

Optimal Periodic Control of a Continuous "Living" Anionic Polymerization II. New Theoretical Results

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Synopsis

In a previous publication,¹ a suboptimal technique was developed to solve the problem of producing polymers with prespecified values of the number-average chain length and the polydispersity, through "living" anionic polymerizations carried out in continuous stirred-tank reactors. The solution of that problem involved the periodic operation of the monomer solution feed and of the initiator solution feed, as well as readjustments in their feedstock concentrations. The present work solves the problem directly, without resorting to laborious "optimization-rescaling" procedures. The objective functional considers not only the polymer quality, but also the required polymer production. Compared with the previous results,¹ the present solutions are better and obtained with less computational effort. The proposed technique may be applicable to other optimal periodic control problems with nonconventional objective functionals.

INTRODUCTION

When a "living" anionic polymerization is carried out in a continuous stirred-tank reactor (CSTR) operated in the steady-state (SS), then (1) the number-average chain length μ_n (or the weight-average chain length μ_w) may be altered by adjusting the flow ratio between the monomer solution and the initiator solution; and (2) the polymer produced ideally exhibits a Schultz-Flory distribution with a fixed polydispersity $D_n (= \mu_w/\mu_n)$ of 2.

With respect to the SS operation, the periodic operation (PO) of continuous polymerization reactors provides enhanced flexibility in the quality of the average polymer produced. The forced feed oscillations of CSTR in which living anionic polymerizations are carried out has been previously investigated in several publications,¹⁻⁵ but only References 1 and 5 have considered its optimal periodic control problem. In general, this type of control has been studied by several authors, from both a theoretical⁶⁻¹⁴ and an applied viewpoint.¹⁵⁻²¹

The present work provides new results for the problem proposed in Frontini et al.¹ In that work, the production of polymers with any prespecified number-average chain length and polydispersity was intended when living anionic polymerizations were carried out in CSTR operated under periodic forcing of the feed flows. To that effect, a suboptimal objective functional related to the average polydispersity was employed. The functional was maximized and minimized in order to determine the feasible range of the

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average polydispersity, around the SS value of 2. In principle, polymers with any average polydispersity within that range could be produced, by adjustment of the step of the iterative numerical procedure employed in the optimization. Also, both the desired average values of the polydispersity and the number-average chain length could be obtained in a doubly iterative procedure involving the readjustment of the initial SS value of the flows and/or the readjustment of the feedstock concentrations. In the present work, an optimal objective functional is utilized to provide the desired product, at the required production rate, in a single optimization stage. To this effect, the theoretical tools described in Watanabe et al.²⁰ are utilized in conjunction with an adaptation of the numerical algorithm in the classic paper by Horn and Lin.⁶ As far as the authors are aware, this is the first application in which such a combination of techniques is employed.

THE SYSTEM MODEL AND THE OPTIMAL OBJECTIVE FUNCTIONAL

As in Reference 1, the following state model for a nonterminated anionic solution homopolymerization carried out in an isothermal and homogeneous CSTR is considered:

$$\frac{d[I(t)]}{dt} = \frac{1}{V}f_I(t)[I'] - \frac{f_I(t) + f_M(t)}{V}[I(t)] - k_i[I(t)][M(t)] \quad (1a)$$

$$\begin{aligned} \frac{d[M(t)]}{dt} = & \frac{1}{V}f_M(t)[M'] - \frac{f_I(t) + f_M(t)}{V}[M(t)] - k_i[I(t)][M(t)] \\ & - k_p[M(t)]\lambda_0(t) \end{aligned} \quad (1b)$$

$$\frac{d\lambda_0(t)}{dt} = k_i[I(t)][M(t)] - \frac{f_I(t) + f_M(t)}{V}\lambda_0(t) \quad (1c)$$

$$\frac{d\lambda_1(t)}{dt} = k_i[I(t)][M(t)] - \frac{f_I(t) + f_M(t)}{V}\lambda_1(t) + k_p[M(t)]\lambda_0(t) \quad (1d)$$

$$\begin{aligned} \frac{d\lambda_2(t)}{dt} = & k_i[I(t)][M(t)] - \frac{f_I(t) + f_M(t)}{V}\lambda_2(t) \\ & + k_p[M(t)](2\lambda_1(t) + \lambda_0(t)) \end{aligned} \quad (1e)$$

where:

$[I(t)], [M(t)]$ = concentrations of the initiator solution and the monomer solution, respectively, in mol/dm³

