

Optimal Operations of Semibatch Solution Polymerization of Acrylamide with Molecular Distribution as Constraints

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SYNOPSIS

In this work, optimal control profiles of a semibatch solution polymerization of an acrylamide system are investigated for the first time. The control variables are the monomer and initiator feed rates. The objective function is the operating time of each batch. One of the operating constraints is the maximum of the polymerization rate of the reaction, which is important due to the limitation of the heat-removal equipment. The expected number-average molecular weight and molecular weight distribution are also included as constraints in order to guarantee the quality of the products. A nonlinear programming approach developed by Jang and Yang is used for solving the equations. Several simulation and experimental runs show that the operation of this semibatch system is very smooth and conversions are fitted well by the model. The molecular weights and molecular weight distributions of the polymer products are also well controlled. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyacrylamide has been widely used in industry since its long chains have an expanded configuration in aqueous solutions. In batch processes, it is frequently desired to minimize the operating time of each batch while not drastically reducing final product quality. However, as shown later, due to the highly exothermic property of the reaction, it is not possible to operate at too high a reaction rate. Further, as will be derived later, it is desired to use a lower initiator and higher monomer composition in order to generate higher polymer molecular weights. In this article, we have defined the minimum end time monomer feed rate as well as initiator feed-rate conditions using a nonlinear programming collocation polynomial method derived by Jang and Yang.¹ The paper focuses on the semibatch nature of this problem and adds molecular weight constraints that were not used in our previous works.^{1,2} Furthermore, this is the first time an acrylamide polymerization been discussed in the area of optimal control.

The kinetics of the solution polymerization of acrylamide with persulfate initiators was first derived by Kolthoff and Miller.³ Riggs and Rodriguez,⁴ in turn, elucidated the equation of reaction rate as a function of monomer and initiator concentrations. Kim and Hamielec⁵ discussed the kinetics of this solution system in higher monomer composition situations. They considered the chemical-controlled termination and diffusion termination situations and provided the reaction-rate equations in these two situations. Hunkeler and Hamielec,⁶ with Hunkeler,⁷ going one step further, provided the complete mechanism and interpretations of experimental data.

Physical models of molecular weights of polyacrylamide have been developed by Hamielec and co-workers. Duerksen et al.⁸ and Hui and Hamielec⁹ derived the molecular weight models directly from the reaction mechanism and proved their results using experimental data. Shawki and Hamielec¹⁰ revised the previous model by considering the chain-transfer constants. Hunkeler and Hamielec¹¹ improved the detecting tools using laser scattering and a so-called one-point method.

The molecular weight distribution of the polymer product is one of the major concerns of product quality. Previously, there has been extensive work

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on molecular weight control in batch reactors (e.g., Baillagou and Soong¹² and Ellis et al.¹³), semibatch reactors (e.g., Alassia et al.¹⁴), and continuous reactors (e.g., Lee and Mallinson¹⁵). However, these works concentrated on obtaining operating conditions of reactors so that the molecular weights of polymer products can be located at a desired range. Economic issues were not studied.

As mentioned earlier, there has been no work on the optimal control of an acrylamide system; however, there exists much work on the optimal control of polymer reactors. Chen and co-workers (e.g., Chen and Jeng¹⁶⁻¹⁸ and Chen and Hsu¹⁹) derived the optimal conditions for batch reactors directly from the maximum principle, but the computational time becomes very cumbersome using this analytical approach if the process model is very complicated. Similar work on different systems also exists (e.g., Farber and Laurence,²⁰ Ponnuswamy et al.,²¹ and Kiparissides et al.²²). Kozub and Macgregor²³ concentrated on the feedback control in a semibatch reactor of a copolymer.

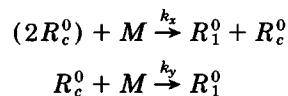
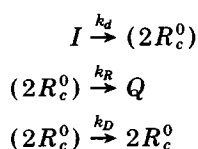
Jang and co-workers (Jang and Yang¹ and Jang and Lin²) used a nonlinear programming collocation polynomial approach to solve continuous and discontinuous policies for a batch latex system. This approach is implemented herein to solve the equations of a semibatch reacting system. Molecular weight distribution is a function of monomer composition in this acrylamide polymerization system; therefore, in this work, the monomer feed stream is manipulated to optimize the operation, i.e., a semibatch approach is implemented. On the other hand, the polymerization reaction rate should be restricted to control heat generation in a very short time period, and this is the other reason to implement a semibatch operation for this polymerization reaction.

