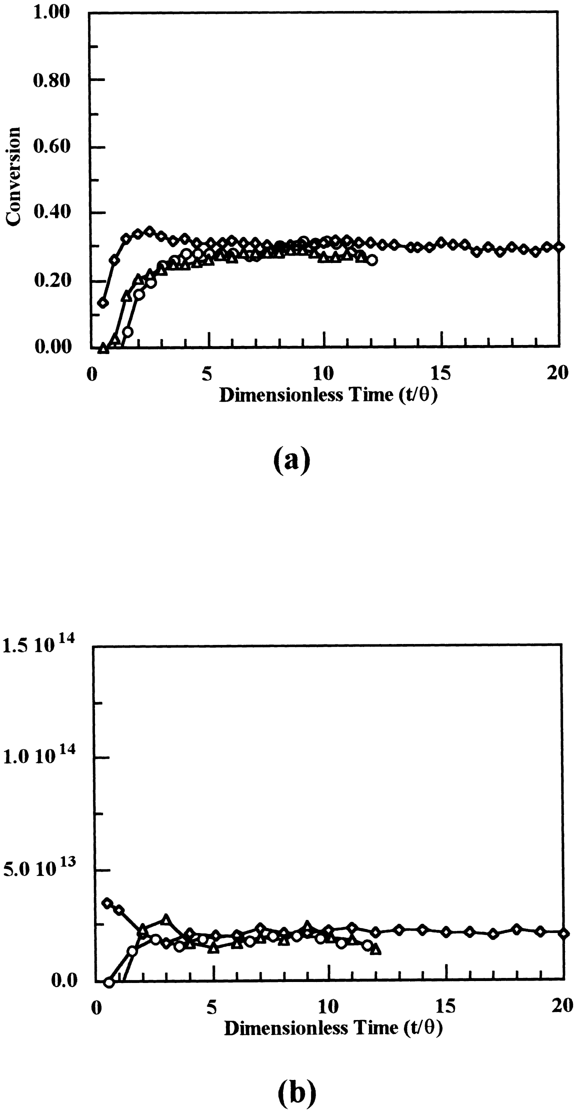

Fig. 5. Effect of the start-up procedure in the miniemulsion process. Time evolution of the conversion (a) and number of particles (b). Legend: (○) M-1, water; (◇) M-2, water and initiator; (△) M-3, all the ingredients.

initiator solution. Most of the conventional emulsion experiments exhibit oscillation, whereas miniemulsions do not. The different behaviour is well explained when the evolution of the number of polymer particles is studied (Fig. 7). In all the conventional emulsion systems, oscillations of the number of polymer particles are observed, the frequency of oscillations being the same as that of the conversion profiles. However, there is almost no variation in the miniemulsion systems. This behaviour is caused by different nucleation mechanisms. While in conventional emulsion there is an intermittent nucleation caused by fluctuations in the emulsifier concentration, in the miniemulsion polymerization there is a continuous nucleation, which takes part almost exclusively in the monomer droplets.

Under most conditions, miniemulsions give a higher number of particles than emulsions. This difference is clear at low surfactant concentrations (S1H1,S1H2 and S1H3). At medium concentrations (S2H1, S2H2 and S2H3) the number of particles of the miniemulsion runs are still on average higher. At the highest surfactant level (S3H1, S3H2 and S3H3), although miniemulsions give a higher number of particles, there is almost no difference between the two systems. This behaviour can be explained by estimating the number of droplets, micelles or particles that the surfactant can stabilize.

Assuming that the average droplet size of the miniemulsions is 150 nm, 1.3×10^{14} droplets can be formed. For the two lowest surfactant levels (0.005 and 0.010 M), there is not enough surfactant to cover the entire droplet surface, hence, there will be no free surfactant available to form micelles. At high surfactant concentrations (0.04 M) however, there is enough free surfactant to form micelles. Assuming that the aggregation number of SDS is 50 molecules/micelle [7], 5.3×10^{16}micelles can be formed. It can be argued that at low surfactant concentrations, the miniemulsion droplets can coalesce, decreasing their number. However, the time that the miniemulsion spends between sonication and entry into the reactor is very short, around 15 s. Hence, it can be assumed that the number of droplets remains almost constant.

