

Molecular Weight Control of a Batch Suspension Polymerization Reactor

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ABSTRACT

This paper concerns molecular weight control of a batch polymerization reactor where suspension polymerization of methyl methacrylate (MMA) takes place. For this purpose, a cascade control structure with two control loops has been selected. The slave loop is used for temperature control using on-line temperature measurements, and the master loop controls the average molecular weights based on its estimated values. Two different control algorithms namely proportional-integral (PI) controller and globally linearizing controller (GLC) have been used for temperature control. An estimator, which has the structure of an extended Kalman filter (EKF), is used for estimating monomer conversion and average molecular weights of polymer using reactor temperature measurements. The performance of proposed control algorithm is evaluated through simulation and experimental studies. The results indicate that a constant average molecular weight cannot be achieved in case of strong gel effect. However, the polydispersity of product will be lower in comparison to isothermal operation. It is also shown that in case of model mismatch, the performance of cascade control is superior compared to the case where only reactor temperature is controlled based on desired temperature trajectory obtained through cascade strategy.

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Key Words:

molecular weight control;
state estimation;
suspension polymerization;
batch reactor;
cascade control.

INTRODUCTION

In industrial polymerization there is considerable economic incentive to produce polymers with desired end-use properties. The development of operating policies that will result in the production of polymers with desired end-use properties is called

quality control. The final polymer properties (e.g. melt index, impact strength, tensile strength, chemical resistance, thermal stability, etc.) are related to a molecular property of polymer described as molecular weight distribution (MWD)[1].

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Therefore, the main objective in controlling polymerization reactors is to meet the final polymer properties at some desired values.

The desired MWD of a polymer can be achieved by applying open-loop or closed-loop control schemes. Time optimal open-loop control can provide monomer, initiator and temperature trajectories that will result in the production of polymers with desired properties [2-7]. Unfortunately, these optimal trajectories are only valid when the dynamic model provides perfect prediction of the actual process dynamics, no disturbances enter the process and the assumed initial operating conditions are correct. This implies that the operation of a polymer reactor based on these off-line calculated trajectories will likely be suboptimal and will suffer from poor product reproducibility. Thus, feedback controllers are required to ensure the realization of the final polymer properties in the presence of initialization errors, model/plant mismatch and disturbances.

A major problem in closed loop control of MWD is the lack of on-line measurements. Although instruments for measuring the MWD are available, these instruments are very expensive and possess substantial measurement delays [8]. By using state estimation techniques, some of these difficult-to-measure variables can be estimated with the aid of certain easily measurable variables such as temperature, viscosity and density of the reaction mixture [9-13].

Limited work has been reported regarding the development of inferential feedback control strategies for polymer reaction processes, among them are Kozub and MacGregor[14], Tsen et al.[15], Ellis et al.[16], Chang and Liao[17].

In this paper, the inferential feedback control of average molecular weights based on temperature measurements is studied. A batch polymerization reactor, in which suspension polymerization of MMA takes place, is selected for this investigation.

The article is organized as follows. First, the experimental system is described and then the mathematical model is given. Next, the structure of control algorithm and estimator are reviewed briefly. Finally, the performance of the controller is examined through simulation and experimental studies.

Experimental System

Figure 1 depicts the schematic diagram of experimental system. The reactor is a 5L stainless steel jacketed vessel. The reacting mixture is mixed by a three-paddle

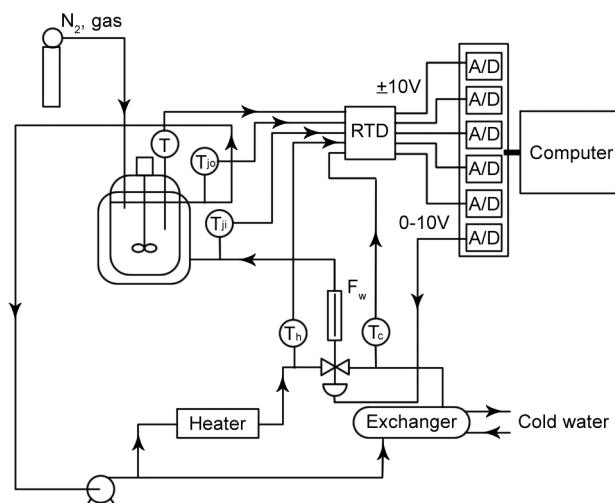


Figure 1. Experimental set-up.

agitator at 600 rpm during the polymerization.

