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TIME-OPTIMAL CONTROL OF MMA-MA COPOLYMERIZATION IN A CSTR FOR GRADE CHANGE

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Abstract – The time-optimal control of MMA-MA copolymerization in a CSTR is treated for a grade-change operation. The control objective is to bring system specifications, such as polymer production rate and polymer composition, to desired values in minimum time. The initiator concentration is chosen as a manipulated variable. Two cases are considered: One is to get the time optimal control for both a desired polymer production rate and a desired weight composition of MA in dead copolymer; the other is only for a desired polymer production rate. In numerical calculation, the final $t_f^{(i)}$ is chosen at each iteration as the time at which the system reached steady-state. This allows us to use a more easily manipulatable form of the performance index and at the same time not directly use the free final time boundary condition.

Key words: *Time-Optimal Control, MMA-MA Copolymerization, Grade Change Operation, Minimum Principle*

INTRODUCTION

A grade change operation involves the production of two or more products with different properties or specifications in one reactor system by changing operating conditions. The frequency and magnitude of grade changes are determined by both prices and market demand. Recently, growing environmental regulations and ever-increasing public awareness have forced companies to pay attention to pollution prevention. Since off-specification products during transient time usually cause serious treatment problems, we want to shorten, as much as possible, the time required for the grade change and thereby minimize off-specification products during the transient time. The time-optimal control of a polymerization process involves finding the control input trajectory for polymer properties, such as molecular weight and composition, or system specification, such as polymer production rate and conversion, to reach desired values in minimum time.

Studies on the optimal control of a polymerization reaction mostly deal with optimal control of homopolymerization in a batch with a relatively simple model. Sacks et al. [1972] applied the minimum principle to determine optimal temperature and initiator addition policies that minimize reaction times for chain addition polymerizations in batch reactors. Ponnuswamy et al. [1987] also applied the minimum principle for the time optimal control of the free radical solution polymerization of MMA in a batch reactor. The minimum principle requires numerically intensive computation of nonlinear differential equations to solve two point boundary value problems. Therefore, Chang and Lai [1992] proposed a modified two step method to determine the time profiles of reactor temperature and initiator concentration for a prescribed molecular weight distribution (MWD) in a free radical polymerization batch reactor.

In spite of the importance of a grade change operation in a continuous polymerization process, only a few studies have been performed. McAuley and MacGregor [1992] determined optimal open-loop policies for optimal grade transitions in a gas phase fluidized-bed polyethylene reactor using a control parameterization approach that discretized control input and approximated it as a ramp function in each interval. Lee et al. [1997] obtained time-optimal control policies based on a parameterization approach for the start-up or grade change operation of a copolymerization system using genetic algorithms with converging range on control inputs. However, the result obtained by the parameterization approach is just an approximation of the optimal control input trajectory.

Therefore, we propose a method for obtaining an optimal control input trajectory rigorously based on the minimum principle even for highly complicated nonlinear polymerization reactions. We here deal with the time-optimal control of the isothermal free radical solution copolymerization of MMA (Methyl Metacrylate)-MA (Methylacrylate) in CSTR.

REACTION MECHANISM OF MMA-MA COPOLYMERIZATION

We consider one initiation step, four propagation steps, three termination steps and two chain transfer reactions [Lee, 1995]. The initiation step is

$$I \xrightarrow{k_i} 2R$$

The propagation steps are

$$A_{i,j}\cdot + A \xrightarrow{k_{paa}} A_{i+1,j}\cdot$$

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$$A_{i,j}\cdot + B \xrightarrow{k_{pab}} B_{i,j+1}\cdot$$
$$B_{i,j}\cdot + A \xrightarrow{k_{pba}} A_{i+1,j}\cdot$$
$$B_{i,j}\cdot + B \xrightarrow{k_{pbb}} B_{i,j+1}\cdot$$

The termination steps by combination are

$$A_{i,j}\cdot + A_{n,m}\cdot \xrightarrow{k_{taa}} P_{i+n,j+m}$$
$$A_{i,j}\cdot + B_{n,m}\cdot \xrightarrow{k_{tab}} P_{i+n,j+m}$$
$$B_{i,j}\cdot + B_{n,m}\cdot \xrightarrow{k_{tbb}} P_{i+n,j+m}$$

where $k_{tab}=\sqrt{k_{taa}k_{tbb}}$, and the chain transfer reactions are

$$A_{i,j}\cdot + T \xrightarrow{k_{Ta}} P_{i,j} + T\cdot$$
$$B_{i,j}\cdot + T \xrightarrow{k_{Tb}} P_{i,j} + T\cdot$$

