Emulsion Copolymerization in a Tubular Reactor

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ABSTRACT: A study was conducted on the emulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor. It was performed at a constant temperature of 60°C and at different fluid velocities and feed compositions. Conversion, particle size distribution, and copolymer composition were measured, respectively, with gravimetric method, laser light scattering, and nuclear magnetic resonance. Maximum conversions were found for each of the monomer compositions; this maximum conversion varied, however, with the recipe used. The amount of butyl acrylate has a direct effect on the number of particles and on the final conversion. In lower levels of butyl acrylate particle size distribution is wide and bimodal. High levels of butyl acrylate leads to narrow and monomodal particle size distribution. Therefore the level of butyl acrylate and the velocity of fluid flowing inside the tube have strong effects on the shape (monomodal-bimodal) and the width of particle size distributions. This effect may vary at different levels of butyl acrylate and flow rate. The results obtained from copolymer composition show that an alternating block copolymer is made during the reaction. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 833–842, 2000

Key words: copolymerization, emulsion, butyl acrylate, vinyl acetate, tubular reactor

INTRODUCTION

Emulsion polymerization has been well studied in batch systems and to a lesser extent in continuous stirred tank reactors (CSTRs); however, there has been very little work done with tubular reactors. This is surprising in the light of potential advantages of such a system.

In 1939, Mark[1] was the first to use a tubular reactor, and in 1946 Calcott and Starkweather[2] improved the reactor. Emulsion copolymerization of styrene and butadiene was done by Feldon et al.[3] in laminar flow. Lanthier[4] in his patent described a continuous loop recycle reactor in which the recycle loop flow rate was much greater than the reactor feed flow rate. A plug flow reactor (PFR) was used to produce seed particles for a CSTR by Ueda et al.[5] Ghosh and Forsyth[6] used a tubular reactor for polystyrene and formulated a model. Rollin et al.[7] studied the influence of the Reynolds number on the rate of polymerization of polystyrene in a closed-loop reactor. Vatanatham and Forsyth[8] studied the emulsion copolymerization of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) in a tube. Rollin et al.,[9] for the first time, used a helical reactor in open loop. In 1981, Lynch and Kiparissides[10] simulated the turbulent experiments of Rollin et al.[7] Lee and Forsyth[11] studied the seeded polymerization of vinyl acetate in the reactor built by Vatanatham and Forsyth.[8] Bataille et al.[12] studied the copolymerization of styrene and α-methyl styrene in an open-loop reactor. Lee and Poehlein[13] used a Teflon-coated tubular reactor as a seed reactor for a CSTR. Shoaf and Poehlein[14] studied the copolymerization of ethyl acrylate and methacrylic acid in batch, CSTR, and tubular reactors. Bataille and Dalpé[15] studied the polymerization of vinyl acetate in a closed-loop reactor. Lee et al.[16] investigated the polymerization of styrene in a
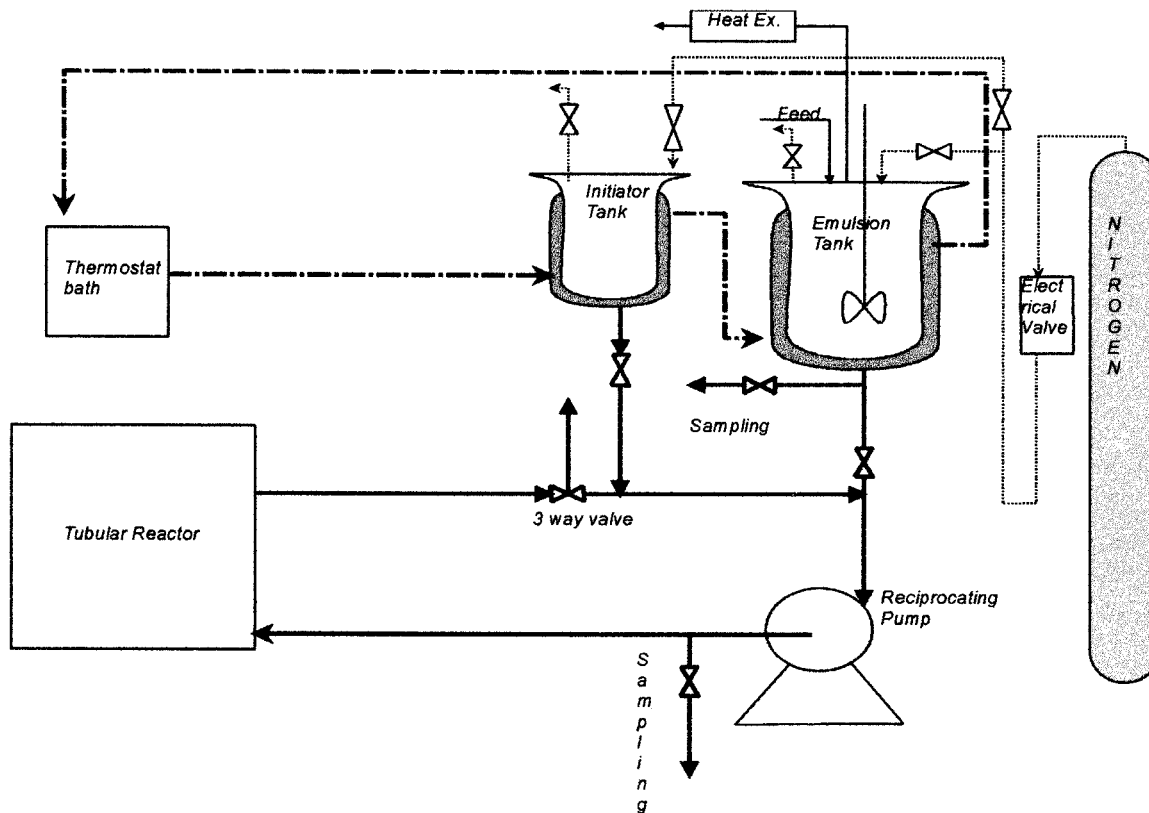
Figure 1 Reactor design.

