

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 weight, 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 three feed (solvent, monomer solution and initiator solution) streams and reactor temperature that minimize a multi-objective performance index, are calculated. The reactor is operated in real-time according to the calculated optimal recipe and measurements are made to validate the true optimality of the recipe. The real-time studies are carried out at DuPont Marshall Laboratory.

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 traditional batch processes are equipped with minimum 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].

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 are feasible range of optimizing variables, balance equations, product quality limits, instrument limitations, and 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 process-model mismatch and/or disturbances 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 operation. The inadequacy of the low-temperature mechanistic models is a consequence of the profound effect of secondary reactions, that are negligible 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 weight, and number of terminal double bonds and branching points per 100 monomer units. 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 solvent, monomer solution, and initiator solution feed 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

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of the recipe.

II. EXPERIMENTAL FRAMEWORK

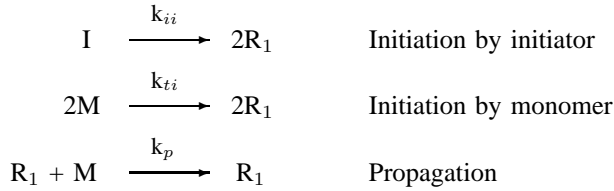
The polymerization system being considered is the thermal solution polymerization of n-butyl acrylate in xylene. Polymerizations are carried out at 160 and 180 °C and low monomer concentration (20-40 monomer wt%) in a 2-Liter calorimeter. Details of the experimental setup and spectroscopic analyses can be found in [12]. Experiments are carried out at DuPont Marshall Laboratory, Philadelphia, PA.

III. MODEL DEVELOPMENT

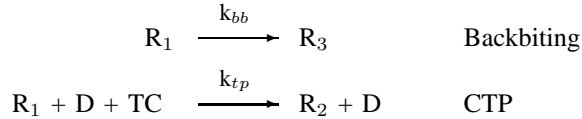
A. Kinetic Scheme and Rate Laws

Reaction mechanism postulated for the polymerization of nBA is based on the characterization results on different polymer micro-structures. The tendency modeling method [13] is partially used in this work. The method assumes that rate of 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.

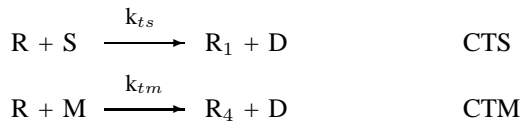
1) *Thermal self-initiation and propagation*: n-Butyl Acrylate has been observed to undergo polymerization in the absence of thermal initiators [12]. Here the self-initiation reaction is assumed to be second-order with respect to monomer concentration:



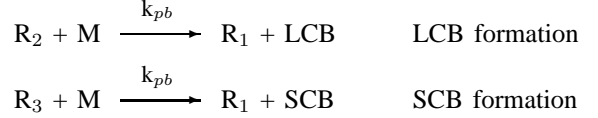
2) *Inter- and intra-molecular chain transfer*: Backbiting and chain-transfer to polymer (CTP) have been observed to be dominant at low and high initial monomer concentrations, respectively [14]:



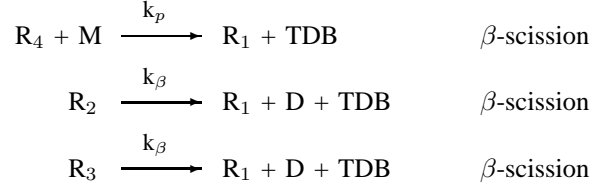
3) *Chain-transfer to small molecules*: Assuming that amount of impurities in solution polymerization is kept to a minimum, the only chain-transfer reactions to be considered are chain-transfer to monomer (CTM) and solvent (CTS):



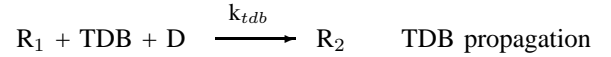
4) *Long and short chain-branching formation*: Formation of long chain-branching (LCB) and short chain-branching (SCB) have been observed in solution polymerization of nBA at the high temperatures [2].



