

Experimental Validation of the Optimal Trajectory of Initiator Concentration in a Batch MMA Polymerization Reactor

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ABSTRACT: This article presents a method to determine the trajectory of initiator concentration that will produce polymer with desired number- and weight-average molecular weights at a prespecified level of monomer conversion. The optimal control theory is applied to the mathematical model for a batch methymethacrylate (MMA) solution polymerization reactor system. By imposing the constraint that initiator concentration should decrease within the range of self-consumption by the initiation reaction, one can obtain the initiator concentration trajectory that can be tracked by feeding the initiator alone. A control scheme is constructed with a cascade proportional-integral-derivative (PID) control algorithm for temperature control and a micropump is installed to manipulate the initiator feed rate. The experimental results show satisfactory tracking control performance despite the nonlinear features of the polymerization reactor system. Also, the monomer conversion and the average molecular weights measured are found to be in fairly good agreement with those of model prediction, respectively. In conclusion, the polymer having desired molecular weight distribution can be produced by operating the batch reactor with the initiator supplement policy calculated from the model. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1256–1266, 2000

Key words: methylmethacrylate (MMA); initiator concentration trajectory; batch reactor; molecular weight distribution (MWD); tracking experiment

INTRODUCTION

The batch polymerization process is widely used in industries for its availability and flexibility in operation. The main objective in the batch polymerization process is to obtain the desired polymer properties as well as to reduce the batch reaction time. However, it is very difficult to achieve both high monomer conversion and large polymer molecular weight simultaneously by merely increasing the amount of initiator concen-

tration for rapid polymerization because it would result in a lower polymer molecular weight and discoloration of polymer product due to the subsequent decomposition of a large amount of initiator residues. Similar problems are encountered when the polymerization is driven to its full extent in a short reaction time by increasing the reaction temperature.¹ For this reason, it is desirable to control the reactor temperature or the feed rate of initiator so as to track a predetermined trajectory that would yield high-quality polymer.

In industrial practice, the recipe is usually determined by trial and error experience. One of the less common but potential approaches for deter-

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mining the recipe is to use polymerization models along with optimal control methodologies. During the past score of years there have been a considerable amount of works on the optimal control of batch polymerization reactors.²⁻¹⁰ The main objective of these works was to obtain a polymer product with desired properties in a minimum time. Most of the investigators have simplified the model by introducing various assumptions such as constant density of the reactor contents, no chain transfer to monomer, and so on, because application of the optimal control theory to the mathematical model results in a great deal of iterative calculation.

Several works have been reported in the literature particularly with respect to the optimization of batch polymerization process using initiator.⁶⁻¹⁰ Sacks et al.⁶ employed the maximum principle to calculate the optimal initiator addition policy achieving a predetermined conversion and number average degree of polymerization in a free radical polymerization batch, isothermal reactor. Their policy was, however, limited to the case of maintaining a constant initiator concentration in the reactor.

Thomas and Kiparissides⁷ applied the minimum principle to a batch polymerization reactor for poly(methylmethacrylate) (PMMA). By minimizing the performance index composed of deviations of conversion and zero and second moments of dead polymer concentration, they obtained the optimal trajectory of initiator concentration that would produce polymer having desired average molecular weights set a priori. However, they were not able to implement their policy experimentally owing to the difficulty encountered in producing a decrease in the initiator concentration as it is required.

The use of photoinitiation method was explored by Louie and Soong⁸ because it may be difficult to disperse added initiator uniformly into the reacting mixture due to the high viscosity encountered at moderate and high conversions. Based on a very simple model, Ponnuswamy et al.⁹ proposed that for a given temperature the optimal initiator concentration be constant during the polymerization as in the work of Sacks et al.⁶ and further that for a very slow initiator decomposition rate, the optimal initiator policy be reduced to a single optimal charge of initiator at the beginning of polymerization.

It was reported by Hsu and Chen¹⁰ that the piecewise initiator addition policy for minimizing the total reaction time under a given set of final

monomer conversion and number average chain length would be to charge an equal amount of the initiator into the reactor at every equal time interval. Experimental verification of their theoretical findings revealed that there was a good agreement between experimental and calculated final conversion values, but there existed an appreciable deviation between experimental and calculated values of the number- and weight-average chain lengths.

However, these studies have treated the polymerization processes at relatively low temperature and low monomer conversion with simplified models. Although many experiments on the temperature trajectory have been performed to validate the temperature control policy,¹¹⁻¹⁴ few experiments have been undertaken for tracking the trajectory of initiator concentration. This is because there is no adequate method to make the initiator concentration decrease without any effect on living polymer concentration.

In a recent study, Elicabe and Meria¹⁵ proposed a cascade model-reference adaptive algorithm to control a continuous polymerization reactor, which is operated under forced oscillations of its feeds. Also, conversion control in the presence of reactive impurities in continuous solution methylmethacrylate polymerization reactor was explored by Chien and Penlidis¹⁶ using initiator flow rate as the manipulated variable. More recently, Scali et al.¹⁷ simulated the regulation control of the product quality of free radical polymerization of methylmethacrylate in a continuous stirred tank reactor by using state estimators (Extended Kalman Filters). These authors' studies aimed not to implement the optimal policy with a batch polymerization reactor but to regulate the product quality or to track periodic trajectory in a continuous polymerization reactor.

In this work, we impose a constraint on the variation of initiator concentration in such a way that the initiator concentration should decrease within the range of self-consumption by the initiation reaction. The optimal control theory is then applied to the batch MMA polymerization reactor model with the proposed constraint to calculate the optimal trajectory of initiator concentration that would produce the polymer product with desired number- and weight-average molecular weights at a prespecified level of monomer conversion. We also propose an initiator feeding scheme that enables us to track the optimal trajectory of initiator concentration. The ultimate goal is to demonstrate experimentally that the

optimal initiator supplement policy so determined really yields polymer product having desired properties set a priori.

