

Application of Optimal Temperature Trajectory to Batch PMMA Polymerization Reactor

SUNG-MO AHN, SOON-CHEOL CHANG, HYUN-KU RHEE

Department of Chemical Engineering, Seoul National University, Kwanak-ku, Seoul 151-742, Korea

Received 16 May 1997; accepted 3 September 1997

ABSTRACT: A mathematical model is developed for the polymerization of methyl methacrylate (MMA) in a batch reactor. The model includes chain transfers to the monomer and solvent and termination by both combination and disproportionation and also takes into account the density change of the reactor contents and the gel effect. The usual pseudo-steady-state assumption is relaxed here. The validity of the proposed model is tested by an isothermal experiment of batch PMMA polymerization. Indeed, the experimental results show that the proposed model can describe the real polymerization system very well in view of both monomer conversion and average molecular weights. The optimal control theory is applied together with Pontryagin's minimum principle to calculate the optimal temperature trajectory for a batch polymerization reactor system which would lead to a polymer product having the desired properties set *a priori*. The performance index of the control system is composed of three factors—the desired monomer conversion and number- and weight-average molecular weights. The desired values of number- and weight-average molecular weights are obtained at a specified monomer conversion within acceptable error ranges. Control experiments are conducted to track the optimal temperature trajectory obtained from the model and the results are found to be in good agreement with the desired values. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 59–68, 1998

Key words: methyl methacrylate (MMA); batch free-radical polymerization; temperature trajectory; optimal control theory; control experiment

INTRODUCTION

The batch polymerization process is widely used in industries for its availability and flexibility in operation. The main objective of the industrial batch polymerization reactor operation is to control the reactor temperature or initiator feed rate so as to track a predetermined trajectory which is obtained *a priori*. One of the potential approaches for determining the recipe is to use polymerization models along with optimal control methodologies. The optimal control theory has been applied by several authors to determine the

recipe that minimizes the reaction time and produces a polymer with a desired average molecular weight and molecular weight distribution.^{1–5} Application of the optimal control theory to the mathematical model results in a two-point boundary value problem that requires a great deal of iterative calculation. Therefore, most of the investigators have simplified the model by introducing assumptions such as constant density of the reactor contents, no chain transfer to monomer, termination by disproportionation only, and a pseudo-steady-state for a living polymer.

Hicks et al.¹ attempted to solve the optimal control problem using two control variables, temperature and initiator concentration, in vain due to severe computational problems. The minimum principle was applied to a polymerization reactor

Correspondence to: H.-K. Rhee.

by Yosimoto et al.² but they used a simple model which did not take into account the gel effect. More recently, Chang and Lai³ modified the two-step method to find an algorithm that could be used in real polymerization systems. The approach, however, was not corroborated by experiment. Application of the minimum principle to the free-radical polymerization reactor can be found in the work of Thomas and Kiparissides.⁴ These authors minimized the performance index representing the deviation of conversion and those of the zero moment and second moment of the dead polymer concentration and thereby obtained the optimal temperature trajectory that would give a polymer product having the desired average molecular weights set *a priori*. O'Driscoll and Ponnuswamy⁵ applied the same methodology to the free-radical polymerization reactor including the cost of the initiator in the performance index. These studies were commonly confined to the cases of simple models with simple correlations for the gel effect and left out the experimental validation of their approaches.

Despite all these theoretical developments, there have been only a few published reports on the actual implementation of such optimal policies to the polymerization reactor systems. The minimum end-time problem for the free-radical solution polymerization of styrene in a batch reactor was studied by Chen and Huang.⁶ Experimental verification of their theoretical findings revealed that an appreciable deviation existed between experimental and calculated average molecular weights. Ponnuswamy et al.⁷ developed an alternative procedure which substantially simplified the calculation of the optimal policies. These authors demonstrated that the optimal temperature policies obtained from the simplified model were almost identical with those calculated by the gradient method. However, the calculated optimal temperature trajectory was close to the isothermal one because the gel effect was not taken into account.

In a recent study, Maschio et al.⁸ corroborated their model by experiment and used it to obtain the optimal temperature trajectory that would yield the assigned values of the weight-average molecular weight and minimum polydispersity. But the optimal policy was not implemented experimentally. Scali et al.⁹ determined an optimal temperature profile that guarantees products having a controlled molecular weight distribution and the desired values of average molecular

weights. Here, only a simplified version of the optimal temperature profile was implemented.

From the review of earlier works, it is apparent that what is in demand is not only a more rigorous mathematical treatment of the optimal control problem but also the actual implementation of the approach on the polymerization reactor systems.

In this study, we aimed to develop a more elaborate model for a batch PMMA polymerization reactor and applied the optimal control theory to the model to calculate the optimal temperature trajectory that would produce the polymer product with the desired number- and weight-average molecular weights at a prespecified monomer conversion. The main objective was to demonstrate experimentally that the optimal temperature trajectory can be tracked by applying the conventional PID control algorithm and that this optimal policy really yields a polymer product having desired properties set *a priori*.

