

Multiobjective Dynamic Optimization of Batch Free Radical Polymerization Process Catalyzed by Mixed Initiator Systems

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SYNOPSIS

The optimal control policies for batch free radical polymerization of styrene catalyzed by a binary mixture of monofunctional initiators have been determined using a multiobjective dynamic optimization technique. The process objectives considered in the optimization include monomer conversion, polymer molecular weight, initiator residue level, and total reaction time. It is illustrated through model simulations and experiments that the performance of the batch polymerization process can be improved significantly through the use of optimal initiator mixture and polymerization temperature programming. This paper also illustrates how the multiobjective optimization technique can be used effectively to solve complex polymerization reactor optimization problems with detailed reaction models.

INTRODUCTION

High molecular weight resins containing residual monomers have certain undesirable end-use properties such as shrinkage at high temperature, low resistance to heat distortion, and discoloration due to oxidation of leftover monomers.¹ Similarly, initiator residues in the final polymer product may decompose during the polymer processing stage, leading to the discoloration of the polymers. Any attempts to purify the polymers by removing unreacted monomers and undecomposed initiators from the polymers after the reaction will be very costly. Therefore, it would be highly desirable to minimize the concentrations of monomers and initiator residues in the reaction stage.

In batch polymerization processes, reducing the batch reaction time and obtaining the desired polymer properties is also required. Although one can use both high-temperature and high-initiator concentration to achieve a near-complete monomer

conversion in a short reaction time, it is often difficult to achieve both high monomer conversion and desired high polymer molecular weight simultaneously by doing so. It has been well known that merely increasing the amount of initiator for rapid polymerization results in lower polymer molecular weight, gelation, and discoloration of polymer product due to the subsequent decomposition of a large amount of initiator residues. Similar problems are encountered when higher operating temperature is employed to drive the polymerization to its full extent in a short reaction time: The polymer molecular weight decreases with an increase in reaction temperature.

Therefore, it is desirable to select the proper initiator type and its concentration and polymerization temperature profile to obtain a high-quality polymer. It is known that many industrial polymerization processes employ a mixture of two or more organic free radical initiators to improve the polymer yield and product properties. The idea of using mixed initiator systems with different thermal reactivities to produce high molecular weight polystyrene with better heat shrinkage properties was introduced some years ago by D'alelio.² Doak³ reported the method of producing commercial-grade polystyrenes in a considerably reduced reaction time by increasing

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the rate of polymerization and concomitantly controlling the concentration of free radicals at all times during the polymerization. It was claimed that the concentration of free radicals can be controlled by selecting the proper composition of the initiator mixture having different thermal stabilities. Kamath and Harpell⁴ suggested a similar approach of using mixed initiators and progressively increasing the reaction temperature to produce commercial-grade high molecular weight polystyrene by suspension and bulk polymerization. They reported that polystyrenes of better quality were obtained with shorter reaction times than with conventional single-initiator systems. The use of mixed-initiator systems for free radical polymerization processes is also reported in several Japanese patents.⁵⁻⁸ In Ref. 5, the use of mixed-initiator systems at two different temperature levels is reported to produce a copolymer of methyl methacrylate (MMA) and methacrylic acid. It has been claimed that the copolymer with improved heat distortion temperature is obtained by such a method. In Ref. 6, a mixture of three initiators is used for suspension polymerization of styrene with a stepwise temperature programming ranging from 100 to 135°C. Such a method yielded polystyrene with better intrinsic viscosity, less residual monomer content, and improved bending strength, impact strength, and heat distortion temperature. Yoshida et al.⁷ have reported the use of a mixture of benzoyl peroxide (BPO) and *tert*-butyl perbenzoate (TBPB) with a multistage temperature (90–120°C) to produce polystyrene granules with narrow pellet size distribution. Fuku et al.⁸ reported the process of producing polystyrene with high molecular weight, good flow properties, and improved mechanical strength using the mixture of initiators and a two-stage temperature program.

The nonisothermal polymerization techniques described in many of the aforementioned studies are based on the experience of those skilled in the art. In this study, we shall investigate the optimal control strategies for the batch styrene polymerization process with a binary mixture of monofunctional initiators and illustrate the potential advantages of using such a system for various operating conditions.

POLYMERIZATION WITH MIXED-INITIATOR SYSTEMS

The nature and the concentration of the initiators and the reaction temperature conditions under which the polymerization reaction is carried out af-

fects the mechanical, rheological, and physical properties of the final polymer product. Karaenev et al.⁹ reported an experimental study describing the influence of reaction temperature and mixed initiators on the styrene polymerization and the resulting properties of the polymer. They studied the suspension polymerization of styrene initiated by BPO and TBPB, and a combination of BPO, TBPB, and 2,5-dimethyl-2,5 ditertiary butylperoxy hexane (DBH). Their experimental results indicate that polystyrene with higher fluidity and impact strength is obtained with a reduction in batch time. Recently, Chen et al.¹⁰ reported a study of free radical polymerization with a mixed-initiator system to control the polymerization at a prescribed rate. They derived equations to determine the type and the concentration of the initiators to maintain a constant polymerization rate. For binary-initiator systems, they determined several sets of initiator pairs and their concentrations for polymerization of MMA at the given rates. However, their work was limited to isothermal reactor operations only.

To take advantage of a mixed-initiator system, developing a methodology for optimally selecting the composition and concentration of the initiators and the reaction temperature profiles is required. This task involves the development of a kinetics model for polymerization with mixed initiators and the determination of the optimal initial reaction conditions and optimal temperature program to achieve the desired objectives.

During the past years, many papers have been published on the kinetics and modeling of free radical vinyl polymerization processes.¹¹⁻¹⁵ In developing a kinetics model for styrene polymerization under industrial process conditions, it is important to incorporate key chemical and physical factors such as thermal initiation, volume contraction, and gel effect into the model. It is also important, particularly for high conversion styrene polymerization, to consider the effects associated with initiator and free radical concentrations (e.g., induced decomposition of initiators and primary radical termination) on the monomer conversion and polymer molecular weight. There is a dearth of literature that have considered all the factors mentioned above in developing the models for the polymerization of styrene and other vinyl monomers. Many works have also been reported in the literature regarding the optimization of batch polymerization of vinyl monomers using a single initiator¹⁶⁻²¹; however, most of them deal with the polymerization at relatively low temperature and low monomer conversion with simplified models.

With rapid progress in computer technology and its application in engineering design, there is an increasing need to use more accurate, but perhaps more complex, reaction models for the design of optimal polymerization strategies. When mixed-initiator systems are used in free radical homopolymerization, the reactor operator will have an additional degree of freedom in choosing optimal reactor operating variables. Then, one must decide (i) the best choice of two initiators having different thermal decomposition rates, (ii) the best total initial concentration of initiators and their compositions, (iii) the optimal temperature profiles to achieve process goals such as minimum residual monomer concentration, desired polymer molecular weight, and molecular weight distribution (MWD), minimum concentration of undecomposed initiator species, etc. Evidently, the classical process optimization techniques such as the minimum principle or the control vector parameterization method will be ineffective in handling such complex practical problems. In this paper, we shall use a multiobjective dynamic optimization technique to develop optimal reactor control policies for the batch styrene polymerization process catalyzed by mixed initiator systems. The kinetics model we shall employ in this study encompasses most of the reported features of the high-conversion bulk polymerization of styrene. The process objectives to be considered in this work will be chosen in such a way that they are very similar to the objectives of many industrial polystyrene processes. In what follows, the details of the kinetics model, the optimization procedure, and some case studies will be presented.

MODELING OF POLYMERIZATION KINETICS

Low-conversion free radical polymerization of styrene can be adequately described by a simple kinetics scheme including initiation, propagation, chain transfer, and chain termination steps. However, extensive works of many researchers^{12,14,22-25} indicate that the simple kinetics scheme is not satisfactory in describing the high-conversion and high-temperature polymerization of styrene. One of the important factors to be considered in modeling high-conversion free radical polymerization is the gel effect or diffusion-controlled termination, which will have an enormous impact on the progress of polymerization and resulting polymer properties. This phenomenon has been studied extensively by many workers in the past.^{24,26,27} In our modeling, we will

use a semiempirical gel effect correlation proposed by Friis and Hamielec.²⁶ Besides this autoacceleration phenomenon, induced decomposition (chain transfer to initiators) and primary radical termination are also important in high-conversion free radical styrene polymerization.²⁸⁻³¹

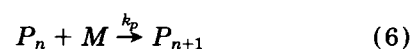
In our study, benzoyl peroxide (BPO) and *t*-butyl perbenzoate (TBPB) are used. These initiators have been reported to show significant induced decomposition at high monomer conversion. Many researchers have also studied the importance of the primary radical termination in styrene polymerization.^{23,31-34} Again, it can be shown that for nonisothermal polymerization of styrene with mixed initiators, the primary radical termination becomes more important at the final stage of polymerization. The overall effect of primary radical termination is to decrease the final monomer conversion and to lower the polymer molecular weight. Berger et al.³⁰ proved the occurrence of primary radical termination in styrene polymerization with BPO using the ¹⁴C-labeled BPO. In our modeling, we have considered the effects of both induced decomposition and primary radical termination. The chain transfer to monomer is also included in the kinetics scheme. In our simulation, the polymerization temperatures used are in the range of 90–140°C; hence, the thermal initiation of styrene is also included in the kinetics scheme.³⁵ Finally, the change in the density of the reaction mass is also considered in the kinetics modeling.

