

Optimal Control of a High-Temperature Semi-Batch Solution Polymerization Reactor

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Abstract—This paper deals with the calculation and real-time implementation of optimal temperature and feed flow rate policies for a high-temperature, n-butyl acrylate, semi-batch, solution, polymerization reactor. A mechanistic model for solution polymerization of alkyl acrylates in a (semi) batch reactor is derived based on a proposed complex reaction mechanism. The model parameters (reaction rate constants) are estimated from off-line measurements of conversion, average molecular weights, number of terminal double bonds and number of branching points. The model is validated against measurements made in regions different from those of the measurements used for the parameter estimation. By using the model, optimal profiles of reactor temperature and three feed (solvent, monomer solution and initiator solution) flow rates that minimize a multi-objective performance index, are calculated.

I. INTRODUCTION

Batch reactors are widely used in the commercial production of polymer solutions (resins), especially in low-volume production of high-quality resins [1], [2]. While batch processes are usually equipped with little instrumentation [1], efforts have been made to use advanced non-conventional analytical methods such as near-infrared spectroscopy to measure monomer conversion and polymer average molecular weights in batch solution polymerization of styrene [3].

Optimal control of batch polymerization reactors has received considerable attention over the past several decades. Choices of monomer(s), solvent(s), initiator(s) and operating conditions dictate the underlying polymerization reaction mechanism and the complexity of the dynamics of the polymerization system (e.g., homo- vs. co-polymerization, solution vs. emulsion polymerization, absence vs. presence of the gel effect, etc.). Recent optimal control studies on batch polymerization systems include solution and emulsion polymerization of styrene [4], [5], solution and bulk polymerization of methyl methacrylate [6], [7], and semi-batch emulsion copolymerization of vinyl acetate/butyl acrylate [8]. Almost all of advanced optimal control studies/implementations have been carried out in academia. On

the other hand, the optimal policies/profiles that are being implemented in the polymer industry have very simple shapes mostly for the ease of their implementation. Time-invariant or piece-wise time-invariant (with a very few changes) policies are very common.

Optimal control problems in batch polymerization reactors are inherently multi-objective. Optimizing variables often have competing effects on an objective function. An optimizing variable sometimes has opposite effects on two objective functions. While the optimization problem can be formulated and solved in a number of ways, choices are limited by computational expense [1]. Constraints of the optimization problem include (a) upper and lower limits (that describe the feasible ranges) of the optimizing variables, (b) mass, energy and structural character balance equations, (c) product quality limits, (d) instrument limitations, and (e) safety limits. Advances have been made to improve numerical algorithm (e.g., genetic algorithm [7], [8], [9]) and to develop alternative optimization approaches (e.g., extended iterative dynamic programming [10] and measurement inclusion [11]).

Most optimization studies are based on first-principle (mechanistic) models, derived from knowledge of a predominant set of polymerization reaction mechanism. The need for reliable process models in the presence of uncertainties has motivated the use of hybrid models such as a combination of neural networks and a first-principles model [6].

This paper presents a study on optimal control of high-temperature (ca. above 140°C) semi-batch solution polymerization of alkyl acrylates. Challenges in the high-temperature polymerization include the inadequacy of low-temperature mechanistic models for the high temperatures and the limited industrial experience in high-temperature batch polymerization. The inadequacy of the low-temperature mechanistic models is a consequence of the profound effect of secondary reactions [12], that are less significant at low temperatures, on the reactor dynamics at the high temperatures. Motivated by these, in this work, a mechanistic semi-batch reactor model based on a proposed reaction mechanism for n-Butyl Acrylate (nBA) is derived. The model parameters (reaction rate constants) are estimated from off-line measurements of conversion, average molecular weights, and number of terminal double bonds and branching points per 100 monomer units. The model is validated against measurements made in regions

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different from those of the measurements used for the parameter estimation. By using the model, optimal feed (solvent, monomer solution, and initiator solution) flow rate and reactor temperature profiles that minimize a multi-objective performance index, are calculated. The reactor is operated in real-time according to the optimal recipe and measurements are made to validate the optimality of the recipe. The optimization validation results were not available at the time of the final submission of this paper; they will be presented at the conference.