THEORY

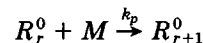
Model and Analysis

The kinetics of a free-radical solution polymerization of acrylamide systems can be described as the following (see Kim and Hamielec⁵):

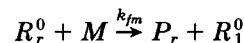
1. Initiation:



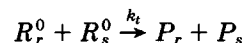
2. Propagation:



3. Chain transfer:



4. Termination:



Riggs and Rodriguez⁴ experimentally defined the following rate equation:

$$R_p = k_{1.25}[I]^{0.5}[M]^{1.25} \quad (1)$$

Kim and Hamielec⁵ showed that the above equation is valid if the monomer composition is less than 2.2 mol/L using the above model. They also showed that the number-average and weight-average length of polyacrylamide at a particular time are given by

$$r_N(t) = 1/\tau \quad (2)$$

$$r_W(t) = 2/\tau \quad (3)$$

where

$$\tau = \frac{k_t R_p}{k_p^2 [M]^2} + \frac{k_{fm}}{k_p} \quad (4)$$

If we substitute the rate eq. (1) into (4), and set $c_1 = k_t k_{1.25} / k_p^2$, $c_2 = k_{fm} / k_p$, we have

$$\tau = c_1 [I]^{0.5} [M]^{-0.75} + c_2 \quad (5)$$

and the number and weight averages of the polymer products in a period in which the monomer conversion varies from 0 to x are

$$\bar{r}_N = \frac{x}{\int_0^x \tau dx} \quad (6)$$

$$\bar{r}_W = \frac{2}{x} \int_0^x \frac{1}{\tau} dx \quad (7)$$

It can be shown in (5) that the number and weight averages are larger if τ is kept small during the op-

eration, i.e., monomer composition is kept high while the initiator is kept low. On the other hand, the molecular weight distribution $U = \bar{r}_w/\bar{r}_n$ is also an important factor. It can be shown that

$$U = \frac{2}{x^2} \int_0^x \frac{1}{\tau} dx \int_0^x \tau dx \quad (8)$$

If conversion x is fixed,

$$U \propto \int_0^x \frac{1}{\tau} dx \int_0^x \tau dx \quad (9)$$

As (9) shows, U can be minimized if τ is kept constant during the operation. However, it is not possible to keep τ constant during each batch. According to our experience, if U is less than 4.5, the quality of polyacrylamide is satisfactory.

Problem Formulation

We may assume that the operating cost of a batch system can be expressed simply as the operating time of each batch, i.e.:

$$COST = t_f \quad (10)$$

Further, if the objective is to minimize the end time of each batch, it is accomplished by manipulating control variables that include the feed rate of the monomer $u(t)$ mol/min and the feed rate of the initiator $v(t)$ mol/min at any time t . In this work, we have assumed that the total amount of monomer added to a batch is a constant, whereas the total amount of initiator is only limited by an upper bound, i.e.:

$$\int_0^{t_f} u(t) dt = M_{tot} \quad (11)$$

$$\int_0^{t_f} v(t) dt \leq I_{tot,U} \quad (12)$$

It is assumed that the reaction of each batch is terminated at the time when the conversion of total monomer added reaches a point such as 0.99, i.e.:

$$x(t_f) = 0.99 \quad (13)$$

It is natural that an upper bound for a heat-generation amount exists due to limitation in heat-removal resources. Since the propagation reaction is highly exothermic, it is also natural to restrict the polymerization rate during the operation, i.e., the

following constraint should be imposed for good temperature control:

$$R_p(t) \leq R_{p,U} \quad (14)$$

Besides, as indicated before, it is also very important to restrict the molecular weight and molecular weight distributions to guarantee product quality. We can therefore set an arbitrary upper bound to the molecular weight distribution:

$$\bar{M}_{N,L} \leq \bar{M}_N(t_f) \leq \bar{M}_{N,U} \quad (15)$$

$$U(t_f) \leq 4.5 \quad (16)$$

If the dynamics of the semibatch system is introduced, one can formulate the optimization problem as the following:

$$\min_{u(t),v(t)} t_f \quad (17)$$

S.T.

