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High solids content miniemulsion polymerization of vinyl acetate in a continuous stirred tank reactor

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Abstract

The dynamics of high solids content miniemulsion polymerization of vinyl acetate produced in a continuous stirred tank reactor (CSTR), under different emulsification processes and hydrophobes were studied. In order to gain more insight into the process, a previous kinetic study in a batch reactor was performed. In addition, the rheological behavior of latexes produced by miniemulsion was compared with those obtained by conventional emulsion. From the experiments made in batch mode, it was observed that poly(vinyl acetate) or polystyrene as the sole hydrophobes were able to create miniemulsions as far as the time elapsed between sonication and polymerization was small. The same behavior was observed in the CSTR, where the feasibility of those systems to eliminate the oscillatory performance of CSTR reactors, also at high solids content was demonstrated. The sonication itself or the sole presence of hydrophobe — without sonication — was not enough to avoid the oscillatory behavior. Further, it was shown that the viscosity of miniemulsions at the beginning of the CSTR process is notably lower than emulsions, thus preventing the initial mixing and heating problems. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Miniemulsion polymerization; Continuous stirred tank reactor; High solids content

1. Introduction

Continuous stirred tank reactors (CSTR) are widely used in the industry when high production rates are desired. In the case of emulsion polymerization, however, the complex dynamics, essentially oscillation mechanisms and multiple steady states have restricted their commercial use.

In a previous article, the feasibility of miniemulsion polymerization as a strategy to eliminate the oscillatory behavior of CSTR reactors was extensively demonstrated [1]. The mentioned work was carried out with low solids content. However, in industrial practice, latexes with high solids content are produced, because they offer numerous advantages, i.e. low shipping costs and there is no need to remove water.

One of the major difficulties encountered in the production of these latexes is the increase in viscosity once a certain value of particle volume fraction is achieved. For monodisperse latexes, the viscosity approaches infinity as the volume fraction of the polymer particle approaches 0.62 [2]. Polydisperse latexes, however, show a lower viscosity because the small particles fit within the voids of the array of large particles. The likelihood for these latexes to achieve higher solids content is enhanced.

In the miniemulsion polymerization, nucleation occurs in the small monomer droplets [3]. This unique particle nucleation mechanism leads to a broader particle size distribution than the conventional emulsion polymerization, when the reaction is carried out in a batch process, allowing the production of latexes with very high solids content. Unzué and Asua [4] produced a 65% butyl acrylate, methyl methacrylate and vinyl acetate terpolymer by using miniemulsion polymerization in a semibatch process. Lopez de Arbina and Asua [5] and Masa et al. [6] compared high solids content emulsion and miniemulsion terpolymers. They found that the viscosity of the 55% solids content latex produced by conventional emulsion was 6.5 times higher than the latex obtained using the miniemulsion process. Leiza et al. [7] presented a new approach to prepare high solids content latexes, based on the synthesis of broad seeded semicontinuous miniemulsion polymerization, followed by further polymerization in batch or semibatch. The approach was used to prepare fluid and coagulum-free poly(*n*-butyl acrylate) latexes up to solids content of 61 wt%.

In addition, this different nucleation mechanism could

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change the performance of the emulsion polymerization in the CSTR reactors at the beginning of the reaction. The small particles with narrow distribution formed during the initial stage of the high solids content conventional emulsion polymerization could lead to thermal runaway and coagulum formation caused by the sudden increase in viscosity. The broad particle distribution of the miniemulsion, however, produced latexes with lower viscosity, which could overcome this initial problem.

On the other hand, fatty alcohols [8–10] (cetyl alcohol) and long-chain alkanes (hexadecane) [11] have been commonly used to stabilize the miniemulsion small droplets against monomer diffusion, that is, to minimize the Ostwald ripening effect. Those low-molecular-weight compounds remain in the particles after polymerization and can plasticize the polymer, affecting its properties. Furthermore, the slow evaporation of these hydrophobes pollutes the atmosphere. Recently, different authors [8,12,13] have studied the feasibility of the preformed polymer to stabilize the monomer droplets. Thus, Miller et al. [8] reported that when polymer was added to the monomer and subsequently homogenized into the surfactant solution, a fully creamed solution was observed in few hours. Furthermore, they observed a turbid water phase, which may indicate the presence of small particles. In fact, when they polymerized this emulsion, they obtained a substantially higher rate of polymerization than the conventional emulsion. This was explained assuming that two different nucleation mechanisms took part: micellar nucleation and the formation of some polymer particles during the homogenization. Reimers and Schork [12] observed that the addition of a monomer-soluble polymer to an emulsion (poly(methyl methacrylate) to methyl methacrylate) slowed the effects of Ostwald ripening long enough to allow a predominant droplet nucleation. The same conclusion was obtained by Aizpurua et al. [13] in the low solids content batch miniemulsion polymerization of vinyl acetate using poly(vinyl acetate) or polystyrene as hydrophobes.

In this work, the study of the feasibility of miniemulsion polymerization to eliminate the oscillatory behavior of CSTR reactors will be extended to high solids content emulsion polymerization of vinyl acetate. In addition, due to the deleterious effect of the commonly used low-molecular-weight cosurfactants, the effectiveness of emulsification processes without any hydrophobe and with polymeric hydrophobes for achieving steady-state operation in the CSTR emulsion polymerization will be explored. Finally, the feasibility of miniemulsion polymerization to prevent the mixing and heat-transfer problems in the initial stage of high solids content emulsion polymerization in CSTR reactors will be analyzed through the study of the rheological behavior of latexes with 60% solids content.

In order to gain more insight into the process, a previous kinetic study in a batch reactor under different emulsification conditions has been carried out.

2. Experimental

2.1. Materials

Vinyl acetate (VAc) was washed with 1% NaOH three times to remove the inhibitor (hydroquinone, 10 ppm). The treated monomer was further washed with deionized water and dried with $CaCl_2$. Butyl acrylate (BA) was distilled under reduced pressure (10 mmHg, 35°C). Both monomers were stored no longer than three days at -18°C.

