

Shaping of Molecular Weight Distribution Using B-spline Based Predictive Probability Density Function Control

Hong Yue, Jinfang Zhang, Hong Wang and Liulin Cao

Abstract—Issues of modelling and control of molecular weight distributions (MWDs) of polymerization products have been studied under the recently developed framework of stochastic distribution control, where the purpose is to design the required control inputs that can effectively shape the output probability density functions (PDFs) of the dynamic stochastic systems. The B-spline Neural Network has been implemented to approximate the function of MWDs provided by the mechanism model, based on which a new predictive PDF control strategy has been developed. A simulation study of MWD control of a pilot-plant styrene polymerization process has been given to demonstrate the effectiveness of the algorithms.

I. INTRODUCTION

The molecular weight distribution (MWD) of a polymer is one of the most important variables to be controlled in industrial polymerization processes because it directly affects many of polymer's end-use properties such as thermal properties, stress-strain properties, impact resistance, strength and hardness, etc [1], [2]. Therefore, there has been much incentive to control MWD accurately during polymerization. The research into the modelling and control of MWD in polymerization has constituted an important area in process control for a decade, where the aim is to select proper control strategies that can effectively control the shape of the molecular weight distribution following the quality requirements of the end-use polymer.

Information of molecular weight distributions for control and optimization is normally obtained from mathematical models because so far MWD is still very difficult to measure on-line. Mechanistic MWD models are developed based on the mass balance and energy balance principles, which include a set of differential equations describing the dynamics of the reaction species such as initiator, monomer, radicals and polymers of different chain length. These equations are functions of kinetic mechanism and reaction operation conditions of the polymerization process [3]. The control inputs can be chosen as initiator concentration, feed rate of monomer and/or chain transfer agent, reactor pressure and temperature, etc [4], [5]. As

This work is supported by Chinese NSFC grant 60128303 and UK's Leverhulme Trust grant F/00038/D

H. Yue and H. Wang are with the Control Systems Centre, University of Manchester Institute of Science and Technology, Manchester M60 1QD, The United Kingdom h.yue@umist.ac.uk; hong.wang@umist.ac.uk

J. Zhang is with the Institute of Automation, Chinese Academy of Sciences, Beijing 100080, China jinfang.zhang@mail.ia.ac.cn

L. Cao is with the Department of Chemical Automation, Beijing University of Chemical Technology, Beijing 100029, China caoll@fht

the polymer chain length of interests is usually a huge number up to millions, direct solution of these hundreds of thousands of differential equations is unfeasible in most real situations and therefore various numerical techniques have been devised to solve this problem. An adaptive orthogonal collocation algorithm has been developed for the computation of the entire MWD which allows broad, bimodal and fast changing distributions [6]. This technique has been implemented for the modelling of the dynamic evolution of MWDs during nonlinear emulsion polymerization reactions [7]. The method of finite molecular weight moments has been proposed for the calculation of MWD in free radical polymerization [8]. Some polymerization systems have also been modelled by statistical methods such as Markov chain [9], [10], [11], Weibull distribution [12], [13] and Schultz-Zimm distribution [14]. For a large number of practical problems of linear polymerization under steady-state or quasi-steady state conditions, the MWD of polymer chains can be described satisfactorily by the generalized Schulz-Flory distribution [3], [15], [16].

In recent years, various control strategies have been developed for the MWD control of polymerization processes. The time optimal monomer and chain-transfer agent feed profiles were computed and implemented experimentally for the MWD control in non-linear emulsion copolymerization systems [5]. An optimal control solution to get the desired MWD of linear polymers within a minimum time has been developed based on on-line reaction calorimetry [17]. The two-step method was proposed in [18] and then modified and validated by an experimental study, which aims for getting the reactor temperature so as to obtain a polymer with a prescribed MWD in a free-radical polymerization batch reactor [1], [19]. The disturbance rejection has been considered in the on-line two-step method for MWD control [20]. Batch-to-batch modifications combined with multivariate statistical process control have been implemented to update manipulated variable trajectories so that the desired MWD can be achieved after several batches [21]. State estimation techniques such as extended Kalman filtering have been implemented when it is desirable to monitor on-line MWD and other time-varying model parameters or unknown conditions [2], [22], [23], [24].