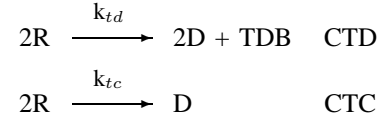
5) *Terminal double bond (TDB) formation*: Scission reactions are in competition with the branching-formation reactions [2]. Note that TDB is also formed in CTD:



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, the following rate laws are derived:

$$\begin{aligned} r_M &= -2k_{ti}[M]^2 - k_p[M]R_1 - k_{pb}[M](R_2 + R_3) \\ &\quad - k_{tm}[M]R - k_p[M]R_4 \\ r_I &= -k_{ii}[I] \\ r_S &= -k_{ts}[S]R \\ r_{TDB} &= k_p[M]R_4 + k_\beta(R_2 + R_3) - 2k_{tdb}[TDB]R_1 \\ &\quad + k_{td}\{R_1R + R_2(R_2 + R_3) + R_3^2\} \\ r_{SCB} &= k_{pb}[M]R_3 \\ r_{LCB} &= k_{pb}[M]R_2 \\ r_D &= k_{tm}[M]R + k_{ts}[S]R + k_\beta(R_2 + R_3) \\ &\quad + (k_{tc} + 2k_{td})\{R_1R + R_2(R_2 + R_3) + R_3^2\} \\ &\quad - 2k_{tdb}[TDB]R_1 \end{aligned} \quad (1)$$

where by invoking the quasi-steady-state-assumption on all radical concentrations, we end up with:

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

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

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

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

$$R_4 = \left\{ \frac{k_{tm}}{k_{tp}} \right\} R \quad (6)$$

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

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

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

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

B. Process Model

An isothermal semi-batch solution polymerization process model can then be derived:

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

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

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

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

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

IV. PARAMETER ESTIMATION AND MODEL VALIDATION

Reaction rate constants are then estimated from the four types of measurements shown in Figure 1. The parameter values 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 peroxide; $k_{ii} = 3.15 \times 10^{14} \exp\left(\frac{-1.38 \times 10^5}{RT}\right) s^{-1}$. The quality of the model predictions is shown in Figure 1.

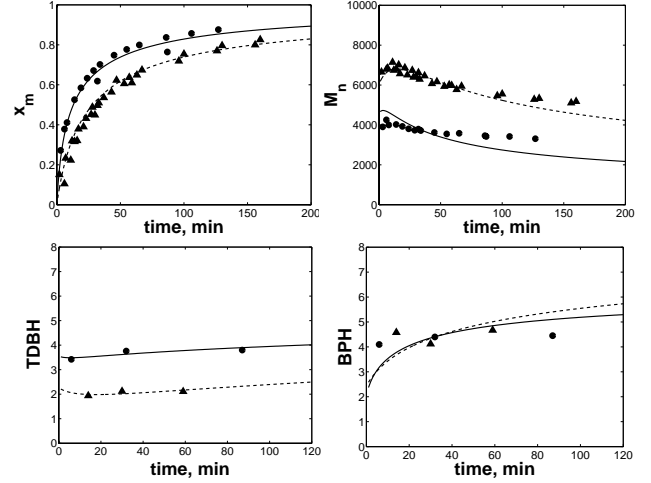


Fig. 1. Measurements and model predictions of monomer conversion (x_m), number-average molecular weight (M_n), number of terminal double bond per 100 monomer units (TDBH) and number of branching points per 100 monomer units (BPH) when the reactor is operated isothermally. The dashed and solid lines represent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

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. It is desired maintain the number of branching points batch-to-batch constant.

- **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 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 the most expensive component in the resin production recipe. 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:

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

where $\omega_1, \dots, \omega_5$ are the weights on the individual objectives. Each weight is set according to the importance of its corresponding objective function.

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 how steep change in temperatures can be.