II. EXPERIMENTAL FRAMEWORK

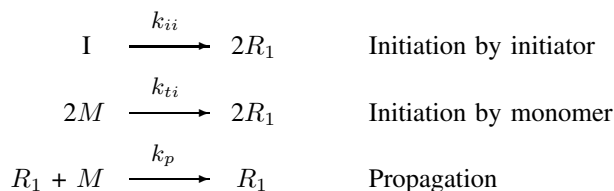
The specific polymerization system being considered here is the thermal solution polymerization of n-butyl acrylate in xylene. Polymerizations are carried out at 160 and 180 °C and low monomer concentration (20-40 monomer wt%) in a 2-liter calorimeter. Details of the experimental setup and spectroscopic analyses can be found in [13]. Experiments are carried out at DuPont Marshall Laboratory, Philadelphia, PA.

III. MODEL DEVELOPMENT

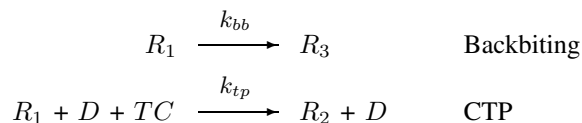
A. Kinetic Scheme and Rate Laws

Reaction mechanism postulated for the polymerization of nBA is based on the characterization results on different polymer micro-structures. The characterization study was carried out at DuPont Marshall Lab. The tendency modeling method [15] is partially used in this work. The method assumes that rates of the reactions are only dependent upon concentrations of micro-structural entities that are involved in the reaction. Reactivity of propagating radicals is also assumed to be independent of chain length.

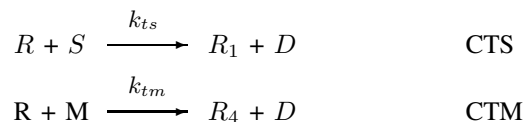
1) *Thermal initiation and propagation*: n-Butyl Acrylate has been observed to undergo polymerization in the absence of thermal initiators [13], [17]. Here the self-initiation reaction is assumed to be second-order with respect to monomer concentration:



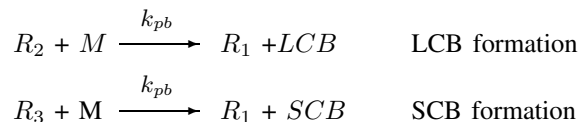
2) *Inter- and intra-molecular chain transfer*: Backbiting and chain-transfer to polymer (CTP) have been observed to be dominant at low and high monomer concentrations, respectively [16]:



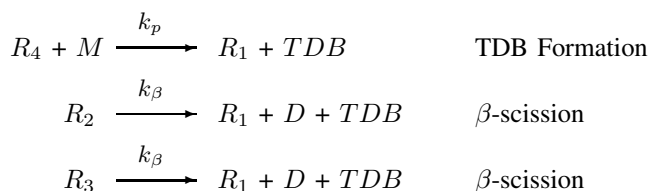
3) *Chain-transfer to small molecules*: Assuming that amount of impurities in solution polymerization is kept to a minimum, the only chain-transfer reactions to be considered are chain-transfer to monomer (CTM) and solvent (CTS):



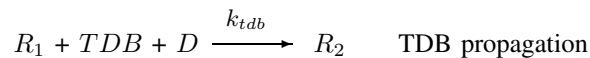
4) *Long and short chain-branching formation*: Formation of long chain-branching (LCB) and short chain-branching (SCB) have been observed in solution polymerization of nBA at the high temperatures [2].



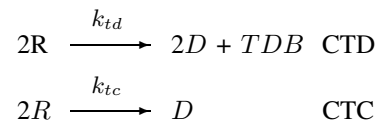
5) *Terminal double bond (TDB) formation*: Scission reactions are in competition with the branching-formation reactions [2]. Note that TDB is also formed in CTD:



6) *TDB propagation*: The existence of TDBs allows for further polymerization (such as cross-linking reactions) to take place at another stage. TDB propagation is in competition with the scission reactions [2]:



7) *Chain termination*: Both known modes of chain-termination is assumed to occur in this work; termination by combination (CTC) and by disproportionation (CTD):



