

Numerical Inversion Techniques in the Recovery of Molecular Weight Distribution Expressed in Different Transformed Domains. Experimental Validation

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In this work we analyze the feasibility of using numerical inversion techniques for recovering MWD of actual polymers from a transformed domain, specifically the one defined by probability generating functions. We start from known experimental MWDs, transform them, and then apply two different numerical techniques to recover the MWD. We analyze the influence of noise in the calculated probability generating functions on the quality of the recovered molecular weight distributions. We also study how the range of molecular weight selected for the inversion procedure affects the results. We compare the recovered distributions obtained by both methods and suggest a criterion for establishing the reliability of a given solution. We find that this general strategy is appropriate for the recovery of MWDs whether they are monomodal, multimodal, wide or narrow. This provides a tool for the treatment of actual polymerization systems for which there is no analytical solution for the mass balance equations.

INTRODUCTION

In the modeling of polymer reaction systems, mass balances for each one of the species involved are usually set up. However, since in a polymerizing system there are infinitely many such species, one ends up with an infinitely large system of equations. Several techniques are available to reduce their number. If one is only interested in the calculation of average quantities, the moment method is appropriate (1–3). Other techniques must be sought if the calculation of the molecular weight distribution (MWD) is necessary. For example, it is possible to apply Laplace transforms to the balance equations (4), or other transforms such as generating functions.

Miller *et al.* (4) inverted Laplace transforms of mass balances using two different numerical techniques. They were applied to several theoretical examples: living polymerization, simple addition polymerization,

and linear and branched addition polymerization. The numerical inversion methods required working in the complex plane. The authors reported that their work improved on previous applications of Laplace transforms to mass balances, which had been performed mostly for systems that had an analytical transform and were therefore limited to relatively simple systems.

A special type of generating function was used by Jackson *et al.* (5) to predict the average molecular weights of a polymer obtained by free radical reaction in a continuous, perfectly stirred reactor. For two particular kinetic schemes, recursive expressions for the number distribution of molecular weight were reported. They solved the system for the average molecular weights. The authors concluded that the most promising way to obtain the complete molecular size distribution would be to invert the generating function presented in their work. They did not perform the proposed inversion.

The z-transform has also been used in several works (6–8). The z-transform is defined for discrete functions, such as the MWD, but its transformed variable

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is complex. The inversion algorithms require a contour integration in the complex plane, something difficult to do numerically except for relatively simple kinetic schemes, without the presence of branching reactions.

Recently, Whiteley and Garriga (9) analyzed the performance of the inversion algorithm reported by Gaver (10) and its applicability for obtaining theoretical MWDs from their Laplace transforms. Using different analytical functions they tested the sensibility of the method to the numerical accuracy used to perform the calculations. They also studied the influence of the order of quadrature used on the calculated solutions. They obtained good results when applying the method to the calculation of MWD where the Laplace transforms at definite values of the transformed variable are obtained by integration of the mass balance equations for the theoretical polymerization reported in Jackson *et al.* (5).

In this work we study the feasibility of using numerical inversion techniques on probability generating function (pgf) transforms in order to calculate complete polymer MWD. Generating functions in general have a long history of use in the theory of probability (11). The probability generating functions have been used in polymer science either for evaluation of moments of the MWD and average molecular weights (12, 13), as a means of evaluating network parameters (14) or as a tool to model complex polymerization reactions (15, 16). They have not, to our knowledge, been used so far for the calculation of the complete MWD. The pgf transforms are defined for discrete distributions, and their transformed variable z is real and bounded. These characteristics make pgfs an attractive alternative to the Laplace or the z -transforms.

In practice, the pgf would be obtained from a treatment of the infinitely many mass balance equations for a given polymerization system, which would be transformed to yield a finite set of equations. In most cases there would be no analytical solution to the transformed equations; a discrete set of values of pgf would be obtained instead. This leads unavoidably to numerical inversion. If the inversion method is inappropriate, or if it is not correctly applied, this step may be accompanied by significant error propagation. The reason is that many inversion procedures require the subtraction of very large quantities of the same order of magnitude.

In order to make the analysis of the inversion techniques independent from the particular details of the application of pgf transforms to mass balance equations, in this work we start from known experimental MWDs obtained in our laboratories. We transform them, and then apply two different numerical techniques to try to recover the MWD. We use "clean" transformed MWDs as well as others where errors have been incorporated, so as to simulate the uncertainty in the transformed domain that would result from numerical calculation. In particular, we analyze the numerical inversion techniques originally developed by Gaver (10) and by Stehfest (17, 18). Both of

them require the user to fix one arbitrary parameter, the value of which is crucial to obtain appropriate MWD. We discuss the quality of the recovered distributions and suggest guidelines for establishing the reliability of a given solution. The fundamentals developed here served as a base to the successful application of this technique to the inversion of pgf obtained in the modeling of industrial autoclave reactors for polyethylene and EVA production (19). That is a system where branched polymers are produced, and where the kinetics are so complex that it is impossible to find an analytical solution to the transformed equations with the methods currently available. The proposed method is useful for the treatment of any free radical polymerization system.

INVERSION ALGORITHMS FOR LAPLACE AND PGF TRANSFORMS OF MWD

We use in this work the inversion formulas proposed by Gaver (10) and by Stehfest (17, 18) that were originally intended to treat Laplace transforms.

The well known Laplace transform of any given function $f(t)$ is given by Eq 1.

$$L\{f(t)\} = \int_0^{\infty} e^{-st} f(t) dt \quad (1)$$

Formally, the MWD can be considered as a periodic pulse function, with pulses of unitary width and period 1. If this is the case, it can be shown that the corresponding Laplace transform is given by Eq 2, where $f^*(t)$ stands for the periodic function.

$$L\{f^*(t)\} = \sum_{t=0}^{\infty} e^{-st} f^*(t) \quad (2)$$

On the other hand, the probability generating function $\psi(z)$ is defined in Eq 3.

$$\psi(z) = \sum_{t=0}^{\infty} z^t P^*(t) \quad (3)$$

where $P^*(t)$ represents the probability of an event " t " and z is the transformed variable, defined to be real, $0 \leq z \leq 1$. In the case of a molecular weight distribution, $P^*(t)$ would be the probability that the degree of polymerization of a molecule is t . This probability could be the weight or number fraction of molecules with degree of polymerization t . Please note that Eq 3 is

different from the z -transform expression, $\sum_{t=0}^{\infty} r^{-t} P^*(t)$, where r is the complex dummy variable.

If the expression for $\psi(z)$ is known analytically, then it is possible to recover as many terms of $P^*(t)$ as desired using the expression (20) given in Eq 4:

$$P^*(t) = \frac{1}{t!} \left. \frac{d^t \psi(z)}{dz^t} \right|_{z=0} \quad (4)$$

If, however, only a finite number of pgf values is known, as is the case when the pgf is found numerically, the

former equation is not appropriate. A different strategy is needed to perform the inversion.

It can be shown that, with an appropriate change of variables, the probability generating function (pgf) is equivalent to the Laplace transform of the MWD. If we look at their definitions (Eqs 2 and 3), if $f^*(t)$ is the same as $P^*(t)$ the equivalence is obtained when $z = e^{-s}$.

