Optimal Policies for BMA Polymerization in Nonisothermal Batch Reactor

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ABSTRACT: In this paper, the optimal policies for bulk polymerization of *n*-butyl methacrylate (BMA) are determined in a nonisothermal batch reactor. Four objectives are realized for BMA polymerization based on a detailed process model. The objectives are: (i) maximization of monomer conversion in a specified operation time, (ii) minimization of operation time for a specified, final monomer conversion, (iii) maximization of monomer conversion for a specified, final number average polymer molecular weight, and (iv) maximization of monomer conversion for a specified, final weight average polymer molecular weight. For each objective, the optimal temperature policy of heat-exchange fluid inside reactor jacket is determined. The temperature of the heat-exchange fluid is considered as a function of a specified variable. Necessary equations are provided to suitably transform the process model in terms of a specified variable other than time, and to evaluate the elements of Jacobian to help in the accurate solution of the process model. A genetic algorithm-based optimal control method is applied to realize the objectives. The resulting optimal policies of this application reveal considerable improvements in the batch production of poly (BMA). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2799–2809, 2006

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INTRODUCTION

Polymerization in batch reactors is carried out extensively in polymer industry because of its operational simplicity and production adaptability. The determination of optimal policies for batch polymerization is very useful to polymer industry, which is always looking for new strategies to enhance the performance of polymer production. During batch polymerization, process variables undergo significant changes with time. The optimal performance of a process is determinable by optimizing an objective function subject to process and safety constraints under time-varying conditions. The determination of optimal parameters requires the satisfaction of a process model comprising differential and (or) algebraic equations. In case of batch reactors, the objective function typically varies with time as an independent variable. However, an independent variable could be any function of process variables.

The efficiency of batch reactors, and the properties of their products are strong functions of reaction temperature. This fact was recognized very early by Denbigh[1] and Aris.[2] Since then, the determination of optimal policies of batch reactors has received a lot of attention as summarized by Sundaram et al.[3] The optimal policies guide as to how certain process variables should be changed with time to achieve desired objectives. Moreover, these policies provide valuable information on the design of batch reactors, and the upper limits to their expected performance. For batch polymerization, many researchers have investigated the determination of optimal operation policies.[3–11] The objectives range from the minimization of operation time to the production of polymer with desired number and weight average molecular weights. No such study, however, is reported for the batch polymerization of *n*-butyl methacrylate (BMA).

In this work, the optimal policies of free radical, bulk polymerization of (BMA) are determined in a nonisothermal batch reactor using monofunctional 2,2′-azobis-isobutyronitrile (AIBN) as an initiator. Four different objectives are realized subject to process model and constraints. Each objective involves the optimization of a variable simultaneously with the specification of another. The objectives are: (i) maximization of monomer conversion in a specified operation time, (ii) minimization of operation time for specified, final monomer conversion, (iii) maximization of monomer conversion for a specified, final number average polymer molecular weight, and (vi) maximization of monomer conversion for a specified, final weight average polymer molecular weight. The temperature policy of heat-exchange fluid strongly influences the reaction temperature, and

therefore is optimally determined to attain the above-mentioned objectives. A robust optimal control method based on genetic algorithm[12] is employed for this purpose.

MATHEMATICAL MODEL

The mathematical model is provided below for the bulk polymerization of BMA in a nonisothermal batch reactor. The model comprises the equations of change of the volume (V) and temperature (T) of reactants, and the concentrations of monomer (m), initiator (i), inhibitor (z), and of the first three moments of radicals and dead polymer radicals. The equations are based on a free-radical polymerization reaction mechanism of Villalobos et al.,[13] and Dhib et al.[14] (Appendix). The symbols in following expressions are defined in Nomenclature.

$$\frac{dV}{dt} = -K_p m \lambda_0 V M_m \left[\frac{1}{\rho_p} - \frac{1}{\rho_m} \right] \tag{1}$$

$$\frac{dT}{dt} = \frac{-\Delta H K_p m \lambda_0}{\rho_m C_p} - \frac{UA(T - T_j)}{V \rho_m C_p} \tag{2}$$

$$\frac{dm}{dt} = -K_p m \lambda_0 - \frac{m}{V} \frac{dV}{dt} \tag{3}$$

$$\frac{di}{dt} = -K_d i - \frac{i}{V} \frac{dV}{dt} \tag{4}$$

$$\frac{dz}{dt} = -K_{tf,z} z \lambda_0 - \frac{z}{V} \frac{dV}{dt} \tag{5}$$

For the moments of polymer radicals:

$$\frac{d\lambda_0}{dt} = 2fK_d i - K_t \lambda_0^2 - K_{tf,z} z \lambda_0 - \frac{\lambda_0}{V} \frac{dV}{dt} \tag{6}$$

$$\frac{d\lambda_1}{dt} = 2fK_d i + K_p m \lambda_0 - K_t \lambda_0 \lambda_1 + k_{tf,m} m(\lambda_0 - \lambda_1)$$
$$- K_{tf,z} z \lambda_1 - \frac{\lambda_1}{V} \frac{dV}{dt} \tag{7}$$

$$\frac{d\lambda_2}{dt} = 2fK_d i + K_p m(\lambda_0 + 2\lambda_1) - K_t \lambda_0 \lambda_2$$
$$+ K_{tf,m} m(\lambda_0 - \lambda_2) - K_{tf,z} z \lambda_2 - \frac{\lambda_2}{V} \frac{dV}{dt} \tag{8}$$

For the moments of dead polymer:

$$\frac{d\mu_0}{dt} = \frac{K_t \lambda_0^2}{2} + (K_{tf,m} m + K_{tf,z} z) \lambda_0 - \frac{\mu_0}{V} \frac{dV}{dt} \tag{9}$$

$$\frac{d\mu_1}{dt} = K_t \lambda_0 \lambda_1 + (K_{tf,m} m + K_{tf,z} z) \lambda_1 - \frac{\mu_1}{V} \frac{dV}{dt} \tag{10}$$

$$\frac{d\mu_2}{dt} = K_t(\lambda_0 \lambda_2 + \lambda_1^2) + (K_{tf,m} m + K_{tf,z} z) \lambda_2 - \frac{\mu_2}{V} \frac{dV}{dt} \tag{11}$$

