Dynamic Optimization of Molecular Weight Distribution in Industrial Batch Polymerization [★]

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Abstract: Market demand for high-performance polymers often requires flexibility to customize product properties with a high degree of consistency. Batch processes are often used to produce high-performance polymers due to their flexibility. The product properties are related to molecular weight distribution (MWD). However, due to the nature of dynamic within batch and batch-to-batch variability, controlling MWD is challenging, leading to inconsistent product properties. Additionally, changes in polymer properties often require cumbersome formulation development, which in practice is not flexible enough to meet downstream requirements for polymer property customization. To address these issues, a mechanistic model of an industrial batch polymerization process is developed, and a dynamic optimization problem is designed on this model. Within the framework of dynamic optimization, it is demonstrated that the MWD can be adjusted by manipulating the initial concentration and flow rate of the chain transfer agent at a constant reaction temperature, which provides the basis and direction for the subsequent development of control strategies to the MWD.

Keywords: Dynamic optimization; Molecular weight distribution; Batch polymerization process; Chain transfer agent

1. INTRODUCTION

High-performance polymers are extensively utilized across various industries due to their exceptional chemical resistance, high thermal stability, and favorable mechanical properties (Gilbert, 2016). Molecular weight distribution (MWD) is a crucial metric for evaluating the properties of polymerization products, as it directly affects several important end-use properties of polymers, including thermal behavior, stress-strain performance, impact resistance, strength, and hardness (Yue et al., 2004).

High-performance polymers require consistent product properties. However, since the formation of individual polymer chains represents a minor portion of the total batch processing time, variations in initial conditions can result in inconsistencies in the final polymer product properties. Additionally, real-time measurement of the MWD is often challenging in many batch and semi-batch polymerization processes, which can result in inconsistent product properties and low yields of high-performance polymer products (Richards and Congalidis, 2006).

In industrial production, fluctuating market demands for polymer product properties require adjustments to the production formulations across different batches. When these formulations are implemented in batch polymerization, challenges such as batch-to-batch variability and difficulties in real-time MWD control often lead to suboptimal operations. To address these issues, dynamic optimization methods should be employed to identify optimal manipulation strategies, enabling the production of polymers with customized MWD while minimizing production costs to meet market demands.

Currently, various approaches have been developed for optimizing MWD. Ma et al. (2019) proposed two optimization formulas aimed at minimizing transition time and reducing the production of off-specification materials, leading to the development of a hierarchical transition optimization model for MWD. Shin et al. (2024) introduced a global optimization framework combining agent-based model optimization with computational fluid dynamics (CFD) reactor models. Sayer et al. (2001) applied iterative dynamic programming (IDP) in the optimal feeding strategy for monomers and chain transfer agents (CTA) to produce copolymers with constant composition and well-

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defined MWD. Apostolos et al. (2006) derived an optimal temperature-setting strategy to ensure compliance with polymer properties specifications and economic process regulations. Based on the above research, we recognize that research on MWD dynamic optimization primarily focuses on continuous processes, analyzing the combined effects of variables such as temperature, monomer feed rate, initiator, and CTA. In contrast, batch process studies often examine individual variables in isolation, neglecting their integrated simultaneous effects. To effectively address MWD requirements across different batches, it is essential to account for the interaction of all relevant manipulated variables.

However, in industrial polymerization, the temperature is typically held constant to ensure process stability, as temperature fluctuations can significantly impact polymerization and product properties. Consequently, this study aims to explore whether MWD requirements can be met through dynamic optimization, specifically by adjusting the initial concentration and flow rate of the CTA while keeping the temperature constant. Two experimental strategies are proposed and both approaches consider all manipulated variables while maintaining a constant temperature for the dynamic optimization of MWD. The findings of this study provide valuable insights for the development of more efficient control strategies for MWD in industrial batch polymerization.

The contribution of this paper is summarized as follows:

(1) This work presents the establishment of a batch polymerization reaction model based on the polymerization mechanism and industrial processes, along with the formulation of a dynamic optimization problem for the MWD derived from the model;
(2) By solving the dynamic optimization problem of MWD under various conditions, it has been determined that the MWD can be controlled by adjusting the initial concentration and flow rate of the CTA, provided that the reaction temperature is maintained within a certain range.

