

Optimal Temperature for the Control of the Product Quality in Batch Polymerization: Simulation and Experimental Results

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SYNOPSIS

A method to determine an optimal temperature profile that guarantees products having controlled molecular weight distribution (MWD) and desired values of molecular weight (M_w) is presented. The base case is the batch polymerization of MethylMethAcrylate, initiated by AIBN. On the basis of the kinetic model, the optimal temperature profile is determined by imposing that the value of the instantaneous chain length is maintained constant, thus counteracting the effects of the increase of viscosity, which leads to broad MWD. Some approximations permit to express, in a straightforward way, the relationship between the optimal temperature and the conversion as a function of the initial conditions. The validity of the simplifying hypotheses that have been assumed is confirmed first by simulation results and then by a comparison with experimental runs conducted in a lab-scale unit, with determination of MWD made by means of GPC. The obtained results suggest that it is possible to decouple the problem: acting on the operating temperature to control the MWD, acting on initial temperature, and initiator concentration to influence the M_w . The possibility of application to industrial reactors has also been investigated, taking into account their peculiarities and constraints. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The demand for polymer products having specific predeterminate properties (tailor-made polymers) requires the control of microscopic characteristics during the reaction, as posttreatments are expensive and not efficient in many respects. Main mechanical and thermal properties of polymeric products are correlated with the value of the molecular weight (M_w) and of the molecular weight distribution (MWD). A typical goal in the optimization of polymerization reactors is to achieve values of greater than a required minimum value and a final value of polydispersity (PD , index of the MWD), less than a fixed maximum value.

The possibility of assuring a product having constant properties is particularly difficult in batch reactors, where, during the course of the reaction, concentrations and reactivities of the different species and physical properties of the system undergo large changes. For example, in the free radical polymerizations carried out in concentrated solution and bulk (or in suspension, kinetically equivalent to bulk), the increase of viscosity leads to the so called gel and glass effect. Both phenomena can play an important role affecting the reaction rate and the molecular weight distribution of the polymer.¹⁻³ Therefore, the final product is a mixture of polymer chains that were formed in very different situations during the batch.

One additional difficulty is given by the fact that variables that are indices of the final polymer quality are not available in real time, owing to problems of measurement or analysis. They must be inferred by other intermediate variables (such as conversion and

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temperature), which are easier to obtain, by means of a model of the system.

The global optimization is included in the objective function, in addition to the control of the polymer quality; also, the achievement of high productivity (high conversion, short reaction times), and the respect of the operation safety. Main operating variables are: the initial concentration of monomer and initiator, the temperature, the rate of feeding solvent, monomer, and initiator, the use of inhibitor, or chain transfer agents. Constraints that are present in industrial reactors are very important to define the range of variation of parameters and to disregard possible solutions that might be interesting in a theoretical approach to the problem.

The optimization of batch polymerization reactors has found wide interest in literature. A review of previous work is reported by Louie and co-workers.² The authors distinguish between two partial optimizations: minimum end time, which minimizes the batch time but leaves the MWD uncontrolled, and minimum *PD*, which minimizes *PD* but leaves the M_w and the batch time uncontrolled. In their articles, a rich analysis of different optimal strategies for bulk and solution polymerization is presented. The effect of monomer and solvent addition, of different initiator (including photoinitiation), and temperature profiles is examined, and considerations about relative merits are drawn, pointing out advantages and disadvantages of each.

A complete work about solution polymerization of MMA is reported by Ref. 4. Time optimal policy for different operating variables are determined mathematically to achieve different objectives. Several closed-loop algorithms are applied to achieve the required control strategies, and a good agreement between theoretical predictions and experimental results, obtained on a lab-scale unit, is shown. Takamatzu⁵ proposes a method to obtain prescribed MWD by acting on temperature and initiator concentration; the possibility of obtaining the desired time profile by using adaptive controllers is shown by simulation. Chang and Lai⁶ present a method to determine the optimal temperature profile to obtain a specified MWD of the product for bulk and solution polymerization of MMA. A two-step procedure is adopted in order to find an algorithm that can be used in a real polymerization system. No experimental results are given.

In this article the attention is focalized to the case of batch polymerization of MMA in suspension, for which a detailed model has been developed in previous work.⁷ The main objective is to investigate the possibility of controlling the product quality by

acting on the temperature. An optimal temperature profile will be derived starting from the kinetics of the process. Some assumptions will allow to simplify the model and to obtain the optimal temperature profile in a direct way. Predicted results will be compared with simulation using the full order model and with experimental runs. Also, possible applications of the proposed strategy will be analyzed taking into account main features of industrial reactors.

MODEL OF THE SYSTEM

Previous activity about polymerization of MMA in batch reactors has allowed development of a detailed model of the system. The model starts from the kinetics of the reactions and includes the dynamic simulation of industrial reactors. The kinetic model has been validated by experimental runs of bulk and suspension polymerization in a wide range of operating conditions.⁷⁻⁹

The model evaluates the average weight molecular weight (\bar{M}_w), the average number molecular weight (\bar{M}_n), and the Polydispersity ($PD = \bar{M}_w / \bar{M}_n$), which is an index of the MWD variance, under isothermal and nonisothermal conditions. The method of the generating functions has been adopted as proposed by Ray¹⁰ and Hamielec.^{11,12} The main differences between the two approaches is that, while Ray takes into account the contribution of both growing and dead polymer chains to the final product quality, Hamielec considers only the dead ones. As in the free radical polymerization reaction the average lifetime of growing chains is negligible with respect to polymerization time, results obtained by the two methods are almost coincident. In addition to these considerations, the simpler Hamielec's approach originates a system of differential equations that showed to be numerically more robust, and for these reasons has been adopted in this study.

For the growing and the dead polymer chains, the two generating functions are defined respectively as:

$$G(s, t) = \sum_{i=1}^{\infty} s^i P_i(t); F(s, t) = \sum_{i=1}^{\infty} s^i M_i(t) \quad (1)$$

P_i is the concentration of polymer growing and M_i is the concentration of dead polymer of length i .

From generating functions, the j th order moments of the MWD can be deducted, for the growing and dead polymer chains, respectively as:

$$\lambda_j = (d^j G(s, t) / ds^j)_{s=1}; \mu_j = (d^j F(s, t) / ds^j)_{s=1} \quad (2)$$

(\bar{M}_w), (\bar{M}_n) and (PD) are obtained from the leading moments as:

$$\bar{M}_n = \frac{\mu_1}{\mu_0} W; \bar{M}_w = \frac{\mu_2}{\mu_1} W; PD = \frac{\mu_2 \mu_0}{\mu_1^2} \quad (3)$$

where W is the molecular weight of the monomer. About the physical meaning of the leading moments: λ_0 is the concentration of growing chains, μ_0 is the concentration of dead polymer chains, μ_1 is the number of monomer units in dead polymer chains.

Reaction rates for all the reacting species, including moments of the MWD, are given below (for a complete list of symbols, see Table V):

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

$$r_m = -2k_d f I - (k_p + k_{tr,m}) M \lambda_0 \quad (5)$$

$$r_{\lambda_0} = 2k_d f I - k_t \lambda_0^2 \quad (6)$$

$$r_{\lambda_1} = 2k_d f I - k_{tr,m} M (\lambda_1 - \lambda_0) + k_p M \lambda_0 - k_t \lambda_0 \lambda_1 \quad (7)$$

$$r_{\lambda_2} = 2k_p M \lambda_1 - (k_{tr,m} M + k_{t,d} \lambda_0) \lambda_0 \quad (8)$$

$$r_{\mu_0} = 0.5 k_{t,c} \lambda_0^2 + (k_{tr,m} M + k_{t,d} \lambda_0) \lambda_0 \quad (9)$$

$$r_{\mu_1} = (k_{tr,m} M + k_t \lambda_0) \lambda_1 + (k_{tr,m} M + k_{t,d} \lambda_0) \lambda_0 \quad (10)$$

$$r_{\mu_2} = k_{t,c} \lambda_1^2 + (k_{tr,m} M + k_t \lambda_0) \lambda_2 + (k_{tr,m} M + k_{t,d} \lambda_0) \lambda_1 \quad (11)$$

In previous expressions, the kinetic constants: k_d , k_{tr} , k_p , k_t refer to typical steps of the free radical polymerization, respectively: initiator decomposition, chain transfer, propagation, and termination. Values of k_p , k_t , and $k_{tr,m}$ are affected by diffusion and then change with conversion and as a consequence of the onset of gel and glass effect.

