

Alternatives for Multiobjective Optimization of a Polymerization Process

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ABSTRACT: The optimal control policies for a polymerization process, particularly for batch free-radical polymerization of methyl methacrylate, were determined using a multiobjective optimization technique. The process objectives considered in the optimization include monomer conversion, polydispersity index, polymerization degree, and total reaction time, weighted and combined in a scalar objective function. The decision variables were the initial concentration of the initiator and the temperature represented by isothermal steps. For solving the optimization problem, several methods based on sequential quadratic programming and a genetic algorithm were used and compared.

Combining them into a hybrid method (the genetic algorithm provided the initial values for the traditional iterative method) led to the best results. The aims of this study were to develop an approach for optimizing the polymerization process and to describe alternatives for formulating and solving this problem, emphasizing the importance of user decision in choosing solutions based on technological criteria. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3680–3695, 2006

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INTRODUCTION

Process optimization can have a significant strategic impact on polymer plant operability and economics. Polymer production facilities face increasing pressures for production cost reductions and higher-quality requirements. The demand for polymer products having specific predetermined properties requires the control of microscopic characteristics during the reaction as post-treatments are expensive and not efficient in many respects. The main mechanical and thermal properties of polymeric products are correlated with molecular weight and molecular weight distribution. These two important parameters characterizing polymer quality can be controlled by adopting a suitable operating strategy for the reactor and by choosing the initial conditions of the operation.

The batch polymerization technique is widely used in industry for its availability and flexibility in operation. Being able to assure a product that has constant properties is particularly difficult in batch reactors, in which large changes occur in the concentrations and reactivities of different species and in the physical properties of a system during a reaction. For example, in free-radical polymerization carried out in concen-

trated solution and in bulk, increased viscosity leads to so-called gel and glass effects. Both phenomena can have an important effect on the reaction rate and molecular weight distribution of the polymer. The final product is a mixture of polymer chains that were formed in very different situations during the batch. The deficiency of accurate online sensors for the measurement of polymer properties coupled with the nonlinearity of the system's behavior represents others drawbacks of batch and semibatch polymerization reactor control. Therefore, the precise control of polymer properties during the batch manufacture process requires advanced techniques for specification of optimal control strategies.

There have been many attempts to optimize batch polymerization because of the numerous and complex problems involved: different types of optimization problems regarding objectives and decision variables, mathematical solving methods, and mathematical models included in the optimization procedure, as well as the recent problem of multiobjective optimization accomplished in a vectorial or scalar fashion.

In addition to control of polymer quality, global optimization requires the achievement of high productivity (high conversion, short reaction time) and respect for operations safety. The commonly studied optimization problem is to obtain reaction conditions that minimize the total reaction time and/or the polydispersity index of the polymer, while simultaneously

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requiring the final monomer conversion and the final number-average chain length to meet certain specifications (called desired values).¹⁻⁵ Some approaches have included minimizing residual monomer and initiator, which can affect the end-use properties of the polymer.^{6,7} Special attention is given to optimal control of molecular weight distribution as one of the important polymer property indices.^{8,9}

To obtain a polymeric material with a prespecified molecular weight and other important properties, at least two decision variables should be manipulated: initiator or monomer addition and reactor temperature. Consideration of constraints in industrial reactors is very important for defining the range of variation of parameters and for being able to disregard possible solutions that might be interesting only in a theoretical approach to the problem.

The optimization of batch free-radical polymerization is multiobjective in nature because it normally has several objectives that must be satisfied at the same time. The performance of the system depends on a large number of criteria, which are often conflicting and noncommensurable. In the last several years research on the optimization of polymerization reactors using multiple objective functions and constraints and its use in online optimizing control has been reported in the literature.^{4,6,7}

Multiobjective optimization can be defined as the problem of finding a vector of decision variables that satisfy constraints and optimize a vector function whose elements represent the objectives' functions. In such cases, instead of obtaining a unique optimal solution, a set of equally good optimal solutions is usually obtained. These are referred to as Pareto sets. A decision maker can choose any one of these nondominant optimal solutions based on additional information.¹⁰ So, multiobjective optimization can be considered as being carried out in two phases: an objective, or mathematical phase and a subjective, or decision-making phase. Some examples of the vectorial approach to multiobjective optimization for polymerization reactors are given in Garg et al.,⁵ Merquior et al.,⁷ and Zhou et al.¹⁰

A great number of multiobjective optimization problems have been studied in terms of a single scalar objective function that combines all identifiable performance measures with appropriate weighting factors.^{3,4,6,11} This "scalarization" of a vector objective function allows simple algorithms to be used for solving the problem but suffers from several drawbacks. One is that the results depend largely on the values of the weighting factors used, which are difficult to assign on an a priori basis. Even more important is the risk of losing some optimal solutions.¹⁰

Computer-aided optimization methods have been widely employed in chemical process industries. Traditional optimization methods can be classified into

two distinct groups: direct and gradient-based methods. In direct search methods, only objective function and constraint values are used to guide the search strategy, whereas gradient-based methods use first- and/or second-order derivatives of the objective function and/or constraints to guide the search process. Because derivative information is not used, direct search methods are usually slow, requiring many function evaluations for convergence. For the same reason, they can be applied to many problems without a major change in the algorithm. On the other hand, gradient-based methods quickly converge to an optimal solution but are not efficient in nondifferentiable or discontinuous problems.¹² Deb emphasized some of the common difficulties with most of the traditional direct and gradient-based techniques: (1) the convergence to an optimal solution depends on the chosen initial solution; (2) most algorithms tend to get stuck to a suboptimal solution; and (3) an algorithm efficient in solving one optimization problem may not be efficient in solving a different optimization problem.¹² Most of the studies on optimization of polymerization reactors have used classical optimization methods.^{8,9,11,13}

In recent years, because of the rapid progress in the computing technology available, new numerical search algorithms are becoming popular. In particular, there is a growing interest in optimization techniques based on genetic and evolutionary algorithms. Because of their flexibility, ease of operation, minimal requirements, and global perspective, these algorithms have been successfully used in a wide variety of multiobjective problems.¹⁴ Multiobjective optimization of polymerization processes is an example of their application.^{3,4,5,10,14,15} These techniques do not need any initial guesses and converge to the global optimum even when with several local optima present. In addition, genetic algorithms use information about the objective function and not its derivatives (such as with traditional optimization techniques), nor do they require any other auxiliary knowledge.¹⁰ Different types of genetic algorithms and their applications in chemical reaction engineering, including polymerization processes, have been described in some review works.¹⁶⁻¹⁹

In the present study, we explored the feasibility of an optimizing control scheme for a sample polymerization system, poly(methyl methacrylate) (PMMA). The procedure developed could easily be used for other free-radical polymerization reactors. The same problem has been approached differently by different research groups. Ahn et al.¹¹ applied optimal control theory with Pontryagin's minimum principle to calculate the optimal temperature trajectory for a batch MMA polymerization reactor system that would lead to a polymer product having the desired properties (monomer conversion and number- and weight-average molecular weights) set a priori. Chakravarthy et

al.³ used a genetic algorithm to obtain optimal temperature histories for methyl methacrylate polymerizations. The reaction time was minimized while simultaneously requiring attainment of design values of the final monomer conversion and number-average chain length. Garg et al.⁴ established the feasibility of implementing online optimizing control of free-radical polymerization reactors (PMMA semibatch reactors) in order to produce polymers of the desired properties in the shortest reaction time. A genetic algorithm was used for this purpose. All three of these attempts used a scalar multiobjective function. Garg and Gupta⁵ developed a multiobjective optimization technique for free-radical bulk polymerization reactors (MMA polymerization) using a nondominated sorting genetic algorithm. The two objective functions that were minimized were total reaction time and the polydispersity index of the polymer product.