Table 4 shows the number of polymer particles of average size 150 nm that the surfactant can cover, neglecting the surfactant necessary to stabilize the droplets, in the case of emulsion polymerization. It is clear that the number of particles that the two lowest surfactant levels can stabilize is not very large, in both cases lower than the number of droplets formed. In the emulsion procedure, at low surfactant level the surfactant disappears very soon once the particles nucleate, and no new particles will be formed for some time. In the miniemulsion, although not all the droplets are stable during the entire run and some of them coagulate, others nucleate. In general, a higher number of particles is created at low surfactant concentration in the miniemulsion procedure than in the emulsion. At high levels, the number of particles that can be formed in emulsion increases greatly. In miniemulsion, the number of micelles is also high, so polymerization occurs in both droplets and micelles, the latter probably being the main process. Therefore, under these conditions, both processes give a similar number of particles.

From the analysis of the data, the following approximate relationship between polymerization rate and the emulsifier and initiator concentration is obtained for both emulsion and miniemulsion polymerization of VAc:

$$\textit{Emulsion: } R_{p_e} \div [S]^{0.16-0.20}[I]^{1.3-1.6}.$$
$$\textit{Miniemulsion: } R_{p_m} \div [S]^{0.16-0.25}[I]^{0.7-1.0}.$$

The dependencies found for the emulsion procedure are quite similar to the ones obtained by Greene et al. [8], particularly for the surfactant.