This equivalence allows the use of the same inversion techniques on Laplace and pgf transforms to recover the original, untransformed functions. With respect to the inversion techniques themselves, those employed here belong to a group of methods that compute a sample, as explained in an extensive review on inversion of Laplace transforms (21). The numerical inversion is accomplished by solving Eq 5:

$$I_n(t) = \int_0^\infty \delta_n(t, s) f(s) ds \quad (5)$$

where $\delta_n(t, s)$ is a convergent sequence that approaches $f(t)$ as n approaches infinity. Gaver (10) proposed Eq 6 to evaluate $\delta_n(t, s)$.

$$\delta(t, s) = \frac{(2n)!}{n!(n-1)!} \frac{\ln(2)}{t} [1 - e^{-(\ln(2)/t)s}]^n e^{-n(\ln(2)/t)s} \quad (6)$$

As it stands, Eq 6 presents a slow rate of convergence (21). Gaver proposed to expand the expression in inverse powers of n so the result could be improved by extrapolation. As a result, the final form of Gaver's formula is given by Eqs 7 and 8:

$$f(t) \approx P_0(n) = \frac{(2n)!}{n!(n-1)!} \frac{\ln(2)}{t} \sum_{k=0}^n \binom{n}{k} (-1)^k F(s_k) \quad (7)$$

where $F(s_k)$ is the Laplace transform of the function $f(t)$ to be recovered at the value t of the independent variable. The values s_k are calculated as $s_k = (n + k) \ln(2)/t$.

$$f(t) \approx P_h(n) = \frac{2^h P_{h-1}(n) - P_{h-1}(n/2)}{2^h - 1}, \quad n = 2^h \quad (8)$$

Equation 8 corresponds to the asymptotic improvement formula used by Gaver (10), where h , the method parameter, is the quadrature approximation order.

Stehfest (17, 18) proposed a different extrapolation formula, given by Eqs 9 and 10.

$$f(t) \approx \ln(2)/t \sum_{n=1}^N K_n F(s_n); \quad s_n = n \ln(2)/t \quad (9)$$

where

$$K_n = (-1)^{n+N/2} \sum_{k=\lceil (n+1)/2 \rceil}^{\min(n, N/2)} \frac{k^{N/2} (2k)!}{(N/2 - k)! k! (k-1)! (n-k)! (2k-n)!} \quad (10)$$

Each method has one parameter that has to be fixed: h for Gaver's formula, and N for Stehfest's formula.

The quality of the inversion depends on these parameters. Gaver's and Stehfest's formulas are equivalent for $h = 1$ and $N = 4$ only. This fact may be easily verified by expanding both formulas for several values of h or N .

In order to implement the methods explained above for the inversion of a pgf that describes a MWD, the variable t is taken to be the degree of polymerization (DP), and the transformed function F is the pgf evaluated at the values of the transformed variable required by the chosen method. These values are $z = e^{-s_k}$ for Gaver's method and $z = e^{-s_n}$ for Stehfest's method.

TREATMENT OF EXPERIMENTAL INFORMATION

Several polymers of very different molecular weight distributions were selected to carry out our work. Two polyethylenes (PE-1 and PE-2) were produced in Repsol-YPF's autoclave reactors as reported in our previous work (22). Another three polyethylenes (M2, M3, and M7) and two polystyrene samples (PS-a and PS-b) belong to the data collection of PLAPIQUI's labs. PS-a and PS-b are molecular weight calibration standards from Polymer Laboratories and TOSOH, respectively.

Polymer samples were analyzed by Size Exclusion Chromatography (SEC) in a Waters 150C instrument with both refractive index and intrinsic viscosity detectors. For polyethylene samples, trichlorobenzene (TCB) at 145°C was used as solvent, with 0.04 wt% of Irganox 1010 added as stabilizer. The operating conditions were as follows: flow rate 0.7 mL/min, sample concentration 5 mg/mL and injection volume 150 μ L. This information was used for calculation of molecular weight distributions (MWD), molecular weights, polydispersities, and branching parameters according to the method proposed by Foster *et al.* (23). The use of the Foster method was unnecessary in the case of the polystyrene samples used, since they are linear calibration standards.

The experimental molecular weight distributions are shown in Fig. 1. The abscissas are the molecular weights of each fraction (M_i). The distributions are expressed in chromatographic basis, which means that the ordinates (c_i) are proportional to the mass times the molecular weight. The distributions may also be expressed in number (n_i) or weight fraction (w_i), according to the user's needs. The measured average molecular weights are reported in Table 1. In what follows we will refer to the number MWD as MWDn, to the weight MWD as MWDw and to the chromatographic MWD as MWDc.

SEC results reported as pairs of data (A_i , B_i) were used to perform the conversion of ordinates. A_i corresponds to the decimal logarithm of the molecular weight of the considered fraction, and B_i to a quantity proportional to the mass present in that fraction. The degree of polymerization for each fraction is calculated as $DP_i = 10^{A_i}/M_{mon}$, where M_{mon} is the average molecular weight of the monomer.

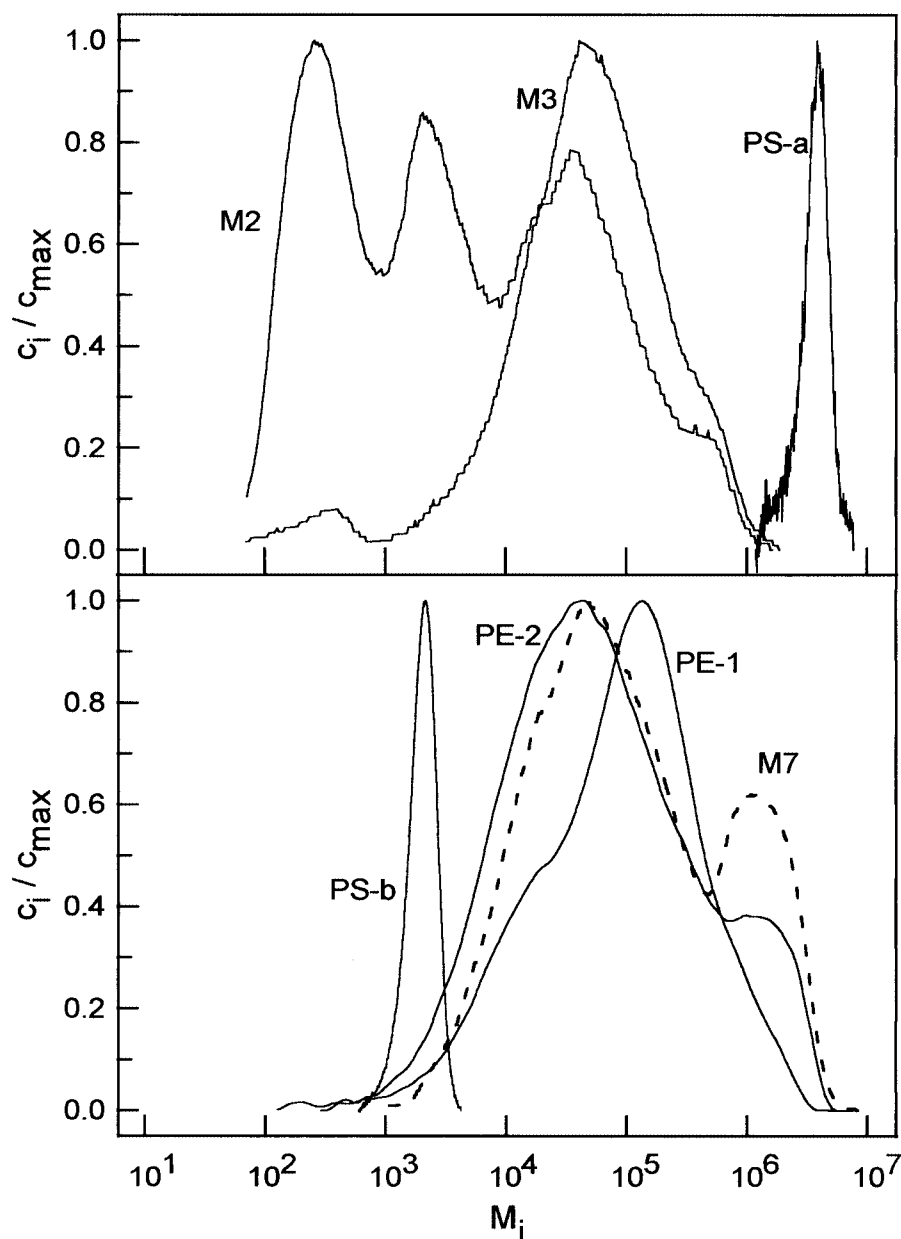


Fig. 1. Normalized experimental chromatographic MWDs of seven polymer samples.