$\lambda_n = \sum_j j^n [P_j]$ ($n = 0, 1, \text{ and } 2$), the first three moments of the number-chain length distribution $[P_j]$ versus j , where P_j is the living polymer of chain length j

V = reaction volume, in dm³

$f_I(t), f_M(t)$ = feed flow rates of the initiator solution and the monomer solution, respectively, in dm³/h

k_i, k_p = initiation and propagation constants, respectively, in dm³/g-mol-h

f = superscript indicates feedstock conditions

The quality of a polymer obtained under PO is represented by the average properties obtained under periodicity conditions of the accumulated effluent along a period of oscillation T_p . We shall indicate these properties by an asterisk (*). For example, the average moments are

$$\lambda_n^* = \frac{\int_t^{t+T_p} [f_I(\tau) + f_M(\tau)] \lambda_n(\tau) d\tau}{\int_t^{t+T_p} [f_I(\tau) + f_M(\tau)] d\tau} \quad n = 0, 1, 2 \quad (2)$$

and therefore,

$$\mu_n^* = \frac{\lambda_1^*}{\lambda_0^*} \quad (3)$$

$$D_n^* = \frac{\lambda_0^* \lambda_2^*}{(\lambda_1^*)^2} \quad (4)$$

Other important properties are the average reagent conversions and the polymer production per unit time z . For example, the average monomer conversion and the average production (in g/h) may be calculated from

$$\eta_M^* = 1 - \frac{\int_t^{t+T_p} (f_I(\tau) + f_M(\tau)) [M(\tau)] d\tau}{\int_t^{t+T_p} f_M(\tau) [M^I] d\tau} \quad (5)$$

and

$$z = \frac{W_M}{T_p} \int_t^{t+T_p} [f_I(\tau) + f_M(\tau)] \lambda_1(\tau) d\tau \quad (6)$$

where W_M is the monomer molecular weight in g/g-mol.

The optimal functional to be minimized can be written, for example, as the sum of three terms, corresponding to deviations from their desired values (represented by the superscript d) of μ_n , D_n , and z , as follows:

$$J = \frac{w_1}{(D_n^d)^2} \left[\frac{\lambda_0^* \lambda_2^*}{(\lambda_1^*)^2} - D_n^d \right]^2 + \frac{w_2}{(\mu_n^d)^2} \left[\frac{\lambda_n^*}{\lambda_0^*} - \mu_n^d \right]^2 + \frac{w_3}{(z^d)^2} [W_M \lambda_1^* - z^d]^2 \quad (7)$$

where w_1 , w_2 , and w_3 are adjustable weights. Note that each term is squared (in order to avoid cancellations) and normalized (in order to make the terms comparable). Ideally, our aim is finding the periodic feed flows $f_M(t)$ and $f_I(t)$ such that the functional of eq. (7) is zero.

**THE OPTIMAL PERIODIC CONTROL WITH
NONCONVENTIONAL OBJECTIVE FUNCTIONALS**

In Horn and Lin,⁶ a method for solving the optimal periodic control problem is developed for an objective functional j consisting of a time-average value over a period of oscillation of a nonlinear scalar function m , depending on the n vector of states $\mathbf{x}(t)$ and on the s vector of controls or manipulated variables $\mathbf{f}(t)$:

$$j = \frac{1}{T_p} \int_0^{T_p} m[\mathbf{x}(t), \mathbf{f}(t)] dt \quad (8)$$

where T_p is considered fixed. In Frontini et al.,¹ a suboptimal objective functional consisting of the time-average value of the instantaneous polydispersity was adopted, in order to fit to the general form of eq. (8). Obviously, the functional of eq. (7) with the definitions of eqs. (2) and (6) falls into a more general class than that of eq. (8) and may be represented as

$$J = g(\mathbf{j}) \quad (9a)$$

where g is a nonlinear scalar function of the r vector,

$$\mathbf{j} = \frac{1}{T_p} \int_0^{T_p} \mathbf{m}[\mathbf{x}(t), \mathbf{f}(t)] dt \quad (9b)$$

and \mathbf{m} is an r vector of nonlinear functions. The extremization of J is subject to the restrictions imposed by the model represented by eq. (1), which may be symbolized as

$$\frac{d\mathbf{x}(t)}{dt} = \mathbf{a}[\mathbf{x}(t), \mathbf{f}(t)] \quad (10)$$

where in our case, $\mathbf{x}(t) = [[I(t)], [M(t)], \lambda_0(t), \lambda_1(t), \lambda_2(t)]^T$: is the state vector and $\mathbf{f}(t) = [f_I(t), f_M(t)]^T$: is the control vector. The periodicity condition

$$\mathbf{x}(0) = \mathbf{x}(T_p) \quad (11)$$

must be also verified.

