

## Computation of Near-Optimal Control Policies for Free-Radical Polymerization Reactors

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### Synopsis

A polymer is characterized by the average degree of polymerization and the molecular weight distribution. Approximate optimization of temperature control, or catalyst feed rate control, or both are performed to attain not only the desired average degree of polymerization but also the desired molecular weight distribution. This near-optimal policy, which is a function of time only for a batch polymerization reactor, is first expressed by a polynomial, and the coefficients of the polynomial are estimated by a pattern search technique. This coefficient's estimation method coupled with a nonlinear search technique was found to be suitable for solving this type of our optimization problem involving complex chemical kinetics.

### INTRODUCTION

Many physical properties of a polymer are related to the average degree of polymerization and the molecular weight distribution (MWD). Because the MWD is a function of the reaction conditions, namely, temperature, catalyst (initiator) concentration, and monomer concentration, one or more of these variables must be manipulated to control the polymerization.

In principle, the MWD of a polymer can be narrowed by maintaining the instantaneous average degree of polymerization (DP) constant throughout the polymerization reaction, or by maintaining the instantaneous kinetic chain length, that is, the ratio of the propagation rate to the initiation rate, constant. Hoffman et al.<sup>1</sup> considered the problem of maintaining the DP constant by feeding the monomer or catalyst. Tadmor and Bisenberger<sup>2</sup> also kept DP constant to obtain a narrower MWD. Hoffman's treatment is not applicable to the more complicated case in which the reaction kinetics involve a chain transfer. Osakada<sup>3</sup> and Shiotsuka and Terauchi<sup>4</sup> applied Hoffman's treatment to a general case with more complex reaction kinetics to obtain the desired polymer. Shiotsuka and Terauchi<sup>5</sup> investigated the effect of injecting a catalyst at a certain time interval and showed that this could improve polymer quality in terms of DP. Lee et al.<sup>6</sup> determined the optimal reactant feed policy to maintain the instantaneous average kinetic chain length constant during the start-up of a continuous stirred tank

reactor (CSTR). Lee et al.<sup>7</sup> also showed that the computations of the MWD are greatly simplified by the use of the kinetic chain length.

The MWD of the polymer can also be narrowed if the polydispersity of the product polymer, that is, the ratio of the number-average chain length to the weight-average chain length, approaches unity. Ray<sup>8</sup> used a search technique to obtain a set of optimal control variables, i.e., temperature, catalyst concentration, and holding time at each tank of a CSTRs-in-series system to produce a polymer with the desired average degree of polymerization and polydispersity. Ray<sup>9</sup> and Hicks et al.<sup>10</sup> used the maximum principle technique to determine the optimal temperature and catalyst control policy to determine the desired average degree of polymerization and polydispersity for a batch reactor and a CSTR which is in the start-up period. It should be noted that polydispersity is not a good criterion for specifying the MWD of a polymer, since polydispersity changes with the average degree of polymerization for the same width of the MWD.

Usually two moments, i.e., the average degree of polymerization and the variance of the MWD, are sufficient to specify the desired MWD. Using these two moments, Zeman and Amundson<sup>11</sup> studied the effects of temperature and initial concentrations of catalyst and monomer on the MWD parametrically, using a continuous variable technique. Mimasu and Ayabe<sup>12</sup> also carried out a parametric study of polymerization reactors following the approach proposed by Zeman and Amundson. They also indicated the possibility of optimizing design and operation of the polymerization reactors by manipulating the temperature, catalyst concentration and/or reactor volume. Nishimura and Yokoyama<sup>13,14</sup> used calculus of variations in an attempt to minimize the variance by controlling the temperature for a simplified kinetic model in which they assumed that all reactant concentrations remain constant. Their results show that the optimal temperature policy, which maintains DP constant throughout the reaction, is identical with the minimum variance policy.

By using the maximum principle technique, Nishimura and Yokoyama<sup>13</sup> also solved the minimal-time control problem to obtain the specified conversion and average degree of polymerization, where the temperature and/or catalyst concentration is chosen as a control variable. In reality, however, the catalyst concentration can not be controlled directly. A more realistic control variable may be the catalyst feed rate. A similar optimal-time control problem was solved by Yoshimoto et al.<sup>15</sup> by the maximum principle technique in which temperature was chosen as a control variable. Nishimura and Yokoyama<sup>13</sup> and Yoshimoto<sup>15</sup> considered only the first-order decomposition of catalyst, whereas Imoto and Lee,<sup>16</sup> who also solved a similar optimal-time control problem by the maximum principle technique, considered the higher-order decomposition of catalyst. The first-order decomposition of catalyst is a special case of the higher-order decomposition. Yoshimoto et al.<sup>17</sup> also solved a similar optimal-time control problem for a different kinetic model which represents a free-radical thermal polymerization system by using the maximum principle technique. King and

Skates<sup>18</sup> investigated the two-position control of a batch bulk polymerization reactor and developed a coolant temperature switching program which achieves 10% polymerization of the monomer in minimum time.