Most of the research studies are based on simulated reactors. Industry-scale closed-loop control of MWD is still a challenging subject not only because the lack of on-line measurement of MWD, but also due to lack of systematic solutions of output distribution control. In this paper, the idea of closed-loop control of output probability density

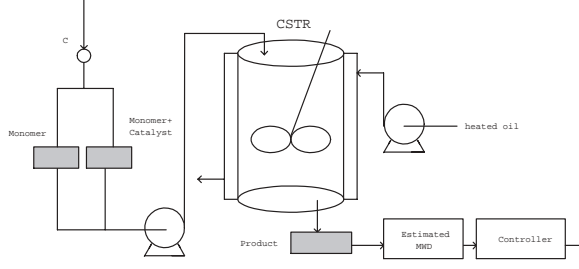


Fig. 1. styrene polymerization system in a CSTR pilot reactor

function (PDF) for non-Gaussian stochastic systems [25], [26], [27] has been introduced to develop control strategies for MWD control of polymerization processes, where the B-spline neural network is used to approximate MWDs obtained from the physical model. The key advantage of using the B-spline decoupling models is that the obtained weights model of the MWD can be made *mathematically* equivalent to any existing physical models for MWD systems subjected to a pre-specified small modelling error. A predictive control algorithm has been proposed to realize the dynamic tracking of the desired output distribution.

II. PROCESS MECHANISM MODELLING

The process in concern is a styrene bulk polymerization reaction in a pilot-plant continuous stirred tank reactor (CSTR) as shown in figure 1, in which styrene is the monomer for polymerization and azobisisobutyronitrile is used as the initiator. These two flows are injected into the CSTR with a certain ratio adjusted by a Bruker HPLC pump. The energy for the reaction is provided by the heated oil in the CSTR's jacket and the oil temperature is controlled by a Tool-Temp temperature control unit TT-162E. To simplify the process, the reaction temperature is assumed to be kept constant. The total flow rate to the system, F , is composed of the flow of monomer, F_m , and the flow of initiator, F_i , i.e., $F = F_m + F_i$. The monomer input ratio is defined as $c = F_m/(F_i + F_m)$. Both F and c can be changed by the control system. In this work, adjustment of c is considered to be the means to control the MWD shape of the polystyrene product.

The following free radical polymerization mechanisms are considered.

- Initiation $I \xrightarrow{K_d} 2R^*$
 $R^* + M \xrightarrow{K_i} R_1$
- Chain propagation $R_j + M \xrightarrow{K_p} R_{j+1}$
- Chain transfer to monomer $R_j + M \xrightarrow{K_{trm}} P_j + R_1$
- Termination by combination $R_j + R_i \xrightarrow{K_t} P_{j+i}$

where I is the initiator, M is the monomer, R^* is the primary radical, R_j is the live polymer radical with chain length j , P_j is the dead polymer with chain length j . K_d ,

K_i , K_p , K_{trm} and K_t are reaction rate constants. A set of mass balance equations can be derived to describe the concentrations of the reaction species.

$$\frac{dI}{dt} = (I^0 - I)/\theta - K_d I \quad (1)$$

$$\frac{dM}{dt} = (M^0 - M)/\theta - 2K_i I - (K_p + K_{trm})MR \quad (2)$$

$$\frac{dR_1}{dt} = -R_1/\theta + 2K_i I - K_p MR_1 + K_{trm}M(R - R_1) - K_t R_1 R \quad (3)$$

$$\frac{dR_j}{dt} = -R_j/\theta - K_p M(R_j - R_{j-1}) - K_{trm}MR_j - K_t R_j R \quad (j \geq 2) \quad (4)$$

$$\frac{dP_j}{dt} = K_{trm}R_j M + \frac{K_t}{2} \sum_{l=1}^{j-1} R_l R_{j-l} - P_j/\theta \quad (j \geq 2) \quad (5)$$

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

$$R = \sum_{j=1}^{\infty} R_j \quad (6)$$

is the total concentration of the radicals. By denoting

$$P = \sum_{j=2}^{\infty} P_j \quad (7)$$

as the total concentration of the polymers, the following formulation for the total concentrations of radicals and polymers can be obtained from (3) to (7) as

$$\frac{dR}{dt} = -R/\theta + 2K_i I - K_t R^2 \quad (8)$$

$$\frac{dP}{dt} = -P/\theta + K_{trm}MR + \frac{K_t}{2} R^2 \quad (9)$$

The initial concentrations of the initiator and monomer are related to the monomer input ratio c through $I^0 = (1-c)I^{00}$ and $M^0 = cM^{00}$. I^{00} and M^{00} are the initial concentrations decided by the chemical system design and the ratio c can be adjusted according to the controller design algorithm.

