Molecular Weight Control of a Batch Polymerization Reactor: Experimental Study

Jyh-Shyong Chang* and Po-Hsun Liao

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, 3rd Sec., Taipei, Taiwan, Republic of China

A parameter estimation procedure was developed to fit a kinetic model with the experimental data obtained from methyl methacrylate (MMA) solution polymerization in a 10 L batch reactor. For molecular weight control, we applied the modified two-step method in calculating the optimal temperature trajectory on the basis of the identified kinetic model. Application of a conventional proportional-integral (PI) controller to track the temperature trajectory proved to be acceptable in a conventional batch reactor with both heating and cooling systems. Experimental results revealed that the identified model is accurate; therefore, one can rely on the calculated optimal temperature trajectories to ensure that the polymer product quality conforms to the specification.

Introduction

Many independent studies revealed that the mechanical properties of polymers strongly depend on the molecular weight distribution (MWD).[1−6] Therefore, the MWD control is highly desirable in operating a polymerization reactor. For the MWD control, the operation of a batch polymerization reactor is expected to obtain a prespecified conversion at the end of each batch cycle. The polymeric product will possess the desired averaged molecular weight and the polydispersity. Achievement of this goal hinges on both a reliable kinetic model and an efficient optimization method. Chang and Lai[7] proposed a modified two-step method for estimating the temperature trajectory of the reacting medium in order to obtain a polymer that has a prescribed molecular weight distribution.[3] First, profiles of the instantaneous average chain length and the polydispersity to give the desired MWD are estimated. Next, the time profile of reactor temperature is obtained via efficient tracking of the profile of the instantaneous average chain length only. In this study, we try to prove the applicability of the modified two-step method experimentally in a conventional batch reactor with both heating and cooling systems. For the solution polymerization of MMA, the solvent and initiator are toluene and azobis(isobutyronitrile) (AIBN), respectively. The chemicals of industrial grades are used to simulate the industrial conditions. It is expected to obtain a reliable kinetic model based on a set of isothermal reaction data. Although the isothermal experiments are conducted in a 10 L reactor because of the available control system provided in the experimental system, one can also perform an isothermal reaction in a smaller reactor system.

Experimental System

Figure 1 provides a schematic diagram of the experimental apparatus. The reactor is a 0.0122 m^3 (10 L) stainless steel cylindrical vessel with a 0.0254 m (1 in.) drain centered at the bottom. Computer control and the installed instrumentations for the experimental apparatus are also shown in Figure 1. Details of the reactor system including the specifications of the equipment and the instrumentations can be found in our previous work.[8]

Heating of the reaction mixture is achieved by adjusting the flow rate of hot water, F_{wj}, through the jacket-side of the reactor with a 3.72 kW centrifugal pump. Heat removal is carried out by manipulating the flow rate of coolant, F_{wc}, through the internal helical coil with another 3.72 kW centrifugal pump. Two pneumatic control valves, two flowmeters, and two rotameters are installed in the flow control loops. At the inlets and outlets of the jacket and the coil, four temperature sensors are located. The reactor temperature is measured by an RTD of the same type.

One vessel, V1, is used to provide the coolant. Another vessel, V2, is installed to serve as the heating medium. Still another vessel, V3, is used to provide a lower temperature coolant (about 8 °C) than V1 by circulating the water of this vessel through a chiller. These three vessels are about 0.08 m^3 in volume. An overflow pipe is inserted to maintain a constant head for each vessel. During the reaction, if the coolant flowrate is raised to above 10 L/min, the temperature of water in V1 is considered to be too high. Then the temperature in V1 would be adjusted with the external cooling water by an ON/OFF solenoid valve. On the other hand, if the coolant flow rate is reduced to below 5 L/min, the temperature of water in V1 is found too low and would be adjusted with an electric heater controlled by a solid-state relay (SSR). Meanwhile, the electric heater installed in V2 is also adjusted with an SSR to maintain the desired temperature of the heating medium.

There are two stainless steel ports (i.d. = 0.04 m) on the head of the reactor. One is adopted as the feeding port, and the other is used for monitoring the reaction. A stainless steel tube (i.d. = 0.01 m) is also located on the reactor head. This tube is used for the outlet of the vapor stream. Two Pyrex Graham condensers (i.d. = 0.025 m, length = 0.3 m) with drip-tip are connected in series, attached to the outlet of this tube, and are used to condense the vaporized solvent and monomer back

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* To whom correspondence should be addressed. E-mail: jschang@che.ttit.edu.tw. Fax number: +886-2-25861939. Telephone number: +886-2-25925252-3451.

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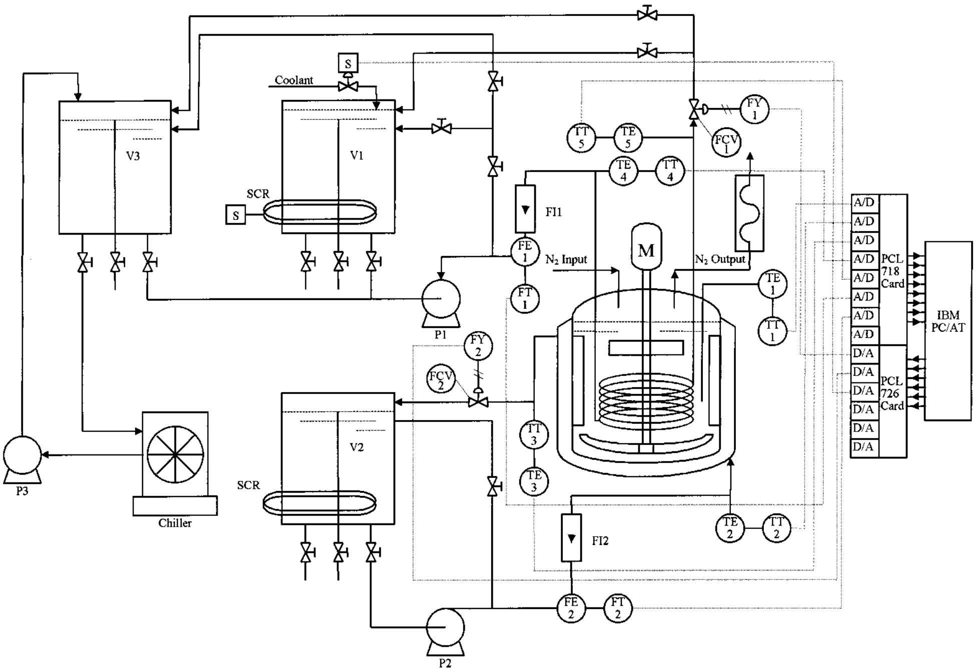

Figure 1. Schematic diagram of the experimental apparatus.

into the reactor. To purge the oxygen dissolved in solution, which is a reaction inhibitor, out of the system, we bubble the nitrogen gas into the mixture of reactants (MMA + toluene) through a glass tube (i.d. = 0.005 m; length = 0.32 m) inserted through the feeding port. This arrangement is designed to prevent any incoming of the oxygen component from the atmosphere of the reactor. During the polymerization reaction, a shorter glass tube (i.d. = 0.005 m; length = 0.05 m) is used for introducing blanking nitrogen. An immersion cooler (model CC-100II, NESLAB instruments, Inc.) provides the condenser with the coolant (5 °C). A vacuum pump located at the outlet of the condenser is used to vacuumize the batch reactor to pump out any gas bubble which is dissolved in the reacting mixture. Note that the existence of any bubble in the reacting medium will affect the accuracy in density measurement and the quality of the polymer product. During the reaction, we maintain the pressure around 30 mmHg (vacuum) by adjusting the power of the vacuum pump through an alterable resistor ranging from 0 to 140 V.