The number, weight and chromatographic fractions of molecules in the i^{th} fraction of the chromatogram are shown in Eqs 11–13, respectively.

$$n_i = \frac{B_i / 10^{A_i}}{\sum_{k=1}^{kmx} B_k / 10^{A_k}} \quad (11)$$

$$w_i = \frac{B_i}{\sum_{k=1}^{kmx} B_k} \quad (12)$$

$$c_i = \frac{B_i \cdot 10^{A_i}}{\sum_{k=1}^{kmx} B_k \cdot 10^{A_k}} \quad (13)$$

Here kmx is the total number of fractions in the chromatogram.

To calculate the pgfs ($\psi_j(z)$) ($j = n, w, c$) of number (n), weight (w) and chromatographic (c) distributions Eqs 14–16 were employed. These equations result from applying the definition of pgf (Eq 3), where the probability $P^*(t)$ is either the number fraction, the weight fraction or the chromatographic fraction of

Table 1. SEC Characterization of the Polymer Samples.

Sample	Mn	Mw	PD
M2	669	46,000	68.8
M3	4910	114,119	23.2
M7	27,925	438,502	15.7
PS-a	3,395,120	3,751,662	1.1
PS-b	1868	2032	1.1
PE-1	15,574	222,442	14.0
PE-2	15,700	300,840	19.0

molecules of length t . It was also taken into account that the fractions n_t , w_t and c_t only have nonzero values for $DP_1 \leq t \leq DP_{max}$.

$$pgfn(z) = \psi_n(z) = \sum_{t=DP_1}^{DP_{max}} n_t z^t \quad (14)$$

$$pgfw(z) = \psi_w(z) = \sum_{t=DP_1}^{DP_{max}} w_t z^t \quad (15)$$

$$pgfc(z) = \psi_c(z) = \sum_{t=DP_1}^{DP_{max}} c_t z^t \quad (16)$$

To accomplish the summations indicated in Eqs 14–16 it was necessary to evaluate the distribution beginning at the lowest available degree of polymerization (DP_1) and move forward one by one. Cubic splines (24) were applied to the experimental data to obtain all the information needed to calculate Eqs 14–16. We have used cubic splines even when the data points were not very smooth because we are not interested in modeling this data, we want to recover as much of it as possible from its transformed version. Therefore no attempt at filtering or otherwise improving the data was made.

The pgfs calculated as described above are considered clean or noise-free pgfs. Different types of errors were added to the pgf transforms in an attempt to evaluate the incidence of error propagation, inherent in the pgf calculation through mass balances, on the inversion step. The resulting pgfs were considered “noisy.”

Once either the clean or the noisy pgf transforms were calculated, they were inverted using the two algorithms described above. When Gaver's method was used, we considered all values of h from 1 to 4. For Stehfest's method, N was varied from 2 to 24 with step 2. Using either method, the MWD is recovered at a finite number of DP points. The recovered distributions are different depending on the pgf used. From $pgfn$, $pgfw$ and $pgfc$ the recovered $f(t)$ are MWDn, MWDw and MWDc, respectively. Please keep in mind that the independent variable t corresponds to DP . Since it is always possible to go from one type of MWD to any other type by direct calculation (see Eqs 11–13), we not only recovered each MWD from its own transform, but also calculated it by manipulating the inversions of the other two. After the inversion step all calculated values were compared with the experimental data.

RESULTS AND DISCUSSION

We select M7 as an example to demonstrate the capabilities of both inversion methods. A strategy to select the optimum solution is also presented. In the following results, $pgfc$ is inverted to obtain the corresponding MWDc. Knowledge of the molecular weight range of the sample is assumed. Figure 2a compares the experimental MWDc with the ones obtained by means of Stehfest's formula with parameter N ranging from 2 to 24. A badly deteriorated solution results for $N > 20$. When using $N = 20$ there is no resolution for the high molecular weight tail of the MWD. At the other end of the spectrum, the use of $N = 2$ results in an overestimation of the lower molecular weight material and an insensitivity to the high molecular weight shoulder. For $2 < N < 20$ the high molecular weight shoulder appears in the calculated distributions clearly and shows reproducibility, while the lower molecular weight region up to the peak agrees almost exactly with the experimental distribution. If the experimental distributions were not known, it would be very difficult to decide which of the reasonable distributions obtained for $4 \leq N \leq 16$ would best represent the actual polymer.

Figure 2b shows similar results when using Gaver's formula. The parameter h , in this case, was varied from $h = 1$ to $h = 4$. Larger values of h lead to violently oscillating solutions. With $h = 4$ a large peak appears at the high molecular weight tail, distorting the real peak and shoulder of the experimental distribution. Results for $h = 1$ to $h = 3$ are very reasonable. The best curves are obtained for $h = 2$ and $h = 3$. Again, without previous knowledge of the experimental MWD it is impossible to decide a priori which one of these two values gives the best calculated MWDc. It is worth noting that Whiteley and Garriga (9) found that Gaver's method implemented in a symbolic mathematical language gives better accuracy when using $h = 4$ and 22 or more significant digits. When using 16 digits the best results they obtained were for $h = 3$. In view of their results, the authors suggested that $h = 4$ with 22 decimal places would be the best choice. In the present work we intend to construct a basis for a more complex and much larger problem, the inversion of pgfs obtained from the resolution of mass balance equations in industrial polymerization reactors. A symbolic language seems inappropriate for such a memory-demanding problem, so we are limited to 16 digits, the maximum precision allowed in the Fortran language.

In order to quantify the goodness of the solutions for both methods, two errors were evaluated. The first one corresponds to the sum of squares of the differences between experimental and calculated curves (SSQ). The second one corresponds to the sum of the squares of the differences between two successive calculated curves (SSQ1). Figure 3 shows these errors for Stehfest's formula and Fig. 4 for Gaver's formula. It appears that the minimum for both SSQ and SSQ1 may fall at similar values of either N or h . In this particular case the values of N at the minima coincide.

