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Comparison of Vinyl Acetate - Butyl Acrylate Emulsion Copolymerizations Conducted in a Continuous Pulsed Sieve Plate Column Reactor and in a Batch Stirred Tank Reactor

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Summary: In this work, vinyl acetate/butyl acrylate emulsion copolymerizations carried out in a continuous tubular reactor (pulsed sieve plate column, PSPC) were compared to those conducted in a semibatch stirred tank reactor under similar operational conditions. In order to minimize the compositional drift along the PSPC, reactions were carried out with different numbers (2, 3 and 4) of lateral feed streams of the more reactive monomer (butyl acrylate). For comparison, fed batch reactions were conducted with the same number of intermittent shot additions of butyl acrylate, at the corresponding batch times. Both systems (tubular and semibatch) with distributed feeding of more reactive monomer are able to reduce composition drift thus providing more uniformity in copolymer composition. In addition, the tubular reactor presents much better control of temperature than the tank reactor, which is important to achieve higher productivity.

Keywords: computer modeling; copolymer composition control; copolymerization; emulsion polymerization; tubular reactor

Introduction

Many polymeric materials of large use, such as coatings, paints, varnishes and adhesives, are produced by emulsion polymerization processes. The main advantage of this kind of polymerization is the fact that it is performed in a heterogeneous medium using water as dispersing medium, thus facilitating the heat removal, and also reducing the contaminating waste products. The resulting product (called latex) is in form of nanometric particles composed by high molecular weight polymer. Because of this, this process presents many advantages in comparison to other free radical polymerization processes. In industrial scale, the emulsion polymerization processes are performed in stirred batch tanks or in semicontinuous stirred tanks as they provide high operational flexibility.[1] According to economical aspects, continuous processes are preferable for larger productions and for reducing quality fluctuations that can occur in batch processes. Continuous stirred tanks (CSTR) and tubular reactors are potential candidates for these cases. A potential advantage of tubular reactor over the stirred tank reactors is the larger area-to-volume ratios for enhance heat removal in highly exothermic polymerization processes. On the other hand, the possibility of reactor clogging (due to the viscosity increase in reaction medium) can weak these advantages.[2] This risk is higher for systems with low colloidal stability and with poor temperature control of the reaction medium. Furthermore, the reactor

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geometrical factors and limiting operational conditions enhance not only the clogging risk but also copolymer composition deviation and the presence of high temperature points along the continuos tubular reactor. Several studies [3–5] indicate an interesting option: a pulsed packed column (PPC) tubular reactor with the purpose of reducing these problems. These studies have emphasized that good local agitation, radial mixing and pulsation conditions in such reactors allow to reach considerably high conversions in relatively low residence time in comparison to a CSTR. However, risk of clogging and differences in temperature can occur. Simultaneously, other researches [6–10] developed a new tubular reactor type, a pulsed sieved plate column (PSPC), in which different internal devices (sieved plates), combined with pulsed (oscillatory) flow, are used to promote effective radial mixing, good local agitation, and good heat dissipation in tubular reactors.

Further studies have explored the possibilities of both PPC and PSPC for emulsion copolymerization processes. Scholtens et al.[11] studied the use of three lateral feeds of styrene (S) and methyl acrylate (MA) during an emulsion polymerization process performed in a pulsed packed column in order to produce S-MA particles with bimodal chemical composition distribution. The authors concluded that polymer with an intermediate chemical composition is obtained as a consequence of the applied backmixing in the PPC. Sallares et al.[12] carried out simulations of vinyl acetate (VA) and butyl acrylate (BA) emulsion copolymerization using a mathematical model that represents the PSPC tubular reactor. As these monomers present very different reactivity ratios, this system is prone to strong composition drift. Additional four lateral feedings along the tubular reactor may be used to control the copolymer composition and contributes to the production of copolymers with a desired composition. Furthermore, the authors also point out that temperature profiles could be used to reduce residence time, thus improving the process productivity. The simulation results presented in [12] were not compared to experimental data of batch, semi-batch, or continuous runs.