When a similar study of the dependence of the

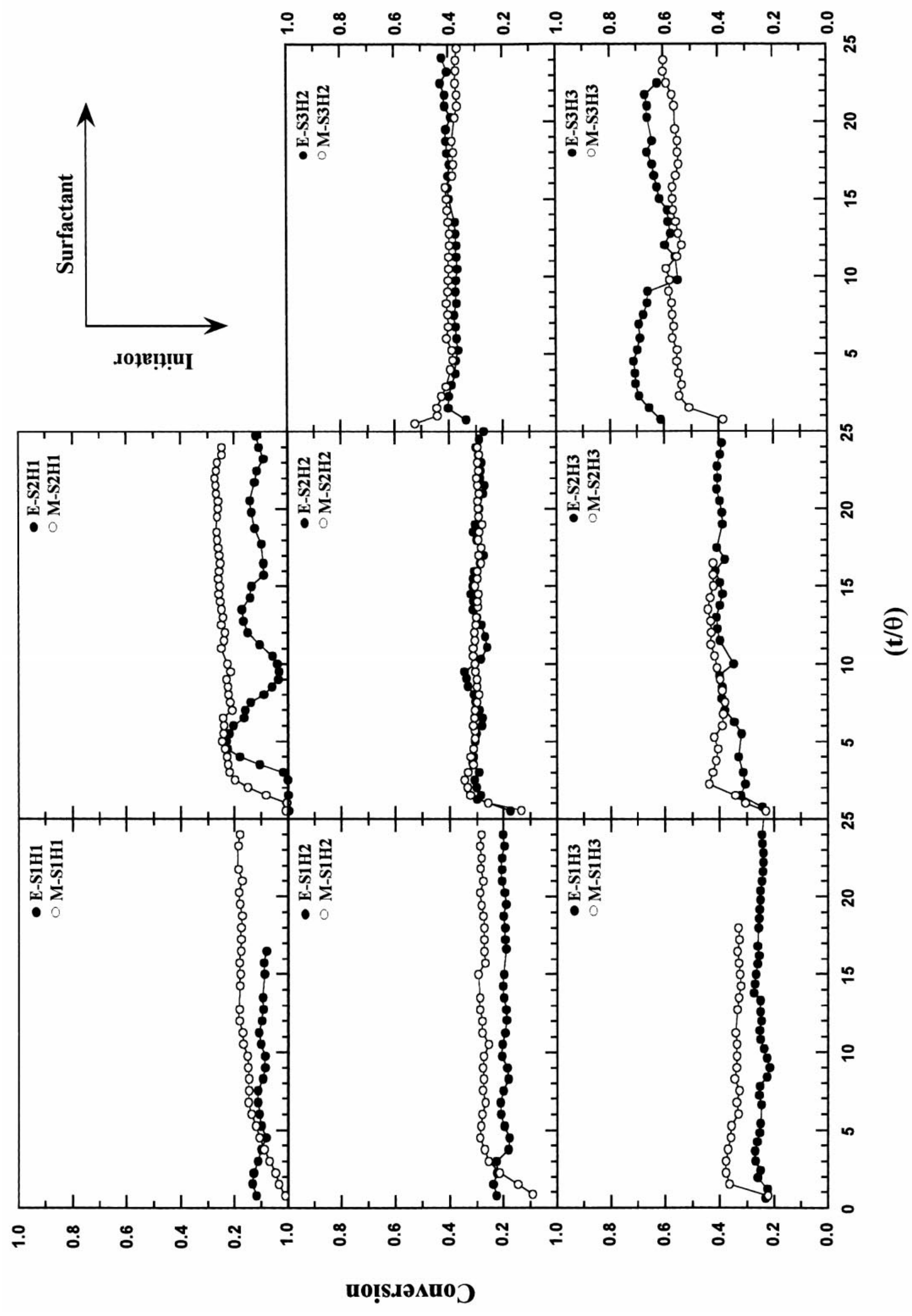

Fig. 6. Time evolution of the conversion for emulsion and miniemulsion processes at different surfactant and initiator concentrations.

