

Control of Molecular Weight Distribution in Emulsion Polymerization Using On-Line Reaction Calorimetry

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The molecular weight distribution (MWD) of linear polymers was controlled based on on-line reaction calorimetry. A method to estimate the MWD from reaction calorimetry when chain transfer to a chain-transfer agent is the main termination event was developed and its robustness assessed by simulation. Following this method, the desired final MWD was decomposed in a series of instantaneous MWDs to be produced at different stages of the process. An optimization algorithm was used to calculate the set-point trajectories to produce the desired MWD in a minimum time. A nonlinear model based controller was used to track these trajectories. The control scheme was validated by preparing polystyrene latexes of widely different predefined MWD.

Introduction

The control of the molecular weight distribution (MWD) of emulsion polymers by means of closed-loop strategies is a challenging subject because the feasibility of the on-line measurement of the MWD for emulsion systems remains to be demonstrated. In addition, the compartmentalized nature of the emulsion polymerization makes, generally speaking, the MWD nonobservable from usually available on-line measurements (monomer conversion and temperatures). 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 chain transfer to CTA. Storti and Morbidelli¹ produced polystyrene latexes of constant molecular weight by maintaining the ratio CTA [carbon tetrachloride (CCl₄)]/styrene along the conversion (measured on-line by densimetry) at a given value. Saldivar and Ray² proposed an open-loop control strategy to simultaneously control constant composition and molecular weights. They tested the strategy for an emulsion copolymerization of methyl methacrylate/vinyl acetate. They also proposed a nonlinear model predictive control algorithm to on-line calculate optimal trajectories, but its real-time implementation was not discussed. Finally, Echevarría et al.³ used on-line gas chromatography to measure the unreacted amounts of styrene and CCl₄, and a nonlinear controller was used to track trajectories of styrene and CCl₄ that ensured the production of a polystyrene latex with a desired MWD. Thus, narrow, broad, and even bimodal distributions were successfully prepared. Nevertheless, in both cases (Storti and Morbidelli¹ and Echevarría et al.³) the on-line measurement

of styrene and CTA was carried out using invasive techniques that are difficult to implement in an industrial environment.

Reaction calorimetry (Regenass,⁴ Wu,⁵ MacGregor,⁶ Moritz,⁷ Schuler and Schmidt,⁸ Urretabizkaia et al.,⁹ Sáenz de Buruaga et al.,^{10–13} Févotte et al.,^{14,15} and Gugliotta et al.^{16,17}) is an appropriate technique for on-line monitoring of polymerizations, because these reactions are very exothermic. The measurement is noninvasive, rapid, and robust because it is based on temperature measurements. Reaction calorimetry does not provide a direct measurement of the unreacted amount of monomer in the reactor, but state observers and estimators allow the estimation of the unreacted amounts of monomers. Gugliotta et al.^{16,17} and Sáenz de Buruaga et al.^{10–13} used open-loop observers for this purpose, and they showed that the estimation of the unreacted amount of monomers in batch and semicontinuous emulsion polymerizations is accurate enough to be used in strategies to control the composition of co/terpolymers. Hammouri et al.¹⁸ used a high-gain observer to infer the unreacted amounts of monomers and the concentration of radicals in the polymer particles. This estimator requires to tune one parameter to accurately estimate the states. To control the MWD, the estimation of unreacted amounts of both monomer and CTA are needed, but no attempt to estimate the unreacted CTA from calorimetric measurements has been reported.

In this work open-loop observers were used to estimate the unreacted amounts of monomer and CTA in the reactor based on the on-line measurement of the heat of reaction obtained from a modified RC1 calorimeter. The estimates were used in a closed-loop control strategy aimed at tracking the trajectories of monomer and CTA that yielded the following MWDs of the polymer: (1) polystyrene with a weight-average molecular weight (\bar{M}_w) of 400 000 and minimum polydispersity, PI = 2; (2) polystyrene with \bar{M}_w = 750 000 and a broad polydispersity, PI = 4; (3) polystyrene with bimodal distribution (mode 1, \bar{M}_{w1} = 1 200 000 and PI₁ = 2; mode 2, \bar{M}_{w2} = 120 000 and PI₂ = 2).

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The manuscript is organized as follows: First, the open-loop observer used to infer the unreacted amounts of monomer and CTA is presented, and its sensitivity to errors in the parameters is illustrated by simulation. Second, the design of the closed-loop control strategy is shown. Finally, the control strategy is validated by preparing polystyrene latexes of predefined MWDs using two CTAs that significantly differ in reactivity.

Estimation of the Unreacted Amount of Monomer and CTA from Calorimetric Data

In the modified Mettler RC1 reactor calorimeter used in this work, the heat of reaction, Q_r , can be determined on-line every 2 s (Sáenz de Buruaga et al.).¹⁰ The heat of polymerization, Q_r , is related to the polymerization rate as

$$Q_r = R_p(-\Delta H_r) \quad (1)$$

where R_p is the rate of polymerization and $-\Delta H_r$ is the enthalpy of polymerization of the monomer. Equation 1 considered that the heat produced by transfer to CTA reaction was negligible. This was checked in batch experiments carried out with different amounts of CTA.

The amounts of unreacted monomer and CTA were inferred using an open-loop observer. This observer is based on the material balances for monomer and CTA in a semicontinuous emulsion polymerization:

$$\frac{dM}{dt} = F_M - R_p = F_M - k_p[M]_p \frac{\bar{n}N_p}{N_A} \quad (2)$$

$$\frac{dCTA}{dt} = F_{CTA} - R_{CTA} = F_{CTA} - k_{tr,CTA}[CTA]_p \frac{\bar{n}N_p}{N_A} \quad (3)$$

where k_p and $k_{tr,CTA}$ are the propagation rate constant and the chain-transfer rate coefficient, respectively, $[M]_p$ and $[CTA]_p$ are the concentrations of the monomer and CTA in the polymer particles, F_M and F_{CTA} are the feed rates of the monomer and CTA, \bar{n} is the average number of radicals per particle, N_p is the total number of polymer particles, and N_A is Avogadro's number.

Combining eqs 1–3, the material balances for the monomer and CTA can be written as a function of the heat released by polymerization and the reactivity ratio of the CTA, $C_{tr,CTA} = k_{tr,CTA}/k_p$, as follows:

$$\frac{dM}{dt} = F_M - \frac{Q_r}{-\Delta H_r} \quad (4)$$

$$\frac{dCTA}{dt} = F_{CTA} - \frac{Q_r}{-\Delta H_r} C_{tr,CTA} \frac{[CTA]_p}{[M]_p} \quad (5)$$

The open-loop observer given by eqs 4 and 5 was used to estimate monomer and CTA concentration from the heat released by polymerization. The rate of convergence of the estimation is not adjustable, and it is given by the process model itself (Soroush).¹⁹ If the observer error at $t = 0$ is zero, it will remain zero during the process (as far as the model is good enough). All of the model contributions in eqs 4 and 5 are given by $C_{tr,CTA}$ and $-\Delta H_r$ that can be accurately known from independent experiments.