The remainder of this paper is organized as follows: Section 2 presents the model for batch polymerization. Section 3 introduces the MWD optimization of batch polymerization. Section 4 provides the simulation results. Finally, Section 5 outlines the main conclusions and suggests directions for future research.

2. POLYMERIZATION MODEL

The batch polymerization model was abstracted from an actual industrial process, and the specific material names have been omitted for reasons of commercial confidentiality. The batch polymerization model consists of the kinetic equations, the polymer moment equations and the mass and energy balance equations.

2.1 Kinetic Equations of Polymerization

The batch polymerization process involves chain initiation, chain growth, chain termination and chain transfer reactions. The chain transfer reactions include both the transfer of the polymer chain to the monomer and to the CTA, while the termination reaction consists solely of coupling termination. The reaction types of polymerization are presented in Table 1, where A represents the polymer monomer, B represents the initiator, C represents the CTA and R^* represents the free radical. P_1, P_n and P_m represent active polymer, D_n and D_{n+m} represent dead polymer, n and m represent the chain length of polymers. $k_\mathrm{d}, k_\mathrm{i}, k_\mathrm{p}, k_{tr,\mathrm{A}}, k_{tr,\mathrm{C}}, k_\mathrm{t}$ represent the reaction rate constant of initiator decomposition reaction, initiation of monomer free radical, chain growth reaction, chain transfer reaction to monomer, chain transfer reaction to CTA, and coupling termination reaction, respectively. The relationship between the reaction rate constant and temperature follows the Arrhenius Eq. (1):

$$k = A_r \exp(\frac{-E_a}{RT_r}). \tag{1}$$

where k represents the reaction rate constant, A_r represents the prefactor, E_a represents the activation energy of the reaction, R represents the molar gas constant, and T_r represents the temperature of reaction. The kinetic parameters for each reaction are provided in Table 1.

2.2 Polymer Moment Equations

Since the chain length n can be very large, the number of differential equations for the concentration variation of active polymers is infinite. To facilitate calculation, the method of moments is introduced (Zhang et al., 2015), which converts infinite differential equations to finite differential equations. We denote

$$[\lambda_j] = \sum_{n=1}^{\infty} n^j [\mathrm{P}_n], j = 0, 1, 2, ... \tag{2}$$

$$[\mu_j] = \sum_{n=1}^{\infty} n^j [\mathrm{D}_n], j = 0, 1, 2, ... \tag{3}$$

where $[\cdot]$ represents the concentration of a substance in liquid phase, j represents the order of polymer moments, λ_j and μ_j represent the j order moments of active and dead polymers, respectively.

$$\begin{aligned} \frac{1}{V_\mathrm{l}}\frac{d\mathrm{n}_{\lambda_j}}{dt} = \sum_{j=1}^{\infty}\frac{d[\mathrm{P}_j]}{dt} &= k_i[\mathrm{A}][\mathrm{R}^*] + k_{\mathrm{tr,A}}[\mathrm{A}]([\lambda_0] - [\lambda_j]) \\ &- k_{tr,\mathrm{C}}[\mathrm{C}][\lambda_j] + k_\mathrm{p}[\mathrm{A}]\sum_{i=1}^{j} C_j^i[\lambda_{j-i}] - k_\mathrm{t}[\lambda_0][\lambda_j] \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{1}{V_\mathrm{l}}\frac{d\mathrm{n}_{\mu_j}}{dt} = \sum_{j=1}^{\infty}\frac{d[\mathrm{D}_j]}{dt} &= k_{tr,\mathrm{A}}[\mathrm{A}][\lambda_j] + k_{tr,\mathrm{C}}[\mathrm{C}][\lambda_j] \\ &+ \frac{1}{2}k_t\sum_{i=1}^{j} C_j^i[\lambda_{j-i}][\lambda_i] \end{aligned} \tag{5}$$

According the Eq. (2),(3) polymer moment equations can be expressed by Eq. (4),(5), where V_l is the liquid volume of reactor, n_{λ_j} and n_{μ_j} represent mole of j order moments of active and dead moments, respectively. $[\mathrm{P}_j]$ and $[\mathrm{D}_j]$ represent the concentration of active and dead polymers with j order respectively.

The number-average molecular weight $\mathrm{M_n}$ and the weight-average molecular weight $\mathrm{M_w}$ can be calculated by the following equations:

Table 1. Polymerization reaction types and kinetic parameters.