C. Optimization

Different batch times are selected and evaluated. Each batch time is divided into N equal time intervals, and each feed flow rate and temperature profile is discretized into M equally-spaced constant values. Thus, the feed flow rate and temperature profiles are piece-wise constant. Since we have 3 different flow rate (monomer, solvent and initiator), 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:

$$\sum_{i=1}^N \frac{F_{i,j}}{F_i} = 1, \quad j = M, S \quad (16)$$

$$\sum_{i=1}^N \frac{F_{i,j}}{F_i} \leq 1, \quad j = I \quad (17)$$

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
$M_{n,set}$	= 2000
$TDBH_{set}$	= 5
BPH_{set}	= 10
$(\Delta T)_{set}$	= 5

$$\sum_{i=1}^N \frac{F_{i,j}}{F_i} \geq 0, \quad j = I \quad (18)$$

$$F_{i,j} > 0, \quad j = M, S, \quad i = 1, \dots, N \quad (19)$$

$$F_{i,j} \geq 0, \quad j = I, \quad i = 1, \dots, N \quad (20)$$

$$T_i - T_{i+1} \geq (\Delta T)_{set}, \quad i = 1, \dots, N \quad (21)$$

$$T_i - T_{i+1} \leq (\Delta T)_{set}, \quad i = 1, \dots, N \quad (22)$$

$$T_i > 0, \quad i = 1, \dots, N \quad (23)$$

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 $(\Delta T)_{set}$ 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). An optimal reactor feed policy subject to an isothermal condition is first calculated. Subsequently, based on the optimal feed policy, different temperature profiles are simulated to obtain a better optimum. 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 optimal control studies.

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

TABLE III
OPTIMAL FEED AND TEMPERATURE POLICIES AND BATCH-END
PROPERTIES

Time (min)	100	200	300	400
Fraction of monomer added	0.5	0.25	0.25	0.75
	0.5	0.25	0.25	0.25
	0	0.5	0.5	0
	0	0	0	0
Fraction of solvent added	1	1	0.75	0.5
	0	0	0	0.5
	0	0	0	0
	0	0	0.25	0
Fraction of initiator added	0	0	0	0
	0	0	0	0.5
	0.5	0	0	0
	0	0.5	0.5	0
Temperature (°C)	170	170	170	170
	165	175	175	175
	160	175	180	180
	155	175	180	175
x_m	100%	100%	100%	100%
M_n	2253	2099	1997	1978
TDBH	5.4	5.0	5.0	4.8
BPH	7.8	8.7	9.2	10.2
Initiator used (kg)	0.005	0.005	0.005	0.005
J	0.8089	0.7534	0.7409	0.7387

index that is formulated based on desired micro-structural 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 reveals control policies which allow for the production higher quality polymer resins at lower costs.

VII. NOTATION

A or [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
F _A	Volumetric flow rate of species A, A = M, S, I
k _{bb}	Reaction rate constant of backbiting reaction
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

k _{ti}	terminal double bond reaction
k _{tm}	Reaction rate constant of self-initiation reaction
k _{tp}	Reaction rate constant of chain-transfer to monomer reaction
k _{ts}	Reaction rate constant of chain-transfer to polymer reaction
k _β	Reaction rate constant of chain-transfer to solvent reaction
LCB	Reaction rate constant of β-scission reaction
LCBH	Long chain-branching
m _I	Long chain-branching per 100 monomer unit
m _{I_t}	Total mass of initiator used in reaction
M	Maximum amount of initiator that can be consumed in each batch cycle
M _n	Monomer
M	Number-average molecular weight
N	Number of discretized values for different feed flow rates
r _A	Number of equal batch time intervals
r _A	Rate of reaction of species A, A = M, TDB, etc.
R ₁	Rate of reaction of species A, A = M, TDB, etc.
R ₂	Secondary propagating radical
R ₃	Tertiary mid-chain propagating radical
R	Tertiary near-chain-end propagating radical
S	Propagating radical = R ₁ + R ₂ + R ₃
SCB	Solvent
SCBH	Short chain-branching
t	Short chain-branching per 100 monomer unit
TC	Reaction time
TDB	Tertiary carbon in a polymer chain
TDBH	Terminal double bond
V	Terminal double bond(s) per 100 monomer unit
(MW) _m	Volume of reactor
x _m	Molecular weight of monomer
ω _i	Monomer conversion
	Weighting factor of an objective in the performance index

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