$$\frac{d[M]}{dt} = -k_{1.25}[I]^{0.5}(t)[M]^{1.25}(t) + \frac{[M]_{in}u(t)}{V(t)} \quad (18)$$

$$\frac{d[I]}{dt} = -k_d[I](t) + \frac{[I]_{in}u(t)}{V(t)} \quad (19)$$

$$\tau = \frac{k_t k_{1.25}}{k_p^2} [I]^{0.5}(t)[M]^{-0.75}(t) + \frac{k_{fm}}{k_p} \quad (20)$$

$$\bar{M}_N = \bar{r}_N W = \frac{x(t)W}{\int_0^{x(t)} \tau dx} \quad (21)$$

$$\bar{M}_W = \bar{r}_w W = \frac{2W}{x(t)} \int_0^{x(t)} \frac{1}{\tau} dx \quad (22)$$

$$\int_0^{t_f} u(t) dt = M_{tot} \quad (23)$$

$$\int_0^{t_f} v(t) dt \leq I_{tot,U} \quad (24)$$

$$\bar{M}_{N,L} \leq \bar{M}_N(t_f) \leq \bar{M}_{N,U} \quad (25)$$

$$\bar{M}_{W,L} \leq \bar{M}_W(t_f) \leq \bar{M}_{W,U} \quad (26)$$

$$R_p(t) \leq R_{p,U} \quad (27)$$

$$0.6 \leq u(t) \leq 110; \text{ otherwise } u(t) = 0 \text{ (mL/min)} \quad (28)$$

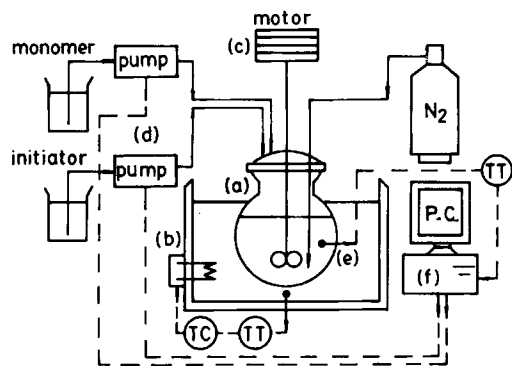


Figure 1 The schematic plot of the experimental setup.

$$0.3 \leq v(t) \leq 63; \text{ otherwise } v(t)$$

$$= 0 \text{ (mL/min)} \quad (29)$$

where the upper and lower bounds of the control variables are necessary due to the limitations of the feed pump operation range. It should also be noted that the constraints on molecular weight distribution U are replaced by the constraints on weight-average molecular weight for convenience.

The Solution Method

As we stated in the previous work (Jang and Yang¹), the solution of the optimization problem of eqs. (17)–(29) is not an easy task. Very frequently, if

the system is not very complicated, it can be solved using a maximum principle. However, in this work, although the dynamics are easy, the constraints (25), (26), and (27) are so-called state constraints, i.e., they are not only implicit functions of state variables $[M]$ and $[I]$, but, as shown before, functions of control. Therefore, it is very difficult to solve analytically. Hence, we use the same approach as in our previous work by assuming

$$u(t) = \sum_{i=1}^{NC} u_i l_i(t) \quad (30)$$

$$v(t) = \sum_{i=1}^{NC} v_i l_i(t) \quad (31)$$

where $l_i(t)$ are Lagrange multipliers at the i th collocation point. Hence, the continuous variables $u(t)$ and $v(t)$ are discretized and the optimization problem can be rewritten by

$$\min_{u_1, u_2, \dots, u_{NC}, v_1, v_2, \dots, v_{NC}} t_f \quad (32)$$

s.t. (19)–(29).

Since in eq. (32) the dimension of control variables becomes finite, one can implement any nonlinear programming packages for solutions. In this work, the above problem is solved using a general reduced gradient package GRG2.

