

**SCHEDULED OPTIMIZATION OF AN MMA  
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**Abstract:** In this study, attention is focused on the design of a scheduled-optimization strategy for a batch MMA polymerization process. The objective of this strategy is to track an optimal temperature, despite uncertainties in the heat transfer and the gel effect. This strategy makes use of an (uncertain) physical model and on-line temperature measurements. The uncertain parameters are re-estimated on line, so as the optimal temperature trajectory. The good decoupling (in time) between the two major disturbances allows good performance to be achieved.

**Keywords:** Polymerization, batch control, process control, optimization.

**1. INTRODUCTION**

From an industrial viewpoint, the methyl methacrylate (or *MMA*, in the abbreviated form) polymer compounds hold an important place in the production of plastics. In this area as in other sectors of the chemical industry, batch processes have gained much interest essentially thanks to better production flexibility, easier scale-up from laboratory setup and increased safety (reduced dimensions).

From a scientific viewpoint, polymerization processes are relevant, essentially because complex temperature-dependent chain reactions and heat

transfers lead to highly nonlinear algebraic and differential equations. In addition, control design for batch processes is a challenging task since 1) in pure batch, no influential input (e.g., feed) allows to alter the reactor contents, only the reaction rates can be modified by adjustment of the reactor temperature 2) only a few variables (temperatures) can be measured on line, the polymer properties being usually measured at the end of the batch only. Batch processes are often run in open loop using a predefined (often heuristic) trajectory. Several variants of this strategy are proposed in the literature, such as classical feedback allowing an optimal trajectory to be tracked, repeated estimation-optimization during the batch, batchwise enhancement of the trajectories (run-to-run optimization). Whatever the technique, the calculation of a trajectory satisfying well-defined

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end-of-batch properties requires that a physical, first-principles model of the process be developed. However, due to time and cost constraints, the model is often of limited accuracy, so that the control strategy has to take the model-plant mismatch into account and to enhance robustness, eventually in detriment of nominal performance. These industrial and scientific aspects are abundantly covered in previous works, such as (Kiparissides, 1996) and (Terwiesch *et al.*, 1994; Bonvin, 1998) and the references therein.

An MMA batch polymerization process is under study, which is a laboratory scale plant at the Aristotle University (Thessaloniki, Greece), and a nonlinear state space model is used, which describes the gel effect using a deterministic law (Kiparissides *et al.*, 2002; Mourikas, 1998). In contrast with G. Mourikas' approach, attention is focused on the more common situation where only temperature measurements are available on line and the model is subject to two sources of uncertainty: one affects a gel effect parameter (e.g., due to an inaccurate identification), the other influences the heat exchange coefficient between the reactor wall and the solution (e.g., due to fouling). When a robust worst-case approach is used, improved performance is achieved in the pure open-loop variant (Lepore *et al.*, 2004; Nagy and Braatz, 2004), i.e., the best input profile is calculated so as to minimize the worst criterion value obtained when the gel parameter ranges within specified limits (min-max problem). However, in the less conservative variant, which uses a feedback controller for immediate disturbance rejection, the feedback required for the gel effect must be positive and cannot deal with the heat exchange disturbance. For these reasons, we have selected a scheduled-optimization approach, which uses on-line measurements in order to estimate both the time-varying parameters (gel effect and heat exchange) and to update the model, so that a new optimal trajectory is calculated. If the heat exchange disturbance occurs batchwise, decoupled effects of the disturbances on the solution temperature are used to obtain accurate, reliable estimates of the coefficients.

The paper is organized as follows. In section 2, the process is described and a nonlinear state space model is derived from mass and energy balances. Section 3 is devoted to the definition of the control objectives. Section 4 describes and assesses the worst-case strategy used to incorporate the model uncertainties. In section 5, the principle of the scheduled-optimization strategy is presented and some results are discussed. Finally, conclusions are drawn in section 6.

## 2. PROCESS DESCRIPTION AND MODELLING

The reactor depicted in figure 1 contains the reactant (monomer) and the product (polymer) just mixed with water. The solution is continuously stirred, and its temperature is adjusted by feeding the jacket with hot and cold water. Two independent valves are regulated by a split range controller (low-level control of the jacket temperature  $T_J$ ). The main process characteristics are:

- the process is of the bulk type, i.e., the solution consists of pure monomer and water, no other agent or solvent is added,
- a homogeneous mixture is considered, i.e., the monomer is miscible with its polymer,
- the reaction kinetics is based on a free-radical mechanism, i.e., intermediate, active radicals, generated from a monomer unit and a catalyst (initiator), grow or propagate by addition of monomer units, then terminate into polymer chains.

