On-Line Terpolymer Composition Control in Semicontinuous Emulsion Polymerization

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A closed-loop strategy for terpolymer composition control in semicontinuous emulsion polymerization of high solids content systems is presented. This strategy is based on a nonlinear adaptive controller that calculates the flow rate of the more reactive monomers to be added into the reactor to produce a terpolymer of a given composition. The nonlinear adaptive controller is based on a simplified mathematical model of the process that includes the on-line estimation of an adjustable parameter. The addition of a conventional feedback proportional-integral (PI) controller to the prediction of the nonlinear controller was studied by simulation. It is shown that the contribution of the PI controller is negligible. The controller was checked by computer simulation and also experimentally verified during the semicontinuous emulsion terpolymerization of high solids content (55 wt. %) of vinyl acetate, methyl methacrylate and butyl acrylate.

Introduction

The production of a large number of specialty emulsion polymers is of great importance in industrial practice and usually involves the polymerization of more than two monomers. However, despite the importance of emulsion terpolymers, only limited attention has been paid to the study of emulsion terpolymerization (Ríos et al., 1980; Ríos and Guillot, 1982; Jerman and Janovic, 1984; Huo et al., 1988; Matejicek et al., 1988; Storti et al., 1989a,b; Masa et al., 1993a,b; López de Arbina and Asua, 1992; Unzué and Asua, 1993). On the other hand, the problem of obtaining polymers with specific properties requires polymerizations to be carried out under controlled conditions. During the last few years considerable effort has been devoted to develop strategies and experimental setups to control and monitor the properties of polymers in polymerization reactors. Focusing on polymer composition control, in most cases, open-loop control strategies based on a mathematical model of the process without any on-line measurement of the polymer composition have been used.

Broadhead et al. (1985), Hamielec et al. (1987), and Arzamendi and Asua (1989) have proposed minimum-time monomer addition policies for composition control in emulsion copolymerization systems for reactors with large heat removal rates, namely, laboratory reactors. In these studies, the reactor was initially charged with all of the less reactive monomer plus the amount of the more reactive monomer needed to initially form a copolymer of the desired composition. Then, the remaining more reactive monomer was added at a flow rate that ensured the formation of a homogeneous copolymer. To calculate the flow rate of the remaining more reactive monomer, the evolution of the polymerization rate during the process was required. However, the theoretical calculation of the polymerization rate is often unreliable because of the uncertainties associated with the parameters of the model. In order to overcome this difficulty Arzamendi and Asua (1990) developed a semiempirical method to determine the optimal flow rate. This method was experimentally verified for different comonomer systems (Arzamendi and Asua, 1990; Arzamendi et al., 1991; Leiza et al., 1993a). A variation of the original method (Arzamendi and Asua, 1990) has been used by Van Doremaele et al. (1992). For reactors with a limited heat removal rate, both monomers should be added into the reactor at a controlled feed rate (different for each monomer) (Arzamendi et al., 1991).

Arzamendi et al. (1992) have also proposed an optimal monomer addition policy for composition control in emulsion terpolymerization systems. They found that, if the rate of heat removal is greater than the rate of heat generation, a homogeneous terpolymer was obtained in a minimum process time when the reactor was initially charged with all the amount of

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one monomer plus some amounts of the other two monomers, and the remaining monomers were added at controlled feed rates. The monomer to be completely included in the reactor is usually the least reactive monomer. When reactors with limited capacity for heat removal are used, only a fraction of the three monomers can be included in the initial charge, feeding the remaining monomers at a controlled flow rate.

Implementation of these open-loop control policies as a preprogrammed trajectory throughout the time of reaction poses some problems. First, the deterministic models used by these policies are often poor. Secondly, there are unmodeled elements such as monomer impurities, unexpected variations in reactor temperature, or inhibition periods which can cause these policies to fail. Therefore, a feedback control using online measurements of the polymerization is needed to compensate for the effect of unmodeled dynamics in order to have a well controlled process. Thus, during the last few years, several closed-loop strategies based on feedback controllers have been reported for polymer composition control in emulsion polymerization systems.

Guyot et al. (1981) used on-line gas chromatography measurements of the residual monomers in a feedback scheme to obtain homogeneous copolymers during the emulsion copolymerization of styrene and acrylonitrile. The same technique was used by Ríos and Guillot (1982) for the emulsion terpolymerization of acrylonitrile-styrene-methyl acrylate. In this case, the reactor was initially charged with all of both acrylonitrile and methyl acrylate, and the styrene was fed at a flow rate that was controlled by the gas chromatography measurements. The authors reported that the styrene content of the terpolymer slightly increased as the polymerization proceeded. This suggests that the controlled addition of more than one monomer is required to obtain homogeneous terpolymers.

A more advanced closed-loop strategy can be obtained by combining a nonlinear controller, which is based on a mathematical model of the process that calculates the monomer addition feed rate profile to produce a polymer of the desired composition, and a conventional feedback controller (P, PI, and PID). Kravaris et al. (1989) developed a general nonlinear feedforward-feedback control methodology for set-point tracking in batch processes. Vega (1993) using this technique calculated the feed rate profile of the more reactive monomer to obtain a homogeneous copolymer in a simulated emulsion copolymerization of acrylonitrile and butadiene. Dimitratos et al. (1989a,c) developed a feedforward-feedback control strategy to control the copolymer composition in emulsion copolymerization systems. The feedforward part of the algorithm is a controller that adjusts the feed rate profile on the basis of the concentrations of the monomers in the polymer particles estimated by means of an extended Kalman filter for state estimation. The authors experimentally tested the controller in the semicontinuous emulsion copolymerization of vinyl acetate and butyl acrylate. Kozub and MacGregor (1992a) have proposed a nonlinear inferential feedback control strategy for semibatch emulsion copolymerization. They showed the usefulness of the strategy in the simulated control of the properties of styrene/butadiene rubber.

Recently, Leiza et al. (1993b) have presented a nonlinear adaptive plus proportional-integral controller for composition control in emulsion copolymerization systems. The nonlinear part of the controller used the estimated values of the amounts of monomers in the polymer particles to calculate the flow rate of the more reactive monomer to be added into the reactor to produce a copolymer of a given composition. The estimated values were calculated by means of an extended Kalman filter from on-line gas chromatography measurements of the unreacted monomers in the reactor. The strategy was checked by computer simulation and experimentally in the semicontinuous emulsion copolymerization of ethyl acrylate and methyl methacrylate.

In this work this nonlinear adaptive plus proportional-integral strategy has been modified and applied to obtain homogeneous terpolymers in semicontinuous emulsion terpolymerization systems. The nonlinear adaptive part of the controller is based on a simplified version of the mathematical model for the semicontinuous emulsion terpolymerization developed by Urretabizkaia et al. (1992). The controller updates its prediction using the estimates of the amounts of monomers in the polymer particles calculated by means of a nonlinear optimization algorithm (Jang et al., 1986) that allows a parameter related to the polymerization rate to be adjusted. This parameter is also updated in the mathematical model of the nonlinear adaptive part of the controller. The nonlinear optimization scheme minimizes the difference between the online gas chromatography measurements of the amounts of unreacted monomers in the reactor and the prediction of those amounts calculated by means of a mathematical model of the process. The proportional-integral controller is a conventional feedback controller, which compares the desired terpolymer composition (set point) with the estimated value, and adds its action to the output of the nonlinear part of the controller. This strategy was experimentally verified in the semicontinuous emulsion terpolymerization of vinyl acetate, methyl methacrylate, and butyl acrylate of high solids content using the computer controlled experimental setup developed by Leiza et al. (1993c) for on-line measurement of polymer composition.

Description of the Experimental Setup

Several experimental setups have been reported for on-line monitoring of emulsion polymerization systems (Guyot et al., 1981, 1984; Schork and Ray, 1981, 1983; Dimitratos, 1989a; Van Doremaele, 1990; Kourti et al., 1990; Chien and Penlidis, 1990; Canegallo et al., 1993). In most cases, samples are taken from a circulation loop of the reactor mixture by means of an injection valve and samples are then introduced into a measurement device such as a gas chromatograph (Guyot et al., 1981, 1984; Dimitratos, 1989; Van Doremaele, 1990). In some cases the measurement device is included in the circulation loop (Schork and Ray, 1981, 1983; Canegallo et al., 1993). In all of the experimental setups the authors reported clogging problems in pipes, pumps, and injection valves when solids concentrations between 25–33 wt. % were reached. Therefore, in none of the experimental installations reported in the literature has it been possible to work as is industrial practice, that is, at high solids content (~55 wt. %). In the present work the experimental setup developed by Leiza et al. (1993c) has been used. This experimental setup overcomes the clogging problems encountered in sampling devices that use pump-driven circulation of the reaction mixture through a sampling valve and, therefore, the equipment allows high solids content emulsion polymerizations to be monitored. However, special

