On-Line Control of a Semibatch Emulsion Polymerization Reactor Based on Calorimetry

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In this work, on-line calorimetry was used to estimate the conversion and the copolymer composition in emulsion polymerization systems. Real-time feedback control of the polymer composition during the semibatch emulsion copolymerization of vinyl acetate and butyl acrylate was carried out. Both homogeneous copolymers and copolymers with previous defined composition profiles were obtained. It was shown that the feedback control was able to avoid monomer accumulation in the reactor, and hence potentially dangerous thermal runaways, without any deleterious effect on the polymer composition, when a sudden inhibition was caused by deliberately adding a solution of hydroquinone. The use of feedback control for the maximization of the production rate under safe conditions in the unseeded emulsion copolymerization of vinyl acetate and VeoVa10 (an alkyl vinyl ester from Shell) is also presented.

Introduction

Emulsion polymerization is currently the predominant process used in industry to produce a great variety of polymers with many uses (paints, adhesives, coatings, binders) that only a few years ago were prepared by other polymerization processes. The importance of the emulsion polymerization process is that, because of its multiphase and compartmentalized nature, it offers the possibility of preparing polymers with unique properties that cannot be produced by other polymerization techniques. In addition, environmental regulations have led to the substitution of solvent-based polymers by waterborne latexes, increasing the importance of emulsion polymerization. As a consequence, more and more products are prepared by emulsion polymerization, and the quality and properties of such products are a matter of great importance. Therefore, considerable effort has been devoted to controlling the properties of polymers produced by emulsion polymerization processes. However, developments in the monitoring and control of emulsion polymerization processes have been even slower than those in other polymerization processes where homogeneous reactions are carried out. The main difficulty encountered is the lack of robust, on-line sensors to measure the properties of the polymers.

At first sight, it may seem that because of the relatively low viscosity of polymeric emulsions, the development of on-line sensors for emulsion polymerization is easier than for bulk and solution processes. However, on-line sensors for emulsion polymerization are more difficult to develop, due to the thermodynamically unstable nature of the latex particles (Chien and Penlidis, 1990). Consequently, most of the control strategies developed in the last two decades have been 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., 1993a; Van Doremaele et al., 1992; Schoonbrood et al., 1993; Canu et al., 1994; Gugliotta et al., 1995b). On the other hand, few closed-loop strategies using on-line measurements have been reported in the literature (Dimitratos, 1989; Dimitratos et al., 1989; Guyot et al., 1981; Kozub and MacGregor, 1992; Soroush and Kravaris, 1992; Leiza et al., 1993; Urretabizkaia et al., 1994).

Gas chromatography (GC) has been successfully applied to on-line measurement and control of copolymer composition (Guyot et al., 1981). This measurement technique was combined with an extended Kalman filter (Leiza et al., 1993b) to estimate monomer concentrations and calculate the required monomer feed rates at low-to-medium latex solids contents ($< 35\%$). Urretabizkaia et al. (1994) used a nonlinear adap-

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tive controller in combination with nonlinear on-line optimization to control industrial-like solids content (55%) emulsion terpolymerizations. 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.

Reaction calorimetry (Regenass, 1985; Wu, 1985; MacGregor, 1986; Moritz, 1989; Schuler and Schmidt, 1992) is an appropriate technique for on-line measurement of polymerizations, since these reactions are very exothermic. The measurement is noninvasive, rapid, and robust, being based on temperature measurements. It does not give direct measurements of either the rate of polymerization or the polymer composition, although these can be inferred from calorimetric data (Urretabizkaia et al., 1993; Gugliotta et al., 1995a,b). In the latter work, an open-loop iterative method was shown to be able to control copolymer compositions under semi-starved conditions in four reactions, using only the enthalpies of homopolymerization of the monomers and their reactivity ratios.

However, open-loop control cannot account for changes in the expected reaction kinetics, which can arise from effects such as varying monomer inhibition due to batch-to-batch variations, incorrect initiator level, poor temperature control, poor mixing in the reactor, or the presence of impurities. In such cases, monomer accumulation can occur, which leads to a subsequent sudden heat release when polymerization recommences, producing poor-quality product (wrong composition and low molecular weight), and in extreme cases, thermal runaway (Hoppe and Grob, 1989). On-line reaction calorimetry can avoid this potentially dangerous condition, since monomer accumulation corresponds to a fall in the heat of reaction, which is rapidly detected and can be corrected by reducing or even stopping reagent addition.

Industrial-scale reactors have a relatively more limited heat-removal capacity than laboratory-scale setups, due to their lower heat-exchange surface area to volume ratio. This, coupled with the high enthalpies of polymerization reactions and the high viscosities of the latexes produced in many industrial processes can lead to heat-removal problems. Hence the rate of heat output in large-scale reactors, and therefore the rate of polymerization, must be limited. If the maximum polymer production rate is to be achieved, the rate of polymerization should be matched to the corresponding heat-removal capacity at all stages of reaction. The ability to estimate both reaction-heat-production rate and conversion is thus extremely useful in estimating the maximum permitted rate of reaction on-line.

In this work, on-line calorimetry was used to estimate the conversion and the copolymer composition in emulsion polymerization systems. Real-time feedback control of the polymer composition during the semibatch emulsion copolymerization of vinyl acetate and butyl acrylate was carried out. Both homogeneous copolymers and copolymers with previously defined composition profiles were obtained. It was shown that the feedback control was able to avoid monomer accumulation in the reactor, and hence potentially dangerous thermal runaways, without any deleterious effect on the polymer composition, when a sudden inhibition was caused by deliberately adding a solution of hydroquinone. The use of feedback control for the maximization of the production under safe conditions in the unseeded emulsion copolymerization of vinyl acetate and VeoVa10 (an alkyl vinyl ester from Shell) is also presented.

The organization of the article is as follows. First, in the theoretical section, the basis of reaction calorimetry and its application to the particular equipment (RC1, Mettler-Toledo) used in this work are discussed: it is shown how the conversion and copolymer composition can be estimated from calorimetric data; optimal monomer feed profiles are determined; and the maximum polymer production rate under safe conditions is discussed. Second, the experimental aspects are discussed. Finally, experimental examples of feedback strategies based on calorimetric measurements for copolymer composition control, thermal runaway control, and maximum polymer production under safe conditions are presented.

Theory

Calorimetric measurements

Reaction calorimetry is based on the energy balance for the material inside the calorimeter (Figure 1):

$$\left(C_{p_{\text{ins}}} + \sum_j m_j c_{p_j}\right)\frac{dT_r}{dt} = \sum_i F_i c_{p_i}(T_i - T_r) + Q_r - Q_f + Q_s + Q_c - Q_l, \quad (1)$$

in which $C_{p_{\text{ins}}}$ is the heat capacity of the reactor inserts (stirrer, calibration heater, measuring devices, etc.); m_j and c_{p_j} are the mass and specific heat capacity, respectively, of the jth component in the reaction mixture; T_r the temperature of the reaction mixture; t time; F_i, T_i, and c_{pi} the mass flow rate, feed temperature, and specific heat capacity, respectively, of the ith reactor feed; Q_r is the heat-generation rate due to the chemical reaction; Q_f is the heat flux across the reactor wall; Q_s and Q_c represent the heating due to stirring and the calibration heater, respectively; and Q_l represents heat loss to the surroundings. The term on the left-hand side of Eq. 1 is known as the heat accumulated in the reactor. The heat of reaction, Q_r, can be calculated from the other terms, if these can be calculated with sufficient accu-

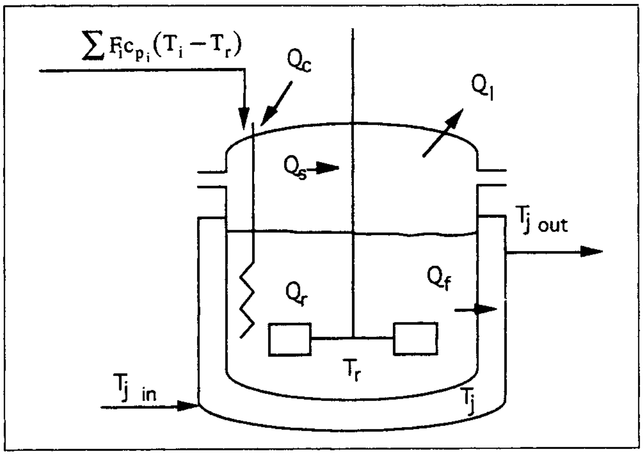

Figure 1. Jacketed stirrer-tank calorimetric semibatch reactor.

racy, this being the essence of reaction calorimetry. The largest of these terms, Q_f, is the heat flow from the reaction mixture to the reactor wall, which in the case where the refrigerant circulates slowly and there is a difference between the inlet and outlet temperatures, is given by

$$Q_f = \int h_r (T_r - T_{w_{x=0}})\, dA, \tag{2}$$

where h_r is the film transfer coefficient between the reaction mixture and the internal wall; T_r the reactor temperature; T_w the wall temperature; x represents the distance from the internal surface across the reactor wall; and A the heat transfer area. The problem with this equation is that $T_{w_{x=0}}$ cannot be measured (in addition to the uncertainties associated with h_r, discussed later).