Denote

$$\alpha = 1 + \frac{K_{trm}}{K_p} + \frac{K_t R}{K_p M} + \frac{1}{K_p M \theta} \quad (10)$$

the static solutions to the concentrations of the reaction species can be derived from (1)-(3) and (8)-(9) as

$$I = \frac{I^0}{1 + K_d \theta} \quad (11)$$

$$R = \frac{-1/\theta + \sqrt{1/\theta^2 + 8K_t K_i I}}{2K_t} \quad (12)$$

$$M = \frac{M^0}{1 + (K_p + K_{trm})R\theta} \quad (13)$$

$$R_1 = \frac{2K_i I + K_{trm}MR}{K_p M \alpha} \quad (14)$$

$$P = \theta(K_{trm}MR + \frac{K_t}{2}R^2) \quad (15)$$

The dynamic model of MWDs with respect to time has been set up by the moment method together with a statistical distribution. The moments of the number chain-length distributions of radicals and polymers are defined as

$$U_m = \sum_{j=1}^{+\infty} j^m R_j, \quad m = 0, 1, 2, \dots \quad (16)$$

$$Z_m = \sum_{j=2}^{+\infty} j^m P_j, \quad m = 0, 1, 2, \dots \quad (17)$$

It can be seen from (16) and (17) that $U_0 = R$ and $Z_0 = P$. The differential equations of the leading moments are derived using the generation function technique as follows :

$$\frac{dU_0}{dt} = 2K_i I - K_t U_0^2 - U_0/\theta \quad (18)$$

$$\begin{aligned} \frac{dU_1}{dt} &= 2K_i I + K_p U_0 M - K_t U_0 U_1 \\ &\quad + K_{trm} M (U_0 - U_1) - U_1/\theta \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{dU_2}{dt} &= 2K_i I + K_p M (2U_1 + U_0) - K_t U_0 U_2 \\ &\quad + K_{trm} M (U_0 - U_2) - U_2/\theta \end{aligned} \quad (20)$$

$$\frac{dZ_0}{dt} = K_{trm} M (U_0 - R_1) + \frac{K_t}{2} U_0^2 - Z_0/\theta \quad (21)$$

$$\frac{dZ_1}{dt} = K_{trm} M U_1 + K_t U_0 U_1 - Z_1/\theta \quad (22)$$

$$\frac{dZ_2}{dt} = K_{trm} M U_2 + K_t U_0 U_2 + K_t U_1^2 - Z_2/\theta \quad (23)$$

Once the moments of the dead polymer are obtained, the calculation of MWD can be carried out through a statistical distribution, chosen empirically in order to resemble the MWD of the actual solution. In this work, the well-known Weibull distribution

$$W(n) = \begin{cases} \frac{g}{x_0} (n - \delta)^{g-1} \exp\left(-\frac{(n-\delta)^g}{x_0}\right) & n \geq \delta \\ 0 & n < \delta \end{cases} \quad (24)$$

is used, in which $n = 1, 2, \dots$ stands for the discrete points of the distribution variable. The link between the leading moments (Z_0, Z_1, Z_2) and the three Weibull parameters (g, x_0, δ) can be established in the same way as described in [13].