The heating/cooling system of the reactor consists of an electrical heater with power of about 6.0 kW, a shell and tube heat exchanger, a motorized three-way control valve, a circulating pump and temperature sensors (four 0-100 C resistance temperature detectors, RTD). The reactor temperature is measured by a RTD of the same type. The circulating pump maintains a constant jacket flow rate. The temperature of the heater is controlled by an on/off controller around 80 C.

The experimental system is connected to a computer by an I/O interface board (Axiom, Inc.; model AX5411).

Mathematical Model

The kinetic mechanism for free radical polymerization of MMA initiated by benzoyl peroxide is given in Table 1 [18]. In order to obtain average molecular weights of the growing radicals and resulting polymers the method of moments is used. These moments are defined below:

$$\lambda_k = \sum_{n=1}^{\infty} n^k R_n \quad \text{and} \quad \mu_k = \sum_{n=1}^{\infty} n^k P_n \quad (1)$$

where R_n and P_n are concentrations of live radical and dead polymer chain with n monomer units, respectively.

Using the kinetic mechanism and performing mass and energy balances the following set of ordinary differential equations are obtained:

$$\frac{dx_m}{dt} = (1 - x_m)(k_p + k_m)\lambda_0 \quad (2)$$

$$\frac{dx_i}{dt} = (1 - x_i)k_d \quad (3)$$

$$\frac{dT}{dt} = \frac{(-\Delta H_p)k_p\lambda_0 C_m V + UA(T_j - T)}{mc} \quad (4)$$

$$\frac{d(\mu_0 V)}{dt} = \lambda_0 V(k_m C_m + k_t \lambda_0) - 0.5k_{tc} \lambda_0^2 V \quad (5)$$

$$\frac{d(\mu_1 V)}{dt} = \lambda_1 V(k_m C_m + k_t \lambda_0) \quad (6)$$

$$\frac{d(\mu_2 V)}{dt} = \lambda_2 V(k_m C_m + k_t \lambda_0) + k_{tc} \lambda_1^2 V \quad (7)$$

where,

$$\lambda_0 = \left(\frac{2f k_d C_i}{k_t} \right)^{0.5} \quad (8)$$

$$\lambda_1 = \lambda_0 \left(1 + \frac{k_p C_m}{k_m C_m + k_t \lambda_0} \right) \quad (9)$$

$$\lambda_2 = \lambda_1 \left(1 + \frac{2k_p C_m}{k_m C_m + k_t \lambda_0} \right) \quad (10)$$

$$C_m = \frac{(1 - x_m)C_{m0} V_0}{V} \quad (11)$$

$$C_i = \frac{(1 - x_i)C_{i0} V_0}{V} \quad (12)$$

$$V = V_0 (1 + \varepsilon x_m) \quad (13)$$

In the above equations, X_m and X_i are monomer and initiator conversion, respectively. The volume expansion factor is given by:

$$\varepsilon = \phi_{m0} \left(\frac{\rho_m}{\rho_p} - 1 \right) \quad (14)$$

To obtain average molecular weights from the moments the following equations can be used:

$$M_n = W_m \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} \approx W_m \frac{\mu_1}{\mu_0} \quad (15)$$

$$M_w = W_m \frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1} \approx W_m \frac{\mu_2}{\mu_1} \quad (16)$$

To introduce the gel and glass effects in the model, the correlation proposed by Chiu et al. [19] are used.

