

# Optimization of Batch Solution Polymerizations: Simulation Studies Using an Inhibitor and a Chain-Transfer Agent

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**ABSTRACT:** Multiobjective constrained optimizations are carried out to compute optimal operation policies for batch solution polymerizations of styrene. It is shown by simulations how specified values for conversion, average molecular weight, and polydispersity may be achieved through the proper manipulation of the temperature profile and the initial amounts of the initiator, chain-transfer agent (modifier), and inhibitor. The optimizations show that the use of inhibitors and/or modifiers is seldomly required, unless the process economics is taken into consideration or the high-molecular weight chain fraction of the final polymer resin is to be minimized. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1137–1152, 1998

**Key words:** polymerization; reactor; optimization; inhibitor; chain-transfer agent

## INTRODUCTION

The determination of optimal operation policies for batch polymerization systems has been extensively researched. Most of the works in this field involve the calculation of continuous and/or discrete profiles and initial conditions which drive the process to a desired state in minimum time. The objective of the optimization is frequently put into the form of a quadratic functional in which the polymer characteristics and end-use properties are expressed in terms of its average molecular weight and polydispersity. A survey on the advanced control of polymerization systems was presented recently by Embiruçu et al.<sup>1</sup>

Among the most frequent control variables, one may cite the reactor temperature profile and the initiator feed rate. Other common choices are the best temperature for an isothermal reaction,

monomer and solvent feed rates, and initial concentrations. Although the use of chain-transfer agents for control purposes has been a common practice for a long time, it has seldomly been used as a manipulated variable for reaction optimization. Kammel et al.<sup>2</sup> proposed that an inhibitor be used to control polymerization reactors in a situation of thermal runaway. They worked toward the project of a safety device and, based on fluid dynamic and kinetic considerations, showed that use of an inhibitor is adequate in such a situation. It seems that the only article which proposed the use of an inhibitor to optimize the operation of polymerization reactors is the one by Cavalcanti and Pinto.<sup>3</sup> In investigating plant data, these authors observed that optimum operation policies obtained by adding either inhibitors or chain-transfer agents to the reaction environment were very similar. As inhibitors are usually much cheaper than are modifiers, they suggested that using inhibitors to control polymer average molecular weights might be encouraged.

The dynamic optimization methods are usually based on the theory of variational calculus<sup>4–9</sup> or on sequential optimization and solution strate-

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gies.<sup>3,10-14</sup> Secchi et al.<sup>8</sup> showed that the gel effect and restrictions imposed on the system are of primary importance to the reactor performance analysis and that most of the times the control programs obtained with the use of Pontryagin's minimum principle are not easy to implement in an industrial environment. This observation is of utmost importance and encourages the use of sequential optimization and solution methods. In this work, the optimal control problem is converted into a standard nonlinear programming (NLP) problem which can be solved by a variety of methods already implemented and tested in standard computer routine libraries. This is accomplished through the discretization of the reactor temperature profile in the form of a piecewise linear function.

To investigate the use of inhibitors and chain-transfer agents (modifiers) as control variables, the batch styrene solution polymerization was chosen. It is shown here that specified polymer average molecular weight and polydispersity and monomer conversion may be always attained in minimum time by simply manipulating the temperature profile and initiator initial amount. However, inhibitors may be useful to increase the homogeneity of the polymer resin and reduce the high molecular weight chain fraction. Besides, it is also shown that modifiers are important when the process economics is taken into consideration.

## PROBLEM STATEMENT

The optimal control problem consists of determining the batch temperature profile and the amounts of initiator and inhibitor or initiator and modifier that should be added to the reactor at the beginning of the batch in order to drive the system to a desired state at  $t_f$  in minimum time. The optimization goals may be represented by an objective functional of  $\mathbf{x}(t_f)$  to be minimized such that

$$\begin{aligned} \mathcal{J}[\mathbf{x}(t_f)] = & \rho_1 \left( \frac{X(t_f) - X_d}{X_d} \right)^2 \\ & + \rho_2 \left( \frac{Mn(t_f) - Mn_d}{Mn_d} \right)^2 \\ & + \rho_3 \left( \frac{D(t_f) - D_d}{D_d} \right)^2 \quad (1) \end{aligned}$$

where each term represents the difference from desired values of conversion, number-average molecular weight, and polydispersity at  $t_f$ , respectively.

The process mathematical model described in the Appendix may be represented by a set of ordinary differential equations (ODEs) in vector form as

$$\begin{aligned} \dot{\mathbf{x}} &= f[\mathbf{x}(t), \mathbf{u}(t), \mathbf{p}] t \in [t_{k-1}, t_k], \\ k &= 1, 2, \dots, n \quad (2) \end{aligned}$$

$$\mathbf{x}_0 = \mathbf{x}(0)$$

where  $\mathbf{x} \in X \subset R^p$  is the vector of state variables;  $\dot{\mathbf{x}}$ , the time derivative of  $\mathbf{x}(t)$ ;  $\mathbf{u}(t) \in U \subset R^q$ , the continuous control variable to be optimized; and  $\mathbf{p} \in P \subset R^m$ , a vector of parameters which may also be subject to optimization. The system parameters and the control variables may have their values limited to the ranges

$$\begin{aligned} \mathbf{u}_i^L &\leq \mathbf{u}_i(t) \leq \mathbf{u}_i^U \quad i = 1, \dots, q \\ p_i^L &\leq p_i \leq p_i^U \quad i = 1, \dots, m \quad (3) \end{aligned}$$

Restrictions may be imposed on state variables by the use of penalty functions. The procedure to take these constraints into account will be exemplified later in this work.

In this work, the vector of continuous control variables  $\mathbf{u}(t)$  has only one element which is the reactor temperature. The vector of parameters to be optimized  $\mathbf{p}$  is composed of the initial amounts of initiator ( $I_0$ ) and inhibitor ( $W_0$ ) or initiator ( $I_0$ ) and modifier ( $Z_0$ ). To simplify the optimization problem, the amounts of solvent and monomer charged to the reactor are fixed. All the optimizations are based on a solution with a weight fraction of 70% of styrene in toluene, because a lower monomer/solvent proportion would not be interesting for an industrial application. The initial volume of the reaction medium is considered to be 1 L, so that the optimizations lead to results that may be tested in laboratory scale in the near future. Results may also be regarded as normalized values for industrial applications. The values chosen for the monomer/solvent proportion and reactor volume result in a batch with 5.86 mol of styrene and 2.84 mol of toluene.

To solve the problem, the time interval  $[0, t_f]$  is divided into  $n$  stages of equal length  $L$  and a search for a piecewise linear control policy  $\mathbf{u}(t)$  within each interval  $(t_{k-1}, t_k)$  by

$$u_i(t) = u_i(k-1) + \left( \frac{u_i(k) - u_i(k-1)}{L} \right) (t - t_{k-1}),$$

$$i = 1, \dots, q; \quad k = 1, \dots, n \quad (4)$$

where  $u(k)$  and  $u(k-1)$  are the values of  $u(t)$  at  $t = t_k$  and  $t = t_{k-1}$ , respectively. The piecewise linear approximation was chosen for  $u(t)$  because it can be easily implemented in practice.

By discretizing the continuous control variable, the optimal control problem is transformed into an NLP problem, where the decision variables are the initial amounts  $I_0$  and  $Z_0$  or  $I_0$  and  $W_0$  and the values of  $u(k)$ ,  $k = 1, 2, \dots, n$ . In fact, we could have  $k$  varying from 0 to  $n$ , but in order to resemble a situation encountered in industrial practice, where every batch must start at the same temperature,  $u(0)$  will not be optimized. This constraint is related to common operation procedures, as the initial temperature usually is the ambient temperature, due to discharging, cleaning, and charging of the reactors between successive batches. It is important to emphasize that ambient temperature here means the temperature which is used for discharging, cleaning, and charging of the reactors, which will be assumed to be equal to 42°C in our case.