Table I The Simulation and Experimental Results of Optimal Control Runs of the Semibatch Reaction System of Solution Polymerization of Acrylamide

Reaction Run	Upper Limit of Exothermic (kJ/min)	Reaction Mole No.	Constraints		Reaction Time (min)	Conversion (%)			$M_n \times 10^{-5}$			$M_w \times 10^{-5}$				
			$M_n \times 10^{-5}$	$M_w \times 10^{-5}$		(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)		
R051	1	0.5			71	99.0	98.8	98.7								
R051n	1	0.5	2.9–3.1		99	99.0	99.0	97.4	2.90	2.9	2.71					
R051w	1	0.5		6.1–7.1	91	99.0	99.0	97.8				6.10	5.99	5.43		
R051nw	1	0.5	2.5–3.5	8.75–15.75	120	99.0	99.1	98.3	2.73	2.53	2.15	12.2	12.2	8.48		
R052	2	0.5			56	99.0	98.9	98.0								
R052n	2	0.5	2.9–3.1		79	99.0	98.7	98.3	2.90	3.14	1.93					
R052w	2	0.5		7.7–8.7	66	99.0	98.8	97.9				7.70	7.84	8.28		
R232	2	2.3			103	99.0	99.2	99.2								
R232n	2	2.3	2.1–2.3		119	99.1	98.9	99.5	2.10	1.97	2.5					
R232w	2	2.3		7.2–8.2	105	99.1	99.1	98.3				7.20	6.56	7.27		
R232nw	2	2.3	1.9–2.5	7.22–10.5	114	99.1	98.8	98.8	1.99	1.93	2.53	8.14	7.88	8.02		
R231	1	2.3			196	99.1	99.0	99.2								

(A) is the result of simulation under constant temperature; (B), the result of simulation with real process temperature; and (C), the result of experiment. R05xxx is the run with $M_{tot} = 0.5$ mol; R23xxx, the run with $M_{tot} = 2.3$ mol; Rxx1xx, the run with $R = 1$ kJ/min; Rxx2xx, the run with $R = 2$ kJ/min; Rxxxn, the run where only M_n constraint exists; Rxxxw, the run where only M_w constraint exists; and Rxxxnw, the run where both M_n and M_w constraints exist.

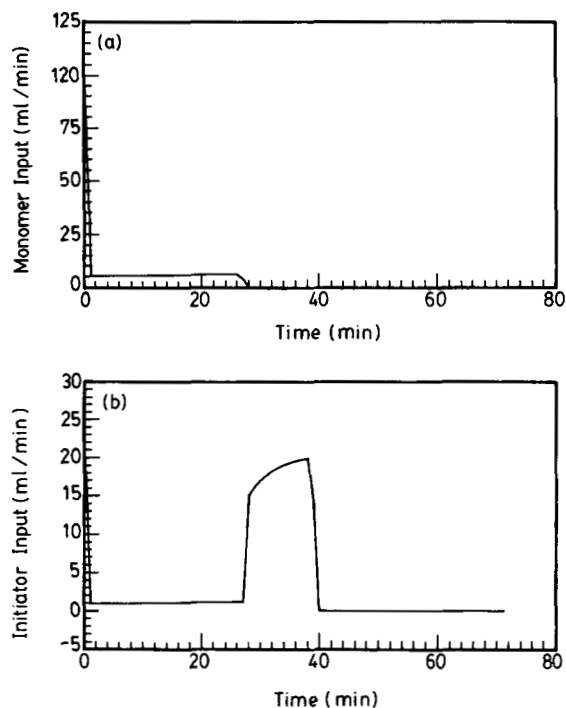


Figure 2 The optimal operation policies for R051: (a) monomer and (b) initiator feed rates as a function of time.

EXPERIMENTAL

A schematic plot of experimental configuration is given by Figure 1. The volume of the glass reactor is 1 L, and the temperature of the reactor was controlled by a separate temperature controller at 75°C as shown in Figure 1. The monomer and initiator were pumped into the reactor according to a program that is a solution of eq. (32). The history of the temperature of each batch was recorded by the computer through an A/D converter. The product was sampled at periodic time intervals.