By quasi-steady state approximation, the concentrations of free radicals are

$$C_A\cdot = \sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}}$$
$$C_B\cdot = \chi C_A\cdot \qquad (1)$$

where $\chi=\frac{k_{pab}C_B}{k_{pba}C_A}$. Reaction rates are obtained by using the long chain hypothesis.

$$R_A=\left(k_{paa}\sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}} + k_{pba}\chi\sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}}\right)C_A$$
$$R_B=\left(k_{pab}\sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}} + k_{pbb}\chi\sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}}\right)C_B$$
$$R_T=\left(k_{Ta}\sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}} + k_{Tb}\chi\sqrt{\frac{2k_iC_i}{k_{taa}+2\chi k_{tab}+\chi^2k_{tbb}}}\right)C_T$$
$$R_{PA}=-R_A$$
$$R_{PB}=-R_B \qquad (2)$$

The kinetic parameter values are k_i=0.01, k_{paa}=262.71, k_{pab}=155.50, k_{pba}=1000.0, k_{pbb}=340.0, k_{taa}=1.4967e+6, k_{tbb}=1.1196e+6, k_{Ta}=102.19, k_{Tb}=23.767 [Lee, 1995].

TIME-OPTIMAL CONTROL FOR A GRADE CHANGE

We consider the time-optimal control of MMA-MA copolymerization in a CSTR for a grade-change operation. We want to obtain the time optimal initiator concentration profile which makes both polymer production rate and weight composition of MA in the dead copolymer reach the desired values in minimum time and stay there as steady state values for a continuous system. The usual practice is to define a performance index (J) for optimal control of a continuous system as in the following formula [Luus, 1993; McAuley and McGregor, 1992]:

$$J=\int_{t_0}^{t_f} w_1(X(t)-X_d)^2+w_2(Y_{MA}(t)-Y_{MA,d})^2\,dt \qquad (3)$$

where, W_d=0.6, $Y_{MA,d}$=0.07 and w_1, w_2 are weight factors which denote the relative importance of each term in the performance index J. The polymer production rate and the weight composition of MA in the dead copolymer are defined as

$$X=\frac{R_AM_A+R_BM_B}{(F_A+F_B)/V} \qquad (4)$$

$$Y_{MA}=\frac{C_{PB}M_B}{C_{PA}M_A+C_{PB}M_B} \qquad (5)$$

where C_{PA} and C_{PB} are the concentrations of two monomers MMA(A), MA(B) in the dead copolymer, respectively.

However, since the integrand of the performance index is very complicated and highly nonlinear, as is often the case in a copolymerization process [MacGregor and Hamielec, 1984; Ray, 1986], it is quite difficult to apply the minimum principle directly. In a numerical calculation, if we integrate the state equations until they reach steady state and take the time required to reach the steady state as the final time $t_f^{(i)}$ at each iteration and then modify it from iteration to iteration, we can obtain the same results for a continuous system by using the following performance index:

$$J=\int_{t_0}^{t_f} dt+w_1(X_{t_f}-X_d)^2+w_2(Y_{MA,t_f}-Y_{MA,d})^2 \qquad (6)$$

More details will be discussed later in the numerical procedure. We choose a control variable u(t) as the concentration of initiator:

$$u(t)=C_i(t) \qquad (7)$$

The following state equations are derived from the material balances for two monomers **MMA**, **MA**, chain-transfer agent (T) and the concentrations of two monomers **MMA**, **MA** in the dead copolymer, C_{PA} and C_{PB}, with the initial values:

$$\frac{dC_k}{dt}=\frac{C_{k_f}-C_k}{\theta_\tau}-R_k \quad C_k(0)=C_{k_0},\quad k=A,\ B,\ T,\ PA,\ PB \qquad (8)$$

where the residence time θ_τ depends on the feed flow rates. The flow rate of the initiator is very small compared with the total feed flow rate. Therefore, the change of the initiator flow rate has no significant effect on the total feed flow rate and is negligible. Since we manipulate only the flow rate of the initiator, we assume that the total feed flow rate and the residence time are constant. Next we define the Hamiltonian H as