Note that it is necessary to know  $t_f$  in advance and so the minimum final time is obtained by optimizing the system with different values of  $t_f$  and taking the one which leads to the smallest performance index. Two NLP methods were used, so that their results could be compared: the Powell's conjugate gradient method and the flexible polyhedron method.<sup>15</sup> As the results obtained were always very similar, references to the optimization method will be omitted. The numerical algorithm used is described below:

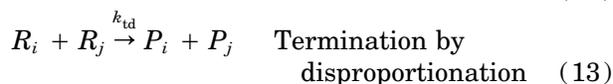
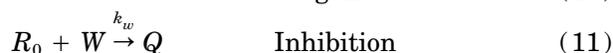
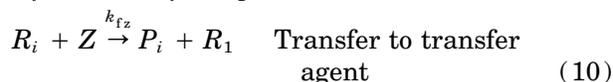
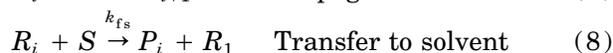
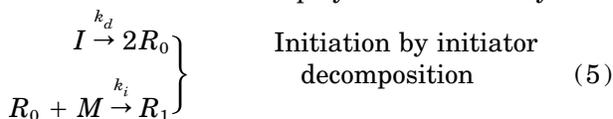
### Algorithm

1. Choose  $t_f$ .
2. Divide the batch time into  $n$  intervals of equal length  $L$ .
3. Choose an initial value for the decision variables.
4. Using the initial control policy, integrate the system from  $t_0$  to  $t_f$ .
5. Using the NLP method, choose new values for the decision variables in order to minimize  $J$  until convergence is attained.
6. If  $J$  is less than a specified tolerance  $\theta$ , then

reduce  $t_f$  until no further decrease in time is possible without making  $J > \theta$ ; otherwise, increase  $t_f$  until  $J \leq \theta$ .

### MODELING

The usual free-radical kinetic mechanism is used to describe the solution polymerization of styrene:

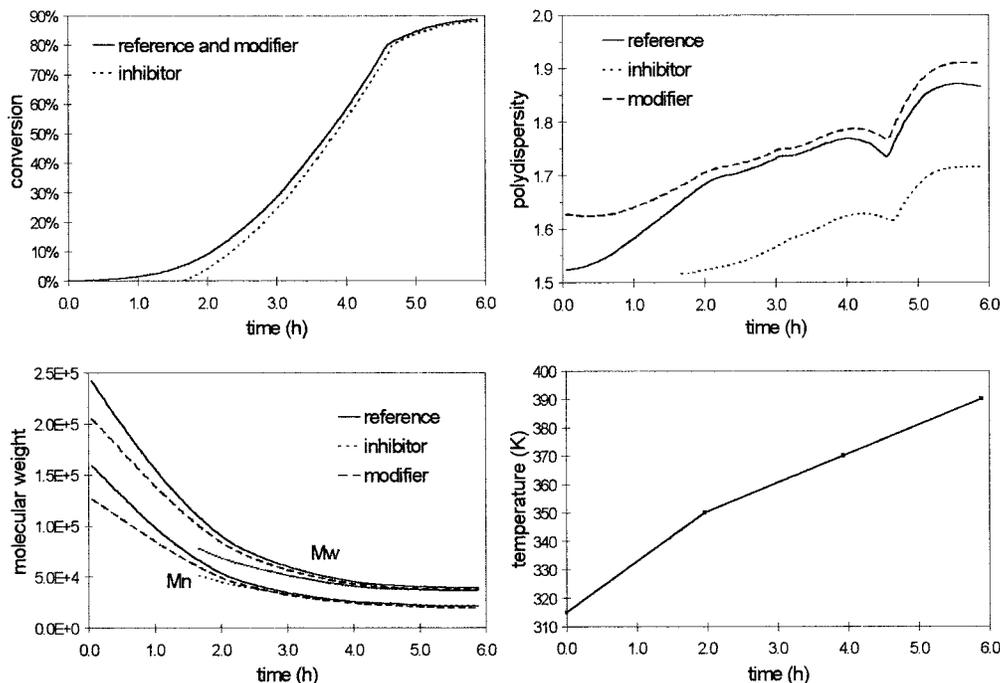


Svec et al.<sup>16</sup> noticed that at temperatures below 130°C termination occurs mostly by a combination of radicals, while disproportionation only becomes significant at higher temperatures.<sup>17</sup>

### Simulations

Results shown here were obtained when the batch duration was divided into three intervals, in order to keep the dimensionality of the NLP problem low and allow the implementation of optimum profiles at actual industrial operation. Dividing the batch time into a larger number of intervals leads to very similar results in shorter times. Besides, as the conclusions of this work are to be drawn from the comparison of the optimization results, it is more important that the discretization be the same in every optimization than having a larger number of intervals to approximate the continuous profile.

The lower and upper limits for the reactor temperature are fixed at 300 K (cooling water temperature) and 400 K (toluene normal boiling point), respectively. As already mentioned, the initial re-



**Figure 1** Effect of adding an inhibitor (0.001 mol) or a chain-transfer agent (0.5 mol); 0.035 moles of initiator were used.

action temperature is the same for all calculations and should be a little higher than the temperature of the monomer supply. This happens because batches are programmed in series, so that when one batch is beginning the reactor jacket, which is still hot due to the previous batch, exchanges some heat with the monomer being charged. Therefore, the initial batch temperature is considered to be 315 K. It is also important to say that initial guesses used for decision variables were always the same, unless stated otherwise. Initial guesses for temperature profiles were equal to 315 K, while initial guesses for initial additive concentrations were equal to zero.

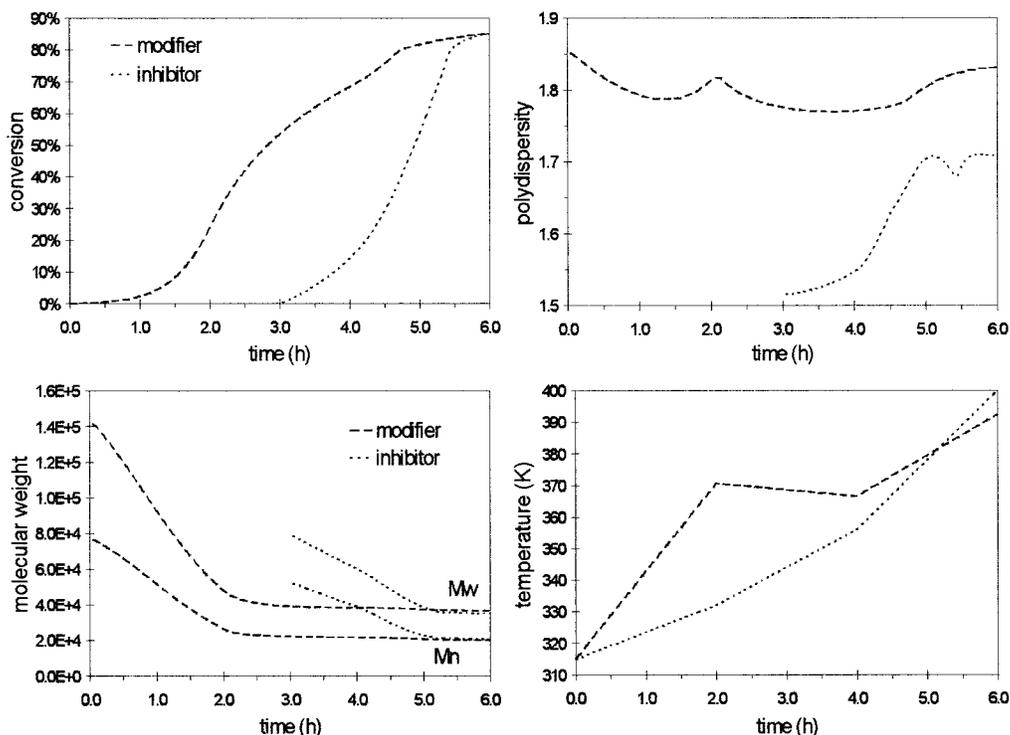
Three simulations were carried out to illustrate how the addition of an inhibitor or a chain-transfer agent affects the batch product. The first simulation did not consider the use of any of these additives and serves as a reference for the other two calculations, one with an inhibitor and another one with a modifier. Figure 1 shows the results obtained for both controlled and manipulated variables.

When the inhibitor is used, no reaction takes place in the beginning of the batch, avoiding the formation of the high molecular weight polymer. This stage is frequently called the induction period and results from the fact that an inhibition

reaction occurs much faster than does initiation. Thus, addition of an inhibitor may be interpreted as a way to start the reaction at higher temperatures. Although it reduces the polymerization duration, the use of an inhibitor has little effect on the conversion because reaction rates are lower at the early stages of the batch due to the lower temperature. As may be observed, the modifier does not influence conversion at all.

