Optimal Periodic Control of a Continuous "Living" Anionic Polymerization. I. Theoretical Study

G. L. FRONTINI, G. E. ELIÇABE, D. A. COUSO, and G. R. MEIRA,*
*INTEC (CONICET and Universidad Nacional del Litoral), C.C. 91, (3000)
Santa Fe, Argentina*

Synopsis

Within certain limitations, this work shows that the production of polymers with any prespecified number average chain length and polydispersity is theoretically feasible when "living" anionic polymerizations are carried out in continuous stirred tank reactors (CSTRs) which are under optimal periodic forcing of the feed flows. The optimal periodic control problem was solved adopting a suboptimal objective function and a novel iterative numerical procedure. When the objective function is minimized in order to reduce the time average polydispersity, then the operation tends to become a sequential semibatch process. Conversely, if the objective is to maximize these variables, then the reagent concentrations inside the reactor tend to be 180° out of phase. Different periods of oscillation must be selected depending on whether the required average polydispersities are above or below the steady state value of 2. The greatest flexibility in the MWD control is obtained with fast kinetics, and, in this case, average polydispersities between 1.06 and 9.2 may be required.

INTRODUCTION

Under ideal conditions, when a "nonterminated" anionic homopolymerization is carried out in a CSTR operated in the steady-state (SS), then the produced polymer exhibits a Schultz–Flory molecular weight distribution (MWD), with a fixed polydispersity D_n $(= \mu_w/\mu_n)$ of 2. The average chain lengths μ_n and μ_w may be altered, however, by adjusting the flow ratio between the monomer solution and the initiator solution.

The periodic operation (PO) of continuous polymerization reactors has shown certain advantages with respect to the SS operation,[1] and the particular problem of the forced feed oscillations in CSTRs where "living" anionic polymerizations are carried out has been previously studied at several opportunities. The first work[2] indicated that, with slow independent oscillations of the monomer and the initiator concentrations, the time average polydispersity could be increased with respect to the SS value. Bandermann[3] showed that, through sinusoidal oscillations of the "living" ends concentration inside the reactor, average polydispersities both above and below 2 could be produced, by simply altering the mean level of the oscillation. In a very recent publication,[4] square oscillations of the reagent feeds 180° out of phase and over a wide range of frequencies were considered. The average polydispersity could be varied between 1.75 at intermediate frequencies up to about 10 at the low frequency limit. Under certain conditions, the monomer conversion is always higher with PO than in the SS.

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* To whom correspondence should be sent.

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The optimal periodic control problem has been studied by several authors, both from a theoretical[5-13] and from an applied viewpoint.[14-20] In particular, the optimal periodic control of a continuous anionic polymerization was investigated by Langner and Bandermann.[21] In that work, an objective function was minimized with the aim of operating the reactor in an intermediate fashion between a normal CSTR and a batch reactor, and in order to obtain polymers with polydispersities between 1.375 and 1.9. The control variables were the feed flows and the reactor outlet flow, and consequently the reactor volume oscillated cyclically. A suboptimal form of the theoretical solution was experimentally evaluated, and the polymer produced exhibited a polydispersity of 1.19.

In the present work, the same chemical system as in the above-mentioned article by Langner and Banderman is theoretically investigated, but with the more general objective of producing polymers with predetermined average values of both the polydispersity and the number average chain length, by forcing the feed flows only. Average polydispersities both below and above 2 can be prespecified.

THE DYNAMIC MODEL

Consider a nonterminated anionic solution homopolymerization carried out in an isothermal and ideally-stirred CSTR. Assuming (a) a reaction mechanism consisting of simple initiation and propagation, (b) propagation constants independent of the polymer chain length, (c) a polymer density independent of chain length, (d) all kinetics are first order in each reagent, (e) constant reaction volume, and (f) outlet reactor flow instantaneously equal to the sum of the feed flows; then the following mass balance may be written[4]:

$$\frac{d[\mathrm{I}]}{dt} = \frac{1}{V} f_\mathrm{I}\,[\mathrm{I}^f] - \frac{f_\mathrm{I} + f_\mathrm{M}}{V}\,[\mathrm{I}] - k_i\,[\mathrm{I}]\,[\mathrm{M}] \tag{1a}$$

$$\frac{d[\mathrm{M}]}{dt} = \frac{1}{V} f_\mathrm{M}\,[\mathrm{M}^f] - \frac{f_\mathrm{I} + f_\mathrm{M}}{V}\,[\mathrm{M}] - k_i\,[\mathrm{I}]\,[\mathrm{M}] - k_p[\mathrm{M}]\lambda_0 \tag{1b}$$

$$\frac{d\lambda_0}{dt} = k_i[\mathrm{I}]\,[\mathrm{M}] - \frac{f_\mathrm{I} + f_\mathrm{M}}{V}\,\lambda_0 \tag{1c}$$

$$\frac{d\lambda_1}{dt} = k_i\,[\mathrm{I}]\,[\mathrm{M}] - \frac{f_\mathrm{I} + f_\mathrm{M}}{V}\,\lambda_1 + k_p[\mathrm{M}]\lambda_0 \tag{1d}$$

$$\frac{d\lambda_2}{dt} = k_i[\mathrm{I}]\,[\mathrm{M}] - \frac{f_\mathrm{I} + f_\mathrm{M}}{V}\,\lambda_2 + k_p[\mathrm{M}]\,(2\lambda_1 + \lambda_0) \tag{1e}$$

where [I] and [M] are the concentrations of the initiator and the monomer solutions, respectively, (mol/dm^3), $\lambda_n = \Sigma_j j^n\,[\mathrm{P}j]$ ($n = 0$, 1, and 2) are the first three moments of the number chain length distribution P_j vs. j, where P_j is the "living" polymer of chain length j, V is the reaction volume (dm^3), f_I and f_M are the feed flow rates of the initiator and the monomer solutions, respectively (dm^3/h), k_i and k_p are the initiation and propagation constants, respectively, (dm^3/g mol h), and the superscript f indicates feed stock conditions. From eqs. (1), the instantaneous number average chain length and polydispersity may be calculated as follows:

$$\mu_n(t) = \frac{\lambda_1(t)}{\lambda_0(t)} \tag{2a}$$

$$D_n(t) = \frac{\lambda_0(t)\lambda_2(t)}{\lambda_1^2(t)} \tag{2b}$$

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

$$\lambda_n^* = \frac{\int_t^{t+T_p} [f_I(\tau) + f_M(\tau)]\lambda_n(\tau)\, d\tau}{\int_t^{t+T_p} [f_I(\tau) + f_M(\tau)]\, d\tau} \quad (n = 0, 1, 2) \tag{3}$$

and therefore

$$\mu_n^* = \frac{\lambda_1^*}{\lambda_0^*} \tag{4a}$$

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

Defining the simple time average of a variable $x(t)$ by

$$\bar{x} = \frac{1}{T_p}\int_t^{t+T_p} x(\tau)\, d\tau \tag{5}$$

note that $\bar{\lambda}_n \neq \lambda_n^*$; and, therefore, $\bar{\mu}_n \neq \mu_n^*$; $\bar{D}_n \neq D_n^*$.