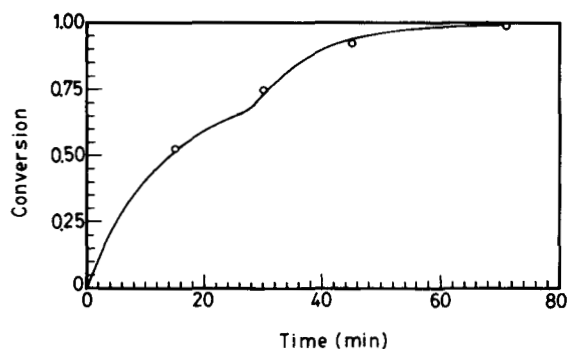


Figure 3 The history of conversion of R051, where the line is the simulation; symbols are experimental data.

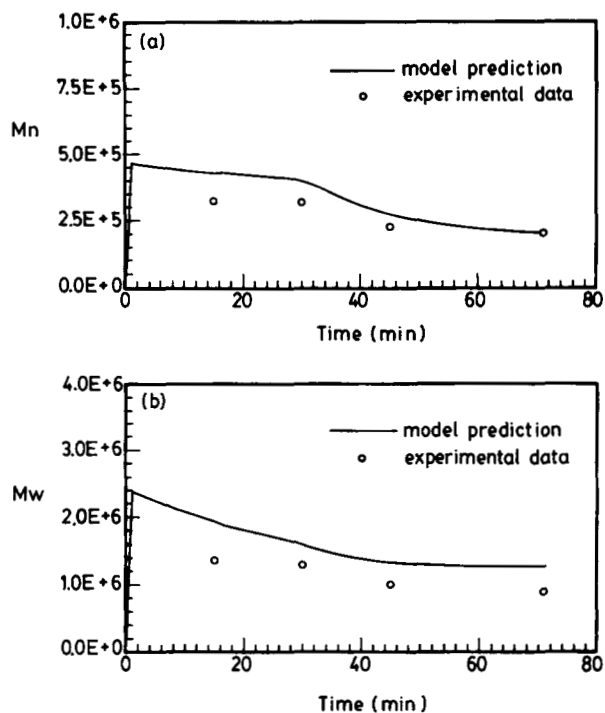


Figure 4 The molecular weights of R051 as a function of time: (a) number-average and (b) weight-average molecular weights, where lines are simulations and symbols are experimental data.

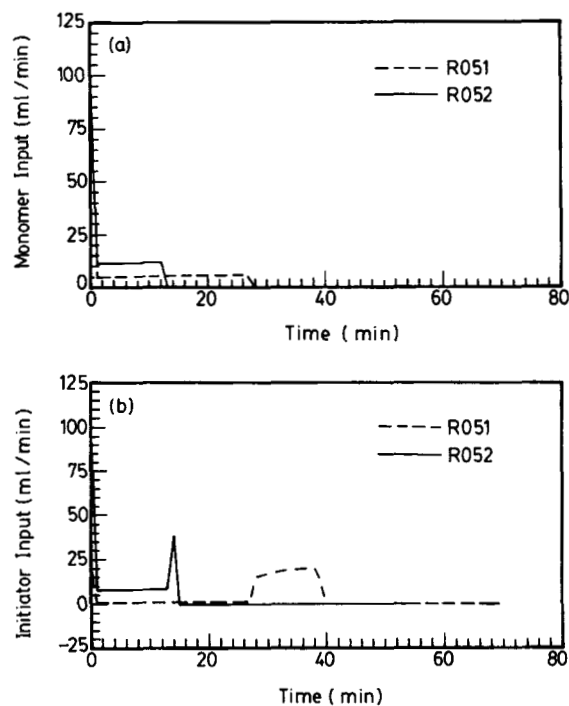


Figure 5 The comparisons of optimal (a) monomer and (b) initiator inputs between runs R051 and R052.