Both additives have the effect of lowering the average molecular weight, but while the modifier tends to increase the polydispersity, the inhibitor lowers this value, which is usually related to improved polymer properties. This is not surprising, as molecular weight distributions are controlled by transfer reactions in the first case (so that the instantaneous polydispersity of living free radicals is equal to 2) and by bimolecular termination in the second case (so that the instantaneous polydispersity of living free radicals is equal to 1.5). These simulations show, however, that both the inhibitor and the chain-transfer agent may be added to the reaction in order to control the properties of the polymer product, especially if lower average molecular weights are desired.

The molecular weight of most commercial polymers ranges from  $10^4$  to  $10^6$ . To investigate the use of an inhibitor and a modifier as a control



**Figure 2**  $M_{nd} = 20,000$ ,  $X_d = 85\%$ ,  $t_f = 6$  h. (Dotted line)  $W_0 = 0.0015$  mol and  $I_0 = 0.035$  mol; (dashed line)  $Z_0 = 2.41$  mol and  $I_0 = 0.0225$  mol.

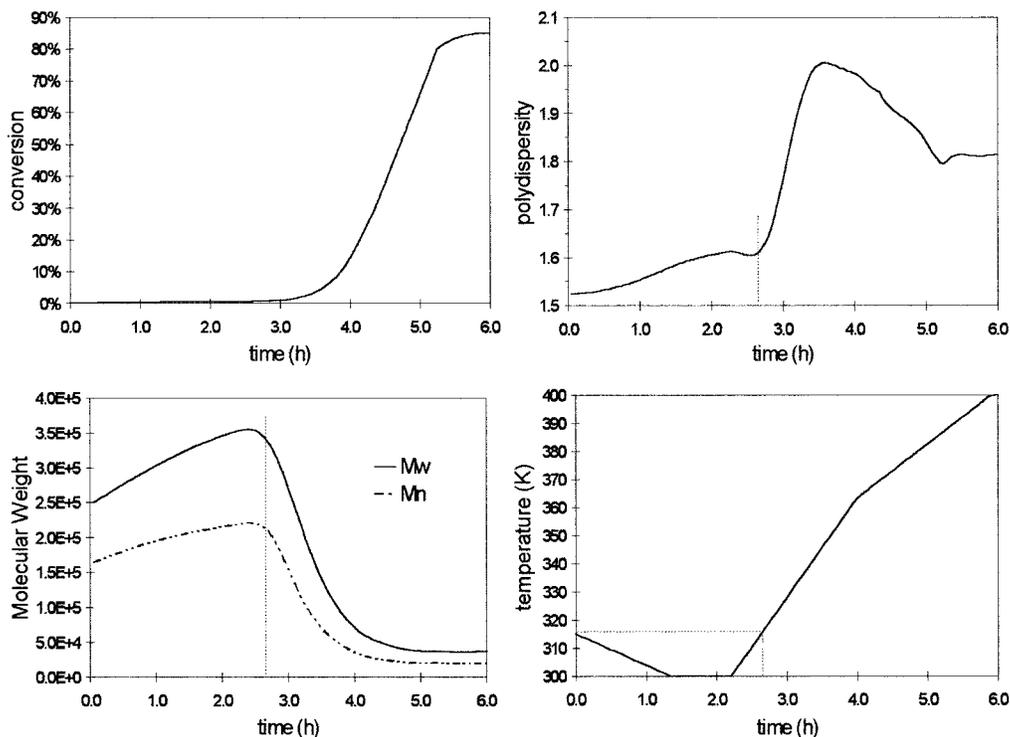
variable in the polymerization process, the desired values for  $M_n$  were kept close to the lower limit of the commercial molecular weight range. It is assumed that adding inhibitors or modifiers would not be beneficial if a higher molecular weight was to be obtained. At first, the production of a polymer with  $M_n = 20,000$  was considered, with a monomer conversion of 85% in minimum time. The first step of the proposed algorithm is choosing an arbitrary value for  $t_f$ , say 6 h. The optimization results for a 6-h batch are shown in Figure 2. Notice that it is possible to achieve the desired objective using either an inhibitor or a modifier.

Figure 3 shows the optimization results obtained at similar conditions with different initial values for the decision variables. In this case, the initial concentrations of the chain-transfer agent and inhibitor were forced to be equal to zero. Note that additives are not needed. Of course, this is not an optimal profile from a practical point of view, but the goals are attained. Note that until approximately 2.6 h had elapsed almost no monomer was converted. In fact, at this time, the temperature is the same as it was in the beginning of the batch and one can imagine a new simulation

similar to what we see at the right side of the dashed line. This is a clear indication that we can achieve our objective in less than 6 h.

The three simulations presented in Figures 2 and 3 represent local minima of the objective function. It may be concluded that many strategies may be adopted in order to achieve the objective in a 6-h batch. According to the optimization algorithm, the batch time should be gradually reduced until the proposed goals are not attainable. As shown in Figure 4, the batch time may be reduced to approximately 2.78 h. For this value of  $t_f$ , the optimizations with the modifier and with the inhibitor lead to the same values for  $I_0$  and to the same temperature profile. The calculated amounts of the initiator, inhibitor, and modifier are 0.035, 0, and 0 mol, respectively. The optimal values of  $W_0$  and  $Z_0$  show that optimum results are obtained when no additives are added to the system.

Up to this point, the polydispersity was left free, that is,  $\rho_3 = 0$  in eq. (1). If it were also necessary to control the polydispersity of the product, while keeping the other goals unchanged, the procedure described so far should be repeated with  $\rho_3 \neq 0$  and  $D_d$  equal to some predetermined



**Figure 3**  $M_{n_d} = 20,000$ ,  $X_d = 85\%$ ,  $t_f = 6$  h,  $I_0 = 0.035$  mol.

value. Figure 5 shows the results of the optimizations of a 6-h batch with  $\rho_3 = 1$  and  $D_d = 2.0$ , which is not much higher than the  $D(t_f)$  obtained in Figure 4 but different enough to allow the observation of the effect on the optimization results. In a real situation, if one should be interested in controlling  $D(t_f)$ , one would like this value to be as low as possible or to be in a higher range, usually from 6 to 10.

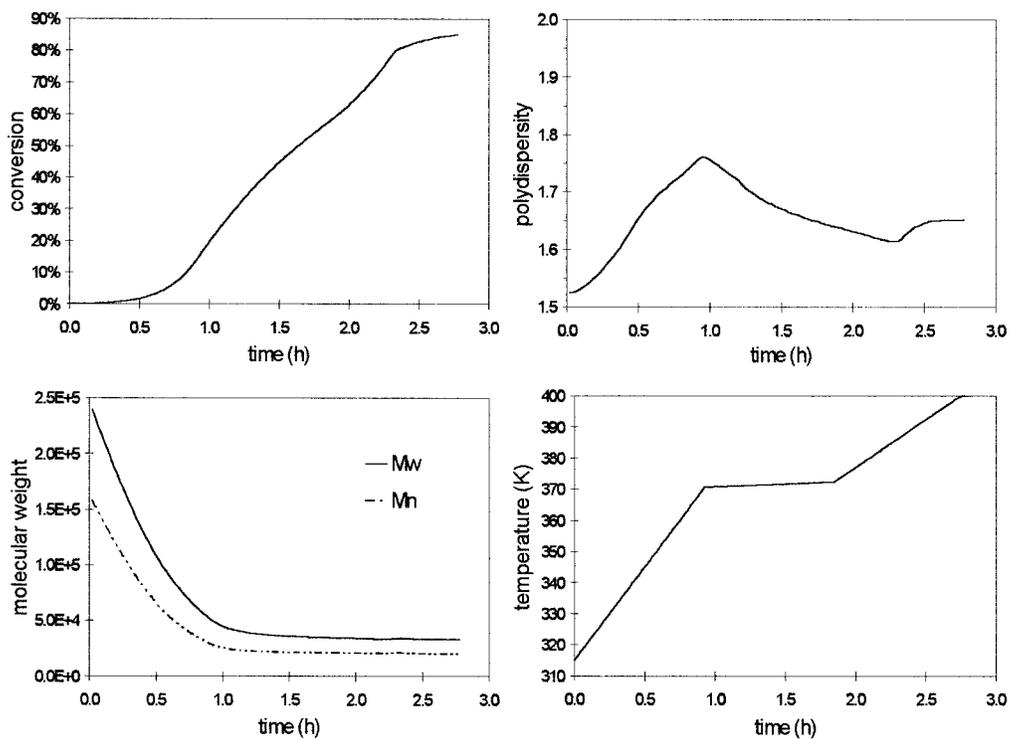
At this point, batch time should be reduced until the proposed values for  $M_{n_d}$ ,  $X_d$ , and  $D_d$  are not met. The optimized batch in minimum time is shown in Figure 6. The introduction of a desired value for  $D(t_f)$  into the objective function did not change the optimal amounts of the initiator, inhibitor, or modifier, which means that the new goal may be achieved by just manipulating the temperature profile and the reaction duration.