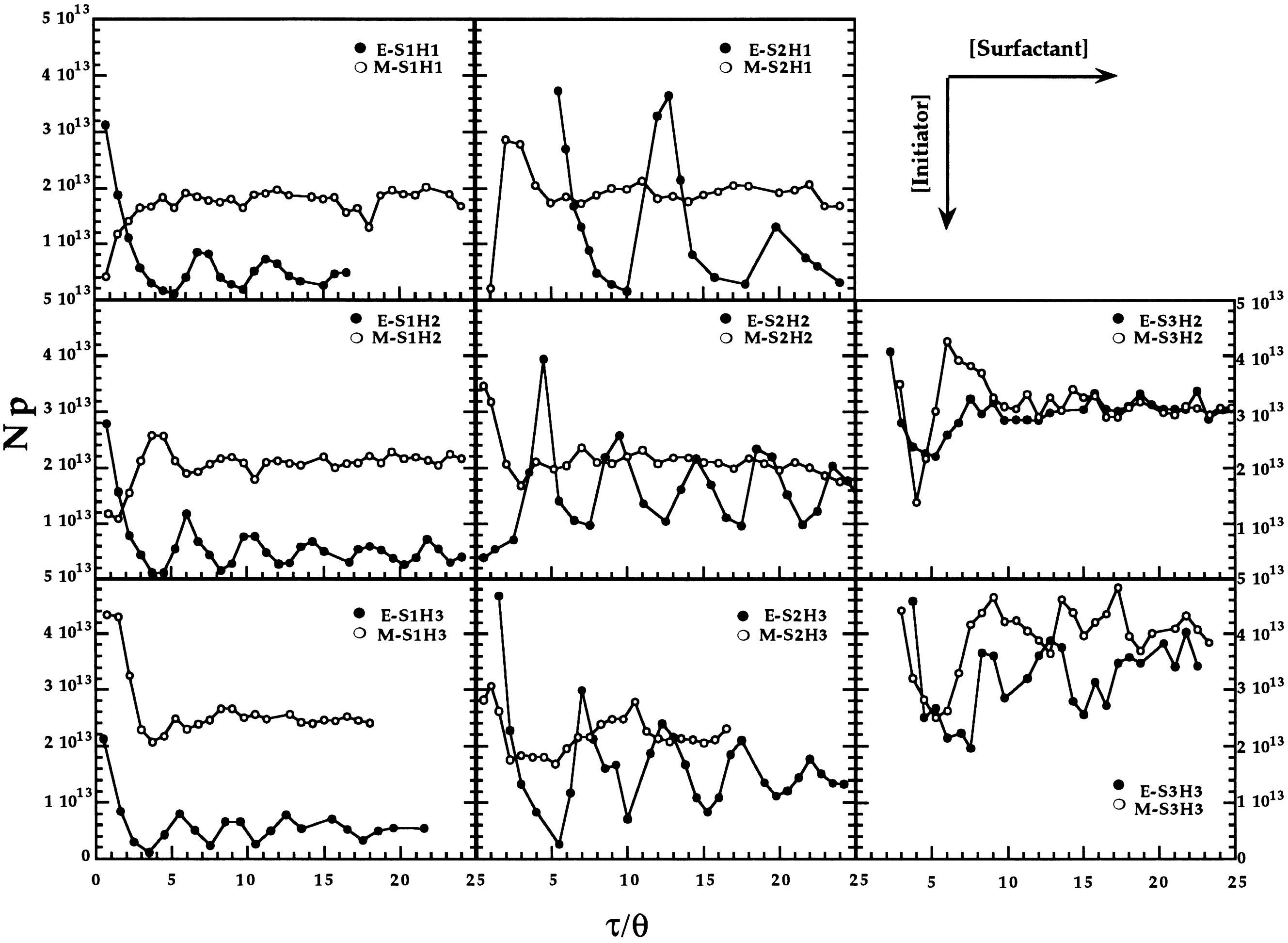

Fig. 7. Time evolution of the number of particles for emulsion and miniemulsion processes at different surfactant and initiator concentrations.

independent variables on the particle number is made, there is a difficulty to overcome. The evolution of the particle number along the emulsion polymerization run changes a lot as a result of the intermittent nucleation. In order to have just a rough estimation of such a dependency, the average particle number of the emulsions obtained after the initial five residence times has been considered, and the following dependencies have been obtained:

Emulsion: $N_{p_e} \div [S]^{0.7}[I]^{0.03}$.
Miniemulsion: $N_{p_m} \div [S]^{0.25}[I]^{0.22-0.4}$.

These results are similar to the dependencies obtained by Delgado et al. [9] for the 50/50 vinyl acetate/butyl acrylate system, except for the initiator concentration in the miniemulsion polymerization, for which they found a higher dependence. Again it is shown that a different nucleation mechanism takes place in each process. The high dependence of the particle number on the surfactant concentration and the almost no dependence on the initiator concentration of the emulsion process suggest that a homogeneous nucleation mechanism is predominant in the conventional process. The particle number is only dependent on the surface of the oligoradicals that can be covered by the surfactant. However, the much lower dependence of the particle number on the surfactant concentration and the strong dependence on the initiator concentration in the miniemulsion process indicate nucleation in the monomer droplets. On increasing the initiator concentration, the radical flux to the monomer droplets increases and hence, the number of droplets being initiated is larger.

More evidence for the different behaviour of conventional emulsion and miniemulsion polymerization is observed when the particle size distributions are analysed. Fig. 8 shows the time evolution of the particle size distribution (in volume) for runs E-S1H2 and M-S1H2. In

Table 4
The number of polymer particles of average size 150 nm that the surfactant can cover

[SDS] (M)	Number of particles
0.005	2.92×10^{13}
0.01	5.96×10^{13}
0.04	2.38×10^{14}