POLYMERIZATION REACTOR MODEL

The polymerization system considered here is a batch solution polymerization of methylmethacrylate (MMA) using benzoylperoxide (BPO) as the initiator and ethylacetate (EA) as the solvent. The kinetic mechanism is the free radical polymerization including chain transfer reactions to monomer and solvent. One can derive the following mass balance equations to describe the dynamic behavior of the polymerization reactor (see Ahn et al.¹³):

$$\frac{1}{V} \frac{d(IV)}{dt} = -k_d I \quad (1)$$

$$\frac{1}{V} \frac{d(MV)}{dt} = -2fk_d I - k_p M G_0 - k_{trm} M G_0 \quad (2)$$

$$\frac{1}{V} \frac{d(SV)}{dt} = -k_{trs} S G_0 \quad (3)$$

$$\frac{1}{V} \frac{d(G_0 V)}{dt} = 2fk_d I - k_t G_0^2 \quad (4)$$

$$\begin{aligned} \frac{1}{V} \frac{d(G_1 V)}{dt} &= 2fk_d I + k_p M G_0 - k_t G_0 G_1 \\ &+ (k_{trm} M + k_{trs} S)(G_0 - G_1) \quad (5) \end{aligned}$$

$$\begin{aligned} \frac{1}{V} \frac{d(G_2 V)}{dt} &= 2fk_d I + k_p M(G_0 + 2G_1) - k_t G_0 G_2 \\ &+ (k_{trm} M + k_{trs} S)(G_0 - G_2) \quad (6) \end{aligned}$$

$$\frac{1}{V} \frac{d(F_0 V)}{dt} = \frac{1}{2} (k_t + k_{td}) G_0^2 + (k_{trm} M + k_{trs} S) G_0 \quad (7)$$

$$\frac{1}{V} \frac{d(F_1 V)}{dt} = k_t G_0 G_1 + (k_{trm} M + k_{trs} S) G_1 \quad (8)$$

$$\begin{aligned} \frac{1}{V} \frac{d(F_2 V)}{dt} &= k_{tc}(G_0 G_2 + G_1^2) + k_{td} G_0 G_2 \\ &+ (k_{trm} M + k_{trs} S) G_2 \quad (9) \end{aligned}$$

Here I , M , and S represent the concentrations of initiator, monomer, and solvent, respectively. Also, G_k and F_k denote the k -th moments of living

and dead polymer concentrations, respectively, and are defined as follows:

$$G_k = \sum_{n=1}^{\infty} n^k R_n(t), \quad k = 0, 1, 2 \quad (10)$$

$$F_k = \sum_{n=1}^{\infty} n^k P_n(t), \quad k = 0, 1, 2 \quad (11)$$

Once the G_k and F_k are known, the number average molecular weight (Mn), the weight average molecular weight (Mw), and the polydispersity (PD) can be determined by the following formulae:

$$Mn = M_m \times \frac{(G_1 + F_1)}{(G_0 + F_0)} \quad (12)$$

$$Mw = M_m \times \frac{(G_2 + F_2)}{(G_1 + F_1)} \quad (13)$$

$$PD = \frac{Mw}{Mn} \quad (14)$$

As the monomer is converted to the polymer, the density of the reaction mixture increases and thus the volume V of the reactor contents shrinks as the reaction proceeds. Rearranging the total mass balance equation, one can obtain the following equations that can be used to calculate the change in the volume of the reaction mixture, i.e.,

$$\frac{dV_p}{dt} = -\frac{1}{\rho_p} \left[M_m \frac{d(MV)}{dt} + M_s \frac{d(SV)}{dt} \right] \quad (15)$$

$$V = (MV) \frac{M_m}{\rho_m} + (SV) \frac{M_s}{\rho_s} + V_p \quad (16)$$

Gel effect is taken into account by the correlations proposed by Schmidt and Ray¹⁸ and the detailed correlations can be found in Ahn et al.¹³ The kinetic parameters are taken from the literature (see, for example, Ahn et al.¹³) and listed in Table I. The physical properties are also taken from the literature.¹¹⁻¹³

OPTIMAL CONTROL

The process model may be represented by the following state equations with totally specified initial conditions:

$$\frac{dx}{dt} = f(x, u, t), x(t_0) = x_0 \quad (17)$$

where $u(t)$ is the vector of control input corresponding to the initiator concentration and $x(t)$ is the vector of internal states which consists of nine components as given by

$$x = [M, S, G_0, G_1, G_2, F_0, F_1, F_2, V] \quad (18)$$

The problem is to find a control input $u^*(t)$, $t_0 \leq t \leq t_f$, in such a way that a properly defined performance index $J(t_f)$ is minimized. In the polymer production the physical and mechanical properties of the final product are normally related to the shape of the molecular weight distribution (MWD) whereas the amount of product obtained is determined by the monomer conversion X . Hence, it would be appropriate to define the performance index $J(t_f)$ as follows:

$$J(t_f) = \rho_1 \left[\frac{Mn(t_f)}{Mn_d} - 1 \right]^2 + \rho_2 \left[\frac{Mw(t_f)}{Mw_d} - 1 \right]^2 + \rho_3 \left[\frac{X(t_f)}{X_d} - 1 \right]^2 \quad (19)$$

where ρ_i denotes the weighting factor and the subscript d represents the desired value at the final time t_f .