The present work investigates experimentally the effect of lateral monomer feed and the effect of reaction temperature along a pulsed sieved plate column on the performance of VA-BA copolymerization. The results are compared to those obtained in a batch process and a semibatch process. The semibatch process is carried out with intermittent monomer feeds, which are equivalent to the column lateral feed in the tubular reactor. In both cases, the more reactive monomer (BA) is added in the lateral feedings (tubular reactor) or in the intermittent feeds (semibatch reactor). In order to compare both processes, the times at which intermittent feeds are applied in the semibatch process are chosen as the corresponding value of space-time in the tubular reactor (or position of the lateral feeding along the tubular reactor divided by the average flow velocity). The main difference of this work in comparison to other previous ones is the fact that the results obtained from the continuous process were compared to a batch or a semibatch process under similarly equivalent operating conditions.

Pulsed Sieved Plate Column Reactor

The PSPC consists on five vertically mounted stainless steel sections, each one is 1000 mm long and 40 mm inner diameter. The plates, also made of stainless steel, have each one 39 holes placed in triangular arrangement, resulting in 23% of free area in each plate. Plate spacing between any two consecutive plates is 50 mm, resulting in a reactor void fraction of 95.7%. Figure 1 presents the tubular reactor used in this work. In order to prevent possible polymer deposits on reactor walls or on its internals (“fouling”) and, as a consequence, a possible reactor clogging, a pulsation is applied to axial flow. The pulsator is located at the

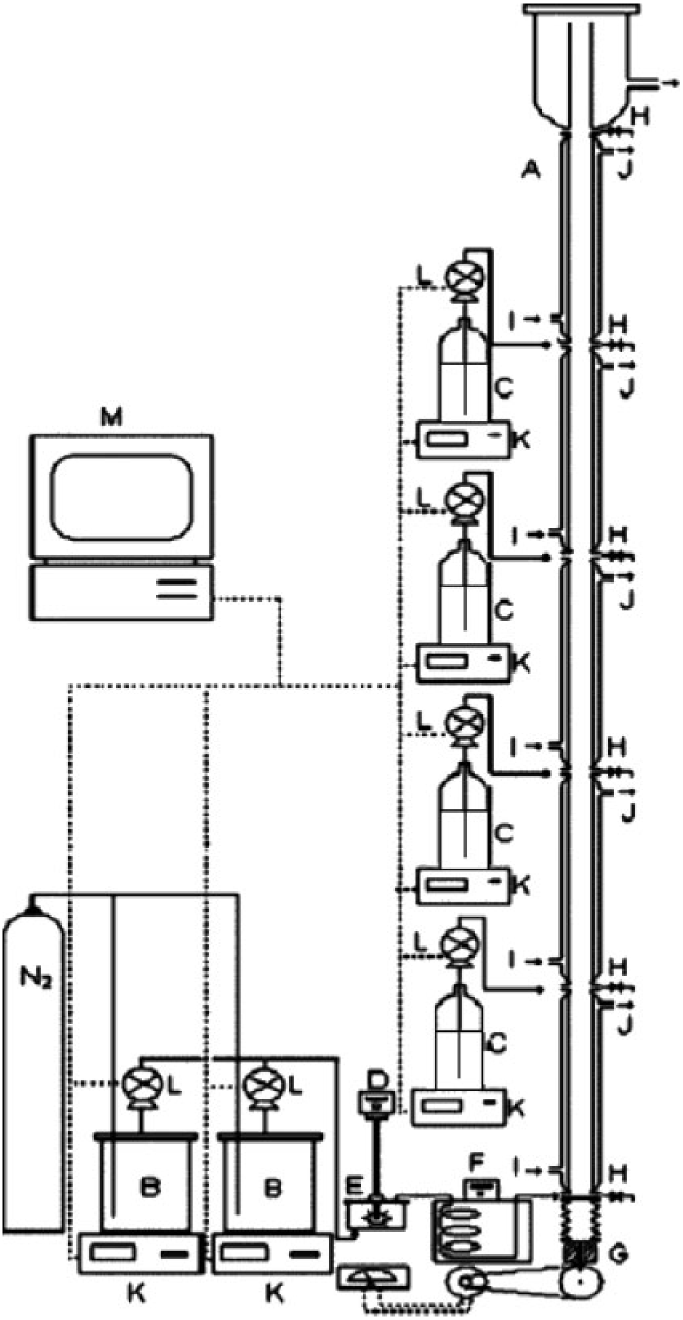

Figure 1.
Continuous Pulsed Sieve Plate Tubular Reactor: A-Reactor, B,C-feed tanks, D-agitator, E-pre-mixing tank, F-heater, G-pulsator, H-sampling points, I- jacket entrances, J- jacket outlet, K-balances, L-metering pumps, M-computer.

bottom of the column and the amplitude and frequency of pulses can be set to corresponding ranges from 5 to 25 mm and 0.2 to 3.5 Hz, respectively. The feeding flow rates of all reactants are controlled by a computer, using metering pumps and electronic balances.