MODEL DEVELOPMENT

The bulk and solution polymerization of methyl methacrylate in a batch reactor is considered with benzoyl peroxide (BPO) as the initiator. The reaction kinetics are assumed to follow the free-radical polymerization mechanism including chain-transfer reactions to both solvent and monomer. The free-radical polymerization mechanism is summarized in Table I.

Table I Free-radical Polymerization Mechanism

Initiation	$I \xrightarrow{k_d} 2\varphi \cdot$
	$\varphi \cdot + M \xrightarrow{k_i} R_1 \cdot$
Propagation	$R_1 \cdot + M \xrightarrow{k_{p1}} R_2 \cdot$
	$R_j \cdot + M \xrightarrow{k_{pj}} R_{j+1} \cdot$
Termination by combination	$R_i \cdot + R_j \cdot \xrightarrow{k_{tc}} P_{i+j}$
Termination by disproportionation	$R_i \cdot + R_j \cdot \xrightarrow{k_{td}} P_i + P_j$
Chain transfer to monomer	$R_i \cdot + M \xrightarrow{k_{trm}} P_i + R_1 \cdot$
Chain transfer to solvent	$R_i \cdot + S \xrightarrow{k_{trs}} P_i + S \cdot$

From the above mechanism, the following mass balance equations can be derived for each of initiator, monomer, and solvent:

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

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

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

in which V denotes the volume of the reaction mixture, and I , M , S , and G_0 represent the concentrations of initiator, monomer, solvent, and living polymer, respectively.

The method of moments was adopted to calculate the number-average molecular weight (M_n) and the weight-average molecular weight (M_w). The definitions of the moments are as follows:

$$G_k = \sum_{n=1}^{\infty} n^k R_n(t) \quad k = 0, 1, 2 \quad (4)$$

$$F_k = \sum_{n=1}^{\infty} n^k P_n(t) \quad k = 0, 1, 2 \quad (5)$$

where G_k and F_k are the k th moments of living and dead polymer concentrations, respectively. One can derive balance equations for the first three moments of the living polymer and dead polymer concentrations as follows:

$$\frac{1}{V} \frac{d(G_0 V)}{dt} = 2fk_d I - k_t G_0^2 \quad (6)$$

$$\frac{1}{V} \frac{d(G_1 V)}{dt} = 2fk_d I + k_p M G_0 - k_t G_0 G_1 + (k_{trm} M + k_{trs} S)(G_0 - G_1) \quad (7)$$

$$\frac{1}{V} \frac{d(G_2 V)}{dt} = 2fk_d I + k_p M(G_0 + 2G_1) - k_t G_0 G_2 + (k_{trm} M + k_{trs} S)(G_0 - G_2) \quad (8)$$

$$\frac{1}{V} \frac{d(F_0 V)}{dt} = \frac{1}{2} (k_t + k_{td}) G_0^2 + (k_{trm} M + k_{trs} S) G_0 \quad (9)$$

$$\frac{1}{V} \frac{d(F_1 V)}{dt} = k_t G_0 G_1 + (k_{trm} M + k_{trs} S) G_1 \quad (10)$$

$$\frac{1}{V} \frac{d(F_2 V)}{dt} = k_{tc} (G_0 G_2 + G_1^2) + k_{td} G_0 G_2 + (k_{trm} M + k_{trs} S) G_2 \quad (11)$$

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, that is:

$$\frac{dV_p}{dt} = -\frac{1}{\rho_p} \left[W_m \frac{d(MV)}{dt} + W_s \frac{d(SV)}{dt} + V_p \frac{\partial \rho_p}{\partial T} \frac{dT}{dt} \right] \quad (12)$$

$$V_m = (MV) \frac{W_m}{\rho_m}, \quad V_s = (SV) \frac{W_s}{\rho_s} \quad (13)$$

In this study, the gel effect is taken into account by introducing the free-volume correlations proposed by Schmidt and Ray.¹⁰ The propagation and termination rate constants for the PMMA polymerization reaction system may be expressed as

$$k_p = g_p k_{p0}, \quad k_t = g_t k_{t0} \quad (14)$$

$$g_p = \begin{cases} 1.0, & V_f > V_{fpc} \\ 7.1 \times 10^{-5} \exp(171.53 V_f), & V_f \leq V_{fpc} \end{cases} \quad (15)$$

where $V_{fpc} = 0.05$

$$g_t = \begin{cases} 0.10575 \exp(17.15 V_f - 0.01715 \\ \quad \times (T - 273.15)), & V_f > V_{fpc} \\ 0.23 \times 10^{-5} \exp(75 V_f), & V_f \leq V_{fpc} \end{cases} \quad (16)$$

where $V_{fpc} = 0.1856 - 0.2956 \times 10^{-3} (T - 273.15)$. Here, g_p and g_t are the gel effect correlation coefficients and subscript 0 denotes the value at zero conversion. V_{fpc} and V_{fsc} are the critical free volumes, at which the diffusion-controlled reaction begins. The free volume of the mixture is determined by the weighted sum, that is:

$$V_f = 0.025 + \alpha_p (T - T_{gp}) \Phi_p + \alpha_m (T - T_{gm}) \Phi_m + \alpha_s (T - T_{gs}) \Phi_s \quad (17)$$

in which α_i is the difference between the thermal expansion coefficients above and below the glass transition temperature T_{g_i} , and Φ_i is the volume fraction of the component i in the solution. The subscripts p , m , and s denote the polymer, monomer, and solvent, respectively.