The termination and, at higher conversion, the propagation, and the transfer rates are controlled by diffusion phenomena.^{2,15,16} The gel effect is originated from the fact that termination reactions among the large polymer growing chains are controlled by diffusion. This slows termination rate compared with propagation and, therefore, causes an increase in the polymerization rate. At higher conversions, when the temperature is below the glass transition temperature of the polymer, the propagation and transfer reaction also may become controlled by diffusion: this glass effect causes a sudden decrease in the reaction rate. Their direct consequences on the molecular weight distributions are the following: (a) during the gel effect time the instantaneous molecular weight goes up rapidly; the

weight average molecular weight (\bar{M}_w) increases more than the number average molecular weight (\bar{M}_n), so that the polydispersity ($PD = \bar{M}_w / \bar{M}_n$) will be larger; (b) during the glass effect time, on the contrary, \bar{M}_n decreases more than \bar{M}_w , but the final results will be, again, a larger value of PD .

Diffusion phenomena are heavily affected by temperature: so the reactor temperature plays an important role on the onset and on the extent of the two effects.

A quantitative evaluation of the onset of gel and glass effect can be achieved by modeling the reaction kinetics in terms of free volumes.^{15,16}

The free volume of the reacting system (ν_f) is computed by free volumes of the two species (monomer: $\nu_{f,m}$ and polymer: $\nu_{f,p}$) and their volume fractions (ϕ_m , ϕ_p), which depend mainly on conversion:

$$\phi_m = \frac{1 - X}{1 + \delta X}; \phi_p = 1 - \phi_m; \nu_{f,m} \phi_m + \nu_{f,p} \phi_p \quad (12)$$

Values of ν_f are compared with critical values ($\nu_{f,cr}$ and $\nu'_{f,cr}$, for gel and glass effect) and the propagation, transfer, and termination rate constants (k_p , k_{tr} , k_t) assume different values, according to the change of the values of system free volume compared with the critical values. Numerical values of all kinetic constants appearing in reaction rates are given in Table I. k_p , k_t , and $k_{tr,m}$ are expressed as a ratio with respect to their values in the absence of diffusive control, at zero conversion (k_{p0} , k_{t0} , and $k_{tr,m0}$).

It should be noted that monomer and polymer free volumes ($\nu_{f,m}$ and $\nu_{f,p}$) increase with temperature while the critical value decreases. Therefore, by acting on the temperature, it is possible to operate above critical values and, as matter of principle, to counteract gel and glass effect consequences. In the sequel, it will be shown how that can be exactly done.

In developing the model, reference has been made to industrial units, where the suspension polymerization of MMA is carried out batchwise. The reaction mixture is stirred by means of a continuous system and warmed up to the desired temperature. Once the reaction starts, the heat generated is removed by means of a jacket cooling system: the reactor temperature is controlled, through the inlet temperature of the cooling water in the jacket, by mixing an external flow of subcooled water with a recycle from the jacket. Hypotheses of perfect mixing for the reactor and the jacket have been assumed and the thermal capacity of the jacket has been neglected. The dynamic behavior of the system is de-

Table I Kinetic Constants Values for Free Radical Polymerization of MMA (Initiator AIBN)

| | |
|--|--|
| $k_d = 1.33 \cdot 10^{15} \cdot e^{-(30700/RT)}$ | $k_{p0} = 4.41 \cdot 10^5 \cdot e^{-(4350/RT)}$ |
| $k_{tr,m0} = 4.67 \cdot 10^{-2} \cdot e^{-(888/RT)}$ | $k_{t0} = 6.50 \cdot 10^7 \cdot e^{-(700/RT)}$ |
| $k_{t,c}/k_{t,d} = 3.956 \cdot 10^{-4} \cdot e^{(4090/RT)}$ | $k_{t,d} = k_t - k_{t,c}$ |
| $\nu_{f,m} = 0.025 + 0.001(T - 167.16)$ | $(k_p/k_{p0}) = 72.23e^{(175\nu_f - 7.41 - 40.2\nu_{f,cr})}; (\nu_f \leq \nu'_{f,cr})$ |
| $\nu_{f,p} = 0.025 + 0.00048(T - 387.16)$ | $(k_p/k_{p0}) = 1; (\nu_f \geq \nu'_{f,cr})$ |
| $\nu_{f,cr} = 0.186 - 2.96 \cdot 10^{-4}(T - 273.16)$ | $(k_t/k_{t0}) = 0.683e^{(80.4(\nu_f - \nu_{f,cr}))}; (\nu_f \leq \nu_{f,cr})$ |
| $\nu'_{f,cr} = 0.055$ | $(k_t/k_{t0}) = 0.135e^{(17.15\nu_f - 0.017(T - 273.16))}; (\nu_f \geq \nu_{f,cr})$ |
| $(k_{tr,m}/k_{tr,m0}) = 72.23e^{(175\nu_f - 7.41 - 40.2\nu_{f,cr})}; (\nu_f \leq \nu'_{f,cr})$ | $(k_{tr,m}/k_{tr,m0}) = 1; (\nu_f \geq \nu'_{f,cr})$ |

scribed by the set of balance equations reported in Table II. A complete list of symbols is given in Table V. By substituting the thermal balance with an imposed temperature profile (adiabatic, isothermal, or programmed as a function of the conversion or time), it is possible to simulate the effects of any operating strategy. The variation of the physical properties of the system as function of temperature and conversion are also accounted for in the model.

Also, the molecular weight distribution of the polymer are evaluated by the model. The classical theory developed by Flory¹³ is applied to the case under study. The instantaneous number distribution function of the polymer chains is given by Ref. 14: $F_i(n) = a \cdot e^{(-a \cdot n)}$; $F_i(n)$ represents a fraction of polymer consisting of n monomers units: $\sum F_i(n) = 1$. The parameter a is defined as the inverse of the average polymerization degree:

$$a = \frac{1}{\bar{x}_n} = \frac{\lambda_0}{\lambda_1} \quad (13)$$

The instantaneous weight distribution function, F_i^w represents a normalized weight fraction of polymer consisting of n monomer units $\sum F_i^w$ and is given by:

$$F_i^w = \frac{n \cdot F_i(n)}{\int (n \cdot F_i(n))} = a^2 \cdot n \cdot e^{(-a \cdot n)} \quad (14)$$

The cumulative MWD curve at a given conversion X_f , can be obtained by a convolution of the instantaneous weight distribution function in the previous N intervals where the variation of conversion is ΔX_j :

$$F_\sigma^w = \sum_{j=1}^N \frac{\Delta X_j}{X_f} F_i^w \quad (15)$$

THE OPTIMAL TEMPERATURE PROFILE

The target is to obtain a constant value of the molecular weight (M_w) during the batch and, consequently, to control the final MWD of the polymer, which largely influences the product quality, by maintaining PD as close as possible to its minimum value. During the course of the batch reaction, different phenomena affect various steps of the polymerization and lead to an increase of M_w and PD , as explained above. For radical polymerization, the average lifetime of polymer chain can be considered about 0.5–5 s, while the batch time is about 1 h.

Therefore, the final product characteristics depend on polymer chains that have been formed in very different situations inside the reactor.

To achieve a product with a constant value of M_w and consequently of PD , the basic idea is to maintain the value of the instantaneous chain length $\nu(t)$ almost constant during the reaction, by acting on the temperature profile.

Table II Balance Equation for the Batch Reactor

| | | |
|---|---|---|
| $dV/dt = -(V_0 \delta dM/dt)$ | $dI/dt = \xi I dM/dt + r_i$ | $dM/dt = r_m / (1 - \xi M)$ |
| $d\lambda_0/dt = \xi \lambda_0 dM/dt + r_{\lambda_0}$ | $d\lambda_1/dt = \xi \lambda_1 dM/dt + r_{\lambda_1}$ | $d\lambda_2/dt = \xi \lambda_2 dM/dt + r_{\lambda_2}$ |
| $d\mu_0/dt = \xi \mu_0 dM/dt + r_{\mu_0}$ | $d\mu_1/dt = \xi \mu_1 dM/dt + r_{\mu_1}$ | $d\mu_2/dt = \xi \mu_2 dM/dt + r_{\mu_2}$ |
| $CdT/dt = \Gamma_r - \Gamma_j$ | $\Gamma_r = -\Delta H_r V_0 \tau r_m$ | $\Gamma_j = U_d A X (T - T_j)$ |

When $k_{t,d} \gg k_{t,c}$, as in the case of MMA, it can be expressed as a ratio between the moments:

$$\nu(t) \cong x_n = \frac{\lambda_1}{\lambda_0} \quad (16)$$

λ_0 and λ_1 should be computed as function of time from the differential equations [Eqs. (9) and (10)]. By assuming that the rates of activation and deactivation of polymer chains are almost equal (Quasi-Steady State Approximation), λ_0 and λ_1 assume algebraic equations.