We apply the Pontryagin's minimum principle to eqs. (17)–(19) and solve the resulting two point boundary value (TPBV) problem with initial values for the state equations and the final values for the costate equations. Thereupon we can obtain the solution to the optimal control problem.¹⁶

Hard nonlinearity of the polymerization system renders an analytic solution for the TPBV problem difficult. For this reason, the discrete control method (DCM) is used, where the total reaction time is divided into n equal subintervals

Table I Reaction Rate Constants Used in the Model for MMA Polymerization

Rate Constants	Expression
k_d [s ⁻¹]	$1.25 \times 10^{18} \exp(-35473/RT)$
k_{p0} [l/(mol s)]	$2.94 \times 10^6 \exp(-5656/RT)$
k_{t0} [l/(mol s)]	$5.20 \times 10^8 \exp(-1394/RT)$
k_{td0}/k_{t0}	$1.83 \times 10^{27} \exp(-44467/RT)$
k_{trm} [l/(mol s)]	$9.32 \times 10^4 \exp(-13971/RT)$
k_{trs} [l/(mol s)]	$8.79 \times 10^{-5} \exp(-42.6/RT)$

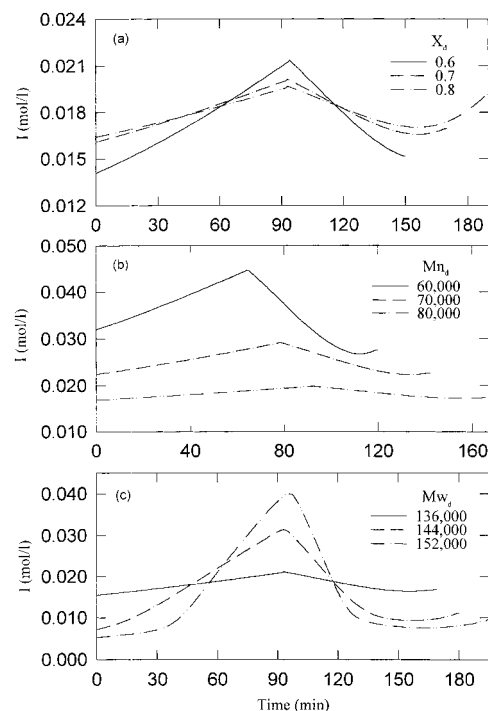


Figure 1 Optimal trajectories of initiator concentration for various sets of desired values; (a) $Mn_d = 80\,000$, $Mw_d = 136\,000$; (b) $X_d = 0.7$, $PD_d = 1.7$; (c) $X_d = 0.7$, $Mn_d = 80\,000$.

and the control variables remain constant in each interval. It is to be noted that depending on the choice of initial trajectory and final time t_f , optimal control may not exist and even if it exists, it may not be unique.^{4,13}

The trajectories for various desired sets (X_d , Mn_d , Mw_d) are calculated at constant temperature of 70°C as shown in Figure 1. Corresponding to a certain desired set the minimum reaction time is found by solving the same problem repeatedly for different final times and selecting the smallest time for which convergence is guaranteed within a satisfied tolerance range.

In Figure 1a the trajectories of initiator concentration are shown for various desired monomer conversions. The number- and weight-average molecular weights are set to be 80 000 and 136 000, respectively, at final time t_f . One may notice that the minimum reaction time becomes longer and the initiator concentration in the latter part of the reaction course becomes higher as the desired value of monomer conversion increases. Figure 1b shows the trajectories for various desired number average molecular weights. It is observed that as the desired value of number

average molecular weight increases, the trajectory consistently maintains lower initiator concentration and the minimum reaction time becomes longer. When the desired monomer conversion and the desired number average molecular weight are fixed at $X_d = 0.7$ and $Mn_d = 80\,000$, respectively, initiator concentration trajectories for various desired weight-average molecular weights are shown in Figure 1c. As the desired polydispersity increases, the trajectory tends to take more curved form.

In fact, one may try to produce a polymer having predetermined properties by controlling the initial charge of initiator. However, it is difficult to produce a polymer with desired number- and weight-average molecular weights at a prespecified level of monomer conversion by only changing the initial charge of initiator. Therefore, in order to obtain a polymer with desired properties, one needs to calculate the trajectory of initiator concentration that would yield polymer product with desired properties.

If a constant initiator concentration of 0.037 is set in Figure 1b, a polymer of number-average molecular weight 60 000 can be obtained after 130 min. However, the weight-average molecular weight and the monomer conversion of the final product turn out to be 99 587 and 0.777, respectively, whereas the desired weight-average molecular weight and the desired monomer conversion are 102 000 and 0.7, respectively. Therefore, it becomes evident that a polymer having the desired monomer conversion, the number-average molecular weight, and the weight-average molecular weight cannot be obtained by only keeping the initiator concentration constant.

IMPLEMENTATION

Optimal Trajectory of Initiator Concentration with Constraint

The purpose here is to obtain polymer product with the desired MWD by tracking a given trajectory of initiator concentration. Because the initiator concentration cannot be measured on-line, the given trajectory of initiator concentration must be tracked in an open loop manner. In the process of tracking the initiator concentration trajectory, one can feed the initiator dissolved in solvent for the part of increasing concentration but cannot take an appropriate control action for the part of decreasing concentration. The reason