The present model is an improved one in the sense that the density change of the reactor contents is taken into account and the usual pseudo-steady-state assumption for moments of the living polymer concentrations is relaxed. The physical and mechanical properties of polymers are related to number- and weight-average molecular weights. These properties can be obtained from the moment equations of living and dead polymer concentrations. Based on the mass balance equations, the number- and weight-average molecular weights and polydispersity are defined by the following equations:

$$Mn = W_m \times \frac{(G_1 + F_1)}{(G_0 + F_0)} \quad (18)$$

$$Mw = W_m \times \frac{(G_2 + F_2)}{(G_1 + F_1)} \quad (19)$$

$$PD = \frac{Mw}{Mn} \quad (20)$$

The physical properties and the kinetic parameters are taken from the literature¹⁰⁻¹² and are listed in Table II.

FORMULATION OF OPTIMAL CONTROL PROBLEM

The mass balance equations can be rearranged to give the following set of ordinary differential equations:

$$\begin{aligned} \frac{dx}{dt} &= f(x, u, t), \quad x(t_0) = x_0 \\ x &= [I, M, S, G_0, G_1, G_2, F_0, F_1, F_2, V_p] \\ u &= \text{control input} \end{aligned} \quad (21)$$

If the control input u is chosen, the solution for the above set of equations is determined with an initial condition x_0 . An admissible control input $u^*(t)$ should be formed in such a way that the performance index J , defined by the following equation, is minimized:

Table II Parameters Used in the Model for MMA Polymerization

Parameters	Values	Reference
<u>Physical properties</u>		
W_m [g/mol]	100.12	11
W_s [g/mol]	88.11	11
W_I [g/mol]	242.23	11
	$965.4 - 1.09T - 9.7$	
ρ_m [g/L]	$\times 10^{-4} T^2$	11
ρ_s [g/L]	$925.0 - 1.239T$	11
ρ_p [g/L]	$1180.0 - 1.0T$	11
T_{g_m} [K]	167.15	10
T_{g_s} [K]	181.15	10
T_{g_p} [K]	387.15	10
α_m [K ⁻¹]	1.0×10^{-3}	10
α_s [K ⁻¹]	1.0×10^{-3}	10
α_p [K ⁻¹]	4.8×10^{-4}	10
<u>Rate constants</u>		
	1.25×10^{18}	
k_d [s ⁻¹]	$\exp(-35473/RT)$	12
	2.94×10^6	
k_{p0} [L mol ⁻¹ s ⁻¹]	$\exp(-5656/RT)$	12
	5.20×10^8	
k_{t0} [L mol ⁻¹ s ⁻¹]	$\exp(-1394/RT)$	12
	1.83×10^{27}	
k_{td0}/k_{t0}	$\exp(-44467/RT)$	12
	9.32×10^4	
k_{trm} [L mol ⁻¹ s ⁻¹]	$\exp(-13971/RT) \times k_p$	12
	8.79×10^{-5}	
k_{trs} [L mol ⁻¹ s ⁻¹]	$\exp(-42.6/RT) \times k_p$	12

$$\begin{aligned} J(t_f) &= \omega_1 \left[\frac{X(t_f)}{X_d} - 1 \right]^2 + \omega_2 \left[\frac{Mn(t_f)}{Mn_d} - 1 \right]^2 \\ &\quad + \omega_3 \left[\frac{Mw(t_f)}{Mw_d} - 1 \right]^2 \end{aligned} \quad (22)$$

where X and ω_i denote the monomer conversion and the weighting factor, respectively. The subscript d represents the desired value to be obtained at the final time, t_f . The control input $u^*(t)$ that minimizes the performance index is called the optimal control input and then $x^*(t)$ is the optimal trajectory.

