Discrete Optimal Control of Molecular Weight Distribution in a Batch Free Radical Polymerization Process

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Traditionally, molecular weight averages and polydispersity have been used as polymer property indices in controlling the polymer molecular weight properties. In this paper, a new method is presented for the control of weight chain length distribution of polymer in a batch free radical polymerization process. The weight chain length distribution is directly calculated using the *method of finite molecular weight moments* in which the weight fraction of polymers is computed over a number of finite chain length intervals covering the theoretically infinite chain length domain. Task level control of chain length distribution is achieved using nonlinear programming to compute a suboptimal sequence of reactor temperature set points which lead to the best match of a given target weight chain length distribution.

1. Introduction

Synthetic polymers are composed of macromolecules with different chain lengths. This distribution of chain lengths affects end-use physical properties of polymers and, as such, is one of the most important polymerization control variables. In operating a batch free radical polymerization process, a typical task involves manipulation of reactant concentrations, temperatures, and other manipulated variables to achieve a desired objective which can usually be expressed in terms of productivity, conversion, chain length distribution (CLD), and perhaps residual impurities. With regard to the CLD, much attention in the past has focused on control of the leading averages of the molecular weight distribution, usually number and weight average molecular weights (Hoffman *et al.*, 1964; Ponnuswamy *et al.*, 1987; Kim and Choi, 1991; Kozub and MacGregor, 1992; Ogunnaike, 1994). This is primarily because the molecular weight averages represent compact, convenient characterizations of the polymer chain length distribution. For example, Ellis *et al.* (1994) used a finite element method and the continuous variable approximation to model the CLD for free-radical polymerization of methyl methacrylate (MMA) in a batch reactor. Their model included chain length dependent termination, and a two-time scale extended Kalman filter was used to incorporate fast monomer conversion and temperature measurements as well as delayed molecular weight (chain length) measurements for feedback control. They implemented this estimator for weight average molecular weight control in a laboratory batch reactor using conventional PID controllers. However, there are some cases where controlling these average molecular weight properties is not sufficient. For example, for broad, highly skewed, or bimodal distributions, specification of number and weight average molecular weight does not uniquely characterize a polymer's CLD (Ray, 1972). Little has been reported in open literature on methods for controlling a polymer's chain length distribution.

In industry, a common method for controlling molecular weight distribution (MWD) in batch polymerization reactors is to predetermine the desired control variable trajectories by some means and attempt to execute these trajectories during the batch. Various techniques have been reported in literature on the design of optimal reactor operating conditions. The necessary conditions for an optimal control trajectory, derived from variational calculus and the minimum principle, have been used in many polymerization processes for optimal control synthesis (Hicks and Ray, 1971; Sacks *et al.*, 1973; Tirrell and Gromley, 1981; Thomas and Kiparissides, 1984; Ponnuswamy *et al.*, 1987). Sacks *et al.* (1973) used the maximum principle to determine the types of temperature variations which minimize or maximize the breadth of the CLD for free-radical polymerizations in batch reactors. They found that, for batch free radical polymerizations, reactor temperature policies which maximize polydispersity will consist of one or at most two step changes in the reactor temperature between the upper and lower temperature bounds. Approximate methods of optimal control trajectory synthesis include control vector parameterization (Hicks and Ray, 1971; Choi and Butala, 1991) and nonlinear programming (Tabak and Kuo, 1969; Cuthrell and Biegler, 1989).

As shown by some workers, it is possible that molecular weight measurements could be incorporated using state estimation but it would then be necessary to recalculate control variable trajectories on line. On line optimization using the maximum principle is computationally time consuming and often infeasible for complex polymerization models and therefore is generally not an option for this purpose. Furthermore, the work of Sacks *et al.* (1973) suggests that control of molecular weight distribution by computing discrete temperature set points may be a good method for broad molecular weight distributions.

In this paper, we shall present a new approach for task level control of polymer chain length distribution (not molecular weight averages) in a batch free radical polymerization reactor. A detailed polymerization model is used in conjunction with the method of finite molecular weight moments (Crowley and Choi, 1997) to determine a sequence of reactor temperature set points which lead to the desired MWD. The suboptimal temperature set point sequence is computed using sequential quadratic programming. The MWD itself is characterized by a finite number of weight fractions over a preselected range of molecular weights. Incorporating

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Table 1. Kinetic Scheme for Free-Radical Polymerization of MMA

initiation	$I \xrightarrow{k_d} 2R$
	$R + M \xrightarrow{k_i} P_1$
propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$
chain transfer to monomer and solvent	$P_n + M \xrightarrow{k_{fm}} D_n + P_1$
	$P_n + S \xrightarrow{k_{fs}} D_n + P_1$
termination (disproportionation only)	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$

this control strategy with an on line execution level controller will be the subject of a forthcoming paper.

2. Free-Radical Polymerization Model

A kinetic scheme for free-radical solution polymerization of MMA is given in Table 1. Key features of this scheme include the formation of reactive radicals by decomposition of the initiator in the initiation step, reactive addition of monomer units to radical polymer chains in the propagation step, and deactivation of polymer radicals by reaction with other polymer radicals in the termination step. In this scheme, it is assumed that primary radical termination is negligible and termination occurs by the disproportionation mechanism only.