continuous recycle reactor. Paquet et al.[17,18] studied emulsion polymerization in a pulsed tubular reactor. They performed their experiments in batch, CSTR, closed-loop, and a pulsed open-loop tubular reactor. Iabbadène and Bataille[19] studied the emulsion polymerization in a pulsed tubular reactor.

No work, however, is reported on the emulsion copolymerization of vinyl acetate-butyl acrylate in a tubular reactor. The object of this paper is to fill this gap and try to understand how and why the polymerization operating conditions will affect the polymer properties.

Reactor Geometry

Most of the studies mentioned here have been done in essentially straight tubular reactors, the curved parts (the elbows) constituting only a very small proportion of the total length. A reactor of commercial interest operated with a Reynolds number in the vicinity of 2100 would be of the order of 60–600 meters in length depending on the tube diameter. The benefits of good heat transfer and temperature control of emulsion polymerization are generally realized by the immer-

sion of the reactor in a heat transfer medium of substantial thermal capacity. This is difficult and costly to achieve with a linear tubular reactor and a helical configuration; however, it might be considered as a viable alternative. According to the works of Eustice,[20] Dean,[21] Taylor,[22] and Srinvasan et al.[23] the curvature of the tube decreases flow perturbations and increases the value of the Reynolds number at which the laminar-turbulent transition occurs. Iabbadène[24] calculated this critical Reynolds number in the vicinity of 7500 and in this work this calculation is used as a basis to design the reactor and operation.

EXPERIMENTAL

Tubular Reactor

All experiments were done in the tubular reactor shown in Figure 1. This system consists of an emulsion tank, an initiator tank, a purging system, a heat exchanger, a tubular reactor, a reciprocating pump, and a data acquisition system. The emulsion tank with a capacity of 3 L was jacketed and equipped with a pitch blade (P-6)

Table I Recipes Used in Experiments Based on 100 Parts of Vinyl Acetate and Butyl Acrylate

Material	Recipe 1	Recipe 2	Recipe 3
Vinyl acetate (monomer)	95	85	75
Butyl acrylate (monomer)	5	15	25
Distilled water	321.8	321	324.7
Sodium lauryl sulfate (surfactant)	1.75	1.75	1.75
Potassium persulfate (initiator)	0.24	0.24	0.24
NOPCO (Antifoaming agent)	10 drops	10 drops	10 drops

impeller and with four vertical baffles that were 10 mm in width, 200 mm in length, and 1 mm clearance to help better mixing. The initiator tank with a capacity of 1 L was also jacketed. Each tank had openings for thermocouples, feeding, nitrogen inlet, mixer shaft, and for a heat exchanger.

The thermostat bath is a cylindrical glass vessel that is used to heat the jacketed vessel to the desired temperature.

The tubular reactor is a 5-m Teflon-lined tube with an 2.23-cm inside diameter (ID) surrounded by a stainless steel mesh, 43 cm coiled, placed in a thermostat bath, equipped with a calibrated reciprocating pump. The reciprocating pump permits to change the velocity of the circulating fluid by changing the pump speed. Temperatures of different sites of the system are recorded by means of a data acquisition system. Each part of the system can be purged separately with nitrogen.

Materials

Inhibited monomers, vinyl acetate (VAc) and butyl acrylate (BuA), and the other materials were used as received. The general formulations used are given in Table I.

Procedure

Emulsifier was dissolved in 1000 mL distilled water together with 10 drops of an antifoaming agent, NOPCO, from Heukel Corp. The initiator was dissolved in 200 mL distilled water. All parts of the system including tubes, emulsion tank, and initiator tank were purged with nitrogen. The solution of emulsifier, and the required amounts of vinyl acetate, butyl acrylate, and 1500 mL of distilled water were poured inside the emulsion tank. Emulsification was performed using the mixer, and continued for 50 min to make sure the emulsification was complete. The emulsion was then transferred to the tube. The reciprocating pump was turned on

and set at the highest speed in order to reach quickly 60°C. This took between 15 and 25 min depending on the recipe. When the temperature in the tube reached 60°C, the pump was set at the desired speed to obtain the required Reynolds number. The liquid was mixed for about 30 min so that it reaches a constant velocity profile. After this period, the warmed initiator solution was injected inside the tube by means of nitrogen exerted through the initiator tank. This is considered as t = 0 for the emulsion copolymerization. The copolymerization proceeds for up to 2 h. During the reaction, samples were collected through the sampling valve and the reaction short-stopped with hydroquinone. Finally the pump was turned off and the produced latex was discharged through the sampling valve. The three-way valve was opened and the entire system was washed with water.

