

Control of Molecular Weight Distribution and Tensile Strength in a Free Radical Styrene Polymerization Process

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ABSTRACT: A new method is presented for modeling and controlling polymer molecular weight distribution (MWD) and tensile strength in a batch suspension polymerization of styrene. The molecular weight distribution is modeled by computing the weight fraction of the polymer in different chain length intervals. Tensile strength is then related to the modeled molecular weight distribution using a correlation available in the literature and based on the concept of a threshold molecular weight. This method enables the design of operating conditions for a batch suspension polymerization reactor, which will theoretically yield amorphous polystyrene with a desired tensile strength. Two numerical examples are presented to illustrate the feasibility of the proposed method. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1017–1026, 1998

Key words: styrene polymerization; molecular weight distribution; tensile strength; method of finite molecular weight moments; reactor control; optimization

INTRODUCTION

There is much interest in controlling the molecular weight distribution (MWD) of synthetic polymers in industrial polymerization processes because the MWD affects rheological properties and many important end-use polymer properties. Unfortunately, the relationship between MWD and specific polymer properties, such as impact resistance and tensile strength, is often imprecise or only qualitative. However, if a quantitative relationship between the MWD and a polymer property exists, it should be possible to indirectly control the property of interest by controlling the MWD during polymerization reactor operation.

In recent years, there has been a large number of publications on the modeling and control of polymer molecular weight properties, particularly number-average and weight-average poly-

mer molecular weights. It was implicitly assumed that somehow these molecular weight averages and/or polydispersity (M_w/M_n) can be correlated to final end-use polymer properties. However, it is important to recognize that end-use properties and rheological properties are often dependent on the chain length distribution in a manner that cannot be accurately expressed by simply using molecular weight averages only. For example, tensile strength is an important polymer property that specifies a material's failure strength in tension and also gives some indication of its overall toughness. Recent experimental work with amorphous polystyrene¹ has shown that tensile strength correlates well with the following molecular weight parameter:

$$\sigma = \sigma_{\infty} \left(1 - \frac{M_T}{\overline{M}_n^*} \right) \phi \quad (1)$$

where σ is the tensile strength, σ_{∞} is the limit tensile strength at very high molecular weights, ϕ

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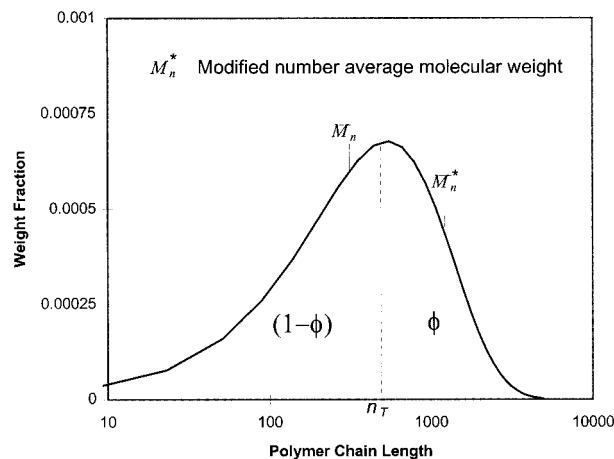


Figure 1 Threshold molecular weight.

is the weight fraction of polymers with molecular weights greater than the threshold value (M_T), and \bar{M}_n^* is the number-average molecular weight for that part of the molecular weight distribution greater than M_T . The threshold molecular weight (M_T) is a key parameter in this simple tensile failure model, which assumes that polymer molecules with molecular weights less than M_T do not contribute to a polymer's tensile strength. This is presumably due to their ineffectiveness in forming chain bridging entanglements, which can retard crack growth in the amorphous polymer. Figure 1 illustrates this concept using an arbitrary molecular weight distribution as an example. This figure illustrates that the modified number-average molecular weight, \bar{M}_n^* , is a number-average molecular weight evaluated using only the fraction of the total polymer molecular weight distribution with molecular weights above the threshold value. In the work by Bersted and Anderson,¹ a value of 59,000 g/mol was determined for the M_T of amorphous polystyrene which, given a monomer molecular weight of 104 g/mol, corresponds to a threshold chain length of $n_T = 567$. They refer to the quantity $\left(1 - \frac{M_T}{\bar{M}_n^*}\right)\phi$ as the failure property parameter. Although this parameter can be evaluated from gel permeation chromatography (GPC), it is not immediately apparent how this parameter could be computed for reactor or process design purposes using the method of molecular weight moments or any of the other available molecular weight modeling techniques.