Strong nonlinearity of MMA polymerization kinetics is due in large part to diffusion limitations at high monomer conversion and reaction medium viscosity. Under these conditions, polymer radicals and, to a lesser extent, monomer molecules become less mobile in the reaction medium. Consequently, the termination rate constant, k_t, and propagation rate constant, k_p, decrease. Diffusion of polymer molecules can be significantly impaired due to their size, and therefore, the termination reaction rate can decrease dramatically at high conversions. This "gel effect" has been studied extensively, and several semiempirical correlations have been developed to predict its effect on polymerization rates. The gel effect parameter, g_t, accounts for diffusion-controlled termination. In this work, the gel effect correlation proposed by Ross and Laurence (1976) is used:

$$g_t = \begin{cases} 0.10575 \exp[17.15 v_f - 0.01715(T - 273.16)] \\ \qquad\qquad\qquad \text{if } v_f \geq v_{fcr} \\ 2.3 \times 10^{-6} \exp[75 v_f] \qquad \text{if } v_f \leq v_{fcr} \end{cases} \quad (1)$$

Here, v_f represents free volume and v_{fcr} the critical free volume. They are given by (Schmidt and Ray, 1981):

$$v_f = 0.025 + 0.001(T - 167)\phi_m + \\ 0.001(T - 181)\phi_s + 0.00048(T - 387)\phi_p$$

$$v_{fcr} = 0.186 - 2.96 \times 10^{-4}(T - 273.16) \quad (2)$$

where ϕ_m, ϕ_s, and ϕ_p represent the volume fractions of the monomer, solvent, and polymer, respectively, and

are given by the following:

$$\phi_m = \frac{x_m M_t}{\rho_m V}$$

$$\phi_p = \frac{x_p M_t}{\rho_p V} \quad (3)$$

$$\phi_s = 1 - \phi_m - \phi_p$$

where x_j represents the mass fraction of component j, M_t the total mass, and ρ_j the density of component j. The total reactor volume, V, is assumed to be an ideal mixture of its components and is given by

$$V = \left(\frac{x_m}{\rho_m} + \frac{x_p}{\rho_p} + \frac{x_s}{\rho_s} + \frac{x_i}{\rho_i}\right)M_t \quad (4)$$

The modeling equations for a batch MMA polymerization reactor and cooling jacket consist of the following mass balances:

$$\frac{dx_m}{dt} = -(k_p + k_{fm})x_m P \quad (5)$$

$$\frac{dx_I}{dt} = -k_d x_I \quad (6)$$

$$\frac{dx_s}{dt} = -k_{fs} x_s P \quad (7)$$

The total concentration of live polymers (P) is derived by applying the quasi-steady-state approximation to live radical species which yields

$$P = \left(\frac{2 f_i k_d I}{k_{td}}\right)^{1/2} \quad (8)$$

where f_i is the initiator efficiency factor. The kinetic rate equation for dead polymers of chain length n can be derived from the kinetic scheme shown in Table 1:

$$\frac{d[D_n V]}{dt} = V[k_{td}P + k_{fm}M + k_{fs}S]P_n \quad (9)$$

Let us define the probability of propagation (α) as

$$\alpha \equiv \frac{k_p M}{k_p M + k_{fm}M + k_{fs}S + k_{td}P} \quad (10)$$

Here, it should be noted that the monomer molar concentration and likewise the solvent concentration are related to the corresponding mass fractions:

$$M = \frac{x_m M_t}{w_m V} \quad (11)$$

where w_m is the molecular weight of the monomer. It is also easy to show that the following equation holds:

$$P_n = \alpha P_{n-1} = (1 - \alpha)\alpha^{n-1} P \quad (12)$$

Since our primary objective is to control polymer chain length distribution, we need a method to compute the polymer CLD. In the following, we present the method of finite molecular weight moments (Crowley and Choi, 1997). Let us consider the following function that defines the weight fraction of the polymer within the

chain length interval (m,n):

$$f(m,n) = \frac{\sum_{i=m}^{n} iD_iV}{\sum_{i=2}^{\infty} iD_iV} \quad (13)$$

Here, we ignore the contribution of live polymers because their concentrations are very small. Then, we can derive the following equation:

$$\frac{df(m,n)}{dt} = \frac{1}{\lambda_1}\sum_{i=m}^{n} i\frac{d[D_iV]}{dt} - \frac{\sum_{i=m}^{n}[iD_iV]}{\lambda_1^2}\frac{d\lambda_1}{dt}$$

$$= \frac{1}{\lambda_1}\sum_{i=m}^{n} i\frac{d[D_iV]}{dt} - \frac{f(m,n)}{\lambda_1}\frac{d\lambda_1}{dt} \quad (14)$$

Here, λ_1 is the first moment of the molecular weight distribution. Using eqs 9 and 10, the summation term above becomes

$$\sum_{i=m}^{n} i\frac{d[D_iV]}{dt} = Vk_pM\frac{(1-\alpha)}{\alpha}\sum_{i=m}^{n} iP_i \quad (15)$$

The term, $\sum_{i=m}^{n} iP_i$, is evaluated as follows:

$$\sum_{i=m}^{n} iP_i = \sum_{i=m}^{\infty} iP_i - \sum_{i=n+1}^{\infty} iP_i \quad (16)$$

where these summations are evaluated by making use of the relationship, $P_n = \alpha P_{n-1}$:

$$\sum_{i=m}^{\infty} iP_i = \left[\frac{m(1-\alpha)+\alpha}{(1-\alpha)^2}\right]P_m \quad (17)$$

Using this result and the relationship $P_n = (1-\alpha)\alpha^{n-1}P$ yields:

$$\sum_{i=m}^{n} iP_i = \left[\frac{m(1-\alpha)+\alpha}{(1-\alpha)}\right]\alpha^{m-1}P -$$
$$\left[\frac{(n+1)(1-\alpha)+\alpha}{(1-\alpha)}\right]\alpha^n P \quad (18)$$