III. B-SPLINE PDF MODEL

Consider a continuous probability density function $\gamma(y, u_k)$ defined on $[a, b]$ interval, the linear B-spline neural network can be used to give an approximation of $\gamma(y, u_k)$ [26]:

$$\gamma(y, u_k) = \sum_{i=1}^n \omega_i(u_k) B_i(y) + e_0 \quad (25)$$

where u_k is the control input at sample time k ; $B_i(y)$ ($i = 1, \dots, n$) are the pre-specified basis functions defined on the interval $y \in [a, b]$; n is the number of basis functions; $\omega_i(u_k)$ ($i = 1, \dots, n$) are the expansion weights; e_0 represents the approximation error which satisfies $|e| < \delta_1$ (δ_1 is

a known small positive number). To simplify the expression, e_0 is neglected in the following. Due to the fact that the integration of a PDF over its definition domain should be 1, there are only $n - 1$ independent weights out of the original n weights [25]. Denote

$$L(y) = \frac{B_n(y)}{\int_a^b B_n(y) dy} \quad (26)$$

$$c_i(y) = B_i(y) - L(y) \int_a^b B_i(y) dy, \quad i = 1, \dots, n - 1 \quad (27)$$

$$C(y) = [c_1(y), c_2(y), \dots, c_{n-1}(y)] \quad (28)$$

$$V_k = [\omega_1(u_k), \omega_2(u_k), \dots, \omega_{n-1}(u_k)]^T \quad (29)$$

the static B-spline PDF model (25) can be represented in a compact form as

$$\gamma(y, u_k) = C(y) V_k + L(y) \quad (30)$$

Equation (30) is the static PDF model approximated by the B-spline neural network, in which $C(y)$ is known when the basis functions $B_i(y)$, ($i = 1, \dots, n$) are chosen and fixed. Denote

$$f_k(y) = \gamma(y, u_k) - L(y) \quad (31)$$

then (30) is transformed into

$$f_k(y) = C(y) V_k \quad (32)$$

For dynamic systems, it is assumed that the weights vector in (29) is dynamically related to the system by

$$V_{k+1} = E V_k + F u_k \quad (33)$$

where E and F are known matrices with appropriate dimensions. Equation (33), together with the B-spline approximation in (30), constitute the state-space dynamic model of the deterministic control input u_k and the output PDF $\gamma(y, u_k)$. As $\gamma(y, u_k)$ is related to $f_k(y)$ by (31), the output PDF can be derived from (32) and ((33) to be

$$f_k(y) = C(y) (I - z^{-1} E)^{-1} (F u_{k-1}) \quad (34)$$

This can be expanded to the following form according to matrix theory [26]

$$f_k(y) = \sum_{i=1}^{n-1} a_i f_{k-i}(y) + \sum_{j=0}^{n-2} C(y) D_j u_{k-1-j} \quad (35)$$

where

$$C(y) D_j u_{k-1-j} = \sum_{i=1}^{n-1} d_{j,i} u_{k-1-j} B_i(y) \quad (36)$$

All the parameters a_i , ($i = 1, \dots, n - 1$) and d_{ji} , ($j = 0, \dots, n - 2, i = 1, \dots, n - 1$) can be estimated by a standard least-square identification algorithm [26].

IV. PREDICTIVE CONTROL OF OUTPUT PDF

The purpose of control algorithm design is to choose a control sequence u_k such that the actual output PDF $\gamma(y, u_k)$ is made as close as possible to a desired PDF $g(y)$. For the general control of output PDF, the following performance function is formulated that primarily contains a measure of the distance between the output PDF and the target PDF

$$J_1 = \int_a^b (\gamma(y, u_k) - g(y))^2 dy + \frac{1}{2} \lambda u_k^2 \quad (37)$$

where $\lambda > 0$ is a pre-specified weighting factor that imposes an energy constraint for the control input. For the performance index (37), solutions to both static and dynamic PDF systems are given in [26], where the static approach is based on gradient search and the dynamic control algorithm provides a compact global optimization solution.

In this paper, a new PDF control strategy is proposed based on the long-range predictive control principle. Let z^{-1} be used as the unit back-shift operator, i.e., $z^{-1}u_k = u_{k-1}$, then (35) can be reformulated as

$$\alpha(z^{-1})f_k(y) = \beta(z^{-1}, y)u_{k-1} \quad (38)$$

where

$$\alpha(z^{-1}) = 1 + \sum_{i=1}^{n-1} a_i z^{-i} \quad (39)$$

$$\beta(z^{-1}, y) = \sum_{j=0}^{n-2} C(y) D_j z^{-j} \quad (40)$$

In order to invent the predictive control strategy, the following Diophantine equation is introduced:

$$1 = G_q(z^{-1})\alpha(z^{-1}) + H_q(z^{-1})z^{-q} \quad (41)$$

where q is the predictive step and

$$G_q(z^{-1}) = 1 + \sum_{i=1}^{q-1} g_{q,i} z^{-i} \quad (42)$$

$$H_q(z^{-1}) = \sum_{j=0}^{n-2} h_{q,j} z^{-j} \quad (43)$$

By multiplying $G_q(z^{-1})$ on both sides of (38), there is

$$G_q(z^{-1})\alpha(z^{-1})f_k(y) = G_q(z^{-1})\beta(z^{-1}, y)u_{k-1} \quad (44)$$