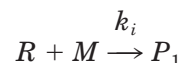
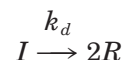
From the foregoing, we can say that being able to estimate or calculate the tensile strength of

polymer during polymerization may be useful in improving process productivity and product quality. In this work, we shall show that the method of finite molecular weight moments² can be easily and conveniently applied to the calculation and control of the failure property parameter in a free radical styrene polymerization process.

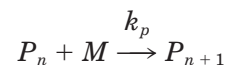
POLYMERIZATION PROCESS MODEL

To calculate polymer chain length distribution, a kinetic model is needed. The kinetic scheme for bulk free radical polymerization of styrene with azo or organic peroxide initiator can be represented as follows.

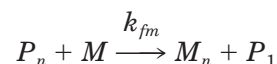
Initiation:



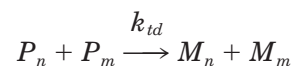
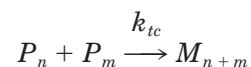
Propagation:



Chain transfer to monomer:



Chain termination:



The following empirical gel effect correlation has been used to account for diffusion-controlled chain termination at high conversion³:

$$g_t \equiv \frac{k_t}{k_t^0} = \exp[-2(Ax_c + Bx_c^2 + Cx_c^3)] \quad (2)$$

where x_c is the fractional conversion of monomer,

$$A = 2.57 - 5.05 \times 10^{-3}T, B = 9.56 - 1.76 \times 10^{-2}T, \text{ and } C = -3.03 + 7.85 \times 10^{-3}T. \quad (3)$$

In the above, k_t^0 is the termination rate constant at zero monomer conversion, and T is in K.

For the kinetic scheme shown above, we can derive the following rate expressions for initiator, primary radicals, monomer, live polymer radicals, and dead polymers.

$$r_I = -k_d I \quad (4)$$

$$r_R = 2f_i k_d I - k_i R M \quad (5)$$

$$r_M = -k_i R M - k_p M P - k_{fm} M P \quad (6)$$

$$r_{P_1} = k_i R M - k_p M P_1 + k_{fm} M (P - P_1) - (k_{tc} + k_{td}) P P_1 \quad (7)$$

$$r_{P_n} = k_p M (P_{n-1} - P_n) - k_{fm} M P_n - (k_{tc} + k_{td}) P P_n \quad (8)$$

$$r_{M_n} = k_{fm} M P_n + \frac{k_{tc}}{2} \sum_{r=1}^{n-1} P_r P_{n-r} + k_{td} P P_n \quad (9)$$

where P is the total live polymer concentration, and f_i is the initiator efficiency factor. P_n is the live polymer radical with n monomer units, and M_n is the dead polymer with n monomer units. When the quasi-steady-state approximation is applied to primary radicals and polymer radicals, the expressions for P_1 and P_n are reduced to

$$P_1 = (1 - \alpha)P \quad (10)$$

$$P_n = \alpha P_{n-1} = (1 - \alpha)\alpha^{n-1}P \quad (11)$$

where α is the probability of propagation defined as

$$\alpha \equiv \frac{k_p M}{k_p M + k_{fm} M + (k_{tc} + k_{td})P} \quad (12)$$

In this article, the free radical polymerization of styrene in a batch suspension polymerization reactor is chosen to illustrate the design of reactor controls to obtain a desired tensile strength value. The suspension of monomer droplets in an aqueous phase enables polymerization to reach high monomer conversion with ease of temperature control and product removal. In the simplest case, each droplet may be modeled as a well-mixed microbatch reactor. Other factors, such as particle size distribution or mixing effects, are not considered in this work.

The above modeling equations can also be expressed in terms of mass fractions of each constituent. For example, the mass balance equations for monomer and initiator in terms of their mass fractions (x_m and x_I) are expressed as

$$\frac{dx_m}{dt} = -(k_p + k_{fm})x_m P \quad (13)$$

$$\frac{dx_I}{dt} = -k_d x_I \quad (14)$$

The total reaction volume V is assumed to be an ideal mixture of its components and is given by

$$V = \left(\frac{x_m}{\rho_m} + \frac{x_p}{\rho_p} + \frac{x_I}{\rho_I} \right) m_t \quad (15)$$

where x_p is the total polymer weight fraction, and m_t is the total reaction mass. ρ_j is the density of component j . The dead polymer mass balance equation is expressed as

$$\frac{d(VM_n)}{dt} = V \left(k_{fm} M + \frac{k_{tc} P}{2\alpha} (1 - \alpha)(n - 1) + k_{td} P \right) \times (1 - \alpha)\alpha^{n-1}P \quad (16)$$

To calculate the polymer chain length distribution, one can directly solve the above kinetic equations for all possible values of n . Computationally, such a method may not be practical, particularly for reaction control purposes. There are also other methods, such as using a moment generating function, z-transform, continuous variable transformation, and Markov chain approaches. In what follows, we shall describe how the polymer chain length distribution can be easily calculated using the above kinetic model.