Finally, eq 14 becomes

$$\frac{df(m,n)}{dt} = \frac{k_pMV}{\lambda_1}\left(\left[\frac{m(1-\alpha)+\alpha}{\alpha}\right]\alpha^{m-1} - \right.$$
$$\left.\left[\frac{(n+1)(1-\alpha)+\alpha}{\alpha}\right]\alpha^n\right)P - \frac{f(m,n)}{\lambda_1}\frac{d\lambda_1}{dt} \quad (19)$$

Equation 19 is then integrated together with other kinetic equations at a discrete number of chain length intervals to calculate the entire weight chain length distribution (WCLD). One can choose any number of chain length intervals. In this work, 15 chain lengths

were chosen to bound the chain length intervals using the following arbitrary formula:

$$m = 2 + a(i-1)i \quad (20)$$

$$n = 1 + ai(i+1) \quad (21)$$

$$i = 1, ..., 15$$

The value of a can be selected such that it satisfies a criterion such as

$$f(2, 1+15a(15+1))|_{x_c=x_{cf}} = 0.999 \quad (22)$$

Which means that a is selected such that the weight fraction of the polymer bounded by the chain lengths 2 to $(1 + 15a(15 + 1))$ is 99.9% of the total polymer produced at final monomer conversion. Equation 20 increases the interval between successive chain lengths as the chain length is increased.

Number average and weight average molecular weights are calculated from the three leading moments of the weight chain length distribution for the dead polymer. The moments, λ_k, are defined as

$$\lambda_k \equiv \sum_{n=2}^{\infty} n^k D_n V \quad (23)$$

and are computed from the following equations:

$$\frac{d\lambda_0}{dt} = k_pMV(1-\alpha)P \quad (24)$$

$$\frac{d\lambda_1}{dt} = k_pMV(2-\alpha)P \quad (25)$$

$$\frac{d\lambda_2}{dt} = \frac{k_pMV(\alpha^2 - 3\alpha + 4)P}{(1-\alpha)} \quad (26)$$

Number and weight average molecular weights are given by

$$\bar{M}_n = w_m\frac{\lambda_1}{\lambda_0} \quad (27a)$$

$$\bar{M}_w = w_m\frac{\lambda_2}{\lambda_1} \quad (27b)$$

Here it is assumed that the contribution of live polymer radicals to the molecular weight averages is negligible because the instantaneous polymer radical concentration, P, is far smaller than the dead polymer concentration.

3. Control of Chain Length Distribution

For control of WCLD during batch MMA polymerization, the reactor temperature set point is chosen as a task level manipulated variable because the polymer chain length is very sensitive to temperature. Of course,

this is based on the assumption that the reactor temperature can be controlled effectively during the course of polymerization. However, it is generally infeasible to solve for the continuous control trajectory $u(t)$ on line. In this work a sequence of discrete temperature set points is determined instead to approximate the optimal solution. The next step is defining a mathematical objective function which adequately describes the real objective. In the case of a batch homopolymerization, the real control objective in terms of polymer properties might be something like "Produce polymer with the desired WCLD at a final monomer conversion of 40%". This is an end-point problem with the final time unknown. Actually, the objective would also likely be to minimize the time required to produce the desired polymer but this does not significantly alter the approach and batch time minimization is omitted in the objective of this example.

One difficulty associated with this end-point problem is that the final batch time is unknown. To simplify this problem, time is replaced by monomer conversion as the independent variable in the model used for optimization. This is accomplished by dividing eqs 5−7 and eq 19 at 15 discrete chain lengths, by the following equation for monomer conversion.

$$\frac{dx_c}{dt} = \frac{(k_p + k_{fm})x_m P}{x_{m0}} \tag{28}$$

This procedure enables the final value of the independent variable, monomer conversion, to be anchored at its desired final value in all computations.

The dynamic model used for optimization computations becomes

$$\frac{dx_m}{dx_c} = -x_{m0} \tag{29}$$

$$\frac{dx_I}{dx_c} = -x_{m0}\frac{k_d x_I}{(k_p + k_{fm})x_m P} \tag{30}$$

$$\frac{dx_s}{dx_c} = -x_{m0}\frac{k_{fs} x_s P}{(k_p + k_{fm})x_m P} \tag{31}$$

$$\frac{df(m,n)}{dx_c} = \left[\frac{x_{m0}k_p MV}{\lambda_1}\left(\left[\frac{m(1-\alpha)+\alpha}{\alpha}\right]\alpha^{m-1} - \left[\frac{(n+1)(1-\alpha)+\alpha}{\alpha}\right]\alpha^n\right)P\right]/(k_p + k_{fm})x_m P$$
$$- \frac{x_{m0}\frac{f(m,n)}{\lambda_1}\frac{d\lambda_1}{dt}}{(k_p + k_{fm})x_m P} \tag{32}$$