Other important properties are the average conversion of a reagent and the average polymer production per unit time z. For example, the average monomer conversion is obtained through

$$\eta_M^* = 1 - \frac{\int_t^{t+T_p} (f_M(\tau) + f_M(\tau))\, [M(\tau)]\, d\tau}{\int_t^{t+T_p} f_M(\tau)[M^f]\, d\tau} \tag{6}$$

while the average production (g/h) may be calculated from

$$z = \frac{W_M}{T_p} \int_t^{t+T_p} \{[M^f] f_M(\tau) - [M(\tau)] (f_I(\tau) + f_M(\tau))\} \, d\tau \tag{7}$$

where W_M is the monomer molecular weight (g/g mol).

THE OPTIMAL PERIODIC CONTROL PROBLEM

In this section, the optimization of a suboptimal functional is first considered. Then, an iterative procedure which permits the production of polymers with any prespecified μ_n^* and D_n^* is proposed.

The Objective Function

Ideally, one would require minimization of an objective function consisting of the sum of three terms, corresponding to deviations from their desired values of μ_n^*, D_n^*, and z. However, optimal periodic control theory is as yet unable to deal with such complicated functionals, and even the simpler problem of extremizing D_n^* seems yet unsolvable. For this reason, Langner and Bandermann[21] considered the minimization of the following cost function:

$$J = \overline{D}_n = \frac{1}{T_p} \int_0^{T_p} \frac{\lambda_0(t)\lambda_2(t)}{\lambda_1^2(t)} \, dt \tag{8}$$

i.e., the simple time average of $D_n(t)$ along a period of oscillation. The selection was justified from the fact that, in all cases studied, when minimizing J, D_n^* always decreased. In the present work, the cost function of eq. (8) is also adopted, not only for obtaining polymers with average polidispersities below 2, but also for producing average polydispersities above that SS value. Denoting the SS condition with the superscript s, note that $J^s = D_n^s = 2$.

Extremization of the Suboptimal Functional

Consider the problem of extremizing,

$$J = \frac{1}{T_p} \int_0^{T_p} m(\mathbf{x}(t), \mathbf{f}(t)) \, dt \tag{9}$$

with T_p assumed fixed, and 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, $\mathbf{f}(t) = [f_I(t), f_M(t)]^T$ is the control vector, and $m = \lambda_0(t)\lambda_2(t)/\lambda_1^2(t)$. The extremization of J is subject to the restrictions imposed by the state model represented by eqs. (1), which may be symbolized by

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

The Hamiltonian is defined by

$$H = m + \boldsymbol{\gamma}^T(\mathbf{t})\mathbf{a}(\mathbf{x}(\mathrm{t}),\mathbf{f}\,(\mathrm{t})) \tag{11}$$

where $\boldsymbol{\gamma}(t)$ is the vector of costates, obtained from

$$\frac{d\boldsymbol{\gamma}(t)}{dt} = -\left[\frac{\partial H}{\partial \mathbf{x}}\right]^T = -\left[\frac{\partial m}{\partial \mathbf{x}}\right]^T - \frac{\partial \mathbf{a}}{\partial \mathbf{x}}\boldsymbol{\gamma}\,(t) \tag{12}$$

In our case, eq. (12) yields

$$\frac{d\gamma_1}{dt} = \left(\frac{f_{\mathrm{I}} + f_{\mathrm{M}}}{V} + k_i[\mathrm{M}]\right)\gamma_1 + k_i[\mathrm{M}]\gamma_2 - (\gamma_3 + \gamma_4 + \gamma_5)\,k_i[\mathrm{M}] \tag{13a}$$

$$\frac{d\gamma_2}{dt} = k_i\,[\mathrm{I}]\gamma_1 + \left(\frac{f_{\mathrm{I}} + f_{\mathrm{M}}}{V} + k_i[\mathrm{I}] + k_p\,\lambda_0\right)\gamma_2 - k_i[\mathrm{I}]\gamma_3$$

$$- (k_i[\mathrm{I}] + k_p\lambda_0)\gamma_4 - [\,k_i[\mathrm{I}] + k_p(2\lambda_1 + \lambda_0\,)\boldsymbol{\gamma}_5 \tag{13b}$$

$$\frac{d\gamma_3}{dt} = -\frac{\lambda_2}{\lambda_1^2} + k_p[\mathrm{M}]\gamma_2 + \frac{f_{\mathrm{I}} + f_{\mathrm{M}}}{V}\gamma_3 - k_p[\mathrm{M}]\gamma_4 - k_p[\mathrm{M}]\,\gamma_5 \tag{13c}$$

$$\frac{d\gamma_4}{dt} = 2\frac{\lambda_0\lambda_2}{\lambda_1^3} + \frac{f_{\mathrm{I}} + f_{\mathrm{M}}}{V}\gamma_4 - 2\,k_p[\mathrm{M}]\lambda_5 \tag{13d}$$

$$\frac{d\gamma_5}{dt} = -\frac{\lambda_0}{\lambda_1^2} + \frac{f_{\mathrm{I}} + f_{\mathrm{M}}}{V}\gamma_5 \tag{13e}$$