In all runs performed in PSCP the temperature control was used only to keep the cooling jacket temperature constant (56–57 °C), and the temperature of the reacting fluid was not controlled.

Stirred Tank Batch Reactor

Figure 2 represents the automated experimental unit, which consists of a 3-liter jacketed stirred tank. The reactor is equipped with a stirrer and a reflux condenser, a sampling valve, a nitrogen injection system (blanketing) and computer controlled system for both temperature (jacket with hot and cold water) and feeding streams (metering pumps and balances). The agitation speed was kept at 200 rpm. A PID controller was employed to control the temperature of the reacting mixture (to a set point 55 °C), by adjusting the jacket temperature by mixing hot and cold water.

Experimental Conditions

In order to evaluate the reaction kinetics in PSPC and in the semibatch reactor, samples were taken at intervals of 5 or 10 minutes. The conversion was evaluated by gravimetry and copolymer composition was calculated from residual monomer concentrations measured by GC employing a headspace gas chromatograph (Shimadzu HS-GC-17 A).

The initial batch system temperature was set to 55 °C. In all sections of the continuous reactor, the inlet cooling jacket temperatures were kept between 56 ± 1 °C and the VA/BA monomer ratio of the final product was fixed in 85/15. Table 1 shows the recipe (reactant weight fraction) of the

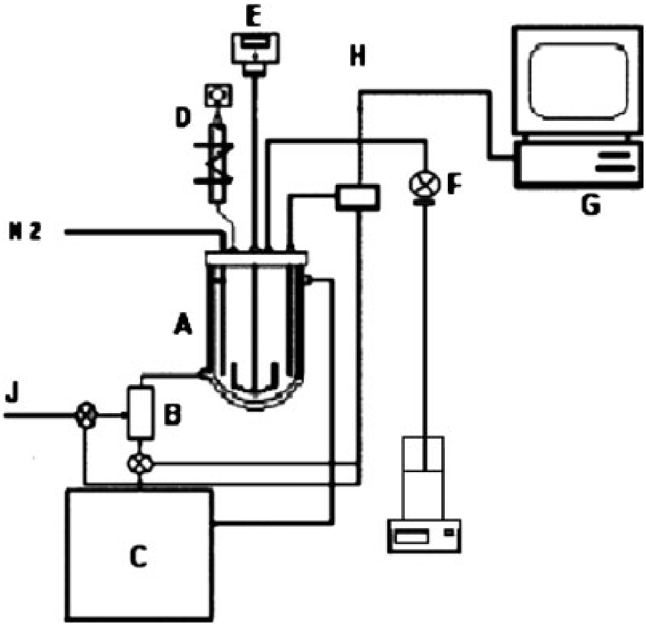

Figure 2.
Stirred Tank Reactor: A-Reactor, B-Water mixer, C-Heater, D-Condenser, E-Agitator, F-pump, G-Microprocessor, H-Temperature controller, I-Balance, J-Cooling water.

Table 1.
Copolymerization recipe.

Reactants	Weight Fraction
Vinyl Acetate (VA)	0.1574
Butyl Acrylate (BA)	0.0279
Water (H_2O)	0.7958
Sodium Lauril Sulfate (SLS)	0.0119
Sodium Persulfate ($Na_2S_2O_8$)	0.0057
Sodium Carbonate (Na_2CO_3)	0.0014

Table 3.
Experimental Reactions.

Reaction Code	Description
BRVABA	Batch
IBVABA	Semibatch with 4 intermittent feeds
PSPC1	PSPC without lateral feeds
PSPC2	PSPC with 2 lateral feeds
PSPC3	PSPC with 3 lateral feeds
PSPC4	PSPC with 4 lateral feeds

BA/VA copolymerization system used in both reactors. Table 2 lists the main operational conditions of both reactors. Each intermittent feed applied to the semibatch reactor lasted 1 minute and was applied at times 6, 12, 18 and 24 minutes. These time intervals are equivalent to the space time (axial position divided by flow velocity) at each feeding point in the PSPC tubular reactor.