The ratio between the value of the polymer chain length at any time $\nu(t)$ and the initial value ν_0 , can be expressed as (details in Appendix):

$$\beta = \alpha \frac{K_0}{K} \frac{1-X}{1+\delta X} \left(\frac{I}{I_0} \right)^{0.5} \quad (17)$$

with the self acceleration parameter $\alpha = g_p g_t^{0.5}$, has been introduced to represent the overall effect of diffusion phenomena.

With some approximations β become a function of temperature, conversion, and initial conditions; by imposing: $\beta(T, X, IC) = 1$, it is possible to compute an optimal temperature profile $T^*(X)$, which will depend only on the initial conditions T_0 , I_0 , and

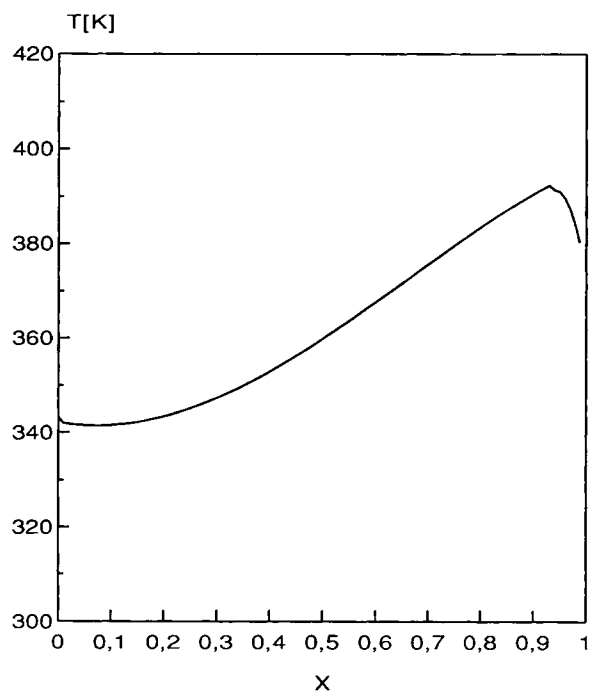


Figure 1 Optimal temperature profile $T^*(X)$ ($T_0 = 343$ K, $M_0/I_0 = 400$).

is able to guarantee constant value of the polymer chain $\nu(t)$, during the course of the polymerization.

The optimal temperature profile $T^*(X)$ is reported in Figure 1, for assigned value of the initial condition T_0 and initiator concentration M_0/I_0 .

In the initial part of the reaction, the required temperature is almost constant (a decreasing profile may be required, according to initial conditions). Then the temperature shows an increase with conversion that becomes larger when the conversion and, consequently, the viscosity increases owing to gel effect, which slows the termination rate compared with the propagation rate.

In the final part of the reaction, owing to the diminution of initiator and monomer concentration, the polymerization rate is strongly reduced and a decrease of temperature is required.

In the case illustrated in Figure 1, the final temperature (T_f) is above the glass transition temperature (T_g), so the glass effect does not affect the reaction. In cases when $T_f < T_g$, the glass effect becomes active and an even lower temperature is required in the final part of the reaction.

RESULTS OF SIMULATION AND DISCUSSION

The molecular weight $M_w(X)$ and the Polydispersity $PD(X)$, calculated by the detailed model of the polymerization process, by imposing the optimal temperature profile $T^*(X)$ [Eq. (17)], are reported in Figure 2.

This behavior confirms that the hypotheses, which have been adopted in developing the optimal profile, are correct.

The optimal temperature profile $T^*(X)$ allows us to obtain constant values of molecular weight and polydispersity, up to large conversions. The M_w has low values, because it is maintained constant at initial values, and this can be a drawback for the final product quality.

Among the several different operating variables that can be used to control the M_w , here attention is devoted to initial temperature (T_0) and concentration of initiator expressed as the initial monomer/initiator ratio (M_0/I_0).

The effects of four different initial temperatures T_0 are reported in Figure 3. The optimal temperature profile $T^*(X)$ shifts by an amount that is almost equal to the initial difference in temperature [Fig. 3(a)].

A decrease of the initial temperature is favorable, as it allows an increase of molecular weight M_w [Fig.

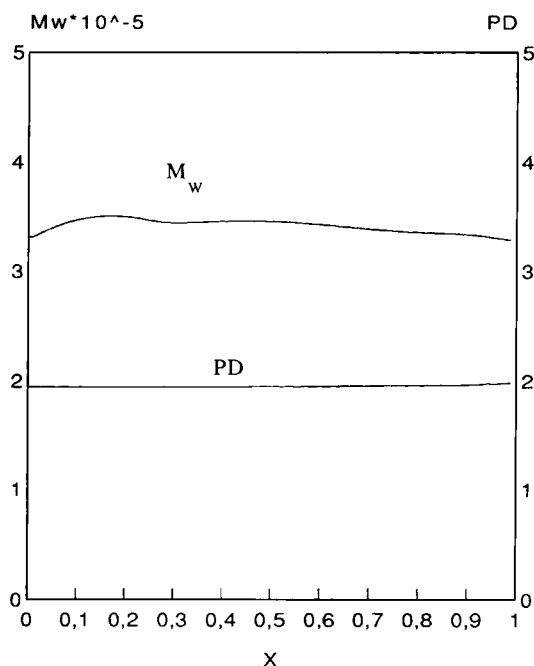


Figure 2 Molecular weight $M_w(X)$ and polydispersity $PD(X)$; ($T_0 = 343$ K, $M_0/I_0 = 400$).

3(c)], while PD still remains constant [Fig. 3(b)]. Another advantage is that the reactor temperature reaches lower final values. The disadvantage lies in the fact that polymerization reaction is slower, and then the batch time will be longer (see Table III).

The effects of different initiator concentrations M_0/I_0 on the molecular weight of the product are reported in Figure 4. A decrease of initiator concentration (i.e., an increase of M_0/I_0) has an effect that is qualitatively analogous to a decrease of the initial temperature, as it leads to an increase of the molecular weight. In this case, too, the drawback lies in longer batch times (see Tables III and IV).

The optimal temperature profile $T^*(X)$ does not change because, as illustrated in the statement of the problem, it is very weakly influenced by the initiator concentration.

The optimization problem can then be restated as: given a minimum value of molecular weight of polymer, find initial conditions (temperature: T_0 and monomer/initiator ratio: M_0/I_0) and the temperature profile $T^*(X)$, in order to maintain a constant value of PD .

EXPERIMENTAL

In order to confirm theoretical results obtained by the model concerning the influence of operating

temperature on the process dynamics and the polymer quality, some experimental runs of bulk polymerization of MethylMethAcrylate (MMA), initiated by a radical initiator (AIBN) AzobisIsoButyrronitrile have been carried out.^{17,18}

The hypotheses of perfect mixing, which is acceptable for suspension polymerization reactors, can be considered still valid for the case of bulk polymerization in very small laboratory units.

Bulk polymerization reactions were executed in glass flasks ($\cong 2$ mL volume) placed in a thermostatic bath in order to perform experiments under isothermal conditions and with programmed temperature profiles. Before experiments the stabilized, commercial MMA (Aldrich Chem) was washed with 10% wt. aqueous solution of NaOH to remove inhibitor, dried, and distilled. The purified monomer was stored in a freezer (-15°C) for a maximum of 12 h. The radical initiator was dissolved and recrystallized from ethyl alcohol and dried under reduced pressure and used immediately. Before each run, the monomer was purged with nitrogen in order to remove the dissolved oxygen and to ensure an inert atmosphere during the batch.

During the polymerization, conversion was determined gravimetrically by sampling flasks at intervals of time. The flasks were cooled rapidly and a solution of methyl alcohol and hydroquinone was introduced in order to stop the reaction and to precipitate the polymer. The polymer was dissolved in ethyl acetate and reprecipitated in methyl alcohol in order to remove any monomer in the polymer.