No reason for adding an inhibitor or a modifier to the reactor charge was detected so far. This may be related to the desired values used on the optimizations ( $M_{n_d}$ ,  $X_d$ , and  $D_d$ ) or to the proposed objectives. The additives could be useful for producing polymers with an even lower molecular weight. To test the influence of reducing the desired average molecular weight on the optimization results, the procedure was repeated with

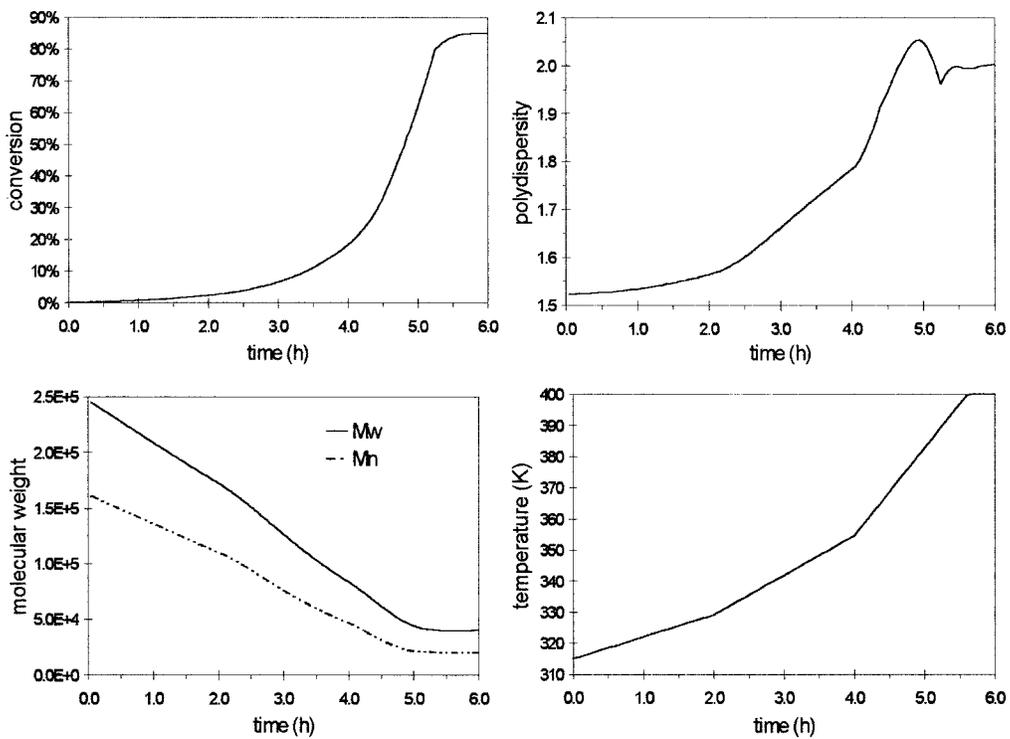
$M_{n_d} = 10,000$  and the same values for  $X_d$  and  $D_d$ . Figure 7 shows the time behavior of the optimized batch for this case and, again, it was not necessary to use any additive. Instead of requiring a modifier, the reduction in  $M_{n_d}$  demanded an amount of initiator greater than that used in the batch of Figure 6.

Similar results are obtained for any values of  $D$ . This is mainly due to two reasons: First, inhibitors lead to the appearance of an induction period, which tends to increase the batch time. Second, modifiers require lower temperatures for the same molecular weights to be attained. It may be concluded that one can drive the system to the desired values of average molecular weight, conversion, and polydispersity at  $t = t_f$  in minimum time simply by manipulating the reactor temperature and initial amount of initiator.

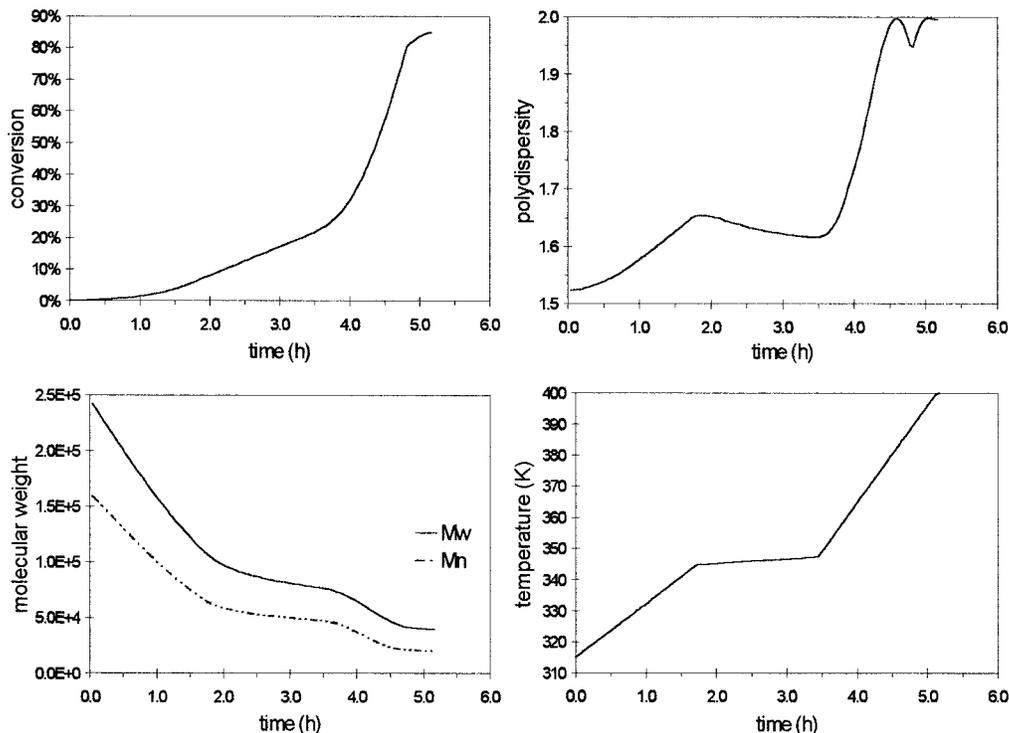
Occasionally, there may be constraints that should be posed on state variables throughout the duration of the batch rather than at  $t = t_f$ . One could be forced to prevent  $M_n$  to be greater than a fixed value in order to produce a more homogeneous product and to avoid posterior processing problems like fish-eye. To restrain the molecular weight to a maximum value, the



**Figure 4**  $M_{n_d} = 20,000$ ,  $X_d = 85\%$ ,  $D_d = 2.0$ ,  $I_0 = 0.035$  mol,  $t_f = 2.78$  h (minimum time).



**Figure 5**  $M_{n_d} = 20,000$ ,  $X_d = 85\%$ ,  $D_d = 2.0$ ,  $t_f = 6$  h,  $I_0 = 0.035$  mol.



**Figure 6**  $M_{nd} = 20,000$ ,  $X_d = 85\%$ ,  $D_d = 2.0$ ,  $I_0 = 0.035$  mol,  $t_f = 5.17$  h (minimum time).

objective function could be rewritten in the form of eq. (14) as to penalize those simulations in which  $M_n(t)$  assumes values greater than allowed:

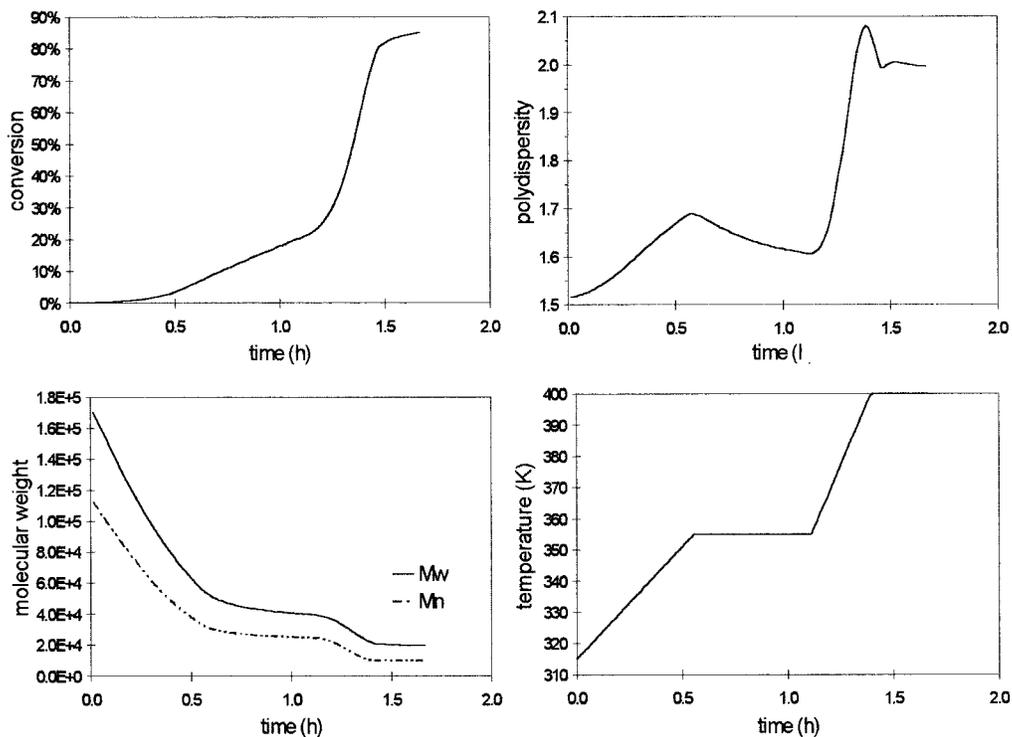
$$\begin{aligned} \mathcal{J}[t_f] = & \rho_1 \left( \frac{X(t_f) - X_d}{X_d} \right)^2 \\ & + \rho_2 \left( \frac{M_n(t_f) - M_{nd}}{M_{nd}} \right)^2 + \rho_3 \left( \frac{D(t_f) - D_d}{D_d} \right)^2 \\ & + \rho_4 \sum_{n=0}^k (M_n(t_n) - M_{n_{\max}}) \quad (14) \end{aligned}$$

where  $\rho_4 = 0$  if  $M_n(t) \leq M_{n_{\max}}$  or  $\rho_4 = 1$  if  $M_n(t) > M_{n_{\max}}$ .

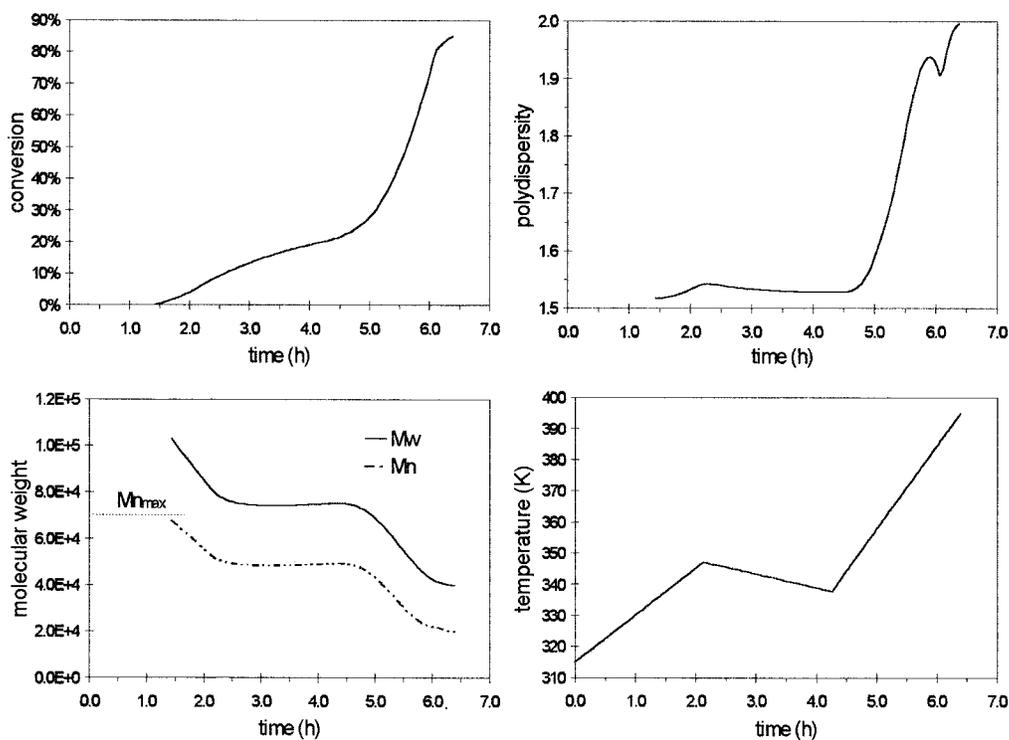
Inhibitors and chain-transfer agents are natural candidates to restrain  $M_n(t)$  to a maximum value. While the use of transfer agents for this particular purpose has been known for a long time, use of an inhibitor has never been reported in the literature. The transfer agent terminates the live molecules prematurely and thus dead polymer chains are shorter. The inhibitor halts the polymerization reaction during the period of

high molecular weight polymer production. As an example, optimizations with the same objectives of Figure 6 and an upper limit of 70,000 for  $M_n(t)$  were carried out with an inhibitor and with a modifier. The results of these calculations are depicted in Figures 8 and 9, respectively.

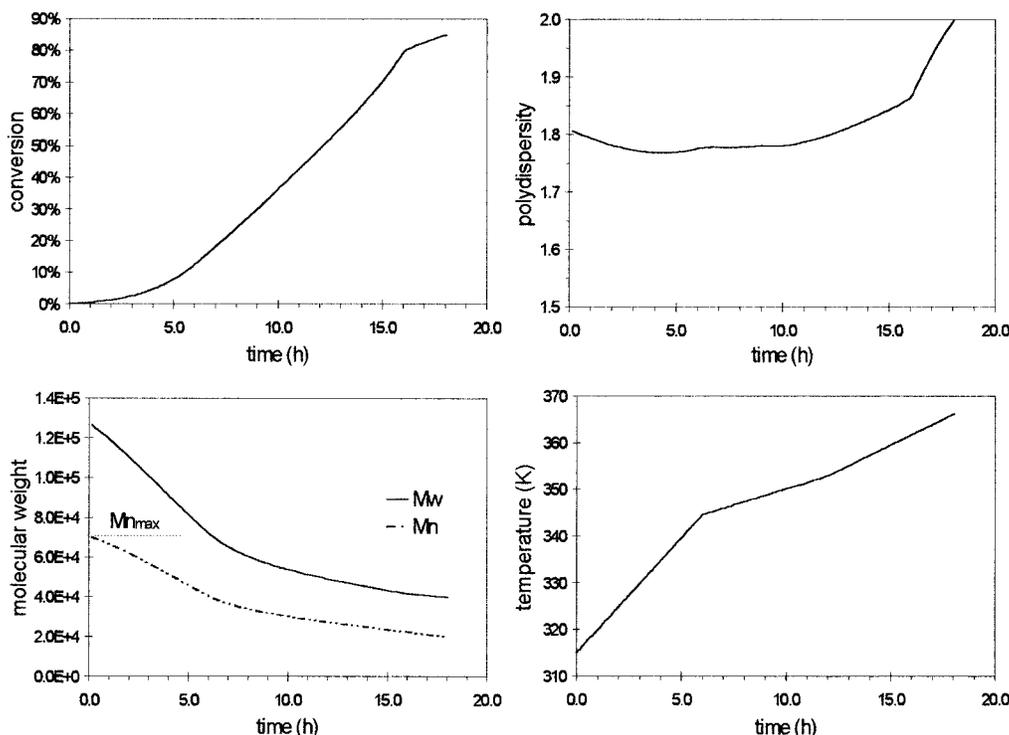
Figure 8 shows that  $M_n(t)$  may be kept lower than 70,000 by using an inhibitor. However, there were two important side effects: The minimum batch time was increased from 5.17 (Fig. 6) to 6.39 h and the amount of initiator increased from 0.035 to 0.036 mol. As a consequence, the batch in which molecular weight was restrained is more expensive than the one without this restriction. If the modifier is used instead of the inhibitor, Figure 9 shows that the duration of the reaction is increased by a much greater extent and that less initiator is needed. These results point to the inhibitor as the best choice for limiting  $M_n(t)$ . Although the use of the modifier requires less initiator, which is good from an economic point of view, batch time is extremely stretched, which leads to a great loss in productivity. Similar results are obtained whenever a maximum value of  $M_n$  is defined, indicating that inhibitors are of



**Figure 7**  $M_{n,d} = 10,000$ ,  $X_d = 85\%$ ,  $D_d = 2.0$ ,  $I_0 = 0.072$  mol, no inhibitor or modifier,  $t_f = 1.67$  h (minimum time).



