NAIST-IS-DD0661030

Doctoral Dissertation

Optimal Quality Control of Continuous Polymerization Reactor

Qing Guo

February 5, 2009

Department of Information Systems
Graduate School of Information Science
Nara Institute of Science and Technology

A Doctoral Dissertation
submitted to the Graduate School of Information Science,
Nara Institute of Science and Technology
in partial fulfillment of the requirements for the degree of
Doctor of Engineering.

Thesis Committee:

Professor Hirokazu Nishitani	(Supervisor)
Professor Kenji Sugimoto	(Co-supervisor)
Associate Professor Masaru Noda	(Co-supervisor)

Optimal Quality Control
of Continuous Polymerization Reactor

Qing Guo

Abstract

A continuous stirred tank reactor (CSTR) is widely used to produce various polymers in the chemical industry. The same reactor is often operated in multiple operating conditions to produce several different grades of the same polymer according to the demand of customers. In this situation, not only steady-state operation but also grade transition operation play important roles in effective polymer production. In this thesis, optimal quality control of the CSTR is discussed from the perspectives of both the optimal steady-state operation and the optimal grade transition operation.

First, a mathematical model is developed for describing the dynamic behavior of a general free radical polymerization in the CSTR. As the specification of polymer quality, the weight-based molecular weight distribution (MWD) function is usually defined by using the concentrations of dead polymers with different chain lengths. We show that the MWD profile is characterized by three parameters: the number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersity index (*PDI*). We also show that these parameters are calculated by using three moments of the polymer system.

Second, the optimal steady-state operating condition to produce polymers with the best match to a specified MWD profile is discussed. Through a study of typical types of free radical polymerization, we find that an operating point can be determined by specifying two MWD parameters, M_n and *PDI,* when the termination by combination reaction is included. However, the simultaneous specification of M_n and *PDI* cannot determine an operating point when the termination reaction by combination is not included. In this case, we need to specify another parameter to determine an operating point. We also show that an appropriate objective function must be selected to determine an optimal operating condition by taking account of the relationship between the specified polymer quality parameters and decision variables.

Finally, the optimal grade transition policy is essential when several grades of polymers are produced in the same CSTR. We discuss an optimal grade transition to minimize the raw material and energy costs during the grade transition operation as well as to shorten the transition time. We show that a combination of feed-forward and regulatory control systems provides a good solution. As a result, we can achieve optimal production of different grades of polymers by applying the steady state optimization and the optimal grade transition policy.

Keywords:

CSTR, free radical polymerization, optimal polymer production, optimal grade transition, polymer quality control, optimization, molecular weight distribution

---

.*Doctoral Dissertation, Department of Information Systems, Graduate School of Information Science, Nara Institute of Science and Technology, NAIST-IS-DD0661030, February 5, 2009.

List of Publications

Journal Paper

1. Guo, Q., M. Noda and H. Nishitani; Optimization of Operating Conditions for Polymer Quality Control in a Continuous Stirred Tank Reactor, *J. Chem. Eng. Japan*, 41, 394-402 (2008)

Proceedings of International Conferences

2. Guo, Q., M. Noda, H. Nishitani and L. L. Cao. Optimal Polymer Production in the CSTR. *Proceedings of PSE Asia* 2007 (CD-ROM), Xi'an, China, Aug. 15-18, (2007)
3. Guo, Q., M. Noda and H. Nishitani. Operating Condition of a CSTR to Produce Polymers with Best Match to Specified MWD Parameters. *Proceedings of FOCAPO 2008*, pp. 271-274, Boston, USA, June 29 - July 2 (2008)

Preprints of Demestic Conferences

4. Guo, Q., M. Noda and H. Nishitani. Operating Condition for Specified Molecular Weight Distribution in Continuous Free Radical Polymerization. SCEJ 39th Autumn Meeting. Sapporo, Sept. 13-15, 2007
5. Guo, Q., M. Noda and H. Nishitani. Optimization of Operating Condition of Continuous Polymerization Reactor. SCEJ 73rd Annual Meeting. Shizuoka, Mar. 17-19, 2008

Contents

List of Figures

List of Tables

Chapter 1

Introduction

1.1 Polymer and polymer property

Polymer chemistry is an important part of chemical technology, and polymer has become an indispensable section in everyday living. Plastic, fibers, coatings, rubber, protein—these are all common terms in our modern vocabulary, and all a part of the polymer chemistry. The polymer industry represents an important segment of the chemical processing industry with around 100 million tons/year produced worldwide (Ray and Villa, 2000).

Polymer properties, including physical and chemical properties, such as rheologic performance, elasticity and viscosity, crystallization performance, thermal properties and so on, are the result of complex polymer architecture and composition formed in reaction (Richards and Congalidis, 2006). Consistent polymer properties are of significant important to end-user manufactures who must produce the polymer in its final form and shape for the intended application. Because the bulk properties dictate how the polymer actually behaves on a macroscopic scale, the bulk properties of a polymer are those most often of end-use interest.

Polymers are large molecules made up of simple units, i.e. molecules named monomers. Polymer molecular weight is an extremely important variable because it directly influences many of the characteristics of polymer product, such as its physiclal properties including bulk properties (Stevens, 1999). In general, the higher the molecular weight is, the tougher the polymer is; however, too high a moelcular weight can lead to processing difficulties. In general, the polymers are thought of having molecular weight that runs from the low thousands up to the millions. The optimum molecular weight depends on the application for which it is intend.

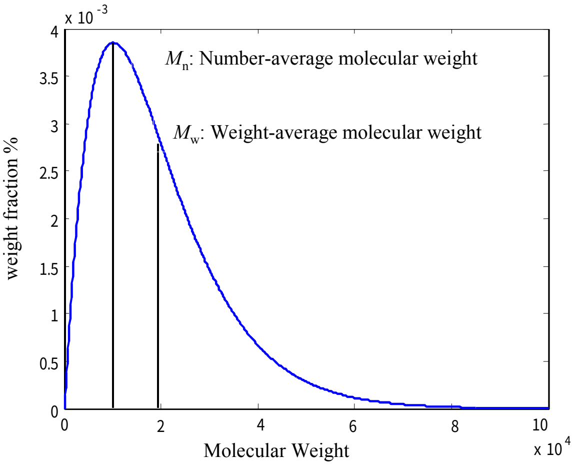

Fig. 1.1 Typical figure of molecular weight distribution

Polymer is a kind of mixture containing moleclules with various chain length or molecular weight, thus the molecular weights of polymers are not a single value, but a kind of distribution called molecular weight distribution (MWD). Polymer MWD can be described in terms of number-average molecular weight (M_n), weight-average molecular weight (M_w), polydispersity index (*PDI*), chain length distribution (CLD) or MWD of whole range. The essential feature of weight-based MWD, M_n and M_w are shown in Figure 1.1.

Techniques commonly used for determining polymer molecular weights include osmometry, light scattering, and ultracentrifugation (Inoue, 1996). However, because of expessive largescale equipment and rigorous analysis conditions, these measurment techniques are unable to be used routinely in industrial plants. Measurements of dilute solution viscosity provide the simplest and most widely used technique for routinely determining molecular weights. But it is not an absolute method and can be used only in conjunction with one of the techniques of measuring absolute molecular weights (usually by lighting scattering).

Molecular weight values obtained depend on the method of measurement. Methods that depend on osmometry give rise to the number-average molecular weight, M_n, and is defined as:

$$M_\mathrm{n} = \frac{\Sigma N_j M_j}{\Sigma N_j} \tag{1.1}$$

where N_j is the number of molecules having molecular weight M_j. Light scattering and ultracentrifugation are methods of determining molecular weight based on mass of the species present. The value obtained is the weight-average molecular weight, M_w, and is expressed as:

$$M_\mathrm{w} = \frac{\Sigma W_j M_j}{\Sigma W_j} = \frac{\Sigma N_j M_j^2}{\Sigma N_j M_j} \tag{1.2}$$

where W_j is the total weight of molecules having molecular weight M_j. It can be derived that M_w is always greater that M_n, except that all molecules are of the same weight (*e.g.* the native rubber), then $M_\mathrm{w} = M_\mathrm{n}$.

The narrower the molecular weight range, the closer are the values of M_w and M_n. The polydispersity index, *PDI*, is defined to indicate the breath of the molecular weight range in a polymer sample as follows:

$$PDI = M_\mathrm{w} / M_\mathrm{n} \tag{1.3}$$

Often in practice, a single molecular weight average (M_w or M_n) is enough to describe the polymer properties such as tensile strength, impact strength and so on. In other cases, a single molecular weight is insufficient, the breadth of molecular weight range (*i.e. PDI*) need to be measured. Moreover, the molecular weight distribution is necessary to give a complete description of the molecular charactoristic of the polymer. For example, molecular weight averages can be misleading when the MWD presents bimodalities, which are common in polymerization systems where transfer reactions to polymer chains and other branching reactions take place (Sayer *et al.*, 2001). The technique mostly used for determining MWD of polymers is size exclusion chromatography (SEC), or gel permeation chromatography (GPC).

In practice, measurement of MWD properties, however, requires sampling, dilution, off-line analysis (~15–20min), and date processing (Zeaiter *et al.*, 2006). These off-line methods are impractical for online monitoring and control applications. Several different approaches therefore have been proposed to implement online control and estimation of polymer qualities. For example, densitometer and viscometer (Ahn *et al.*, 1999) or near infrared spectroscopy (Othman and Févotte, 2004) is used to estimate polymer MWD on line as a supplementary instrument. Reaction calorimetry is another technique for online monitoring of polymerizations (Vicente *et al.*, 2001). In most cases, a process model is used as soft-sensor to predict MWD or MWD parameters on line, and model-based control strategies have been widely applied to the polymerization process control (Alhamad *et al.*, 2005; Richards and Congalidis, 2006).

1.2 Optimization and quality control in polymerization process

Polymer manufacture is one of the most important industries worldwide, and is constantly growing in sales volume. Due to increasingly stringent requirements governing high-quality polymers, there is a strong incentive to implement precise quality control for polymer production. That is, optimal operating conditions for producing polymers with the desired MWD should be determined. At the same time, varying demands of customers require more agile operation of plants to meet increased productivity requirement with flexible operating conditions. The polymer reactor needs to operate in multiple operating conditions to manufacture several different grades of polymers with different chemical and physical characteristics according to the demand of customers. Therefore, not only the design of steady-state operation but also grade transition policies should be considered for the development of effective polymer production strategies.

One of the most common problems encountered in the polymer production is the quality control problem. The main task consists of keeping the quality-relevant variables at their desired set points, despite disturbances, in order to stay within the bounds specified by the end-user properties. However, polymerization processes are difficult to control effectively due to their severe nonlinearity. As a result, several kinds of nonlinear control strategies have been developed. Due to good robust stability properties, the model predictive control (MPC) technology is applied to solve the quality control problem in batch, semi-batch or continuous polymerization reactor (for example, Jeong *et al.*, 2001; Prasad *et al.*, 2002; Zeaiter *et al.*, 2006; Ekpo and Mujtaba, 2008). Bindlish and Rawlings (2003) presented a target linearization model controller (TLMPC) for achieving process objectives in a prototypical industrial polymerization process in the presence of disturbances and plant-model mismatch. The neural network based controller was studied based on a previously developed rigorous dynamic model of a continuous acrylonitrile polymerization reactor (Atasoy *et al.*, 2006). The control results presented a comparison of two typical neural network controllers: model predictive control and NARMA-L2 control.

Off-line optimization problems have been formulated and solved for operating condition specification and polymer grade transitions. The off-line dynamic optimization is used commonly to generate optimal set point profile for batch polymerization, in which the set point profile is usually temperature trajectory during batch time, and the specified monomer conversion must be satisfied at the end of batch time (Crowley and Choi, 1997; Yoo *et al.*, 1999; Chang and Hung, 2002; Kiparissides *et al.*, 2002). Asteasuain *et al.* (2001) analyzed the start-up and shutdown strategies and perform flexibility analysis in the tubular polymerization reactor. Based on a dynamic model that predicts average molecular weights, monomer conversion, concentrations and temperature as function of time and axial reactor length, a dynamic optimization problem was formulated for studying start-up strategies. Another example considered the optimization of steady-state operation of the styrene polymerization in a three–section tubular reactor (Costa Jr. *et al.*, 2003). With the wall temperature of each reactor section is used as the only manipulated variable, the multi-objective optimization problem was solved to find maximum conversion with minimum polydispersity.

In the polymer production, profitability depends not only on steady-state operation, but also on grade transition policies. Usually, several polymer grades are produced with the same polymer reactor by changing the operating condition. Transitions between different grades result in the production of a considerable amount of off-specification polymer. Dynamic optimization is thereby implemented to minimize grade transition time, and reduce the amount of off-specification product during grade transition operation (Lee *et al.*, 1999; Kadam *et al.*, 2007; Padhiyar *et al.*, 2006). BenAmor *et al.* (2004) presented the application of an industrial real-time optimization package to the nonlinear model predictive control (NLMPC) of a simulated polymer grade transition. Two simulated polymerization cases were studied. In the continuous methyl methacrylate (MMA) process, the M_n was controlled by manipulating volumetric flow rate of initiator. In the second case of a gas-phase polyethylene reactor, the NLMPC regulated melt index, density, reactor pressure, and production rate by manipulating the flow rates of nitrogen, hydrogen, comonomer and catalyst. Asteasuain *et al.* (2006) presented a comprehensive approach to the simultaneous design and control of a continuous stirred tank reactor (CSTR) for styrene solution polymerization. A multi-objective optimization was implemented to achieve the simultaneous selection of the polymerization reactor, the structure and tuning parameters of multivariable feedforward-feedback controllers, the steady states and the transition paths between different steady states. The cost function of steady-state operation comprised an annualized reactor cost, and an average of the operating costs for producing polystyrenes of two grades. The objective function for grade transition optimization was formulated to minimize the production of off-specification polymer and the transition time between steady states.

From the review of earlier works, usually two distinct types of approaches, control and optimization, are used to solve the problem of polymer production with quality performance and flexible operation demand. In this work, we aim to perform off-line optimization strategy to solve the steady-state operation and grade transition problem encountered in polymer production.

1.3 Research objective

For purpose of implementing flexible polymer production in continuous polymerization reactor, the off-line steady state and dynamic optimization is considered in this thesis. The optimal polymer production problem comprises two parts, determination of steady-state operating condition and optimal manipulated variable profiles during grade transition.

The dissertation is divided into five main chapters.

In Chapter 2, the mathematical model is developed for description of dynamic and static behavior of a general free radical polymerization in CSTR. Based on the simulated polymer reactor, following optimization research studies are carried out.

In Chapter 3, the off-line optimization problem is formulated for a pilot-plant jacketed CSTR in the space of two operating conditions of the reactor temperature and the monomer feed ratio. The objective functions are formulated to determine an optimal operating point to produce polymers with the best match to a target MWD profile.

In Chapter 4, in order to explain the degree of freedom problem for determining an operating condition, the mathematical models of several typical free radical polymerization processes are analyzed. A thorough study is carried out to reveal the relationship between the operating condition and specified polymer quality parameters.

In Chapter 5, the optimal grade transition problem is considered for polymer production in CSTR. The off-line dynamic optimization is carried out to generate the optimal transition trajectories for input variables in the presence of constraints on input, output and state variables.

Finally, Chapter 6 summarizes the main achievement of this doctoral dissertation.

Chapter 2

Mathematical Model of a General Free Radical Polymerization in CSTR

2.1 Continuous polymerization reactor

Vinyl polymers are the most important of all polymer types. A wide variety of vinyl polymers and copolymers are produced by free radical polymerization (Stevens, 1999). The CSTR is widely used to produce synthetic polymer, operating at low conversions. In this section, a mathematical model is developed to describe the steady state and dynamic characteristic of a general free radical polymerization in CSTR, which was employed by many works for polymer quality control in CSTR or batch reactor (Ahn *et al.*, 1999; Yoo *et al.*, 1999; Kiparissides *et al.*, 2002).

The CSTR employed for free radical solution polymerization is illustrated in **Figure 2.1**. The reactor temperature is manipulated by regulating the flow rate of coolant in the jacket. F_j is the flow rate of coolant, and T_jf and T_j are respectively the temperature of feed coolant and jacket. T_f and T are the temperature of feed stream and reactor respectively. The monomer and the initiator are well mixed with the solvent before being fed into the reactor. F_m and F_i are respectively the flow rates of monomer and initiator. It is assumed that the monomer flow rate F_m is constant, and the flow rate at the inlet is the same as that of the product stream (i.e., $F = F_\mathrm{m} + F_\mathrm{i}$), and the total volume of all reactants in the reactor V is constant. I^{00} and M^{00} are respectively concentrations of initiator and monomer in feed solution. S_m^{00} and S_i^{00} are respectively concentrations of solvent in monomer and initiator feed solution. I^{00}, M^{00}, S_m^{00} and S_i^{00} are assumed to be constant. I^0 and M^0 are respectively the concentrations of initiator and monomer in the feed mixture. I, M, S, R and P are respectively the concentrations of the initiator, monomer, solvent, live and dead polymers.