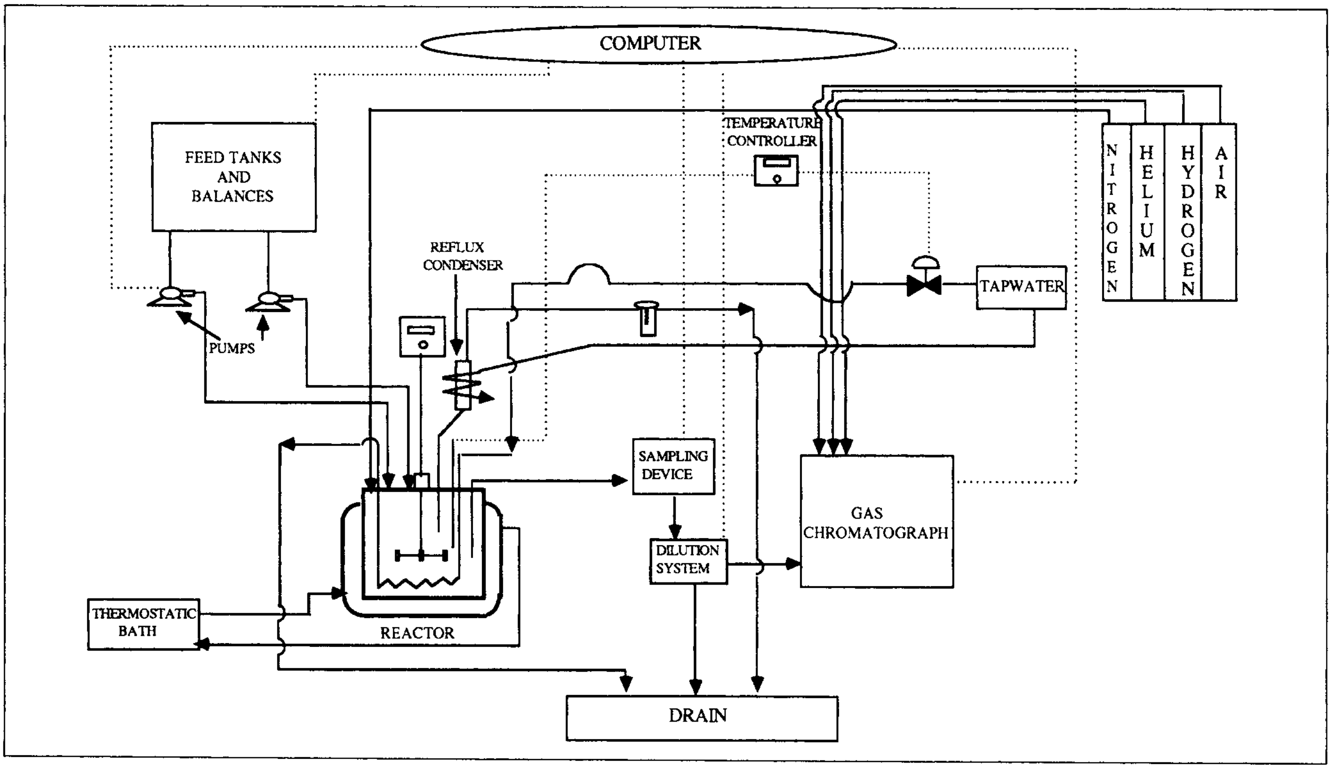


Figure 1. Experimental setup.

care should be taken in some parts of the installation, for example, the water-jet aspirator pump used to withdraw the sample from the reactor should be cleaned after five to seven reactions, because of clogging with the polymer. The chromatographic injection valve should also be cleaned carefully after each reaction with acetone or tetrahydrofuran. The following is a brief description of the experimental setup. A detailed description can be found elsewhere (Leiza, 1991; Leiza et al., 1993c).

A representation of the experimental installation is presented in Figure 1. The main elements of the installation are: polymerization reactor; reactants feed system; sampling and dilution system; chromatographic analysis system; and computer data acquisition and control system.

Polymerization reactor

The reactor is a 2 liter jacketed stainless-steel equipped with a reflux condenser, stainless-steel stirrer, internal coiling coil, two reactant inlets, nitrogen inlet, on-line sampling outlet, and off-line sampling device. The reaction mixture was continuously heated by circulating hot water through the reactor jacket by means of a thermostatic bath (Grant W6 KD). A proportional controller (Transmetal, TFN) was used to maintain the desired temperature inside the reactor by manipulating the flow of cold water through a coil placed inside the reactor.

Reactants feed system

This system is based on computer-driven positive displacement pumps (FMI QV-OSSY with a V-107 stroke rate controller), balances (Sartorius U 4100 S), and the reactant tanks. The flow rate of the reactants (monomers, emulsifier, and water) is adjusted by controlling the speed of the pumps through the computer by means of a BASIC program. The balances are used to monitor the total amount of the reactants added into the reactor.

Sampling and dilution system

Samples are taken from the reactor using vacuum and the content of the sample loop transferred to the dilution system. After homogenization, the sample is injected into the gas chromatography.

Chromatographic analysis system

The unreacted monomer of the reaction mixture is measured by gas chromatography. This measurement together with the monomer material balances were used to calculate the on-line conversion and copolymer composition during the polymerization. A gas chromatograph (Shimadzu G.C. 8A) equipped with flame ionization detector and integrator (HP 3396 A) was used. The samples were injected into the gas chromatograph by means of an automatic injection valve (E^{ts} Grayel) located on the top of the injection port of the gas chromatograph. A glass insert filled with glass wool was inserted in the injection port to retain the polymer of the latex and avoid clogging of the column. The glass wool was changed after each polymerization. The separation of the monomers was achieved by means of a semi-capillary "wide-bore" column (S.G.E. 25 QC5/BP5-1, 5% diphenyl dimethyl siloxane, of 25 m in length, 1 μ thickness, and 0.53 mm ID). The monomer contents of the sample are calculated using calibration curves with 1-pentanol as internal standard and then these data are sent to the computer using an RS-232-C interface.

Data acquisition and computer control system

The whole installation is controlled by an Olivetti M290 personal computer (12 MHz 80286 microprocessor). The computer is equipped with two RS-232-C serial ports, a digital/analog board (D/A Metrabyte DDA06), a digital input/output module (DGH 1111), and a parallel port for the printer. A program written in BASIC (Quick BASIC Microsoft) and operating under MS DOS is used to support the data acquisition and control all the elements of the installation during the real-time experiments.

An important characteristic of this setup is that several actions can be carried out in parallel. Thus, the sampling system is cleaned and a new sample taken while the gas chromatography analysis of the previous sample is performed. For the emulsion polymerization system studied in this work, sampling, gas chromatography analysis, and computer calculations takes 18 min. Therefore, there is a dead time of 18 min between sampling and the time when the controller acts. Nevertheless, because several actions are carried out in parallel, samples are taken every 10 min.

Controller Design

The aim of the work reported here was to develop a closed-loop control strategy to produce homogeneous terpolymers in semicontinuous emulsion polymerization systems of high solids content. Therefore, the instantaneous terpolymer composition must be maintained constant during the whole polymerization. The manipulated variables of the process are the three monomer flow rates (F_A, F_B, and F_C) and the controlled variables are the amounts of monomers in the polymer particles (A_p, B_p, and C_p).

In order to maintain the instantaneous terpolymer composition constant, the amounts of monomers in the polymer particles (A_p, B_p, and C_p) should be controlled. This is achieved by maintaining the ratios of the amounts of monomers in the polymer particles A_p/B_p and A_p/C_p at previously determined values. It should be pointed out that if the ratios A_p/B_p and A_p/C_p are set, the ratio B_p/C_p will also be fixed. In order to control the amounts of the three monomers in the polymer particles, it is necessary to manipulate the three monomer feed rates (F_A, F_B, and F_C). However, if one of the output variables (A_p, B_p, and C_p) is arbitrarily fixed (for example: A_p), only two of the variables F_B and F_C need to be used in order to control the polymer composition.

Polymer composition control in emulsion polymerization often results in strategies in which the concentration of one of the monomers in the reactor is fixed. An important example is that of the minimum-time monomer addition policies to produce homogeneous polymers. These strategies have been extensively applied in emulsion copolymerization systems (Broadhead et al., 1985; Hamielec et al., 1987; Arzamendi and Asua, 1989, 1990; Arzamendi et al., 1991; Van Doremaele et al., 1990, 1992). In this works, and in the case of reactors with a large heat removal rate, the reactor is initially charged with the total amount of the less reactive monomer plus the amount of the more reactive monomer needed to initially form a copolymer of the desired composition. Thereafter, the remaining more reactive monomer is added at the time-dependent flow rate that ensures the formation of a homogeneous copolymer. In such a case, $F_A = 0$ and A_p is determined by the polymerization rate (A being the less reactive monomer). When reactors with limited capacity for heat removal are used, Arzamendi and Asua (1991) have found that only a fraction of the less reactive monomer plus the necessary amount of the more reactive monomer are needed in the initial charge. The remaining two monomers are added in such a way that the feed rate of the less reactive monomer is limited by the reactor heat removal rate, and the feed rate of the more reactive monomer is adjusted to maintain the ratio B_p/A_p at the value that ensures the formation of a copolymer of the desired composition. When the reactor heat removal rate is constant, Arzamendi and Asua (1991) found that the feed rate of the less reactive monomer was constant. Therefore, only the feed rate of the more reactive monomer is required to achieve the control.