In this process, the viscosity of the mix causes poor heat transfer characteristics within the solution and with the jacket (due to polymer deposits on the reactor wall).

A particular phenomenon, well known as the *gel effect* may cause, if ignored, poor properties of the final product or very low conversion. In fact, when the monomer conversion is sufficient, the termination reactions become *diffusion-controlled*, i.e., large free-radical chains terminate hardly, whereas the propagation phenomenon accelerates. A natural counteraction consists in heating the solution.

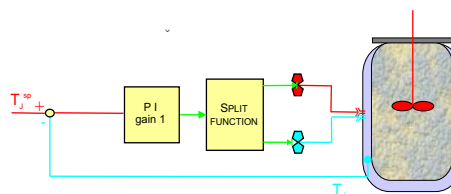


Fig. 1. Polymerization reactor: equipment and low-level control.

The process objectives are mainly concerned with final-product quality (specific physical properties), process performance (conversion percentage and/or batch time), safety (temperature limitations). The disturbances (model uncertainties) affecting the process behaviour are of several types: wrong initial conditions (e.g., initiator), varying coefficients due to impurities or polymer deposits (heat exchange between the metal wall and the solution, initiator efficiency), poor accuracy when identifying the gel effect. Only temperature measurements are available at sufficient rate and reliable, whereas the polymer properties are accurately measured at the end of the batch only.

Denoting  $R_i$  and  $P_i$  the molar concentration of the free-radical and the polymer species, respectively, the general  $k^{\text{th}}$  noncentered moments are:

$$k = \sum_{i=1}^{\infty} i^k R_i \quad (1a)$$

$$k = \sum_{i=1}^{\infty} i^k P_i. \quad (1b)$$

With  $\boldsymbol{\lambda} = [0 \ 1 \ 2]^T$  and  $\boldsymbol{\mu} = [0 \ 1 \ 2]^T$ , mass balances expressed in terms of the first three noncentered moments lead to the following set of differential-algebraic equations (DAEs):

$$\frac{d\boldsymbol{\xi}_1}{dt} = \mathbf{f}_1(\boldsymbol{\xi}_1; \boldsymbol{\theta}_1) \quad (2a)$$

$$\mathbf{g}_1(\boldsymbol{\lambda}, \boldsymbol{\xi}_1; \boldsymbol{\theta}_1) = 0 \quad (2b)$$

$$\boldsymbol{\xi}_1(0) = \boldsymbol{\xi}_{1;0}, \quad (2c)$$

where:

- $\boldsymbol{\xi}_1 = [c_M I (\boldsymbol{\mu}^T V)]^T$ ,  $c_M$  is the monomer conversion factor,  $I$  is the initiator molar concentration,  $V$  is the sum of the monomer and polymer volumes,
- $\boldsymbol{\xi}_{1;0} = [0 \ I_0 \ 0 \ 0 \ 0]^T$ ,  $I_0$  is the initial molar concentration of the initiator,
- $\boldsymbol{\theta}_1$  is the parameter vector, related to the reaction rates.

Due to the faster dynamics of the free-radical species, the quasi-steady state assumption (QSSA) holds for the free-radical chains, leading to the purely algebraic equations (2b).

Another set of equations derives from thermodynamic balances between the physical components of the reactor. According to (Mourikas, 1998) and the references therein, one can assume that 1) the temperatures of the metal wall and of the solution are uniform (efficient stirring); the sensor for the solution temperature is modelled by a first-order system 2) as the heat exchange coefficient between the jacket and the metal wall highly depends on the jacket temperature distribution, the jacket is discretized into four zones where the heat exchange parameters are lumped. Expressing the variations of the internal energy as the net amount of heat transfer leads to ordinary differential equations (ODEs) for variables  $T_R$  (reacting solution),  $T_M$  (metal wall),  $T_{J;k}$ ,  $k = 1..4$  (jacket zones) and  $T_S$  (sensor).

$$\frac{d\boldsymbol{\xi}_2}{dt} = \mathbf{f}_2(\boldsymbol{\xi}_2, \mathbf{F}_w; \boldsymbol{\theta}_2) \quad (3a)$$

$$\boldsymbol{\xi}_2(0) = \boldsymbol{\xi}_{2;0}, \quad (3b)$$

where:

- $\boldsymbol{\xi}_2 = [T_R \ T_{J;1} \ T_{J;2} \ T_{J;3} \ T_{J;4} \ T_S \ T_M]^T$ ,

- $\boldsymbol{\xi}_{2;0;i} = 300 \text{ K}$ ,  $i = 1..7$ ,
- $\mathbf{F}_w$  is the two-component vector of hot and cold water flow rates,
- $\boldsymbol{\theta}_2$ , the parameter vector, contains the heat exchange and specific heat coefficients, which are complex functions of the temperature.

One element of  $\boldsymbol{\theta}_2$ , the heat exchange coefficient between the metal wall and the solution, noted  $h_{ms}$ , can vary during the batch or batchwise due to accumulation of impurities (fouling).

A deterministic law, which describes the termination rate coefficient, is defined as follows (Mourikas, 1998):

$$k_t = k_{t0} g_t, \quad (4a)$$

$$g_t = f_{gel}(T_R, \rho, c_M; A), \quad (4b)$$

where  $k_t$  and  $k_{t0}$  are the real and low-conversion termination rate coefficients, respectively,  $\rho$ , according to (1a), is the total concentration in the free-radical species,  $A$  is a scalar parameter which accounts here for the inaccuracy when identifying the gel effect.  $A$  can vary between two bounds (lower and upper).

Assembling equations (2) and (3), and augmenting them with one variable, named  $\eta$ , and one equation accounting for the low-level control allows to redefine a new, complete system:

$$\frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x}, u; \mathbf{p}), \quad (5a)$$

$$\mathbf{x}(0) = \mathbf{x}_0, \quad (5b)$$

where:

- $\mathbf{x}^T = [\boldsymbol{\xi}_1^T \ \boldsymbol{\xi}_2^T \ \eta]$ ,  $\mathbf{x}_0^T = [\boldsymbol{\xi}_1^T \ \boldsymbol{\xi}_2^T \ 0]$ ,
- $u$  is the jacket temperature setpoint  $T_J^{sp}$ ,
- $\mathbf{p} = [p_h \ p_g]^T$  accounts for the two aforementioned model uncertainties, i.e.,  $p_h$  is such that the heat exchange coefficient between the metal wall and the solution  $h_{ms}^{real} = h_{ms}^{nom}(1 + p_h)$ ,  $p_g$  affects the model of the gel effect through parameter  $A$  in relation (4b) as  $A^{real} = A^{nom}(1 + p_g)$ .

### 3. CONTROL OBJECTIVES

The control objective consists of a trade-off between several end-of-batch properties related to product quality and quantity. As in (Thomas and Kiparissides, 1984) and (Mourikas, 1998; Kiparissides *et al.*, 2002), a terminal cost  $\Phi(\mathbf{x}(t_f))$  is defined as follows:

$$\Phi(\mathbf{x}(t_f)) = \epsilon_{c_M}^2 + \epsilon_{Mn}^2 + \epsilon_{Mw}^2 \quad (6a)$$

$$\epsilon_{c_M} = \left(1 - \frac{c_M(t_f)}{c_{Md}}\right) \quad (6b)$$

$$\epsilon_{Mn} = \left(1 - \frac{Mn(t_f)}{Mn_d}\right) \quad (6c)$$

$$\epsilon_{Mw} = \left(1 - \frac{Mw(t_f)}{Mw_d}\right). \quad (6d)$$

In expressions (6),  $c_M(t)$  is the conversion factor,  $Mn(t)$  and  $Mw(t)$  are the *number average molecular weight* and the *weight average molecular weight*, respectively:

$$Mn(t) = MW \frac{1(t)}{0(t)} \quad (7a)$$

$$Mw(t) = MW \frac{2(t)}{1(t)}, \quad (7b)$$

where  $MW$  is the molar weight of the monomer.  $Mn(t)$  is exactly the mean length of the polymer chains, whereas  $Mw(t)$  encompasses the length and the dispersion of the polymer chains. In expressions (6),  $c_{Md}$ ,  $Mn_d$  and  $Mw_d$  are the target (or desired) values.