Based upon the foregoing discussion, the following kinetics is used in this study:

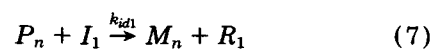
Initiation:



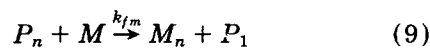
Propagation:



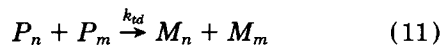
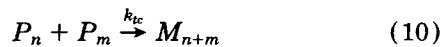
Induced Decomposition of Initiator:



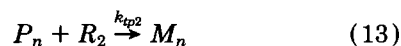
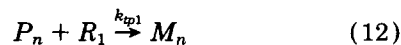
Chain Transfer to Monomer:



Chain Termination:



Primary Radical Termination:



In styrene polymerization, combination termination is the predominant mechanism of chain termination. With the kinetics scheme proposed above, we can derive the following modeling equations for the batch polymerization of styrene with mixed initiators:

$$\frac{dM}{dt} = -k_p(1 + C_m)PM \left[\frac{M_0 + \epsilon M}{M_0} \right] \quad (14)$$

$$\frac{DI_1}{dt} = -(k_{d1}I_1 + k_{id1}P) - \frac{\epsilon I_1 M}{M_0} P k_p(1 + C_m) \quad (15)$$

$$\frac{DI_2}{dt} = -(k_{d2}I_2 + k_{id2}P) - \frac{\epsilon I_2 M}{M_0} P k_p(1 + C_m) \quad (16)$$

where M is the monomer concentration; I_1 and I_2 , the initiator concentrations; ϵ , the volume contraction factor; C_m , the characteristic constant for chain transfer to monomer ($\triangleq k_{fm}/k_p$); and P , the total concentration of live polymers. The molecular weight averages and the polydispersity are computed using the method of moments. After applying the quasi steady-state approximation for the live polymer species and the radical species, we can derive

the following equations for the dead polymer moments:

$$\frac{d\lambda_0^d}{dt} = \left(\frac{k_t}{2} P + k_p\beta_1 + k_p\beta_2 + k_{fm}M + k_{id1}I_1 + k_{id2}I_2 \right) P - k_p(1 + C_m)P \frac{\epsilon M}{M_0} \lambda_0^d \quad (17)$$

$$\frac{d\lambda_1^d}{dt} = (k_t P + k_p\beta_1 + k_p\beta_2 + k_{fm}M + k_{id1}I_1 + k_{id2}I_2) \lambda_1^d - k_p(1 + C_m)P \frac{\epsilon M}{M_0} \lambda_1^d \quad (18)$$

$$\frac{d\lambda_2^d}{dt} = (k_t P + k_p\beta_1 + k_p\beta_2 + k_{fm}M + k_{id1}I_1 + k_{id2}I_2) \lambda_2^d + k_t \lambda_1^d - k_p(1 + C_m)P \frac{\epsilon M}{M_0} \lambda_2^d \quad (19)$$

The k -th moment of dead polymers is defined as

$$\lambda_k^d = \sum_{n=2}^{\infty} n^k M_n \quad (20)$$

where

$$\beta_1 = R_1 \frac{k_{tp1}}{k_p} = \frac{(2f_1 k_{d1} I_1 + k_{id1} I_1 P) K_1}{M + K_1 k_p P} \quad (21)$$

$$\beta_2 = R_2 \frac{k_{tp2}}{k_p} = \frac{(2f_2 k_{d2} I_2 + k_{id2} I_2 P) K_2}{M + K_2 k_p P} \quad (22)$$

and

$$\lambda_1^l = \frac{\alpha(P + \gamma)}{(1 - \alpha)} \quad (23)$$

$$\lambda_2^l = \frac{\alpha(P + \gamma + 2\lambda_1^l)}{(1 - \alpha)} \quad (24)$$

where

$$\alpha = \frac{M}{M + \beta_1 + \beta_2 + \frac{k_{id1}I_1}{k_p} + \frac{k_{id2}I_2}{k_p} + C_m M + \frac{(k_{tc} + k_{td})}{k_p} P} \quad (25)$$

$$\gamma = \frac{2f_1 k_{d1} I_1}{k_p (M + K_1 k_p P)} + \frac{2f_2 k_{d2} I_2}{k_p (M + K_2 k_p P)} + \frac{2k_{dm} M^2}{k_p} + C_m P \quad (26)$$

$$C_m = \frac{k_{fm}}{k_p} \quad (27)$$

The number-average chain length (NACL or the degree of polymerization X_N) and the polydispersity (X_W/X_N) are calculated as follows:

$$X_N = \frac{\lambda_1^d + \lambda_1^l}{\lambda_0^d + \lambda_0^l} \quad (28)$$

$$\frac{X_W}{X_N} = \frac{(\lambda_2^d + \lambda_2^l)(\lambda_0^d \lambda_0^l)}{(\lambda_1^d + \lambda_1^l)^2} \quad (29)$$

The detailed derivation of the modeling equations is reported in Butala.³⁵ The symbols are defined in the Notation.

OPTIMIZATION OF BATCH POLYMERIZATION PROCESSES

To take full advantage of different thermal reactivities of different initiators, it is desirable to operate the styrene polymerization reactor (initiated by mixed initiators) nonisothermally so that the batch reaction time can be reduced and the desired polymer properties can be obtained. It is also important that the total initiator concentration and composition of the initiator mixture should also be selected optimally. Such nonisothermal temperature profiles and initial operating conditions can be determined by formulating and solving the open-loop optimal control problem to obtain the desired polymer properties in the minimum reaction time. One of the techniques one may use to solve such problems is the weighted sum approach in which the single-cost function is a weighted sum of various performance objectives. However, this method has the disadvantage of hiding the physical significance of the objectives during the course of optimization. As described earlier, some control variables in free radical polymerization have contradictory effects on the different objectives, e.g., increased temperature results in high monomer conversion but lowered molecular weight. A single weighted sum approach also requires *a priori* knowledge of the weights to vary the emphasis given to each objective and adjusting them is often difficult.

In recent years, several publications on the optimization of polymerization processes initiated by a single initiator have been reported.¹⁶⁻²¹ Although there are a few papers dealing with multiobjective optimization of copolymerization processes,^{36,37} the multiobjective optimization of homopolymerization reactors has not been reported in the literature. Moreover, little has been reported on the optimization of polymerization processes initiated by mixed initiators. In this paper, we shall use a mul-

tiobjective dynamic optimization technique used in our previous work.³⁷ This method was successfully applied to the optimal control of semibatch copolymerization of SAN. In this study, optimal temperature policy, optimal initiator concentration, and composition are computed to obtain the desired prespecified polymer properties in the minimum possible batch reaction time. The detailed description of the feasible direction algorithm and the criteria used in defining the design specifications is described in Nye and Tits.³⁸ The methodology used in defining the objectives and constraints is presented here and a brief summary of the actual optimization algorithm is given in the Appendix.

The central idea in this methodology is to emphasize designer intuition in an optimization-based approach to engineering design. It handles multiobjective design problems where some of the objectives or the constraints could be "functional." This means that the specification could also be a function of an independent variable and that the specification needs to be optimized or satisfied for all values of the independent variable in a given set. The delivery of designer intuition and knowledge pertaining to the design problem is through an application-oriented problem formulation. The procedure of the problem formulation can be summarized as follows:

1. Partition of the various specifications into three categories:
 - (a) Hard (functional) constraint—a specification whose satisfaction is considered essential and, hence, achieving it should proceed with the utmost priority. For our design problem, a good example of hard constraints is the limit of polymerization temperature. It is clear that the resulting design has no engineering value if the limits on maximum or minimum reaction temperature are violated.
 - (b) Soft (functional) constraint—a specification that involves a desired or target value, which the designer should try to approach and reach if possible, but such that no further gain would be obtained if the specification overachieved its target value. A soft constraint could be the product quality specifications. A slight violation of the constraint would probably not jeopardize the value of the whole design, even though a design satisfying the constraint would be preferable.
 - (c) (Functional) objective—a specification for which some quantity should be min-

imized or maximized. Minimization of deviation of product specification from their prespecified values and minimization of reaction time will be our objectives.

Based on the above definition of constraints and objectives, the algorithm proceeds in three phases. In the phase I, only the hard constraints are considered; when all the hard constraints are satisfied, the second phase starts. In the phase II, objectives and soft constraints compete simultaneously, while hard constraints remain satisfied. The third phase starts only when all the soft constraints are satisfied, all objectives have reached at least their good values (see below), and hard constraints are still maintained satisfied. In the phase III, effort is made to improve the objectives, while all hard and soft constraints are still kept satisfied.