In our study, a more general kinetic model than that employed by other investigators in optimization studies of polymerization processes is considered. More specifically, the chain transfer step is taken into account, which was neglected by Nishimura and Yokoyama.<sup>13</sup> A frequently made assumption that all the reactant concentrations are kept constant throughout the polymerization is not made. In this work, all reactant concentrations are considered to change as the reaction proceeds in a batch reactor. Temperature and/or catalyst feed rate is chosen as the control variable for manipulating not only the average degree of polymerization but also the MWD. Two moments of the MWD, i.e., the average degree of polymerization and the variance of the MWD, are used to specify the MWD. Computational time is reduced by approximating the optimal control policy by a polynomial, and the coefficients of the polynomial are evaluated by the simplex pattern search technique.<sup>19</sup> It appears that this simple approach has not been employed so far for optimizing a polymerization system. This coefficient estimation method coupled with a search technique can be considerably more efficient and convenient for optimizing the type of complex reaction system considered in this work than other optimization techniques such as the dynamic programming,<sup>20</sup> maximum principle,<sup>21,22</sup> and gradient technique.<sup>23,24</sup>

### MECHANISM OF POLYMERIZATION

A free-radical polymerization reaction can be represented by a chain process consisting of four stages, namely, initiation (formation of radicals), propagation (chain growth), termination (chain stopped), and chain transfer.<sup>25</sup> In the present work, a homogeneous bulk polymerization reaction in a batch is considered, and the reaction mechanism represented by the following kinetic model is assumed:

Stage	Material equation
Initiation	$C \xrightarrow{k_d} 2C^*$
	$C^* + M \xrightarrow{k_{ic}} R_1^*$
Propagation	$R_1^* + M \xrightarrow{k_p} R_2^*$
	$R_r^* + M \xrightarrow{k_p} R_{r+1}^*$
Termination by disproportion	$R_r^* + R_q^* \xrightarrow{k_t} P_r + P_q$
Chain transfer	$R_r^* + M \xrightarrow{m k_{tr}} P_r + M^*$

where  $C$ ,  $C^*$ ,  $M$ ,  $R_r^*$ ,  $R_q^*$ ,  $P_r$  and  $P_q$  denote the catalyst (initiator), catalyst radical, monomer, active  $r$ -mer, active  $q$ -mer, dead  $r$ -mer and dead  $q$ -mer concentrations, respectively; and  $k_d$ ,  $k_i$ ,  $k_p$ ,  $k_t$ , and  ${}_m k_{tr}$  are specific reaction rate constants for catalyst decomposition, initiation, propagation, termination, and chain transfer, respectively. It is assumed that these specific reaction rate constants are independent of the chain length.

Assuming the existence of a steady state for the radicals and a sufficiently long chain length, the initiation rate  $I$  and the concentration of all radicals  $R^*$  are:<sup>25</sup>

$$I = 2fk_d C \quad (1)$$

$$R^* = \left( \frac{2fk_d C}{k_t} \right)^{1/2} \quad (2)$$

where  $f$  denotes the catalyst efficiency.

The rate equations for monomer  $M$ , catalyst (initiator)  $C$ , polymer  $P$ , and  $r$  degrees of polymer  $P_r$ , are expressed as follows:<sup>25</sup>

$$-\frac{dC}{dt} = k_d C \quad (3)$$

$$-\frac{dM}{dt} = K'(C^{1/2})M \quad (4)$$

$$\frac{dP_r}{dt} = \left( \frac{2fk_d C}{k_t} \right)^{1/2} \frac{\{C_m k_p M + (2fk_d k_i C)^{1/2}\}^2 (k_p M)^{r-1}}{\{k_p M + C_m k_p M + (2fk_d k_i C)^{1/2}\}^r}, \quad r = 1, 2, 3, \dots \quad (5)$$

$$\frac{dP}{dt} = \sum_{r=1}^{\infty} \frac{dP_r}{dt} = C_m K' C^{1/2} M + 2fk_d C \quad (6)$$

with initial conditions

$$\left. \begin{aligned} C &= C_0 && \text{at } t = 0 \\ M &= M_0 && \text{at } t = 0 \\ P_r &= 0, \quad r = 1, 2, 3, \dots && \text{at } t = 0 \\ P &= 0 && \text{at } t = 0 \end{aligned} \right\} \quad (7)$$

where  $K'$  is

$$K' = \frac{k_p (2f)^{1/2} (k_d)^{1/2}}{k_t^{1/2}} \quad (8)$$

and  $C_m$  is the monomer chain transfer constant and is defined as

$$C_m = \frac{{}_m k_{tr}}{k_p} \quad (9)$$

The instantaneous average degree of polymerization  $DP$  is defined as follows:

$$DP = \frac{-(dM/dt)}{dP/dt} = \frac{1}{C_m + K'(k_i/k_p^2) (C^{1/2}/M)} \quad (10)$$

Assuming that the specific reaction rates follow Arrhenius' law,

$$\left. \begin{aligned} k_d &= k_{d0} \exp(-E_d/RT) \\ k_p &= k_{p0} \exp(-E_p/RT) \\ k_t &= k_{t0} \exp(-E_t/RT) \\ {}_m k_{tr} &= {}_m k_{tr0} \exp(-{}_m E_{tr}/RT) \end{aligned} \right\} \quad (11)$$

where  $k_{d0}$ ,  $k_{p0}$ ,  $k_{t0}$ , and  ${}_m k_{tr0}$  are the frequency factors of decomposition, propagation, termination, and chain transfer, respectively;  $E_d$ ,  $E_p$ ,  $E_t$ , and  ${}_m E_{tr}$  are the activation energies of decomposition, propagation, termination, and chain transfer, respectively;  $R$  is the gas constant; and  $T$  is absolute temperature.

