Modeling and Control of Free Radical Co-Polymerization

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Abstract: In this work, we develop a model and a control system for a 4 monomer acrylate - methacrylate - styrene free-radical co-polymerization reaction. The model was implemented in PREDICI, and parameter estimation was carried out using nonlinear optimization from semi-batch experiments. Molecular weight distribution (MWD) determine utility. Stringent control over reactor conditions is critical. An inventory control scheme was demonstrated to work well for this complex polymerization process. A correlation mapping among the steady state initiator and monomer concentrations, molecular weight distributions and poly-dispersity was used to assign set-points for the inventory controller.

Keywords: polymerization, process control, passivity, automotive paint.

1. INTRODUCTION

We have developed a kinetic model for the free-radical polymerization of the Hydroxypropyl acrylate/ Styrene/ Butyl acylate/ Butyl methacrylate (HPA/ Sty/ BA/ BMA) copolymerization system. Unknown model parameters were estimated using data from semi-batch experiments and an inventory control strategy has been proposed for operation in continuous mode. The kinetic model has been implemented in PREDICI while the control system was implemented in MATLAB. The motivation of this current work stems from the need for effective operation of industrial continuous polymerization reactors to make resins from acrylates, methacrylates and styrene. These resins are an important constituent of automotive coatings.

Homopolymerization and butyl acrylate systems have previously been studied, and rate-constants are available in literature (Beuermann and Buback (2002), Maeder and Gilbert (1998), Curteanu (2003), Curteanu and Bulacovschi (2005)). For example, Congling Quan and Grady (2003) have developed a kinetic model of the high-temperature free-radical polymerization of butyl acrylate capable of predicting polymer molecular weight for a semi-batch process. D. Li and Hutchinson (2005) developed kinetic models for butyl acrylate - butyl methacrylate free radical polymerization system. In this study, the modeling tool PREDICI was used to show good predictions for the outputs, without a need for further refinement of the kinetic parameters. However, it is uncommon to find models with parameters that have been refined using a combination of experimentation and parameter optimization for this system.

The processability and utility of polymer products depend upon reactor operating conditions, and, good control is needed to achieve desired properties (Amrehn (1977), Elicabe and Meira (1988), MacGregor (1986)). Several promising control strategies applied to polymerization processes such as adaptive control (W. R. Cluett (1985)), optimal control (Choi (1997)), output feedback control (Soroush and Zambare (2000)) and nonlinear model predictive control (H. Seki (2001)) have been proposed. None of these approaches however, have been applied to very complex polymerization systems with several monomer inputs and few advanced schemes have found industrial application.

The purpose of our paper is to investigate the feasibility of using inventory control to control polymer properties. Inventory control is based on the idea of manipulating process flows so that the inventories follow their set points. The operator mapping flows to inventories in a macroscopic system is passive and any input strictly passive (ISP) feedback controller can be used in order to achieve input-output stability. The inventory control approach, which can be viewed as a way to chose candidate measured and manipulated variables for output linearization, was proposed by C. A. Farschman (1998). The method has been applied to transport reaction systems by M. Ruszkowski (2005). M. D. Díez (2007) applied the method to control particulate systems and Ydstie and Jiao (2006) applied the method to control a float glass plant for automotive windshield production. The HPA/ Sty/ BA/ BMA copolymerization system central to our work, has not been previously studied in literature from a modeling and control point of view. The model we propose combines literature data with experimental studies using nonlinear optimization.

2. KINETIC MODEL FOR FREE-RADICAL POLYMERIZATION

The model for free-radical polymerization consists of the following sets of reactions: Initiation, Propagation, Chain-transfer and Termination.

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Initiation: The initiator used in this study is Di-*t*-amyl peroxide (DTAP) with a half life of 2 minutes at 160 °C (AkzoNobel (2006)). It decomposes with an efficiency f, to form two free radicals that can initiate propagation by reaction with any of the four monomers present in the system, abstract hydrogen atoms from other species in the system or recombine to form the initiator. Equation (1) represents the initiator decomposition reaction

$$I \xrightarrow{k_d} 2\, f\, I^{\cdot} \tag{1}$$

The dissociation rate constant k_d for DTAP is known to be given by eq (2) (AkzoNobel (2006))

$$k_d = 4.08 \times 10^{15} e^{-\frac{17831.36}{T}} \quad (s^{-1}) \tag{2}$$

The free radicals generated by initiator decomposition can initiate polymerization by reacting with the monomer species present in the solution. This process is described by the initiation reactions as shown in eq (3).

