

# Optimization of a Batch Polymerization Reactor at the Final Stage of Conversion. II. Molecular Weight Constraint

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## Synopsis

A mathematical model for the free radical batch solution polymerization of methyl methacrylate that takes depropagation into account was developed. This model was then used to derive optimal temperature and initiator concentration policies to reduce residual monomer concentration to desired levels, producing at the same time a polymer with the desired number average molecular weight. An objective function was formulated to take account of the cost of the initiator with respect to the cost of time of reaction. It was observed that when the cost of initiator increased, optimal initiator concentration decreased whereas optimal temperature increased. Finally temperature reached a limiting value above which polymer with desired number average molecular weight could not be produced. These results give insight into the factors that determine the policies that could be employed in optimizing the operation of a reactor.

## INTRODUCTION

In an earlier paper<sup>1</sup> we derived optimal isothermal and nonisothermal policies to optimize the operation of a batch polymerization reactor at the final stage of conversion. The objective was to reduce the residual monomer concentration to low levels in a minimum possible time in order to increase throughput of a batch reactor. It was found that in polymerization reactions in which depropagation is also important, optimal isothermal policies were limited by either the "dead end" effect arising from the depletion of the initiator or by the depropagation reaction becoming important at higher temperatures.

Though it is essential to reduce the residual monomer concentration to low levels, at times it is also important to control the molecular weight of the polymer formed to achieve a desired quality of the product. It is well known that the molecular weight distribution and its averages such as number average and weight average molecular weights determine many of the physical and processing properties of the polymer formed.

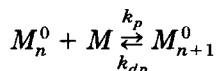
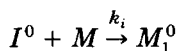
Many researchers studied the problems of optimization of batch polymerization reactor using temperature variations or semicontinuous operations involving adding combinations of initiator, monomer, transfer agent, or chain stopper.<sup>2-4</sup> A detailed literature survey on batch reactor optimization is given in our earlier paper.<sup>1</sup> None of the above efforts considered depropagation effects in combination with the optimal reactor problem. This paper is concerned with the development of optimal temperature and initial initiator

concentration policies to reduce residual monomer concentration to the desired levels and producing at the same time polymer with desired number average molecular weight. These optimal policies are derived based on a mathematical model that also takes depropagation into account. The effect of relative cost of the initiator on the optimal policies is analyzed.

### PROBLEM FORMULATION

It is assumed that most of the monomer has undergone solution polymerization in a batch reactor, resulting in a high solids content and a relatively low monomer concentration, herein designated  $M_0$ . At this point a certain amount of initiator is to be added to bring the initiator concentration to  $I_0$ . It is desired to reduce the monomer concentration  $M_0$  (around 5 vol %) to a final concentration  $M_f$  (around 0.5 vol %) in the minimum possible time and at the same time produce a final desired number average molecular weight  $M_{nf}$  by a proper choice of a temperature and an initial initiator concentration  $I_0$ . We do not consider the influence of diffusion control on the termination or other rate processes because such effects may be small when in a solution which is sufficiently dilute or when the polymer is of low molecular weight.

Free radical polymerization of MMA is a well-understood process. The kinetic mechanism neglecting chain transfer reaction is given as follows<sup>5,6</sup>:



From the above reaction mechanism, it is possible to derive a mathematical model as given in eqs. (1)–(4):

$$\frac{dI}{dt} = -k_d I, \quad I(0) = I_0 \quad (1)$$

$$\frac{dM}{dt} = -k_p \sqrt{2fk_d I/k_t} (M - M_e), \quad M(0) = M_0 \quad (2)$$

$$\frac{d\mu_0}{dt} = 2fk_d I, \quad \mu_0(0) = 0 \quad (3)$$

$$\frac{d\mu_2}{dt} = 2 \frac{k_p^2}{k_t} (M - M_e)^2 + k_p \sqrt{2fk_d I/k_t} (M - M_e), \quad \mu_2(0) = 0 \quad (4)$$