2. Choose a good value (curve) and a bad value (curve) for each specification by the uniform satisfaction/dissatisfaction rule: Having all the various (functional) objectives and soft (functional) constraints achieve their corresponding good values (curves) should provide the same level of satisfaction to the designer for each, whereas achieving the bad values (curves) should provide the same level of dissatisfaction. Having all of the various hard (functional) constraints achieve their corresponding good values (curves) should provide the same level of satisfaction to the designer for each, whereas achieving the bad values (curves) should provide the same level of dissatisfaction. The use of good and bad values in this way provides a very simple way to do trade-off analysis; if the designer is dissatisfied with the performance level achieved by a particular objective or constraint, he simply changes what he considers to be satisfactory (good value) or unsatisfactory (bad value).

With this problem formulation, comparison between various scaled specifications becomes meaningful; namely, under the assumption that the levels of satisfaction are affine functions of the specifications, we can say that the i th specification is more satisfied than the j th, if $f_s^i > f_s^j$ and vice versa. Hence, the maximal scaled value of all specifications

represents an index of the quality of the design. Therefore, we consider the following nonlinear programming problem:

$$\min_x \max_i f_s^i(x) \quad (30)$$

subject to

$$g_s^j(x) \leq 0, \quad j = 1, 2, \dots$$

where x is the design parameter vector and f_s^i and g_s^j are the i th "scaled" (functional) objective and the j th (functional) constraint, respectively. The "scaled" (functional) objective is defined by

$$f_s^i = \frac{f^i - f_{\text{good}}^i}{f_{\text{bad}}^i - f_{\text{good}}^i} \quad (31)$$

where f^i is the i th (functional) objective and f_{good}^i , f_{bad}^i are its good value (curve) and bad value (curve), respectively. With this transformation, 0 and 1 correspond, respectively, to the specified good and bad values. A similar definition applies to the "scaled" (functional) constraint. In case of the functional objective, f_s^i stands for the maximal value of all possible values of the independent variable and, similarly, for the functional constraint, $g_s^j \leq 0$ means that the constraint must be satisfied for all possible values of the independent variable. The methodology mentioned above has been implemented in the CAD package CONSOLE.³⁸⁻⁴¹ CONSOLE is used in this study to obtain optimal reactor control policies.

FORMULATION OF BATCH POLYMERIZATION OPTIMIZATION PROBLEM

The optimal reactor operating policies for the bulk or suspension free radical styrene polymerization process is studied for several different cases. For each case, the obtainment of specified end properties (e.g., monomer conversion and number-average chain length [NACL]) in minimum time is desired. Reactor operating temperature is a control variable and is parameterized to the third-order polynomial in time:

$$T = \sum_{i=1}^4 a_i t^{i-1} \quad (32)$$

Once the time-varying reactor temperature program is obtained, one can implement such a program in a process control computer. Although this parameterization approach may give a suboptimal solution, this method has the advantage that no adjoint equations need to be solved and complex process models, such as those described in this paper, can be used for process optimization by allowing a parameter optimization scheme to select experiments to be performed on the process model. In other words, existing process models do not have to be modified in order to perform optimal control calculations. When one has *a priori* knowledge about optimal control policies, a simple functional form as eq. (32) with only a few coefficients should be adequate.⁴² This method is applicable to many practical problems characterized by complexity of the process models.^{42,43} In our work, higher-order polynomials (up to eighth order) have been tried and it was found that the third-order polynomials were sufficient in describing the optimal control trajectories. Hicks and Ray⁴³ describe how the control vector parameterization can be modified when the control policy is of a mixed type having both bang-bang and unconstrained portions.

The coefficients of the polynomial in eq. (32) are considered as design parameters. For some cases, total initiator concentration may also be selected optimally and, hence, it becomes one of the design parameters. For the case of a mixed initiator system, the composition of initiator mixture is selected optimally; thus, the initial mol fraction of one of the initiators is also a design parameter. The constraints on reactor operating temperature are defined as upper and lower bounds. Although the polymer properties are specified only at the final time, the constraints on the reaction temperature are observed

throughout the reaction period. For the optimization calculations, the entire span of reaction time is divided into a finite number of intervals. As the number of intervals increases, the problem approaches the actual dynamic optimization problem. In our case, 20 discrete points to cover the whole reaction period have been found satisfactory. According to this convention, the time-dependent quantity (i.e., reactor temperature) is considered as a functional quantity. Now its values will be considered only at a finite number of time instants (mesh points). This allows us to specify the good and bad values of functional objectives and functional constraints at each mesh point corresponding to the desired value of the independent variable (i.e., time). The optimization algorithm will try to satisfy the functional constraints at each individual mesh point. The constraints on reaction temperature are defined as hard constraints.

The objectives of achieving the properties at the final time are defined as soft constraints, whereas the final batch time itself is defined as objective and as one of the design variables. These different definitions (hard constraints, soft constraints, and objectives) are used for the different specifications so that they will match with the theme of the Phase I-II-III algorithm. For more details on the Phase I-II-III algorithm, refer to Nye and Tits.³⁸ This algorithm proceeds in a way that objectives are improved only after the hard constraints and soft constraints are satisfied. Thus, our problem definition corresponds to our aim of achieving the desired end properties (soft constraints) in minimum time (objective); in other words, to minimize the reaction time (objective) only if specified hard constraints (temperature) and specified soft constraints (end properties) are achieved. In mathematical notation, the general problem can be formulated as follows:

<i>Objectives:</i>	$\min t_f$	Total batch time
<i>Soft Constraints:</i>	$\left[\frac{X_{Nd} - X_N(t_f)}{X_N(t_f)} \right]^2 \leq 0.05$	NACL
<i>Hard Constraints:</i>	$x(t_f) \geq x_d$ $[-OO-]t_f \leq 10 \text{ ppm}$ $343 \text{ K} \leq T(t) \leq 413 \text{ K}$ $(0 \leq t \leq t_f)$	Monomer conversion Peroxide residue concentration Reaction temperature
<i>Design Parameters:</i>	Coefficients, a_j ($j = 1, 2, 3, 4$) Batch time, t_f Total initiator concentration, I_t ($t = 0$) Mol fraction of BPO in initiator mixture, y_1	

Here, X_N represents the number-average chain length and subscript d denotes the desired value. Other symbols are defined in the Notation.

RESULTS AND DISCUSSION

For our simulation study, styrene polymerization in suspension is selected. The polymerization reaction temperature range of 70–140°C is used for all the simulation studies. The selected temperature range is within the operating range of the industrial styrene polymerization in suspension.⁴⁴ The similar temperature range for styrene polymerization in suspension is reported in the patent literature discussed earlier. However, the simulation results are also valid for the bulk polymerization of styrene. Although the industrial processes for styrene polymerization in bulk may employ higher temperatures than in our selected temperature range, the experimental work of bulk polymerization of styrene was performed to illustrate the effect of the mixed initiator system.

A. Experimental Procedure

For each experiment, styrene (Aldrich) is passed through a column of ion-exchange resins (Amberlyst, Rohm and Haas Co.) to remove inhibitors. A measured amount of initiators (BPO [Aldrich] and TBPB [Aldrich]) are added to the purified styrene to prepare the reaction mixture. The reaction mixture is then filled into 8–10 break-seal ampules. Each ampule is purged with nitrogen to remove air from the ampule. While continuously purging with nitrogen, each ampule is sealed air tight using a flame torch. A heating bath containing oil is used to keep the ampules at the desired temperature. Once the heating bath reaches the desired initial reaction temperature, all the ampules are dipped (80% of the length) into the heating bath. Since the diameter of the ampules is very small (o.d.: 10 mm), it is assumed that a quick steady state is obtained between the heating bath temperature and the temperature inside the ampules. The whole optimal temperature profile is divided in several intervals of 10 min each. Then, within each interval, the temperature is kept constant. At the end of the 10 min time period, the temperature set point for the heating bath is changed to the temperature corresponding to the next interval. Since the optimal temperature profiles to follow vary slowly, this method results in a very accurate tracking of such temperature profiles. At each spec-

ified sampling time, an ampule is removed from the heating bath and quenched rapidly. The polymer sample from the ampule is then analyzed for monomer conversion and molecular weights. The monomer conversion is measured by the standard gravimetric method and the polymer molecular weight by the gel permeation chromatography.

A binary mixture of monofunctional initiators with different thermal reactivities, benzoyl peroxide (BPO) with a 1 h half-life at 84°C and *t*-butyl perbenzoate (TBPB) with a 1 h half-life at 125°C, is used in numerical simulations and experimental study. The kinetic constants used in our simulations are listed in Table I. The optimal polymerization reactor operating policies have been determined for several different cases. First, the simplest problem of obtaining the optimal temperatures profile for a given total initiator concentration and initiator mixture composition is solved, where the objective is to achieve a desired monomer conversion and NACL at the end in a minimum batch reaction time. Successively more specifications in terms of soft constraints are added to the problem definition. Next, the composite problem including all the specifications is solved. The effects of variation in design specifications are also examined. Finally, the performance of styrene polymerization with mixed initiators is compared with that of the polymerization with single initiator only (BPO or TBPB). In what follows, these case studies will be discussed to illustrate the effect of using the mixed initiator system in batch styrene polymerization.

B. Polymerization with Mixed Initiators

Case 1: Optimization with prespecified initiator concentration and initiator composition.