## OPTIMIZATION OF BATCH POLYMERIZATION REACTOR

### Optimization of Molecular Weight Distribution

The physical properties of a polymer are directly related to the average degree of polymerization  $\bar{P}_n$  and the variance of the MWD  $V_{ar}$ , which are defined as follows:

$$\bar{P}_n = \frac{\sum_{r=1}^{\infty} r P_r}{\sum_{r=1}^{\infty} P_r} \quad (12)$$

$$V_{ar} = \frac{\sum_{r=1}^{\infty} (r - \bar{P}_n)^2 P_r}{\sum_{r=1}^{\infty} P_r} \quad (13)$$

The objective of optimization is to obtain the average degree of polymerization of the product,  $\bar{P}_n$ , and variance of the MWD of the product,  $V_{ar}$ , as close as possible to the specified desired values,  $\bar{P}_{nd}$  and  $V_{ard}$ , respectively, by controlling the catalyst feed rate, or temperature, or both. If the catalyst feed rate is chosen as the control variable, the rate equation for the catalyst can be rewritten as

$$\frac{dC}{dt} = -k_d C + \frac{F}{V} \quad (14)$$

with the initial condition

$$C = C_0 \text{ at } t = 0,$$

where  $F$  is the catalyst feed rate and  $V$  is the reactor volume;  $V$  is assumed to be constant since the amount of catalyst fed during the reaction is usually

negligible. The objective function to be minimized can be generally written as

$$S = w_1(\bar{P}_n - \bar{P}_{nd})^2 + w_2(V_{ar} - V_{ara})^2 \quad (15)$$

where  $w_1$  and  $w_2$  denote weights which represent the relative importance of the average degree of polymerization and the variance of the MWD and have positive values.

Now the optimization problem becomes one of minimizing the objective function  $S$  defined by eq. (15) subject to the performance equations and equality constraints given by eqs. (3) through (14) and the following inequality constraints:

$$\left. \begin{aligned} 0 &\leq t \leq t_f \\ T_l &\leq T \leq T_u \\ M &> 0 \\ C &> 0 \\ F &> 0 \end{aligned} \right\} \quad (16)$$

where  $t_f$  is the final time of reaction and  $T_l$  and  $T_u$  are the lower and upper limits of temperature, respectively.

The maximum principle and other variational techniques appear to be very convenient for this problem. However, the use of a variational technique gives rise to a split boundary value problem through the introduction of adjoint variables. The constraints imposed on the state variables often gives rise to a computational difficulty. To overcome these difficulties, a very naive but convenient approximate approach for optimization is introduced.<sup>23</sup> In this approach optimal policies are approximately expressed by the polynomials

$$F_{opt} = a_1 + a_2 \left(\frac{t}{t_f}\right) + a_3 \left(\frac{t}{t_f}\right)^2 + a_4 \left(\frac{t}{t_f}\right)^3 + \dots \quad (17)$$

and

$$T_{opt} = b_1 + b_2 \left(\frac{t}{t_f}\right) + b_3 \left(\frac{t}{t_f}\right)^2 + b_4 \left(\frac{t}{t_f}\right)^3 + \dots \quad (18)$$

where  $F_{opt}$  and  $T_{opt}$  are the optimal catalyst feed rate and optimal temperature, respectively; and  $a_1, a_2, a_3, \dots$  and  $b_1, b_2, b_3, \dots$  are constant coefficients which should be evaluated such that the objective function  $S$  in eq. (15) is minimized.

These coefficients can be evaluated by any of the available nonlinear search techniques. Experience indicates that the use of a pattern search technique is preferable. Specifically, the simplex pattern search technique is used in this study.<sup>19</sup> Note that the original dynamic problem has now been changed to a static problem. The dimensions and the computational time for the problem are reduced by the use of this coefficient estimation method coupled with the pattern search technique.

### Optimization of Instantaneous Average Degree of Polymerization

Qualitatively, the MWD is narrowed by keeping the instantaneous average degree of polymerization,  $DP$ , constant throughout the reaction. Hence, the objective of optimization is to obtain the  $DP$  as close as possible to the desired instantaneous average degree of polymerization,  $DP_d$ , by controlling the catalyst feed rate or the temperature throughout the polymerization reaction. This is equivalent to minimizing the following objective function:

$$S_3 = \int_0^{t_f} (DP - DP_d)^2 dt \quad (19)$$

The optimization problem is now transformed to that of minimizing the objective function  $S_3$  of eq. (19) subject to the performance equations and equality constraints of eq. (15). The total reaction time,  $t_f$ , is divided into  $N$  time stages, and approximately optimal piecewise control policies are determined at each time stage by the simplex pattern search technique. Results of the optimization are compared with those of the preceding optimization problem which takes into account both the average degree of polymerization and the variance of the MWD as expressed by eq. (15).

**Example:** Consider a vinyl acetate polymerization in a batch reactor;  $\alpha, \alpha'$ -azobisisobutyronitrile (AZN) is used as the catalyst. This system follows the preceding polymerization mechanism and has the following specific reaction rate constants and catalyst efficiency<sup>25-29</sup>:

$$\left. \begin{aligned} k_d &= 7.9 \times 10^{16} \exp(-34000/RT) \text{ sec}^{-1} \\ k_p &= 2.43 \times 10^8 \exp(-7320/RT) \text{ l. mole}^{-1} \text{ sec}^{-1} \\ k_t &= 2.08 \times 10^{11} \exp(-5240/RT) \text{ l. mole}^{-1} \text{ sec}^{-1} \\ m k_{tr} &= 3.63 \times 10^3 \exp(-5687/RT) \text{ l. mole}^{-1} \text{ sec}^{-1} \\ f &= 0.5 \end{aligned} \right\} \quad (20)$$

It is also assumed that the initial monomer concentration is 10.85 mole l.<sup>-1</sup> and the reactor volume is 1 liter, that is,  $M_0 = 10.85$  mole l.<sup>-1</sup> and  $V = 1$  liter.

