

PHYSICAL PROPERTY CONTROL FOR A BATCH POLYMERIZATION REACTOR

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Abstracts A method to determine an optimal temperature trajectory that guarantees polymer products having controlled molecular weight distribution and desired values of molecular weight is presented. The coordinate transformation method and the optimal control theory are applied to a batch PMMA polymerization system to calculate the optimal temperature trajectory. Coordinate transformation method converts the original fixed-end-point, free-end-time problem to a free-end-point, fixed-end-time problem. The idea is that by making the reactor temperature track the optimal temperature trajectory one may be able to produce polymer products having the prespecified physical property in a minimum time. The on-line control experiments with the PID control algorithm have been conducted to establish the validity of the scheme proposed in this study. The experimental results show that prespecified polymer product could be obtained with tracking the calculated optimal temperature trajectory.

Keywords Batch polymerization reactor, Optimal control, Coordinate transformation method, Control experiment, Temperature trajectory tracking.

1. INTRODUCTION

The typical goal in operating a polymerization reactor system is to get the polymer product with prespecified physical properties. A good number of studies have been reported on the control and optimization of polymerization reactor system[1]. In particular, Thomas and Kiparissides[2] applied the optimal control theory to obtain near-optimal strategy for reaction temperature and initiator feed rate in a batch PMMA polymerization system. Kwon and Evans [3] suggested the coordinate transformation method for minimum-time control problems. However, experimental studies on the physical properties control for the polymerization reactor system seem to be rather scarce.

In this study, the coordinate transformation method and the optimal control theory are applied to a batch PMMA polymerization system to calculate the optimal temperature trajectory with minimum reaction time. The optimal temperature trajectory are corroborated by conducting the on-line digital control experiments for tracking the trajectory.

2. MODEL DEVELOPMENT

The solution polymerization of MMA in a batch reactor with ethyl acetate solvent and benzoyl peroxide initiator is to be considered. The kinetics is assumed to follow the free radical polymerization mechanism including chain transfers to solvent and to monomer, respectively. From the mass balance the following differential equations can be derived for initiator(I), monomer(M), solvent(S), living polymer(G), and dead polymer(F).

$$\begin{aligned} \frac{1}{V} \frac{d(I)V}{dt} &= -k_d I \\ \frac{1}{V} \frac{d(M)V}{dt} &= -2fk_d I - k_p MG - k_{trm} MG_0 \\ \frac{1}{V} \frac{d(S)V}{dt} &= -k_{trs} SG_0 \\ \frac{1}{V} \frac{d(G_0)V}{dt} &= 2fk_d I - k_t G_0^2 \\ \frac{1}{V} \frac{d(G_1)V}{dt} &= 2fk_d I + k_p MG_0 - k_t G_0 G_1 \\ &\quad + k_{trm} M(G_0 - G_1) + k_{trs} S(G_0 - G_1) \\ \frac{1}{V} \frac{d(G_2)V}{dt} &= 2fk_d I + k_p M(G_0 + 2G_1) - k_t G_0 G_2 \\ &\quad + k_{trm} M(G_0 - G_2) + k_{trs} S(G_0 - G_2) \end{aligned} \quad (1)$$

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$$\begin{aligned}
\frac{1}{V} \frac{d(F_0 V)}{dt} &= \frac{1}{2} k_i G_0^2 + \frac{1}{2} k_{td} G_0^2 + k_{trm} M G_0 + k_{trs} S G_0 \\
\frac{1}{V} \frac{d(F_1 V)}{dt} &= k_i G_0 G_1 + k_{trm} M G_1 + k_{trs} S G_1 \\
\frac{1}{V} \frac{d(F_2 V)}{dt} &= k_{tc} (G_0 G_2 + G_1^2) + k_{td} G_0 G_2 + k_{trm} M G_2 \\
&\quad + k_{trs} S G_2
\end{aligned} \quad (2)$$

Here, G_k and F_k are the k -th moments of living and dead polymer concentrations. The consideration for the volume contraction is included.

It is well-known that free radical polymerization kinetics exhibit the gel effect, which results from the self-acceleration of the polymerization rate and from the diffusion controlled termination reaction among the large polymer radicals. At high conversion, the propagation rates may be also diffusion controlled when the polymerization temperature is below the glass transition temperature of the polymer being synthesized. In this work we adopted the gel effect correlation proposed by Schmidt and Ray[4].

The temperature dependence of the rate constants is assumed to follow the Arrhenius law. The kinetic data used for the simulation of this study are taken from Chang[5].