Potassium peroxodisulfate (KPS) (Merck), sodium acid disulfite (SDA) (Panreac PA), Alipal CO436 (ammonium 8-[4-(*n*-nonyl)phenoxy]-3,6-dioxaoctyl sulfate) (Rhône-Poulenc), Arkopal N230 (2-{ω-[4-(*n*-nonyl)phenoxy]polyethyleneoxy} ethanol) (Hoechst), hydroxyethyl cellulose (HEC) (Quimidroga) and hexadecane (HD) (Aldrich) were used as received. Deionized water was used through the work.

Two polymeric hydrophobes were used: poly(vinyl acetate) (PVAc) ($M_w = 110\,000$, Aldrich) was used as supplied. Polystyrene (PS) ($M_n = 70\,000$, $M_w = 104\,000$), was synthesized in our laboratory by emulsion polymerization, separated by coagulation and washed by solution/precipitation with tetrahydrofuran/heptane.

Table 1
Summary of experiments carried out in batch reactor

Reaction	VAc (g)	H_2O (g)	Arkopal (g)	Alipal (g)	HEC (g)	KPS (g)	HD (g)	PVAc (g)	PS (g)	Sonic
B-∅	100	81.81	1	0.75	0.1	1.05	–	–	–	No
B-∅S	100	81.81	1	0.75	0.1	1.05	–	–	–	Yes
B-H	100	81.81	1	0.75	0.1	1.05	2	–	–	Yes
B-P1a[a]	100	81.81	1	0.75	0.1	1.05	–	1	–	Yes
B-P1b[b]	100	81.81	1	0.75	0.1	1.05	–	1	–	Yes
B-P2	100	81.81	1	0.75	0.1	1.05	–	–	1	Yes
B-E	100	81.81	2	1.5	0.1	1.05	–	–	–	No
B-M	100	81.81	2	1.5	0.1	1.05	2	–	–	Yes

[a] Elapsed time between sonication and polymerization: 15 min.

[b] Elapsed time between sonication and polymerization: 45 min.

2.2. Polymerization processes

2.2.1. Batch process reactions

Batch reactions were performed under nitrogen, at 60°C, in a 0.75 l jacketed glass reactor, equipped with an anchor stirred. It was closed by a stainless steel cover and sealed with a viton® toroidal joint. Reaction temperature was set constant by controlling the temperature of the fluid in the jacket by means of a thermostatic bath and a heat exchanger.

Water phase (water and emulsifiers) and organic phase (monomer and hydrophobe, if any) were prepared in separate flasks and they were mixed by a magnetic stirrer. This emulsion was sonicated for 10 min using a Branson 450 sonifier and immediately after sonication, miniemulsions were transferred to the batch reactor and they were stirred and kept under nitrogen (Alphagaz UN-45) for 10 min, until reaction temperature was reached. The reaction was initiated by the addition of the aqueous solution initiator system.

Samples were withdrawn at regular intervals through a three-way stopcock. Polymerization in the sample was shortstopped with hydroquinone and conversion (gravimetry) and particle size (Dynamic Light Scattering Coulter N4 Plus) were measured.

The experiments performed in this section are summarized in Table 1. Reactions with different type of polymeric hydrophobes (poly(vinyl acetate) and polystyrene) were synthesized to elucidate the stabilizing capacity of the miniemulsion droplets (runs B-P1 and BP-2, respectively). A reaction applying sonication to the emulsion — without any hydrophobe — was performed, to evaluate the effect on the kinetics of the sonication itself (run B-∅S). The influence of the interval between the sonication and the reaction start up, when poor stabilizers are used, was also analyzed to verify the stabilization with time of the miniemulsion (runs B-P1a and B-P1b). In order to establish a basis of comparison, a reaction with the commonly used cosurfactant hexadecane and a conventional emulsion polymerization were carried out (B-H and B-∅).

In the previously described reactions, and with the aim to work close to industrial conditions, very low concentration of surfactants were used, and some products coagulated after the reaction. Due to this fact, two new reactions with double amount of emulsifiers were done (Reactions B-E and B-M in Table 1). Those products were used to compare the rheological behavior of conventional emulsion and miniemulsion polymerization batch processes.

2.2.2. Continuous process reactions

Experiments were performed in a 0.47-l jacketed tank reactor equipped with a six-blade turbine, and inlet and outlet tubes [1]. The reactants were fed into the reactor through a 1/4-inch stainless steel tube located near the turbine. The reactants were fed in two streams. One was an aqueous solution of initiator and emulsifiers and the other was an organic solution (mixture of monomer and hydrophobe when required). In the miniemulsion preparation, both streams were mixed and subjected to sonication into a cooled continuous sonicated chamber (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-inch tube, located at the top of the reactor. There was no head-space in the reactor, which ensured a constant volume.

Temperature control was achieved through a cascade control. The temperature inside the reactor was measured 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, that is, an electrical resistance placed in the circuit of the thermal fluid and an electrovalve, which controls the flow of the tap water. The whole experimental set-up was controlled by a PC. This system allows to control the reactor temperature in a ±0.2°C range.

Because of the major influence of any external perturbation in the performance of the polymerization, the same procedure was used in all the experiments. Before starting the process, the reactor was completely filled with the reaction mixture. This solution was kept for 30 min under a N_2 atmosphere at 60°C. The aqueous and organic solutions were continuously purged with N_2. All the reactions were performed at 60°C and mean residence time (θ) of 20 min. Samples were withdrawn and analyzed as in the batch reactions.