The periodicity condition must be verified by both state and costate vectors; i.e.,

$$\mathbf{x}(t) = \mathbf{x}\,(t + T_p) \tag{14a}$$

$$\boldsymbol{\gamma}(t) = \boldsymbol{\gamma}(t + T_p) \tag{14b}$$

In order to find the controls $\mathbf{f}(t)$ that extremize J, the numerical method proposed by Horn and Lin[5] with the modification suggested by Denn[22] to normalize the iteration steps was utilized. In summary, the control vector in the kth iteration $\mathbf{f}|_k$ may be found from its value at iteration k-1 as follows:

$$\mathbf{f}|_k = \mathbf{f}|_{k-1} + \Delta\mathbf{f}|_k = \mathbf{f}|_{k-1} + \mathrm{sg.}\epsilon\left[\frac{\partial \mathbf{a}}{\partial \mathbf{f}}\right]^T\boldsymbol{\gamma} \tag{15a}$$

where

$$\mathrm{sg.} = \begin{cases} +1 \text{ for maximizing } J \\ -1 \text{ for minimizing } J \end{cases} \tag{15b}$$

ϵ is the step length coefficient obtained through

$$\epsilon = \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix} \tag{15c}$$

with

$$\epsilon_i = \frac{c_i}{\left\{ \int_0^{T_p} [[\partial \mathbf{a}/\partial \mathbf{f}]^T \boldsymbol{\gamma}]_2 \, dt \right\}^{1/2}} \qquad (i = 1,2) \tag{15d}$$

In eq. (15d), c_i is an adjustable step length coefficient weight of the appropiate dimensions, and the denominator is included in order to normalize $[\partial \mathbf{a}/\partial \mathbf{f}]^T \boldsymbol{\gamma}$. The coefficients c_1 and c_2 should be relatively low values, and may be readjusted between iterations. In our case, the correction $\Delta \mathbf{f}$ yields:

$$\Delta f_{\mathrm{I}} = \frac{c_1}{\left[\int_0^{T_p} h_1^2(t) \, dt \right]^{1/2}} h_1(t) \tag{16a}$$

$$\Delta f_{\mathrm{M}} = \frac{c_2}{\left[\int_0^{T_p} h_2^2(t) \, dt \right]^{1/2}} h_2(t) \tag{16b}$$

with

$$h_1(t) = \left(\frac{[\mathrm{I}^f]}{V} - \frac{[\mathrm{I}]}{V} \right) \gamma_1 - \frac{[\mathrm{M}]}{V} \gamma_2 - \frac{\lambda_0}{V} \gamma_3 - \frac{\lambda_1}{V} \gamma_4 - \frac{\lambda_2}{V} \gamma_5 \tag{16c}$$

$$h_2(t) = -\frac{[\mathrm{I}]}{V} \gamma_1 + \left(\frac{[\mathrm{M}^f]}{V} - \frac{[\mathrm{M}]}{V} \right) \gamma_2 - \frac{\lambda_0}{V} \gamma_3 - \frac{\lambda_1}{V} \gamma_4 - \frac{\lambda_2}{V} \gamma_5 \tag{16d}$$

In order to start the iterative procedure, a small periodic perturbation must be superimposed around an optimum SS value. In our particular problem, any arbitrary initial SS condition is adequate for the optimization, because J^s is invariant for any given combination of the SS inputs.

The Period of Oscillation and the Initial Perturbation

For a given set of feed profiles, the period of oscillation has a great influence on μ_n^* and D_n^*, thus indicating the importance of adequately selecting this parameter.[4] In this work, the definition of T_p and of the initial perturbation necessary to start the iterative procedure is based on a sensitivity analysis due to Sinčić and Bailey.[18] Assume that the initial control is obtained by imposing a small periodic perturbation $\delta \mathbf{f}(t)$ about a certain

SS value $\mathbf{f}^s$:

$$\mathbf{f}(t) = \mathbf{f}^s + \delta\mathbf{f}(t) \tag{17}$$

Then, to first approximation, the corresponding change in the objective function J is proportional to its second variation, i.e.,

$$\Delta J \cong \frac{1}{2}\delta^2 J \tag{18}$$

If the initial perturbations are assumed sinusoids with small amplitudes and an adjustable phase T, i.e.,

$$\delta f_{\mathrm{I}}(t) = a_{\mathrm{I}} \sin \omega\, (t\text{-}T) \tag{19a}$$

$$\delta f_{\mathrm{M}}(t) = a_{\mathrm{M}} \sin \omega\, t \tag{19b}$$

then, it can be shown[18] that

$$\delta^2 J = \frac{1}{2}\{\rho_{11}(\omega)\, a_{\mathrm{M}}^2 + 2a_{\mathrm{I}}a_{\mathrm{M}}\, \mathrm{Re}[\rho_{12}(\omega)\exp(-j\omega T)] + \rho_{22}(\omega)a_{\mathrm{I}}^2\} \tag{20}$$

where ρ_{ik} denotes a typical entry in the follwing (2 × 2) Hermitian π-matrix:

$$\pi(\omega) = G^T(-\mathrm{j}\omega)PG(\mathrm{j}\omega) + Q^TG(\mathrm{j}\omega) + G^T(-j\omega)\,Q + R \tag{21a}$$

with

$$A = \frac{\partial \mathbf{a}}{\partial \mathbf{x}}(\mathbf{x}^s, \mathbf{f}^s) \tag{21b}$$

$$B = \frac{\partial \mathbf{a}}{\partial \mathbf{f}}(\mathbf{x}^s, \mathbf{f}^s) \tag{21c}$$

$$P = \frac{\partial^2 H}{\partial \mathbf{x}^2}(\mathbf{x}^s, \mathbf{f}^s, \boldsymbol{\gamma}^s) \tag{21d}$$

$$Q = \frac{\partial^2 H}{\partial \mathbf{f}\,\partial \mathbf{x}}(\mathbf{x}^s, \mathbf{f}^s, \boldsymbol{\gamma}^s) \tag{21e}$$

$$R = \frac{\partial^2 H}{\partial \mathbf{f}^2}(\mathbf{x}^s, \mathbf{f}^s, \boldsymbol{\gamma}^s) \tag{21f}$$

$$G(s) = (sI_n - A)^{-1}B \tag{21g}$$

In our case, the sensitivity analysis is used as follows: (a) For different values of the phase shift, eq. (20) is solved over a wide frequency range; (b) the phase shift and the frequency providing the highest maximum in $\delta^2 J$

are adopted for maximizing J; and (c) the phase shift and the frequency that produce the lowest minimum of $\delta^2 J$ are adopted for minimizing J.