Collected samples were analyzed for conversion, particle size distribution, and copolymer composition. Particle size distribution was measured by using a laser light scattering from Brookhaven Instruments Corporation (Holtsville, NY), connected to a BIMODAL-203AT digital correlator, where the data could be collected. For this analysis, dust-free doubled-distilled water was used. The measurements were carried out by maintaining the samples in a paraffin bath at 25°C. The data obtained from this instrument was processed in order to have a distribution curve based on the particles fraction.

A Brucker (Billerica, MA) WH400 spectrometer (400.13 MHz) was used to obtain the molar composition of latex by nuclear magnetic resonance (NMR) spectra. Knowing the CH group resonance in vinyl acetate (5.22 ppm) and -O-CH$_2$ group resonance in butyl acrylate (4.13 ppm), the composition was calculated from the area under each peak.[25]

Reynolds numbers of 6500, 7500, 8600, and 9700 were applied to each set of experiments. The
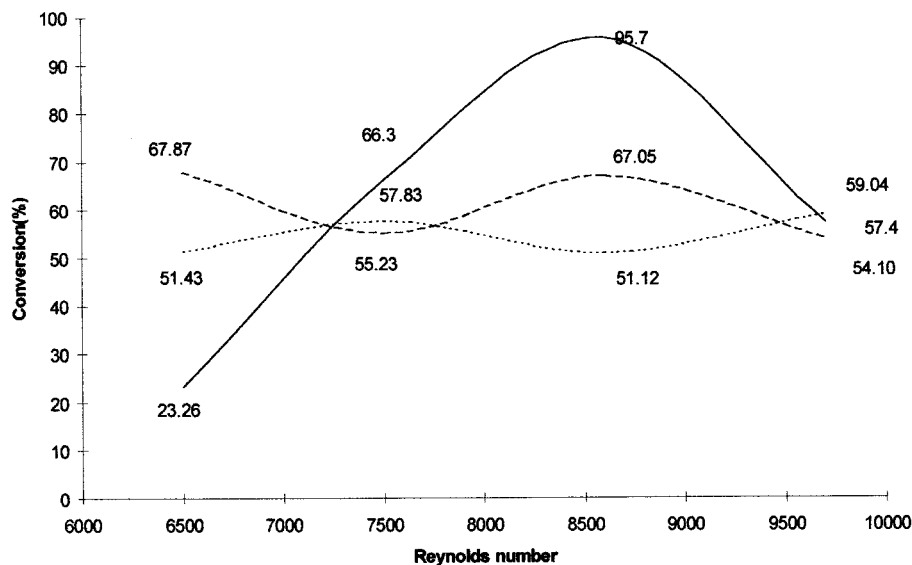
Figure 2 Total conversion as a function of Reynolds number in the emulsion copoly-merization of vinyl acetate and butyl acrylate. Vinyl acetate-Butyl acrylate ratios: (—) 95/5, (····) 85/15, (- - ---) 75/25.

reciprocating pump was calibrated with water at 60°C.

RESULTS AND DISCUSSION

Conversion

Iabbadène and Bataille[19] showed that in emulsion copolymerization of vinyl acetate a maximum conversion was reached in the laminar-turbulent transition flow region. The copolymerization of vinyl acetate and butyl acrylate treated in a similar way and the results for final conversion versus Reynolds number are given in Figure 2. The results of each of the monomer feed compositions are given in this figure.

The results of experiments with tubular reactor compared with those in batch rectors[26] show that the conversion obtained in tubular reactor are below the conversion obtained in the batch reactor.

In all cases maxima are obtained. The location and the amplitude of these maxima are functions of the feed composition and the agitation.

With 5% wt of butyl acrylate the maximum is in the turbulent flow region with a conversion of about 96% wt. When the concentration of butyl acrylate is increased to 15% wt two maxima appear with, however, a decrease in conversion to about 67%. Interesting enough, one of the maxi-

mum occurs in the turbulent flow region, suggesting two different reaction mechanisms. When the level of butyl acrylate is increased to 25% wt we have a further flattening of the conversion curve but again two peaks appear, one in the laminar flow region and the other in the turbulent flow region.

By increasing the amount of butyl acrylate in the feed one can notice a shift of the maximum conversions towards the turbulent flow region. The butyl acrylate has a negative effect on the final conversion in some regions and a positive effect in other regions.