Let us define normalized state variables as follows:

$$\check{V} = 1 - \frac{V}{V^0} \qquad \check{T} = 1 - \frac{T + 273.15}{T^0 + 273.15} \qquad \check{m} = 1 - \frac{m}{m^0} \qquad \check{i} = 1 - \frac{i}{i^0}$$

$$\check{z} = 1 - \frac{z}{z^0} \qquad \check{\lambda}_j = 1 - \frac{\lambda_i}{\lambda_j^0} \qquad \check{\mu}_j = 1 - \frac{\mu_j}{\mu_j^0} \qquad j = 0, 1, 2 \tag{12}$$

where V^0, T^0, m^0, i^0, and z^0 are the initial values of V, T, m, i, and z, respectively, and μ^0 is a parameter used to normalize radical and polymer moments. Then, the equations of change for the normalized state variables are given by

$$\frac{d\check{y}_j}{dt} = \begin{cases} -\frac{1}{y_j^0} \frac{dy_j}{dt}, & \text{if } y_j^0 \neq 0 \\ 0, & \text{if } y_j^0 = 0 \end{cases}; \quad j = 0, 1, 2, \ldots, 10 \tag{13}$$

where $\check{y}_j$ is the normalized form of a state variable, y_j, with the normalization factor, y_j^0.

OBJECTIVES

Based on the above unsteady state model, it is desired to realize the following four objectives for batch BMA polymerization reactor:

1. Maximization of monomer conversion for a specified operation time.
2. Minimization of batch operation time for a specified monomer conversion.
3. Maximization of monomer conversion for a specified number average polymer molecular weight.
4. Maximization of monomer conversion for a specified weight average polymer molecular weight.

For the above objectives, the temperature policy of heat-exchange fluid (or ''jacket temperature'') is considered to be a function of a specified parameter. An inequality constraint limiting the reaction temperature has to be satisfied as follows:

$$T \leq T_{\max} \tag{14}$$

There are two additional inequality constraints on jacket temperature as follows:

$$T_{j,\min} \leq T_j \leq T_{j,\max} \tag{15}$$

Objective 1

The first objective is to determine the control policy for jacket temperature that would maximize monomer conversion in a specified batch operation time (t_f), i.e., the performance index,

$$\underset{\max}{J} = X(t_f) = X_f \tag{16}$$

In eq. (16), X is monomer conversion given by

$$X = 1 - \frac{mV}{m^0 V^0} = 1 - (1 - \check{m})(1 - \check{V}) \tag{17}$$

This objective requires the satisfaction of eqs. (1)–(6), or their normalized counterparts.

Objective 2

In this case, it is desired to determine the control policy for jacket temperature that would minimize operation time for a specified, final monomer conversion expressed in terms of fractional reduction in monomer concentration ($\check{m}_f$) i.e., the performance index,

$$\underset{\min}{J} = t(\check{m}_f) = t_f \tag{18}$$

This objective requires the transformation of eqs. (1)–(11), so that the independent variable is fractional reduction in monomer concentration ($\check{m}$). The transformed equations are given by

$$\frac{dt}{d\check{m}} = \left[\frac{d\check{m}}{dt}\right]^{-1} \tag{19}$$

$$\frac{d\check{y}_j}{d\check{m}} = \left(\frac{d\check{m}}{dt}\right)^{-1} \frac{d\check{y}_j}{dt}; \quad j = 0, 1, 3, 4, \ldots, 10 \tag{20}$$

with time as a new state variable replacing $\check{m}$.

Objective 3

The third objective is to determine the control policy for jacket temperature that would maximize monomer con-

version for a specified, final weight average polymer molecular weight ($\overline{M}_{n,f}$), i.e., the performance index,

$$\underset{\max}{J} = X(\overline{M}_{n,f}) = X_f \tag{21}$$

This objective requires the satisfaction of eqs. (1)–(11) after their transformation so that the independent variable is number average polymer molecular weight ($\overline{M}_n$). The transformed equations are given by

$$\frac{d\check{y}_j}{d\overline{M}_n} = \left(\frac{d\overline{M}_n}{dt}\right)^{-1} \frac{d\check{y}_j}{dt}; \quad j = 0, 1, 2, \ldots, 10 \tag{22}$$

where

$$\overline{M}_n = M_m \left(\frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0}\right) \tag{23}$$

$$\frac{d\overline{M}_n}{dt} = \frac{M_m \mu^0}{\mu_0 + \lambda_0} \left[\overline{M}_n \left(\frac{d\check{\mu}_0}{dt} + \frac{d\check{\lambda}_0}{dt}\right) - \left(\frac{d\check{\mu}_1}{dt} + \frac{d\check{\lambda}_1}{dt}\right)\right] \tag{24}$$

The additional equation of change for time as a state variable is given by

$$\frac{dt}{d\overline{M}_n} = \left[\frac{d\overline{M}_n}{dt}\right]^{-1} \tag{25}$$

Objective 4

The last objective is to determine the control policy for jacket temperature that would maximize monomer conversion for a specified, final weight average polymer molecular weight ($\overline{M}_{w,f}$), i.e., the performance index,

$$\underset{\max}{J} = X(\overline{M}_{w,f}) = X_f \tag{26}$$

This objective requires the satisfaction of eqs. (1)–(11) after their transformation, so that the independent variable is weight average polymer molecular weight ($\overline{M}_w$). The transformed equations are given by

$$\frac{d\check{y}_j}{d\overline{M}_w} = \left[\frac{d\overline{M}_w}{dt}\right]^{-1} \frac{d\check{y}_j}{dt} \quad j = 0, 1, 2, \ldots, 10 \tag{27}$$

where

$$\overline{M}_w = M_m \left(\frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1}\right) \tag{28}$$

$$\frac{d\overline{M}_w}{dt} = \frac{M_m \mu^0}{\mu_1 + \lambda_1} \left[\overline{M}_w \left(\frac{d\check{\mu}_1}{dt} + \frac{d\check{\lambda}_1}{dt}\right) - \left(\frac{d\check{\mu}_2}{dt} + \frac{d\check{\lambda}_2}{dt}\right)\right] \tag{29}$$

The additional equation of change for time as a state variable is given by

$$\frac{dt}{d\overline{M}_w} = \left[\frac{d\overline{M}_w}{dt}\right]^{-1} \tag{30}$$

For Objectives 2–4, the transformations of the process model, eqs. (1)–(11), enable its integration in the range of a selected independent variable (other than time) up to its desired, final value.