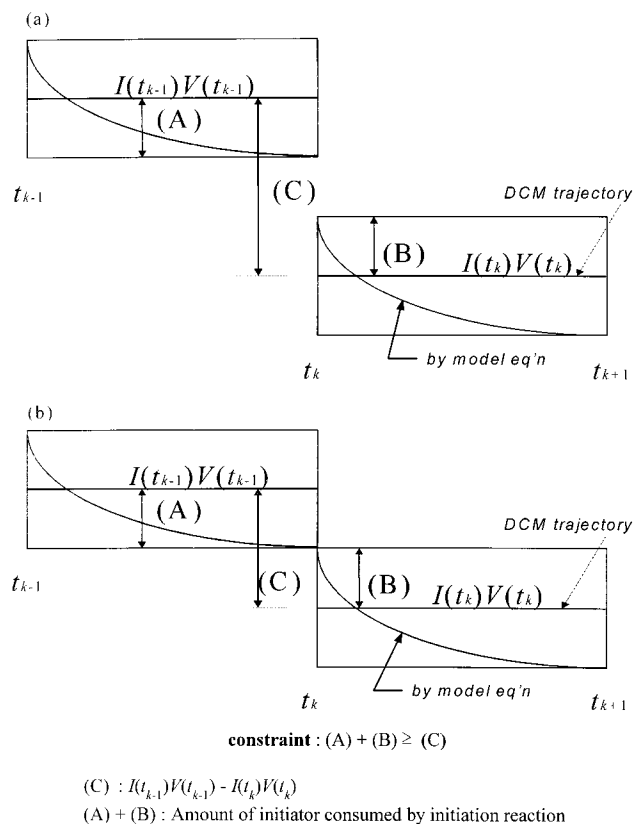


Figure 2 Constraint imposed on the scheme of calculating $I(t_k)$ that can be tracked by initiator feeding alone. (a) Constraint is not imposed. (b) Constraint is imposed.

is that it is practically impossible to decrease exclusively the initiator concentration without decreasing the concentrations of free radicals. Therefore, we impose the constraint that the initiator concentration should decrease within the range of self-consumption by the initiation reaction. In this way, we need not remove the initiator when tracking the descending part of trajectory.

The scheme of this constraint is depicted in Figure 2. Because the trajectory of initiator concentration is calculated by using the DCM, the initiator concentration remains constant during a certain time interval (e.g., 1 min). In Figure 2, $I(t_{k-1})$ and $I(t_k)$ represent the constant values of initiator concentration during their respective time intervals. Because the costate equation with final conditions develops backward, $I(t_{k-1})$ is calculated after $I(t_k)$ is determined. The problem comes into existence when the increased amount from $I(t_k)$ to $I(t_{k-1})$ exceeds the allowable limit, that can be tracked by feeding initiator alone, as illustrated in Figure 2a. Here it is assumed that

in each time interval, the volumes, $V(t_{k-1})$ and $V(t_k)$, remain constant and $I(\cdot)V(\cdot)$ represents the average value of the amount of initiator.

In the polymerization process, the initiator concentration decreases nearly exponentially during each time interval according to eq. (1). One may assume that $I(\cdot)V(\cdot)$ is the same as the arithmetic mean of the initial and final amounts of initiator in each time interval. As a result, one can determine the initial amount of initiator in each time interval from the given trajectory of initiator concentration. Then, the self-consumption of initiator in the neighborhood of time t_k can be expressed as the sum of one half of the decreased amount in the interval (t_{k-1}, t_k) and that in the interval (t_k, t_{k-1}) . In Figure 2, (A) and (B) represent the former and the latter, respectively, and (C) corresponds to the increased amount from $I(t_k)V(t_k)$ to $I(t_{k-1})V(t_{k-1})$. If (C) is larger than (A) + (B) as in Figure 2a, the constraint reduces $I(t_{k-1})$ until (C) becomes equal to (A) + (B) as shown in Figure 2b. Consequently, one can express the constraint by eqs. (20) and (21), where eq. (20) corresponds to Figure 2a. By equalizing the two sides of eq. (20), we obtain $I(t_{k-1})$ satisfying the constraint as given by eq. (21).

$$[I(t_{k-1})V(t_{k-1}) - I(t_k)V(t_k)] > 0.5\{I(t_{k-1})V(t_{k-1}) \times [1 - \exp(-k_d \times 60(\text{sec}))] + I(t_k)V(t_k) \times [1 - \exp(-k_d \times 60(\text{sec}))]\} \quad (20)$$

$$I(t_{k-1}) = \frac{1.5 - 0.5 \times \exp(-k_d \times 60(\text{sec}))}{0.5 + 0.5 \times \exp(-k_d \times 60(\text{sec}))} \times I(t_k) \times \frac{V(t_k)}{V(t_{k-1})} \quad (21)$$

Figure 3 shows the effect of applying the constraint. As a result of applying the constraint, the rate of decrease in the descending part of trajectory becomes smaller and the reaction time becomes longer in comparison to those without constraint. With the application of constraint one can implement the tracking control by feeding the initiator dissolved in solvent alone.

Initiator Feeding Scheme for Tracking the Trajectory of Initiator Concentration with Constraint

In order to implement the trajectory of initiator concentration one must keep the initiator concentration constant during a short time interval, but

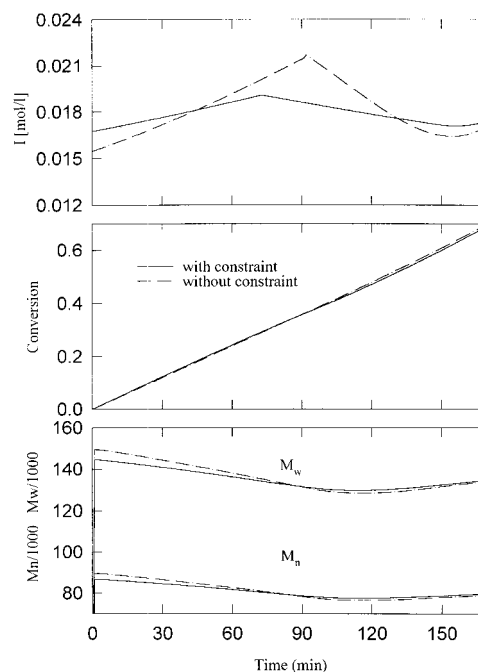


Figure 3 Comparison between the trajectories of initiator concentration with and without constraint ($X_d = 0.7$, $Mn_d = 80\,000$, $Mw_d = 136\,000$).

it is not an easy matter because of the continuous consumption of initiator. We therefore propose as an alternative that the constant value of the amount of initiator $I(\cdot)V(\cdot)$ in a short time interval be equal to the average value of the amount of initiator during that short time interval.