Plotted in Figures 3 and 4 are the number of particles in one drop of laser light scattering sample as a function of time at laminar-turbulent transition flow region and turbulent flow, and at three levels of monomer feed compositions. For the laminar-turbulent transition flow system (Fig. 3) the number of particles produced is the highest when the feed composition is at 5% wt butyl acrylate and 95% wt vinyl acetate. As the butyl acrylate is increased to 15% wt and then to 25% wt, there is a general drop in the number of particles formed. This type of ordering is similar to the one for the final conversion given in Figure 2. For the turbulent flow as shown in Figure 4, the highest level of particles is obtained initially with 15% wt butyl acrylate and 85% wt vinyl acetate after 20 min; however, the order of importance of the
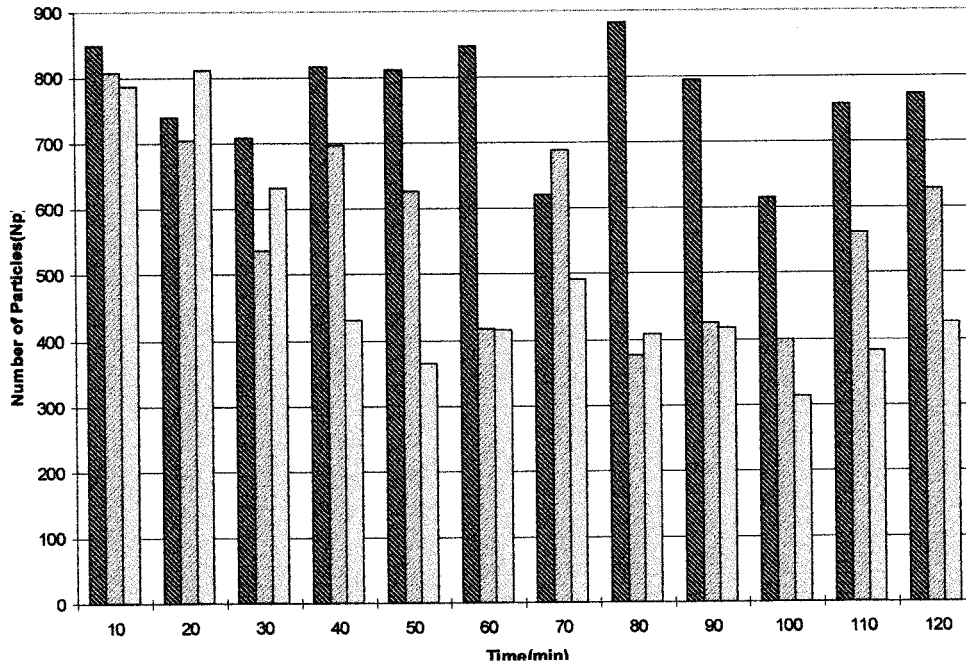
Figure 3 Number of particles at different times of reaction [Re = 7500, laminar-turbulent transition flow]. Vinyl acetate -Butyl acrylate ratios: (▨) 95/5, (▨) 85/15, (▨) 75/25.