In the approach by Watanabe et al.,²⁰ this problem is solved by defining a Hamiltonian:

$$H = \mathbf{p}^T \mathbf{m} + \gamma^T \mathbf{a} \quad (12a)$$

where \mathbf{p} is a real r vector calculated through

$$\mathbf{p} = \frac{\partial g}{\partial \mathbf{j}} \quad (12b)$$

and $\gamma(t)$ is an n vector of periodic functions (called the costates vector),

which can be obtained through the differential system

$$\frac{d\gamma(t)}{dt} = \frac{\partial H}{\partial \mathbf{x}} \quad (12c)$$

with

$$\gamma(0) = \gamma(T_p) \quad (12d)$$

The problem represented by eqs. (9) through (12) may be numerically solved through a gradient technique equivalent to that described in Horn and Lin.⁶ In our case, this technique, with the modification suggested in Denn,²² is employed; that is, the necessary controls are calculated through the iterative procedure

$$f(t)|_{\text{new}} = f(t)|_{\text{old}} - \epsilon \frac{\partial H}{\partial \mathbf{f}} \quad \epsilon > 0 \quad (13a)$$

with

$$\epsilon = \text{diagonal}(\epsilon_1, \dots, \epsilon_i, \dots, \epsilon_s) \quad (13b)$$

and

$$\epsilon_i = \frac{c_i}{\left[\int_0^{T_p} \left(\frac{\partial H}{\partial f_i} \right)^2 dt \right]^{1/2}} \quad (13c)$$

In eq. (13c), c_i is an adjustable coefficient for the step length.

The variational analysis from which the equations are obtained is developed in Appendix A. Appendix B provides the expressions of eqs. (9), (12), and (13) for the problem under study.

As explained in Frontini et al.,¹ the "best" period of oscillation T_p and the initial perturbation to start the iterative procedure may be found by application of the sensitivity analysis developed in Sinčić and Bailey.¹⁹ The initial perturbation must be added to an optimal SS condition. In our particular problem, and through appropriate SS designs, it is always possible to obtain the desired production and number-average chain length; the polydispersity will be always 2, however. For this reason, any design with $\mu_n^s = \mu_n^d$ and $z^s = z^d$ is an optimal SS. (We use the superscript s to indicate the SS condition.)

In summary, the optimization of a periodic process may be performed as follows:

1. Design an optimal SS operation (in our case based on μ_n^d and z^d).
2. Choose T_p and the initial control perturbation through the method suggested in Frontini et al.¹
3. Find the solution to the state equation (10), subject to eq. (11).
4. Solve the costate equation (12c), subject to eq. (12d).
5. Improve the control through eq. (13).
6. Iteratively repeat steps 3–6 until no significant improvement in J is obtained.

TABLE I
 Optimal SS Conditions

Raw data	SS values
$V = 0.9 \text{ dm}^3$	$[I]^s = 0.0001454 \text{ g-mol/dm}^3$
$k_i = 21.4 \text{ dm}^3/\text{g-mol-h}$	$[M]^s = 0.4819 \text{ g-mol/dm}^3$
$k_p = 4284 \text{ dm}^3/\text{g-mol-h}$	$D_n^s = 2$
$[I^f] = 0.003 \text{ g-mol/dm}^3$	$\mu_n^s = 1860$
$[M^f] = 6 \text{ g-mol/dm}^3$	$z^s = 165 \text{ g/h}$
$f_i^s = f_M^s = 0.5 \text{ dm}^3/\text{h}$	$\eta_f^s = 0.90$
$W_M = 65.12 \text{ g/g-mol}$	$\eta_M^s = 0.84$
	$\theta^s = 0.9 \text{ h}$

 TABLE II
 Characteristics of the Required Polymers

	D_n^d	μ_n^d	$z^d \text{ (g/h)}$
Polymer A	4.0	1860	170
Polymer B	1.5	1860	170

THE SIMULATION RUNS

Consider, as in Frontini et al.,¹ the polymerization of isoprene in *n*-heptane with *n*-butyllithium as initiator at 25°C. Table I provides the basic raw data and the results of a SS operation (θ represents the reactor mean residence time). The solution in Table I may be taken as the initial optimal SS when the polymers with the characteristics indicated in Table II must be produced. Also, the straight maximization and minimization of the average polydispersity will be investigated. In this case, we shall take $J = D_n^*$, and again the optimal SS condition of Table I. The computer programs were written in FORTRAN for a VAX 11/780. Owing to the "stiffness" of the state equations, one of Gear's integration routines was employed.