Objectives:

$$\min t_f$$

Product Specifications:

$$X_{Nd} = 1000$$

$$x_d \geq 0.99$$

Reaction Conditions:

$$I_t(t = 0) = 0.011 \text{ mol/L}$$

$$y_1(0) = 0.8$$

$$T(t) = \text{free}$$

Table I Numerical Values of Kinetics Parameters for Bulk Polymerization of Styrene

Reaction	Parameter (g, mol, L, s, cal, K)	Ref.
Initiation	BPO: $f_1 = 1.0$	12
	$k_{d1} = 1.44 \times 10^{13} \exp(-14700/T)$	
	TBPP: $f_2 = 1.0$	45
	$k_{d2} = 8.315 \times 10^{13} \exp(-16162/T)$	
	Thermal: $k_{dm} = \bar{k}_i = 2.19 \times 10^5 \exp(-13810/T)$	34
Propagation	$k_p = k_{p0} = 1.06 \times 10^7 \exp(-3569/T)$	46
Chain transfer to monomer	$C_m = \left(\frac{k_{fm}}{k_p}\right) = \left(\frac{k_{fm}}{k_p}\right)_0 + B_1 x$	34
	$k_{fmo} = 2.31 \times 10^6 \exp(-6377/T)$	
	$B_1 = -1.013 \times 10^{-3} \log_{10} \left(\frac{473.12 - T}{202.5}\right)$	
Induced decomposition of initiator	BPO: $k_{id1} = 3.116 \times 10^9 \exp(-6359/T)$	30
	TBPP: $k_{id2} = 1.62 \times 10^{13} \exp(-9518/T)$	
Chain termination	$k_t = k_{tc} = k_{t0} g_t$	46
	$k_{t0} = 1.25 \times 10^9 \exp(-847/T)$	
Gel effect	$g_t = \exp[-2(A_1 x + A_2 x^2 + A_3 x^3)]$	26
	$A_1 = 2.57 - 5.05 \times 10^{-3} T, A_2 = 9.56 - 1.76 \times 10^{-2} T$	
	$A_3 = 3.63 + 7.85 \times 10^{-3} T$	
Primary radical termination	BPO: $K_1 = \left(\frac{k_{tp1}}{k_{i1} k_p}\right) = 3.44 \times 10^{-14} \exp(14022/T)$	30
	TBPP: $K_2 = \left(\frac{k_{tp2}}{k_{i2} k_p}\right) = K_1$	
Density of styrene and polystyrene	$\rho_m = 924.0 - 0.918(T - 273.1)$	34
	$\rho_p = 1084.8 - 0.605(T - 273.1)$	

The initial reaction conditions (total initiator concentration and initiator mixture composition) reported by Sanchez⁴⁷ are used in deriving the optimal control profiles for styrene polymerization using the mixture of BPO (I_1) and TBPP (I_2) as initiators. Thus, only the optimal time-varying temperature profile will be computed. The initiator mixture consists of 80% BPO and 20% TBPP. The performance of the optimal control policy in the open-loop batch polystyrene process is shown in Table II and Figure 1, where the symbols indicate the experimental results and the solid lines indicate the simulation results. Figure 1 shows that a very good agreement between the simulation results and the experimental data has been obtained. However, the final value of NAEL ($X_N = 780$) is lower than the desired value ($X_{Nd} = 1000$). This is because, with the given product specifications and initial reaction conditions, trade-off is reached between the competing specifications for monomer conversion,

NAEL, and the requirement for minimum batch time. The error bound for the specification of monomer conversion is tighter than the error bound for the specification of NAEL; hence, more deviation in X_N from the desired value (X_{Nd}) is observed. In all our experiments, no bimodal molecular weight distribution was observed. The results shown in Figure 1 also indicate that the conversion of TBPP (I_2) is only 25% and a large amount of initiator residue remains (680 ppm) in polymer. As mentioned above, this is a quite undesirable situation. Thus, in our next example, we shall select both the initial initiator composition and total initiator concentration in an optimal manner.

Case 2: Optimization with prespecified initiator concentration.

Objectives:

$$\min t_f$$

Table II Styrene Polymerization with Mixed Initiators; Comparison of Different Optimal Control Case Studies

Reaction Parameters	Results of Optimization Case 1	Results of Optimization Case 2	Results of Optimization Case 3(a)	Results of Optimization Case 3(c)
I_0 (mol/L)	0.011	0.011	0.00575	0.00316
BPO mol % (I_1)	80.0	69.2	39.4	47.8
TBPB mol % (I_2)	20.0	30.8	60.6	52.2
Temperature (°C)	87–103	94–107	119–133	103–131
Reaction time (h)	6.04	5.13	3.04	4.89
Monomer Conversion (%)	98.4	98.5	99.0	98.4
$X_N(X_{Nd})$	780 (1000)	782 (1000)	930 (1000)	1327 (1500)
Initiator residue (ppm)	680	660	8	5

Product Specifications:

$$X_{Nd} = 1000$$

$$x_d \geq 0.99$$

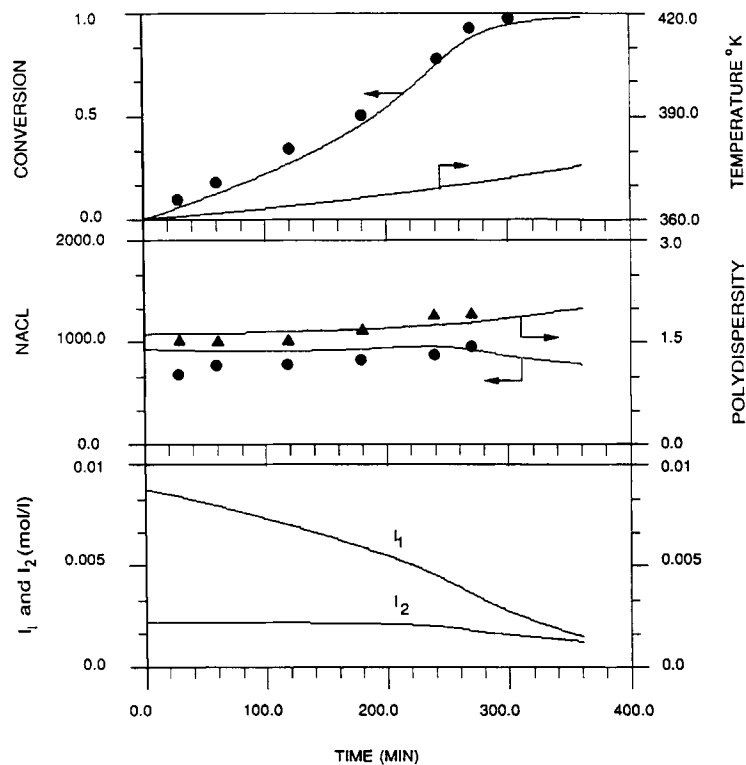
Reaction Conditions:

$$I_t(t = 0) = 0.011 \text{ mol/L}$$

$$y_1(0) = \text{free}$$

$$T(t) = \text{free}$$

In this case, the total initiator concentration is fixed as in Case 1, whereas the initial composition of the mixed initiator system is selected optimally. All the other product quality specifications are same as in Case 1. It has been found that the optimal composition of the initiator mixture is $y_1(0) = 0.7$, which is different from the one used in the previous case [$y_1(0) = 0.8$], and the total reaction time has been reduced by 15% (from 6 to 5.1 h). The performance of this optimal control policy is illustrated in Figure 2. Again, a good agreement between the

**Figure 1** Optimal polymerization with mixed initiators: Case 1.

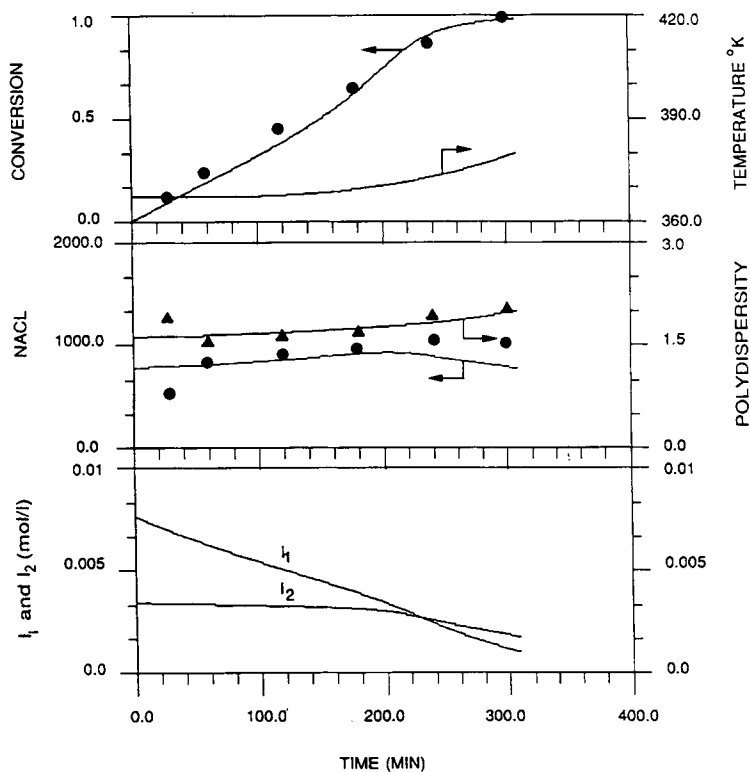


Figure 2 Optimal polymerization with mixed initiators: Case 2.

experimental results and the model predictions is observed. Note that the reactor is operated at slightly higher temperature than in Case 1. For this case, also, the deviation in X_N from X_{Nd} is observed. The reason for the deviation in X_N is same as discussed for Case 1. The results shown in Figure 2 indicate that the final conversion of TBPB is still less than 25%. Therefore, it is necessary to select the total initiator concentration optimally so that the amount of initiator residues can be reduced to a minimum permissible level.