The residence time employed in the PSCP was 30 minutes, and the total run time of each continuous reaction was 600 minutes, which is equivalent to 5 residence times. Table 3 presents the descriptions of operational conditions of all reactions carried out in this work.

The temperature control systems of each reactor, including valves and temperature sensors, are both of the same type. On the other hand, the employed control parameters were not the same for each reactor because of their different heat exchange area-to-volume ratios. In the present work, in the PSPC reactions only the jacket temperature was controlled, while in the stirred tank the controller of the reacting mixture temperature was active.

Table 2.
Operational Conditions.

Batch Reactor with and without intermittent feed	
Stirring speed	200 rpm
Temperature setpoint	55 °C
Pulsed Reactor column with and without lateral feed.	
Peclet number	61
Amplitude	18 mm.
Frequency	2.1 Hz.
Cooling Temperature*	56–57 (°C)
Residence time	30 min.
Number of residence times	5

* Reactions without temperature control, but with constant cooling jacket entrance temperatures.

Results

The performance of batch and semibatch reactions is compared to the corresponding continuous reactions performed in PSPC, in terms of monomer conversion and copolymer composition. The evolution of these variables as a function of time in batch and semibatch reactions was compared to the evolution of the same properties along the PSPC length expressed as space time *z/v* where *z* is the axial position and *v* is the average linear fluid velocity, at steady state conditions.

Global Conversion

Figures 3–6 compare the evolution of global monomer conversion during the first 30 minutes of batch and semibatch reactions. Batch reaction presented a higher reaction rate at the first 15 minutes in comparison to the other reactions. This behavior probably has the following explanations.

1) axial dispersion in PSPC induces to axial gradients reduction and also induces to a reduction in reaction rate along the column length in comparison to the behavior observed during a batch reaction (note that an ideal plug-flow reactor would present the same behavior as a batch reactor);
2) comparing to intermittent semibatch reaction (Figure 4), BA is quickly consumed as a consequence of the intermittent BA feed which controls the VA

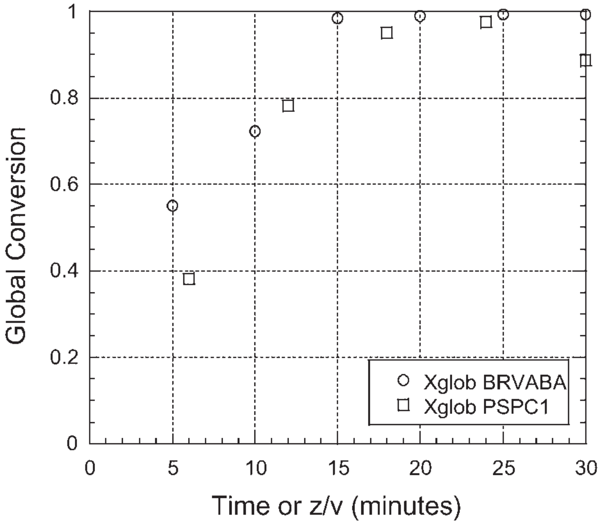

Figure 3.
Evolution of global conversion in batch reaction (BRVABA) as function of time and continuous reactor without lateral feed (PSPC1) as function of space time.

polymerization rate. Hence, the global conversion in intermittent the batch reaction is lower than in batch reaction.

Another interesting comparison that can be observed (Figure 5) is the difference between the achieved conversion in the intermittent feed semibatch reaction (IBVABA) and the reaction performed in the PSPC with 4 lateral feed streams (PSPC4). Figure 5 shows that the reaction rate (over the time in intermittent semibatch reactor and along the reactor length in PSPC reactor) presents a similar beha-