Method of Finite Molecular Weight Moments

At this point, it is necessary to develop a method for calculating the molecular weight distribution, which can also be used to evaluate the failure property parameter. This failure property parameter requires that we calculate the weight fraction of the entire distribution with molecular weights larger than the threshold value (M_T). To do so, let us first define the following function which represents the weight fraction of polymer within a finite chain length interval (m, n)²:

$$f(m, n) \equiv \frac{\sum_{i=m}^n iM_iV}{\sum_{i=2}^{\infty} iM_iV} = \frac{\sum_{i=m}^n iM_iV}{\lambda_1} \quad (17)$$

where $\lambda_1 \left(\equiv \sum_{i=2}^{\infty} iM_iV \right)$ represents the first moment of the molecular weight distribution for dead polymers. Here, we ignore the contribution of live polymer radicals because their concentrations are negligibly small. Then, we obtain the following differential equation for $f(m, n)$:

$$\frac{df(m, n)}{dt} = \frac{1}{\lambda_1} \sum_{i=m}^n i \frac{dM_iV}{dt} - \frac{f(m, n)d\lambda_1}{\lambda_1 dt} \quad (18)$$

The first term in the right-hand side can be easily derived² and the resulting equation is expressed as The shape of the MWD can then be modeled by choosing a number of different chain length intervals and calculating the weight fraction of polymer in these intervals using eq. (19) and the kinetic mass balance equations. Since the entire range of polymer chain length is discretized using finite chain length intervals, the number of equations to solve is quite small. Our experience suggests that even 15 intervals would be sufficient to express the shape of the chain length distribution. Notice in eq. (19) that only m and n values are varied; therefore, when we develop a computer program, different chain length intervals are specified, and the same equations with different m and n values are integrated. If a large number of chain length intervals are used, the resulting MWD will become close to a continuous distribution curve. This method is different from simply discretizing the polymer population balance equations to a finite difference form for numerical calculations. The main advantage of the method of finite molecular weight moments is that the differential equation for the weight fraction of polymer in any finite chain length interval is explicitly expressed in terms of kinetic and process variables and parameters.

The property parameter ϕ can immediately be identified with the function $f(m, n)$ as

$$\phi = f(n_T, \infty) \quad (20)$$

$$\frac{df(m, n)}{dt} = \frac{V}{\lambda_1} \left\{ \frac{k_{tc}}{2\alpha} P^2 (1-\alpha) \left[\frac{m^2(1-\alpha)^2 + 2\alpha m(1-\alpha) + \alpha^2 + \alpha}{(1-\alpha)^2} \alpha^{m-1} + \left[\frac{(n+1)(1-\alpha) + \alpha}{1-\alpha} \right] \alpha^n - \left[m + \frac{\alpha}{1-\alpha} \right] \alpha^{m-1} - \left[(n+1)^2 + 2(n+1) \frac{\alpha}{1-\alpha} + \frac{\alpha(\alpha+1)}{(1-\alpha)^2} \right] \alpha^n \right] \right. \quad (19)$$

$$\left. + \left(k_{fm}M + k_{td}P \right) P \left(\left[m + \frac{\alpha}{1-\alpha} \right] \alpha^{m-1} - \left[n+1 + \frac{\alpha}{1-\alpha} \right] \alpha^n \right) \right\} - \frac{f(m, n) d\lambda_1}{\lambda_1 dt}$$

where n_T is the threshold polymer chain length ($n_T = M_T/w_m \cong 567$), and w_m is the molecular weight of monomer. Thus, it follows that

$$\phi = f(n_{T,\infty}) = \frac{\sum_{i=n}^{\infty} iM_iV}{\lambda_1} \quad (21)$$

The following differential equation is then obtained for $f(n_{T,\infty})$:

$$\begin{aligned} \frac{df(n_{T,\infty})}{dt} = & \frac{V}{\lambda_1} \left\{ \frac{k_{tc}}{2\alpha} (1-\alpha) P \left(\left[n_T^2 + 2\alpha n_T \frac{1}{1-\alpha} \right. \right. \right. \\ & \left. \left. \left. + \frac{\alpha(1+\alpha)}{(1-\alpha)^2} \right] - \left[n_T + \frac{\alpha}{1-\alpha} \right] \right) + (k_{fm}M \right. \\ & \left. + k_{td}P) \left[n_T + \frac{\alpha}{1-\alpha} \right] \right\} \alpha^{n_T-1} P \\ & - \frac{f(n_{T,\infty})d\lambda_1}{\lambda_1 dt} \quad (22) \end{aligned}$$

where the terms multiplied by α^∞ have been eliminated because $0 < \alpha < 1$. The first moment can be computed by solving the following moment equation:

$$\frac{d\lambda_1}{dt} = \left[\frac{k_{tc}P}{1-\alpha} + (k_{fm}M + k_{td}P) \frac{\alpha(2-\alpha)}{1-\alpha} \right] PV \quad (23)$$