number of particles formed reverts back to the one formed for the laminar-turbulent transition flow. It could be said that in tubular reactor the amount of butyl acrylate in system has a direct effect on the number of produced particles and on final conversion.
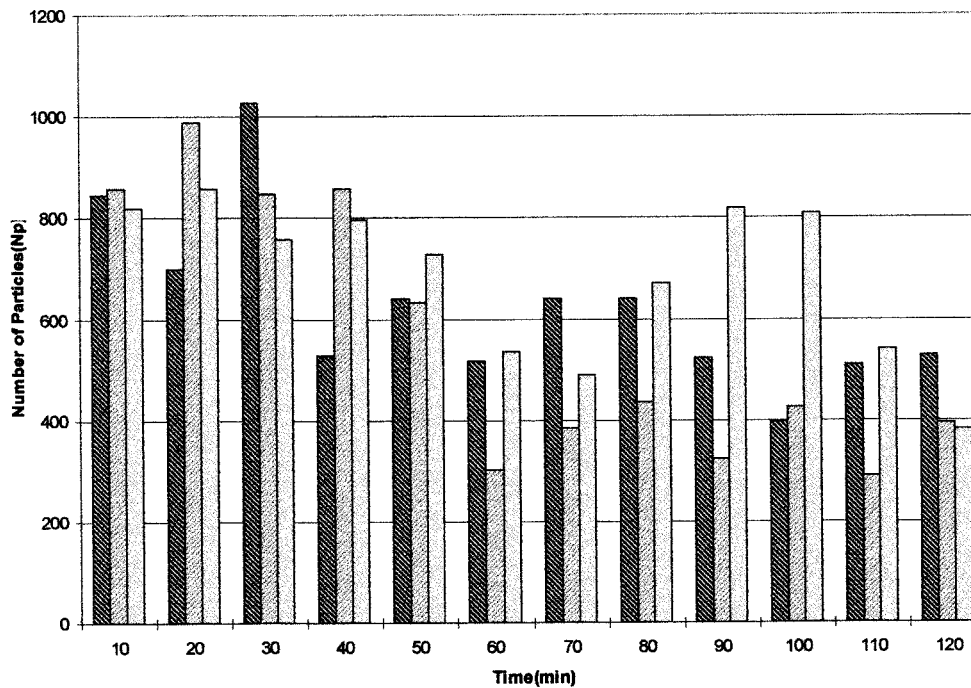
Figure 4 Number of particles at different times of reaction [Re = 9700, highly-turbulent flow]. Vinyl acetate -Butyl acrylate ratios: (▨) 95/5, (▨) 85/15, (▨) 75/25.
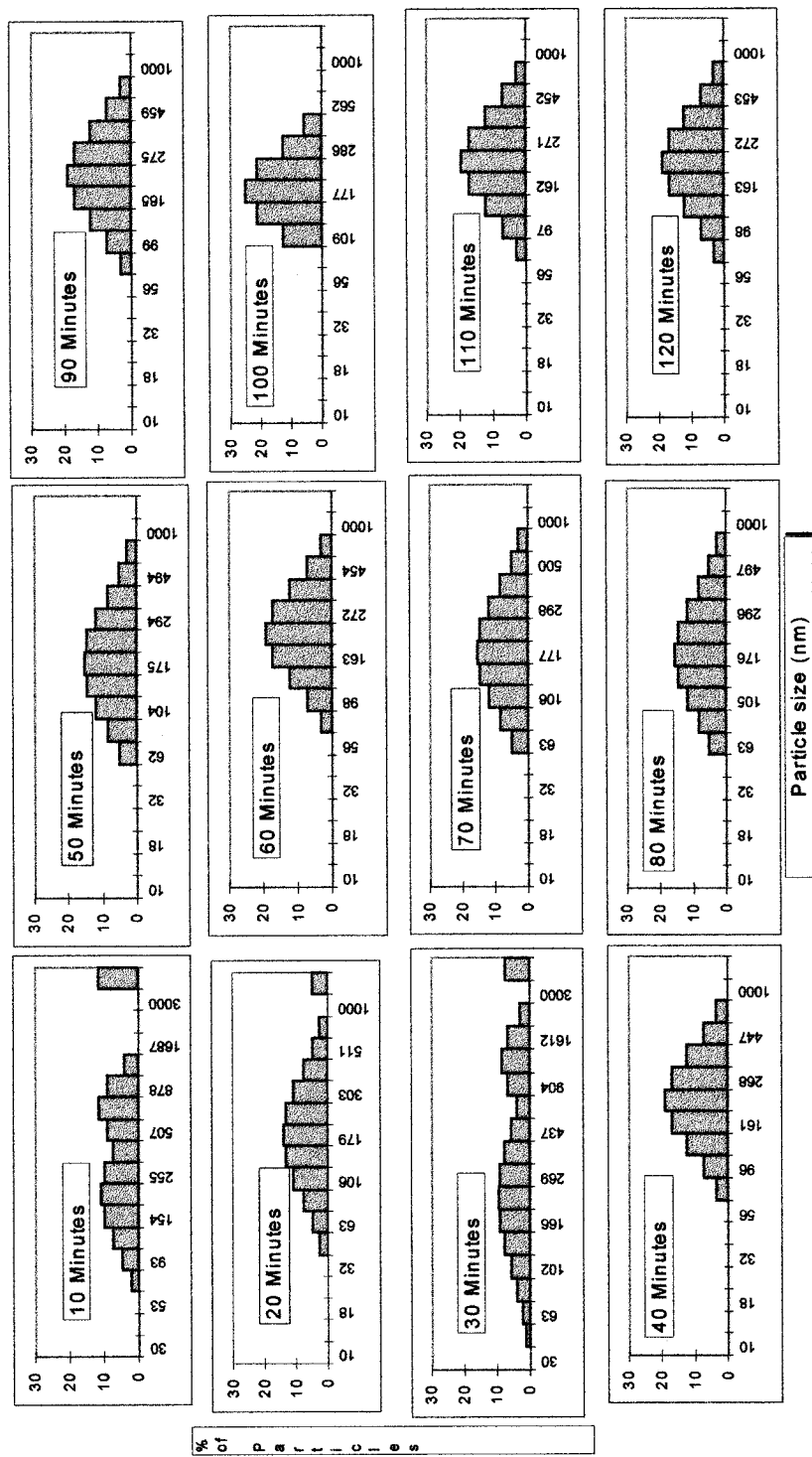
Figure 5 The evolution of particle size distribution in emulsion copolymerization of 95wt % vinyl acetate and 5 wt % butyl acrylate in highly-turbulent flow (Re = 9700).
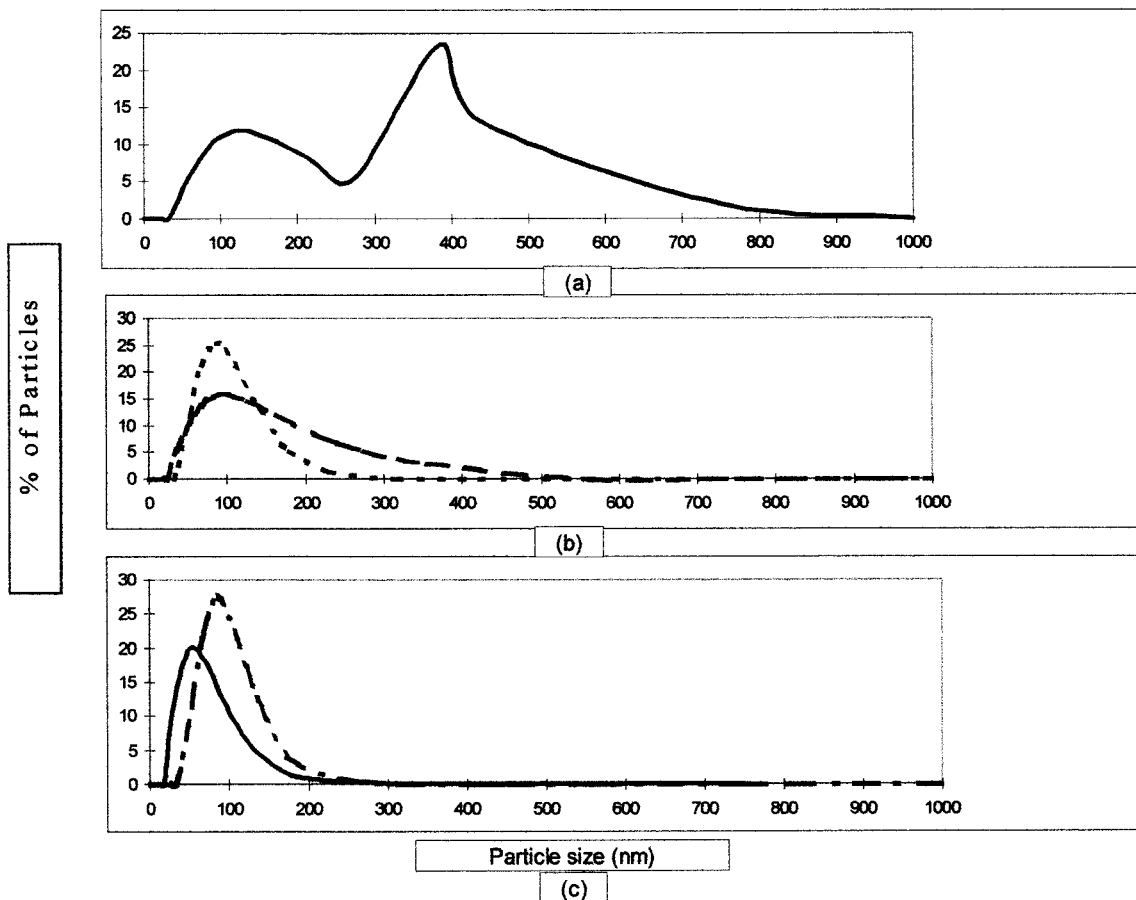
Figure 6   Final particle size distributions related to the cases with maximum conversion. (a) 5 wt % butyl acrylate, (——) Re = 8600; (b) 15 wt % butyl acrylate, (- - - -) Re = 7500, (····) Re = 9700; (c) 25 wt % butyl acrylate, (- - - - -) Re = 6500, (——) Re = 8600.