While any appropriate values can be assigned to  $w_1$  and  $w_2$  in eq. (15), for optimizing the MWD in the present examples the following objective functions are specifically considered:

$$S_1 = (\bar{P}_n - \bar{P}_{nd})^2 + (V_{ar} - V_{ard})^2 \quad (21)$$

and

$$S_2 = (\bar{P}_n - \bar{P}_{nd})^2 \quad (22)$$

where  $\bar{P}_{nd}$  is specified as 4500 and  $V_{ard}$  as zero. It should be noted that  $\bar{P}_n$  and  $V_{ar}$  are controlled in an optimal manner in minimizing  $S_1$ , and only  $\bar{P}_n$  is controlled in minimizing  $S_2$ .

The following values are assigned to the initial catalyst and monomer concentrations when only the temperature is controlled:

$$C_0 = 0.005 \text{ mole l.}^{-1}$$

$$M_0 = 10.85 \text{ mole l.}^{-1}$$

When both the temperature and catalyst feed rate are controlled, the following values are assigned to the initial concentrations:

$$C_0 = 0 \text{ mole l.}^{-1}$$

$$M_0 = 10.85 \text{ moles l.}^{-1}$$

The inequality constraints are

$$\left. \begin{aligned} 0 &\leq t \leq 6000 \text{ sec} \\ 303 &\leq T \leq 373^\circ\text{K} \\ C &> 0 \text{ mole l.}^{-1} \\ M &> 0 \text{ mole l.}^{-1} \end{aligned} \right\} \quad (23)$$

The optimal policies are approximated by the following third-order polynomials:

$$F_{opt} = a_1 + a_2 \left(\frac{t}{t_f}\right) + a_3 \left(\frac{t}{t_f}\right)^2 + a_4 \left(\frac{t}{t_f}\right)^3 \quad (24)$$

and

$$T_{opt} = b_1 + b_2 \left(\frac{t}{t_f}\right) + b_3 \left(\frac{t}{t_f}\right)^2 + b_4 \left(\frac{t}{t_f}\right)^3 \quad (24)$$

This means that a four-dimensional search must be carried out when only the temperature is controlled, and an eight-dimensional search must be carried out when both the temperature and the catalyst feed rate are controlled. It should be noted that the accuracy of the results can be improved by using higher-order polynomials.

For the optimization of the instantaneous degree of polymerization,  $DP$ , the objective function  $S_3$  in eq. (19) is minimized by specifying  $DP_a = 4500$ . For computational purposes, the reaction time  $t_f$  is divided into 20 time stages, and at each time stage the piecewise approximate optimal policies are determined by the simplex pattern search technique. If the number of time stages is increased, a more accurate result can be obtained.

## RESULTS AND DISCUSSIONS

The optimal results of five optimization problems are tabulated in Table I along with the values of objective functions. The results of unoptimized batch operations are tabulated in Table II for comparison. The optimal policies for the five cases are also shown in Figures 1 through 5, and the resultant optimal MWD and percentage conversions for cases 1 and 2 are



TABLE I  
Results of Optimization

Control	Controlled variables	Optimal policy	Minimized objective function value	Values of other objective functions corresponding to policies in column 3
MWD				
Case 1	temperature <sup>a</sup>	in Fig. 1	$S_1 = 0.7435 \times 10^{13}$	$S_2 = 0.2021 \times 10^8$ $S_3 = 0.3349 \times 10^9$
Case 2	temperature catalyst feed rate	in Fig. 2	$S_1 = 0.5377 \times 10^8$	$S_2 = 0.2024 \times 10^8$
Case 3	temperature <sup>a</sup>	in Fig. 3	$S_2 = 0.1914$	$S_1 = 0.4570 \times 10^{15}$
DP				
Case 4	temperature <sup>a</sup>	in Fig. 4	$S_3 = 0.9036 \times 10^4$	$S_1 = 0.2096 \times 10^{15}$ $S_2 = 0.8348 \times 10^6$
Case 5	catalyst feed rate <sup>b</sup>	in Fig. 5	$S_3 = 0.1248 \times 10^7$	

<sup>a</sup> Initial catalyst concentration,  $C_0 = 0.005$  g-mole/l.

<sup>b</sup> Temperature is kept at 60°C throughout the polymerization reaction.

TABLE II  
Results of Unoptimized Batch Operation<sup>a</sup>

	Unoptimized policy				
	Temp, °C	Initial catalyst concn, g-mole/l.	Objective function value		
			$S_1 \times$ $10^{-15}$	$S_2$	$S_3 \times$ $10^{-7}$
Case 6	50	0.005	0.4617	$0.2171 \times 10^3$	0.9565
Case 7	60	0.005	0.4308	$0.6052 \times 10^4$	0.5165
Case 8	70	0.005	0.2494	$0.5563 \times 10^6$	3.397
Case 9	60	0.0025	0.5236	$0.3506 \times 10^5$	2.485
Case 10	60	0.010	0.3169	$0.2106 \times 10^6$	0.597

<sup>a</sup> Catalyst is not fed during the polymerization rejection.

shown in Figures 6 through 9, together with those of corresponding unoptimized batch operations which have the same initial catalyst and/or monomer concentration as the optimized operations.