Kinetic Model for MMA Solution Polymerization. In a previous study of ours, the mechanisms of initiator decomposition, initiation, propagation, chain transfer to monomers and solvents, and terminations by disproportionation and combination were considered.[7] In the derivation of the mass balance equation for the different species, the rate constants are usually assumed to be independent of different chain lengths. However, the effect of volume contraction of the reaction mixture is not negligible. On the basis of the generalized free-radical polymerization mechanism,[7] the mass balance equations for the different species in the reactor can be derived.

Initiator. The mass balance for initiator is

$$\frac{\mathrm{d}[I]}{\mathrm{d}t} = -k_{\mathrm{d}}[I] - ([I]/V)(\mathrm{d}V/\mathrm{d}t) \tag{1}$$

Monomer, *i*th Moment of Living Radicals, and Dead Polymer Distributions. The monomer fractional conversion and the *i*th moment of living radicals and dead polymer distributions are defined as follows:

$$X(t) = \frac{V(0)[M(0)] - V(t)[M(t)]}{V(0)[M(0)]} \tag{2}$$

$$\lambda_i(t) = \sum_{n=1}^{\infty} n^i [P_n^{\bullet}(t)] \quad i = 0, 1, 2, ... \tag{3}$$

$$\mu_i(t) = \sum_{n=1}^{\infty} n^i [D_n(t)] V(t) \quad i = 0, 1, 2, ... \tag{4}$$

Furthermore, the number-average degree of polymerization $P_{\mathrm{N}}(t_{\mathrm{f}})$ and polydispersity $HI(t_{\mathrm{f}})$ of a polymer product are defined as

$$P_{\mathrm{N}}(t_{\mathrm{f}}) = \frac{\mu_1(t_{\mathrm{f}})}{\mu_0(t_{\mathrm{f}})} \tag{5}$$

$$HI(t_{\mathrm{f}}) = \frac{\mu_0(t_{\mathrm{f}})\mu_2(t_{\mathrm{f}})}{\mu_1^{\,2}(t_{\mathrm{f}})} \tag{6}$$

In the meantime, the next two equations are to be used in the following discussion:

$$\bar{M}_{\mathrm{n}} = P_{\mathrm{N}} MW_{\mathrm{M}} \tag{7}$$

$$\bar{M}_{\mathrm{w}} = \bar{M}_{\mathrm{n}} HI \tag{8}$$

Consumption of monomers goes through propagation, initiation, and transfer to monomer reactions. The mass balance for conversion of monomers is

$$\frac{\mathrm{d}X}{\mathrm{d}t} = (k_{\mathrm{p}} + k_{\mathrm{tm}})(1 - X)\lambda_0 \tag{9}$$

while those for the ith moment of living radical distributions are

$$\frac{\mathrm{d}(\lambda_0 V)}{\mathrm{d}t} = V(2fk_\mathrm{d}[I] - k_\mathrm{t}\lambda_0^{\,2}) \tag{10}$$

$$\frac{\mathrm{d}(\lambda_1 V)}{\mathrm{d}t} = V\{2fk_\mathrm{d}[I] + k_\mathrm{p}[M]\lambda_0 + (k_\mathrm{tm}[M] + k_\mathrm{ts}[S])(\lambda_0 - \lambda_1) - k_\mathrm{t}\lambda_0\lambda_1\} \tag{11}$$

$$\frac{\mathrm{d}(\lambda_2 V)}{\mathrm{d}t} = V\{2fk_\mathrm{d}[I] + k_\mathrm{p}[M](2\lambda_1 + \lambda_0) + (k_\mathrm{tm}[M] + k_\mathrm{ts}[S])(\lambda_0 - \lambda_2) - k_\mathrm{t}\lambda_0\lambda_2\} \tag{12}$$

If one adopts the quasi-steady-state approximation (QSSA) for the moment of $\lambda_i V|_{i=0,1,2}$, the rate change terms of eqs 10−12 can be set to be zero. Then, the moments of $\lambda_i|_{i=0,1,2}$ can be derived as

$$\lambda_0 = \left\{\frac{2fk_\mathrm{d}[I]}{k_\mathrm{tc} + k_\mathrm{td}}\right\}^{1/2} \tag{13}$$

$$\lambda_1 = \frac{\{(k_\mathrm{tc} + k_\mathrm{td})\lambda_0 + k_\mathrm{p}[M] + k_\mathrm{tm}[M] + k_\mathrm{ts}[S]\}\lambda_0}{k_\mathrm{tm}[M] + k_\mathrm{ts}[S] + k_\mathrm{t}\lambda_0} \tag{14}$$

$$\lambda_2 = \left\{1 + \frac{2k_\mathrm{p}[M]}{k_\mathrm{tm}[M] + k_\mathrm{ts}[S] + k_\mathrm{t}\lambda_0}\right\}\lambda_1 \tag{15}$$

The corresponding moments for the dead polymers are

$$\mathrm{d}\mu_0/\mathrm{d}t = V\{(k_\mathrm{tm}[M] + k_\mathrm{ts}[S])\lambda_0 + (k_\mathrm{td} + 0.5k_\mathrm{tc})\lambda_0^{\,2}\} \tag{16}$$

$$\mathrm{d}\mu_1/\mathrm{d}t = V\{(k_\mathrm{tm}[M] + k_\mathrm{ts}[S])\lambda_1 + k_\mathrm{t}\lambda_0\lambda_1\} \tag{17}$$

$$\mathrm{d}\mu_2/\mathrm{d}t = V\{(k_\mathrm{tm}[M] + k_\mathrm{ts}[S])\lambda_2 + k_\mathrm{t}\lambda_0\lambda_2 + k_\mathrm{tc}\lambda_1^{\,2}\} \tag{18}$$

Equations 1, 5, 6, 9, and 13−18 are model equations of the batch polymerization reaction adopted.

Parameter Estimation. We design a two-stage optimization phase for the parameter estimation problem. In the first phase, the isothermal measurements of monomer conversion, number-average degree of polymerization, and polydispersity are used to search for the rate constants. This is done by the following minimization problem:

Objective

$$\min_{k} \sum_{j=1}^{N_\mathrm{e}} \left\{ \left(\frac{\tau_{X_j} - y_{X_j}}{S_X}\right)^2 + \left(\frac{\tau_{P_{Nj}} - y_{P_{Nj}}}{S_{P_N}}\right)^2 + \left(\frac{\tau_{HI_j} - y_{HI_j}}{S_{HI}}\right)^2 \right\}$$

subject to the system equations (eqs 1, 5, 6, 9, and 13−18) and

$$\boldsymbol{k}_\mathrm{min} \le \boldsymbol{k} \le \boldsymbol{k}_\mathrm{max} \tag{19}$$

where $\boldsymbol{k}^\mathrm{T}$=[k_d, k_p, k_t, k_tm, k_tc, k_tcd]. Note that all the terms in eq 19 should be prescaled so that they are put on an equal basis in the evaluation of the objective function. By this way we can avoid the issue of the order of magnitude differences between the variables.