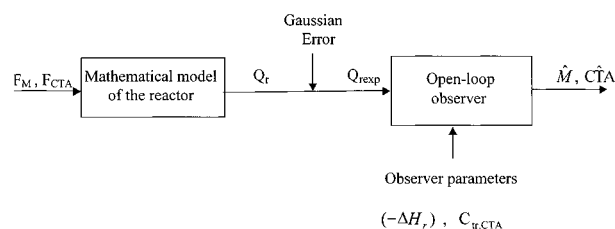


Figure 1. Simulation scheme for the sensitivity analysis of the open-loop observer.

The overall (X) and instantaneous (X_{ins}) gravimetric conversions were calculated as follows:

$$X = \frac{M_0 + \int_0^t F_M dt + CTA_0 + \int_0^t F_{CTA} dt - M_t - CTA_t}{M_T + CTA_T} \quad (6)$$

$$X_{ins} = \frac{M_0 + \int_0^t F_M dt + CTA_0 + \int_0^t F_{CTA} dt - M_t - CTA_t}{M_0 + \int_0^t F_M dt + CTA_0 + \int_0^t F_{CTA} dt} \quad (7)$$

where M_0 and CTA_0 are the initial amounts of monomers and CTA in the reactor and M_T and CTA_T the total amounts of monomer and CTA in the formulation, respectively.

As shown in the appendix, chain transfer to CTA is the main termination event when there is enough CTA in the reactor. Under these circumstances, the instantaneous ($\bar{M}_{n,ins}$) and cumulative ($\bar{M}_{n,cumul}$) number-average molecular weights are given by (see the appendix)

$$\bar{M}_{n,ins} = \frac{k_p[M]_p}{k_{tr,CTA}[CTA]_p} P_m \quad (8)$$

$$\bar{M}_{n,cumul} = \frac{M_0 + \int_0^t F_M dt - M_t}{CTA_0 + \int_0^t F_{CTA} dt - CTA_t} P_m \quad (9)$$

where P_m is the molecular weight of the repeating unit.

Sensitivity Analysis of the Open-Loop Observer. To check the robustness of the proposed estimation scheme, a sensitivity analysis was carried out to study the effect of the model parameters (transfer rate constant, $C_{tr,CTA}$, and enthalpy of polymerization, $-\Delta H_r$) on the estimated values of the unreacted amounts of monomer and CTA and on the estimated molecular weights. This study was done by simulation using a mathematical model to simulate the calorimeter reactor and generate data of the heat of reaction. The heat of reaction was used as input of the open-loop observer. Figure 1 summarizes the simulation scheme, and Table 1 presents the parameters used in the mathematical model.

Simulations were carried out using two different CTA: a high reactive CTA, BuM; and a low reactive CTA, CCl_4 . Seeded semibatch experiments were simulated according to the recipe presented in Table 2. Monomer and CTA were added to the reactor in 500 min (for CCl_4 the addition time was only 120 min), and the total number of particles of the seed was 1×10^{18} .

Table 1. Values of the Parameters Used in the Sensitivity Analysis of the Open-Loop Observer ($T = 60$ °C)^a

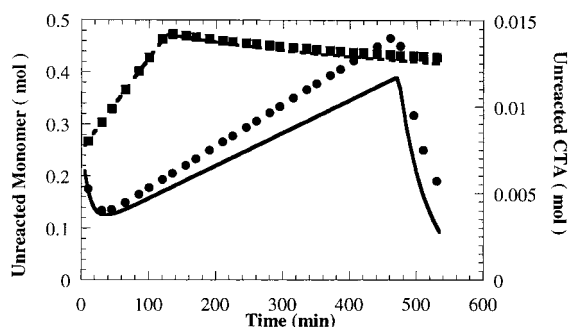
k_p (L mol ⁻¹ s ⁻¹) ²⁴	275		
C_{tr,CCl_4} , ³ $C_{tr,BuM}$ ²⁰	9.8×10^{-3}	21	
$K_{P,W}^M$, $K_{P,W}^{CCl_4}$, $K_{P,W}^{BuM}$, ^{3,25}	1500	3650	450
$K_{D,W}^M$, $K_{D,W}^{CCl_4}$, $K_{D,W}^{BuM}$, ^{3,25}	2700	4860	700
N_p , ρ_{pol} (g L ⁻¹) ²¹	1×10^{18}	1050	
$M_{w,M}$, M_{w,CCl_4} , $M_{w,BuM}$ (g mol ⁻¹) ²¹	104.1	154.4	90.2
ρ_M , ρ_{CCl_4} , ρ_{BuM} (g L ⁻¹) ²¹	904	1596	842
$-\Delta H_M$ (J/mol) ²⁶	73×10^3		

^a $K_{i,j}^K$ = partition coefficient of reagent K between phases i and j .

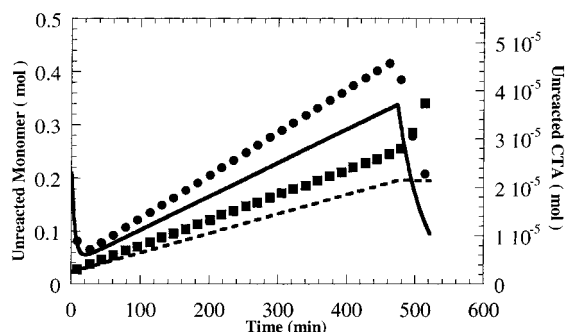
Table 2. Recipe Used for the Simulations of the Open-Loop Observer

	initial charge	flow rate (mol/s)	total
styrene (mol)	0.25	1.6×10^{-4}	4.8
CCl ₄ (mol)	0.0075	10^{-6}	0.015
BuM (mol)	10^{-6}	2×10^{-7}	0.006
water (mol)	44.44	0	44.44
K ₂ S ₂ O ₈ (mol)	2.48×10^{-3}	0	2.48×10^{-3}
SLS (mol)	2.77×10^{-2}	0	2.77×10^{-2}
seed ^a (g)	35	0	35

^a $N_{p,seed} = 1 \times 10^{18}$ particles.



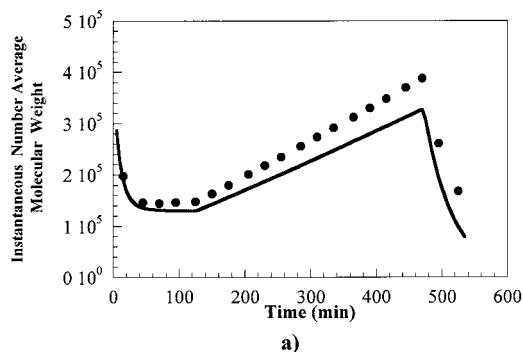
a)



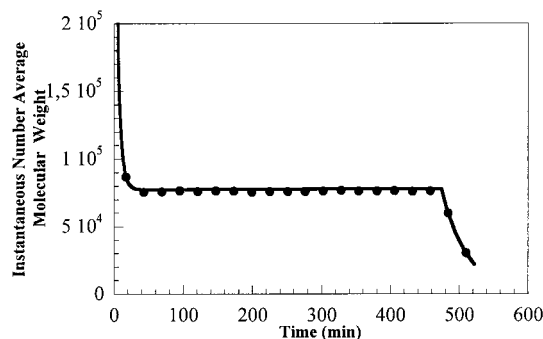
b)

Figure 2. Estimation of the unreacted amount of the monomer and CTA for a 2% error in the enthalpy of polymerization: (a) CCl₄; (b) BuM. Legend: estimated (●) and actual (—) monomer; estimated (■) and actual (---) CTA.