Solution of the optimal control problem can be obtained by solving the two-point boundary value problem with initial boundary conditions for the state equation and the final boundary conditions for the costate equation, while minimizing the Hamiltonian.¹³ It should be noted that optimal

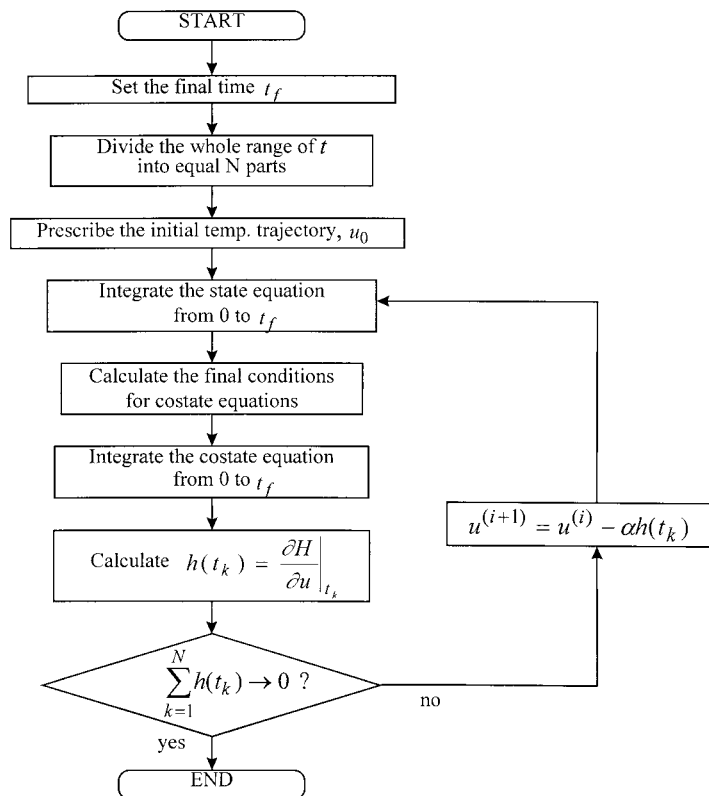


Figure 1 Flow chart to calculate the optimal temperature trajectory.

control may not exist, and even if it exists, it may not be unique. The calculation procedure to determine the optimal control $u^*(t)$ is described in Figure 1, in which H denotes the Hamiltonian.

EXPERIMENTAL

Figure 2 shows the schematic diagram of the batch PMMA polymerization reactor system used in this study. The jacketed stainless-steel reactor has a capacity of 2 L and is equipped with a 45° pitched-turbine stirrer for the mixing of the reactants. An inverter is adopted to maintain the stirring speed at 300 rpm. The reactor temperature is controlled by regulating the flow rates of hot and cold water supplied to the jacket by a split-range control and a cascade PID control algorithm. Part of the coolant is recirculated to reduce disturbance in the jacket temperature. An IBM 486 personal computer and PLC(TI505) are employed for data acquisition and control of the polymerization reactor system.

The methyl methacrylate is treated by using a 0.1M NaOH solution to remove the inhibitor. The

solvent is ethyl acetate and the initiator is benzoyl peroxide (BPO), which is dissolved in chloroform and then recrystallized in methanol to remove impurities. Nitrogen is bubbled through the reaction mixture for about 1 h to purge the monomer and solvent of oxygen.

The samples taken out every 15 min are quenched with cold methanol. The monomer conversion is determined by the gravimetric method while the average molecular weights are measured by gel permeation chromatography, a Waters GPC system equipped with an RI detector, and two Ultrastyrigel columns (Styrigel HR4, HR5E). For column calibration, PMMA standards with a narrow molecular weight distribution are used. The essential features of the polymerization reactor system and the more detailed experimental procedure are described elsewhere (see Rho et al.¹⁴).

MODEL VALIDATION

The proposed model is tested for its validity by conducting polymerization reaction experiments

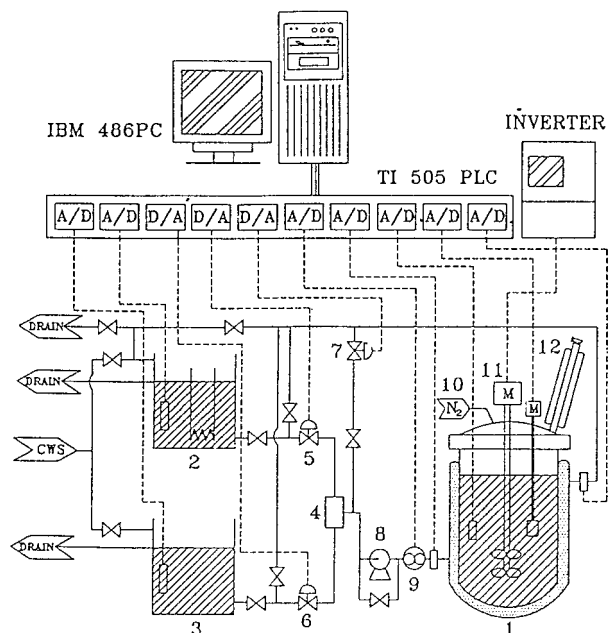


Figure 2 Schematic diagram of the polymerization reactor system: (1) batch polymerization reactor; (2) hot water supply tank; (3) cold water supply tank; (4) mixing chamber; (5) hot water control valve; (6) cold water control valve; (7) recycled water control valve; (8) circulation pump; (9) flowmeter; (10) N_2 inlet; (11) motor; (12) reflux condenser.

under the isothermal conditions and comparing the results with the model predictions. Figure 3 shows the comparison between the experimental (filled keys) and simulation (curves) results at three different temperatures. In all cases, the two are in fairly good agreement not only in terms of the monomer conversion but also in view of the number- and weight-average molecular weights. Good agreement between the experimental results and the model predictions is again confirmed in Figure 4, which presents the results obtained at 70°C with three different initial charges of the initiator. Therefore, it may be concluded that the model developed in this study is adequate to describe the batch PMMA polymerization reactor system under consideration.