Table 1. Objectives Used in MWD Control

control objective	derived control objective
$X^*(t_\mathrm{f})$	$\mu_{0\mathrm{f}}^* \equiv V(0)[M(0)]X^*(t_\mathrm{f})/P_\mathrm{N}^*(t_\mathrm{f})$
$P_\mathrm{N}^*(t_\mathrm{f})$	$\mu_{1\mathrm{f}}^* \equiv V(0)[M(0)]X^*(t_\mathrm{f})$
$HI^*(t_\mathrm{f})$	$\mu_{2\mathrm{f}}^* \equiv V(0)[M(0)]X^*(t_\mathrm{f})P_\mathrm{N}^*(t_\mathrm{f})\ HI^*(t_\mathrm{f})$

The rate constants used in the system equations are represented by Arrhenius' law:

$$\ln k = \ln k_0 - E/RT \tag{20}$$

Equation 20 denotes a linear relationship between $1/T$ and $\ln k$, in which the slope is $-E/R$ and the intercept is $\ln k_0$. Note that the initiator efficiency f is assumed to be 0.58.[9] Any discrepancy between this assumed f and the real value of the reaction system may bias the estimated rate constants. After the isothermal rate constants are found in the first phase, we adopt eq 20 to fit the parameters k_0 and E for each rate constant. The second phase optimization procedure is to search for optimal k_0 and E for each rate constant by the next minimization programming, where the initial guess of each parameter is provided by the parameters determined in the first phase.

Objective

$$\min_{\boldsymbol{k}_0, \boldsymbol{E}} \sum_{i=1}^{N_\mathrm{b}} \sum_{j=1}^{N_\mathrm{e}} \left\{ \left(\frac{\tau_{X_{ij}} - y_{X_{ij}}}{S_X}\right)^2 + \left(\frac{\tau_{P_{Nij}} - y_{P_{Nij}}}{S_{P_N}}\right)^2 + \left(\frac{\tau_{HI_{ij}} - y_{HI_{ij}}}{S_{HI}}\right)^2 \right\}$$

subject to system equations (eqs 1, 5, 6, 9, and 13−18) and

$$\boldsymbol{k}_{0\mathrm{min}} \le \boldsymbol{k}_0 \le \boldsymbol{k}_{0\mathrm{max}}$$
$$\boldsymbol{E}_\mathrm{min} \le \boldsymbol{E} \le \boldsymbol{E}_\mathrm{max} \tag{21}$$

where $\boldsymbol{k}_0^{\ \mathrm{T}} = [k_\mathrm{d0}, k_\mathrm{p0}, k_\mathrm{t0}, k_\mathrm{tm0}, k_\mathrm{ts0}, k_\mathrm{tcd0}]$ and $\boldsymbol{E}^\mathrm{T} = [E_\mathrm{d}, E_\mathrm{p}, E_\mathrm{t}, E_\mathrm{tm}, E_\mathrm{ts}, E_\mathrm{tcd}]$. The minimization programming is executed by the nonlinear programming routine GRG2.[10]

Optimal Temperature Set-Point Policy for MWD Control. A specified cumulative average chain length and polydispersity are the desired control objectives: $X^*(t_\mathrm{f})$, $P_\mathrm{N}^*(t_\mathrm{f})$, and $HI^*(t_\mathrm{f})$ at the end of the batch process. The relationship between the desired control objectives and the derived control objectives $\mu_{0\mathrm{f}}^*$, $\mu_{1\mathrm{f}}^*$, and $\mu_{2\mathrm{f}}^*$ is tabulated in Table 1. Therefore, given the control objectives and initial conditions, Table 1 can be used for determining the derived control objectives. Conversely, if the derived control objectives are achieved by adjusting the manipulated variables of the batch reactor, the control objectives for MWD control can then be attained.

The number-average degree of polymerization, $\tilde{p}_\mathrm{n}$, and the polydispersity, $\tilde{h}_\mathrm{i}$, of an instantaneous polymer are defined, respectively, as

$$\tilde{p}_\mathrm{n} \cong (\mathrm{d}\mu_1/\mathrm{d}t)/(\mathrm{d}\mu_0/\mathrm{d}t) \tag{22}$$

$$\tilde{h}_\mathrm{i} \cong (\mathrm{d}\mu_0/\mathrm{d}t)(\mathrm{d}\mu_2/\mathrm{d}t)/(\mathrm{d}\mu_1/\mathrm{d}t)^2 \tag{23}$$

From eqs 22 and 23, we obtain

$$d\mu_1/d\mu_0 = \tilde{p}_n \tag{24}$$

$$d\mu_2/d\mu_0 = \tilde{h}_i\tilde{p}_n^{\,2} \tag{25}$$

In a free-radical polymerization reaction scheme, the chain transfer to the polymer reaction is not involved. Therefore, a dead polymer does not disappear. Consequently, the final MWD of the polymer in the batch polymerization reaction becomes a cumulative MWD of the instantaneous dead polymer during the operating period. When the derived control objectives μ_{0f}*, μ_{1f}*, and μ_{2f}* are attained, the following equations hold:

$$\mu_{1f}{}^* = \int_0^{\mu_{0f}^*} \tilde{p}_n \, d\mu_0 \tag{26}$$

$$\mu_{2f}{}^* = \int_0^{\mu_{0f}^*} \tilde{h}_i\tilde{p}_n^{\,2} \, d\mu_0 \tag{27}$$

For simplicity of calculation, $\tilde{h}_i(\mu_0)$ is fixed at the constant value $\bar{h}_i$. Under this condition, the following two equations must be satisfied:

$$\mu_{1f}{}^* = \int_0^{\mu_{0f}^*} \tilde{p}_n \, d\mu_0 \tag{28}$$

$$\frac{\mu_{2f}{}^*}{\bar{h}_i} = \int_0^{\mu_{0f}^*} \tilde{p}_n^{\,2} \, d\mu_0 \tag{29}$$

Equations 28 and 29 give two degrees of freedom for designing the possible solution form. On the basis of this observation, the following three types of solutions of $\tilde{p}_n{}^*(\mu_0)$ are studied by Takamatsu et al.:[3] (a) a rectangular type in terms of μ_0, (b) a second-order polynomial in terms of μ_0, and (c) a mixed type of zero- and first-order polynomials in terms of μ_0. In this work $\tilde{p}_n(\mu_0)$ is chosen to be type b:

$$\tilde{p}_n(\mu_0) = \tilde{p}_n(0) + a_1\mu_0 + a_2\mu_0^{\,2} \tag{30}$$

$\tilde{p}_n(0)$ in the above equation can be calculated using the given initial conditions for eqs 16−18. Given the proper control objectives (Table 1), eq 30 is inserted into eqs 28 and 29 to obtain the undetermined parameters a_1 and a_2 by solving the nonlinear algebraic equations. The resulting optimal path is defined as $\tilde{p}_n{}^*(\mu_0)$. After the solution of $\tilde{p}_n{}^*(\mu_0)$ is calculated, $T_b{}^*(\mu_0)$, which gives the profile of $\tilde{p}_n(\mu_0)$, can be calculated based on the process model. If the value of $\tilde{p}_n$ can keep track of $\tilde{p}_n$* along [0, μ_{0f}*] closely, then the MWD control objective can be achieved. Using eqs 16, 17, and 24, $\tilde{p}_n(\mu_0)$ can be derived as

$$\tilde{p}_n(\mu_0) = \frac{\{(k_{tm}[M] + k_{ts}[S])\lambda_1 + k_t\lambda_0\lambda_1\}}{\{(k_{tm}[M] + k_{ts}[S])\lambda_0 + (k_{td} + 0.5k_{tc})\lambda_0^{\,2}\}} \tag{31}$$