Under steady-state conditions, Q_f is also given by the following equations, in which all of the temperatures can be measured:

$$Q_f = UA\overline{\Delta T} \tag{3}$$

$$Q_f = F_{c_f} c_{p_{c_f}} (T_{j_{\text{out}}} - T_{j_{\text{in}}}), \tag{4}$$

where U is the overall heat transfer coefficient per unit surface area; $\overline{\Delta T}$ is the appropriate mean temperature difference; F_{c_f} the mass flow rate of the cooling fluid; $c_{p_{c_f}}$ its specific heat capacity; $T_{j_{\text{out}}}$ its outlet temperature and $T_{j_{\text{in}}}$ its inlet temperature.

The term heat-flow calorimetry is used when Q_f is calculated from Eq. 3, whereas in heat-balance calorimetry Q_f is determined by means of Eq. 4. In the latter case, the jacket must be thermally insulated.

Under nonsteady-state conditions, Eqs. 3 and 4 do not provide an accurate measurement of Q_f because of the heat accumulation in the reactor wall. For a given wall material, the smaller the reactor-wall/reactor-mixture mass ratio, the more accurate Eqs. 3 and 4 are. Hence these equations can be more safely applied to industrial-scale reactors than to lab-scale reactors.

If Eqs. 3 and 4 were sufficiently accurate (e.g., industrial-scale reactors operating under conditions such that the sudden variations of the temperature are avoided), heat-balance calorimetry would be more advantageous because all the terms in Eq. 4 can be accurately measured, whereas Eq. 3 includes U that cannot be directly measured on-line [although on-line estimation is possible using a temperature-oscillating calorimeter (Carloff et al., 1994)] and, in many cases, varies during the process.

In the case of lab-scale reactors, such as the RC1 heat-flow reactor calorimeter (Mettler-Toledo) used in this work, neither Eq. 3 nor Eq. 4 are, in general, accurate enough, because of the substantial amount of heat that can be accumulated in the reactor wall. On the other hand, in lab-scale reactors the cooling fluid mass-flow rate can be high enough to make $T_{j_{\text{out}}} \sim T_{j_{\text{in}}}$. Under these conditions, Eq. 2 reduces to

$$Q_f = h_r A (T_r - T_{w_{x=0}}), \tag{5}$$

which still includes the nonmeasurable $T_{w_{x=0}}$. In this work, $T_{w_{x=0}}$ is calculated on-line by solving the following equation for one-dimensional heat flow through the reactor wall:

$$\rho_w c_{p_w} \frac{\partial T_w}{\partial t} = k_w \frac{\partial^2 T_w}{\partial x^2} \tag{6}$$

with the initial boundary conditions

$$t = 0 \qquad T_w(x) = T_w^0(x) \tag{7}$$

$$x = 0 \qquad -k_w \left. \frac{\partial T_w}{\partial x} \right|_{x=0} = h_r (T_r - T_{w_{x=0}}) \tag{8}$$

$$x = d_w \qquad -k_w \left. \frac{\partial T_w}{\partial x} \right|_{x=d_w} = h_j (T_{w_{x=d_w}} - T_j), \tag{9}$$

where ρ_w, c_{p_w}, and k_w are the density, specific heat capacity, and thermal conductivity, respectively, of the reactor wall, and h_j is the film transfer coefficient between the heat-transfer medium and the outer reactor-wall surface, whose temperature is $T_{w_{x=d_w}}$. The determination of h_r and h_j is detailed in the experimental part.

A three-point orthogonal collocation (Villadsen and Michelsen, 1978) algorithm was used to calculate the partial derivatives in the on-line solution of the heat balance at the reactor wall (Eqs. 6–9). A similar approach to calculate Q_f was used by Karlsen and Villadsen (1987), and by Bonvin et al. (1989). It has to be pointed out that this is a general approach to calculate Q_f. In the particular case of isothermal reactions, using a high mass-flow rate of the cooling system ($T_{j_{\text{out}}} \sim T_{j_{\text{in}}}$), Q_f can be more easily calculated as follows:

$$Q_f = UA(T_r - T_j). \tag{10}$$

The approach used in this work to calculate Q_f differs from that used by the commercial RC1 that uses the following equation:

$$Q_f = UA(T_r - T_a), \tag{11}$$

T_a being the "apparent" temperature of the reactor jacket. The temperature T_a is defined by Mettler-Toledo in order to account for unsteady heat-flow through the wall, and the way in which it is calculated is not detailed in the equipment manual. Under isothermal conditions, T_a is equal to T_j. Nevertheless, the main drawback for the purposes of this work is that in the control software provided with the RC1, T_a is calculated accurately at the end of the reaction, and hence Eq. 11 cannot be used for on-line calorimetric measurements.

Another important term in Eq. 1 is Q_l, the heat loss to the surroundings. Q_l depends on the geometry (size) of the reactor, the temperature difference between the reaction mixture and the surroundings. Because of the geometric effect, this term is proportionally much smaller in industrial-scale reactors than in lab-scale reactors, and this makes reaction calorimetry in large reactors less complicated. The value of Q_l can be determined by filling the reactor with a nonreacting mixture and solving Eq. 1 in the steady state while maintaining the reactor temperature constant. For an industrial-scale reactor, a calibration of this type may be appropriate because of the relatively modest contribution of Q_l in Eq. 1. However, for a lab-scale reactor, this is not always enough and the reproducibility of the measurements improves significantly by keeping the surrounding conditions (e.g., using a thermostated reactor lid, avoiding air currents in the laboratory) constant.

The derivative of the temperature in the accumulation term of Eq. 1 is numerically calculated on-line (see details in the experimental section). The heat due to stirring may be easily determined in nonreacting systems (see experimental section).

In conclusion, it is possible to accurately determine on-line the heat released by polymerization, Q_r, by calculating all the terms of Eq. 1 as mentioned earlier. Note that for an industrial-scale reactor, the solution of Eq. 1, and hence obtaining Q_r on-line, is even simpler than for a lab-scale reactor, since Q_f can, in many cases, be determined by using Eq. 4, and the heat-loss term, Q_l, is of much lesser importance than in lab-scale reactors.

Estimating conversion and copolymer composition from calorimetric data

The global polymerization heat, Q_r, is related to the rates of reaction of the individual monomers by Eq. 12, assuming that the heats of cross-propagation are equal to those of homopolymerization (Urretabizkaia et al., 1994):

$$Q_r = R_{pA}(-\Delta H_A) + R_{pB}(-\Delta H_B), \tag{12}$$

where R_{pA} and R_{pB} are the rates of polymerization of the two monomers A and B, and $(-\Delta H_A)$ and $(-\Delta H_B)$ the enthalpies of polymerization of monomers A and B, respectively. For a small time interval, Δt, such that R_p does not change significantly, Eq. 12 can be rewritten as

$$\frac{Q_{r_{t-1}} + Q_{r_t}}{2} = \frac{A_{t-1} + \Delta A - A_t}{\Delta t}(-\Delta H_A) + \frac{B_{t-1} + \Delta B - B_t}{\Delta t}(-\Delta H_B), \tag{13}$$

where Q_{r_t} is the overall rate of heat generation at time t, A_t and B_t are the amounts of A and B present in the reactor at time t, and ΔA and ΔB represent the moles of monomers A and B, respectively, added into the reactor during Δt.

Assuming that the extent of the aqueous-phase polymerization is negligible, the polymerization rate of monomer i is given by

$$R_{pi} = (k_{pAi}p_A + k_{pBi}p_B)[i]_p \frac{\bar{n}N_T}{N_A}; \qquad i = A, B, \tag{14}$$

where k_{pij} is the propagation rate constant of monomer i with monomer j; p_j the time-averaged probability of finding a free radical with ultimate unit of type j in the polymer particles; $[i]_p$ the concentration of monomer i in the polymer particles; $\bar{n}$ the average number of radicals per particle; N_T the total number of polymer particles; and N_A Avogadro's constant.