Equation (4) is a simplified version of the more exact equation and can be obtained by following an order of magnitude study similar to the one shown by Ponnuswamy.<sup>7</sup> Conversion, number average and weight average molecular weights are obtained as

$$x = (M_0 - M)/M \quad (5)$$

$$M_n = W_m(M_0x)/\mu_0 \quad (6)$$

$$M_w = W_m\mu_2/(M_0x) \quad (7)$$

Equilibrium monomer concentration  $M_e$  is given as<sup>8</sup>

$$M_e = \exp(-\Delta S/R) \exp(\Delta H/RT) = C \exp(\Delta H/RT) \quad (8)$$

### OPTIMIZATION PROBLEM

The following optimization problem can be formulated. For a given initial monomer concentration  $M_0$ , determine an optimal isothermal temperature ( $T$ ) and initial initiator concentration ( $I_0$ ) that will produce a polymer with desired conversion ( $x_f$ ) and number average molecular weight ( $M_{nf}$ ) in minimum time. The desired conversion  $x_f$  and the desired number average molecular weight  $M_{nf}$  can be transformed into the desired monomer concentration ( $M_f$ ) and the desired zeroth moment of dead polymer ( $\mu_{0f}$ ) by the following equations:

$$M_f = M_0(1 - x_f) \quad (9)$$

$$\mu_{0f} = W_m(M_0x_f)/M_{nf} \quad (10)$$

Since the model equations are written in terms of monomer concentration ( $M$ ) and zeroth moment ( $\mu_0$ ), it is convenient to work with these quantities.

### Isothermal Policy Development

If the temperature remains constant, Eqs. (1)–(3) can be integrated to get

$$I_f = I_0 \exp(-k_d t_f) \quad (11)$$

$$\mu_{0f} = 2fI_0[1 - \exp(-k_d t_f)] \quad (12)$$

$$\ln\{(M_0 - M_e)/(M_f - M_e)\} = 2(k_0 I_0)^{1/2}[1 - \exp(-k_d t_f/2)] \quad (13)$$

where

$$k_0 = 2fk_p^2/k_t k_d = A_0 \exp(-E_0/RT) \quad (14)$$

In Eq. (13) we can assume  $M_0 \gg M_e$ . From eq. (12) we can obtain the final time  $t_f$  as

$$t_f = -\frac{1}{k_d} \ln(1 - \mu_{0f}/2fI_0) \quad (15)$$

Our objective is to minimize the final time  $t_f$  subjected to the equality constraint given by the eq. (13). We are required to find two variables subjected to one equality constraint and hence there is only 1 degree of freedom for optimization. It can be shown easily that eq. (4) giving the rate of change of second moment is dependent on eqs. (2) and (3) and hence it is not possible to control weight average molecular weight in this problem.

Since  $t_f$  is given by eq. (15), we can incorporate the equality constraint given by eq. (13) using Lagrange multiplier in an adjoint objective function given as<sup>9</sup>

$$J = -\frac{1}{k_d} \ln\left(1 - \frac{\mu_{0f}}{2fI_0}\right) + \lambda \left\{ \ln\left(\frac{M_0}{M_f - M_e}\right) - 2(k_0I_0)^{1/2} \left[ 1 - \left(1 - \frac{\mu_{0f}}{2fI_0}\right)^{1/2} \right] \right\} \quad (16)$$

In eq. (16)  $\lambda$  is the Lagrange multiplier. The objective function  $J$  has to be minimized by a proper choice of the initial initiator concentration  $I_0$  and temperature  $T$ . Optimality conditions are given by the following equations:

$$\frac{\partial J}{\partial I_0} = 0 \quad (17)$$

$$\frac{\partial J}{\partial T} = 0 \quad (18)$$

From the optimality conditions given by eqs. (17) and (18), it is possible to solve for optimum isothermal temperature and optimum initial initiator concentration ( $I_0$ ) as given in Appendix A. After solving for  $I_0$  and  $T$ , final time  $t_f$  can be obtained from eq. (15).