3. FORMULATION OF OPTIMAL CONTROL PROBLEM

Consider the system described by

$$\dot{\mathbf{x}}(t) = \mathbf{f}[\mathbf{x}, \mathbf{u}(t)], \quad \mathbf{x}(t_0) = \mathbf{x}_0 \quad (3)$$

$$\begin{aligned}
\mathbf{x} &= [V, I, M, S, G_0, G_1, G_2, F_0, F_1, F_2] \\
\mathbf{u} &= [T] \text{ (control input, temperature)} \\
t &= \text{time}
\end{aligned}$$

If the control input \mathbf{u} is selected, the solution to the equation is uniquely determined with the initial condition \mathbf{x}_0 . Consider the performance index J defined as

$$\begin{aligned}
J(t_f) &= \omega_1 \left[\frac{X(t_f)}{X_d} - 1 \right]^2 + \omega_2 \left[\frac{M_n(t_f)}{M_{nd}} - 1 \right]^2 \\
&\quad + \omega_3 \left[\frac{M_w(t_f)}{M_{wd}} - 1 \right]^2
\end{aligned} \quad (4)$$

where X , M_n and M_w denote the conversion, number average molecular weight and weight average molecular weight, respectively. The subscript d represents the desired value and t_f the final time, and ω_1 , ω_2 and ω_3 denote the weighting factors. It is required to find an admissible control $\mathbf{u}^*(t)$ which minimizes the performance index J . Then such a control $\mathbf{u}^*(t)$ is called the optimal control and $\mathbf{x}^*(t)$ the

optimal trajectory. The classical calculus leads to the following solution. Define the Hamiltonian H as :

$$\begin{aligned}
H(\mathbf{x}, \mathbf{u}, t) &= \lambda^T \mathbf{f}(\mathbf{x}, \mathbf{u}, t) \\
&= \sum_{i=1}^{10} \lambda_i f_i \\
&= \lambda_1 f_1 + \dots + \lambda_{10} f_{10}
\end{aligned} \quad (5)$$

where λ_i is called the costate vector or adjoint vector. The costate vector must satisfy the canonical equation.

$$-\dot{\lambda} = \frac{\partial H}{\partial \mathbf{x}} \Rightarrow -\dot{\lambda}_i = \frac{\partial \left(\sum_{i=1}^{10} \lambda_i f_i \right)}{\partial x_i} \quad (6)$$

($t \leq t_f$) t_f : final time

A necessary condition for optimality, derived from the classical calculus is the gradient of the Hamiltonian H relative to the control vector \mathbf{u} must be zero along the optimal trajectory.

$$0 = \frac{\partial H}{\partial \mathbf{u}} = \frac{\partial \mathbf{f}^T}{\partial \mathbf{u}} \lambda \quad (7)$$

The final boundary condition of costate equation is given by

$$\lambda^T(t_f) = \frac{\partial J}{\partial \mathbf{x}} \bigg|_{t_f} \quad (8)$$

Solution to the optimal problem can be obtained by solving the two point boundary value problem for the state equation and the costate equation

4. COORDINATE-TRANSFORMATION METHOD

The minimum-time optimal control problem is referred to as a fixed-end-point, free-end-time problem for all of the state variables are specified at the end of interval, but the length of the interval is unspecified and is, in fact, to be minimized by an optimal choice of the control inputs. The coordinate transformation method proposed herein converts the minimum-time control problem to an equivalent free-end-point, fixed-end-time problem. The necessary condition for coordinate transformation is that at least one state variable is monotone (that is, its time derivative does not change sign during the time interval of interest). In polymerization reactor system, the monomer conversion may be chosen as the monotone variable.

Consider an n -th order system

$$\begin{aligned}
\dot{\mathbf{x}}(t) &= \mathbf{f}[\mathbf{x}, \mathbf{u}(t)] \\
\mathbf{x}(t_0) &= \mathbf{x}_0 \\
\mathbf{x}(t_f) &= \mathbf{x}_f
\end{aligned} \quad (9)$$

where \mathbf{x} is the n vector of state variables($x_1, x_2, x_3, \dots, x_n$), and \mathbf{u} is the m vector of control inputs. The state variables can be rearranged, such that x_1 is the monotone variable which will be substituted for the independent variable. We can then make the coordinate transformation as follows:

$$\tau \leftarrow x_1, y_1 \leftarrow t, y_i \leftarrow x_i \quad (i > 1)$$

Thus the system equation becomes

$$\dot{\mathbf{y}}(\tau) = \mathbf{F}(\mathbf{y}, \mathbf{u}, \tau) \quad (10)$$

where

$$\begin{aligned} F_1 &= 1/f_1, & F_i &= f_i/f_1 \quad (i > 1) \\ y_1(\tau_0) &= t_0, & y_i(\tau_0) &= x_{i0} \quad (i > 1) \\ y_1(\tau_f) &= \text{free}, & y_i(\tau_f) &= x_{if} \quad (i > 1) \\ \tau_0 &= x_{10}, & \tau_f &= x_{1f} \quad (\text{fixed}) \end{aligned}$$