The same experimental conditions tested in the batch processes were studied in CSTR. Table 2 summarizes the polymerizations carried out. In addition, a new reaction was performed to explore if adding polymer had any effect on

Table 2
Summary of experiments carried out in CSTR

Reaction	VAc (g)	H_2O (g)	Arkopal (g)	Alipal (g)	HEC (g)	KPS (g)	HD (g)	PVAc (g)	PS (g)	Sonic
C-∅	100	81.81	1	0.75	0.1	1.05	–	–	–	No
C-P$	100	81.81	1	0.75	0.1	1.05	–	1	–	No
C-∅S	100	81.81	1	0.75	0.1	1.05	–	–	–	Yes
C-H	100	81.81	1	0.75	0.1	1.05	2	–	–	Yes
C-P1	100	81.81	1	0.75	0.1	1.05	–	1	–	Yes
C-P2	100	81.81	1	0.75	0.1	1.05	–	–	1	Yes

Table 3
Summary of experiments carried out in CSTR to study the emulsion and miniemulsion rheological behavior

	Vac (g)	H_2O (g)	Alipal (g)	Arkopal (g)	HEC (g)	KPS (g)	SDA (g)	BA (g)	HD
C-E	100	66.7	0.75	1	0.1	0.2	0.2	1	–
C-M	100	66.7	0.75	1	0.1	0.2	0.2	1	2

the polymerization mechanism. In this case, the polymeric hydrophobe was dissolved in monomer and the solution was fed directly without any prior sonication (Reactions C-P$ in Table 2).

The previous CSTR reactions were run at low conversions, and some phase separation occurred during the viscosity measurement. Furthermore, due to the different conversion of the above-mentioned runs, the solids percent was different, and so was the viscosity. Therefore, two new reactions were conducted in the CSTR, aiming to obtain both high solids content and high conversions. The recipes used are shown in Table 3. Both reactions were run at 60°C, with 40 min as residence time to ensure high conversion. A small amount of HEC and BA was added to improve colloidal stability. In those experiments, the particle size distribution was measured by disc centrifugue photosedimentometer, BI-DCP, Brookhaven, and the viscosity with a Brookfield ELV-8 viscosimeter.

3. Results and discussion

The results will be discussed under two major headings, namely "Batch processes" and "Continuous stirred tank reactor processes". Each of these two sections will be subdivided into discussion of the kinetics and rheological behavior.

3.1. Batch processes

3.1.1. Kinetics

Fig. 1 shows the time evolution of the conversion for the reactions specified in Table 1. Conventional emulsion is the fastest, followed by the sonified emulsion, the miniemulsion with polymeric hydrophobe and the miniemulsions with HD. Those small differences become clearer when the evolution of the particle size is analyzed (Fig. 2). At the beginning of the reaction, the runs containing hydrophobe (B-H and B-P1a) present bigger particle diameter than conventional emulsion (B-∅) and the pseudo miniemulsion sonicated without any hydrophobe (B-∅S). As a consequence, when the number of particles is analyzed (Fig. 3), it is seen that the conventional emulsion and the sonicated one have much higher number of particles than miniemulsions. Those results are due to the different nucleation mechanism. When no additional stabilizer is added (B-∅, B-∅S), the nucleation occurs on the monomer-swollen micelles or by self-precipitation of oligomers in aqueous phase, yielding small particles. In the other reactions, the added hydrophobe stabilizes miniemulsions and nucleation takes place in monomer droplets and larger particles are obtained. Comparing hexadecane with the polymeric hydrophobe, although the latter is not a good swelling agent [8], it seems to stabilize the miniemulsion time long enough for the nucleation to occur also in monomer droplets.

The time elapsed between sonication and the polymerization seems to be an important factor when poor stabilizers, such as PVAc polymer hydrophobe, are used. If the time elapsed is large, the small droplets can disappear by diffusion degradation and as result, the system can lose the

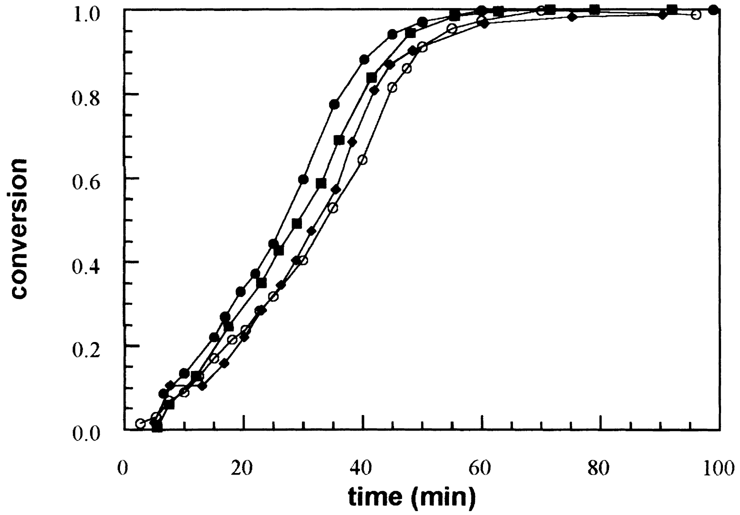


Fig. 1. Time evolution of conversion in batch mode. (●) B-∅, conventional emulsion; (■) B-∅S, sonicated with no hydrophobe; (○) B-H, 2% HD; (◆) B-P1a, 1% PVAc.