Based on the postulated reaction mechanism, one can derive the following rate laws:

$$\begin{aligned} r_M &= -2k_{ti}[M]^2 - k_p[M][R_1] - k_{pb}[M]([R_2] \\ &+ [R_3]) - k_{tm}[M][R] - k_p[M][R_4] \\ r_I &= -k_{ii}[I] \\ r_S &= -k_{ts}[S][R] \\ r_{TDB} &= k_p[M][R_4] + k_\beta([R_2] + [R_3]) \\ &- 2k_{tdb}[TDB][R_1] + k_{td}\{[R_1][R] + \\ &[R_2]([R_2] + [R_3]) + [R_3]^2\} \\ r_{SCB} &= k_{pb}[M][R_3] \\ r_{LCB} &= k_{pb}[M][R_2] \\ r_D &= k_{tm}[M]R + k_{ts}[S][R] + k_\beta([R_2] + [R_3]) \\ &+ (k_{tc} + 2k_{td})\{[R_1][R] + [R_2]([R_2] + [R_3]) \\ &+ [R_3]^2\} - 2k_{tdb}[TDB][R_1] \end{aligned} \quad (1)$$

Making the quasi-steady-state-assumption for all radical concentrations leads to:

$$[R] = \left\{ \frac{k_{ti}[M]^2 + 2k_{ii}[I]}{k_{tc} + k_{td}} \right\}^{\frac{1}{2}} \quad (2)$$

$$[R_1] = \frac{[R]}{1 + \alpha + \beta} \quad (3)$$

$$[R_2] = \alpha[R_1] \quad (4)$$

$$[R_3] = \beta[R_1] \quad (5)$$

$$[R_4] = \frac{k_{tm}}{k_{tp}}[R] \quad (6)$$

$$\alpha = \frac{(k_{tp}[TC] + k_{tdb}[TDB])}{(k_{pb} + k_{tm})[M] + k_{ts}[S] + k_{\beta} + (k_{tc} + k_{td})[R]} \quad (7)$$

$$\beta = \frac{(k_{bb} + k_{tdb}[TDB])}{(k_{pb} + k_{tm})[M] + k_{ts}[S] + k_{\beta} + (k_{tc} + k_{td})[R]} \quad (8)$$

$$[TC] = [M]_f - [M] - [TDB] - [SCB] - [LCB] \quad (9)$$

B. Process Model

With the assumption of constant density, one can derive the following first-principles, semi-batch, solution polymerization, reactor model:

$$\begin{aligned} \frac{dV}{dt} &= F_T \\ \frac{d[M]}{dt} &= \frac{1}{V} \{F_M[M]_M + r_M V - [M]F_T\} \\ \frac{d[I]}{dt} &= \frac{1}{V} \{F_I[I]_I + r_I V - [I]F_T\} \\ \frac{d[S]}{dt} &= \frac{1}{V} \{F_S[S]_S + F_I[S]_I + r_S V - [S]F_T\} \\ \frac{d[TDB]}{dt} &= \frac{1}{V} \{r_{TDB} V - [TDB]F_T\} \\ \frac{d[SCB]}{dt} &= \frac{1}{V} \{r_{SCB} V - [SCB]F_T\} \\ \frac{d[LCB]}{dt} &= \frac{1}{V} \{r_{LCB} V - [LCB]F_T\} \\ \frac{d[D]}{dt} &= \frac{1}{V} \{r_D V - [D]F_T\} \end{aligned} \quad (10)$$

where $F_T = F_M + F_S + F_I$. The measured variables are given by:

$$x_m = \frac{[M]_f - [M]}{[M]_f} \quad (11)$$

where $[M]_f = \frac{1}{V} \int_0^t F_M[M]_M dt$,

$$M_n = \frac{[M]_f - [M]}{[D]} \times (MW)_m \quad (12)$$

$$TDBH = \frac{[TDB]}{[M]_f - [M]} \times 100 \quad (13)$$

$$BPH = \frac{[SCB] + [LCB]}{[M]_f - [M]} \times 100 \quad (14)$$

TABLE I
VALUES OF THE ESTIMATED PARAMETERS

Parameter	unit	160 °C	180 °C
k_{ti}	$Lmol^{-1}s^{-1}$	1.33E-10	1.33E-09
k_p	$Lmol^{-1}s^{-1}$	1.73E+02	9.25E+02
k_{tp}	$Lmol^{-1}s^{-1}$	1.57E-01	1.69E+00
k_{bb}	s^{-1}	2.15E+01	1.20E+02
k_{tm}	$Lmol^{-1}s^{-1}$	3.38E-04	9.05E-03
k_{ts}	$Lmol^{-1}s^{-1}$	1.18E-01	1.47E+00
k_{pb}	$Lmol^{-1}s^{-1}$	8.47E+00	1.14E+01
k_{β}	s^{-1}	1.84E+01	3.06E+01
k_{tdb}	$Lmol^{-1}s^{-1}$	3.97E+02	1.63E+03
k_{tc}	$Lmol^{-1}s^{-1}$	5.76E+00	2.02E+02
k_{td}	$Lmol^{-1}s^{-1}$	1.76E+01	7.96E+01

IV. PARAMETER ESTIMATION AND MODEL VALIDATION

The reaction rate constants are then estimated from the four types of measurements shown in Figure 1. The least-squared-error parameter estimates are given in Table I. The rate of thermal initiator decomposition that is used in this study is a typical decomposition rate of t-butyl peroxy acetate; $k_{ii} = 3.15 \times 10^{14} \exp\left(\frac{-1.38 \times 10^5}{RT}\right) s^{-1}$. The quality of the model predictions is shown in Figure 1. The model is capable of predicting conversion, number-average molecular weight at the lower temperature, and number of terminal double bonds very well. The predictions of number-average molecular weight at the higher temperature and number of branching points can be improved at the expense of the accuracy of the other predictions.

V. OPTIMIZATION AND OPTIMIZATION VALIDATION

A. Performance Index

The performance index to be minimized is formulated by considering typical resin recipes and general knowledge of industrial polymerization processes. In particular, it is desirable to achieve the following objectives:

- **Monomer conversion.** A monomer conversion of 100% is desirable, since unreacted monomers can undergo further (unwanted) polymerization and/or be wasted.
- **Number-average molecular weight.** Low viscosity resins are desired for automotive coatings applications, which generally translates to lower number-average molecular weight resins. In a typical batch production of resins, a certain number-average molecular weight is desired.
- **Number of branching points.** Effect of branching on the polymer properties in general is still not well understood yet. Currently production is based on experience and/or lab experiments. Batch-to-batch consistency in number of branching points is desired.
- **Number of terminal double bonds.** The existence of terminal double bonds create opportunities for the production of macromonomers that have adequate reactivity to take part in further polymerization reactions

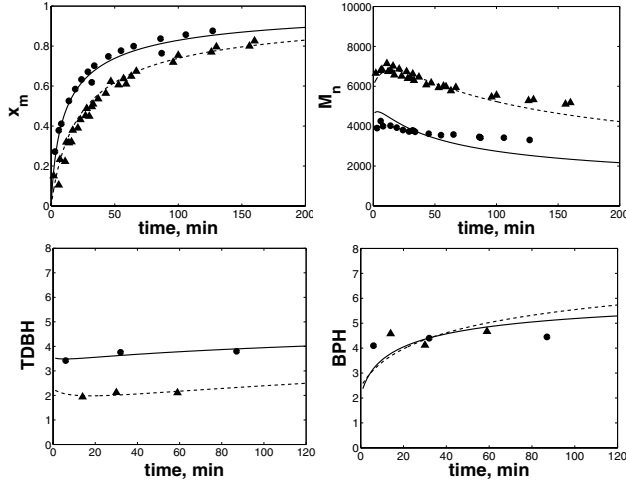


Fig. 1. Measurements and model predictions of monomer conversion (x_m), number-average molecular weight (M_n), number of terminal double bond per 100 monomer units (TDBH) and number of branching points per 100 monomer units (BPH) when the reactor is operated isothermally. The dashed and solid lines represent model predictions at 160 and 180°C, respectively, and the triangles and circles represent measurements at 160 and 180°C, respectively.

such as cross-linking reactions. Manufacturers would ultimately like to have control over number of terminal double bonds in the end product.