The M_w and MWD of polymer were determined by gel permeation chromatography (GPC), using a Varian 4400 liquid chromatograph equipped with three Ultrastyrigel columns Waters (10^{-4} , 10^{-5} , and 10^{-6} Å). In nonisothermal runs, at a certain time the heat exchange capacity of the thermostatic bath was drastically reduced, thus obtaining a sharp increase of temperature in the flasks in order to approximate the optimal temperature profile $T^*(X)$.

The experimental temperature profiles under

Table III Effect of Different Initial Temperature T_0 on the Batch Time ($\tau_{90\%}$), $M_0/I_0 = 400$

| T_0 [K] | $\tau_{90\%}$ (min) |
|-----------|---------------------|
| 333 | 90 |
| 343 | 52 |
| 353 | 28 |
| 363 | 15 |

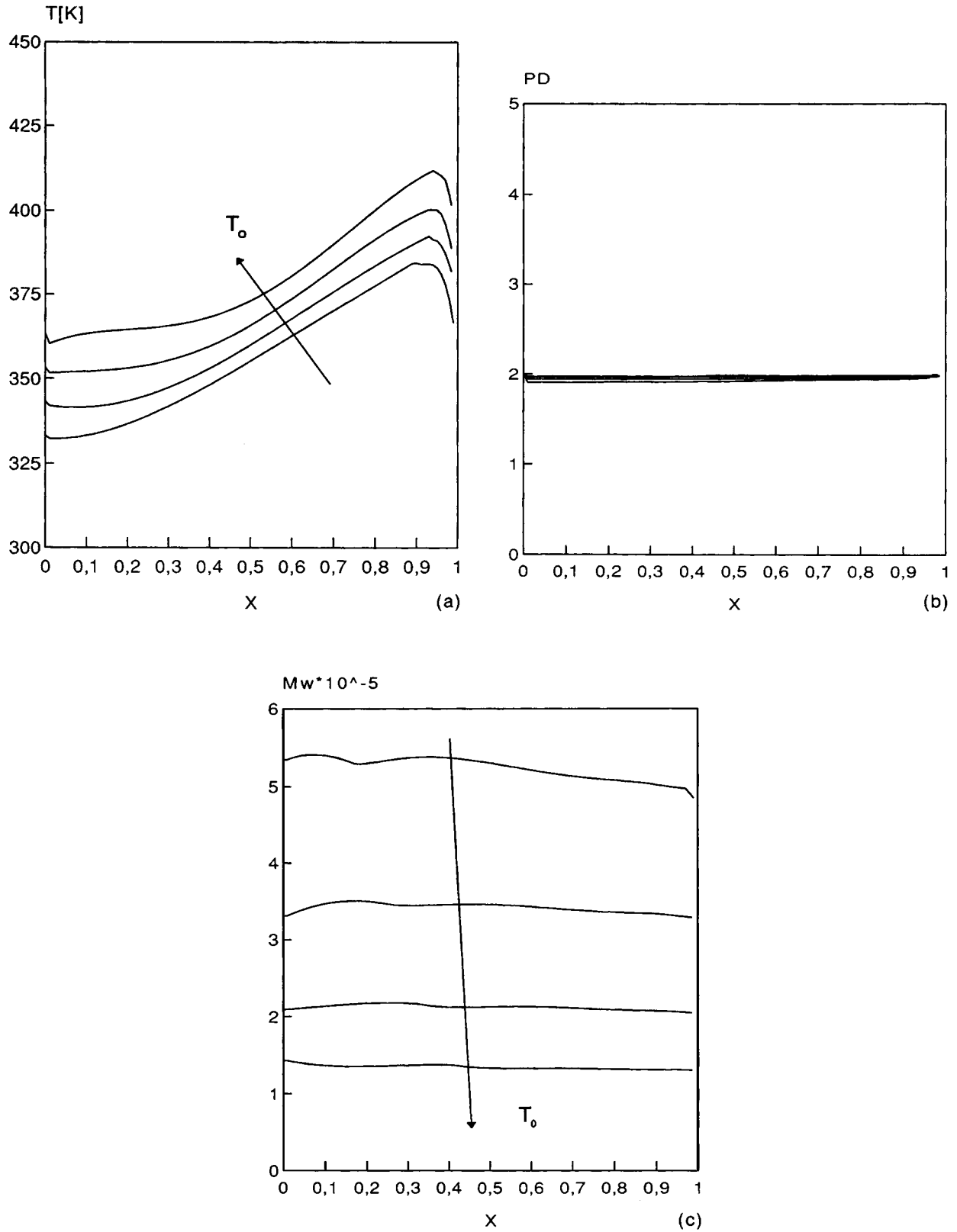


Figure 3 The effect of different initial temperature $T_0 = 333, 343, 353, 363$ K for ($M_0/I_0 = 400$) on: (a) optimal temperature profile $T^*(X)$; (b) polydispersity $PD(X)$; (c) molecular weight M_w .

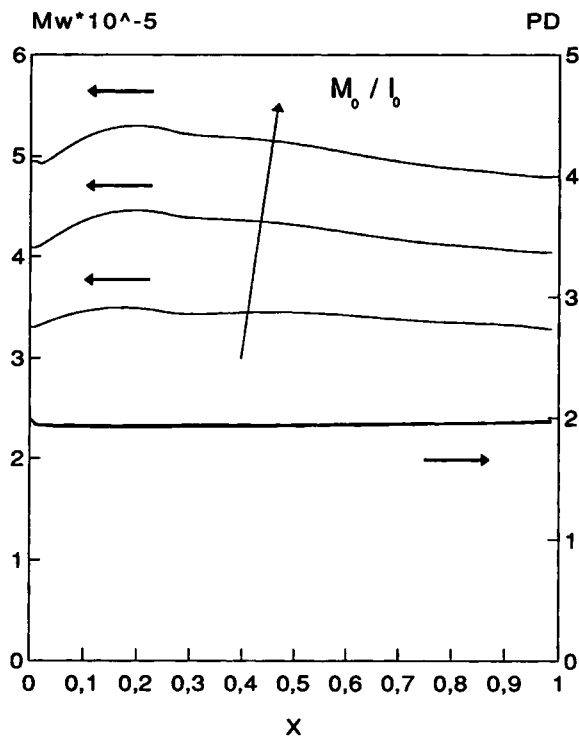


Figure 4 The effect of different initiator concentration for ($T_0 = 343$ K) on molecular weight M_w and polydispersity $PD(X)$: (1) $M_0/I_0 = 400$, (2) $M_0/I_0 = 700$, (3) $M_0/I_0 = 1000$.

isothermal and nonisothermal runs are shown in Figure 5, as functions of the conversion. It can be noted that isothermal conditions can be obtained with very good accuracy, while the optimal temperature profile can only be obtained with some approximation.

A physically based understanding of the evolution of the polymerization from the beginning to the end of the reaction can be achieved by an analysis of the MWD curves obtained by GPC.

In order to determine the shape of the GPC curve and to obtain a correlation with simulation results, an approximately linear dependence is assumed be-

Table IV Effect of Different Initial Temperature T_0 and Initial Ratio M_0/I_0 on the Molecular Weight

| T_0 [K] \ M_0/I_0 | 164 | 400 | 700 | 1000 |
|-----------------------|--------|--------|--------|--------|
| 333 | 350000 | 540000 | 680000 | 800000 |
| 343 | 230000 | 345000 | 440000 | 520000 |
| 353 | 150000 | 210000 | 275000 | 335000 |
| 363 | 125000 | 140000 | 190000 | 230000 |

tween the retention time τ_R of the peaks of narrowly distributed polymer fractions used for GPC calibration and logarithms of their n values:¹⁴

$$\tau_R = a - b \cdot \log(n) \quad (20)$$

The basic equation of the GPC technique gives the following relationship between F_σ^w , defined in the modeling section and computed as a function of the instantaneous MWD curves [Eq. (6)], and the experimentally determined function τ_R , which describes the height of the GPC curve at different τ_R :

$$F_\sigma^w = H(\tau_R) \left(\frac{d\tau_R}{dn} \right) \quad (21)$$

Differentiation of Eq. (20) and introduction of Eq. (21) gives the following equation for a GPC curve of a Flory-distributed polymer:

$$H(\tau_R) \cong a^2 \cdot n^2 \cdot e^{-a \cdot n} \quad (22)$$

This equation states that a GPC curve can be correlated as: $a^2 \cdot n^2 \cdot e^{-a \cdot n}$ vs. $\log(n)$.