It was checked that when correct model parameters and the initial values of monomer and CTA were used, the observer provided the correct values of both monomer and CTA (not shown). Figure 2 shows the estimated amounts of the monomer and CTA when a 2% error in $-\Delta H_r$ was considered. As can be seen, this error affected both monomer and CTA estimation and this effect is cumulative. In addition, the extent of the effect on the estimation of CTA depended on the reactivity of the CTA. Thus, when a slow reactive CTA was used (Figure



a)



b)

Figure 3. Estimation of the instantaneous \bar{M}_n for a 2% error in the enthalpy of polymerization: (a) CCl₄; (b) BuM. Legend: (●) estimated value; (—) actual value.

2a), the effect of the error in $-\Delta H_r$ was almost negligible because CCl₄ scarcely reacts; i.e., its concentration remains almost constant during the process. On the other hand, a larger error was made in the estimation of the highly reactive CTA, that was affected in a way similar to that of the monomer. It is worthy to explain how a 2% error in the enthalpy of polymerization yielded at the end of the feeding period a 24% error in both the unreacted monomer and highly active CTA. For a conversion of 90% at the end of the feeding period, a 2% error in $-\Delta H_r$ yields a 2% error in the estimated gravimetric conversion ($X_{estimated} = 88.2\%$), which is quite a good estimation. However, when the unreacted monomer is considered, the induced error is substantially larger. Thus, for the example given above, the estimated unreacted monomer is 11.8%, whereas the actual amount is 10%, namely, an 18% error. The error in the estimated unreacted monomer increases as the semicontinuous process becomes more starved. A similar reasoning applies to the highly reactive CTA.

For the purposes of the present work, the critical magnitude is the monomer/CTA ratio because this is what controls the polymer molecular weight (see eq 8). Figure 3 present a comparison between the estimated and actual $\bar{M}_{n,ins}$ for a 2% error in $-\Delta H_r$. It can be seen that a perfect matching was observed for the highly reactive CTA, because both monomer and CTA were similarly affected by the 2% error. On the other hand, the estimated value of $\bar{M}_{n,ins}$ was affected by a 18% error when a slow reactive CTA (CCl₄) was used, because the estimation of the monomer was more affected than that of the CTA by the error in the enthalpy of polymerization.

Figure 4 presents the effect of a 30% error in $C_{tr,CTA}$ when CCl₄ is used. It can be seen that the estimation of the unreacted amount of CTA was only slightly affected (Figure 4a) because CCl₄ scarcely reacted.

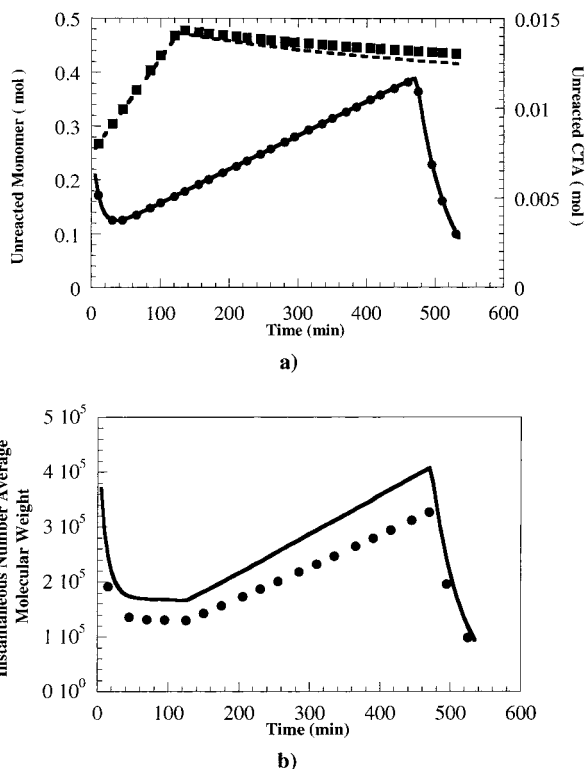


Figure 4. (a) Estimation of the unreacted amount of the monomer and CTA and (b) instantaneous \bar{M}_n for a 30% error in $C_{tr,CTA}$ when CCl_4 was used as the CTA. Legend: (a) estimated (●) and actual (—) monomer; estimated (■) and actual (---) CTA; (b) (●) estimated value; (—) actual value $\bar{M}_{n,ins}$.

However, the error in $C_{tr,CTA}$ substantially affected the estimation of the molecular weight (Figure 4b). Figure 5 presents the effect of a 30% error in $C_{tr,CTA}$ when BuM was used. It can be seen that this leads to a significant error in the concentration of CTA (Figure 5a), but this error was compensated by that of the $C_{tr,CTA}$ in the calculation of $\bar{M}_{n,ins}$, yielding an accurate estimation of the molecular weight.

In conclusion, the molecular weights can be accurately estimated from calorimetric measurements when a highly reactive CTA is used, whereas the estimation approach is more sensitive to model errors when a low reactive CTA is employed. It is important to stress that this refers only to linear polymers under conditions in which chain transfer to CTA is the main termination event.

Control Strategy

Figure 6 summarizes the control scheme. Reactions were carried out in a modified Mettler RC1 calorimeter that allows for the on-line determination of the heat of polymerization (Sáenz de Buruaga et al.).¹¹ This value was used in the open-loop observer described in the previous section to estimate the amounts of monomer and CTA in the reactor. These values are compared with the set point calculated by means of an off-line optimization, and then a nonlinear model based controller was used to calculate the control actions.

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

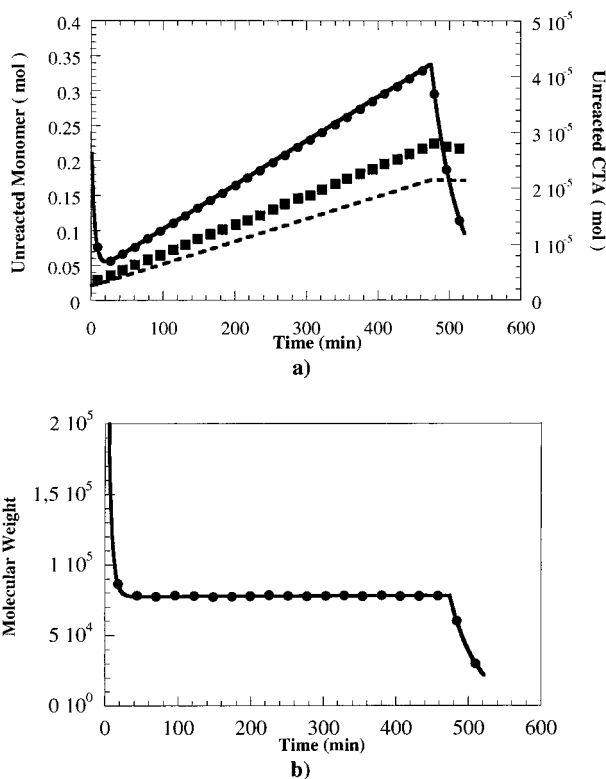


Figure 5. (a) Estimation of the unreacted amount of the monomer and CTA. (b) Instantaneous \bar{M}_n for a 30% error in $C_{tr,CTA}$ when BuM was used as the CTA. Legend: (a) estimated (●) and actual (—) monomer; estimated (■) and actual (---) CTA; (b) (●) estimated value; (—) actual value $\bar{M}_{n,ins}$.