According to this scheme, the amount of initiator F_I to be fed at the beginning of each time interval can be calculated from the trajectory of initiator concentration and state variables as illustrated in Figure 4. Figure 4a corresponds to the case of ascending part of the trajectory. The amount $F_I(t_k)$ of initiator charged at the beginning of the k -th time interval (t_k, t_{k+1}) is calculated from $I(t_k)$ and $I(t_{k-1})$ as

$$F_I(t_k) = I(t_k)V(t_k) - I(t_{k-1})V(t_{k-1}) + 0.5\{I(t_{k-1})V(t_{k-1}) \times [1 - \exp(-k_d \times 60(\text{sec}))] + I(t_k)V(t_k) \times [1 - \exp(-k_d \times 60(\text{sec}))]\} \quad (22)$$

Figure 4b corresponds to the case of descending part of the trajectory and $F_I(t_k)$ can be calculated similarly as in the case of Figure 4a. Whereas Figure 4b shows the case in which the constraint is not imposed, Figure 4c represents the case in

which the constraint is imposed, where A and B in Figure 4b coincide with each other, and $F_I(t_k)$ becomes zero.

In actual experiment, the initiator dissolved in solvent is fed into the reactor by using a micropump. Here the volume of solvent added is assumed negligible compared to the total volume of the reaction mixture. Once the trajectory of $F_I(t_k)$ is given, the direct digital controller equipped with FIX-DMACS converts $F_I(t_k)$ to the period during which the micropump works from the beginning of every interval. The flow rate and the concentration of the initiator dissolved in solvent are kept constant over the time interval. Figure 5 depicts the mode of intermittent operation of pump. Here F_s denotes the amount of

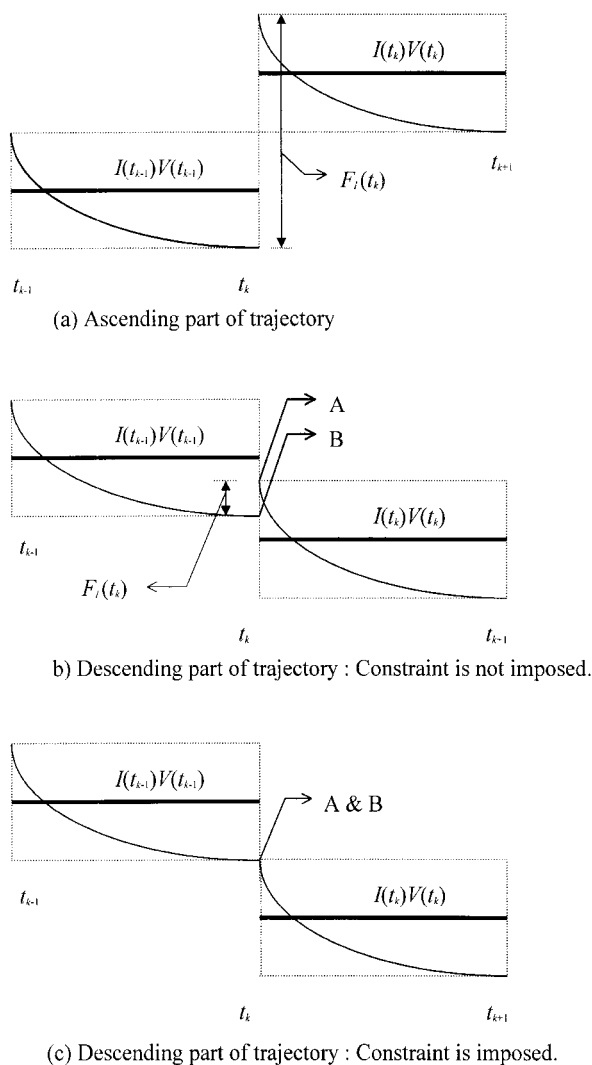


Figure 4 Amount of initiator to be fed (F_I) at the beginning of each time interval of 1 min.

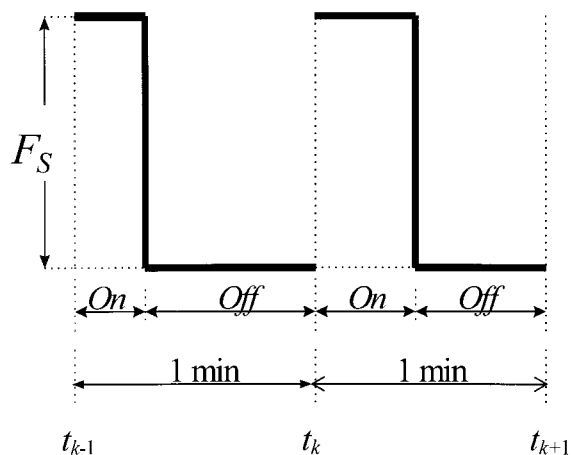


Figure 5 Schematic diagram of the initiator feeding scheme.

initiator charged per second. The pump works only during the period 'On' of each interval. The duration of the period 'On' of each interval is determined in proportion to the value $F_I(t_k)$.

Experimental

Figure 6 depicts the schematic diagram of the batch MMA polymerization reactor system equipped with initiator feeding device. The reactor has a volume of 2l. The jacket inlet temperature is manipulated by changing the ratio of flow-rates of hot and cold water supplied to the jacket by split-range control with cascade proportional-integral-derivative (PID) control algorithm. A stirrer with 2-blade 45° pitched-turbine is installed for mixing reactants and the agitation speed is maintained at 300 rpm by an inverter. An IBM 486 personal computer and programmable logic controller (PLC) (TI505) are used for data acquisition and control of the polymerization reactor system.