Taking (41) into (44), the following predictive formulation of the output PDF can be obtained:

$$f_{k+q}(y) = H_q(z^{-1})f_k(y) + G_q(z^{-1})\beta(z^{-1}, y)u_{k+q-1} \quad (45)$$

$q = 1, 2, \dots, p$

Considering the following expansion

$$G_q(z^{-1})\beta(z^{-1}, y) = \sum_{i=0}^{n+q-3} s_{q,i} z^{-i} \quad (46)$$

(45) can be further represented as

$$\Pi(y, k, p) = \bar{H} f_k(y) + \Omega(y)U_k + \Phi \bar{U}_k \quad (47)$$

where

$$\Pi(y, k, p) = [f_{k+1}(y) f_{k+2}(y) \cdots f_{k+p}(y)]^T \quad (48)$$

$$\bar{H} = [H_1(z^{-1}) H_2(z^{-1}) \cdots H_p(z^{-1})]^T \quad (49)$$

$$\Omega(y) = \begin{bmatrix} s_{1,0} & 0 & \cdots & 0 \\ s_{2,1} & s_{2,0} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ s_{p,p-1} & s_{p,p-2} & \cdots & s_{p,0} \end{bmatrix} \quad (50)$$

$$U_k = [u_k u_{k+1} \cdots u_{k+p-1}]^T \quad (51)$$

$$\Phi = \begin{bmatrix} s_{1,1} & s_{1,2} & \cdots & s_{1,n-2} \\ s_{2,2} & s_{2,3} & \cdots & s_{2,n-2+1} \\ \vdots & \vdots & \ddots & \vdots \\ s_{p,p} & s_{p,p+1} & \cdots & s_{p,n+p-3} \end{bmatrix} \quad (52)$$

$$\bar{U}_k = [u_{k-1} u_{k-2} \cdots u_{k-n+2}]^T \quad (53)$$

The following performance index is formulated for the purpose of predictive PDF control:

$$J_2 = \int_a^b [\Pi(y, k, p) - A(y)]^T [\Pi(y, k, p) - A(y)] dy + U_k^T \bar{R} U_k \quad (54)$$

where $A(y) = [a(y), a(y), \dots, a(y)]^T \in R^p$ corresponds to the target distribution by $a(y) = g(y) - L(y)$ when the same basis functions to approximate $\gamma(y, u_k)$ have been used. \bar{R} is the weighting matrix for the control input. Taking (47) into (54) and denote

$$\xi(y) = \bar{H} f_k(y) + \Phi \bar{U}_k \quad (55)$$

as the known term at the sample time k , the optimization solution to (54) can be obtained by making $\partial J_2 / \partial U_k = 0$ to be

$$U_k = -(\int_a^b \Omega(y)^T \Omega(y) dy + \bar{R})^{-1} \int_a^b (\xi(y) - A(y)) dy \quad (56)$$

The coefficients $g_{q,i}$ and $h_{q,j}$ in the Diophantine equation (41) can be obtained with a recursive derivation which is not given in detail here due to the page limit. Interested readers may contact the authors for the further information.

V. SIMULATION

The styrene bulk polymerization process is described in section II, whose main parameters used are listed in table 1. Seven fourth-order univariate B-spline functions [28] are chosen to formulate the basis functions. The range of the control input, i.e., the monomer input ratio c , is [0.2, 0.8]. Simulation results are shown in figures 2 - 6. Comparing fig.2 with fig. 3, it can be seen that the B-spline MWD model agrees well with the result from the mechanistic model. Figures 5-6 show how the target MWD is achieved

by the predictive PDF control strategy after some control steps.