The modified molecular weight moments are defined as

$$\lambda_0^* \equiv \sum_{i=n_T}^{\infty} M_iV$$

and

$$\lambda_1^* \equiv \sum_{i=n_T}^{\infty} iM_iV.$$

Then the dynamic moment equations can be derived as follows:

$$\frac{d\lambda_0^*}{dt} = \left[\frac{k_{tc}}{2\alpha} P \{ (n_T - 1)(1 - \alpha) + \alpha \} + (k_{fm}M + k_{td}P) \right] \alpha^{n_T-1} PV$$

$$\begin{aligned} \frac{d\lambda_1^*}{dt} = & \frac{k_{tc}}{2\alpha} P \left[\frac{n_T^2(1-\alpha)^2 + 2\alpha n_T(1-\alpha) - n_T(1-\alpha)^2 + 2\alpha^2}{1-\alpha} \right] \\ & \times \alpha^{n_T-1} PV + (k_{fm}M + k_{td}P) \\ & \times \left(n_T + \frac{\alpha}{1-\alpha} \right) \alpha^{n_T-1} PV \quad (25) \end{aligned}$$

The number-average molecular weight of the polymer fractions above the threshold value is then calculated according to

$$\bar{M}_n^* = w_m \frac{\lambda_1^*}{\lambda_0^*} \quad (26)$$

Thus, we can directly calculate the weight fraction of polymers and the number-average molecular weight above the threshold chain length. The polymer tensile strength is then calculated directly using eq. (1).

Control of MWD and Tensile Strength

In this section, we shall illustrate how the MWD modeling method above can be incorporated into the design of operating policies for a batch polymerization reactor with obtaining a desired value of polymer's tensile strength as a major objective. Since it is difficult to add or remove reactants from polymer particles in a batch suspension polymerization reactor, the reactor temperature is practically the only variable that can be adjusted during polymerization to change the final polymer molecular weight distribution. Therefore, in our simulations, discrete reactor temperature set-point sequences are determined, which will lead to the best match of predicted tensile strength at final conversion to a target tensile strength. Of course, this approach assumes that the resulting temperature set-point sequence can be tracked reasonably well by a real-time process controller.

The control strategy is an end-point problem with the final batch time unknown. In this work, time is replaced by monomer conversion as the

Table I Kinetic Parameters for Bulk Styrene Polymerization

$k_d = 1.13 \times 10^{19} \exp(-34,277/RT)$ (min^{-1}) ^a
$k_p = 6.31 \times 10^{11} \exp(-7,060/RT)$ ($L \text{ kmol}^{-1} \text{ min}^{-1}$) ^b
$k_{fm} = 1.58 \times 10^{10} \exp(-10,280/RT)$ ($L \text{ kmol}^{-1} \text{ min}^{-1}$) ^b
$k_{tc}^0 = 7.56 \times 10^{13} \exp(-1,680/RT)$ ($L \text{ kmol}^{-1} \text{ min}^{-1}$) ^b
$f_i = 0.6$
$\rho_m = 0.924 - 9.18 \times 10^{-4} T$ (kg/L)
$\rho_p = 1.085 - 6.05 \times 10^{-4} T$ (kg/L)
$\rho_I = \rho_{If} = 1.18$ (kg/L)
$\rho_{mf} = \rho_m$ (25°C)