Our approach used a complete model for batch, bulk MMA polymerization, a multiobjective function in a scalar form, which includes minimization of reaction time, minimization of polydispersity index, and achievement of some desired values for conversion and number-average polymerization degree. Three optimization methods were used for comparison: a traditional method based on sequential quadratic programming, a genetic algorithm, and a hybrid method that combined the first two approaches. The difficult task of choosing the appropriate weights enabled pointing out some of the proposed objectives. On the basis of the technique used and the results obtained, this study has demonstrated that the hybrid method favors scalarization of the objective function. Choosing the weights of the objective function can be considered in the scalar optimization as the equivalent of the decision-making phase in the vectorial multiobjective optimization, with an additional level of difficulty for the former.

Unlike other articles that focused on particular aspects of optimization, our article includes most polymerization objectives and a complete mathematic model for polymerization exhibiting gel and glass effects. Also, the optimal solution is represented by two or three temperature steps, three solving methods are used and compared, and the influence of weights in optimization is emphasized. In addition, the association between a scalar objective function and a hybrid solving method for the optimization problem can be considered an acceptable alternative to multiobjective optimization because of its simplicity and its accurate results. In the following, an optimization method based on a scalar objective function in which the weights of the objectives must be chosen and on a hybrid solving method that combines the advantages of sequential quadratic programming and genetic algorithm is illustrated on a polymerization process.

TABLE I
Kinetic Scheme for MMA Free-Radical Polymerization

Initiation	$\begin{cases} I \xrightarrow{k_d} 2R^* \\ R^* + M \xrightarrow{k_i} P_1^* \end{cases}$
Propagation	$P_n^* + M \xrightarrow{k_p} P_{n+1}^*$
Chain transfer to monomer	$P_n^* + M \xrightarrow{k_{tm}} D_n + P_1^*$
Termination by disproportionation	$P_n^* + P_m^* \xrightarrow{k_t} D_n + D_m$

Model development

Chemical-initiated free-radical polymerization of methyl methacrylate (MMA) is considered to occur in a batch bulk process. This system follows the standard kinetic scheme, which includes formation of reactive radicals by decomposition of the initiator [azobisisobutyronitrile (AIBN)], the reactive addition of monomer units to radical polymer chains in the propagation step, deactivation of polymer radicals by reaction with other polymer radicals in the termination step (disproportionation), and chain transfer to monomer, shown in Table I, where I , M , and R^* represent the initiator, monomer, and primary radical, respectively; P_n^* and D_n are the macroradical and the dead polymer with n monomer units, respectively; and k_d , k_i , k_p , k_{tm} , and k_t are the rate constants for the initiator decomposition, initiation, propagation, chain transfer to monomer, and termination by disproportionation, respectively.

The mass balance equations for monomer conversion, x , initiator concentration, I , and moments of chain length for radicals, λ_k and dead polymer, μ_k ($k = 0, 1, 2$), represent the kinetic model of the polymerization process:

$$\frac{dI}{dt} = -k_d I - I\varepsilon \frac{1-x}{1+\varepsilon x} \lambda_0 (k_p + k_{tm}) \quad (1)$$

$$\frac{dx}{dt} = (k_p + k_{tm})(1-x)\lambda_0 \quad (2)$$

$$\frac{d\lambda_0}{dt} = 2fk_d I - k_t \lambda_0^2 - \lambda_0^2 \varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) \quad (3)$$

$$\begin{aligned} \frac{d\lambda_1}{dt} = & 2fk_d I + k_p M_0 \frac{1-x}{1+\varepsilon x} \lambda_0 - k_t \lambda_0 \lambda_1 \\ & - \lambda_0 \lambda_1 \varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) - \\ & - k_{tm} M_0 \frac{1-x}{1+\varepsilon x} (\lambda_1 - \lambda_0) \quad (4) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_2}{dt} = & 2fk_dI + k_pM_0 \frac{1-x}{1+\varepsilon x} (2\lambda_1 + \lambda_0) - k_t\lambda_0\lambda_2 \\ & - \lambda_2\lambda_0\varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) - \\ & - k_{tm}M_0 \frac{1-x}{1+\varepsilon x} (\lambda_2 - \lambda_0) \quad (5) \end{aligned}$$

$$\frac{d\mu_0}{dt} = k_t\lambda_0^2 - \mu_0\lambda_0\varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) + k_{tm}M_0 \frac{1-x}{1+\varepsilon x} \lambda_0 \quad (6)$$

$$\begin{aligned} \frac{d\mu_1}{dt} = & k_t\lambda_0\lambda_1 - \mu_1\lambda_0\varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) \\ & + k_{tm}M_0 \frac{1-x}{1+\varepsilon x} \lambda_1 \quad (7) \end{aligned}$$

$$\begin{aligned} \frac{d\mu_2}{dt} = & k_t\lambda_0\lambda_2 - \mu_2\lambda_0\varepsilon \frac{1-x}{1+\varepsilon x} (k_p + k_{tm}) \\ & + k_{tm}M_0 \frac{1-x}{1+\varepsilon x} \lambda_2 \quad (8) \end{aligned}$$

where it is assumed that no monomer is consumed in the initiation process and that the quasi-steady state approximation for the initiator fragment balance is valid and where ε is a parameter accounting for the variation in volume that accompanies polymerization; f is the initiator efficiency; and M_0 is the monomer concentration at time $t = 0$.

Gel, glass, and cage effects are exhibited in the bulk polymerization of MMA. The gel effect arises because of the decrease in the termination rate constant at high monomer conversion, associated with increased diffusional resistance to the growing radicals. It is manifested as a sudden increase in conversion, as well as in weight-average molecular weight with time, after some polymerization has occurred. Similarly, the glass effect is associated with a decrease in the propagation rate constant because of increased diffusional resistance to the movement of the monomer toward a growing radical. This leads to the polymerization stopping short of complete monomer conversion, even though the reactions are irreversible.

To describe the decrease in the termination (k_t) and propagation (k_p) rate constants during polymerization, Chiu et al.²⁰ proposed models that consider diffusional constraints as an integral part of these reactions even from the beginning of the process:

$$\frac{1}{k_t} = \frac{1}{k_{t0}} + \theta_t \frac{\lambda_0}{\exp\left[\frac{2.303(1-x)}{A+B(1-x)}\right]} \quad (9)$$

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \theta_p \frac{\lambda_0}{\exp\left[\frac{2.303(1-x)}{A+B(1-x)}\right]} \quad (10)$$

$$\theta_t = \frac{\theta_t^0}{I_0} \exp\left(\frac{E_{\theta t}}{RT}\right) \quad (11)$$

$$\theta_p = \theta_p^0 \exp\left(\frac{E_{\theta p}}{RT}\right) \quad (12)$$

$$A = C_1 - C_2(T - T_{gp})^2 \quad (13)$$

where k_{t0} and k_{p0} are the rate constants for termination and propagation, respectively, in the absence of the gel and glass effects; θ_t and θ_p are the characteristic migration times; θ_t^0 and θ_p^0 are the preexponential factors for θ_t and θ_p ; $E_{\theta t}$ and $E_{\theta p}$ are the activation energies for θ_t and θ_p ; T is the temperature; T_{gp} is the glass-transition temperature of the polymer; B , C_1 , and C_2 are the constants; and R is the universal gas constant.