### Optimization Including Cost of Initiator

The previous optimization procedure assumed that the cost of the initiator is insignificant and hence was concerned only with minimization of time. The following objective function is proposed to incorporate the cost of the initiator:

$$J' = \alpha_1 t_f + \alpha_2 I_0 \quad (19)$$

In eq. (19),  $\alpha_1$  and  $\alpha_2$  are the cost factors associated with time and initial initiator concentration, respectively. It is assumed that the optimization is

carried out for a reactor volume of 1 L. Hence  $J'$  represents costs associated with 1 L of the reactor. Equation (19) can be modified to take account of the relative cost of time and initiator concentration as follows.

$$J_1 = (J'/\alpha_1) = t_f + (\alpha_2/\alpha_1)I_0 = t_f + \alpha I_0 \quad (20)$$

In eq. (20),  $\alpha$  represents the relative cost of the initiator with respect to the cost associated with the time of reaction and is given in the units of s/mol. It can easily be seen that optimization of objective functions given in eqs. (19) and (20) are equivalent. A procedure very similar to the one used in the earlier section can be used to derive optimal control policies.

## RESULTS AND DISCUSSION

A series of simulations were performed to determine the optimal temperature and initial initiator concentration to produce polymer with desired conversion and number average molecular weight in minimum time. It was assumed that initially the polymerization mixture contained 5 vol % monomer, the rest of the mixture being solvent and low molecular weight polymer formed earlier. It was required to reduce the monomer concentration from 5 to 0.5 vol %, producing polymer with a desired number average molecular weight in minimum time. The kinetic and thermodynamic parameters used are similar to those of free radical polymerization of MMA. These parameter values are given in Appendix B.<sup>10</sup>

Table I and also Figure 1 gives the optimum temperature and optimum initial initiator concentration for various desired number average molecular weights ranging from 1000 to 5000. It is well known that higher molecular weight polymer could be produced by decreasing temperature and also decreasing initial initiator concentration. However, in either case, the minimum time required to reach the desired conversion and  $M_n$  would increase. We note that when the  $M_n$  increases from 1000 to 5000, the minimum time increases

TABLE I  
Optimal Isothermal and Initial Initiator Policies To Produce Polymer with Desired conversion ( $x_f$ ) and Number Average Molecular Weight ( $M_{nf}$ )<sup>a</sup>

$M_{nf}$	$I_0$ (mol/L)	$T$ (°C)	$t_f$ (min)
1000	0.2325	75.2	152
475	0.2325	86.2	100
2000	0.0620	75.0	304
1100	0.0620	85.2	220
3000	0.0325	74.4	458
1800	0.0325	84.2	338
4000	0.0250	74.3	614
2240	0.0250	83.6	406
5000	0.0146	73.8	773
3450	0.0146	82.1	612

<sup>a</sup> $x_f = 0.90$ ;  $M_0 = 0.47$  mol/L. Second line in each block of data gives results for the case when  $M_{nf}$  was not controlled.