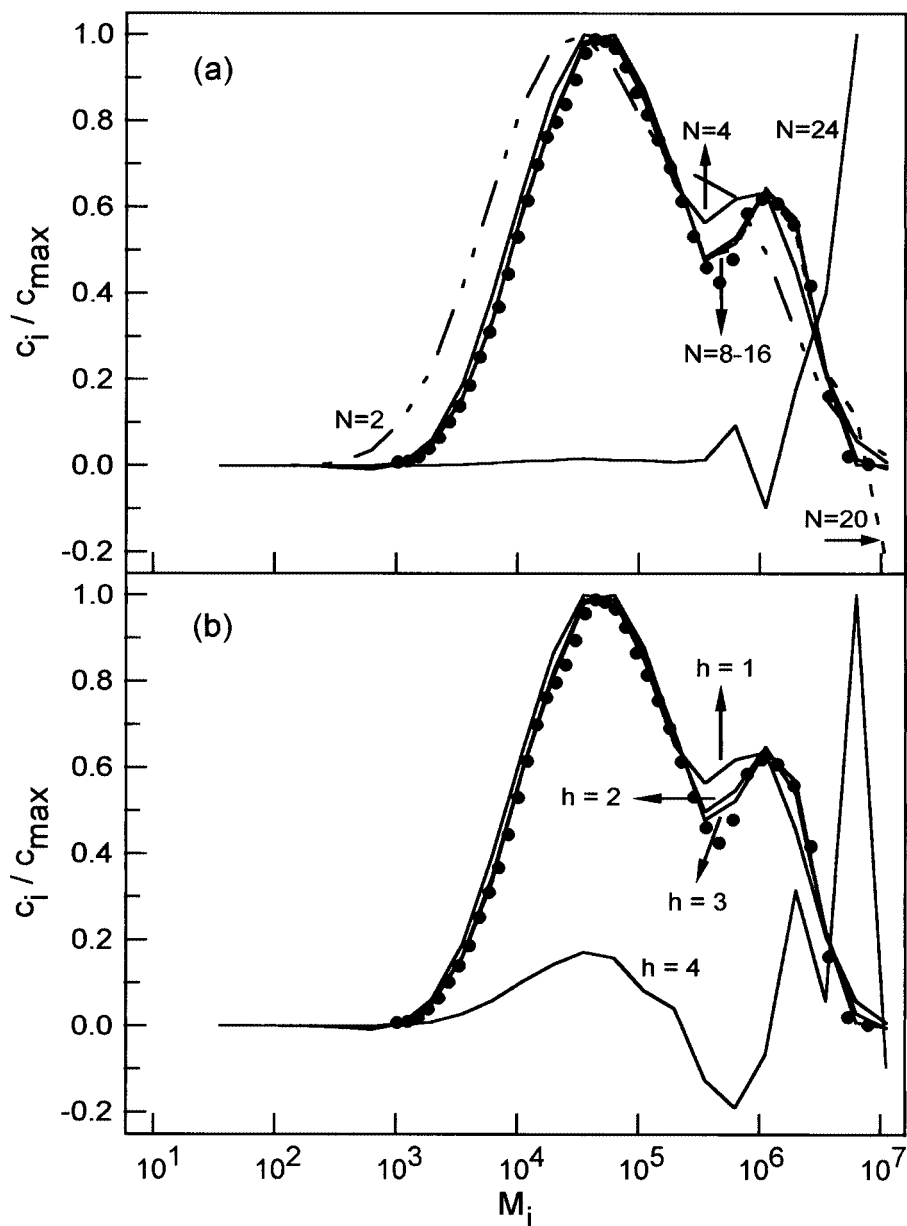


Fig. 2. Normalized chromatographic MWDs for M7, with (●) indicating experimental data. (a) Calculated MWDs as functions of Stehfest's parameter N . (b) Calculated MWDs as functions of Gaver's parameter h .

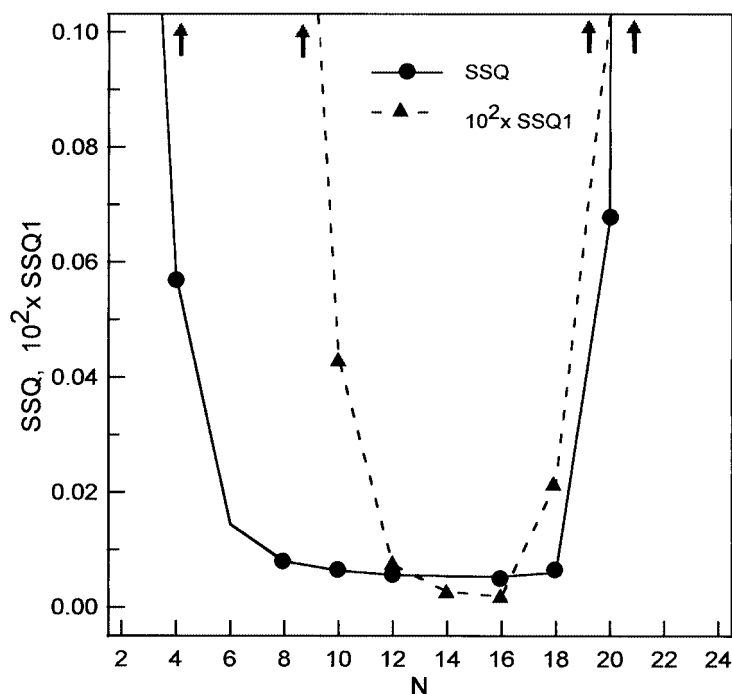
The same holds for h . This indicates that in the present example $N = 16$ and $h = 3$ are the best parameter values. The minimum values of SSQ are very similar for both inversion methods, indicating that both result in distributions of comparable quality. The use of Stehfest's formula, on the other hand, results in a smoother transition to the minimum value of SSQ1 than the one provided by Gaver's formula. This may be observed by comparing the curves in Figs. 3 and 4.

The same kind of analysis was performed starting from each one of the pgfs to recover the three types of distributions. A similar trend to the one shown in Figs. 3 and 4 was obtained when analyzing MWDn and MWDw predictions. In the case of MWDw and Stehfest's formula, a larger difference in the location of minimum SSQ and SSQ1 was observed. Nevertheless

the quality of the prediction was of the same order in both cases. In consequence, for cases where the real distribution is not known it seems reasonable to select the value of the curve for which SSQ1 reaches a minimum. Moreover, Stehfest's formula appears to be more robust than Gaver's formula because it provides a smoother transition to the minimum of SSQ1.

Next, we analyze which pgf is the best to employ in the recovery of each type of MWD. The following analysis is based on the assumption that no experimental information is available so SSQ1 is the only measure of goodness to be considered. Table 2 presents the minimum SSQ1 values obtained by using Stehfest's and Gaver's formulas for different polymers. We may observe in Table 2 that the lowest value in SSQ1—indicated in bold—is found when recovering each

Fig. 3. Influence of Stehfest's parameter N on parameters SSQ and $SSQ1$.



distribution from its own pgf and using Stehfest's formula. We discussed above that when comparing the recovered distributions with the experimental values, the minimum value reached for SSQ was of the same order of magnitude for either Stehfest's or Gaver's formula. However, Stehfest's formula gave a smoother transition to the minimum. This may be observed in Table 2, where for all cases Stehfest's formula results in a value of $SSQ1$ at the minimum that is at least an order of magnitude lower than the one given by Gaver's formula. This only indicates that the recovered curves are closer to each other when using Stehfest's formula. We found the same trends for all other polymers. In view of these findings, the optimum policy seems to be to recover each distribution from its own pgf, and use Stehfest's formula for the inversion step. We may also comment that when inverting pgfw reasonable recoveries of all types of MWDs are achieved. This may be important from a computational viewpoint. When calculating pgf from mass balances, pgfn must be calculated prior to pgfw, which in turn must be calculated before pgfc. This is so because a system of coupled equations results. The number of equations in the system doubles each time a new type of pgf is added to the unknowns. If computer storage and time are limited, one could calculate pgfn and pgfw only, since it is possible to obtain reasonable recoveries of all types of MWD from pgfw.

Figures 5 to 7 show the experimental number, weight and chromatographic distributions of the remaining polymers used in this work, compared to those obtained through inversion of the respective pgf using Stehfest's formula.

Figures 5a to c show the three types of distributions recovered for PE-1, which presents a polydispersity of 14. The inversion of the pgf was sensitive to special features of this distribution at the low molecular weight region. The quality of the recovery was excellent, taking into account that no experimental information except the rough molecular weight range was used to decide which were the best solutions. With respect to PE-2, which presents a shoulder in the high molecular weight tail, the recovery was done under the same conditions

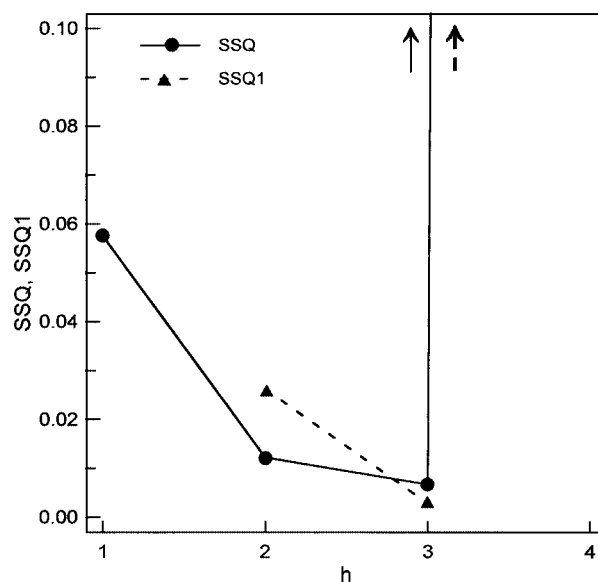


Fig. 4. Influence of Gaver's parameter h on SSQ and $SSQ1$.

Table 2. Minimum SSQ1 Values for M7 and Different Combinations of pgf and MWD Types.