For the rate constant of chain transfer to monomer, a decrease similar to that of the propagation rate constant was proposed¹³ because both reactions involve the same diffusion mechanism—monomer molecules migrating toward the growing macroradicals:

$$k_{tm} = k_{tm0} \frac{k_p}{k_{p0}} \quad (14)$$

where k_{tm0} is the rate constant for chain transfer to monomer in the absence of the glass effect.

Genetic algorithm

Genetic algorithm (GA) is a problem-solving technique inspired by the process of natural evolution, in which the fittest species survive and propagate, whereas the less successful tend to disappear. The main idea is to represent a set of potential solutions as a population of individuals represented by chromosomes. The chromosomes in GA are similar to biological chromosomes, as their genes reflect different aspects of the solution. Chromosomes consist of genes, which are blocks of DNA. Each gene produces a particular protein that will shape a certain trait. Possible variations of a gene are called alleles. Each gene has its own position in the chromosome, called a locus. The complete set of genetic material (all chromosomes) is called the genome.

Unlike other methods, evolution is not a directed process but an heuristic one, in which the purpose of the individuals is to compete in order to propagate their genetic material to the next generation. In the biological case, the fitness of an individual results from its interaction with the environment. Genetic

algorithms use a fitness function instead to compute how close a potential solution is to the desired solution.

The three fundamental procedures in a typical genetic algorithm are selection, crossover, and mutation.

Selection establishes the way in which parents will be chosen for the offspring that will form the next generation. In this phase, the fitness of all individuals in the population is evaluated. Individuals with higher fitness must have more chances to reproduce. For each individual to be created in the next generation, two parents are thus selected.

Crossover is the operation that ensures the genetic diversity of the population. After two parents have been selected, their chromosomes are combined to produce an offspring. In nature, crossover occurs when corresponding chromosomes of a parent exchange genetic material by the breaking and reuniting of DNA molecules. In this case, each parent has two strings of chromosomes (the double helix), and one string from a parent is combined with one string from the other. In GA, an individual has only one set of chromosomes. Thus, the chromosome of the offspring is built by taking different parts of the parents' chromosomes and binding them together. The many variants for performing this operation largely depend on the problem.

After crossover, a small change in the chromosome of the offspring can be applied. The importance of this operation—mutation—is still a matter of debate. It is believed that its role is to get the system out of local extremes or to accelerate convergence, although genetic algorithms do not need differential functions and gradient descent methods for convergence.

The first generation is randomly generated. Then, using the above operations, a new population is created. The old population is abandoned, and the subsequent generation is produced using the new population. There is no theoretical reason for this clear distinction between generations. There is no such phenomenon in nature, where individuals from different generations usually coexist. This restriction is only an implementation model that simplifies the computation. The process is repeated until a convenient solution is found. Normally, the best (fittest) individual of its generation represents the solution given by the genetic algorithm at a certain moment.

Although GAs rely highly on stochastic processes (selection, crossover, and mutation are performed with certain probability rates), they are not random searches. Evolutionary mechanisms definitely have better results than random exploration, and these results are achieved with faster convergence.

Given that the overall structure of a GA is somehow standardized, solution encoding remains the most difficult part of the design because it highly depends on the problem. More natural encoding is more efficient

and produces better solutions. A number of representations have been successfully used in different situations: binary encoding, permutation encoding, value encoding, tree encoding.

Considering the population size, it was discovered that very big population usually did not improve the performance of GA. An acceptable population size is about 20–30; however, sometimes 50–100 has been reported as best.

Description of GA model

In our GA model, we used real value encoding for the chromosomes. There are other approaches for MMA polymerization using binary solution representation,³ as it is the simplest type of encoding, in which chromosomes are composed only of ones and zeros. Thus, even the number of alleles is rather small (two), so this encoding is very common because it is very easy to use. However, value encoding is more general because genes are real numbers. Some experiments²¹ have shown that real-value encoding is more time efficient, with better precision of the solutions.

Binary encoding is a frequent choice in genetic algorithms. It has the advantage of simplicity, and it is reminiscent of the four-nucleotide alphabet of the biological DNA. However, it may not yield optimal performance for problems such as ours that involve real-number solutions. Even if crossover and mutation operators are straightforward, this encoding may have several disadvantages. Binary encoding utilizes the representational capabilities of a positional number system, in which the leftmost digits are more important than the rightmost ones. When mutation is performed, any digit may be changed with equal probability, that is, a small change is equally probable to a big one. This may be beneficial at first, when the population must explore greatly, but may prevent quick convergence later on.

Real encoding is a better alternative for our optimization problem. Not only does it provide a more flexible expression of parameter values, but the chromosomes have a more localized character, as they actually investigate definite regions of the solution space. In this case, mutation mainly has the role of fine-tuning the solution in order to increase precision. It is the role of crossover to lead the actual search, which seems more natural than the randomly generated diversity of mutation-based exploration.

We used a population of 30 individuals whose initial values were random numbers with uniform distribution between the lower and upper limit of the parameters involved in the polymerization process.

A roulette-wheel selection technique was implemented. In this strategy,²² the parents are selected proportionally to their fitness. The probability of an individual, i , being chosen is

TABLE II
Genetic Algorithm Parameters Used in MMA Optimization

Population size	30 individuals
Maximum number of generations	100
Crossover probability	80%
Mutation probability	2%
Number of children/crossovers	1

$$P_i = \frac{F_i}{\sum_{j=1}^n F_j} \quad (15)$$

where F_i is the fitness of individual i and n is the number of individual in the population. Because roulette wheel is basically a stochastic process, there is a good chance that the individual with the best fitness is selected both as mother and as father. Thus, to diminish the loss of genetic diversity, we imposed a rule that the two parents be different individuals.

We used arithmetic crossover with a probability of 0.8. Arithmetic real-value crossover produces a linear combination of the parents. Given a uniform random number $r \in [0,1]$,

$$C = r \cdot M + (1 - r) \cdot F \quad (16)$$

or

$$C = r \cdot F + (1 - r) \cdot M \quad (17)$$

where C is the real-value chromosome of the child, and M and F are the chromosomes of the parents.

After a new individual has been created, a mutation is performed on it. Given the chosen solution encoding, we employed a uniform mutation that randomly changed a gene to a uniform random value from a interval: $x'_i = U(\min_i, \max_i)$. The interval we used was $[0.95x_i, 1.05x_i]$, where x_i is the current value of the gene. We did not use absolute boundaries for the interval in order to not constrain this genetic operator.

The GA parameters are summarized in Table II, in which we used a predefined number of generations as a termination criterion.