The monomer, MMA, is treated using 0.1M NaOH solution to remove the inhibitor and dissolved in the solvent, EA. The initiator, benzoylperoxide (BPO), is dissolved in chloroform and recrystallized in methanol to remove impurities and moisture. The initial charges of monomer, solvent and initiator are set at 0.8l, 0.8l, and 8.0g, respectively. The samples are taken out of the reactor at every 15 min and quenched with cold methanol.

The monomer conversion is determined by the gravimetric method, while the average molecular weights are measured by gel permeation chroma-

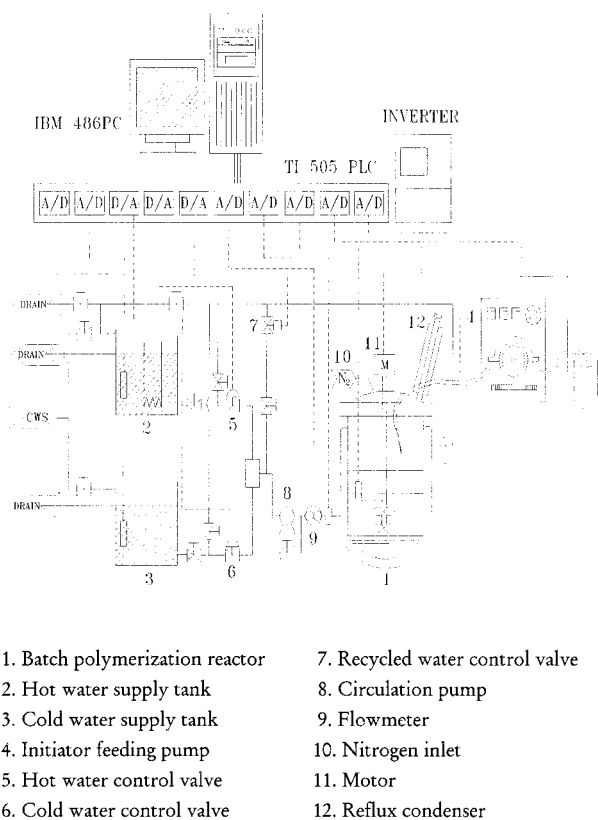


Figure 6 Schematic diagram of the polymerization reactor system equipped with the initiator feeding device.

tography (Waters GPC). The PMMA standards with narrow molecular weight distribution are used for the calibration of molecular weights vs. retention time of column set. The detailed experimental procedures are described elsewhere.¹²

RESULTS AND DISCUSSION

Here the constraint on the variation of initiator concentration is imposed and we obtain the trajectories of initiator concentration for two different cases that are specified in Table II, respectively. The trajectories (1) and (2) are presented in Figures 7a and 9a, respectively. In both cases, the reaction time becomes about 3 min longer and the slope of descending part becomes smaller in comparison to those without constraint.

To establish the validity of the initiator supplement policy proposed in this work, the time variation of the initiator concentration are calculated by applying this policy to the model and the result is compared with those of the original trajectory

Table II Target Values and Batch Time for Two Different Cases

Trajectory	X_d	Mn_d	Mw_d	PD_d	Batch Time (t_f)
Case (1)	0.7	80 000	136 000	1.7	170 min
Case (2)	0.7	100 000	170 000	1.7	228 min

with constraint in Figure 7a and Figure 9a. Here the solid curve represents the trajectory of initiator concentration calculated by using the optimal control theory, whereas the dash-dotted curve indicates the variation of initiator concentration obtained by simulating the proposed control scheme. The open circle represents the amount of initiator $F_I(t_k)$ to be fed from the beginning of every interval of 1 min to realize the proposed control scheme. It is noticed that the initiator concentration obtained by using the initiator supplement policy is consistently lower

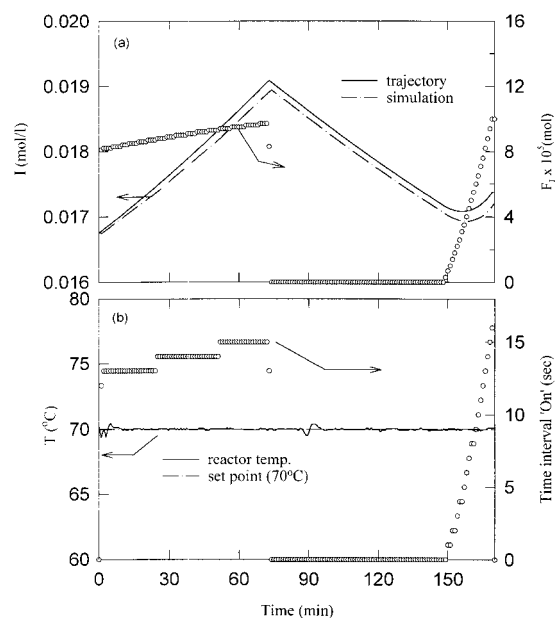


Figure 7 The results of tracking control for the Case (1) of Table II. (a) The optimal trajectory of initiator concentration calculated by the model (solid curve), the time profile of initiator concentration obtained by applying the initiator feeding scheme of this work (dash-dotted curve), and the variation in the amount of initiator to be fed (open circle). (b) The time profiles of the reactor temperature and the time interval 'On' for the initiator feed pump required to track the optimal trajectory.