- **Initiator.** Thermal initiators are relatively expensive components in resin production. Thus, it is desirable to minimize the amount of initiator used in the resin production.

Based on the above considerations, the following performance index is formulated:

$$J = \omega_1(1 - x_m)^2 + \omega_2\left(\frac{M_n}{M_{n,des}} - 1\right)^2 + \omega_3\left(\frac{BPH}{BPH_{des}}\right) + \omega_4\left(\frac{TDBH}{TDBH_{des}} - 1\right)^2 + \omega_5\left(\frac{m_I}{m_{I_t}}\right) \quad (15)$$

where $\omega_1, \dots, \omega_5$ are the weights on the individual objectives, and the subscript *des* denotes the desired value of the final batch product property. The weights are set according to their relative importance.

B. Optimization Constraints

The above performance index is minimized at the end of the batch cycle time subject to:

- **Optimizing variable constraints.** These constraints represent the feasible ranges of the optimization variables.
- **Balance equations.** These are the conservation equations that govern the process.
- **Hardware and safety limits.** Safety concerns and instrumentation capabilities are represented as limits on reactor temperature changes.

C. Optimization Solution

To solve the optimization problem, a very simple gridding approach is used. Since the current practice is to operate the reactors at constant or piece-wise constant (with a very few changes) temperature and feed flow rates, our initial objective has been to show that considerable improvement in product quality can be made with optimal policies/profiles that are still piece-wise constant but have a higher frequency of change in the optimizing variables.

Different batch times are selected and evaluated. Each batch time (t_b) is divided into N equal time intervals of duration $\Delta t = t_b/N$, and each feed flow rate and temperature profile is discretized into M equally-spaced constant values; that is, the profiles are time- and magnitude-discretized. Thus, the feed flow rate and temperature profiles are piece-wise constant and take a limited number of values. Since we have 3 different (monomer, solvent and initiator) flow rates, we end up with $4 \times M \times N$ optimizing variables. When choosing N and M one should take into account the computational cost of the optimization. In other words, N and M should be large enough such that the performance index is minimized adequately. The optimization constraints are as follows:

$$\sum_{i=1}^N f_{i,j} = f_j, \quad j = M, S \quad (16)$$

$$\sum_{i=1}^N f_{i,I} \leq f_I \quad (17)$$

$$0 \leq f_{i,j} \leq f_j, \quad j = M, S, I, \quad i = 1, \dots, N \quad (18)$$

$$|T_i - T_{i+1}| \leq (\Delta T)_{des}, \quad i = 1, \dots, N \quad (19)$$

$$393.2 \leq T_i \leq 573.2, \quad i = 1, \dots, N \quad (20)$$

where $f_{i,j}$ is the constant flow rate of the j stream over the i th time interval, T_i is the constant reactor temperature over the i th time interval, and $(\Delta T)_{des}$ is the maximum allowable change in reactor temperature over two successive time intervals.

In this study, the minimum is obtained by simulating all possible profiles subject to the defined constraints (simulation), and subsequently, searching through the list of the resulting performance indices for a minimum (optimization). Polymerization recipe used in the optimization and optimization condition is given in Table II. Optimization results are shown in Table III.

Optimization results will be validated experimentally. Challenges in experimental validation include (i) limited experience in carrying out high-temperature experiments, (ii) possible existence of process-model mismatch, (iii) sub-optimal control policies and (iv) limited experience in utilization of modern polymer characterization techniques in

TABLE II
OPTIMIZATION SETTINGS

Monomer (n-butyl acrylate)	= 490 kg
Solvent (xylene)	= 210 kg
Initiator (t-butyl peroxide)	= 0.049 kg
Solvent in initiator solution	= 0.245 kg
$\omega_1 = \omega_2 = \omega_3 = \omega_4 = \omega_5$	= 1
$N = M$	= 4
$M_{n,des}$	= 2000
$TDBH_{des}$	= 5
BPH_{des}	= 10
$(\Delta T)_{des}$	= 5

optimal control studies. The optimization validation results were not available at the time of the final submission of this paper; they will be presented at the conference.