Selection of T_p and of the Initial Perturbation

Let the initial flow perturbations be sinusoids of small amplitudes of an adjustable frequency $\omega = 2\pi/T_p$ and of an adjustable phase T . By means of the sensitivity analysis due to Sinčić and Bailey,¹⁹ as applied in Frontini et al.,¹ one may find the best combination of T_p and T for the optimization algorithm. The values of T_p and T providing the maximum negative variation of the functional ΔJ are chosen to minimize J . Similarly, those values providing the maximum positive variation of J are adopted for the maximization of J .

Let J_A and J_B be the functional of eq. (7) associated with polymers A and B in Table II, respectively, with the weights $w_1 = w_2 = w_3 = 1$. The sensitivity analyses for the functional taken as J_A , J_B , and D_n^* are represented in Figures 1a, 1b, and 1c, respectively. For the different cases under study, the adopted combinations of T_p and T are indicated in Table III. It is interesting to note that, irrespective of the functional structure, the results are identical

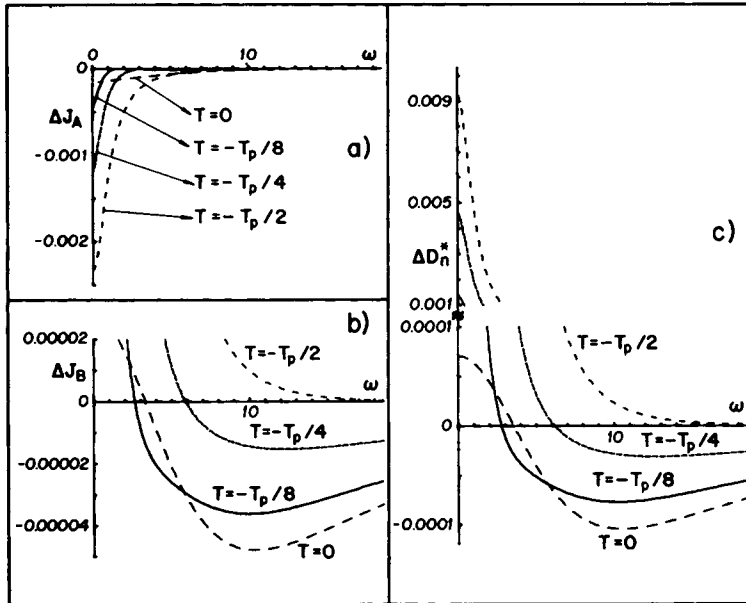


Fig. 1. Sensitivity analyses for the specification of T_p and T . (a) Production of polymer A. (b) Production of polymer B. (c) Extremization of D_n^* .

TABLE III
Selected Combinations of T_p and T for the Different Optimization Cases Considered

	ω (L/h)	T_p (h)	T
min J_A	0.31	20	$T_p/2$
min J_B	10.5	0.6	0
min D_n^*	10.5	0.6	0
max D_n^*	0.31	20	$T_p/2$

when an average polydispersity greater than 2 is required, and the same is true when an average polydispersity below 2 is specified. This indicates that D_n^* is the principal variable affected by T_p and T , the reason perhaps being that any desired μ_n^* and z may be obtained directly in the SS. The sensitivity analysis requires that when $D_n^d > 2$, then $T_p \rightarrow \infty$ should be selected. This would signify an infinitely large collecting tank for the reactor effluent, and the selected period ($T_p = 20$ h) implies a compromise between the two conflicting effects.