$$H=1+\sum_k P_k\left(\frac{C_{k_f}-C_k}{\theta_\tau}-R_k\right),\quad k=A,\ B,\ T,\ PA,\ PB \qquad (9)$$

and the costate equations as

$$\frac{\partial P_k}{\partial t}=-\frac{\partial H}{\partial C_k},\quad k=A,\ B,\ T,\ PA,\ PB$$

$$\frac{\partial P_A}{\partial t}=\left\{-P_A\left(\frac{1}{\theta_\tau}+\frac{\partial R_A}{\partial C_A}\right)-P_B\frac{\partial R_B}{\partial C_A}-P_T\frac{\partial R_T}{\partial C_A}+P_{PA}\frac{\partial R_A}{\partial C_A}+P_{PB}\frac{\partial R_B}{\partial C_A}\right\}$$

$$\frac{\partial P_B}{\partial t}=\left\{-P_A\frac{\partial R_A}{\partial C_B}-P_B\left(\frac{1}{\theta_\tau}+\frac{\partial R_B}{\partial C_B}\right)-P_T\frac{\partial R_T}{\partial C_B}+P_{PA}\frac{\partial R_A}{\partial C_B}+P_{PB}\frac{\partial R_B}{\partial C_B}\right\}$$

$$\frac{\partial P_T}{\partial t}=-\left\{-P_T\left(\frac{1}{\theta_\tau}+\frac{\partial R_T}{\partial C_T}\right)\right\}$$

$$\frac{\partial P_{PA}}{\partial t}=\frac{P_{PA}}{\theta_\tau}$$

$$\frac{\partial P_{PB}}{\partial t}=\frac{P_{PB}}{\theta_\tau}\tag{10}$$

Although the final polymer production rate and the final weight composition of MA in the dead copolymer are fixed, the final states are not completely fixed according to Eqs. (4) and (5). This problem is therefore a free terminal state problem. So we obtain the following boundary conditions at t_f.

$$P_k(t_f)=\frac{\partial\{w_1(X-X_d)^2+w_2(Y_{MA}-Y_{MA,d})^2\}}{\partial C_k}\Big|_{t=t_f},$$

$$k=A,\ B,\ T,\ PA,\ PB$$

$$P_A(t_f)=\frac{2w_1(X-X_d)}{(F_A+F_B)/V}\left(\frac{\partial R_A}{\partial C_A}M_A+\frac{\partial R_B}{\partial C_A}M_B\right)\Big|_{t=t_f}$$

$$P_B(t_f)=\frac{2w_1(X-X_d)}{(F_A+F_B)/V}\left(\frac{\partial R_A}{\partial C_B}M_A+\frac{\partial R_B}{\partial C_B}M_B\right)\Big|_{t=t_f}$$

$$P_T(t_f)=0.0$$

$$P_{PA}(t_f)=-\frac{2w_2(Y_{MA}-Y_{MA,d})(C_{PB}M_AM_B)}{(C_{PA}M_A+C_{PB}M_B)^2}\Big|_{t=t_f}$$

$$P_{PB}(t_f)=\frac{2w_2(Y_{MA}-Y_{MA,d})M_B(C_{PA}M_A+C_{PB}M_B)}{(C_{PA}M_A+C_{PB}M_B)^2}-\frac{2w_2(Y_{MA}-Y_{MA,d})C_{PB}M_B^2}{(C_{PA}M_A+C_{PB}M_B)^2}\Big|_{t=t_f}\tag{11}$$

Because the terminal t_f is not specified, we can obtain another boundary condition,

$$H(t_f)+\frac{\partial\{w_1(X-X_d)^2+w_2(Y_{MA}-Y_{MA,d})^2\}}{\partial t}\Big|_{t=t_f}=H(t_f)=0\tag{12}$$

If the control input is not constrained, it should satisfy the following necessary condition to minimize the performance index.

$$\frac{\partial H}{\partial C_i}=-P_A\frac{\partial R_A}{\partial C_i}-P_B\frac{\partial R_B}{\partial C_i}-P_T\frac{\partial R_T}{\partial C_i}+P_{PA}\frac{\partial R_A}{\partial C_i}+P_{PB}\frac{\partial R_B}{\partial C_i}=0\tag{13}$$