The Algorithms for Obtaining Any Prespecified Polymer

When maximizing J, it is expected that the final D_n^* will have increased with respect to its original value; and the opposite is expected when J is minimized. Thus, the extremizations of the cost function provide the upper and lower limits of D_n^* within which any intermediate value of this quantity could be, in principle, produced. Through an appropiate manipulation of the step coefficient weights along the optimization process, convergence to any intermediate value of J or D_n^* is possible; but the magnitude of the final μ_n^* will have changed with respect to its original value, however. Indicating desired values with the superscript d, the problem therefore consists in simultaneously obtaining $\mu_n^* = \mu_n^d$ and $D_n^* = D_n^d$. In simpler situations, this problem may be solved by the independent application of any of the algorithms that follow; but in more complex cases, both techniques may have to be sequentially utilized.

Algorithm 1

This numerical method is schematically illustrated by Figure 1. Basically, the desired goal is achieved through an iterative procedure which appropiately readjusts the feed stock concentrations $[I^f]$ and $[M^f]$ after each optimization process, in order to produce the desired μ_n^*.

Algorithm 2

Figure 2 represents a flow sheet of this method. Here, the objective is met through an iterative optimization-rescaling procedure. The rescaling stage implies an appropiate readjustment of $f_I(t)$ and/or $f_M(t)$.

A SIMULATED EXAMPLE

Consider the polymerization of isoprene in n-heptane with n-butyllithium as initiator at 25°C. Under SS conditions, and utilizing the raw data of the first column of Table I, the dependent variables indicated in the remaining columns of that table may be calculated (Θ represents the reactor mean residence time). The given SS is chosen as the basic starting condition for the different problems that are considered below. In all cases, the control variables were bounded as follows: $\mathbf{f} > 0$. The computer programs were written in FORTRAN for a VAX 11/780. Due to the "stiffness" of the state equations under certain conditions, one of Gear's integration routines was employed.

Selection of T_p and of the Initial Perturbation

Consider the perturbations about the SS represented by eqs. (19), with $a_I = a_M = 0.01$. Solving eqs. (21) for the given SS condition, and replacing the results in eq. (20), one may finally obtain an expression for $\delta^2 J$ with

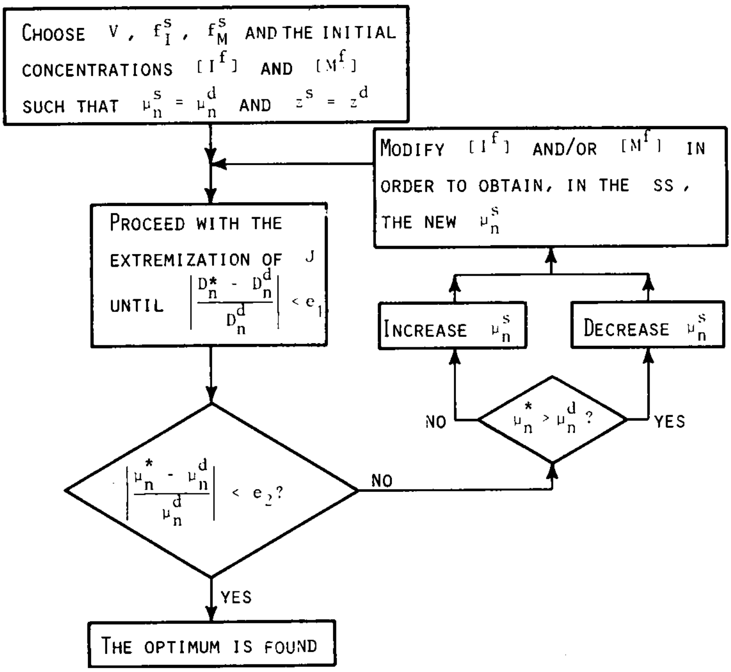


Fig. 1. Algorithm 1 for the obtention of (μ_n^d, D_n^d).

the frequency ω and the phase shift T as independent variables. Figure 3(a) shows the graph of $\delta^2 J$ vs. ω for several values of T. From such curves, the set of values ($T_{mx} = -T_p/2$; $T_{p,mx} = 5.7$ h) and $T_{mn} = -T_p/8$; $T_{p,mn} = 1.25$ h) are respectively selected for maximizing and for minimizing J. In order to verify the validity of the selected periods of oscillation, J was extremized at various frequencies around the corresponding stationary points of $\delta^2 J$. The results are shown in Figure 3(b) (the superscript + indicates optimal results). The stationary points of $\delta^2 J$ occur at the same frequencies as those of J^+, thus validating the preselected periods. The resulting initial perturbations are illustrated in Figure 4.

Consider the evolution of the objective function and of D_n^* along the optimization procedure when J is maximized [Fig. 5(a)] and when it is minimized [Fig. 5(b)]. It is observed that $D^*{}_n$ generally increases (up to a final value of 6.40) in the first case, and that it decreases (down to 1.19) in the second.

Maximization of *J*

The first row of Table II, together with the optimal profiles of Figure 6, contain the results of the maximization of J. Note the following:

a. μ_n^* has increased slightly with respect to the corresponding SS value.

b. $\overline{\Theta}$ has decreased with respect to Θ^s, but the production and the two conversions have all dropped with respect to the corresponding SS conditions.