On the basis of eq 31, $\tilde{p}_n(\mu_0)$ can be calculated once the states of the system, $T_b{}^*(\mu_0)$, $X(\mu_0)$, [I](μ_0), and [S](μ_0), are known. The whole process can be solved stepwise by the nonlinear programming routine.[11] At the same time, the following equation can be coupled with system equations in mapping the obtained $T_b(\mu_0)$ into $T_b(t)$:

$$dt/d\mu_0 = \{V[(k_{tm}[M] + k_{ts}[S])\lambda_0 + (k_{td} + 0.5k_{tc})\lambda_0^{\,2}]\}^{-1} \tag{32}$$

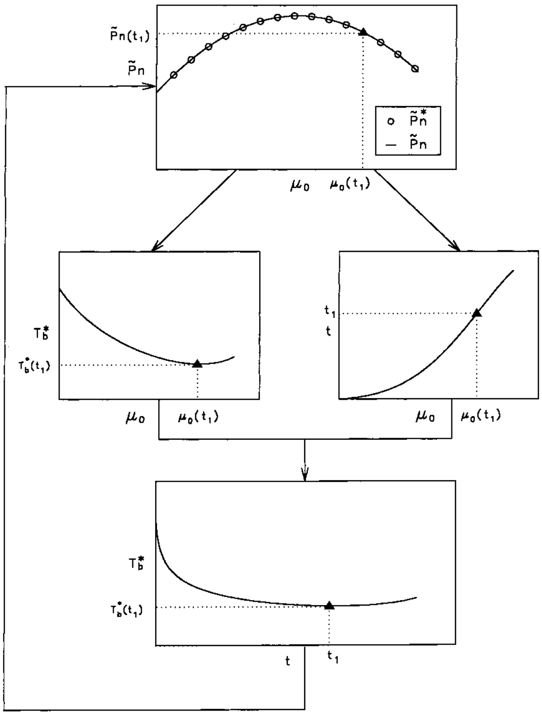

Figure 2. Computation of an optimal temperature trajectory for operating a batch polymerization reactor based on the modified two-step method.

The entire picture for illuminating the modified two-step discussed above is depicted in Figure 2. Similar analysis can be found in the subject of phase plane analysis.[12]

Trajectory Tracking via a Conventional PI Controller. The control law for the conventional PI controller is

$$u(t) = K_c e(t) + \frac{K_c}{\tau_1}\int_0^t e(\tau)\, d\tau \tag{33}$$

$$e(t) = T_b^*(t) - T_b(t) \tag{34}$$

To track a reference temperature trajectory closely in a batch reactor, both heating and cooling of the process are necessary. Therefore, the experimental apparatus (Figure 1) is designed to meet this requirement. As we know, to control a single output (T_b) through these two manipulated variables (F_{wj} and F_{wc}) the control system will be excessively determined. One way of solving this difficulty is to introduce a single parametric variable u[13] such that

$$\begin{aligned} F_{wj} &= (F_{wj,max} - F_{wj,min})u + F_{wj,min} \\ F_{wc} &= (F_{wc,min} - F_{wc,max})u + F_{wc,max} \end{aligned} \tag{35}$$

Clearly, $u = 0$ represents the maximum cooling, and $u = 1$, the maximum heating of the system. This parametric variable is used as a single control variable for this tracking problem. Prevention of reset windup is implemented through the developed rest feedback scheme. The tuning parameter used in the PI controller can be obtained by trial and error on the basis of the simulator if it is available or on the basis of reactor system loaded with water.

Table 2. Loading Conditions of the Experimental Studies

W_M (MMA)	3.492 kg
W_S (toluene)	5.239 kg
[I] (AIBN)	0.05 mol/L ($W_I = 0.082$ kg)

Table 3. Temperature Dependence of MMA, Toluene, and PMMA

ρ_M (kg/m^3) = 996.5 − 1.1T (°C)
ρ_S (kg/m^3) = 883.0 − 0.9T (°C)
ρ_P (kg/m^3) = 1200[9]

Experimental Section

Toluene and MMA are both of industrial grades. AIBN is from Zuitop Co. Because it is sold in purified condition, it is dosed for polymerization directly. We use anhydrous sodium sulfate to remove water contained in the commercial MMA. Furthermore the inhibitor (hydroquinone monomethyl ether) is removed by passing the MMA through an iron exchange resin (Amberlyst-27 from Aldrich) column. The loading conditions (Table 2) are the same as those given by Ponnuswamy and Shah[4] in the following experimental studies. By adoption of these loading conditions, the Trommsdroff or gel effect is not significant.[4] Reproducibility of the experiment is ensured by adopting the experimental procedures shown in the Appendix strictly.

Measurement of Monomer Conversion. Because the density of the polymer product is higher than that of the monomer, the density of the reacting mixture increases during the polymerization reaction. As a consequence, a measurement of the density is a convenient means to monitor the conversion history of the monomer during the polymerization reaction. A densitometer with accuracy ±1 × 10^{-1} kg/m^3 (DA-200, Kyoto Electronics, Kyoto, Japan) is applied to measure the density of the reacting medium. Conversion of monomers can be calculated by

$$X = \frac{W_{T0}/\rho_{mix}(T) - (W_{M0}/\rho_M(T) + W_{S0}/\rho_S(T) + W_{I0}/\rho_I(T))}{W_{M0}/\rho_M(T)(\rho_M(T)/\rho_P(T) - 1)} \quad (36)$$

In the above equation, the densities of the monomer and solvent used in the experiment are measured at different temperatures. The correlation of the density with temperature is shown in Table 3.

Molecular Weight Measurements. Molecular weight distribution ($\bar{M}_n$ and HI) of a polymer product is measured off line by the gel permeation chromatography (GPC; model WAT 610, Waters Ltd.). A refractive-index detector is used for measuring polymer concentration in the carrier stream as it eludes from the separation columns connected in series (Tosoh TSK-GEL G4000HXL and G7000HXL). The range for measuring the weight-average molecular weight of a polymer product by these two separation columns is 1 × 10^4−10^5 and 4 × 10^5−10^8, respectively. To protect the separation columns from being contaminated by any impurity, a guard column (Tosoh TSK-GEL, HXL type) is located before the first column. By this arrangement, the separation efficiency can be guaranteed.

We use the GPC to establish the calibration curve[14] of the molecular weight (MW) of a polymer product with respect to the retention time. A set of PMMA standards (Polymer Standards Service-USA, Inc.) whose MW's range from 2.5 × 10^3 to 8.53 × 10^5 are used.