In the same way, performing energy balances for the jacket, heater and exchanger result the following equations:

$$\frac{dT_j}{dt} = \left[UA(T - T_j) + U_{\infty} A_{\infty} (T_{\infty} - T_j) + \frac{F_w \rho_w c_w}{1 - \gamma} (T_{ji} - T_j) \right] / m_j c_w \quad (17)$$

$$\frac{dT_c}{dt} = \left[U_c A_c (T_w - T_c) + (1 - a_v) F_w \rho_w c_w (T_{jo} - T_c) \right] / m_c c_w \quad (18)$$

$$\frac{dT_h}{dt} = \left[Q_h + a_v J_w \rho_w c_w (T_{jo} - T_h) \right] / m_h c_w \quad (19)$$

where,

$$T_{ji} = a_v T_h + (1 - a_v) T_c \quad (20)$$

$$T_{jo} = (T_j - \gamma T_{ji}) / (1 - \gamma) \quad (21)$$

In the above equations T_j , T_c and T_h are temperatures of jacket, cold and hot streams, respectively. T_{ji} and T_{jo} are inlet and outlet jacket temperatures. T_{jo} is a function of T_{ji} and T_j . This functionality has been obtained through experimental data and it is given by (eqn 21). This equation is used in jacket energy balance (eqn17).

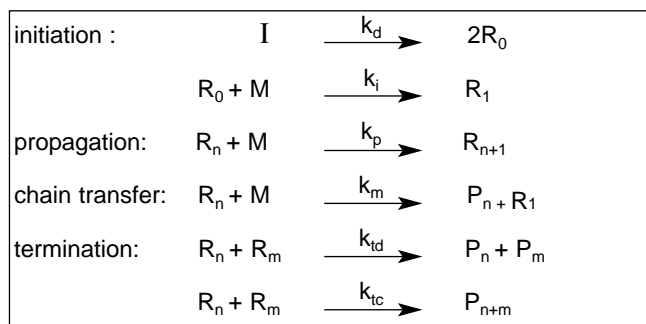
If a_v is defined as the opening fraction of the three-way control valve (when the a_v is one, then the hot stream way is fully open), then it can be related to the control signal (u_f) as given by the following equation:

$$a_v = \begin{cases} 0.089u_f^{1.078} & \text{if } , u_f \leq 7.6 \\ 0.519u_f - 3.152 & \text{if } , u_f > 7.6 \end{cases} \quad (22)$$

Q_h in eqn (19) is the variable power of heater and can be calculated by the following empirical equation:

$$Q_h = 6.45 + 0.7(T_h^* - T_h) + 0.007 \int_0^t (T_h^* - T_h) dt \quad (23)$$

Table 1. Free radical polymerization mechanism.

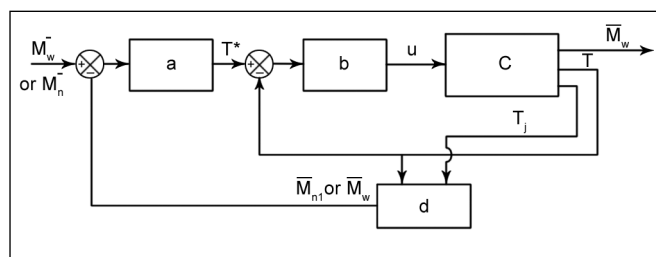


where, T_h^* is the desired value of T_h . The physical properties and other parameters of jacket energy balance equations, eqns(17-19), are given in Table 2. The parameters given in Table 2 are calculated through experimental data using least square technique.

CONTROLLER STRUCTURE

The schematic diagram of the proposed control scheme, which has a cascade structure, is shown in Figure 2. The master loop is used for controlling the molecular weight at the desired value. Since the on-line measurement of molecular weight is not available, its estimated value is used. The output of the master controller is the set point of the slave controller that controls the reactor temperature by manipulating the jacket inlet temperature.