Formulation of optimization problem

The mass balance equations gave the following set of ordinary differential equations:

$$\frac{dz}{dt} = f(z, u, t) \quad z(t_0) = z_0 \quad (18)$$

where $z(t)$ is the state variable vector defined, for bulk polymerization, by

$$z = [I, x, \lambda_0, \lambda_1, \lambda_2, \mu_0, \mu_1, \mu_2] \quad (19)$$

and $u(t)$ is the control variable vector, with temperature and initial concentration of the initiator as components:

$$u(t) = [T_1, T_2, I_0] \quad \text{or} \quad u(t) = [T_1, T_2, T_3, I_0] \quad (20)$$

An admissible control input, $u^*(t)$ should be formed in such a way that the performance indices, J_1 and J_2 , defined by the following equations, are minimized:

$$\text{Min } J_1[u(t)] = w_i \cdot t_f + w_x \cdot (1 - x_f) + w_Q \cdot Q_f \quad (21)$$

or

$$\text{Min } J_2[u(t)] = w_i \cdot t_f + w_Q \cdot Q_f + w_x \cdot \left(1 - \frac{x_f}{x_d}\right)^2 + w_{DP_n} \cdot \left(1 - \frac{DP_{nf}}{DP_{nd}}\right)^2 \quad (22)$$

subject to

$$dz/dt = f(z, u, t) \quad (23)$$

$$u_{\min} \leq u(t) \leq u_{\max} \quad (24)$$

where

$$DP_n = \frac{\lambda_1 + \mu_1}{\lambda_0 + \mu_0} \quad (25)$$

$$x_f = x(t_f) \quad \text{and} \quad DP_{nf} = DP_n(t_f) \quad (26)$$

where, in the above equation, J is the objective function to be minimized, w is the weighting factor, Q is the polydispersity index, x_d and DP_{nd} are the desired values of monomer conversion and number-average chain length, respectively, at $t = t_f$; and x_f and DP_{nf} are the actual values corresponding to the final reaction time, t_f .

An important objective function for the polymerization system is minimization of the final reaction time, which leads to higher productivity. The other objective included in the same function is minimization of the polydispersity index of the polymer product. This ensures good physical properties of the polymer manufactured. The end-point requirement on monomer conversion forces the amount of unreacted monomer to be small and hence keeps postreactor separation and recycling costs low. The constraint on DP_n leads to the production of polymer with the desired properties because several physical properties of polymers are related to their values of DP_n .

Many authors have suggested using vectorial objective functions, with which more solutions are ob-

TABLE III
Parameters Used in MMA Polymerization

$k_d^0 = 1.053 \times 10^{15} \text{ s}^{-1}$ (for initiation with AIBN);
$k_{p0}^0 = 4.917 \times 10^2 \text{ m}^3/(\text{mol s})$;
$k_{t0}^0 = 9.8 \times 10^4 \text{ m}^3/(\text{mol s})$; $k_{tm0}^0 = 4.66 \times 10^6 \text{ m}^3/(\text{mol s})$;
$E_d = 1.2845 \times 10^5 \text{ J/mol}$;
$E_p = 1.822 \times 10^4 \text{ J/mol}$; $E_t = 2.937 \times 10^3 \text{ J/mol}$;
$E_{tm} = 7.428 \times 10^4 \text{ J/mol}$;
$f = 0.58$ (AIBN); $\varepsilon = [0.1946 + 0.16 \times 10^{-3} \times T \text{ (}^\circ\text{C)}]$;
$C_1 = 0.15998$; $C_2 = 7.812 \times 10^{-6}$;
$B = 0.03$; $T_{gp} = 387 \text{ K}$; $\theta_p^0 = 3.99822 \times 10^{-12} \text{ s}$;
$E_{op} = 1.02451 \times 10^5 \text{ J/mol}$;
$\theta_t^0 = 2.8883 \times 10^{-18} \text{ (mol s)/m}^3$;
$E_{ot} = 1.48924 \times 10^5 \text{ J/mol}$;
$k_d = k_d^0 \exp[-E_d/(RT)]$; $k_{p0} = k_{p0}^0 \exp[-E_p/(RT)]$;
$k_{t0} = k_{t0}^0 \exp[-E_t/(RT)]$;
$k_{tm0} = k_{tm0}^0 \exp[-E_{tm}/(RT)]$

tained, each “specialized” for a certain criterion. Although this approach has the benefit of emphasizing the equilibrium regions of the decision space, eventually it is the user who must decide to choose an appropriate solution if the problem requires a single result. In our case, the user must take into account several technological criteria. Using a scalar function with user-chosen objective weights proved to be a simpler approach, one better suited to our investigation. In addition, the hybrid method that combines sequential quadratic programming with genetic algorithm promoted the scalarization of objective function. The discussion of the results will provide evidence of these statements.

RESULTS AND DISCUSSION

A good process model is a necessary prerequisite for application of the optimal control strategy. Consequently, the kinetic model has been validated by experimental runs of bulk polymerization in a wide range of operating conditions. Our previous works^{23,24} found good agreement between the simulation results and the experimental data.

At each step of the optimization procedure, model equations were integrated using a special function for solving *stiff* differential equation, *ode15* from Matlab 7.0. Integration led to conversion and number- and weight-average molecular weight histories for $t_{\text{init}} \leq t \leq t_f$.

The numerical values for solving the model of MMA polymerization are given in Table III.

The polymerization process was conducted for a fixed time of 400 s in a perfect-mix batch reactor. Limit ranges for the reaction temperature, T , and the initiator concentration feed, I_0 , were established on the basis of the experimental data: $40^\circ\text{C} \leq T \leq 90^\circ\text{C}$ and $10 \text{ mol/m}^3 \leq I_0 \leq 50 \text{ mol/m}^3$.

The optimal control problem assumes determination of the nonisothermal temperature profile and the initial operating conditions (total initiator concentration) in order to obtain maximum conversion and minimum polydispersity index in a minimum reaction time according to the objective function (function 21) or to obtain the desired degree of polymerization, and desired monomer conversion, minimum polydispersity index in a minimum reaction time (function 22). The optimization procedure was performed in parallel for the two objective functions, J_1 and J_2 .

One obvious problem with this approach, which combines objectives into a single function, is that it may be difficult to generate a set of weights that properly scales the objectives when little is known about the problem. A single weighted sum approach requires a priori knowledge of the weights in order to vary the emphasis given to each objective. Thus, our results assumed the use of different values for the weights of the objective function, accompanied by a series of discussions whose main purpose was the correlation of weight values with optimal solutions. Although the objective functions do not have simple forms (in the sense that they impose simultaneous attainment of several objectives), choosing the best weights according to the established main objectives is not a difficult task because the best values of the parameters are precisely known: polydispersity has an ideal value of 1, conversion must be as close as possible to 1, and reaction time depends on temperature and has a maximum of 400 s, imposed from the beginning. In our optimization, for practical purposes, the temperature profile was considered to be composed of two or three isothermal steps.

Task level control was achieved by using nonlinear programming (SQP method), a genetic algorithm, and a hybrid method that combines them.

Sequential quadratic programming (SQP) methodology mimics Newton’s method for constrained optimization in that at each major iteration, an approximation is made of the Hessian of the Lagrangian function using a quasi-Newton updating method. This is then used to generate a QP subproblem whose solution is used to form a search direction for a line search procedure. The method is implemented in Matlab through the *fmincon* function.