RESULTS AND DISCUSSION

The target is to obtain a product having the desired monomer conversion (X_d), the number-average molecular weight (Mn_d), and the weight-average molecular weight (Mw_d). The optimal temperature trajectory is obtained by applying the

iterative scheme shown in Figure 1 to the mathematical model developed in this study. The initial temperature trajectory is assumed to be the isothermal one.

Figure 5 shows the progressive change of the temperature trajectory as the iteration number increases when X_d , Mn_d , and Mw_d are specified *a priori* as 0.7, 100,000, and 175,000, respectively. In this case, the initial temperature trajectory is set at 70°C and the total reaction time is 223 min. As the iteration number increases, the trajectory becomes more curved and converges to the optimal trajectory after 22 iterations. The discrepancy between the desired and calculated values of Mn and Mw depends on the number of iterations. In this case, the calculated values converge to the desired ones within the range of 1% error after 22 iterations. In actual application, however, tighter tolerance is recommended because of experimental inaccuracy and unknown disturbance.

Presented in Figure 6 are the temperature tra-

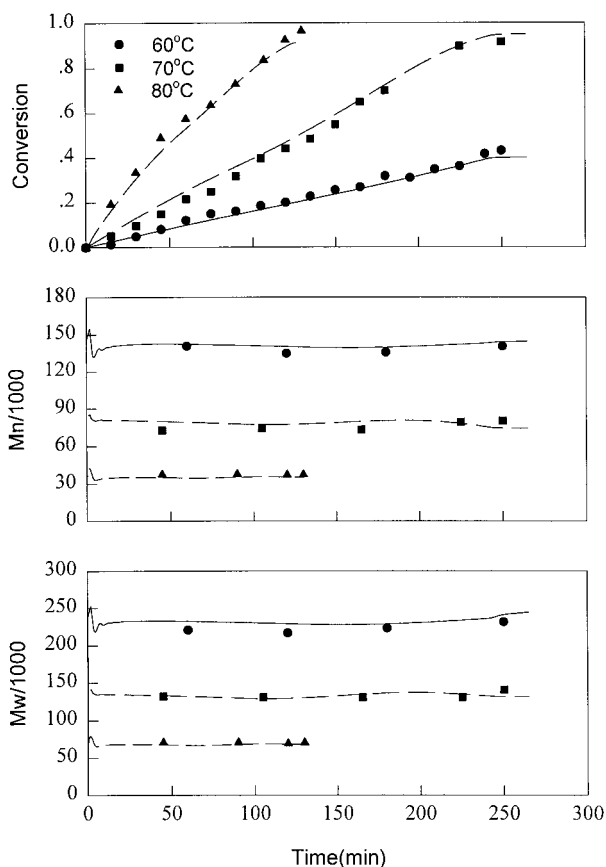


Figure 3 Experimental results (filled keys) compared to the model predictions (curves) under various isothermal conditions. Monomer: 0.8 L; solvent: 0.8 L; initiator: 8.0 g.

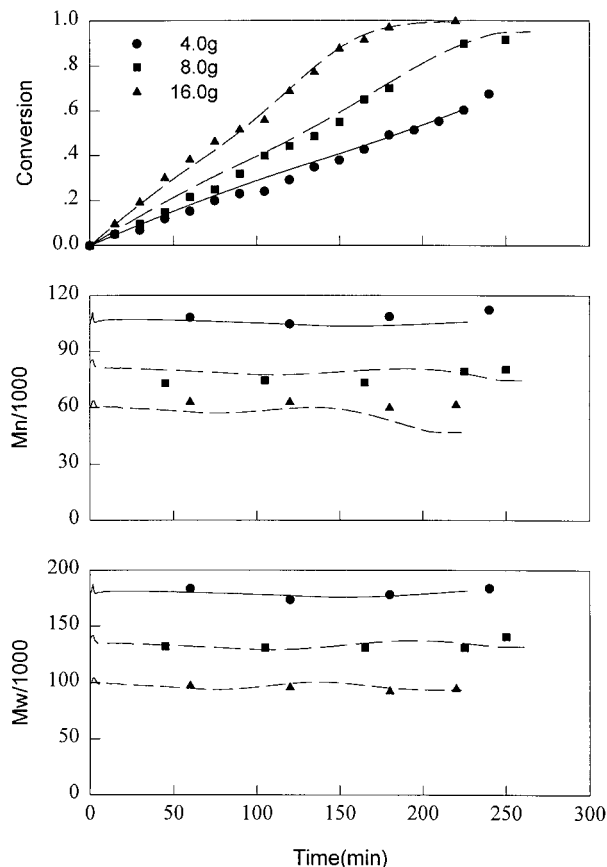


Figure 4 Comparison between the experimental (filled keys) and simulation (curves) results obtained at the reaction temperature of 70°C with three different initial charges of initiator. Monomer: 0.8 L; solvent: 0.8 L.