In the terpolymerization case, the situation is more complex, however, Arzamendi et al. (1992) found that the minimum-time addition policies are similar to that of the copolymer case. Thus, when the reactor heat removal rate is greater than the heat generation rate, the minimum-process time is obtained when the reactor is initially charged with the total amount of one of the monomers, and the remaining monomers are fed in a controlled way to the reactor. The authors gave a criterion to choose which of the monomers should be totally charged into the reactor. Usually, this monomer is the less reactive one. When a reactor with limited capacity for heat removal is used, the maximum feed rate of the key monomer is limited by the reactor heat removal rate and the remaining two monomers are fed to maintain the ratios A_p/B_p and A_p/C_p at the desired values and hence to produce a homogeneous terpolymer. Therefore, in any type of reactor, both with and without limited heat removal capacity, the feed rate of two of the monomers must be manipulated, in order to produce a homogeneous terpolymer in a minimum process time.

The problem of obtaining a terpolymer of homogeneous composition in semicontinuous emulsion polymerization results in a multiple input-multiple output (MIMO) control system. The process has two manipulated inputs, namely, the flow rates of the most reactive monomers, F_B and F_C, and two controlled outputs, namely, the ratios of the monomer amounts in the polymer particles A_p/B_p and A_p/C_p. In general, in any MIMO process control system with N manipulated inputs and N controlled outputs there are $N!$ different ways to form the control loops, that is, to pair the manipulated and controlled variables. In this particular case where $N=2$, there are two different configurations of pairing A_p/B_p and A_p/C_p with F_B and F_C. The best configuration should be the one with minimum interaction between the control loops. In order to select the best configuration of the control loop the relative gain matrix methodology proposed by Bristol (1966) has been applied. The relative gain matrix was obtained by simulation using the model without any linearization. Because the model is nonlinear the gains depend to some extent on the size of the step taken. In order to check this point, steps of 8% and 100% of the values of the monomer feed rates were simulated finding that the relative gain matrix was almost independent of the step size.

Step size: 8%

$$\lambda = \begin{array}{cc} \begin{bmatrix} 0.9887 & 0.0113 \\ 0.0113 & 0.9887 \end{bmatrix} & \begin{array}{c} (A_p/B_p) \\ (A_p/C_p) \end{array} \\ \begin{array}{cc} F_B \qquad & F_C \end{array} & \end{array}$$

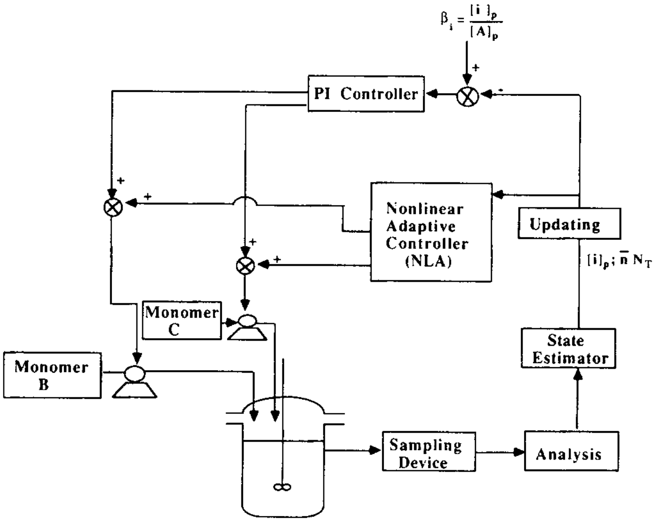


Figure 2. Representation of the control design.

Step size: 100%

$$\lambda = \begin{array}{ccl} 0.9977 & 0.0023 & (A_p/B_p) \\ 0.0023 & 0.9977 & (A_p/C_p) \\ F_B & F_C & \end{array}$$

The result indicates that there is almost no interaction between the loop formed by F_B with (A_p/B_p) and F_C with (A_p/C_p), that is, the process gain of one loop is the same when the other loop is open or closed. Consequently, and following Bristol pairing rule, the selected pairs are F_B with (A_p/B_p) and F_C with (A_p/C_p), whose elements in the relative gain matrix are the closest to one.

The control scheme is summarized in Figure 2. The unreacted monomer concentrations in the reactor are measured by on-line gas chromatography. In order to estimate the amounts of monomer in the polymer particles from these experimental measurements, a state estimation technique can be used. Different state estimation techniques have been reported in the literature. Both filtering algorithms such as the Kalman filter (Schuler and Suzhen, 1985; Dimitratos et al., 1989b, 1991; MacGregor et al., 1986; Kozub and MacGregor, 1992b; Leiza et al., 1993b) and nonlinear optimization algorithms (Jang et al., 1986) have been used. In this work, the nonlinear optimization algorithm approach has been used. This nonlinear optimization algorithm allows the estimated states of the amount of monomer in the polymer particles, A_p, B_p, and C_p, to be calculated as well as the product of the average number of radicals per particle ($\bar{n}$) and the number of polymer particles (N_T). This product is proportional to the polymerization rate. These results are used by the nonlinear adaptive controller (NLA), which is based on a simplified mathematical model of the emulsion terpolymerization, to calculate the flow rates of the monomers. In addition, a conventional proportional-integral (PI) feedback controller is included to compensate for possible errors introduced by the NLA part of the controller.

State estimation using a nonlinear optimization algorithm

The amounts of the residual monomers from the on-line measurements are used to adjust the predicted values given by a mathematical model of the process. The prediction of the model acts as a filter for the experimental error, and allows an estimation of the states of the reactor to be obtained. The following objective function is minimized:

$$J = \sum_{t=1}^{m} \sum_{j=A,B,C} [i_{\exp}(t) - i_{\text{the}}(t)]^2 \tag{1}$$

where m is the total number of samples available, A, B, and C the monomers, $i_{\exp}$ the amounts of unreacted monomer in the reactor measured by means of on-line gas chromatography, and i_{the} the corresponding values predicted by the mathematical model of the process.

The value i_{the} is calculated by the mathematical model as follows:

$$\frac{di_{\text{the}}}{dt} = -(k_{PAi}P_A + k_{PBi}P_B + k_{PCi}P_C)\frac{[i]_p}{N_A}\bar{n}N_T + F_i \qquad i = A, B, C \tag{2}$$

where the first term on the righthand side represents the consumption of monomer i by polymerization, F_i the molar feed rate of monomer i, $[i]_p$ the concentration of monomer i in the polymer particles, k_{pij} the propagation rate constant, $\bar{n}$ the average number of radicals per particle, N_T the number of polymer particles, and P_i the probability of finding a free radical with ultimate unit of type i. These probabilities are given by the following equations (Arzamendi et al., 1992):

$$P_A = \frac{\alpha}{\alpha + \beta + \gamma} \tag{3}$$

$$P_B = \frac{\beta}{\alpha + \beta + \gamma} \tag{4}$$

$$P_C = 1 - P_A - P_B \tag{5}$$

$$\alpha = (k_{PCA}k_{PBA}[A]_p + k_{PBA}k_{PCB}[B]_p + k_{PCA}k_{PBC}[C]_p)[A]_p \tag{6}$$

$$\beta = (k_{PAB}k_{PCA}[A]_p + k_{PAB}k_{PCB}[B]_p + k_{PCB}k_{PAC}[C]_p)[B]_p \tag{7}$$

$$\gamma = (k_{PAC}k_{PBA}[A]_p + k_{PBC}k_{PAB}[B]_p + k_{PAC}k_{PBC}[C]_p)[C]_p \tag{8}$$

Considerable effort has been devoted to study the mechanisms involved that control the average number of radicals per particle, $\bar{n}$, (Ugelstad and Hansen, 1976; Nomura, 1982; Gilbert and Napper, 1983; Penboss et al., 1986; Asua et al., 1989, 1990; Asua and de la Cal, 1991; Barandiaran et al., 1992). Nevertheless, the current state of knowledge is not sufficient to predict accurately the evolution of $\bar{n}$ during the process. On the other hand, and despite the important improvements made on the particle nucleation theory (Fitch and Tsai, 1971; Hansen and Ugelstad, 1978, 1979; Feeney et al., 1984, 1987), the prediction of the number of polymer particles, N_T, is even less accurate than that of $\bar{n}$. Therefore, the product $\bar{n} \times N_T$ has been used as a tuning parameter to minimize the objective function of Eq. 1. For this purpose the product $\bar{n} \times N_T$ was approximated by the following equation:

$$\bar{n} \times N_T = k_1 + k_2 t + k_3 t^2 \tag{9}$$

and the parameters k_1, k_2, and k_3 were tuned to minimize the objective function J using an optimization algorithm for systems of nonlinear ordinary differential equations (Senfield and Lapidus, 1974). In this way the objective function weights past data and more recent data equally in determining the parameters. Several processes like secondary nucleation, particle coagulation and gel effect might cause the shape of the variation of $\bar{n} \times N_T$ to be not fitted by a quadratic function, as Eq. 9, if all the experimental data are used. In order to overcome this problem, McAuley and MacGregor (1991) have proposed a method to slowly forget past data and hence to weigh more heavily the most recent data in order to minimize the objective function. In the present work, only the 14 most recent data were used to estimate on-line the value of $\bar{n} \times N_T$. This increased the flexibility of the estimation approach to fit abrupt changes in $\bar{n} \times N_T$ and had the additional advantage of reducing the computer time in the real-time experiments.

Once the parameters of Eq. 9 are tuned, the predictions of the mathematical model are used to estimate A_p, B_p, and C_p. It should be pointed out that in this last calculation the partition coefficients of monomers between the different phases must be known.

