Simultaneous Control of Copolymer Composition and MWD in Emulsion Copolymerization

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Copolymer composition and molecular-weight distribution of linear copolymers were controlled simultaneously by maintaining concentrations of the monomers and chain-transfer agent (CTA) at calculated values. The unreacted amounts of monomers and CTA were inferred by on-line measurements of the reaction heat. Styrene/n-butyl acrylate emulsion copolymers of predefined constant compositions and MWDs (narrow and broad monomodal, and bimodal with different polydispersities index in each mode) were obtained by this control approach using tertdodecyl mercaptan as CTA.

Introduction

Emulsion polymerization is currently the predominant process used in industry to produce a large variety of polymers for multiple uses (e.g., paints, adhesives, coatings, varnishes, carpet backings, and binders). Many applications of these polymer latexes require the formation of a continuous film with high mechanical strength. Both the film formation process and the mechanical properties of the film strongly depend on the chemical composition and molecular-weight distribution (MWD) of the polymer. Chemical composition mainly determines the glass transition temperature (T_g) of a copolymer (Odian, 1991). On the other hand, MWD affects important end use properties of the film, such as elasticity, strength, toughness, and solvent resistance.

Copolymer composition is by far the molecular property of polymer latexes that have been more often controlled. To achieve this goal, an *a priori* simple but not always easily attainable condition must be fulfilled, namely that the ratio of the comonomers in the polymerization loci should be controlled. Most of the control strategies implemented to achieve this goal were open-loop, based on mathematical models of the process or on extensive experimental work (Broadhead et al., 1985; Hamielec et al., 1987; Arzamendi and Asua, 1989, 1990, 1991; Arzamendi et al., 1991; Leiza et al., 1993; Van Doremaele et al., 1992; Schoonbrood et al., 1993). The reasons for using open-loop control strategies stem from the difficulty in developing robust and fast on-line sensors to measure either the copolymer composition or the unreacted monomers, the lack of robust nonlinear feedback controllers to deal with the important nonlinearities arising in batch and semibatch emulsion polymerization processes (Bequette, 1991; Leiza and Asua, 1997), and the still limited knowledge of the mechanisms involved in emulsion polymerization.

Closed-loop control strategies have been used to control the copolymer composition. Thus, gas chromatography (GC) has been successfully applied to on-line monitoring and control of copolymer composition (Guyot et al., 1981; Dimitratos et al., 1989; Leiza et al., 1992; Urretabizkaia et al., 1994). Dimitratos et al. (1989) and Leiza et al. (1992) combined GC with an extended Kalman filter for on-line estimation of the concentration of unreacted monomers, and hence controlling copolymer composition. Urretabizkaia et al. (1994) used the same equipment as Leiza et al. (1992) to control the terpolymer composition of emulsion polymerizations carried out at high solids contents. The main problem with on-line GC is that only relatively infrequent and delayed data are available, and therefore it cannot be applied to fast processes. Besides, the lack of robustness of the sampling and diluting device employed to inject samples into the GC make its industrial implementation unreliable.

A different approach to control the copolymer composition of emulsion polymerization processes has been proposed by Canu et al. (1994) and Sáenz de Buruaga et al. (1996, 1997a,b,

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2000). In this approach, optimal monomer addition profiles were obtained as a function of conversion by solving an optimization problem off-line where one of the constraints was the copolymer composition requirement. Canu et al. (1994) used densimetry and sound velocity to obtain an on-line estimation of conversion, and Sáenz de Buruaga et al. (1996, 1997a,b, 2000) used on-line reaction calorimetry. These approaches cannot be seen as a true classic feedback-control strategy, since the measurement of the copolymer composition was not directly used in the feedback controller.

The on-line measurement of the MWD may be achieved through the use of automated size-exclusion chromatography (SEC). Although experimental setups capable of performing this task for solution polymerization have been reported (Ponnuswamy et al., 1988; Budde and Reichert, 1988; Ellis et al., 1988, 1994), to our knowledge, no such application has been implemented for emulsion polymerization. The lack of hardware sensors might be overcome by the use of software sensors, namely by estimating the MWD from the measurements of other variables that are available on-line. Although some success has been obtained in solution polymerization systems (Jo and Bankoff, 1976; Schuler and Suzhen, 1985; Schuler and Papadopoulou, 1986; Ellis et al., 1988; Adebekun and Schork, 1989; Crowley and Choi, 1997) generally speaking, the compartmentalized nature of emulsion polymerization makes the MWD nonobservable from usually available on-line measurements (monomer conversions and temperature). Nevertheless, under some conditions of practical significance, the MWD of emulsion polymers is not affected by the compartmentalization of the system. A typical example is when a chain-transfer agent (CTA) is used and the kinetic chain length is controlled by the chain-transfer reaction to CTA. This feature has been exploited by Storti and Morbidelli (1997), Echevarria et al. (1998), and Vicente et al. (2001). Storti and Morbidelli (1997) used densimetry to monitor conversion on-line, and polystyrene latexes of constant molecular weight were produced by maintaining the styrene/CTA (CCl_4) ratio at a given value. Echevarría et al. (1998) used on-line gas chromatography to measure the unreacted amount of styrene and CCl_4, and then a nonlinear controller was used to track trajectories of styrene and CCl_4 that ensured the production of a polystyrene latex with a given MWD. Thus, narrow, broad, and even bimodal distributions were successfully prepared. Nevertheless, neither densimetry nor gas chromatography are robust enough to be implemented in an industrial environment. Vicente et al. (2000) have demonstrated that noninvasive techniques such as on-line reaction calorimetry can control the MWD of polystyrene latexes using the control strategy developed by Echevarria et al. (1998). In addition, they showed that CTAs having a reactivity higher than carbon tetrachloride (for example,1-butyl mercaptan) are more suitable to control the MWD of polystyrene latexes because of the lower influence of its calorimetric estimation and the shortest process times required.

Reaction calorimetry (Regenass, 1985; Wu, 1985; MacGregor, 1986; Moritz, 1989; Schuler and Schmidt, 1992; Urretabizkaia et al., 1993; Sáenz de Buruaga et al., 1996, 1997a,b, 2000; Févotte et al., 1996, 1998) is a technique that is well-suited for on-line monitoring of polymerizations, since these reactions are very exothermic. The measurement is noninvasive, rapid, and robust, as it is based on temperature measurements. In addition, this technique can be easily implemented in industrial reactors. The main drawback of this technique is that it does not provide a direct measurement of either the unreacted amounts of monomer or the CTA, which are necessary for applying strategies to control the copolymer composition and the MWD of polymer latexes. Nevertheless, it has been shown that the on-line measurement of the heat of reaction can be used as input for state observers or estimators that allow the estimation of the unreacted amounts of monomers. Gugliotta et al. (1995a,b) and Sáenz de Buruaga et al. (1996, 1997a,b, 2000), using open-loop observers for this purpose, showed that, if the observer parameters (mainly reactivity ratios) are accurate enough, the estimation of the unreacted amount of monomers in batch and semicontinuous emulsion polymerization is good enough to be implemented in strategies to control the composition of co/terpolymers. Similarly, Vicente et al. (2001) have recently shown that if the chain-transfer reactivity ratio ($C_{tr,\mathrm{CTA}}$) and the enthalpy of polymerization of the monomer ($-\Delta H_r$) are known within a reasonable accuracy, an accurate estimation of the CTA is possible. In addition, they have also demonstrated that for polymerization processes where the chain transfer to CTA is the controlling termination rate, the estimation of the instantaneous molecular weight from calorimetric data is more accurate as the reactivity of the CTA increases.