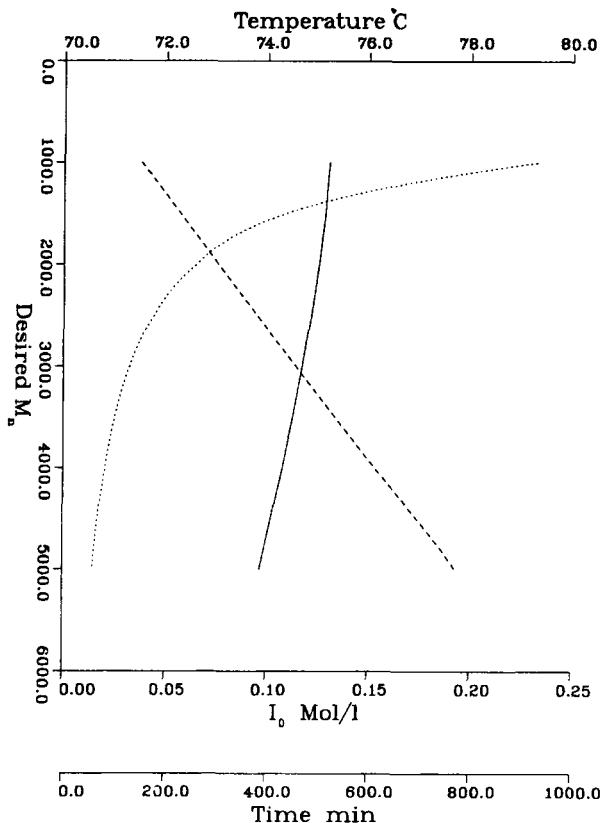


Fig. 1. Optimum temperature and initial initiator concentration policies as a function of desired  $M_n$ :  $x_f = 0.90$ ;  $M_0 = 0.47$  mol/L. (—) Temperature ( $^{\circ}\text{C}$ ); ( $\cdots$ )  $I_0$  (mol/L); and (---) time (min).

from 152 to 773 min. It can be observed that the optimum temperature does not decrease very much whereas the optimum initial initiator concentration decreases considerably from 0.2325 to 0.0146 mol/L. We also compared the results with the optimal isothermal policy when the same initial initiator concentration was used but the  $M_n$  was not controlled. In Table I, the second line in each block of data gives the optimal temperature and other data

TABLE II  
Effect of Initiator Cost on Optimal Temperature and Initial Initiator Concentration Policies<sup>a</sup>

$\alpha$ (s/mol)	$I_0$ (mol/L)	$T$ ( $^{\circ}\text{C}$ )	$t_f$ (min)
$1.0 \times 10^4$	0.01456	73.9	773
$1.0 \times 10^5$	0.01394	74.5	774
$1.0 \times 10^6$	0.01147	77.2	791
$1.0 \times 10^7$	0.00918	81.2	917
$1.0 \times 10^8$	0.00856	83.5	1211
$1.0 \times 10^9$	0.00847	84.4	1614
$1.0 \times 10^{10}$	0.00846	84.6	2101

<sup>a</sup> $M_{nf} = 5000$ ;  $x_f = 0.90$ ;  $M_0 = 0.47$  mol/L.

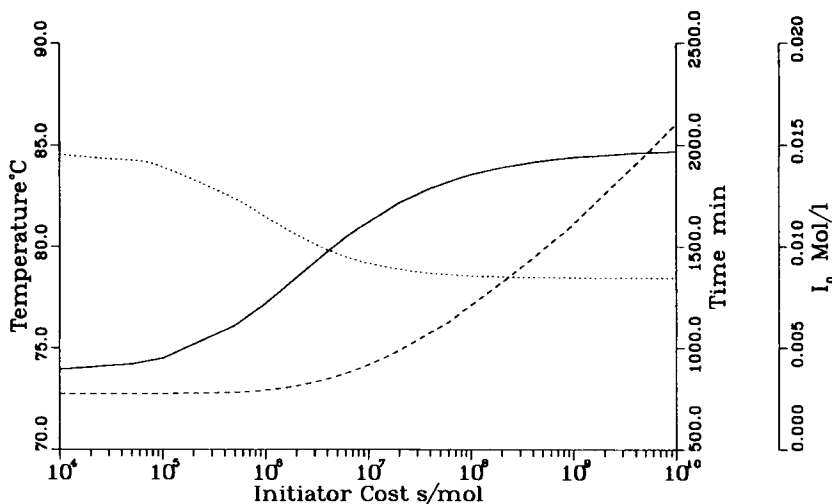


Fig. 2. Effect of initiator cost on optimal temperature and initial initiator concentration policies:  $M_{nf} = 5000$ ;  $x_f = 0.90$ ;  $M_0 = 0.47$  mol/L. (—) Temperature ( $^{\circ}\text{C}$ ); ( $\cdots$ )  $I_0$  (mol/L); (---) time (min).

obtained when  $M_{nf}$  was not controlled. In each case, as could be expected, isothermal temperature increased considerably, producing lower molecular weight polymer but decreasing the optimum time of operation considerably.