Updating of the state estimates

The estimated amounts of monomers in the polymer particles (A_p, B_p, and C_p) correspond to that of the sampling time. Due to the dead time of the sampling and chromatographic analysis ($\simeq$ 18 minutes) the estimated states need to be updated. This is done by integrating the mathematical model of the emulsion terpolymerization from the sampling time to the current time. The dependence on time of the product $\bar{n} \times N_T$ calculated by means of Eq. 9 was used in the integration.

Nonlinear adaptive (NLA) controller

The instantaneous terpolymer composition can be calculated as the ratio of the individual monomer consumption rates. For example, the instantaneous composition with respect to the less reactive monomer (A) is given by:

$$Y_{\text{inst}\,A} = \frac{R_{PA}}{R_{PA} + R_{PB} + R_{PC}} \tag{10}$$

Dividing each term on the righthand side of Eq. 10 by R_{PA} gives:

$$Y_{\text{inst}\,A} = \frac{1}{1 + \dfrac{1}{C_{\text{inst}\,AB}} + \dfrac{1}{C_{\text{inst}\,AC}}} \tag{11}$$

where

$$C_{\text{inst}\,Ai} = \frac{R_{PA}}{R_{Pi}} = \frac{\left(k_{PAA}P_A + \sum_j (k_{PjA}P_j)\right)\dfrac{A_P}{V_p}\bar{n}\dfrac{N_T}{N_A}}{\left(k_{PAi}P_A + \sum_j (k_{Pji}P_j)\right)\dfrac{i_p}{V_p}\bar{n}\dfrac{N_T}{N_A}} \tag{12}$$

where V_p is the volume of the monomer swollen polymer particles.

Furthermore, the ratios of the amounts of monomer i and monomer A in the polymer particles, β_i, which ensure the formation of a terpolymer of the desired composition are defined as follows:

$$\beta_i = \frac{i_p}{A_p} \tag{13}$$

The values of the ratios β_B and β_C as a function of $C_{\text{inst}\,AB}$, $C_{\text{inst}\,AC}$ and the propagation rate constants can be calculated by solving the nonlinear algebraic equations obtained from Eq. 12.

Therefore, in order to produce a terpolymer of homogeneous composition, $Y_{\text{inst}\,i}$, the ratios β_B and β_C should be kept constant during the polymerization process.

After an on-line gas chromatography measurement, the monomer molar ratios in the reactor estimated by means of the nonlinear optimization algorithm are B/A and C/A. These ratios may or may not produce a terpolymer of the desired composition. The controller developed in this work calculates the constant flow rate of the more reactive monomers (F_B and F_C) required to ensure that after a sampling interval, Δt, the monomer ratios in the polymer particles, B_p/A_p and C_p/A_p, are the desired ones, β_B and β_C.

The material balances for monomers are:

$$\frac{di}{dt} = F_i - R_{Pi} \quad i = A, B, C \tag{14}$$

where i is the total number of moles of monomer i in the reactor, F_i the flow rate of monomer i and R_{pi} the polymerization rate of monomer i. The differential Eqs. 14 can be approximated by the following difference equations:

$$\Delta i = i_{n+1} - \hat{i}_n = (F_i - R_{Pi})_n \Delta t \quad i = A, B, C \tag{15}$$

where $\hat{i}_n$ is the amount of moles of monomer i in the reactor at the beginning of the time increment, Δt, and i_{n+1} the value at the end of the time increment. Dividing Eq. 15 for $i = A$, by the same equation using $i = B$ and C, one obtains:

$$\left(\frac{A}{B}\right)_{n+1} = \frac{\hat{A}_n + (F_A - R_{PA})_n \Delta t}{\hat{B}_n + (F_B - R_{PB})_n \Delta t} \tag{16}$$

$$\left(\frac{A}{C}\right)_{n+1} = \frac{\hat{A}_n + (F_A - R_{PA})_n \Delta t}{\hat{C}_n + (F_C - R_{PC})_n \Delta t} \tag{17}$$

From Eqs. 16 and 17, explicit algebraic equations for the flow rate of the more reactive monomers, F_B and F_C, can be obtained as follows:

$$F_B = \left[\frac{\hat{A}_n}{\Delta t} + (F_A - R_{pA})_n\right]\left(\frac{B}{A}\right)_{n+1} - \frac{\hat{B}_n}{\Delta t} + R_{pBn} \tag{18}$$

$$F_C = \left[\frac{\hat{A}_n}{\Delta t} + (F_A - R_{PA})_n\right]\left(\frac{C}{A}\right)_{n+1} - \frac{\hat{C}_n}{\Delta t} + R_{PCn} \tag{19}$$

Equations 18 and 19 give the flow rate of the more reactive monomers, F_B and F_C, such that at the end of the time increment, Δt, the ratios $(i/A)_{n+1}$ will be the desired ones. It should be noted, that in these equations, the flow rate of the less reactive monomer, F_A, is included to give the equation a more general form.

The goal of the controller is to adjust the ratios B/A and C/A in order to produce a terpolymer of composition, $Y_{\text{inst}\,i}$. $Y_{\text{inst}\,i}$ is related to the monomer ratio in the polymer particles, β_B and β_C, by means of Eqs. 11, 12, and 13. Therefore, relationships between B/A and C/A, and β_B and β_C are required. The amount of monomer i in the reactor is related to the amount of that monomer in the polymer particle, i_p, through the following equation (Leiza, 1991):

$$i = i_p\left(1 + \frac{V_{\text{aq}}}{V_p k^i}\right) \quad i = A,\ B,\ C \tag{20}$$

where k^i is the partition coefficient of monomer i between the polymer particles and the aqueous phase, and V_{aq} is the volume of the aqueous phase. Implicit in Eq. 20 is the assumption that no monomer droplets are present in the system. Combining Eq. 20 for $i = A$, with those for $i = B$ and C, the following equations are obtained:

$$\left(\frac{B}{A}\right) = \frac{k^A}{k^B}\left(\frac{V_p k^B + V_{\text{aq}}}{V_p k^A + V_{\text{aq}}}\right)\beta_B \tag{21}$$

$$\left(\frac{C}{A}\right) = \frac{k^A}{k^C}\left(\frac{V_p k^C + V_{\text{aq}}}{V_p k^A + V_{\text{aq}}}\right)\beta_C \tag{22}$$

Substitution of Eqs. 21 and 22 into Eqs. 18 and 19, provides a general form for the prediction of the flow rates of the more reactive monomers, F_B and F_C, to be added into the reactor during the time Δt to make sure that at the end of that time interval, the monomer ratios of the polymer particles are the ones that form a terpolymer of the desired composition.

Conventional feedback proportional-integral (PI) controller

A feedback controller was incorporated to compensate for possible errors associated with the NLA controller. The addition of conventional feedback controllers to nonlinear controllers has been already reported in the literature (Kravaris et al., 1989; Dimitratos et al., 1989a,c; Leiza et al., 1993b). The action of the conventional feedback controller is added to that predicted by the NLA controller when an error is detected between the desired terpolymer composition (set point) and the estimated terpolymer composition. In this work, a conventional proportional-integral algorithm was used:

$$F_{PI_i} = k_{C_i}\left\{\text{Error}_i(t) + \frac{1}{\tau_{I_i}}\int_0^t \text{Error}_i(t)\,dt\right\} \quad i = B,\ C \tag{23}$$

where k_{C_i} is the proportional gain, τ_{I_i} the integral time constant and $\text{Error}_i(t)$ is defined as:

$$\text{Error}_i(t) = \beta_i - \frac{\hat{i}_p}{\hat{A}_p} \quad i = B,\ C \tag{24}$$

where β_i are the monomer ratios in the polymer particles needed to produce a terpolymer of the desired composition and $\hat{i}_p/\hat{A}_p$ are the estimated values calculated from the measurements.

The flow rates of the more reactive monomers calculated by the nonlinear adaptive proportional-integral (NLAPI) controller accounts for the action of both controllers and are given by the following equation:

$$F_{i(\text{NLAPI})} = F_{i(\text{NLA})} + k_{C_i}\left\{\text{Error}_i(t) + \frac{1}{\tau_{I_i}}\int_0^t \text{Error}_i(t)\,dt\right\} \quad i = B,\ C \tag{25}$$

Assessment of the Control Strategy by Numerical Simulation

Prior to its application to real-time experiments, the NLAPI controller was assessed by computer simulation. On-line measurements were simulated using the detailed model of the semicontinuous emulsion terpolymerization developed by Urretabizkaia et al. (1992). This model takes into account the possibility that monomer droplets can be present in the system. The experimental setup provides measurements each 10 min with a dead time of 18 min, for the emulsion polymerization studied in this work. In the simulation and for the sake of programming simplicity, they were assumed to be available every 9 min and the dead time assumed was 18 min. To make these measurements more realistic, a random error was also included. The control strategy was simulated, as is shown in Figure 3. The emulsion terpolymerization of vinyl acetate, methyl methacrylate and butyl acrylate was considerated in the simulation. Thereafter, the same terpolymerization system was used to validate experimentally the proposed control strategy. The values of the parameters used in both the extended and simplified models are presented in Table 1.

The control design was checked in two stages. Initially, the performance of the NLA controller was assessed and thereafter that of the NLAPI controller.