Reaction type	Reaction equation	Prefactor A_r (1/s)	Activation energy E_a (J/mol)
Initiator decomposition	$\mathrm{B} \overset{k_\mathrm{d}}{\to} 2\mathrm{R}^*$	1.13×10^{17}	1.35×10^{5}
Initiation	$\mathrm{A} + \mathrm{R}^* \overset{k_\mathrm{i}}{\to} \mathrm{P}_1$	3.62×10^{15}	1.20×10^{5}
Propagation	$\mathrm{P}_n + \mathrm{R}^* \overset{k_\mathrm{p}}{\to} \mathrm{P}_{n+1}$	5.49×10^{7}	1.74×10^{4}
Chain transfer to monomer	$\mathrm{P}_n + \mathrm{A} \overset{k_{\mathrm{t}r,\mathrm{A}}}{\to} \mathrm{D}_n + \mathrm{P}_1$	9.96×10^{7}	5.30×10^{4}
Chain transfer to CTA	$\mathrm{P}_n + \mathrm{C} \overset{k_{\mathrm{t}r,\mathrm{C}}}{\to} \mathrm{D}_n + \mathrm{P}_1$	3.15×10^{6}	2.00×10^{4}
Termination by combination	$\mathrm{P}_n + \mathrm{P}_m \overset{k_\mathrm{t}}{\to} \mathrm{D}_{n+m}$	3.38×10^{9}	1.36×10^{4}

$$\mathrm{M_n} = \mathrm{M_A} \frac{n_{\mu_1} + n_{\lambda_1}}{n_{\mu_0} + n_{\lambda_0}} \tag{6}$$

$$\mathrm{M_w} = \mathrm{M_A} \frac{n_{\mu_2} + n_{\lambda_2}}{n_{\mu_1} + n_{\lambda_1}} \tag{7}$$

where n_{λ_0}, n_{λ_1}, n_{λ_2} and n_{μ_0}, n_{μ_1}, n_{μ_2}, represent mole of 0, 1, 2 order moments of active polymers and 0, 1, 2 order moments of dead polymers, respectively. $\mathrm{M_A}$ is the molecular weight of monomer A.

Assume that the MWD follows the lognormal distribution (Williamson et al., 2016), $\mathrm{M_n}$ and $\mathrm{M_w}$ can be calculated as:

$$\mathrm{M_n} = \exp(\mu_M - \frac{\sigma_M^2}{2}), \quad \mathrm{M_w} = \exp(\mu_M + \frac{\sigma_M^2}{2}) \tag{8}$$

Here, μ_M and σ_M represent the mean and variance of the actual MWD, and they can be used to describe the MWD. Taking the logarithm of both sides of Eqs (8) yields the following results:

$$\sigma_M = \ln(\frac{\mathrm{M_w}}{\mathrm{M_n}}), \quad \mu_M = \ln(\frac{\mathrm{M_w}}{\exp(\frac{\sigma_M^2}{2})}) \tag{9}$$

2.3 Mass Balance and Energy Balance

The polymer monomer is added to the reactor in gaseous form, which is lighter than the water phase and is dispersed as bubbles. Mechanical agitation in the reactor facilitates the transfer of monomers into the reaction medium and subsequently into the growing polymer particles (Mendez Ecoscia et al., 2019). The transfer of monomer from the bubbles into the continuous water phase within the reactor follows the gas-liquid mass transfer Eq. (10) (Gelinski et al., 2024):

$$V_\mathrm{l} \frac{d[\mathrm{A}]}{dt} = \kappa_\mathrm{l} s V_\mathrm{l}([\mathrm{A}^*] - [\mathrm{A}]) - \frac{R_\mathrm{A}}{\mathrm{M_A}} - \frac{F_\mathrm{out}}{\mathrm{M_A}}[\mathrm{A}]. \tag{10}$$

where $[\mathrm{A}^*]$ represents the ideal concentration of monomer in liquid phase, t is the time, κ_l is the liquid mass transfer coefficient, s is the gas–liquid interfacial area per unit of volume of the dispersion. Since the change in $\kappa_\mathrm{l} s$ is negligible under pressure variations ranging from 10 to 100 atmospheres, $\kappa_\mathrm{l} s$ is treated as a constant (Teramoto et al., 1974). F_out is the exit flow rate of liquid phase. The reaction rate R_A is defined as the A monomer consumption rate in the reactor, which can be calculated as

$$R_\mathrm{A} = (k_i[\mathrm{A}][\mathrm{R}^*] + (k_p + k_{\mathrm{t}r,\mathrm{A}})[\mathrm{A}][\lambda_0]) V_\mathrm{l} \mathrm{M_A} \tag{11}$$