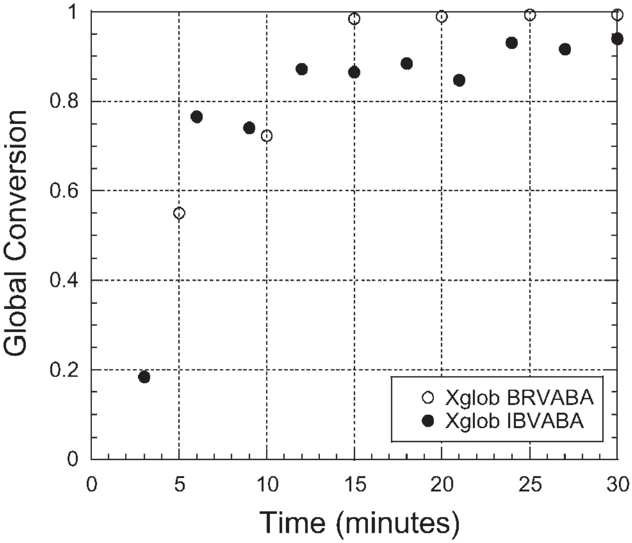

Figure 4.
Evolution of global conversion in batch reaction (BRVABA) and intermittent feed semi batch reaction (IBVABA) as function of time.

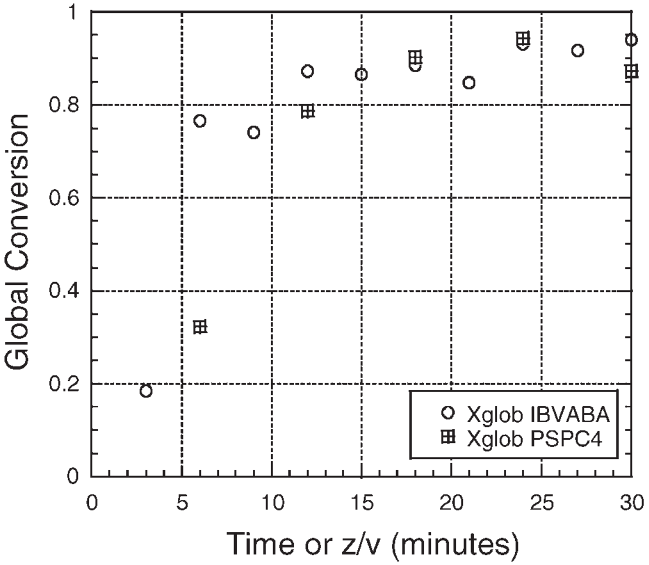

Figure 5.
Global conversion evolution of intermittent feed semibatch reaction (IBVABA) as function of time and continuous reactor with lateral feed (PSPC4) as function of space time.

vior in both cases. This behavior is due to the fact the BA amounts of the feed streams of the last sections, in the continuous reactor are equivalent to the same amounts employed in intermittent feed in the batch reactor. Both reactions cannot achieve the total monomer conversion in comparison to batch reaction (BRVABA), once the monomer feeding over the time increases the monomer weight in the reacting medium.

Figure 6 presents the global conversion evolution as a function of residence time for

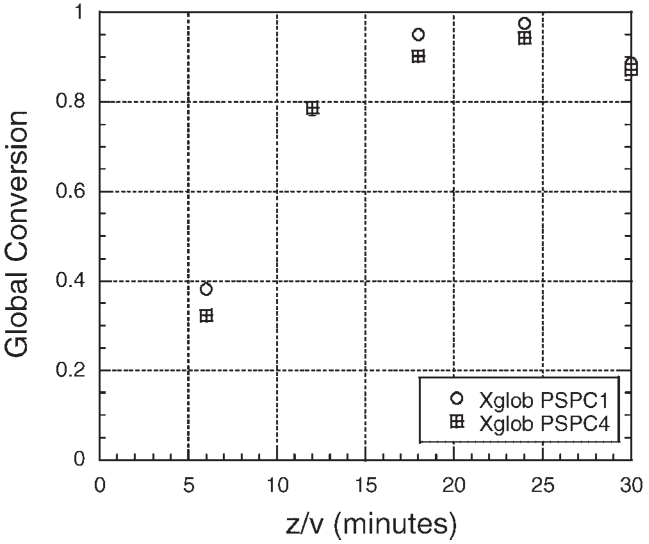

Figure 6.
Global conversion evolution of column reactor without lateral feed (PSPC1) and with lateral feed (PSPC4) as function of space time.

a reaction performed in the continuous reactor. In this case, global conversion in PSPC1 (without lateral feed) is slightly higher than the obtained in the reaction with 4 lateral feed (PSPC4). This lower conversion in PSPC4 can be regarded to the relatively higher amount of monomer in lateral feed at the final part of the reactor.