c. The optimal profiles are such that when $[I(t)]$ is at its maximum, $[M(t)]$

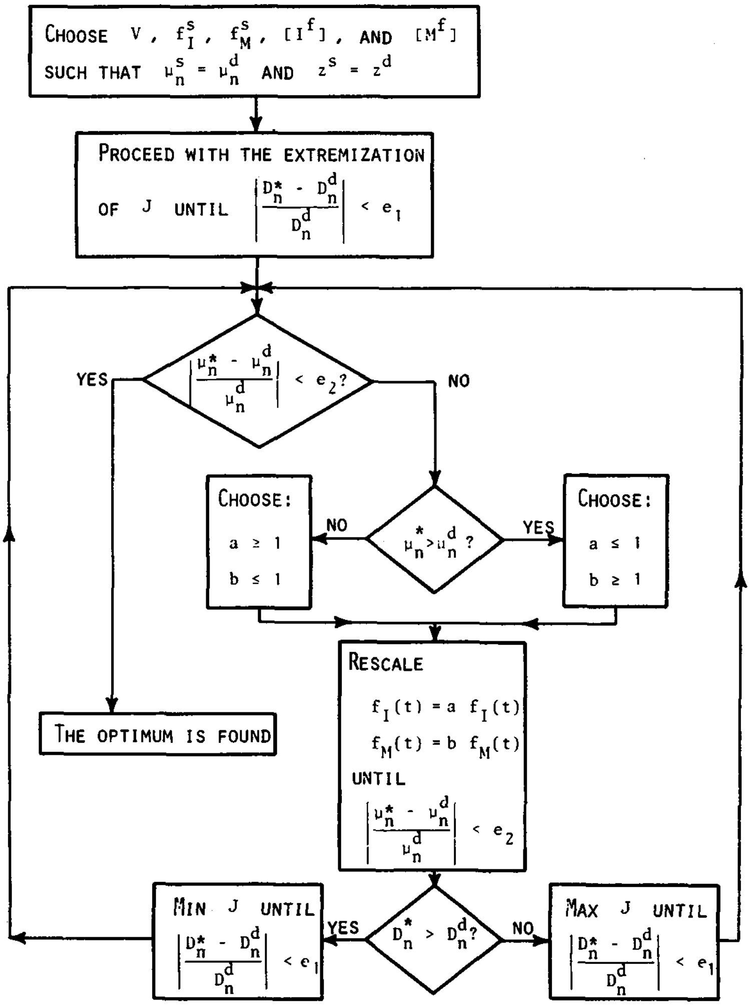


Fig. 2. Algorithm 2 for the obtention of (μ_n^d, D_n^d).

is at its minimum, and vice versa. In this manner, a polymer with a very short average chain length is produced during appoximately half the period of oscillation, and a polymer with a relatively high average molecular weight during the remaining fraction. This result is reasonable from the point of view of maximizing D_n^*.[23]

As $\omega \rightarrow 0$, Figure 3(a) indicates that no increments in J with respect to the SS value are to be expected. This is not the case for D_n^*, however. As previously reported,[4] in fact the greatest increases in D_n^* are observed in the limit of very low frequencies, when square feed profiles 180° out of phase are employed. This may be easily interpreted as follows. Assume that the feed profiles of Figure 7(a) are applied around the previously mentioned SS condition, where the time is represented in units of T_p. Figures 7(b) and 7(c) illustrate the resulting $\mu_n(t)$ and $D_n(t)$ profiles, when the period is increased from 5.7 (the value selected for the maximization of J) up to 200. In the limit of $T_p \rightarrow \infty$, J will tend to 2, whereas D_n^* will tend towards

TABLE I
SS Conditions

Raw data	States	Derived variables	Costates
$V = 0.9$ dm^3	$[I]_s = 0.0001454$ g mol/dm^3	$\mu_n^s = 1860$	$\gamma_1^s = -0.4492$
$k_i = 21.4$ dm^3/g mol h	$[M]^s = 0.4819$ g mol/dm^3	$D^s = J^s = 2$	$\gamma_2^s = -0.7133$
$k_p = 4284$ dm^3/g mol h	$\lambda_0^s = 0.001355$ g mol/dm^3	$\eta_I^s = 0.90$	$\gamma_3^s = 1.923 \times 10^{-4}$
$[I^f] = 0.003$ g mol/dm^3	$\lambda_1^s = 2.518$ g mol/dm^3	$\eta_M^s = 0.84$	$\gamma_4^s = -1.034$
$[M_f]$cb $= 6$ g mol/dm^3	$\lambda_2^s = 9349.5$ g mol/dm^3	$z^s = 165$ g/h	$\gamma_5^s = 1.3597 \times 10^{-3}$
$f_I^s = f_M^s = 0.5\ dm^3/h$		$\Theta^s = 0.9$ h	

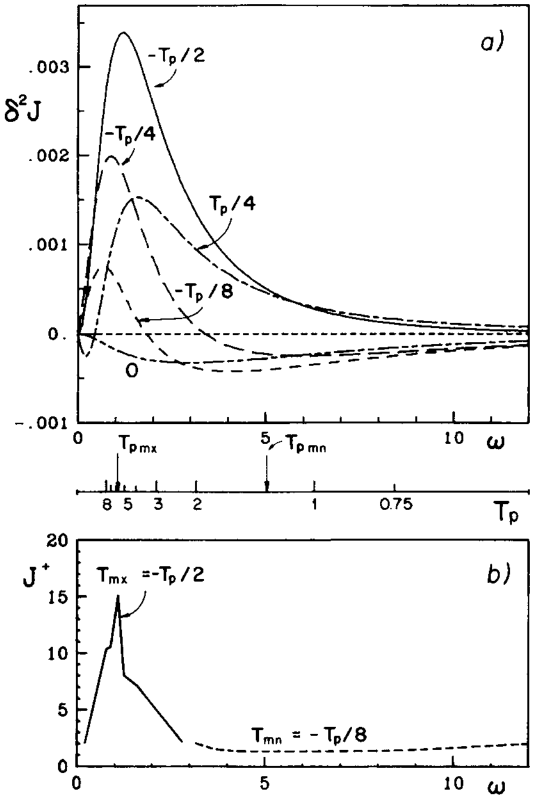


Fig. 3. Selectivity analysis for the selection of (T_{mn}; $T_{p,mn}$) and (T_{mx}; $T_{p,mx}$): (a) $\delta^2 J$ vs. ω with T as parameter; (b) J^+ vs. ω with $T = T_{mn}$ and $T = T_{mx}$.

some large finite number (in this case, 9.39). Furthermore, this last value could be still augmented by increasing the amplitude of the oscillations. Thus, the chosen suboptimal objective function J is unable to generate very large values of D_n^*, which could be better produced through increased periods of oscillation. It is interesting to note, however, that when T_p becomes very large with respect to $\overline{\Theta}$, then the averaging tank required to mix the reactor effluent along a period of oscillation becomes intolerably large. For

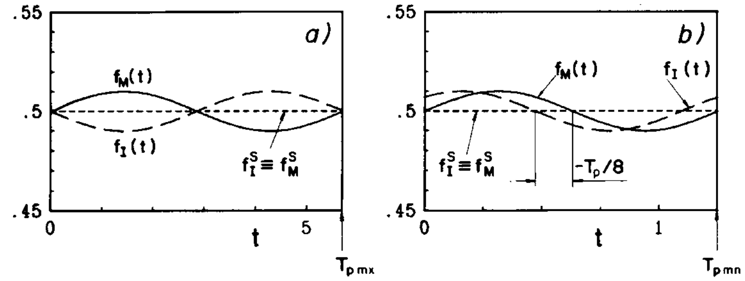


Fig. 4. Initial inputs adopted for: (a) maximizing J; (b) minimizing J.