INTEGRATION OF THE PROCESS MODEL

The four objectives described earlier require the integration of the process model with appropriate independent variables (t, $\breve{m}$, $\overline{M}_n$, and $\overline{M}_w$) for performance index evaluations. These equations are very stiff and nonlinear. In this work, they were numerically integrated using semi-implicit Bader-Deuflhard algorithm, and adaptive step-size control.[15] Analytical expressions for Jacobians were employed for integration. The equations to evaluate the elements of Jacobian corresponding to each objective are provided in the next section.

Equations for Jacobian evaluations

Jacobians are provided for the normalized state variables, and time (for Objectives 2–4) with respect to the independent variable depending on an optimal control objective. Using the start-up values, y_j^0, and the basic Jacobian elements, $d/dy_k\left(dy_j/dt\right)$, $j,k = 0, 1, 2, \ldots, 10$, the Jacobian elements are sequentially calculable as described below for each optimal control objective.

Jacobian for Objective 1

For all state variables, the elements of the Jacobian are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{d\breve{y}_j}{dt}\right) = \begin{cases} \dfrac{y_k^0}{y_j^0}\dfrac{d}{dy_k}\left(\dfrac{dy_j}{dt}\right) & \text{if } y_j^0 > 0 \\ 0, & \text{if } y_j^0 = 0 \end{cases};$$

$$j, k = 0, 1, 2, \ldots, 10 \tag{31}$$

This Jacobian is same for other optimal control objectives until the independent variable of eqs. (1)–(11), which initially is time, is replaced with $\breve{m}$, $\overline{M}_n$, and $\overline{M}_w$ for Objectives 2, 3, and 4, respectively. Time then becomes a new state variable of the transformed process model. For this transformation, the new independent variable must be nonzero. The Jacobians for Objectives 2–4 are then sequentially calculable as follows:

Jacobian for Objective 2 after transformation

In this case, the independent variable is the normalized monomer concentration $\breve{m}$. The Jacobian elements for time, corresponding to $j = 0$, are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{dt}{d\breve{m}}\right) = -m^0 y_k^0 \left[\frac{dm}{dt}\right]^{-2}\frac{d}{dy_k}\left(\frac{dm}{dt}\right);$$

$$k = 0, 1, 2, \ldots, 10 \tag{32}$$

The Jacobian elements for remaining state variables, corresponding to $j = 1, 2, \ldots, 10$, are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{d\breve{y}_j}{d\breve{m}}\right) = -\frac{1}{y_j^0}\frac{dy_j}{dt}\frac{d}{d\breve{y}_k}\left(\frac{dt}{d\breve{m}}\right) + \alpha$$

$$k = 0, 1, 2, \ldots, 10 \tag{33}$$

where

$$\alpha = \begin{cases} -m^0\left[\dfrac{dm}{dt}\right]^{-1}\dfrac{y_k^0}{y_j^0}\dfrac{d}{dy_k}\left(\dfrac{dy_j}{dt}\right), & \text{if } y_j^0 > 0 \\ 0, & \text{if } y_j^0 = 0 \end{cases} \tag{34}$$

Jacobian for Objective 3 after transformation

In this case, the independent variable is the number average polymer molecular weight, $\overline{M}_n$. The basic Jacobian elements for $\overline{M}_n$ are given by

$$\frac{d}{dy_k}\left(\frac{d\overline{M}_n}{dt}\right) = \frac{M_m}{\mu_0 + \lambda_0}\left[\frac{d}{dy_k}\left(\frac{d\mu_1}{dt}\right) + \frac{d}{dy_k}\left(\frac{d\lambda_1}{dt}\right)\right] - \frac{M_m}{\mu_1 + \lambda_1}\left[\frac{d}{dy_k}\left(\frac{d\mu_0}{dt}\right) + \frac{d}{dy_k}\left(\frac{d\lambda_0}{dt}\right)\right]$$

$$+ \beta_0 \quad k = 0, 1, 2, \ldots, 10 \tag{35}$$

where

$$\beta_0 = \begin{cases} \dfrac{-M_m}{(\mu_0 + \lambda_0)^2}\left[\left(\dfrac{d\mu_1}{dt} + \dfrac{d\lambda_1}{dt}\right) - 2\overline{M}_n\left(\dfrac{d\mu_0}{dt} + \dfrac{d\lambda_0}{dt}\right)\right], & \text{for } y_k = \mu_0, \lambda_0 \\[4mm] \dfrac{-M_m}{(\mu_0 + \lambda_0)^2}\left(\dfrac{d\mu_0}{dt} + \dfrac{d\lambda_0}{dt}\right), & \text{for } y_k = \mu_1, \lambda_1 \\[4mm] 0, & \text{for all other } y_k s \end{cases} \tag{36}$$