According to Henry's law (Sander, 2023), the dissolution rate of monomer, denoted as F_gl, can be expressed by Eq. (12):

$$F_\mathrm{gl} = \kappa_\mathrm{l} s V_\mathrm{l} \mathrm{M_A}([\mathrm{A}^*] - [\mathrm{A}]) = \kappa_\mathrm{l} s V_\mathrm{l} \mathrm{M_A}(\frac{P}{\mathrm{H}} - [\mathrm{A}]). \tag{12}$$

where P represents the pressure of reaction, H represents the Henry coefficient.

Based on the mass balance, the differential equation for mole of free radical n_{R^*}, monomer n_A, initiator n_B, CTA n_C, monomer in gas phase of reactor $n_{g,\mathrm{A}}$ can be expressed by Eq. (13) ∼ (17).

$$\frac{1}{V_\mathrm{l}} \frac{dn_{\mathrm{R}^*}}{dt} = 2k_\mathrm{d}[\mathrm{B}] - k_\mathrm{i}[\mathrm{A}][\mathrm{R}^*] + k_{\mathrm{t}r,\mathrm{C}}[\mathrm{C}][\lambda_0] \tag{13}$$

$$\frac{1}{V_\mathrm{l}} \frac{dn_\mathrm{A}}{dt} = \frac{F_\mathrm{gl} - R_\mathrm{A}}{\mathrm{M_A} V_\mathrm{l}} \tag{14}$$

$$\frac{1}{V_\mathrm{l}} \frac{dn_\mathrm{B}}{dt} = \frac{F_\mathrm{B}}{\mathrm{M_B} V_\mathrm{l}} - 2k_\mathrm{d}[\mathrm{B}] \tag{15}$$

$$\frac{1}{V_\mathrm{l}} \frac{dn_\mathrm{C}}{dt} = \frac{F_\mathrm{C}}{\mathrm{M_C} V_\mathrm{l}} - k_{\mathrm{t}r,\mathrm{C}}[\mathrm{C}][\lambda_0] \tag{16}$$

$$\frac{dn_{g,\mathrm{A}}}{dt} = \frac{F_\mathrm{A} - \mathrm{max}}{\mathrm{M_A}} \tag{17}$$

where F_A, F_B, F_C represent the feed rate of monomer, initiator and CTA respectively. $\mathrm{M_A}$, $\mathrm{M_B}$, $\mathrm{M_C}$ represent the molecular weight of A, B, C, respectively.

Accumulated feed weight of monomer, initiator and CTA: $m_{\mathrm{A_{in}}}$, $m_{\mathrm{B_{in}}}$ and $m_{\mathrm{C_{in}}}$ can be calculated by Eq. (18) ∼ (20):

$$\frac{dm_{\mathrm{A_{in}}}}{dt} = F_\mathrm{A} \tag{18}$$

$$\frac{dm_{\mathrm{B_{in}}}}{dt} = F_\mathrm{B} \tag{19}$$

$$\frac{dm_{\mathrm{C_{in}}}}{dt} = F_\mathrm{C} \tag{20}$$

According to the ideal gas equation of state $PV_\mathrm{g} = n_{g,\mathrm{A}} R T_r$, the differential equation for P can be expressed by Eq. (21):

$$\frac{dP}{dt} = \frac{R}{V_\mathrm{g}}(n_{g,\mathrm{A}} \frac{dT_r}{dt} + T_r \frac{dn_{g,\mathrm{A}}}{dt}) \tag{21}$$

where V_g represents the gas volume of reactor. And $V_\mathrm{g} = V - V_\mathrm{l}$, where V=6000 L represents the total volume of reactor.