All of the previously discussed control strategies were developed to control a single polymer property. Only few works have been published on the simultaneous control of MWD and copolymer composition in free radical copolymerization (Tsoukas et al., 1982; Congalidis et al., 1989; Kozub and MacGregor, 1992; Crowley and Choi, 1999; Choi and Butala, 1991; Saldívar and Ray, 1997; Sayer et al., 2000), and only the last three were experimentally verified. Tsoukas et al. (1982) used simulation to investigate the impact of various control schemes, including temperature, monomer, and initiator addition as manipulated variables, on the performance of a multiobjective function optimization technique in a free radical copolymerization of styrene and acrylonitrile (S/AN). Congalidis et al. (1989) designed a control system for a solution copolymerization of MMA/VAc in a continuous stirred-tank reactor using a combination of feedforward, ratio, and feedback control to regulate polymer production rate, copolymer composition, molecular weight, and reactor temperature. They tested the control strategy on a nonlinear model of the process for set point changes and compensation of unmeasured reactor disturbances. Kozub and MacGregor (1992) treated the multivariable polymer quality-control problem by computer simulation. Their inferential nonlinear feedback-control strategy was able to successfully simulate the simultaneous control of the overall conversion, instantaneous copolymer composition and instantaneous weight average molecular weight, in a styrene–butadiene semibatch emulsion polymerization. Crowley and Choi (1999) presented a method to design optimal control policies for a semibatch free radical solution copolymerization with copolymer composition and hydrodynamic volume distribution as the main control objectives, but unfortunately this work was not validated experimentally. Choi and Butala (1991) developed an open-loop control strategy for a semibatch solution copolymerization of MMA/VAc, where varying monomer feed rates and reactor temperature produced copolymers of the desired composition and average molecular weights. Saldívar and Ray (1997) studied the simultaneous control of instantaneous copolymer composition and average molecular weights in an emulsion polymerization of MMA/VAc in semibatch reactors tracking optimal open-loop monomer and CTA trajectories. Also a nonlinear model-predictive control scheme, which used the instantaneous property technique to recompute optimal trajectories on-line, was tested by simulation. Recently, Sayer et al. (2000) have investigated the effect of different strategies for copolymer composition control on the MWD and gel fraction in the emulsion copolymerization of MMA/*n*-BA. The authors assessed the feasibility of simultaneous control of the copolymer composition and the MWD.

In this work, we present a control strategy for the simultaneous control of the cumulative copolymer composition and the MWD. The control of these properties was achieved by maintaining both the comonomer ratio and the ratio of the overall unreacted monomer concentration to CTA at the values that ensured the production of the copolymer of the desired quality. Unreacted amounts of monomers and CTA in the reactor were estimated by means of on-line measurements of the heat of reaction obtained in a modified Mettler-Toledo RC1 calorimeter. The estimates were then used in a closed-loop control strategy that aimed at tracking trajectories of monomers and CTA that ensure a certain desired copolymer composition and MWD of the polymer.

To validate the control strategy, the following copolymers were prepared:

1. Styrene/*n*-butyl acrylate copolymer with a composition in styrene $Y = 0.25$, and weight-average molecular weight ($\overline{M}_w$) of 650,000 and minimum attainable polydispersity index, $PI = 2$.
2. Styrene/*n*-butyl acrylate copolymer with a composition in styrene $Y = 0.5$, and weight-average molecular weight ($\overline{M}_w$) of 400,000 and minimum attainable polydispersity index, $PI = 2$.
3. Styrene/*n*-butyl acrylate copolymer with a composition in styrene $Y = 0.5$, and bimodal MWD: Mode 1; $\overline{M}_{w1} =$ 1,050,000 and $PI = 2.5$, and Mode 2; $\overline{M}_{w2} = 115{,}000$ and $PI = 3$.
4. Styrene/*n*-butyl acrylate copolymer with a composition in styrene $Y = 0.15$ and weight-average molecular weight of 625,000 and a broad MWD, $PI = 5$.

The manuscript is organized as follows: First, the open-loop observer used to infer the unreacted amounts of monomers and CTA is presented. Second, the design of the closed-loop control strategy is shown. Finally, the control strategy is validated by preparing styrene/*n*-butyl acrylate copolymer latexes of given copolymer composition and MWD using *tert*-dodecyl mercaptan as the CTA.

Estimation of Unreacted Amount of Monomer and CTA from Calorimetric Data

Reaction calorimetry is a powerful technique for monitoring on-line polymerization processes. It is noninvasive, rapid, robust, and can be conveniently applied to industrial reactors. Unfortunately, only the overall polymerization rate can be directly obtained from the heat of reaction. This is an important drawback if one wishes to use this sensor to control copolymer composition and/or MWD. The reason is that the control strategies require the individual amounts of each comonomer and also the CTAs in the case where one wishes to control the MWD. This drawback can be overcome by using either state estimators or observers to infer those states from calorimetric measurements. Different approaches have been explored in the literature. Both estimators and observers (Sáenz de Buruaga et al., 1996, 1997a,b, 2000; Vicente et al., 2001; Hammouri et al., 1999; McKenna et al., 2000) have been applied to estimate unreacted amounts of monomers in solution and emulsion co/terpolymerization. In this work an open-loop observer similar to that used in Sáenz de Buruaga et al. (1996, 1997a,b, 2000) and Vicente et al. (2001) was used to infer the unreacted amounts of monomers and the concentration of CTA from the calorimetric data obtained in a Mettler-Toledo RC1 calorimetric reactor.

The overall heat of polymerization, Q_r, was determined on-line almost continuously from the calorimeter reactor [details about the calorimeter used in this work can be obtained elsewhere (Sáenz de Buruaga et al., 1997a)]. The heat of polymerization, Q_r, is related to the polymerization rates of the individual monomers as follows

$$Q_r = R_{pA}(-\Delta H_A) + R_{pB}(-\Delta H_B), \tag{1}$$

where R_{pA} and R_{pB} are the rates of polymerization of the monomers A and B, respectively, and $(-\Delta H_A)$ and $(-\Delta H_B)$ are the corresponding enthalpies of polymerization.

The material balances for monomers in a semicontinuous emulsion polymerization reactor are given by

$$\frac{di}{dt} = F_i - R_{pi} = F_i - \bar{k}_{pi}[i]_p \frac{\bar{n}N_p}{N_A} \quad i = A, B, \tag{2}$$

where $[i]_p$ is the concentration of monomer i in the polymer particles; $\bar{n}$ is the average number of radicals per particle; N_p is the total number of polymer particles; N_A is Avogadro's constant; and $\bar{k}_{pi}$ is the overall propagation rate constant of monomer i, and can be expressed as follows (Forcada and Asua, 1985)

$$\bar{k}_{pi} = k_{pAi}P_A + k_{pBi}P_B; \quad i = A, B \tag{3}$$

$$P_j = \frac{k_{pij}[j]_p}{k_{pij}[j]_p + k_{pji}[i]_p}, \tag{4}$$

$$P_i = 1 - P_j, \tag{5}$$

where k_{pij} is the propagation rate constant of monomer i, with monomer j and P_j the time-averaged probability of finding a free radical with terminal unit of type j in the polymer particles.

From Eqs. (2–5), the well-known Mayo-Lewis equation for the instantaneous copolymer composition in emulsion copoly-

Table 1. Parameters Used in the Reactions

Parameter	Value
$K_{d,w}^{A}$ (Echevarría et al., 1998)	2,700
$K_{d,w}^{B}$ (Gugliotta et al., 1995a)	705
$K_{d,w}^{\mathrm{CTA}}$ (Nomura et al., 1994)	4.9×10^{7}
$K_{p,w}^{A}$ (Echevarría et al., 1998)	1,500
$K_{p,w}^{B}$ (Gugliotta et al., 1995a)	460
$K_{p,w}^{\mathrm{CTA}}$ (Nomura et al., 1994)	$3.18\ \times 10^{7}$
k_{pA} (L/mol·s) (Buback et al., 1988)	275
k_{pB} (L/mol·s) (Plessis et al., 2000)	4,600
r_A (Sáenz de Buruaga et al., 2000)	0.75
r_B (Sáenz de Buruaga et al., 2000)	0.2
$k_{tr,CTAA}$ $k_{tr,CTAB}$ (L/mol·s) (Estimated in this work)	460
$(-\Delta H_A)$ (J/ mol) (Varela et al., 1996)	73.0×10^{3}
$(-\Delta H_B)$ (J/ mol) (Brandrup and Immergut, 1989)	78.2×10^{3}

A = styrene
B = n-butyl acrylate
$K_{i,j}^{K}$ = partition coefficient of reagent K between phases i and j

merization systems can be obtained

$$Y_A = \frac{Rp_A}{Rp_A + Rp_B} = \frac{r_A + \dfrac{[B]_P}{[A]_P}}{r_A + 2\dfrac{[B]_P}{[A]_P} + r_B\left(\dfrac{[B]_P}{[A]_P}\right)^2}, \tag{6}$$

where r_A and r_B are the reactivity ratios of monomer A and B, respectively.