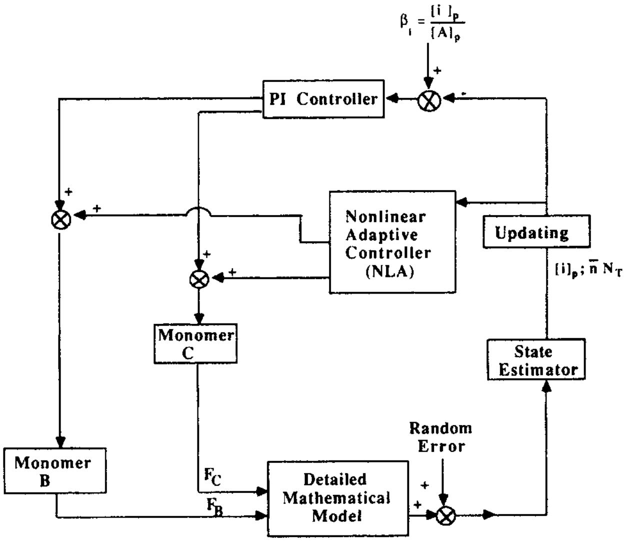


Figure 3. Representation of the simulated control strategy used in the semicontinuous emulsion terpolymerization of VAc/MMA/BuA.

Table 1. Parameters Used in Detailed and Simplified Modeling for the Controller Simulation

k_{pAA}, k_{pBB} (Walling, 1957); k_{PCC} (Dimitratos, 1989) ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	3.29	0.29	0.247
r_{AB} (Brandrup and Immergut, 1989); r_{AC} (Delgado, 1986), r_{BA} (Brandrup and Immergut, 1989)	0.07	0.037	22.21
r_{BC}*, r_{CA} (Delgado, 1986); r_{CB}*	2.64	6.35	0.315
k_{tAA}, k_{tBB} (Walling, 1957); k_{tCC} (Dimitratos, 1989) ($\times 10^{-4}$) ($m^3 \cdot mol^{-1} \cdot s^{-1}$)	3.49	1.91	0.00016
k_A^p, k_B^p, k_C^p (Gardon, 1968)	0.0339	0.0232	0.0022
k_A^d, k_B^d, k_C^d (Gardon, 1968)	0.0288	0.017	0.0014
k_I (s^{-1}), f (Walling, 1957)		2.0×10^{-4}	0.5
k_a ($m^3 \cdot mol^{-1} \cdot s^{-1}$), a_1, b_1**(Urretabizkaia et al., 1992)	2.04×10^6	−3.32	−1.54

* Experimentally calculated.

** $k_t = k_t(a_1 \phi_p^p + b_1 \phi_p^{p2})$.

Simulation of the performance of the NLA controller

In order to study the performance of the NLA controller, the contribution of the proportional-integral (PI) part was set to zero. The three cases presented in Table 2 were considered. This table shows that in each case the reactor was initially charged with all of the less reactive monomer, vinyl acetate (VAc), (that is, $F_A = 0$). In addition, in the initial charge, the necessary amount of butyl acrylate (BuA) and varying amounts of the most reactive monomer, methyl methacrylate (MMA) were charged. The initial amounts of MMA were as follows: *Case a*: The MMA initial charge was that required to obtain a terpolymer of a molar composition VAc/MMA/BuA = 15/35/50 (this amount of MMA and the initial amount of BuA used in each case were calculated by the method proposed by Arzamendi et al. (1992)); *Case b*: A large excess of MMA was charged at $t = 0$; *Case c*: The initial amount of MMA was much smaller than that of *Case a*. In all three simulations, the remaining monomers, MMA and BuA, were added in two separate streams of flow rates calculated by means of the NLA controller. In a third stream, emulsifier, initiator and water were added to the reactor at constant flow rate.

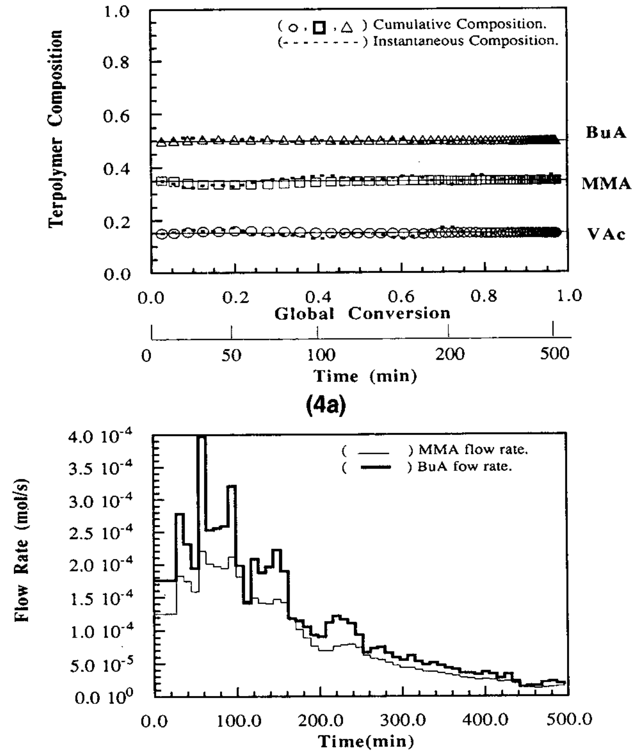
Figure 4a presents the evolution of the instantaneous and cumulative terpolymer compositions obtained using the NLA controller for the simulation of *Case a*, namely, when the initial amount of MMA was that calculated to give a terpolymer of the desired composition. It can be seen that the instantaneous compositions are very close to those required throughout the polymerization, showing a slight oscillation about the desired values. Consequently, the cumulative terpolymer compositions are homogeneous. The slight oscillation observed is due to the dead time between sampling and the time when the controller acts. Figure 4b shows the MMA and the BuA flow rates calculated by the NLA controller. The flow rates were calculated every 9 min, when the simulated measurements were available, and kept constant between samples. It can be seen that during the first 27 min the flow rates of both monomers remain constant. This is because the first sample is assumed to be taken after 9 min of polymerization and hence due to the dead time of 18 min, the first action taken by the NLA controller is that of 27 min. The initial flow rates were calculated following the method proposed by Arzamendi et al. (1992) for open-loop control strategies.

Figure 5a shows the evolution of the instantaneous and cumulative terpolymer compositions obtained using the NLA controller for the simulation of *Case b*, namely, when the initial charge contained an excess of MMA. This shows that in spite of the fact that the terpolymer formed at the beginning of the polymerization deviated from the desired compositions, the NLA controller was able to bring the instantaneous terpolymer compositions to the desired values after a few control actions. As in *Case a*, the instantaneous compositions oscillated about the desired values, but in this case the oscillation was more pronounced than in *Case a* (Figure 4a). These oscillations are basically due to the dead time (18 min) and as a result, the greater the polymerization rate, the more pronounced are the oscillations. Because of this, the oscillations practically disappear at the end of polymerization. Similar behavior but with less pronounced oscillations is observed in the cumulative compositions.

The flow rates of MMA and BuA calculated by the NLA controller for *Case b* are presented in Figure 5b. Due to the fact that the MMA is in excess in the reactor, in the first control action, the NLA controller practically stopped the flow rate of the MMA. As can be seen in Figure 5a, the amount of BuA in the reactor was initially less than that desired, but the NLA controller reduced drastically the flow rate of BuA which might appear surprising. The reason for this behavior is that, to produce a terpolymer of the desired composition, the amounts of all three monomers in the polymer particles should be kept at the desired values. Therefore, to maintain the ratio of butyl acrylate to that of vinyl acetate, whose amount was also smaller

Table 2. Recipe Used for the Simulation of the Emulsion Terpolymerization of VAc/MMA/BuA

	Seed	Initial Charge	Stream 1	Stream 2	Stream 3
Vinyl acetate (kg)	0.010	0.101	—	—	—
Methyl methacrylate (kg)	0.027	13.09×10^{-3} a 23.09×10^{-3} b 3.09×10^{-3} c	0.262	—	—
Butyl acrylate (kg)	0.048	0.053	—	0.449	—
Water (kg)	0.181	0.550	—	—	0.080
Emulsifier (Alipal CO-436) (kg)	1.75×10^{-3}	8.0×10^{-3}	—	—	2.0×10^{-3}
Initiator ($K_2S_2O_8$) (kg)	0.17×10^{-3}	3.0×10^{-3}	—	—	2.60×10^{-3}

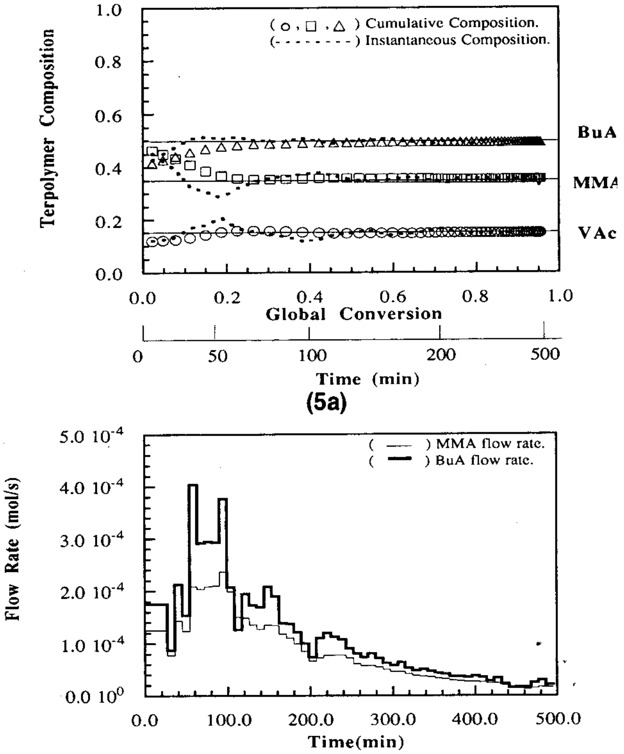


(4a)

(4b)

Figure 4. (a) Evolution of the instantaneous and cumulative terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA; (b) MMA and BuA flow rate profiles.