The heat transfer process in polymerization can be mainly divided into two parts: jacket transfer and reactor transfer. The temperature change of the reactor can be calculated as Eq. (22).

$$\begin{aligned} \frac{dT_r}{dt} = \frac{1}{m_t C_p} [& F_\mathrm{A} C_{p,\mathrm{A}}(T_\mathrm{A} - T_r) + US(T_\eta - T_r) \\ & + \frac{\Delta H R_\mathrm{A}}{\mathrm{M_A}} - a(T_r - T_{amb})^b + Q_{stir}] \end{aligned} \tag{22}$$

where m_t represents the mass of materials in the reactor, C_p and $C_{p,\mathrm{A}}$ represent the heat capacity of water and monomer A, respectively. T_A, T_η, T_{amb} represent the feed temperature of monomer A in the reactor, the temperature of jacket and the temperature of environment, respectively. US represents the multiplier of Heat-transfer coefficient U and Heat-transfer area S. ΔH is the standard reaction heat. a and b are the constant of environmental heat transfer. Q_{stir} represents the stirring heat.

The temperature change of the jacket can be calculated as Eq. (23).

$$\begin{aligned}\frac{dT_\eta}{dt} = &\frac{1}{m_\eta C_{p,\eta}}[F_{\eta,c}C_{p,\eta}(T_{\eta,c} - T_\eta) \\ &+ F_{\eta,h}C_{p,\eta}(T_{\eta,h} - T_\eta) - US(T_\eta - T_r)]\end{aligned} \tag{23}$$

where m_η represents the mass of materials in the jacket, $C_{p,\eta}$ represents the heat capacity of jacket water, $F_{\eta,h}$ and $F_{\eta,c}$ represent the flow of hot water and cold water in jacket, $T_{\eta,h}$ and $T_{\eta,c}$ represent the temperature of hot water and the temperature of cold water. The values of parameters are shown in Table 2.

Table 2. The parameters of polymerization model.

Parameter	Unit	Value	Parameter	Unit	Value
R	$\mathrm{J/(mol \cdot K)}$	8.314	T_{amb}	K	293
$\kappa_{\mathrm{l}}s$	1/s	0.1405	$T_{\eta,h}$	K	363
F_{out}	kg/s	0	$T_{\eta,c}$	K	283
H	$\mathrm{Pa \cdot m^3/mol}$	700	$T_{r,sp}$	K	351
$\mathrm{M_A}$	g/mol	100	ΔH	J/mol	2.73×10^5
$\mathrm{M_B}$	g/mol	228	US	J/K	2.69×10^4
$\mathrm{M_C}$	g/mol	202.4	a	-	1
m_t	kg	4000	b	-	2
m_η	kg	2000	Q_{stir}	J/s	0.5
C_p	$\mathrm{J/(kg \cdot K)}$	4200	$F_{\eta,h\mathrm{max}}$	kg/s	1
$C_{p,\mathrm{A}}$	$\mathrm{J/(kg \cdot K)}$	804	$F_{\eta,h\mathrm{min}}$	kg/s	0
$C_{p,\eta}$	$\mathrm{J/(kg \cdot K)}$	4200	$F_{\eta,\mathrm{cmax}}$	kg/s	10
T_{A}	K	333	$F_{\eta,\mathrm{cmin}}$	kg/s	0

3. MWD DYNAMIC OPTIMIZATION FORMULATIONS

3.1 General Dynamic Optimization

A general dynamic optimization can be expressed in the following form:

$$\begin{aligned}\min_{u(t)} J =&\Phi(x(t_f), t_f) + \int_{t_0}^{t_f} L(x(t), u(t))dt \\ &s.t. \\ &\quad \dot{x}(t) = f(x(t), u(t)) \\ &\quad g_s(x(t), u(t)) \geq 0 \\ &\quad g_t(x(t), u(t)) \geq 0 \\ &\quad x(t_0) = x_0, t \in [t_0, t_f]\end{aligned} \tag{24}$$

where $x(t)$ is a vector of the state variables, $u(t)$ is a vector of the manipulated variables, t_0 and t_f are initial time and terminal time. The initial value of the state variables is given by x_0, f are the differential equations of $x(t)$, $g_s(x(t), u(t))$ represents path constraints and $g_t(x(t), u(t))$ represents terminal constraints. J is the objective function, where Φ is terminal object function and L is path objective function.