To estimate the molecular weight, an estimation scheme which uses jacket and reactor temperatures has been proposed. The block diagram of the proposed estimator, which has two parts, is shown in Figure 3. The first part is an EKF for estimating of the observable states (monomer conversion; x_m , initiator conversion; x_i and reactor temperature; T), and the second part is an open loop observer for estimation of detectable states (average molecular weights). The estimator properties



(a)Master controller; (b)slave controller; (c)polymerization reactor (d)estimator

Figure 2. Block diagram of selected control structure.

Table 2. Physical properties and other parameters of heating/cooling system.

UA= 0.097	$U_{\infty} A_{\infty} = 0.02$	$U_c A_c = 0.165$
$m_j = 1.7$	$m_c = 6.5$	$m_n = 5.5$
$C_w = 4.2$	$F_w = 2.33 \times 10^{-4}$	$\gamma = 0.75$
$T_{\infty} = 293.7$	$T_w = 294.2$	$\rho_w = 983$

are discussed by Shahrokhi and Fanaei [21].

Different control algorithms can be used for the inner loop. To investigate the effect of slave controller on the overall performance, two different controllers, namely PI and GLC are used. The details of GLC algorithm used in this study are discussed by Shahrokhi and Fanaei [20].

For the master loop, a conventional PI controller is used to maintain the average molecular weight at its desired value by adjusting the reactor temperature set point. Although different types of control schemes (e.g., model predictive controller; MPC) can be used, a conventional PI due to its simple structure is selected.

RESULTS

In this section, the performance of the proposed control algorithm is evaluated through simulation and experimental studies. In all runs, the sampling period is 5. The selected tuning parameters of GLC (slave loop) and PI (master loop) controllers are given in Table 3. These parameters are obtained by minimizing the integral of absolute value of the error. Because of physical

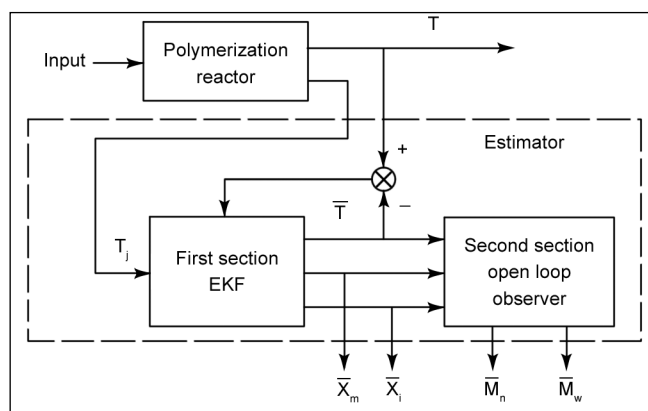


Figure 3. Block diagram of the designed estimator.

Table 3. Control parameters used in slave and master loops.

Controller	K_c	τ_i (s)	β (s)	Set point	Controlled variable
GLC	2.1	150	150	variable	T
PI	-1.25×10^{-4}	100	----	5.0×10^5	\bar{M}_w
PI	-2.5×10^{-4}	100	----	2.5×10^5	\bar{M}_n

limitations, the output of the master controller is constrained ($45\text{--}75^\circ\text{C}$).

Simulation Results

The number average molecular weight (\bar{M}_n) or weight average molecular weight (\bar{M}_w), can be selected as a controlled variable. In all simulation runs the controller of inner loop is a GLC. The simulation results for controlling \bar{M}_n and \bar{M}_w are shown in Figures 4 and 5, respectively. As can be seen, the produced polymer has lower polydispersity if \bar{M}_n is controlled. Also, it may be noted that the constant average molecular weight cannot be achieved due to strong gel effect. In batch suspension polymerization reactors, most of the polymer is produced in the gel effect region. Therefore, after this region the molecular weight distribution cannot be affected considerably. In addition, for comparison, the molecular weights (\bar{M}_n , \bar{M}_w) of produced polymer for isothermal operation are shown in Figures 4 and 5. The results indicate that polydispersity of polymer pro-