$$I^{\cdot} + M_i \xrightarrow{k_{p_{ii}}} P_1^{i\cdot} \tag{3}$$

Propagation: The polymer chain is then propagated by the products of the initiation reactions by reaction with monomers via the propagation reactions given in eq (4).

$$P_n^{i\cdot} + M_j \xrightarrow{k_{p_{ij}}} P_{n+1}^{j\cdot} \tag{4}$$

The rate constants for the homo-polymerization reactions, $k_{p_{ii}}$ (Asua (2007); D. Li and Hutchinson (2005)) were evaluated at 433 K and 10 psi. $k_{p_{11}}$ was assumed to be identical to $k_{p_{33}}$ because of lack of literature values. $k_{p_{33}}$ (and hence $k_{p_{11}}$) was assumed to be insensitive to pressure. Where possible, $k_{p_{ii}}$ were calculated using (6) and (5).

$$k_{p_{ii}} = A_i\, e^{-\frac{E_i + 1\times 10^{-6} \Delta V_p\, P}{R\, T}} \qquad \forall i \in \{2, 4\} \tag{5}$$

$$k_{p_{ii}} = A\, e^{-\frac{E_a}{R\, T}} \qquad \forall i \in \{1, 3\} \tag{6}$$

The rate constants for the hetero-propagation reactions, $k_{p_{ij}}$, are obtained by defining reactivity ratios, r_{ij}, as shown in (7)

$$r_{ij} = \frac{k_{p_{ii}}}{k_{p_{ij}}} \tag{7}$$

Reactivity ratios were obtained from literature (Ham (1964); Chow (1975)). For the particular set of monomers present in the HPA/Sty/BA/BMA system, it was difficult to obtain reactivity ratios at the desired temperature. The values obtained from literature or calculated from *Q*-*e* data are available at temperatures different from the reactor temperature and hence, were treated as estimates.

Chain Transfer: Chain transfer in the context of free-radical polymerization involves the transfer of the radical from a live polymer chain to any other species present in the system which may be initiator, monomer, solvent molecules, dead polymer or live polymer or another species specifically added to the system which behaves as a chain transfer agent (CTA) (Asua (2007)). In this work, three types of chain transfer reactions are considered - chain transfer to monomer, chain transfer to solvent and chain transfer to live polymer.

Chain Transfer to Monomer: Chain transfer to monomers that contain aliphatic hydrogens such as acrylates and methacrylates involves H-atom abstraction to form an unsaturated radical (Asua (2007)). This unsaturated radical may then undergo further reaction as shown in eq (8). Transfer to monomer rates were not available in literature and were calculated using eq (9).

$$P_n^{i\cdot} + M_j \xrightarrow{k_{tr_{ij}}^{mon}} P_1^{j\cdot} + D_n \tag{8}$$

$$k_{tr_{ij}}^{mon} = \frac{k_{p_{ij}}}{C_{tr}^{mon}} \tag{9}$$

C_{tr}^{mon} is the coefficient for chain-transfer to monomer and typically lies in the range $1 - 50 \times 10^{-5}$ (Asua (2007)). For this work, the value C_{tr}^{mon} was taken to be 1×10^{-5}.

Chain-transfer to solvent: Chain transfer to solvent occurs according to reactions eq (10) and eq (11). In this system, for lack of literature values, we assume that both the solvents behave identically, and hence, have identical rate constants. The rate constants for chain transfer to solvent are obtained from eq (12) using a value for $C_{tr}^{S_k}$ is taken to be 3.16×10^{-5}, which is the logarithmic mean of the range in which it lies in 1×10^{-6} - 1×10^{-3}.

$$P_n^{i\cdot} + S_k \xrightarrow{k_{tr_{ii}}^{S_k}} S_k^{\cdot} + D_n \tag{10}$$

$$S_k^{\cdot} + M_i \xrightarrow{k_{ii}^{S_k}} P_1^{i\cdot} \tag{11}$$

$$k_{tr_{ii}}^{S_k} = \frac{k_{p_{ii}}}{C_{tr}^{S_k}} \tag{12}$$

Further, for lack of literature values, the rate constants $k_{ii}^{S_k}$, are assumed to be identical to the rate constant for propagation.