3.2 MWD Problem Formulation

The dynamic optimization problem for the batch polymerization is given in (24). The optimal trajectory for F_{A}, F_{B}, F_{C}, and the heating/cooling auxiliary variable α can be determined by solving the optimization problem. α can be expressed as follow:

$$\begin{cases} F_{\eta,c} = \max(-\alpha, 0) \times (\mathrm{F}_{\eta,\mathrm{cmax}} - \mathrm{F}_{\eta,\mathrm{cmin}}), \alpha \in [-1, 0] \\ F_{\eta,h} = \max(\alpha, 0) \times (\mathrm{F}_{\eta,\mathrm{hmax}} - \mathrm{F}_{\eta,\mathrm{hmin}}), \alpha \in (0, 1] \end{cases}$$

The notation $\max(\cdot, \cdot)$ denotes the maximum value of the two values contained within the parenthesis. $F_{\eta,h\mathrm{max}}$ and $F_{\eta,h\mathrm{min}}$ represent the maximum and minimum value of hot water. $F_{\eta,\mathrm{cmax}}$ and $F_{\eta,\mathrm{cmin}}$ represent the maximum and minimum value of cold water. The value of $F_{\eta,h\mathrm{max}}$, $F_{\eta,h\mathrm{min}}$, $F_{\eta,\mathrm{cmax}}$, $F_{\eta,\mathrm{cmin}}$ are shown in Table 2.

The following outlines the state variables:

$$\begin{aligned} x = [&n_{\lambda_0}, n_{\lambda_1}, n_{\lambda_2}, n_{\mu_0}, n_{\mu_1}, n_{\mu_2}, n_{\mathrm{R}^*}, n_{\mathrm{A}}, n_{\mathrm{B}}, \\ &n_{\mathrm{C}}, T_r, n_{g,\mathrm{A}}, P, T_\eta, m_{\mathrm{A_{in}}}, m_{\mathrm{B_{in}}}, m_{\mathrm{C_{in}}}, V_{\mathrm{l}}]\end{aligned}$$

The initial values of state variables are shown in Table 3.

Table 3. Initial conditions and state constraints.

Variable	Unit	Min	Max	Initial Value
n_{λ_0}	mol	0	inf	0
n_{λ_1}	mol	0	inf	0
n_{λ_2}	mol	0	inf	0
n_{μ_0}	mol	0	inf	0
n_{μ_1}	mol	0	inf	0
n_{μ_2}	mol	0	inf	0
n_{R^*}	mol	0	inf	0
n_{A}	mol	0	inf	914
n_{B}	mol	0	inf	3.63×10^{-4}
n_{C}	mol	0	inf	8.4
T_r	K	320	373	340
$n_{g,\mathrm{A}}$	mol	0	1.00×10^4	113
P	Pa	1.5×10^5	1.6×10^6	1.6×10^5
T_η	K	283	373	340
$m_{\mathrm{A}_{in}}$	kg	0	0	3250
$m_{\mathrm{B}_{in}}$	kg	0	2.00×10^{-3}	0
$m_{\mathrm{C}_{in}}$	kg	0	2	0
V_{l}	L	2000	6000	4000

The optimal solution is required to satisfy the following path and terminal constraints:

1. Path constraints: The batch polymerization process should meet the safety constraints, the safety constraint refers to the constraint of the state variables and manipulated variables in the model. The path constraints are as follows:

$$g_s(x(t), u(t)) = \begin{cases} x^L \leq x(t) \leq x^U \\ u^L \leq u(t) \leq u^U \end{cases}$$

where the superscripts L and U denote the lower and upper bounds respectively, on a given variable. The maximum and minimum of variables are shown in Table 3 and Table 4.

Table 4. Bounds on the manipulated variables.

Variable	Unit	Min	Max
F_{A}	kg/s	0.694	0.694
F_{B}	kg/s	0	4.00×10^{-7}
F_{C}	kg/s	0	5.60×10^{-3}
α	-	-1	1

2. Terminal constraints: At the end of the reaction, the monomer quantity should reach $m_{\mathrm{A,end}}$, and the reactor

pressure must be below the bleed pressure P_b. The terminal constraints are as follows:

$$g_t(x(t), u(t)) = \begin{cases} m_{\mathrm{A,end}} \leq m_{\mathrm{A_{in}}} \leq m_{\mathrm{A,max}} \\ P \leq P_b \end{cases}$$

where $m_{\mathrm{A,end}}$ is 3249 kg, $m_{\mathrm{A,max}}$ is 3250 kg and P_b is 10 bar.