Simulation results for the instantaneous MWD curves at different conversions are reported in Figure

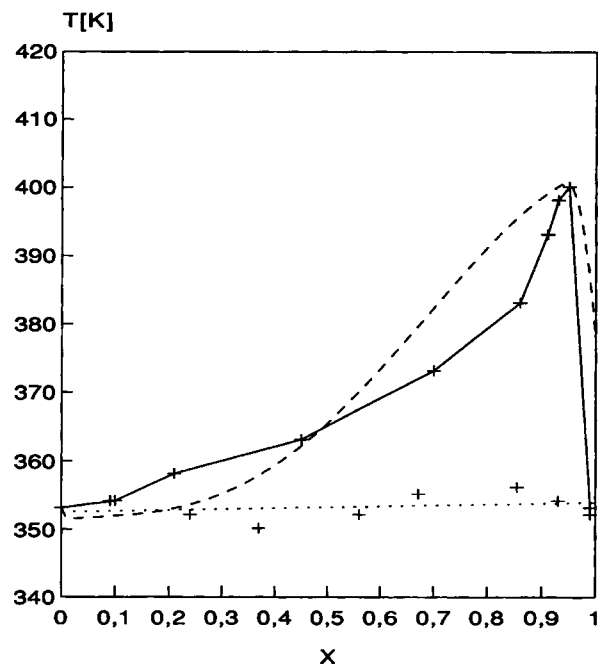


Figure 5 Experimental temperature profiles for polymerization of MMA: initiated by AIBN ($M_0/I_0 = 328$) compared with simulation. (Initial temperature $T_0 = 353$ K). Isothermal (\cdots), nonisothermal ($-$), optimal ($--$).

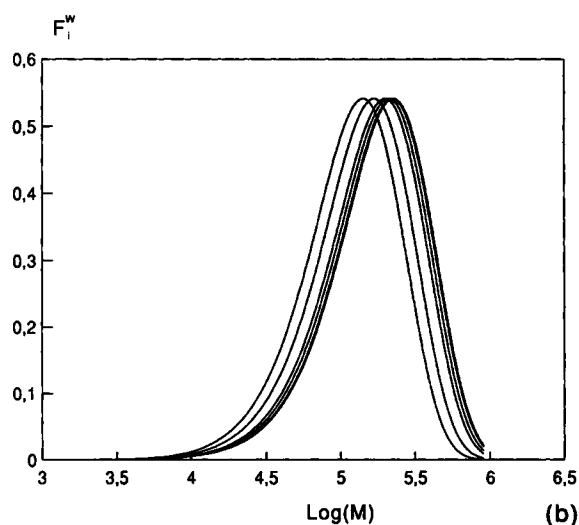
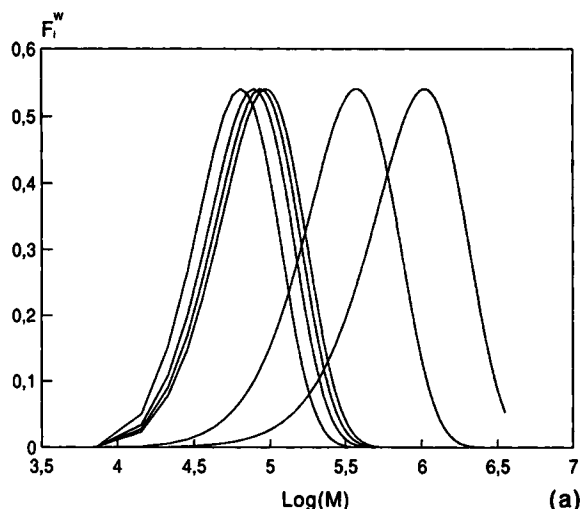


Figure 6 Simulation results for polymerization of MMA, initiated by AIBN ($M_0/I_0 = 328$): instantaneous molecular weight distribution curve at increased conversions. (a) Isothermal run ($T_0 = 378$ K). (b) Optimal temperature profile $T^*(X)$; (initial temperature $T_0 = 353$ K).

6(a) for the isothermal case and in Figure 6(b) for the optimal temperature profile. Figure 7(a) and (b) report the corresponding cumulative MWD curves.

It can be noted that all instantaneous MWD curves are unimodal. In the isothermal case, the peak of these curves changes location, as a function of the conversion, to mean different chain length before and after the onset of the gel effect. For the optimal temperature profile $T^*(X)$, the peak maintain a constant position, to indicate an almost constant chain length.

As a consequence, the cumulative MWD curves are regular at low conversion in both cases. As con-

version increases, in the isothermal case the distribution becomes broader, and at higher conversions, a bimodal distribution curve is observed. For the $T^*(X)$ case, the MWD curve maintains a narrow unimodal distribution throughout the conversion range investigated, as a consequence of the fact that the value of the instantaneous chain length remains almost constant during the batch.

Experimental results are reported in Figure 8(a) (isothermal case) and in Figure 8(b) (for the non-isothermal profile, which approximates the optimal one). It can be noted that experimental results are similar to simulation results for the cumulative MWD curves.

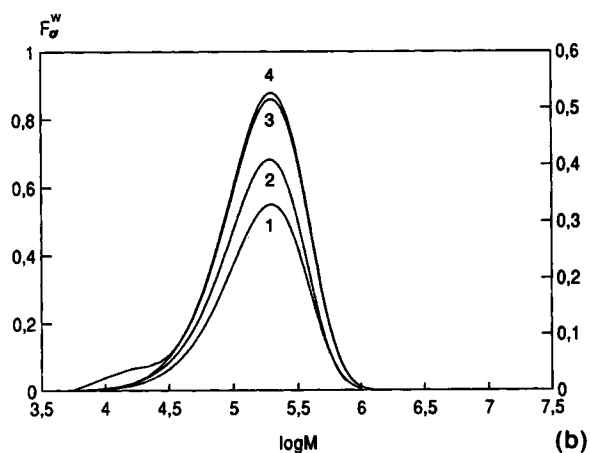
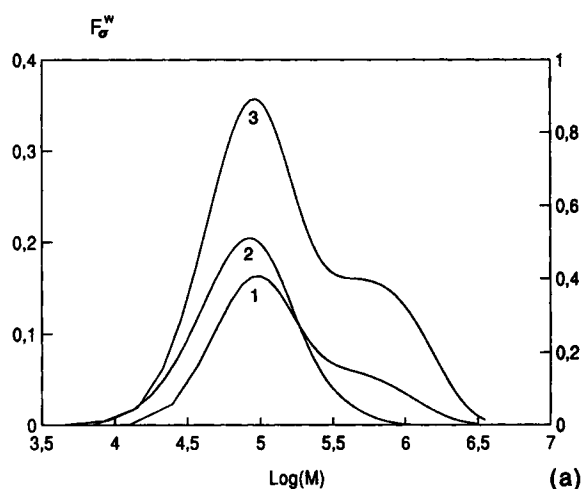


Figure 7 Simulation results for polymerization of MMA, initiated by AIBN ($M_0/I_0 = 328$): cumulative molecular weight distribution curve at different conversions. (a) Isothermal run ($T_0 = 378$ K). 1: $X = 10\%$, 2: $X = 35\%$, 3: $X = 95\%$. (b) Optimal temperature profile $T^*(X)$; (initial temperature $T_0 = 353$ K). 1: $X = 10\%$, 2: $X = 70\%$, 3: $X = 90\%$, 4: $X = 95\%$.