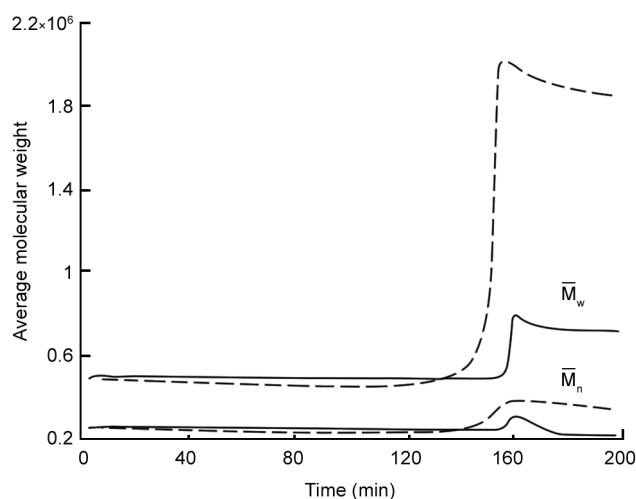


Figure 4a. Variations of polymer molecular weights for isothermal operation (dash line) and cascade loop controlling \bar{M}_n (solid line).

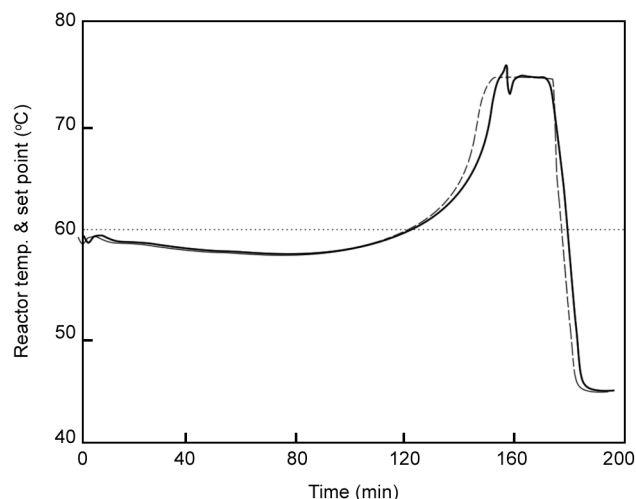


Figure 4b. Temperature profiles for isothermal operation (dot line) and cascade control (reactor temperature: solid line and set point: dash-dot line).

duced by isothermal operation is higher than polymer obtained using cascade control. The polydispersity of produced polymer is 5.3 for isothermal operation while it is 4.5 or 3.3 if \bar{M}_w or \bar{M}_n is controlled, respectively. In the remainder of this paper \bar{M}_n is selected as a controlled variable.

If the temperature trajectory shown in Figure 4b is used as desired profile by a single temperature control loop, the performance of this control scheme will be the same as cascade loop in case of no model mismatch. When there is modeling error, the polydispersity of

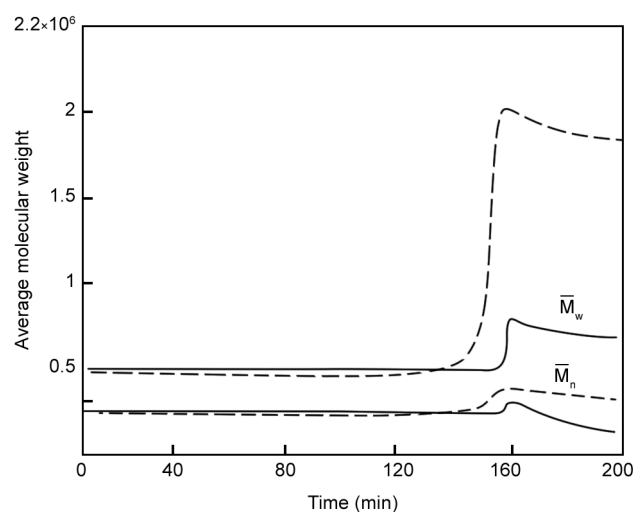


Figure 5a. Variations of polymer molecular weights for isothermal operation (dash line) and cascade loop controlling \bar{M}_w (solid line).