T in K , $R = 1.987$ kcal/kmol - K

^a Product Bulletin (DuPont).⁵

^b Brandrup and Immergut, 1975.⁶

independent variable in the model used to compute the reactor temperature set-point sequence. This is accomplished by dividing eqs. (13) and (14), (22), (23), and (25) by the following equation for monomer conversion (x_c):

$$\frac{dx_c}{dt} = \frac{(k_p + k_{fm})x_m P}{x_{m0}} \quad (27)$$

where x_{m0} is the initial mass fraction of monomer. It would also be useful to minimize the overall batch time if possible, so an additional state variable, x_b , representing batch time, is included to compute the batch time for different reactor temperature set-point sequence. This procedure enables the final value of the independent variable, monomer conversion, to be anchored at its desired final value in all computations. Using this transformation, the dynamic model equations used for optimization computations take the following form:

$$\frac{dx_m}{dx_c} = -x_{m0} \quad (28)$$

$$\frac{dx_I}{dx_c} = -\frac{x_{m0}k_a x_I}{(k_p + k_{fm})x_m P} \quad (29)$$

$$\begin{aligned} \frac{df(n_T, \infty)}{dx_c} = & \frac{x_{m0}V\alpha^{n_T-1}}{(k_p + k_{fm})x_m\lambda_1} \left\{ \frac{k_{tc}}{2\alpha}(1-\alpha) \left(\left[n_T^2 \right. \right. \right. \\ & + \left. \frac{2\alpha n_T}{1-\alpha} + \frac{\alpha^2 + \alpha}{(1-\alpha)^2} \right] - \left[n_T + \frac{\alpha}{1-\alpha} \right] \right) + (k_{fm}M \\ & + k_{td}P) \left(n_T + \frac{\alpha}{1-\alpha} \right) \left. \right\} - \frac{f(n_T, \infty)d\lambda_1}{\lambda_1 dx_c} \quad (30) \end{aligned}$$

$$\frac{d\lambda_1}{dx_c} = \left[\frac{k_{tc}P}{1-\alpha} + (k_{fm}M + k_{td}P) \frac{\alpha(2-\alpha)}{1-\alpha} \right] \frac{x_{m0}V}{(k_p + k_{fm})x_m} \quad (31)$$

$$\frac{d\lambda_0^*}{dx_c} = \left[\frac{k_{tc}P}{2\alpha} \{ (n_T - 1)(1 - \alpha) + \alpha \} + (k_{fm}M + k_{td}P) \right] \frac{\alpha^{n_T-1}x_{m0}V}{(k_p + k_{fm})x_m} \quad (32)$$

$$\begin{aligned} \frac{d\lambda_1^*}{dx_c} = & \frac{k_{tc}P}{2\alpha} \left[\frac{n_T^2(1-\alpha)^2 + 2\alpha n_T(1-\alpha)}{1-\alpha} - n_T(1-\alpha)^2 + 2\alpha^2 \right] \\ & \times \frac{\alpha^{n_T-1}x_{m0}V}{(k_p + k_{fm})x_m} + (k_{fm}M + k_{td}P) \\ & \times \left(n_T + \frac{\alpha}{1-\alpha} \right) \alpha^{n_T-1} \frac{x_{m0}V}{(k_p + k_{fm})x_m} \quad (33) \end{aligned}$$

$$\frac{dx_t}{dx_c} = \frac{x_{m0}}{(k_p + k_{fm})x_m P} \quad (34)$$

The objective function can then be defined in terms of the fixed final monomer conversion.

Let us consider a free radical suspension polymerization of styrene in a batch reactor. The objective is to design polymerization conditions to achieve a prespecified polymer tensile strength at the final monomer conversion. In suspension polymerization processes, near 100% monomer

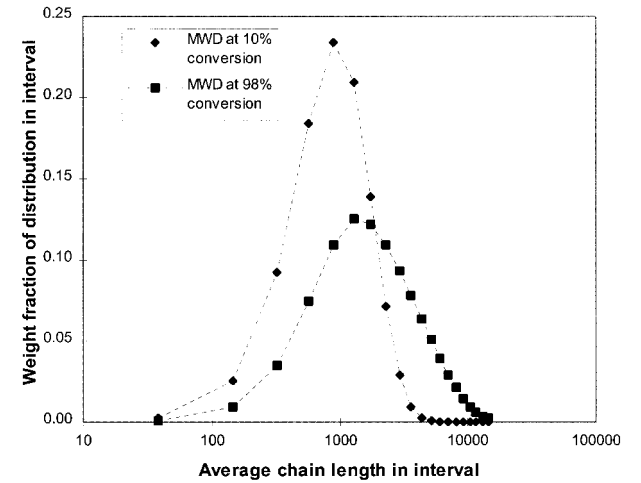


Figure 2 Polymer weight chain length distributions at 10% and 98% conversions at 78°C.