Case 3(a): Optimization with optimally chosen initial initiator concentration and composition and prefixed residual initiator concentration.

Objectives:

$$\min t_f$$

Product Specifications:

$$X_{Nd} = 1000$$

$$x_d \geq 0.99$$

$$[-OO-]_{t_f} \leq 10 \text{ ppm}$$

Reaction Conditions:

$$I_t(t = 0) = \text{free}$$

$$y_1 = \text{free}$$

$$T(t) = \text{free}$$

In this example, more flexibility in the design parameters is introduced by optimally selecting the total initiator concentration and initiator mixture composition. As mentioned earlier, high initiator residue level in the final polymer product is not desirable. Thus, one more design specification (soft constraint) is included in the problem definition: maximum allowed level of initiator residues at $t_f = 10$ ppm. The results of reactor simulation are shown in Figure 3 along with the experimental data. First, note that there is a drastic reduction in total reaction time from 5 h (Case 2) to about 3 h. Moreover, the total initial concentration of the initiator mixture (I_0) is about 50% less than the previous cases. The final value of NACL (X_N) obtained is very close to the desired value of NACL (X_{Nd}). The final concentration of peroxides was 8 ppm which is within

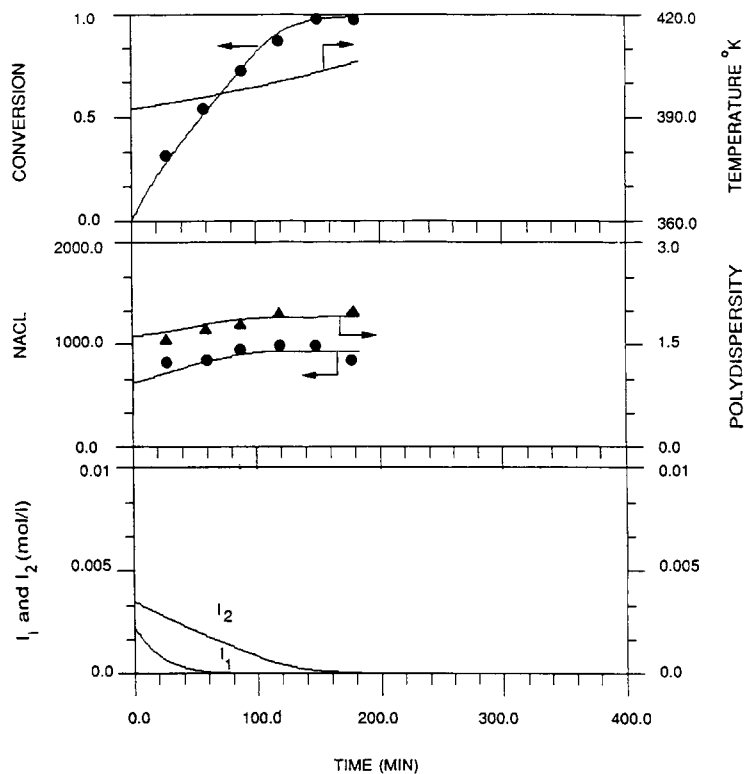


Figure 3 Optimal polymerization with mixed initiators: Case 3(a).

the specified limit. The agreement between experimental results and the model simulation is also excellent. The results indicate that when both initiator parameters are selected optimally there is a significant improvement in the reactor operation. It is also observed that the reactor is operated at higher temperature levels than the previous two design cases.

The performances of the batch styrene polymerization processes for the Cases 1, 2 and 3(a) are compared in Table 2. The comparison of the results suggests that the total initial initiator concentration (I_0) used for Cases 1 and 2 is not appropriate to obtain the desired product specifications. Apparently, I_0 used for Cases 1 and 2 is too high, which leads to low NACL. Hence, low-temperature polymerization is required to obtain high molecular weight polystyrene in these cases. When the lower initiator concentration is used as in Case 3(a), higher temperature can be employed to reduce the batch time without lowering the polymer molecular weight. The use of low initiator concentration also decreases residual peroxide group concentration. This example illustrates that by adding the flexibility in the selection of the initial reaction condi-

tions one can improve the performance of batch styrene polymerization processes. Our analysis of styrene polymerization with three different optimal control cases indicated that to realize the full advantage of the mixed initiator system it is necessary to select optimally the initial reaction conditions as well as the reaction temperature profile.

Case 3(b): Effect of change in the specification of final monomer conversion.

Here, the desired monomer conversion at final time is specified as 90%. The optimization computation is started again by keeping all the other specifications as in Case 3(a). The same results are obtained as in the Case 3(a), the reason being that when the constraint on residual peroxide concentration is specified the constraint on monomer conversion is not active. In other words, high monomer conversion (> 99%) is the consequence of higher initiator conversion (> 90%).

Case 3(c): Effect of change in the specification of NACL.

The same problem as described in Case 3(a) is solved again with the different design specification for NACL. A new target value of NACL is 1500, which is higher than all the other previous cases

(i.e., 1000). The reactor simulation results obtained after the application of the open-loop optimal control are shown in Figure 4. Note that all the design parameters have been changed to accommodate the change in the design specification for NACL. The total initiator concentration is reduced by 45%, and lower polymerization temperature is used to obtain higher molecular weight polymers. However, the use of lower reaction temperature than in Case 3(a) leads to longer reaction time (4.5 h) than in Case 3(a). In computing the optimal reaction conditions, the trade-off has been made between the requirements of high NACL and low residual initiator concentration, hence, some deviation in NACL (X_N) from the desired value is observed. The results for the Cases 3(a)–3(c) illustrate that more changes in reactor variables are required when one changes the specification of desired polymer molecular weight than when monomer conversion requirement is changed.

C. Polymerization with Single Initiator

Case 4: Optimization with optimally chosen initial concentration of BPO or TBPB.

Objectives:

$$\min t_f$$

Product Specifications:

$$X_{Nd} = 1000 \text{ or } 1500$$

$$x_d \geq 0.99$$

$$[-OO-]_{t_f} \leq 10 \text{ ppm}$$

Reaction Conditions:

$$I_i(t=0) (\text{BPO or TBPB}) = \text{free}$$

$$T(t) = \text{free}$$

For comparison of the polymerization performance with mixed initiators and with single initiators, the optimal control policies have also been determined for single monofunctional initiator systems (benzoyl peroxide only and with *t*-butyl perbenzoate only). The simulation results of the optimal controls of styrene polymerization with BPO only and TBPB only are shown in Tables III–V.

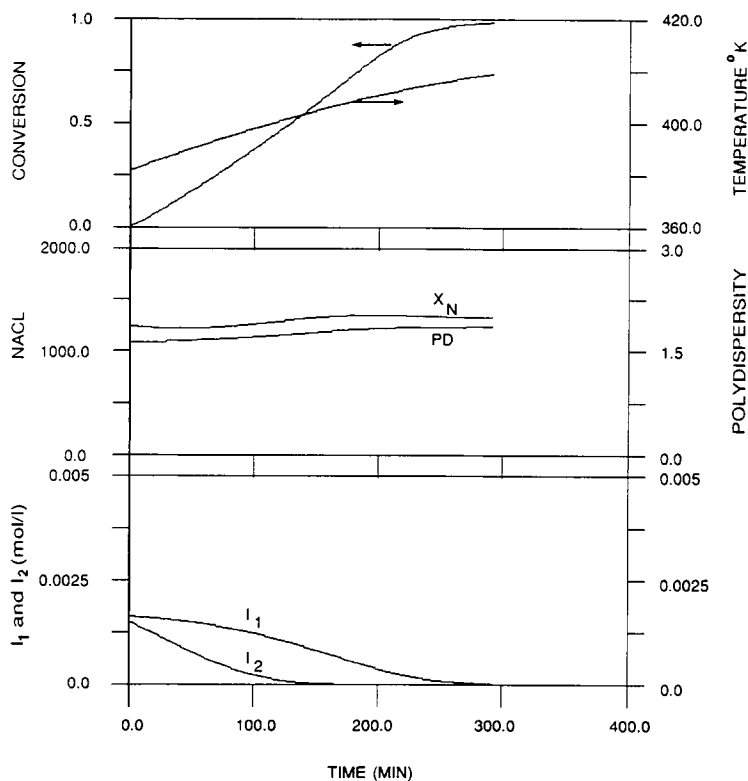


Figure 4 Optimal polymerization with mixed initiators: Case 3(c).