Note that the temperature is maintained almost constant throughout the polymerization reaction for the MWD control. It can be clearly seen that the quality of the polymer is improved by controlling the temperature and/or the catalyst feed rate. The optimal objective function values in Table I are smaller than those of the corresponding unoptimized batch operations given in Table II. Tables I and II also show that the changes of the initial catalyst concentration and temperature can only slightly re-

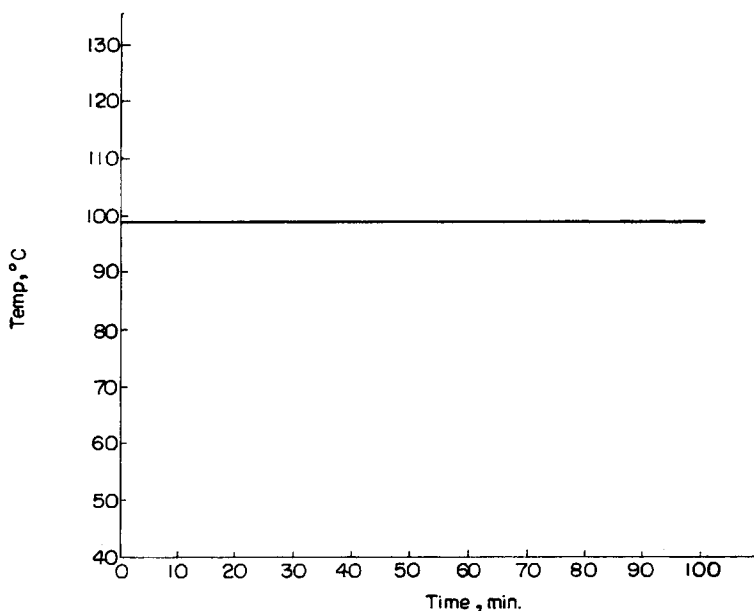


Fig. 1 Optimal temperature policy of Case 1.

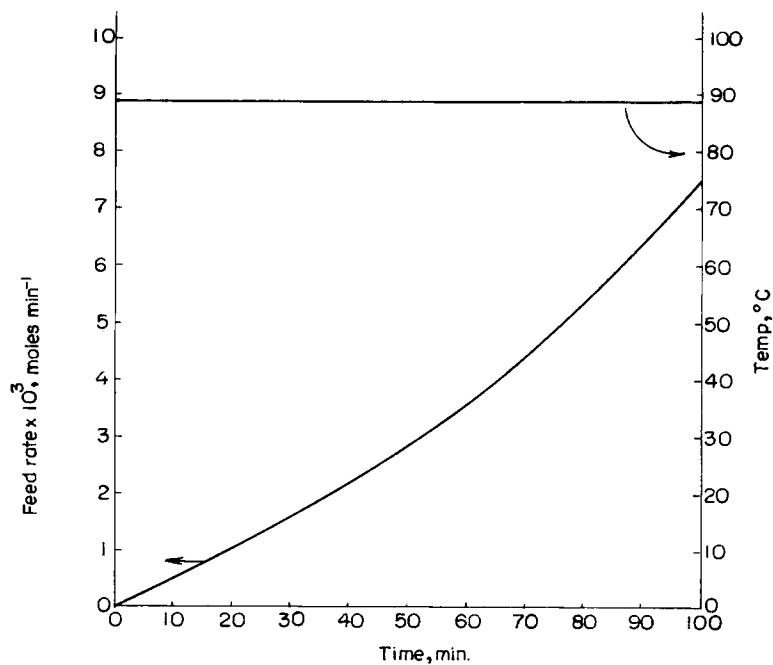


Fig. 2. Optimal temperature and catalyst feed policy of Case 2.

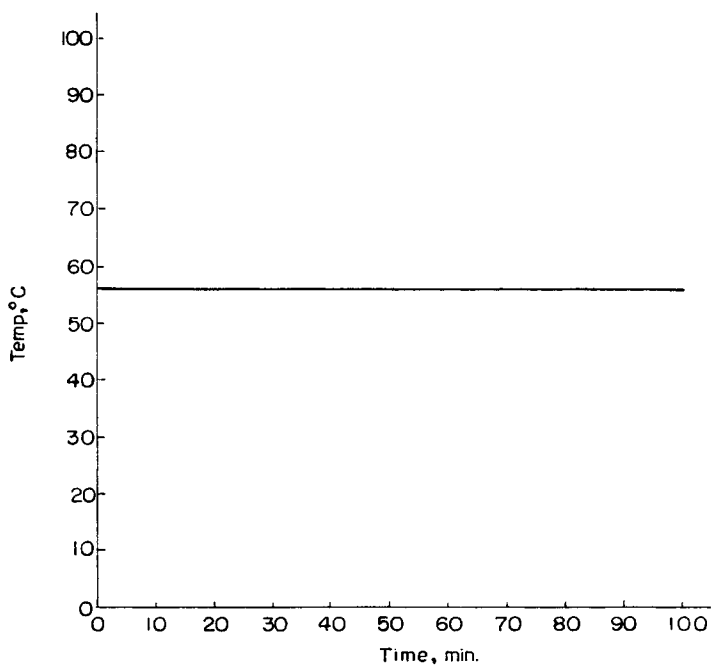


Fig. 3. Optimal temperature policy of Case 3.