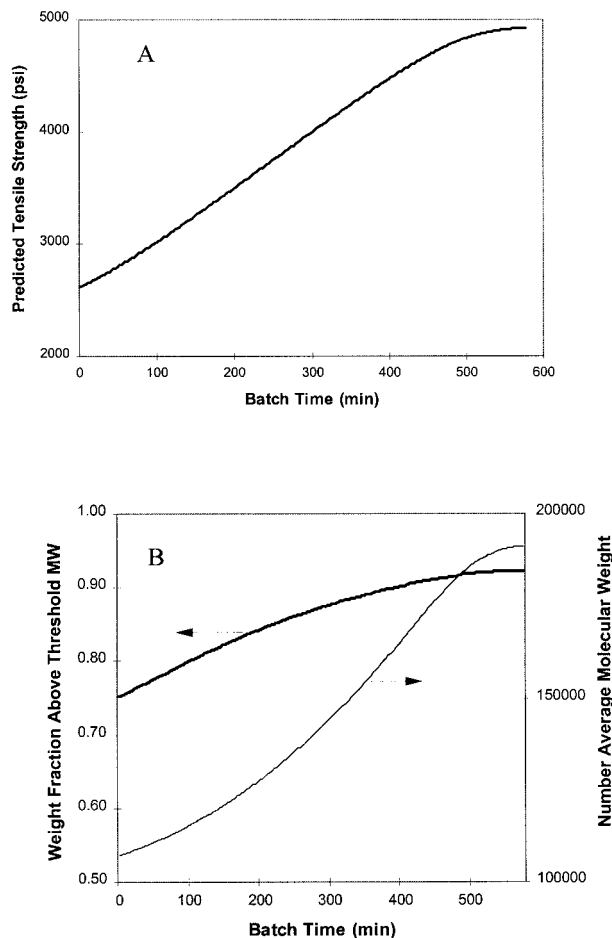


Figure 3 Molecular-weight-dependent tensile strength and tensile strength variation during polymerization for isothermal operation at 78°C.

conversion is achievable. To illustrate how the method of finite molecular weight moments can be applied to designing optimal reaction conditions, we shall consider both isothermal and nonisothermal reactor operations.

To design an optimal nonisothermal reactor operating policy, the reactor temperature sequence, T_j ($j = 1, \dots, N$), and initial initiator concentration are taken as the decision variables in an optimization problem defined by the objective function,

$$\min_{x_t(0), T_1, T_2, \dots, T_N} J(x_{cf}) + \left(\frac{\sigma(x_{cf}) - \sigma_{set}}{\sigma_{set}} \right)^2 + [x_t(x_{cf})W_t]^2 \quad (35)$$

subject to bounds on the discrete temperature levels, T_j , as follows:

$$40^\circ\text{C} \leq T_j \leq 100^\circ\text{C} \quad (36)$$

where $x_t(0)$ = initial initiator weight fraction, T_j = j -th reactor temperature set-point in the reactor temperature setpoint sequence, $\sigma(x_{cf})$ = tensile strength at the final polymer weight fraction of 98%, $x_t(x_{cf})$ = batch time (min) required to reach 98% polymer weight fraction, W_t = weighting factor set equal to 10^{-4} , σ_{set} = target tensile strength, and x_{cf} = final target monomer conversion of 98%.

The reactor temperature set-points are discretized in conversion rather than time. Therefore, each T_j in the temperature set-point sequence represents a temperature at which the reactor will be controlled for a fixed fraction of the total polymer to be produced. For example, if the final desired conversion were 40% and if the total

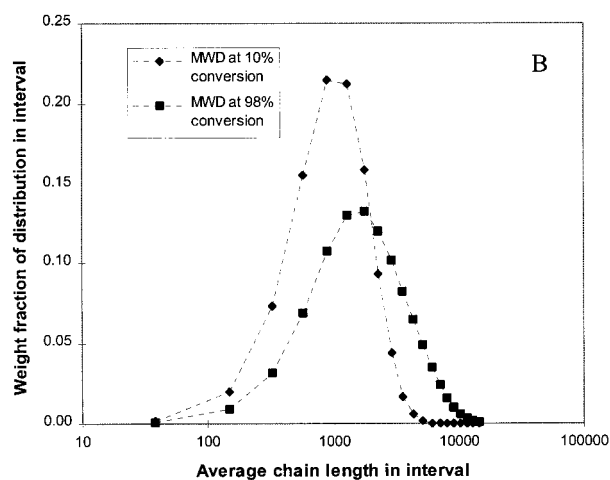
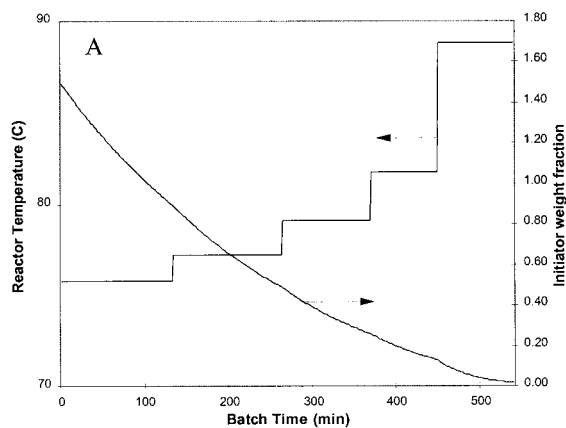


Figure 4 Reactor temperature set-point program and weight chain length distributions at 10% and 98% monomer conversion.