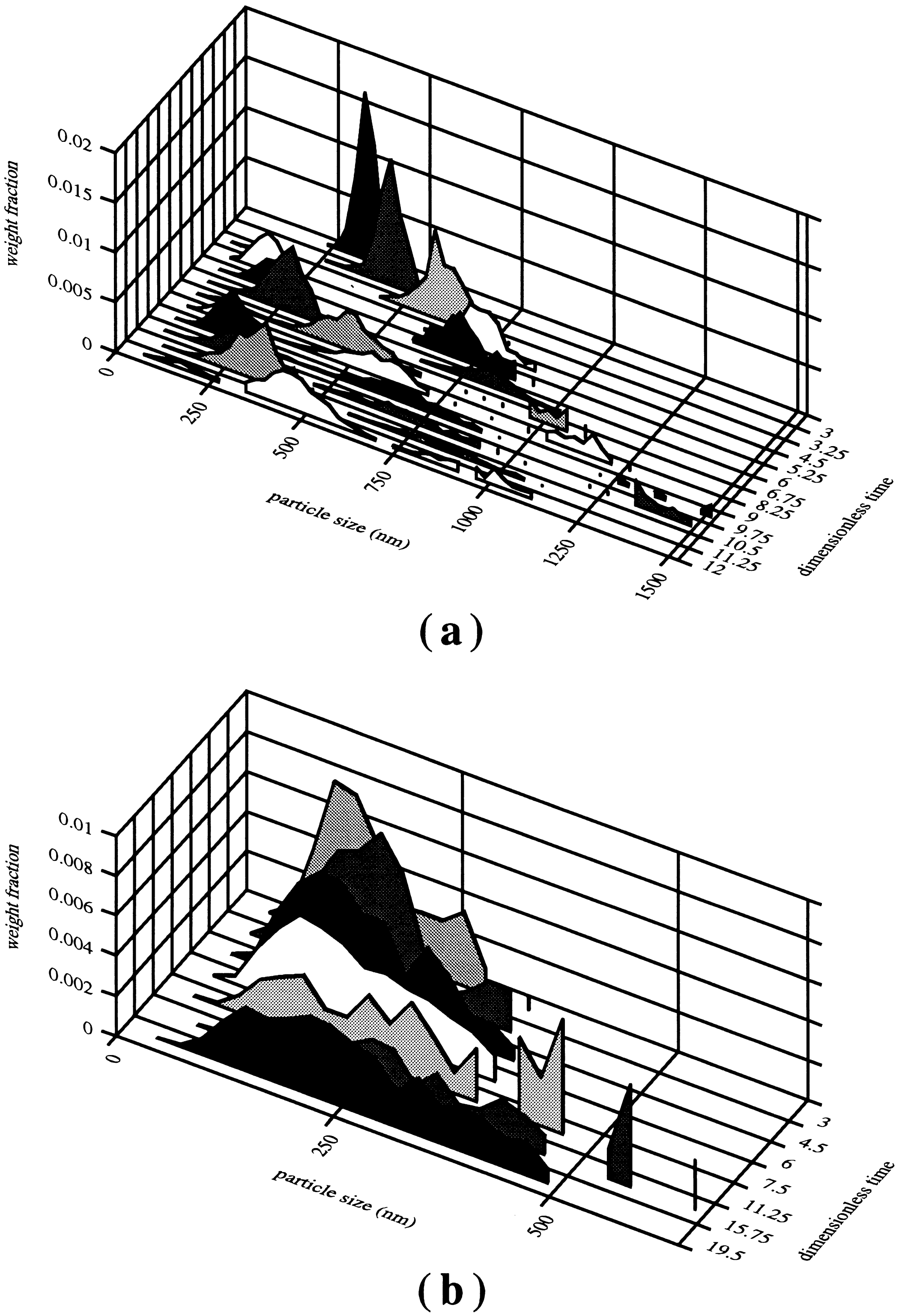

Fig. 8. Time evolution of the particle size distribution for E-S1H2 emulsion (a) and M-S1H2 miniemulsion (b) processes.

the miniemulsion process there is only one particle population, whose distribution barely changes during the reaction, as a result of the continuous nucleation process. In the conventional emulsion, a single population was found in the early samples. Later, new nucleations appeared and more than one population existed during the entire run, as a consequence of the intermittent nucleation.