Chain transfer to Polymer: Chain transfer to polymer occurs according to reaction eq (13). In this system, for lack of literature values, we assume that the chain transfer to polymer is similar to chain transfer to monomer, and hence, has similar rate constants. The rate constants for chain transfer to polymer are obtained from eq (14), using a value of C_{tr}^{pol} equal to 1×10^{-5} which is the logarithmic mean of the range in which it lies 1×10^{-6} - 1×10^{-4}.

$$P_n^{i\cdot} + D_m \xrightarrow{k_{tr_{ij}}^{pol}} P_m^{j\cdot} + D_n \tag{13}$$

$$k_{tr_{ij}}^{pol} = \frac{k_{p_{ij}}}{C_{tr}^{pol}} \tag{14}$$

Termination: Termination occurs via two competing routes - combination (eqn (15)) and disproportionation (eqn (16)). Termination by combination results in the formation of a single dead polymer chain from two live polymer chains, whereas, termination by disproportionation results in the formation of one dead polymer chain and a live polymer chain with an unsaturated terminal residue which may react further.

$$P_n^{i\cdot} + P_r^{j\cdot} \xrightarrow{k_{tc_{ij}}} D_{n+r} \tag{15}$$

$$P_n^{i\cdot} + P_r^{j\cdot} \xrightarrow{k_{td_{ij}}} D_n + D_r \tag{16}$$

The termination rate constant is defined as the sum of the individual rate constants for termination by combination and disproportionation (eq (17)).

$$k_t = k_{tc} + k_{td} \tag{17}$$

Termination rates for free radical polymerization are diffusion controlled (Asua (2007)) and any available estimates are system specific. Thus, for the HPA/Sty/BA/BMA system, termination rates that were obtained from literature (Asua (2007)) were treated as estimates. The rate constant for homo-termination for M_1 was not available in literature and was assumed to be identical to that of M_3.

The relative importance of the mechanism of termination by disproportionation versus termination by combination is measured using a parameter δ, which is defined in eq (18).

$$\delta = \frac{k_{td}}{k_{tc} + k_{td}} \tag{18}$$

δ_{ij} values for styrene and acrylates lie in the range of 0.05 - 0.2 while those for methacrylates lie in the range 0.5 - 0.8 (Asua (2007)). In this work, δ_{ii} for acrylates and styrene is taken to be 0.05, while that for methacrylates is taken as 0.65 (D. Li and Hutchinson (2005)). δ_{ij} value was evaluated as the arithmetic mean of δ_{ii} and δ_{jj}. The values for δ_{ii} were taken to be 0.05 for acrylates, 0.65 for methacrylates.

For the copolymerization reactions, $k_{tc_{ij}}$ and $k_{td_{ij}}$ are calculated using equations (19), (20) and (21). Equation (19) was obtained by generalizing eq (16) from D. Li and Hutchinson (2005) for the case of more than 2 monomers. Here, f_i represents the instantaneous mole fraction of M_i.

$$k_{t,copo_{ij}} = k_{t_{ii}}^{f_i}\, k_{t_{jj}}^{f_j} \tag{19}$$

$$k_{tc_{ij}} = (1 - \delta_{ij})\, k_{t,copo_{ij}} \tag{20}$$

$$k_{td_{ij}} = \delta_{ij}\, k_{t,copo_{ij}} \tag{21}$$

3. EXPERIMENTAL DATA AND PARAMETER ESTIMATION

Polymerization of the HPA/Sty/BA/BMA system was carried out in a well mixed, semi-batch reactor. The feed to the reactor consists of four monomers and an inhibitor dissolved in two solvents. The polymerization is carried out in semi-batch mode, in a 4000 mL vessel isothermally at a temperature of 160 °C and pressure of 10 Psi. The temperature of the vessel is maintained constant using electrical heating.

The reactor is initially charged with solvent mix (76 g S_1, 549.4 g S_2) and heated to 210 °C and then allowed to cool to 160 °C at atmospheric pressure. Feed A (293.6 g S_1 and 65 g I) and Feed B (827.2 g M_1, 393.9 g M_2, 374.2 g M_3 and 374.3 g M_4) are then fed to the reactor simultaneously for a period of 125 min and 120 min respectively. For the semi-batch process the outputs of interest are the residual monomer concentrations, weight average molecular weight (MW_w), number average molecular weight (MW_n), z-average molecular weight (MW_z) and the polydispersity index (PDI). Experimental data was obtained from two different sets of experiments. In one set, only data for the first 1000 seconds was collected and in the second set, data for times from 1000 - 7000 seconds was collected.