The advantage of GA lies in its being able to work without requiring much information about the system, in contrast to traditional techniques, which need gradients, initial guesses. In addition, the GA-based method provides very good initial points for starting other techniques that require excellent initial guesses (SQP, in our case). We call this procedure the hybrid method (HM). These three techniques were applied in parallel for different types of objective functions and different weights, emphasizing the best results from these points of view (method, objectives, and

TABLE IV
Optimization of MMA Polymerization Achieved with Objective Function J_1 in Two Temperature Steps

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP_n	J_1	Observations (weights, method)
1	16	83.7 54.5	0.83 0.90	31.30 81.03	3.92	1610	4.01845	$w_x = 1; w_Q = 1; w_t = 0$ GA
2	50	90 66.2	0.87 0.94	14.74 60.09	3.29	511	3.92415	$w_x = 10; w_Q = 1;$ $w_t = 0$ GA
2'	10	80.6 90	0.38 0.98	34.68 73.87	4.55	1174	4.7121	$w_x = 10; w_Q = 1;$ $w_t = 0$ SQP
2''	39.1	106.1 74.8	0.93 0.96	8.80 35.38	2.83	278	3.24374	$w_x = 10; w_Q = 1;$ $w_t = 0$ HM
3	10.9	95.4 103	0.31 0.99	10.43 38.98	3.41	718	3.70249	$w_x = 10; w_Q = 1;$ $w_t = 10^{-4}$ GA
3'	10	82.7 90	0.39 0.98	30.82 69.72	4.56	1152	5.14191	$w_x = 10; w_Q = 1;$ $w_t = 10$ SQP
4	18.3	70.3 42.2	0.17 0.17	26.53 26.64	1.99	1671	18.2366	$w_x = 10; w_Q = 5;$ $w_t = 0$ GA

weights). The genetic algorithm was also implemented with Matlab.

The tables that show the results of the optimizations contain the following columns: the current number to which the optimization refers (this is why numbering continues throughout different tables); the values of the decision variables, I_0 and T (two or three temperature values), obtained from optimization; conversion, x ; time, t , in minutes; the polydispersity index, Q ; the number-average degree of polymerization, DP_n (all these resulted from solving the model in the conditions, I_0 and T , established through the optimization procedure); the value of the objective function, J_1 or J_2 , and an observation column, which notes weight values and the method employed. The optimization methods—SQP, GA, and HM—can also be identified by the optimization number. Thus, n ($n = 1, 2, \dots$) identifies a GA-based optimization, n' shows an SQP optimization and n'' an optimization based on the HM, meaning that the initial point of the SQP method was found by the GA. In an optimization, two or three values are shown for conversion and time. The first one or two represent the values of the intermediate steps of temperature, and the last—the value obtained at the end of the reaction, when using optimal parameters. Also, particular cases of the objective function are included in the tables by assigning zero values to the weights of some objectives.

Table IV presents the optimization results achieved with function J_1 , which aimed to minimize the reaction time and the polydispersity index and to maximize monomer conversion. For temperature as a decision variable, two isothermal steps were set initially. Some

of these results are displayed in order to demonstrate how results and weight values were chosen. User decision was easy to make, given sufficient information from the optimization results. Also, we considered this decision-making phase to be beneficial because it allowed the introduction of a technological criterion, as optimization supposes the approximation of reality by the mathematical model used and by stating the optimization problem (choosing and assembling the objectives into a function and choosing the decision variables and the solving method). Selecting the conditions that corresponded to the minimum of the objective function was not required, but selecting those that correspond to the established technological goals were. In this way, this article mainly aims at presenting the methodology of optimization and at discussing and comparing the computational methods and the obtained results. The hybrid method was only applied when that proved best chance to provide results worth considering.

It can be seen that the pair $w_x = 10$ and $w_Q = 1$ in optimization 2, variant 2'', provided the best results—high conversion and low polydispersity index. Optimization 2 was performed with the GA method, 2' with SQP, and 2'' with HM (SQP used solution 2 as its initial values). These two optimizations, 2 and 2', provided acceptable values for monomer conversion, but high values for the polydispersity index. The hybrid method enhanced the optimization results, also improving polymer polydispersity.

Introducing time into objective function J_1 in order to minimize it is shown in case 3. The results in Table IV demonstrate that time was not an important pa-

TABLE V
Optimization of MMA Polymerization Achieved with Objective Function J_2 in Two Temperature Steps

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP_n	J_2	Observations (weights, method)
5	38.2	59.6 67.1	0.28 0.94	73.6 148.6	5.81	1800	0.00496	$w_x = 10; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500$ $x_d = 0.96; DP_{nd} = 1800$ GA
5'	19.6	74.2 71.3	0.361 0.95	38.67 101	6.35	1800	0.00118	$w_x = 10; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500$ $x_d = 0.96; DP_{nd} = 1800$ SQP
5''	10.3	84.4 75.7	0.42 0.96	29.2 83.8	6.65	1800	2.22×10^{-8}	$w_x = 10; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500$ $x_d = 0.96; DP_{nd} = 1800$ HM
6	30.3	57.9 71.6	0.54 0.95	125.1 177.8	7.04	1800	0.00096	$w_x = 10; w_Q = 0;$ $w_t = 0; w_{DP_n} = 50$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
6'	10	81.9 77.7	0.72 0.96	39.9 85.6	5.05	1800	0.00021	$w_x = 10; w_Q = 0;$ $w_t = 0; w_{DP_n} = 50$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
7	22.2	77.5 119.9	0.63 0.99	37.4 46.0	8.39	357	0.01838	$w_x = 10; w_Q = 1;$ $w_t = 10^{-4}; w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
7'	25	70 90	0.30 0.98	40.5 80.8	5.88	539	0.16196	$w_x = 10; w_Q = 1;$ $w_t = 10^{-4}; w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
7''	22.2	77.7 90	0.63 0.98	37.3 70.2	7.23	630	0.16194	$w_x = 10; w_Q = 1;$ $w_t = 10^{-4}; w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
8	10.5	83.8 76.9	0.22 0.96	16.25 88.9	5.92	1905	19.5205	$w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
10'	10	70.9 82.6	0.36 0.97	63.3 112.4	4.86	1799	14.6343	$w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
10''	10	86.5 59.4	0.88 0.95	33.8 70	3.718	1797	11.2179	$w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM

parameter in MMA optimization; small values also were obtained when $w_t = 0$.

To increase the importance of the objective that imposed the minimization of Q , we tried to increase w_Q in optimization 4. However, the results were not acceptable, as improvement in Q greatly impeded the

conversion value. This characteristic is known to be an effect of multiobjective optimization, that is, improving one objective implies deterioration of another.

The thermal regime obtained in optimization contained an increasing or a decreasing number of temperature steps. We considered as favorable a situation in

TABLE VI
Optimization of MMA Polymerization Achieved with the Objective Function J_1 in Three Temperature Steps

