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Recovery of molecular weight distributions from transformed domains. Part II. Application of numerical inversion methods

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Abstract

This work is a part of a study aiming at developing tools for the prediction of complete molecular weight distributions (MWDs) of polymers at the exit of a reactor. This reactor may be a synthesis reactor or one used to modify a preexisting resin. In this work, we analyse the suitability of three methods for the numerical inversion of probability generating functions (pgfs), those due to Papoulis, de Hoog and Garbow. The three methods have been proposed in the literature for the inversion of Laplace transforms. We show how to adapt them to the problem at hand, and apply them to two situations. The first one is the recovery of experimentally measured MWDs, through a process that consists of finding the pgf of the distribution, numerically inverting it and comparing the result with the known MWD. The second one is to solve the pgf balances of polymerisation systems with known MWDs, and comparing those MWD with the ones that result from the inversion with the three methods. We discuss the relative advantages of each inversion method and propose guidelines for their proper use with unknown MWD functions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular weight distributions; Pgf transforms; Numerical inversion

1. Introduction

This is the second part of an investigation that aims at developing alternative tools for the calculation of molecular weight distributions (MWD) in reactive processes where polyolefins are either produced or modified. If one sets out to write mass balances and discriminates species by chain length, an infinitely large system of equations results. In Part I of this work [1] we review the techniques available to deal with infinite mass balances and present a detailed description of the use of probability generating functions (pgfs) for solving MWD both in polymerisation and post-reactor systems. The method results in a finite set of pgf balances, which must then be solved using either analytical or numerical methods. The pgf is really a transform technique, and when dealing with polymerisation systems the resulting transform function contains information on the complete MWD. An inversion step must follow in order to recover this MWD. If the system of pgf balances had to be solved numerically, as is usually the case with polymer systems, no analytical expression for the pgf is available, and a numerical inversion must be performed. We have already shown [2] that under certain conditions, pgf transforms are equivalent to the Laplace transform. For the latter, there is much work published on numerical inversion methods [3].

As part of this investigation, we have already performed an experimental validation of two numerical inversion methods [2], the ones proposed by Gaver [4] and Stehfest [5,6] for Laplace transforms. They were applied to recover the MWD from pgf transforms in low-density polyethylene autoclave reactors [7] with very promising results. However, they sometimes produce negative responses when the pgf is affected by numerical noise [2], and in a few of the cases analysed [7] they fail to reproduce accurately the complete MWD. In the latter situation it could not be determined whether the error was due to the inversion algorithm itself, to an inaccurate kinetic mechanism, to error propagation in the integration of the differential equations, or to experimental uncertainties. As Davies and Martin [3] recommend in their extensive review of Laplace transform inversion methods, it is convenient to use more than one method on an unknown function, to increase confidence in the results. This seems to be the only way to rule out the inversion algorithm as the source of inaccuracies in the predicted MWD.

Since the inversion methods are numerical, the MWD is recovered not as a continuous function but as a set of values at particular degrees of polymerisation. If one wants to change the degree of polymerisation (DP) at which the

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MWD should be calculated (to have more points, for example) both Gaver's and Stehfest's algorithms require evaluation of the pgf at different values of the independent variable. This means that as more points of the MWD are calculated, a larger system of pgf balances must be solved and inverted. There are other algorithms that do not present this drawback [3]. These facts encouraged us to continue testing other inversion methods.

In this work, we analyse the feasibility of applying some of those inversion methods for the special case of pgf transforms that describe MWD. Specifically, we study the methods developed by Papoulis [8], de Hoog [9] and Garbow et al. [10,11] to work with Laplace transforms. We implement Papoulis' algorithm in Fortran code. The other two algorithms are used as implemented in commercial software [12]. First, we perform a validation of the inversion methods using measured polymer MWDs covering a wide range of polydispersities. We start from these MWD, transform them, and then apply the numerical techniques to try to recover the distribution. We use 'clean' transformed distributions as well as others where noise has been incorporated, with the aim of simulating the uncertainty in the transformed domain that would result from numerical calculation. We develop techniques to tune the performance of the inversion methods with this special kind of functions (MWD), and also determine their accuracy. All the methods studied here, as well as the two previously presented, require the user to fix the value of some arbitrary parameters, which turn out to be crucial to obtain appropriate results. We discuss the quality of the recovered distributions and suggest guidelines for establishing the reliability of a given solution. We also make a comparative analysis between all the considered methods.

As a further test we apply the validated methods to calculate MWD from polymerisation reaction mass balances, solving some examples presented by Miller et al. [13]. The pgf balances for those examples were developed in Part I of this work [1].

2. Adaptation of inversion algorithms for the Laplace transform for the recovery of MWDs described by pgf

In general, $F(s) = \int_0^\infty \mathrm{e}^{-st} f(t)\mathrm{d}t$ is the well known Laplace transform of a function $f(t)$.