**Figure 8** Use of an inhibitor to restrain  $M_n(t)$ .  $M_{n,d} = 20,000$ ,  $X_d = 85\%$ ,  $D_d = 2.0$ ,  $M_{n,max} = 70,000$ ,  $I_0 = 0.036$  mol,  $W_0 = 2.78 \times 10^{-4}$  mol,  $t_f = 6.39$  h (minimum time).



**Figure 9** Use of a chain-transfer agent to restrain  $M_n(t)$ .  $M_{n_d} = 20,000$ ,  $X_d = 85\%$ ,  $D_d = 2.0$ ,  $M_{n_{max}} = 70,000$ ,  $I_0 = 0.0261$  mol,  $Z_0 = 2.311$  mol,  $t_f = 18.05$  h (minimum time).

great value when high molecular weight chain fractions are to be avoided in batch polymerizations during temperature increase.

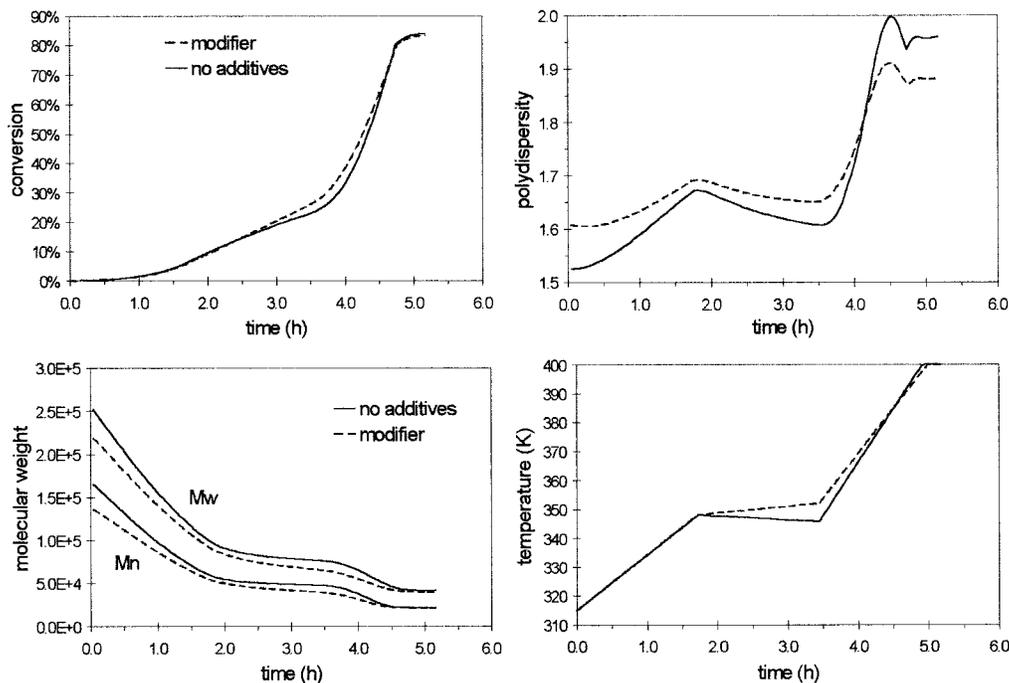
Due to its high costs, the total amount of the initiator used in the polymerization is another important issue in polymerization reactions. An ideal objective function would take into account not only the desired properties of the polymer but also the economical factors of the process. An economical character may be posed on the objective function by adding a term representing the “cost” of the initiator:

$$\begin{aligned} \mathcal{J}(t_f) = & \rho_1 \left( \frac{X(t_f) - X_d}{X_d} \right)^2 \\ & + \rho_2 \left( \frac{M_n(t_f) - M_{n_d}}{M_{n_d}} \right)^2 + \rho_3 \left( \frac{D(t_f) - D_d}{D_d} \right)^2 \\ & + \rho_4 \sum_{n=0}^k (M_n(t_n) - M_{n_{max}}) + \rho_5 I_0 \quad (15) \end{aligned}$$

where  $\rho_4 = 0$  if  $M_n(t) \leq M_{n_{max}}$  or  $\rho_4 = 1$  if  $M_n(t) > M_{n_{max}}$  and  $\rho_5$  would act as the molar price of the initiator.

Figure 10 presents the results of two optimizations carried out with this objective function in the same conditions of the one presented in Figure 6:  $t_f = 5.17$  h,  $M_{n_d} = 20,000$ , and  $X_d = 85\%$ , and  $D_d = 2.0$ . One of them considers the use of an inhibitor, and the other, a transfer agent. The former resulted in an initial amount  $W_0 = 0$ , which could be expected because the presence of the inhibitor requires that a little bit more of the initiator be used. The latter resulted in a lower value for the performance index, indicating that the use of a modifier in industrial plants may be attributed to economical reasons, as it allows the use of smaller amounts of the initiator, in spite of the longer reaction times.

By adding the cost of the initiator to the objective function, the nature of the optimization problem has been changed. Up to now, there has been a search for a temperature profile and the amount of the initiator and/or certain additives that would make  $J$  smaller than a very small tolerance, completely achieving the optimization goals, in minimum time. This has been done through inspection of  $J(t_f)$  for various values of  $t_f$ . From now on, there is a compromise between the physi-



**Figure 10** (Solid line)  $M_n = 21,350$ ,  $X = 84.0\%$ ,  $D = 1.96$ ,  $I_0 = 0.032$  mol; (dashed line)  $M_n = 20,200$ ,  $X = 83.4\%$ ,  $D = 1.88$ ,  $I_0 = 0.030$  mol,  $Z_0 = 0.374$  mol.

cal characteristics of the product and economical factors of the process and it has to be determined how much polymer properties may differ from the desired values. This tolerance together with the value of the performance criterion must be used to determine the minimum batch time. Notice that  $J$  will no longer be as close to 0 as desired because it is always necessary that some initiator be used and the product does not meet its specifications as tightly as before. Table I presents the simulation results obtained when  $\rho_5$  is equal to 1 for both cases presented in Figure 10.

It may be concluded that if a chain-transfer agent is used less initiator is necessary and that in both cases, with or without this modifier, the final state of the system is not as close to the desired values as it was with the other objective functions. So, the choice of using a modifier and the search for the shortest batch duration is condi-

tioned by the margin set for the product specification and by the cost of the initiator.

## CONCLUSIONS

It was shown through simulation studies that if the most important aspect of the batch optimization is to drive the system to specified values of average molecular weight and polydispersity of the polymer in minimum time then there is no need to use an inhibitor or a chain-transfer agent in the polymerization environment. It was also observed that both the inhibitor and the modifier may be used to restrain the average molecular weight to a maximum value but that the use of the inhibitor is preferable over the modifier. In this case, the amount of the inhibitor to be used has to be carefully calculated as it also affects the

**Table I** Optimal Simulation Results as Presented in Figure 10

Case	$Z_0$	$X$	$M_n$	$D$	$I_0$	$J$
Without chain-transfer agent		84.0%	21,350	1.96	0.0323	0.168
With chain-transfer agent	0.372	83.4%	21,202	1.88	0.0305	0.163

amount of initiator needed. The main reason for using a modifier in polymerizations is of economical nature, as it allows the reduction of the total amount of the initiator used.