This model was implemented in PREDICI (Polyreaction Distributions by Countable System Integration), a comprehensive simulation package for the numerical integration of differential equations arising out of the kinetic equations describing polymerization systems. The results for the integration of the differential equations generated for the semi-batch process model in PREDICI are compared with the experimental data. The integration was performed in the *moment mode* with the values for the rate constants as listed in the tables and the relevant outputs were tracked. The model matches the experimental results poorly using literature data for the kinetic parameters.

Sensitivity and Estimability Analyses: The kinetic model for the HPA/Sty/BA/BMA system has a total of 79 parameters which can be estimated. To improve the fit of the model predictions and the experimental data, parameter estimation was carried out. The set of estimable parameters was obtained following the methodology of K. Zhen Yao (2003). Hence, as a first step toward identifying estimable parameters, a sensitivity study was carried out to identify the sensitivity of the model outputs with respect to the set of parameters as functions of time. The estimable parameters represent the set of parameters that affect the relevant set of outputs the most, among all the parameters, based on the initial values of the parameters at which the sensitivity derivatives are evaluated. The algorithm use to identify this set is called the Estimability analysis (K. Zhen Yao (2003)).

In order to be able to compare the measure of the sensitivity of a parameter, the sensitivity derivatives are non-dimensionlized using a scaling factor φ_{ijk} defined so that

$$\tilde{S}_{ijk} = \varphi_{ijk}\frac{\Delta y_{i,k}}{\Delta\theta_j}, \quad \varphi_{ijk} = \frac{\hat{\theta}_j}{\hat{y}_{i,k}} \tag{22}$$

$\hat{\theta}_j$ and $\hat{y}_{i,k}$ are used for scaling because they reflect the approximate magnitudes of changes in parameter estimates and model predictions respectively. Here, θ_j represents the j^{th} paramater and $y_{i,k}$ represents the value of the i^{th} output at the k^{th} time point.

It is important to note that the number of estimable parameters depends on the number of output variables, the number of observations per output variable and the linear dependence of the parameters on each other. Further, the global identifiability of the parameters depends on the size of the space of input-output variable values in which experimental data is available. For the purpose of estimability calculations, the scaled sensitivity derivatives defined in eq (**??**) were used to construct the *Scaled Sensitivity Matrix,* $\tilde{S}$ given in eq (23).

$$\tilde{S} = \begin{bmatrix} \varphi_{111}\dfrac{\partial y_{1,1}}{\partial\theta_1} & \cdots & \varphi_{1p1}\dfrac{\partial y_{1,1}}{\partial\theta_p} \\ \vdots & \ddots & \vdots \\ \varphi_{r11}\dfrac{\partial y_{r,1}}{\partial\theta_1} & \cdots & \varphi_{rp1}\dfrac{\partial y_{r,1}}{\partial\theta_p} \\ \varphi_{112}\dfrac{\partial y_{1,2}}{\partial\theta_1} & \cdots & \varphi_{1p2}\dfrac{\partial y_{1,2}}{\partial\theta_p} \\ \vdots & \ddots & \vdots \\ \varphi_{r1n}\dfrac{\partial y_{r,n}}{\partial\theta_1} & \cdots & \varphi_{rpn}\dfrac{\partial y_{r,n}}{\partial\theta_p} \end{bmatrix} \tag{23}$$

The cut-off (ϵ) value for which the algorithm is terminated is fairly arbitrary. From the estimability analysis for an $\epsilon = 1 \times 10^{-2}$, only 8 parameters may be estimated with $\mathcal{L} \equiv \{f, k_{t_{22}}, k_{p_{23}}, k_{p_{21}}, k_{p_{11}}, \delta_{22}, k_{p_{31}}, k_{p_{24}}\}$ in order of estimability.

Parameter Estimation: The parameter estimation algorithm was implemented by combining PREDICI and MATLAB using an MS Excel interface. The PREDICI-Excel link was set up to integrate the differential equations based on initial conditions for parameters obtained from literature values. Updated estimates for the parameters were obtained from a weighted non-linear least squares Gauss - Newton algorithm with line search implemented in MATLAB. Table 1 shows the optimized values of the parameters.