To From	MWDn		MWDw		MWDc	
	SSQ1	N or h	SSQ1	N or h	SSQ1	N or h
pgfn (S)	7.10×10^{-4}	12	6.96×10^{-5}	14	1.22×10^{-3}	14
pgfn (G)	7.51×10^{-3}	3	2.35×10^{-3}	3	1.44×10^0	3
pgfw (S)	8.60×10^{-4}	22	5.41×10^{-5}	12	2.96×10^{-5}	14
pgfw(G)	3.66×10^{-3}	4	6.54×10^{-4}	3	5.08×10^{-3}	3
pgfc(S)	1.03×10^{-3}	24	9.38×10^{-5}	20	1.01×10^{-5}	16
pgfc(G)	1.40×10^{-2}	4	3.24×10^{-3}	3	2.93×10^{-3}	3

as in PE-1. It appears that MWDn is not predicted as well as the others (Figs. 5d to f), probably because of an experimental noise level that becomes more evident in Fig. 5e. In contrast, the calculated MWDc and MWDw (Figs. 5e and f) agreed very well with the experimental data.

Results presented in Figs. 6a to f show the potential of the method in recovering very polydisperse distributions. The agreement between all experimental and calculated distributions is very good for M2 and M3 polyethylenes, which present polydispersities of 69 and 23, respectively.

With respect to narrow distributions Figs. 7a to f present the results for PS-a and PS-b, two polystyrene calibration standards of polydispersity around 1.1. For both cases, excellent agreement between calculated and experimental distributions was obtained.

Setting the molecular weight range may result crucial to the success of the recovery procedure, especially for narrow distributions. The results shown in Figs. 5 and 6 were obtained assuming a wide molecular weight range ($1.45 < \log(M_i) < 7.10$). The calculated distributions shown in Fig. 7 for the polystyrene standards were obtained assuming $6.0 < \log(M_i) < 7.0$ for PS-a and $2.5 < \log(M_i) < 3.7$ for PS-b. These ranges were selected in view of our previous knowledge of the type of experimental distributions. If there is no previous information about the possible range of molecular weights, an iterative procedure must be followed as explained below. In the case of narrow distributions such as PS-a and PS-b the problem is more evident. Figure 8 shows the effect of the range on the calculated MWDc. For each range, 23 points of the distribution were evaluated. This requires the calculation of the pgf at up to 23N distinct values of the transformed variable z . Both for PS-a (Fig. 8a) and PS-b (Fig. 8b) we started with the maximum range for which the inversion method was implemented (\blacktriangle symbols). When comparing with the actual distributions, only around four \blacktriangle points lay on them, the others being outside the actual distribution ranges. As the range became more bounded, more and more calculated points fell on the actual distribution. It is surprising to find that the experimental distribution is recovered correctly from points calculated using different molecular weight ranges. When using an inappropriate range, computational effort is being wasted. That may become a particularly bad problem when calculating all pgf values from mass balances, which

are computationally expensive to evaluate. Similar results as those shown in Fig. 8 were obtained when analyzing the effect of the range using Gaver's formulas. In the latter case the pgf must be evaluated in up to $2^{h+1} \times 23$ values of z .

In all the cases presented up to this point the pgfs were calculated directly from actual experimental information, and were considered numerically noise-free even though the small numerical error associated with any ordinary algebraic calculation is present. If the pgfs had been obtained through mass balance calculations, they should have been noisier due to the larger inherent error involved in the numerical resolution of a system of equations. In order to estimate the influence of noise on the quality of the recovered MWD curves, we added different types of errors to the pgf. The maximum error at each z was set at 0.5% of the value of the clean pgf in all cases. We added errors that were all the same sign and whose absolute values either increased or decreased with z , both in a linear and an exponential fashion. No significant difference was found on the respective recovered MWDs when analyzed either in raw or in normalized form (ordinates are normalized to unity, abscissas are left unchanged). The same result was obtained when constant or bell-shaped errors were added to the pgfs. When a sign change was forced in the error added at one particular value of z , by use of a step function at $z=0.5$, again no significant change on the recovered normalized MWDs was observed. Finally, we solved several problems in single precision arithmetic, where there are at most 8 significant digits, and compared the results with those obtained with double precision arithmetic. The recovered MWDs had more extra sudden peaks in the case of single precision arithmetic, a feature that we also found when recovering MWD from pgf balances (19). This suggests that the inversion procedures are sensitive to roundoff error present in the pgf. This is the kind of error that may change sign from one point to the next. In order to further evaluate the sensitivity of the inversion method to this rapidly fluctuating type of error in the pgf transform solution, random noise was added to the clean pgfs at two levels: a maximum of 0.1% or 0.5% of the calculated clean values. Then we inverted the resulting pgfs using both inversion methods. In the remainder of the paper, "noisy" pgfs will be those with random noise added to them. Table 3 shows the optimum method parameters and the corresponding value of SSQ1 for both inversion methods

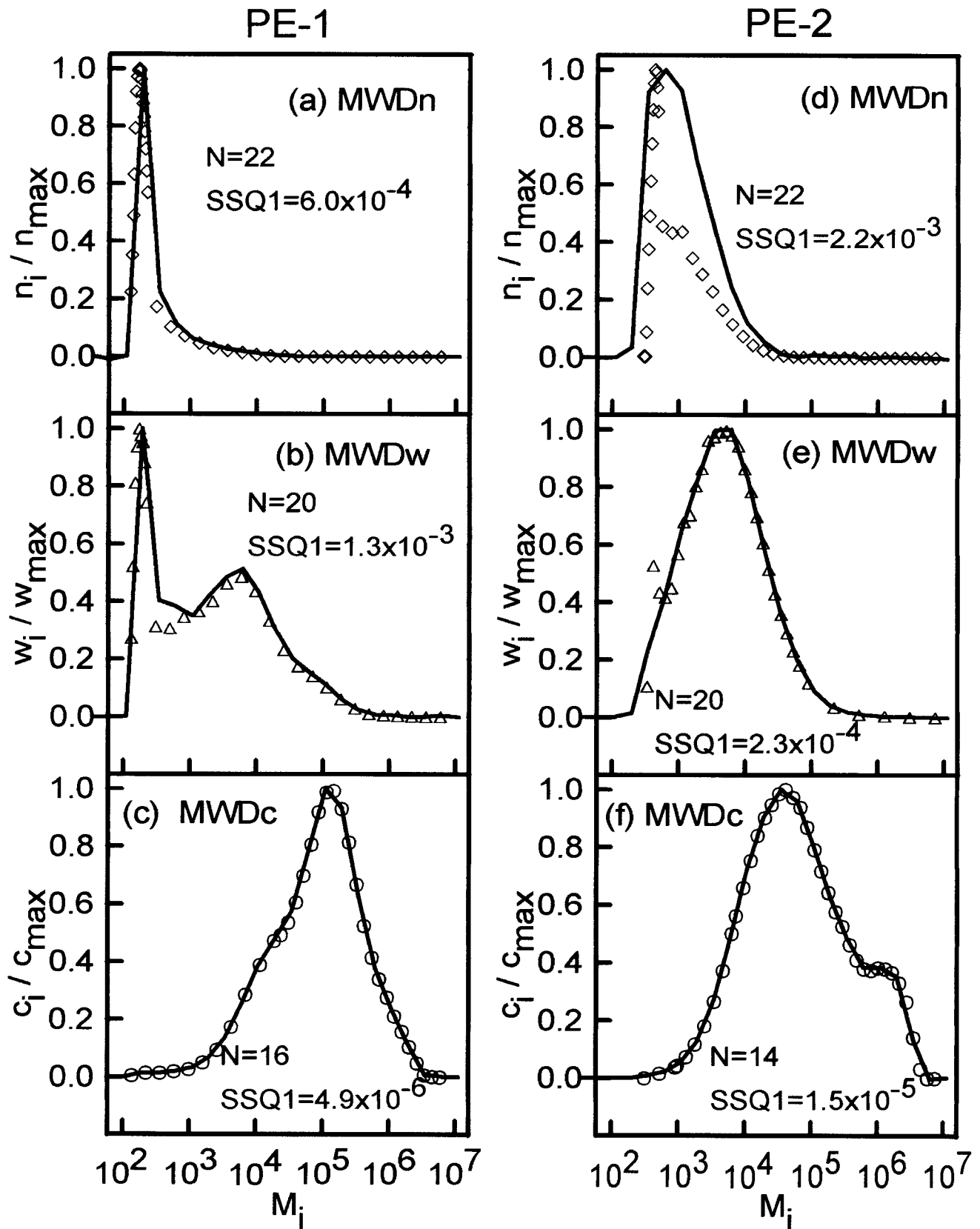


Fig. 5. Experimental (symbols) and optimum calculated (—) MWDs using Stehfest's method. (a) to (c) PE-1, (d) to (f) PE-2.