(Echevarría et al.).³ 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. To calculate the \bar{X}_{ni} value that has to be produced at each value of X , the final MWD is discretized as

$$W_c^*(n) = \frac{1}{X_f} \sum_{j=1}^k W_j(n) \Delta X_j = \frac{\Delta X^k}{X_f} \sum_{j=1}^k \frac{n}{\bar{X}_{ni}^2} \exp\left(-\frac{n}{\bar{X}_{ni}}\right) \quad (10)$$

where X_f is the final overall conversion, \bar{X}_{ni} , the instantaneous number-average chain length produced in the conversion increment j , $W_j(n)$ the instantaneous MWD produced in the conversion increment j (a constant value of ΔX_j (ΔX) is used in eq 10), and k the number of increments in which X_f is divided. For a given number of conversion increments, the required values of \bar{X}_{ni} can be calculated by minimizing the equation

$$\text{Min}_{\bar{X}_{ni}} \left[\sum_n (W_c^d(n) - W_c^*(n))^2 \right] \quad (11)$$

where $W_c^d(n)$ and $W_c^*(n)$ are the desired and the calculated MWDs (eq 10). 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,

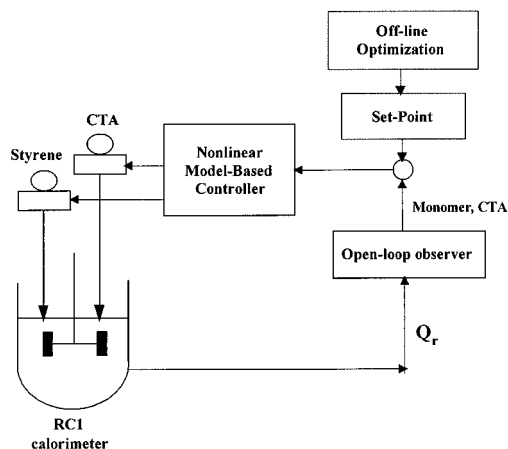


Figure 6. Closed-loop control scheme.

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 2 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 (see the appendix). 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 11 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 a low reactive CTA accumulates in the reactor, precluding the formation of high molecular weight polymer at the end of the process. Therefore, the only achievable sequence for a low reactive CTA, as CCl_4 , is to produce a continuously decreasing molecular weight polymer during the process (an exception to this rule is the production of a MWD of minimum polydispersity index (PI) 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.

Off-Line Optimization. The goal of the off-line optimization is to calculate the set-point trajectories of the controlled variables that ensure the production of an emulsion polymer of the desired MWD in a minimum process time. This was carried out by minimizing the objective function

$$\text{Min}_{[M]_p} \left[\int_0^t \frac{1}{R_p} dX \right] \quad (12)$$

where R_p is the polymerization rate and X the overall conversion defined as the ratio between the polymer in the reactor and the monomer in the recipe. This means that to maximize the polymerization rate, it is necessary to work at any time at the maximum allowable concentration of monomer in the particles.

The minimization of eq 12 is subjected to the following constraints:

(i) The polymer produced must have the desired final MWD ($W_c^d(n)$). This is equivalent to produce the required \bar{X}_{ni} at each conversion interval. A polynomial fitting of the decreasing sequence of the \bar{X}_{ni} calculated in the minimization was used for simplicity in the optimization algorithm.

$$\bar{X}_{ni} \propto \frac{[M]_p}{[CTA]_p} = f(X) \quad (13)$$

(ii) The maximum amounts of monomer and CTA that can be added into the reactor are the total amount in the recipe, M_T and CTA_T , respectively.

$$M + M_{pol} \leq M_T \quad (14)$$

$$CTA + CTA_{pol} \leq CTA_T \quad (15)$$

where the subscript pol stands for the polymerized amounts.

(iii) The monomer and CTA already charged into the reactor cannot be removed.

$$\frac{d[M + M_{pol}]}{dX} \geq 0 \quad (16)$$

$$\frac{d[CTA + CTA_{pol}]}{dX} \geq 0 \quad (17)$$

(iv) The amount of monomer and, hence, that of CTA in the latex particles should be limited. The presence of droplets should not be allowed because the excess of monomer or CTA, which is in the monomer droplets, does not contribute to increase the polymerization rate but causes a significant loss of control capacity. Temperature control and safety are other reasons to limit the amount of free monomer in the reactor.

The optimization provides the amounts of both monomer and CTA in the reactor at any overall conversion. The resulting curves monomer vs X and CTA vs X are independent of the polymerization rate of the process and can be regarded as master curves.

Nonlinear Model Based Controller. Although nearly continuous measurements of Q_r are available, control actions (changes in the flow rates of the feeding pumps) were implemented for each control interval ($\Delta t = 20$ s). The role of the nonlinear model based controller is to calculate the feed rates of the monomer (F_M) and CTA (F_{CTA}) for each control interval. The controller is based on the discretized material balances

$$M_{t+1} = \hat{M}_t + (F_M - R_p)\Delta t \quad (18)$$

$$CTA_{t+1} = \hat{CTA}_t + (F_{CTA} - R_{CTA})\Delta t \quad (19)$$

where \hat{M}_t and \hat{CTA}_t are the estimated values of monomer and CTA at the beginning of the control interval and M_{t+1} and CTA_{t+1} are the desired values of these variables at the end of the interval as given by the optimization presented previously:

$$M_{t+1} = f(X_{t+1}) \quad (20)$$

$$CTA_{t+1} = f(X_{t+1}) \quad (21)$$

$$X_{t+1} = \frac{M_t + F_M \Delta t - M_{t+1} + \text{CTA}_t + F_{\text{CTA}} \Delta t - \text{CTA}_{t+1}}{M_T + \text{CTA}_T} \quad (22)$$

Equations 18–22 are a set of five nonlinear algebraic equations with five unknowns, M_{t+1} , CTA_{t+1} , X_{t+1} , F_M , 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 MWD.

Several constraints were imposed on the maximum and minimum levels of the manipulated variable, F_M and F_{CTA} , and also on the rate of change of those variables:

$$F_{i,\min} \leq F_i(t) \leq F_{i,\max}; \quad i = \text{monomer and CTA} \quad (23)$$

$$F_i(t-1) - \Delta F_{i,\max} \leq F_i(t) \leq F_i(t-1) + \Delta F_{i,\max}; \\ i = \text{monomer and CTA} \quad (24)$$

where $\Delta F_{i,\max} = 0.3F_i(t)$.