The objective function can then be defined in terms of the final batch WCLD alone:

$$J(\mathbf{u}, x_{cf}) = \sum_{i=1}^{15}\left(\frac{f(2 + a(i-1)i, 1 + ai(i+1)) - f_{i,set}}{f_{i,set}}\right)^2 \tag{33}$$

where $\mathbf{u}$ is a vector representing the sequence of reactor temperature set points during the batch which must be found by the as yet undescribed optimization procedure, x_{cf} the fixed desired final monomer conversion, $f_{i,set}$ the
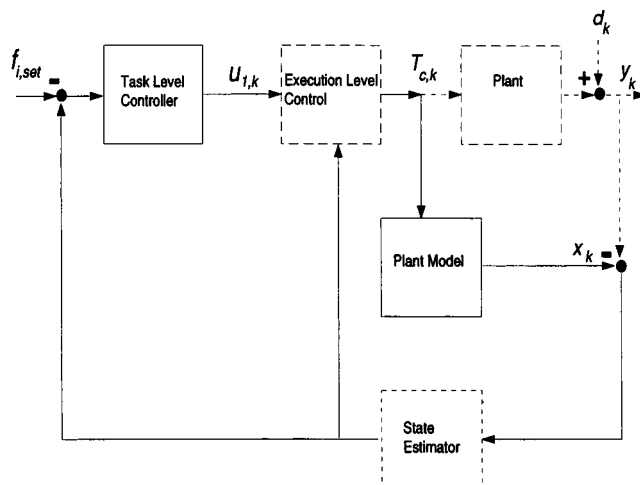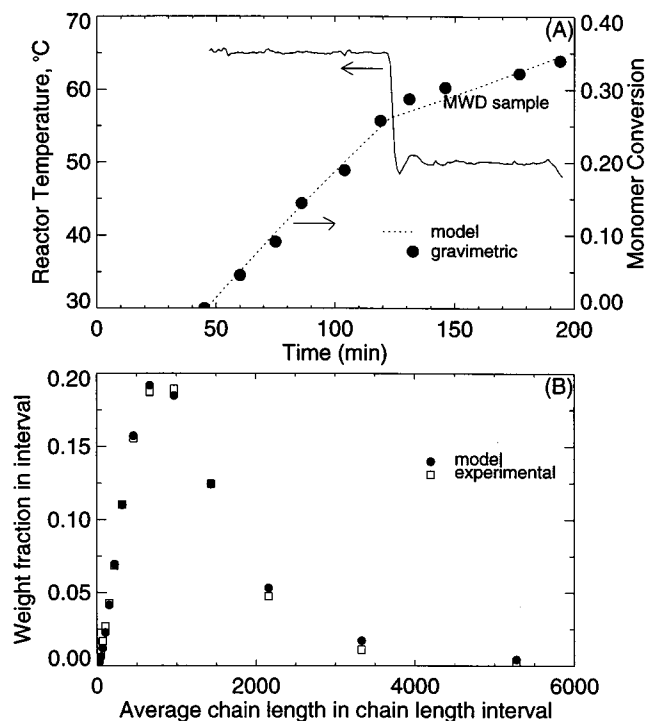

Figure 1. Block diagram of discrete MWD control.

Figure 2. Validation of conversion and MWD model predictions; $I_0 = 0.046$ mol L^{-1}, $\phi_{m0} = 0.5$, and $\phi_{s0} = 0.5$.

desired WCLD values; the denominator in the summation is to normalize the weight fraction values which are relatively small at the lower and upper ends of chain length and large in the midrange. Each element of the vector $\mathbf{u}$ is chosen to be a temperature set point at which the reactor will be controlled for a fixed fraction of the total polymer to be produced. For example, if the final desired monomer conversion were 40%, then if the dimension of $\mathbf{u}$ is 4, the first element of $\mathbf{u}$ would represent an optimized temperature set point at which the reactor would be operated during polymerization from 0% to 10% monomer conversion, the second element of $\mathbf{u}$ would represent the optimized temperature for conversion from 10% to 20%, the third element would represent the optimized temperature during polymerization from 20% to 30% monomer conversion, and finally, the fourth element would represent the optimized reactor temperature from 30% to the final desired conversion.