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## NOMENCLATURE

$f$	initiator efficiency
$fr$	mass fraction of monomer in solution
$g$	empirical correlation for gel effect
$I$	initiator, also number of moles of
$I_0$	initial number of moles of initiator
$J$	performance criterion
$k_d$	kinetic constant for initiator decomposition
$k_{dm}$	kinetic constant for thermal initiation
$k_{fm}$	kinetic constant for chain transfer to monomer
$k_{fs}$	kinetic constant for chain transfer to solvent
$k_{fz}$	kinetic constant for chain transfer to modifier
$k_p$	kinetic constant for propagation
$k_t$	kinetic constant for termination within gel effect range
$k_{t0}$	kinetic constant for termination
$k_{tc}$	kinetic constant for termination by combination
$k_{td}$	kinetic constant for termination by disproportionation
$k_w$	kinetic constant for inhibition
$L$	length of each stage
$M$	monomer, also number of moles of
$M_n$	number-average molecular weight
$M_w$	weight-average molecular weight
$MW$	molecular weight of monomer
$n$	number of stages into which the total time is divided
$D$	polydispersity
$P_i$	dead polymer particle with length $i$ , also number of moles of
$R$	gas law constant
$R_0$	primary radical resulting from initiator decomposition, also number of moles of
$R_i$	live polymer particle with length $i$ , also number of moles of
$S$	solvent, also number of moles of
$T$	reactor temperature
$t_f$	final time
$t_k$	time at the end of the $n$ th stage

$T^l$	lower limit for $T$
$T^u$	upper limit for $T$
$V$	reaction volume
$V_{m0}$	monomer initial volume
$V_s$	solvent volume
$W$	inhibitor, also number of moles of
$W_0$	initial number of moles of inhibitor
$X$	monomer conversion
$\mathbf{x}$	vector of state variables
$\mathbf{x}_0$	initial values for $\mathbf{x}$
$Z$	chain-transfer agent, also number of moles of
$Z_0$	initial number of moles of modifier

## Greek Letters

$\alpha$	parameter of the gel effect correlation
$\beta$	parameter of the gel effect correlation
$\gamma$	parameter of the gel effect correlation
$\varepsilon$	volume contraction factor
$\mu_i$	dead polymer chain length distribution $i$ th moment
$\lambda_i$	live polymer chain length distribution $i$ th moment
$\rho_m$	monomer density
$\rho_s$	solvent density
$\rho_i$	weight of the $i$ th term of the performance criterion
$\theta$	tolerance for $J[\mathbf{x}(t_f)]$

## APPENDIX: MODEL EQUATIONS

The following assumptions were made in order to write the model equations:

- Reactions are irreversible.
- Kinetic constants do not depend on chain size.
- The material in the reactor is perfectly mixed.
- The quasi-steady-state assumption (QSSA) is valid for radicals.<sup>18</sup>
- Monomer consumption on the propagation phase is much larger than on other steps (long-chain hypothesis).
- The rate of formation of primary radicals by thermal decomposition of the monomer is not significant when compared to the rate of initiator decomposition.

For the free-radical polymerization mechanism, the material balances for the species taking part in the reaction, in moles, are

$$\frac{dI}{dt} = -k_d I \quad (\text{A.1})$$

$$\begin{aligned} \frac{dM}{dt} = & -3 \frac{k_{dm}}{V^2} M^3 - \frac{k_i}{V} MR_0 \\ & - \frac{(k_p + k_{fm})}{V} M \sum_{i=1}^{\infty} R_i \quad (\text{A.2}) \end{aligned}$$

$$\frac{dS}{dt} = -\frac{k_{fs}}{V} S \sum_{i=1}^{\infty} R_i \quad (\text{A.3})$$

$$\frac{dZ}{dt} = -\frac{k_{fz}}{V} Z \sum_{i=1}^{\infty} R_i \quad (\text{A.4})$$

$$\frac{dW}{dt} = -\frac{k_w}{V} W \sum_{i=0}^{\infty} R_i \quad (\text{A.5})$$

$$\frac{dR_0}{dt} = 2fk_d I - \frac{k_i}{V} MR_0 \quad (\text{A.6})$$

$$\begin{aligned} \frac{dR_1}{dt} = & 2 \frac{k_{dm}}{V^2} M^3 + \frac{k_i}{V} MR_0 - \frac{k_p}{V} MR_1 \\ & + \frac{(k_{fm}M + k_{fs}S + k_{fz}Z)}{V} \left( \sum_{i=1}^{\infty} R_i - R_1 \right) \\ & - \frac{(k_{tc} + k_{td})}{V} R_1 \sum_{j=1}^{\infty} R_j \quad (\text{A.7}) \end{aligned}$$

$$\begin{aligned} \frac{dR_i}{dt} = & \frac{k_p}{V} M(R_{i-1} - R_i) \\ & - \frac{(k_{fm}M + k_{fs}S + k_{fz}Z)}{V} R_i \\ & - \frac{(k_{tc} + k_{td})}{V} R_i \sum_{j=1}^{\infty} R_j, \quad i \geq 2 \quad (\text{A.8}) \end{aligned}$$

$$\begin{aligned} \frac{dP_i}{dt} = & \frac{(k_{fm}M + k_{fs}S + k_{fz}Z)}{V} R_i + \frac{k_{td}}{V} R_i \sum_{j=1}^{\infty} R_j \\ & + \frac{1}{2} \frac{k_{tc}}{V} \sum_{j=1}^{i-1} (R_j R_{i-j}), \quad i \geq 2 \quad (\text{A.9}) \end{aligned}$$

Assuming the QSSA for radical formation,<sup>18</sup>

$$\begin{aligned} \frac{dR_0}{dt} \cong 0 = & 2fk_d I \frac{k_i}{V} MR_0 \\ \text{or } \frac{k}{V} MR_0 = & 2fk_d I \quad (\text{A.10}) \end{aligned}$$

According to Ray,<sup>18</sup> the  $k$ th moments of the live and dead polymer chain-length distributions may be written as

$$\lambda_k = \sum_{i=1}^{\infty} i^k R_i \quad (\text{A.11})$$

$k$ th moment of the live polymer

$$\mu_k = \sum_{i=1}^{\infty} i^k P_i \quad (\text{A.12})$$

$k$ th moment of the dead polymer

deriving the equations for the moments of the live polymer distribution and applying eqs. (A.10)–(A.12), we have

$$\begin{aligned} \frac{d\lambda_0}{dt} = & \sum_1^{\infty} \frac{dR_i}{dt} \\ = & 2 \left( \frac{k_{dm}}{V^2} M^3 + fk_d I \right) - \frac{(k_{tc} + k_{td})}{V} \lambda_0^2 \quad (\text{A.13}) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_1}{dt} = & \sum_{i=1}^{\infty} i \frac{dR_i}{dt} = 2 \left( \frac{k_{dm}}{V^2} M^3 + fk_d I \right) \\ & + \frac{k_p}{V} M \lambda_0 - \frac{(k_{tc} + k_{td})}{V} \lambda_0 \lambda_1 \\ & + \frac{(k_{fm}M + k_{fs}S + k_{fz}Z)}{V} (\lambda_0 - \lambda_1) \quad (\text{A.14}) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_2}{dt} = & \sum_{i=1}^{\infty} i^2 \frac{dR_i}{dt} = 2 \left( \frac{k_{dm}}{V^2} M^3 + fk_d I \right) \\ & + \frac{k_p}{V} M (\lambda_0 + 2\lambda_1) - \frac{(k_{tc} + k_{td})}{V} \lambda_0 \lambda_2 \\ & + \frac{(k_{fm}M + k_{fs}S + k_{fz}Z)}{V} (\lambda_0 - \lambda_2) \quad (\text{A.15}) \end{aligned}$$

From the QSSA for radical formation, we have

$$\frac{d\lambda_0}{dt} \cong 0, \quad \frac{d\lambda_1}{dt} \cong 0, \quad \frac{d\lambda_2}{dt} \cong 0$$

and eqs. (A.13)–(A.15) become

$$\lambda_0 = \left( \frac{(k_{dm}M^3/V + fk_d IV)}{k_t} \right)^{1/2} \quad (\text{A.16})$$

$$\lambda_1 = \lambda_0 + \frac{k_p M \lambda_0}{k_{fm}M + k_{fs}S + k_{fz}Z + k_t \lambda_0} \quad (\text{A.17})$$

$$\lambda_2 = \lambda_0 + \frac{k_p M \lambda_0 + 2k_p M \lambda_1}{k_{fm}M + k_{fs}S + k_{fz}Z + k_t \lambda_0} \quad (\text{A.18})$$

with  $k_t = k_{tc} + k_{td}$ .