Calculated using the NLA controller for *Case a* in Table 2.



(5a)

(5b)

Figure 5. (a) Evolution of the instantaneous and cumulative terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA; (b) MMA and BuA flow rate profiles.

Calculated using the NLA controller for *Case b* in Table 2.

than that required (Figure 5a), the controller reduced the flow rate of BuA. The ability to stop monomer flow when an excess is detected is a powerful feature of the NLA controller. This avoids monomer accumulation in the reactor and hence the risk of reactor runaway. In subsequent controller actions, more MMA and BuA were required to be added to the reactor.

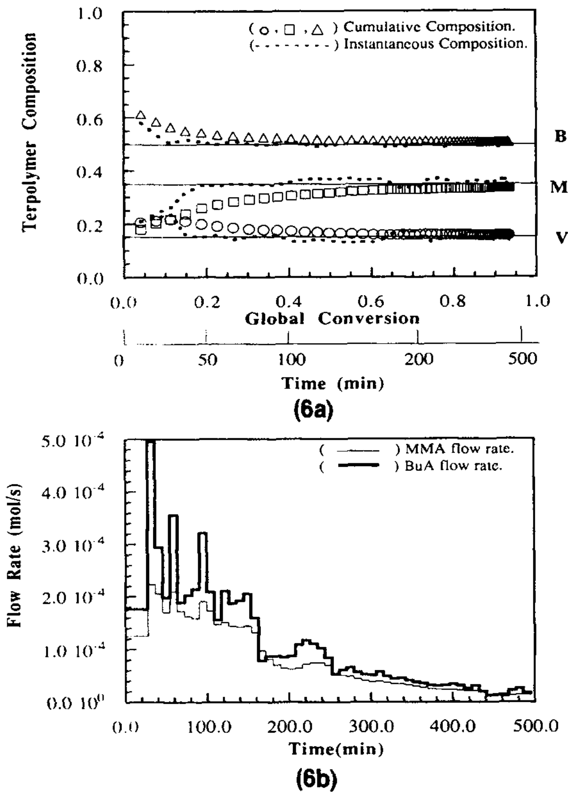
Figure 6a presents the evolution of the instantaneous and cumulative terpolymer compositions using the NLA controller when the initial amount of MMA is less than the adequate value (*Case c*, Table 2). It can be seen that the NLA controller was able to bring the instantaneous terpolymer composition to the set points after a few control actions, and then to maintain the compositions during the rest of the polymerization. As in the previous cases the evolution of the cumulative terpolymer compositions were similar to the instantaneous compositions but with oscillations of lesser magnitude.

Figure 6b shows the flow rates of MMA and BuA calculated using the NLA controller for *Case c*. As in the other two simulated reactions the flow rates were constant during the first 27 min. Once the first "measurement" was available, the flow rate of MMA was significantly increased to compensate for the deficit of MMA in the initial charge. Comparison with Figure 4b shows that the amount of MMA fed to reactor is larger than that fed when the correct initial charge was used. In addition, the flow rate of BuA is also increased even when, as Figure 6a shows, there was an apparent excess of BuA in the reactor. The reason for this behavior is that VAc was also in excess, and to maintain the ratio of the three monomers in the polymer particles, an increase in the BuA flow rate was required.

Simulation of the performance of the whole controller (NLAPI)

Simulations were carried out using the same conditions than those for the NLA controller, that is, measurements were available every 9 min and a dead time of 18 min was assumed. The first sample was taken at 9 min and hence the flow rates were not changed during the first 27 min. The three cases presented in Table 2 were simulated following the strategy presented in Figure 3. Note that the amounts of monomers under the headings stream 1, 2, and 3, represent the total quantities of these monomers added into the reactor after the initial charge.

Figure 7a presents a comparison between the instantaneous terpolymer compositions obtained using NLA and NLAPI controllers for *Case a* in Table 2, that is, when the correct amount of MMA to produce a terpolymer of molar composition VAc/MMA/BuA = 15/35/50 was initially charged in the reactor. It can be seen that both controllers produced the desired instantaneous composition. The instantaneous compositions oscillated slightly about the set point, but the oscil-

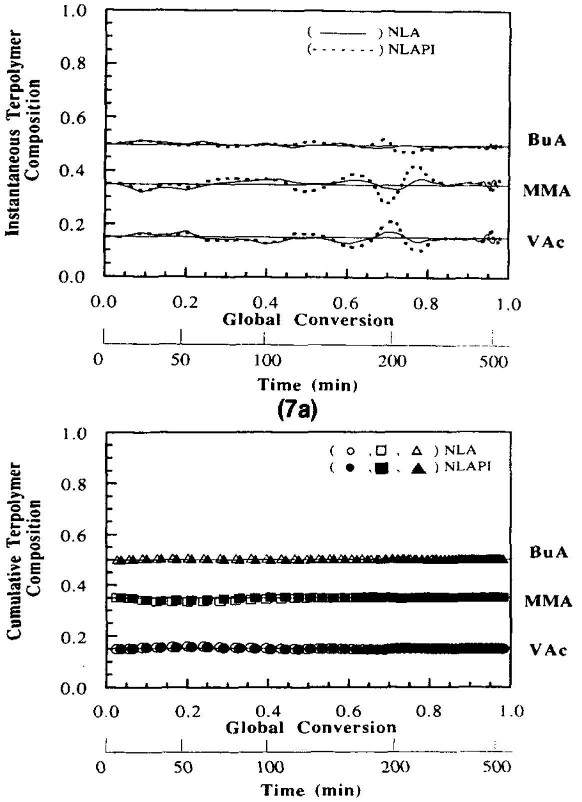


(6a)

(6b)

Figure 6. (a) Evolution of the instantaneous and cumulative terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA; (b) MMA and BuA flow rate profiles.

Calculated using the NLA controller for *Case c* in Table 2.



(7a)

(7b)

Figure 7. (a) Evolution of the instantaneous terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA; (b) evolution of the cumulative terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA.

Both NLA and NLAPI controllers are used for *Case a* in Table 2.

lations were larger for the NLAPI controller (dashed lines) than for the NLA controller.

Figure 7b shows the evolution of the cumulative terpolymer composition obtained using both NLA and NLAPI controllers for *Case a*. As it was expected, homogeneous terpolymers of the desired composition were obtained. In addition, there are no noticeable differences between the two controllers.

Figures 8a and 8b show a comparison of the evolution of the cumulative and instantaneous terpolymer compositions, respectively, obtained using the NLAPI controller for *Case b*, with those obtained with the NLA controller. It can be seen in Figure 8a that the PI contribution led to a slightly faster approach to the desired cumulative terpolymer composition. However, as it is shown in Figure 8b, this faster approach is achieved by producing a more heterogeneous instantaneous terpolymer composition. Figure 8b shows that the oscillations about the desired value are larger for the NLAPI controller than for the NLA controller. In addition, it should be pointed out that this faster performance of the NLAPI controller is attained using excessively large PI controller parameters ($k_{CB}=1{,}2\times10^{-4}$ mol/s; $\tau_{IB}=92$ s; $k_{CC}=6{,}0\times10^{-4}$ mol/s; $\tau_{IC}=135$ s). On the other hand, when reasonable values of the PI controller parameters ($k_{CB}=7{,}1\times10^{-5}$ mol/s; $\tau_{IB}=92$ s; $k_{CC}=5{,}0\times10^{-5}$ mol/s; $\tau_{IC}=135$ s) were used the contribution of the PI controller was negligible.

The evolution of the cumulative and instantaneous terpolymer compositions are shown in Figures 9a and 9b, respectively, comparing the NLAPI and the NLA controllers for *Case c*. The result is similar to that obtained for *Case b*. The contribution of the PI part of the controller gives a faster approach to the cumulative terpolymer composition set points (Figure 9a) but at the expense of a more heterogeneous instantaneous terpolymer composition (Figure 9b). A similar behavior was reported by McAuley and MacGregor (1992) in a gas-phase polyethylene reactor and by Leiza et al. (1993b) for emulsion copolymerization. More recently, MacAuley and MacGregor (1993) have shown that in control strategies having a suitable parameter updating scheme, an additional integral action did not report any advantage in product property controllers.

In the foregoing, it has been shown that: the NLA controller allows to produce a terpolymer of the desired composition even if a mistake in the initial charge of monomers in the reactor is made; the PI part of the controller does not provide any additional advantage; the control strategy avoids the accumulation of monomer in the reactor and hence reduces the risk of thermal runaway.