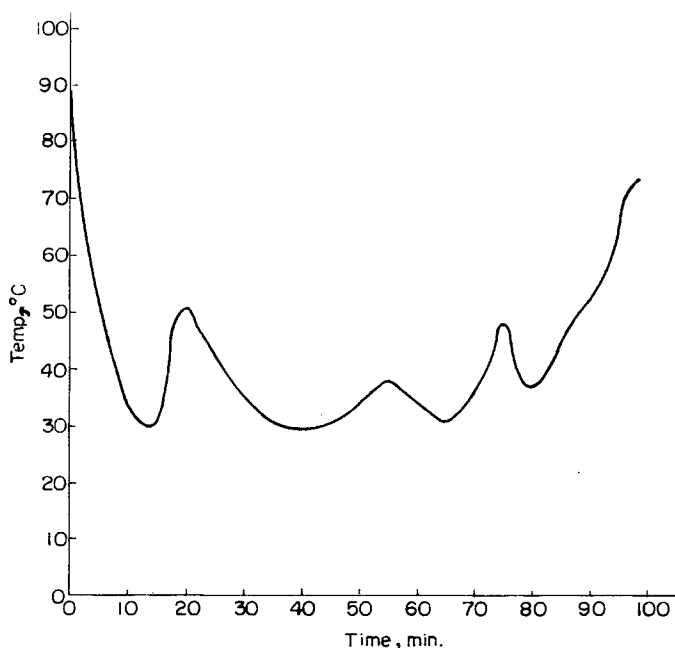


Fig. 4. Optimal temperature policy of Case 4.

duce the values of the objective functions for the unoptimized batch operation, but the control of temperature and/or the catalyst feed rate can drastically reduce the values of the objective functions for the optimal operation.

Comparison of cases 1 and 2 in Table I shows that the objective function value of case 2 with two control variables is much smaller than that of case 1 with a single control variable. The resultant optimal MWDs for cases 1 and 2 are compared respectively in Figures 6 and 8 with the MWD resulting from the corresponding unoptimized batch operation. In the unoptimized batch operation, the temperature is kept at the arbitrarily chosen level of 60°C, and the catalyst is not fed during the operation. Figures 6 and 8 clearly show that the width of the MWD of each optimized system is much narrower than that of the corresponding unoptimized batch operation. Figures 7 and 9 illustrate that the conversion of each optimized system for cases 1 and 2 is greater than that of the corresponding unoptimized batch operation.

It has been said<sup>1</sup> that the MWD becomes narrower if the instantaneous average degree of polymerization,  $DP$ , is kept constant throughout the reaction. However, a comparison of the results of cases 1 and 4 in Table I shows that the optimal policy which minimizes the objective function  $S_2$  does not always minimize the objective function  $S_1$ . This implies that even if  $DP$  is controlled, the MWD is not always improved. Similarly, the policy which minimizes the objective function  $S_1$  does not always minimize the objective function  $S_2$  or vice versa, as shown in Table I.

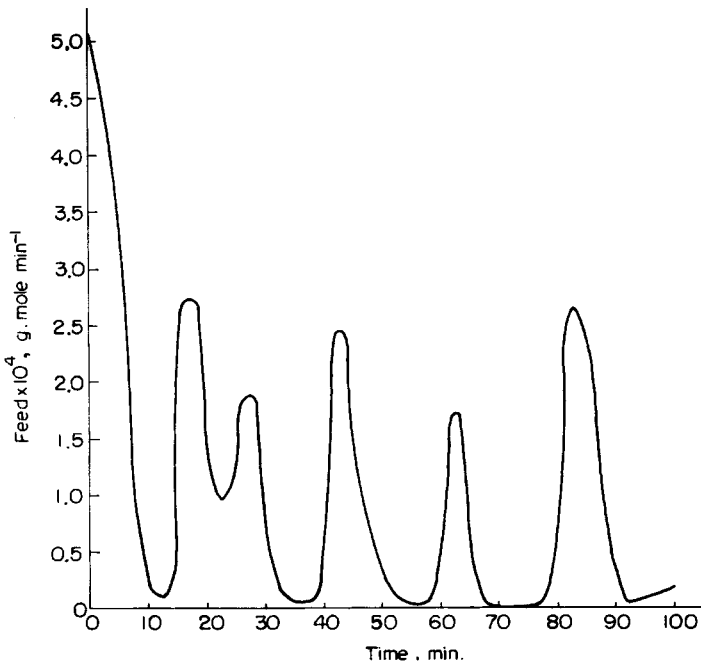


Fig. 5. Optimal catalyst feed policy of Case 5.