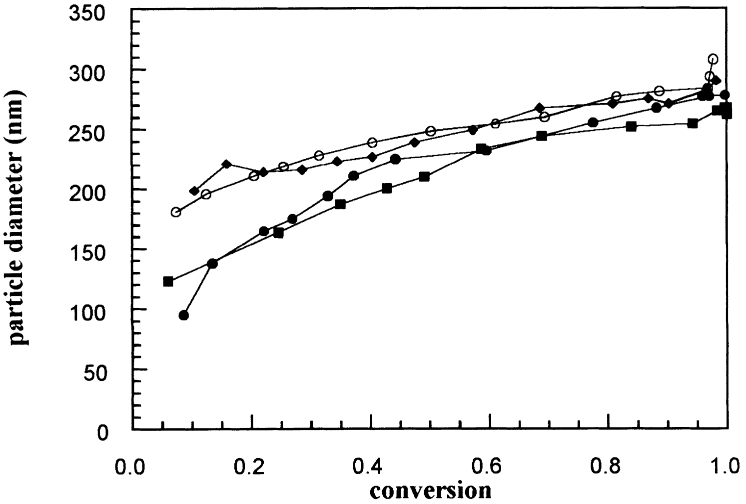


Fig. 2. Time evolution of particle diameter in batch mode. (●) B-∅, conventional emulsion; (■) B-∅S, sonicated with no hydrophobe; (○) B-H, 2% HD; (◆) B-P1a, 1% PVAc.

miniemulsion characteristics. In order to check this phenomenon, two reactions with PVAc as the only hydrophobe and with different time elapsed between sonication and polymerization were compared: reactions B-P1a, with 15 min elapsed, and B-P1b, with 45 min elapsed (see Table 1). Figs. 4 and 5 show the behavior of those reactions, compared with the conventional emulsion and miniemulsion. While reaction B-P1a, with the smaller period of elapsed time, behaves similar to the conventional miniemulsion, the evolution of reaction B-P1b is closer to the emulsion. Therefore, it can be concluded that PVAc can produce miniemulsion latexes only if the time elapsed between sonication and polymerization is small enough to keep the Ostwald ripening effect negligible.

The ability of other polymeric hydrophobes to stabilize the VAc monomer droplets during the 55 wt% solids content miniemulsion polymerization was also tested. Fig. 6 shows the time evolution of the conversion of the miniemulsion stabilized with polystyrene (B-P2). For the sake of comparison, the data corresponding to the miniemulsions stabilized with PVAc (B-P1a) is shown. Both have nearly the same polymerization rate and present similar particle sizes. Those results suggest that polymers other than PVAc can be used as hydrophobe in the high solids content miniemulsion polymerization of VAc with almost the same result.

3.1.2. Rheological behavior

Table 4 shows the viscosity of the emulsion and miniemulsion latexes obtained under the reaction conditions described in Table 1. The measurements were done at different shear rates. Both emulsion and miniemulsion present the

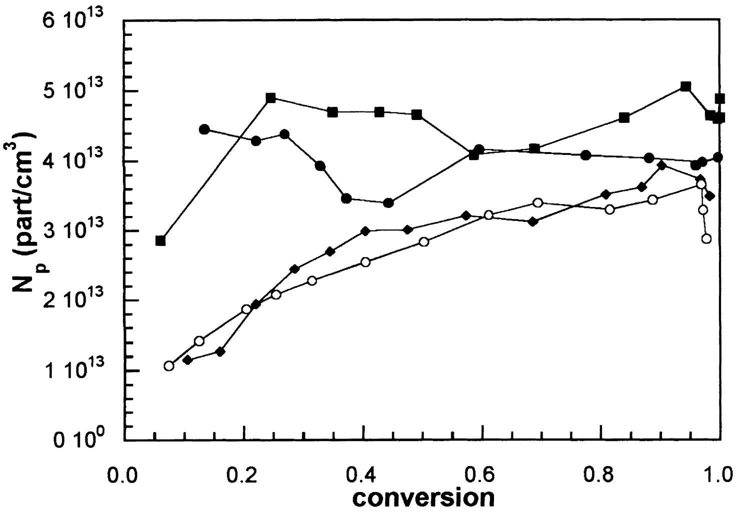


Fig. 3. Time evolution of number of particles in batch mode. (●) B-∅, conventional emulsion; (■) B-∅S, sonicated with no hydrophobe; (○) B-H, 2% HD; (◆) B-P1a, 1% PVAc.

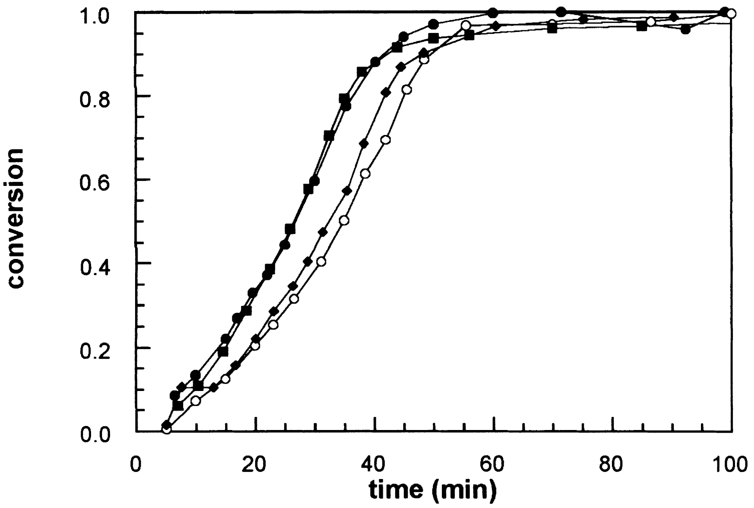


Fig. 4. Effect of the time elapsed between sonication and polymerization on the conversion evolution of VAc polymerization in batch. (●) B-∅, conventional emulsion; (○) B-H, 2% HD; (◆) B-P1a, 1% PVAc (15 min); (■) B-P1b, 1% PVAc (45 min).

usual pseudoplastic behavior. However, miniemulsion latex has lower viscosity than emulsion.

Fig. 7 shows the weight particle size distribution of both latexes, measured by BI-DCP. It can be observed that the size distribution of the miniemulsion is much broader than the emulsion. Due to the quite short nucleation period of conventional emulsion, most of the particles are formed at the same period of time, and they have a similar period to grow, leading to particles with rather homogeneous sizes. In the miniemulsion case, however, the broad distribution of monomer droplet size together with the longer nucleation period leads to such a broad particle size distribution, which conducts to a lower viscosity.