Experimental Validation of the Control Strategy

The control strategy was experimentally tested during the seeded emulsion terpolymerization of vinyl acetate, methyl

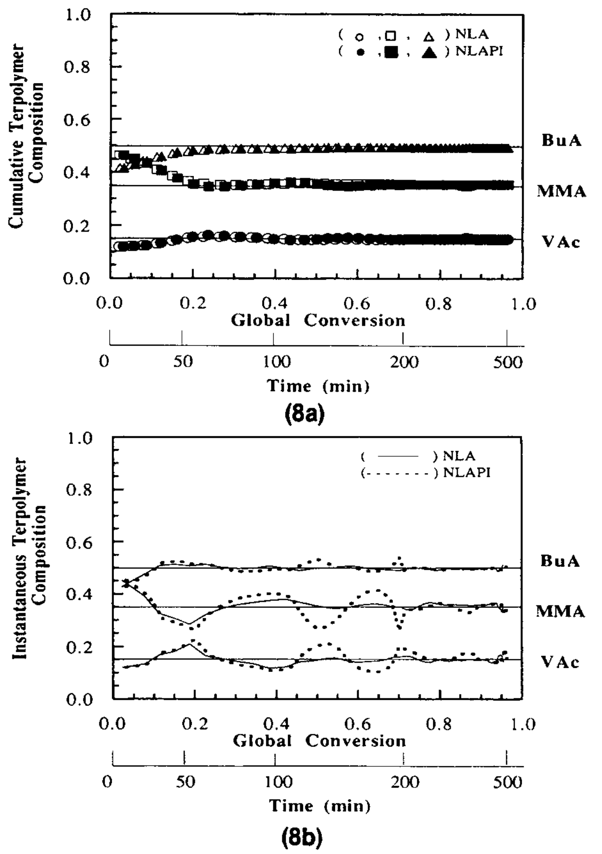


Figure 8. (a) Evolution of the cumulative terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA; (b) evolution of the instantaneous terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA.

Both NLA and NLAPI controllers are used for *Case b* in Table 2.

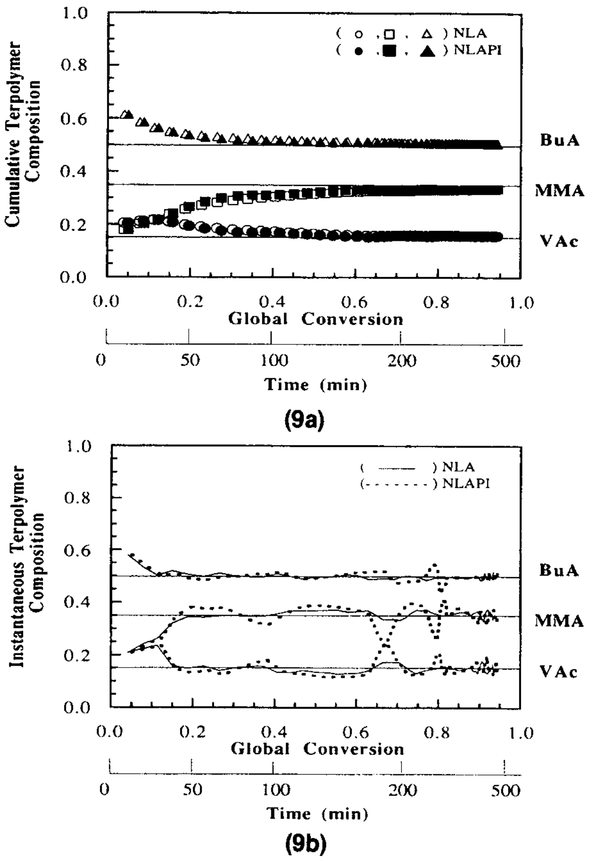


Figure 9. (a) Evolution of the cumulative terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA; (b) evolution of the instantaneous terpolymer composition simulated in the emulsion terpolymerization of VAc/MMA/BuA.

Both NLA and NLAPI controllers are used for *Case c* in Table 2.

methacrylate, and butyl acrylate. Polymerizations were carried out as in industrial practice, namely, at high solids content (55 wt. %). The goal was to produce a homogeneous terpolymer with molar composition VAc/MMA/BuA of 15/35/50. Since the simulations predicted that the NLAPI controller does not provide any advantage over the NLA strategy, only the NLA controller was used in real-time experiments.

Experimental procedure

Inhibited monomers, vinyl acetate (VAc), methyl methacrylate (MMA), butyl acrylate (BuA), and acrylic acid (AA) (hydroquinone in the vinyl acetate and p-methoxyphenol in the acrylic monomers) were used. Small amounts of polar monomers, such as acrylic acid, are included in many emulsion polymerization recipes because they enhance the latex stability, improve the wetting properties, and exhibit an increase of the adhesion with aging. The emulsifier was Alipal CO-436 (ammonium salt of sulfated nonylphenol poly(ethylenoxy) ethanol (4 ethylenoxyde) Rhône-Poulenc) and the initiator $K_2S_2O_8$. All materials were used as received. Distilled and deionized water (DDI) was used throughout. Polymerizations were carried out in the apparatus developed by Leiza et al. (1993c) and described earlier on. In some cases, the cumulative terpolymer composition was also measured off-line by means of ^{1}H NMR. The seed latex was prepared in a semicontinuous process under starved conditions at 80°C. The recipe used is given in Table 3.

Two experiments, A-1 and A-2, were carried out to verify the control strategy. The recipes of the two experiments are presented in Tables 4 and 5, respectively. As in Table 2, the amounts of monomers under the headings stream 1, 2, and 3 represent the total quantities of these monomers added into the reactor after the initial charge. In both cases the final solids content of the polymer obtained was 55 wt. %. In experiment A-1, the minimum-time policy for composition control in reactors with heat removal capacity larger than the maximum heat generation was performed. The initial monomer charges and initial monomer flow rates were calculated by means of the method developed by Arzamendi et al. (1992). Therefore, the experimental run was similar to that simulated for the *Case a* in Table 2. On the other hand, in run A-2, the case of reactors with limited heat removal capacity was considered. In addition, a constant heat removal rate was assumed. As reported by Arzamendi et al. (1992), in those cases only a fraction of the less reactive monomer can be included in the initial charge and the rest has to be fed at a constant flow rate. Table 5 shows that only a fraction of vinyl acetate is initially charged into

Table 3. Recipe Used for the Seed

	Initial Charge	Stream 1	Stream 2
Vinyl acetate (kg)	—	0.067	—
Methyl methacrylate (kg)	—	0.182	—
Butyl acrylate (kg)	—	0.324	—
Acrylic acid (kg)	—	5.8×10^{-3}	—
Water (kg)	0.180	0.740	0.280
Emulsifier (Alipal CO-436) (kg)	1.26×10^{-3}	9.1×10^{-3}	1.26×10^{-3}
Initiator ($K_2S_2O_8$) (kg)	0.12×10^{-3}	—	1.03×10^{-3}
Buffer ($NaHCO_3$) (kg)	0.12×10^{-3}	—	1.03×10^{-3}

Table 4. Recipe Used in the Experiment A-1 Carried Out to Experimentally Check the Control Strategy

	Seed	Initial Charge	Stream 1	Stream 2	Stream 3
Vinyl acetate (kg)	0.010	0.101	—	—	—
Methyl methacrylate (kg)	0.027	0.013	0.262	—	—
Butyl acrylate (kg)	0.048	0.053	—	0.449	—
Acrylic acid (kg)	0.86×10^{-3}	1.67×10^{-3}	2.621×10^{-3}	4.492×10^{-3}	—
Water (kg)	0.181	0.550	—	—	0.080
Emulsifier (Alipal CO-436) (kg)	1.75×10^{-3}	8×10^{-3}	—	—	2×10^{-3}
Initiator ($K_2S_2O_8$) (kg)	0.175×10^{-3}	3×10^{-3}	—	—	2.6×10^{-3}
Buffer ($NaHCO_3$) (kg)	0.175×10^{-3}	3×10^{-3}	—	—	2.6×10^{-3}

$T = 70°C$.

Table 5. Recipe Used in the Experiment A-2 Carried Out to Experimentally Check the Control Strategy

	Seed	Initial Charge	Stream 1	Stream 2	Stream 3	Stream 4
Vinyl acetate (kg)	0.010	0.016	—	—	0.085	—
Methyl methacrylate (kg)	0.0275	2.083×10^{-3}	0.272	—	—	—
Butyl acrylate (kg)	0.049	7.935×10^{-3}	—	0.494	—	—
Acrylic acid (kg)	0.86×10^{-3}	0.266×10^{-3}	2.72×10^{-3}	4.94×10^{-3}	0.85×10^{-3}	—
Water (kg)	0.181	0.490	—	—	—	0.140
Emulsifier (Alipal CO-436) (kg)	1.75×10^{-3}	6×10^{-3}	—	—	—	4×10^{-3}
Initiator ($K_2S_2O_8$) (kg)	0.175×10^{-3}	1.8×10^{-3}	—	—	—	3.6×10^{-3}
Buffer ($NaHCO_3$) (kg)	0.175×10^{-3}	1.8×10^{-3}	—	—	—	3.6×10^{-3}