As a special case of the previous problem, we also obtain the time optimal initiator concentration profile that minimizes the required time to reach only a desired polymer production rate. We define the performance index J as

$$J=\int_{t_0}^{t_f}dt+w(X_{t_f}-X_d)^2\tag{14}$$

where X_d=0.7. The polymer production rate **X** is defined as

$$X=\frac{R_AM_A+R_BM_B}{(F_A+F_B)/V}\tag{15}$$

We choose a control variable u(t) as the concentration of initiator again:

$$u(t)=C_i(t)\tag{16}$$

The state equations are again obtained from the material balances for two monomers MMA, MA and chain-transfer agent with the following initial values:

$$\frac{dC_k}{dt}=\frac{C_{k_f}-C_k}{\theta_\tau}-R_k\quad C_k(0)=C_{k_0},\quad k=A,\ B,\ T\tag{17}$$

Here the residence time θ_τ is constant for the same reason as in the previous problem. Next we define the Hamiltonian H as

$$H=1+\sum_k P_k\left(\frac{C_{k_f}-C_k}{\theta_\tau}-R_k\right),\quad k=A,\ B,\ T\tag{18}$$

and the costate equations as

$$\frac{\partial P_k}{\partial t}=-\frac{\partial H}{\partial C_k},\quad k=A,\ B,\ T$$

$$\frac{\partial P_A}{\partial t}=-\left\{-P_A\left(\frac{1}{\theta_\tau}+\frac{\partial R_A}{\partial C_A}\right)-P_B\frac{\partial R_B}{\partial C_A}-P_T\frac{\partial R_T}{\partial C_A}\right\}$$

$$\frac{\partial P_B}{\partial t}=-\left\{-P_A\frac{\partial R_A}{\partial C_B}-P_B\left(\frac{1}{\theta_\tau}+\frac{\partial R_B}{\partial C_B}\right)-P_T\frac{\partial R_T}{\partial C_B}\right\}$$

$$\frac{\partial P_T}{\partial t}=-\left\{-P_T\left(\frac{1}{\theta_\tau}+\frac{\partial R_T}{\partial C_T}\right)\right\}\tag{19}$$

Although the final polymer production rate is fixed, the final states are not completely fixed because of Eq. (15). This problem therefore becomes a free terminal state problem. We obtain the following boundary conditions at t_f.

$$P_k(t_f)=\frac{\partial\{w(X-X_d)^2\}}{\partial C_k}\Big|_{t=t_f},\quad k=A,\ B,\ T$$

$$P_A(t_f)=\frac{2w(X-X_d)}{(F_A+F_B)/V}\left(\frac{\partial R_A}{\partial C_A}M_A+\frac{\partial R_B}{\partial C_A}M_B\right)\Big|_{t=t_f}$$

$$P_B(t_f)=\frac{2w(X-X_d)}{(F_A+F_B)/V}\left(\frac{\partial R_A}{\partial C_B}M_A+\frac{\partial R_B}{\partial C_B}M_B\right)\Big|_{t=t_f}$$

$$P_T(t_f)=0.0 \tag{20}$$

Because the terminal time t_f is not specified, we need the boundary condition

$$H(t_f)+\frac{\partial\{w(X-X_d)^2\}}{\partial t}\Big|_{t=t_f}=H(t_f)=0 \tag{21}$$

If the control input is not constrained, it should satisfy the following necessary condition:

$$\frac{\partial H}{\partial C_i}=-P_A\frac{\partial R_A}{\partial C_i}-P_B\frac{\partial R_B}{\partial C_i}-P_T\frac{\partial R_T}{\partial C_i}=0 \tag{22}$$