Table 1. Optimized values of the estimable parameters

Parameter	Optimal value
f	0.95
$k_{t_{22}}$	1×10^9
$k_{p_{23}}$	8483. 5
$k_{p_{21}}$	426. 6
$k_{p_{11}}$	3.5114×10^5
δ_{22}	0.2
$k_{p_{31}}$	100
$k_{p_{24}}$	2136

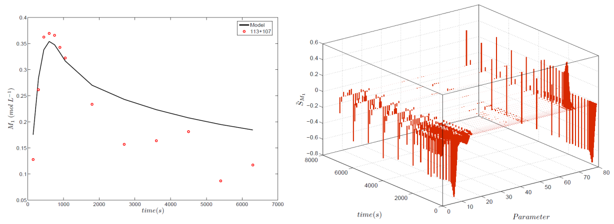

Fig. 1. Model results (solid) vs experiments (circles) for Monomer 1 (Left). Scaled sensitivity for Mononmer 1 shown with respect to time and the 79 parameters (Right).

Comparison plots shows that the model over-predicts some of the outputs and under-predicts some others. A typical result is shown in Figure 3.The sensitivity plot Figure 3 in shows that the sensitivity derivatives for the set of estimable parameters are of the same sign. This necessarily implies, that there is a trade-off between the outputs for which the model over-predicts and those for which the model under-predicts. This means that we can only obtain ‘good’ fits for either the set of outputs which are over-predicted or the set of outputs which are under-predicted. We conclude that the model we have developed misses some reaction mechanisms and that good fit with the semi-batch data is not possible.

4. CONTROL SYSTEM FOR THE COPOLYMERIZATION SYSTEM

Let the vector x represents the state of a process system, m a vector of control variables, d a vector of disturbance variables and y a vector of measurements. An inventory for the system described above is defined to be an additive continuous function $v \colon \mathbf{X} \rightarrow \Re$. For the system described above and using the nomenclature introduced in C. A. Farschman (1998) we have:

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \phi(m, x, d) + p(x), \qquad v = g(z) \tag{24}$$

where $v \in \mathbb{R}_{+}^{dimv}$ are the inventories (mass, component mass,...). C. A. Farschman (1998) showed that the synthetic input and output pair

$$u = \phi + p + \frac{\mathrm{d}v^*}{\mathrm{d}t} \qquad e = (v - v^*) \tag{25}$$

is passive with the storage function $\psi = \frac{1}{2}(v-v^*)^T(v-v^*)$. C. A. Farschman (1998) implement a feedback-feedforward control in the form

$$u = -\mathbf{C}(e) = \phi(m, z, d) + p(z, d) + \frac{\mathrm{d}v^*}{\mathrm{d}t} \tag{26}$$

This control law is input strictly passive (ISP). Khalil (2002) showed that when a passive system is connected in feedback with an ISP controller, the closed loop is also passive. Hence the operator $\mathbf{C}$(e), which maps errors into synthetic controls, should be strictly passive. Most controllers in use are strictly passive. The control law is easy to implement if the inventories can be estimated from process data and the mapping $\phi(m, z, d)$ can be inverted with respect to the control variables m. In the simulations below we use a proportional controller ($\mathbf{C}(e) = Ke$ where K is a positive constant). It can be observed that an inventory controller linearizes the system dynamics.

In our application, the manipulated variables are the input flows of monomers (F_{M_1} to F_{M_4}) and initiator (F_I). The concentrations of the monomers and initiator are selected as the inventories and are forced to track their respective set-points. This gives a 5×5 multivariable control system for our system. Using the differential equation model (Equations 24 and 25), we generate the control equations for the required manipulated variables which force the concentration of the initiator and the respective monomers to its set-point. The control scheme generated is shown below: Control equation for initiator I,

$$F_{I_{in}} = F_{I_{out}} + k_d I V - K(I - I^*) \tag{27}$$

Control equations for the monomers,

$$F_{M_{1,in}} = F_{M_{1,out}} + \Big(2 f k_d I + \sum_{j=1}^{4} P_n^{j\cdot} M_1 (k_{p_{j1}} + $$

$$k_{tr_{j1}} + \sum_{l=1}^{2} k_{11}^{S_l} S_l M_1)\Big) V - K(M_1 - M_1^*) \tag{28}$$