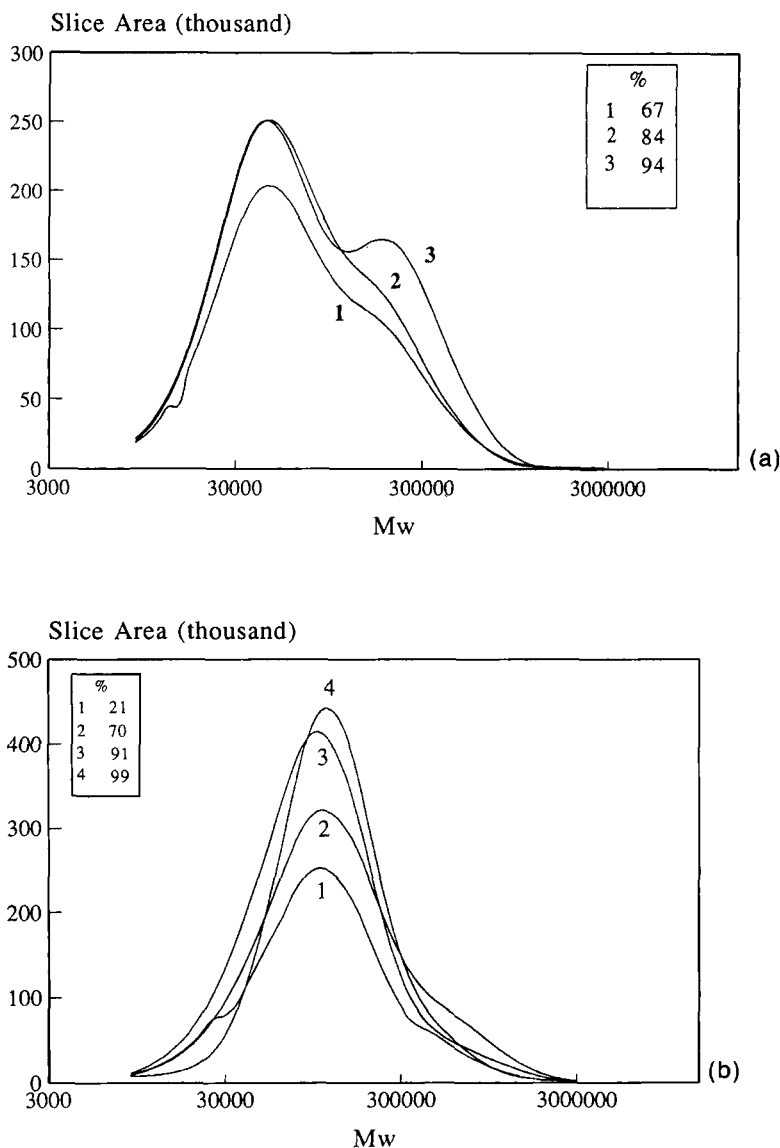


Figure 8 Experimental results for polymerization of MMA, initiated by AIBN ($M_0/I_0 = 328$): molecular weight distribution curve at different conversions. (a) Isothermal run; ($T_0 = 378$ K). (b) Nonisothermal run; (initial temperature $T_0 = 353$ K).

Better fitting between experimental and simulation results might be obtained: (a) by a better calibration of GPC factors; (b) by adopting distribution functions more suitable than Flory's for the case under study; simulation performed by adopting Peebles¹⁹ and a modification Peebles distribution curves²⁰ brought very similar results; (c) by adopting a modified kinetic scheme in which different values are used for the termination constant k_t for different polymer radicals, according to their size, as presented by Brooks.²¹

More important to stress, it is the positive effect on MWD curves played by an increase of temper-

ature that can be predicted by our model. An increase of temperature on the beginning of the gel effect, also if different from the optimal one $T^*(X)$ is able to maintain the corresponding MWD curve very close to the unimodal shape.

ANALYSIS OF INDUSTRIAL APPLICATIONS

The optimal profile $T^*(X)$ is then able to give a solution to the problem of controlling the molecular weight distribution of the product, with limits explained above.

The determination of $T^*(X)$ is based only on the kinetics of the polymerization and then it is valid for the two equivalent cases of bulk and suspension. The proposed model of the reactor, based on the hypothesis of perfect mixing, allows the simulation of an industrial size reactor in the case of suspension polymerization.

The possibility of applications of previous results to the case of suspension polymerization in industrial reactors is now analyzed. The main operating parameters in an industrial operation are: temperature, initiator concentration (M/I), and ratio between water and monomer (Z). The batch time and the characteristics of the product are mainly controlled by the initial values of these parameters and by the temperature profile during the batch, as reported in Tables III and IV. A careful selection of the values of these parameters is necessary in order to reduce the batch time and to obtain the desired polymer quality.

Usually in industrial processes, polymerization runs are carried out using the following procedure. The reactor is charged, at low temperature (30–35°C), with organic phase (monomer, initiator, etc.) and a part of suspending media (water and suspending agent); an adequate mixing permits the formation of a stable suspension. A second part of suspending media at high temperature (100°C) is added in order to rapidly reach a temperature close to the operating temperature (T_0); an initial heating by means of steam circulating in the jacket may be required. At this time, the conversion can be considered very small. After the startup, the polymerization run is carried out under isothermal conditions up to the time when the heat generated overcomes the heat removed by the cooling system. An increase of the temperature happens when the reaction becomes self accelerating, owing to gel effect, and most of the polymerization takes place.

Hard constraints to the maximum cooling load are given by heat exchange surface (A) and coefficients (U_d), by flow rates, and temperature of the cooling medium. The slope of the temperature vs. conversion curve and the maximum cooling load are functions of the heat capacity of the system which, for a fixed amount of monomer and potentiality of the cooling system, depends on the value of the parameter Z . The range of variation of Z is limited by operating considerations suggested by the economicity of the plant ($Z = 1-2.5$).

Finally, the maximum reactor temperature must be limited in order to prevent increase of pressure, which can be brought towards unsafe conditions. The increase of pressure, as a function of the temperature, closely follows the increase of vapor pres-

sure of the water, which is the suspending medium. A value of $T_m = 385$ K ($P_m = 1.5$ bar), can be assumed as maximum. In addition, at high temperature, also the suspension may become unstable.

A simulation of temperature profiles in an industrial size reactor ($V = 15$ m³, $Z = 2$), is reported in Figure 9(a), in order to analyze the influence of the heat transfer parameter (U_d^*A). The corresponding values of MWD are reported in Figure 9(b).

The temperature profiles obtained in these cases differ considerably with respect to the optimal one. The profiles that are closer to the optimal temperature $T^*(X)$ are those corresponding to less cooling load. Note that different profiles are almost parallel, showing that, when the heat generated overcomes the maximum cooling load of the reactor, the operating conditions do not differ very much from adiabatic.

The MWD of the product presents a bimodal shape, but the second peak is less evident as values of U_d^*A decrease. To narrow the MWD curves, an increase of temperature during the batch is required.

On the basis of previous considerations, different operating strategies can be compared. They differ in the initial part of the operation, while the final part is carried on under adiabatic conditions: (1) isothermal operation as far as possible ($X = X_1$), for a given cooling load (U_d^*A); U_d is calculated from the physical properties of the system. (2) Isothermal operation up to a prefixed value of conversion ($X_2 < X_1$). (3) Reactor maintained at the optimal temperature profile $T^*(X)$, up to a larger value of conversion (X_3). (4) Adiabatic operation from the beginning. In addition, also the case of isothermal (5) and optimal temperature profile for the whole batch time (6), are reported as limit cases.

Note that case (1) is very close to the actual industrial operation, as previously described. Values of X_2 and X_3 , which depend on the maximum allowable temperature and on the amount of liquid in the reactor, have been chosen in order to have a comparison at the same final temperature (T_m) between cases (2) and (3).

Figure 10(a) and (b) show, respectively, temperature profiles, as a function of the conversion X , and MWD curves of the product that correspond to the different operating strategies. In all the cases, the resulting temperature profile differs from the optimal one. This cannot be achieved without supplying heat to the system, because the slope of the $T^*(X)$ curve is even larger than the slope of adiabatic curves. Moreover, the final temperature exceeds the maximum allowable value T_m , which has been assumed for the suspension process. Anyway, significant improvements, in terms of narrowing the