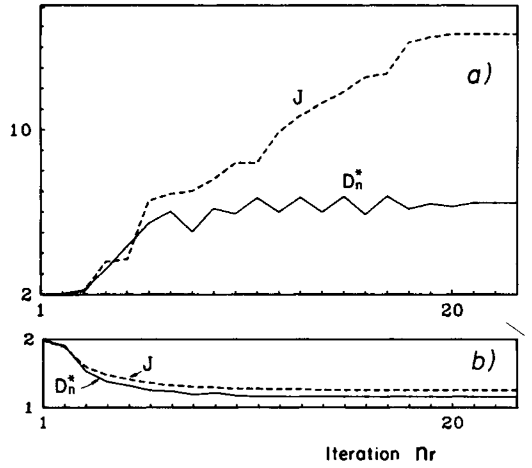


Fig. 5. Evolution of J and D_n^* along an optimization path when: (a) J is maximized and (b) J is minimized.

example, in the table of Figure 7(c), the volume V' eluted from the reactor along a complete period of oscillation, is indicated together with the resulting values of J and D_n^*.

Minimization of J

The second row of Table II and the profiles of Figure 8, contain the results of the minimization of J. Note the following:

a. μ_n^* has dropped considerably with respect to μ_n^s.

b. The monomer conversion increases slightly with respect to the SS values, while the initiator conversion and the polymer production notably decrease.

c. The optimal flow rates indicate that the process will tend towards a sequence of semibatch operations. In effect, the monomer is fed during a very short period of time at the point when the initiator concentration is at its maximum. Then, while the monomer is propagating, no regent is added. Only after the monomer concentation has dropped to zero, the initiator is rapidly incorporated, and consequently $[I(t)]$ quickly increases again up to its peak. This process is totally consistent with the fact that the narrowest distributed polymers are produced in semibatch reactors,[24] in a way which is equivalent to that described. Note that during most of the period, $D_n(t)$ is very near its lowest bound of 1.

Production of Polymers with Predetermined Values of μ_n^* and D_n^*

Suppose one is required to produce two different polymers whose specifications are given in Table III. In both cases, μ_n^* coincides with the SS value from which the optimizations are commenced.

From the extremization results, μ_n^* is more sensitive to minimizations of J than to maximizations of that functional. Thus, one could *a priori* expect less difficulties in solving polymer A than polymer B. This was confirmed

TABLE II

Results for the Extremizations of J and for the Productions of the Desired Polymers when $k_i = 21.48$ dm^3/g mol h and $k_p = 4284$ dm^3/g mol h

	$[I^f]$	$[M^f]$	T_p	T	μ_n^*	D_n^*	J^+	η_I^*	η_M^*	$\bar{\Theta}$	z
Maximization of J	0.003	6.0	5.7	$-T_p/2$	2044	6.40	15.24	0.54	0.60	0.823	132.5
Minimization of J	0.003	6.0	1.25	$-T_p/8$	708	1.19	1.24	0.22	0.86	0.22	81.48
Production of polymer A, method 1	0.003	6.0	5.7	$-T_p/2$	1851	3.997	3.03	0.838	0.774	0.806	153.4
Production of polymer A, method 2	0.003	6.0	5.7	$-T_p/2$	1867	3.990	7.42	0.37	0.74	0.776	139.5
Production of polymer B (methods 1 + 2 combined)	0.0025	9.0	1.25	$-T_p/8$	1840	1.50	1.41	0.48	0.79	0.717	88.4

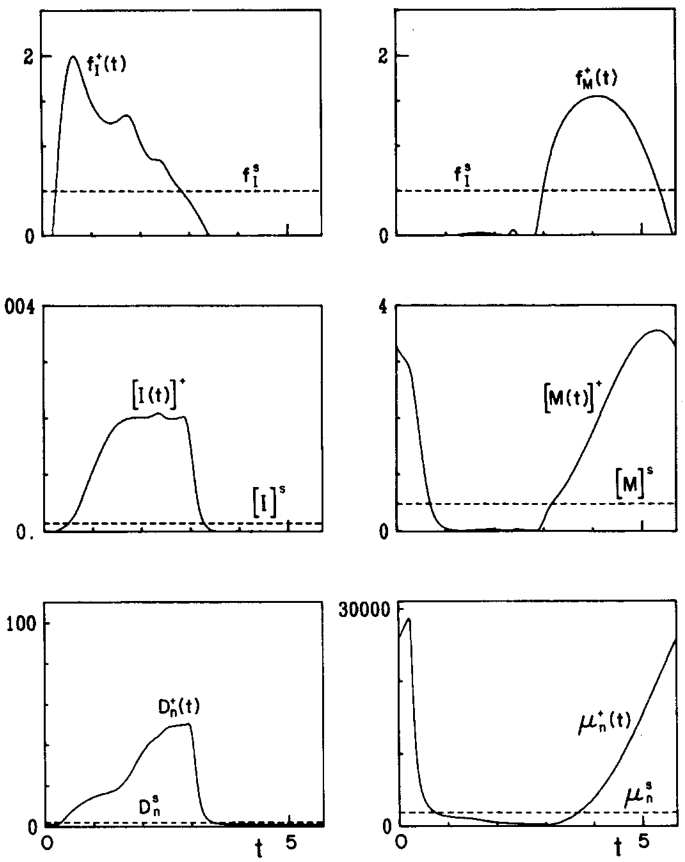


Fig. 6. Maximization of J: optimal periodic profiles.

by the fact that solutions for polymer A were readily obtained by the independent application of method 1 or of method 2 previously described, with relatively low computational effort. In contrast, in the case of polymer B, the two methods had to be sequentially combined, and a relatively large number of iterations were required.