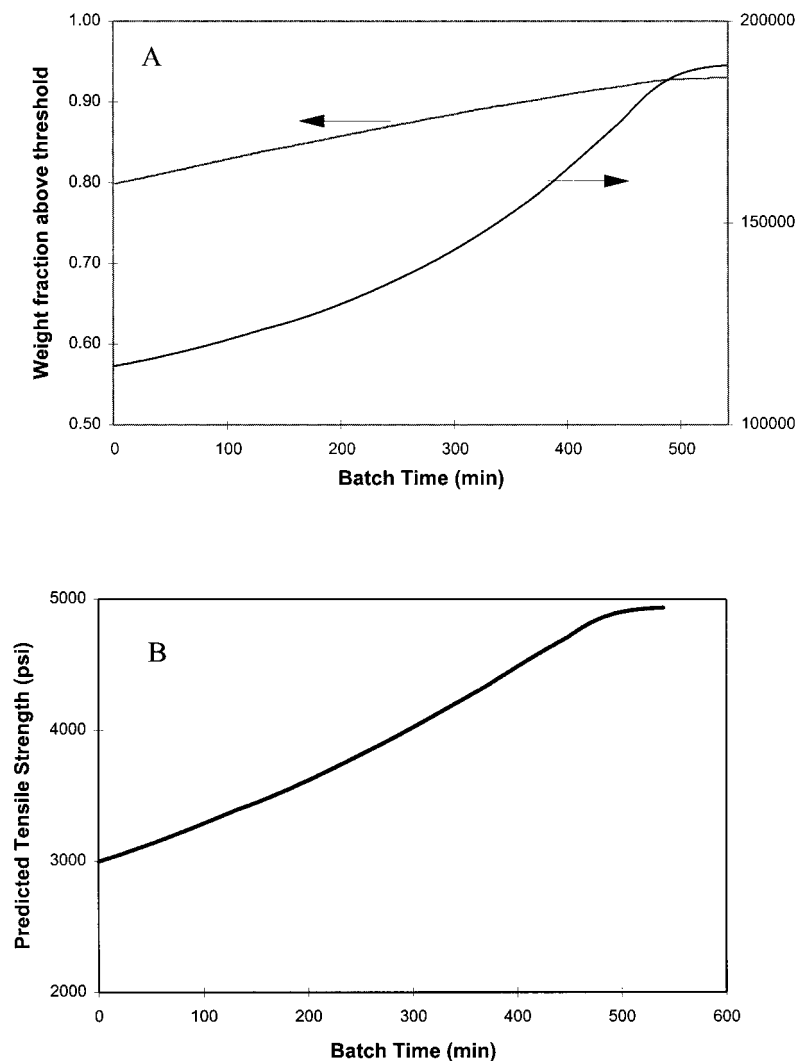


Figure 5 Molecular-weight-dependent tensile strength parameters and tensile strength variation during polymerization for nonisothermal operation.

number of temperature levels N is specified as 4, then T_1 would represent an optimized temperature set-point at which the reactor would be operated during polymerization from 0 to 10% monomer conversion, T_2 would represent the optimized temperature for conversion from 10 to 20%, T_3 for polymerization from 20 to 30% monomer conversion, and, finally, T_4 would represent the optimized reactor temperature from 30% to the final desired conversion.

The optimization problem defined by eqs. (35) and (36) is solved using a sequential quadratic programming algorithm, FSQP.⁴ 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. Other similar optimization techniques can also be used. The numerical values for the kinetic and physical parameters are listed in Table I. The initiator employed in our numerical simulations is 2,2'-azobis(2-methyl-butanenitrile). In our model simulations, it is assumed that chain termination occurs predominantly via combination termination mechanism (that is, $k_{td} \approx 0$).