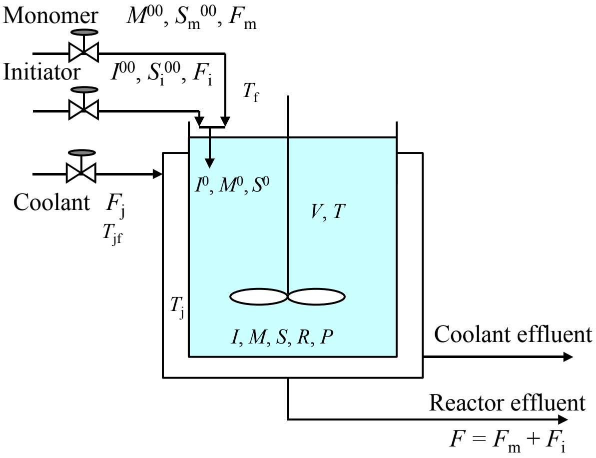

Fig. 2.1. Solution polymerization in a CSTR

2.2 Free radical polymerization mechanism

The free radical polymerization mechanism generally includes elementary reactions as initiation, propagation, transfer and termination reaction (Inoue, 1996; Stevens, 1999). An important assumption for simplifying mechanism of free radical polymerization is that the rates of initiation, propagation, and termination are all different, but that each propagation step goes at the same rate, independent of chain length. Similarly, it is assumed that the rates of termination by combination and by disproportionation are independent of chain length.

The elementary reactions are described as follows:

1) Initiation $I \xrightarrow{K_\mathrm{d}} 2R^+$

$R^+ + M \xrightarrow{K_\mathrm{i}} R_1$

2) Propagation $R_j + M \xrightarrow{K_\mathrm{p}} R_{j+1}$

3) Transfer to monomer $R_j + M \xrightarrow{K_\mathrm{trm}} P_j + R_1$

4) Transfer to solvent $R_j + S \xrightarrow{K_\mathrm{trs}} P_j + R_1$

5) Termination by combination $R_j + R_i \xrightarrow{K_\mathrm{tc}} P_{j+i}$

6) Termination by disproportionation $R_j + R_i \xrightarrow{K_\mathrm{td}} P_j + P_i$

where, I is the initiator, M is the monomer and S is the solvent. R^+ is the primary radical; R_j and P_j are the live and the dead polymers with chain length j respectively. K_d, K_i, K_p, K_trm, K_trs, K_tc and K_td are the reaction rate coefficients of corresponding elementary reactions, *i.e.* initiator decomposition, initiation reaction, propagation, transfer to monomer, transfer to solvent, termination by combination, and termination by disproportionation, respectively. All these coefficients are assumed to satisfy the Arrhenius equation, $K = A\exp(-E/R'T)$, where R' is the gas constant.

2.3 Dynamic model of polymerization

It is assumed that the flow rate of the inlet is the same as that of the product stream, and the total volume of all reactants in the reactor is constant. From the general free radical polymerization mechanism, the following set of mass balance equations therefore can be derived to describe the concentrations of the reaction species (Ahn *et al.*, 1999).

$$\frac{dI}{dt} = (I^0 - I)/\theta - K_{\mathrm{d}} I \tag{2.1}$$

$$\frac{dM}{dt} = (M^0 - M)/\theta - 2K_{\mathrm{i}} I - (K_{\mathrm{p}} + K_{\mathrm{trm}}) MR \tag{2.2}$$

$$\frac{dS}{dt} = (S^0 - S)/\theta - K_{\mathrm{trs}} SR \tag{2.3}$$

$$\frac{dR_1}{dt} = -R_1/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{p}} MR_1 + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)(R - R_1) - K_{\mathrm{t}} R_1 R \tag{2.4}$$

$$\frac{dR_j}{dt} = -R_j/\theta - K_{\mathrm{p}} M(R_j - R_{j-1}) - (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S) R_j - K_{\mathrm{t}} R_j R \qquad (j \geq 2) \tag{2.5}$$

$$\frac{dP_j}{dt} = -P_j/\theta + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S + K_{\mathrm{td}} R) R_j + \frac{K_{\mathrm{tc}}}{2} \sum_{l=1}^{j-1} R_l R_{j-l} \qquad (j \geq 2) \tag{2.6}$$

where, $\theta = V/F$ is the average residential time of the reactant in the CSTR, and

$$R = \sum_{j=1}^{\infty} R_j \tag{2.7}$$

is the total concentration of the live polymers. The rate constant, $K_{\mathrm{t}} = K_{\mathrm{tc}} + K_{\mathrm{td}}$, represents the summation of K_{tc} and K_{td}. By denoting

$$P = \sum_{j=2}^{\infty} P_j \tag{2.8}$$

as the total concentration of the polymers, the following formulation for the total concentrations of live polymers and dead polymers is obtained.

$$\frac{dR}{dt} = -R/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{t}} R^2 \tag{2.9}$$

$$\frac{dP}{dt} = -P/\theta + (K_{\mathrm{trm}}M + K_{\mathrm{trs}}S)R + (\frac{K_{\mathrm{tc}}}{2} + K_{\mathrm{td}})R^2 \tag{2.10}$$

The temperature dependence of the rate constants is assumed to follow the Arrhenius equations. The temperature of reactor and jacket is described using following energy balance equations:

$$\frac{dT}{dt} = \frac{F}{V}(T_{\mathrm{f}} - T) + \frac{-\Delta H_{\mathrm{r}}}{\rho \mathrm{Cp}} K_{\mathrm{p}} M U_0 - \frac{U_{\mathrm{r}} A_{\mathrm{r}}}{\rho \mathrm{Cp} V}(T - T_{\mathrm{j}}) \tag{2.11}$$

$$\frac{dT_{\mathrm{j}}}{dt} = \frac{F_{\mathrm{j}}}{V_{\mathrm{j}}}(T_{\mathrm{jf}} - T_{\mathrm{j}}) + \frac{U_{\mathrm{r}} A_{\mathrm{r}}}{\rho_{\mathrm{j}} \mathrm{Cp}_{\mathrm{j}} V_{\mathrm{j}}}(T - T_{\mathrm{j}}) \tag{2.12}$$

where ΔH_{r}, U_{r} and A_{r} denote the heat of reaction for propagation, the overall heat transfer coefficient and the heat transfer area.

To describe the molecular weight distribution, it isn’t necessary to solve the infinite number of equations for the concentration of polymer chains of each length. Instead, the method of moments is adopted to calculate the number-average molecular weight (M_{n}), weight-average molecular weight (M_{w}) and polydispersity index (*PDI*). The moments of the live and dead polymers are defined as

$$U_m = \sum_{j=1}^{+\infty} j^m R_j \quad \text{and} \quad Z_m = \sum_{j=2}^{+\infty} j^m P_j, m = 0,1,2,\cdots \tag{2.13}$$

where, U_m and Z_m are the *m*th moments of live and dead polymer concentrations, respectively. It can be seen that $U_0 = R$ and $Z_0 = P$, which are total concentration of the live and dead polymers respectively. One can derive balance equations for the first three moments of the live and dead polymer concentrations as follows:

$$\frac{dU_0}{dt} = -U_0/\theta + 2K_{\mathrm{i}}I - K_{\mathrm{t}}U_0^2 \tag{2.14}$$

$$\frac{dU_1}{dt} = -U_1/\theta + 2K_\mathrm{i}I + K_\mathrm{p}U_0M - K_\mathrm{t}U_0U_1 + (K_\mathrm{trm}M + K_\mathrm{trs}S)(U_0 - U_1) \qquad (2.15)$$

$$\frac{dU_2}{dt} = -U_2/\theta + 2K_\mathrm{i}I + K_\mathrm{p}M(2U_1 + U_0) - K_\mathrm{t}U_0U_2 + (K_\mathrm{trm}M + K_\mathrm{trs}S)(U_0 - U_2) \qquad (2.16)$$

$$\frac{dZ_0}{dt} = -Z_0/\theta + (K_\mathrm{trm}M + K_\mathrm{trs}S + K_\mathrm{td}U_0)U_0 + \frac{K_\mathrm{tc}}{2}U_0^2 \qquad (2.17)$$

$$\frac{dZ_1}{dt} = -Z_1/\theta + (K_\mathrm{trm}M + K_\mathrm{trs}S + K_\mathrm{td}U_0)U_1 + K_\mathrm{tc}U_0U_1 \qquad (2.18)$$

$$\frac{dZ_2}{dt} = -Z_2/\theta + (K_\mathrm{trm}M + K_\mathrm{trs}S + K_\mathrm{td}U_0)U_2 + K_\mathrm{tc}(U_0U_2 + U_1^2) \qquad (2.19)$$

The number and weight average molecular weight and polydispersity index are then calculated using above moments as

$$M_\mathrm{n} = M_\mathrm{m}\frac{Z_1 + U_1}{Z_0 + U_0} \qquad (2.20)$$

$$M_\mathrm{w} = M_\mathrm{m}\frac{Z_2 + U_2}{Z_1 + U_1} \qquad (2.21)$$

$$PDI = M_\mathrm{w}/M_\mathrm{n} \qquad (2.22)$$

where, M_m is the molecular weight of the monomer. Since the concentrations of live polymers are far smaller than the concentrations of dead polymers, the contribution of live polymers to the overall polymer molecular weight is negligibly small. As a result, the number and weight average molecular weight and *PDI* are calculated by using the dead polymer moments as follows:

$$M_\mathrm{n} = M_\mathrm{m}Z_1/Z_0,\ \ M_\mathrm{w} = M_\mathrm{m}Z_2/Z_1, \text{ and }\ PDI = M_\mathrm{w}/M_\mathrm{n} = \frac{Z_0Z_2}{Z_1^2} \qquad (2.23)$$

2.4 Static model of polymerization

By imposing left of above dynamic equations on 0, the steady state model of the continuous polymerization process is obtained. The reactant concentrations in steady state are expressed by a set of mass balance equations as follows:

$$(I^0 - I)/\theta - K_{\mathrm{d}} I = 0 \tag{2.24}$$

$$(M^0 - M)/\theta - 2K_{\mathrm{i}} I - (K_{\mathrm{p}} + K_{\mathrm{trm}})MR = 0 \tag{2.25}$$

$$(S^0 - S)/\theta - K_{\mathrm{trs}} SR = 0 \tag{2.26}$$

$$-R_1/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{p}} MR_1 + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)(R - R_1) - K_{\mathrm{t}} R_1 R = 0 \tag{2.27}$$

$$-R_j/\theta - K_{\mathrm{p}} M(R_j - R_{j-1}) - (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)R_j - K_{\mathrm{t}} R \cdot R_j = 0 \quad (j \geq 2) \tag{2.28}$$

$$-P_j/\theta + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S + K_{\mathrm{td}} R)R_j + \frac{K_{\mathrm{tc}}}{2} \sum_{l=1}^{j-1} R_l R_{j-l} = 0 \qquad (j \geq 2) \tag{2.29}$$

$$-R/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{t}} R^2 = 0 \tag{2.30}$$

$$-P/\theta + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)R + (\frac{K_{\mathrm{tc}}}{2} + K_{\mathrm{td}})R^2 = 0 \tag{2.31}$$

The first three moments of live and dead polymers are calculated using following equations:

$$-U_0/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{t}} U_0^2 = 0 \tag{2.32}$$

$$-U_1/\theta + 2K_{\mathrm{i}} I + K_{\mathrm{p}} MU_0 - K_{\mathrm{t}} U_0 U_1 + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)(U_0 - U_1) = 0 \tag{2.33}$$

$$-U_2/\theta + 2K_{\mathrm{i}} I + K_{\mathrm{p}} M(2U_1 + U_0) - K_{\mathrm{t}} U_0 U_2 + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)(U_0 - U_2) = 0 \tag{2.34}$$

$$Z_0 = \theta \cdot \{(K_{\mathrm{trm}} M + K_{\mathrm{trs}} S + K_{\mathrm{td}} U_0)U_0 + \frac{K_{\mathrm{tc}}}{2} U_0^2\} \tag{2.35}$$

$$Z_1 = \theta \cdot \{(K_{\mathrm{trm}} M + K_{\mathrm{trs}} S + K_{\mathrm{td}} U_0)U_1 + K_{\mathrm{tc}} U_0 U_1\} \tag{2.36}$$

$$Z_2 = \theta \cdot \{(K_{\mathrm{trm}} M + K_{\mathrm{trs}} S + K_{\mathrm{td}} U_0) U_2 + K_{\mathrm{tc}} (U_0 U_2 + U_1^2)\} \tag{2.37}$$

One can derive the molecular weight distribution function from above mass balance equations. The concentration of live polymers with a chain length of one is calculated as follows:

$$R_1 = \frac{2K_{\mathrm{i}} I + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S) R}{K_{\mathrm{p}} M \varphi} \tag{2.38}$$

where, $\varphi = 1 + \frac{K_{\mathrm{trm}}}{K_{\mathrm{p}}} + \frac{K_{\mathrm{trs}} S}{K_{\mathrm{p}} M} + \frac{K_{\mathrm{tc}} R}{K_{\mathrm{p}} M} + \frac{K_{\mathrm{td}} R}{K_{\mathrm{p}} M} + \frac{1}{K_{\mathrm{p}} M \theta}$ (2.39)

Combining Eqs. (2.27) and (2.28) gives following expression for the concentration of live polymers with chain length j.

$$R_j = R_{j-1} \cdot \varphi^{-1} = R_1 \cdot \varphi^{-(j-1)}; j \geq 2 \tag{2.40}$$

If Eq. (2.40) is substituted into Eq. (2.29), the concentration of dead polymers with chain length j is then derived as follows:

$$P_j = \theta \cdot [(K_{\mathrm{trm}} M + K_{\mathrm{trs}} S + K_{\mathrm{td}} R) R_1 \cdot \varphi^{-(j-1)} + \frac{1}{2} K_{\mathrm{tc}} R_1^2 \cdot \varphi^{-(j-2)} (j-1)] \tag{2.41}$$

The maximum value of j is selected such that it satisfies a criterion such as

$$\sum_{j=2}^{\max} P_j / P = 0.999 \tag{2.42}$$

When j of Eq. (2.41) is set from 2 to the maximum value calculated by Eq. (2.42), the concentrations of dead polymers with different chain length are obtained. The weight-based MWD function can then be described using following equation:

$$f_{\mathrm{w}}(j) = jN_j / \Sigma jN_j = \frac{jP_j}{\sum_{j=2}^{\max} jP_j} = \frac{jP_j}{Z_1}; j = 2,3,\cdots \tag{2.43}$$

Chapter 3

Steady-state Optimization of Operating Conditions for Polymer Quality Control in Continuous Free Radical Polymerization Reactor

3.1 Introduction

Polymer molecular weight distribution (MWD) is one of the most important properties in industrial polymerization processes. For a specific polymer, its physical and chemical properties, such as thermal, rheological, and crystallization characteristics, strongly depend on the polymer MWD (Crowley and Choi, 1997a). Due to increasingly stringent requirements governing high-quality polymers, there is a strong incentive to implement precise quality control for polymer production. That is, optimal operating conditions for producing polymers with the desired MWD should be determined. The polymer MWD generally cannot be observed online. As a result, model-based control strategies have been widely applied to the polymerization process control.

An appropriate objective function plays an important role in both offline and online control strategies. Polymer MWD can be described in terms of the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (*PDI*). Often, in practice, only the average molecular weight properties (*e.g.*, M_n or M_w) are selected as the major controlled variables (Ahn *et al.*, 1999; Park and Rhee, 2001). In some industrial cases, it is regarded that the control of a single molecular weight average is not sufficient, and it is necessary to control the shape of the polymer MWD. Since an MWD profile is more complex than MWD parameters, selecting an appropriate function to describe the MWD profile is a challenge. A stochastic distribution control strategy that aims to control the shape of the output probability density function (PDF) for general non-Gaussian stochastic systems was applied to MWD control in polymerization processes (Yue and Wang, 2003). Yue *et al.* (2004) reported a B-spline-based neural network model, which was implemented to approximate the shape of MWD for a styrene bulk polymerization in a pilot-plant continuous stirred tank reactor (CSTR). An objective function containing a measure of the distance between the output PDF (*i.e.* polymer MWD) and the target PDF was formulated. The control input was the monomer feed ratio. Crowley and Choi (1997b) presented a weight-fraction method to describe the MWD for a batch free radical polymerization, in which the objective function was defined as the discrepancy between the product weight chain length distribution (WCLD) and a given target WCLD. A suboptimal sequence of reactor temperature set points was calculated using nonlinear programming.

Generally, in batch polymerization processes, the desired monomer conversion is used as an important parameter to determine the final batch time (Crowley and Choi, 1997b; Yoo *et al.*, 1999; Kiparissides *et al.*, 2002). An online two-step method was used to obtain the polymer product with the desired MWD when there was a process disturbance in a batch styrene polymerization reactor. The controlled variables were the number-average degree of polymerization and *PDI* at the final batch time. The manipulated variable was the reactor temperature (Yoo *et al.*, 1999). The model predictive control (MPC) strategy was proposed for the online optimal control of key polymer properties, the particle size distribution (PSD) and MWD, in a semi-batch styrene emulsion polymerization. The monomer flow rate and the reactor temperature were used as the manipulated variables, and the controlled variables were the particle size polydispersity index (PSPI) and M_n (Zeaiter *et al.*, 2006).

Many authors have focused on grade transition operation and control of continuous polymerization processes, in which the steady state is usually specified in terms of product properties, such as M_n, M_w, *PDI*, polymer melt index and density, or cost performance (Yi *et al.*, 2003; Padhiyar *et al.*, 2006); the selection of appropriate parameters as specifications depends on the performance demands. In these cases, the monomer conversion is less important than polymer quality properties and is not considered as a main specification parameter. In the dynamic optimization of methyl-methacrylate vinyl acetate (MMA-VA) copolymerization in a continuous reactor, the objective function was formulated as an integration of the total absolute discrepancy between the desired and achieved values of M_w and the monomer composition of VA in dead copolymers during the transition time (Lee *et al.*, 1999). Prasad *et al.* (2002) focused on the free radical styrene polymerization in a jacket CSTR. The manipulated inputs were the coolant, initiator, monomer, and solvent flow rates. The controlled variables were the reactor temperature, the zeroth moment of the polymer distribution λ_0 (*i.e.*, polymer concentration), M_n and *PDI,* because the choice of these parameters reflects the desire to control polymer product quality.

