OPTIMAL CONTROL OF EMULSION COPOLYMERIZATION: APPLICATION TO A PILOT-SCALE REACTOR UNDER A DCS ENVIRONMENT

B. Alhamad, R.Willis, J. A. Romagnoli*, V. G. Gomes

Laboratory for Process Systems Engineering (PSE)
Department of Chemical Engineering,
The University of Sydney
NSW 2006, Australia

ABSTRACT

A detailed model was developed for the emulsion copolymerization of styrene and MMA to predict the evolution of the particle size distribution (PSD) and molecular weight distribution (MWD) over the entire range of monomer conversion. A system exhibiting zero-one kinetics was employed. The model was used to optimise the emulsion copolymerization process in order to maximize particle size polydispersity index (PSPI) and Molecular weight polydispersity index (MWPI). Five variables were used as manipulated variables, styrene monomer feed rate, MMA monomer feed rate, surfactant feed rate, initiator feed rate, and the temperature of the reaction by controlling the jacket temperature. The results from optimization were validated against experimental and found to show good agreement. The whole strategy has been developed within a gPROM-Excel/OPC-DCS environment allowing for direct transfer of the technology to a general industrial application.

Keywords: Optimization, Copolymerization, PSPI, PSD, MWPI, MWD

1. INTRODUCTION

Emulsion copolymerisation is widely used in industry to produce products ranging from paints, adhesives through to tyres and wet-suits. To improve the efficiency and safety of the process, model development becomes necessary to ensure optimized processes and product quality. However, the modelling of emulsion copolymerisation is a challenging task, since it involves complex physico-chemical sub-processes, some of which are not well-understood. Especially, the particle formation mechanism and inclusion of two or monomers increases the complexity. Moreover, it is a multi-phase environment consisting of an aqueous phase, surfactants, initiators, buffers, monomer droplets and polymer particles. The reaction mechanisms are yet to be fully elucidated under various reaction conditions. The goal is to develop a practical tool to predict polymer production rate and key product attributes for ultimate application in industry.

There is relatively little literature on the control of the full PSD, and it is even littler for the copolymerization process. In contrast, there is a considerable number of studies reported in the literature on the control of lumped properties. (Semino and Ray, 1995b, Semino and Ray, 1995a) addressed the very pertinent issue of the controllability of population balance systems. They found in their system the controllability of the distributions for the unconstrained case is ensured by employing the feed concentration of surfactant, initiator and inhibitor as manipulated variables. (Kozub and Macgregor, 1992) applied the idea of a two-tier control strategy-open loop feed forward generation of an optimal recipe, which is then recomputed online based on feedback from process measurements to a semibatch emulsion polymerization system , for the multivariable control of composition and average molecular weight. (Saldivar and Ray, 1997) studied the control of copolymer composition and averaged molecular weight for semi-continuous emulsion polymerization. (Clarke-Pringle and MacGregor, 1998) presented a batch to batch adjustment strategy for the control of molecular weight distribution (MWD) to reoptimize the inputs for the next batch based on end-point measurement of the MWD. (Crowley et al., 2001) used a hybrid modelling strategy in batch to batch optimization for PSD control. (Crowley et al., 2000) are among the first researchers to address the control of the full particle size distribution. (Immanuel and Doyle, 2002) presented an open loop optimization study for the control of the full PSD in the emulsion copolymerization of vinyl acetate and butyl acrylate. (Zeaiter et al., 2002) developed a model for emulsion polymerization of styrene to optimise and control the PSD.

A comprehensive dynamic model for a copolymerization reactor was developed by (Alhamad et al., 2003, Alhamad et al., 2004), which allows the prediction of key polymer properties such as: average particle size, conversion, PSD, MWD, M_n, and M_w. A modified zero-one kinetic model is used in the formulation allowing prediction of secondary nucleation under starving monomer conditions. In this work, based on this comprehensive model, a multi-layer model-based framework was developed and implemented within an industrial distributed control system environment, to optimize the Particle Size Polydispersity Index (PSPI) and Molecular Weight Polydispersity Index (MWPI).