jectories and the corresponding variations in the monomer conversion and the number- and weight-average molecular weights obtained for different values of prespecified number- and weight-average molecular weights. Here, the conversion and polydispersity are set to be 0.7 and 1.75, respectively, at the final time t_f . In the computational procedure, the trajectory tends to diverge if t_f becomes smaller than a certain value, which we call here the minimum reaction time. The results shown in Figure 6 are all for their respective minimum reaction time. As the desired value of the number-average molecular weight increases, the trajectory consistently maintains a lower temperature and the minimum reaction time becomes longer.

When the desired monomer conversion is fixed at $X_d = 0.8$, the temperature trajectories for various desired molecular weights are shown in Figure 7. In this case, the desired polydispersities

are 1.7, 1.8, and 2.0, respectively. As the desired polydispersity increases, the temperature trajectory tends to assume a higher temperature and to take a more curved form. From this result, it may be deduced that a somewhat severe variation of the reaction temperature would be required for the production of a polymer with a broad molecular weight distribution.

The calculated optimal temperature trajectories are implemented on the batch PMMA polymerization reactor system with the cascade PID controller. Figures 8 and 9 show the results of on-line digital control experiments for tracking two of the optimal temperature trajectories obtained in this study. The PID control algorithm with fixed tuning performs quite satisfactorily for the temperature control in both cases. Table III shows a comparison between the measured and the desired values of number- and weight-average molecular weights.

For the experiment to track the first trajectory (cf. Fig. 8), the PID controller can track the opti-

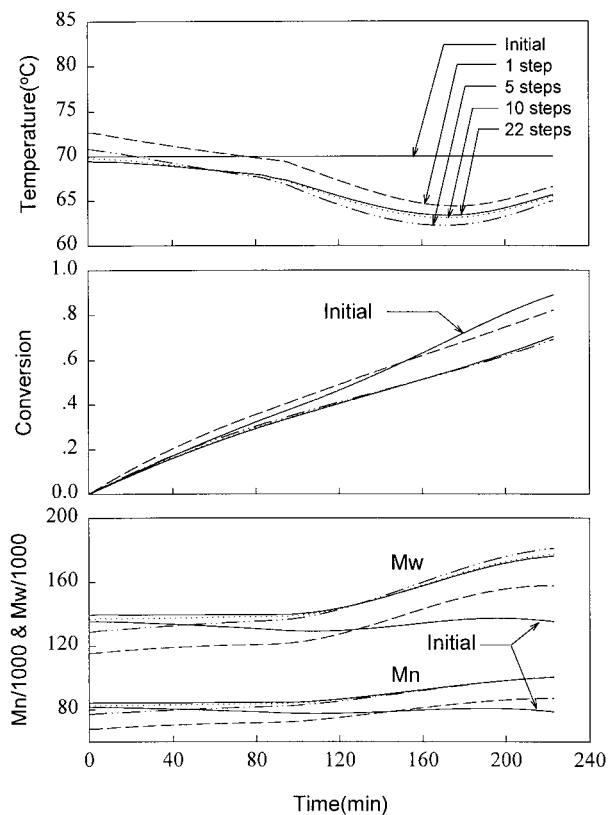


Figure 5 Progressive change of the temperature trajectory and corresponding variations in monomer conversion and average molecular weights as the iteration number increases. $X_d = 0.7$, $Mn_d = 100,000$; $Mw_d = 175,000$.