In this Chapter, we consider the optimal polymer production problem in the space of two operating conditions of the reactor temperature and the monomer feed ratio in a simulated pilot-plant jacketed CSTR. The objective is to obtain an operating point for producing polymers with the best match to a target MWD profile described using finite weight fractions (Crowley and Choi, 1997a). The optimization algorithm is used to solve the simultaneous nonlinear algebraic equations of the mathematical model. A thorough study to find an appropriate objective function for obtaining the optimal operating point is carried out based on the relationship among the decision variables and specified polymer quality parameters. Two cases are studied in this work: free radical styrene polymerization and free radical MMA polymerization.

3.2 Problem formulation of off-line optimization

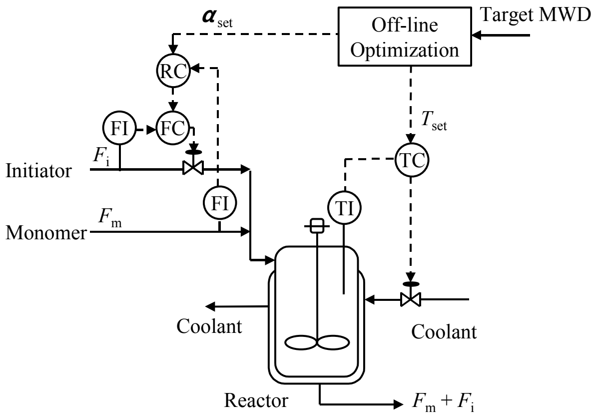

Fig. 3.1 Control scheme of a pilot-plant jacketed CSTR

Figure 3.1 shows the control scheme for a pilot-plant jacketed CSTR. The reactor is equipped with a stirrer for mixing the reactants. The off-line optimization calculates the optimal reactor temperature and the initiator-to-monomer flow rate ratio for the target MWD. These parameters are used as the set-point signals of the regulatory controllers. The reactor temperature is manipulated by regulating the flow rate of coolant in the jacket. A ratio controller is used to control the flow rate of the initiator solution. The flow rate of the monomer is fixed. The monomer and the initiator are well mixed with the solvent before being fed into the reactor.

The off-line optimization of the operating conditions is performed under the assumption that the regulatory controllers are properly designed and work effectively to track the set points. The optimization target is to obtain a product with the best match to the given target MWD profile. Instead of the initiator-to-monomer flow rate ratio in the above control scheme, the monomer feed ratio (α) and the reactor temperature (T) are used as decision variables in the optimization problem. The monomer feed ratio is defined as follows:

$$\alpha = \frac{F_\mathrm{m}}{F_\mathrm{m} + F_\mathrm{i}} \tag{3.1}$$

where, F_m and F_i are the flow rates of monomer and initiator, respectively. The concentrations of monomer and initiator in the feed solution are assumed to be constant.

The objective function J_1 was constructed by using a set of L weight fractions of polymers, directly approximating the MWD profile as follows (Crowley and Choi, 1997a):

$$J_1 = \sum_{i=1}^{L} \left(\frac{f(m_i, n_i)^* - f(m_i, n_i)}{f(m_i, n_i)^*} \right)^2 \tag{3.2}$$

Where, $f(m_i, n_i)$ is the weight fraction of polymers within a chain length interval (m_i, n_i). $f(m_i, n_i)^*$ denotes the desired weight fraction. In this work, 15 chain length intervals are selected using the following formula:

$$\left.\begin{aligned} m_i &= 2 + a(i-1)i \\ n_i &= 1 + a(i+1)i \end{aligned}\right\} i = 1, 2, \cdots, 15 \tag{3.3}$$

where, the value of a is chosen to ensure that a set of 15 weight fractions expresses the MWD profile. Each weight fraction is defined as follows:

$$f(m_i, n_i) = \frac{\sum_{j=m_i}^{n_i} jN_j}{\sum_{j=2}^{\infty} jN_j} = \frac{\sum_{j=m_i}^{n_i} jP_j}{\sum_{j=2}^{\infty} jP_j} \tag{3.4}$$

where, N_j and P_j are the number and the concentration of dead polymers with chain length *j*, respectively. The contribution of live polymers is ignored because their concentrations are much lower than that of dead polymers.

The off-line steady-state optimization problem was solved using the CVP_SS solver in gPROMS^{TM}. The CVP_SS solver implements a single-shooting dynamic optimization algorithm, which employs a sequential quadratic programming (SQP) method for the solution of the nonlinear programming problem. The CVP_SS solver involves the following steps:

1. The optimizer chooses the duration of each control interval, and the values of the control variables over it;

2. Starting from the initial point at time $t = 0$, the dynamic system model is solved over the entire time horizon to determine the time-variation of all variables in the system;

3. The above information is used to determine the values of the objective function to be optimized and any constraints that have to be satisfied by the optimization;

4. Based on above steps, the optimizer revises the choices it made at the first step, and the procedure is repeated until convergence to the optimum is achieved.

The CVP_SS solver supports both steady-state and dynamic optimization problems. In this chapter, the off-line optimization problem is a steady-state ones, so the steady-state mathematical model presented in Chapter 2.4 is used.

3.3 Case study for free radical styrene polymerization

3.3.1 Problem statement

In free radical styrene polymerization, azobisisobutyronitrile and toluene are used as the initiator and the solvent, respectively. The physical properties and kinetic parameters are referred from the literature (Yoo *et al.*, 1999) and listed in **Table 3.1**. By substituting above parameters into the steady-state model developed in Chapter 2, we obtained the mathematical model for steady-state off-line optimization of free radical styrene polymerization. The simulation results show that the polymer concentration is negligible when the chain length is greater than 1800 for the free radical styrene polymerization under the presented conditions. Therefore, the chain length j from 1 to 1800 was selected to obtain the steady-state polymerization model. M^{00} and I^{00} are concentrations of monomer and initiator in the feed solution.

Table 3.1 Parameters of styrene polymerization model

K_d [L·mol/min]	$9.48 \times 10^{16} \exp(-30798.5/1.987T)$
K_i [L·mol/min]	$0.6K_d$
K_p [L·mol/min]	$6.306 \times 10^{8} \exp(-7067.8/1.987T)$
K_{trm} [L·mol/min]	$7.116 \times 10^{8} \exp(-12671.1/1.987T)$
K_{tc} [L·mol/min]	$7.5 \times 10^{10} \exp(-1680/1.987T)$
M_m [g/mol]	100.12
M^{00} [mol/L]	4.8
I^{00} [mol/L]	0.0106
F_m [L/min]	0.02
V [L]	3.927

The target MWD properties or MWD profile are usually specified according to laboratory analysis of sample products with the desired polymer properties. In this work, in order to avoid complicated consideration of the optimization result, the target polymer MWD was specified under a predefined reactor temperature (T = 345 K) and a monomer feed ratio (α = 0.55). **Figure 3.2** shows a set of 15 weight fractions of the target MWD that approximates the desired MWD profile. The optimal operating conditions are obtained by minimizing J_1 of Eq. (3.2). We can find the predefined operating condition as an optimal point by formulating an appropriate objective function. The search area of the decision variables is shown in **Table 3.2**.

Table 3.2 Search area of decision variables for styrene polymerization

Decision Variables	Lower Bound	Upper Bound
α	0.3	0.8
T [K]	330	355

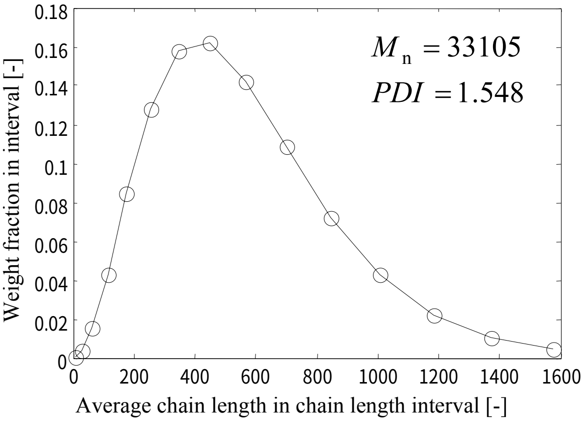

Fig. 3.2 15 weight fractions of a target MWD (styrene)

3.3.2 Results of J_1 minimization

We searched for the optimal solution of J_1 from seven initial points in the operating condition space. These searches stopped on various points denoted by "○" in **Figure 3.3**, depending on the starting points. These points are on a curve that passes through the predefined optimal point. **Table 3.3** summarizes two MWD parameters with the monomer conversion (Xc) for each converged point. The monomer conversion is calculated as follows:

$$Xc = (M^0 - M) / M^0 \tag{3.5}$$

These values in Table 3.3 were calculated from the simulation results for the operating conditions converged. The two MWD parameters must coincide with the desired values as described in the next section. The discrepancies between the desired and the achieved values of the two MWD parameters indicate the difficulty of numerical minimization of J_1.

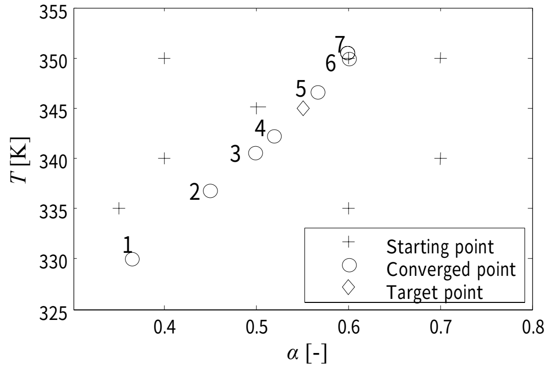

Fig. 3.3 Searches for J_1 minimization (styrene)

Table 3.3 Simulated MWD for converged points of J_1 (styrene)

No.	α	T [K]	M_n	*PDI*	Xc [%]
1	0.36	330	33129	1.532	2.1
2	0.45	337	33102	1.539	4.4
3	0.50	341	33106	1.543	6.4
4	0.52	342	33116	1.545	7.4
5	0.57	347	33104	1.550	10.3
6	0.59	350	33085	1.556	13.1
7	0.60	351	33111	1.556	13.1

3.3.3 Introduction of objective function J_2

To consider the results of J_1 minimization, we introduced the following objective function J_2 represented by two MWD parameters, M_n and *PDI*.

$$J_2 = \left(\frac{M_\mathrm{n}^* - M_\mathrm{n}}{M_\mathrm{n}^*}\right)^2 + \lambda\left(\frac{PDI^* - PDI}{PDI^*}\right)^2 \tag{3.6}$$

where, λ is the weighting factor. The target MWD profile $f(m_i, n_i)^*$ in Figure 3.2 corresponds to $M_\mathrm{n}^* = 33105$ and $PDI^* = 1.548$.

The operating points that satisfy the desired value of M_n form a contour of constant M_n in the space of operating conditions. Similarly, the operating points that satisfy the desired value of *PDI* form a contour of constant *PDI*. **Figure 3.4** shows both contours of M_n and *PDI*. When either M_n or *PDI* is specified at M_n^* or PDI^*, the solution is on the contour of M_n^* or PDI^*. When both M_n and *PDI* are specified simultaneously, the cross point of the two contours of M_n and *PDI* is obtained.

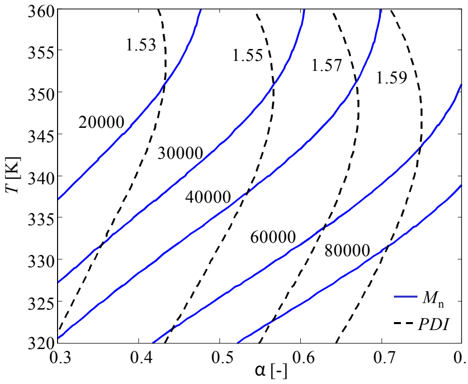

Fig. 3.4 Contour map of M_n and *PDI* (styrene)

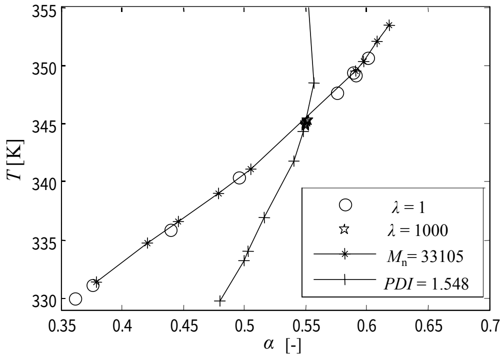

Fig. 3.5 Searches for J_2 minimization with different λ (styrene)

Although the optimal point is determined from the specified M_n and *PDI*, care must be taken when minimizing J_2. The result of the search strongly depends on the weighting factor λ. **Figure 3.5** illustrates the results of J_2 minimization for different values of λ. If λ is 1, the search will converge on a curve denoted by "○" in Figure 3.5, which is the contour of M_n^* seen in the results on J_1. When λ is set as 1000, the optimization result denoted by "✯" converges on the predefined optimal operating point ($\alpha = 0.55$, $T = 345\,\mathrm{K}$). Obviously, the resulting point is the cross point of the contours of M_n^* and PDI^*.

In the following, the above results for the optimization problem of J_2 are considered. The gradient of J_2 with respect to x can be expressed by following equation:

$$\frac{\partial J_2}{\partial x} = -\frac{2}{M_\mathrm{n}^*} \cdot \frac{M_\mathrm{n}^* - M_\mathrm{n}}{M_\mathrm{n}^*} \cdot \frac{\partial M_\mathrm{n}}{\partial x} - \frac{2\lambda}{PDI^*} \cdot \frac{PDI^* - PDI}{PDI^*} \cdot \frac{\partial PDI}{\partial x} \tag{3.7}$$

Here, $x = [T \quad \alpha]^T$ denotes the vector of manipulated variables. At the optimal point, M_n and *PDI* satisfy the condition: $\partial J_2 / \partial x = 0$. It is clear from Figure 3.4 that all elements of $\partial PDI / \partial x$ are much smaller than those of $\partial M_\mathrm{n} / \partial x$ in the search area of the operating conditions. Also, the second term of Eq. (3.7), excluding λ, is about 10^{-3} times smaller than the first term of Eq. (3.7). Therefore, when λ in the second term is small, the second term of Eq. (3.7) is negligible in the calculation of the gradient vector. As a result, the searching point moves so that the first term of Eq. (3.7) becomes a zero vector. This means that the optimization search of J_2 is easily trapped near the curve of $M_\mathrm{n} - M_\mathrm{n}^* = 0$. When λ is large, the search point moves to satisfy both requirements of M_n and *PDI* simultaneously. In other words, the search converges to the cross point of the contours of M_n^* and PDI^*, which is the optimal point. We can reason that the very low sensitivity of the decision variables to the objective function J_2 or J_1 generated trapping near the curve satisfying $M_\mathrm{n}^* = M_\mathrm{n}$.

3.4 Case study for free radical MMA polymerization

3.4.1 Problem statement

In this case study, the off-line optimization is implemented for a methyl methacrylate (MMA) polymerization in CSTR. Ethyl acetate (EA) and vazo 67 (2-methylbutanenitrile) are used as solvent and initiator respectively. It is necessary to assign appropriate values to m and n in Eqs. (3.3) and to replace the infinite chain length domain with a finite range bounded by a maximum chain length. In this case, according to the simulation results, the polymer concentration is very low while the chain length is greater than 4000 for the target MWD, so if 15 chain lengths were chosen to bind the chain length intervals, the value of a in Eqs. (3.3) is set as 16.

The target polymer MWD was specified under a predefined operating condition ($\alpha = 0.55$, $T = 340\text{K}$); thus, it is a feasible MWD. The search area of the decision variables is listed in **Table 3.4**. The physical properties and kinetic parameters are referred from the literature (Crowley and Choi, 1997) and listed in **Table 3.5**. **Figure 3.6** shows the 15 weight fractions of the target MWD for the free radical MMA polymerization.

Table 3.4 Search area of decision variables for MMA polymerization

Decision Variables	Lower Bound	Upper Bound
α	0.3	0.8
T [K]	320	350

Table 3.5 Parameters of MMA polymerization model

K_d [L·mol/min]	$1.14\times10^{19}\exp(-34277/1.987T)$
K_i [L·mol/min]	$0.21K_\mathrm{d}$
K_p [L·mol/min]	$4.2\times10^{8}\exp(-6300/1.987T)$
K_trm [L·mol/min]	$1.74\times10^{13}\exp(-17957/1.987T)$
K_trs [L·mol/min]	$6.12\times10^{10}\exp(-15702/1.987T)$
K_tc [L·mol/min]	0
K_td [L·mol/min]	$1.06\times10^{11}\exp(-2800/1.987T)$
M_m [g/mol]	104.15
M^{00} [mol/L]	4.694
I^{00} [mol/L]	0.025
S_m^{00} [mol/L]	5.09
S_i^{00} [mol/L]	10.18
F_m [L/min]	0.02
V [L]	3.927

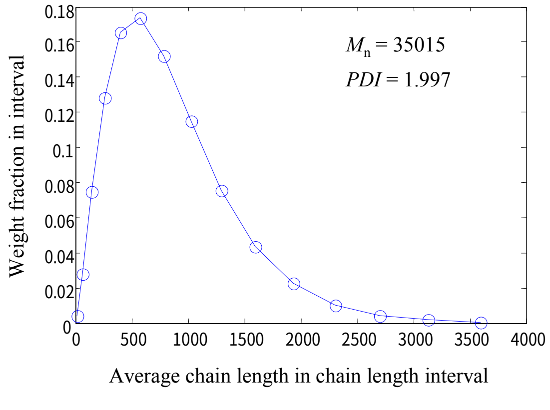

Fig. 3.6 Weight fraction of a target MWD (MMA)

3.4.2 Results of J_1 and J_2 minimization

We assumed six initial points to obtain an optimal solution for J_1. These searches stopped at various points 1-6 denoted by "○" in **Figure 3.7**, and depended on the starting points. These points converge on a curve that passes through the predefined optimal point. **Table 3.6** summarizes two MWD parameters with the monomer conversion for each convergence point. It is clear from Table 3.6 that all the simulation results approximately satisfy the requirements of both M_n and *PDI* targets. This result is distinct from that of J_1 in the case of styrene polymerization.