Generally, a dynamic optimization problem is stated as follows: given the desired values  $c_{Md}$ ,  $Mn_d$  and  $Mw_d$ , find the input profile  $u(t)$  which minimizes  $\Phi(\mathbf{x}(t_f))$ , while satisfying the system constraints (5), input constraints, path and terminal constraints. In the following, the dynamic optimization problem is solved using a direct single-shooting method, i.e., the input  $u(t)$  is parameterized with  $N$  linear segments and box constraints apply on the input only. On the other hand, it is considered that the constant input of 337 K is optimal in the nominal case ( $\mathbf{p} = \mathbf{0}$ ) for a batch of 120 min.

#### 4. ROBUST WORST-CASE STRATEGIES

In a standard worst-case strategy, one solves an optimization problem, which accounts for the model uncertainty. In our case, it is assumed that the gel effect is unknown (with no loss of generality,  $p_g$  is between 0.0 and 0.05). Due to the structure of the cost function (a sum of square deviations from target values), the optimization problem is of type min-max:

$$\min_{u(t)} \max_{p_g} \Phi(\mathbf{x}(t_f)), \quad (8)$$

subject to the system constraints (5) and subject to input and disturbance bounds,  $u^{min} \leq u \leq u^{max}$  and  $0.0 \leq p_g \leq 0.05$  respectively.

In the pure open-loop variant, the minimization is performed using the input profile only. Figure

2 shows the evolution of the terminal cost, as a function of the gel effect parameter  $p_g$ , either in the nominal design (i.e., no uncertainty is accounted for, which leads to a classical open-loop optimization) or in the worst-case design. It is noted that 1) the decrease in the terminal cost is significant when applying the worst-case input for higher values of  $p_g$  2) the worst-case input yields some degradation for lower values of  $p_g$ , however not very significant. Robustness of the strategy is also exhibited with respect to perturbations in the heat transfer. In regards of this conservative variant, another variant is of major interest, which uses an internal feedback controller for immediate disturbance rejection (whose parameters may also be optimized). However, the rejection of the (residual) gel effect requires a positive reaction, which is not compatible when dealing with the heat exchange disturbance.

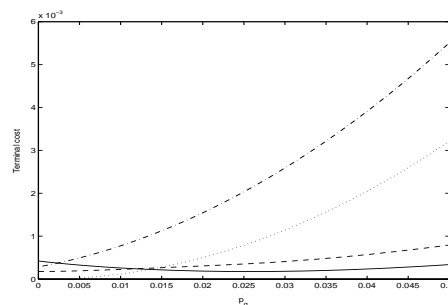


Fig. 2. Terminal cost corresponding to optimal open-loop input. No heat exchange disturbance: nominal (dotted) and worst-case (solid) design ; heat exchange disturbance: nominal (dash-dotted) and worst-case (dashed) design.

#### 5. SCHEDULED-OPTIMIZATION STRATEGY

This strategy lies on the principle of estimation-optimization, i.e., the uncertain parameters are estimated on line and a new trajectory is calculated using the adapted model. In our investigation, we consider that the batch preparation is ideal, i.e., the initial conditions are known. The algorithm is designed to deal efficiently with two disturbances in the same batch, which are in the heat exchange and in the gel effect and both vary batchwise only. In fact, the gel effect exhibits only when the monomer conversion is sufficient whereas the heat exchange has an impact during the whole batch, especially at the beginning where the input contains sufficient excitation (strong heating). Therefore, decoupled, reliable estimation can be achieved, according to the following output least-square error problem (9).

$$\min_{p \in \mathcal{P}} \int_{t_0}^{t^{EOT}} (y(\tau) - y_m(\tau))^2 d\tau, \quad (9)$$

subject to system constraints:

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, u; p), \quad (10a)$$

$$\mathbf{x}(t_0) = \mathbf{x}_0, \quad (10b)$$

$$y = h(\mathbf{x}, u), \quad (10c)$$

where:

- $t_0$  is the initial time of the measurement sequence and  $t^{EOT}$  is the estimation-optimization time (last time in the measurement sequence),
- $y(t)$  and  $y_m(t)$  are the model and measured solution temperatures at time  $t$ , respectively.