The Jacobian elements for time as a state variable, corresponding to $j = 11$, are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{dt}{d\overline{M}_n}\right) = y_k^0\left[\frac{d\overline{M}_n}{dt}\right]^{-2}\frac{d}{dy_k}\left(\frac{d\overline{M}_n}{dt}\right);$$
$$k = 0, 1, 2, \ldots, 10 \quad (37)$$

$$\frac{d}{dt}\left(\frac{dt}{d\overline{M}_n}\right) = 0 \quad (38)$$

The Jacobian elements for remaining state variables, corresponding to $j = 1, 2, \ldots, 10$, are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{d\breve{y}_j}{d\overline{M}_n}\right) = -\frac{1}{y_j^0}\frac{dy_j}{dt}\frac{d}{d\breve{y}_k}\left(\frac{dt}{d\overline{M}_n}\right) + \gamma_0;$$
$$k = 0, 1, 2, \ldots, 10 \quad (39)$$

$$\frac{d}{dt}\left(\frac{d\breve{y}_j}{d\overline{M}_n}\right) = 0 \quad (40)$$

where,

$$\gamma_0 = \begin{cases}\left[\frac{d\overline{M}_n}{dt}\right]^{-1}\frac{y_k^0}{y_j^0}\frac{d}{dy_k}\left(\frac{dy_j}{dt}\right), & \text{if } y_j^0 > 0 \\ 0, & \text{if } y_j^0 = 0\end{cases} \quad (41)$$

Jacobian for Objective 4 after transformation

In this case, the independent variable is the weight average polymer molecular weight, $\overline{M}_w$. The basic Jacobian elements for $\overline{M}_w$ are given by

$$\frac{d}{dy_k}\left(\frac{d\overline{M}_w}{dt}\right) = \frac{M_m}{\mu_1 + \lambda_1}\left[\frac{d}{dy_k}\left(\frac{d\mu_2}{dt}\right) + \frac{d}{dy_k}\left(\frac{d\lambda_2}{dt}\right)\right] - M_m\frac{\mu_2 + \lambda_2}{(\mu_1 + \mu_2)^2}\left[\frac{d}{dy_k}\left(\frac{d\mu_1}{dt}\right) + \frac{d}{dy_k}\left(\frac{d\lambda_1}{dt}\right)\right] + \beta_1;$$
$$k = 0, 1, 2, \ldots, 10 \quad (42)$$

where,

$$\beta_0 = \begin{cases}\dfrac{-M_m}{(\mu_1 + \lambda_1)^2}\left[\left(\dfrac{d\mu_2}{dt} + \dfrac{d\lambda_2}{dt}\right) - 2\overline{M}_w\left(\dfrac{d\mu_1}{dt} + \dfrac{d\lambda_1}{dt}\right)\right], & \text{for } y_k = \mu_1, \lambda_1 \\[4mm] \dfrac{-M_m}{(\mu_1 + \lambda_1)^2}\left(\dfrac{d\mu_1}{dt} + \dfrac{d\lambda_1}{dt}\right), & \text{for } y_k = \mu_2, \lambda_2 \\[4mm] 0, & \text{for all other } y_k s\end{cases} \quad (43)$$

The Jacobian elements for time as a state variable, corresponding to $j = 11$, are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{dt}{d\overline{M}_w}\right) = y_k^0\left[\frac{d\overline{M}_w}{dt}\right]^{-2}\frac{d}{dy_k}\left(\frac{d\overline{M}_w}{dt}\right)$$
$$k = 0, 1, 2, \ldots, 10 \quad (44)$$

$$\frac{d}{dt}\left(\frac{dt}{d\overline{M}_w}\right) = 0 \quad (45)$$

The Jacobian elements for remaining state variables, corresponding to $j = 1, 2, \ldots, 10$, are given by

$$\frac{d}{d\breve{y}_k}\left(\frac{d\breve{y}_j}{d\overline{M}_w}\right) = -\frac{1}{y_j^0}\frac{dy_j}{dt}\frac{d}{d\breve{y}_k}\left(\frac{dt}{d\overline{M}_w}\right) + \gamma_1;$$
$$k = 0, 1, 2, \ldots, 10 \quad (46)$$

$$\frac{d}{dt}\left(\frac{d\breve{y}_j}{d\overline{M}_w}\right) = 0 \quad (47)$$

where,

$$\gamma_1 = \begin{cases}\left[\frac{d\overline{M}_w}{dt}\right]^{-1}\frac{y_k^0}{y_j^0}\frac{d}{dy_k}\left(\frac{dy_j}{dt}\right), & \text{if } y_j^0 > 0 \\ 0, & \text{if } y_j^0 = 0\end{cases} \quad (48)$$

For the integration of equations of change for Objectives 3 and 4, μ^0 was adjusted so that the difference between value of independent variable (e.g., $\overline{M}_n$), and that calculated using other state variables [e.g., from eq. (23)] is negligible. For Objectives 2–4, the transformation of process model was done as soon as the new independent variable achieved a finite value lying within the first stage of temperature policy.

Various parameters used in calculations are provided in Table I. The reactants for BMA polymerization are monomer, *n*-butyl methacrylate or BMA, monofunctional initiator, 2,2′-azobisisobutyronitrile or AIBN, and some impurity as an inhibitor. The product is the polymer, poly(BMA). It may be noted that the gel effect in the BMA polymerization is suppressed[22] and

TABLE I
Model Parameters Used in Calculations

Parameter	Value or expression	Reference
f	0.6	Present study
i^0 (mol/L)	1.829×10^{-2}	
m^0 (mol/L)	6.035	
T^0 (°C)	60 (Objectives 1 and 2), 0 (Objectives 3 and 4)	
T_{max} (°C)	90	
$T_{j,max}$ (°C)	120	
$T_{j,min}$ (°C)	4 (Objectives 1 and 2), 20 (Objectives 3 and 4)	
z^0 (mol/L)	4.5×10^{-5}	
V^0 (L)	1	
μ^0	10^{-6}	
$K_{tf,z}$ (L/mol min)	$1.4 \times 10^3\, K_p$	
M_m (kg/kmol)	142.2 (for BMA)	
K_d (L/mol min)	4.26×10^{-4}	16
K_p (L/mol min)	$2 \times 10^8 \exp[-2.8057 \times 10^3/(T + 273.15)]$	17
UA (cal/min K)	156.49	13
$-\Delta H$ (cal/mol)	1.3743×10^4	
$K_{tf,m}$ (L/mol min)	$1.4 \times 10^{-5}\, K_p$	18
ρ_m (g/L)	$286.91 \times 0.2545^{-[1-(T+273.15)/616]^{0.2857}}$	
C_p (cal/g K)	$0.22417 + 1.8179 \times 10^{-3}(T + 273.15) - 5.0421$ $\times 10^{-6}(T + 273.15)^2 + 6.1489 \times 10^{-9}\,(T + 273.15)^3$	19
K_t (L/mol min)	$2 \times 10^{11} \exp[-1,803.8/(T + 273.15)]$	20
ρ_p (g/L)	$1,187 - (T + 273.15)$	21