The dimension of $\mathbf{u}$, denoted j, the number of reactor temperature set points over which the objective function is minimized at each sampling point, is chosen as a
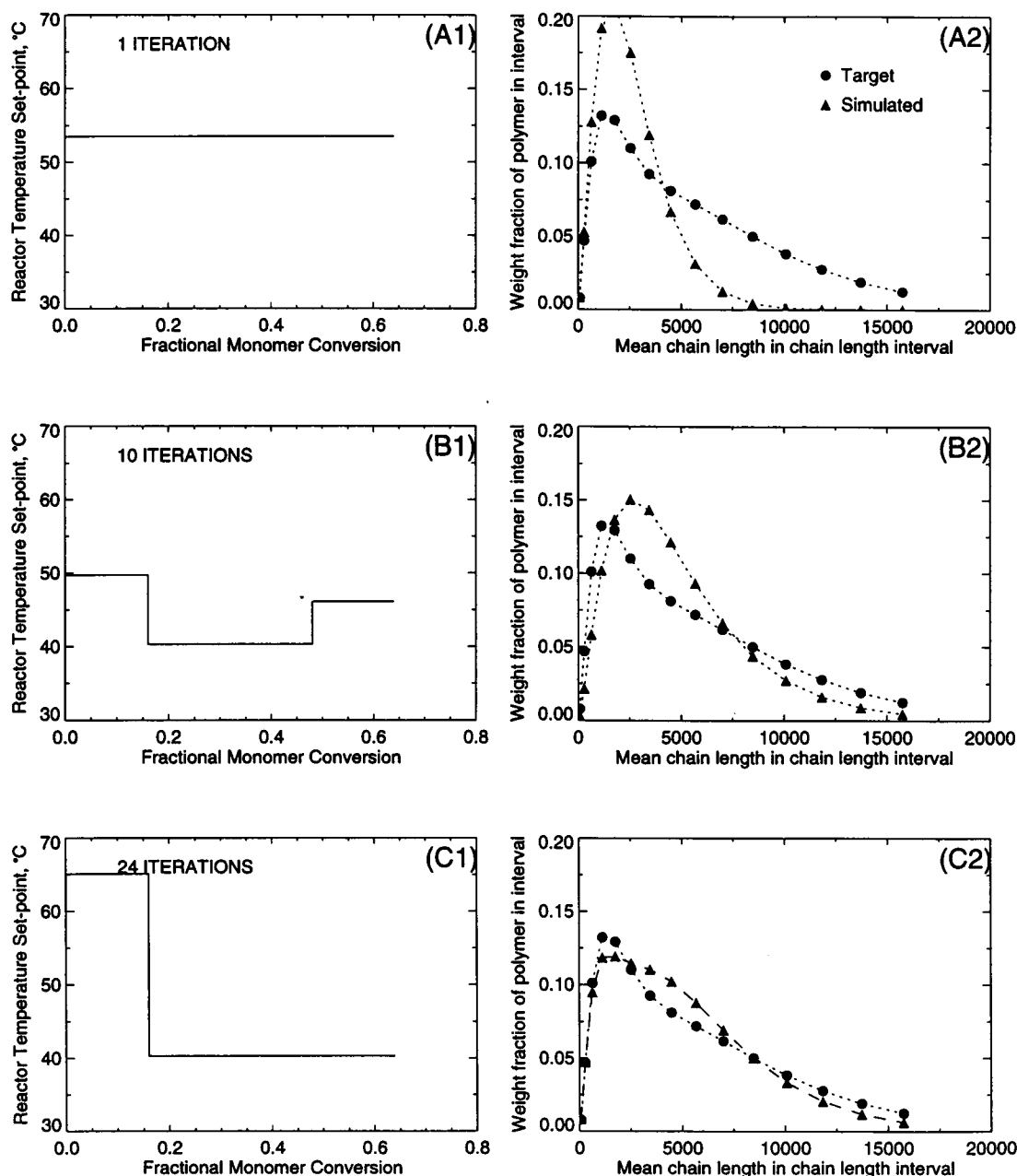
Figure 3. Illustration of iterative optimization.

compromise of control precision with computational speed. For all simulations, j was set equal to 4. The objective can be expressed more succinctly as

$$\min J_k(u_j(j=1,4),x_{cf}) =$$
$$\sum_{i=1}^{15} \left(\frac{f(2 + a(i-1)i, 1 + ai(i+1)) - f_{i,\text{set}}}{f_{i,\text{set}}} \right)^2 \quad (34)$$

subject to bounds on the task level manipulated variables, u_j

$$40\ ^\circ C \leq u_j \leq 70\ ^\circ C$$

In the above, the u_j represents a sequence of reactor temperature set points up to the final desired weight fraction and J_k represents the task level objective function at the kth sampling time.

This objective function is minimized using FSQP (feasible sequential quadratic programming) (Panier and Tits, 1993). FSQP solves a given optimization problem by iteratively calculating a feasible search

direction which is the solution to a quadratic program and which yields a decrease in the objective function. In its simplest form, sequential quadratic programming (SQP) solves the problem (Bazaraa *et al.*, 1993)

$$\min J(\mathbf{u})$$

subject to
$$g_i(\mathbf{u}) \leq 0 \qquad i = 1, ..., m$$

$$h_i(\mathbf{u}) = 0 \qquad i = 1, ..., l$$

by sequentially solving at each interation, k, the quadratic subproblem

$$\min \nabla J(\mathbf{u}_k)^t \mathbf{d} + {}^1/_2 d^t \nabla^2 L(\mathbf{u}_k) \mathbf{d}$$

subject to
$$g_i(\mathbf{u}_k) + \nabla g_i(\mathbf{u}_k)^t \mathbf{d} \leq 0 \qquad i = 1, ..., m$$

$$h_i(\mathbf{u}_k) + \nabla h_i(\mathbf{u}_k)\mathbf{d} = 0 \qquad i = 1, ..., l$$

which yields a search direction, $\mathbf{d}$. The next iterate can then be computed using a linear or nonlinear update

equation such as a line search of the form

$$\mathbf{u}_{k+1} = \mathbf{u}_k + s\mathbf{d} \qquad (35)$$

Here, s represents a step length in the search direction $\mathbf{d}$ which may satisfy some convergence criterion, L represents the Lagrangian function, and g and h represent inequality and equality constraints, respectively. The form of this quadratic subproblem is such that it drives the solution toward a Karush-Kuhn-Tucker (KKT) point, which is a necessary condition for local optimality and drives the solution toward beneficial (i.e., local minima) KKT points when more than one exist. Problems can arise using this method because the quadratic subproblem may generate infeasible iterates and a suitable method is required in the search step (eq 35) to ensure convergence. FSQP addresses the feasibility and convergence problems which can arise in sequential quadratic programs. It should be noted that other similar optimization methods can also be used.

In this work, the objective function is evaluated by integrating eqs 29–32 from the current monomer conversion to the final desired monomer conversion. Figure 1 shows a block diagram of the control algorithm. In this figure, $T_{c,k}$ represents a manipulated variable such as coolant temperature which would be determined by an execution level controller to regulate reactor temperature, d_k represents unknown disturbances, y_k represents plant measurements, and x_k represents model predictions. It should be again noted that design of the task level control block, depicted in Figure 1, is the sole subject of this paper. Here, the subscript k represents the kth sampling point for a batch reactor operated under digital control. $\mathbf{u}_{1,k}$ represents output from the task level controller block at the kth sampling time because only the first optimal temperature set point in the optimal sequence would be actually implemented by an execution level controller.