The Optimization Results

Consider first how to obtain polymers A and B of Table II. The resulting optimal periodic profiles are represented in Figure 2, and the average properties are indicated in Table IV. For the given set of data, the solution corresponding to polymer A may be readily obtained. In the case of polymer B and for the original set of data, a solution with a value of J very close to zero could not be found, in spite of having investigated with different

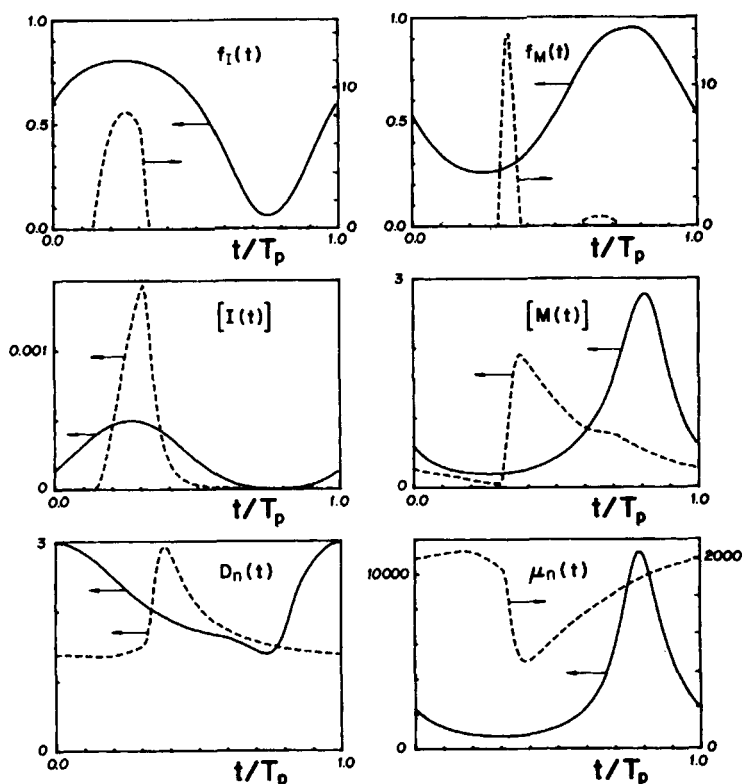


Fig. 2. Optimal profiles for the production of polymer A (—) and for the obtainment of polymer B (---).

TABLE IV
Average Properties Obtained When Polymers A and B Were Required

	$[I^I]$	$[M^I]$	D_n^*	μ_n^*	z	η_i^*	η_M^*	θ	J
Production of polymer A	0.003	6.0	3.99	1866	169.8	0.85	0.72	0.82	4×10^{-5}
Production of polymer B	0.003	6.0	1.58	1840	206	0.55	0.80	0.55	0.0078

combinations of the weights w_i . This is consistent with the difficulties previously observed in Frontini et al.¹ and probably indicates that a solution with $J = 0$ may simply not exist for the given data set.

Consider now the straightforward maximization and minimization of D_n^* . The results may be found in Figure 3, and under Kinetics 1 of Table V. Clearly, polymers with any value of D_n^* between 1.13 and 12.7 could be produced with the system under study. The optimal profiles are qualitatively equivalent to those obtained in Frontini et al.,¹ thus validating the suboptimal functional selected in that opportunity. The enhanced flexibility obtained here with respect to the maximum value of D_n^* is mainly determined by the change in T_p . (In the paper mentioned, a large T_p could not be used to produce