COMPUTATION SCHEME

Among many numerical iteration methods [Kirk, 1970; Stengel, 1986], we use the steepest-descent algorithm based on the gradient search direction method with some modification to implement our approach. At first, we assume the initial control input trajectory $C_i^{(0)}(t)$, then integrate the state Eq. (8) with the initial conditions and previous control input using Gear's method, and store the resulting state trajectory and $\frac{\partial R_A}{\partial C_A}$, $\frac{\partial R_A}{\partial C_B}$, $\frac{\partial R_B}{\partial C_A}$, $\frac{\partial R_B}{\partial C_B}$, $\frac{\partial R_T}{\partial C_A}$, $\frac{\partial R_T}{\partial C_B}$, $\frac{\partial R_T}{\partial C_T}$, $\frac{\partial R_A}{\partial C_i}$, $\frac{\partial R_B}{\partial C_i}$, $\frac{\partial R_T}{\partial C_i}$ values. Unlike the conventional approach, we select the final time $t_f^{(i)}$ as the time at which the system reaches steady-state (i.e., when the system state variables do not vary any more within the given accuracy). This means that $t_f^{(i)}$ is not fixed during the entire numerical calculations, but it is fixed at each iteration step. Thus $t_f^{(i)}$ is modified from iteration to iteration. This technique allows us to use the performance index in Eq. (6) instead of that in Eq. (3) and to regard the problem as a fixed final time and free terminal state problem during the numerical calculation. Thus, it allows us to disregard the final time boundary conditions $H(t_f)+\frac{\partial\{w(X-X_d)^2\}}{\partial t}\big|_{t=t_f}=0$. The next step is to calculate $P_k(t_f^{(i)})$ using boundary conditions (11). Then using this value $P_k(t_f^{(i)})$ as the initial conditions of backward integration and with the stored values, we integrate the costate Eq. (10) from $t_f^{(i)}$ to t_0 by evaluating $\frac{\partial H}{\partial C_i}$ and modifying the value of the control input variable by the relationship, $C_i^{n+1}(t)=C_i^n(t)-\varepsilon\frac{\partial H(t)}{\partial C_i(t)}$. Note that we set the control input value after $t_f^{(i)}$ as constant (value at $t_f^{(i)}$) to guarantee that the states after $t_f^{(i)}$ are steady states at each iteration. The stopping criteria are checked next, $\sum_{t=t_0}^{t_f}\{C_i^n(t)-C_i^{n-1}(t)\}^2<\varepsilon_1$, where

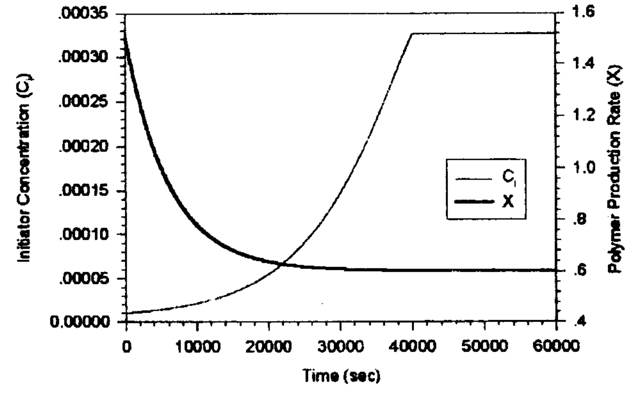

Fig. 1. Initiator concentration and polymer production rate as functions of time.

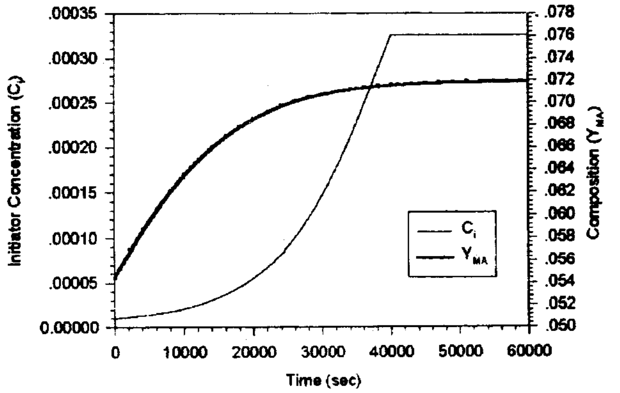

Fig. 2. Initiator concentration and weight composition of MA as functions of time.

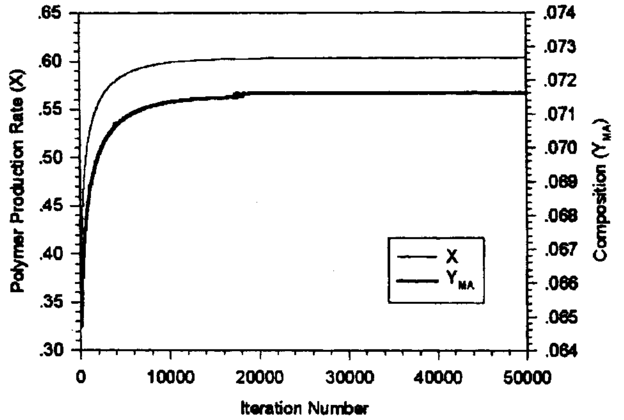

Fig. 3. Polymer production rate and weight composition of MA as functions of iteration number.