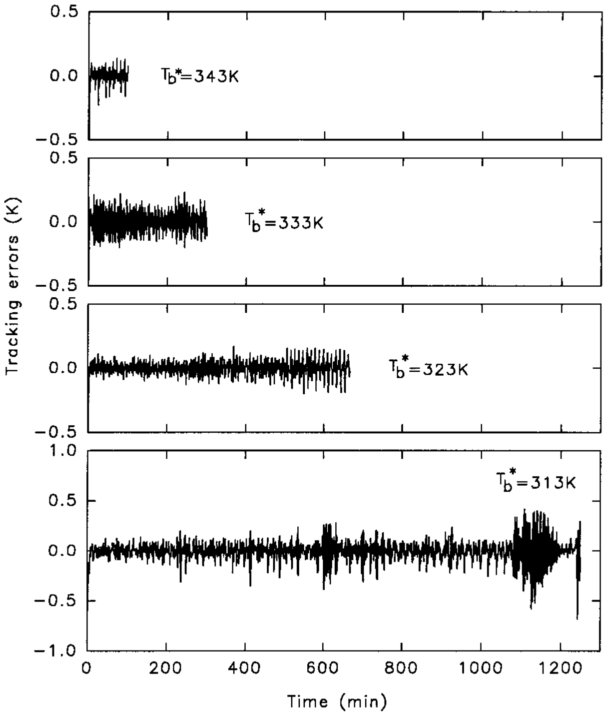

Figure 3. Isothermal solution polymerization of MMA.

Table 4. Initial Guesses for Rate Constant Estimation (T_b^* = 40 °C)

	lower bound	initial guess	upper bound
k_d	1 × 10^{-9}	0.2 × 10^{-7}	1 × 10^{-4}
k_p	1 × 10^{1}	0.2 × 10^{3}	1 × 10^{5}
k_t	1 × 10^{5}	0.2 × 10^{7}	1 × 10^{9}
k_{tm}	1 × 10^{-7}	0.2 × 10^{-4}	1 × 10^{-1}
k_{ts}	1 × 10^{-6}	0.2 × 10^{-2}	1
k_{tcd}	1 × 10^{-5}	0.8 × 10^{-2}	1 × 10^{-1}

Table 5. Estimated Rate Constants (1st Phase)

k_d (s^{-1}) = 4.063 × 10^{15} exp[−1.323 × 10^5 (kJ/kmol)/RT (K)]
k_p (m^3/(s kmol)) = 2.353 × 10^{14} exp[−7.216 × 10^4 (kJ/kmol)/RT (K)]
k_t (m^3/(s kmol)) = 1.413 × 10^{22} exp[−9.000 × 10^4 (kJ/kmol)/RT (K)]
k_{tm} (m^3/(s kmol)) = 5.221 exp[−3.815 × 10^4 (kJ/kmol)/RT (K)]
k_{ts} (m^3/(s kmol)) = 3.092 × 10^6 exp[−9.153 × 10^4 (kJ/mol)/RT (K)]
$k_t = k_{tc} + k_{td}$
$k_{tcd} = k_{tc}/k_{td}$ = 1.128 × 10^{-11} exp[6.007 × 10^4 (kJ/kmol)/RT (K)]

Parameter Estimation for the Kinetic Model. Figure 3 depicts the results of isothermal trajectory-tracking experiments (T_b^* = 40, 50, 60, and 70 °C) by a conventional PI controller. By the adoption of suitable tuning parameters ($K_c = 1$, $\tau_I = 100$), the tracking errors (Figure 3) performed by the PI controller are acceptable for these four temperature levels; therefore, the corresponding measurements of X, $\bar{M}_W$ and $\bar{M}_n$ (Figures 4−6) can be used for the parameter estimation of the kinetic model. After executing the first phase parameter estimation with the initial guesses (one example is shown in Table 4 for T_b^* = 40 °C), we can obtain the fitting of ln k versus 1/T for each rate constant (Figure 7). The estimated k_0 and E for each rate constant (Table 5) are used as the initial guess for the second phase of the parameter estimation. Table 6 gives these estimated kinetic parameters. The estimated rate constants obtained in the second phase estimation are similar to those obtained in the first phase estimation.

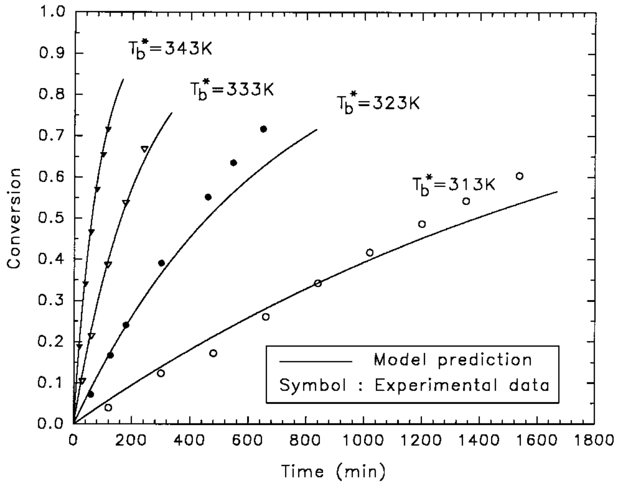

Figure 4. Isothermal solution polymerization of MMA.

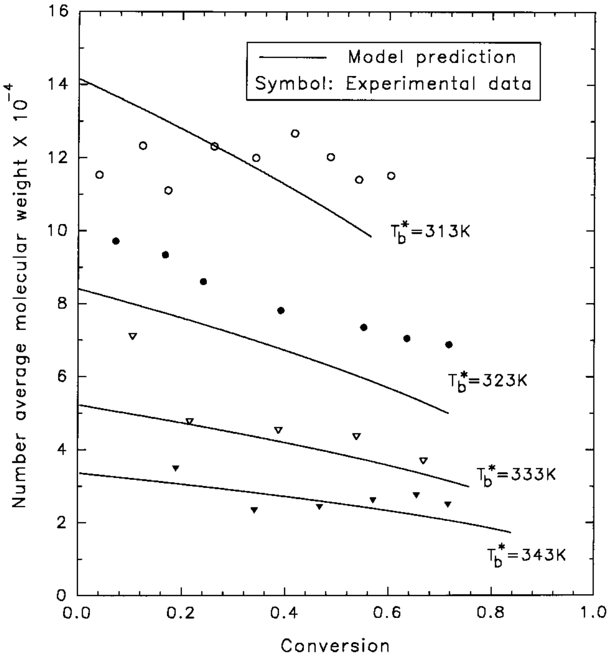

Figure 5. Isothermal solution polymerization of MMA.

Table 6. Estimated Rate Constants (2nd Phase)

$k_d(s^{-1}) = 9.592 \times 10^{15} \exp[-1.343 \times 10^5 \text{ (kJ/kmol)}/RT \text{ (K)}]$
$k_p \text{ (m}^3\text{/(s kmol))} = 1.310 \times 10^{14} \exp[-7.065 \times 10^4 \text{ (kJ/kmol)}/RT \text{ (K)}]$
$k_t \text{ (m}^3\text{/(s kmol))} = 8.498 \times 10^{21} \exp[-8.851 \times 10^4 \text{ (kJ/kmol)}/RT \text{ (K)}]$
$k_{tm} \text{ (m}^3\text{/(s kmol))} = 2.886 \times 10^{1} \exp[-4.268 \times 10^4 \text{ (kJ/kmol)}/RT \text{ (K)}]$
$k_{ts} \text{ (m}^3\text{/(s kmol))} = 4.487 \times 10^{6} \exp[-6.816 \times 10^4 \text{ (kJ/kmol)}/RT \text{ (K)}]$
$k_t = k_{tc} + k_{td}$
$k_{tcd} = k_{tc}/k_{td} = 7.976 \times 10^{-12} \exp[6.125 \times 10^4 \text{ (kJ/kmol)}/RT \text{ (K)}]$

This is attributed to the effectiveness of the proposed method in obtaining initial guesses for k_0 and E. The model predictions for X, $\bar{M}_W$, and $\bar{M}_n$ from the identified kinetic model are plotted on the same figures for comparison with the experimental data (Figures 4–6). The identified kinetic model fits nicely with the experimental measurements of X for these four temperature levels ($T_b^* = 40$, 50, 60, and 70 °C). However, there seems to exist a discrepancy between the model prediction and the experimental data for $\bar{M}_W$ and $\bar{M}_n$, especially at the low-temperature level ($T_b^* = 40$ °C).