2. EXPERIMENTAL SETUP

2.1 Data Acquisition and Control Environment

The polymer lab consists of a 5 litre jacketed stirred reactor; a Julabo heating circulator to provide heat to the reactor through the jacket; 4 solenoid dosing pumps for providing the monomers, surfactant and initiator to the reactor; 3 RTDs for monitoring temperature; and 4 precision balances to determine the quantities of the reactants used. The polymer lab is controlled by a Honeywell C200 controller on a Honeywell Plantscape DCS. The uploading and configuration of the control schemes to the controller is done using the Control Builder from the Honeywell Plantscape r500.1. The polymer lab I/O consists of 3 RTDs, 3 analogue inputs, 5 analogue outputs, 4 digital outputs and a 4 port serial to Ethernet converter. The RTDs are the jacket inlet temperature, the jacket outlet temperature, and the internal reactor temperature. The analogue inputs are the impeller speed within the reactor; the Julabo heating circulator operating temperature; and the user specified setpoint temperature from the Julabo. The analogue outputs are setpoint temperature for the Julabo heating circulator, and the dosing frequencies or stroke rates for each of the dosing pumps. The digital outputs are used to stop or resume the dosing pumps from pumping. The 4 port serial to Ethernet converter is used in conjunction with software developed within the PSE group to send flowrates or differential weight readings from the balances to the controller. All the manipulated variables profiles are put into the Control Builder to be operated automatically.

Data Acquisition and control of the polymerization reactor was performed using Honeywell's Plantscape R300 software residing on a server. This developed set-up allows the configuration and implementation of multilayer control scheme for advanced operation and control of the process and a client station is used for operator manipulations. The lower level control consists of a series of conventional PID controllers to control the monomer feeds, surfactant, and initiator as well as to control the temperature. The inputs to the PID controllers are the set-point (upper-layer) provided from either one of the following three sources: 1) *Manual set-point:* this is used when the key polymerization variables are required to be set at a constant temperature (used during model validation), 2) *Rampsoak set-point:* this is a set-point varying with time and it changes according to an operator built-in profile (used during off-line optimization) and 3) *External set-point:* this is used when an external program is used to provide the set-point (this is the case in our environment when implementing the real-time optimizing control using an MPC strategy).
The model developed is used within the proposed strategy to provide the optimal set-points (off-line) in case 2 and to provide optimal trajectories and as a real-time soft sensor to control PSD and MWD in case 3.

An intelligent control hierarchy is formulated for such distributed parameter system incorporating three different levels; offline optimization, on-line DMC and regulatory control successively. The novelty of this approach is the incorporation of a validated high order dynamic model as a soft sensor for on-line feedback of the PSD and MWD. Figure 1 shows the schematic diagram of the overall control hierarchy.

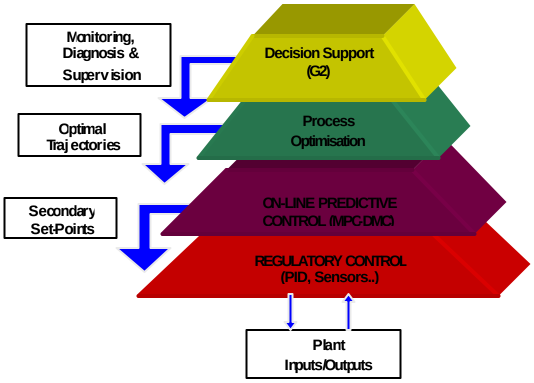

Figure 1: Overall Control Hierarchy

2.2 Sample Preparation and Characterization

Styrene (99% purity, inhibited with 4-tert-butylcatechol) and MMA (99% purity, inhibited with hydroquinone) monomers were obtained from Fluka, while the water used was purified to a Milli-Q standard. Surfactant (sodium dodecyl sulfate) and initiator (potassium persulfate) were both obtained from Sigma-Aldrich. Semi-batch emulsion copolymerisations of styrene and MMA were carried out at 70, 75, 80 and 85 ^{o}C under slight nitrogen pressure. Note that the monomers were purifed using an inhibitor column, which is also obtained from Sigma Aldrich. Monomer conversion was gravimetrically determined off-line by taking samples from the reactor. The MWD of the polymer samples was determined off-line by GPC, while most of the PSDs were obtained using the zetasizer and the CHDF.