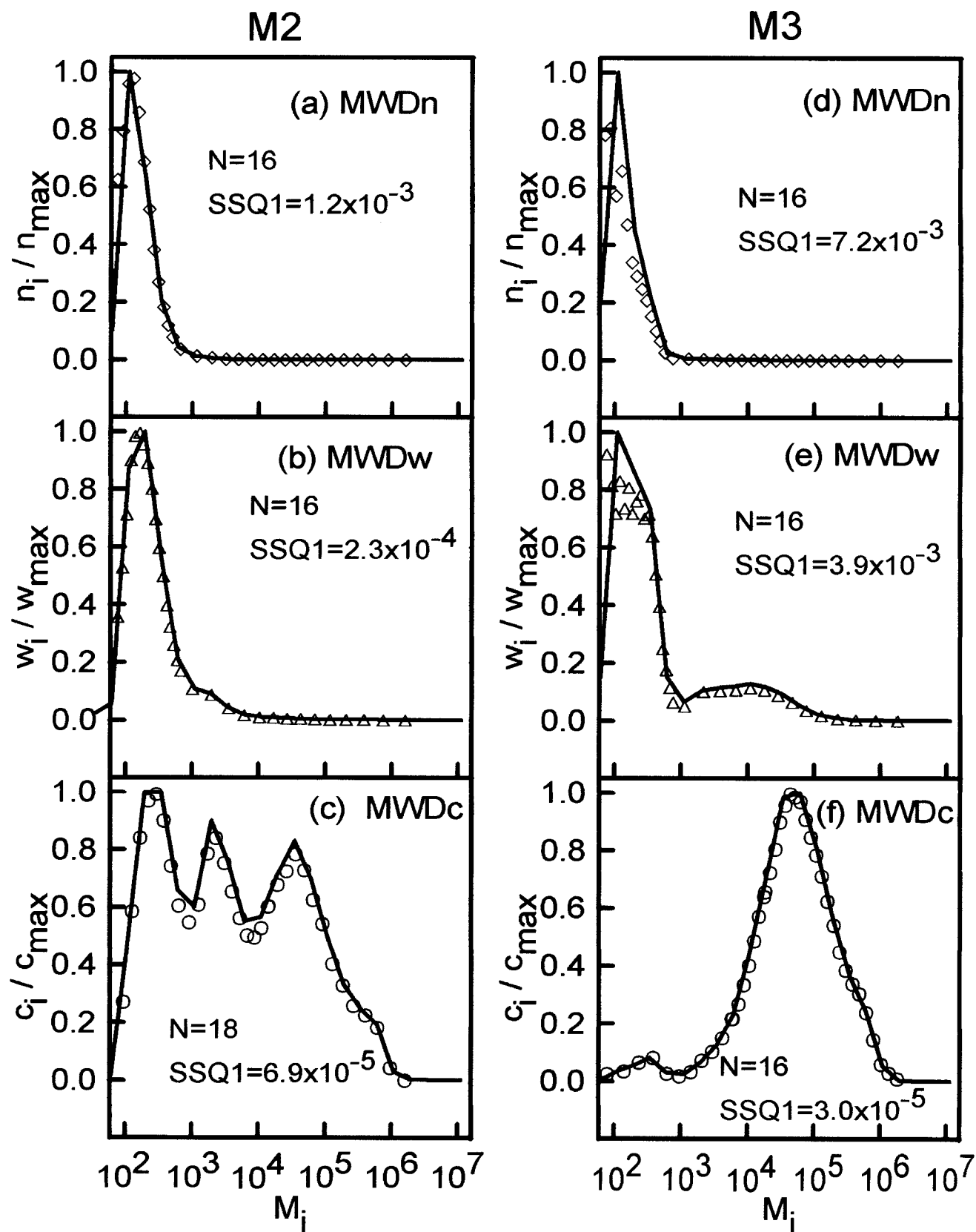


Fig. 6. Experimental (symbols) and optimum calculated (—) MWDs using Stehfest's method. (a) to (c) M2, (d) to (f) M3.

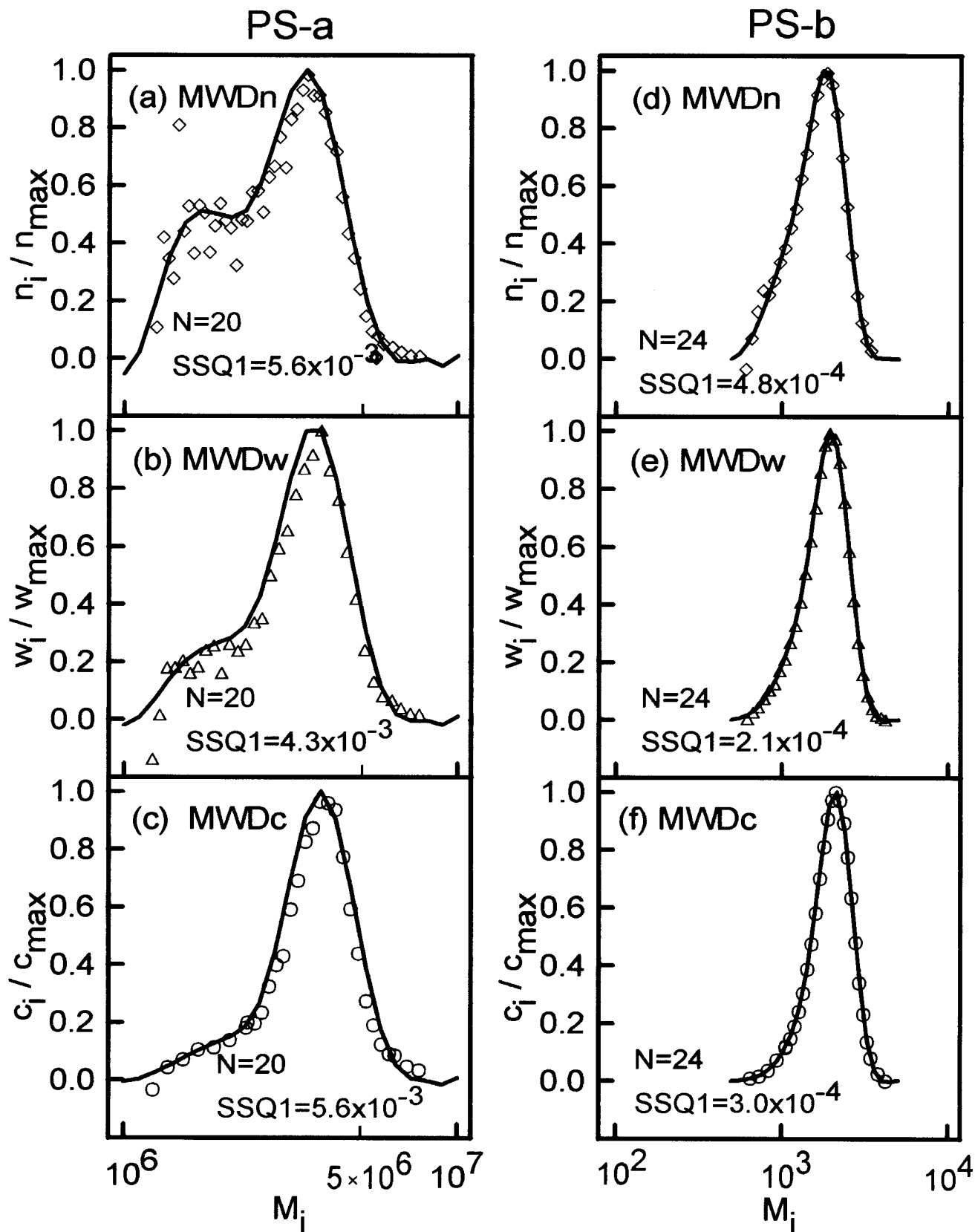


Fig. 7. Experimental (symbols) and optimum calculated (—) MWDs using Stehfest's method. (a) to (c) PS-a, (d) to (f) PS-b.