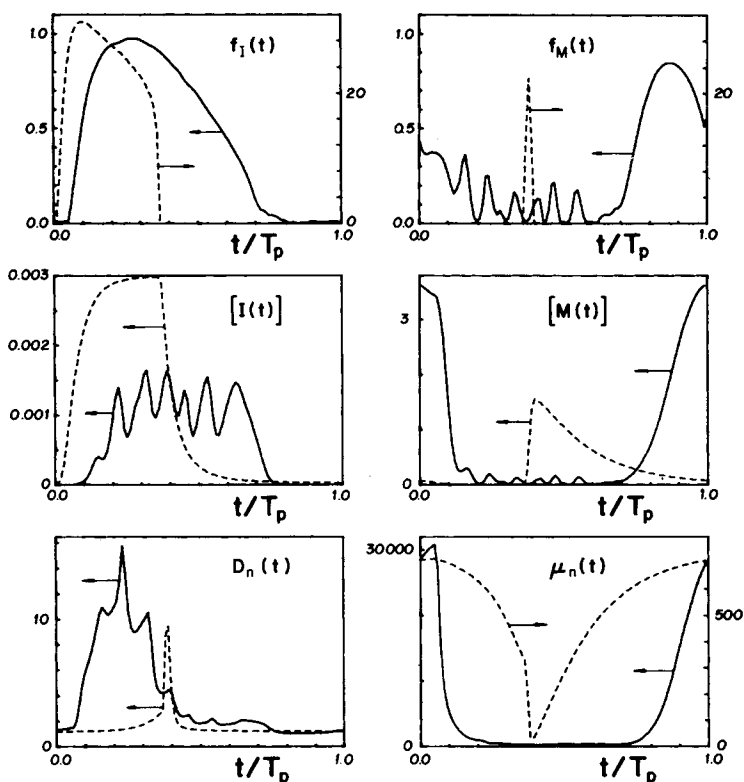


Fig. 3. Optimal profiles for the maximization of D_n^* (—) and for the minimization of D_n^* (- -).

TABLE V
Results of the Extremizations of D_n^* for the Simulated Example (Kinetics 1) and for Other Combinations of the Rate Constants

		T_p (h)	T	D_n^s, D_n^*	μ_n^s, μ_n^*	z^s, z (g/h)	η_I^s, η_I^*	η_M^s, η_M^*	θ^s, θ (h)
Kinetics 1	SS	—	—	2	1860	171	0.903	0.839	0.9
$(k_i = 24.47$ and $k_p = 4284)$	max D_n^*	20	$T_p/2$	12.7	1244	86.5	0.656	0.669	1.08
	min D_n^*	0.6	0	1.13	679	161	0.132	0.83	0.097
Kinetics 2	SS	—	—	2	1705	174	0.99	0.853	0.9
$(k_i = 42840$ and $k_p = 4284)$	max D_n^*	20	$T_p/2$	43.8	483	58.4	0.993	0.656	1.1
	min D_n^*	0.16	0	1.06	2102	100	1.0	0.007	0.025
Kinetics 3	SS	—	—	2	3170	199	0.614	0.9726	0.9
$(k_i = 21.47$ and $k_p = 42840)$	max D_n^*	20	$T_p/2$	17.5	4122	175	0.442	0.716	0.84
	min D_n^*	1.4	0	1.29	1507	125	0.12	0.97	0.24
Kinetics 4	SS	—	—	2	1967	201	0.99	0.983	0.9
$(k_i = 42840$ and $k_p = 42840)$	max D_n^*	20	$T_p/2$	43.95	1612	139	0.98	0.8	1.05
	min D_n^*	0.06	$-T_p/6$	1.04	1.04	0.044	0.54	0.009	0.95

the largest possible values of D_n^* because the suboptimal functional did not increase under those conditions.)

In order to determine the feasible ranges of the average polydispersity for different combinations of the kinetic constants, D_n^* was extremized under kinetics 2–4 in Table V, with the other parameters remaining unaltered. In all

cases, the ranges observed in D_n^* are wider than those calculated in Frontini et al.¹ Note that, with fast initiation and propagation, a useless trivial solution (with $\mu_n^* \cong 1$) is obtained when minimizing D_n^* .

CONCLUSIONS

This work reconsiders an optimal periodic control problem previously solved suboptimally in Frontini et al.¹ In that publication, a "classic" objective functional was utilized and the periodic policy necessary to produce a prespecified polymer quality was calculated by means of ad hoc iterative procedures. Here, an optimization technique for non-conventional functionals is employed that allows one to solve the problem of producing the desired polymer at the required production rate in a straightforward manner, without resorting to "special" numerical algorithms. It should be emphasized that the proposed method is quite general and could be applied to many other optimal periodic control problems.

Through an adequate SS design, polymers with practically any desired average chain length and production are relatively easy to obtain. This is not the case with the polydispersity, however, and for this reason D_n^* is the most important optimization variable. For example, selection of the period of oscillation and of the initial perturbation seems to depend only on whether an average polydispersity above or below 2 is required.

Under certain design conditions (i.e., for a given combination of the rate constants, the reactor volume, the feedstock concentrations, and so on), polymers with exactly the prespecified values of the average chain length, the polydispersity, and the production can be produced. Otherwise, the optimization algorithm will converge to some "best possible" solution, which is a compromise between the different requirements. Such compromise may be adjusted through the functional weights. Furthermore, the objective functional could include more terms (e.g., a required monomer conversion), and the solution will again be a compromise between potentially conflicting factors. Also, the system model could be extended to include higher moments of the number chain length distribution. In this way, the polymer quality could be more finely specified.

Experimental validation of the proposed technique and the development of a closed-loop adaptive control for the periodic operation²³ are at present being investigated.