Tracking Optimal Trajectories via a Conventional PI Controller. On the basis of the identified kinetic model, the modified two-step method is then applied to the calculation of an optimal temperature trajectory in achieving a polymer product with a specified cumulative average chain length and polydispersity (Table 7). First, $T_b^*(0)$ is set to be 70 °C and the optimal

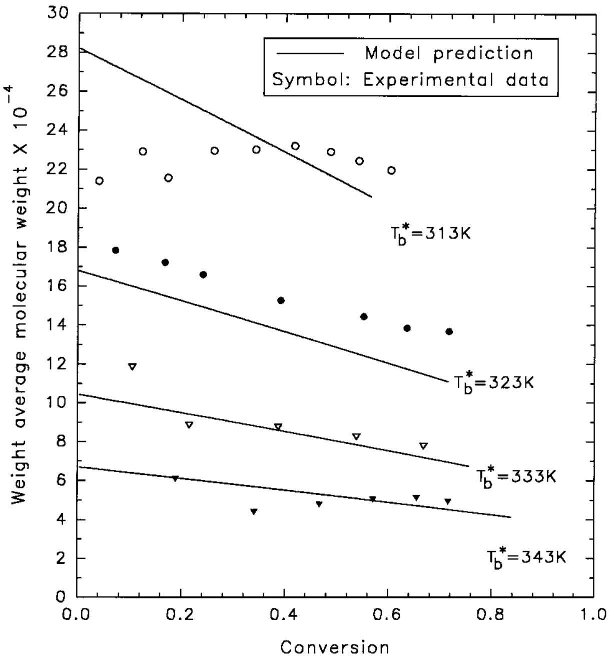

Figure 6. Isothermal solution polymerization of MMA.

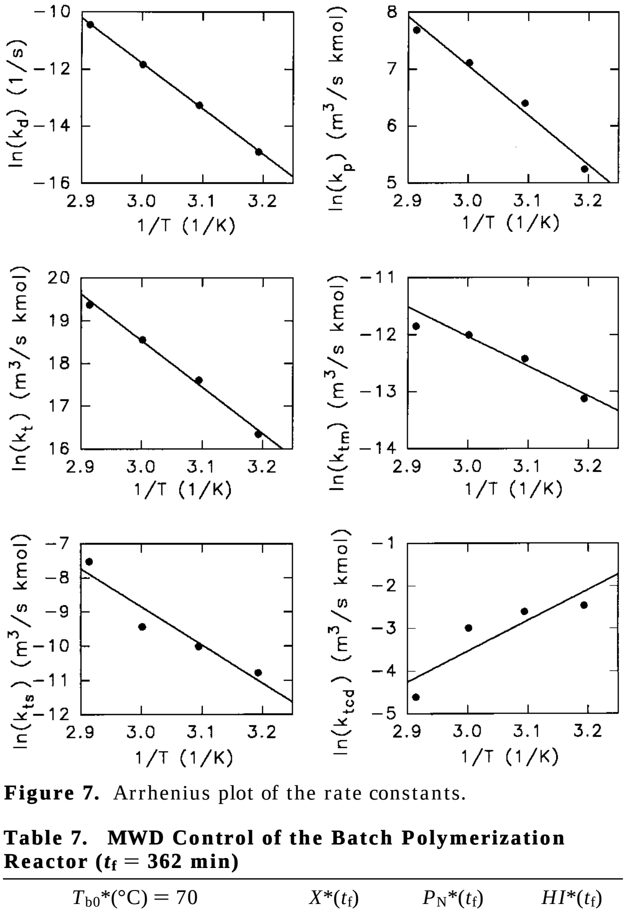

Figure 7. Arrhenius plot of the rate constants.

Table 7. MWD Control of the Batch Polymerization Reactor (t_f = 362 min)

T_{b0}^*(°C) = 70	$X^*(t_f)$	$P_N^*(t_f)$	$HI^*(t_f)$
control target	0.5	500	2
model output based on two-step method	0.512	498.8	2.03
exptl measmts	0.5314	548.9	2.09

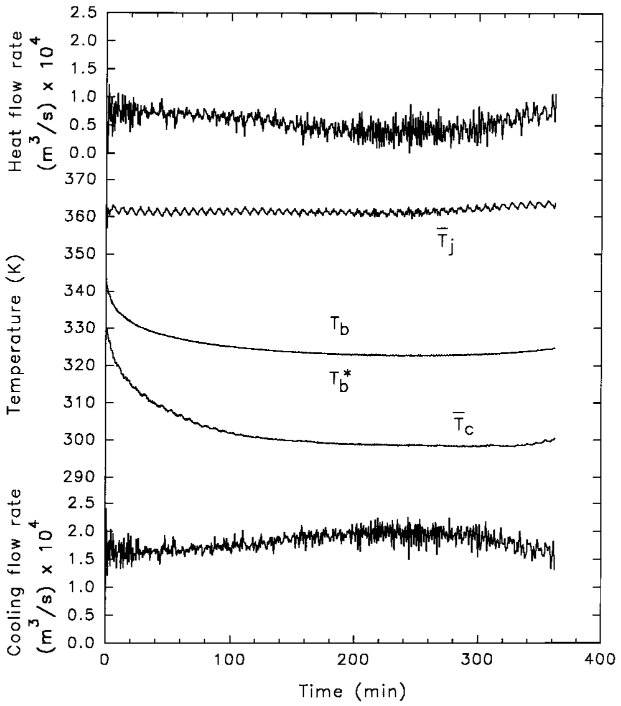

Figure 8. Trajectory tracking of an optimal path by a PI controller (T_{b0}* = 70 °C).

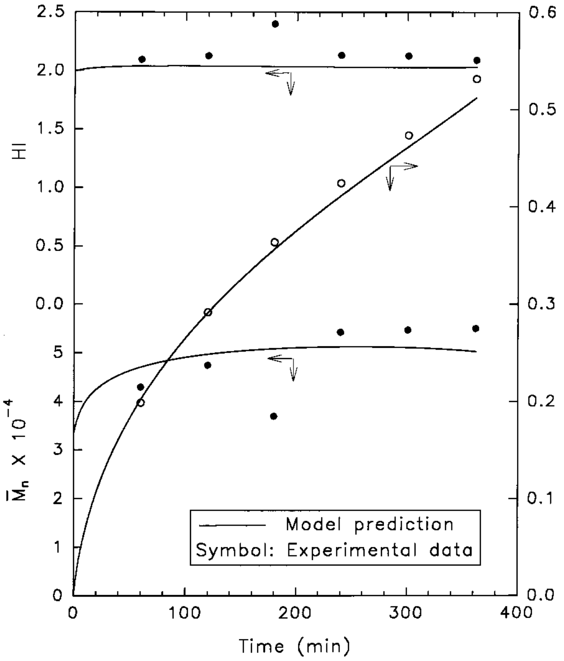

Figure 9. Comparison of theoretical and experimental results for an optimal path (T_{b0}* = 70 °C).

temperature trajectory calculated T_b*(t) is shown in Figure 8. By tracking this optimal trajectory with a conventional PI controller (K_c = 1, τ_I = 100), we obtain the end product (Table 7). From the performance of the PI controller shown in Figure 8, the trajectory is tracked closely; therefore, the quality of the identified kinetic model is reflected in the measurements of X, $\bar{M}_n$ and HI (Figure 9). The experimental data shown in Figure 9 reveal that the identified kinetic model is reliable; as a result, we have a chance of achieving the objectives of the MWD control.