3. OPTIMAL CONTROL STUDIES

3.1. Model Development

The population balance equations (PBE), based on particle formation through both homogeneous and micellar nucleation, provide estimates for the PSD. The PBEs for the three types of particles: those containing no radicals (type n_0 particles), those containing one monomeric radical (type n_1^M particles), and those containing one polymeric radical (type n_1^P particles), are given by:

$$\begin{aligned}\frac{\partial n_1^P(V,t)}{\partial t} &= k_p^1 C_P n_1^M + r_{init} n_0 - r n_1^P - k_{tr} C_P n_1^P - \frac{\partial (K n_1^P)}{\partial V} \\ &+ d(V-V_o)\left[C_{micelle} \sum_{i=z}^{j_{crit}-1} \left[k_{e,micelle}^{i} [IM_i]\right] - k_{p,aq}^{j_{crit-1}} C_W [IM_{j_{crit}-1}]\right] \\ &+ \int_0^\infty B(V,V-V')[n_0(V')n_1^P(V-V') + n_1^P(V')n_0(V-V')]dV' \\ &- n_1^P(V)\int_0^\infty B(V,V')[n_0(V') + n_1^P(V')]dV' \qquad \textbf{(1)}\end{aligned}$$

$$\begin{aligned}\frac{\partial n_0(V,t)}{\partial t} &= r[n_1^P + n_1^M - n_0] + k_{dM} n_1^M + \int_0^\infty B(V,V-V')[n_0(V')n_0(V-V') \\ &+ n_1^P(V')n_1^P(V-V')]dV' - n_0(V)\int_0^\infty B(V,V')[n_0(V') + n_1^P(V')]dV' \qquad \textbf{(2)}\end{aligned}$$

$$\frac{\partial n_1^M(V,t)}{\partial t} = k_{tr} C_P n_1^P + k_{eE}[E]n_0 - (k_p^1 C_P + k_{dM} + r)n_1^M \qquad \textbf{(3)}$$

Total number particles are given by:

$$n(V,t) = n_1^P(V,t) + n_0(V,t) + n_1^M(V,t) \qquad \textbf{(4)}$$

The term $C_{micelle}$ is the micelle concentration, which is determined by the rate of surfactant consumption. The terms k_p, k_e, k_{tr}, are the kinetic rate coefficients for the propagation, entry and transfer respectively.

The transient monomer molar balance for semi-batch reactor operation is given by:

$$\frac{dN_{m,A}}{dt} = F_{mA,in} - R_{pAp}V_p - R_{pAw}V_w \qquad \textbf{(5)}$$

where $R_{p,A,p}$ and $R_{p,A,w}$ are the rate of reactions of reactions of the polymer for monomer A and B in the particle and water phase, respectively. The rate of constant are defined as follows:

$$R_{pAp} = \frac{\left(kp_{AA} \cdot kp_{BB} \cdot (r_A \cdot C_{pA}{}^2 + C_{pA} \cdot C_{pB})\right)}{k_{pBB} \cdot r_A \cdot C_{pA} + k_{pAA} \cdot r_B \cdot C_{pB}} \bullet \frac{\bar{n} \cdot N_{tot}}{N_a \cdot V_p} \qquad \textbf{(6)}$$

$$R_{pAw} = \frac{\left(kp_{AA} \cdot kp_{BB} \cdot (r_A \cdot C_{wA}{}^2 + C_{wA} \cdot C_{wB})\right)}{k_{pBB} \cdot r_A \cdot C_{wA} + k_{pAA} \cdot r_B \cdot C_{wB}} \bullet T \qquad \textbf{(7)}$$

where k_p is the propagation coefficient, N_{tot} is the total number of particles, N_a is the Avogadro's number, r_A is the reactivity ratio, T is the total number of radicals, and V_p is the volumer of the polymer phase.