The probabilities are given by (Forcada and Asua, 1985):

$$p_j = \frac{k_{pij}[j]_p}{k_{pij}[j]_p + k_{pji}[i]_p} \tag{15}$$

$$p_i = 1 - p_j. \tag{16}$$

From Eqs. 14–16, the following equation can be derived:

$$\frac{R_{pA}}{R_{pA} + R_{pB}} = \frac{r_A + \dfrac{[B]_p}{[A]_p}}{r_A + 2\dfrac{[B]_p}{[A]_p} + r_B\dfrac{[B]_p^2}{[A]_p^2}}, \tag{17}$$

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

$$r_i = \frac{k_{pii}}{k_{pij}}. \tag{18}$$

As earlier, for small time increments, Eq. 17 can be rewritten as

$$\frac{A_{t-1} + \Delta A - A_t}{A_{t-1} + \Delta A - A_t + B_{t-1} + \Delta B - B_t} = \frac{r_A + \left[\dfrac{[B]_p}{[A]_p}\right]_a}{r_A + 2\left[\dfrac{[B]_p}{[A]_p}\right]_a + r_B\left[\dfrac{[B]_p}{[A]_p}\right]_a^2}, \tag{19}$$

where the subscript a refers to the average concentrations between time samples $t-1$ and t.

The concentration of the monomers in the polymer particles can be easily calculated using the equilibrium equations and the overall material balances by means of an iterative algorithm (Omi et al., 1985; Urretabizkaia and Asua, 1994). Here, the equilibrium equations were written in terms of partition coefficients as follows:

$$K_{j,k}^i = \frac{[i]_j}{[i]_k}, \tag{20}$$

where $K_{j,k}^i$ is the partition coefficient of monomer i between phases j and k; and $[i]_j$ and $[i]_k$ are the concentrations of monomer i in phases j and k, respectively. The three phases —water, particles, and droplets—are presented by w, p, and d, respectively.

Equations 13 and 19 are a set of two algebraic equations with two unknowns, A_t and B_t. Their solution gives the time evolution of the amounts of free monomers A and B during the course of polymerization, from which conversion and copolymer composition are readily calculated (Gugliotta et al., 1995a).

Determining the optimal monomer feed profile

The instantaneous composition of copolymer in the polymer particles for a given pair of monomers is determined by the ratio of the concentrations of the two monomers in the polymer particles, being independent of the absolute values (Arzamendi and Asua, 1989, 1990). It follows that to produce a homogeneous copolymer, it is sufficient to maintain that concentration ratio constant throughout the reaction. One method of achieving uniform copolymers is that of the so-called starved conditions (Snuparek, 1972; Snuparek and Krska, 1976, 1977), in which the monomers are fed into the reactor at such a low rate that the rates of polymerization are equal to the monomer feed rates, which therefore determine the instantaneous copolymer composition. The main disadvantage of this approach is that very long reaction times can be needed, especially in the case of pairs of monomers with widely different reactivities. Arzamendi and coworkers (Arzamendi and Asua, 1989, 1990, 1991; Arzamendi et al., 1991) have developed minimum-time strategies for controlled copolymer production, for both seeded and unseeded emulsion polymerizations. Their work is readily applicable to calorimetric estimation and control of copolymer composition (Gugliotta et al., 1995b), and is extended here to include safety aspects, through the on-line control of the amount of unreacted monomer in the reactor.

Ignoring the effect of the monomer concentration on the number of polymer particles and on the number of free radicals per particle, the minimum process time to obtain a homogeneous copolymer is obtained by minimizing the following objective function:

$$F = \int \frac{dx_T}{\sum\limits_{A,B} (k_{p_{A_i}} p_A + k_{p_{B_i}} p_B)[i]_p}, \tag{21}$$

where x_T is the global molar conversion defined as

$$x_T = \frac{A_0 + \int_0^t F_A\, dt + B_0 + \int_0^t F_B\, dt - A_t - B_t}{A_T + B_T}, \tag{22}$$

where A_0 and B_0 are the initial amounts of monomers A and B in the reactor; F_A and F_B the flow rates of monomers A and B at time t; and A_T and B_T the total amounts of monomers A and B in the formulation, respectively.

The following constraints must be held:

1. The copolymer must have the desired composition:

$$\frac{[A]_p}{[B]_p} = f(x_T). \tag{23}$$

In the case of homogeneous copolymers, $f(x_T)$ is a constant, but can be any function, depending on the copolymer composition profile.

2. There is a limit to the maximum swelling of the particles by monomer:

$$[i]_p \le [i]_{p_{\text{ref}}} \qquad i = A, B. \tag{24}$$

Table 1. Parameters Used in the On-line Control Strategy

Parameter	Value
$K^A_{w,d}$ (Gugliotta et al., 1995c)	0.027
$K^B_{w,d}$ (Gugliotta et al., 1995c)	0.00135
$K^A_{w,p}$ (Gugliotta et al., 1995c)	0.0323
$K^B_{w,p}$ (Gugliotta et al., 1995c)	0.0208
k_{pA} (L/mol·s) (Delgado, 1986)	2.35×10^3
k_{pB} (L/mol·s) (Delgado, 1986)	1.26×10^2
r_A (Urretabizkaia et al., 1993)	0.037
r_B (Urretabizkaia et al., 1993)	6.36
$(-\Delta H_A)$ (J/mol) (Brandrup and Immergut, 1989)	89.5×10^3
$(-\Delta H_B)$ (J/mol) (Brandrup and Immergut, 1989)	78.2×10^3

A: Vinyl acetate; B: butyl acrylate.

There are two main reasons for imposing such a limit $[i]_{p_{\text{ref}}}$. First, it is one way of controlling the rate of heat generation, but also in some polymerizations, such as those in which transfer to polymer is significant, the molecular weight of the polymer depends on the ratio of monomer to polymer. A maximum swelling for a given monomer, lower than its equilibrium solubility limit in polymer, also implies that there will be no droplet phase in the system. Note that the presence of monomer droplets in the system implies the loss of control ability, and hence should be avoided.

3. Monomer cannot be removed from the reactor

$$\frac{\partial i}{\partial x_T} \ge 0 \qquad i = A, B. \tag{25}$$

4. There is a finite limit to the amount of monomer that can be added to the reactor:

$$i_t + i_{\text{pol}} - i_T \le 0 \qquad i = A, B, \tag{26}$$

where i_{pol} is the amount of polymer, and i_T the total amount of monomer i in the formulation.

Using the parameters of Table 1, the system of Eqs. 21–26 can be solved by the method of de la Cal et al. (1995), leading to monomer feed profiles such as those presented in Figure 2, in which the amounts of each monomer that must have been fed into the reactor are shown as a function of conversion for two different swelling limits for the unseeded emulsion copolymerization of VAc and BuA. The values at zero conversion represent the monomer that must be initially present in the reactor. The only data needed to calculate these feed profiles are the monomer reactivity ratios and their partition coefficients. The monomer feed profile can be calculated *a priori*, in which case, the on-line control strategy requires only that these profiles be followed, using the on-line estimate of conversion to determine the amounts of monomer that ought to be in the reactor at any time. This can be seen as a typical trajectory-tracking control issue, the monomer flow rates being the manipulated inputs to achieve such a goal. In addition, it is worth noting that the optimum trajectories are independent of the polymerization rate and that they can be seen as master curves for each comonomer pair system for the operation conditions considered.

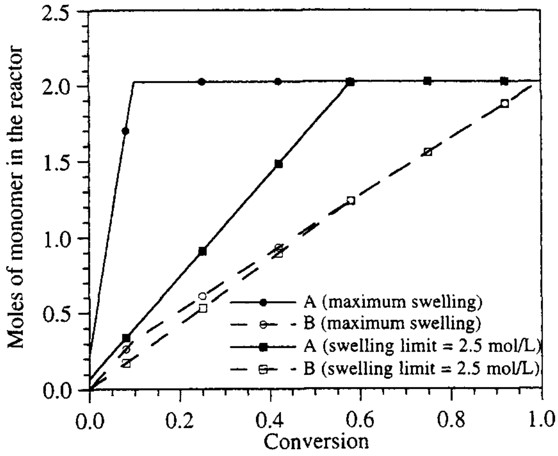

Figure 2. Monomer feed profiles for a molar 50/50 VAc/BuA copolymer for different particle-swelling limits.

Maximum production rate under safe conditions

The maximum polymer production rate can be achieved if the heat-generation rate is held at the safe maximum heat-removal capacity of the reactor. The safe maximum heat-removal capacity of an isothermal stirred-tank reactor can be expressed as $Q_{\mathrm{lim}_x} = \alpha UA(T_r - T_{c_{\min}})$, where α is a safety coefficient (< 1) and $T_{c_{\min}}$ is the lowest achievable reactor coolant temperature. Additional safety margins are obtained when the reactor is operated at above-ambient temperatures from the heat losses and cooling effects of the feeds. The overall heat transfer coefficient between the reactor contents and the reactor wall, U, is determined by a number of factors, stirrer speed and viscosity being the most important for a given formulation. Viscosity changes in the polymerization to produce high-solids-content latexes are such that U, and hence the heat-removal capacity, fall as the polymer content increases. In batch and semibatch isothermal processes, this is equivalent to a decreasing heat-removal capacity with conversion, since $T_r - T_{c_{\min}}$ is constant. The curve of the maximum heat-removal capacity with overall conversion can be calculated beforehand, by determining the dependence of the overall heat-transfer coefficient on the solids content, as explained in the experimental section below. Figures 13 and 15 (seen later) present examples of these plots. It is worth pointing out that these curves are independent of the polymerization rate and that they can be seen as master curves for a given dependence of U on the solids content. Obviously, this is not the case if massive coagulation or severe reactor-wall fouling occurs, namely the present control strategy is only applicable to formulations leading to stable latexes.