The material balance for CTA in a semicontinuous emulsion polymerization reactor is given by

$$\frac{d\mathrm{CTA}}{dt} = F_{\mathrm{CTA}} - R_{\mathrm{CTA}} = F_{\mathrm{CTA}} - \bar{k}_{tr,\mathrm{CTA}}[\mathrm{CTA}]_P \frac{\bar{n}N_p}{N_A}, \tag{7}$$

where $\bar{k}_{tr,\mathrm{CTA}}$ is the overall chain-transfer rate constant to the CTA that can be expressed as follows

$$\bar{k}_{tr,\mathrm{CTA}} = k_{tr,\mathrm{CTAA}}P_A + k_{tr,\mathrm{CTAB}}P_B, \tag{8}$$

where $k_{tr,\mathrm{CTAA}}$ and $k_{tr,\mathrm{CTAB}}$ are the chain-transfer rate constant to the CTA of monomer A and B, respectively. In this work, $k_{tr,\mathrm{CTAA}} = k_{tr,\mathrm{CTAB}}$, as given in Table 1.

Besides, as shown in the Appendix, the instantaneous number-average chain length of a polymer produced when chain transfer to CTA is the main termination event is given by

$$\bar{X}_{ni} = \frac{\bar{k}_{pA}[A]_P + \bar{k}_{pB}[B]_P}{\bar{k}_{tr,\mathrm{CTA}}[\mathrm{CTA}]_P}. \tag{9}$$

Combining Eqs. 1–9, the material balances for the monomers and the CTA can be written as a function of the heat released by polymerization, monomer reactivity ratios, and the reactivity ratios of the CTA, $C_{tr,\mathrm{CTA}i} = k_{tr,\mathrm{CTA}i}/k_{pi}$, where $i = A$, B, as follows:

$$\frac{dA}{dt} = F_A - \frac{Q_r}{(-\Delta H_A) + (-\Delta H_B)\dfrac{(1-Y_A)}{Y_A}} \tag{10}$$

$$\frac{dB}{dt} = F_B - \frac{Q_r}{(-\Delta H_A)\dfrac{Y_A}{(1-Y_A)} + (-\Delta H_B)} \tag{11}$$

$$\frac{d\mathrm{CTA}}{dt} = F_{\mathrm{CTA}} - (R_{p_A} + R_{p_B})\left(\frac{\bar{k}_{tr,\mathrm{CTA}}[\mathrm{CTA}]_P}{\bar{k}_{p_A}[A]_P + \bar{k}_{p_B}[B]_P}\right). \tag{12}$$

The open-loop observer given by Eqs. 10–12 can be used to estimate monomer and CTA concentration from the heat released by polymerization, although the rate of convergence of the estimation is not adjustable and it is given by the process model itself (Soroush, 1997). In addition, if the error at $t = 0$ is zero, it will remain zero during the process (as long as the model is good enough). All the model contributions in Eqs. 10–12 are given by r_i, $C_{tr,\mathrm{CTA}i}$, and $(-\Delta H_i)$, which can be accurately known from independent experiments.

By solving Eqs. 10–12 simultaneously, it is possible to obtain the unreacted amounts of monomers (A, B) and CTA during the course of polymerization from which overall, X, and fractional conversion, X_f, and instantaneous, Y_{Ai}, and cumulative, $Y_{A,\mathrm{cumul}}$, copolymer composition, and instantaneous and cumulative number-average molecular weights, $\bar{M}_{n,\mathrm{ins}}$ and $\bar{M}_{n,\mathrm{cumul}}$, can be readily calculated, as follows

$$X = \frac{A_0 + \int_0^t F_A dt + B_0 + \int_0^t F_B dt - A_f - B_f}{A_{\mathrm{Tot}} + B_{\mathrm{Tot}}} \tag{13}$$

$$X_f = \frac{A_0 + \int_0^t F_A dt + B_0 + \int_0^t F_B dt - A_f - B_f}{A_0 + \int_0^t F_A dt + B_0 + \int_0^t F_B dt,} \tag{14}$$

$$Y_{Ai} = \frac{\bar{k}_{pA}[A]_P}{\bar{k}_{pA}[A]_P + \bar{k}_{pB}[B]_P} \tag{15}$$

$$Y_{A,\mathrm{cumul}} = \frac{A_0 + \int_0^t F_A dt - A_f}{A_0 + \int_0^t F_A dt - A_f + B_0 + \int_0^t F_B dt - B_f} \tag{16}$$

$$\bar{M}_{n,\mathrm{ins}} = \frac{\bar{k}_{pA}[A]_P + \bar{k}_{pB}[B]_P}{\bar{k}_{tr,\mathrm{CTA}}[\mathrm{CTA}]_P} P_m \tag{17}$$

$$\bar{M}_{n,\mathrm{cumul}} = \frac{A_0 + \int_0^t F_A dt - A_f + B_0 + \int_0^t F_B dt - B_f}{\mathrm{CTA}_0 + \int_0^t F_{\mathrm{CTA}} dt - \mathrm{CTA}_f} P_m, \tag{18}$$

where A_0, B_0, and CTA_0 are the initial amounts of monomers and CTA in the reactor; A_f, B_f, and CTA_f are the unreacted amounts of monomers and CTA present in the

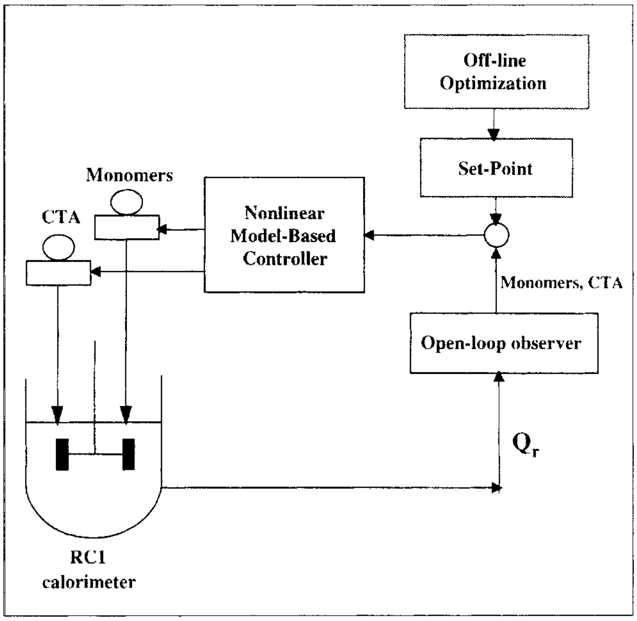


Figure 1. Closed-loop control scheme.

reactor; F_A, F_B, and F_{CTA} are the corresponding flow rates; A_{Tot} and B_{Tot} are the total amounts of monomers in the formulation; and P_m is the averaged molecular weight of the repeating unit.

Control Strategy

In this work the approach of Echevarría et al. (1998) was adopted to control the MWD of copolymer latexes. This approach requires the measurement of the unreacted amounts of monomer and CTA. These values were inferred by means of the open-loop observer described in the previous section and then compared with the setpoint calculated by means of an off-line optimization (see below). Finally, a nonlinear model-based controller was used to calculate the control actions for the next time interval. Figure 1 summarizes the control scheme.