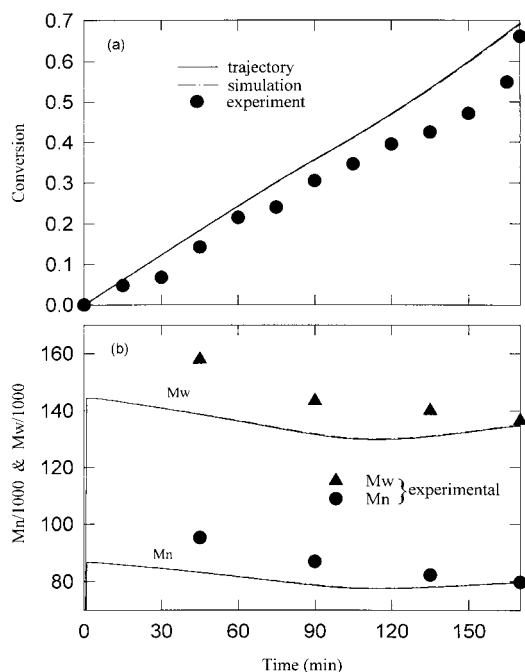


Figure 8 The time profiles of monomer conversion and average molecular weights obtained by simulation (dash-dotted curve) and by experiment (filled keys) for tracking control for the Case (1) of Table II.

than that of the original trajectory. This may be attributed to the fact that, instead of feeding the amount of initiator instantly at the beginning of each interval, the present policy makes the initiator fed continuously over the period 'On' of the interval as depicted in Figure 5.

Figure 7b shows the time variations of the reactor temperature and the time interval 'On' regulated by the micro pump to track the optimal trajectory. One may note that the cascade PID controller with fixed tuning keeps the reactor temperature at the setpoint (70°C) and the operating time of initiator feeding pump is nearly proportional to the amount $F_I(t_k)$ of initiator to be supplied. It is clearly seen that there is no need to supply additional initiator during the descending part of the trajectory.

The variation of monomer conversion is presented in Figure 8a. The solid curve, which results from the optimal trajectory of initiator concentration, coincides almost completely with the dash-dotted curve obtained by simulation with the initiator feeding scheme proposed in this work. The experimental data marked by the solid circles register more or less lower values than the two trajectories especially in the latter part of the reaction course. This discrepancy may be ascribed

to the imperfect mixing of initiator in the reaction mixture due to the effect of significantly increased viscosity. Another factor of this discrepancy may be the presence of a small amount of impurities in the reactor system that slows down the polymerization somewhat and increases the average molecular weights.

It is also shown in Figure 8b that the average molecular weights determined from the trajectory (solid curve) and by simulation with the initiator feeding scheme of this study (dash-dotted curve) overlap with each other. Here again, the experimental result marks higher values although both the number- and weight-average molecular weights reach their respective target values at the final time.

Figures 9 and 10 present the simulation and experimental results for the case of trajectory (2). Here the optimal trajectory of initiator concentration takes a more curved form and gives a longer reaction time because the desired average molecular weights are larger than in the previous case. The overall feature is found almost the same as in

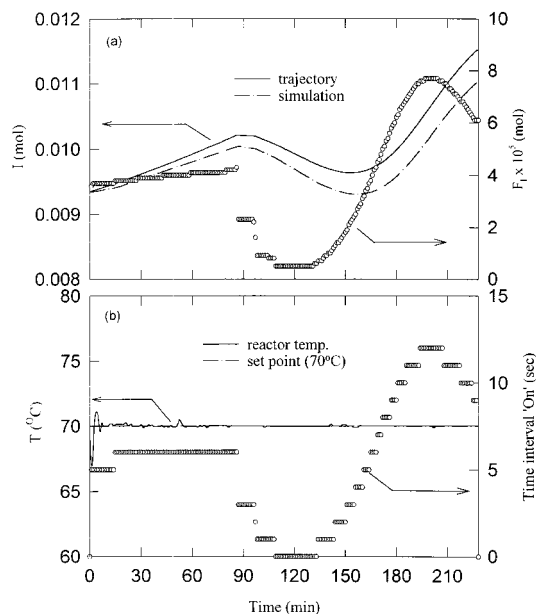


Figure 9 The results of tracking control for the Case (2) of Table II. (a) The optimal trajectory of initiator concentration calculated by the model (solid curve), the time profile of initiator concentration obtained by applying the initiator feeding scheme of this work (dash-dotted curve), and the variation in the amount of initiator to be fed (open circle). (b) The time profiles of the reactor temperature and the time interval 'On' for the initiator feed pump required to track the optimal trajectory.

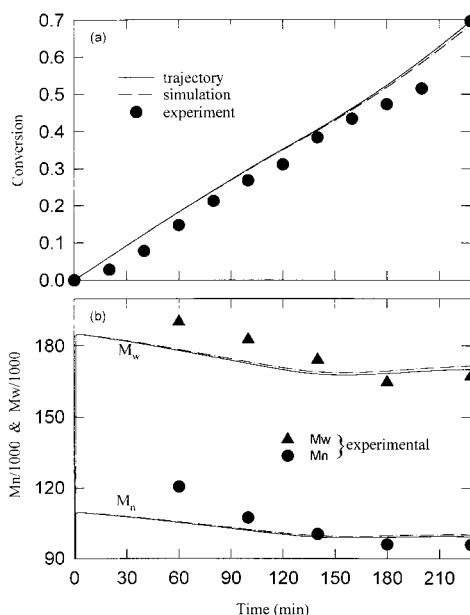


Figure 10 The time profiles of monomer conversion and average molecular weights obtained by simulation (dash-dotted curve) and by experiment (filled keys) for tracking control for the Case (2) of Table II.

Figures 7 and 8 with less discrepancy between the measured values and the simulation results.

These two examples clearly illustrate that the initiator feeding scheme proposed in this study can be applied effectively to produce polymer having desired average molecular weights by tracking control of the initiator concentration.