The volume of polymer particles is defined for two separate regimes: when monomer droplets exit (*Vp*) and when there are no longer any droplets. So the copolymer particle volume is calculated by two different equations in two stages. The first regime is calculated by:

$$\frac{dV_p}{dt} = \frac{M_{w,A} \cdot (R_{p,A,p} \cdot V_p + R_{p,A,w} \cdot V_w) + M_{w,B} \cdot (R_{p,B,p} \cdot V_p + R_{p,B,w} \cdot V_w)}{d_p} \qquad \textbf{(8)}$$

whereas the second regime is calculated by the following:

$$\begin{aligned}\frac{dV_p}{dt} &= \frac{M_{w,A} \cdot (R_{p,A,p} \cdot V_p + R_{p,A,w} \cdot V_w) + M_{w,B} \cdot (R_{p,B,p} \cdot V_p + R_{p,B,w} \cdot V_w)}{d_p} \qquad \textbf{(9)} \\ &- \left[M_{w,A} \cdot R_{p,A,p} \cdot V_p \cdot \left(\frac{1}{d_{m,A}} - \frac{1}{d_{p,A}}\right) + M_{w,B} \cdot R_{p,B,p} \cdot V_p \cdot \left(\frac{1}{d_{m,B}} - \frac{1}{d_{p,B}}\right)\right]\end{aligned}$$

P_A and P_B are the time-averaged probabilities of finding a free radical with ultimate unit of type A and B, respectively. They are calculated as follows:

$$P_A = \frac{k_{pBA} \cdot C_{p,A}}{k_{pBA} \cdot C_{p,A} + k_{pAB} \cdot C_{p,B}} \qquad \textbf{(10)}$$

$$P_B = 1 - P_A \qquad \textbf{(11)}$$

where $C_{p,A}$ and $C_{p,B}$ are the concentrations of monomers A and B in the particle phase. They are obtained by using the partition coefficients (K) between the three phases, water (w), monomer (m) and particles (p).

$$C_{p,A} = MIN\left(C_{p,A}^{sat}, \frac{N_{m,A}}{K_{A,mw} \cdot K_{A,wp} \cdot V_m + K_{A,wp} \cdot V_w + V_p}\right) \qquad \textbf{(12)}$$

where N_m is the number of moles and V is the volume.

3.2 Optimization Strategy Setup

As stated previously, the main objective in this study is to investigate the use of a detailed (validated) mechanistic model (Alhamad et al., 2003, Alhamad et al., 2004) to develop an advanced control strategy for the optimal operation of the reactor. The proposed strategy will provide set-point trajectories for the manipulated variables (for example, monomer feed rate and reactor temperature) so as to ensure the production of a copolymer with a defined PSD and MWD in the minimum reaction time.

Several objective functions were studied, in terms of both PS and MW. For the purpose of obtaining the desired broad PSD, a polydispersity index was chosen as an objective function to be maximized. For MW both MWPI as well as simply the molecular weight were investigated as the objective functions to be optimized. The particle concentration densities, particle diameter, temperature shift, copolymer composition and the total amount of monomer to be added to the reactor were included as constraints along with the reaction time.

The objective functions are optimized by using the five manipulated variables, styrene feed rate, MMA feed rate, surfactant feed rate, and initiator feed rate and temperature. The temperature was used as a manipulated variable for maximizing MWPI, since the molecular weight is largely affected by the temperature, rather than the PSPI, which is not significantly affected by the temperature. The MWPI was also maximized without the temperature as a manipulated variable investigate the actual effect of temperature.

A polydispersity index indicates the spread of the distribution. The particle size polydispersity index (PSPI) is estimated as follows:

$$PSPI = \frac{<r^2>}{<r>^2} \qquad \textbf{(13)}$$

The number average radius was computed from

$$\langle r \rangle = \frac{\sum (r_{uns} \cdot n)}{\sum n} \qquad \textbf{(14)}$$

The objective functions to be optimized were defined as: Max [PSPI(r, t_{final})] and Max[MWPI(r, m, t_{final}]. Where: m is the molecular weight and t_{final} is the processing time. For operational reasons, the monomers, surfactant, initiator feed rates and temperature (for molecular weight optimisation) were specified within the following upper and lower bounds:

$$0.12815\ g/s \le F_{m,A} \le 0.2\ g/s \qquad \textbf{(15)}$$

$$0.12815\ g/s \le F_{m,B} \le 0.2\ g/s \qquad \textbf{(16)}$$

$$0.12815\ g/s \le F_S \le 0.2\ g/s \qquad \textbf{(17)}$$

$$0.12815\ g/s \le F_I \le 0.2 g/s \qquad \textbf{(18)}$$

$$343\ ^oC \le T_{reac} \le 358\ ^oC \qquad \textbf{(19)}$$

The final PSD shape was included in this optimisation in the form of end point inequality constraints formulated in terms of the final molar concentration density of particles