Experimental Validation of the Control Strategy

The control strategy was experimentally validated for the unseeded emulsion polymerization of styrene using two different CTAs (CCl_4 and BuM). Experiments were carried out in a modified Mettler RC1 reaction calorimeter equipped with the HP60 stainless steel reactor. Details on the experimental setup and on the on-line determination of the heat released by polymerization can be found elsewhere (Sáenz de Buruaga et al.).¹¹ Polymerization samples were taken during the reaction for the off-line measurement of the MWD by size-exclusion chromatography (SEC) and conversion by gravimetry. The SEC apparatus was a Waters equipped with a pump (Waters 510, Milford, MA), a refractometer detector (Waters 2410) and two columns in series (Styragel HR4 and HR6 of 10^4 and 10^6 Å). The chromatograph was operated at 30 °C, the flow rate of tetrahydrofuran (THF) was 1 mL/min, and samples were diluted in THF prior to injection.

The production of polystyrene latexes with three different MWDs was considered:

C1. Polystyrene with PI = 2 and $\bar{M}_w = 4.0 \times 10^5$.

C2. Polystyrene with PI = 4 and $\bar{M}_w = 7.5 \times 10^5$.

C3. Polystyrene with bimodal MWD: $\bar{M}_{w1} = 1.2 \times 10^6$ and PI = 2 and $\bar{M}_{w2} = 1.2 \times 10^5$ and PI = 2.

The polystyrene of case C3 was produced using both CTAs, CCl_4 and BuM, and that of the cases C1 and C2 was produced by using only CCl_4 . The formulations used are given in Table 3.

Case C1. In this case the production of a polystyrene with $\bar{M}_w = 4.0 \times 10^5$ and minimum PI was considered. To produce this constant molecular weight polymer, the monomer/CTA ratio has to be kept constant during the entire process. The trajectories obtained in the optimization indicated that all of the CCl_4 should be included in the initial charge and that the monomer flow rate should be controlled to maintain the desired monomer/CTA ratio. Figure 7a shows the average cumulative molecular weights obtained during run 1 using the styrene feed rates given in Figure 8. It can be seen that the desired polymer was produced. A more detailed comparison of the polymer required and that produced

are given in Figure 7b where the entire MWD is shown at different gravimetric conversions.

Case C2. In case C2 (run 2), the production of polystyrene with a broad distribution was attempted. CCl_4 was used as CTA in this run. Figure 9a presents the sequence of the instantaneous \bar{M}_n 's that ensured the production of the desired final MWD (calculated using eqs 10 and 11). Once the evolution of the required instantaneous \bar{M}_n is known, the optimization algorithm allowed one to calculate the optimal trajectories for styrene and CTA to be tracked by the nonlinear model based controller (Figure 9b). All of the CTA should be in the reactor at an overall conversion of about 30%.

Figure 10 shows the flow rates of monomer and CTA calculated on-line by the nonlinear model based controller at each control interval (20 s was considered). Monomer and CTA flow rates were high during the first 40 min to follow the trajectories of Figure 8b. The flow rate of CCl_4 stopped at 45 min.

Figure 11 shows a comparison between the desired MWD and that actually obtained during run 2. It can be seen that the desired MWD of the final latex was obtained.

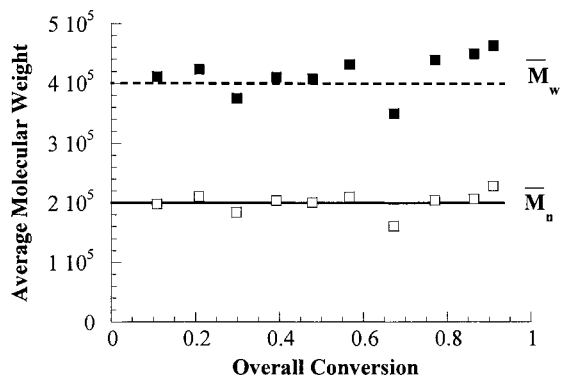
Case C3. In this case, a bimodal distribution with two peaks of minimum polydispersity and containing the same amounts of polymer was attempted. According to the optimal process, the peak of high molecular weight with constant instantaneous MWD should be produced during the first part of the polymerization. The low molecular weight peak should be produced during the second half of the process. This is the only way to produce such a bimodal polymer if a low reactive CTA is used. The reason is that CTA accumulates in the reactor, and hence high molecular weights cannot be produced at high overall conversions, namely, when the amount of monomer in the reactor is low. For a reactive CTA, such as BuM, this is not a constraint and other policies may be adopted to produce the bimodal polystyrene. Nevertheless, this policy was also considered when BuM was employed. Table 3 shows the recipes used in runs 3 and 4 for the production of such a bimodal polymer. Note that the amount of BuM required was almost 7 times lower than that of CCl_4 . BuM was added to the reactor as a highly diluted preemulsified stream because the flow rate required was very low. In addition, BuM could not be directly dissolved in the monomer because the addition of the monomer should be stopped before that of the mercaptan (Figure 12).

Figure 12 presents the optimal trajectories for styrene and CTA required to produce the bimodal polystyrene of case C3 for both CCl_4 and BuM. The differences in reactivity (see Table 1) are clearly evidenced in the optimal trajectories.

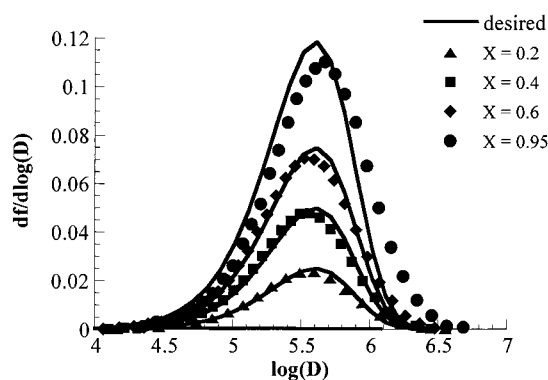
Figure 13 shows the results obtained for run 3, when CCl_4 was used as CTA. It can be seen that the final MWD is bimodal, although the low molecular weight mode had a larger PI than desired. This deviation was likely due to diffusional limitations affecting the CCl_4 added to reactor as a shot when polymerization reached 50% gravimetric conversion. This made the monomer/CTA ratio in the polymer particles higher than required, and hence too high molecular weights were produced after the CTA shot. This hypothesis was supported by the results observed when the mixing in the reactor was modified. In the experiments described previously, a Fluidfoil impeller (Lightning mixers) at 400 rpm was used. This impeller was substituted by an anchor