The objective function J_2 was used to further investigate the optimization result of J_1, where $M_\mathrm{n}^* = 35015$ and $PDI^* = 1.997$ correspond to the target MWD profile $f(m_i, n_i)^*$ in Figure 3.6. As shown in Figure 3.7, the search results "✳" still converge on the curve that passes through the predefined optimal point in accordance with J_1, but not on the target point, even with a large weighting factor ($\lambda = 10000$).

Figure 3.8 illustrates both contours of M_n and *PDI*. In contrast to the styrene polymerization, in the case of free radical MMA polymerization, the contours of M_n and *PDI* are almost parallel. In particular, the two contours of $M_\mathrm{n} = 35015$ and $PDI = 1.997$ almost coincide. It is, therefore, impossible to determine an optimal point even if M_n and *PDI* are specified simultaneously. The optimizing searches of J_1 and J_2 stop on the contour satisfying desired values of M_n and *PDI*, but not on the target point. Therefore, an additional constraint, *e.g.*, dead polymer concentration, must be introduced into the objective function to obtain an optimal point. This constraint is equivalent to give a constraint of the polymer production rate.

Table 3.6 Simulated MWD for search results of J_1 (MMA)

No.	α	T [K]	M_n	*PDI*	*Xc* [%]
1	0.349	334	35022	1.997	8.5
2	0.429	336	34992	1.997	11.8
3	0.494	338	35016	1.997	14.8
4	0.561	340	35015	1.997	17.7
5	0.600	341	35035	1.997	19.3
6	0.779	346	35039	1.997	24.4

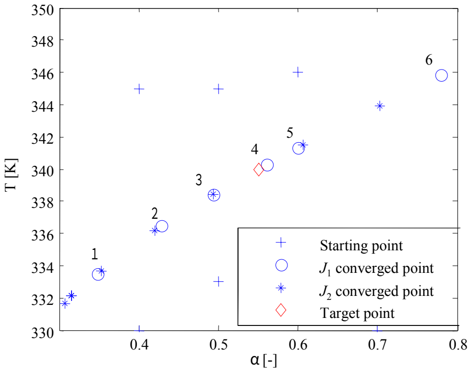

Fig. 3.7 Searches for J_1 and J_2 (MMA)

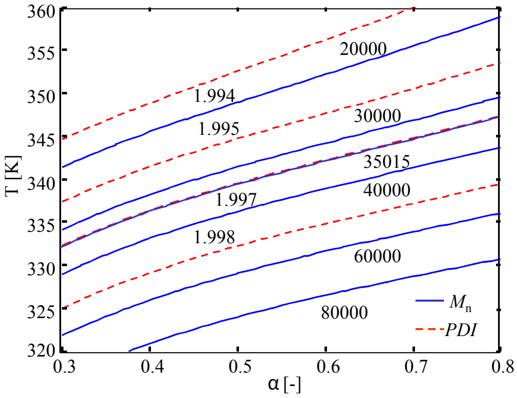

Fig. 3.8 Contour map of M_n and *PDI* (MMA)

3.4.3 Introduction of objective function J_3

When customers specify M_n and *PDI* of the polymers, the first three moments of molecular weight can be calculated using Eqs. (2.23) with a specified dead polymer concentration Z_0. We formulated objective function J_3 describing the discrepancy of three moments of dead polymer, i.e., Z_0, Z_1, and Z_2.

$$J_3 = \left(\frac{Z_0^* - Z_0}{Z_0^*}\right)^2 + \left(\frac{Z_1^* - Z_1}{Z_1^*}\right)^2 + \left(\frac{Z_2^* - Z_2}{Z_2^*}\right)^2 \tag{3.8}$$

Here, the output dead polymer concentration under the predefined operating condition is selected. J_3 is not only related to the MWD profile, but also to the dead polymer concentration.

As a result, almost the same solution was obtained in the search despite starting from different points, as shown in **Figure 3.9**. When the dead polymer concentration is introduced into the objective function, the optimal solutions converge on the target point.

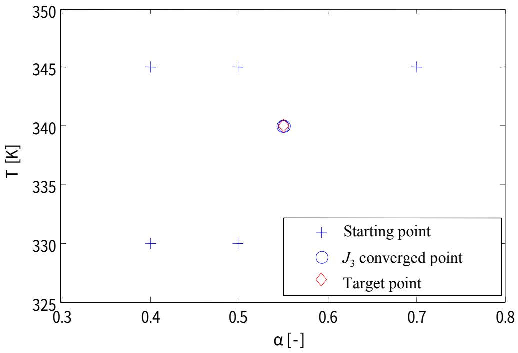

Fig. 3.9 Searches for J_3 (MMA)

3.5 Discussion

Off-line optimization for the polymer quality control in a CSTR was considered in this Chapter. The objective functions were formulated to determine an optimal operating point to produce polymers with the desired MWD. These objective functions were investigated according to two cases: the free radical styrene polymerization and free radical MMA polymerization.

The optimization results of J_1, which is constructed by a set of 15 weight fractions of polymers approximating the MWD profile, stopped near a curve that passes through the predefined optimal point instead of the target point in both cases. Another objective function J_2 composed of two MWD parameters was introduced to investigate the result of J_1. In the case of styrene polymerization, the optimal operating condition with the specified value of M_n or PDI is on the contour of M_n^* or PDI^*. When M_n and PDI are specified simultaneously, the cross point of the two contours becomes the optimal point. We also showed that the partial differentiation of PDI, with respect to the decision variables x, is numerically far smaller than that of M_n. For this reason, when λ in J_2 is small, the optimization of J_2 could not reach the optimal point, but converged on the curve satisfying the desired value of M_n. We must choose the weighting factor λ appropriately in order to obtain the target point.

In the case of free radical MMA polymerization, different from that of styrene polymerization, optimization searches of J_2 cannot reach the target point, and stopped near a curve even with a large weighting factor. This is because the contours of M_n and PDI are almost parallel. To solve this problem, we need to add another constraint to the optimization problem. As an example, the objective function J_3 in view of three moments of dead polymer was formulated to solve this problem. These parameters are not only related to the MWD profile, but also to dead polymer concentration or polymer production rate. As a result, the target point was reached despite starting from different points.

Chapter 4

Analysis of Correlation between Operating Condition and Polymer Quality Specifications

4.1 Introduction

Polymer MWD is an extremely important variable because it relates directly to polymer's physical properties. In order to implement precise quality control in polymerization process, one must determine the operating conditions needed to produce polymers with a specified MWD. In many studies, the MWD parameters, such as M_n, M_w and *PDI* are used as a substitute for MWD in polymerization processes. The MWD parameters, especially M_n or melt index, which is used as an online measurement displacing online immeasurable MWD, are often employed as the polymer grade specification to obtain the steady-state operating point of CSTR (Yi *et al.*, 2003; Asteasuain *et al.*, 2006).

In single-input-single-output (SISO) cases of polymer quality control in CSTR, the average molecular weight, M_n or M_w, is generally used as the only controlled variable. However, in multi-input-multi-output (MIMO) cases, in addition to the average molecular weight or substitute parameter (*e.g.* melt index or viscosity), other related variables, such as monomer conversion, polymer density and production rate, are used as controlled variables depending on the process requirement (Ahn *et al.*, 1999; Park and Rhee, 2001; BenAmor *et al.*, 2004). Prasad *et al.* (2002) focused on the free radical styrene polymerization in a jacket CSTR. The manipulated inputs were the coolant, initiator, monomer, and solvent flow rates. The controlled variables were the reactor temperature, the zeroth moment of the polymer distribution λ_0 (*i.e.*, polymer concentration), M_n and *PDI*, since the choice of these parameters reflects the desire to control polymer product quality.

The optimization studies of operating conditions in a pilot-plant jacket CSTR were discussed in **Chapter 3**. Based on the case studies of free radical styrene polymerization and free radical MMA polymerization, the objective functions for determining operating point to produce a polymer with the best match to a target MWD profile are investigated. The optimization results of objective function J_1 in view of finite weight fraction stopped near a curve that passes through a predefined optimal point instead of the target point for both cases. Objective function J_2 was formulated on basis of two MWD parameters M_n and *PDI*. In the case of styrene polymerization, the optimization searches of J_2 converged on the optimal point. On the other hand, in the case of free radical MMA polymerization, the optimal point cannot be obtained by minimizing J_2. In this case, an additional constraint such as polymer concentration is needed to determine an optimal solution.

In this Chapter, we seek to promote the investigation of the problem of determining an operating condition for producing polymers with a specified set of MWD-related parameters, M_n and *PDI*. In view of the mathematical model of typical free radical polymerization processes in CSTR, we seek to reveal mathematically the correlation between operating conditions and MWD specifications for several types of free radical polymerization processes. Three cases are studied to illustrate the mathematical analysis results: free radical styrene polymerization and two types of free radical methyl methacrylate (MMA) polymerization.

4.2 Determination of Operating Conditions for typical free radical polymerization processes

Based on the mathematical model of typical free radical polymerizations, we seek to determine an operating condition for producing polymers with a specified set of MWD related parameters, M_n and *PDI*. It is well known that the reactant concentrations and reactor temperature have great impact on the product MWD. The reactor temperature T and the monomer feed ratio α, which effects on the reactant concentrations, are selected as the manipulated variables to compose the operating condition space. The monomer feed ratio is defined as

$$\alpha = \frac{F_\mathrm{m}}{F_\mathrm{m} + F_\mathrm{i}} \tag{4.1}$$

The free radical polymerization principally includes elementary reactions of initiation, propagation, transfer to monomer, transfer to solvent, termination by combination and termination by disproportination. For most particular polymerization processes, usually only part of these transfer or termination reactions occurs depending on combination of monomer, initiator, solvent and operating condition. In view of the mathematical model of typical free radical polymerization processes in CSTR, we seek to reveal mathematically the relevance of operating conditions to MWD specification for several types of free radical polymerization processes. Four types of typical free radical polymerization processes are shown in **Table 4.1**.

Table 4.1 Free radical polymerization types

Elementary reaction	general	type 1	type 2	type 3
Initiation	○	○	○	○
Propagation	○	○	○	○
Transfer to monomer	○	○	○	○
Transfer to solvent	○	×	×	○
Termination by combination	○	○	○	×
Termination by disproportination	○	○	×	○

○ Elementary reaction occurs

× Elementary reaction does not occur

4.2.1 General free radical polymerization

The free radical polymerization general includes elementary reactions as initiation, propagation, transfer to monomer, transfer to solvent, and termination by combination and by disproportination. The mathematical model of a general free radical polymerization is proposed in Chapter 2. Substituting the expression of first three moments of live and dead polymer (*i.e.* Eqs. (2.32)-(2.37)) into Eqs. (2.23), the following equations are derived for the calculation of M_n, M_w and *PDI*:

$$M_\mathrm{n} = M_\mathrm{m}\frac{Z_1}{Z_0} = M_\mathrm{m}\cdot\left(\frac{U_1}{U_0}+\frac{U_1\cdot K_\mathrm{tc}/2}{K_\mathrm{trm}M+K_\mathrm{trs}S+K_\mathrm{td}U_0+K_\mathrm{tc}U_0/2}\right) \tag{4.2}$$

$$M_\mathrm{w} = M_\mathrm{m}\frac{Z_2}{Z_1} = M_\mathrm{m}\cdot\left(\frac{U_2}{U_1}+\frac{K_\mathrm{tc}\cdot U_1}{K_\mathrm{trm}M+K_\mathrm{trs}S+K_\mathrm{td}U_0+K_\mathrm{tc}U_0}\right) \tag{4.3}$$

$$PDI = M_\mathrm{w}/M_\mathrm{n} = \frac{Z_0 Z_2}{Z_1^2} = \frac{\dfrac{U_2}{U_1}+\dfrac{K_\mathrm{tc}U_1}{K_\mathrm{trm}M+K_\mathrm{trs}S+K_\mathrm{td}U_0+K_\mathrm{tc}U_0}}{\dfrac{U_1}{U_0}+\dfrac{K_\mathrm{tc}U_1/2}{K_\mathrm{trm}M+K_\mathrm{trs}S+K_\mathrm{td}U_0+K_\mathrm{tc}U_0/2}} \tag{4.4}$$

Substituting boundary conditions of the jacket CSTR in **Figure 2.1** and operating condition of *α* and *T* into the steady-state equations, the following set of nonlinear algebraic equations is derived:

$$
\begin{aligned}
&M_{\mathrm{n}} = M_{\mathrm{m}} \cdot \left(\frac{U_1}{U_0} + \frac{U_1 K_{\mathrm{tc}}/2}{K_{\mathrm{trm}}M + K_{\mathrm{trs}}S + K_{\mathrm{td}}U_0 + K_{\mathrm{tc}}U_0/2}\right) \\
&PDI = \frac{\dfrac{U_2}{U_1} + \dfrac{K_{\mathrm{tc}}U_1}{K_{\mathrm{trm}}M + K_{\mathrm{trs}}S + K_{\mathrm{td}}U_0 + K_{\mathrm{tc}}U_0}}{\dfrac{U_1}{U_0} + \dfrac{K_{\mathrm{tc}}U_1/2}{K_{\mathrm{trm}}M + K_{\mathrm{trs}}S + K_{\mathrm{td}}U_0 + K_{\mathrm{tc}}U_0/2}} \\
&2K_{\mathrm{i}}I - (K_{\mathrm{tc}} + K_{\mathrm{td}})U_0^2 - U_0/\theta = 0 \\
&U_1 = \frac{2K_{\mathrm{i}}I + (K_{\mathrm{p}}M + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S)U_0}{1/\theta + K_{\mathrm{tc}}U_0 + K_{\mathrm{td}}U_0 + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S} \\
&U_2 = \frac{2K_{\mathrm{i}}I + (K_{\mathrm{p}}M + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S)U_0 + 2K_{\mathrm{p}}MU_1}{1/\theta + K_{\mathrm{tc}}U_0 + K_{\mathrm{td}}U_0 + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S} \\
&(I^0 - I)/\theta - K_{\mathrm{d}}I = 0 \\
&(M^0 - M)/\theta - 2K_{\mathrm{i}}I - (K_{\mathrm{p}} + K_{\mathrm{trm}})MU_0 = 0 \\
&(S^0 - S)/\theta - K_{\mathrm{trs}}SU_0 = 0 \\
&I^0 = I^{00}(1-\alpha) \\
&M^0 = M^{00} \cdot \alpha \\
&S^0 = S_{\mathrm{m}}^{00} \cdot \alpha + S_{\mathrm{i}}^{00}(1-\alpha) \\
&\theta = \alpha \cdot V / F_{\mathrm{m}}
\end{aligned}
\tag{4.5}
$$

Equations (4.5) describe the steady-state relationship between two polymer MWD parameters and operating conditions of *α* and *T*. It should be noted that all of the reaction rate coefficients, K_{d}, K_{i}, K_{p}, K_{trm}, K_{trs}, K_{tc} and K_{td} are assumed to satisfy the Arrhenius equation, *i.e.* these coefficients are functions of reactor temperature *T*. There are 14 variables in this set of equations, *i.e.* M_n, PDI, U_0, U_1, U_2, I, M, S, I^0, M^0, S^0, θ, α and T. The quality of product polymer is determined by solving this set of equations for M_n and PDI, when the manipulated variables α and T are given. Inversely, the problem of obtaining the product with the MWD for which M_n and PDI are specified is to solve Eqs. (4.5) for α and T. In general, one operating point is obtained by solving Eqs. (4.5) for α and T.