The control strategy is based on the fact that for linear polymers produced by free radical polymerization, the polymer chains do not suffer any modification once they are formed. This opens the possibility of decomposing the desired final MWD in a series of instantaneous MWDs to be produced at different stages of the reaction (Echevarría et al., 1998). When chain transfer to CTA is the main termination event, each of those instantaneous MWDs can be characterized by a single parameter, which is the instantaneous number-average chain length, $\bar{X}_{ni}$ (see the Appendix). Therefore the problem reduces to calculating the sequence of the values of $\bar{X}_{ni}$ that provide the desired final MWD. In order to calculate the $\bar{X}_{ni}$ value that has to be produced at each value of X, the final MWD is discretized as follows

$$W_c^*(n) = \frac{1}{X_f} \sum_{j=1}^{k} W_j(n) \Delta X_j = \frac{\Delta X}{X_f} \sum_{j=1}^{k} \frac{n}{\bar{X}_{ni_j}^2} \exp\left(-\frac{n}{\bar{X}_{ni_j}} \right), \tag{19}$$

where X_f is the final overall conversion; $\bar{X}_{ni_j}$ is the instantaneous number-average chain length produced in the conversion increment j; $W_j(n)$ is the instantaneous MWD produced in the conversion increment j [a constant value of ΔX_j (ΔX) is used in Eq. 19]; and k is the number of increments in which X_f is divided. For a given number of conversion increments, the required values of $\bar{X}_{ni_j}$ can be calculated by minimizing the following equation

$$\underset{\bar{X}_{ni}}{\mathrm{Min}} \left\{ \sum_n \left[W_c^d(n) - W_c^*(n) \right]^2 \right\}, \tag{20}$$

where $W_c^d(n)$ and $W_c^*(n)$ are the desired and the calculated MWDs. This is a nonlinear optimization in which the number of values of n should be greater than the number of conversion increments. Typically, 100 values of n were used for $k = 20$. It is worth pointing out that the larger the number of conversion increments, the closer to the desired MWD will be the solution, but the computation time will increase as the number of parameters to be estimated, $\bar{X}_{ni}$, increases.

A priori any MWD, $W_c^d(n)$, with polydispersity equal or higher than two can be prepared by this method. Strictly speaking, the maximum molecular weight achievable with this technique is that produced with the minimum amount of CTA that ensures that termination by chain transfer to CTA is the main termination event (Vicente et al., 2001). In practice this is very close to the molecular weight obtained without CTA. On the other hand, MWDs containing very low molecular weights may require the use of amounts of CTA that exceed the maximum allowable quantities (usually lower than 1 wt. % based on monomer weight) used in industrial practice.

The minimization of Eq. 20 gives the values of $\bar{X}_{ni}$ to be produced at different ΔX, but it does not provide any hint about the sequence in which they have to be produced. For a highly reactive CTA, almost any sequence will be implementable, but in this work, to avoid diffusional problems of the CTA, a sequence where continuously decreasing molecular-weight polymer is produced during the process was considered (an exception to this rule is the production of a MWD of minimum polydispersity index when the same molecular weight has to be produced throughout the process).

Once the function $\bar{X}_{ni} = f(X)$ has been calculated by the described minimization, this function is used as one of the constraints for the optimization of the process.

In what follows the optimization algorithm and the nonlinear model-based controller used are briefly described.

Off-line optimization algorithm

The goal of the off-line optimization algorithm is to calculate the setpoint trajectories of the controlled variables that ensure the production of an emulsion polymer of the desired MWD and copolymer composition in the minimum amount of process time.

The objective function to be minimized to achieve this minimum process time is

$$\underset{[M]_p}{\mathrm{Min}} \left[\int_0^1 \frac{1}{R_p} dX \right], \tag{21}$$

where R_p is the polymerization rate and X is the overall conversion, defined as the ratio between the polymer in the reactor and the monomer in the formulation (Eq. 13).

The minimization of Eq. 21 is subjected to the following constraints:

1. The polymer produced must have the desired copolymer composition and the final MWD $[W_c^d(n)]$. Note that in this case the control of MWD is equivalent to produce the required $\overline{X}_{ni}$ at each conversion interval. A polynomial fitting of the decreasing $\overline{X}_{ni}$ sequence calculated in the minimization was used for simplicity in the optimization algorithm

$$\frac{[A]_p}{[B]_p}=f(X) \tag{22}$$

$$\overline{X}_{ni}\,\alpha\,\frac{[A]_p+[B]_p}{[\mathrm{CTA}]_p}=f(X). \tag{23}$$

2. The maximum amounts of the monomers and CTA that can be added to the reactor are the total amounts of these compounds in the formulation; A_{Tot}, B_{Tot}, and $\mathrm{CTA}_{\mathrm{Tot}}$, respectively

$$A_f + A_{\mathrm{pol}} \leq A_{\mathrm{Tot}} \tag{24}$$

$$B_f + B_{\mathrm{pol}} \leq B_{\mathrm{Tot}} \tag{25}$$

$$\mathrm{CTA}_f + \mathrm{CTA}_{\mathrm{pol}} \leq \mathrm{CTA}_{\mathrm{Tot}}, \tag{26}$$

where the subscripts f and pol stand for free and polymerized amounts, respectively.

3. The monomers and CTA already charged in the reactor cannot be removed

$$\frac{d\lfloor A_f + A_{\mathrm{pol}}\rfloor}{dX} \geq 0 \tag{27}$$

$$\frac{d\lfloor B_f + B_{\mathrm{pol}}\rfloor}{dX} \geq 0 \tag{28}$$

$$\frac{d\lfloor \mathrm{CTA}_f + \mathrm{CTA}_{\mathrm{pol}}\rfloor}{dX} \geq 0. \tag{29}$$

4. The amount of monomers, and hence that of CTA, in the latex particles should be limited. The presence of droplets should not be allowed, as the monomer contained in the monomer droplets does not contribute to increasing the polymerization rate, but causes a significant loss of control capacity. Safety can also be a reason to limit the amount of free monomer in the reactor.

The optimization provides the amounts of monomers and CTA in the reactor at any overall conversion. These profiles are independent of the kinetics of the process and can be regarded as master curves.

Nonlinear model-based controller

The role of the nonlinear model-based controller is to calculate the feed rates of the monomers and CTA until the next measurement of the heat of reaction is available (F_A, F_B, and F_{CTA}). The controller is based on the discretized material balances

$$A_{f_{t+1}}=\hat{A}_{f_t}+(F_A-R_{pA})\Delta t \tag{30}$$

$$B_{f_{t+1}}=\hat{B}_{f_t}+(F_B-R_{pB})\Delta t \tag{31}$$

$$\mathrm{CTA}_{f_{t+1}}=\mathrm{C\hat{T}A}_{f_t}+(F_{\mathrm{CTA}}-R_{\mathrm{CTA}})\Delta t, \tag{32}$$

where $\hat{A}_{f_t}$, $\hat{B}_{f_t}$, and $\mathrm{C\hat{T}A}_{f_t}$ are the estimated values of the monomers and CTA at the beginning of the control interval, Δt; and $A_{f_{t+1}}$, $B_{f_{t+1}}$, and $CTA_{f_{t+1}}$ are the desired values of these variables at the end of the interval, as given by the optimization presented previously

$$A_{f_{t+1}}=f(X_{t+1}) \tag{33}$$

$$B_{f_{t+1}}=f(X_{t+1}) \tag{34}$$

$$\mathrm{CTA}_{f_{t+1}}=f(X_{t+1}) \tag{35}$$

$$X_{t+1}=\frac{A_{T_t}+F_A\Delta t-A_{f_{t+1}}+B_{T_t}+F_B\Delta t-B_{f_{t-1}}}{A_{\mathrm{Tot}}+B_{\mathrm{Tot}}} \tag{36}$$

where A_{T_t} and B_{T_t} are the total amounts of each monomer added into the reactor up to the beginning of the control interval. Equations 30–36 are a set of seven nonlinear algebraic equations with seven unknowns, $A_{f_{t+1}}$, $B_{f_{t-1}}$, $CTA_{f_{t+1}}$, X_{t+1}, F_A, and F_{CTA}. Their solution gives the feed rates of monomer and CTA to be added to the reactor during the control interval that will allow the production of the desired copolymer in terms of composition and MWD.