4. Results and Discussion

A good process model is a necessary prerequisite for application of this suboptimal task level control strategy. To verify the model used for MMA polymerization, a batch free radical solution polymerization of methyl methacrylate has been carried out in a 4 L jacketed stirred tank reactor. The reactor was intially charged with 500 mL of MMA, 500 mL of ethyl acetate as the solvent, and 9 g of 2,2′-azobis(2-methylbutanenitrile) initiator. The reactor was heated to 65 °C, regulated at that temperature to 27% monomer conversion, and then the temperature was decreased to 50 °C to intentionally broaden the molecular weight distribution. Figure 2 represents the experimental reactor temperature and monomer conversions measured off line using the gravimetric method as well as a comparison of experimental and model-predicted molecular weight distributions. The observed induction period in Figure 2A is due to inhibitors in the monomer. Molecular weight measurements were made with a Waters GPC system equipped with an RI detector and three ultrastyragel columns (one 10^4 Å, one 10^3 Å, and a linear column). Narrow MWD poly(methyl methacrylate) standards were used for column calibration. The following kinetic parameters have been used for model calculations (units in mol, L, K, and min): $k_d = 1.14 \times 10^{19} \exp(-34277/RT)$, $k_p = 4.2 \times 10^8 \exp(-6300/RT)$, $k_{fm} = 1.75 \times 10^{13} \exp(-17957/RT)$, $k_{fs} = 6.95 \times 10^{10} \exp(-15702/RT)$, $k_{td} = g_t \times 1.06 \times 10^{11} \exp(-2800/RT)$, and
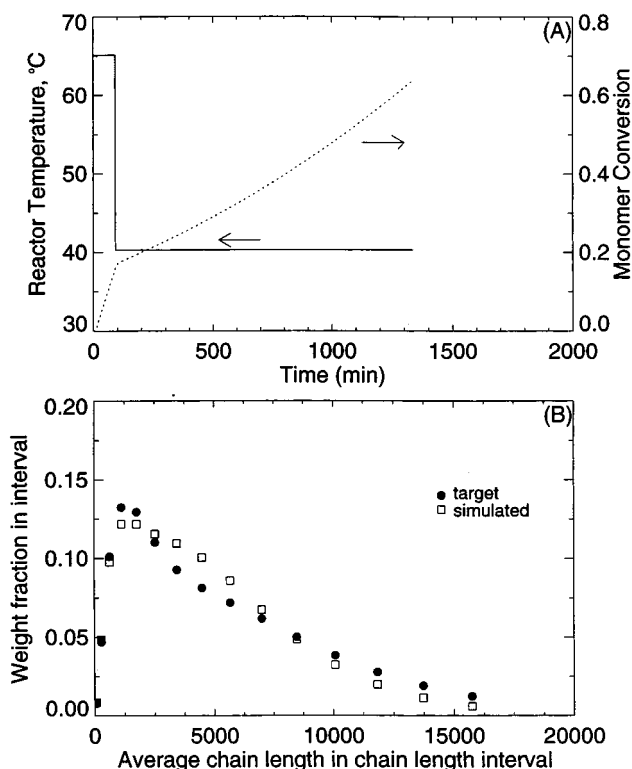

Figure 4. Open loop reactor temperature policy and resulting MWD.

$f_i = 0.21$ (initiator efficiency factor). As seen in Figure 2, good agreement is observed between experimental and model-predicted conversion and molecular weight.

FSQP iteratively finds the sequence of reactor temperature set points which will yield the best match between target and actual polymer WCLD at the end of the batch. To demonstrate application of the proposed method to broad distributions, the optimization procedure was applied to a distribution with a polydispersity of 3.15 and a weight average molecular weight of 417 000. Initial reaction conditions for all polymerization simulations are initiator concentration = 0.015 mol/L, solvent volume fraction = 0.45, and monomer volume fraction = 0.54.