We also conducted some simulations to study the effect of initiator cost on the optimal temperature and initial initiator concentration policies. Table II and Figure 2 shows the results obtained when the desired  $M_n$  was 5000. The objective function shown in eq. (20) was used to develop the optimal policies. When the relative initiator weighting  $\alpha$  is increased, it is expected that the optimal policy would decrease the initiator concentration but at the same time increase the temperature. It can be noted from the objective function that the policy is not a minimum time policy but optimizes a function of time and the cost of the initiator. Hence we observe the optimum time increases when the weighting given to the initiator concentration increases. It is important to note that temperature increases to a limiting value above which the polymer with desired  $M_n$  could not be produced.

## CONCLUSIONS

In this paper we derived a simplified mathematical model of a batch solution polymerization reactor taking into account the depropagation. We formulated and solved the optimal time problem to produce polymer with desired  $M_n$  and at the same time reducing the residual monomer concentration to the desired levels. Optimal isothermal and initial initiator concentration was obtained for various cases of desired  $M_{nf}$  and desired  $x_f$ . It was observed that the initiator concentration changed considerably when the desired  $M_{nf}$  was increased whereas temperature did not change very much.

An objective function was formulated to include the cost of the initiator in the optimization. It was observed that when the weighting given to the initiator was increased, the optimal  $I_0$  decreased whereas the optimal temper-

ature increased. Finally optimal temperature reached a limiting value above which polymer with desired  $M_n$  could not be produced.

These results give insight into the factors that determine the policies that can be employed in optimizing the operation of a batch reactor when constraint in the form of desired  $M_n$  is imposed. An analysis of the reactor equations clearly reveals that only two leading moments of the molecular weight distribution can be controlled. Hence  $M_n$  and  $M_w$  cannot be independently controlled in the reactor optimization. The model of the polymerization reactor used in this work has ignored variation of rate parameters with conversion such as that occurring in the gel effect. Incorporation of such effects would require only a specific model so that  $k_0$  in eq. (14) can be made conversion- and temperature-dependent.

### APPENDIX A

*Objective:* Minimize  $J = t_f$  with respect to  $I_0$  and  $T$  subjected to the equality constraint eq. (13).

Introducing the Lagrange multiplier  $\lambda$ , the adjoint objective function can be written as

$$J = -\frac{1}{k_d} \ln\left(1 - \frac{\mu_{0f}}{2fI_0}\right) + \lambda \left\{ \ln\left(\frac{M_0}{M_f - M_e}\right) - 2(k_0 I_0)^{1/2} \left[ 1 - \left(1 - \frac{\mu_{0f}}{2fI_0}\right)^{1/2} \right] \right\} \quad (21)$$

Optimality conditions are given by

$$\frac{\partial J}{\partial I_0} = -\frac{\mu_{0f}}{2fk_d I_0^2 (1 - \mu_{0f}/2fI_0)} \quad (22)$$

$$+ \lambda \left[ -\left(\frac{k_0}{I_0}\right)^{1/2} \left[ 1 - \left(1 - \frac{\mu_{0f}}{2fI_0}\right)^{1/2} \right] + \left(\frac{k_0}{I_0}\right)^{1/2} \frac{\mu_{0f}}{2fI_0(1 - \mu_{0f}/2fI_0)^{1/2}} \right] = 0$$

$$\frac{\partial J}{\partial T} = \frac{E_d}{RT^2 k_d} \ln\left(1 - \frac{\mu_{0f}}{2fI_0}\right) + \lambda \left[ \frac{-M_e(\Delta H)}{RT^2(M_f - M_e)} - \frac{E_0(k_0 I_0)^{1/2}}{RT^2} \left\{ 1 - \left(1 - \frac{\mu_{0f}}{2fI_0}\right)^{1/2} \right\} \right] = 0 \quad (23)$$