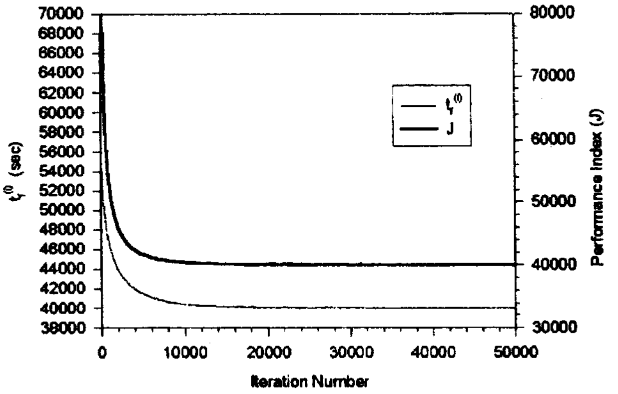

Fig. 4. $t_f^{(i)}$ and performance index J as functions of iteration number.

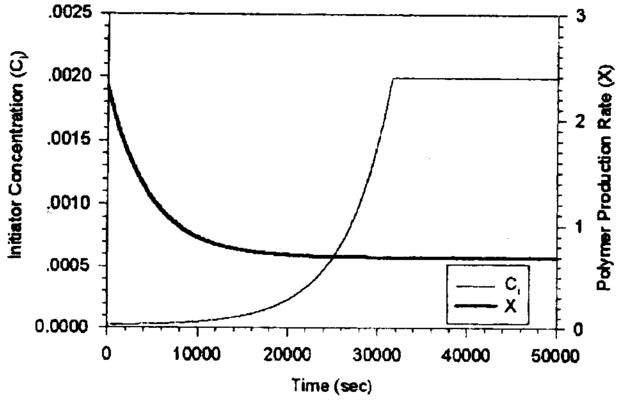

Fig. 5. Polymer production rate and initiator concentration as functions of time.

ε_1 are predefined small positive constants. If the criteria are satisfied, the iteration is stopped; if not, the above procedure is repeated.

RESULTS

Fig. 1-7 show the results of the numerical computations. In Figs. 1 and 2, the initiator concentration trajectories, the change of polymer production rate and weight composition of MA in the dead copolymer as functions of time, are shown. The polymer production rate (X) and weight composition of MA in the dead copolymer (Y_{MA}) reach the desired values (X_d =0.6, $Y_{MA,d}$=0.07) quite well and stay there. We find that we should increase the flow rate of initiator until X and Y_{MA} reach the desired values, then keep it at that steady state value. Fig. 3 shows that X and Y_{MA} reach the desired values as the iteration number increases. In Fig. 4, the values of the performance index (J) and $t_f^{(i)}$ decrease until they reach minimum values as the iteration number increases. There is a point after which the values of X, Y_{MA} and $t_f^{(i)}$ do not vary any more within the given accuracy. Therefore, we can regard the values corresponding to the point as the final values, X_{t_f}, Y_{MA,t_f} and t_f, respectively. We also obtained time as an optimal initiator concentration profile for a desired polymer production rate. Fig. 5 shows the initiator concentration trajectory and the change of polymer production rate as functions of time. The polymer production rate reaches the desired value (X_d=0.7) quite well and stays there. Fig. 6 and Fig. 7 show the polymer production rate (X), $t_f^{(i)}$ and performance index (J) as functions of iteration number. As the iteration number increases, X reaches the desired value, and $t_f^{(i)}$ and J decrease. There is also a point after which the values of X and $t_f^{(i)}$ do not vary any further within the given accuracy, and we can regard these values as the final values, X_{t_f} and t_f.