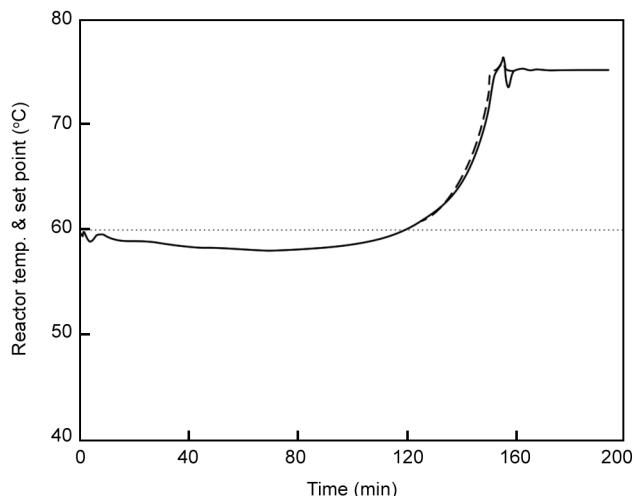


Figure 5b. Temperature profiles for isothermal operation (dotted line) and cascade control (reactor temperature: solid line and set point: dash-dot line).

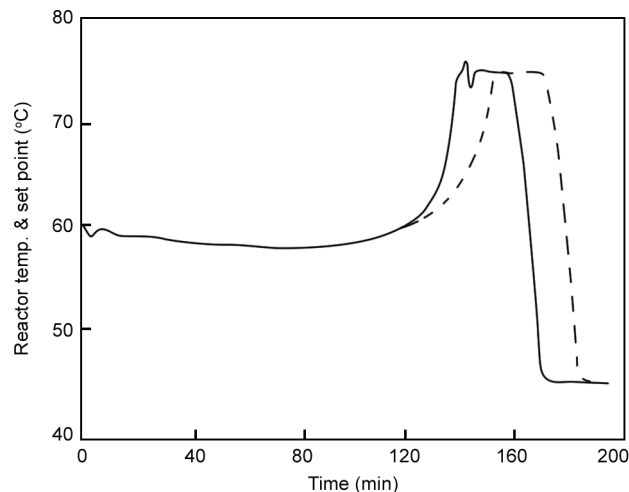


Figure 6b. Reactor temperature profiles for single temperature loop (dash line) and cascade loop (solid line).

produced polymer is lower for cascade loop. The variations of average molecular weights for the above control strategies are shown in Figure 6 for 20 percent error in the initiator efficiency (f). As can be seen from the results, the polydispersity for cascade loop is 3.5 while it is 5.6 for the single temperature control loop.

Note that the estimated value of average molecular weights has bias (Figure 6). This bias exists because \bar{M}_n and \bar{M}_w are detectable and not observable from temperature measurement [21].

Experimental Results

In this section, the performance of proposed control algorithm has been evaluated through real time studies using experimental set-up (Figure 1). The estimated values of average molecular weights and measured reactor temperature are shown in Figures 7a and 7b. As can be seen, the polydispersity of the polymer is about 4. It should be noted that before reaching the gel effect region polydispersity is controlled at the desired value.

To investigate the effect of controller type in the inner loop, the GLC is replaced with a PI controller and the run is repeated. The slave controller parameters are

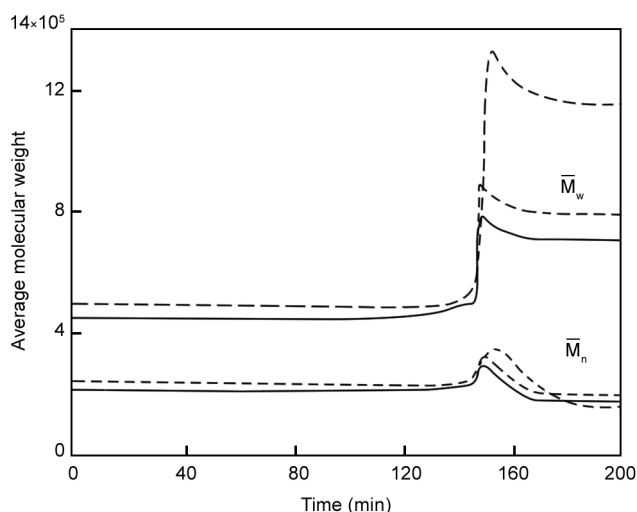


Figure 6a. Variations of polymer molecular weights for single temperature loop (dash-dot line) and cascade loop (dash line) for 20% error in f . Solid lines show real values.