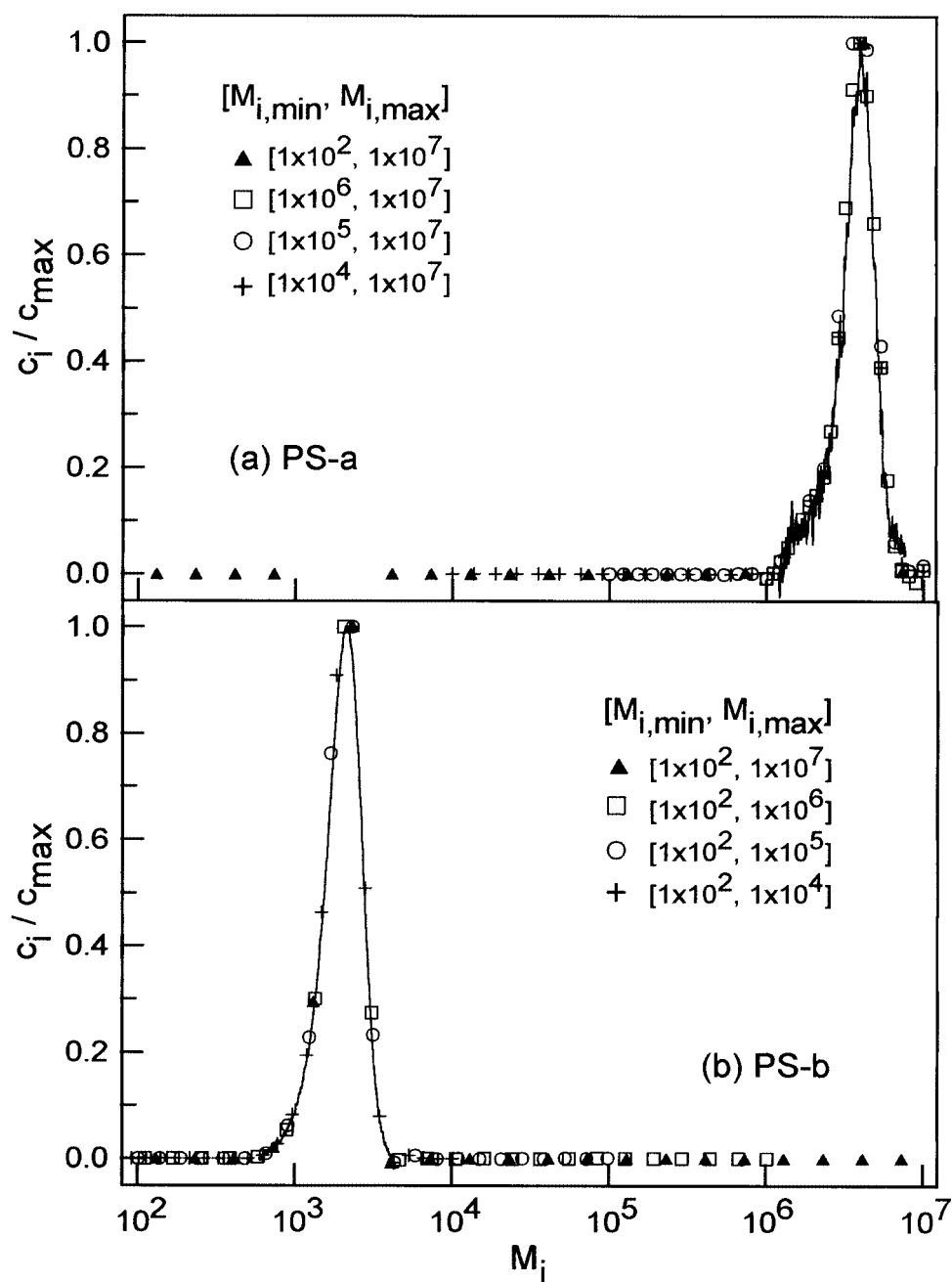


Fig. 8. Experimental (—) and optimum calculated (symbols) MWDs by Stehfest's method for different molecular weight ranges. (a) PS-a, (b) PS-b.

Table 3. Minimum SSQ1 Values for M7 Obtained With Clean and Noisy pgf.

Method	Error	MWDn		MWDw		MWDc	
	$\epsilon \times 100$	N or h	SSQ1	N or h	SSQ1	N or h	SSQ1
Stehfest	0.0	12	7.10×10^{-4}	12	5.40×10^{-5}	16	1.91×10^{-3}
	0.1	6	8.91×10^{-2}	6	6.91×10^{-2}	6	1.77×10^{-1}
	0.5	4	4.43×10^{-1}	4	3.07×10^{-1}	4	3.23×10^{-1}
Gaver	0.0	3	3.75×10^{-3}	3	6.50×10^{-4}	3	2.90×10^{-3}
	0.1	2	3.34×10^{-1}	2	3.91×10^{-1}	2	1.08×10^0
	0.5	2	3.44×10^0	2	5.63×10^0	3	6.21×10^0

when applied to clean and noisy pgfs corresponding to polymer M7. For both methods, the minimum SSQ1 sharply increases as the noise level grows. On the other hand, the values of the inversion parameters (N or h) suffer an important decrease. Similar conclusions may be drawn from the analysis of the other polymer samples.

For Stehfest's method, optimum N values for noisy pgf are much lower than those for the clean pgf. Nevertheless, in most cases it is possible to apply the minimum SSQ1 criterion. In several cases SSQ1 was an increasing function of N , so the optimum value was $N = 4$. Very stable solutions in the presence of noise were obtained with this particular value of N . As we already mentioned, the same results would be obtained with Gaver's formula and $h = 1$. As an example, the three types of distributions calculated in this way are shown in Figs. 9a to c for M7 and Stehfest's formula. Even though the solutions show minor "bumps," they reflect appropriately each one of the experimental MWDs.

For Gaver's method, it may be concluded that: a) if the pgfs are almost clean, the best values to recover the MWD are $h = 3$ or occasionally $h = 4$. This results from the application of the minimum SSQ1 criterion; b) if the pgf are noisy, SSQ1 becomes an increasing function of h . MWD obtained with $h = 2$ may be contaminated with important oscillations and in that case it would be preferable to use $h = 1$. Figures 10a to f include the results for M7 obtained using Gaver's formula. The minimum SSQ1 criterion gives as the optimum parameter $h = 2$ or $h = 3$ (Figs. 10a to c). Important oscillations appear when the level of noise increases. As $h = 1$ is not part of this selection, it is interesting to analyze the results obtained with this particular value. The recovered MWDs are shown in Figs. 10d to f. Very smooth curves are obtained this way, which reflect most of the experimental features of the MWD.

The comments on optimal parameters are applicable to all the polymer samples considered in this work.

CONCLUSIONS

This work provides a demonstration of the recovery of experimental MWD from probability generating functions. Two methods for the numerical inversion of Laplace transforms were adapted to be used with probability generating functions. Since Stehfest's formula gives a smoother transition to the best solution, it is easier to use in the MWD recovery than Gaver's formula, providing a more robust procedure to select the best solution for practical cases where the distribution is not known *a priori*. Nevertheless, the optimal solutions are of the same degree of accuracy when using either inversion method.

From the analysis presented in this work it seems that it is best to calculate each type of MWD from the inversion of the same type of pgf. If necessary, it is possible to obtain reasonable inversions of all MWD types from pgfw only.