$$n_{\min} \le n(r, t_{final}) \le n_{\max} \qquad \textbf{(20)}$$

Above, n_{min} and n_{max} denote the lower and upper limits, respectively, and were specified to match the required distribution. The final copolymer composition required was 50/50, so a condition was specified as follows:

$$0.49 \le \overline{F} \le 0.51 \qquad \textbf{(21)}$$

Since this is a semibatch process with monomer fed to the reactor, the maximization of PSPI and MWPI must also be subjected to additional constraints to account for the total amount of monomer in the recipe ($N_{m,T}$), and the total reaction time. These constraints are defined as follows:

$$N_{m,T} = 8 \text{ mol and } t_{\min} \le t \le t_{\max} \qquad \textbf{(22)}$$

The solution to this constrained optimal control problem was obtained via an interface to the gOPT dynamic optimization code. Five bounded time intervals (of initially equal duration) were specified for the manipulated variables, $F_{m,A}$, $F_{m,B}$, F_S, F_I and T_{reac}, such that it remained constant over a certain time interval, before moving discretely to the value for the next interval. A violation over 0.1°C is put for the temperature, so that the temperature when jumping from one temperature to the other, the temperature rises gradually.

3.3 Results and Discussions

As discussed, the optimal control strategy involved the computation of a monomer feed trajectory which would drive the process to give a PSD with a specified broad distribution. The required PSD was generated by fixing the reactor temperature at 75 °C, and allowing a 25 min (batch) pre-period to allow for initial particle nucleation, before any further addition. Implementation of the optimal control strategy for the reminder of the run was fully automatically achieved through the control and data acquisition strategy developed, using the Rampsoak set-point option from operator built-in profiles. The final shape of the experimental PSD, MWPI and MW was in good agreement with the simulation results. Figure 2 shows the results obtained to maximize PSPI. Figure 3 shows the results obtained in order to maximize MWPI using only the flowrates, that is, temperature was not used as a manipulated variable. Figure 4was used to maximize MWPI using the additional variable, which is the temperature. The MWD, average particle size, PSD and conversion were used as a validation to the optimization process. It can be seen that on maximizing PSPI, a bimodal distribution was produced, since the requirement was to have a very broad distribution. Another observation regarding the molecular weight is that the molecular weight produced with the temperature as a variable was much larger, and that shows the great effect that temperature has on molecular weight. It has also been observed that maximizing the MWPI would result in the maximizing of the M_n