Table III Comparison of Styrene Polymerization with Mixed Initiators BPO Only and TBPB Only [$X_{Nd} = 1000$; $T_0 = \text{free}$]: Case 4

Specifications	BPO Only	TBPB Only
I_0 (mol/L)	0.00578	0.00542
BPO mol % (I_1)	100	—
TBPB mol % (I_2)	—	100
Temperature ($^{\circ}\text{C}$)	84–139	122–133
Batch time (h)	4.4	3.08
Monomer conversion (%)	99.4	99.1
X_N	992	954
Polydispersity	1.77	1.87
Initiator residue (ppm)	0	10

One can compare the results shown in Table III with Case 3(a), where the desired X_N value was 1000. Note that the performances obtained by using the mixed-initiator system [Case 3(c)] and only TBPB (I_2) are very similar, whereas the results obtained with only BPO (I_1) show that a longer reaction time is required to achieve the same product specifications.

Table IV shows the performances of the optimal controls with BPO only and TBPB only when the desired X_{Nd} is 1500. Other design specifications are identical to Case 3(c). Note that when the mixed initiators are used the desired specifications are achieved in less batch time. The performance obtained with TBPB only is comparable to the performance obtained with the mixed-initiator system except that a slightly longer batch time is required. Note that low-temperature operation of 103–131 $^{\circ}\text{C}$ is required with the mixed-initiator system [Case 3(c)], whereas higher temperature operation of 115–137 $^{\circ}\text{C}$ is required for the polymerization with TBPB only. Again, because of the low-temperature operation, longer batch time is required for the polymerization with BPO only. The results shown in Tables III and IV indicate that the use of a mixed-initiator system gives less reaction time and lower reaction temperature level, which can be practically more attractive.

Case 5: Optimization with a constraint on initial reactor temperature.

For all the previous cases, the initial reaction temperature was kept free. Minimization of batch reaction time is the main objective; hence, the highest possible initial reaction temperature is selected by the optimizer. However, in many polymerization processes where larger reactors are used, such a high

initial reaction temperature may not be desirable. Instead, a gradual increase in the polymerization temperature starting from the relatively lower temperature may be preferred for better temperature-control purposes. The polymerization with mixed-initiator systems can be used for selective decomposition of initiators by gradually raising the reaction temperature. In what follows, we shall present the results when the maximum allowed initial reaction temperature is given. For this case, the upper bound of the initial reaction temperature is set at 353 K. All the other specifications are same as in Cases 3(a) and 4 for the polymerization with mixed initiators and the polymerization with a single initiator, respectively.

The results of optimally controlled polymerization with BPO only, TBPB only, and a mixed-initiator system are shown in Table V and Figures 5–7. From Table V, one can first observe that the batch reaction time is almost 1 h less with a mixed initiator system than with either BPO or TBPB only. Also, in all three cases, the optimal initial reaction temperature is 353 K, which is the maximum allowed initial temperature. Such a choice of the initial temperature by the optimizer is due to the requirement of minimum batch reaction time. Note that all the product specifications obtained are very close to the target values. In particular, the polymer molecular weight is almost perfectly on target value when the mixed initiator is used. In Case 3(a) where we have the same molecular weight specification, such a high precision control has not been obtained. Even when a single initiator is used (Table V), the performance improves significantly. From the optimization results for Cases 1, 2, and 3(a), one can conclude that the large deviations in X_N in the Cases 1, 2, and

Table IV Comparison of Styrene Polymerization with Mixed Initiators BPO Only and TBPB Only [$X_{Nd} = 1500$; $T_0 = \text{free}$]

Specifications	BPO Only	TBPB Only
I_0 (mol/L)	0.00373	0.00278
BPO mol % (I_1)	100	—
TBPB mol % (I_2)	—	100
Temperature ($^{\circ}\text{C}$)	100–122	115–137
Batch time (h)	5.66	5.06
Monomer conversion (%)	98.8	98.9
X_N	1372	1362
Polydispersity	1.82	1.88
Initiator residue (ppm)	0	3

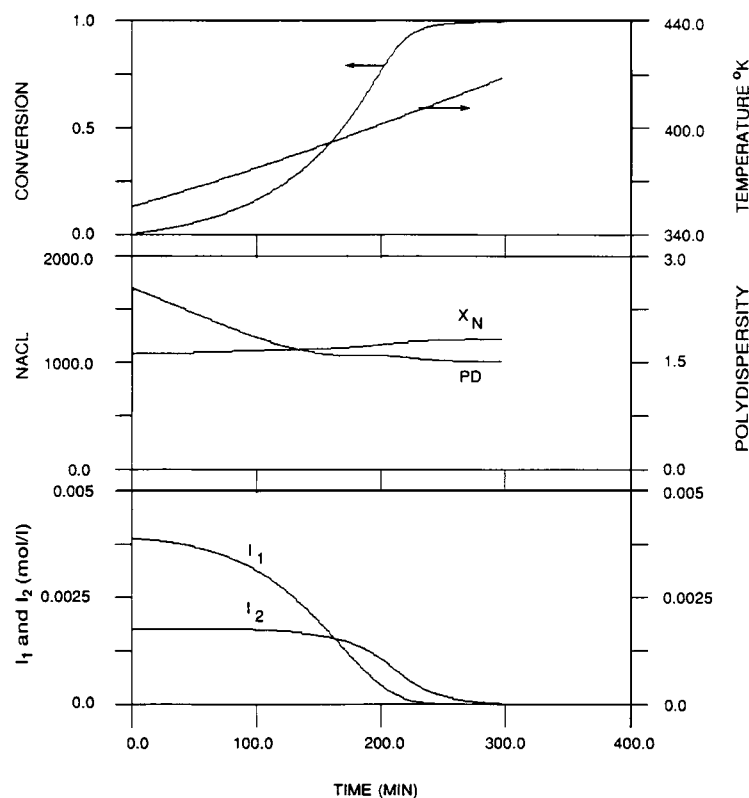
Table V Comparison of Styrene Polymerization with Mixed Initiators BPO Only and TBPB Only [$X_{Nd} = 1000$; $T_0 \leq 353$]: Case 5

Specifications	Mixed Initiators	BPO Only	TBPB Only
I_0 (mol/L)	0.00567	0.00568	0.00533
BPO mol % (I_1)	69.0	100	—
TBPB mol % (I_2)	31.0	—	100
Temperature ($^{\circ}\text{C}$)	80–140	72–140	80–140
Batch time (h)	4.94	5.77	5.88
Monomer conversion (%)	99.6	99.4	99.7
$X_N(X_{Nd})$	994 (1000)	980 (1000)	988 (1000)
Polydispersity	1.83	1.80	2.01
Initiator residue (ppm)	3	0	1

3 (a) are due to the strong requirement of minimum batch time. In other words, the optimizer selected higher initial temperature to minimize the batch time and to obtain high monomer conversion. Table V also shows that when the mixed initiator system is used very narrow molecular weight distribution (polydispersity) is obtained.

Also note that when the slow initiator (TBPB) is used alone, the NACL varies from about 3400 to

1000 during the course of polymerization, whereas with the mixed initiators, the NACL varies from 1700 to 1000. Figure 8 shows the optimal temperature profile and the resulting reactor performance when the maximum initial temperature is set at 363 K. Compared with Figure 5, it shows a significant reduction in the total reaction time and less variation in NACL during the reaction. Both Figures 5 and 8 suggest that the optimal reactor operating


Figure 5 Optimal polymerization with mixed initiators: [$T_0 \leq 353$ K].

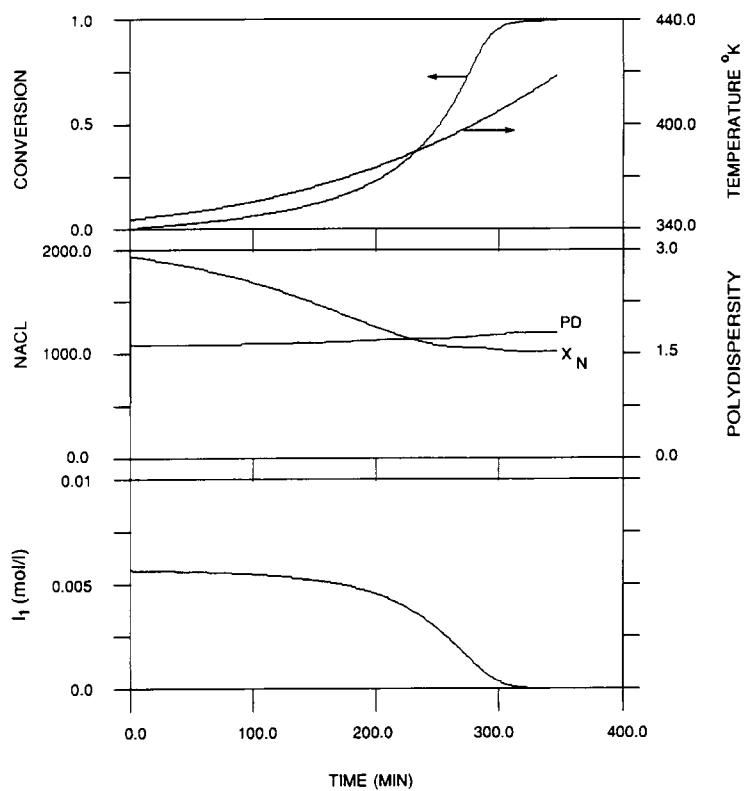


Figure 6 Optimal polymerization with BPO only [$T_0 \leq 353$ K]: Case 5.