Table 1. Model parameters

K_d	$9.48 \times 10^{15} \exp(-30798.5/rT)$
K_i	$0.6K_d$
K_p	$6.306 \times 10^8 \exp(-7067.8/rT)$
K_{trm}	$1.386 \times 10^8 \exp(-12671.1/rT)$
K_t	$3.75 \times 10^{10} \exp(-1680/rT)$
V	3.927
F	0.0238
T	353
I^{00}	0.1E-3
M^{00}	9.6E-3
r	1.987

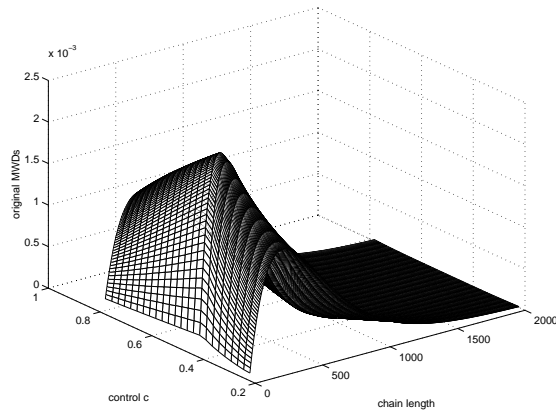


Fig. 2. MWD curves from mechanism model

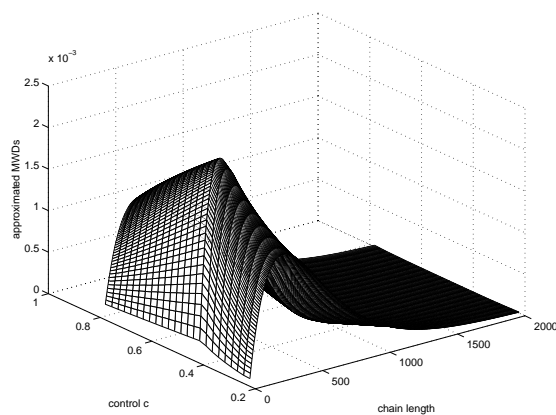


Fig. 3. MWD curves from B-spline model

VI. CONCLUSIONS

In this paper, a B-spline approximation model has been used to decouple the static and dynamic effects of the control input on the output MWD shape. In this context, the control of the MWD shape can be realized through