The objective of batch polymerization optimization is to polymerize a certain amount of monomers added to the reactor into polymer products that meet the properties requirements as soon as possible under the safety constraints, and require the reactor to reach the bleed pressure at the end of the batch.

In the optimization problem, ensuring that polymer product properties meets requirements means that the final MWD of the polymers should closely approximate the ideal MWD. And minimizing production time can be reformulated as maximizing the reaction rate within a specified period. Additionally, given that temperature stability in batch processes significantly impacts MWD, the optimization objective can thus be expressed as follows Eq. (25):

$$\begin{aligned} \min_{u(t)} J =& w_1 \varepsilon_{\mu_M} + w_2 \varepsilon_{\sigma_M} \\ & + \int_{t_0}^{t_f} [-w_3 R_{\mathrm{A}} + w_4 (T_r - T_{r,sp})^2] dt \\ s.t.& \\ & Eqs.\ (4), (5), (13) \sim (23) \\ & x^L \leq x(t) \leq x^U \\ & u^L \leq u(t) \leq u^U \\ & m_{\mathrm{A,end}} \leq m_{\mathrm{A_{in}}} \leq m_{\mathrm{A,max}} \\ & P \leq P_b \\ & x(t_0) = x_0, t \in [t_0, t_f] \end{aligned} \tag{25}$$

where $w_1 = 500$, $w_2 = 1$, $w_3 = 1$, $w_4 = 10$ represent weighting coefficient corresponding to each term. ε_{σ_M} represents the relative deviation between σ_M and σ_0, and ε_{μ_M} represents the relative deviation between μ_M and μ_0, which can be calculated as Eqs (26):

$$\varepsilon_{\mu_M} = (\frac{\mu_M - \mu_0}{\mu_0})^2, \quad \varepsilon_{\sigma_M} = (\frac{\sigma_M - \sigma_0}{\sigma_0})^2 \tag{26}$$

where μ_0 and σ_0 represent the mean and variance of ideal MWD.

4. SIMULATION RESULT

Dynamic optimization problems in process systems engineering are most commonly addressed using direct collocation methods. In this approach, the entire state trajectory is parameterized as piecewise low-order polynomials, which are then integrated as decision variables within the framework of nonlinear programming (NLP). The state and manipulated variables are discretized into 240 points, with an 80-seconds interval between each point. The dynamic optimization problems are formulated using CasADi(Sander, 2019), and IPOPT (Biegler and Zavala, 2009) is used to solve NLP.

To explore whether the MWD requirements can be met by adjusting the initial concentration and flow rate of the chain transfer agent (CTA), while considering the influence of all manipulated variables and maintaining a constant temperature, two dynamic optimization cases are proposed. The details of cases are shown in the following Table 5:

Table 5. Scenario Setting of Two cases.

Case	manipulated variables	Addition method CTA
1	$u = [F_{\mathrm{A}}, F_{\mathrm{B}}, F_{\mathrm{C}}, \alpha]$	in stages*
2	$u = [F_{\mathrm{A}}, F_{\mathrm{B}}, \alpha]$	single addition at the beginning

* A specific amount of CTA is added initially before introducing the monomer, followed by continuous CTA addition.

The effect of CTA on the dynamic optimization of MWD should be expressed by the following indicators:

(1) ε_{μ_M} and ε_{σ_M}(26): the closeness between actual MWD and ideal MWD. A smaller value of ε_{σ_M} and ε_{μ_M} indicate a MWD that is closer to the ideal MWD.
(2) t_e: the time at $P \leq P_b$, which indicating the endpoint of the reaction. A smaller value of t_e signifies a faster reaction termination and corresponds to a higher reaction rate.
(3) $\overline{\Delta T^2}$: the variance between T_r and $T_{r,sp}$. A smaller value of $\overline{\Delta T^2}$ signifies a better temperature stability.
(4) $n_{\mathrm{C}e}$: the total mole of CTA.

In this paper, the optimization results of ε_{σ_M}, ε_{μ_M}, t_e, $\overline{\Delta T^2}$ and $n_{\mathrm{C}e}$ with varying initial values of the CTA are analyzed to evaluate the impact of the CTA on the MWD. The results of Case 1 is presented in the following Table 6.

Table 6. The results of Case 1.