In order to gain more insight into both processes, the

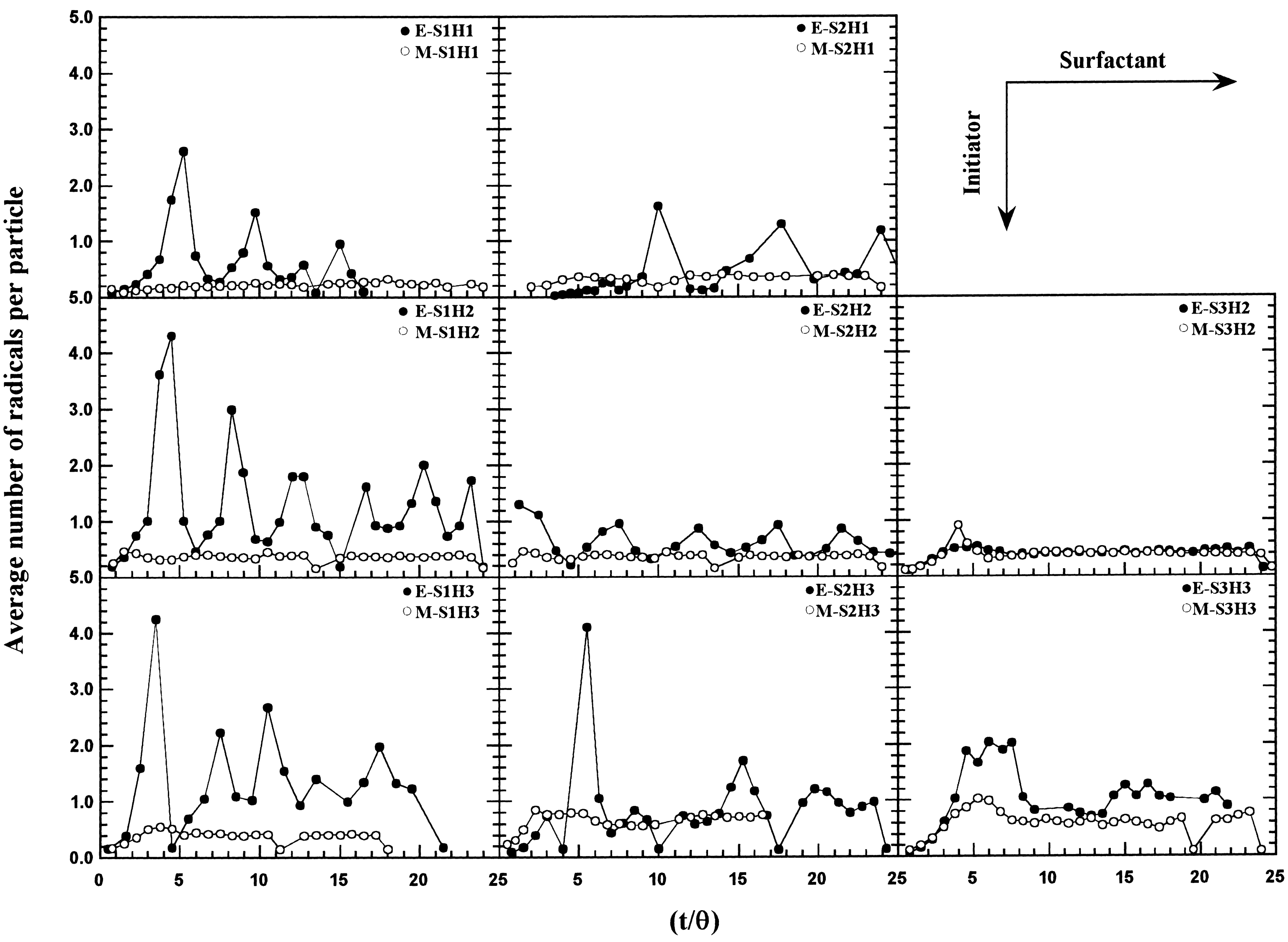

Fig. 9. Time evolution of the average number of radicals per particle for emulsion and miniemulsion processes at different surfactant and initiator concentrations.