VI. CONCLUSIONS

In this study, a class of batch polymerization reactor is investigated. A mechanistic model for an isothermal semi-batch reactor is developed based on a proposed set of reaction mechanism of high-temperature solution polymerization of alkyl acrylates. Optimal control policies are calculated based on minimization of a proposed performance index that is formulated based on desired microstructural properties such as number of terminal double bonds and branching points, and more conventional objectives such as maximization of monomer conversion, minimization of thermal initiator and obtainment of a pre-determined number-average molecular weight. Optimization results reveal control policies which allow for the production of higher quality polymer resins at lower costs. The optimization validation results were not available at the time of the final submission of this paper; they will be presented at the conference.

NOTATION

$[A]$	Concentration of species A in reactor, A = M, TDB, etc.
$[A]_B$	Concentration of species A in feed flow rate of B, B = M, S, I
BP	Chain-branching = SCB + LCB
BPH	Chain-branching per 100 monomer unit = SCBH + LCBH
D	Dead polymer chain
Δt	Batch time divided by N
F_j	Volumetric flow rate of species j , $j = M, S, I$
f_j	Volume of species j to be fed to the reactor over time divided by Δt , $j = M, S, I$
k_{bb}	Reaction rate constant of backbiting reaction

TABLE III
OPTIMAL FEED POLICIES AND TEMPERATURE PROFILES

Time (min)	100	200	300	400
Fraction of monomer added	0.5	0.5	0.75	0.75
	0.5	0.5	0.25	0.25
	0	0	0	0
	0	0	0	0
Fraction of solvent added	1	1	1	0.5
	0	0	0	0.5
	0	0	0	0
	0	0	0	0
Fraction of initiator added	0	0	0	0
	0.5	0	0.5	0.5
	0	0.5	0	0
	0	0	0	0
Temperature ($^{\circ}C$)	170	170	170	170
	165	175	175	175
	160	175	180	180
	155	180	185	175
x_m	100%	100%	100%	100%
M_n	2253	2053	2035	1978
TDBH	5.4	5.1	4.6	4.8
BPH	7.8	8.1	9.7	10.2
Initiator used (kg)	0.002	0.002	0.002	0.002
J	0.8089	0.7708	0.7455	0.7387

k_{ii}	Reaction rate constant of thermal initiator decomposition
k_p	Reaction rate constant of propagation reaction
k_{pb}	Reaction rate constant of chain-branching reaction
k_{tc}	Reaction rate constant of termination by combination reaction
k_{td}	Reaction rate constant of termination by disproportionation reaction
k_{tdb}	Reaction rate constant of propagation on terminal double bond reaction
k_{ti}	Reaction rate constant of self-initiation reaction
k_{tm}	Reaction rate constant of chain-transfer to monomer reaction
k_{tp}	Reaction rate constant of chain-transfer to polymer reaction
k_{ts}	Reaction rate constant of chain-transfer to solvent reaction
k_{β}	Reaction rate constant of β -scission reaction
LCB	Long chain-branching
LCBH	Long chain-branching per 100 monomer unit
m_I	Total mass of initiator used in reaction
m_{I_t}	Maximum amount of initiator that can be consumed in each batch cycle
M	Monomer
M_n	Number-average molecular weight
M	Number of discrete values that the inlet flow rates and temperature can take
N	Number of equal time intervals in a batch cycle
r_A	Rate of production of species A, A = M, TDB, etc.
R_1	Secondary propagating radical
R_2	Tertiary mid-chain propagating radical