3.2. Continuous stirred tank reactor processes

3.2.1. Kinetics

In the experiments made in batch mode, it was demonstrated that the presence of small monomer droplets during a short period of time could be enough to change the nucleation mechanism with respect to the conventional emulsion (run B-P1a). Furthermore, Aizpurua et al. [1] verified that nucleation mechanism change could influence the dynamics of the VAc emulsion polymerization strongly in a CSTR. Therefore, in this part, the effect of the sonication itself — without any hydrophobe — which could create small monomer droplets during a short period of time, and the behavior of different polymeric hydrophobes, able to stabilize the monomer droplets, on the dynamics of the high solids content emulsion polymerization of VAc in the CSTR will be presented. In addition, the effect of the sole presence of hydrophobe, without any emulsification process, will be discussed.

3.2.1.1. Effect of the sole presence of hydrophobe. From an industrial point of view, the high energy required for the

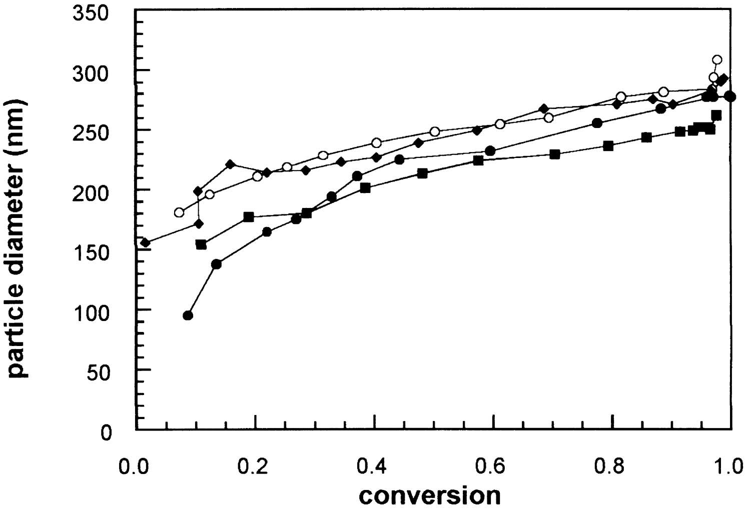


Fig. 5. Effect of the time elapsed between sonication and polymerization on the particle size evolution of VAc polymerization in batch. (●) B-∅, conventional emulsion; (○) B-H, 2% HD; (◆) B-P1a, 1% PVAc (15 min); (■) B-P1b, 1% PVAc (45 min).

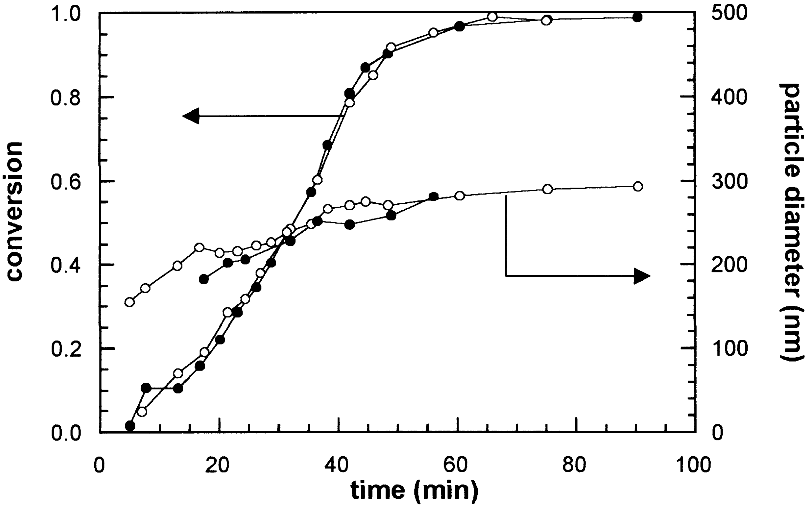


Fig. 6. Effect of the different polymeric hydrophobes on the batch emulsion polymerization of VAc. (○) B-P1a, 1% PVAc; (●) B-P2, 1% PS.

miniemulsification process increases the production costs. Furthermore, it can cause the mixing to be heated, which is not convenient because the reaction can start before entering the reactor. Therefore, the effect of adding polymer to a conventional emulsion was analyzed.

The evolution of the conversion and particle size of the conventional emulsion (C-∅) and the reaction where PVAc was added, without any emulsification process (C-P$), were compared (Fig. 8). Both of them show oscillations in particle size and there is almost no difference in conversion. Those results, therefore, verified that the sole presence of the polymeric hydrophobe does not change the polymerization rate and has no effect on nucleation, whence sustained oscillations persist.

3.2.1.2. Effect of the sonication. In the previous section, it was demonstrated that the batch reaction carried out after sonication, but without any hydrophobe (B-∅S) behaves as the conventional emulsion. In this process, the time elapsed between the sonication and polymerization was around 15 min, time enough for the small droplets to diffuse into the big ones. In the CSTR system, however, the time elapsed between the sonication chamber and the reactor can be much lower (about 1 min in this work), maybe allowing the droplets to maintain their kinetic stability. In order to check this hypothesis, a reaction with a sonicated emulsion without any hydrophobe was carried out (C-∅S).

Table 4
Rheological behavior of emulsion (B-E) and miniemulsion (B-M) produced in batch reactor

	Emulsion	Miniemulsion
Conversion	0.95	0.97
Particle diameter		
$\bar{d}_n$	269 nm	406 nm
$\bar{d}_w$	298 nm	430 nm
Viscosity		
$\omega = 6$ rpm	720 cp	525 cp
$\omega = 12$ rpm	447 cp	338 cp
$\omega = 30$ rpm	256 cp	198 cp
$\omega = 60$ rpm	173 cp	133 cp

The time evolution of the conversion of this reaction (Fig. 9) shows nearly the same conversion as the conventional emulsion (C-∅) and the miniemulsion stabilized with HD (C-H), although miniemulsion (C-H) presents a slightly lower value. However, great differences can be seen in the particle sizes. Whereas conventional emulsion (C-∅) shows great oscillations in particle diameter, a stable particle diameter is obtained in miniemulsion (C-H). The reaction sonicated without any hydrophobe (C-∅S) also presents oscillations, although with a smaller amplitude. Even if small droplets are formed when the emulsion is sonicated, they disappear very quickly due to Ostwald ripening and nucleation takes place mainly in monomer-swollen micelles. This means that sonication is not enough to avoid oscillations, although the time elapsed between the sonication chamber and the reactor is very small.