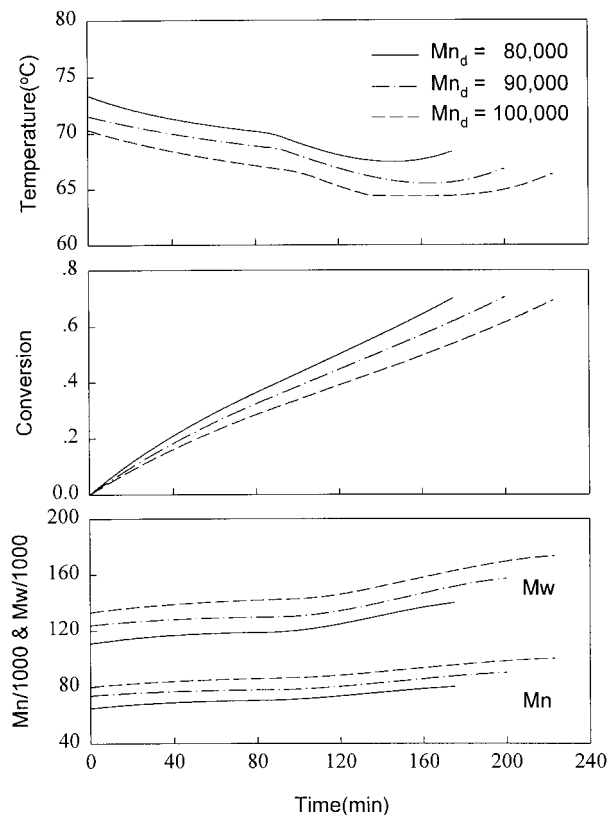


Figure 6 Optimal temperature trajectories and corresponding variations in monomer conversion and average molecular weights for various values of Mn_d where both the desired monomer conversion and polydispersity are fixed at $X_d = 0.7$ and $PD_d = 1.75$.

mal trajectory quite satisfactorily and the offset between the reactor temperature and the set point is kept very small throughout the course of the reaction. At the final time $t_f = 175$ min, the measured values of the average molecular weights are indeed in good agreement with their desired values within the error range less than 4%. This error range may be considered reasonable if one takes into account the measurement precision of GPC.

In Figure 9, the temperature trajectory takes a more curved form than the previous one. Although some offset occurred at the initial stage of the reaction due mainly to the abrupt change in the temperature trajectory, the control performance for tracking the set point appears to be fairly good. The discrepancy between the measured values and desired values of the average molecular weights turns out to be less than 5% at the final time $t_f = 98$ min.

It is also noticed in Figures 8 and 9 that simula-

tion results are in reasonably good agreement with experimental data during the course of the reaction not only in terms of the monomer conversion but also in view of the average molecular weights. The rate of heat generation computed by the model is plotted against the reaction time in the middle parts of Figures 8 and 9. From this plot, one can see when the gel effect becomes significant. As a whole, the strategy of the optimal temperature trajectory is proved to be effective for producing polymers with desired properties.

Although the computational scheme employed in this work requires a rather long computing time, implementation of trajectory tracking is fairly straightforward as demonstrated here. Therefore, if one has a good mathematical model that can describe the actual system adequately, the present approach certainly has 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

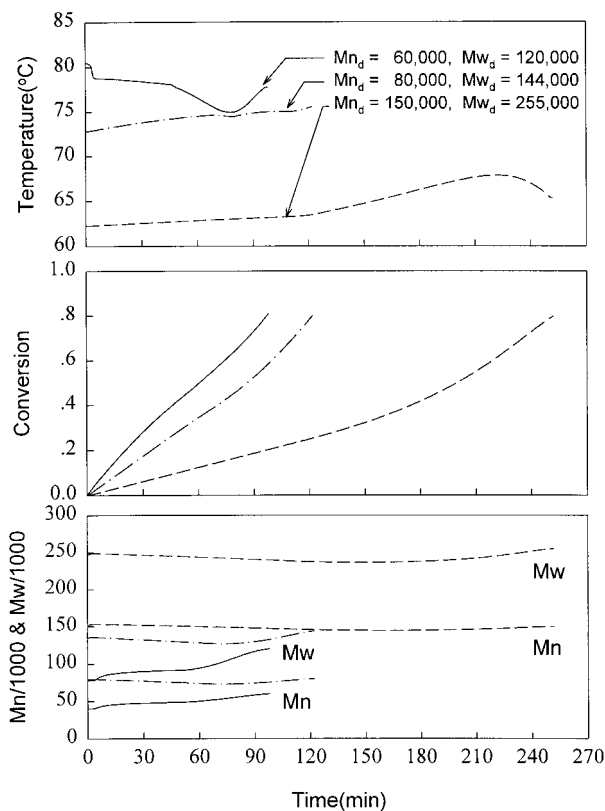


Figure 7 Optimal temperature trajectories and corresponding variations in monomer conversion and average molecular weights for various values of the desired average molecular weights when the desired conversion is fixed at $X_d = 0.8$.

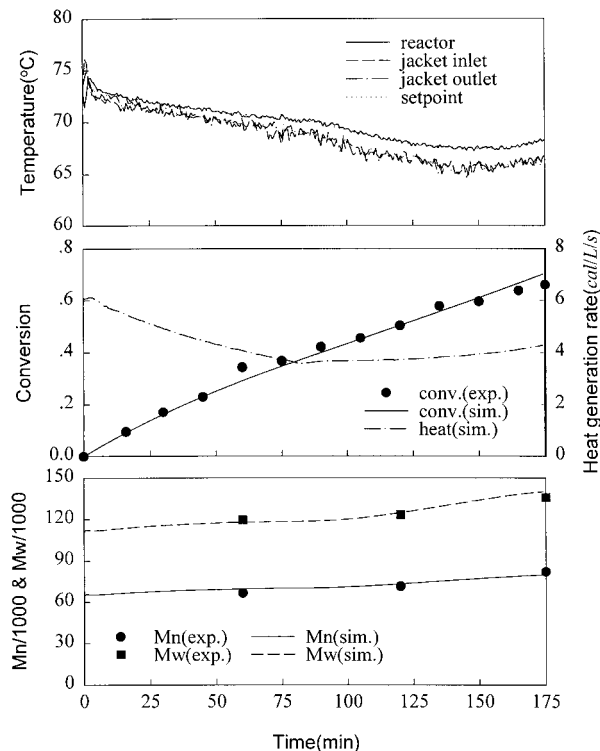


Figure 8 Experimental results for tracking the optimal temperature trajectory when $X_d = 0.7$, $Mn_d = 80,000$, and $Mw_d = 140,000$.