$$F_{M_{2,in}} = F_{M_{2,out}} + \Big(2 f k_d I + \sum_{j=1}^{4} P_n^{j\cdot} M_2 (k_{p_{j2}} + $$

$$k_{tr_{j2}} + \sum_{l=1}^{2} k_{22}^{S_l} S_l M_2)\Big) V - K(M_2 - M_2^*) \tag{29}$$

$$F_{M_{3,in}} = F_{M_{3,out}} + \Big(2 f k_d I + \sum_{j=1}^{4} P_n^{j\cdot} M_3 (k_{p_{j3}} + $$

$$k_{tr_{j3}} + \sum_{l=1}^{2} k_{33}^{S_l} S_l M_3)\Big) V - K(M_3 - M_3^*) \tag{30}$$

$$F_{M_{4,in}} = F_{M_{4,out}} + \Big(2 f k_d I + \sum_{j=1}^{4} P_n^{j\cdot} M_4 (k_{p_{j4}} + $$

$$k_{tr_{j4}} + \sum_{l=1}^{2} k_{44}^{S_l} S_l M_4)\Big) V - K(M_4 - M_4^*) \tag{31}$$

In the above equations, K is a positive constant and I^* and $M_i^* (i \in \{1, 2, 3, 4\})$ are the predetermined set-points for the initiator and monomer concentrations. The theory provides guidance for how to chose K since $1/K$ corresponds to the closed loop time-constant. The control system assumes that the initiator and four monomer concentrations are measured. If these variables are not measured then it is necessary to develop an estimator to estimate these variables from the model.

To illustrate the performance of the control system we have introduced set point changes, first in M_1 at time 330 seconds and then in I at time 510 seconds to study how the system responds to these set point changes after the effect of initial conditions have died out. The results for the setpoint tracking performance for initiator and 3 monomers are shown in Figure 2[1]. The proportional gain for all four controllers is $K = 0.01$ so that the closed loop time constant for all the four outputs is equal to 100 secs. The results show that the inventory controller decouples the response so that a setpoint change in one variable does not lead to a change in the other variables[2]. In practice there will be a mismatch between the real system and the controller equations and it may not be possible to achieve perfect decoupling.

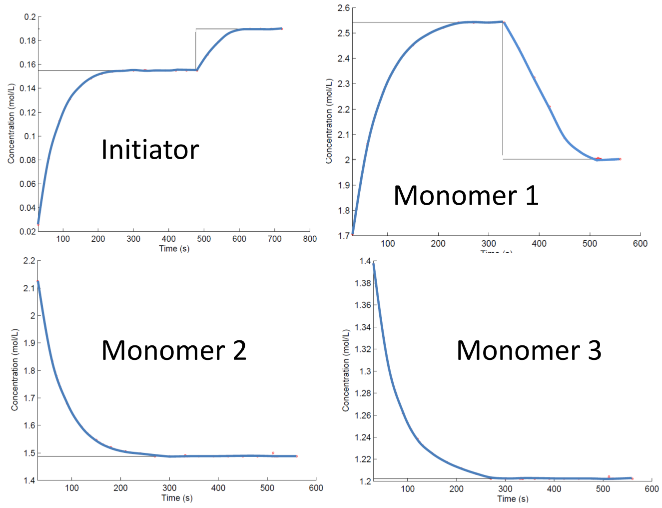

Fig. 2. Initiator, 3 Monomer Concentrations and Setpoints

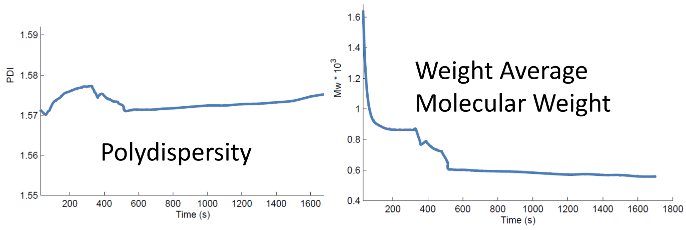

Fig. 3. Polydispersity and Weight Average Molecular Weight

5. THE CORRELATION MAPPING

The inventory control scheme allows the user to define setpoints in terms of inventories. In our case these are the initiator concentration and concentrations of monomers inside the reactor. These variables are related to the flow variables in a passive manner and they are easy to control. In practice it is often necessary to control secondary variables like molecular weight and polydispersity. These variables are more difficult to control since the relative degree of the control system now may be much higher. In this work we have solved the problem by developing a correlation mapping to identify how the steady state monomer set points correspond to target molecular weights and polydispersity for use in the inventory control scheme. The idea now is to use the mapping to generate inventory setpoint and control to the calculated setpoints. Model uncertainty can be compensated for using a separate estimation algorithm to fit the mapping to the data in real time.