3.2.1.3. Effect of the polymeric hydrophobe. In the batch experiments, it was shown the positive effect of the polymeric hydrophobe as cosurfactant on stabilizing the monomer droplets, when the time elapsed between sonication and polymerization is low. This point suggested the possibility of using this hydrophobe to stabilize the monomer droplets in the CSTR process. Fig. 10 reproduces the evolution of the conversion and mean particle size for the miniemulsion (with sonication) carried out with PVAc (C-P1) and with PS (C-P2) as the only hydrophobe. For the sake of comparison, the conventional emulsion (without sonication) (C-∅) and miniemulsion (C-H) are also displayed.

Although the time evolution of the conversion presents a similar behavior, with no apparent oscillations, the differences on the dynamics appear clearly when the particle

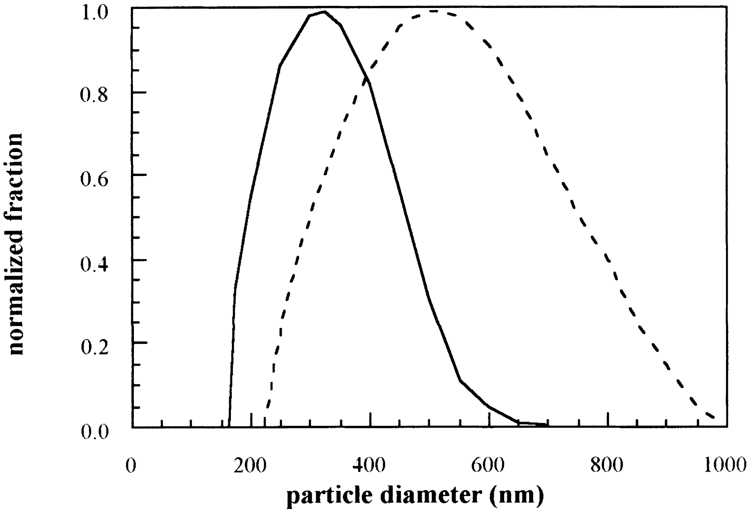


Fig. 7. Weight particle size distribution of batch emulsion (run B-E) (—) and miniemulsion (run B-M) (- - -).

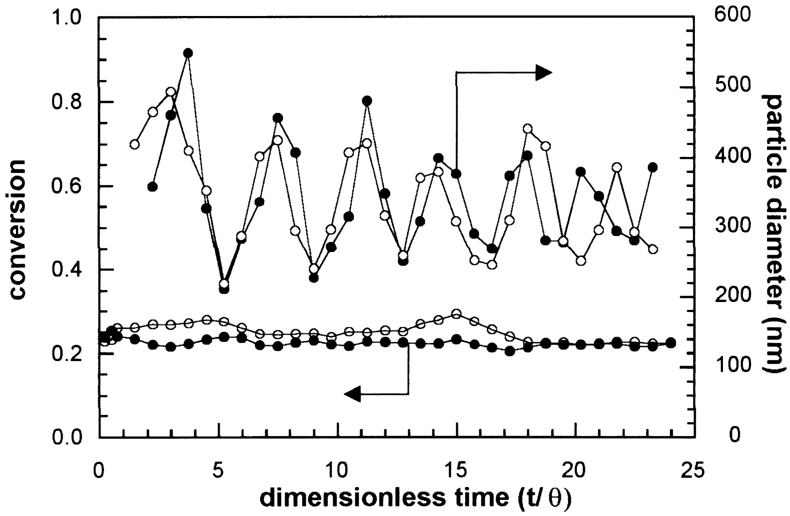


Fig. 8. Effect of the sole presence of hydrophobe on the kinetics of VAc emulsion polymerization in CSTR reactor. (●) C-∅, conventional emulsion, (○) C-P$ reaction with 1% of PVAc but not sonicated.