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APPENDIX A

Our optimal periodic control problem consists in minimizing the functional represented by eq. (9), subject to the constraints imposed by eqs. (10) and (11). From eq. (9), the variations of J and j are

$$\delta J = \frac{\partial g}{\partial j} \delta j \quad (\text{A.1})$$

and

$$\delta j = \frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial \mathbf{m}}{\partial \mathbf{x}} \delta \mathbf{x} + \frac{\partial \mathbf{m}}{\partial \mathbf{f}} \delta \mathbf{f} \right) dt \quad (\text{A.2})$$

Substituting (A.2) into (A.1) and bearing in mind that

$$\delta \dot{\mathbf{x}} = \frac{\partial \mathbf{a}}{\partial \mathbf{x}} \delta \mathbf{x} + \frac{\partial \mathbf{a}}{\partial \mathbf{f}} \delta \mathbf{f} \quad (\text{A.3})$$

then, one can write

$$\delta J = \frac{\partial g}{\partial j} \frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial \mathbf{m}}{\partial \mathbf{x}} \delta \mathbf{x} + \frac{\partial \mathbf{m}}{\partial \mathbf{f}} \delta \mathbf{f} \right) dt - \frac{1}{T_p} \int_0^{T_p} \gamma \left(\delta \dot{\mathbf{x}} - \frac{\partial \mathbf{a}}{\partial \mathbf{x}} \delta \mathbf{x} - \frac{\partial \mathbf{a}}{\partial \mathbf{f}} \delta \mathbf{f} \right) dt \quad (\text{A.4})$$

and

$$\delta J = \frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial g}{\partial j} \frac{\partial \mathbf{m}}{\partial \mathbf{x}} \delta \mathbf{x} + \frac{\partial g}{\partial j} \frac{\partial \mathbf{m}}{\partial \mathbf{f}} \delta \mathbf{f} - \gamma \delta \dot{\mathbf{x}} + \gamma \frac{\partial \mathbf{a}}{\partial \mathbf{x}} \delta \mathbf{x} + \gamma \frac{\partial \mathbf{a}}{\partial \mathbf{f}} \delta \mathbf{f} \right) dt \quad (\text{A.5})$$

Integrating the third term of the integrand by parts, one obtains

$$\begin{aligned} \delta J = & \frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial g}{\partial j} \frac{\partial \mathbf{m}}{\partial \mathbf{x}} + \gamma \frac{\partial \mathbf{a}}{\partial \mathbf{x}} + \dot{\gamma} \right) \delta \mathbf{x} dt - \frac{1}{T_p} \left(\gamma(T_p) \delta \mathbf{x}(T_p) - \gamma(0) \delta \mathbf{x}(0) \right) \\ & + \frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial g}{\partial j} \frac{\partial \mathbf{m}}{\partial \mathbf{f}} + \gamma \frac{\partial \mathbf{a}}{\partial \mathbf{f}} \right) \delta \mathbf{f} dt \end{aligned} \quad (\text{A.6})$$

Define the Hamiltonian as in eqs. (12a) and (12b). From the periodicity condition, we get $\gamma(T_p) \delta \mathbf{x}(T_p) = \gamma(0) \delta \mathbf{x}(0)$. Thus, eq. (A.6) may be written

$$\delta J = \frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial H}{\partial \mathbf{x}} + \dot{\gamma} \delta \mathbf{x} + \frac{\partial H}{\partial \mathbf{f}} \delta \mathbf{f} \right) dt \quad (\text{A.7})$$

Substituting eq. (12c) into eq. (A.7), we find

$$\delta J = \frac{1}{T_p} \int_0^{T_p} \frac{\partial H}{\partial \mathbf{f}} \delta \mathbf{f} dt \quad (\text{A.8})$$

By choosing

$$\delta \mathbf{f} = -\epsilon \frac{\partial H}{\partial \mathbf{f}} \quad \epsilon > 0 \quad (\text{A.9})$$

then

$$\delta J = -\frac{1}{T_p} \int_0^{T_p} \epsilon \left(\frac{\partial H}{\partial \mathbf{f}} \right)^2 dt \quad (\text{A.10})$$

will be always negative, thus ensuring the minimization of J .