R ₃	Tertiary near-chain-end propagating radical	[15] J. Villermaux, L. Blavier, M. Pons, "A new method for modeling free radical polymerization and predicting polymer quality," in <i>Polymer reaction engineering: influence of reaction engineering on polymer properties</i> , K. H. Reichert, W. Geiseler, eds., pp. 1-20, 1983.
R ₄	Secondary radical with one monomer-unit length	[16] N. M. Ahmad, F. Heatley, P. A. Lovell, "Chain transfer to polymer in free-radical solution polymerization of n-butyl acrylate studied by NMR spectroscopy," <i>Macromolecules</i> , vol. 31, pp. 2822-2827, 1998.
R	Propagating radical = R ₁ + R ₂ + R ₃	[17] C. L. Quan, M. Soroush, M. C. Grady, "Mathematical modeling of high-temperature, free-radical polymerization of butyl acrylate," <i>AIChE Annual Meeting, Reno, NV</i> , November, 2001.
S	Solvent	
SCB	Short chain-branching	
SCBH	Short chain-branching per 100 monomer unit	
t	time	
t _b	batch time	
TC	Tertiary carbon in a polymer chain	
TDB	Terminal double bond	
TDBH	Terminal double bond(s) per 100 monomer unit	
V	Volume of reactor	
(MW) _m	Molecular weight of monomer	
x _m	Monomer conversion	
ω _i	Weighting factor of objective <i>i</i> in the performance index	

REFERENCES

- [1] B. Srinivasan, S. Palanki, D. Bonvin, "Dynamic optimization of batch processes I. Characterization of the nominal solution," *Computers Chem. Eng.*, vol. 27, pp. 1-26, 2003.
- [2] M. C. Grady, W. J. Simonsick, R. A. Hutchinson, "Studies of higher temperature polymerization of n-Butyl Methacrylate and n-Butyl Acrylate," *Macromol. Symp.*, vol. 182, pp. 149-168, 2002.
- [3] J. M. R. Fontoura, A. F. Santos, F. M. Silva, M. K. Lenzi, E. L. Lima, J. C. Pinto, "Monitoring and control of styrene solution polymerization using NIR spectroscopy," *J. App. Pol. Sci.*, vol. 90, pp. 1273-1289, 2003.
- [4] A. R. Karagoz, H. Hapoglu, M. Alpbaz, "Generalized minimum variance control of optimal temperature profiles in a polystyrene polymerization reactor," *Chemical Engineering and Processing*, vol. 39, pp. 253-262, 2000.
- [5] C. Gentric, F. Pla, J. P. Corriou, "Experimental study of the nonlinear geometric control of a batch emulsion polymerization reactor," *Computers Chem. Eng.*, vol. 21, pp. S1043-S1048, 1997.
- [6] J. Zhang, "A reliable neural network model based optimal control strategy for a batch polymerization reactor," *Ind. Eng. Chem. Res.*, vol. 43, pp. 1030-1038, 2004.
- [7] S. Garg, S. K. Gupta, "Multiobjective optimization of a free radical bulk polymerization reactor using genetic algorithm," *Macromol. Theory Simul.*, vol. 8, pp. 46-53, 1999.
- [8] C. D. Immanuel, F. J. Doyle III, "Open-loop control of particle size distribution in semi-batch emulsion copolymerization using a genetic algorithm," *Chem. Eng. Sci.*, vol. 57, pp. 4415-4427, 2002.
- [9] Y. Tian, J. Zhang, J. Morris, "Modeling and optimal control of a batch polymerization reactor using a hybrid stacked recurrent neural network model," *Ind. Eng. Chem. Res.*, vol. 40, pp. 4525-4535, 2001.
- [10] F. S. Wang, T. L. Shieh, "Extension of iterative dynamic programming to multiobjective optimal control problems," *Ind. Eng. Chem. Res.*, vol. 36, pp. 2279-2286, 1997.
- [11] B. Srinivasan, D. Bonvin, E. Visser, S. Palanki, "Dynamic Optimization of batch processes II. Role of measurements in handling uncertainty," *Comp. Chem. Eng.*, vol. 27, pp. 27-44, 2002.
- [12] A. N. F. Peck, R. A. Hutchinson, "Secondary reactions in the high-temperature free radical polymerization of butyl acrylate," *Macromolecules*, vol. 37, pp. 5944-5951, 2004.
- [13] C. L. Quan, M. Soroush, M. C. Grady, J. E. Hansen, W. J. Simonsick, "High-temperature homo-polymerization of n-butyl acrylate and ethyl acrylate: polymer characterization," *Macromolecules*, submitted (2004).
- [14] F. S. Rantow, C. L. Quan, M. Soroush, M. C. Grady, "Mechanistic modeling of high-temperature homo-polymerization of n-butyl acrylate and ethyl acrylate," *Polymer Engineering and Science*, to be submitted (2005).