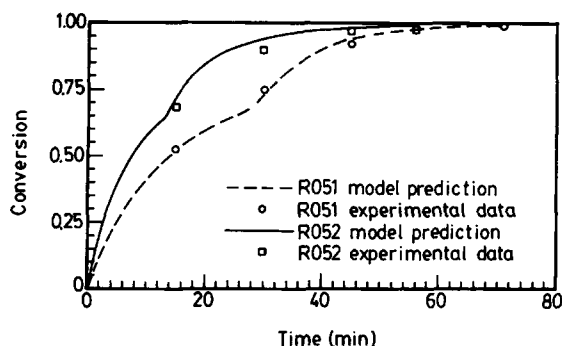


Figure 6 The comparison of conversion profiles between runs R051 and R052; lines are simulations and symbols are experimental data.

The initiator used was potassium persulfate. The conversion of each sample was determined using the so-called bromate-bromide method (see, e.g., Norris²⁴), whereas the molecular weights were measured with a GPC.

RESULTS

Equation (32) was solved for 13 different conditions. The numerical solutions as well as experimental data

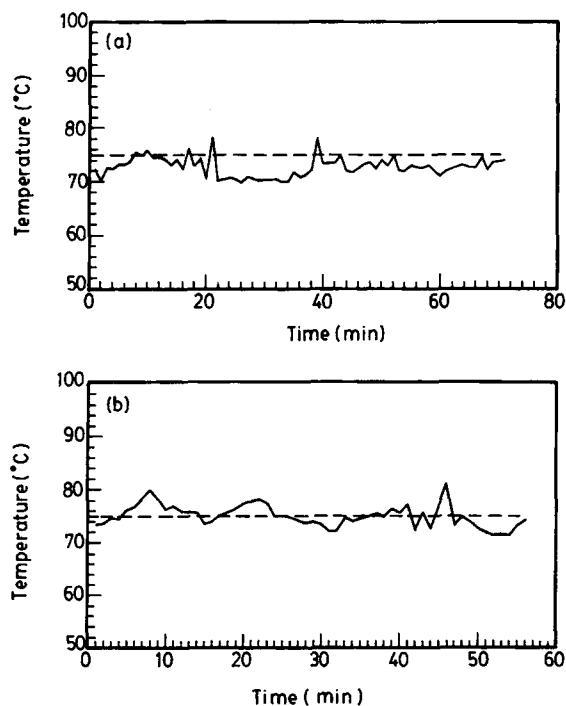


Figure 7 The comparisons of temperature control quality between (a) R051 and (b) R052.

are listed in Table I. In these simulation runs, we assumed that the upper bounds of heat generation were 1 kJ/min or 2 kJ/min separately. With higher heat-generation rates, the system becomes uncontrollable. The total moles of monomer were assumed to be 0.5 mol or 2.3 mol for purpose of comparison. The condition of terminating the reaction is 99% conversion of the total monomer added. In Table I, one can see that most results of experiments and simulation fit very well.

The monomer and initiator conditions for run R051, which set the upper bound of heat generation at 1 kJ/min and total monomer concentration of 0.5 mol without any constraint on the molecular weights, are given in Figure 2 (a) and (b). The conversion and molecular weights as a function of time are given in Figures 3 and 4 (a) and (b), respectively. It can be seen that the experimental data and simulations are consistent.

Figure 5 (a) and (b) compares the conditions with different upper bounds of heat generation, 1 kJ/min for R051 and 2 kJ/min for R052, but without molecular weight constraints. Figure 6 shows the experimental and simulation conversions as a function of time, while Figure 7 (a) and (b) gives the tem-