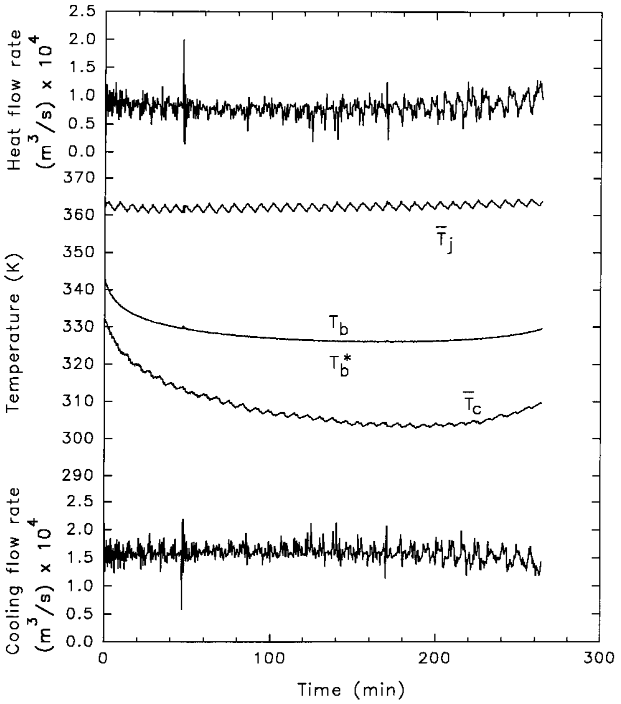

Figure 10. Trajectory tracking of an optimal path by a PI controller (T_{b0}* = 70 °C).

Table 8. Estimated Rate Constants (Revised)

k_d (s^{-1}) = 9.592 × 10^{15} exp[−1.343 × 10^5 (kJ/kmol)/RT (K)]
k_p (m^3/(s kmol)) = 1.310 × 10^{14} exp[−7.065 × 10^4 (kJ/kmol)/RT (K)]
k_t (m^3/(s kmol)) = 8.498 × 10^{21} exp[−8.851 × 10^4 (kJ/kmol)/RT (K)]
k_{tm} (m^3/(s kmol)) = 2.886 × 10^1 exp[−4.268 × 10^4 (kJ/kmol)/RT (K)]
k_{ts} (m^3/(s kmol)) = 4.487 × 10^6 exp[−6.816 × 10^4 (kJ/kmol)/RT (K)]
$k_t = k_{tc} = k_{td}$
$k_{tcd} = k_{tc}/k_{td}$ = 6.629 × 10^{-11} exp[−6.125 × 10^4 (kJ/kmol)/RT (K)]

Table 9. MWD Control of the Batch Polymerization Reactor (t_f = 264 min)

T_{b0}*(°C) = 70	X*(t_f)	P_N*(t_f)	HI*(t_f)
control target	0.5	500	2
model output based on two-step method	0.5098	501.2	1.998
exptl measmts	0.5282	523.4	1.992

Table 10. MWD Control of the Batch Polymerization Reactor (t_f = 264 min)

T_{b0}*(°C) = 70	X*(t_f)	P_N*(t_f)	HI*(t_f)
control target	0.5	500	2
model output based on two-step method	0.5098	501.2	1.998
exptl measmnts	0.5247	529.9	2.002

Furthermore, the parameter estimation is executed again on the basis of the measurements shown in Figure 9 as well as the isothermal measurements in Figures 4−6. We obtain revised kinetic parameters (Table 8). Note that the parameters are maintained with the exception of k_{tdc0}. This is a reasonable result because the experimental data are suitably modeled by the previous identified parameters (Table 6). On the basis of kinetic parameters (Table 8), a revised optimal path is calculated with T_b*(0) = 70 °C (Figure 10) and a qualified end product is obtained after the path is tracked (Table 9). The experimental data are acceptable, as shown in Figure 11. To check the reproducibility of the experiment, the same trajectory is tracked again. A similar end product (Table 10) is obtained.

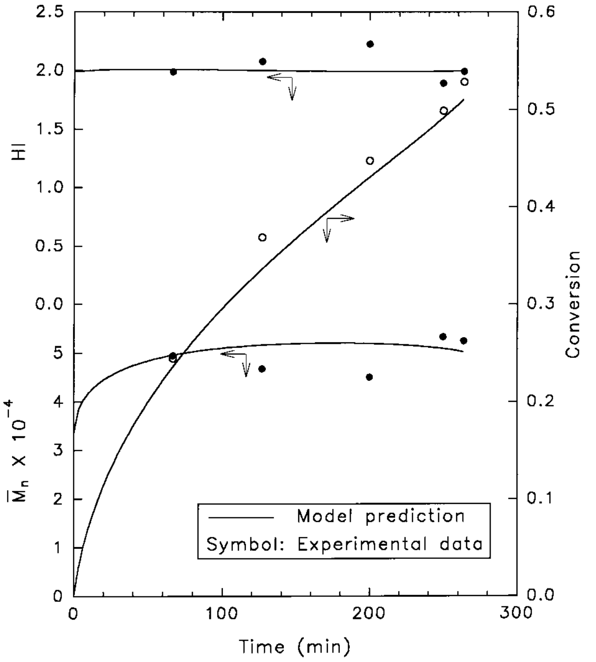

Figure 11. Comparison of theoretical and experimental results for an optimal path (T_{b0}^* = 70 °C).

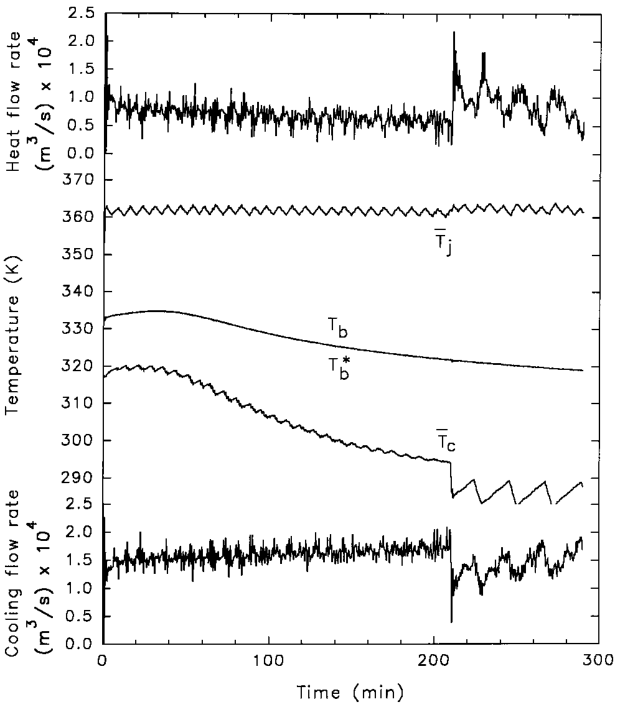

Figure 12. Trajectory tracking of an optimal path by a PI controller (T_{b0}^* = 60 °C).