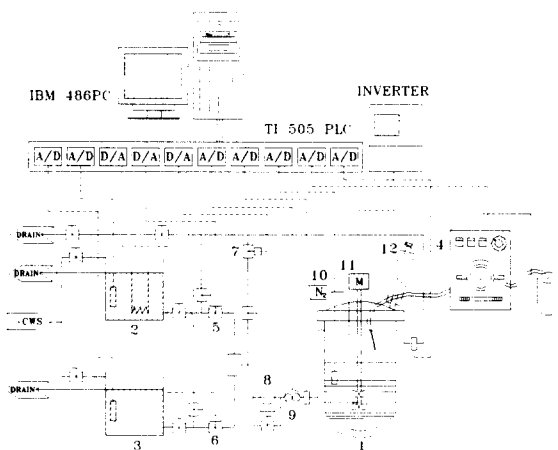
$$J(\tau_f) = \rho_1 y_1^2 + \rho_2 \left[\frac{Mn(\tau_f)}{Mn_d} - 1 \right]^2 + \rho_3 \left[\frac{Mw(\tau_f)}{Mw_d} - 1 \right]^2 \quad (11)$$

Now we have the control problem with free-end-point, fixed-end-time as follows:

$$\begin{aligned} \dot{\mathbf{y}}(\tau) &= \mathbf{F}(\mathbf{y}, \mathbf{u}, \tau) \\ \mathbf{y}(\tau_0) &= \mathbf{y}_0, \quad \mathbf{y}(\tau_f) = \text{free}, \quad \tau_f : \text{fixed} \end{aligned} \quad (12)$$

5. EXPERIMENTAL

Fig.1 is the schematic diagram of the batch PMMA polymerization system used in this study. The reactor temperature was controlled by regulating the flowrates of hot water and cold water supplied to the jacket by



1. Polymerization reactor
2. Hot water reservoir
3. Cold water reservoir
4. mixing chamber
5. Hot water control valve
6. Cold water control valve
7. Recycle water control valve
8. Coolant circulation pump
9. Coolant flowmeter
10. N₂ inlet
11. Stirrer motor
12. Reflux condenser

Fig. 1. Schematic diagram of the batch PMMA polymerization system.

split-range control. Part of coolant was recirculated to reduce disturbance in the jacket temperature. The samples taken out every 20 minutes were quenched by using cold methanol, and the monomer conversion was determined by gravimetry while the average molecular weights were measured by gel permeation chromatography.

6. RESULTS AND DISCUSSION

The temperature trajectories are obtained by applying the Pontryagin's maximum principle and the coordinate-transformation method. The performance index is composed of the reaction time and the number- and weight-average molecular weights. Figure 2 shows the sequence of temperature trajectories as the weighting factor ρ_1 increases. The temperature trajectories show gradual rise with the progress of time regardless of the value of ρ_1 . Increase of ρ_1 means that the reaction time is becoming more and more important, so there may be errors in number- and weight-average molecular weights in the case of larger value of ρ_1 than in the case of smaller value of ρ_1 . As the value of ρ_1 increases, the minimum reaction time decreases and the errors in the number- and weight-average molecular weights become larger as expected.

Presented in Fig. 3 are the temperature trajectories and the corresponding variations in monomer conversion, number- and weight-average molecular weights for different values of prespecified number-and

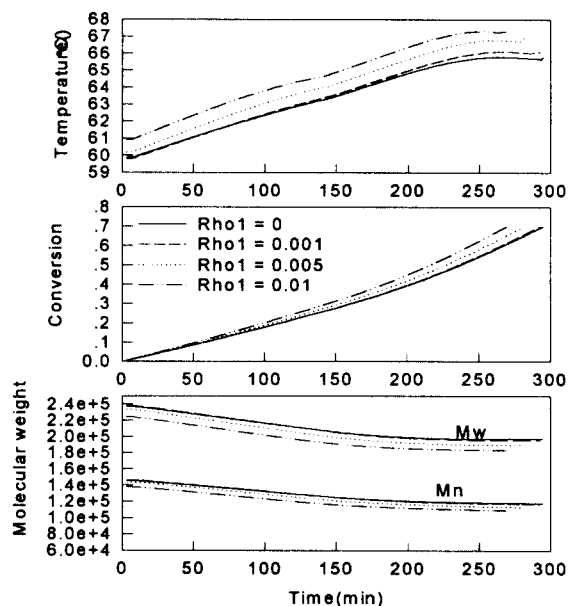


Fig. 2. Temperature trajectories and corresponding variations in conversion, number- and weight-average molecular weights for various values of ρ_1 ($X_d=0.7$, $Mn_d=120,000$, $PD_d=1.7$).