insignificant up to about 40% monomer conversion.[16,23] Furthermore, appropriate gel effect models for termination and propagation rate coefficients are not available at the present time. Therefore, the present work has been limited to the realm of maximum 40% BMA conversion where the gel effect is insignificant. The reference for the comparison of optimal results is the "base case" of isothermal, BMA polymerization with AIBN initiator at 60°C, which was simulated and verified from the experimental data published by Nair and Muthana.[16]

OPTIMAL CONTROL METHOD

The mathematical model of bulk, batch polymerization reactor is highly nonlinear. Furthermore, due to the inequality constraints of eqs. (14) and (15), the relation between the performance index and jacket temperature for Objectives 1–4 would not necessarily be unimodal and continuous for the four objectives. To overcome these difficulties, a robust optimal control method based on genetic algorithm[12] was applied. This optimal control method iteratively uses the three genetic operations of selection, crossover and mutation in the size-varying domain of control function with logarithmic and linear mappings. The method does not require any input of feasible control solution, or any auxiliary condition. Selection picks control functions stochastically from their population on the basis of performance index or "fitness." A control function with better fitness has a greater probability to populate a new set of control functions. Crossover works on the

new set or population, which has a larger proportion of control functions with better fitnesses. Crossover recombines the building blocks of these control functions expressed as binary digits, or bits. This operation results in a newer population of "children," some of which are likely to be better than their "parents." Finally, mutation changes the bits of children with a very low probability, and is equivalent to a local search for the control functions of even better fitnesses.

This method has been successfully applied earlier to determine optimal policies for ethylene polymerization in an industrial tubular reactor,[24] and methyl methacrylate polymerization in batch reactors.[3,4] Further details of this method may be found in Ref. 12. In this work, the policy to be optimally determined was the temperature of heat-exchange fluid inside reactor jacket (or jacket temperature) as a function of specified independent variable. Jacket temperature was considered to be a series of five discrete step values equispaced in the range of independent variable. The number of step values (or control stages), the mathematical model of bulk, batch polymerization reactor with its parameters, and the process constraints of eqs. (14) and (15) were the inputs to the optimal control method. These inputs are needed to evaluate the performance index (fitness) for a given control function. The application of the method yielded the optimal control function by stochastically applying genetic operations on a randomly generated set (population) of control functions constrained by eq. (15). Since the method generates optimal control functions within the control domain, the constraints of eq. (15) are satisfied automatically. The method eliminates any control function for

TABLE II
Summary of Optimal Results

Objective	Specification	J in base case	Optimal J
1	$t_f = 70$ min	$X_f = 25.5\%$	$X_f = 36.5\%$ max
2	$X_f = 40\%$	$t_f = 119.1$ min	$t_f = 79.1$ min min
3	$\overline{M}_{n,f} = 5 \times 10^5$	$X_f = 7.8\%$	$X_f = 38.6\%$ max
4	$\overline{M}_{w,f} = 9.4 \times 10^5$	$X_f = 1.5\%$	$X_f = 2.6\%$ max

which any other process constraint [eq. (14) in this application] is violated during the evaluation of corresponding performance index.

RESULTS

The optimal results for the four objectives are summarized and compared with the base case in Table II. The results show significant performance improvements in the performance of the batch polymerization process.

Results for Objective 1

To realize this objective, monomer conversion in the batch polymerization reactor was maximized for the specified operation time of 70 min. The optimal policy for jacket temperature (i.e., optimal jacket temperature versus time) is presented in Figure 1. The figure shows the evolution of jacket temperature from a random series of step values of jacket temperature to its optimal level as the iterations of the optimal control method continue with progressive increase in final monomer conversion. It is observed that the optimal jacket temperature is close to its upper limit of 90°C. Optimal monomer conversion is 36.5%, which is an improvement of 43% over that in the base case.
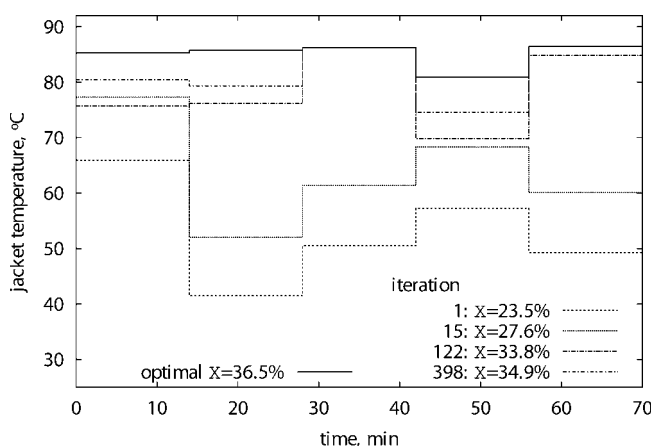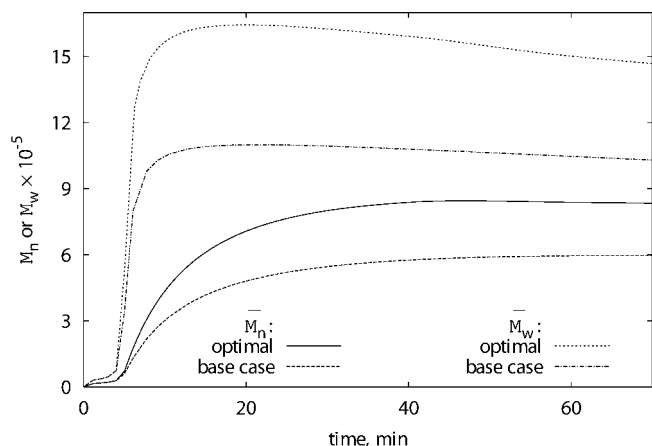