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP _n	J_1	Observations (weights, method)
11	19.6	59.9	0.44	120.3	2.53	3953	3.58666	$w_x = 10; w_Q = 1; w_t = 0;$ GA
		80.6	0.80	124.8				
		53.1	0.89	180.4				
11'	10	70.4	0.44	72.6	2.54	2876	3.21353	$w_x = 10; w_Q = 1; w_t = 0;$ SQP
		90	0.86	77.1				
		65.1	0.93	124.7				
11''	10	70.4	0.44	72.6	2.54	2876	3.21353	$w_x = 10; w_Q = 1; w_t = 0;$ HM
		90	0.86	77.1				
		65.1	0.93	124.7				
12	35.6	100.3	0.95	13.0	3.137	362	3.91177	$w_x = 20; w_Q = 1; w_t = 0;$ GA
		46.8	0.96	400				
12'	50	90	0.88	15.1	3.39	488	4.19749	$w_x = 20; w_Q = 1; w_t = 0;$ SQP
		53.9	0.96	384.6				
		53.5	0.96	400				
12''	10	71.9	0.43	65.0	2.6	2458	3.80261	$w_x = 20; w_Q = 1; w_t = 0;$ HM
		90	0.87	70.0				
		70.5	0.95	116.9				
13	16.1	60.2	0.42	124.6	2.43	4127	8.50162	$w_x = 10; w_Q = 3; w_t = 0;$ GA
		81.9	0.83	130.1				
		48.4	0.88	174.3				
13'	10	69.2	0.45	78.9	2.42	3239	8.12611	$w_x = 10; w_Q = 3; w_t = 0;$ SQP
		90	0.85	83.1				
		58.6	0.91	129.4				
13''	50	71.4	0.49	38.4	2.34	1102	8.01123	$w_x = 10; w_Q = 3; w_t = 0;$ HM
		90	0.84	40.9				
		55.2	0.90	87.8				
14	20.1	61.2	0.41	105.0	2.55	3220	9.63184	$w_x = 20; w_Q = 3; w_t = 0;$ GA
		82	0.82	110.8				
		55.1	0.90	164.7				
14'	21	70.3	0.47	56.5	2.47	1917	9.05126	$w_x = 20; w_Q = 3; w_t = 0;$ SQP
		90	0.85	59.9				
		60.3	0.92	108.1				
14''	10	69.8	0.44	75.6	2.47	3049	8.9322	$w_x = 20; w_Q = 3; w_t = 0;$ HM
		90	0.86	79.9				
		62.4	0.93	127.5				
15	18.6	58.6	0.42	133.5	2.49	4070	9.76352	$w_x = 20; w_Q = 3; w_t = 10^{-5};$ GA
		80.7	0.81	138.9				
		52.2	0.89	192.7				
15'	21.3	70.5	0.47	55.6	2.47	1892	9.11573	$w_x = 20; w_Q = 3; w_t = 10^{-5};$ SQP
		90	0.85	58.9				
		60.3	0.92	107.1				
15''	10	70	0.44	74.7	2.48	3028	9.00829	$w_x = 20; w_Q = 3; w_t = 10^{-5};$ HM
		90	0.86	78.9				
		62.5	0.93	126.3				

which the first temperature was high, which would mean a big conversion, followed by a decrease in temperature, necessary for a narrow polydispersity. Case 2'' is representative, with $T_1 = 106^\circ\text{C}$ and $T_2 = 75^\circ\text{C}$.

For the situation shown in Table IV (objective function J_1 and two temperature steps), $w_x = 10$, $w_Q = 1$, and HM are recommended.

Table V shows optimizations based on objective function J_2 , achieved in two temperature steps.

In optimizations 5 and 6, because $w_t = 0$ and $w_Q = 0$, we sought to reach some imposed final values for conversion and degree of polymerization. If, as in optimization 5, reaching the objectives required use of

the hybrid method, in optimization 6, in which the weight of polymerization degree was decreased, the SQP method led to the imposed values of conversion and number-average degree of polymerization.

In optimizations 7 and 8, the objective function was supplemented by introducing values for the weights attached to time and the polydispersity index. A value too small for degree of polymerization compared to the imposed value (in optimization 7) determined an increase in the weight of this parameter in optimization 8, in which greater importance also was given to the polydispersity index by increasing its weight threefold. Thus, optimization 10'', based on the hybrid

TABLE VII
Comparison of Three Techniques Used in MMA Optimization: GA, SQP, and HM

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP_n	J_2	Observations (weights, method)
16	23.7	64.2 68.6 72.7	0.33 0.67 0.95	69.2 84.2 134.6	6.44	1800	0.00105	$w_x = 20; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
16'	24.8	69.9 69.9 69.7	0.25 0.64 0.95	34.8 57.9 111.2	6.14	1800	0.00444	$w_x = 20; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
17	21.1	60.5 73.5 71	0.23 0.71 0.95	73.6 96.1 147.7	5.22	2000	0.00017	$w_x = 20; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 2000$ GA
17'	23.9	69.2 69.8 68.1	0.28 0.91 0.94	41.1 81.8 111.9	5.72	2000	0.0017	$w_x = 20; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 2000$ SQP
18	37.2	66.2 84.9 69.7	0.32 0.86 0.95	48.2 57.4 104.2	3.48	999	0.00071	$w_x = 20; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 1000$ GA
18'	40.5	77 76.9 68.6	0.10 0.84 0.94	6.1 33.3 82.5	4.76	1000	0.00119	$w_x = 20; w_Q = 0; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 1000$ SQP
19	33.6	66.7 88 49.1	0.46 0.79 0.88	60.7 63.6 119.9	2.59	1846	8.23271	$w_x = 10; w_Q = 3; w_t = 10^{-5};$ $w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
19'	33	67.5 88.6 48.3	0.48 0.84 0.88	58.7 61.5 102.3	2.36	1799	7.15048	$w_x = 10; w_Q = 3; w_t = 10^{-5};$ $w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
19''	33.6	67.3 88.4 47.9	0.48 0.84 0.88	59.08 61.87 102.3	2.36	1799	7.21131	$w_x = 10; w_Q = 3; w_t = 10^{-5};$ $w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
20	32.7	66.8 79.9 65	0.47 0.73 0.93	61.3 64.2 119.9	3.75	1810	11.2814	$w_x = 10; w_Q = 3; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
20'	35.9	66.5 87.7 47.6	0.48 0.84 0.88	60.7 63.6 104.7	2.36	1799	7.1494	$w_x = 10; w_Q = 3; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
20''	32,3	67.7 88.8 48.5	0.48 0.84 0.88	58.5 61.2 102.3	2.36	1799	7.1495	$w_x = 10; w_Q = 3; w_t = 0;$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM

Table VII Continued

TABLE VII
Continued

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP_n	J_2	Observations (weights, method)
21	31.1	66.1	0.47	65.8	3.65	1840	11.9527	$w_x = 20; w_Q = 3; w_t = 10^{-5};$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ GA
		80	0.74	68.7				
		66	0.94	123.5				
21'	10	86.7	0.89	33.9	3.67	1797	13.4317	$w_x = 20; w_Q = 3; w_t = 10^{-5};$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ SQP
		43.3	0.99	400				
21''	26.6	70.1	0.48	52.3	2.37	1799	7.78648	$w_x = 20; w_Q = 3; w_t = 10^{-5};$ $w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
		90	0.85	56.1				
		48.2	0.88	88.9				

method, showed the best results for the objectives of the J_2 function.

For the optimizations shown in Table V (function J_2 and two temperature steps), good results were obtained with $w_x = 10, w_Q = 3, w_{DP_n} = 500$, and $w_t = 10^{-5}$. From the point of view of the thermal regime, increased or decreased temperatures could be used because J_2 supposes many objectives to be reached simultaneously.

The same procedure (the use of objective functions J_1 and J_2) was applied to obtain the initiator concentration and three temperatures as decision variables. Table VI presents several examples of such optimizations, corresponding to the objective function J_1 .

Optimizations 11–14 had two objectives, combined in a weighted manner in J_1 function: monomer conversion and polymer polydispersity at the end of the reaction. In the last optimization (groups 15, 15', 15''), time minimization was added as an objective. Optimization 12 was achieved in two temperature steps (the values of temperatures T_2 and T_3 were found to be equal).

A first observation concerning the data in Table VI is that all the optimizations corresponding to the hybrid method had a thermal regime in which $T_1 < T_2 > T_3$, that is, an increase followed by a decrease in temperature. This was the most frequently encountered case, but not the only one. Other optimizations (not included in Table VI) showed a different hierarchy of the three temperature steps.