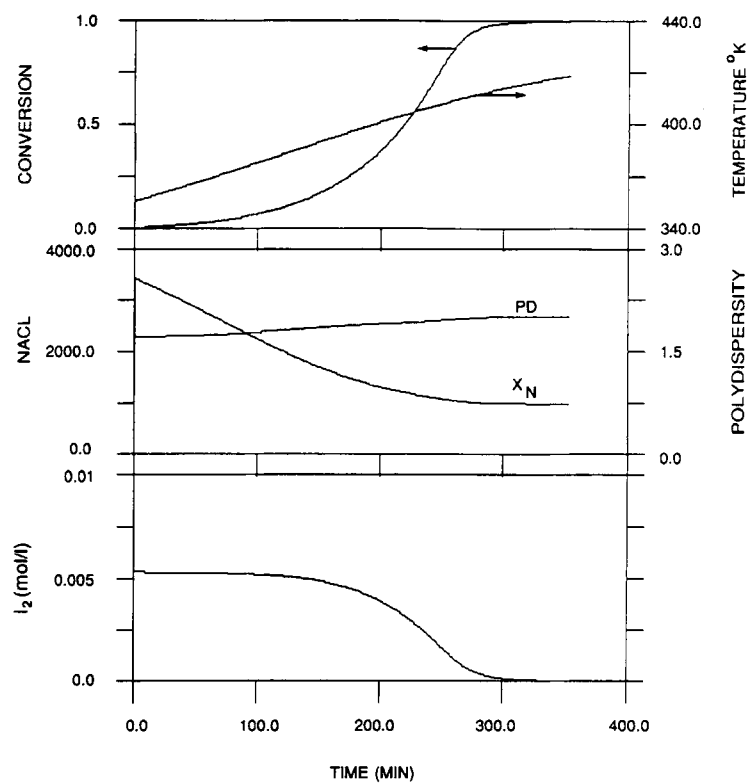


Figure 7 Optimal polymerization with TBPB only [$T_0 \leq 353$ K]: Case 5.

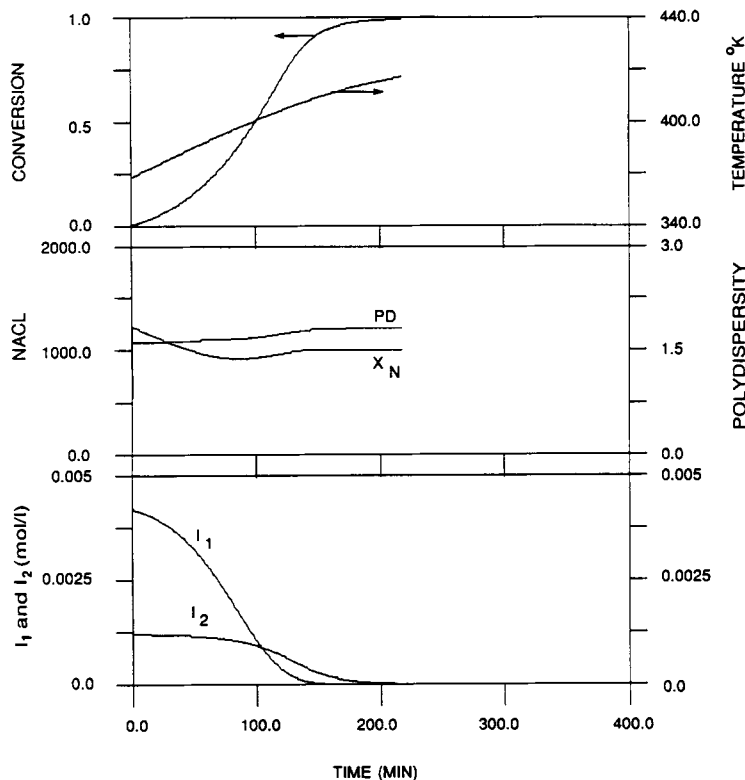


Figure 8 Optimal polymerization with mixed initiators [$T_0 \leq 363$ K]: Case 5.

policies are quite sensitive to the choice of initial reaction temperature.

CONCLUDING REMARKS

Optimal control of bulk or suspension batch polymerization of styrene with a binary mixture of initiators has been studied using a detailed kinetics model. The multiobjective dynamic optimization approach used in this study for obtaining the optimal reactor control strategies provides a convenient way to do trade-off analysis between the conflicting control objectives. The computer simulations and the experimental tests for various design specifications support the fact that the batch polymerization process can be improved significantly by using an optimally selected initial initiator concentration and initiator mixture composition with the time-varying temperature profile. It has also been shown that the specifications of soft constraints and objectives affect the optimal reactor operating policies to a large extent. Perhaps a further improvement would also be possible by adding more initiators (e.g., chaser

catalyst) and using optimal reactor operating policies as illustrated in this paper.

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APPENDIX

Feasible Direction Algorithm³⁸

In the following, a brief summary of the feasible direction algorithm implemented in the "CONSOLE" is presented.

The nonlinear mathematical problem can be stated as

$$\min_x \{ \max_{k \in M} f_k | g_j(x) \leq 0 \quad \forall j \} \quad (33)$$

where

$$k = 1, 2, \dots, m; \quad m = \text{number of objectives} \quad (34)$$

$$j = 1, 2, \dots, n; \quad n = \text{number of constraints} \quad (35)$$

The following definitions are used in building the feasible direction algorithm:

(1) The point x in the parameter space is a feasible point if

$$g_j(x) \leq 0 \quad \text{for } j = 1, 2, \dots, n \quad (36)$$

(2) The point x^* is a feasible point and there is no other point nearby that decreases some f_j without increasing any others; then, x^* is a noninferior point. In mathematical terms, there exists a $\delta \leq 0$ such that there is no other $x \in B(x^*, \delta)$ having the following properties:

$$g_j(x) \leq 0 \quad j = 1, 2, \dots, n \quad (37)$$

$$f_j(x) \leq f_j(x^*) \quad j = 1, 2, \dots, m \quad (38)$$

(3) The ϵ -active specifications [$J_{f_i(x)}$ and $J_{g_i(x)}$] are defined as below for any $\epsilon \geq 0$:

$$\varphi_f(x) \triangleq \max f_j(x) \quad \text{for } j = 1, 2, \dots, m \quad (39)$$

$$J_{f_i(x)} \triangleq \{j = 1, 2, \dots, m \mid f_j(x) \geq \varphi_f(x) - \epsilon\} \quad (40)$$

$$J_{g_i(x)} \triangleq \{j = 1, 2, \dots, n \mid g_j(x) \geq -\epsilon\} \quad (41)$$

(4) A feasible point \hat{x} is a stationary point for the problem defined above if there exist semipositive vectors μ_f and μ_g , such that

$$0 \in \sum_{j=1}^m \mu_{f_j} \nabla f_j(\hat{x}) + \sum_{j=1}^n \mu_{g_j} \nabla g_j(\hat{x}) \quad (42)$$

$$\mu_{g_j} g_j(\hat{x}) = 0 \quad \text{for } j = 1, 2, \dots, n \quad (43)$$

$$\mu_{f_j} (\varphi_f(\hat{x}) - f_j(\hat{x})) = 0 \quad \text{for } j = 1, 2, \dots, m \quad (44)$$

Now, the following proposition is made:

"If ($f_j \mid j = 1, 2, \dots, m$) and ($g_j \mid j = 1, 2, \dots, n$) are continuously differentiable and if x^* is a locally noninferior point, then x^* is a stationary point for the above-stated nonlinear programming problem."

The search direction function h_ϵ and the optimality function θ_ϵ are defined as

$$h_\epsilon \triangleq \frac{h}{\|h\|} \quad (45)$$

$$\theta_\epsilon \triangleq -\|h\| \quad (46)$$

with h computed as the vector opposite to the nearest point to the origin in the convex hull of the set of gradients of ϵ -active f and g functions. Thus, the computation of h determines the descent direction for both the cost and the active constraints. By using the search direction function h_ϵ , which gives a descent direction, a scalar step size λ can

always be found such that the $x_i + h_\epsilon \lambda$ remains feasible and the following condition is satisfied:

$$\varphi_f(x_i + \lambda h_\epsilon(x_i)) - \varphi_f(x_i) \leq \alpha \lambda \theta_\epsilon(x_i) \quad (47)$$

where $\alpha \in (0, 1)$. The trial values of λ that satisfy the above condition are generated using

$$\lambda = \beta^k \quad \text{for } k = 0, 1, \dots; \quad \beta \in (0, 1) \quad (48)$$

Now the algorithm can be described by the following procedure:

1. Initialize $\delta, \epsilon_0, \alpha, \beta$, and x .
2. Start iteration by setting $i = 0$
3. set $\epsilon = \epsilon_0$.
4. If $\theta_\epsilon(x_i) = 0$, then STOP.
5. If $\theta_\epsilon(x_i) < -\delta \cdot \epsilon$, then go to (7).
6. $\epsilon = \epsilon/2$; obtain h and go to (5).
7. Set $k = 0$.
8. Check if $\varphi_g[x_i + \beta^k \cdot h_\epsilon(x_i)] \leq 0$ and $\varphi_f(x_i + \beta^k \cdot h_\epsilon(x_i)) - \varphi_f(x_i) \leq \alpha \beta^k \theta_\epsilon(x_i)$ are satisfied, then go to (10).
9. $k = k + 1$; go to (8).
10. $x_{i+1} = x_i + \beta^k \cdot h_\epsilon(x_i)$.
11. $i = i + 1$; go to (3).