To follow the Q_{lim_x} vs. conversion curves basically requires that the polymerization rate be controlled. The control of a derivative quantity, such as the *rate* of polymerization, is much more difficult than the control of an integral quantity such as cumulative copolymer composition, because the derivative is much more sensitive to small variations in the operation conditions in the reaction mixture (viscosity, temperature, and monomer feed rates, for example).

Control of the polymerization rate was carried out using the feed rate of monomer as the manipulated variable. The strategy used is outlined in Figure 3. Note that polymerization rate control is not independent of composition control unless one selects a pair of monomers with really close reactivity ratios. In this work, VAc and VeoVa10 were chosen because of their close reactivity ratios and hence polymerization rate was the only controlled variable.

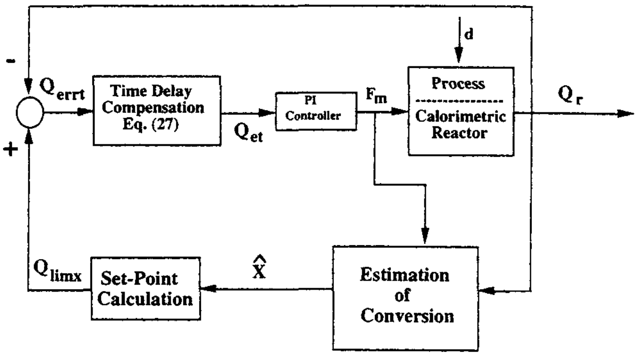

Figure 3. Control design devised for maximum copolymer production rate under safe conditions.

At each sampling interval, a measurement of the heat released by polymerization, Q_r, is first used to estimate conversion, as explained earlier. Once an estimate of conversion is available, the maximum safe heat-removal capacity, Q_{lim_x}, is inferred from the plot Q_{lim_x} vs. conversion calculated beforehand and used as the setpoint. Both Q_{lim_x} and the actual heat released, Q_r, are compared and the difference, Q_{err_t}, is used by a conventional proportional-integral feedback controller to calculate the required amount of monomer to be added into the reactor. However, and as can be seen in the block diagram, the difference, Q_{err_t} is not directly used by the controller. The scheme includes a time-delay compensation in order to take into account the diffusional limitations of the monomer to reach the polymerization loci, that is, the polymer particles. In the time-delay compensation block the actual difference, Q_{err_t}, is extrapolated forward by a time delay, t_{del}, using the following equation:

$$Q_{e_t} = Q_{\mathrm{err}_t} + (Q_{\mathrm{err}_t} - Q_{\mathrm{err}_{t-1}})t_{\mathrm{del}}/\Delta t, \tag{27}$$

where t_{del} represents the overall time delay; Δt is the time between control actions; and Q_{e_t} is the estimated difference between the heat generated by the reaction and the heat-removal limit, which is used as the input to the discrete control algorithm in incremental form:

$$F_{A_{t+1}} = F_{A_t} + k_{Qp}(Q_{e_t} - Q_{e_{t-1}}) + k_{Qi}(Q_{e_t} + Q_{e_{t-1}})/2, \tag{28}$$

in which; F_{A_t} is the current mass flow rate of monomer A; $F_{A_{t+1}}$ the new rate; $Q_{e_{t-1}}$ the previous values of Q_{e_t}; and k_{Qp} and k_{Qi} are the proportional and integral gains, respectively. Equation 28 is written for a single monomer, although it can be readily applied to copolymerization systems.

Experimental

Operation of the RC1 reaction calorimeter

Figure 4 presents the setup, based on a commercial reaction calorimeter (RC1, Mettler-Toledo), used to carry out

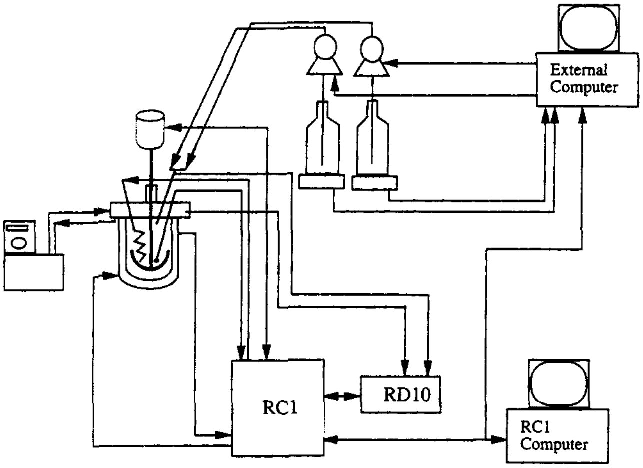

Figure 4. Modified RC1 calorimetric reactor.

semicontinuous unseeded emulsion polymerizations. It is equipped with a 1.5-L stainless-steel jacketed reactor vessel (HP60, Mettler-Toledo) fitted with anchor stirrer, platinum resistance thermometer, electrical calibration heater, and sampling tube. In addition to the RC1 computer, an external computer was attached to the installation, to solve on-line the material and energy balances of the reactor as explained in the Theory section, and to monitor and control the reaction according to the strategies previously described using balances and pumps also connected to this computer. The monomer flow rate was adjusted every 5 s by means of a $P + I$ algorithm, and the heat balance was determined at 20-s intervals. The RC1 was operated in isothermal mode at a set reactor temperature of 60°C. A separate thermostatically controlled bath was used to circulate water at 65°C through the reactor head.

An initial charge was added to the reactor, and after reaching thermal equilibrium, the overall heat-transfer coefficient was determined by means of a calibrated electrical heater immersed in the initial charge. By equating the electrical energy dissipated to that determined calorimetrically, a value of UA was obtained from Eq. 29, as explained in the RC1 operating manual.

$$UA\int_{t_1}^{t_2}(T_r - T_a)\,dt = \int_{t_1}^{t_2} Q_c\,dt, \qquad (29)$$

where t_1 and t_2 are the starting and end times of the calibration. This value of UA determined from the initial charge changes considerably during the polymerization because both A and U vary. The heat-transfer area, A, varies because of the semicontinuous operation; U varies because of the viscosity increase. The viscosity mainly depends on the solids content and, less strongly, on the particle-size distribution (PSD) (Krieger, 1985). The equipment used does not allow the evolution of the UA during the reaction to be estimated. Only the initial and final values of UA can be measured accurately by a calibration procedure. The variation of A can be calculated from the material balances in the reactor and from the effect of stirring (see below). In order to obtain the evolution of U, previously prepared latexes having different PSD and solids content were used to estimate the dependence of the overall heat-transfer coefficient on these variables. It was found that for the range of PSDs studied, U was mainly a function of the solids content. This means that for a particular semicontinuous process, the curve U vs. conversion is quite insensitive and may be used as a master curve.

To calculate Q_f on-line, Eqs. 6–9 must be solved. The term h_j was determined beforehand by Wilson's method (Choudhury and Utiger, 1989), and h_r was calculated from the dependence of the overall heat-transfer coefficient vs. the solids contents obtained previously for the system under study. The remaining terms are measured on-line by the RC1 and transferred to the external computer (T_r and T_j) or are known (k_w).

Once Q_f is calculated, Eq. 1 is easily solved for Q_r in the external computer as explained in the Theory section. Measurements at different stirred speeds indicated that the heat produced by stirring is negligible for the range of experimental conditions used.

The correct operation of the RC1 imposes minimum and maximum volumes on the reactor contents. The lower limit is due to the initial volume required in the reactor to perform correctly a calibration of the overall heat transfer coefficient, U. To obtain an accurate value, the volume of the initial charge must immerse the calibration heater at least 5 cm, and at 150 and 350 rpm, is approximately 0.6 and 0.8 L, respectively, for the 1.5-L reactor vessel (HP60) used in this work. The increased vortex at higher stirring speeds is the cause of this difference, since the heater tip is situated near the central axis of the vessel. The upper limit is a consequence of the configuration of the cooling jacket around the reactor. The jacket does not cover the entire volume of the reactor, and hence, when the reactor liquid level rises above the available heat-transfer area, the reaction heat rate measured is not accurate. For a typical 55% solids content latex, this value is approximately 1.45 L at 150 rpm and is 1.3 L at 350 rpm. These values were determined by wetting paper strips attached to the inner reactor wall.