One example of such a correlation is shown in Figure 4. The x-axis consists of the different molecular weight distributions. the numbers 1 to 3 are indices corresponding to M_w, M_n and M_z respectively. The z-axis shows the number value of each of the molecular weight distributions, while the y-axis shows the values of the input flow rates. These maps provide a means to chose set points for monomer inventories to achieve desired polymer properties. Similar plots were developed for the initiator and the other monomers.

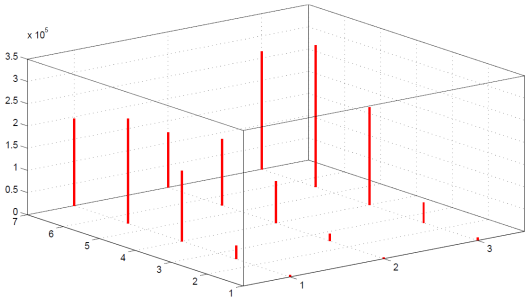

Fig. 4. M1-MWD correlation plot

Table 2. Simulation Results for varying M1

Flow rate of $M1$(kg/s)	M_w	M_n	M_z
1	4574	2439	6844
2.5	30003	15813	44928
4	158560	93652	219070
5.5	235980	149230	319110
7	195670	123340	264750

6. CONCLUSIONS

A kinetic model for free radical polymerization of the monomers in HPA/Sty/BA/BMA was developed and implemented in PREDICI. Kinetic parameters obtained from literature were found to predict the experimental data poorly. Further refinement was carried by implementing a parameter estimation algorithm based on nonlinear optimization. A sensitivity study and an estimability analysis were carried out to identify the set of estimable parameters. The estimable parameters were then optimized using a weighted, constrained non-linear least squares Gauss-Newton algorithm with backtracking line search. The optimized values of the parameters were found to yield better fits for the experimental data. However, there seems to be

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[1] Due to space limitation we do not show the 4th monomer which is similar to the third and fourth.

[2] The simulated controller used a sampling time of 30 sec during the period when the setpoints were constant. It was decreased to one sample every 2 seconds for a brief period during the setpoint change

a trade-off between the two types of outputs (molecular weights and residual monomer concentrations) that may be optimized. It is possible to fit only either set of outputs very well, using this model. Certain features of the experimental data were not captured, indicating that the need for further refinement of the model by adding other reactions that are relevant to the process. An inventory control approach was proposed to force monomer concentrations to track some pre-determined set points. These set points can be appropriately selected based on the requirements using a correlation mapping such as the one performed in this study.

NOMENCLATURE

I ≡ Initiator
M_i, M_j ≡ Monomer
S_k ≡ Solvent
$P_n^{i\cdot}$, $P_r^{i\cdot}$, $P_{n+r}^{i\cdot}$, $P_m^{i\cdot}$ ≡ Live Polymer Chain
D_n, D_r, D_m, D_{n+r} ≡ Dead Polymer Chain
φ_{ijk} ≡ Scaling factor

Sets

$\mathcal{M} \equiv \{M_1, M_2, M_3, M_4\}$ ≡ set of all monomers
$\mathcal{A} \equiv \{M_1, M_2, M_3\}$ ≡ set of Acrylate monomers
$\mathcal{MA} \equiv \{M_4\}$ ≡ the set of Methacrylate monomers
$\mathcal{P} \equiv \{P_n^{i\cdot}, P_r^{i\cdot}, P_m^{i\cdot}, P_{n+r}^{i\cdot}\}$ represents the set of Live Polymer Chains
$\mathcal{S} \equiv \{S_1, S_2\}$ represents the set of solvents
$\mathcal{D} \equiv \{D_n, D_r, D_m, D_{n+r}\}$ represents the set of dead polymer chains

Indices

$i,\ j \in \{1,2,3,4\}, \quad k \in \{1,2\}, \quad n,\ r,\ m \in [1,\dots,\infty)$

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