Figure 3 illustrates snapshots of the iterative optimization process at three selected iterations. Graphs on the left-hand side of this figure represent the computed sequence of reactor temperature set points at selected iterations, and graphs on the right-hand side represent the resulting WCLD at final conversion compared with the target distribution. Figure 3A1 (labeled 1 Iteration) represents the initialized values for the reactor temperature set point sequence at zero batch time. Here, all values of $\mathbf{u}_j$ have been initialized at an arbitrary temperature of 53 °C. The WCLD modeling equations are then integrated from 0% monomer conversion to the final desired monomer conversion of 64% to compute the resulting WCLD which is shown in Figure 3A2 along with the target distribution. Since the initialized temperature profile is not optimal, the resulting polymer chain length distribution is significantly off from the target chain length distribution. Then, the deviations in the chain length distributions are used to recalculate the reactor temperature set points. Figure 3B1 represents the sequence of reactor temperature set points computed by FSQP at the 10th iteration point and Figure 3B2 shows the resulting WCLD. Compared with Figure 3A2, the computed polymer chain length distribution is closer to the target
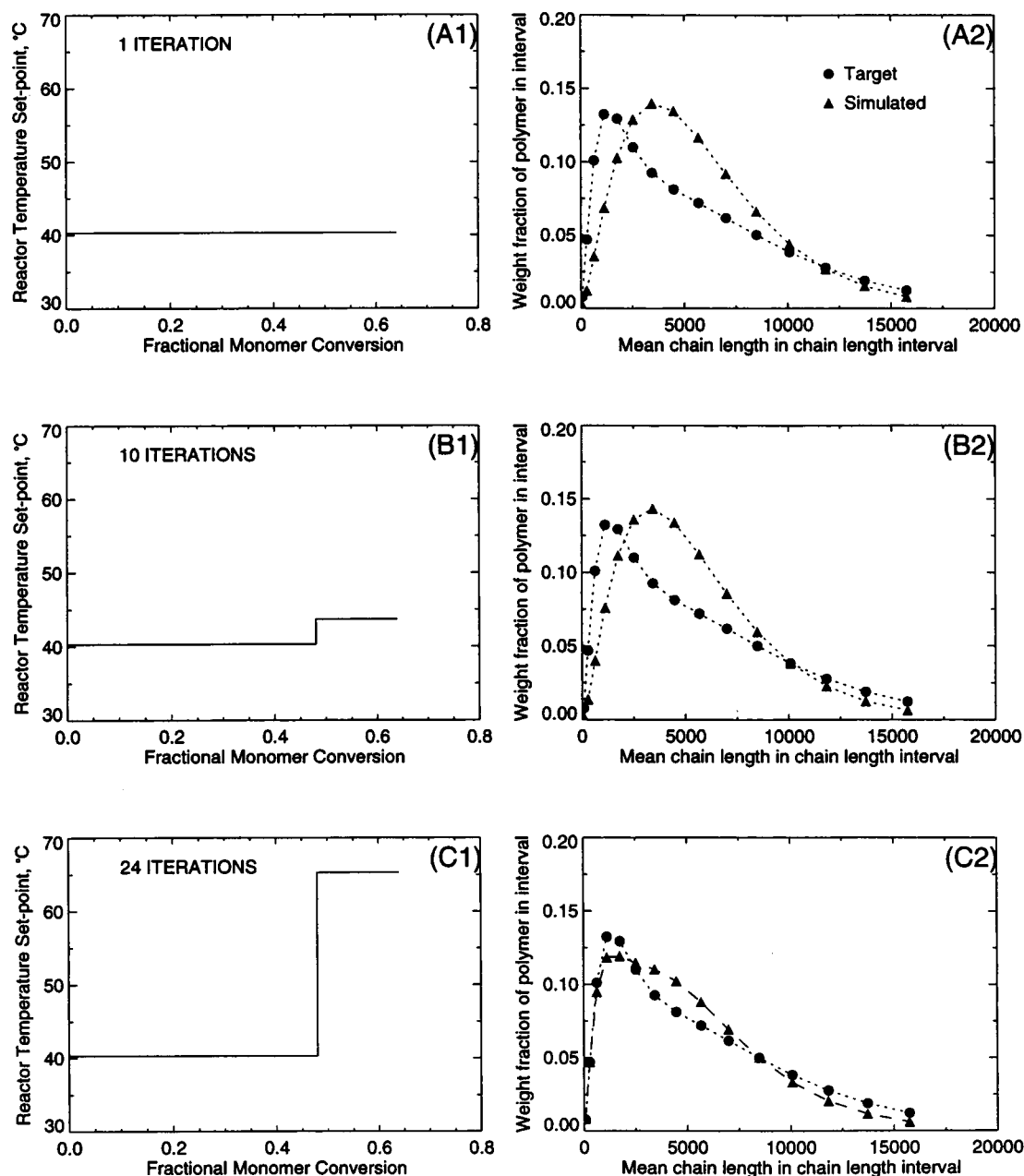
Figure 5. Iterative optimization with different initialization.

value. Convergence is achieved at the 24th iteration in this example, and the suboptimal reactor temperature set point sequence is shown in Figure 3C1 along with the corresponding comparison of simulated and target WCLD in Figure 3C2. The reactor temperature profile shown in Figure 3C1 can then be implemented in the actual polymerization process. The execution level controller is then designed to follow the task level control trajectory as closely as possible. If there is significant model–plant mismatch, the optimal temperature set points calculated off line may have to be adjusted during the batch operation.

Of course, if a computed suboptimal reactor temperature sequence was applied to a batch reactor without on line monomer conversion measurements (e.g., on line densitometry), the sequence of reactor temperature set points would be implemented in terms of time rather than monomer conversion. Figure 4A represents the same suboptimal temperature sequence as that in Figure 3C1 but plotted against batch time rather than monomer conversion. Figure 4B represents simulated polymer WCLD at the end of a batch reaction operated

according to the temperature history given in Figure 4A. Notice that the reactor temperature is maintained high initially and then lowered afterward. After about 16% monomer conversion, the reactor is operated isothermally at about 40 °C.

Remarks. Although this suboptimal task level control strategy has theoretically yielded promising results, it should be noted that the optimization algorithm, FSQP, may find local rather than global minima. As such, solutions can be sensitive to initial conditions when more than one minimum exists in the solution space. For example, in the preceeding control simulation, the intitialization guess for the optimal reactor temperature set point sequence was

$$\mathbf{u}_0 = [T(k) = 53\ ^\circ\text{C} \qquad (k = 1, 4)]$$

However, as shown in Figure 5, the following initial temperature profile leads to a different solution:

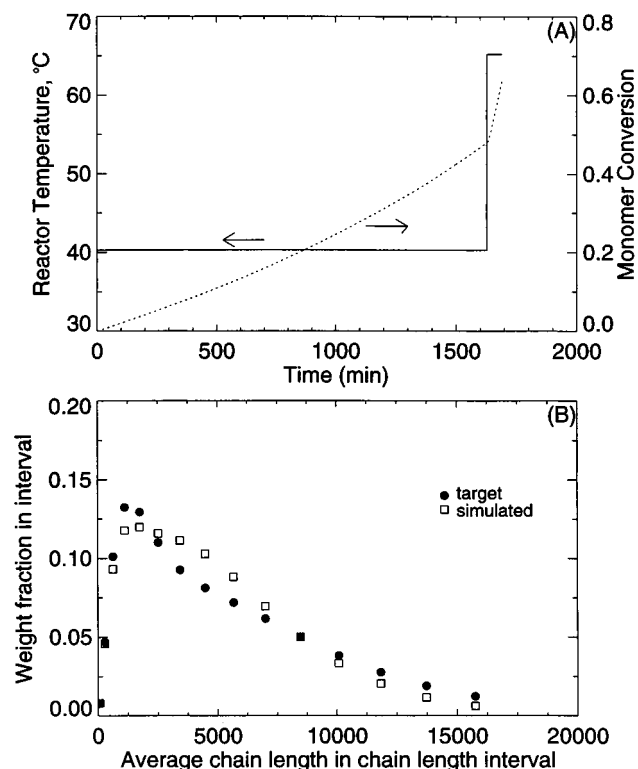$$\mathbf{u}_0 = [T(k) = 40\ ^\circ\text{C} \qquad (k = 1, 4)]$$

Figure 6. Open loop reactor temperature policy.

Notice that the latter initialization leads to temperature set points which start at a lower temperature and end at a higher temperature which is opposite to the trend seen for the former initialization. Also, the latter initialization leads to an overall longer batch time. Therefore, it would often be necessary to properly intialize the optimization procedure when local minima are expected to exist and to evaluate any process constraints (e.g., heat removal capacity) associated with these control designs.

5. Concluding Remarks

In this paper, a new method has been proposed for the design of task level control of polymer chain length distribution in a batch free radical polymerization process. The proposed method is a departure from other methods reported in literature in that a complete chain length distribution instead of molecular weight averages is controlled. The method of finite molecular weight moments allows the designer to calculate reactor temperature profiles that yield a desired polymer chain length distribution at the end of batch polymerization. A sequence of reactor temperature set points is computed using an optimization program on the basis of sequential quadratic programming. Certainly, other optimization techniques can also be used. It has been found that the design of reactor temperature set point profiles is dependent on the initial temperature values when multiple minima exist. Obviously, different temperature profiles result in different batch times to achieve a target monomer conversion. Therefore, it will be necessary to find optimal initial temperature profiles that give rise to minimum batch times while meeting product specifications. The process constraints should also be considered in determining the most effective control design. The proposed method can also be used to design the reactor control algorithm that will control the certain regions of a polymer's molecular weight distribution.

Nomenclature

D_n = dead polymer concentration with n repeating units, mol L^{-1}

$f(m,n)$ = weight fraction of polymer in chain length interval from m,n

$f_{i,\text{set}}$ = target weight fraction for ith fraction of WCLD

f_i = initiator efficiency factor

g_t = gel effect parameter

I = initiator concentration, mol L^{-1}

I_0 = initial initiator concentration, mol L^{-1}

$J(\mathbf{u},x_{\text{cf}})$ = objective function for weight chain length distribution control

$J_k(\mathbf{u}_k,x_{\text{cf}})$ = value of objective function at kth sampling time

J_k = objective function for reactor temperature control

k_d = initiator decomposition rate constant, min^{-1}

k_{fm} = chain transfer to monomer rate constant, L mol^{-1} min^{-1}

k_{fs} = chain transfer to solvent rate constant, L mol^{-1} min^{-1}

k_i = primary radical formation rate constant, L mol^{-1} min^{-1}

k_p = propagation rate constant, L mol^{-1} min^{-1}

k_{td} = disproportionation termination rate constant, L mol^{-1} min^{-1}

M = monomer concentration, mol L^{-1}

M_t = total reaction mass, g

M_n = dead polymer concentration with n repeating units, mol L^{-1}

$\bar{M}_n$ = number average molecular weight, g mol^{-1}

$\bar{M}_w$ = weight average molecular weight, g mol^{-1}

M_0 = initial monomer concentration, mol L^{-1}

n_{max} = maximum chain length for molecular weight distribution modeling

P = total concentration of live polymer radicals, mol L^{-1}

P_n = live polymer radical concentration with n repeating units, mol L^{-1}

R = primary radical concentration, mol L^{-1}

S = solvent concentration, mol L^{-1}

T = reactor temperature, K

v_f = free volume

v_{fcr} = critical free volume

$\mathbf{u}$ = vector of optimized reactor temperature set points

$\mathbf{u}_k$ = vector of optimized reactor temperature set points at kth sampling time

$\mathbf{u}_0$ = initial values for sequence of reactor temperature set points

u_j = jth element of vector $\mathbf{u}$

$u_{j,k}$ = jth element of vector $\mathbf{u}_k$

V = reactor volume, L

w_m = monomer molecular weight, g mol^{-1}

x_c = monomer conversion

x_{cf} = final monomer conversion

x_j = weight fraction of component j

x_{m0} = initial monomer weight fraction

Greek Letters

α = probability of propagation

λ_k^l = kth moment of live polymer molecular weight distribution

λ_k = kth moment of dead polymer molecular weight distribution

ϕ_m = monomer volume fraction

ϕ_{m0} = initial monomer volume fraction

ϕ_s = solvent volume fraction

ϕ_{s0} = initial solvent volume fraction
ϕ_p = polymer volume fraction
ρ_j = density of component j

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