RESULTS

The first simulation was carried out for an isothermal polymerization. The target tensile

strength of the polymer to be produced is 5000 psi. Then, the objective is to find the optimal isothermal reaction temperature and initiator concentration to obtain the desired tensile strength in minimum batch time. Mathematically, isothermal polymerization can be simulated simply by setting $N = 1$ in eq. (35). 78°C was found to be the optimal polymerization temperature for the isothermal operation. Figure 2 shows the weight chain length distribution curves at 10 and 98% monomer conversion at 78°C, respectively. It is seen that the polymer molecular weight distribution changes significantly with conversion. Recall that the threshold chain length is 567. Figure 3(A) shows the weight fraction of polymers above the threshold molecular weight and the number-average molecular weight of the polymers having the chain lengths larger than the threshold value. Also shown in Figure 3(B) is the tensile strength variation during polymerization. Since the objective function used is defined such that the desired tensile strength should be reached at the final target monomer conversion, the tensile strength of 5,000 psi is indeed reached at the end of the batch.

In the second simulation, the reactor is operated nonisothermally, and the optimal nonisothermal reaction conditions (that is, the temperature set-point sequence) will be designed. Figure 4(A) shows the optimized nonisothermal reactor temperature sequence and the initiator concentration profile. The resulting chain length distributions at 10% and 98% monomer conversion are shown in Figure 4(B). The nonisothermal optimization calculation was carried out with $N = 5$ (5 control intervals). Figure 5(A) shows the polymer weight fraction above the threshold polymer chain length and the number-average molecular weight of the polymers having the chain lengths larger than the threshold value. Again, the target tensile strength is obtained at the end of batch polymerization [Fig. 5(B)]. It is seen that, compared to isothermal operation (Fig. 3), the total batch time for nonisothermal operation is reduced by about 30 min. In Figure 6(B), the weight chain length distributions for isothermal and nonisothermal polymerizations are compared. Although it appears that these 2 distributions are quite similar, the initiator concentration at the end of polymerization in each operation is quite different [Fig. 6(A)]. It is seen that the residual

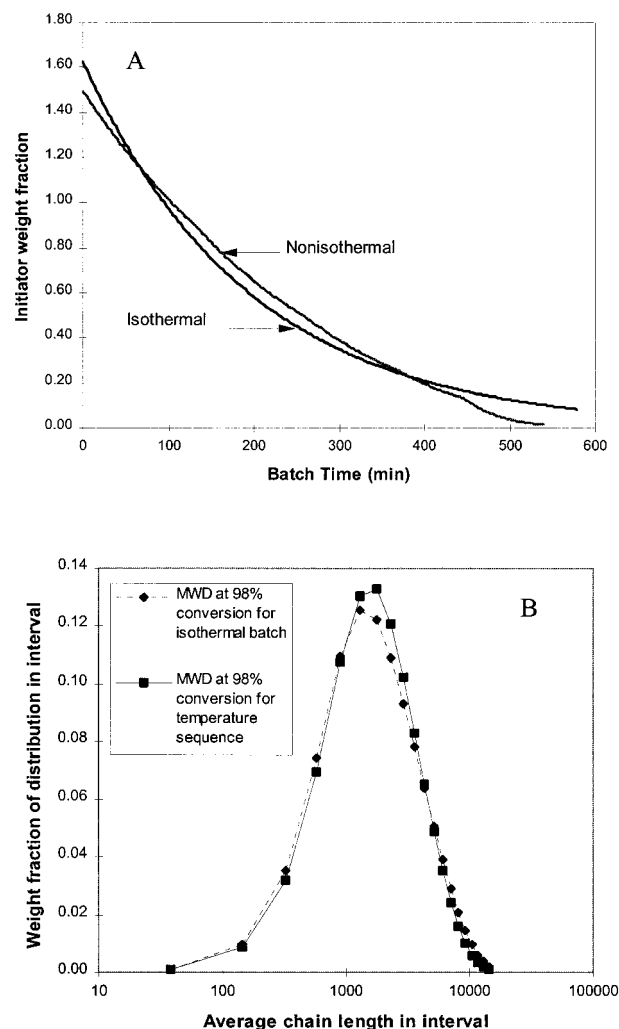


Figure 6 Comparison of final initiator concentration and weight chain length distribution for isothermal and nonisothermal polymerizations.

initiator concentration is higher in isothermal polymerization than in nonisothermal polymerization.

CONCLUSIONS

In this article, it is illustrated that the method of finite molecular weight moments can be conveniently used to calculate the molecular weight distribution of polymer above a threshold chain length. This enables one to predict the tensile strength of the final amorphous polymer during polymer synthesis. The batch suspension polymerization of styrene is used as a simulation ex-

ample. Through the comparison of 2 different reactor operations (that is, isothermal and nonisothermal polymerizations), it has been shown that one can design various types of reactor operating policies and assess the molecular weight properties, as well as the overall batch time and residual initiator concentration. The method presented in this article can be easily extended to continuous polymerization systems.

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