Materials and experimental procedure

The technical grade monomers VAc, BuA, and VeoVa10 as supplied, are inhibited with hydroquinone, *p*-methoxy phenol and hydroquinone, respectively. When purified, monomers were washed with dilute sodium hydroxide solution, then distilled at reduced pressure. Filtered, deionized water was used throughout. All other reagents were used as supplied. Sodium lauryl sulfate (SLS, Merck, > 90% activity) was used as emulsifier in the controlled composition reactions at 30% solids content. A mixture of ionic (Alipal CO436–88% activity, Rhône-Poulenc) and nonionic (Arkopal–N230, Hoechst) emulsifiers was used, together with hydroxyethyl cellulose (Aldrich) as colloid protector in the high solids content VAc/VeoVa10 polymerizations. Sodium bicarbonate (99.5%, Fluka) was the buffer; potassium persulfate (98%, Merck) was the initiator; and for the redox initiator systems, the latter was used with sodium disulfite (Panreac, 96%).

Controlled-composition reactions

Vinyl acetate (VAc) and butyl acrylate (BuA) were chosen for their widely differing reactivity ratios (0.037 and 6.36, re-

Table 2. Recipe Used to Obtain VAc/BuA Copolymers

	Initial Molar Composition Amount (kg)			
Component	50/50—Runs 1 and 5	70/30—Run 2	90/10—Run 3	10/90—Run 4
H_2O	0.82000	0.82000	0.82000	0.82000
SLS	0.00400	0.004	0.00400	0.00400
$K_2S_2O_8$	0.00200	0.002	0.00200	0.00200
VAc	0.01315 + 0.15885*	0.2644	0.02154 + 0.15046*	0.00595 + 0.16803*
BuA	0.00010 + 0.25590*	0.01038 + 0.25902*	0.00001 + 0.25894*	0.00072 + 0.25823*
Stirrer speed	150	150	150	250

*Initial charge + amount fed into the reactor during the reaction.

spectively), which makes it difficult to control the composition of their copolymers, even under starved conditions. Both technical and purified (inhibitor-free) monomers were used, and a range of copolymer compositions, both constant and linearly dependent on conversion, were sought.

The following procedure was implemented. The reactor was initially charged with all but 50 g of the water, all the emulsifier, and a proportion of the two monomers taken from the monomer feed profiles at zero conversion (see Figure 2). The RC1 software was used to raise the reactor temperature to 60°C, and when the reaction heat base line calculated by the RC1 was stable, the external PC was used to calibrate the initial heat-transfer coefficient, U, and calculate a base line, Q_l. The preheated solution of initiator in 50 g of water was added, and on stabilizing once again the base line, the monomer feed algorithm was started by the external PC, according to the predetermined conversion-based profiles calculated by the method presented in the theory section.

Constant 50/50 and 70/30 molar VAc/BuA copolymers (Runs 1 and 2) and two gradient copolymers, linear with respect to conversion, with initial VAc/BuA compositions of 90/10 and 10/90 (Runs 3 and 4), and a final equimolar cumulative copolymer composition, were prepared, according to the recipes of Table 2.

Thermal runaway control

One of the major concerns in industrial polymerization reactors is the production of polymers of the desired quality under strict safety considerations. Difficult and risky situations in emulsion polymerization reactors are usually related to monomer accumulation and the subsequent thermal runaway when polymerization recommences. Monomer accumulation can originate, for example, from the variation of the inhibitor level in the monomer feedstock, batch-to-batch variability, incorrect initiator level, poor mixing in the reactor, and the presence of impurities.

An experiment (Run 5) was carried out to show the ability of on-line calorimetry and the devised monomer addition policy to produce copolymers of the desired composition and to handle situations that can lead to poor-quality products and thermal runaway. The experiment was carried out using the recipe and procedure of Run 1, in which a 50/50 molar VAc/BuA copolymer was sought. To check the robustness of the strategy, a solution of hydroquinone was deliberately added into the reactor after 20 min of reaction, during a strongly exothermic phase, to simulate a sudden inhibition.

Maximum production rate under safe conditions

VAc/VeoVa10 copolymerizations were carried out, with the aim of maintaining the rate of heat release by polymerization at a steadily decreasing predetermined level as a function of conversion, which might represent the fall in the heat-transfer capacity of an industrial-like reactor as its polymer content increases. The recipe for these reactions, a commercially derived 74.5/24.5/1 wt. % VAc/VeoVa10/acrylic acid formulation, of 55 wt. % solids content, based on the work of Abad et al. (1995), is given in Table 3. The small amount of acrylic acid is found to improve the latex stability. Note that VAc and VeoVa10 have reactivities close to 1, and hence strategies to control the copolymer composition, such as in the case of VAc and BuA, are not required.

The monomers were premixed and fed into the reactor as a single stream. A redox initiator system of potassium persulfate and sodium disulfite was used. All reagents were used as supplied. The initial reactor charge comprised 670 g of water, the emulsifiers, colloid protector, and buffer. The external PC was then used to determine the overall heat-transfer coefficient U of the reactor contents, and the base line. The initial charge of monomer (35 g, 4% of total) was fed into the reactor over 3 min, and the redox initiator feeds were immediately started at constant feed rates of 0.243 (persulfate) and 0.204 (bisulfite) g/min, also using the PC. Controlled monomer addition according to Eq. 28 did not begin until 30% of the initial monomer charge had been polymerized. In this way, the reaction commenced smoothly, and excess monomer accumulation in the reactor was avoided. The monomer feed required typically 210 min, and the initiator feeds were maintained for a further 50 min to ensure complete conversion.

Table 3. Recipe Used to Obtain a 75/25 wt. % VAc/VeoVa10 Copolymer with a Predefined Reaction Rate Limit (Runs 6, 7 and 8)

Component	Amount (kg)
H_2O	0.58000 + 0.07886*
Alipal	0.01155
Arkopal	0.01540
Monomers	0.03500 + 0.74770*
Hydroxyethyl cellulose	0.00077
$NaHCO_3$	0.00100
$K_2S_2O_8$	0.0 + 0.00754*
$Na_2S_2O_5$	0.0 + 0.00637*

*Initial charge + amount fed into the reactor during the reaction.

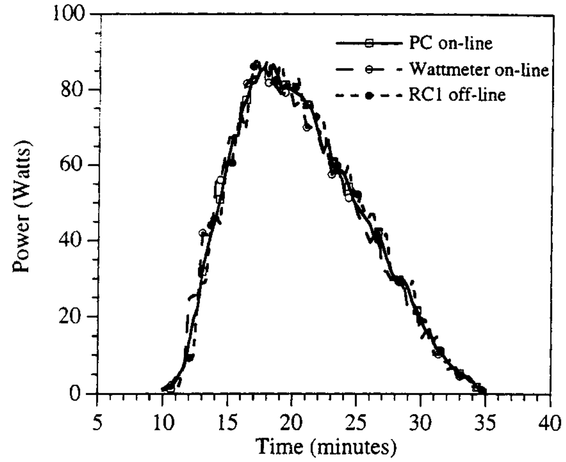

Figure 5. Comparison of the heat released by an electrical heater calculated on-line (PC and wattmeter) and off-line (RC1) for a simulated slow reaction.

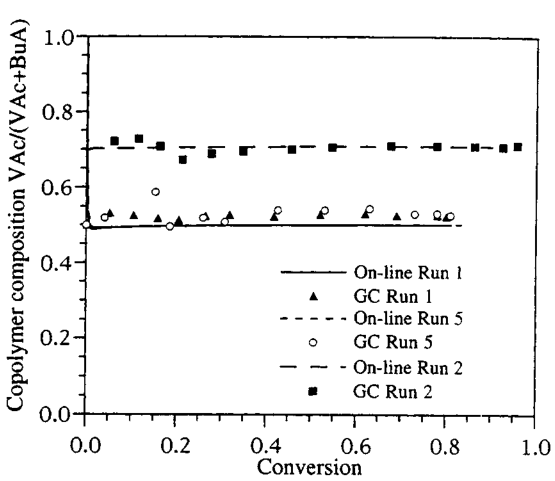

Figure 7. On-line composition control with different types of monomer inhibition.

Results and Discussion

Validation of the on-line calculation of the heat of reaction

To determine the accuracy of the on-line measurements, an isothermal chemical reaction was simulated with a variable-voltage electrical heater inserted in a known mass of water in the reactor, whose energy consumption was measured by a calibrated wattmeter. The initial value of *UA* was determined from the calibration heat Q_c calculated by the RC1, but also available to the external PC. On-line heats of reaction from the PC and the wattmeter, and off-line values from the RC1 software are shown in Figures 5 and 6 for two simulated reactions, of 25- and 11-min duration. An excellent agreement can be seen between the different measurements.