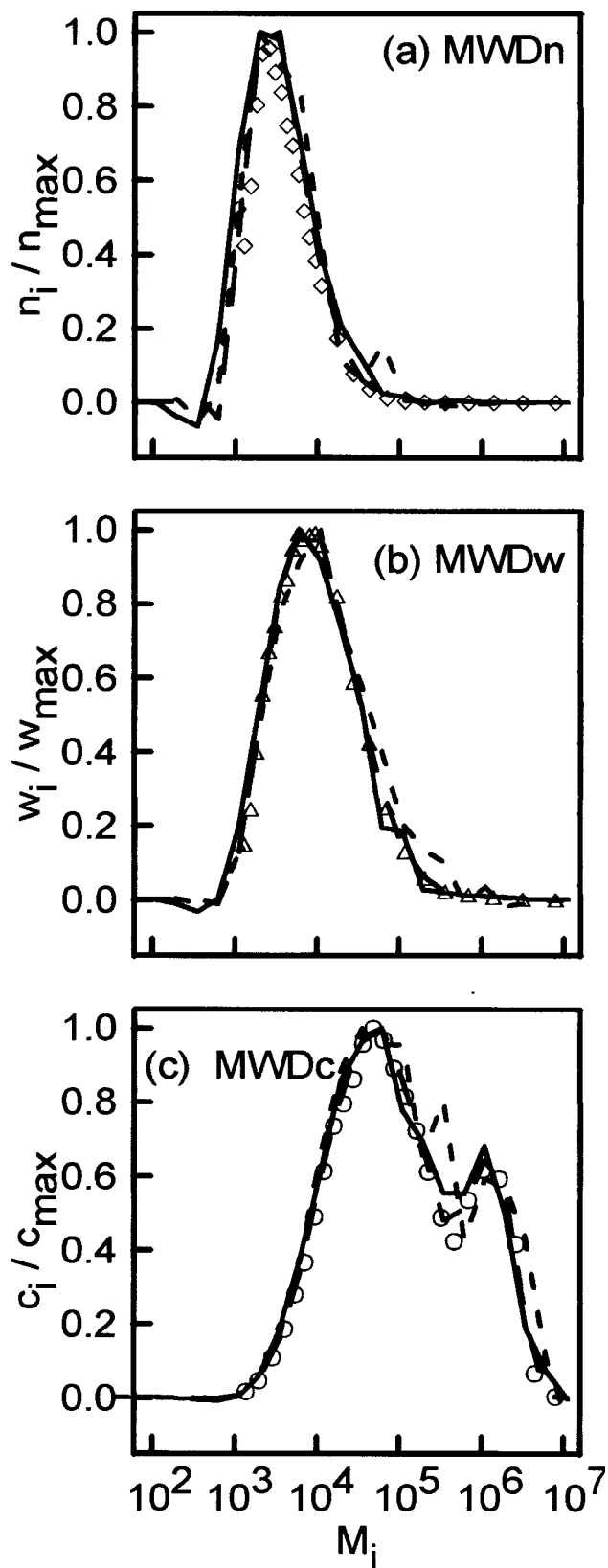


Fig. 9. Experimental (symbols) and optimum calculated (lines) MWDs for M7 using Stehfest's method for different levels of noise in the pgfs. $|\text{noise}| < \epsilon \cdot \text{pgf}$, where (—): $\epsilon = 0$, (---): $\epsilon = 0.001$, (.....): $\epsilon = 0.005$.

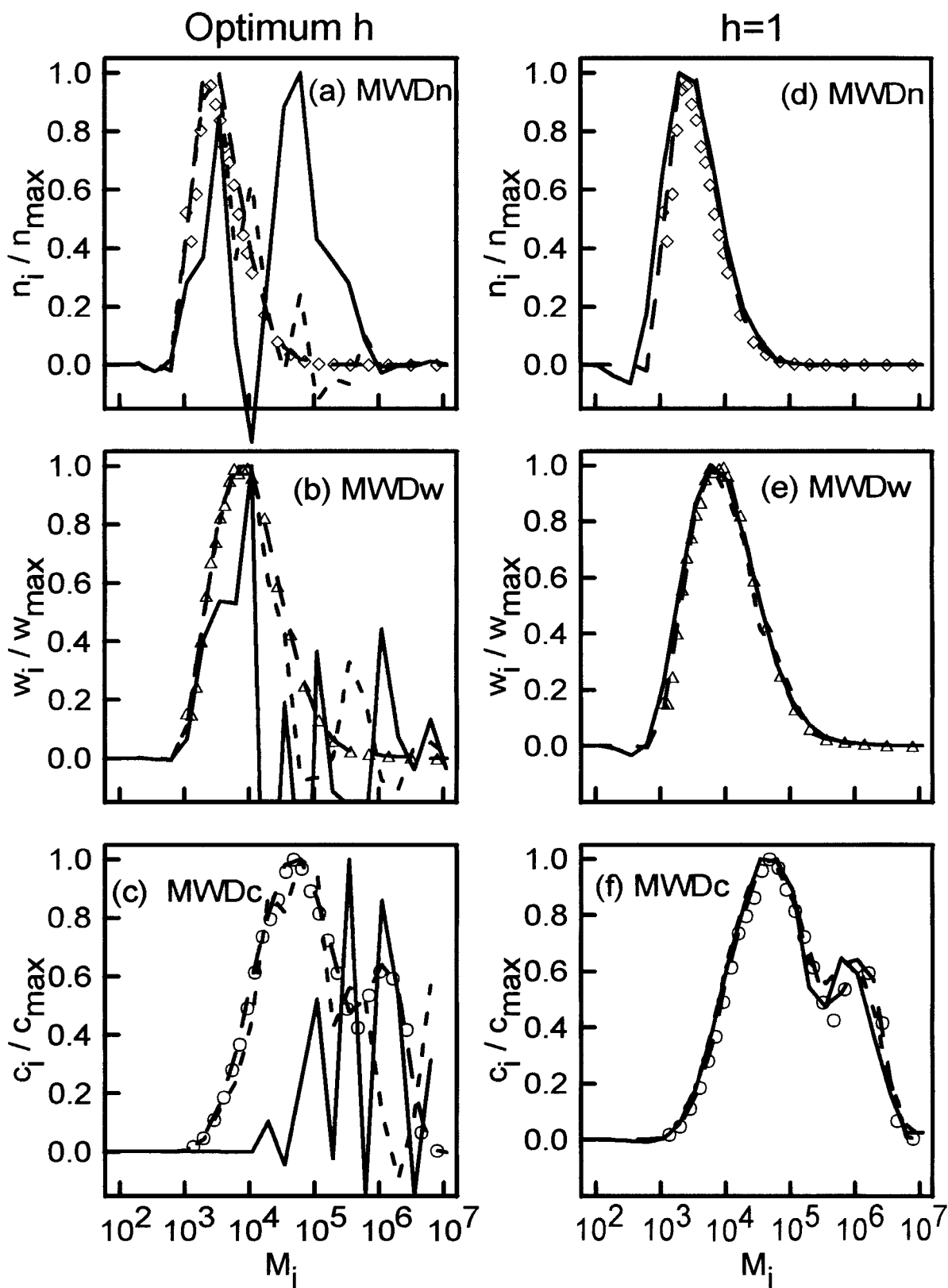


Fig. 10. Experimental (symbols) and calculated (lines) MWDs for M7 using Gaver's method for different levels of noise in the pgfs. $|\text{noise}| < \varepsilon \cdot \text{pgf}$, where (—): $\varepsilon = 0$, (---): $\varepsilon = 0.001$, (-.-): $\varepsilon = 0.005$. (a), (b) and (c) obtained with optimum values of h according to the SSQ1 criterion; (d), (e) and (f) obtained with $h = 1$.

The addition of noise to the original pgfs and the subsequent inversion of the noisy transforms show that rapidly fluctuating errors such as those produced by rounding off are the ones for which the inversion method is most sensitive. Error propagation must be carefully analyzed when starting the inversion from pgfs obtained through mass balance resolution. In the case of noisy pgfs good results are obtained using either Gaver's formula with $h = 1$ or Stehfest's formula with $N = 4$ or $N = 6$.

The results and conclusions presented in this paper may also be applied in the case of the inversion of Laplace transforms. The corresponding results, which are completely analogous to the ones for pgf transforms, were not presented here because of space limitations. The choice of transform to be used with a particular polymerization problem would depend on the mathematical form of the mass balances.

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