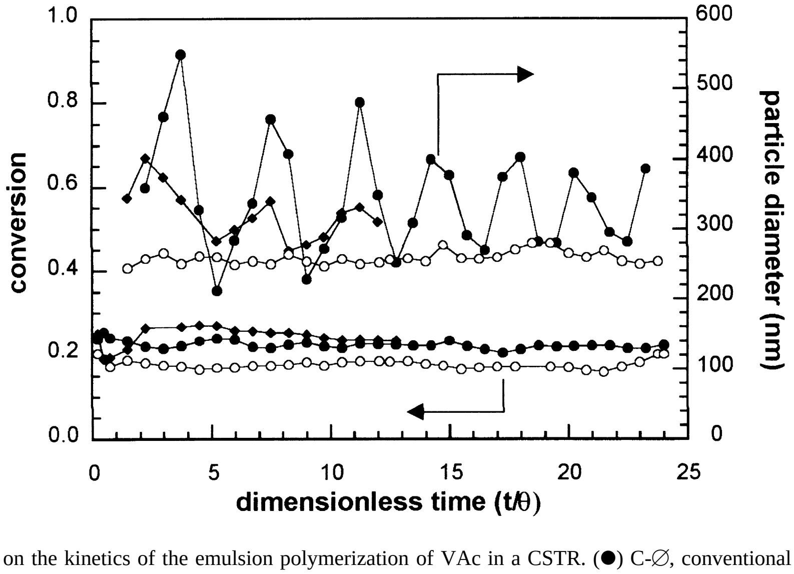
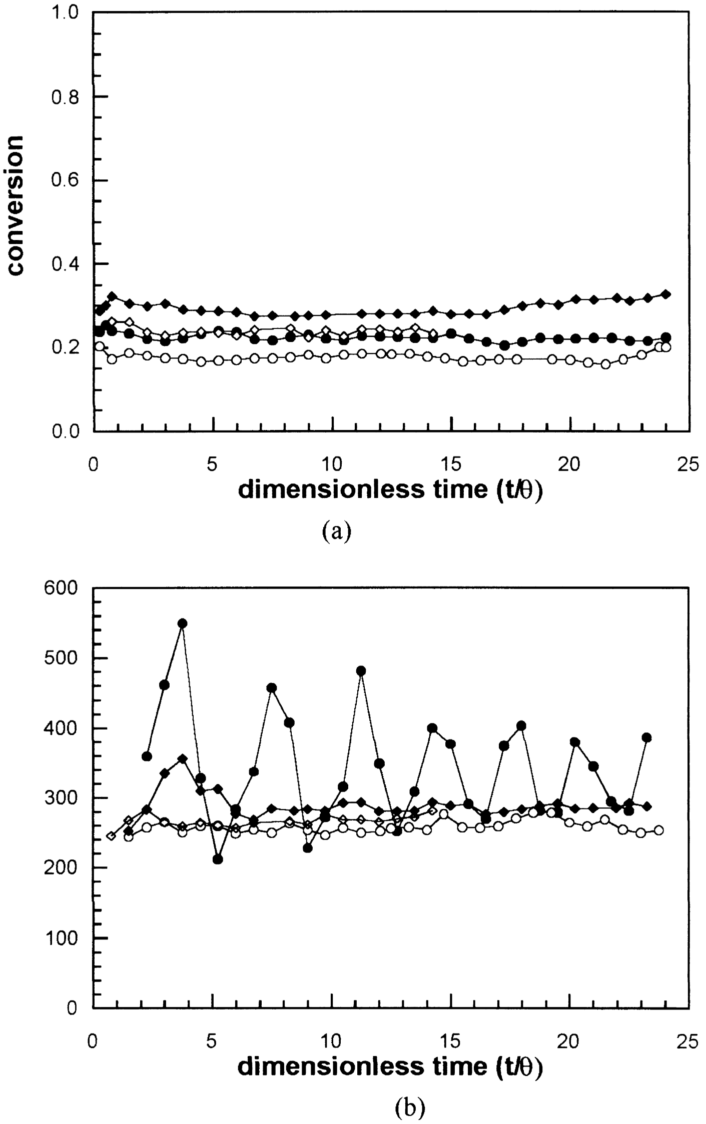


Fig. 9. Effect of the sonication on the kinetics of the emulsion polymerization of VAc in a CSTR. (●) C-∅, conventional emulsion, (◆) C-∅S sonicated conventional emulsion, (○) C-H 2% hexadecane.



(a)

(b)

Fig. 10. Effect of the polymeric hydrophobe on the conversion (a) and particle size (b) of VAc emulsion polymerization in CSTR. (●) C-∅, conventional emulsion;. (○) C-H, 2% hexadecane; (◆) C-P1, 1% PVAc, (◇) C-P2, 1% PS.

diameter evolution is analyzed. The miniemulsions prepared with polymeric hydrophobe present a stable dynamic, similar to the conventional miniemulsion, whereas the emulsion has big oscillations. Those results indicate that the polymeric hydrophobes can be used instead of the traditional low-molecular-weight cosurfactants to obtain steady-state operation in CSTR emulsion polymerization, also when high solids content processes are carried out.

3.2.2. Rheological analysis

Polymerizations in dispersed media in CSTRs yield broad particle size distributions due to the different residence time of each particle in the reactor. Both emulsion and miniemulsion processes should produce broad particle distributions when polymerized but the different nucleation mechanism could change the properties of the latex at the beginning of the polymerization process.

In the initial stage of the high solids content emulsion polymerization, the increase in viscosity can be very high if the particles are small and the distribution very narrow. This phenomenon can cause mixing and heat-transfer problems, producing thermal runaway and coagulum formation.

In this section, the feasibility of the miniemulsion to overcome this initial problem wanted to be checked. Two 60 wt% solids content emulsion and miniemulsion polymerization were carried out in a CSTR, following the recipe given in Table 3. The evolution of the conversion of both reactions is almost the same and close to complete conversion.

In Fig. 11, the evolution of viscosity for both reactions is plotted. Viscosity is almost constant for miniemulsion polymerization but it is about five times higher for emulsion at the beginning of the reaction. Viscosity of emulsion

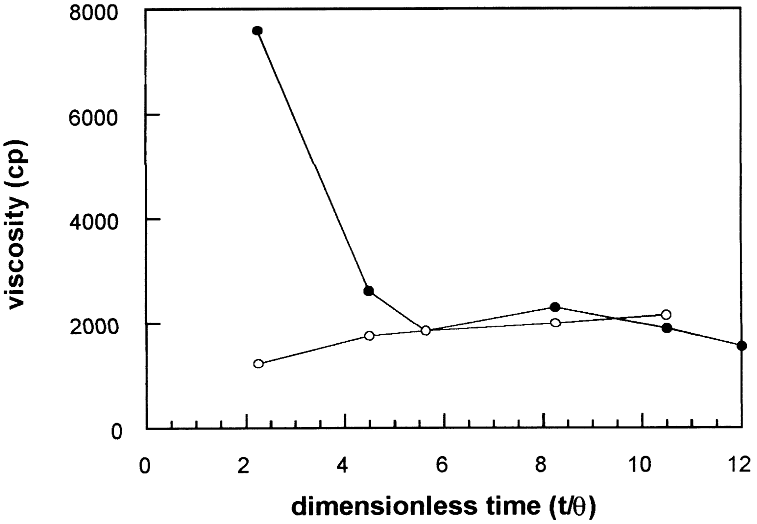


Fig. 11. Time evolution of viscosity in high solids content VAc reactions polymerized in a CSTR. (●) C-E, emulsion; (○) C-M, miniemulsion.

decreases to the same values of miniemulsion as reaction goes on. This phenomenon can be explained looking at the particle size distribution. Fig. 12a shows the particle size distribution for emulsion and miniemulsion at a residence time value of three. The initial miniemulsion particles are bigger and the distribution is broader than the emulsion, thus leading to a lower viscosity. As particles are washed out from the reactor and a new nucleation begins in the emulsion process, due to the oscillatory behavior of the system, particle size distribution is broader and viscosity decreases. As reaction goes on, there is almost no difference between emulsion and miniemulsion particle size distribution as shown in Fig. 12b (samples taken at a residence time value of 10.5), and consequently, the viscosity is similar.