Copolymer Composition

Figure 7 presents the evolution of copolymer composition (VA weight fraction in copolymer) over the time (for a batch reaction, BRVABA) or over the space-time (for a continuous reaction without lateral feed, PSPC1). The results show a deviation at the first 15 minutes of reaction. This deviation is stronger in PSPC1 because the batch reaction is faster (Figure 3) and, as a consequence, the final composition is achieved earlier in this case. Figure 8 shows similar composition curves as function of conversion for two runs, PSPC1 and BRVABA.

In Figure 9, the composition evolutions for the intermittent feed semibatch reaction (IBVABA) and for the continuous reaction carried out with 4 lateral feed (PSPC4) are compared. Positive deviations in composition are obtained at the first 15 minutes of reaction run when these results are compared to those ones obtained from batch reaction and continuous reaction without lateral feed (Figure 7). Moreover, it can be observed that there is a similar behavior between these reactions. In the same way, this behavior can also be observed in Figure 10, which shows composition in relation to global conversion.

The use of lateral feedings in the tubular reactor (PSPC4), as well as the use of intermittent feedings in semibatch reactor (IBVABA), reduces composition drifts and improves the copolymer composition uniformity in comparison to the cases of tubular reactor with no lateral feeding (PSPC1) or fully batch reactor (BRVABA).

Figure 11 shows the evolution of copolymer composition as a function of space time for two continuous reactions, PSPC4 and PSPC1. A slight negative deviation can be observed in composition values in the beginning of PSPC1 and also a positive deviation in the beginning of PSPC4.

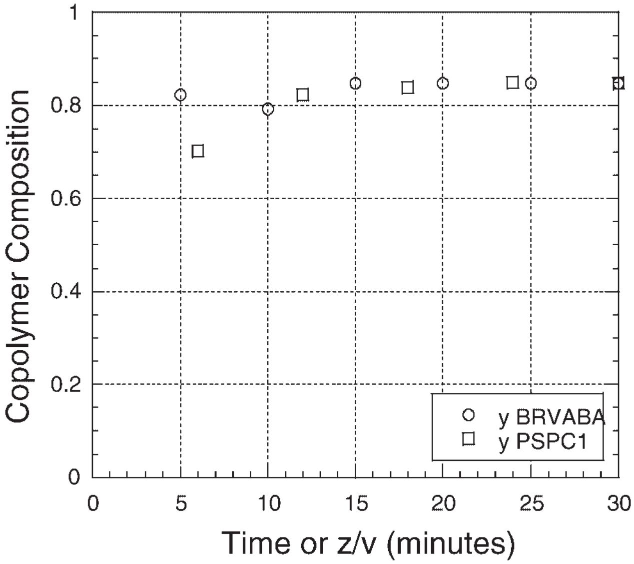

Figure 7.
Copolymer composition of batch reaction (BRVABA) as function of time and of a continuous reactor without lateral feed (PSPC1) as function of space time.

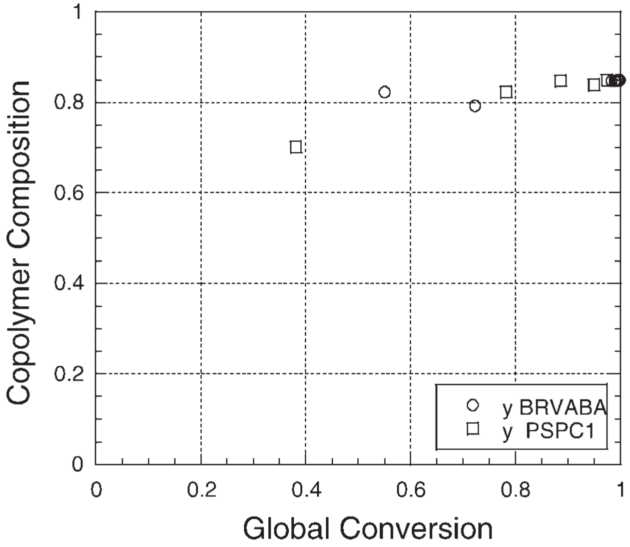

Figure 8.
Copolymer composition as function of global conversion of a batch reaction (BRVABA) and of a continuous reaction without lateral feed (PSPC1).