4.2.2 Type 1: free radical polymerization without transfer to solvent reaction

Since the chain transfer reaction to solvent may not arise in some free radical polymerization, we consider a free radical polymerization without transfer to solvent reaction as type 1 to investigate the effect of transfer to solvent reaction on the convergence characteristic of the operating condition problem. When the transfer to solvent reaction is not included in the elementary reactions of free radical polymerization, *i.e.* the reaction rate coefficient K_{trs} is 0, the nonlinear Eqs. (4.5) for the calculation of M_n and PDI are converted as follows:

$$M_{\mathrm{n}} = M_{\mathrm{m}} \cdot \left(\frac{U_1}{U_0} + \frac{U_1 K_{\mathrm{tc}}/2}{K_{\mathrm{trm}} M + K_{\mathrm{td}} U_0 + K_{\mathrm{tc}} U_0 / 2}\right)$$

$$PDI = \frac{\dfrac{U_2}{U_1} + \dfrac{K_{\mathrm{tc}} U_1}{K_{\mathrm{trm}} M + K_{\mathrm{td}} U_0 + K_{\mathrm{tc}} U_0}}{\dfrac{U_1}{U_0} + \dfrac{K_{\mathrm{tc}} U_1 / 2}{K_{\mathrm{trm}} M + K_{\mathrm{td}} U_0 + K_{\mathrm{tc}} U_0 / 2}}$$

$$2K_{\mathrm{i}} I - (K_{\mathrm{tc}} + K_{\mathrm{td}}) U_0^2 - U_0 / \theta = 0$$

$$U_1 = \frac{2K_{\mathrm{i}} I + (K_{\mathrm{p}} M + K_{\mathrm{trm}} M) U_0}{1/\theta + K_{\mathrm{tc}} U_0 + K_{\mathrm{td}} U_0 + K_{\mathrm{trm}} M}$$

$$U_2 = \frac{2K_{\mathrm{i}} I + (K_{\mathrm{p}} M + K_{\mathrm{trm}} M) U_0 + 2K_{\mathrm{p}} M U_1}{1/\theta + K_{\mathrm{tc}} U_0 + K_{\mathrm{td}} U_0 + K_{\mathrm{trm}} M} \qquad (4.6)$$

$$(I^0 - I)/\theta - K_d I = 0$$

$$(M^0 - M)/\theta - 2K_i I - (K_p + K_{trm}) M U_0 = 0$$

$$I^0 = I^{00}(1-\alpha)$$

$$M^0 = M^{00} \cdot \alpha$$

$$\theta = \alpha \cdot V / F_m$$

In the absence of transfer to solvent reaction, the solvent concentration is irrelevant to polymer MWD, and thus the solvent concentration and the corresponding equations are removed from the nonlinear algebraic equations. There are 12 variables and 10 equations in Eqs. (4.6), *i.e.* M_n, *PDI,* U_0, U_1, U_2, I, M, I^0, M^0, θ, α and T. If M_n and *PDI* are specified simultaneously, one operating point (α and T) is obtained by solving Eqs. (4.6) for α and T. Therefore, the absence of transfer to solvent reaction does not essentially change the convergence relationship of operating conditions and specified set of M_n and *PDI*.

4.2.3 Type 2: free radical polymerization without transfer to solvent and termination by disproportination reaction

Two principal ways that termination may occur in free radical polymerization are radical combination and disproportionation. Whether termination occurs by combination or by disproportionation depends in large measure on monomer structure or, more exactly, on the structure of the chain-end radical. Polystyryl radicals undergo combination almost exclusively at low temperatures, whereas poly(methyl methacrylate) radicals mainly undergo disproportionation; However, in general, both processes occur (Stevens, 1999).

In some styryl-polymerizations, neither transfer to solvent nor termination by disproportination reaction occurs. By setting both the reaction rate coefficients K_{trs} and

K_{td} in Eqs. (4.5) to 0, the nonlinear algebraic equation set is derived for the calculation of M_{n} and *PDI* for free radical polymerization of type 2, in which neither transfer to solvent nor termination by disproportination reaction is included in the elementary reactions. The equation set is omitted here, as it is similar to Eqs. (4.5).

There are 12 variables and 10 equations in the nonlinear algebraic equation set of this polymerization type, i.e. M_{n}, *PDI*, U_0, U_1, U_2, I, M, I^0, M^0, θ, α and T. When M_{n} and *PDI* are specified simultaneously, one operating point is obtained by solving the equation set for α and T, as that in general free radical polymerization and type 1. Although the equation set is simplified by removing K_{td} and K_{trs}, hardly essential deviation arises in the convergence relationship of operating conditions and specified set of M_{n} and *PDI* in the absence of termination by disproportination reaction.

4.2.4 Type 3: free radical polymerization without termination by combination reaction

Termination reaction occurs mainly by disproportionation than by combination in certain free radical polymerization, such as MMA polymerization. When the termination by combination reaction does not occur, *i.e.* the rate coefficient K_{tc} is 0, and thus the Eqs. (4.2)–(4.4) for calculating M_{n}, M_{w} and *PDI* are converted to the following formulations:

$$M_{\mathrm{n}} = M_{\mathrm{m}} Z_1 / Z_0 = M_{\mathrm{m}} U_1 / U_0 \tag{4.7}$$

$$M_{\mathrm{w}} = M_{\mathrm{m}} Z_2 / Z_1 = M_{\mathrm{m}} U_2 / U_1 \tag{4.8}$$

$$PDI = \frac{Z_2 Z_0}{Z_1^2} = \frac{U_2 U_0}{U_1^2} \tag{4.9}$$

Equations (2.32)-(2.34), *i.e.* equations for calculation of the first three moments of live polymers, are simplified as follows:

$$-U_0/\theta - K_{\mathrm{td}}U_0^2 + 2K_{\mathrm{i}}I = 0 \tag{4.10}$$

$$\begin{aligned} U_1 &= \frac{2K_{\mathrm{i}}I + (K_{\mathrm{p}}M + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S)U_0}{1/\theta + K_{\mathrm{td}}U_0 + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S} \\ &= (1 + \frac{K_{\mathrm{p}}M}{1/\theta + K_{\mathrm{td}}U_0 + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S})U_0 = (1 + \frac{1}{\varphi - 1})U_0 \end{aligned} \tag{4.11}$$

$$\begin{aligned} U_2 &= \frac{2K_{\mathrm{i}}I + (K_{\mathrm{p}}M + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S)U_0}{1/\theta + K_{\mathrm{td}}U_0 + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S} + \frac{2K_{\mathrm{p}}MU_1}{1/\theta + K_{\mathrm{td}}U_0 + K_{\mathrm{trm}}M + K_{\mathrm{trs}}S} \\ &= U_1 + \frac{2}{\varphi - 1}U_1 \end{aligned} \tag{4.12}$$

where, $\varphi = 1 + \frac{K_{\mathrm{trm}}}{K_{\mathrm{p}}} + \frac{K_{\mathrm{trs}}S}{K_{\mathrm{p}}M} + \frac{K_{\mathrm{td}}R}{K_{\mathrm{p}}M} + \frac{1}{K_{\mathrm{p}}M\theta}$ (4.13)

Thus, for free radical polymerization without termination by combination, the MWD parameters can be calculated by using the following reduced formulations:

$$M_{\mathrm{n}} = (1 + \frac{1}{\varphi - 1})M_{\mathrm{m}} \tag{4.14}$$

$$M_{\mathrm{w}} = (1 + \frac{2}{\varphi - 1})M_{\mathrm{m}} \tag{4.15}$$

$$PDI = M_{\mathrm{w}}/M_{\mathrm{n}} = 1 + \frac{1}{\varphi} \tag{4.16}$$

It is worth noting that φ is a function of the reactant concentrations (M, S, R) and the reaction rate coefficients. The latter depends on the reactor temperature. From the equations above, it is obvious that the three MWD parameters, M_{n}, M_{w} and PDI, are interdependent. The values of three MWD parameters can be determined, when φ is given. On the other hand, when termination by combination reaction is not included in the elementary reactions of free radical polymerization, the equation set for the calculation of M_{n} and PDI is then derived as follows:

$$
\begin{aligned}
&M_{\mathrm{n}} = (1+\frac{1}{\varphi-1})M_{\mathrm{m}} \\
&PDI = 1+\frac{1}{\varphi} \\
&\varphi = 1+\frac{K_{\mathrm{trm}}}{K_{\mathrm{p}}}+\frac{K_{\mathrm{trs}}S}{K_{\mathrm{p}}M}+\frac{K_{\mathrm{td}}R}{K_{\mathrm{p}}M}+\frac{1}{K_{\mathrm{p}}M\theta} \\
&-R/\theta+2K_{\mathrm{i}}I-K_{\mathrm{td}}R^2 = 0 \\
&(I^0-I)/\theta-K_{\mathrm{d}}I = 0 \\
&(M^0-M)/\theta-2K_{\mathrm{i}}I-(K_{\mathrm{p}}+K_{\mathrm{trm}})MR = 0 \qquad (4.17) \\
&(S^0-S)/\theta-K_{\mathrm{trs}}SR = 0 \\
&I^0 = I^{00}(1-\alpha) \\
&M^0 = M^{00}\cdot\alpha \\
&S^0 = S_{\mathrm{m}}^{00}\cdot\alpha+S_{\mathrm{i}}^{00}(1-\alpha) \\
&\theta = \alpha\cdot V/F_{\mathrm{m}}
\end{aligned}
$$

There are 13 variables in this set of Eqs. (4.17), i.e. M_{n}, PDI, φ, I, M, R, S, I^0, M^0, S^0, θ, α and T. As the general free radical polymerization, therefore, when both M_{n} and PDI are specified for the free radical polymerization without termination by combination reaction, the operating point should be determined with respect to the two dimensional space of α and T. However, since M_{n} and PDI are interdependent, an operating point cannot be determined by the simultaneous specification of M_{n} and PDI. Another polymer quality-related or performance-related parameter instead of PDI should be specified to determine an operating point.

4.3 Case studies

In order to demonstrate the mathematical analysis in section 4.2, three typical free radical polymerization processes corresponding to three polymerization types are studied in this section. Case 1 deals with free radical MMA polymerization process corresponding to type 1, in which termination reactions occur both by combination and by disproportionation, but in which transfer to solvent reaction does not occur. Case 2 deals with free radical styrene polymerization corresponding to type 2, in which termination reaction occurs only by combination. Case 3 deals with MMA polymerization using different initiator and solvent from case 1, in which termination reaction occurs only by disproportionation. The model parameters of case 1 are shown in **Table 4.2** (Daoutidis *et al.*, 1990). The model parameters of case 2 and 3 are shown in Table 3.1 and Table 3.5 respectively.

Table 4.2 Model Parameters of case 1

Monomer	methyl methacrylate
Initiator	Azobisisobutyronitrile (AIBN)
Solvent	toluene
M_m [g/mol]	104.15
K_d [L·mol/min]	$6.32\times10^{16}\exp(-29975/1.987T)$
K_i [L·mol/min]	$0.58K_\mathrm{d}$
K_p [L·mol/min]	$2.95\times10^{7}\exp(-4367/1.987T)$
K_trm [L·mol/min]	$1.74\times10^{13}\exp(-17957/1.987T)$
K_trs [L·mol/min]	0
K_tc [L·mol/min]	$6.37\times10^{8}\exp(-703/1.987T)$
K_td [L·mol/min]	$5.24\times10^{9}\exp(-703/1.987T)$
M^{00} [mol/L]	4.694
I^{00} [mol/L]	0.025
S_m^{00} [mol/L]	4.704
S_i^{00} [mol/L]	9.40
F_m [L/min]	0.02
V [L]	3.927

4.3.1 Case 1: Free radical MMA polymerization

We first consider determination of operating condition for a free radical MMA polymerization in the jacket CSTR to demonstrate the mathematical analysis of type 1 in section 4.2.2. Azobisisobutyronitrile (AIBN) and toluene are used as the initiator and solvent respectively. The physical properties and kinetic parameters are referred from the literature and listed in Table 4.2 (Daoutidis *et al.*, 1990). The elementary reactions include initiation, propagation, transfer to monomer, termination by combination and by disproportionation. Compared with the general free radical polymerization, transfer to solvent reaction is not included in the elementary reactions.

According to mathematical analysis in section 4.2.2, for the free radical MMA polymerization, in which transfer to solvent reaction is absent, and in which termination reaction occurs both by combination and by disproportionation, when both M_n and *PDI* are specified, one operating point can be calculated by solving Eqs. (4.6). For example, when the MWD parameters are specified as $M_\mathrm{n} = 30000$ and $PDI = 1.994$, the operating point obtained by solving the algebraic equations is $\alpha = 0.622$, $T = 337\mathrm{K}$.

The operating points that satisfy the desired value of M_n form a contour of constant M_n in the space of operating conditions. Similarly, the operating points that satisfy the desired value of *PDI* form a contour of constant *PDI*. When only M_n or *PDI* is specified, there are many possible values of α and T exist, that correspond to M_n or *PDI* contour. **Figure 4.1** illustrates several M_n and *PDI* contours for case 1. When both M_n and *PDI* are specified, an operating condition is determined by the intersection of two contours. According to Figure 4.1, there is one point at which $M_\mathrm{n} = 30000$ and $PDI = 1.994$.

In the free radical MMA polymerization, the termination reaction occurs mainly by disproportination, so that the reaction coefficient of termination by combination K_tc is about 1/10 of the reaction coefficient of termination by disproportionation K_td. It can be seen from Figure 4.1 that the contours of M_n and *PDI* intersect in the feasible operating condition space. The contours of constant M_n extend upward to higher temperature T and increasing monomer feed ratio α. The contours of constant *PDI* appear as much as M_n contours do.

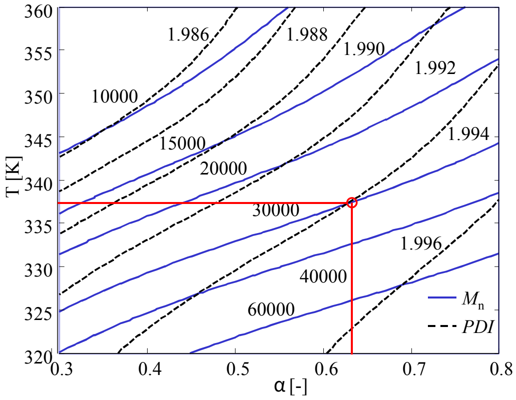

Fig. 4.1. Contours of M_n and *PDI* of case 1

4.3.2 Case 2: free radical styrene polymerization

The free radical styrene polymerization is considered in this section to demonstrate mathematical analysis result of type 2, *i.e.* free radical polymerization without transfer to solvent and termination by disproportination reaction. Azobisisobutyronitrile and toluene are used as the initiator and solvent respectively. The elementary reactions include initiation, propagation, transfer to monomer and termination by combination. The physical properties and kinetic parameters are taken from the literature and listed in Table 3.1 (Yoo et al., 1999).

According to the mathematical analysis in section 4.2.3, as a typical free radical polymerization in which termination reaction occurs by combination, when both M_n and *PDI* are specified for the free radical styrene polymerization, one operating point can be calculated by solving the nonlinear equations. For example, when M_n and *PDI* are specified as $M_n = 40000$ and $PDI = 1.55$, the operating point obtained by solving the nonlinear equations is $\alpha = 0.534$, $T = 338\text{K}$. Whereas, when only one MWD-related parameter is specified, the operating point cannot be obtained. **Figure 4.2** illustrates M_n and PDI contours of styrene polymerization. When both M_n and PDI are specified, an operating condition is determined by the intersection of two contours, for example the intersection point of two contours $M_n = 40000$ and $PDI = 1.55$.

In the free radical styrene polymerization, termination by disproportionation reaction seldom occurs, *i.e.* K_{td} is 0. Only the termination by combination reaction occurs. It can be seen from Figure 4.2 that contours of constant M_n extend upward to higher temperature T when monomer feed ratio α is increased. The contours of PDI, on the other hand, are nearly vertical to x-axis of α; this means that PDI is increased with a higher T, but not sensitive to the change of α. The contours of M_n and PDI intersect in free radical styrene polymerization, but the angels of two M_n and PDI contours are greater than that of free radical MMA polymerization in case 1, in which the reaction rate coefficient of termination by disproportionation K_{td} is greater than 0.

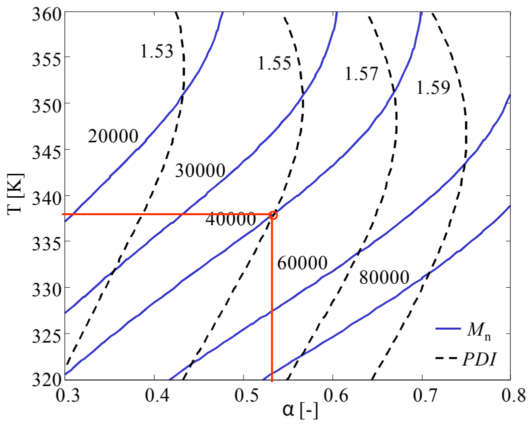

Fig. 4.2 Contours of M_n and PDI of case 2

4.3.3 Case 3: free radical MMA polymerization without termination by combination reaction

In this case, another free radical MMA polymerization process is considered to illustrate the relationship between the specified MWD parameters and operating conditions when termination by combination reaction is not included in the elementary reactions. The physical properties and kinetic parameters are referred from the literature and listed in Table 3.5 (Crowley and Choi, 1997). Vazo 67 (DuPont) and ethyl acetate are used as the initiator and solvent, respectively. The elementary reactions include initiation, propagation, transfer to monomer, transfer to solvent, and termination by disproportionation.

The first attempt is to determine an operating point by solving Eq. (4.17) with specifying M_n and *PDI*. Instead of one operating point, various solutions are obtained. **Figure 4.3** illustrates the contours of M_n, *PDI* and φ. It is shown that the contours of M_n, *PDI* and φ are parallel or overlap each other. Each of the M_n and *PDI* contours corresponds to a value of φ. For example, the contour of $\varphi = 1.003$ matches the contours of $M_\text{n} = 33500$ and $PDI = 1.997$. This is distinct from case 1 and case 2, where the contours of M_n and *PDI* are crossed. Therefore, we cannot obtain an operating point when M_n and *PDI* are specified simultaneously. The simulation result of case 3 coincides with mathematical analysis result of type 3.