This approach can be used to prepare any copolymer one may need to accomplish the end-use properties of the latex, as long as chain transfer to CTA is the controlling mechanism.

Experimental Validation of the Control Strategy

The control strategy was experimentally validated for the unseeded emulsion copolymerization of styrene/*n*-butyl acrylate using *tert*dodecyl mercaptan (TDM) as CTA. In order to check the performance of the control strategy, samples were taken during the reaction and the monomer conversion, copolymer composition, and MWD were determined off-line by using gravimetry, gas chromatography (GC), and size-exclusion chromatography (SEC). The GC apparatus was a Shimadzu GC-14A fitted with a polar column (BP20, SGE; 25 m long and 0.53 mm wide; stationary phase: polyethylene glycol) and Flame Ionization Detector. The SEC apparatus was a Waters 510 (Milford, CT), equipped with a refractometer detector (Waters 2410) and two columns in series (Styragel HR4, HR6; 10^4 and 10^6 Å). It was operated at 30°C, with a THF flow rate of 1 mL/min, and latex samples were dissolved in THF prior to injection. The molecular weight of the samples was calculated using the universal calibration technique using polystyrene standards (Polymer Laboratories).

The production of copolymer latexes with very different copolymer composition and MWDs was considered. For the sake of brevity only four representative cases will be presented in this work:

Table 2. Recipes Used for Producing Copolymer S/*n*-BA Latexes of C1, C2, C3, and C4

	Case C1			Case C2			Case C3			Case C4		
Ingredient (g)	Total	Initial Charge	Feeds	Total	Initial Charge	Feeds	Total	Initial Charge	Feeds	Total	Initial Charge	Feeds
Styrene	85	—	85	180	0	180	180	—	180	50	—	50
n-BA	315	—	315	220	0	220	220	—	220	350	—	350
H_2O	800	775	25	800	760	40	800	714	86	800	700	100
TDM	0.25	—	0.25	0.4	—	0.4	2.14	—	2.14	4	0	4
$K_2S_2O_8$	1	1	—	1	1	—	1	1	—	1	1	—
$NaHCO_3$	1	1	—	1	1	—	1	1	—	1	1	—
SLS	8	7.75	0.25	8	7.6	0.4	8	7.15	0.85	8	7	1

C1—Copolymer with a cumulative copolymer composition styrene/*n*-butyl acrylate = 25/75 (S/*n*-BA = 25/75) and MWD with $PI = 2$ and $\overline{M}_w = 6.5\times10^5$.

C2—Copolymer with a cumulative copolymer composition S/*n*-BA = 50/50 and MWD with $PI = 2$ and $\overline{M}_w = 4\times10^5$.

C3—Copolymer with a cumulative copolymer composition S/*n*-BA = 50/50 and a bimodal MWD: $\overline{M}_{w1} = 1.05\times10^6$ and $PI_1 = 2.5$; $M_{w2} = 1.15\times10^5$ and $PI_2 = 3$.

C4—Copolymer with a cumulative copolymer composition S/*n*-BA = 15/85 and MWD with $PI = 5$ and $\overline{M}_w = 6.25\times10^5$.

Experiments were carried out in a modified RC1 calorimeter equipped with the HP60 stainless-steel reactor. Details of the experimental setup and the on-line determination of the heat released by polymerization can be found elsewhere (Saenz de Buruaga et al., 1997a). Table 1 presents the parameters used in this work.

Case C1

The first case was the production of a copolymer with a constant copolymer composition S/*n*-BA = 25/75, $\overline{M}_w = 6.5\times10^5$, and minimum polydispersity index ($PI = 2$). Table 2 presents the formulation used in Run 1. To produce this constant molecular-weight polymer, the ratio of total unreacted monomer (styrene plus *n*-butyl acrylate) to unreacted CTA has to be kept constant during the entire process. Simultaneously, the copolymer composition was controlled by keeping the comonomer concentration ratios at the required values. Figure 2 presents the profiles of the amounts of monomers and CTA to be fed into the reactor, as calculated by the optimization for this case. Figures 3 and 4 show the evolution of the cumulative copolymer composition and molecular weights, respectively (average molecular weights in Figure 4a and the entire MWD in Figure 4b). It can be seen that a copolymer of the desired quality was obtained.

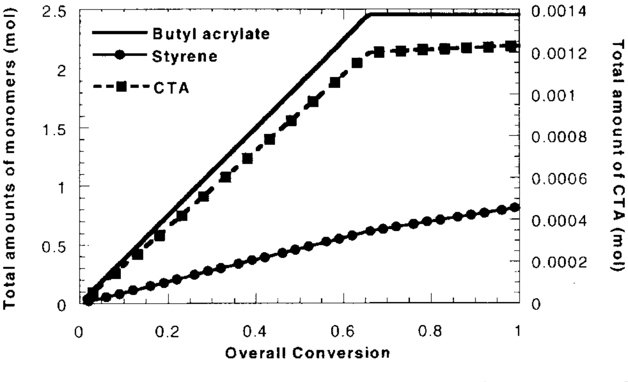


Figure 2. Optimal trajectories for the total amounts of monomers and CTA to produce the copolymer of case C1.

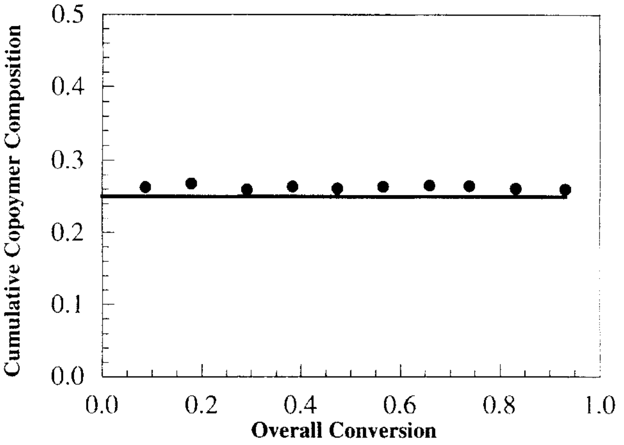


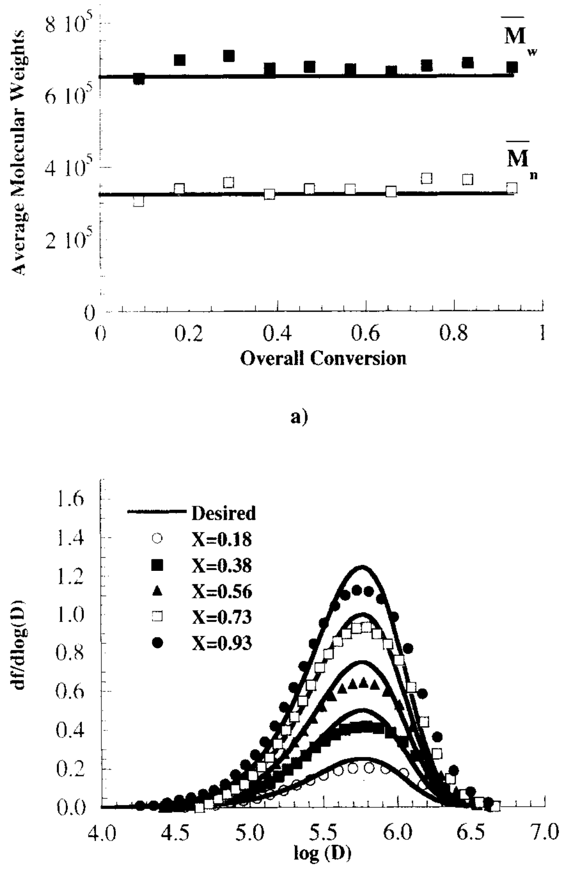
Figure 3. Evolution of the cumulative copolymer composition related to styrene produced in case C1.