Figure 1 Optimal jacket temperature versus time for Objective 1.
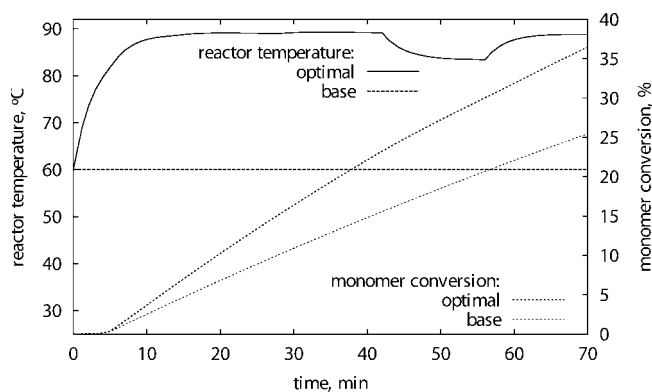

Figure 2 Reactor temperature and monomer conversion versus time for Objective 1.

Corresponding to the optimal jacket temperature of Figure 1, the optimal reactor temperature and monomer conversion with time are shown in Figure 2 along with the variables for the base case. It is observed that the optimal reactor temperature after the first control stage is in phase with the optimal jacket temperature, which indicates its strong influence on reaction temperature. At all times, the optimal reactor temperature is well within the upper limit of 90°C specified through eq. (14). For time greater than zero, the optimal reactor temperature and monomer conversion are higher than those respectively, for the base case.

The optimal values of number and weight average polymer molecular weights ($\overline{M}_n$ and $\overline{M}_w$) are shown in Figure 3 along with those for the base case. It is observed that the initial rate of increase of optimal $\overline{M}_n$ as well as $\overline{M}_w$ with time is significantly higher and more prolonged than that in the base case. In comparison to the base case, the final values of optimal $\overline{M}_n$ and $\overline{M}_w$ are higher by about 38% and 50%, respectively. This increase suggests that the high optimal reactor temperature under the present unsteady state conditions favors the generation of polymer molecules with

Figure 3 Optimal number and weight average molecular weight of polymer versus time for Objective 1.

Figure 4 Optimal jacket temperature versus time for Objectives 2–4.
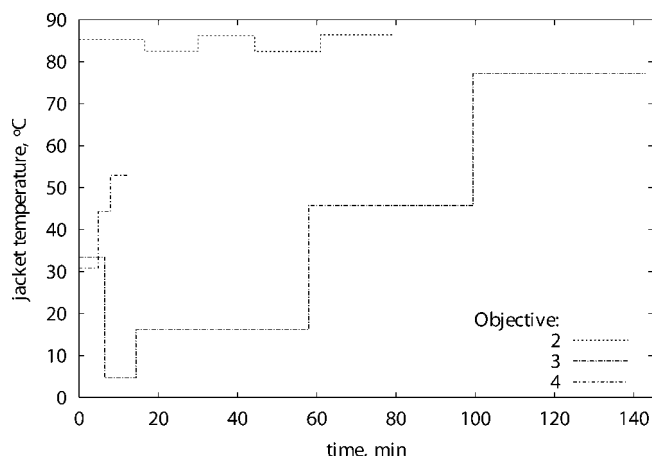
Figure 5 Optimal reactor temperature versus time for Objectives 2–4.

longer chain lengths. In fact, this departure in the values of average polymer molecular weights from the base case motivated the formulation of Objectives 3 and 4, which target the maximization of monomer conversion with specified, final $\overline{M}_n$ and $\overline{M}_w$, respectively.

Results for Objective 2

To realize this objective, the operation time of batch polymerization was minimized for the specified, final monomer conversion of 40%. The optimal policy for jacket temperature is presented in Figure 4. Optimal jacket temperature is close to its upper limit of 90°C, similar to what was observed for Objective 1. Moreover, the time-averaged value of the optimal jacket temperature is approximately same as that in case of Objective 1. This similarity of the optimal jacket temperature is reasonable because the attainment of each of Objectives 1 and 2 demands that the overall rate of monomer conversion be maximized through jacket temperature.

Optimal reactor temperature, shown in Figure 5, closely follows the optimal jacket temperature second control stage onward. This behavior was observed earlier in case of Objective 1. Corresponding to the optimal jacket temperature, the optimal value of the operation time is 79.1 min, which is a reduction by 34% relative to that of the base case.

The optimal number and weight average polymer molecular weights ($\overline{M}_n$ and $\overline{M}_w$) are shown in Figure 6. The change in the average molecular weights with time almost coincides with that in case of Objective 1. The reason is that corresponding optimal reactor and jacket temperatures for Objective 1 and 2 are not much different, and are close to their upper limit.
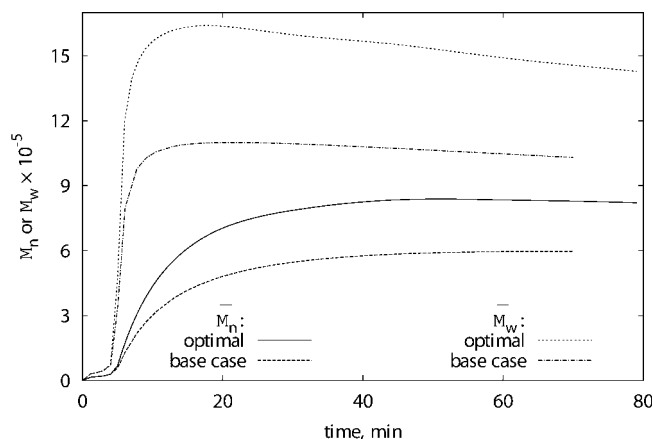
Results for Objective 3