From above investigation, we can conclud that the simultaneous specification of M_n and *PDI* cannot determine an operating point for the free radical MMA polymerization without termination by combination reaction. We have one degree of freedom for determining an operating condition. Another parameter must be specified to obtain an operating point, for example, the zeroth moment of dead polymer, Z_0. This is equivalent to specifying the dead polymer concentration and thus the production rate of dead polymer. As another choice, we can specify the monomer conversion as an additional parameter.

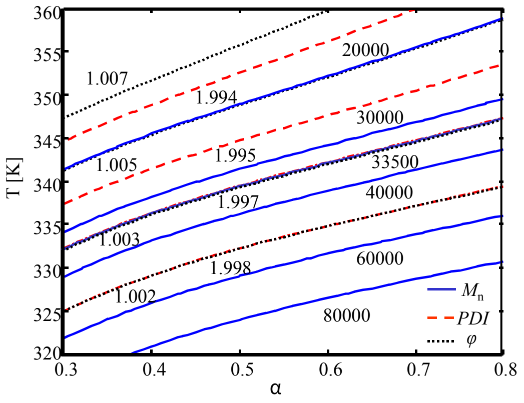

Fig. 4.3 Contours of M_n, *PDI* and φ of case 3

4.4 Discussion

The issue of determining an operating point of CSTR in order to produce a product polymer with the specified MWD was considered in this Chapter. As a substitute for the MWD profile, we used two MWD parameters, M_n and *PDI*. We select the monomer feed ratio α and the reactor temperature T as the manipulated variables. The mathematical model for the general free radical polymerization in the CSTR represents the relationship between the operation conditions and the product quality. We can basically determine an operating condition when the product quality, *i.e.* both M_n and *PDI* are specified.

In view of transfer and termination reactions, three typical types of free radical polymerization are presented to illustrate the relationship between operating conditions and MWD specification. By analyzing the mathematical model of three types, we concluded that the absence of transfer to solvent reaction and termination by disproportination hardly affect the relationship between operating conditions and MWD specification. When the termination by combination reaction occurs, an operating point can be determined by specifying two MWD parameters, M_n and *PDI*. Whereas, when the termination reaction by combination does not occur, an operating point cannot be determined by the simultaneous specification of M_n and *PDI*, since the two parameters are interdependent and related by a polymerization factor φ. We have one degree of freedom for determining an operating condition. Another parameter must be specified to obtain an operating point.

Three cases were studied to demonstrate the mathematical analysis results. In the case of free radical MMA polymerization and the case of free radical styrene polymerization, when both parameters of M_n and *PDI* are specified at the desired values, an operating condition is determined. However, in the case of a free radical MMA polymerization without termination by combination reaction, an operating point cannot be determined by specifying M_n and *PDI* due to overlapping of M_n and *PDI* contours. The mathematical analysis of these three cases of typical free radical polymerization was demonstrated by simulation results.

The relationship between M_n and *PDI* contours in terms of termination by combination reaction rate coefficient were also considered in this work. The M_n contours are similar for all of three cases, but *PDI* contours are different. In case 2, in which the role of termination by combination is the most significant, the *PDI* contours are nearly vertical to x-axis of α, and the angels between M_n and *PDI* contours are the greatest. In case 3, in which K_{tc} is 0, the M_n and *PDI* contours overlap each other. In case 1, in which K_{tc} is about 1/10 of K_{td}, M_n and *PDI* contours intersect, the angles are smaller than that in case 1. As the role of termination by combination reaction gets weaker, therefore, the angles become smaller, until it becomes 0 where K_{tc} is 0.

Chapter 5

Optimal Grade Transition in Continuous Free Radical Polymerization Reactor

5.1 Introduction

Grade transition operation is essential in continuous polymerization plants because many grades of polymers are produced from the same process. The flexible operation of the polymerization plants depends not only on the steady-state operation, but also on the effective grade transition. From the economical point of view, it is important to reduce the amount of the off-specification polymer during the grade transition operation as well as shorten the transition time for the operation of continuous polymerization reactor.

There have been many research works about optimal grade transition operation and control of continuous polymer processes (Chatzidoukas *et al.*, 2003; Padhiyar *et al.*, 2006; Kadam *et al.*, 2007; Prata *et al.*, 2008). Lee *et al.* (1999) proposed a modified differential evolution (MDE) algorithm for the dynamic optimization problem of a continuous methyl methacrylate-vinyl acetate (MMA-VA) copolymerization reactor. The object was to determine the optimal trajectories of control input that minimize the transition time. Controlled variables were the M_w and the monomer composition of VA in dead polymer. A nonlinear control system integrating an off-line optimizer and a nonlinear MPC controller was developed to perform optimal grade transition operation at the industrial polyolefin reactors. The optimal trajectories of both output and input were calculated off-line using the control vector parameterization method with the nonlinear first principles models. The derived optimal input sequence was used as a feedforward signal during the grade transition control (Wang *et al.*, 2000).

Some research works consider the grade transition problem from other views. Yi *et al.* (2003) developed the grade transition strategy for an industrial slurry-phase high-density polyethylene plant in a plantwide viewpoint. In addition to the reactors, the models of downstream processes were also included in the optimization problem. The polymer slurry melt index from reactors and polymer pellet melt index from the pelletizer were used as the properties for grade specification. Asteasuain *et al.* (2006) applied a mixed-integer dynamic optimization approach to the simultaneous design and control of a continuous styrene polymerization process. The steady-state operation and grade transition policies have been determined so as to minimize capital and steady-state operating costs, as well as off-specification product during grade transition. The polymer M_n was used as the only grade specification. BenAmor *et al.* (2004) applied NLMPC algorithm to the polymer grade transition control using an industrial real-time optimization package. Two simulated polymerization cases were studied. In the continuous methyl methacrylate (MMA) process, the M_n was controlled by manipulating flow rate of initiator. In the second case of a gas-phase polyethylene reactor, the NLMPC regulated melt index, density, reactor pressure, and production rate by manipulating the flow rates of nitrogen, hydrogen, comonomer and catalyst.

In this Chapter, a sequential approach is presented to implement optimal polymer production in CSTR. As an important component of the optimal polymer production system, we consider the optimal grade transition problem for a continuous free radical styrene polymerization process. The off-line dynamic optimization is carried out to generate the optimal transition trajectories for input variables in the presence of constraints on input, output and state variables.

5.2 Dynamic optimization approach

In order to implement the optimal grade transition, a dynamic optimization problem should be formulated. The major goal of the optimization task is to determine the best trajectory for input variables from initial steady states to a new grade by minimizing a certain objective function. A general formulation of the optimal grade transition problem is described as follows:

$$\min_{u(t),t_f} J(x(t),t_f) \tag{5.1}$$

$$s.t. \quad \dot{x}(t) = f(x(t),u(t)), \quad x(t_0) = x_0 \tag{5.2}$$

$$y(t) = g(x(t),u(t)) \tag{5.3}$$

$$u^{\min} \le u(t) \le u^{\max} \tag{5.4}$$

$$y^{\min} \le y(t) \le y^{\max} \tag{5.5}$$

$$x^{\min} \le x(t) \le x^{\max} \tag{5.6}$$

where $x(t)$ denotes the vector of state variables with the initial conditions x_0 at the initial moment t_0. $u(t)$ and $y(t)$ denote the vector of input and output variables respectively. Eqs. (5.2) and (5.3) represent the process model and polymer properties model, which are given in the form of differential and algebraic equations. Eqs. (5.4), (5.5) and (5.6) denote the lower and upper bounds on the input, output and state variables, respectively.

A standard mathematical solver for optimization in gPROMS$^{\text{TM}}$, CVP_MS, is used to solve the dynamic optimization problem. The dynamic optimization problem is converted to a standard nonlinear program (NLP) using control vector parameterization (CVP) and then it is solved by a gradient-based optimization method named sequential quadratic programming (SQP). Each input profile is parameterized as a piecewise-constant function. The CVP_MS implements a “multiple-shooting” dynamic optimization algorithm with the following steps:

1) The optimizer chooses the duration of each control interval, the values of the control variables over it, and, additionally, the values of the differential variables $x(t)$ at the start of each control interval other than the first one;

2) For each control interval, starting from the initial point that is either known (for the first interval) or is chosen by the optimizer (for all subsequent intervals), the dynamic system model is solved over this control interval to determine the time-variation of all variables $x(t)$ in the system;

3) The above information is used to determine the values of: the objective function to be optimized, any constraints that have to be satisfied by the optimization, the discrepancies between the computed values of the variables $x(t)$ at the end of each interval and the corresponding values chosen by the optimizer at the start of the next interval;

4) Based on the above, the optimizer revises the choices it made at the first step, and repeats the above procedure until it obtains a point that optimizes the objective function, satisfies all constraints and ensures that all differential variables $x(t)$ are continuous at the control interval boundaries.

5.3 Grade transition in continuous free radical polymerization reactor

5.3.1 Process description

In this section, we consider the optimal polymer production problem for the free radical polymerization in a pilot-plant CSTR. **Figure 5.1** shows a scheme of optimal polymer production system for CSTR. The reactor feed streams is composed of the monomer and initiator streams, and these feed streams are well mixed with the solvent before being fed into the reactor. The cooling water is used to remove the heat generated by the polymerization.

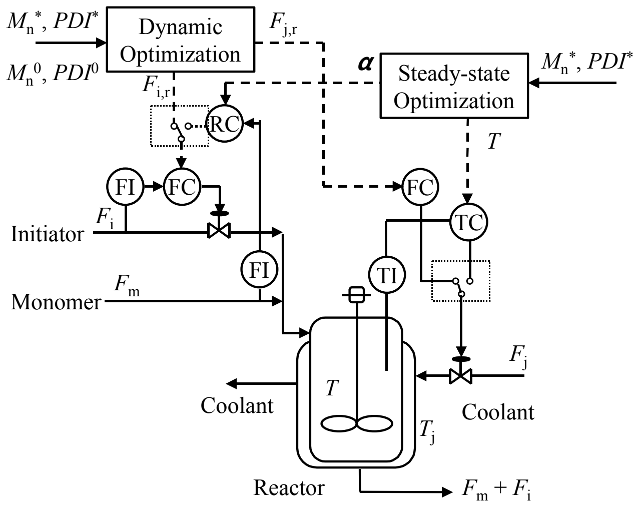

Fig. 5.1 Scheme of optimal polymer production system for CSTR

When the quality specification is determined for a demanded polymer grade, a sequential approach is adapted to implement the optimal polymer production in CSTR with following steps:

1) The target operating condition is determined by off-line optimization on basis of the steady-state mathematical model. The objective function is formulated to satisfy the polymer quality specifications.

2) The optimal transition trajectories of input variables are determined by off-line dynamic optimization system using the mathematical model in the presence of constraints on input, output and state variables. With the calculated optimal trajectories of manipulated variables used as the set point signals, the feedforward controllers drive the polymerization process from the steady state of original grade to a new steady state that satisfies the target grade specifications.

3) When both input and output variables satisfy the target requirements for operating condition and polymer quality specification, the grade transition operation is completed. The feedback control system is then used in the online implementation of routine

operation to account for model errors as well as immeasurable disturbances.

In this Chapter, we focus solely on the grade transition of the optimal polymer production system where optimal transition trajectories are generated using off-line optimization. The polymer grade specification is defined as number-average molecular weight M_n and polydispersity index *PDI*, which must be satisfied at both steady states. The operating condition specification is defined as the monomer feed ratio α and the reactor temperature T. The flow rate of initiator and coolant, F_i and F_j, are selected as manipulated variables for the dynamic optimization.

5.3.2 Dynamic model of free radical polymerization process

A mathematical model is developed to simulate the free radical polymerization in CSTR. The elementary reactions include initiation, propagation, transfer to monomer, transfer to solvent, and termination by combination and by disproportionation. It is assumed that the flow rate of the inlet is the same as that of the product stream, *i.e.* $F = F_\text{i} + F_\text{m}$, and the total volume of all reactants in the reactor is constant. The reactor temperature T and the monomer feed ratio α, which effects on the reactant concentrations, are used to compose the operating condition specification of each steady state. The monomer feed ratio is defined as

$$\alpha = \frac{F_\text{m}}{F_\text{m} + F_\text{i}} \tag{5.7}$$

The following mass balance equations are derived to describe the concentrations of the reaction species:

$$\frac{dI}{dt} = (I^0 - I)/\theta - K_\text{d} I \tag{5.8}$$

$$\frac{dM}{dt} = (M^0 - M)/\theta - 2K_\text{i} I - (K_\text{p} + K_\text{trm}) MR \tag{5.9}$$

$$\frac{dS}{dt} = (S^0 - S)/\theta - K_{\mathrm{trs}} SR \tag{5.10}$$

$$\frac{dR}{dt} = -R/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{t}} R^2 \tag{5.11}$$

$$\frac{dP}{dt} = -P/\theta + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)R + (\frac{K_{\mathrm{tc}}}{2} + K_{\mathrm{td}})R^2 \tag{5.12}$$

where, $\theta = V/F$ is the average residential time of the reactant in the CSTR. The temperature dependence of the rate constants is assumed to satisfy the Arrhenius equations. The temperatures of reactor and jacket are described using following energy balance equations:

$$\frac{dT}{dt} = \frac{F}{V}(T_{\mathrm{f}} - T) + \frac{-\Delta H_{\mathrm{r}}}{\rho C\mathrm{p}} K_{\mathrm{p}} M U_0 - \frac{U_{\mathrm{r}} A_{\mathrm{r}}}{\rho C\mathrm{p} V}(T - T_{\mathrm{j}}) \tag{5.13}$$

$$\frac{dT_{\mathrm{j}}}{dt} = \frac{F_{\mathrm{j}}}{V_{\mathrm{j}}}(T_{\mathrm{jf}} - T_{\mathrm{j}}) + \frac{U_{\mathrm{r}} A_{\mathrm{r}}}{\rho_{\mathrm{j}} C\mathrm{p}_{\mathrm{j}} V_{\mathrm{j}}}(T - T_{\mathrm{j}}) \tag{5.14}$$

The method of moments is adopted to calculate the MWD parameters. The definitions of the moments are as follows:

$$U_m = \sum_{j=1}^{+\infty} j^m R_j \quad \text{and} \quad Z_m = \sum_{j=2}^{+\infty} j^m P_j, m = 0,1,2,\cdots \tag{5.15}$$

where, U_m and Z_m are the mth moments of live and dead polymer concentrations, respectively. One can derive balance equations for the first three moments of the live and dead polymer concentrations as follows:

$$\frac{dU_0}{dt} = -U_0/\theta + 2K_{\mathrm{i}} I - K_{\mathrm{t}} U_0^2 \tag{5.16}$$

$$\frac{dU_1}{dt} = -U_1/\theta + 2K_{\mathrm{i}} I + K_{\mathrm{p}} U_0 M - K_{\mathrm{t}} U_0 U_1 + (K_{\mathrm{trm}} M + K_{\mathrm{trs}} S)(U_0 - U_1) \tag{5.17}$$

$$\frac{dU_2}{dt} = -U_2/\theta + 2K_\mathrm{i}I + K_\mathrm{p}M(2U_1 + U_0) - K_\mathrm{t}U_0U_2 + (K_\mathrm{trm}M + K_\mathrm{trs}S)(U_0 - U_2) \quad (5.18)$$

$$\frac{dZ_0}{dt} = -Z_0/\theta + (K_\mathrm{trm}M + K_\mathrm{trs}S + K_\mathrm{td}U_0)U_0 + \frac{K_\mathrm{tc}}{2}U_0^2 \quad (5.19)$$

$$\frac{dZ_1}{dt} = -Z_1/\theta + (K_\mathrm{trm}M + K_\mathrm{trs}S + K_\mathrm{td}U_0)U_1 + K_\mathrm{tc}U_0U_1 \quad (5.20)$$

$$\frac{dZ_2}{dt} = -Z_2/\theta + (K_\mathrm{trm}M + K_\mathrm{trs}S + K_\mathrm{td}U_0)U_2 + K_\mathrm{tc}(U_0U_2 + U_1^2) \quad (5.21)$$

The average molecular weight and polydispersity index are calculated using the first three moments of dead polymer as follows:

$$M_\mathrm{n} = M_\mathrm{m}Z_1/Z_0,\ M_\mathrm{w} = M_\mathrm{m}Z_2/Z_1, \text{and } PDI = M_\mathrm{w}/M_\mathrm{n} = \frac{Z_0Z_2}{Z_1^2} \quad (5.22)$$

5.3.3 Objective function and constraints

In the optimal polymer production system, the off-line optimization yields the optimal steady-state operating conditions in terms of polymer quality specifications. The grade transition will be optimized to minimize operating cost during transition time.

Two objective functions are formulated to determine the optimal transition trajectory of the manipulated variables. The objective function J_1 aims to minimize the transition time, and is described as follows:

$$J_1 = t_\mathrm{f} \quad (5.23)$$

where t_f denotes the final transition time.

The objective function J_2 focuses the cost performance of the polymerization process by minimizing the consumption of initiator during the transition time. Based on the optimum transition time $t_{\mathrm{f},1}$ obtained using J_1, the time horizon of J_2 is fixed for simplifying the optimization problem, *i.e.* $t_{\mathrm{f},2} = kt_{\mathrm{f},1}$, where k>1. The objective function J_2 is then formulated as follows:

$$J_2 = \int_0^{t_{f,2}} F_i(t)dt \tag{5.24}$$

To solve the dynamic optimization problem by gPROMS, a series of constraints should be specified for the optimization solver CVP_MS. The conditions that the system must satisfy at the end of the operation are called end-point constraints. For instance, in the grade transition of a continuous polymerization reactor, we may require: the M_n of product to be a certain prescribed value; and also the monomer conversion to lie within given limits. In the first case, an equality end-point constraint is defined as:

$$\omega(t_f) = \omega^* \tag{5.25}$$

where ω is one of the system variables (x or y). In the second case, we have an inequality end-point constraint:

$$\omega^{\min} \le \omega(t_f) \le \omega^{\max} \tag{5.26}$$

The interior-point constraints hold at one or more distinct time t_I during the time horizon (*e.g.* in the middle of the horizon). These constraints are represented mathematically as:

$$\omega^{\min} \le \omega(t_I) \le \omega^{\max} \tag{5.27}$$

where t_I is a given time. Both interior and end-point constraints are special cases of point constraints.