Desired value (——); experimental results (●).

Figure 5 shows the flow rates of monomers and CTA implemented on-line by the controller at each sampling interval (20 s was considered) to track the profiles in Figure 2. Monomer and CTA flow rates are high during the first 50 min, then the flow rate of the less reactive monomer (*n*-butyl acrylate) and the CTA were stopped and the flow rate of the more reactive monomer (styrene) was maintained at the values that ensure the production of the copolymer of the desired composition. Note that the flow rates of styrene were much lower than those of *n*-BA, because the required copolymer composition was only 25 mol % in styrene, and styrene is more reactive than *n*-BA.

Case C2

In this case the production of a copolymer with a minimum polydispersity index was also sought, but the average molecular weight was lower than for Case 1 ($\overline{M}_w = 400{,}000$) and the cumulative copolymer composition sought was S/*n*-BA = 50/50 (a common comonomer ratio used for producing latexes for paints). Table 2 presents the formulation used in this case (Run 2). Figure 6 presents the optimal profiles of monomers and CTA to be fed into the reactor. Figure 7 shows



a)

b)

Figure 4. Molecular weights produced in case C1.

(a) Cumulative average molecular weights; (b) MWD produced at different conversions.

the evolution of the cumulative copolymer composition with respect to styrene. It can be seen that a copolymer of the desired composition was obtained. Furthermore, Figure 8a shows the average cumulative molecular weights obtained during Run 2. A more detailed comparison of the polymer sought and that produced is given by Figure 8b, where the entire MWD is shown at different conversions during the controlled process. A fairly good agreement between the desired and obtained MWD was achieved. Finally, Figure 9 shows the flow rates of monomers and CTA fed into the reactor in this case.

Case C3

Case C3 was the production of a copolymer with constant copolymer composition S/*n*-BA = 50/50 and a bimodal MWD with two peaks (50 wt. % of the polymer in each peak) of different polydispersities: $\overline{M}_{w1} = 1.05\times 10^6$ and $PI_1 = 2.5$, and $\overline{M}_{w2} = 1.15\times 10^5$ and $PI_2 = 3$. Table 2 shows the recipe used in Run 3 for the production of this bimodal copolymer.

Figure 10a presents the sequence of the instantaneous number-average molecular weights that ensures the production of the desired final MWD (this was calculated using Eq. 20). Once the evolution of the required instantaneous number-average molecular weight was known, the optimization algorithm allowed calculation of the optimal trajectories for monomers and CTA to be followed during the experiment. These trajectories are shown in Figure 10b. It can be seen that to maintain the comonomer ratio the required amount of *n*-BA was always larger than that of styrene. Moreover, during the production of the first 50% of the polymer, the amount of TDM required was low since the mode with the large molecular weight was prepared first (as shown in Figure 10a). At 50% conversion, a sudden addition of TDM was required to start producing the low molecular-weight mode. Afterwards, more TDM was added to produce the polydispersity required for the low molecular-weight mode.

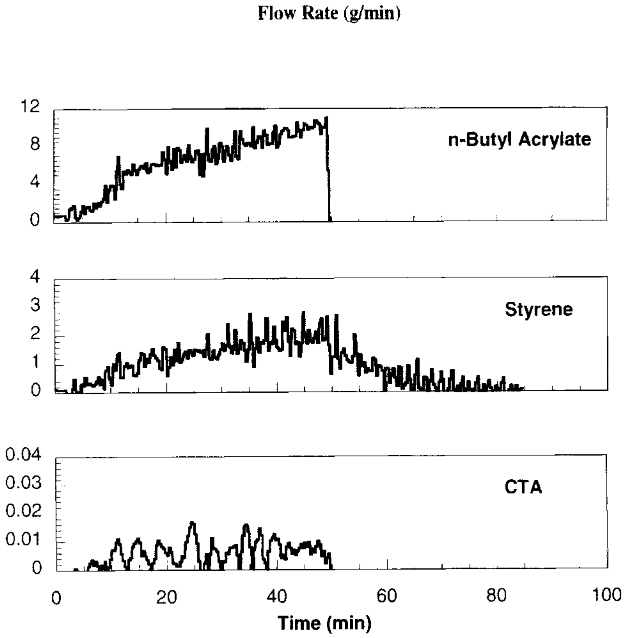


Figure 5. Flow rates of monomers and CTA calculated on-line by the nonlinear controller when a copolymer of case C1 was sought.

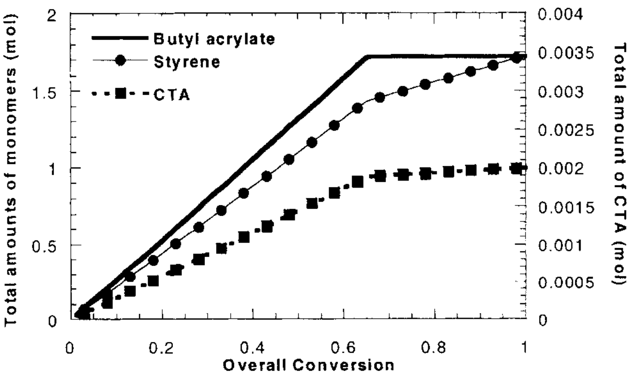


Figure 6. Optimal trajectories for the total amounts of monomers and CTA to produce the copolymer of case C2.

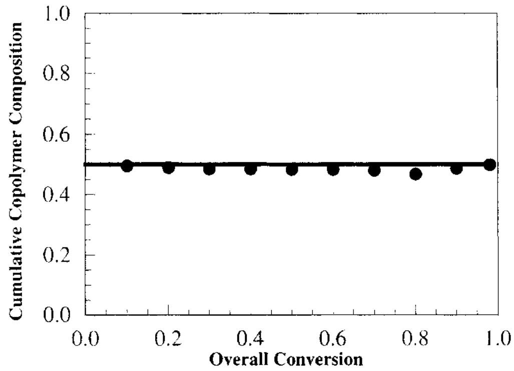
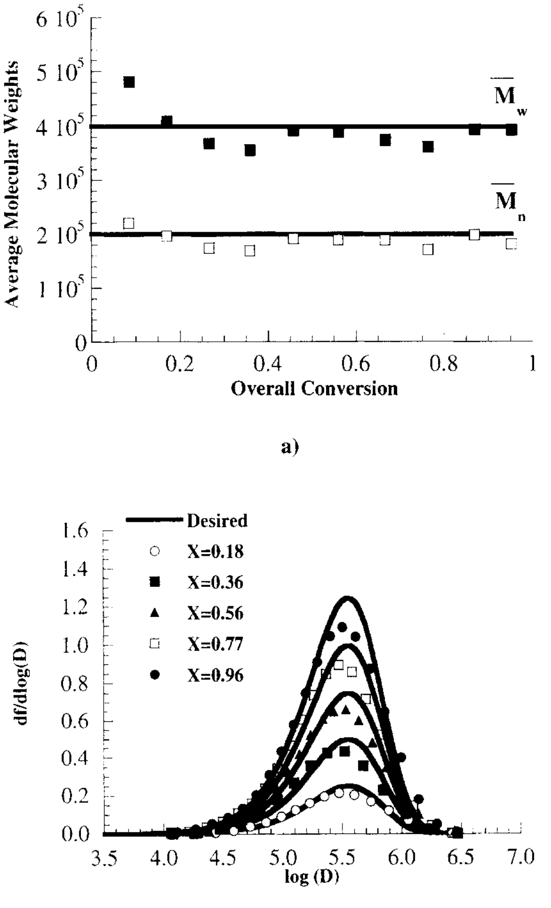


Figure 7. Evolution of the cumulative copolymer composition related to styrene produced in case C2.

Desired value (——); experimental results (●).

Figures 11, 12a, and 12b present a comparison between the desired composition and the molecular weights obtained in the controlled process. It can be seen that the polymer produced had the desired quality.



a)

b)

Figure 8. Molecular weights produced in case C2.