Another optimal path is calculated with $T_b^*(0) = 60$ °C (Figure 12) based on the kinetic parameters shown in Table 8. The temperature level of this trajectory is much lower at the later stage of the batch cycle. The cold resource is changed from vessel V1 to V3 ($T_{V3}(0) \cong$ 15 °C) at $t = 210$ min. By this way the driving forces of the heating and cooling resources are matched comparatively; therefore, the trajectory ($t \geq 250$ min) can be tracked properly. Similarly, a qualified end product is produced (Figure 13 and Table 11).

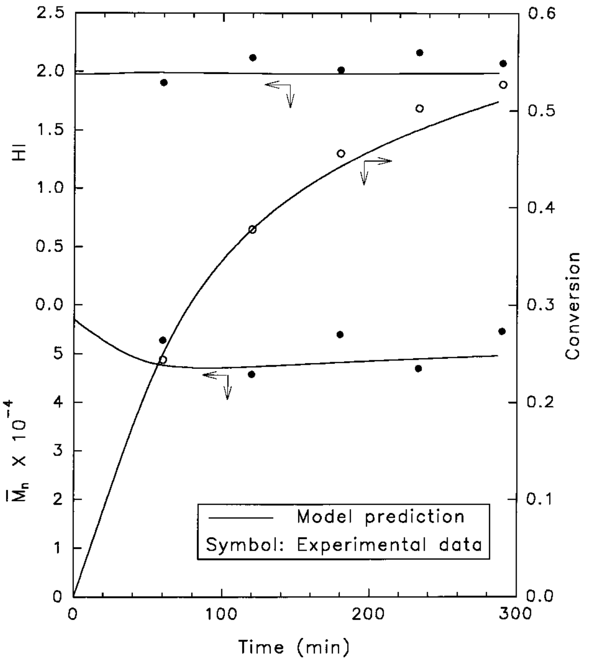

Figure 13. Comparison of theoretical and experimental results for an optimal path (T_{b0}^* = 60 °C).

Table 11. MWD Control of the Batch Polymerization Reactor (t_f = 289 min)

T_{b0}^*(°C) = 60	$X^*(t_f)$	$P_N^*(t_f)$	$HI^*(t_f)$
control target	0.5	500	2
model output based on two-step method	0.5091	495.0	1.987
exptl measmts	0.527	544.9	2.073

Conclusions

In this work, the MWD control of a batch polymerization reactor is considered. The achievement of this goal hinges on a well-established reactor system, a proper model building and parameter estimation strategy, a computational method for determining optimal operating trajectories, a suitable controller for trajectory tracking and experimental details, etc. Chemicals of industrial grades are adopted to test the whole process to see whether the aims of MWD control can be achieved.

A two-phase parameter estimation strategy is developed to identify the reaction model for a batch solution polymerization reactor system. On the basis of a set of isothermal operations of the MMA polymerization in the batch reactor, the frequency factors and the activation energies of the reaction rate constants, k_d, k_p, k_t, k_{tm}, k_{ts}, and k_{tcd} are obtained. Comparisons between model predictions and experimental data reveal that the identified model predicts the isothermal reaction behavior accurately in this experimental system. On the basis of this identified model, the modified two-step method is used to calculate the optimal temperature setpoint for the MWD control.

A conventional PI controller with suitable tuning parameters is applied successfully for tracking the calculated temperature trajectory. The experimental results prove the applicability of the experimental apparatus used in this work.

Finally, as the paths are calculated on the basis of the reliable identified kinetic model, the qualities of the polymer product (conversion, number-average degree of polymerization, and polydispersity) can be produced accurately. The results shown in this work prove that the hardware and software developed in this work are applicable in achieving the MWD control of a batch polymerization reactor.

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Nomenclature

D_n = dead polymer of length n
E = activation energy, kJ/(kmol K)
e = deviation between the set-point and the process variable
f = initiator efficiency
F = flow rate, m^3/s
HI = polydispersity
$\tilde{h}_\mathrm{i}$ = polydispersity of instantaneous polymer
$\bar{h}_\mathrm{i}$ = assumed constant polydispersity of instantaneous polymer
I = initiator
k = rate constant, m^3/s kmol or 1/s
K_c = proportional gain, 1/°C
M = monomer
$\bar{M}$ = average molecular weight, kg/kmol
MW = molecular weight, kg/kmol
N_b = numbers of batch runs
N_e = numbers of measurements per batch run
p_N = number-average degree of polymerization
$p_n^\bullet$ = radical polymer of length n
$\tilde{p}_\mathrm{n}$ = number-average degree of polymerization of instantaneous polymer
t = time, s
S = scaling factor
T = temperature, °C
u = manipulated input
V = volume of reacting mixture, m^3
W = weight, kg
X = conversion of monomer
y = measurement

Greek Symbols

$\mu_i|_{i=0,1,2}$ = ith moment of living radical distribution
$\mu_i|_{i=0,1,2}$ = ith moment of dead polymer distribution
ρ = density, kg/m^3
τ = target value; dummy variable
τ_I = integral time constant, s
[ ] = molar concentration, $kmol/m^3$

Acronyms

AIBN = azobis(isobutyronitrile)
GPC = gel permeation chromatography
i.d. = inside diameter
MMA = methyl methacrylate
MWD = molecular weight distribution
PI = proportional-integral
PMMA = polymethyl methacrylate
QSSA = quasi-steady-state approximation
RTD = resistance temperature detector
SSR = solid-state relay
THF = tetrahydrofuran

Superscript

T = transpose
$*$ = optimal

Subscripts

0 = initial; intrinsic
b = reacting mixture in the batch reactor
c = combination
d = decomposition; disproportionation
f = final
I = initiator
M = monomer
m = monomer
max = maximum
min = minimum
P = polymer
p = propagation
S = solvent
T = total
t = termination; transfer
w = water

Appendix: Experimental Procedures

1. Prepare the reactants using the loading conditions given in Table 3. 2. Prepare the hot water and the coolant in the heating and cooling vessels. 3. Load the toluene prepared in step 1 into the reactor vessel and stir it by the agitator. The nitrogen gas is then bubbled (0.03 L/min) into the solution of toluene to purge any dissolved oxygen from the solution for about 1 h. 4. Drain the solution of toluene (about 2 L) prepared in step 3 into a 3 L glass bottle. 5. Load the initiator into the bottle that contains the solution prepared in step 4. Stir the solution till the initiator is dissolved in the solution completely. 6. Load the solution of MMA prepared in step 1 into the reactor and stir the mixture. The nitrogen gas (0.02 L/min) is then bubbled into the solution to purge any dissolved oxygen from the solution for about 1 h. 7. Preheat the temperature of the solution prepared in step 5 to the desired temperature. Meanwhile, maintain both the heating vessel and the cooling vessel at desired temperatures. 8. Load the solution prepared in step 7 into the reactor and start the control program. Blank the reacting medium with the nitrogen gas (0.04 L/min) to keep oxygen out of the reactor. Sample and measure the initial density of the reaction medium. 9. Sample the reacting mixture (10 mL) and measure the density of the test sample at the sampling time. Add the solution of methanol (80 mL) into the test sample to precipitate the solid product of PMMA for molecular weight analysis. 10. Repeat step 9 till the end of the run. 11. Vacuum and dry the test sample taken in step 9. Dissolve the test sample into the solution of THF (0.003 g/mL). 12. Inject the test sample into GPC (gel permeation chromatography), and analyze the MWD of the test sample.

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