Controlled composition reactions

Homogeneous Composition. Figure 7 shows the evolution of the cumulative copolymer composition with respect to VAc for two polymerizations aimed at producing 50/50 (Run 1) and 70/30 (Run 2) molar VAc/BuA homogeneous copolymers. It can be seen that copolymers of the desired composition were obtained in both cases. Figure 8 shows the evolution of both the on-line calorimetric-based conversion and the off-line gravimetric conversion for Runs 1 and 2. The excellent agreement between on-line and off-line conversions is further support for the accuracy of the calorimetric measurements. In Run 1, the VAc was fed into the reactor over a period of 40 min, whereas the feed of BuA was stopped after 5 h reaction, since the required average feed rate was less than 0.1 g/min. The rapid fall in the rate of reaction after feeding in all the VAc and the consequent decrease in the required BuA feed rate are discussed below.

Composition Profile Control. Figures 9 and 10 show the results of copolymerizations (Runs 3 and 4) in which variable cumulative molar copolymer compositions from initial values of 90/10 and 10/90 (respectively) VAc/BuA to a final value of 50/50, in both cases, were sought, according to the recipe of Table 2, and the experimental procedure described previ-

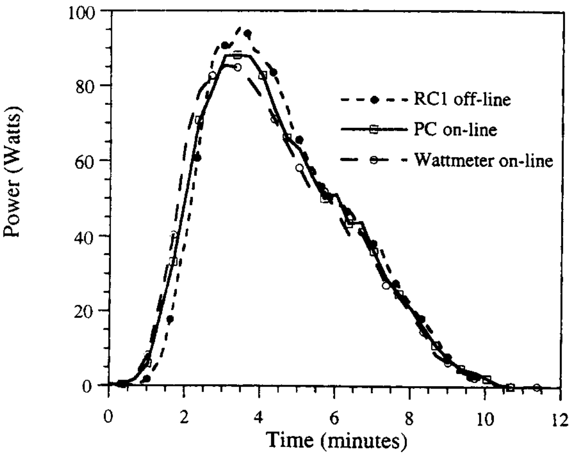

Figure 6. Comparison of the heat released by an electrical heater calculated on-line (PC and wattmeter) and off-line (RC1) for a simulated fast reaction.

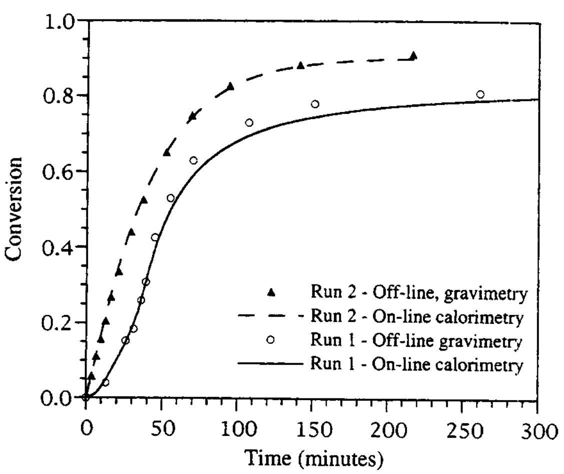

Figure 8. Evolution of conversion in controlled composition emulsion copolymerization with different constant copolymer compositions.

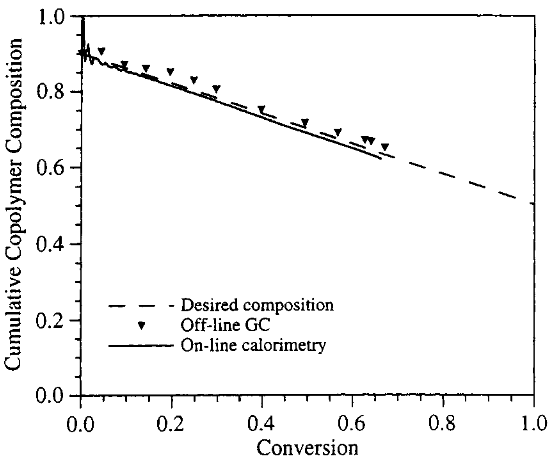

Figure 9. Evolution of the cumulative copolymer VAc composition in a controlled negative-gradient emulsion polymerization (Run 3).

ously. The low final conversion in Run 3 (Figure 9) is a result of the rapid fall in polymerization rate after the addition of all the vinyl acetate at 40% conversion, leading to extremely low BuA feed rates at conversions greater than 60%. This effect is unavoidable, since it arises from the very different reactivity ratios of the two monomers, such that the relative polymerization rate falls rapidly with the molar ratio of VAc to total monomer in the polymer particles, the minimum being found at 93% VAc/7% BuA (Gugliotta et al., 1995b). Hence, since the composition profile of Figure 9 requires an ever-decreasing proportion of VAc in the copolymer formed, the reaction rate decreases more rapidly than in the case of the 50/50 homogeneous copolymer, which achieves a conversion of 85% in 5 h. This effect would be much less pronounced in the case of monomers with less disparate reactivity ratios.

Thermal runaway control

The use of conversion-based feed profiles offers two main advantages over the more common time-based method.

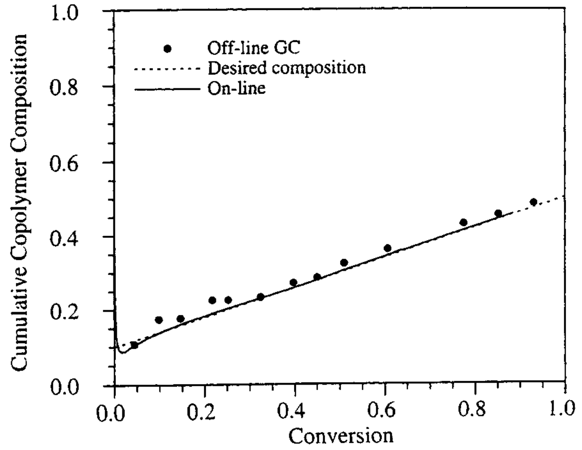

Figure 10. Evolution of the cumulative copolymer VAc composition in a controlled positive-gradient emulsion polymerization (Run 4).

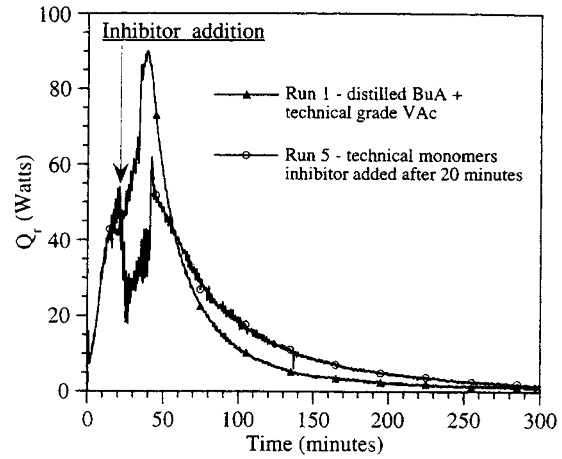

Figure 11. Rate of heat generation for on-line composition control with different types of monomer inhibition.

Batch-to-batch variations in the monomer inhibitor level can easily be accommodated, since a delay in the start of reaction means that either monomer addition is also delayed, or that a lower rate of reaction results in the feed rate being reduced. In the extreme case of the reaction being stopped by an unexpected inhibition, the monomer feeds are also stopped, since the conversion no longer increases. This would avoid monomer accumulation, a potentially dangerous reactor condition. In more common cases of minor fluctuations in the rate of polymerization, the monomer feed rates are adjusted automatically, reducing the amount of off-specification product and hence maintaining the product quality.

These advantages are illustrated in Figures 7, 11 and 12 for an experiment (Run 5) in which hydroquinone was deliberately added to the reactor during a strongly exothermic phase of the reaction. Figure 11 shows the evolution of the heat released during Run 5 and Run 1 (where no inhibitor was added and the BuA was distilled). It can be seen that after the inhibitor addition, the heat rate dropped, but that once the inhibitor had been consumed, and because the strategy did not allow monomer to accumulate in the reactor (as con-

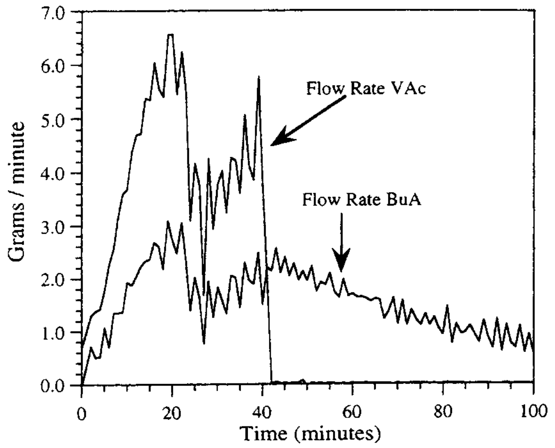

Figure 12. Monomer feed profiles for the inhibited reaction Run 5 of Figure 11.

firmed by the decrease in the flow rates of both monomers in Figure 12), the polymerization proceeded safely without the risk of thermal runaway. Moreover, as can be seen in Figure 7, the quality of the copolymer, as measured by the cumulative copolymer composition, is as good as that in Run 1, in which distilled BuA was used and no hydroquinone was added during the experiment.