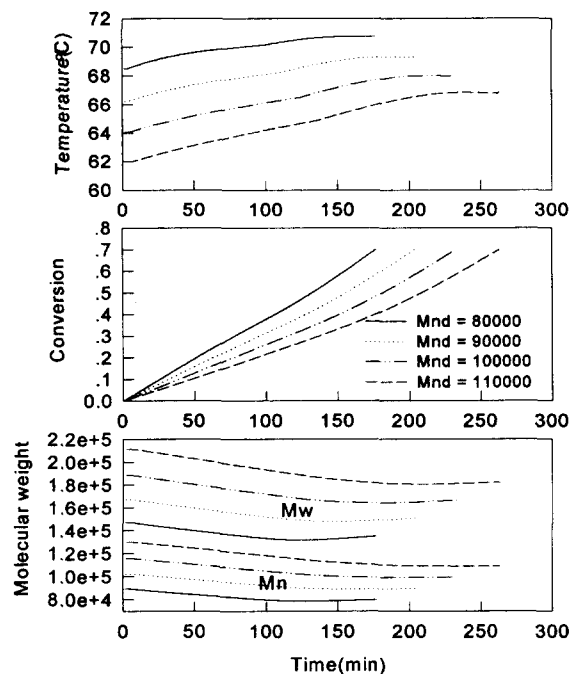


Fig. 3. Temperature trajectories and corresponding variations in conversion, number- and weight-average molecular weights for various conditions ($X_d=0.7$, $PD_d=1.7$).

weight average molecular weights. As the prespecified value of number average molecular weight increases, the trajectory maintains higher temperature and the minimum reaction time becomes shorter.

Figure 4 shows the results of on-line digital control experiments for tracking the optimal temperature trajectory obtained by applying the Pontryagin's maximum principle and the coordinate transformation method. The PID control algorithm with fixed tuning performed quite satisfactorily for the temperature control. Not only the monomer conversion but also the average molecular weights show good agreement between the experimental and simulation results. Consequently, the strategy of optimal temperature trajectory is proven effective for producing polymers having desired properties.

6. CONCLUSIONS

A mathematical method for the optimal temperature trajectory which provide polymer product of desired physical properties in minimum reaction time is presented. The simulation results show that as the desired number average molecular weight increases, the temperature trajectory gets lowered and the minimum reaction time increases. Control experiments are conducted to track the temperature trajectory and the results are found to be in good agreement with the desired values. Consequently, it is proven that the polymer product having desired physical properties can

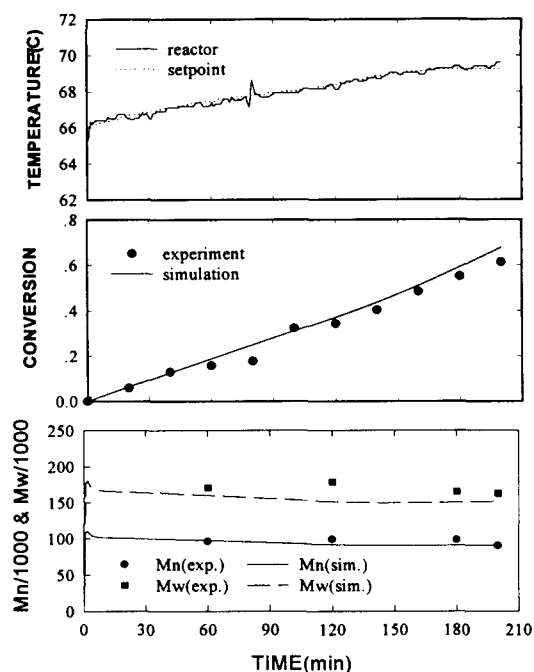


Fig. 4. Experimental results for tracking the optimal temperature trajectory ($X_d=0.7$, $Mn_d=90,000$, $PD_d=1.7$).

be obtained by operating the batch reactor in such a way that the reactor temperature track the temperature trajectory calculated by applying the method presented herein.

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