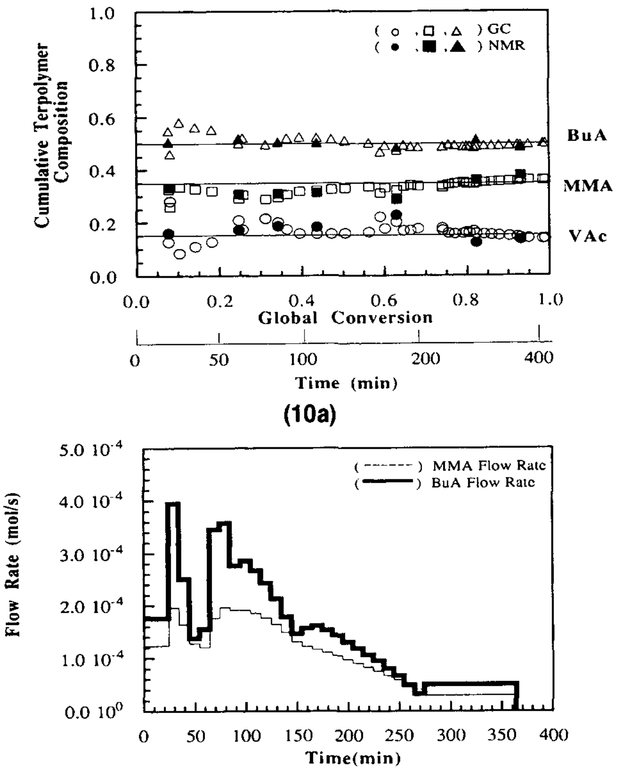
$T = 70°C$.

the reactor and that the remaining vinyl acetate is fed at a constant flow rate during 180 min. During the experiments samples were taken starting at time = 4 min and thereafter every 10 min. The time required to sample, analyze, and calculate the state estimate is approximately 18 min. Accordingly, during the first 22 min the flow rates were held constant. Thereafter, the flow rates were calculated by the controller as the measurements were available. In order to calculate the conversion and the cumulative terpolymer composition, the amount of reaction mixture withdrawn from the reactor by sampling was taken into account. On the other hand, this was not taken into account in the controller (Eqs. 18 and 19) because simulation showed that the error in the total number of moles of VAc was less than 3% when the effect of the sampling was neglected. Notice that for the other monomers the errors should be smaller because they were continually fed into the reactor whereas all of the VAc was in the initial charge.

Figure 10a shows the evolution of the cumulative terpolymer composition obtained in experiment A-1. Both, on-line gas chromatography measurements and off-line ^1H NMR measurements of the cumulative terpolymer composition are shown. A good agreement between on-line and off-line measurements was observed. It should be noted that no monomer droplets were present initially in the system. Nevertheless, in a system having monomer droplets, the monomers ratio in this phase is nearly the same as in the polymer particles and hence the presence of monomer droplets would not represent a perturbation for the control strategy. The flow rates of monomers MMA and BuA were calculated on-line by the controller and are presented in Figure 10b. Figure 10a shows that, apart from some initial oscillations, the control strategy allowed a homogeneous terpolymer of the desired composition to be obtained. Figure 10b shows that during the first 22 min the flow rates of MMA and BuA were constant. Then, the controller changes the flow rates of BuA and MMA in order to account for reactor conditions.

Figure 11a presents the evolution of the cumulative terpolymer composition obtained in run A-2. It can be seen that a homogeneous terpolymer was obtained throughout the polymerization. The flow rates of MMA and BuA calculated online by the nonlinear adaptive controller as well as the constant flow rate of VAc fed during the experiment are presented in Figure 11b. The flow rates of MMA and BuA increased up to the time in which the constant addition of VAc was stopped. This was due to the accumulation of vinyl acetate that occurred in the reactor during the VAc addition period. Once the addition of VAc was stopped, its concentration began to decrease and consequently the flow rates of MMA and BuA decreased.

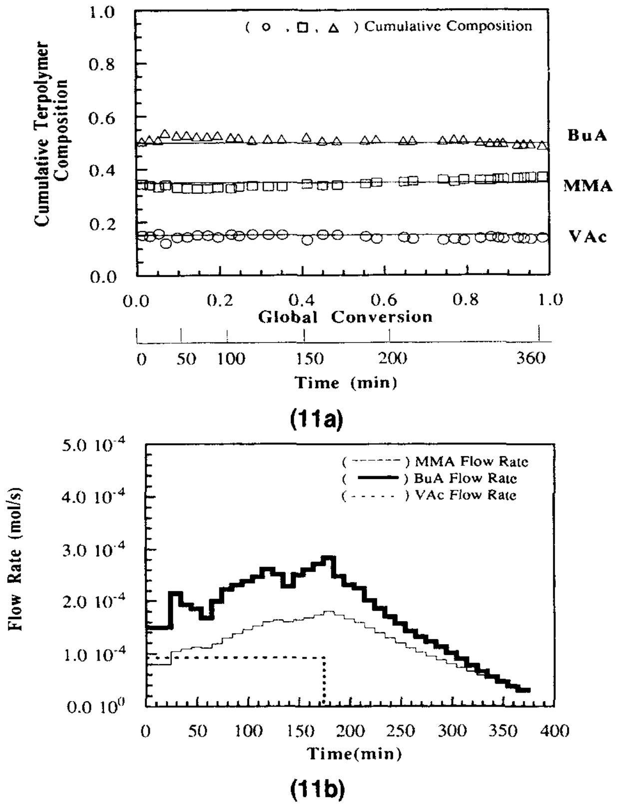
It should be pointed out that these performances were achieved in a high solids content (≈ 55 wt. %) emulsion polymerization and that such control has not previously been reported in the literature.



(10a)

(10b)

Figure 10. (a) Experimental evolution of the cumulative terpolymer composition during experiment A-1 carried out using the recipe given in Table 4; (b) MMA and BuA flow rate profiles calculated by means of the control strategy in experiment A-1.



(11a)

(11b)

Figure 11. (a) Experimental evolution of the cumulative terpolymer composition during experiment A-2 carried out using the recipe given in Table 5; (b) MMA and BuA flow rate profiles calculated by means of the control strategy in experiment A-2.

VAc constant flow rate was used.

Conclusions

A closed-loop strategy for terpolymer composition control in a semicontinuous emulsion polymerization of high solids content is presented. The strategy is based on a nonlinear adaptive (NLA) plus proportional-integral (PI) controller that uses the estimated values of the amounts of monomers in the polymer particles. These estimates are calculated by means of a nonlinear optimization algorithm, which minimizes the difference between the on-line measurements and the prediction of a mathematical model of the process of amounts of unreacted monomers in the reactor. The controller calculates the feed rates of the more reactive monomers that have to be fed into the reactor to make sure that after a sampling time interval, the monomer ratios in the polymer particles lead to the formation of a terpolymer of the desired composition. It was shown that the NLA controller was able to bring the terpolymer composition to the desired value when the polymerization was started with incorrect initial monomer ratios. Moreover, it was found that the addition of the PI part to the NLA controller does not provide any noticeable advantage. The controller was experimentally verified under typical industrial conditions producing a 55 wt. % solids content terpolymer of molar composition VAc/MMA/BuA = 15/35/50. The control strategy provided a homogeneous terpolymer of the desired composition. It should be pointed out that it is the first time in which a homogeneous emulsion terpolymer of the desired composition is produced by controlling the addition of two monomers in emulsion terpolymerization systems. Furthermore, previous published works on related systems have been with latexes of between 25 to 33%.

Acknowledgments

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Notation

a_1, b_1 = parameters used in the termination rate constant to take into account the gel effect (Table 1)
A, B, C = amount of monomers VAc, MMA, and BuA, respectively, in the reactor (mol)
A_p, B_p, C_p = amount of monomers VAc, MMA, and BuA, respectively, in the polymer particles (mol)
$C_{\text{inst}\,ij}$ = ratio of the polymerization rate of monomer i and j respectively (Eq. 12)
$\text{Error}_i(t)$ = difference between the set point and the estimated terpolymer composition
f = efficiency factor for initiator decomposition
F_i = flow rate of monomer i (mol/s)
$[i]_p$ = concentration of monomer i in polymer particles (mol/m^3)

J = objective function
k_a = entry rate coefficient (m^3/mol·s)
k_{C_i} = proportional gain of the PI controller for monomer i
k^i = partition coefficient of monomer i between polymer particles and aqueous phase, respectively (Eq. 20)
k_i^j = partition coefficient of monomer i between the phase j and aqueous phase (Table 1)
k_I = rate constant for initiator decomposition (s^{-1}) (Table 1)
k_{Pij} = propagation rate constant (m^3/mol·s)
k_{tij} = termination rate constant (m^3/mol·s)
k_1, k_2, k_3 = adjustable parameters (Eq. 9)
$\bar{n}$ = average number of radicals per particle
N_A = Avogadro's number
NLA = nonlinear adaptive controller
NLAPI = nonlinear adaptive plus proportional-integral controller
N_T = total number of polymer particles
P_i = time-averaged probability of finding a free radical with ultimate unit of type i
r_{ij} = reactivity ratio of monomer i with monomer j (k_{Pii}/k_{Pij})
R_{Pi} = polymerization rate of monomer i (mol/s)
t = time
V_{aq} = volume of the aqueous phase (m^3)
V_p = total volume of the monomer swollen polymer particles (m^3)
$Y_{inst\,i}$ = instantaneous composition referred to monomer i

Greek letters

α, β, γ = parameters given by Eqs. 6, 7, and 8, respectively
β_i = ratios of monomer i and monomer A in the polymer particles that ensure the formation of a terpolymer of the desired composition (Eq. 13)
Δt = time increment
τ_{I_i} = reset time or integral time for monomer i

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