Maximum production under safe conditions

A first experiment (Run 6) was carried out using the recipe of Table 3 and the strategy devised by Eq. 28. Initially no delay was assumed in the controller, that is $t_{\mathrm{del}} = 0$. The evolution of the heat released by polymerization is shown in Figure 13. As can be seen, significant oscillations occurred during the reaction, which led, during the initial part of the experiment, to what might have been a runaway condition in an industrial reactor. Note that unseeded polymerizations were used to test the strategy, imposing an additional demand on the control strategy, because of the important and unpredictable acceleration of the heat released due to the polymer particle nucleation.

However, the oscillations observed in Figure 13 were not only due to the nucleation of polymer particles, or to the nonlinear nature of the emulsion polymerization process being controlled by a conventional linear feedback technique, but were also due to a significant time delay between two process variables. This is shown in Figure 14, where Figure 13 is enlarged for the first two oscillations and the unreacted amount of monomer present in the reactor is also plotted. It is evident in the figure that there is a significant shift between the maxima in the amount of unreacted monomer and those corresponding to the rate of heat generation, that is, a time delay. A time delay of 120 s was calculated as the average between the maxima of the unreacted monomer and those of the rate of heat generation.

In the two subsequent experiments (Runs 7 and 8), the same strategy was applied, taking into account the time delay estimated from Run 6, that is, $t_{\mathrm{del}} = 120$ s. Figure 15 shows the evolution of the heat released by polymerization as a function of conversion for those reactions. As can be seen, the results were considerably improved and allowed the predetermined profile to be tracked successfully.

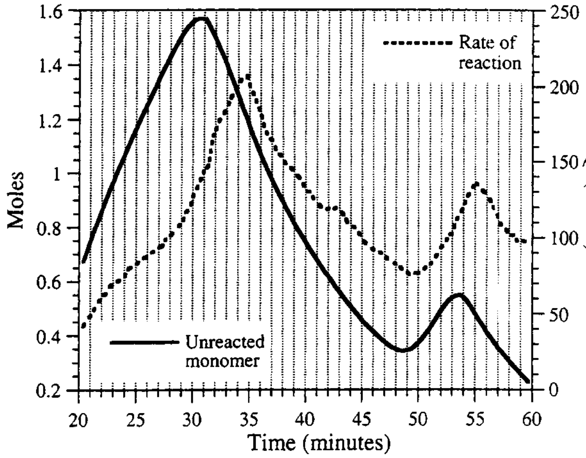

Figure 14. Evolution of the power of reaction and the unreacted monomer during a VAc/VeoVa10 emulsion copolymerization (Run 6) with a variable heat-production limit and conventional PI controller ($t_{\mathrm{del}} = 0$).

Conclusions

A commercial reaction calorimeter was used to thermally monitor and control unseeded semibatch emulsion copolymerization. An external PC, using the information derived from the calorimeter and balances to measure reagent addition, calculated on-line the thermal and material balances of the reactor, and thus the monomer conversions. Based on an optimization approach, trajectories of the amount of monomer required in the reactor to produce copolymers of homogeneous composition (50/50 and 70/30) and non-

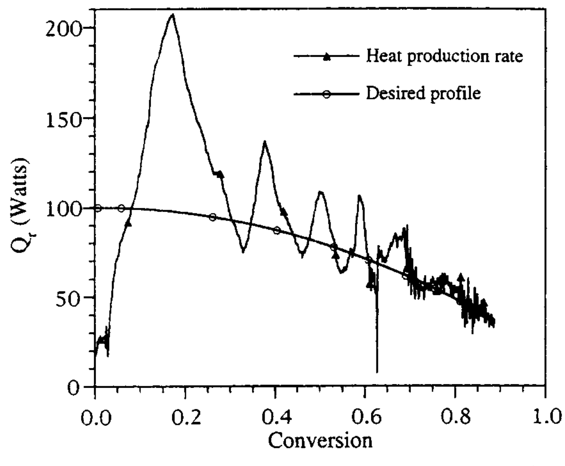

Figure 13. Evolution of the heat released by polymerization during a VAc/VeoVa10 emulsion copolymerization (Run 6) with a variable heat-production limit and conventional PI controller ($t_{\mathrm{del}} = 0$).

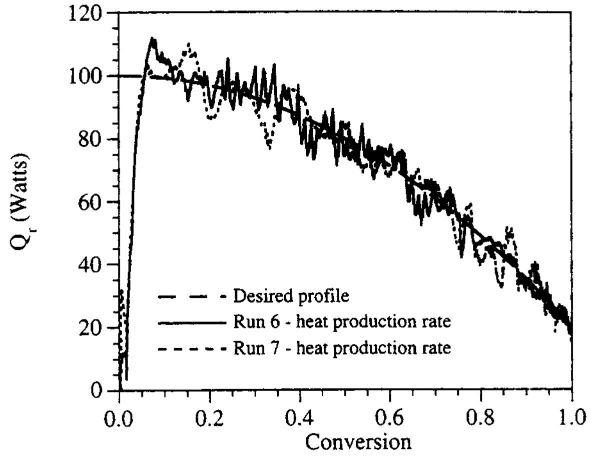

Figure 15. Evolution of the heat of reaction during a VAc/VeoVa10 emulsion copolymerization (Runs 7 and 8) with a variable heat-production limit and conventional PI controller with time delay ($t_{\mathrm{del}} = 120$ s).

uniform compositions (from 10/90 or 90/10 to 50/50) were obtained as a function of the overall conversion for the emulsion copolymerization of VAc/BuA. These trajectories, which are unique for each system under study and the composition required (they can be seen as master curves), were followed by measuring on-line the conversion, based on the rate of heat released by polymerization, and thus controlling on-line the addition of monomer into the reactor. It was shown that the VAc/BuA copolymers sought were successfully produced. In addition, safety considerations were studied to check the robustness of the control strategy. It was also shown that the control strategy devised lends itself to safe operation, since sudden inhibition (deliberately induced by the addition of a radical scavenger during an exothermic phase of the polymerization) did not lead to monomer accumulation or thermal runaway once polymerization recommenced. Furthermore, the quality of the copolymer was maintained at the target value.

Finally, in a separate series of unseeded semicontinuous emulsion copolymerizations of VAc/VeoVa10 at high solids content, optimum process criteria were implemented, that is, polymerizations were carried out at the maximum polymerization rate allowed by an imposed safe maximum polymerization reactor heat-removal capacity. A simple conventional PI controller plus dead-time compensation allowed a predetermined decreasing heat-removal capacity as a function of the solids content, to be followed reasonably well.

Acknowledgments

Financial support from the Diputación Foral de Gipuzkoa and the CICYT (grant TAP 95-1020) is gratefully appreciated. I. Sáenz de Buruaga and A. Echevarría acknowledge fellowships from the Basque Government. P. D. Armitage acknowledges the fellowship from the Human Capital and Mobility program (grant ERB4001GT931751).

Literature Cited

Abad, C., J. C. de la Cal, and J. M. Asua, "Emulsion Copolymerization of Vinyl Esters in Continuous Reactors: Comparison Between Loop and Continuous Stirred Tank Reactors," *J. Appl. Poly. Sci.*, **56**, 419 (1995).

Arzamendi, G., and J. M. Asua, "Monomer Addition Policies for Copolymer Composition Control in Semicontinuous Emulsion Copolymerization," *J. Appl. Poly. Sci.*, **38**, 2019 (1989).

Arzamendi, G., and J. M. Asua, "Copolymer Composition Control During the Seeded Emulsion Copolymerization of Vinyl Acetate and Methyl Acrylate," *Makromol. Chem., Macromol. Symp.*, **35/36**, 249 (1990).

Arzamendi, G., and J. M. Asua, "Copolymer Composition Control of Emulsion Copolymers in Reactors with Limited Capacity for Heat Removal," *Ind. Eng. Chem. Res.*, **30**, 1342 (1993).

Arzamendi, G., J. R. Leiza, and J. M. Asua, "Semicontinuous Emulsion Copolymerization of Methyl Methacrylate and Ethyl Acrylate," *J. Appl. Poly. Sci.*, **29**, 1549 (1991).