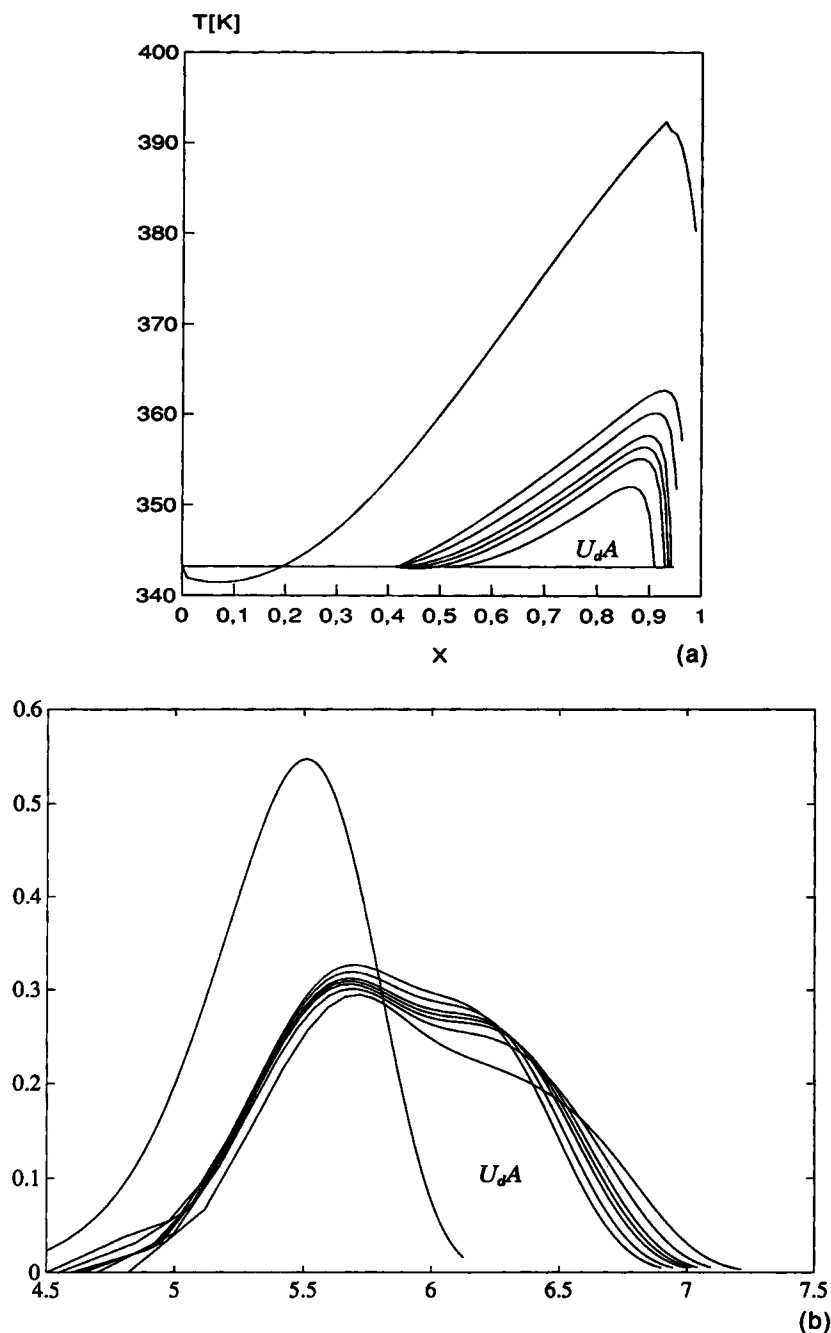


Figure 9 Simulation of industrial operations for different value of $U_d^*A = 5800\text{--}23000$ (W/K). (a) Temperature profiles; (b) MWD.

MWD curves, can be obtained, with respect to the actual operating strategies, by adopting strategies (2) and (3).

Both operating strategies, in order to be actually implemented by a control system, require real time measurements of temperature and conversion. Good quality measurements are possible for the reactor temperature, while difficulties are encountered for conversion. Direct off-line measurements are more

precise, but they involve delay that are not allowable, by considering the fast dynamics of the process. Indirect on-line measurements, by means of densimeters or viscosimeter, etc., can be used, and these are usually preferable for their dynamic characteristics, even if they may be less precise.

Further considerations may be drawn, by taking into account the behavior of the curves $X(t)$ [Fig. 10(c)]. In case (3), the switching from the optimal

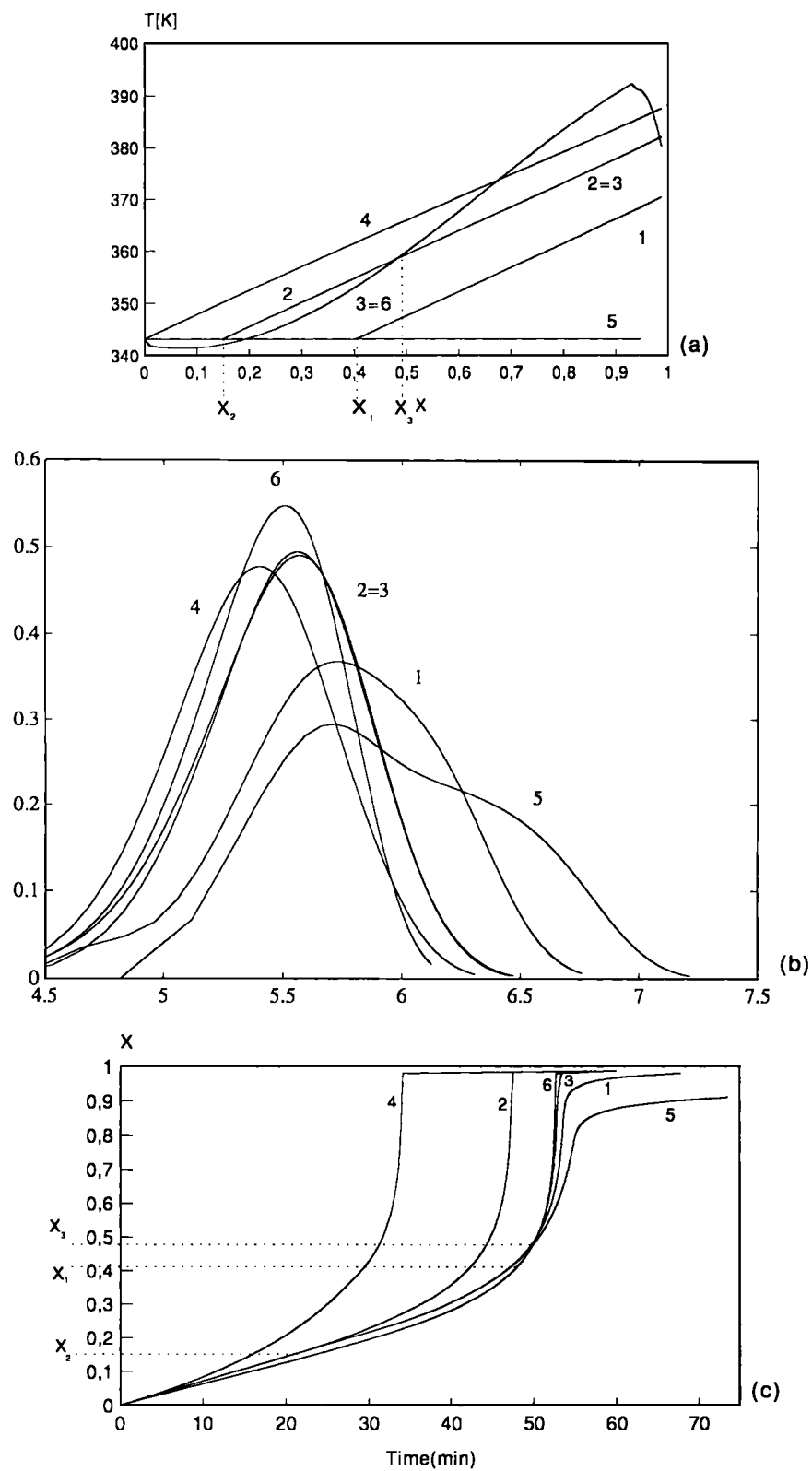


Figure 10 Simulation of different operating strategies. (a) Temperature profiles; (b) MWD; (c) conversion vs. time.

Table V. List of Symbols

| | |
|--------------|---|
| A | heat transfer surface [m ²] |
| f | initiator efficiency: $f = 0.4$ |
| k_d | decomposition rate constant [s ⁻¹] |
| k_t | termination rate constant [m ³ /kmol·s] |
| M | monomer concentration [kmol/m ³] |
| M_n | number aver. mol. weight [kg/kmol] |
| PD | polydispersity |
| r | reaction rate [kmol/m ³ ·s] |
| T | reaction temperature [K] |
| t | time [s] |
| V_0 | initial volume [m ³] |
| W | monomer molecular weight [kg/kmol] |
| β | length chain ratio: $\nu(t)/\nu_0$ |
| δ | vol. contraction: $\delta = \rho_m/\rho_p - 1$ |
| λ_j | growing chains i^{th} order moment |
| ζ | vol. shrinkage: $\zeta = \delta/(Z + 1 + \delta X)$ |
| τ | vol. shrinkage: $\tau = (1 + \delta X)(Z + 1)$ |
| ϕ_m | vol. fraction monomer: $\phi_m = (1 - X)(1 + \delta X)$ |
| Γ_g | heat generation [W] |
| C | thermal capacity [J/K] |
| I | initiator concentration [kmol/m ³] |
| k_p | propagation rate constant [m ³ /kmol·s] |
| k_{tr} | transfer rate constant [m ³ /kmol·s] |
| M/I | ratio: monomer/initiator |
| M_w | weight aver. mol. weight [kg/kmol] |
| M_i | dead polymer chains [kmol/m ³] |
| P_i | growing polymer chains [kmol/m ³] |
| T_j | jacket temperature [K] |
| U_d | global heat transfer coeff. [W/m ² ·K] |
| V | volume [m ³]: $V = V_0(1 + Z + \delta X)$ |
| Z | initial ratio: (aqueous/organic) phase |
| ν | instantaneous chain length |
| ΔH_r | heat of reaction [J/kmol] |
| μ_j | dead polymer chains i^{th} order moment |
| ρ | density [kg/m ³] |
| χ | vol. shrinkage: $\chi = (1 + Z + \delta X)/(Z + 1)$ |
| ϕ_p | vol. fraction polymer: $\phi_p = 1 - \phi_m$ |
| Γ_j | heat removal [W] |