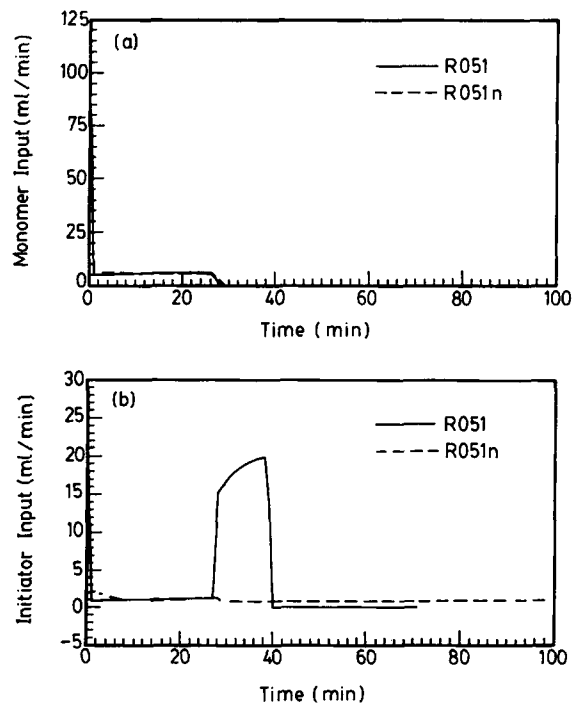


Figure 8 The comparisons of optimal conditions between R051 and R051n: (a) monomer input and (b) initiator input as functions of time.

perature histories of both runs. It can be observed that the batch time of the higher heat-generation run is shorter. The temperature oscillates a little more, and this is reasonable.

Figure 8(a) and (b) compare the monomer and initiator conditions between runs R051 and R051n, where R051n implemented the same constraints on monomer amount and upper bound of heat generation as did R051. However, in R051n, the number-average molecular weight of the polymer product is restricted within the range 2.9×10^5 and 3.1×10^5 . As shown in Table I, the lower bound of this constraint applies. Figure 9(a) compares monomer compositions in the reactor as a function of time. As we derived in the previous sections, the constraints required higher monomer compositions and lower initiator compositions as shown in Figure 9(b) in order to obtain a higher molecular weight. It should be noted that all solutions for the initiator and monomer show similar patterns. The amount of initiator added to the reactor increases quickly at the end of each batch to speed up the reaction. However, only a small amount of initiator is added at the beginning of each batch since the monomer

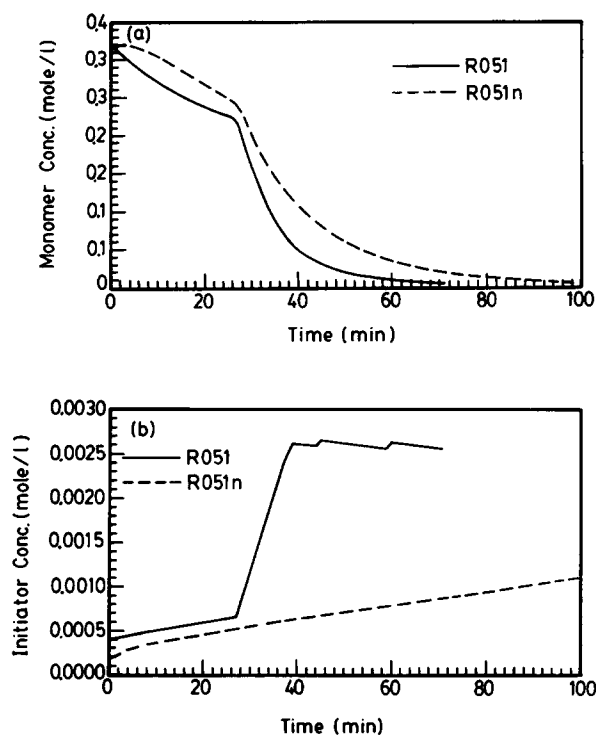


Figure 9 The comparisons of (a) monomer compositions and (b) initiators in the reactors between runs R051 and R051n.

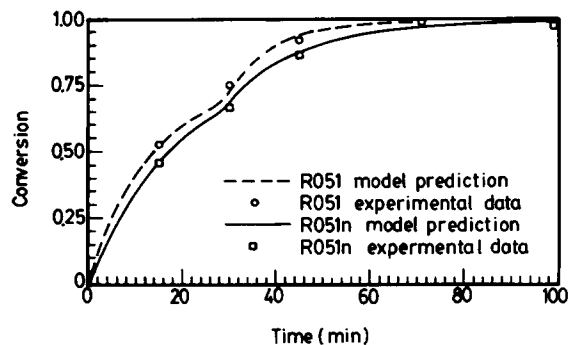


Figure 10 The comparisons of optimal profiles of conversions between R051 and R051n, where lines are simulations and symbols are experimental data.

composition is high at that time and reaction rate is restricted by the constraint. Figure 10 compares the conversions, whereas the number-average molecular weights for both runs are given in Table I.