Although the computational scheme employed in this work requires substantial amount of computational work, implementation of trajectory tracking is fairly straightforward as demonstrated in this study. Therefore, if one has a good mathematical model that can describe the actual system adequately, the present approach certainly has a merit. In many cases, however, the physical properties of the polymer product may substantially differ from the desired values because of the model uncertainty and unknown disturbances. It is then necessary to develop an on-line optimization strategy that can update the trajectory efficiently using the measured states.

CONCLUSION

A detailed mathematical model for the batch MMA polymerization reactor system is developed, which takes into account the volume change of

the reactor contents and relaxes the pseudo steady state assumption for the moments of living polymer concentration.

With this model one can determine the optimal trajectory of initiator concentration required to produce polymer with desired number- and weight-average molecular weights at a prespecified conversion by applying the optimal control theory. To implement the optimal trajectory in practice an additional constraint has to be imposed on the variation of initiator concentration because the initiator concentration cannot be made to decrease faster than the rate of consumption by initiation reaction during the course of polymerization. Thus it is suggested to allow the trajectory to descend only at the rate of initiator consumption by initiation reaction if it is required to descend. This scheme is first validated by simulation study.

Tracking experiments are conducted on a wholly automated experimental reactor system with the initiator feed rate manipulated by using a micropump. The experimental results demonstrate that the tracking control performance is quite satisfactory despite the nonlinear features of the polymerization reactor system. Experimental values of the monomer conversion and average molecular weights of the final product are found to be in good agreement with their respective target values.

It is clearly illustrated that the polymer having desired average molecular weights can be produced by operating the batch reactor with the optimal initiator policy calculated from the model. The off-line approach proposed in this study could provide realistic recipes for industrial reactors and lay the groundwork for on-line adjustment of the trajectory. If a suitable on-line parameter estimation technique is combined with the initiator feeding scheme proposed in this work, the performance of the molecular weight distribution control will be remarkably improved under the model uncertainty and unknown disturbances. We expect that the experimental procedure and its realization by digital computer in this work may provide the basis for the advanced control of polymerization reactors.

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NOMENCLATURE

F_I the amount of initiator feeding [mol]
 F_S the amount of initiator charged per second-
 [mol/sec]

f	initiator efficiency [-]
G_k	k -th moment of living polymer concentration ($k = 0, 1, 2$) [mol/l]
I	initiator concentration [mol/l]
J	performance index [-]
k	reaction rate constant [s^{-1}] or [l/(mol · s)]
M	monomer concentration [mol/l]
M_m	molecular weight of monomer [g/mol]
M_n	number average molecular weight [g/mol]
M_s	molecular weight of solvent [g/mol]
M_w	weight average molecular weight [g/mol]
PD	polydispersity [-]
P_n	dead polymer of chain length n [mol/l]
t_f	final time [sec]
u	control input (initiator concentration trajectory) [mol/l]
V	volume of reaction mixture [l]
V_p	volume of polymer [l]
X	conversion of monomer [-]
x	state vector [-]

Greek Letters

ρ	weighting factor in eq. (19) or density [-] or [g/l]
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Subscripts

d	initiator decomposition or desired value
m	monomer
p	propagation reaction
t	termination
tc	termination by combination
td	termination by disproportionation
trm	chain transfer to monomer
trs	chain transfer to solvent

REFERENCES

1. Butala, D. N.; Liang, W. R. *J Appl Polym Sci* 1992, 44, 1759.
2. Chen, S. A.; Huang, N. W. *Chem Eng Sci* 1981, 36, 1295.
3. Hsu, K. Y.; Chen, S. A. *Chem Eng Sci* 1988, 43, 1311.
4. O'Driscoll, K. F.; Ponnuswamy, S. R. *J Appl Polym Sci* 1990, 39, 1299.
5. Secchi, A. R.; Lima, E. L.; Pinto, J. C. *Poly Eng Sci* 1990, 30, 19.
6. Sacks, M. E.; Lee, S. I.; Biesenberger, J. A. *Chem Eng Sci* 1972, 27, 2281.
7. Thomas, I. M.; Kiparissides, C. *Can J Chem Eng* 1984, 62, 284.
8. Louie, B. M.; Soong, D. S. *J Appl Polym Sci* 1985, 30, 3707.
9. Ponnuswamy, S. R.; Shah, S. L.; Kiparissides, C. A. *Ind Eng Chem Res* 1987, 26, 2229.
10. Hsu, K. Y.; Chen, S. A. *Chem Eng Sci* 1988, 41, 1311.
11. Chang, S. C.; Rho, H. J.; Rhee, H.-K. *Proc 10th Korea Automatic Control Conf, Vol. I*, 374, 1995.
12. Rho, H. J.; Kim, I. S.; Rhee, H.-K. *Hwahak Konghak* 1996, 34, 117.
13. Ahn, S. M.; Chang, S. C.; Rhee, H.-K. *J Appl Polym Sci* 1998, 69, 59.
14. Rho, H. J.; Huh, Y. J.; Rhee, H.-K. *Chem Eng Sci* 1998, 53, 3729.
15. Elicabe, C. E.; Meria, G. R. *Poly Eng Sci* 1989, 29, 374.
16. Chien, D. C. H.; Penlidis, A. *Chem Eng Sci* 1994, 49, 1855.
17. Scali, C.; Morretta, M.; Semino, D. *J Proc Cont* 1997, 7, 357.
18. Schmidt, A. D.; Ray, W. H. *Chem Eng Sci* 1981, 36, 1401.
19. Lewis, F. L. *Applied Optimal Control and Estimation*; Prentice-Hall: Englewood Cliffs, New Jersey, 1992.