temperature profile $T^*(X)$ to adiabatic conditions is required at higher conversions, where a small error or delay in the measurements may imply a large error in the corresponding value of the conversion. In case (2), instead, the switching towards adiabatic conditions is required at smaller conversions, where the slope of the $X(t)$ curves is smaller and then the effect of a measurement error is less crucial. The operating strategy (2), which gives almost the same MWD curves, has to be considered the most reliable to be applied in industrial reactors and can lead to noticeable improvements in the product quality.

CONCLUSION

The molecular weight distribution and the molecular weight of the polymer, which are the two main parameters characterizing the polymer quality, can be controlled, respectively, by adopting a suitable operating strategy of the reactor and by choosing the initial conditions of the operation. The optimal temperature profile is computed on the basis of the kinetic model of the process and requires an increase of temperature before the onset of the gel effect, in order to counteract the effect of the increase of viscosity, which leads to broad MWD curves for the product. The positive effect of an increase of temperature, even if different from the optimal one, is confirmed by experimental results.

The analysis of possible applications to industrial reactors shows that an isothermal operation followed by adiabatic conditions, which can be adopted without too many difficulties by the control system, can give significant improvements in the polymer quality.

APPENDIX

Algebra and Hypotheses Assumed in Computing the Optimal Temperature Profile $T^*(X)$

By adopting the Quasi Steady State Approximation, λ_0 and λ_1 can be computed from (9–10) and for $r_{\lambda_0} = r_{\lambda_1} = 0$ become:

$$\lambda_0 = \left(\frac{2fk_d}{k_t} \right)^{0.5} \cdot I^{0.5} \quad (\text{a-1})$$

$$\lambda_1 = \left(\frac{k_t\lambda_0 + k_pM + k_{tr,m}M}{k_t\lambda_0 + k_{tr,m}M} \right) \cdot \lambda_0 \quad (\text{a-2})$$

Consequently, the value of the polymer length $\nu(t)$ becomes:

$$\nu(t) = \frac{(2fk_d k_t)^{0.5} I^{0.5} + k_pM + k_{tr,m}M}{(2fk_d k_t)^{0.5} I^{0.5} + k_{tr,m}M} \quad (\text{a-3})$$

But $k_pM \gg (2fk_d k_t)^{0.5} I^{0.5} + k_{tr,m}M$ and then:

$$\frac{1}{\nu(t)} \cong K \left(\frac{g_t^{0.5}}{g_p} \right) \frac{I^{0.5}}{M} + C_m \quad (\text{a-4})$$

where:

$$K = \left(\frac{2fk_d k_{t0}}{k_{p0}^2} \right)^{0.5}; C_m = \frac{k_{tr,m}}{k_p} \quad (\text{a-5})$$

Analogously, at the initial time, the initial polymer chain length is:

$$\frac{1}{\nu_0} \cong K_0 \left(\frac{I_0^{0.5}}{m_0} \right) + C_{m0} \quad (\text{a-6})$$

The ratio $\frac{\nu(t)}{\nu_0} = \beta$ becomes:

$$\frac{\nu(t)}{\nu_0} = \beta \cong \frac{K_0 \left(\frac{I_0^{0.5}}{M_0} \right) + C_{m0}}{K \frac{g_t^{0.5}}{g_p} \left(\frac{I^{0.5}}{M} \right) + C_m} \quad (\text{a-7})$$

The ratio β , in addition of initial conditions, is function of temperature T and of concentrations of monomer M and initiator I , which depend on time. It is possible, and more convenient, to eliminate the time dependence of β , with the following observations: (a) Values of C_m are always much smaller with respect to the first term in numerator and denominator of Eq. (a-4) and, therefore, can be neglected. (b) The concentration of monomer can be expressed as a function of the conversion and temperature in a simple way

$$M = M_0 \left(\frac{1 - X}{1 + \delta X} \right) \quad (\text{a-8})$$

(c) The concentration of initiator can be expressed as a function of temperature and conversion, rearranging the expression as follows:

$$\frac{dI}{dX} = \frac{dI}{dt} \bigg/ \frac{dX}{dt} \quad (\text{a-9})$$

From eq.(7)

$$\frac{dI}{dt} = -k_d I \quad (\text{a-10})$$

$$\frac{dX}{dt} \cong \frac{d}{dt} \left(\frac{M_0 + M}{M_0} \right) = \frac{-\frac{dM}{dt}}{M_0}; \cong \frac{k_p M \lambda_0}{M_0}$$

$$\frac{dX}{dt} = \frac{k_p M (2fk_d I)^{0.5}}{M_0 k_t^{0.5}} \quad (\text{a-11})$$

Substituting Eq. (a-10) and (a-11) in the Eq. (a-9):

$$\frac{dI}{dX} = - \left(\frac{k_d k_t}{2fk_p^2} \right)^{0.5} I^{0.5} \left(\frac{1 + \delta X}{1 - X} \right) \quad (\text{a-12})$$

By carrying out a numerical integration of Eq. (a-12) over X , it is possible to obtain the final expression of Eq. (17), which depends only on temperature, conversion, and initial condition, as:

$$\beta \cong \alpha \frac{K_0}{K} \frac{1 - X}{K(1 + \delta X)} \left(\frac{I}{I_0} \right)^{0.5} \quad (17)$$

REFERENCES

1. E. Trommsdorff et al., *Makromol. Chem.*, **1**, 169 (1948).
2. B. M. Louie and D. S. Soong, *J. Appl. Polym. Sci.*, **30**, 3707 (1985).
3. P. E. Baillagou and D. S. Soong, *Chem. Eng. Sci.*, **40**, 75 (1985).
4. S. R. Ponnuswamy et al., *Ind. Eng. Chem. Res.*, **26**, 2229 (1987).
5. T. Takamatzu, S. Shioya, and Y. Okada, *Ind. Eng. Chem. Res.*, **27**, 93 (1988).
6. J. S. Chan and J. L. Lai, *Ind. Eng. Chem. Res.*, **31**, 861 (1992).
7. G. Maschio, T. Bello, and C. Scali, *Chem. Eng. Sci.*, **47**, 2609 (1992).
8. G. Maschio, T. Bello, C. Scali, and S. Zanelli, *Polymer Reaction Engineering*, Vol. 127, Dechema Publ., Berlin, 1992, p. 285.
9. G. Maschio and C. Scali, *Ing. Chim. Ital.*, **74**, 16 (1992).
10. H. W. Ray, *J. Macromol. Sci. Rev.*, **C8** (1972).
11. A. W. Hui and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 749 (1972).
12. A. Husain and A. E. Hamielec, *J. Appl. Polym. Sci.*, **22**, 1207 (1993).
13. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
14. Y. V. Kissin, *Makromol. Chem., Macromol. Symp.*, **66**, 83 (1993).
15. S. K. Soh and S. C. Sundberg, *J. Polym. Sci. Chem. Ed.*, **20**, 1299 (1982).
16. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489 (1982).
17. M. Catalfamo, Thesis, Dipartimento di Chimica Industriale Università di Messina, 1992.
18. T. Bello, Ph.D. Thesis, Dipartimento di Chimica Industriale Università di Messina, 1994.
19. L. H. Peebles, *Molecular Weight Distribution in Polymers*, Interscience, New York, 1971.
20. P. Giusti and G. Maschio, *Chim. Indust.*, **64**, 492 (1982).
21. B. W. Brooks, *Chem. Eng. Sci.*, **40**, 1419 (1985).

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