Additionally, a lower bound on the parameter variance  $\frac{2}{p}$  is given by the inverse of the (scalar) Fisher information matrix and is approximated as follows (Walter and Pronzato, 1997):

$$\frac{2}{p} = \frac{\frac{2}{y}}{\int_{t_0}^{t^{EOT}} \left( \left( \frac{\partial h}{\partial p} \right) (\tau) \right)^2 d\tau} \quad (11)$$

where:

- $\frac{2}{y}$  is the variance of the temperature measurements,
- $\frac{\partial h}{\partial p}$  is the first-order sensitivity function of the temperature variable with respect to the parameter.

The heat exchange coefficient is estimated once at time noted  $t^{he}$  ( $t_0 = 0$  and  $t^{EOT} = t^{he}$ ). The gel effect is estimated at any time  $t^{gel}$  where the solution temperature deviates sufficiently from the most recently-calculated optimal trajectory ( $t_0 = t^{he}$  and  $t^{EOT} = t^{gel}$ ). After each estimation (at time  $t^{EOT}$ ), a new trajectory is calculated by solving problem (12).

$$\min_{u(t)} \Phi(\mathbf{x}(t_f)), \quad (12)$$

subject to system and input constraints :

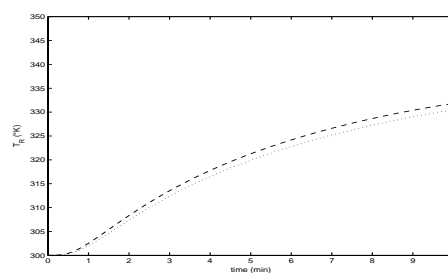
$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, u; \mathbf{p}^{est}), \quad (13a)$$

$$\mathbf{x}(0) = \mathbf{x}_0, \quad (13b)$$

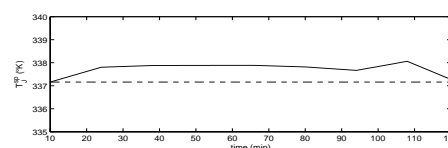
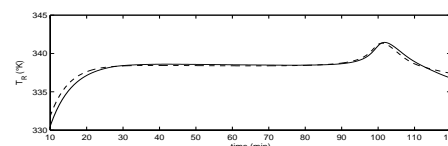
$$u(t) \in [u^{min}, u^{max}]. \quad (13c)$$

An illustrative experiment is performed, under the following operating conditions:

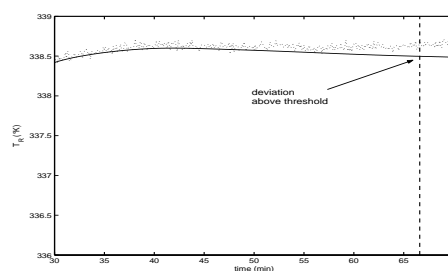
- model uncertainties:  $p_h = 0.5$ ,  $p_g = 0.05$ ,
- measurements of the solution temperature are available every 0.1 min and are affected by white Gaussian noise, with zero mean and 0.033 K standard deviation (maximum error: 0.1 K),
- the estimation-optimization task is performed at time  $t^{he} = 10$  min, accounting for the variation of the heat exchange,



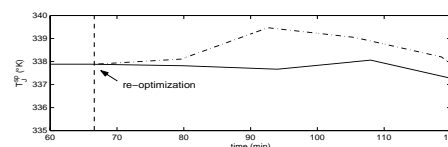
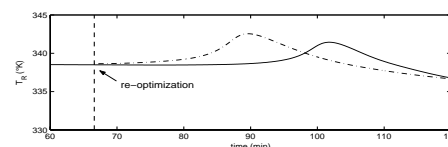
(a) Heat exchange mismatch: deviation between optimal (dashed) and real (dotted) trajectories ( $t \leq 10$ )



(b) Trajectories re-optimized at time 10 (solid) compared to off line-calculated trajectories (dashed)



(c) Gel effect mismatch: deviation between optimal (solid) and real (dotted) trajectories ( $30 \leq t \leq 70$ )



(d) Trajectories re-optimized at time 66.6 (dash-dotted) compared trajectories re-optimized at time 10 (solid)

Fig. 3. Scheduled-optimization strategy: illustration

- the estimation-optimization task is performed at time  $t^{gel}$  where a deviation of 2 times the maximum error is detected, i.e., 0.2 K.