In Figures 8 and 10 copolymer compositions are compared for the PSPC1 and PSPC4 runs. It can be noted that PSPC4 presents a more homogeneous composition. From this fact it can be concluded that a more distributed feed of the more reactive monomer along the tubular reactor length tends to improve the copolymer composition control.

Reaction Temperature

According to Figure 12, during the batch run a strong temperature rise took place at the first 15 minutes as a consequence of the

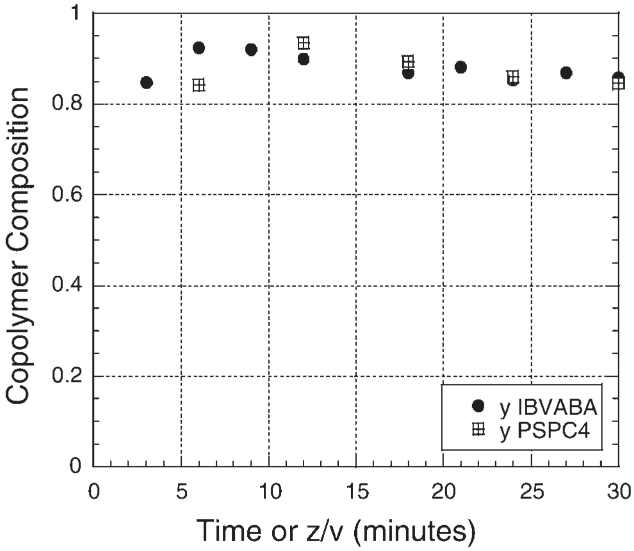

Figure 9.
Copolymer composition of a semibatch reaction with intermittent feed (IBVABA) and of a continuous reaction with 4 lateral feed (PSPC4) as function of space time.

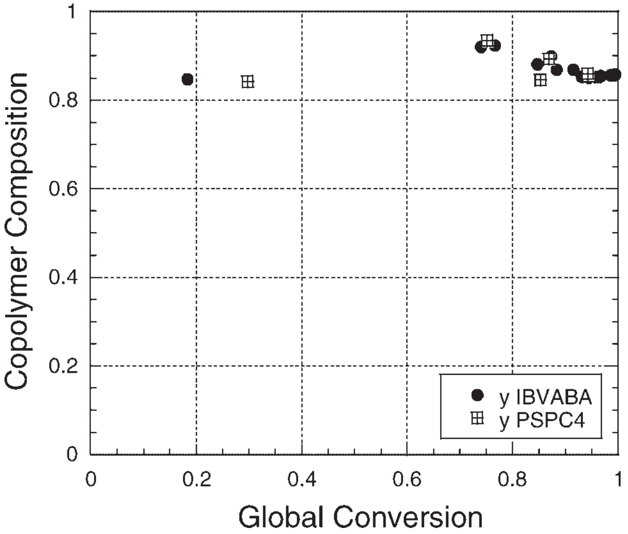

Figure 10.
Copolymer composition as function of global conversion of an intermittent feed semibatch reaction (IBVABA) and of a continuous reaction with 4 lateral feed (PSPC4).

combination of the high exothermic behavior with the high reaction rate present in this kind of copolymerization. Also some temperature rise was observed in the intermittently fed semibatch run. The temperature controller was active, but given the variation observed, one could consider the occurrence of some fortuitous malfunction of the controller in these specific runs. On the other hand, no strong temperature rise was observed in all PSPC runs. This is remarkable because the

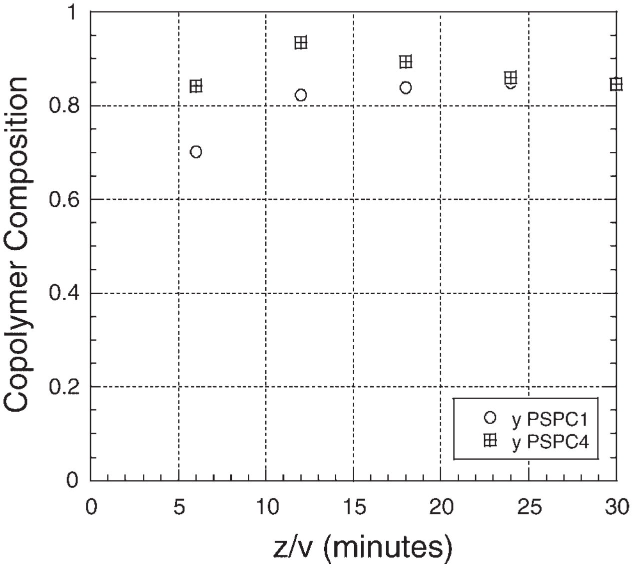

Figure 11.
Copolymer composition in continuous reactions without lateral monomer feed (PSPC1) and with lateral monomer feed (PSPC4) as function of space time.