To realize this objective, monomer conversion in the bulk, batch polymerization of BMA was maximized
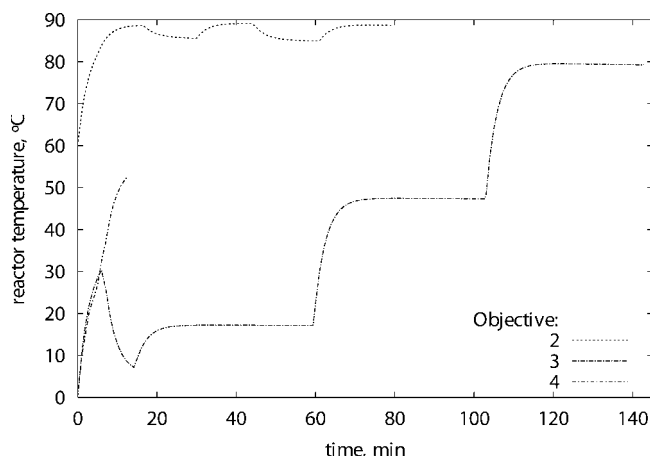
for the specified, final number average molecular weight, $\overline{M}_{nf} = 5 \times 10^5$. For the base case with the constant reactor temperature of 60°C, the time needed to achieve this value of $\overline{M}_{nf}$ is about 22 min with 7.8% monomer conversion as seen in Figures 3 and 2, respectively. Generally, the time needed for a given $\overline{M}_{nf}$ would increase with a decrease in reaction temperature. To enable extended operation time for optimal control through jacket temperature, and to facilitate higher monomer conversion (during longer operation time), the initial temperature of reactor was set at a low value of 0°C. Furthermore, lower temperature range was made available to jacket temperature by reducing its lower limit to −20°C. It may be noted that these settings are provisions for numerical calculations only, and enable the initial generation of feasible policies for subsequent improvement. Several numerical experiments showed that for Objective 3 as well as 4, the initial policies and subsequent optimal results could be generated only with these settings.

Figure 6 Optimal number and weight average molecular weight of polymer versus time for Objective 2.

Figure 4 shows the resulting optimal policy for jacket temperature, which spans 142.9 min of operation time, and yields the final monomer conversion of 38.6%. This conversion is a substantial improvement by approximately four folds over that in the base case. Although the lower limit for jacket temperature is $-20°C$, its lowest optimal value is above $0°C$. Optimal jacket temperature climbs up with time after its initial decline, and is closely followed by corresponding optimal reactor temperature as seen in Figure 5. While lower, initial reactor temperature obviates the early attainment of $\overline{M}_{n,f}$ with low monomer conversion; higher reactor temperature later on boosts the final monomer conversion. The optimal rates of change of $\overline{M}_n$ and $\overline{M}_w$ (Fig. 7) are initially very high, but become more gradual later on.

Results for Objective 4

To realize this objective, monomer conversion in batch polymerization was maximized for the specified, final weight average molecular weight, $\overline{M}_{w,f} = 9.4 \times 10^5$. For the base case with the constant reactor temperature of $60°C$, the time needed to achieve this value of $\overline{M}_{w,f}$ is about 7 min with 1.5% monomer conversion as seen in Figures 3 and 2, respectively. During that short time, the rate of change of $\overline{M}_w$ with time is about an order of magnitude higher than that for $\overline{M}_n$. As a result, the realization of the present objective with high monomer conversions is expected to be very challenging. Optimal control results for this objective were obtained for the same initial reactor temperature, and the lower limit of jacket temperature that were used for Objective 3.

Figure 4 shows the resulting optimal jacket temperature versus time, which spans only 12.7 min of operation time, and effectively comprises three control stages as the second, third, and fourth stages have same jacket temperature. Corresponding final monomer conversion, which although is an improvement by 73% over the base case, is a low value of 2.6%. Optimal
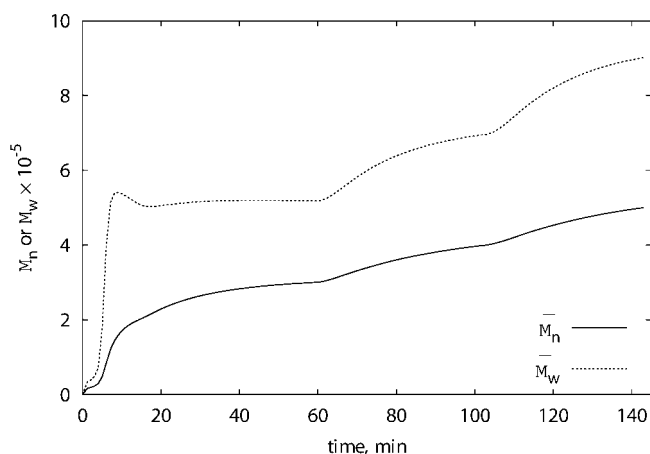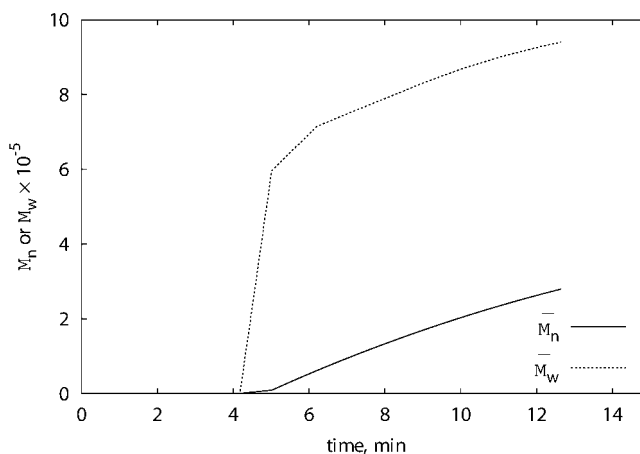
Figure 8 Optimal number and weight average molecular weight of polymer versus time for Objective 4.

jacket temperature increases stagewise with time, and is closely followed by corresponding optimal reactor temperature as seen in Figure 5. Optimal $\overline{M}_n$ and $\overline{M}_w$ (Fig. 8) before 4.3 min are of the order of 10^3. Immediately after, $\overline{M}_w$ increases rapidly with time and is indicative of the severe limitation of short time available for optimal control.