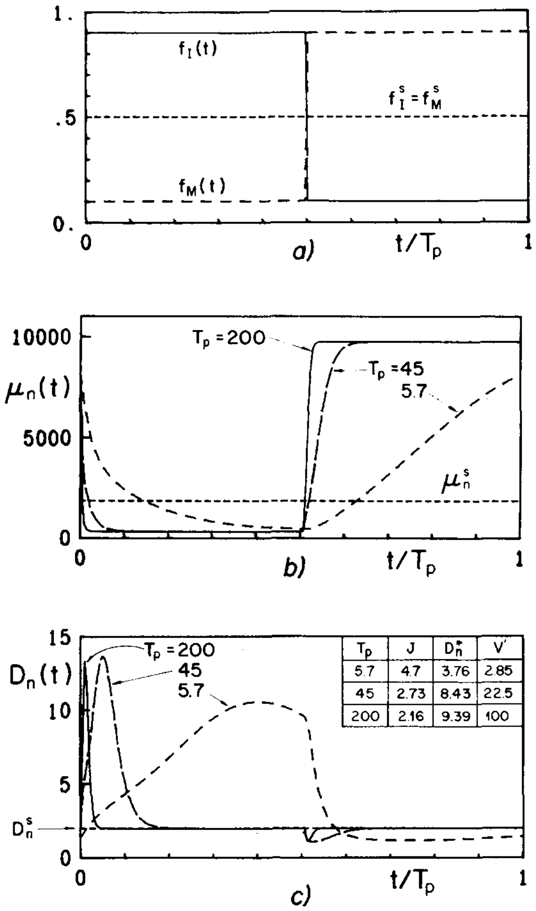
The results corresponding to polymer A with the independent application of each method are given in Table II and Figure 9, while those of polymer B are presented in the last row of Table II and in Figure 10. Note the following:

a. When method 1 was utilized, only the initiator feed concentration was adjusted in the case of polymer A, but the concentration of both reagents were modified for polymer B.

b. When method 2 was utilized, only the initiator feed flow was rescaled.

c. In all cases, μ_n^* and D_n^* were made to converge to values which are as close as required to μ_n^d and D_n^d.

d. In the case of polymer A, the values of J^+ differ significantly according to whether method 1 or method 2 is employed. Also, and as a result of an



T_p	J	D_n^*	V'
5.7	4.7	3.76	2.85
45	2.73	8.43	22.5
200	2.16	9.39	100

Fig. 7. When square feed flows 180° out of phase of increasingly high periods of oscillation are applied (a), it is easy to see that while J tends to 2 (b), D_n^* tends to a high finite value (c).

increase in $[I^f]$ through method 1, the corresponding $f_I^+(t)$ curve is permanently below that of method 2.

e. As expected, when $D_n^* > 2$, the optimal profiles are similar to those corresponding to max J. Conversely, when $D_n^* < 2$, the shapes are similar to those corresponding to min J.

Effects of Variations in k_i and k_p

In order to test the proposed technique for different combinations of k_i and k_p while maintaining the other data unmodified, the cost function was extremized under the kinetics conditions indicated in Table IV. (The set of constants of kinetics 1 correspond to the previously considered simulations.) The SS results, together with the results of the extremizations of J for kinetics 2, 3 and 4, are summarized in Table V. Note the following:

a. The values of T_p obtained from the sensitivity analysis are all quite similar; the same is true for the phase T.

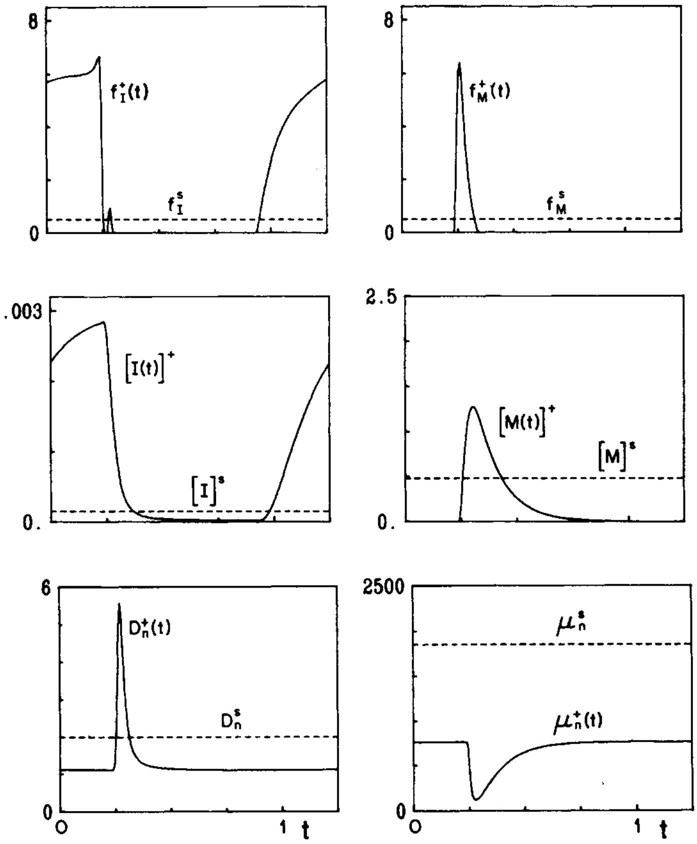


Fig. 8. Minimization of J: optimal profiles.

b. The values of μ_n^* are of the same order as the corresponding μ_n^s's, except when minimizing J with high initiation constants (kinetics 2 and 4).

c. The greatest flexibility in D_n^* is obtained when both k_i and k_p are very high. In this case, values of this parameter as low as 1.06 and as high as 9.2 are observed.

d. The greatest deviations between the numerical values of D_n^* and J^+ occur when J is maximized, because relatively high periods of oscillation are required.

TABLE III
Characteristics of the Required Polymers

	μ_n^*	D_n^*
Polymer A	1860	4
Polymer B	1860	1.5

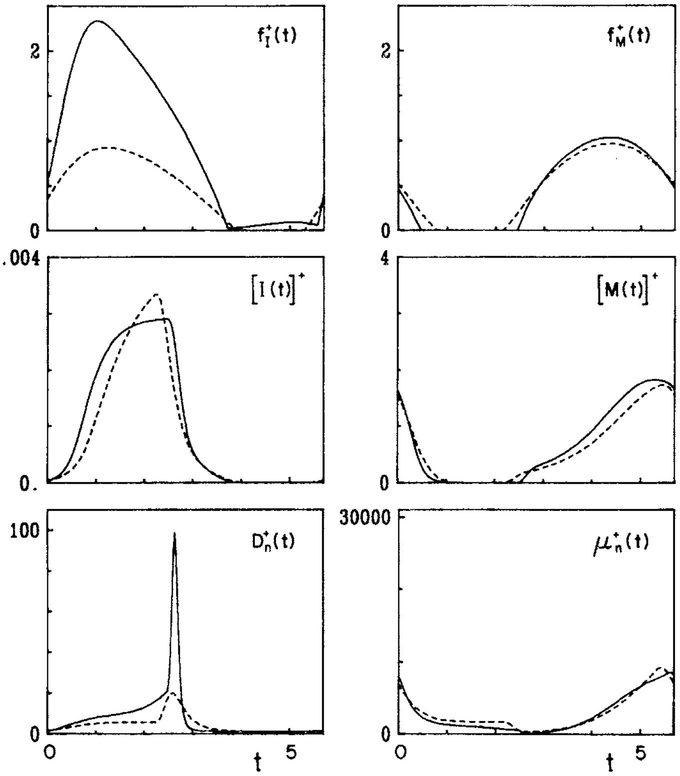


Fig. 9. Profiles for the obtention of polyjer A: (- - -) results for method 1; (—) results for method 2.