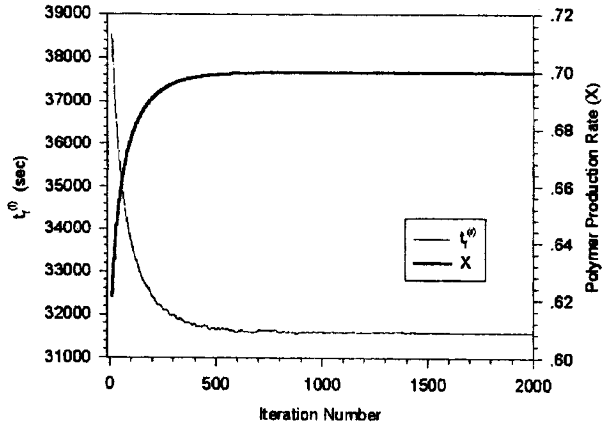

Fig. 6. Polymer production rate and $t_f^{(i)}$ as functions of iteration number.

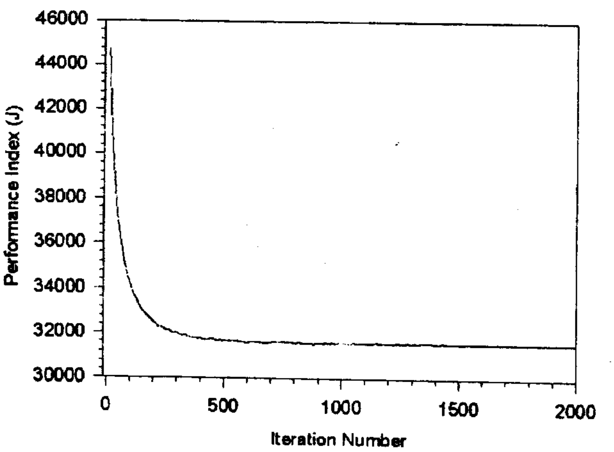

Fig. 7. Performance index J as a function of iteration number.

CONCLUSIONS

It is shown in this study that a modified application of the minimum principle for complicated nonlinear polymerization reactions successfully results in the optimal control trajectory. The time-optimal control of a continuous MMA-MA copolymerization system is treated here for a grade-change operation. We select the initiator concentration as a manipulated variable and obtain the optimal control trajectories, the time-optimal initiator concentration profile for both the desired polymer production rate and desired weight composition of MA in dead copolymer, and the time-optimal initiator concentration profile for the desired polymer production rate. Since highly complex and nonlinear polymer reaction steps are involved, application of the minimum principle is rather messy but leads to the desired optimal trajectories. In numerical calculations, we select at each iteration the final time $t_f^{(i)}$ as the time at which the system reaches steady state. This technique allows us to use a more easily manipulatable form of the performance index and to regard the problem as a fixed final time and free terminal state problem during the numerical calculations. Then the complicated final time boundary condition, $H(t_f)=0$ (usually $H(t_f)+\frac{\partial h}{\partial t}|_{t=t_f}=0$) is not needed. This saves much time and effort in computation. The procedure is also applicable to time-optimal control of other complex and highly nonlinear continuous systems.

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NOMENCLATURE

A : monomer MMA
$A_{i,j}\cdot$: free radical that ends with monomer A
B : monomer MA
$B_{i,j}\cdot$: free radical that ends with monomer B
C_k : concentration of species k [kgmol/m^3]
C_{kf} : feed concentration of species k [kgmol/m^3]
C_{k0} : initial concentration of species k [kgmol/m^3]
$C_k\cdot$: free radical concentration of species k [kgmol/m^3]
F_k : mass flow rate of species k [kg/hr]
H : Hamiltonian
I : initiator
J : performance index
k : reaction rate constant [m^3/kgmol s]
MA : methylacrylate
MMA : methyl methacrylate
M_k : molecular weight of species k
P : dead copolymer
P_k : costate variable of species k
R_k : reaction rate of species k [kgmol/m^3 s]
T : chain transfer agent
t_f : final time [sec]
$t_f^{(i)}$: obtained final time at each iteration [sec]
t_0 : initial time [sec]
V : reactor volume (25 m^3)
w : weighting factor
X : polymer production rate per monomers used
Y_{MA} : weight composition of MA in dead copolymer

Greek Letters

ε : predefined small positive constant
θ_r : residence time [sec]
χ : $\frac{k_{pab} C_B}{k_{pba} C_A}$

Subscripts

A : monomer MMA
a : monomer MMA
B : monomer MA
b : monomer MA
d : desired value
i : initiator
PA : monomer MMA in dead copolymer
PB : monomer MA in dead copolymer
p : propagation step
T : chain transfer agent
t : termination step
t_f : final time

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