(a) Cumulative average molecular weights; (b) MWD produced at different conversions.

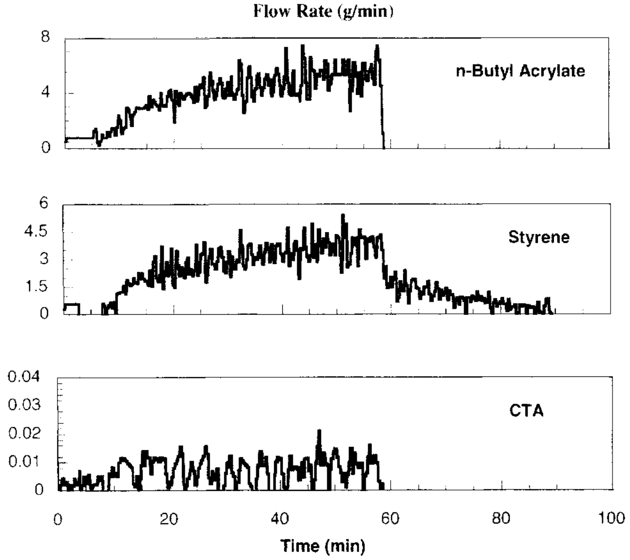


Figure 9. Flow rates of monomers and CTA calculated on-line by the nonlinear controller when a copolymer of case C2 was sought.

Case C4

The last case considered was the production of a copolymer with a broad MWD and low styrene content in the copolymer S/*n*-BA = 15/85 (a common comonomer ratio used for producing pressure-sensitive adhesives). The MWD sought was $\overline{M}_w = 6.25 \times 10^5$ and $PI = 5$. Table 2 presents the recipe used in this case (Run 4).

Figure 13a shows that the required copolymer composition was successfully produced during the process. Furthermore, Figure 13b shows the average cumulative molecular weights obtained during Run 4. The polymer produced had a slightly broader distribution than that required ($\overline{M}_w$ are larger than those sought). The reason for this deviation is that the comonomer ratio used in the experiment is rich in *n*-BA. Polymers containing this monomer in large amounts are apt to suffer polymer chain transfer leading to short- and long-chain branching (Plessis et al., 2000). Therefore, in Run 4 (15 mol % of styrene) it is very likely that chain transfer to polymer occurred to some extent, and hence the molecular weight produced was shifted toward higher values.

Figure 14 shows the flow rates of monomers and CTA calculated on-line by the nonlinear controller at each sampling interval. Monomer flow rates are high during the first 50 min of the process, and the feed rate of CTA is kept low to produce the large molecular-weight fraction of the polymer. Once the total amount of the less reactive monomer was added, the feed rate of styrene decreased, but the flow rate of CTA increased to produce the low molecular-weight fraction of the polymer.

Conclusions

In this work the copolymer composition and the molecular-weight distribution (MWD) of emulsion polymers were on-line controlled simultaneously by maintaining the comonomer ratio and the overall unreacted monomer con-

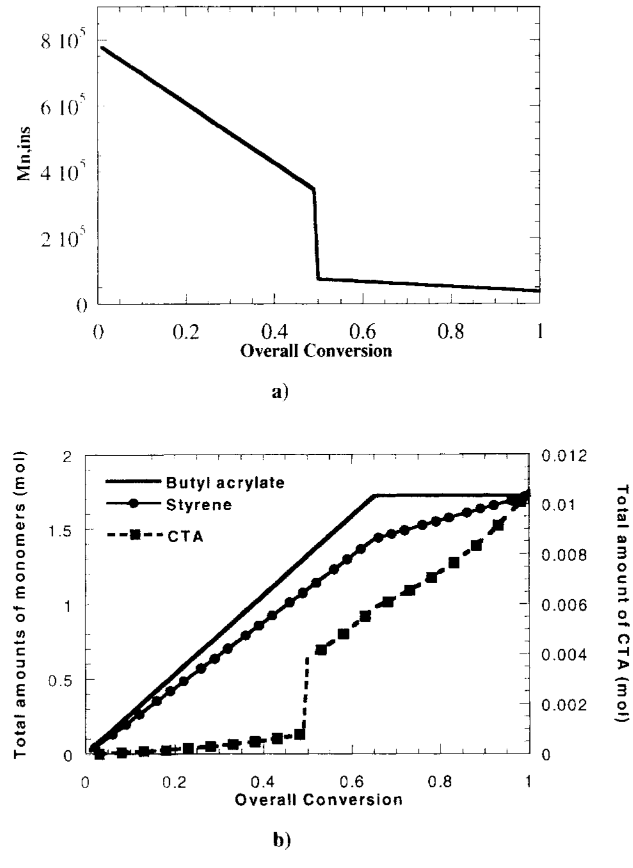


Figure 10. (a) Evolution of the instantaneous average amount of molecular weight required to produce the desired final MWD for case C3; (b) optimal trajectories for the total number of monomers and CTA to produce the copolymer of case C3.

centration of chain-transfer agent (CTA) ratio at calculated values. This was accomplished by means of a closed-loop control strategy that uses the on-line measurement of the heat of polymerization as input of an open-loop observer that provides estimates of the unreacted amounts of monomer and CTA in the reactor. These estimates are used by a nonlinear model-based controller to find the trajectories of the total amount of monomer and CTA required to produce a copolymer of the desired quality (copolymer composition and MWD).

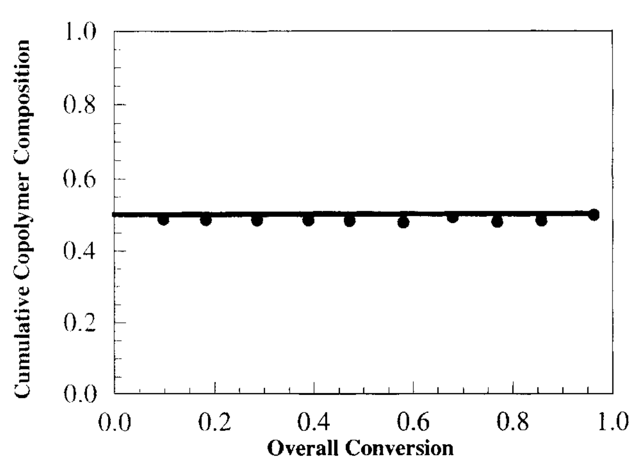


Figure 11. Cumulative copolymer composition related to styrene in case C3

Desired value (——); experimental results (●).

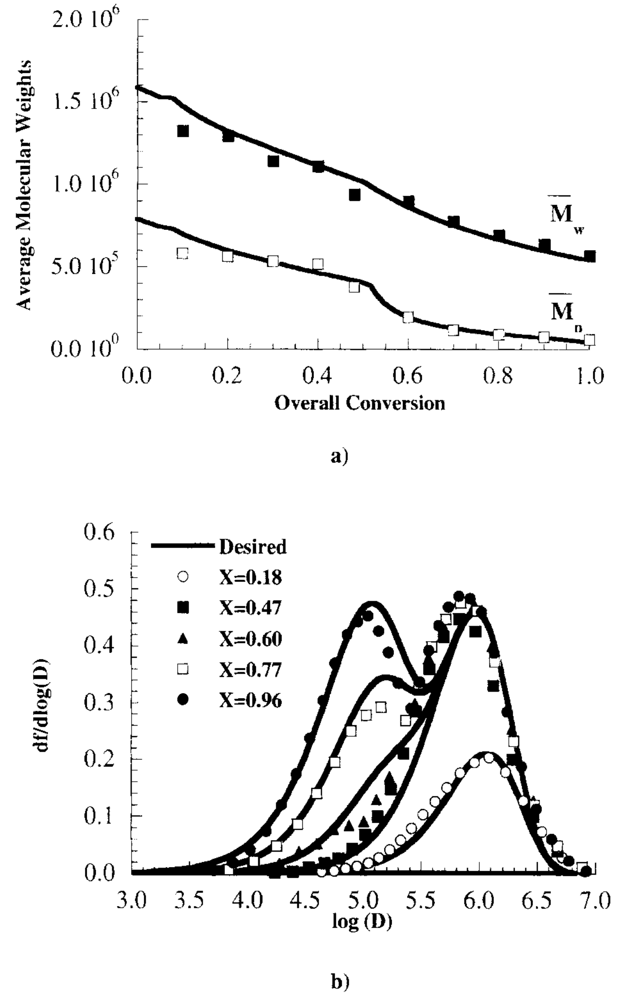


Figure 12. Molecular weights produced in case C3

(a) Cumulative average molecular weights; (b) MWD produced at different conversions.