Multiplying eq. (A.9) by  $i^k$  and summing for  $i = 1$  to  $\infty$ , we have

$$\begin{aligned} \sum_{i=1}^{\infty} i^k \frac{dP_i}{dt} &= \frac{d\mu_k}{dt} = \frac{(k_{\text{fm}}M + k_{\text{fs}}S + k_{\text{tz}}Z)}{V} \\ &\quad \sum_{i=1}^{\infty} i^k R_i + \frac{k_{\text{td}}}{V} \sum_{i=1}^{\infty} i^k R_i \sum_{j=1}^{\infty} R_j \\ &\quad + \frac{1}{2} \frac{k_{\text{tc}}}{V} \sum_{i=1}^{\infty} \left( i^k \sum_{j=1}^{i-1} (R_j R_{i-j}) \right) \end{aligned} \quad (\text{A.19})$$

The final term in eq. (A.19) may be evaluated for  $k = 1, 2, 3$  as

$$k = 0 \quad \sum_{i=1}^{\infty} \left( \sum_{j=1}^{i-1} (R_j R_{i-j}) \right) = \lambda_0 \quad (\text{A.20})$$

$$k = 1 \quad \sum_{i=1}^{\infty} \left( i \sum_{j=1}^{i-1} (R_j R_{i-j}) \right) = 2(\lambda_0 \lambda_1) \quad (\text{A.21})$$

$$k = 2 \quad \sum_{i=1}^{\infty} \left( i^2 \sum_{j=1}^{i-1} (R_j R_{i-j}) \right) = 2(\lambda_0 \lambda_2 + \lambda_1^2) \quad (\text{A.22})$$

Thus, we have

$$\begin{aligned} \frac{d\mu_0}{dt} &= \frac{k_{\text{fm}}M + k_{\text{fs}}S + k_{\text{tz}}Z}{V} \lambda_0 \\ &\quad + \frac{k_{\text{td}}}{V} \lambda_0^2 + \frac{1}{2} \frac{k_{\text{tc}}}{V} \lambda_0^2 \end{aligned} \quad (\text{A.23})$$

$$\begin{aligned} \frac{d\mu_1}{dt} &= \frac{k_{\text{fm}}M + k_{\text{fs}}S + k_{\text{tz}}Z}{V} \lambda_1 \\ &\quad + \frac{k_{\text{tc}} + k_{\text{td}}}{V} \lambda_0 \lambda_1 \end{aligned} \quad (\text{A.24})$$

$$\begin{aligned} \frac{d\mu_2}{dt} &= \frac{k_{\text{fm}}M + k_{\text{fs}}S + k_{\text{tz}}Z}{V} \lambda_2 \\ &\quad + \frac{k_{\text{tc}} + k_{\text{td}}}{V} \lambda_0 \lambda_2 + \frac{k_{\text{tc}}}{V} \lambda_1^2 \end{aligned} \quad (\text{A.25})$$

From the long-chain hypothesis, eq. (A.2) becomes

$$\frac{dM}{dt} = - \frac{(k_p + k_{\text{fm}})}{V} M \lambda_0 \quad (\text{A.26})$$

As conversion may be defined as

$$X = \frac{(M_0 - M)}{M_0} \quad (\text{A.27})$$

we may substitute eq. (A.26) by

$$\frac{dX}{dt} = \frac{(k_p + k_{\text{fm}})}{V} (1 - X) \lambda_0 \quad (\text{A.28})$$

and let the number of moles of monomer be calculated from eq. (A.27):  $M = M_0(1 - X)$ . Equations (A.3) and (A.4) become

$$\frac{dS}{dt} = - \frac{k_{\text{fs}}}{V} S \lambda_0 \quad (\text{A.29})$$

$$\frac{dZ}{dt} = - \frac{k_{\text{tz}}}{V} Z \lambda_0 \quad (\text{A.30})$$

Another simplification may be used if we notice that the number of moles of monomer consumed must be equal to the amount of this species present in live and dead polymer molecules so that

$$M_0 - M = \mu_1 + \lambda_1 \quad (\text{A.31})$$

and considering  $\mu_1 \gg \lambda_1$ , we may substitute eq. (A.24) by

$$\mu_1 = M_0 - M = M_0 X \quad (\text{A.32})$$

As we wish to control the average molecular weight and polydispersity of the product, we have to relate these properties to the moments of the polymer chain length distribution. This can be obtained by the average definitions

$$\begin{aligned} M_n &= MW \frac{\mu_1}{\mu_0}, \quad M_w = MW \frac{\mu_2}{\mu_1}, \\ \text{and } D &= \frac{M_w}{M_n} = \frac{\mu_0 \mu_2}{\mu_1^2} \end{aligned} \quad (\text{A.33})$$

The inhibition reaction occurs at much faster rates than does the initiation reaction; therefore, the presence of an inhibitor in the reactor results in an induction period during which no polymerization takes place. In this work, we considered that all radicals react with the inhibitor instead of propagating and thus the rate of consumption of the inhibitor and the formation of primary radicals are the same. Therefore, instead of eq. (A.5), the rate of consumption of the inhibitor will be described by

**Table II Kinetic Parameters**

Parameter	Unit	Ref.
$k_d = 7.12 \cdot 10^{13} \cdot \exp(-29589/RT)$	$s^{-1}$	21
$k_{dm} = 2.190 \cdot 10^5 \cdot \exp(-27440/RT)$	$L^2/mol^2 s$	22
$k_p = 1.051 \cdot 10^7 \cdot \exp(-7060/RT)$	$L/mol s$	5
$k_{t0} = 1.255 \cdot 10^9 \cdot \exp(-1680/RT)$	$L/mol s$	5
$K_{fm} = 2.31 \cdot 10^6 \cdot \exp(-12670/RT)$	$L/mol s$	5
$k_{fs} = 5.92 \cdot 10^8 \cdot \exp(-17210/RT)$	$L/mol s$	5
$k_{tz} = k_p/500$	$L/mol s$	
$e = 0.1506 + 4.436 \cdot 10^{-4} \cdot \exp(T - 273.15)$		23
$r_m = (0.8075 + 10^{-3} T)^{-1}$	$g/mL$	24
$\rho_s = (1.047 + 4.9 \cdot 10^{-4} T)^{-1}$	$g/mL$	24
$f = 0.72$		25

$$\frac{dW}{dt} = -2fk_dI \quad (\text{A.34})$$

So, if we solve the set of differential algebraic equations (DAE) composed by eqs. (A.1), (A.16)–(A.18), (A.23), (A.25), (A.27)–(A.30), (A.32), and (A.34), we determine the time behavior of the reactor and using eqs. (A.33) we can calculate the value of the performance criterion at the end of the batch  $J[\mathbf{x}(t_f)]$ . To solve this system, we used the code DASSL written by Petzold.<sup>19</sup>

### Gel Effect

The gel or Trommsdorf effect was considered by using an empirical expression valid for conversions ranging from 30 to 80%:

$$g = \left(\frac{k_t}{k_{t0}}\right)^{0.5} = \phi + \beta X + \gamma X^2 \quad \text{with} \quad \begin{aligned} \phi &= 0.5093 \\ \beta &= 2.4645 \\ \gamma &= -3.7473 \end{aligned} \quad (\text{A.35})$$

These values for the parameters were reported by Chen and Huang<sup>20</sup> for the solution polymerization of styrene in toluene with a mass ratio styrene/toluene of 3/1 (mass fraction of 75%) and may be corrected according to the amount of monomer in solution as shown in eq. (A.36):

$$\begin{aligned} \beta &= 2.4645 \frac{4}{3} fr \\ \gamma &= -3.7473 \left(\frac{4}{3}\right)^2 fr^2 \end{aligned} \quad (\text{A.36})$$

where  $fr$  is the monomer/solvent percent mass fraction.

The volume in the reactor was considered to vary linearly with conversion due to the change in the reaction medium density during the course of polymerization. So, the total reaction volume may be expressed as

$$V = V_s + V_{m0}(1 - \varepsilon X) \quad (\text{A.37})$$

Table II presents the kinetic parameters used in this work, as compiled by Fontoura.<sup>9</sup>

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