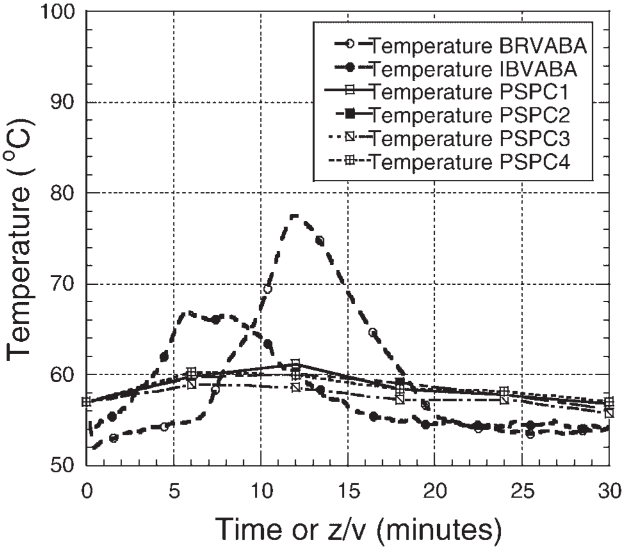

Figure 12.
Temperature of the reaction mixture in all reactions as function of time for batch runs and as a function of space time for continuous runs.

temperature of the reacting mixture was not controlled in the PSCP, only the inlet temperatures of the cooling jackets in each column section were kept constant. Even so, the average temperature of reacting mixture remained closer to the set point (55 °C). The reason for this behavior is the high ratio between heat exchange area and reaction volume of the PSPC, which favors the temperature control in tubular reactors in comparison with tank reactors (batch or semibatch reactors).

Conclusions

The two reactors have been compared for the emulsion copolymerization of vinyl acetate (VA) and butyl acrylate (BA) in order to analyze the feeding strategy of the more reactive monomer (butyl acrylate) in lateral streams of a continuous pulsed sieved plate column, PSPC, and in intermittently fed semibatch reactor. The effects of these different strategies on important variables, which directly affect the final product properties, have also been studied. The studied variables are global conversion, copolymer composition and temperature of reaction medium during the polymerization process. The results show that when batch reactions are carried out, higher polymerization rates are achieved in comparison to the reactions performed in continuous or intermittent semibatch reactors. It is ascribed to a higher amount of butyl acrylate present in the reacting medium and it increases by this way the global conversion. However, this higher amount induces the process to a copolymer composition deviation and a considerable increase on reaction temperature. The intermittently fed semibatch runs have been performed under similar operational conditions employed in the PSPC reactor at steady state conditions (with 30 minutes of residence time), in the way that intermittent feedings in semibatch reactor mimics the lateral feedings in the PSCP tubular reactor operating under steady-state condition. The results show that the polymerization rate in batch reactor is higher than that in the PSPC at the beginning of reaction, due to the axial dispersion effect present in the continuous flow. A similar behavior related to global conversion was observed during the next minutes of reaction time in both reactors. The cause of this fact is the equivalent amounts of BA in the last column sections and in intermittent feed in batch reactor. On the other hand, as a consequence of a lower concentration of the more reactive monomer at the beginning of the intermittent semibatch run, the reaction temperatures achieved lower values compared to those obtained in batch reactions but they still remained higher than in PSPC. Furthermore, in this case, not only reaction temperature but also the copolymer composition deviation was higher in relation to the continuous process. From all these comparisons, it can be concluded that the column reactor has some advantages over the other processes performed in tank reactors. One of these advantages is the higher heat exchange capacity related to the high ratio between heat transfer area and reaction volume in PSPC, which improves reaction rates and allows reducing the total reaction time. Besides, the monomer lateral feed and temperature profiles along the column length can be optimized so that a higher productivity and a better homogeneity in copolymer composition can be achieved simultaneously.

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