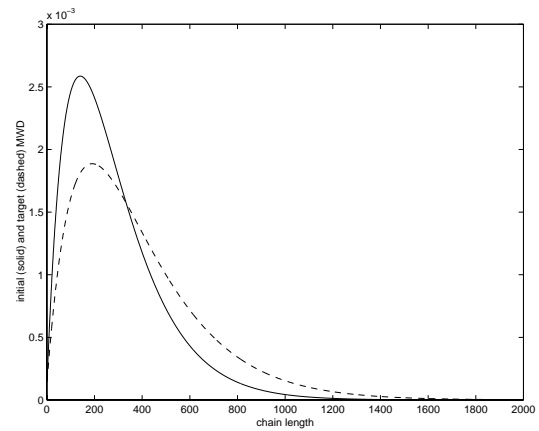


Fig. 4. initial and target MWDs

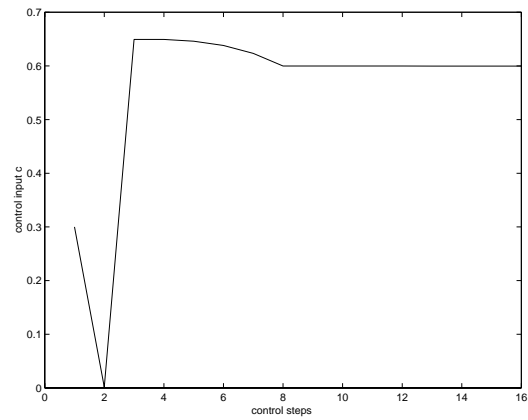


Fig. 5. control input sequence

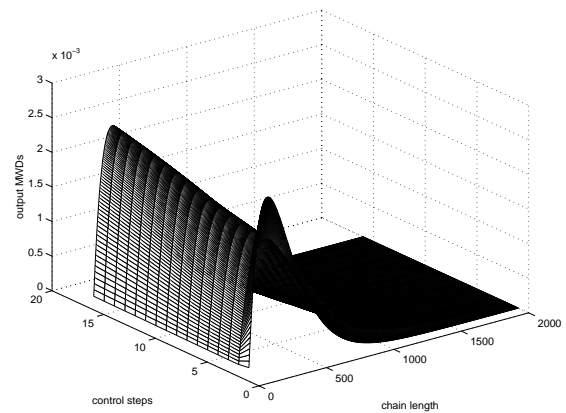


Fig. 6. MWD curves during the control process

the control of the weights (coefficients) in the B-spline expansion on the considered MWD. A physical model of the process was firstly developed and used as a starting point for the establishment of the equivalent B-spline models. This is then followed by a new predictive PDF control method, in which the control input is selected that minimizes a performance measure of the functional error between the target distribution and the estimated MWD. A simulation example is given for the dynamic MWD control system, where desired results have been achieved.

NOTATION

I initiator or its concentration ($mol \cdot L^{-1}$)
 I^{00} initial initiator concentration ($mol \cdot L^{-1}$)
 I^0 controlled ed initial initiator concentration ($mol \cdot L^{-1}$)
 K_d initiator decomposition rate constant (min^{-1})
 K_i initiation reaction constant ($L \cdot mol^{-1} \cdot min^{-1}$)
 K_p propagation rate constant ($L \cdot mol^{-1} \cdot min^{-1}$)
 K_{trm} chain transfer rate constant ($L \cdot mol^{-1} \cdot min^{-1}$)
 K_t termination rate constant ($L \cdot mol^{-1} \cdot min^{-1}$)
 M monomer or its concentration ($mol \cdot L^{-1}$)
 M^{00} initial monomer concentration ($mol \cdot L^{-1}$)
 M^0 controlled initial monomer concentration ($mol \cdot L^{-1}$)
 R_j live polymer of chain length j or its concentration ($mol \cdot L^{-1}$)
 R total concentration of live polymer radicals ($mol \cdot L^{-1}$)
 P_j dead polymer of chain length j or its concentration ($mol \cdot L^{-1}$)
 P total concentration of dead polymer ($mol \cdot L^{-1}$)
 T reaction temperature (K)
 F total feed flow rate ($L \cdot min^{-1}$)
 V volume of reaction mixture (L)
 θ average residential time of reactants in the CSTR (min)