CONCLUSIONS

Four objectives were realized for the bulk polymerization of BMA in a batch reactor based on a detailed nonisothermal process model. The objectives were: (i) maximization of monomer conversion in a specified operation time, (ii) minimization of operation time for specified, final monomer conversion, (iii) maximization of monomer conversion for a specified, final number average polymer molecular weight, and (vi) maximization of monomer conversion for a specified, final weight average polymer molecular weight. The temperature of heat-exchange fluid inside reactor jacket was employed as a control function of a specified independent variable. The process constraints of maximum reactor temperature and the upper and lower limits to the heat-exchange fluid were imposed. The above mentioned objectives were designed to help augment operational efficiency, and achieve a higher degree of product specificity in polymer production. Equations were provided to suitably transform the process model in the range of a specified variable other than time, and to evaluate the elements of Jacobian. Based on the process model, the objectives were realized for the bulk batch polymerization of BMA using a genetic algorithm-based optimal control method. The optimal results showed significant performance improvements in the range, 34–395%. For the last objective, the optimal monomer conversion was not as high as that for other objectives. It was observed that even with low initial reactor temperature, the rate of increase of the

Figure 7 Optimal number and weight average molecular weight of polymer versus time for Objective 3.

weight average polymer molecular weight was extremely high. When its final value was specified for the last objective, this phenomenon limited monomer conversion by drastically reducing the operation time for optimal control.

NOMENCLATURE

A　　heat transfer area, m^2

C_p　　specific heat of reactant mixture, cal/g K

f　　efficiency of initiator

i　　concentration of initiator, mol/L

i^0　　initial i, mol/L

$\check{\imath}$　　normalized i

I　　initiatior

J　　performance index

K_d　　rate coefficient of chemical initiation, 1/min

K_p　　rate coefficient of propagation, L/mol min

K_t　　rate coefficient of termination by combination, L/mol min

$K_{tf,m}$　　rate coefficient of chain transfer to monomer, L/mol min

$K_{tf,z}$　　rate coefficient of chain transfer to inhibitor, L/mol min

m　　monomer concentration, mol/L

m^0　　initial m, mol/L

$\check{m}$　　normalized m

$\check{m}_f$　　final $\check{m}$

M　　monomer

$\overline{M}_n$　　number average molecular weight, g/mol

$\overline{M}_{n,f}$　　final, specified $\overline{M}_n$, g/mol

$\overline{M}_w$　　weight average molecular weight, g/mol

$\overline{M}_{w,f}$　　final, specified $\overline{M}_n$, g/mol

M_m　　monomer molecular weight, g/mol

P_l　　dead polymer with chain length l

$R^{\bullet}_{in}$　　initiator radical

$R^{\bullet}_l$　　radical of chain length l

t　　time, min

t_f　　final, specified operation time, min

T　　temperature of reactants (or reactor), °C

T^0　　initial T, °C

T_{max}　　upper limit to T, °C

$\check{T}$　　normalized T

T_j　　temperature of heat exchange fluid in reactor jacket, °C

$T_{j,max}$　　upper limit to T_j, °C

$T_{j,min}$　　lower limit to T_j, °C

U　　heat transfer coefficient for reactor wall and jacket, cal/m^2·min·K

V　　volume of reactants inside reactor, L

V^0　　initial V, L

$\check{V}$　　normalized V

X　　monomer conversion, %

X_f　　specified, final X

y_k　　k-th state variable

z　　concentration of inhibitor, mol/L

z^0　　initial z, mol/L

$\check{z}$　　normalized z

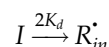Z　　inhibitor

$Z^{\bullet}$　　inactive inhibitor radical

Greek symbols

$-\Delta H$　　heat of polymerization, cal/mol

λ_i　　i-th moment of live polymer radical

$\check{\lambda}_i$　　normalized λ_i

μ_i　　i-th moment of dead polymer

$\check{\mu}_i$　　normalized μ_i

μ^0　　parameter used to normalize radical and polymer moments

ρ_m　　monomer density, g/L
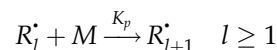
ρ_p　　polymer density, g/L

APPENDIX: FREE RADICAL POLYMERIZATION MECHANISM

Based on the approach of Villalobos et al.,[13] and Dhib et al.,[14] the following free-radical polymerization mechanism is used in this study.
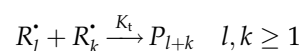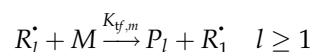
Chemical initiation

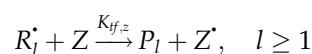$$I \xrightarrow{2K_d} R^{\bullet}_{in}$$

Propagation

$$R^{\bullet}_l + M \xrightarrow{K_p} R^{\bullet}_{l+1} \quad l \geq 1$$

Termination

$$R^{\bullet}_l + R^{\bullet}_k \xrightarrow{K_t} P_{l+k} \quad l,k \geq 1$$

Transfer to monomer

$$R^{\bullet}_l + M \xrightarrow{K_{tf,m}} P_l + R^{\bullet}_1 \quad l \geq 1$$

Transfer to inhibitor (or impurity)

$$R^{\bullet}_l + Z \xrightarrow{K_{tf,z}} P_l + Z^{\bullet}, \quad l \geq 1$$

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