Particle Size

### Particle Size Distribution

The evolution of particle size distribution was monitored continuously during the reaction. Secondary nucleation was observed as a bimodal particle distribution appeared during the early stages of the polymerization. This is shown in Figure 5 for the system of 5% wt butyl acrylate and 95% wt vinyl acetate in the feed at a highly turbulent flow (Re = 9700). The existence of secondary nucleation confirms that there is homogeneous nucleation during the emulsion copolymerization due to the water solubility of vinyl acetate.[27]

All the particle size distributions related to high conversion conditions in different compositions of feed were compared in Figure 6. In this figure it can be seen that the final latex in reaction with 95 wt % vinyl acetate and 5 wt % butyl

acrylate has a broad and bimodal particle size distribution. However the final latex of 85 wt % vinyl acetate, 15 wt % butyl acrylate, and 75 wt % vinyl acetate, 25 wt % butyl acrylate have both narrow and monomodal particle size distribution. In reaction with 85 wt % vinyl acetate it is seen that there is always two different flow regions where a monomodal particle size distribution is obtained, but the particle size distribution obtained in highly turbulent flow is narrower than particle size distribution obtained in laminar-turbulent transition flow.

In case of 75 wt % vinyl acetate, also, both particle size distributions are monomodal but the one obtained in laminar flow is narrower than the one obtained in turbulent flow.