4. Conclusions

In this work, the dynamics of high solids content miniemulsion polymerization of VAc produced in a CSTR, with different type of hydrophobes and emulsification procedures, has been extensively studied. In order to gain more insight into the process, a preliminary study in a batch reactor has also been carried out.

From the experiments made in the batch mode, some interesting conclusions were obtained. On the one hand, it was seen that the small droplets created after sonicating the conventional emulsion suffered from diffusion degradation immediately after homogenization, causing a net decrease in the droplet surface area. As a result, the principal locus of nucleation was likely the monomer-swollen micelles. Furthermore, it was demonstrated that the PVAc as the sole hydrophobe, after sonication, is able to create miniemulsions, as far as the time elapsed between sonication and polymerization is minimized. The same result was obtained when PS was used as hydrophobe. In this way, those polymeric hydrophobes could be used as an alternative to the traditional cosurfactants, as HD, in order to reduce in some extension the low molecular weight contamination and the plasticizing effect. Finally, the rheological study showed that miniemulsions have lower viscosities due to the broader particle size distribution.

The experiments carried out in the CSTR showed the feasibility of miniemulsions to eliminate the oscillatory behavior of CSTR reactors at high solids content. It was seen that the only addition of hydrophobe to the conventional emulsion was not enough to avoid the oscillations. It was also observed that sonication of the conventional emulsion did not avoid the oscillatory behavior, although the time elapsed between the sonication chamber and the reactor was very small. Furthermore, it was observed that polymeric hydrophobes such PVAc and PS were able to stabilize the monomer droplets and allow the system to behave as a miniemulsion during the continuous process.

The different rheological behavior shown by both processes in the CSTR at high solids content at the beginning of the reaction, where the viscosity of the miniemulsion is about five times lower than the conventional emulsion, presents the miniemulsion process as a very useful tool to improve the initial mixing and to avoid heat-transfer problems, both present in high solids content conventional emulsion polymerization process.

The above conclusions should be of significance when large-scale emulsion polymerization processes are considered. The reduction (or elimination) of the oscillatory behavior during a CSTR process should give a more uniform product quality. The reduced viscosity of miniemulsion compared to conventional emulsion is an important factor when energy balance is considered in an industrial-scale process.

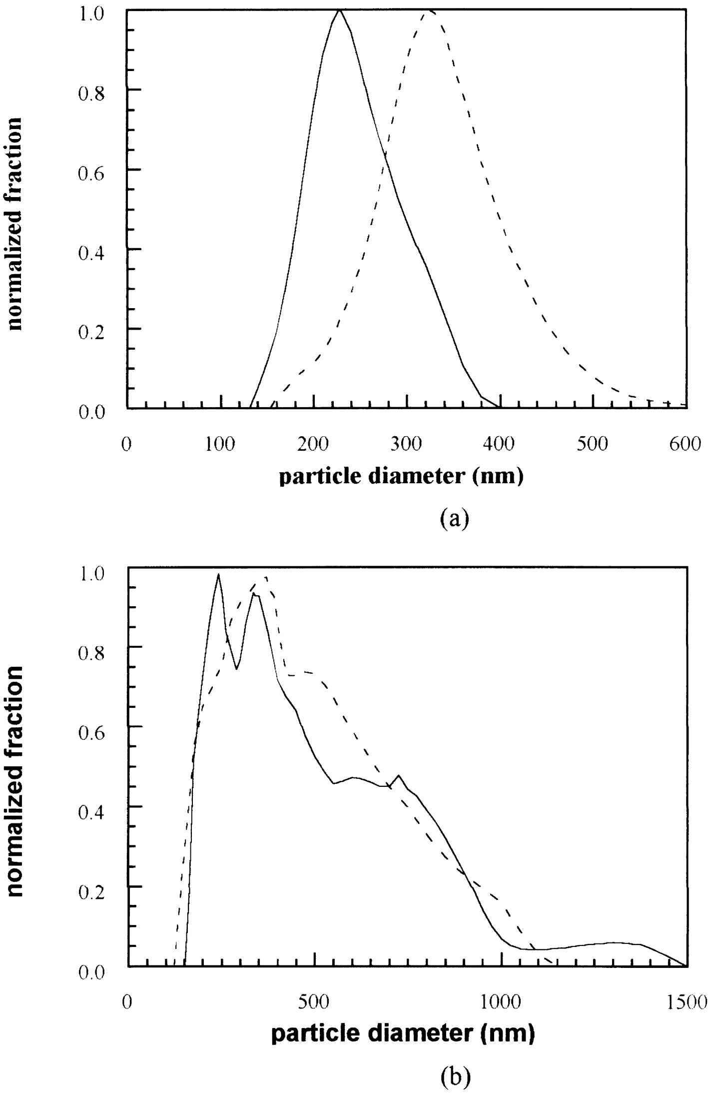


Fig. 12. Particle size distribution of samples withdrawn at (a) $t/\theta = 3$ and (b) $t/\theta = 10.5$. for emulsion (—); and miniemulsion (- - -) of VAc carried out in a CSTR.

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