Optimizations with different weights were achieved, thus increasing the importance of a certain objective. The increase from 10 to 20 of the weight attached to the conversion resulted in a bigger conversion at the end of the reaction (0.96 for $w_x = 20$, case 12', compared to 0.93 for $w_x = 10$, case 11'). Similarly, $w_Q = 3$ compared to $w_Q = 1$ led to smaller values for the polydispersity index of the polymer ($Q = 2.54$ in 11'' and $Q = 2.34$ in 13'').

The minimal value of the J_1 criterion means optimization from the mathematical point of view. However,

the technological factors allow the choosing of an alternative, depending on the aimed purpose, that is, the properties of interest. We must keep in mind that when one objective was improved, the other worsened. For example, increasing the w_x weight from 10 to 20 (optimization 12 compared to optimization 11) caused an increase in conversion, but also an increase in the polydispersity index.

A comparison of optimizations achieved with the same objective function and with the same weight values but using different solving methods (GA and SQP) (Table VI) did not allow a decision to be made as to which of the two methods provided better results. For example, the GA method proved to be better in case 12 and the SQP method in cases 11, 13, 14, and 15. The same thing can be seen in Table V for similar optimizations. In all examples shown in Table VI, it can be seen that the hybrid method led to the best results.

The optimizations presented in Table VI showed different aspects of the multiobjective optimization achieved with a scalar function in which the objectives were combined in a weighted manner. The weights $w_x = 20$ and $w_Q = 3$ were the best values for high conversion and narrow polydispersity.

Table VII shows a comparison of examples of optimizations achieved with objective function J_2 and was solved with the three methods.

In optimizations 16–18, the J_2 function has a particular form, given by $w_Q = 0$ and $w_t = 0$. These optimizations were designed for different imposed values of conversion and number-average polymerization degree (case 16: $x_d = 0.96$ and $DP_{nd} = 1800$; case 17: $x_d = 0.95$ and $DP_{nd} = 2000$; case 18: $x_d = 0.95$ and $DP_{nd} = 1000$), while keeping the weights constant ($w_x = 20, w_{DP_n} = 500$). Because these desired values were met by the GA and SQP methods (cases 16–18), the hybrid method was no longer consid-

ered necessary because its main purpose was to enhance the results of the previous methods.

The thermal regime was different depending on the values imposed for conversion, degree of polymerization, or polydispersity index and their relative importance established through the weights. In most cases, the first temperature step was increasing, followed by a decreasing step.

In optimizations 19–21 minimization of the polydispersity index and the reaction time were sought, in addition to the values imposed for conversion and degree of polymerization.

If a relatively small polydispersity index was obtained (2.4 in optimizations 20' and 21" and the desired value for the degree of polymerization), the objective related to the desired value for conversion was not achieved (20'), even if its weight increased (21"). By accepting a greater polydispersity index (greater than 3, case 20), acceptable values were obtained for conversion and degree of polymerization. It was observed that with the use of a technological criterion for evaluating the results, the value of the objective function was of little importance. Given that the objective function includes four partial objectives, a compromise between these values must be accepted, depending on the practical goals considered.

In Table VII, based on the objective function J_2 , different values for x_d and DP_n , for the weights and different solving methods were chosen. Usually, the optimizations that were compared differed in the value of a single parameter (weight, method, or value imposed) in order to establish its influence.

In most cases, the hybrid method improved the results obtained with GA because it benefitted from good starting points. Table VIII shows the optimizations achieved with the GA and SQP methods in similar conditions, providing additional considerations about the optimization methods we used. Several pairs ($n-n'$) were considered for comparison. In Table VIII the method selected, which was based on the quality of its results, was: GA for the pairs (11–11'), (17–17'), (18–18') and SQP for the pairs (13–13'), (19–19'), and (20–20').

The optimizations retained the same numbers from previous tables. Neither method was found to be better than the other. Optimizations 11" and 13" (Table VI) and 19" and 20" (Table VII) were made by HM, which improved the prior results.

No better results were obtained with the SQP method than with the GA method. The results of the SQP method depend on its starting point. Therefore, it can be applied several times, with different initial values in the search space, or even successively, and the solution found can be a starting point for a new SQP search. Using either SQP or GA, the working procedure can be done in several ways, depending on the user's experience, the goal of the problem, and the

available knowledge about the process. The way the objective function was formulated and the adequate weight chosen must be also considered. The present study mainly focused on presenting a working procedure, and therefore in this article absolute conclusions cannot be formulated, only recommendations.

Most articles in the literature on optimization of polymerization processes with genetic algorithms reported that this method provided better results compared to classical solutions. We have shown that genetic algorithms do not always give the best results; however, the hybrid method, which combines a genetic algorithm with the sequential quadratic procedure, is efficient.

In the present study, optimizations achieved under similar conditions (objective function, weights) were compared, the results of which were represented by two or three temperature steps. Table IX lists several examples that demonstrate that a third temperature step improved the optimization results. The situations compared were grouped and marked two by two. Thus, from comparing 2" to 11", 22" to 13", 23" to 14", 24" to 19", 25" to 20", and 26" to 21", it can be seen that better results occurred with the latter of each pair (11", 13", 14", 19", 20", and 21"), corresponding to a thermal regime formed of three isothermal temperature steps.

Figure 1 presents the thermal regimes of some of the optimizations achieved in three temperature steps; 11" and 13" were obtained with the J_1 function and 19" and 21" with the J_2 function. In most cases, the obtained optimal regime was formed of a temperature step that was increasing, followed by a step that was decreasing. The intermediate temperature corresponded to a short time interval. The optimal thermal regime depended on the conditions in which optimization was achieved: proposed objectives, weight values, or final values imposed for conversion and degree of polymerization.

Choosing the weight values was not a complicated matter. In a few trials, adequate weights for the proposed objectives could be estimated, depending on their relative importance. As the tables with the optimization results show, the most frequent values for the weights in the present study were: $w_x = 10, 20$; $w_Q = 1, 3$; and $w_{DP_n} = 50, 500$. Manipulating these weights allowed the user to have one objective take precedence over another, giving the optimization method flexibility.

CONCLUSIONS

The main goal of this article was to outline a general strategy for applying optimization to polymerization processes, on the basis of the results obtained and the method's accessibility.

In general, optimization of a polymerization process means simultaneously achieving several objectives