There are also certain constraints that must be satisfied at all times during the system operation. These are called path constraints and often inequalities of the form:

$$\omega^{\min} \le \omega(t) \le \omega^{\max}, \forall t \in [0, t_f] \tag{5.28}$$

For instance, in the polymerization reactor, the temperature is required to never exceed a certain value so as to avoid some unwanted side-reactions that are not explicitly considered by the mathematical model.

The definition of end-point constraints is important for the dynamic optimization problem. When two MWD parameters, M_n and *PDI*, are specified as the target polymer grade, the target operating conditions of α and T are determined by steady-state optimization as mentioned in section 5.3.1. There are two conditions the process must satisfy at the end of transition operation. First is the operating condition specification that is defined as the monomer feed ratio α and the reactor temperature T. The second is the steady state specification. If the end-point constraints are formulated to meet the requirement for target operating point and rigorous steady state simultaneously, the polymer product will satisfy the MWD specification. Therefore, the α, T and a set of state variables are specified as the end-point constraints.

5.4 Case study for grade transition in free radical styrene polymerization

The free radical styrene polymerization in a pilot-plant CSTR is considered as a case study for the optimal grade transition approach proposed in section 5.3. The continuous solution polymerization reactor is shown in Figure 5.1. Azobisisobutyronitrile and toluene are used as the initiator and the solvent, respectively. The dynamic optimization is carried out using the mathematical model described in section 5.3.2. The physical properties and kinetic parameters are referred from the literatures and listed in **Table 5.1**.

The polymer grade is specified using two polymer MWD parameters, M_n and *PDI*. The α and T are used to specify the operating condition, and defined as output variables as well. The flow rate of initiator and coolant, F_i and F_j, are used as manipulated variable. Substituting boundary conditions of the jacket CSTR in Figure 5.1 into the polymerization process model, the state vector x, the manipulated input vector u and the output vector y are defined respectively as follows:

$$x = [I, M, U_0, U_1, U_2, Z_0, Z_1, Z_2, T_\mathrm{j}, T]^\mathrm{T} \tag{5.29}$$

$$y = [M_\mathrm{n}, PDI, \alpha, T]^\mathrm{T} \tag{5.30}$$

$$u = [F_\mathrm{i}, F_\mathrm{j}]^\mathrm{T} \tag{5.31}$$

Table 5.1 Parameters of dynamic styrene polymerization model

K_d [L·mol·min^{-1}]	$9.48\times10^{16}\exp(-30798.5/1.987T)$ [a]
K_i [L·mol·min^{-1}]	$0.6K_\mathrm{d}$ [a]
K_p [L·mol·min^{-1}]	$6.306\times10^{8}\exp(-7067.8/1.987T)$ [a]
K_trm [L·mol·min^{-1}]	$7.116\times10^{8}\exp(-12671.1/1.987T)$ [a]
K_tc [L·mol·min^{-1}]	$7.5\times10^{10}\exp(-1680/1.987T)$ [a]
M_m [g·mol^{-1}]	100.12
$\rho C\mathrm{p}$ [cal·L^{-1}·K^{-1}]	360.23 [b]
$\rho_\mathrm{j} C\mathrm{p}_\mathrm{j}$ [cal·L^{-1}·K^{-1}]	966.92 [b]
$-\Delta H\mathrm{r}$ [cal·mol^{-1}]	16710.77 [b]
U_r [cal·min^{-1}·K^{-1}·m^{-2}]	2868 [c]
A_r [m^2]	0.11
M^{00} [mol·L^{-1}]	4.8
I^{00} [mol·L^{-1}]	0.0106
F_m [L·min^{-1}]	0.02
T_f [K]	350
T_jf [K]	293.2
V [L]	3.927
V_j [L]	4.318

[a] Yoo *et al.* (1999) [b] Asteasuain *et al.* (2006) [c] Padhiyar *et al.* (2006)

5.4.1 Specifications of process grades and constraints

The polymer grade specification is defined as the number-average molecular weight M_n and polydispersity index *PDI*, which must be satisfied at both the initial and terminal steady states. The initial polymer grade is defined as $M_\mathrm{n} = 26935$, $PDI = 1.555$, and the target grade as $M_\mathrm{n}^* = 35700$ and $PDI^* = 1.566$.

In order to maintain the operating range within the bounds where the model parameters were obtained, upper bound for the reactor temperature is set. In order to exclude low conversion steady states, lower bound for the reactor temperature is selected. The upper limit for the jacket temperature is selected as safe margin with respect to the boiling point of water. Bounds for the initiator and coolant flow rates are also set. These constraints are used as path constraints that must be satisfied during transition operation and at both steady states. The path constraints are summarized in **Table 5.2**.

Table 5.2 Bounds of path constraint for dynamic optimization

Variable	Lower bound	Upper bound
T [K]	340	370
T_j [K]	—	368
F_i [L/min]	0.002	0.05
F_j [L/min]	0.001	0.01

If the target polymer grade is specified, the steady-state operating point of α and T is determined by the steady-state optimization proposed in Chapter 2; for target polymer grade of $M_\mathrm{n} = 35700$ and $PDI = 1.566$, the operating point is $\alpha = 0.645$ and $T = 354\mathrm{K}$. The jacket temperature T_j and coolant flow rate F_j are calculated using the dynamic model. The initial and target specifications for polymer grade and operating condition are shown in **Table 5.3**.

Table 5.3 Initial and target value of polymer grade and operating conditions

Variable	Initial value	Target value
F_i [L/min]	0.015	0.011
F_j [L/min]	0.003	0.00348
α	0.57	0.645
T [K]	360	354
T_j [K]	359	353.35
M_n	26935	35700
PDI	1.555	1.566

Table 5.4 Initial values of state variables

State variable	Initial value
I [mol/L]	0.0015
M [mol/L]	2.2066
U_0 [mol/L]	6.745×10^{-8}
U_1	9.317×10^{-6}
U_2	0.00256
Z_0 [mol/L]	0.00206
Z_1	0.536
Z_2	217.17
T_j [K]	359
T [K]	360

As the first step of the dynamic optimization, the simulation is carried out to access a steady state, which is used as the initial state of the process. The initial state is obtained by fixing F_i and F_j as 0.015 and 0.003 [L/min] respectively. The initial values of state variables are shown in **Table 5.4**.

The end-point constraints are created on the operating condition of α, T and a set of state variables. Based on the mathematical model of free radical styrene polymerization in the CSTR, dynamic optimization was carried out to find the feasible set of the end-point constraints. We first considered the optimization problem with specifying the target α and T as end-point equality constraints and the derivatives of 6 state variables as end-point inequality constraints. Even though the simulation results of M_n and PDI for the optimized input trajectory were close to the target point, the target point could not be reached. It was difficult to solve the optimization problem with the increase of the number of the constraints. Therefore, instead of constraints on all of the state variables, both M_n and PDI are specified as end-point equality constraints. The polymer grade specification, M_n and PDI, and the operating condition specification, α and T, are specified as the end-point equality constraints in the dynamic optimization solver. As a result, the optimization solution reached the target grade. The specifications of end-point equality constraints are shown in **Table 5.5**.

Table 5.5 Specification of end-point equality constraints

Variable	Constraint specification	value
M_n	Endpoint equality	35700
PDI	Endpoint equality	1.566
α	Endpoint equality	0.645
T [K]	Endpoint equality	354

Table 5.6 Specification of end-point inequality and interior-point constraints

Variable	Constraint specification	Lower bound	Upper bound
dT/dt	End-point inequality	-0.0001	0.0001
dZ_0/dt	End-point inequality	-0.00001	0.00001
dT/dt	Interior point*	-0.0001	0.0001

*Bounds at the last control interval

At the end of grade transition, the polymerization process should not only satisfy the grade specification but also access a steady state. Since the computing cost is high if all of the state variables are monitored, two state variables, Z_0 (i.e. dead polymer concentration) and T are selected to indicate the process state. Since the polymerization process is slow and sensitive to the reactor temperature, T is enforced to maintain at the target value during the last control interval. These variables are specified as end-point inequality and interior-point constraints in CVP_MS optimization solver. **Table 5.6** shows the specification of the end-point inequality and interior-point constraints.

5.4.2 Optimization results of J_1 and J_2

It is well-known the SQP algorithm deployed by the CVP_MS optimization solver in gPROMS^{TM} leads to only a locally optimal solution, and may fail to provide the global optimum if the optimization problem has multiple optima. The grade transition problem of continuous polymerization reactor is characterized by its severe nonlinear behavior that often leads to a nonconvex optimization problem with multiple optima. The optimization solver runs with various sets of time interval and initial guess value of the decision variables to find the global optimal solution for the dynamic optimization problem.

We first determine the shortest transition time by minimizing the objective function

J_1. From the viewpoints of optimal performance and calculation load, 19 control intervals are selected. The horizon of transition time is defined as $t_{f,1} \in [560, 830]$ min. The first 18 control intervals are fixed as 20 or 30 minutes to simplify the optimization. In order to ensure that the process can access the steady state of the target grade, the last control interval is specified much longer than other control intervals as $t_{fl,1} \in [50, 300]$ min. The objective function J_1 is optimized to a final transition time $t_{f,1} = 717$ min.

The transition time horizon of J_2 is set as $t_{f,2} = kt_{f,1}$, where $k>1$. Here, $t_{f,2}$ is set as 730min, and 19 control intervals are selected. The first 18 control intervals are set as 30min each, and the last interval is set as $t_{fl,2} = 190$ min.

Figures 5.2 and **5.3** show the optimized control input trajectories, F_i and F_j, for J_1 and J_2. The optimization result by minimizing J_1 is illustrated by "—". The optimization result by minimizing J_2 is illustrated by "---". The optimized consumption of the initiator by using objective function J_2 appears less than that of J_1. **Table 5.7** shows the optimized value of the two objective functions.

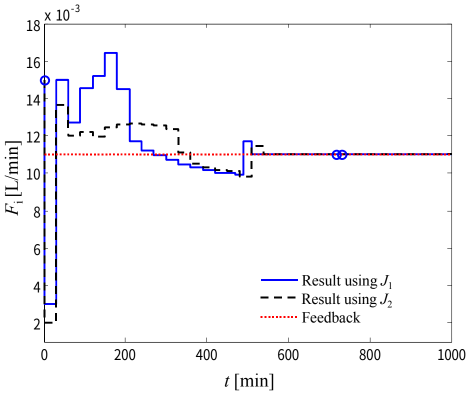

Fig. 5.2 Optimal transition trajectory of F_i

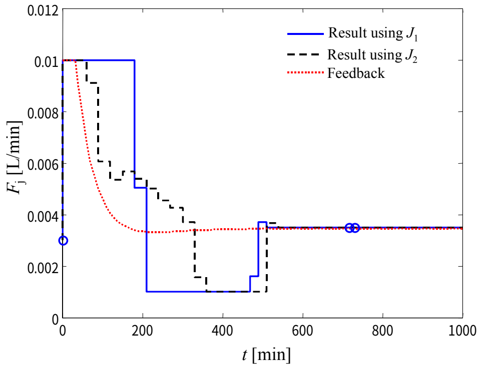

Fig. 5.3 Optimal transition trajectory of F_j

Table 5.7 Optimized value of two objective functions

Objective function	Optimized value	
	t_f [min]	Initiator consumption [L]
J_1	717	8.226
J_2	730	8.11
Feedback	1000	11.01

Simulation study is carried out to verify the optimization results. The optimized transition trajectory of F_i and F_j are used as set points for the feedforward controller from $t=0$ to $t=t_f$. In this work we do not take account of the system error with model mismatch. **Figures 5.4—5.7** show the simulation results of α, T, M_n and *PDI* respectively. The simulation results for J_1 are illustrated by "—". The simulation results on basis of minimizing J_2 are illustrated by "---". It must be noted that the target α and T are used as input variables after the final transition time t_f. For J_1, the profiles show simulation results for optimized F_i and F_j from $t=0$ to $t=t_{f,1}=717$ min; from $t=717$ to $t=1000$ min, the profiles show the simulation results of feedback control with the set points $\alpha=0.645$ and $T=354\text{K}$, and the state at $t_{f,1}$ is used as the initial state. Similarly, the switch time for J_2 is $t_{f,2}=730$ min.

The feedback control responding to the step change of the set point of α and T are compared to the simulation results for optimized transition trajectory of F_i and F_j. The step change is from the initial operating condition of $\alpha=0.57$, $T=360\text{K}$ to the target $\alpha=0.645$, $T=354$ K (*cf.* Table 5.3). The conditions for these case studies are shown in **Table 5.8**. **Figures 5.2** and **5.3** show the trajectories of F_i and F_j that are outputs of the regulatory controllers, and **Figures 5.4—5.7** show simulation results of α, T , M_n and *PDI.*

Table 5.8 Condition for simulation

	Input variable in time horizon t [min]	
Run	Optimized F_i, F_j	Setpoint of Feedback control $\alpha = 0.645$, $T = 354$ K
J_1	[0,717]	[717,1000]
J_2	[0,730]	[730,1000]
Feedback	–	[0,1000]

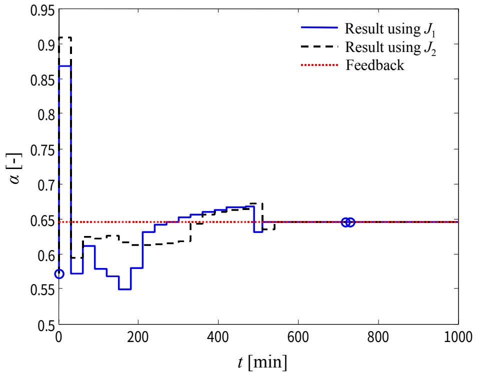

Fig. 5.4 Optimal transition trajectory of α

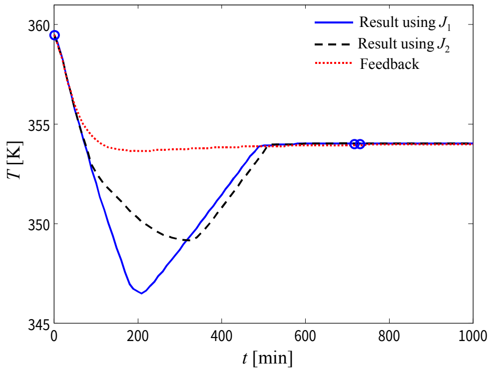

Fig. 5.5 Simulated transition trajectory of T

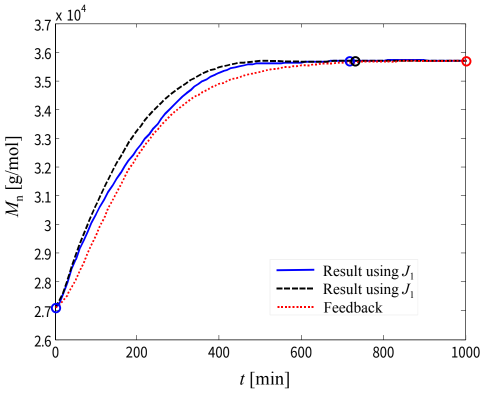

Fig. 5.6 Simulated transition trajectory of M_n

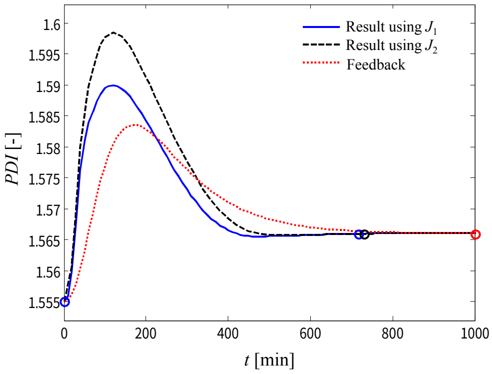

Fig. 5.7 Simulated transition trajectory of PDI

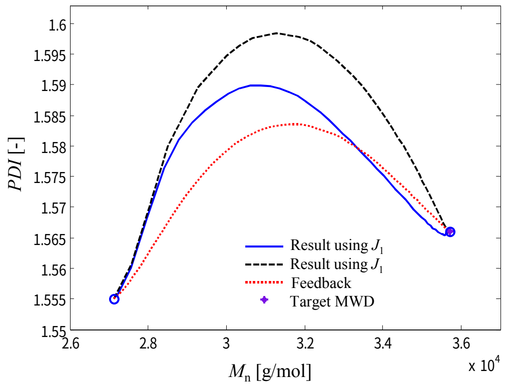

Fig. 5.8 Simulated transition trajectory of M_n and *PDI*

The simulation results show that the control variables are determined to first decrease the reactor temperature for increasing M_n and *PDI*, and then to increase the temperature for narrowing the MWD, *i.e.* decreasing the *PDI*. **Figure 5.8** shows simulated transition trajectory of M_n and *PDI*. The end point values of M_n and *PDI* of all simulation results satisfy the target specifications. The termination time are the final transition time $t_{\text{f},1}$ for J_1 and $t_{\text{f},2}$ for J_2 respectively. However, the termination time for the feedback control for the step response t_f is about 1000 min as shown in Table 5.7.