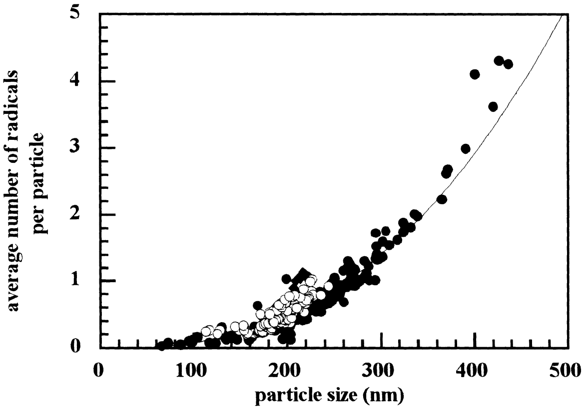

Fig. 10. Average number of radicals per particle vs. mean particle size for the emulsion and miniemulsion processes.

evolution of the average number of radicals per particle ($\bar{n}$) has been estimated, with $k_p = 8.12 \times 10^6 \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1}$ [10]. The results are shown in Fig. 9. In most of the cases, $\bar{n}$ is bigger in the conventional emulsion, especially at low emulsifier concentrations where the mean particle size is much larger than in the corresponding miniemulsion polymerization. The maximum value of $\bar{n}$ reached is almost 5 while miniemulsions present constant values lower than 0.5. Further, the time evolution of $\bar{n}$ for most of the conventional emulsions presents an oscillatory behaviour similar to the evolution of the particle size.

Fig. 10 shows the relationship between $\bar{n}$ and the mean particle size for both conventional emulsion and miniemulsion processes. It can be seen that all the points are located under the same line. The narrow particle size range of the miniemulsion latexes however, makes it difficult to draw any conclusion. The points related to the conventional emulsion polymerizations can be fitted to an exponential function, where the exponent is 2.7. This exponent close to 3 suggests that the number of radicals per particle is proportional to the particle volume. This is in accordance with the Smith–Ewart case 1, that is fulfilled by systems with high propagation constant rates and significant desorption and water-phase termination rates, which is the VAc case.

Table 5
Summary of the average weight molecular weight of conventional emulsion and miniemulsion latexes

Initiator (mM)	Emulsifier (mM) 5	10	40
Emulsion			
5	307,000	288,000	–
7.5	368,000	405,000	421,000
10	376,000	401,000	524,000
Miniemulsion			
5	308,000	373,000	–
7.5	360,000	357,000	423,000
10	390,000	494,000	583,000

Although it has been extensively shown during this work that miniemulsion polymerization is a successful technique for eliminating oscillations in CSTR reactors, it is very important to know how different the product characteristics are. Table 5 shows the average weight molecular weight of conventional emulsion and miniemulsion samples taken at the same residence time (11θ) for runs carried out varying the emulsifier and initiator concentrations. In most of the cases, a little difference between the two systems is observed. This can be justified by the importance of the monomer chain transfer in VAc that dominates the molecular weight at low conversion. When the conversion increases, it can be seen that the molecular weight increases, as a consequence of the higher chain transfer to polymer as a result of a higher concentration of polymer in the reaction.

4. Conclusions

The conventional emulsion and miniemulsion polymerizations of vinyl acetate in a CSTR were studied under a wide range of operating conditions. The feasibility of miniemulsion polymerization as a strategy to eliminate the oscillatory behaviour of CSTR reactors was extensively demonstrated, through the observation of the time evolution of the conversion, particle number and particle size distribution, which showed that a different particle nucleation mechanism takes place in each process. The dependencies of the particle number on the initiator and surfactant concentrations for the two different processes confirm this fact. In the emulsion polymerization, the number of particles is proportional to the 0.7 power of the surfactant concentration whereas in the miniemulsion process it is only proportional to 0.25. In contrast, there is almost no dependence of the particle number on the initiator concentration in the conventional process, and a 0.22–0.40 power dependency in the miniemulsion process. All these results show that while an intermittent homogeneous nucleation mechanism, caused by the fluctuations of the surfactant, is predominant in the conventional emulsion, in the miniemulsion polymerization particle nucleation occurs in the submicron monomer droplets.

Finally, almost no differences in the molecular weights of the latexes obtained by the emulsion and miniemulsion processes were observed, as a consequence of the large monomer chain transfer rate of VAc, which controls the molecular weight at low conversions.

Acknowledgements

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