In general it could be said that in emulsion copolymerization of vinyl acetate and butyl acrylate in tubular reactor, in contrast to the batch reactors[26] and like semicontinuous reactors,[26] by
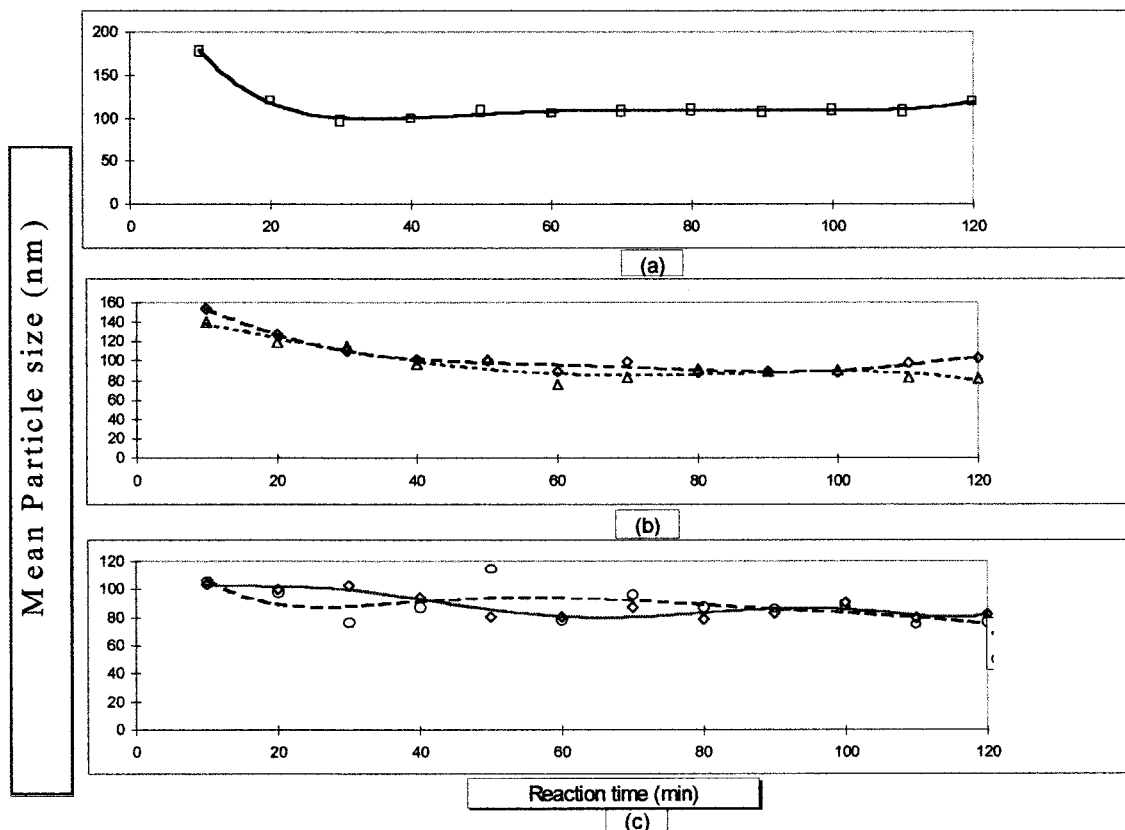
Figure 7 The evolution of mean particle size related to the cases with maximum conversion. (a) 5 wt % butyl acrylate, (□) Re = 8600; (b) 15 wt % butyl acrylate, (◇) Re = 7500, (△) Re = 9700; (c) 25 wt % butyl acrylate, (◇) Re = 6500, (○) Re = 8600.

increasing the quantity of butyl acrylate in feed a narrow particle size distribution is obtained. It was found that the amount of butyl acrylate and the velocity of fluid have strong effects on the shape (monomodal-bimodal) and on the distribution of the particle size. This effect may change with different butyl acrylate contents and fluid velocities. So, it could be said that in addition to the chemical composition of the feed, flow rate has also a dominant effect on the properties of final latex including particle size distribution and mean particle size.

Mean Particle Size

The evolution of mean particle size for the experiments with high conversions are shown in Figure 7.

In all three cases, mean particle size decreases during the reaction and reaches a nearly constant value. Clearly, the amounts of butyl acrylate in the feed and also the fluid velocity have a strong effect on the mean particle size. In all three plots

it can be seen that, like semicontinuous[27] and in contrast to batch reactor,[28] by increasing the butyl acrylate in feed, final mean particle size tends towards smaller diameters.

It is proposed that in all cases during the course of reaction secondary nucleation cause to have old and new particles. As the reaction proceeds the distribution of the new particles shifts gradually such that their average diameter tends towards the mean particle size of old particles. These results suggest the formation of new particles during the polymerization process. The proposed explanation is that, as the conversion in a particle milieu becomes unfavorable to the surfactant, the emulsifier is released permitting the creation of new micelles, and consequently, of new particles.