When the transition time horizon and control interval are selected similarly for J_1 and J_2, the dynamic optimization results of manipulated variables differ, and the simulation trajectory of output variables appears different. The optimized transition times for both J_1 and J_2 are shorter than that of feedback control.

The control system switches from feedforward control to feedback control at the final transition time t_f. Figures 5.6 and 5.7 illustrate that the polymer MWD parameters, M_n and *PDI*, hardly fluctuate after the termination of grade transition operation. **Figure 5.9** shows the trajectory of dead polymer concentration *P* that is selected to indicate whether the polymerization process accesses a steady state. It is shown that the dead polymer concentration is nearly stable. It is demonstrated that the polymerization process reaches the target steady state satisfying the grade specification at the final transition time t_f. The combination of feedforward and regulatory system provides a good solution for the grade transition operation.

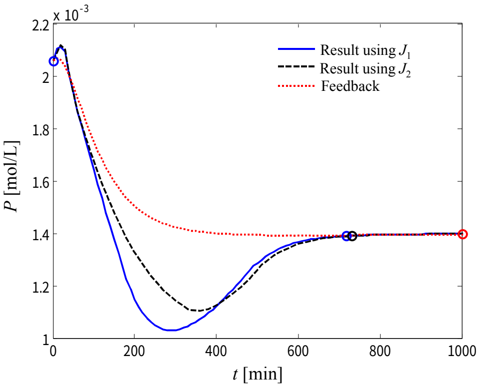

Fig. 5.9 Simulated transition trajectory of dead polymer concentration

5.5 Summary

The grade transition problem for free radical styrene polymerization in a pilot-plant CSTR is considered in this chapter. The polymer grade specification is defined as number average molecular weight M_n and polydispersity index *PDI*. The flow rate of initiator and coolant, F_i and F_j, are selected as manipulated variables in the dynamic optimization. The optimal transition trajectories of input variables are generated using off-line dynamic optimization.

Two objective functions are formulated to determine the optimal trajectory of manipulated variables. The objective function J_1 aims to minimize the transition time, and the objective function J_2 focuses on the cost performance of the polymerization process by minimizing the consumption of initiator during the transition time.

Simulation studies in view of the combination of feedforward and regulatory control system are carried out to verify the optimization result. The polymer MWD parameters, M_n and PDI, satisfy the polymer grade specification at the end of the transition operation. The optimal transition time is much shorter than that of feedback control. It was demonstrated that the combination of feedforward and regulatory control system provides a good solution for the grade transition operation.

Chapter 6

Conclusion

Continuous polymerization reactors are widely used to produce synthetic polymers in industries. The polymer reactor is usually operated in multiple operating conditions to manufacture several different grades of polymers according to demands of customers. The flexible operation of polymerization plants is an important research subject in polymer production. In this thesis, we considered the optimal polymer production problem, in which the optimal steady-state operating condition and the optimal grade transition are achieved.

A mathematical model was developed for description of dynamic and static behavior of a general free radical polymerization in CSTR. The material and energy balance equations were derived with respect to initiator, monomer, solvent, live polymer, dead polymer, reactor temperature, and cooling jacket temperature. Also molecular weight moments are introduced for live and dead polymers. By using three leading dead polymer moments, we calculated the MWD parameters: both the number-average and weight-average molecular weights and the polydispersity index. The weight-based MWD function is calculated using concentrations of dead polymers with different chain lengths.

For purpose of producing polymers with the best match to a specified MWD profile, off-line optimization was carried out to determine the optimal steady-state operating conditions. The monomer feed ratio α and the reactor temperature T are used as the decision variables in this optimization. Three objective functions were investigated in two cases: the free radical styrene polymerization and free radical MMA polymerization.

In order to explain the degree of freedom problem for determining an operating condition, we considered the issue of determining an operating point of CSTR to produce a product polymer with specified MWD parameters in chapter 4. Two MWD parameters, M_n and *PDI* are selected as a substitute for the MWD profile. The mathematical model for the general free radical polymerization in the CSTR represents the relationship between the operation conditions and the product quality. We can basically determine an operating condition when the product quality, *i.e.* M_n and *PDI* are specified.

Three typical types of free radical polymerization were investigated to find the correlation between operating conditions and polymer MWD specification. When the termination by combination reaction occurs, an operating point can be determined by specifying two MWD parameters, M_n and *PDI*. Whereas, when the termination reaction by combination does not occur, an operating point cannot be determined by the simultaneous specification of M_n and *PDI*, because the two parameters are interdependent and related to a polymerization factor φ. In this case, since there is one degree of freedom for determining an operating condition, another parameter must be specified to obtain an operating point.

The optimal grade transition for free radical styrene polymerization in CSTR was considered in chapter 5. The optimal transition trajectories of input variables are determined using off-line dynamic optimization. The polymer grade specification was defined as number-average molecular weight M_n and polydispersity index *PDI*. The flow rate of initiator and coolant, F_i and F_j, were selected as manipulated variables in the dynamic optimization. Two objective functions were formulated to determine the optimal transition trajectory of manipulated variables. The objective function J_1 aims to minimize the transition time, and the objective function J_2 focuses on the cost performance of the polymerization process by minimizing the consumption of initiator during the transition time. The simulation results of polymer MWD parameters, M_n and *PDI*, satisfy the polymer grade specification. The optimal transition time is much shorter than that of feedback control. It was demonstrated that the combination of feedforward and regulatory control system provides a good solution for the grade transition operation.

Acknowledgements

First of all, I would like to express my deepest gratitude to my supervisor, Professor Hirokazu Nishitani for accepting me in his Laboratory and providing me with unlimited support and guidance in my study. His serious and decisive attitude impressed me deeply and will greatly benefit me in the future.

I would like to thank Professor Kenji Sugimoto for his invaluable comments and helpful advices. I am very grateful to Associate Professor Masaru Noda for his constructive comments and practical support. I also thank Dr. Hiroaki Kosaka and Dr. Hisakazu Nakamura for their invaluable advices and continuous help.

I also gratefully acknowledge the Ministry of Education of the People's Republic of China and the Japanese Ministry of Education, Culture, Sport, Science and Technology for the scholarship they offered me, and for the precious opportunity to experience a different life and a new culture in Japan they gave me.

Many thanks to Dr. Masanori Takemoto and my fellow students of the Systems and Control Laboratory for their friendship and kind help. Special thanks go to Dr. Xiwei Liu and Dr. Yoshiyasu Sakakura for their great help and friendly advices.

No words can express my thanks to my parents, my sisters, my brother and all my family members for their endless love and support. Finally and most importantly, I would like to thank my daughter for her love and her existence itself gave me the greatest power to go through the toughest times in my life.

Nomenclatures

A	frequency factor in Arrhenius equation
A_r	overall heat-transfer area
$C\mathrm{p}$	thermal capacitance of reacting mixture
$C\mathrm{p}_\mathrm{j}$	thermal capacitance of coolant
E	Activation energy in Arrhenius equation
F	flow rate
F_i	flow rate of initiator feed stream
F_j	flow rate of coolant
F_m	flow rate of monomer feed stream
$f\,(m_i, n_i)$	weight fraction of polymers within chain length interval (m_i, n_i)
$f_\mathrm{w}(j)$	weight-based molecular weight distribution function
I	initiator or its concentration
I^0	concentration of initiator in feed mixture
I^{00}	concentration of initiator feed stream
J	objective function
j	polymer chain length
K	rate constant
K_d	rate constant of initiator decomposition
K_i	rate constant of initiation
K_p	rate constant of propagation
K_trm	rate constant of transfer to monomer
K_trs	rate constant of transfer to solvent
K_t	rate constant of termination reaction
K_tc	rate constant of termination by combination
K_td	rate constant of termination by disproportination
M	monomer or its concentration
M^0	concentration of monomer in feed mixture
M^{00}	concentration of monomer feed stream

M_j	molecular weight of polymer with chain length j
M_m	molecular weight of monomer
M_n	number-average molecular weight
M_w	weight-average molecular weight
N_j	number of polymers with chain length j
P	total concentration of dead polymers
P_j	dead polymer with chain length j or its concentration
PDI	polydispersity index
R	total concentration of live polymers
R^+	primary radical
R_j	live polymer with chain length j or its concentration
S	solvent and its concentration
S^0	concentration of solvent in feed mixture
S_m^{00}	concentration of solvent in monomer feed stream
S_i^{00}	concentration of solvent in initiator feed stream
T	reactor temperature
T_f	temperature of inlet reactant stream
T_j	jacket temperature
T_jf	temperature of the inlet coolant stream
t	time
t_f	final transition time
U_m	mth moment of live polymer
U_r	overall heat-transfer coefficient
V	reactor volume
V_j	cooling jacket volume
W_j	total weight of polymers with chain length j
$X\mathrm{c}$	monomer conversion
Z_m	mth moment of dead polymer

Greek Letters

α	monomer feed ratio
θ	average residence time
λ	weight factor
ρ	density of reacting mixture
ρ_{j}	density of coolant
$\rho C\mathrm{p}$	density multiplies heat capacity of reacting mixture
$\rho_{\mathrm{j}} C\mathrm{p}_{\mathrm{j}}$	density multiplies heat capacity of coolant
$-\Delta H_{\mathrm{r}}$	heat of propagation reaction

Subscripts

d	initiator decomposition
i	initiator
m	monomer
f	feed stream
p	propagation reaction
s	solvent
t	termination
tc	termination by combination
td	termination by disproportination
trm	chain transfer to monomer
trs	chain transfer to solvent

Literature Cited

Ahn, S. M., S. C. Chang and H. K. Rhee; "Application of Optimal Temperature Trajectory to Batch PMMA Polymerization Reactor," *J. Appl. Polym. Sci.*, 69, 59-68 (1998)

Ahn, S. M., M. J. Park and H. K. Rhee; "Extended Kalman Filter-Based Nonlinear Model Predictive Control for a Continuous MMA Polymerization Reactor," *Ind. Eng. Chem. Res.*, 38, 3942-3949 (1999)

Alhamad, B., J. A. Romagnoli and V. G. Gomes; "On-Line Multi-Variable Predictive Control of Molar Mass and Particle Size Distributions in Free-Radical Emulsion Copolymerization," *Chem. Eng. Sci.*, 60, 6596-6606 (2005)

Asteasuain, M., S. M. Tonelli, A. Brandolin and A. Bandoni; "Dynamic Simulation and Optimisation of Tubular Polymerisation Reactors in gPROMS," *Comp. & Chem. Eng.,* 25, 509-515 (2001)

Asteasuain, M., A. Bandoni, C. Sarmoria and A. Brandolin; "Simultaneous Process and Control System Design for Grade Transition in Styrene Polymerization," *Chem. Eng. Sci.*, 61, 3362-3378 (2006)

Atasoy, I., M. Yuceer and R. Berber; "Molecular Weight Control in Acrylonitrile Polymerization with Neural Network Based Controllers," *Comp. Aided Chem. Eng.*, 21, 1617-1622 (2006)

BenAmor, S., F. J. Doyle Ⅲ and R. McFarlane; "Polymer Grade Transition Control Using Advanced Real-Time Optimization Software," *J. Process Control*, 14, 349-364 (2004)

Bindlish, R., J. B. Rawlings; "Target Linearization and Model Predictive Control of Polymerization Processes," *AICHE J.*, 49, 2885-2899 (2003)

Chang, J. S., B. C. Hung; "Optimization of Batch Polymerization Reactors Using Neural-Network Rate-Function Models," *Ind. Eng. Chem. Res.*, 41, 2716-2727, (2002)

Chatzidoukas, C., J. D. Perkins, E. N. Pistikopoulos and C. Kiparissides; "Optimal Grade Transition and Selection of Closed-loop Controllers in a Gas-Phase Olefin Polymerization Fluidized Bed Reactor," *Chem. Eng. Sci.*, 58, 3643-3658 (2003)

Costa, E. F., Jr., P. L. C. Lage and E. C. Biscaia, Jr.; "On the Numerical Solution and Optimization of Styrene Polymerization in Tubular Reactors," *Comp. & Chem. Eng.,* 27, 1591-1604 (2003)

Crowley, T. J. and K. Y. Choi; "Calculation of Molecular Weight Distribution from Molecular Weight Moments in Free Radical Polymerization," *Ind. Eng. Chem. Res.*, 36, 1419-1423 (1997a)

Crowley, T. J., K. Y. Choi; "Discrete Optimal Control of Molecular Weight Distribution in a Batch Free Radical Polymerization Process," *Ind. Eng. Chem. Res.*, 36, 3676-3684 (1997b)

Daoutidis, P., M. Soroush and C. Kravaris; "Feedforward/Feedback Control of Multivariable Nonlinear Processes," *AICHE J.*, 36, 1471-1484 (1990)

Ekpo, E. E., I. M. Mujtaba; "Evaluation of Neural Networks-Based Controllers in Batch Polymerization of Methyl Methacrylate," *Neurocomputing*, 71, 1401-1412 (2008)

Inoue, S.; Synthetic Polymer Chemistry, Shokabo, Tokyo, Japan (1996)

Jeong, B. G., K. Y. Yoo and H. K. Rhee; "Nonlinear Model Predictive Control Using a Wiener Model of a Continuous Methyl Methacrylate Polymerization Reactor," *Ind. Eng. Chem. Res.*, 40, 5968-5977 (2001)

Kadam, J. V., W. Marquardt, B. Srinivasan and D. Bonvin; "Optimal Grade Transition in Industrial Polymerization Process via NCO Tracking," *AICHE J.*, 53, 627-639 (2007)

Kiparissides, C., P. Seferlis, G. Mourikas and A. J. Morris; "Online Optimizing Control of Molecular Weight Properties in Batch Free-Radical Polymerization Reactors," *Ind. Eng. Chem. Res.*, 41, 6120-6131 (2002)

Lee, M. H., C. Han and K. S. Chang; "Dynamic Optimization of a Continuous Polymer Reactor Using a Modified Differential Evolution Algorithm," *Ind. Eng. Chem. Res.*, 38, 4825-4831 (1999)

Othman, N. S., G. Févotte; "Control of Polymer Molecular Weight Using Near Infrared Spectroscopy", *AIChE J.*, 50, 654-664 (2004).

Othman, N. S., D. Peycelon and G. Févotte; "Monitoring and Control of Free-Radical Polymerization Using Near-Infrared Spectroscopy", *Ind. Eng. Chem. Res.*, 43, 7383-7391 (2004).

Padhiyar, N., S. Bhartiya and R. D. Gudi; "Optimal Grade Transition in Polymerization Reactors: A Comparative Case Study," *Ind. Eng. Chem. Res.*, 45, 3583-3592 (2006)

Park, M. J., H. K. Rhee; "LMI-based Robust Model Predictive Control for a Continuous MMA Polymerization Reactor," *Comp. & Chem. Eng.,* 25, 1513-1520 (2001)

Prasad, V., M. Schley, L. P. Russo and B. W. Bequette; "Product Property and Production Rate Control of Styrene Polymerization," *J. Process Control*, 12, 353-372 (2002)

Ray, W. H. and C. Villa; "Nonlinear dynamics found in polymerization processes—a review," *Chem. Eng. Sci.*, 55, 275-290 (2000)

Richards, J. R.; J. P. Congalidis; "Measurement and Control of Polymerization Reactors," *Comp. & Chem. Eng.,* 30, 1447-1463 (2006)

Sayer, C., G. Arzamendi, J. M. Asua, E. L. Lima and J. C. Pinto; "Dynamic Optimization of Semicontinuous Emulsion Copolymerization Reactions: Composition and Molecular Weight Distribution," *Comp. & Chem. Eng.,* 25, 839-847 (2001)

Stevens, M. P.; Polymer Chemistry — An Introduction, 3rd ed., Oxford University Press, New York, USA (1999)

Vicente, M., S. BenAmor, L. M. Gualiotta, J. R. Leiza and J. M. Asua; "Control of Molecular Weight Distribution in Emulsion Polymerization Using On-Line Reaction Calorimetry," *Ind. Eng. Chem. Res.*, 40, 218-227 (2001)

Wang, Y., H. Seki, S. Ohyama, K. Akamatsu, M. Ogawa and M. Ohshima; "Optimal Grade Transition Control for Polymerization Reactors," *Comp. & Chem. Eng.,* 24, 1555-1561 (2000)

Yi, H. S., J. H. Kim, C. Han, J. Lee and S. S. Na; "Plantwide Optimal Grade Transition for an Industrial High-Density Polyethylene Plant," *Ind. Eng. Chem. Res.*, 42, 91-98 (2003)

Yoo, K. Y., B. G. Jeong and H. K. Rhee; "Molecular Weight Distribution Control in a Batch Polymerization Reactor Using the On-line Two-step Method," *Ind. Eng. Chem. Res.*, 38, 4805-4814 (1999)

Yue, H. and H. Wang; "Recent Developments in Stochastic Distribution Control/ a Review," *Journal of Measurement + Control*, 36, 209-215 (2003)

Yue, H., J. F. Zhang, H. Wang and L. L. Cao; "Shaping of Molecular Weight Distribution Using B-spline Based Predictive Probability Density Function Control," *Proceeding of ACC 2004*, 3587-3592 (2004)

Zeaiter, J., J. A. Romagnoli and V. G. Gomes; " Online Control of Molar Mass and Particle-Size Distributions in Emulsion Polymerization," *AIChE Journal*, 52, 1770-1779 (2006)