e. In all cases considered, η_I^* is lower than the corresponding η_I^s, but the same is not true with the monomer conversion.

f. Even though not showned here, the shapes of the optimal profiles for kinetics 2, 3, and 4 are similar to those of kinetics 1.

CONCLUSIONS

When a "living" anionic polymerization is carried out in a CSTR, it is possible to set an optimal periodic control problem through which the polymer produced may exhibit average polydispersities D_n^* both above and below the SS value of 2. For different data sets, the extremizations of the selected cost function provide the upper and lower limits of D_n^* within which any intermediate value of this property may be obtained. The problem of finding the flow profiles which allow the production of polymers with prespecified values of both D_n^* and μ_n^* may be solved through two novel iterative algorithms that involve readjustments of the feed stock concentations and rescalings of the feed flows.

The preselection of the period of oscillation T_p and of the phase shift T for the initial perturbations, can be based on a sensitivity analysis due to

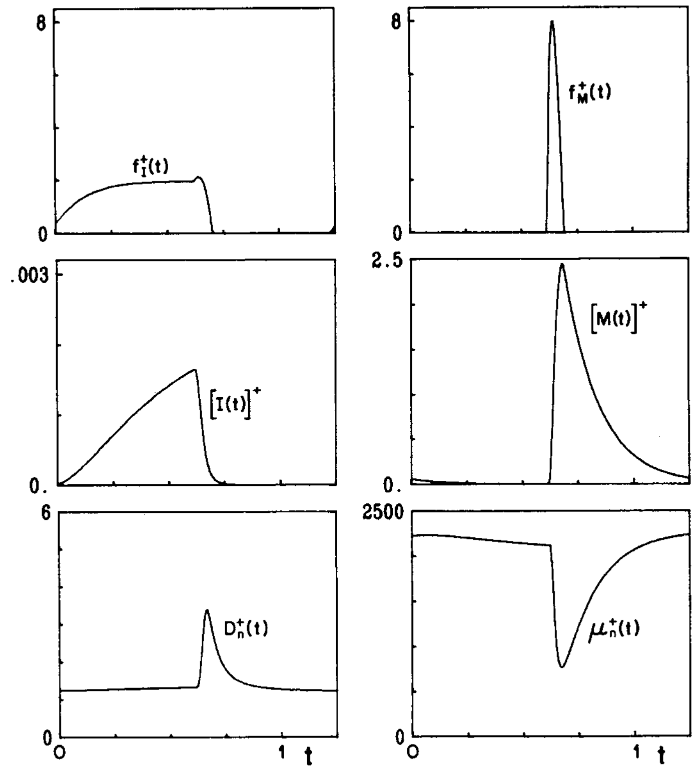


Fig. 10. Profiles for the obtention of polymer B.

Sinčić and Bailey.[18] Extremizations of the cost function for values of T_p in the neighborhood of those obtained through the said sensitivity analysis confirmed the validity of this approach.

The numerical values attained by the adopted suboptimal objective function (J), are in general of the same order as those of D_n^*, except when the period of oscillation is considerably larger than the time average mean residence time $\overline{\Theta}$. In this last case, it is preferable to select periods of oscillation lower than those determined by the sensitivity analysis. Higher frequencies of oscillation are also desirable from the point of view of reducing the volume of the averaging tank which is required to mix the reactor effluent.

The results of the extremizations of J are also interesting from the point

TABLE IV
Set of Considered Kinetics

$k_p k_i$	21.478	42,840
4284	Kinetics 1	Kinetics 2
42,840	Kinetics 3	Kinetics 4

TABLE V
SS and Extremization Results for the New Combinations of k_i and k_p Considered

		T_p	T	μ^s_n, μ^*_n	D^s_n, D^*_n	J^+	η^s_I, η^*_I	η^s_M, η^*_M	$\overline{\Theta}$	z
Kinetics 2										
	SS results	—	—	1697	1.997	1.954	0.99	0.85	0.9	174.2
(k_i = 42840 and k_p = 4284)	max J	5	$-T_p/2$	1522	5.7	10.1	0.99	0.75	0.94	149.3
	min J	1	$-T_p/6$	2.30	1.39	1.37	0.455	0.81	0.29	0.79
Kinetics 3										
	SS results	—	—	3170	1.999	1.99	0.61	0.97	0.9	204.6
(k_i = 21.478 and k_p = 42840)	max J	6.6	$-T_p/2$	7814	5.96	8.98	0.33	0.86	0.875	217.8
	min J	1-.85	$-T_p/4$	2517	1.32	1.287	0.17	0.97	0.37	164.9
Kinetics 4	SS results	—	—	1955	2.0	1.95	0.99	0.98	0.9	203
(k_p = 42840 and k_p = 42840)	max J	5.7	$-T_p/2$	2150	9.2	29.6	0.95	0.95	0.92	206
	min J	1	$-T_p/6$	22.9	1.06	1.06	0.134	0.998	0.13	4.21

of view of D_n^*. When maximizing that cost function, the optimal feed profiles induce oscillations in the reagent concentrations inside the reactor which are approximately 180° out of phase. This has the effect of producing basically a blend of two narrow-distributed polymer species: one of very low and another of very high molecular weight. When minimizing J, the continuous periodic forcing resembles the sequential operation of a semibatch reactor, where a narrow polymer is obtained at the end of each cycle. The greatest variations in D_n^* are observed when the rates of initiation and of propagation are high. In this case, time average polydispersities between 1.09 and 9.2 may be produced.

In summary, the proposed approach provides an increased flexibility for the MWD control, when anionic polymerizations are performed in CSTRs. At present, the experimental validation of the technique is being investigated, and this will be the subject of a future communication.

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