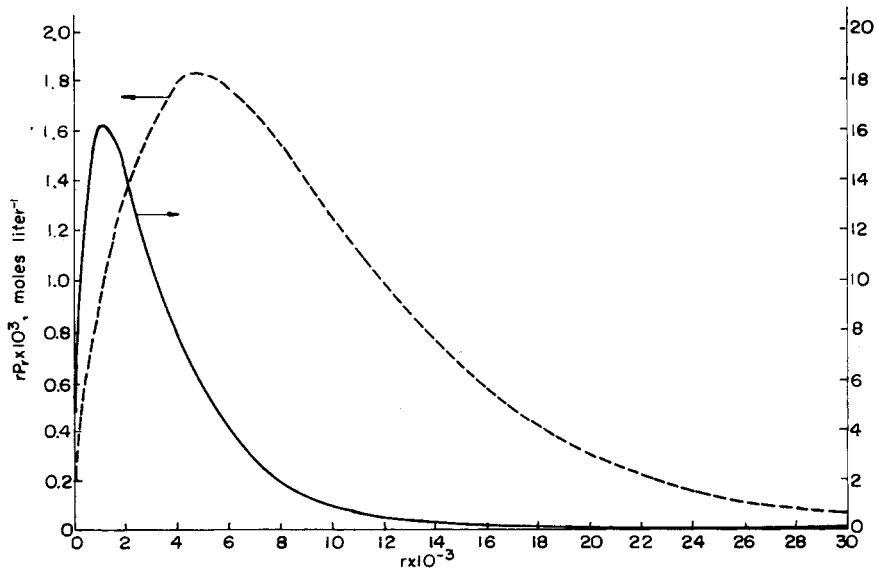


Fig. 6. Molecular weight distribution of batch (Case 7, dashed line) and optimized (Case 1, solid line) operations

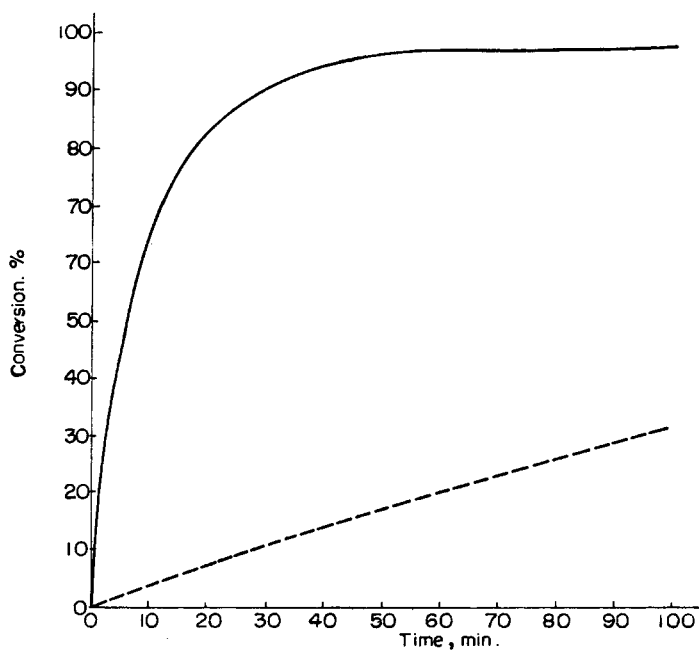


Fig. 7. Conversion vs. time by batch (Case 7, dashed line) and optimized (Case 1, solid line) operations.

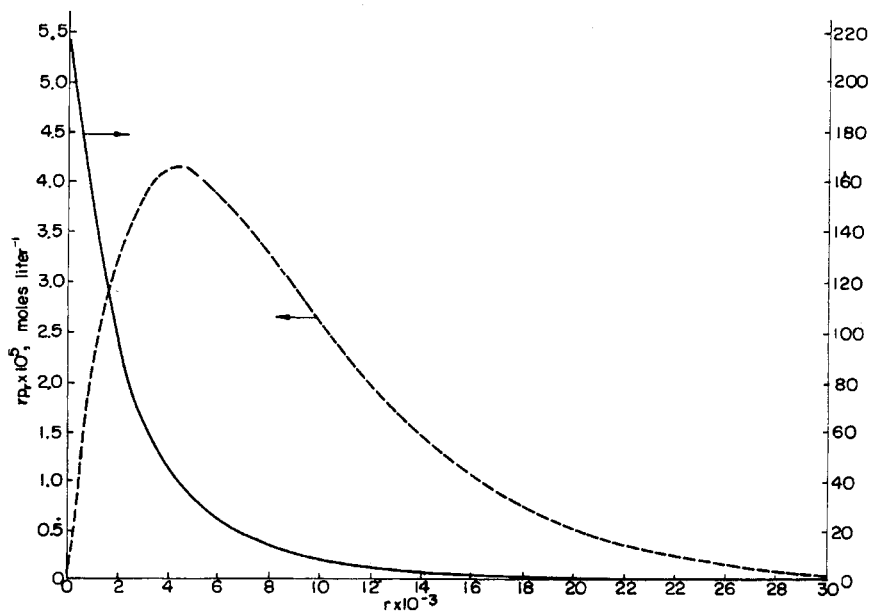


Fig. 8. Molecular weight distribution of batch (Case 10, dashed line) and optimized (Case 2, solid line) operations.