Table 3. Recipes Used for the Production of Polystyrene Latexes of Cases C1–C3

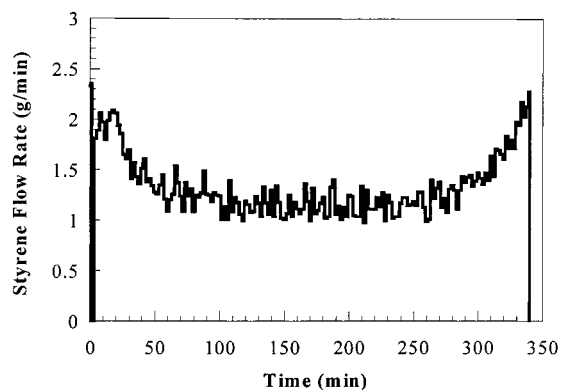
ingredient (g)	run 1, case C1			run 2, case C2			run 3, case C3			run 4, case C3		
	total	initial charge	feed	total	initial charge	feed	total	initial charge	feed	total	initial charge	feed
styrene	500	28.35	471.65	500	14.5	485.5	500	25.54	474.46	500	5	495
H ₂ O	700	700		700	700		700	700		732.5	700	32.5
CCl ₄	2.23	2.23		4.96	0.3	4.62	4.97	0.67	4.264			
BuM										0.722	0	0.722
K ₂ S ₂ O ₈	0.83	0.83		0.83	0.83		0.83	0.83		0.83	0.83	
NaHCO ₃	0.83	0.83		0.83	0.83		0.83	0.83		0.83	0.83	
SLS	10	10		10	10		10	10		10	9.84	0.16



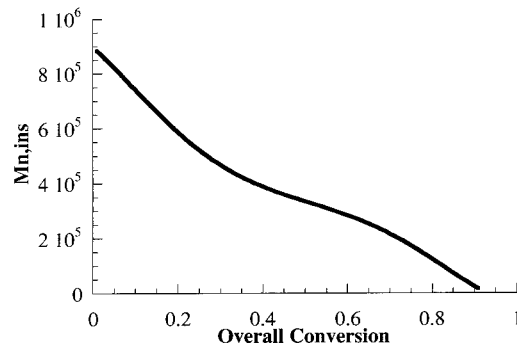
a)



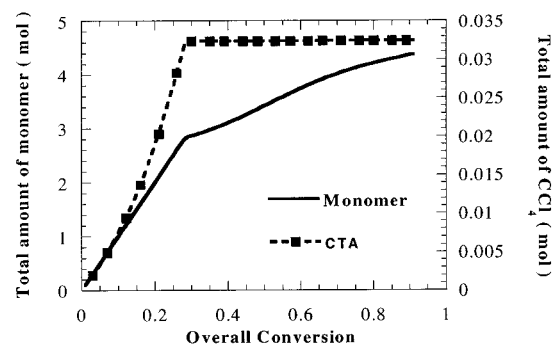
b)

Figure 7. (a) Evolution of the cumulative average molecular weights and (b) MWD produced at different run conversions and comparison with the desired distributions. Run 1 (case C1).**Figure 8.** Flow rate of styrene calculated by the controller for run 1 (case C1).

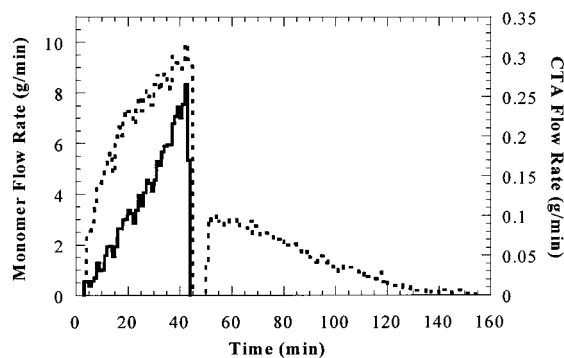
impeller (Mettler-Toledo) working at 300 rpm which gives a poor mixing, obtaining a single-mode broad MWD (Figure 14). This distribution was made broader by adding some amount of hydroquinone (a radical scavenger) at the same time as the shot of CCl₄, i.e.,



a)



b)

Figure 9. (a) Evolution of the instantaneous \bar{M}_n required to produce the desired final MWD. (b) Optimal trajectories for the total amount of styrene and CCl₄. Case C2.**Figure 10.** Flow rates of styrene and CCl₄ calculated by the controller for run 2 where a polystyrene latex of case C2 was sought. Legend: (---) styrene; (—) CCl₄.

allowing more time for CCl₄ to reach the polymer particles (Figure 14).

The results obtained when BuM was used to produce the same bimodal distribution (run 4) are shown in Figure 15. It can be seen that the required polymer was reasonably well produced. In this case, the average molecular weight of the second mode was slightly lower

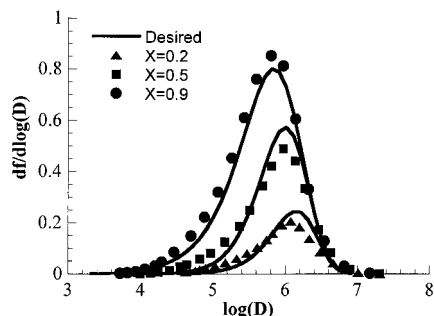


Figure 11. Comparison of the conversion evolution of the MWD produced and desired for run 2, where a polystyrene latex of case C2 was sought.

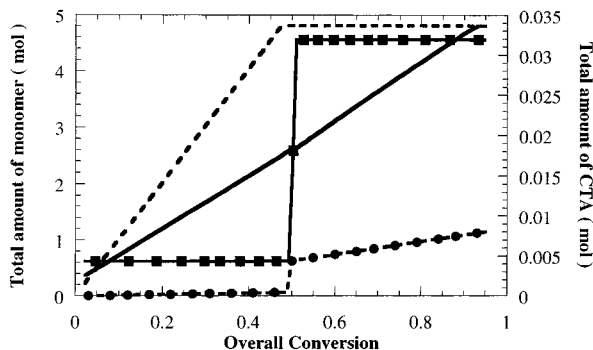


Figure 12. Optimal trajectories for styrene and CTA to produce polystyrene latexes of case C3 using CCl_4 and BuM. Legend: (—) styrene using CCl_4 ; (---) styrene using BuM; (—■—) CCl_4 ; (---●---) BuM.

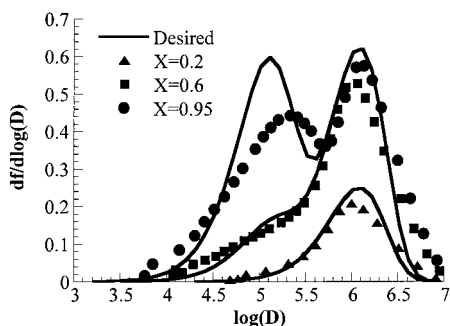


Figure 13. Comparison between the desired and obtained MWDs at different conversions for case C3 when CCl_4 was used as the CTA.

than that required. This deviation may be due to the fact that in this case a very small quantity of CTA had to be fed into the reactor (0.722 g) over the whole reaction, and about half of that quantity was added as a shot at $X = 0.5$. A slightly higher amount of CTA added in that moment could be the reason for that small deviation. It is important to point out that the polymerization required only 120 min in comparison with the 500 min required for run 3 when CCl_4 was used as the CTA.

From a technological point of view, the use of a mercaptan is better suited for industrial-like emulsion polymerization, because it is completely consumed during the process, and the amount required as well and the polymerization time are significantly lower than when CCl_4 is used.