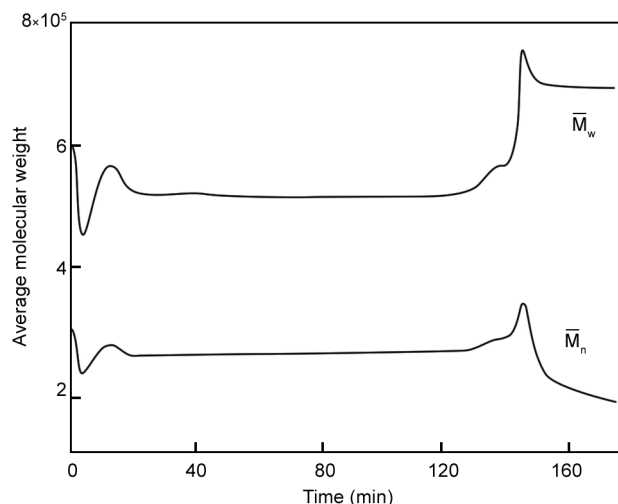


Figure 7a. Experimental results for cascade loop using a GLC for slave loop. Estimated molecular weights.

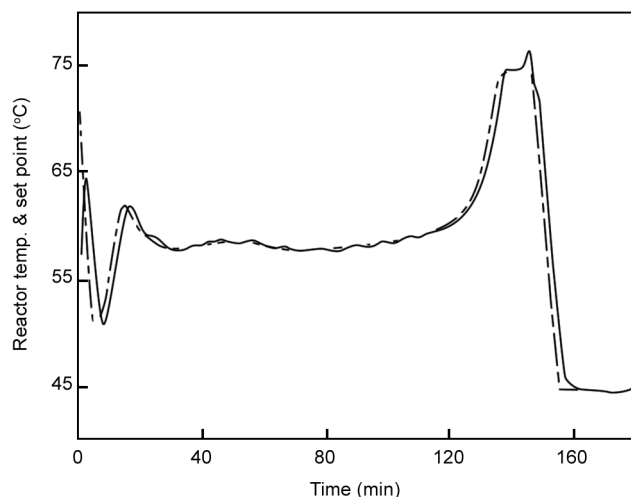


Figure 7b. Experimental results for cascade loop using a GLC for slave loop. Reactor temperature (solid line) and its set point (dash-dot line).

$K_c=1.0$ and $\tau_i=150$ s the master controller parameters are same as before. The estimated values of average molecular weights and measured temperature are shown in Figures 8a and 8b. Comparing the results shown in Figures 7 and 8 it does indicate that the type of slave controller (PI or GLC) has no considerable effect on average molecular weights of produced polymer.

CONCLUSION

In this paper a cascade control strategy for controlling molecular weights (\bar{M}_n and \bar{M}_w) has been proposed and its performance is evaluated through simulation and

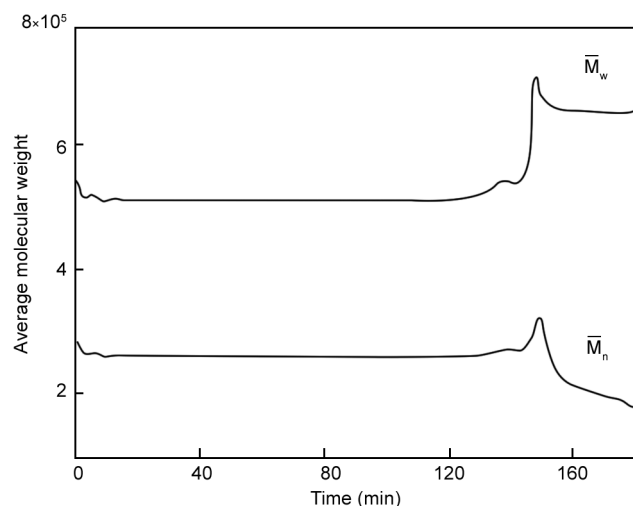


Figure 8a. Experimental results for cascade loop using a PI for slave loop. Estimated molecular weights.