The convergence criteria used in the above procedure can be stated as: "All the iterates constructed by above algorithm are feasible points, and if the sequence of x_i constructed by the above algorithm is finite, then the last point in the sequence is the stationary point. Otherwise, any accumulated point of the sequence x_i is stationary point."

NOTATION

C_m	characteristic constant for chain transfer to monomer [= k_{fm}/k_p]
f_j	initiator efficiency [$j = 1, 2$]
g_t	gel-effect correlation factor [= k_t/k_{t0}]
I_j	initiator concentration [$j = 1, 2$] (mol L ⁻¹)
I_t	total initiator concentration (mol L ⁻¹)
K_j	characteristic constant for primary radical termination [$j = 1, 2$] [= $k_{tpj}/k_{ij}k_p$]
k_{dj}	rate constant for decomposition of initiator [$j = 1, 2$] (s ⁻¹)
k_{dm}	rate constant for thermal initiation (L ² mol ⁻² s ⁻¹)
k_{fm}	rate constant for chain transfer to monomer (L mol ⁻¹ s ⁻¹)
k_{ij}	initiation rate constant [$j = 1, 2$] (L mol ⁻¹ s ⁻¹)

k_{idj}	rate constant for induced decomposition [$j = 1, 2$] ($\text{L mol}^{-1} \text{s}^{-1}$)
k_p	rate constant for propagation ($\text{L mol}^{-1} \text{s}^{-1}$)
k_t	rate constant for termination ($\text{L mol}^{-1} \text{s}^{-1}$)
k_{tc}	rate constant for combination termination ($\text{L mol}^{-1} \text{s}^{-1}$)
k_{td}	rate constant for disproportionation termination ($\text{L mol}^{-1} \text{s}^{-1}$)
k_{t0}	rate constant for termination at zero conversion ($\text{L mol}^{-1} \text{s}^{-1}$)
k_{tpj}	rate constant for primary radical termination [$j = 1, 2$] ($\text{L mol}^{-1} \text{s}^{-1}$)
M	monomer concentration ($\text{L}^{-1} \text{mol}$)
M_n	concentration of dead polymer with n monomer units (mol L^{-1})
M_0	initial monomer concentration (mol L^{-1})
P	total live polymer concentration (mol L^{-1})
P_n	concentration of live polymer with n monomer units (mol L^{-1})
R_j	primary radical concentration [$j = 1, 2$] (mol L^{-1})
T	reaction temperature (K)
T_0	initial reaction temperature (K)
t	reaction time (s)
t_f	final reaction time (s)
V	reaction mass volume (L)
X_N	number-average chain length of polymer
X_{Nd}	desired number-average chain length of polymer at $t = t_f$
x	monomer conversion
x_d	desired monomer conversion at $t = t_f$

Greek Symbols

ϵ	volumer contraction factor
λ_k^d	k th moment of dead polymer
λ_k^l	k th moment of live polymer
ρ_m	density of monomer (g L^{-1})
ρ_p	density of polymer (g L^{-1})

REFERENCES

- R. B. Thompson, and M. J. Jursich, U. S. Pat. 3,414,547 (1968).
- G. F. D'alelio, U. S. Pat. 2,656,334 (1953).
- K. W. Doak, U. S. Pat. 2,907,756 (1958).
- V. R. Kamath and G. A. Harpell, U. S. Pat. 4,129,703 (1978).
- Kyowa Gas Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho JP 81,145,907 (1981); *Chem. Abst.*, 96: 69600 v.
- Denki Kagaku Kogyo K. K., Jpn. Kokai Tokkyo Koho JP 81,167,706 (1981); *Chem. Abst.*, 96:143534 v.
- H. Yoshida, H. Matsui, and N. Taga, Jpn. Kokai Tokkyo Koho JP 62,109,807 (1987); *Chem. Abst.*, 107: 135240 b.
- M. Fuku, Y. Okada, and K. Aoshima, Jpn. Kokai Tokkyo Koho JP 62,197,407 (1987); *Chem. Abst.*, 108: 151150 y.
- S. S. Karaenev, M. D. Petkova, and M. S. Mihailova, *Dokl. Bolg. Akad. Nauk.*, **40**, 69-72 (1987).
- C. Y. Chen, C. S. Chen, and J. F. Kuo, *Polymer*, **28**, 1395-1402 (1987).
- P. E. Baillagou and D. S. Soong, *Chem. Eng. Sci.*, **40**, 75-86 (1985).
- M. Stickler, *Makromol. Chem.*, **184**, 2563-2579 (1983).
- F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489-505 (1982).
- S. K. Soh and D. C. Sunderberg, *J. Polym. Sci. Polym. Chem.*, **20**, 1299-1371 (1982).
- W. H. Ray and R. L. Laurence, in *Chemical Reactor Theory-A Review*, L. Lapidus and N. R. Amundson, Eds., Prentice-Hall, New York, (1977), pp. 532-583.
- M. E. Sacks, S. I. Lee, and J. A. Biesenberger, *Chem. Eng. Sci.*, **27**, 2281-2289 (1972).
- I. M. Thomas and C. A. Kiparissides, *Can. J. Chem. Eng.*, **62**, 284-291 (1984).
- S. A. Chen and K. Y. Hsu, *Chem. Eng. Sci.*, **39**, 177-179 (1984).
- B. M. Louie and D. S. Soong, *J. Appl. Polym. Sci.*, **30**, 3707-3749 (1985).
- J. N. Farber and R. L. Laurence, *Chem. Eng. Sci.*, **46**, 347-364 (1986).
- S. R. Ponnuswamy, S. L. Shah, and C. A. Kiparissides, *Ind. Eng. Chem. Res.*, **26**, 2229-2236 (1987).
- H. K. Mahabadi and K. F. O'Driscoll, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 283-300 (1977a).
- K. Ito, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 1759-1764 (1977).
- F. L. Marten and A. E. Hamielec, *ACS Symp. Ser.*, **104**, 44-69 (1979).
- O. F. Olaja, G. Zifferer, G. Gleixner, and M. Stickler, *Eur. Polym. J.*, **22**, 585-595 (1986).
- N. Friis and A. E. Hamielec, *ACS Symp. Ser.*, **24**, 82-91 (1976).
- R. L. Ross and R. L. Laurence, *AIChE Symp. Ser.*, **72**, 74-79 (1976).
- W. A. Pryor and T. R. Fiske, *Macromolecules*, **2**, 62-70 (1969).
- K. Ito, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 401-413 (1975).
- K. C. Berger, P. C. Deb, and G. Meyerhoff, *Macromolecules*, **10**, 1075-1080 (1977).
- P. C. Deb and S. K. Kapoor, *Eur. Polym. J.*, **15**, 961-963 (1979).
- K. Ito, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 701-707 (1980).

33. H. K. Mahabadi and K. F. O'Driscoll, *Makromol. Chem.*, **178**, 2629–2636 (1977b).
34. A. Husain and A. E. Hamielec, *J. Appl. Polym. Sci.*, **22**, 1207–1223 (1978).
35. D. N. Butala, Ph.D. Thesis, University of Maryland, College Park, MD, 1990.
36. A. Tsoukas, M. Tirrell, and G. Stephanopoulos, *Chem. Eng. Sci.*, **37**, 1785–1795 (1982).
37. D. N. Butala, K. Y. Choi, and M. K. H. Fan, *Comp. Chem. Eng.*, **12**, 1115–1127 (1988).
38. W. T. Nye and A. L. Tits, *Int. J. Cont.*, **43**, 1693–1721 (1986).
39. M. K. J. Fan, J. Koninckx, L. S. Wang, and A. L. Tits, *CONSOLE User's Manual*, University of Maryland, College Park, 1987.
40. M. K. J. Fan, J. Koninckx, L. S. Wang, and A. L. Tits, in *Proc. Am. Con. Conf.*, Atlanta, GA, 1988, pp. 701–706.
41. A. L. Tits, M. K. H. Fan, and E. R. Panier, in *4th IFAC Symposium on CADCS*, Beijing, PRC, 1988.
42. W. H. Ray, *Advanced Process Control*, McGraw-Hill, New York, 1981, pp. 101–105.
43. G. A. Hicks and W. H. Ray, *Can. J. Chem. Eng.*, **49**, 522–528 (1971).
44. W. S. Fong, Polystyrene, Report No. 39, Stanford Research Institute, Menlo Park, CA, 1966.
45. Pennwalt-Lucidol, Peroxyesters, Product Bulletin, New York.
46. J. Brandup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley, New York, 1975, pp. 45–51.
47. T. Sanchez, U. S. Pat. 4,129,704 (1978).

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