APPENDIX B

From eqs. (2), (6), and (7) one may write

$$J = \frac{w_1}{(D_n^d)^2} \left(\frac{j_1 j_3}{j_2^2} - D_n^d \right)^2 + \frac{w_2}{(\mu_n^d)^2} \left(\frac{j_2}{j_1} - \mu_n^d \right)^2 + \frac{w_3}{(z^d)^2} [W_M j_2 - z^d]^2 \quad (\text{B.1})$$

with

$$j_i = \frac{1}{T_p} \int_0^{T_p} (f_I + f_M) \lambda_{i-1} dt \quad i = 1, 2, 3 \quad (\text{B.2})$$

The real multipliers defined by eq. (12b) are

$$\begin{aligned} p_1 &= 2 \frac{w_1}{(D_n^d)^2} \left(\frac{j_1 j_3}{j_2^2} - D_n^d \right) \frac{j_3}{j_2^2} - 2 \frac{w_2}{(\mu_n^d)^2} \left(\frac{j_2}{j_1} - \mu_n^d \right) \frac{j_2}{j_1^2} \\ p_2 &= -4 \frac{w_1}{(D_n^d)^2} \left(\frac{j_1 j_3}{j_2^2} - D_n^d \right) \frac{j_1 j_3}{j_2^3} + 2 \frac{w_2}{(\mu_n^d)^2} \left(\frac{j_2}{j_1} - \mu_n^d \right) \frac{1}{j_1} \\ &\quad + 2 \frac{w_3}{(z^d)^2} (W_M j_2 - z^d) W_M \\ p_3 &= \frac{2w_1}{(D_n^d)^2} \left(\frac{j_1 j_3}{j_2^2} - D_n^d \right) \frac{j_1}{j_2^2} \end{aligned} \quad (\text{B.3})$$

From the Hamiltonian, the costates equations result:

$$\begin{aligned} \frac{d\gamma_1}{dt} &= \left(\frac{f_I + f_M}{V} + k_i[M] \right) \gamma_1 + k_i[M] \gamma_2 - (\gamma_3 + \gamma_4 + \gamma_5) k_i[M] \\ \frac{d\gamma_2}{dt} &= k_i[I] \gamma_1 + \left(\frac{f_I + f_M}{V} + k_i[I] + k_p \gamma_0 \right) \gamma_2 - k_i[I] \gamma_3 \\ &\quad - (k_i[I] + k_p \lambda_0) \gamma_4 - [k_i[I] + k_p (2\lambda_1 + \lambda_0)] \gamma_5 \\ \frac{d\gamma_3}{dt} &= k_p[M] \gamma_2 + \frac{f_I + f_M}{V} \gamma_3 - k_p[M] \gamma_4 \\ &\quad - k_p[M] \gamma_5 - p_1 (f_I + f_M) \\ \frac{d\gamma_4}{dt} &= \frac{f_I + f_M}{V} \gamma_4 - 2k_p[M] \gamma_5 - p_2 (f_I + f_M) \\ \frac{d\gamma_5}{dt} &= \frac{f_I + f_M}{V} \gamma_5 - p_3 (f_I + f_M) \end{aligned} \quad (\text{B.4})$$

Finally, the new controls are obtained through

$$\Delta f_I = \frac{c}{\left[\frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial H}{\partial f_I} \right)^2 dt \right]^{1/2}} \frac{\partial H}{\partial f_I}$$

$$\Delta f_M = \frac{c}{\left[\frac{1}{T_p} \int_0^{T_p} \left(\frac{\partial H}{\partial f_M} \right)^2 dt \right]^{1/2}} \frac{\partial H}{\partial f_M}$$
(B.5)

with

$$\frac{\partial H}{\partial f_I} = \gamma_1 \frac{[I'] - [I]}{V} - \gamma_2 \frac{[M]}{V} - \gamma_3 \frac{\lambda_0}{V} - \gamma_4 \frac{\lambda_1}{V} - \gamma_5 \frac{\lambda_2}{V} + p_1 \lambda_0$$

$$+ p_2 \lambda_1 + p_3 \lambda_2$$

$$\frac{\partial H}{\partial f_M} = -\gamma_1 \frac{[I]}{V} + \gamma_2 \frac{[M'] - [M]}{V} - \gamma_3 \frac{\lambda_0}{V} - \gamma_4 \frac{\lambda_1}{V} - \gamma_5 \frac{\lambda_2}{V} + p_1 \lambda_0$$

$$+ p_2 \lambda_1 + p_3 \lambda_2$$
(B.6)

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