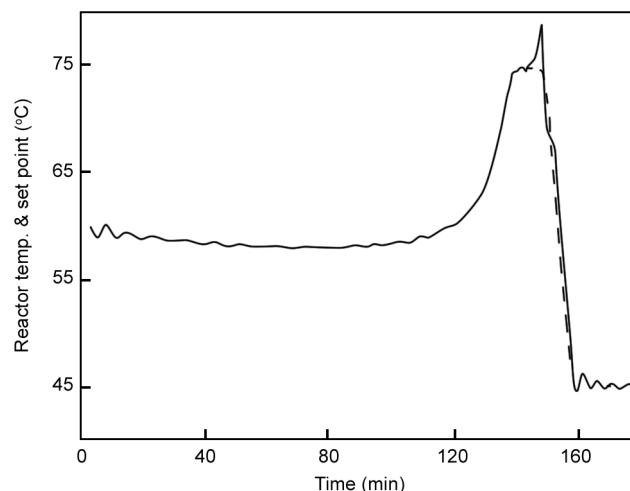


Figure 8b. Experimental results for cascade loop using a PI for slave loop. Reactor temperature (solid line) and its set point (dash-dot line).

real-time studies. It is shown that lower polydispersity can be obtained if \bar{M}_n is controlled instead of \bar{M}_w . The performance of the proposed scheme is superior to isothermal operation. In case of model mismatch, the proposed scheme performs better than single loop temperature controller whose set point trajectory is obtained through the cascade strategy. Finally, it is shown that the type of slave controller has not any considerable effect on the overall performance of control system.

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SYMBOLS AND ABBREVIATIONS

- A, A_∞ = reactor-jacket and surrounding-jacket heat transfer area
- C_i, C_{i0} = concentration of initiator and its initial value
- C_m, C_{m0} = concentration of monomer and its initial value
- c = heat capacity of reactor contents
- c_w = heat capacity of water
- F_w = flow rate of jacket
- f = initiator efficiency

K_c = gain of PI controller
 k_d = rate constant for initiation reaction
 k_m = rate constant for chain transfer to monomer
 k_p = rate constant for propagation reaction
 k_{tc} = rate constant for termination by combination
 k_{td} = rate constant for termination by disproportion
 $k_t = k_{td} + k_{tc}$
 \bar{M}_n, \bar{M}_n^* = number average molecular weights and its desired value
 \bar{M}_w, \bar{M}_w^* = weight average molecular weights and its desired value
 m = mass of reactor contents
 m_j = mass of water in jacket
 T, T^* = reactor temperature and its desired value
 T_c = cold stream temperature
 T_j = jacket temperature
 T_h = hot stream temperature
 T_∞ = surrounding temperature
 t, t_s = time and sampling time respectively
 U, U_∞ = overall heat transfer coefficient of reactor-jacket and surrounding
 V, V_0 = volume of the reacting mixture and its initial value
 X_i, X_m = initiator and monomer conversions, respectively
 W_m = monomer molecular weight

Greek Letters

β = tunable parameter of input/output linearized system
 γ = tunable parameter in calculation of output jacket temperature
 λ_k = kth moment of live polymer chains
 $-\Delta H_p$ = heat of propagation reactions
 ε = polymerization volume expansion
 ϕ_{m0} = initial value of monomer volume fraction
 ρ_m, ρ_p = density of monomer and polymer respectively
 ρ_w = density of water
 μ_k = kth moment of dead polymer chains
 τ_1 = integral time constant of PID controllers

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