REFERENCES

- [1] J.-H. Chang and P.-H. Liao, "Molecular weight control of a batch polymerisation reactor: experimental study," *Ind. Eng. Chem. Res.*, vol.38, 1999, pp.144-153.
- [2] T.J. Crowley and K.Y. Choi, "Experimental studies on optimal molecular weight distribution control in a batch-free radical polymerization process," *Chem. Eng. Sci.*, vol.53, 1998, pp.2769-2790.
- [3] J. C. Pinto, "A matrix representation of polymer chain size distributions, I Linear polymerization mechanisms at steady-state conditions," *Macromol. Theory Simul.*, vol.10, 2001, pp.79-99.
- [4] T. J. Crowley and K. Y. Choi, "Discrete optimal control of molecular weight distribution in a batch free radical polymerization process," *Ind. Eng. Chem. Res.*, vol.36, 1997, pp.3676-3684.
- [5] M. Vicente, C. Sayer, J. R. Leiza, G. Arzamendi, E. L. Lima, J. C. Pinto and J.M. Asua, "Dynamic optimization of non-linear emulsion copolymerization systems open-loop control of composition and molecular weight distribution," *Chemical Engineering J.*, vol.85, 2002, pp.339-349.
- [6] M. Nele, C. Sayer, J. C. Pinto, "Computation of molecular weight distributions by polynomial approximation with complete adaptation procedures," *Macromol. Theory Simul.*, vol.8, 1999, pp.199-213.
- [7] C. Sayer, P. H. H. Araujo, G. Arzamendi, J. M. Asua, E. L. Lima, J. C. Pinto, "Modeling molecular weight distribution in emulsion polymerization reactions with transfer to polymer," *J. Poly. Sci. A: Poly. Chem.*, vol.39, 2001, pp.3513-3528.
- [8] T. J. Crowley and K. Y. Choi, "Calculation of molecular weight distribution from molecular weight moments in free radical polymerisation," *Ind. Eng. Chem. Res.*, vol.36, 1997, pp. 1419-1423.
- [9] L. Christov, G. Georgiev, "An algorithm for determination of the copolymer molecular weight distribution by Markov chain simulation," *Macromol. Theory Simul.*, vol.4, 1995, pp.177-193.
- [10] G. Storti, G. Polotti, M. Cociani, M. Morbidelli, "Molecular weight distribution in emulsion polymerization. I. the homopolymer case," *J. Poly. Sci. A: Poly. Chem.*, vol.30, 1992, pp.731-750.
- [11] G. Storti, G. Polotti, M. Cociani, M. Morbidelli, "Molecular weight distribution in emulsion polymerization. II. the copolymer case," *J. Poly. Sci. A: Poly. Chem.*, vol.30, 1992, pp.751-777.
- [12] L. Cao, H. Yue, "Mathematical models of microscopic quality for polybutadiene production," *J. Beijing Institute of Chem. Tech.*, vol.21, 1994, pp. 65 - 69.
- [13] H. Yue, L. Cao, "Reaction extent modeling of a butadiene polymerization process," in *IFAC Int. Symp. Advanced Control of Chem. Proc.*, Pisa, Italy, June 14-16, 2000, pp. 1043-1048.
- [14] L. Cao, N. Lu, "Modelling of a continuous PET process," *Journal of System Simulation*, vol.13, 2001, pp.536-538.
- [15] M. Nele, J. C. Pinto, "Molecular-weight multimodality of multiple Flory distributions," *Macromol. Theory Simul.*, vol.11, 2002, pp.293-307.
- [16] A. Salazar, L. M. Gugliotta, J. R. Vega, G. R. Meira, "Molecular weight control in a starved emulsion polymerization of styrene," *Ind Eng Chem Res*, vol.37, 1998, pp.3582-3591.
- [17] M. Vicente, S. BenAmor, L. M. Gugliotta, J.R. Leiza and J. M. Asua, "Control of molecular weight distribution in emulsion polymerisation using on-line reaction calorimetry," *Ind. Eng. Chem. Res.*, vol.40, 2001, pp.218-227.
- [18] T. Takamatsu, S. Shioya and Y. Okada, "Molecular weight distribution control in batch polymerization reactor," *Ind. Eng. Chem. Res.*, vol.27, 1998, pp.93-99.
- [19] J. S. Chang, J. L. Lai, "Computation of optimal temperature policy for molecular weight Control in a batch polymerization reactor," *Ind Eng Chem Res*, vol.31, 1992, pp.861-868.
- [20] K. -Y. Yoo, 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.*, vol.38, 1999, pp.4805-4814.
- [21] T.L. Clarke-Pringle and J.F. MacGregor, "Optimization of molecular-weight distribution using batch-to-batch adjustments," *Ind. Eng. Chem. Res.*, vol.37, 1998, pp.3660-3669.
- [22] A. Echevarria, J. R. Leiza, J. C. de la Cal, J. M. Asua, "Molecular weight distribution control in emulsion polymerization," *AIChE J.*, vol.44, 1998, pp.1667-1679.
- [23] M. F. Ellis, T. W. Taylor and K. F. Jensen, "On-line molecular weight distribution estimation and control in batch polymerisation," *AIChE Journal*, vol.40, 1994, pp.445-462.
- [24] C. Kiparissides, P. Seferlis, G. Mourikas and A. J. Morris, "Online optimisation control of molecular weight properties in batch free-radical polymerisation reactors," *Ind. Eng. Chem. Res.*, vol.41, 2002, pp.6120-6131.
- [25] H. Wang, "Robust control of the output probability density functions for multivariable stochastic systems," *IEEE Transaction on Automatic Control*, vol.44, 1999, pp. 2103-2107.
- [26] H. Wang, *Bounded Dynamic Stochastic Systems: Modelling and Control*, Springer-Verlag London Limited, 2000.
- [27] H. Yue and H. Wang, "Recent developments in stochastic distribution control: a review," *Measurement and Control*, vol.36, 2003, pp.209-215.
- [28] Z. Cheng and S. Li, *Numerical Approximation and Numerical Solutions to Differential Equations*, Xian Jiaotong University Press, Xian, China, 2000.