Copolymer Composition

The composition of the copolymer was monitored throughout the polymerization by NMR. Results for the system of 15% butyl acrylate and 85%
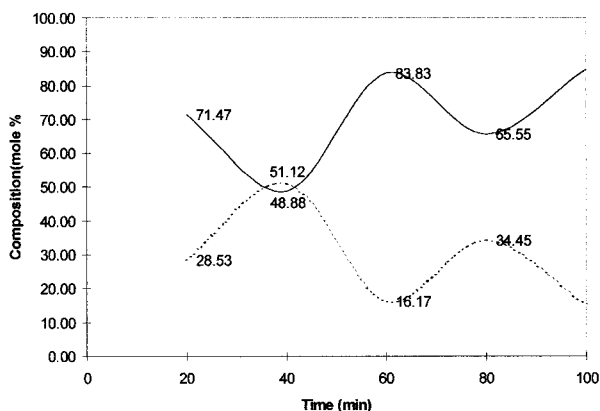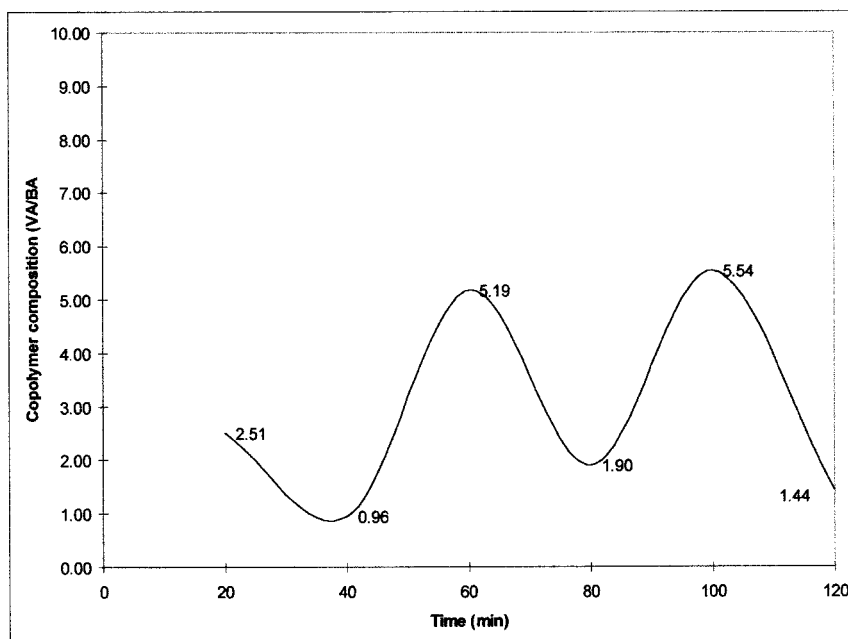
Figure 8 Copolymer composition of poly vinyl acetate-butyl acrylate latex made from feed containing 85 wt % vinyl acetate and 15 wt % butyl acrylate, in turbulent flow (Re = 8600). (——) % of vinyl acetate, (····) % of butyl acrylate.

vinyl acetate at turbulent flow are given in Figure 8. In regard to the reactivity ratios of vinyl acetate ($r_1 = 0.024$) and butyl acrylate ($r_2 = 10.67$),[25] it suggests that the polymer would be constituted of two long chains of vinyl acetate and butyl acrylate attached together, i.e., a block copolymer. Figure 8 shows that the vinyl acetate contents of copolymer sometimes increases and then decreases. This suggests that during the reaction an

alternating block copolymer is made. To confirm this idea the instantaneous copolymer composition was calculated from the NMR data. Instantaneous copolymer composition is being defined here as the ratio of vinyl acetate (electron donor) moles to the butyl acrylate (electron acceptor) moles in copolymer.[29] If instantaneous copolymer composition is between 1 and 2, the latex is an alternating copolymer, and if it exceeds to more than 2 the latex is an alternating block copolymer. Figure 9 confirms this idea. It is seen that during the progress of reaction instantaneous copolymer composition ratio gradually increases. It is suggested that the tendency of monomers to react changes during the reaction and blocks of vinyl acetate and butyl acrylate are made. Finally we can obtain a latex with an alternating block structure. In other words in a tubular reactor it is possible to decrease the composition drift and avoid the large composition drift existing with copolymerization in a batch reactor.[27]

CONCLUSION

Emulsion copolymerization of vinyl acetate and butyl acrylate was done in a tubular reactor at a constant temperature of 60°C and different fluid velocities and feed compositions. It was found

Figure 9 The evolution of instantaneous copolymer composition during emulsion copolymerization (85 wt % vinyl acetate and 15 wt % butyl acrylate), turbulent flow (Re = 8600).

that depending on the monomers composition in feed there is (are) region(s) where conversion is maximum. These regions are not the same for different recipes. Also it was found that the amount of butyl acrylate has a direct effect on the number of particles and on the final conversion. Studies on particle size distribution showed that recipes with lower quantities of butyl acrylate have a wide and bimodal particle size distribution for final latex, and recipes with higher butyl acrylate contents have a narrow and monomodal particle size distribution. So the amount of butyl acrylate and the velocity of fluid flowing inside the tube have strong effects on the shape (monomodal-bimodal) and the width of particle size distributions. This effect may varies in different butyl acrylate contents and fluid velocities. In investigating copolymer composition it was found that an alternating block copolymer is made during the reaction.

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