This control strategy allowed the production of linear copolymers of any copolymer composition and MWD. Thus, for the emulsion polymerization of styrene/*n*-butyl acrylate, copolymers with narrow, broad, and bimodal distributions of different polydispersities and copolymer compositions were produced using *tert*-dodecyl mercaptan as CTA. It is worth noting that the maximum amount of CTA used was 1 wt.%, based on monomer for the broader distribution sought.

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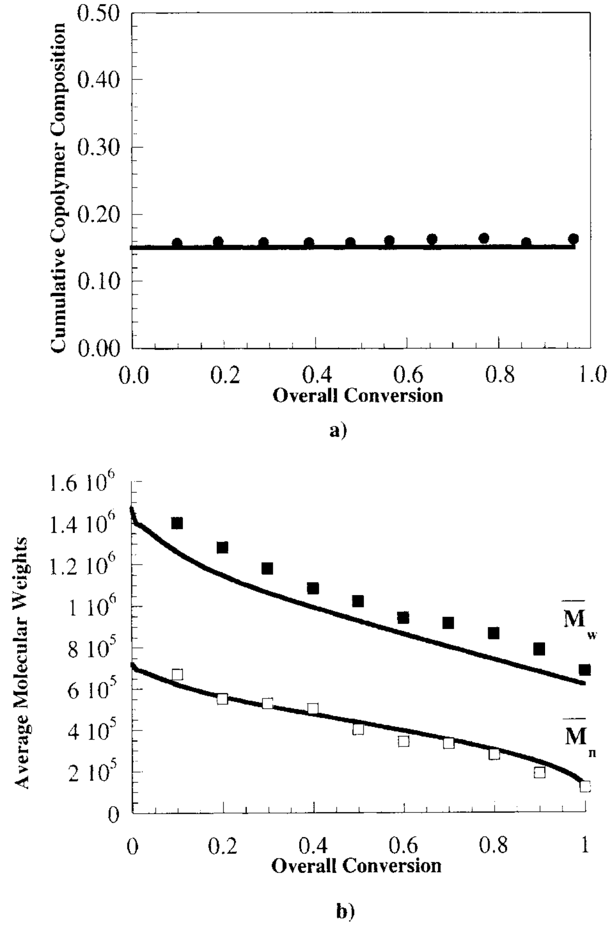

a)

b)

Figure 13. (a) Cumulative copolymer composition; (b) cumulative average molecular weight produced in case C4.

Desired values (——); experimental results (●).

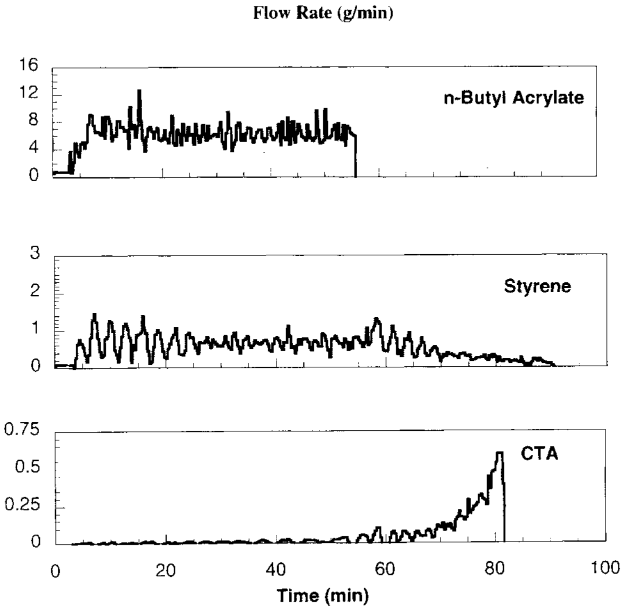

Figure 14. Flow rates of monomers and CTA calculated by the nonlinear controller for Run 4 where a copolymer of case C4 was sought.

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Appendix: Molecular-Weight Distribution in Polymerization Using CTA: Linear Polymers

In free radical polymerization, the instantaneous number-average chain length can be expressed as the ratio between the propagation (R_p) and termination (R_t) reaction rates (Odian, 1991)

$$\bar{X}_n = \frac{R_p}{R_t}. \tag{A1}$$

Assuming that the polymerization in the aqueous phase is negligible, the rate of polymerization of an emulsion copolymerization is given by

$$R_p = R_{pA} + R_{pB} = \left(\bar{k}_{pA}[A]_p + \bar{k}_{pB}[B]_p\right)\frac{\bar{n}N_p}{N_A}, \tag{A2}$$

where $[A]_p$ and $[B]_p$ are the concentration of monomers A and B, respectively, in the polymer particles; $\bar{n}$ is the average number of radicals per particle; N_p is the total number of polymer particles; N_A is Avogadro's constant; and $\bar{k}_{pA}$ and $\bar{k}_{pB}$ are the average propagation rate constant of monomers A and B, respectively.

The termination rate, R_t, can be expressed as a sum of the contribution of homomolecular (chain transfer) and bimolecular termination reactions. When CTA is present, chain transfer to CTA is the main termination event

$$R_t = \bar{k}_{tr,\text{CTA}}[\text{CTA}]_p \frac{\bar{n} N_p}{N_A}, \tag{A3}$$

where $[\text{CTA}]_p$ is the concentration of the CTA in the polymer particles, and $\bar{k}_{tr,\text{CTA}}$ is the overall chain-transfer rate constant to the CTA.

Under these circumstances, the instantaneous number-average chain length can be calculated as a function of the ratio of the concentration of monomers to CTA in the polymer particles as follows

$$\bar{X}_{ni} = \frac{\bar{k}_{pA}[A]_p + \bar{k}_{pB}[B]_p}{\bar{k}_{tr,\text{CTA}}[\text{CTA}]_p}. \tag{A4}$$

Furthermore, the polydispersity index (PI) is equal to two (Billmeyer, 1962)

$$PI = \frac{\bar{X}_{w_i}}{\bar{X}_{n_i}} = 2. \tag{A5}$$

From these values the instantaneous MWD can be calculated by using the Schultz-Flory distribution (Billmeyer, 1962)

$$W(n) = \frac{Y(nY)^z \exp[-nY]}{\Gamma(z+1)} \tag{A6}$$

$$z = \frac{1}{\left(\frac{\bar{X}_{w_i}}{\bar{X}_{n_i}} - 1\right)} \tag{A7}$$

$$Y = \frac{z+1}{\bar{X}_{w_i}}, \tag{A8}$$

where $W(n)$ is the weight fraction of polymer chains of length n, and Γ is the gamma function.

When the instantaneous polydispersity index is equal to 2, Eq. A6 reduces to the most probable distribution

$$W(n) = \frac{n}{\bar{X}_{n_i}^2} \exp\left[-\frac{n}{\bar{X}_{n_i}}\right]. \tag{A-9}$$

In addition the cumulative MWD, $W_c(n)$, can be calculated as follows

$$W_c(n) = \frac{1}{X}\int_0^X W(n)\,dX, \tag{A10}$$

where X is the overall monomer conversion.

Therefore, a polymer with a given desired MWD can be tailored by producing instantaneous fractions of polymer of polydispersity equal to two in such a way that the sum of these fractions provides the desired MWD.

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