Limitations of the Present Approach. The approach presented in this paper opens the possibility for on-line control of MWD of linear emulsion polymers based on reaction calorimetry. This is advantageous

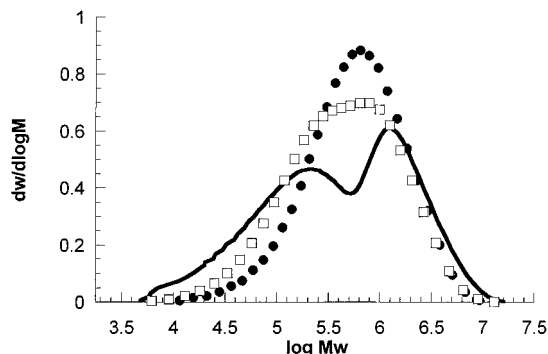


Figure 14. Final MWD of polystyrene latexes prepared using the recipe for run 3 with different mixing conditions. Legend: (—) fluid-foil impeller at 400 rpm; (●) anchor impeller at 300 rpm; (□) anchor impeller plus hydroquinone shot.

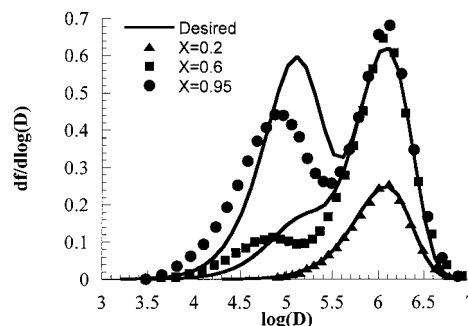


Figure 15. Comparison between the desired and obtained MWDs at different conversions for case C3 when BuM was used as the CTA.

because this on-line monitoring technique is noninvasive, rapid, and robust. The approach also has some limitations that should be mentioned. The first one is that it can only be applied to linear polymers; i.e., polymers that suffer intermolecular chain transfer to polymer cannot be prepared by this method. The reason is that these processes involve inactive polymer chains that, upon chain transfer to polymer, become active radicals modifying their molecular weight. This jeopardizes the strategy of building the desired MWD from a series of well-defined instantaneous MWDs.

The present strategy relies on models for both inferring and controlling the MWD. For well-mixed reactors, the structure of the model is well established and the only source of errors is the value of the parameters. Nevertheless, the sensitivity analysis shows that the approach is not significantly affected by errors in the parameters. The application of the approach to poorly mixed systems is more challenging and would require a good knowledge of the flow pattern in the reactor. In those systems, the production of a polymer with a minimum PI (2) is not possible because different MWDs are produced at different parts of the reactor.

Conclusions

In this work, a method for the on-line control of the MWD of linear emulsion polymers was developed based on reaction calorimetry. Nowadays, the on-line measurements of the MWD of emulsion polymers is not feasible. A method to estimate the MWD from reaction calorimetry when chain transfer to CTA is the main termination event was implemented. The robustness of the estimation approach to errors in the model was assessed by simulation. It was found that the molecular

weights can be accurately estimated from calorimetric measurements when a highly reactive CTA (e.g., a mercaptan) is used. On the other hand, the estimation approach is more sensitive to model errors when a slow reactive CTA is employed.

The control strategy takes advantage of the fact that, for linear polymers produced by free-radical polymerization, the polymer chains do not suffer any modification once they are formed. Therefore, the desired final MWD can be decomposed in a series of instantaneous MWDs to be produced at different stages of the process. An optimization algorithm was used to calculate the set-point trajectories that ensured the production of emulsion polymers of given MWDs in a minimum process time. A nonlinear model based controller was used to track these trajectories.

The control strategy was validated by preparing several polystyrene latexes of predefined MWDs: (i) monomodal, $\bar{M}_w = 400\,000$ and $PI = 2$; (ii) monomodal, $\bar{M}_w = 750\,000$ and $PI = 4$; (iii) bimodal, $\bar{M}_{w1} = 1\,200\,000$ and $PI_1 = 2$; $\bar{M}_{w2} = 120\,000$ and $PI_2 = 2$. Both slow reactive (CCl_4) and highly reactive (BuM) CTAs were used. The desired MWDs were achieved in most cases, although slight deviations were observed. When CCl_4 was added as a shot, mass-transfer limitations were observed. When using BuM, because a very low amount is required because of the higher reactivity, a small error in the amount fed into the reactor can lead to slight MWD deviations. It is important to point out that this would not be a problem in industrial-scale reactors. The application of the approach to poorly mixed systems would require a good knowledge of the flow pattern in the reactor. In those systems, the production of a polymer with a minimum PI (2) is not possible because different MWDs are produced at different parts of the reactor.

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Appendix: Molecular Weight Distribution in Polymerization Using a Chain-Transfer Agent

In 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 (Odián):²⁰

$$\bar{X}_n = R_p/R_t \quad (A-1)$$

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

$$R_p = k_p[M]_p \frac{\bar{n}N_p}{N_A} \quad (A-2)$$

where k_p is the propagation rate constant, $[M]_p$ is the concentration of the monomer in the polymer particles, \bar{n} is the average number of radicals per particle, N_p is the total number of polymer particles, and N_A is Avogadro's number.

In a compartmentalized system, the termination rate is given by

$$R_t = [k_{tr,CTA}[CTA]_p + k_{tr,M}[M]_p + k_a[R]_w] \frac{\bar{n}N_p}{N_A} \quad (A-3)$$

where the first term in the right-hand side member accounts for the termination by chain transfer to CTA, the second for the termination by chain transfer to the monomer, and the third for bimolecular termination with radicals entering from the aqueous phase. In eq A-3, $k_{tr,M}$ is the rate coefficient for chain transfer to the monomer, k_a the rate coefficient for radical entry, and $[R]_w$ the concentration of radicals in the aqueous phase. It is worth pointing out that in eq A-3 it was assumed that instantaneous termination occurred when a radical entered the polymer particle already containing another radical. This overestimated the contribution of bimolecular termination in eq A-3, but it allowed a more conservative calculation of the minimum amount of CTA to ensure that chain transfer to CTA was the main termination event. This would occur when

$$k_{tr,CTA}[CTA]_p/k_{tr,M}[M]_p > 10 \quad (A-4)$$

and

$$k_{tr,CTA}[CTA]_p/k_a[R]_w > 10 \quad (A-5)$$

From eqs A-4 and A-5 the minimum amount of CTA (BuM in the example) needed to ensure that chain transfer to CTA was the main termination event can be calculated as

$$[CTA]_p/[M]_p > 5.2 \times 10^{-6} \text{ mol/L} \quad (A-6)$$

and

$$[CTA]_p > 3.5 \times 10^{-6} \text{ mol/L} \quad (A-7)$$

Using $k_{tr,M} = 0.003 \text{ L/(mol s)}$ (Brandrup and Immergut²¹) and $k_a[R]_w = 0.002 \text{ s}^{-1}$ (Asua et al.),²² one gets $[CTA]_p/[M]_p > 5.2 \times 10^{-6} \text{ mol/L}$ and $[CTA]_p > 3.5 \times 10^{-6} \text{ mol/L}$. These conditions were met in the experiments carried out in this work. Under these circumstances, the termination rate reduces to

$$R_t \approx R_{CTA} = k_{tr,CTA}[CTA]_p \frac{\bar{n}N_p}{N_A} \quad (A-8)$$

The instantaneous number-average chain length can be calculated as a function of $[M]_p/[CTA]_p$ as follows:

$$\bar{X}_{ni} = k_p[M]_p/k_{tr,CTA}[CTA]_p \quad (A-9)$$

Furthermore, the polydispersity index (PI) is equal to 2 (Billmeyer):²³

$$PI = \bar{X}_{wi}/\bar{X}_{ni} = 2 \quad (A-10)$$

From these values the instantaneous MWD can be calculated by using the Schultz-Flory distribution (Billmeyer):²³

$$W(n) = \frac{Y(nY)^z \exp[-nY]}{\Gamma(z+1)} \quad (A-11)$$

$$z = \frac{1}{(\bar{X}_{wi}/\bar{X}_{ni} - 1)} \quad (A-12)$$

$$Y = \frac{z+1}{\bar{X}_{wi}} \quad (\text{A-13})$$

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

When the instantaneous PI is equal to 2, eq A-11 reduces to the most probable distribution:

$$W(n) = \frac{n}{\bar{X}_{ni}^2} \exp\left[-\frac{n}{\bar{X}_{ni}}\right] \quad (\text{A-14})$$

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

$$W_c(n) = \frac{1}{\bar{X}} \int_0^X W(n) dX \quad (\text{A-15})$$

where X is the overall gravimetric conversion.

Therefore, a polymer with a given desired MWD can be tailored by producing instantaneous fractions of polymer of polydispersity equal to 2 in such a way that the sum of these fractions provides the desired MWD.

Literature Cited

- (1) Storti, G.; Morbidelli, M. Open-loop Control of Polymerization Reactors. In *Polymer Dispersions. Principles and Applications*; Asua, J. M., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.
- (2) Saldívar, E.; Ray, W. H. Control of Semicontinuous Emulsion Copolymerization Reactors. *AIChE J.* **1997**, *43*, 2021.
- (3) Echevarría, A.; Leiza, J. R.; de la Cal, J. C.; Asua, J. M. Molecular Weight Distribution Control in Emulsion Polymerization. *AIChE J.* **1998**, *44*, 1667.
- (4) Regenass, W. Calorimetric Monitoring of Industrial Chemical Processes. *Thermochim. Acta* **1985**, *95*, 351.
- (5) Wu, R. S. H. Dynamic Thermal Analyzer for Monitoring Batch Processes. *Chem. Eng. Prog.* **1985**, *81*, 57.
- (6) MacGregor, J. F. On-line Reactor Energy Balances via Kalman Filtering. IFAC Conference on Instrumentation and Automation in Rubber, Plastics and Polymerization Industries, Akron, OH, 1986.
- (7) Moritz, H. U. Polymerization Calorimetry: A Powerful Tool for Reactor Control. *Polymer Reaction Engineering*; Reichert, K. H., Geiseler, W., Eds.; VCH-Verlag: Weinheim, Germany, 1989.
- (8) Schuler, H.; Schmidt, C. U. Calorimetric State Estimators for Chemical Reactor Diagnosis and Control: Review of Method and Applications. *Chem. Eng. Sci.* **1992**, *47*, 899.
- (9) Urretabizkaia, A.; Sudol, E. D.; El-Aasser, M. S.; Asua, J. M. Calorimetric Monitoring of Emulsion Copolymerization Reactions. *J. Polym. Sci., Part A* **1993**, *31*, 2907.
- (10) Sáenz de Buruaga, I.; Armitage, P. D.; Gugliotta, L. M.; Leiza, J. R.; Asua, J. M. On-line Calorimetric Control of Emulsion Polymerization Reactors. *Chem. Eng. Sci.* **1996**, *51*, 2781.
- (11) Sáenz de Buruaga, I.; Echevarría, A.; Armitage, P. D.; de la Cal, J. C.; Leiza, J. R.; Asua, J. M. On-line Control of Semibatch Emulsion Polymerization Reactors Based on Calorimetry. *AIChE J.* **1997**, *43*, 1069.
- (12) Sáenz de Buruaga, I.; Armitage, P. D.; Leiza, J. R.; Asua, J. M. Nonlinear Control for Maximum Production Rate of Latexes of Well-Defined Polymer Composition. *Ind. Eng. Chem. Res.* **1997**, *36*, 4243.
- (13) Sáenz de Buruaga, I.; Leiza, J. R.; Asua, J. M. Model-based Control of Emulsion Terpolymers Based on Calorimetric Measurements: Feasibility Study. *Polym. React. Eng.* **2000**, *8* (1), 39.
- (14) Fèveotte, G.; Barudio, I.; McKenna, T. F. Computed-Aided Parameter Estimation and On-line Monitoring of Emulsion and Solution Polymerization Reactors. *Comput. Chem. Eng.* **1996**, *20*, S581.
- (15) Fèveotte, G.; McKenna, T. F.; Othman, S.; Hammouri, H. Nonlinear tracking of glass transition temperatures for free radical emulsion copolymers. *Chem. Eng. Sci.* **1998**, *53*, 773.
- (16) Gugliotta, L. M.; Leiza, J. R.; Arotçarena, M.; Armitage, P. D.; Asua, J. M. Copolymer Composition Control in Unseeded Emulsion Polymerization Using Calorimetric Data. *Ind. Eng. Chem. Res.* **1995**, *34*, 3899.
- (17) Gugliotta, L. M.; Arotçarena, M.; Leiza, J. R.; Asua, J. M. Estimation of Conversion and Copolymer Composition in Semicontinuous Emulsion Polymerization Using Calorimetric Data. *Polymer* **1995**, *36*, 2019.
- (18) Hammouri, H.; McKenna, T. F.; Othman, S. Applications of Nonlinear Observers and Control: Improving Productivity and Control of Free Radical Solution Copolymerization. *Ind. Eng. Chem. Res.* **1999**, *38*, 4815.
- (19) Soroush, M. Nonlinear state-observer design with application to reactors. *Chem. Eng. Sci.* **1997**, *52*, 387.
- (20) Odian, G. *Principles of Polymerization*; Wiley: New York, 1991.
- (21) Brandrup, J., Immergut, E. M., Eds. *Polymer Handbook*; Wiley: New York, 1989.
- (22) Asua, J. M.; Adams, M. E.; Sudol, E. D. A New Approach for the Estimation of Kinetic Parameters in Emulsion Polymerization Systems. I. Homopolymerization under Zero-One Conditions. *J. Appl. Polym. Sci.* **1990**, *39*, 1183.
- (23) Billmeyer, F. W. *Textbook of Polymer Science*; Wiley: New York, 1962.
- (24) Buback, M.; García Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Ólag, F. J.; Shen, J.; Solomom, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnick, M. A. Consistent Values of Rate Parameters in Free Radical Polymerization Systems. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 293.
- (25) Gardon, J. L. Emulsion Polymerization. VI. Concentration of Monomers in Polymer Particles. *J. Polym. Sci., Part A-1* **1968**, *6*, 2859.
- (26) Varela, L. Emulsion Polymerization of Styrene Using an Automated Reaction Calorimeter. Doctoral Dissertation, Lehigh University, Bethlehem, PA, 1996.

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