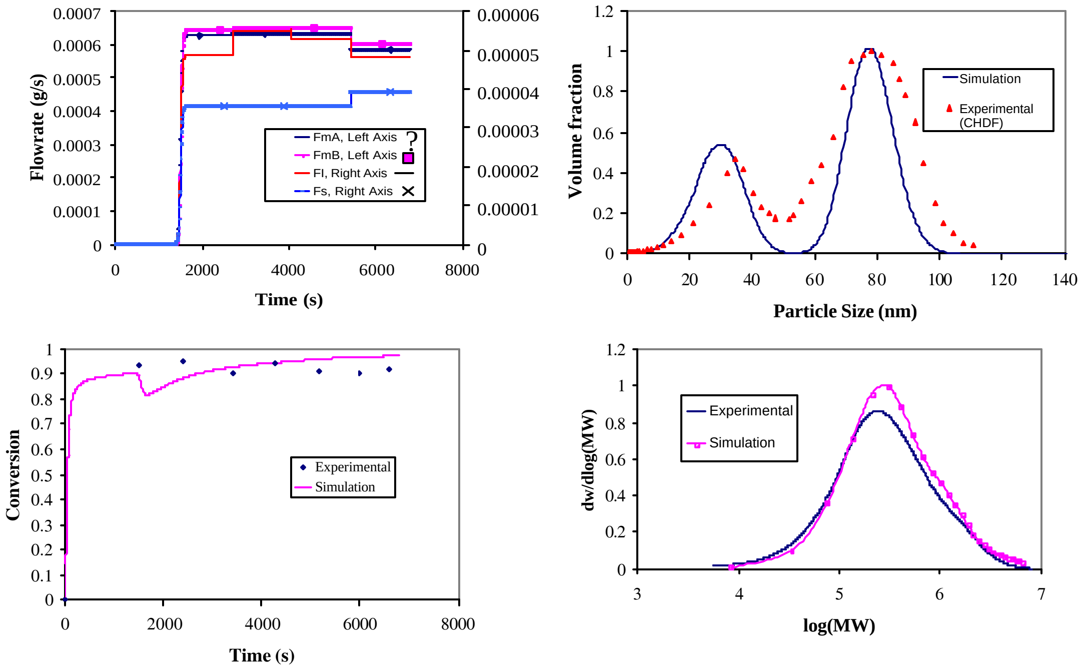

Figure 2. Validation of optimal trajectories to maximize .(a) manipulated variables optimal profile; (b) PSD; (c) Conversion; (d) MWD

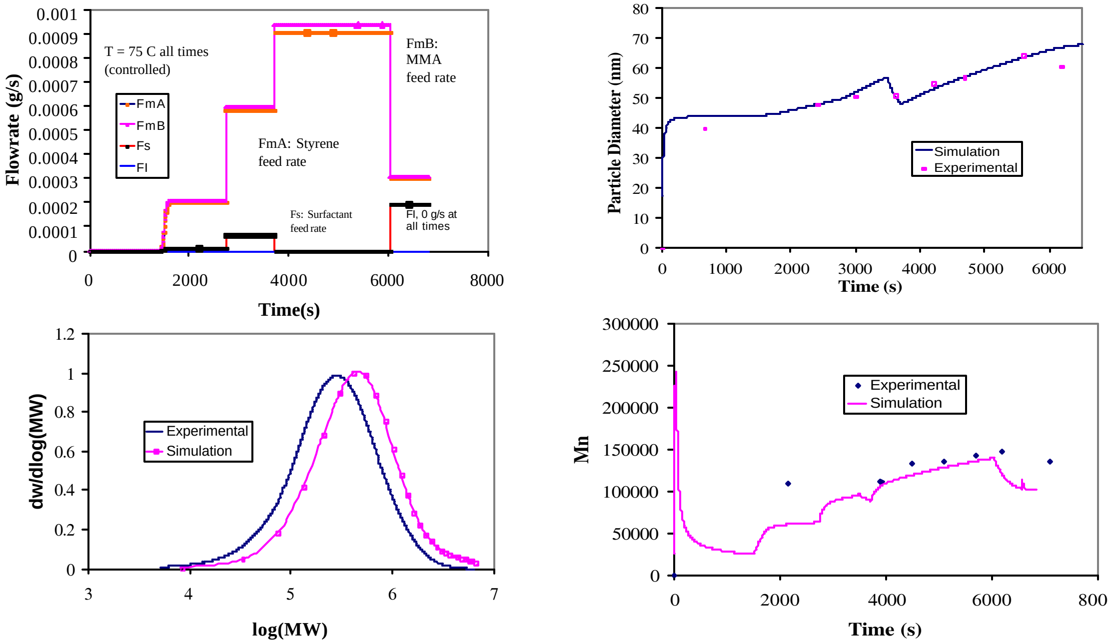

Figure 3: Validation of optimal trajectories to maximize MWPI. (a) manipulated variables optimal profile; (b) Particle diameter; (c) MWD; (d) M_n