Figure 11(a) and (b) compares the monomer and initiator policies between runs R232 and R232nw, where R232nw implements both number- and weight-average molecular weight constraints. Figure

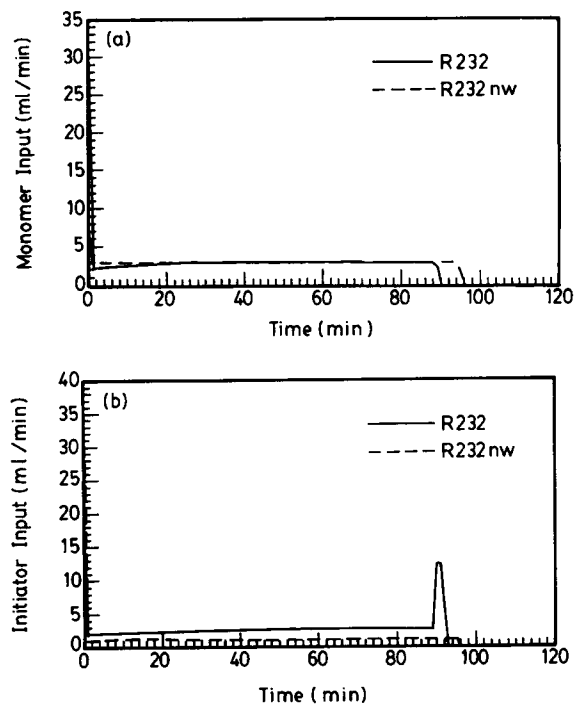


Figure 11 The comparison of optimal (a) monomer and (b) initiator conditions between runs R232 and R232nw.

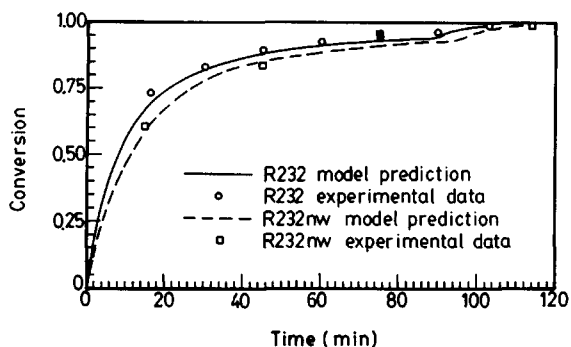


Figure 12 The comparison of conversion profiles as a function of time between runs R232 and R232nw.

12 compares the experimental and simulation results of R232 and R232nw, and molecular weights of both runs are also given in Table I. The results show that the limited experimental data and numerical solutions agree well.

CONCLUSION

A very popular semibatch process, the polymerization of acrylamide, has been optimized. The solution method assumes that the optimal approach uses polynomials. The control variables are the monomer and initiator feed rates. The solutions and experiments show that the system can be operated smoothly and product quality can be guaranteed.

The solutions of the optimization problem minimized the operating time and restricted the heat generation and molecular weight and molecular weight distribution. Experiments were performed to verify the numerical solutions.

NOTATION

$[I]$	initiator concentration
$I_{\text{tot},U}$	upper bound of the total amount of initiator
l_i	Lagrange interpolating function
$k_{1,25}$	rate constant, $1.7 \times e^{-16900/1.987T}$
k_d	decomposition rate constant of the initiator, $2.12 \times 10^{18} e^{-33320/1.987T}$
$[M]$	monomer concentration

M_{tot}	the total amount of monomer
\bar{M}_n	the number-average molecular weight of polyacrylamide
\bar{M}_w	the weight-average molecular weight of polyacrylamide
N_c	number of collocation points
R_p	polymerization rate
$R_{p,u}$	maximum polymerization rate
\bar{r}_n	the number-average length of polyacrylamide
\bar{r}_w	the weight-average length of polyacrylamide
t	time
t_0	initial time
t_f	final time
U	molecular weight distribution
$u(t)$	monomer feed rate
$v(t)$	initiator feed rate
W	molecular weight of acrylamide
x	conversion

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