to develop an on-line optimization strategy which can update the trajectory efficiently using the measured states.

CONCLUDING REMARKS

A mathematical model is developed for the batch PMMA polymerization reactor system. In the present model, the density change of the reactor contents is taken into consideration and the pseudo-steady-state assumption for moments of living polymer concentrations is relaxed. Experimental results show that the proposed model is adequate to describe the batch polymerization reactor system in view of both monomer conversion and average molecular weights.

Application of the optimal control theory plus Pontryagin's minimum principle to the model leads to a computational scheme for the optimal temperature trajectory required to produce a polymer with desired number- and weight-average molecular weights at a prespecified conversion. The optimal temperature trajectory takes different patterns depending upon the desired average

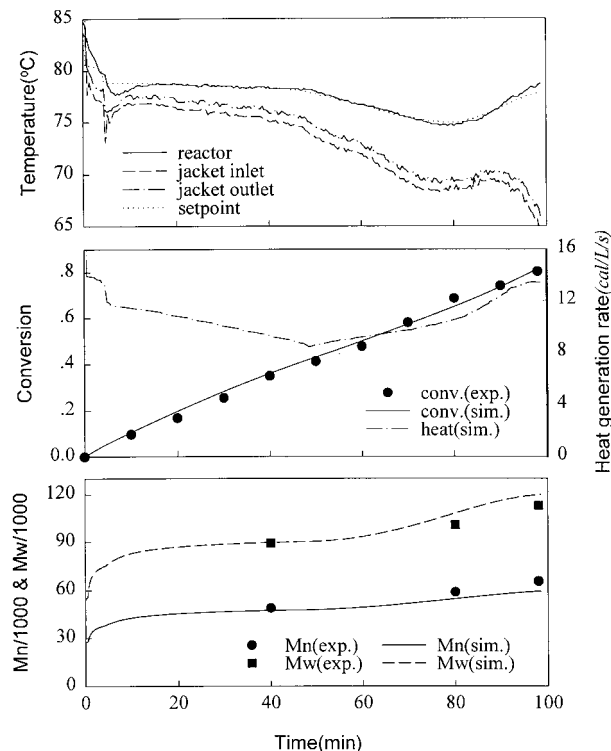


Figure 9 Experimental results for tracking the optimal temperature trajectory when $X_d = 0.8$, $Mn_d = 60,000$, and $Mw_d = 120,000$.

molecular weights specified *a priori*. The desired values of number- and weight-average molecular weights can be reached within a desired error range.

This optimal policy was implemented on a fully automated experimental reactor system. The control performance for tracking the optimal temperature trajectory is found to be quite satisfactory and experimental values of the conversion and average molecular weights turn out to be in good agreement with their respective desired values.

In conclusion, the polymer product having desired molecular weights can be obtained by op-

Table III Comparison Between Measured and Desired Values of Mn and Mw

		Measured Value	Desired Value	Error (%)
Figure 8	Mn	82,142	80,000	2.6
	Mw	135,780	140,000	3.6
Figure 9	Mn	62,759	60,000	4.5
	Mw	114,335	120,000	4.7

erating the batch reactor in such a way that the reactor temperature may track the optimal temperature trajectory calculated by the mathematical model.

NOMENCLATURE

F_k	k -th moment of dead polymer concentration ($k = 0, 1, 2$)
f	initiator efficiency
G_k	k -th moment of living polymer concentration ($k = 0, 1, 2$)
g_p	propagation gel effect correlation factor
g_t	termination gel effect correlation factor
I	initiator or its concentration
J	performance index
k	rate constant
M	monomer or its concentration
M_n	number-average molecular weight
M_w	weight-average molecular weight
PD	polydispersity
P_i	dead polymer of chain length i
R_i	living polymer of chain length i
S	solvent or its concentration
T	temperature
T_g	glass transition temperature
t	time
t_f	final time
u	temperature trajectory
V	volume of reaction mixture
V_f	free volume
V_{fpc}	critical free volume for propagation reaction
V_{ftc}	critical free volume for termination reaction
W	molecular weight
X	conversion

Greek Letters

α	difference in thermal expansion coefficient
ρ	density
Φ	volume fraction
ω	weighting factor in eq. (22)

Subscripts

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

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Automation Research Center at Pohang University of Science and Technology.

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