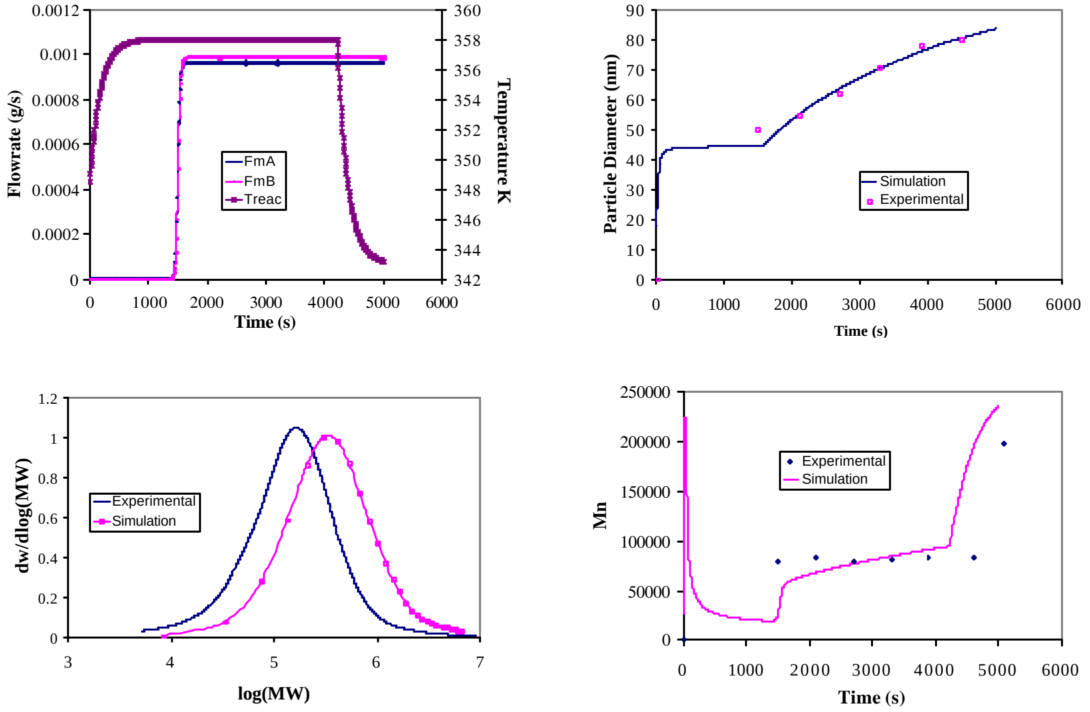

Figure 4: Validation of optimal trajectories to maximize M_n. (a) manipulated variables optimal profile; (b) Particle Diameter; (c) MWD (d) M_n

CONCLUSIONS

A model-based framework to optimally control key copolymerization variables has been developed and implemented within a pilot-scale environment under DCS. Validation results show very good agreement between model prediction and experimental runs. Work is currently underway to implement a simultaneous MWD/PSD control strategy in an on-line environment within a model predictive control scheme.

REFERENCES

Alhamad, B., Romagnoli, J. A. and Gomes, V. G. (2003) In *31st Australasian Chemical Engineering Conference CHEMECA*, Adelaide, South Australia, pp. 138.

Alhamad, B., Willis, R., Romagnoli, J. A. and Gomes, V. G. (2004) In *ESCAPE-14*,Lisbon.

Clarke-Pringle, T. L. and MacGregor, J. F. (1998) *Industrial & Engineering Chemistry Research*, **37**, 3660-3669.

Crowley, T. J., Harrison, C. A. and Doyle III, F. J. (2001) In *2001 American Control Conference, Jun 25-27 2001*, Vol. 2 Institute of Electrical and Electronics Engineers Inc., Arlington, VA, pp. 981-986.

Crowley, T. J., Meadows, E. S., Kostoulas, E. and Doyle, F. J. I. (2000) *Journal of Process Control 14th IFAC World Congress, Jul 5-Jul 9 1999*, **10**, 419-432.

Immanuel, C. D. and Doyle, F. J. I. (2002) *Chemical Engineering Science*, **57**, 4415-4427.

Kozub, D.and Macgregor, J. F. (1992) *Chemical Engineering Science*, **47**, 929-942.

Saldivar, E. and Ray, W. H. (1997) *Aiche Journal*, **43**, 2021-2033.

Semino, D. and Ray, W. H. (1995a) *Chemical Engineering Science*, **50**, 1805-1824.

Semino, D. and Ray, W. H. (1995b) Chemical Engineering Science, 50, 1825-1839.

Zeaiter, J., Romagnoli, J. A., Barton, G. W., Gomes, V. G., Hawkett, B. S. and Gilbert, R. G. (2002) In Chemical Engineering Science, Vol. 57 Elsevier Science Ltd, pp. 2955-2969.