Bonvin, D., P. Valliere, and W. T. Rippin, "Application of Estimation Techniques to Batch Reactors: I. Modelling Thermal Effects," *Comput. Chem. Eng.*, **13**(1/2), 1 (1989).

Brandup, J., and E. M. Immergut, eds., *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York (1989).

Broadhead, T. O., A. E. Hamielec, and J. F. MacGregor, "Dynamic Modeling of the Emulsion Copolymerization of Styrene/Butadiene," *Makromol. Chem. Suppl.*, **10/11**, 105 (1985).

Canu, P., S. Canegallo, G. Storti, and M. Morbidelli, "Composition Control in Emulsion Copolymerization: I. Optimal Monomer Feed Policies," *J. Appl. Poly. Sci.*, **54**, 1889 (1994).

Carloff, R., A. Proβ, and K. H. Reichert, "Temperature Oscillation Calorimetry in Stirred Tank Reactors with Variable Heat Transfer," *Chem. Eng. Tech.*, **17**, 406 (1994).

Chien, D. H. C., and A. Penlidis, "On-line Sensors for Polymerization Systems," *J. Macromol. Sci., Macromol. Chem. Phys.*, **C30**(1), 1 (1990).

Choudhury, S., and L. Utiger, "Heat Transport in Agitated Vessels: Scale-Up Methods," Mettler Publication ME-724218, Mettler-Toledo, Switzerland (1989).

de la Cal, J. C., A. Echevarría, G. R. Meira, and J. M. Asua, "Minimum Time Strategy to Produce Nonuniform Emulsion Copolymers: I. Theory," *J. Appl. Polym. Sci.*, **57**, 1063 (1995).

Delgado, J., "Miniemulsion Copolymerization of Vinyl Acetate and n-Butyl Acrylate," PhD Diss., Lehigh Univ., Bethlehem, PA (1989).

Dimitratos, J., "Modeling and Control of Semicontinuous Emulsion Copolymerization," PhD Diss., Lehigh Univ., Bethlehem, PA (1989).

Dimitratos, J., G. Georgakis, M. S. El-Aasser, and A. Klein, "Control of Product Composition in Emulsion Copolymerization," *Polymer Reaction Engineering*, K. H. Reichert and W. Geissler, eds., Verlag Chemie, New York, p. 33 (1989).

Forcada, J., and J. M. Asua, "Modelling the Microstructure of Emulsion Copolymers," *J. Poly. Sci. Poly., Chem. Ed.*, **23**, 1955 (1985).

Gugliotta, L. M., M. Arotçarena, J. R. Leiza, and J. M. Asua, "Estimation of Conversion and Copolymer Composition in Semicontinuous Emulsion Polymerization Using Calorimetric Data," *Polymer*, **36**, 2019 (1995a).

Gugliotta, L. M., J. R. Leiza, M. Arotçarena, P. D. Armitage, and J. M. Asua, "Copolymer Composition Control in Unseeded Emulsion Polymerization Using Calorimetric Data," *Ind. Eng. Chem. Res.*, **34**, 3899 (1995b).

Gugliotta, L. M., G. Arzamendi, and J. M. Asua, "Choice of the Monomer Partition Model in Mathematical Modeling of Emulsion Copolymerization Systems," *J. Appl. Poly. Sci.*, **55**, 1017 (1995c).

Guyot, A., J. Guillot, C. Pichot, and L. Ríos-Guerrero, "New Design for Producing Constant Composition Copolymers in Emulsion Polymerization. Emulsion Polymers and Emulsion Polymerization," *ACS Symp. Ser.*, Vol. 165, American Chemical Society, Washington, DC (1981).

Hamielec, A. E., J. F. MacGregor, and A. Penlidis, "Multicomponent Free Radical Polymerization in Batch, Semibatch and Continuous Reactors," *Macromol. Chem. Macromol. Symp.*, **10/11**, 521 (1987).

Hoppe, T., and B. Grob, "Heat Flow Calorimetry as a Testing Method for Preventing Runaway Reactions," Int. Symp. Runaway Reaction, Cambridge, MA (1989).

Karlsen, L. G., and J. Villadsen, "Isothermal Reaction Calorimetry—II Data Treatment," *Chem. Eng. Sci.*, **42**, 1165 (1987).

Kozub, D., and J. F. MacGregor, "Feedback Control of Polymer Quality in Semibatch Copolymerization Reactors," *Chem. Eng. Sci.*, **47**, 929 (1992).

Krieger, J. M., "Rheology of Polymer Colloids," *Polymer Colloids*, R. Buscall, T. Corner, and J. F. Stageman, eds., Elsevier, London, p. 219 (1985).

Leiza, J. R., G. Arzamendi, and J. M. Asua, "Copolymer Composition Control in Emulsion Polymerization Using Technical Grade Monomers," *Polym. Int.*, **30**, 455 (1993a).

Leiza, J. R., J. C. de la Cal, G. R. Meira, and J. M. Asua, "On-line Copolymer Composition Control in the Semicontinuous Emulsion Copolymerization of Ethyl Acrylate and Methyl Methacrylate," *Polym. React. Eng.*, **1**, 461 (1993b).

MacGregor, J. F., "On-line Reactor Energy Balances via Kalman Filtering," IFAC Conf. Instrumentation and Automation in Rubber, Plastics and Polymerization Industries, Akron, OH (1986).

Moritz, H. U., "Polymerization Calorimetry—A Powerful Tool for Reactor Control," *Polymer Reaction Engineering*, K. H. Reichert and W. Geiseler, eds., Verlag Chemie, Weinheim, Germany (1989).

Omi, S., K. Kushibiki, M. Negishi, and M. Iso, "Generalized Computer Modeling of Semi-Batch, *n*-Component Emulsion Copolymerization Systems and Its Applications," *Zairyo Gijutsu.*, **3**, 426 (1985).

Regenass, W., "Calorimetric Monitoring of Industrial Chemical Processes," *Thermochim. Acta*, **95**, 351 (1985).

Schoonbrood, H. A. S., H. A. Thijssen, H. M. G. Broons, M. Petrs, and A. L. German, "Semicontinuous Emulsion Copolymerization to Obtain Styrene-Methyl Acrylate Copolymers with Pretermined

Chemical Composition Distributions," *J. Appl. Poly. Sci.*, **49**, 2029 (1993).

Schuler, H., and C. U. Schmidt, "Calorimetric State Estimators for Chemical Reactor Diagnosis and Control: Review of Methods and Applications," *Chem. Eng. Sci.*, **47**, 899 (1992).

Snuparek, J., "Semicontinuous Emulsion Polymerization. II. Copolymerization of Butyl Methacrylate and Butyl Acrylate," *Angew. Makromol. Chem.*, **25**, 113 (1972).

Snuparek, J., and F. Krska, "Semicontinuous Emulsion Copolymerization of Styrene and Butyl Acrylate," *J. Appl. Poly. Sci.*, **20**, 1753 (1976).

Snuparek, J., and F. Krska, "Semicontinuous Emulsion Copolymerization of Acrylonitrile, Butyl Acrylate and Styrene," *J. Appl. Poly. Sci.*, **21**, 2253 (1977).

Soroush, M., and C. Kravaris, "Nonlinear Control of a Batch Polymerization Reactor: An Experimental Study," *AIChE J.*, **38**, 1429 (1992).

Urretabizkaia, A., E. D. Sudol, M. S. El-Aasser, and J. M. Asua, "Calorimetric Monitoring of Emulsion Copolymerization Reactions," *J. Poly. Sci. Part A: Poly. Chem.*, **31**, 2907 (1993).

Urretabizkaia, A., and J. M. Asua, "High Solids Content Emulsion Terpolymerization of Vinyl Acetate, Methyl Methacrylate, and Butyl Acrylate. I. Kinetics," *J. Poly. Sci.: Part A: Poly. Chem.*, **32**, 1761 (1994).

Urretabizkaia, A., J. R. Leiza, and J. M. Asua, "On-line Terpolymer Composition Control in Semicontinuous Emulsion Polymerization," *AIChE J.*, **40**, 1850 (1994).

Van Doremaele, G. H. J., H. A. S. Schoonbrood, J. Kurja, and A. L. German, "Copolymer Composition Control by Means of Semicontinuous Emulsion Copolymerization," *J. Appl. Poly. Sci.*, **45**, 957 (1992).

Villadsen, J. V., and M. L. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation*, Prentice Hall, Englewood Cliffs, NJ (1978).

Wu, R. S. H., "Dynamic Thermal Analyzer for Monitoring Batch Processes," *Chem. Eng. Prog.*, **81**, 57 (1985).

Manuscript received June 3, 1996, and revision received Nov. 11, 1996.