CTA_0 (mol)	ε_{σ_M} $\times 10^3$	ε_{μ_M} $\times 10^8$	t_e (h)	$\overline{\Delta T^2}$ (K^2)	$n_{\mathrm{C}e}$ (mol)
8.4	2.15	1.08	3.09	0.0890	9.17
4.2	2.47	1.09	3.07	0.0874	9.24
1.68	3.16	1.11	3.04	0.0865	9.33
1.4	3.29	1.11	3.04	0.0865	9.35
0.84	3.75	1.13	3.04	0.0867	9.40
0.42	4.33	1.15	3.04	0.0868	9.46
0.21	4.80	1.16	3.04	0.0877	9.52
0.12	5.11	1.18	3.04	0.0881	9.55
0.093	5.21	1.18	3.04	0.0883	9.56
0.084	5.26	1.18	3.04	0.0884	9.57

where CTA_0 represents the initial value of CTA. And the results of Case 2 is presented in the following Table 7.

Table 7. The results of Case 2.

CTA_0 (mol)	ε_{σ_M} $\times 10^3$	ε_{μ_M} $\times 10^8$	t_e (h)	$\overline{\Delta T^2}$ (K^2)	$n_{\mathrm{C}e}$ (mol)
9.2	2.11	0.0234	3.11	0.0627	9.2
9.1	2.11	4.49	3.09	0.133	9.1
9.0	1.88	4.85	3.11	0.138	9.0
8.9	1.67	5.20	3.16	0.144	8.9
8.8	1.48	5.56	3.20	0.150	8.8
8.7	1.30	5.97	3.22	0.155	8.7
8.6	1.14	6.40	3.27	0.161	8.6
8.5	0.986	6.89	3.31	0.168	8.5

Given that the difference between $\varepsilon_{\sigma_M} \times 10^3$ and $\varepsilon_{\mu_M} \times 10^8$ is on the order of $\times 10^5$, the primary manifestation of differences in MWD is captured in ε_{σ_M}. When the

CTA is added in stages, as illustrated in Table 6, ε_{σ_M} gradually increases as the CTA_0 decreases, indicating that the actual MWD deviates from the ideal distribution as the CTA_0 decreases. In the scenario where the CTA is single addition at the beginning, as depicted in Table 7, ε_{σ_M} gradually decreases as the CTA_0 decreases, indicating that the MWD approaches the ideal distribution as the CTA_0 decreases. Therefore, the ideal MWD can be achieved by adjusting the initial concentration of the CTA. The influence of the initial value of the CTA on the MWD is reversed when the agent is either added in stages or single addition at the beginning.

By comparing t_e values of different $n_{\mathrm{C}e}$, it is observed that t_e decreases as $n_{\mathrm{C}e}$ increases. This suggests that the addition of the CTA reduces the rate of chain growth. The reduction in chain growth rate is attributed to the reaction between the monomer and the CTA, which leads to a decrease in the concentration of monomer available for chain growth reactions, thereby decreasing the overall chain growth reaction rate.

Regardless of whether the CTA is single addition at the beginning or added in stages, $\overline{\Delta T^2}$ remains below 0.25. This indicates that the temperature deviation between the reactor and its set point remains within ±0.5°C, suggesting that the temperature can be considered constant throughout the reaction process.

Upon comparing Table 6 and Table 7, it is evident that the addition of CTA results in lower values for both t_e and $\overline{\Delta T^2}$. This observation suggests that optimizing the reaction by simultaneously considering four manipulated variables produces better results than optimizing with only three manipulated variables in these two cases.

5. CONCLUSION

Based on the batch polymerization reaction model, this study designed the dynamic optimization problem concerning the MWD in batch polymerization and solved the optimization outcomes for varying initial values of CTA under two different ways of adding CTA. Analysis of the optimization results revealed that in a polymerization reaction conducted at a constant temperature, the MWD can be effectively controlled by adjusting both the flow rate and the initial concentration of the CTA. From the perspectives of reaction time and temperature stability in two different methods of CTA addition, it is found that the MWD of the polymerization with staged addition of CTA is superior to that with single-step addition. In future work, advanced control methodologies will be employed to predict the optimal initial concentration and flow rate of CTA. Subsequently, efficient control loops will be designed to achieve these optimal strategys, with the primary objectives of ensuring consistent product properties and enhancing the yield of high-performance polymer products.

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