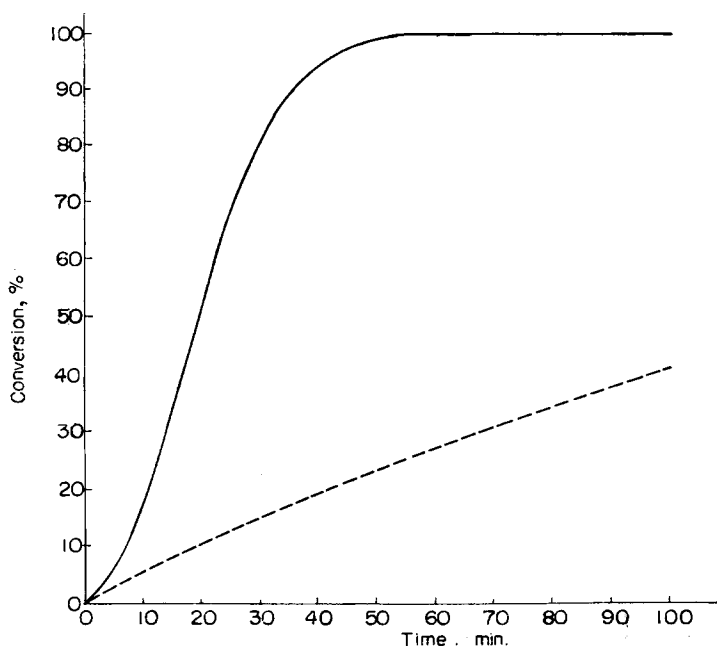


Fig. 9. Conversion vs. time by batch (Case 10, dashed line) and optimized (Case 2, solid line) operations.

In addition to the temperature and catalyst feed rate, the monomer feed rate can also be chosen as a control variable. If so, the problem becomes more complicated since the volume change due to addition of the monomer to the reactor must be taken into account.

In lieu of fixing final time, a final conversion  $x_f$  can be fixed. If the final time is not fixed, a minimal time control problem is created. The objective function becomes

$$S' = w_1(\bar{P}_n - \bar{P}_{nd})^2 + w_2(V_{ar} - V_{ard})^2 + w_3(t_f)^2 \quad (25)$$

where the weights  $w_1$ ,  $w_2$ , and  $w_3$  represent the relative importance of the average degree of polymerization, of the variance of the MWD, and of the final reaction time, respectively.

In this study, the optimal policies are expressed by an ordinary polynomial which is extremely simple. Other more complex polynomials may prove to be as efficient or even more so. For example, the Chebyshev polynomial has the "economization" property, and hence fewer coefficients may need be evaluated to obtain the same degree of precision.<sup>30</sup>

### CONCLUDING REMARKS

The quality of a polymer as characterized by the average degree of polymerization, and the variance of the MWD can be improved drastically by optimally controlling the temperature and/or the catalyst feed rate. It

has been shown that use of an additional control variable gives rise to further improvement in product quality. It has also been found that the optimal policy that controls DP does not always lead to the optimal MWD, or vice versa.

It is possible to express approximately the optimal policies by polynomials and estimate their coefficients by a nonlinear search technique. This simple coefficient estimation method, coupled with a nonlinear search technique, can also be used for solving a complicated optimal control problem in which a more general kinetic model than those employed in this work is considered. This coefficient estimation method can also be applied to other optimization problems.

### Nomenclature

$a_1, a_2, \dots$	coefficients of optimal polynomials of catalyst feed rate, moles/sec
$b_1, b_2, \dots$	coefficients of optimal polynomials of temperature, °K
$C$	catalyst concentration, moles/l.
$C_0$	initial catalyst concentration, moles/l.
$C^*$	catalyst radical concentration, moles/l.
$C_m$	monomer chain transfer constant
$DP$	instantaneous average degree of polymerization
$DP_d$	desired instantaneous average degree of polymerization
$E_d$	activation energy of decomposition, cal/mole
${}_mE_{tr}$	activation energy of monomer chain transfer, cal/mole
$E_p$	activation energy of propagation, cal/mole
$E_t$	activation energy of termination, cal/mole
$F$	catalyst feed rate, moles/sec
$F_{opt}$	optimal catalyst feed rate, moles/sec
$f$	catalyst efficiency
$I$	initiation rate, moles/l. sec
$K'$	defined by eq. (8), $l^{1/2}/\text{mole}^{1/2}$ , sec
$k_d$	decomposition rate constant, $\text{sec}^{-1}$
$k_{d0}$	frequency factor of decomposition, $\text{sec}^{-1}$
$k_{ic}$	initiation rate constant, l./mole sec
${}_m k_{tr}$	monomer chain transfer constant, l./mole sec
${}_m k_{tr0}$	frequency factor of monomer chain transfer, l./mole sec
$k_p$	propagation rate constant, l./mole sec
$k_{p0}$	frequency factor of propagation, l./mole sec
$k_t$	termination rate constant, l./mole sec
$k_{t0}$	frequency factor of termination, l./mole sec
$M$	monomer concentration, moles/l.
$M_0$	initial monomer concentration, moles/l.
$M^*$	radical monomer concentration, moles/l.
$P$	all polymer concentration, moles/l.
$P_q$	concentration of $q$ degree of polymer, moles/l.



$P_r$	concentration of $r$ degree of polymer, moles/l.
$\bar{P}_n$	average degree of polymerization of product
$\bar{P}_{nd}$	desired average degree of polymerization of the product
$\alpha$	degree of polymerization
$R$	gas constant, cal/°K mole
$R^*$	total radical concentration, moles/l.
$R_r^*$	concentration of $r$ degree of radical polymer, moles/l.
$r$	degree of polymerization
$S, S_1, S_2, S_3, S'$	objective functions defined by eqs. (15), (21), (22), (19), and (26), respectively.
$T$	temperature, °K
$T_{opt}$	optimal temperature °K
$T_l$	lower limit of admissible temperature, °K
$T_u$	upper limit of admissible temperature, °K
$t$	time, sec.
$t_f$	final time of the reaction, sec
$V$	reactor volume, liters
$V_{ar}$	variance of MWD of product
$V_{ard}$	desired variance of MWD of product
$w_1, w_2, w_3$	weights in objective functions

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