Figure 3 illustrates the experiment and calls for the following comments:

- in 10 min, sufficient information is available from the real temperature which deviates

sensitively from the optimal temperature trajectory calculated on line (3(a)),

- at time  $t = 10$  min, the heat exchange coefficient is estimated and the state vector is obtained by simulation from the known initial conditions, then new optimal trajectories are calculated based on the adapted model (3(b)),
- at time  $t = 66.6$  min, the solution temperature deviates sensitively from the optimal trajectory (3(c)), which is attributed to the gel effect mismatch,
- the gel effect coefficient is estimated and, again, the state vector is obtained by simulation, then the new optimal trajectories are calculated based on the adapted model (3(d)),
- from time  $t = 66.6$  min on, no more deviations above the threshold are detected.

In this simple experiment, satisfactory end-of-batch performance is achieved (the terminal cost is  $0.33 \cdot 10^{-3}$ ), as well as accurate estimation results, such as:

- estimation of  $p_h = 0.5$ , with a standard deviation of  $7 \cdot 10^{-4}$ ,
- estimation of  $p_g = 0.049$ , with a standard deviation of  $9 \cdot 10^{-4}$ .

If the accuracy of the temperature sensor is lower (higher measurement error) whereas the threshold factor is kept unchanged (for example, equal to 2), a degradation (increase) of the terminal cost can be expected due to the lag in the detection/re-optimization. Figure 4 illustrates the evolution of the detection time and of the terminal cost for various values of the maximum absolute measurement error (from 0.1 to 2.0 K). Clearly, the terminal cost is kept at reasonable values even when the detection is very late (time 85 corresponds to the gel effect phenomenon).

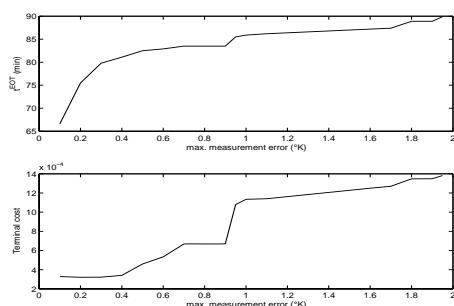


Fig. 4. Scheduled optimization-based strategy: effect of noise on temperature measurements.

## 6. CONCLUSION

This paper reports work on the design of controllers for an MMA polymerization reactor,

based on temperature measurements only. The approach, based on a worst-case analysis (min-max problem), gives acceptable results in open loop. However, it is very conservative unless combined with a feedback controller, which cannot be achieved here since only a positive feedback is suitable for rejection of the gel effect disturbance. Better results are obtained with a scheduled-optimization strategy, i.e., the model parameters are adapted on line, and optimal trajectories are re-evaluated. Provided the reasonable assumption that the parameters vary batchwise only, a decoupled, reliable estimation of these is achieved and this latter approach gives very satisfactory results.

## REFERENCES

- Bonvin, D. (1998). Optimal operation of batch reactors: a personal view. *Journal of Process Control* **8**(5-6), 355–368.
- Kiparissides, C. (1996). Polymerization reactor modeling: a review of recent developments and future directions. *Chemical Engineering Science* **51**(10), 1637–1659.
- Kiparissides, C., P. Seferlis, G. Mourikas and A.J. Morris (2002). On-line optimizing control of molecular weight properties in batch-free polymerization reactors. *Industrial and Engineering Chemistry Research* **41**, 6120–6131.
- Lepore, R., R. Findeisen, Z.K. Nagy, F. Allgöwer and A. Vande Wouwer (2004). Optimal open- and closed-loop control for disturbance rejection in batch process control: a MMA polymerization example. In: *Symposium on Knowledge-driven Batch Processes (BATCH-PRO)*. pp. 235–241. Poros, Greece.
- Mourikas, G. (1998). Modelling, estimation and optimisation of polymerisation processes. PhD thesis. The University of Newcastle. Newcastle upon Tyne, United Kingdom.
- Nagy, Z. K. and R.D. Braatz (2004). Open-loop and closed-loop robust optimal control of batch processes using distributional and worst-case analysis. *Journal of Process Control* **14**, 411–422.
- Terwiesch, P., M. Agarwal and D.W.T. Rippin (1994). Batch unit optimization with imperfect modelling: a survey. *Journal of Process Control* **4**(4), 238–258.
- Thomas, I.M. and C. Kiparissides (1984). Computation of the near-optimal temperature and initiator policies for a batch polymerization reactor. *The Canadian Journal of Chemical Engineering* **62**, 284–291.
- Walter, E. and L. Pronzato (1997). *Identification of parametric models from experimental data*. Springer-Verlag. London.