TABLE VIII
Comparison of the SQP and GA Methods

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP_n	Objective function	Observations (weights, method)
11	19.6	59.9 80.6 53.1	0.44 0.80 0.89	120.3 124.9 180.4	2.53	3953	3.586660	J_1 $w_x = 10; w_Q = 1;$ $w_t = 0; w_{DP_n} = 0;$ GA
11'	10	70.4 90 65.1	0.44 0.86 0.93	72.6 77.1 124.7	2.54	2876	3.21353	J_1 $w_x = 10; w_Q = 1;$ $w_t = 0; w_{DP_n} = 0;$ SQP
13	16.1	60.2 81.9 48.4	0.42 0.83 0.88	124.6 130.1 174.3	2.43	4127	8.501617	J_1 $w_x = 10; w_Q = 3;$ $w_t = 0; w_{DP_n} = 0;$ GA
13'	10	69.2 90 58.6	0.45 0.85 0.91	78.9 83.1 129.4	2.42	3239	8.12611	J_1 $w_x = 10; w_Q = 3;$ $w_t = 0; w_{DP_n} = 0;$ SQP
17	21.1	60.5 73.5 71	0.23 0.71 0.95	73.6 96.1 147.7	5.22	2001	0.000174	J_2 $w_x = 20; w_Q = 0;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 2000;$ GA
17'	23.9	69.2 69.8 68.1	0.28 0.91 0.94	41.0 81.8 111.9	5.72	2000	0.0017	J_2 $w_x = 20; w_Q = 0;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 2000;$ SQP
18	37.2	66.2 84.9 69.7	0.32 0.86 0.95	48.2 57.4 104.2	3.48	999	0.00071	J_2 $w_x = 20; w_Q = 0;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 1000;$ GA
18'	40.5	77 76.9 68.6	0.10 0.84 0.94	6.1 33.3 82.5	4.76	1000	0.001198	J_2 $w_x = 20; w_Q = 0;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.95;$ $DP_{nd} = 1000;$ SQP
19	33.6	66.7 88 49.1	0.461 0.79 0.88	60.7 63.6 119.9	2.59	1846	8.232717	J_2 $w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} =$ 50; $x_d = 0.96;$ $DP_{nd} = 1800;$ GA
19'	33	67.5 88.6 48.3	0.48 0.84 0.88	58.7 61.5 102.3	2.36	1799	7.15048	J_2 $w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} =$ 50; $x_d = 0.96;$ $DP_{nd} = 1800;$ SQP
20	32.7	66.8 79.9 65	0.47 0.73 0.93	61.3 64.2 119.9	3.75	1810	11.2814	J_2 $w_x = 10; w_Q = 3;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800;$ GA
20'	35.9	66.5 87.7 47.6	0.48 0.84 0.88	60.7 63.6 104.7	2.36	1799	7.1494	J_2 $w_x = 10; w_Q = 3;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800;$ SQP

TABLE IX
Comparison of Optimizations Achieved in Two and Three Temperature Steps

No.	I_0 (mol/m ³)	T (°C)	x	t (min)	Q	DP_n	Objective function	Observations (weights, method)
2''	39.1	106.1	0.93	8.80	2.83	278	3.24374	J_1 $w_x = 10; w_Q = 1;$ $w_t = 0$ HM
		74.8	0.96	35.38				
11''	10	70.4	0.44	72.6	2.54	2876	3.21353	J_1 $w_x = 10; w_Q = 1; w_t = 0;$ HM
		90	0.86	77.1				
		65.1	0.93	124.7				
22''	10.1	89.3	0.26	13.2	3.93	857	11.8964	J_1 $w_x = 10; w_Q = 3; w_t = 0;$ HM
		97.4	0.99	49.3				
13''	50	71.4	0.49	38.4	2.34	1102	8.01123	J_1 $w_x = 10; w_Q = 3; w_t = 0;$ $w_t = 0;$ HM
		90	0.84	40.9				
		55.2	0.90	87.8				
23''	10	48	0.37	384.4	2.61	9595	10.3774	J_1 $w_x = 20; w_Q = 3; w_t = 0;$ HM
		72.1	0.87	400				
14''	10	69.8	0.44	75.6	2.47	3049	8.9322	J_1 $w_x = 20; w_Q = 3; w_t = 0;$ HM
		90	0.86	79.9				
		62.4	0.93	127.5				
24''	10	86.7	0.88	33.4	3.71	1773	11.2078	J_2 $w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 50;$ $x_2 = 0.96;$ $DP_{nd} = 1800$ HM
		59.6	0.92	69.5				
19''	33.6	67.3	0.48	59.08	2.36	1799	7.21131	J_2 $w_x = 10; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 50;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
		88.4	0.84	61.87				
		47.9	0.88	102.3				
25''	10	86.5	0.88	33.7	3.72	1773	11.1757	J_2 $w_x = 10; w_Q = 3;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
		59.5	0.92	70.5				
20''	32,3	67.7	0.48	58.5	2.36	1799	7.1495	J_2 $w_x = 10; w_Q = 3;$ $w_t = 0; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
		88.8	0.84	61.2				
		48.5	0.88	102.3				
26''	10	86.5	0.88	33.8	3.72	1797	11.2386	J_2 $w_x = 20; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
		59.9	0.92	70.7				
21''	26.6	70.1	0.48	53.2	2.37	1799	7.78648	J_2 $w_x = 20; w_Q = 3;$ $w_t = 10^{-5}; w_{DP_n} = 500;$ $x_d = 0.96;$ $DP_{nd} = 1800$ HM
		90	0.85	56.1				
		48.2	0.88	88.9				

that are often contradictory in nature. Therefore, solving such a problem is accompanied by difficulties, beginning with the way of formulating the objective

function and continuing with the choice of working procedure and the selection of results from more possible options. It is not sufficient to handle optimization

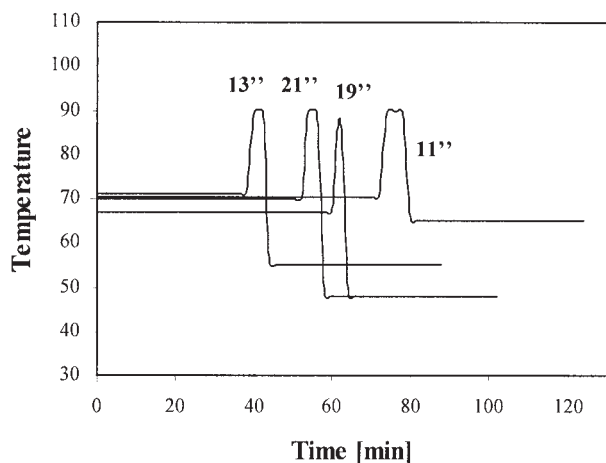


Figure 1 Thermal regimes in MMA polymerization optimization.

from a mathematical point of view alone. This is extremely difficult because of the complexity of the problem. User decision in result selection allows technological considerations to be added to the objective function.

Our study combined several objectives into a scalar function in a weighted manner: minimization of polydispersity index, minimization of reaction time, achievement of imposed values for conversion, and number-average polymerization degree. The decision variables were initial concentration of the initiator and the temperature formed by isothermal steps.

The conclusions came from more than 100 optimizations achieved, only some of which were chosen to be presented as examples. The study did not intend to obtain unique results in the form of the best optimization results from a mathematical point of view; instead, it sought to describe the working procedure, focusing on choosing the optimization method and on the possibility of manipulating and combining the algorithms frequently used in optimization.

Thus, the procedure can be organized into the following steps:

- Attempts are made with different weight values to select those that lead to achievement of the proposed objectives. Often, simultaneous achievement of all the objectives is impossible, as they are contradictory in nature. In such cases, manipulating the weight values is a means to focus interest on user-chosen objectives, in conformity with the technological requirements of the process.
- Different optimization methods were used for comparison, and they were evaluated on the basis of their optimization results and ease with which

they can be used productively. The presented methods, SQP and GA, as well as their combination (e.g., HM), are trustworthy.

- For temperature as a decision variable, several isothermal steps were chosen in order to compromise between their number and the results corresponding to the optimal regime. We tried two and three temperature steps, and the latter is recommended. Increasing the number of temperature steps may be a possible way to improve optimization results.

In conclusion, this study has shown that a multiobjective scalar function, properly manipulated, is easy to use and provides accurate results. Also, the importance of user decision must be emphasized. The presence of this step is not a disadvantage of the optimization, but a favorable opportunity to consider technological criteria.

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