From eq. (23)  $\lambda$  can be obtained as

$$\lambda = \frac{(E_d/k_d)\ln(1 - \mu_{0f}/2fI_0)}{M_e(\Delta H)/(M_f - M_e) + E_0(k_0 I_0)^{1/2} \left[ 1 - \left(1 - \mu_{0f}/2fI_0\right)^{1/2} \right]} \quad (24)$$



Substitute (24) in (22):

$$\begin{aligned} & \frac{\mu_{0f}}{2fk_d I_0^2 (1 - \mu_{0f}/2fI_0)} \\ &= \frac{-(E_d/k_d)\ln(1 - \mu_{0f}/2fI_0)}{M_e(\Delta H)(M_f - M_e) + E_0(k_0 I_0)^{1/2}(1 - \mu_{0f}/2fI_0)^{1/2}} \left(\frac{k_0}{I_0}\right)^{1/2} \\ & \times \left\{ \left[ 1 - \left(1 - \frac{\mu_{0f}}{2fI_0}\right)^{1/2} \right] - \frac{\mu_{0f}}{2fI_0(1 - \mu_{0f}/2fI_0)^{0.5}} \right\} \end{aligned} \quad (25)$$

Solving (25) and eq. (13) simultaneously we get  $I_0$  and  $T$ . Any of the standard numerical procedures can be used to solve the two equations.<sup>11</sup>

## APPENDIX B

$$k_d = 1.64 \times 10^{14} \exp(-126,000/RT)$$

$$k_p = 4.92 \times 10^5 \exp(-18,200/RT)$$

$$k_t = 9.8 \times 10^7 \exp(-2930/RT)$$

$$k_0 = 1.506 \times 10^{-11} \exp(92,380/RT)$$

$$(-\Delta H) = 55 \text{ kJ/mol}$$

$$\Delta S = -123 \text{ J/mol K}$$

$$M_e = \exp(-\Delta S/R)\exp(\Delta H/RT) = 2.828 \times 10^6 \exp(-55,000/RT)$$

$$M_0 = 0.47 \text{ mol/L}$$

$$M_f = 0.047 \text{ mol/L}$$

$$f = 0.50$$

$$R = 8.28 \text{ J/mol K}$$

## APPENDIX C: NOMENCLATURE

$A_d, A_p, A_t$	Arrhenius factor for dissociation, propagation and termination respectively
$C$	$\exp(-\Delta S/R)$
$E_d, E_p, E_t$	activation energy for dissociation, propagation and termination respectively (J/mol)
$f$	initiator efficiency
$I_0$	initial initiator concentration (mol/L)
$I_f$	final initiator concentration (mol/L)
$I$	initiator concentration (mol/L)

$J, J', J_1$	objective function
$k_d$	rate constant for initiator dissociation ( $s^{-1}$ )
$k_{dp}$	rate constant for depropagation (L/mol s)
$k_p$	rate constant for propagation (L/mol s)
$k_t$	termination constant (L/mol s)
$M$	monomer concentration (mol/L)
$M_e$	equilibrium monomer concentration (mol/L)
$M_0$	initial monomer concentration (mol/L)
$M_f$	final monomer concentration (mol/L)
$M_n$	number average molecular weight
$M_{nf}$	desired final number average molecular weight
$M_w$	weight average molecular weight
$R$	gas constant (J/mol K)
$T$	temperature ( $^{\circ}C$ or K)
$t$	time (s)
$t_f$	final time (s)
$W_m$	molecular weight of monomer (g/mol)
$x$	conversion
$x_f$	desired final conversion
$(-\Delta H)$	heat of polymerization (J/mol)
$(\Delta S)$	entropy change of polymerization (J/mol K)
$\alpha$	relative cost the initiator wrt to cost of time of reaction (s/mol)
$\alpha_1$	cost factor for time of reaction (dollars/s)
$\alpha_2$	cost factor for initiator concentration (dollars/mol)
$\mu_0, \mu_2$	zeroth and second moment of dead polymer
$\mu_{0f}$	desired final zeroth moment of dead polymer
$\lambda$	Lagrange multiplier

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