MWDs are discrete functions that can be considered as periodic impulse functions of period one. At this point, this type of distribution may be considered as a generic function $f(t)$. The independent variable t represents the DP; the dependent variable could be any quantity representing number or mass of molecules with a given DP. The corresponding Laplace transform is given by Eq. (1), where $f(t)$ stands for the periodic function.

$$F(s) = \sum_{t=0}^{\infty} \mathrm{e}^{-st} f(t) \tag{1}$$

On the other hand, Eq. (2) defines the pgf for discrete functions.

$$\phi_{N,a}(z) = \sum_{t=0}^{\infty} z^t P_a(N = t) \qquad a = 0, 1, 2 \tag{2}$$

where $P_a(N = t)$ represents the probability of an event t. Subscript a indicates the type of probability [1], as indicated later. In the case of the MWD, $P_a(N = t)$ would be the probability that the DP of a molecule is t (DP $= t$). This probability could be the number ($a = 0$), weight ($a = 1$) or chromatographic ($a = 2$) fraction of molecules with DP t. By chromatographic we mean that the quantity of interest is the weight times the molecular weight.

We have already shown [2] that, with the appropriate variable change, the pgf is equivalent to the Laplace transform of the MWD. If we look at their definitions (Eqs. (1) and (2)), if $f(t)$ is the same as $P_a(N = t)$ the equivalence is obtained when $z = \mathrm{e}^{-s}$. This equivalence allows the use of the same inversion techniques on Laplace and pgf transforms to recover the original, untransformed functions.

In what follows, we proceed to describe the three inversion algorithms analysed in this work. We also describe our findings on how to use them in order to obtain a good recovery of the MWD.

2.1. Papoulis' inversion method [8]

This method consists of approximating the unknown function $f(t)$ as a weighted sum of orthogonal polynomials.

$$f(t) = \sum_{n=0}^{N} a_n P_{2n}(\mathrm{e}^{-rt}) \tag{3}$$

where a_n are constant coefficients, N indicates the number of terms in the sum and $P_{2n}(x)$ are Legendre polynomials of degree $2n$. These polynomials can be calculated with the recursive formula given in Eq. (4), where $x = \mathrm{e}^{-rt}$

$$\begin{aligned} &P_0(x) = 1, \qquad P_1(x) = x \\ &(n+1)P_{n+1}(x) = (2n+1)xP_n(x) - nP_{n-1}(x) \end{aligned} \tag{4}$$

It must be noted that r is a parameter whose selection determines at which points the transform of $f(t)$ must be calculated during the inversion procedure, as shown later. A proper choice of parameter r is required for an accurate inversion.

Taking the Laplace transform $F(s)$ of Eq. (3), and setting the transform variable at the values $s = (2k + 1)r$ with $k = 0, 1, \ldots, N$, the following expression is obtained:

$$rF((2k+1)r) = \sum_{m=0}^{k} \frac{(k-m+1)_m}{2(k+1/2)_{m+1}} a_m \qquad k = 0, 1, \ldots, N \tag{5}$$

where the terms in parentheses at the right hand side of Eq. (5) may be written in generic form as $(j)_l$, and

calculated as follows:

$$(j)_l = \begin{cases} 1 & l = 0 \\ j(j+1)\cdots(j+l-1) & l > 0 \end{cases} \quad (6)$$

From the generic expression in Eq. (5) a system of $N+1$ linear equations is obtained, from which the a_n can be readily solved. The values of the Laplace transforms are the only required data for the calculation of the a_n, since these coefficients depend on the Laplace transform and the parameter r, but not on t. Thus, the whole $f(t)$ can be recovered with a single set of transform values, provided the parameter r is not changed. This feature can save a considerable amount of time when the transform evaluation is time-consuming. Papoulis [8] does not give examples of application of the method. Davies and Martin [3] tested this method among others, covering a wide range of different classical analytical functions, with varying results. According to their results, the method we selected was the most accurate, especially with distribution-type functions. However, Davies and Martin [3] used a small range of the independent variable t in their analysis: from 1 to 30. In MWD functions the independent variable covers a much wider range, which can easily span five orders of magnitude. This fact causes difficulties, especially when assigning suitable values to the parameters.

For our work, we implement the algorithm in double precision Fortran code. Each time $F(s)$ is required by the algorithm, the pgf evaluated at $z = e^{-s}$ must be provided. As explained before, this method requires the user to specify the values of parameters N and r. The unknown function $f(t) = \mathrm{MWD(DP)}$ is obtained from the transform domain by using values of the transform function at a series of equidistant points s_k, determined by r:

$$s_k = (2k+1)r \qquad k = 0, \ldots, N \quad (7)$$

Besides, r also weighs the value of the independent variable t when evaluating the Legendre polynomials in Eq. (4). An inappropriate value of r will cause the inversion formula to fail. In his work, Papoulis suggests calculating r from

$$e^{-rT} = \frac{1}{2} \quad (8)$$

where $0 < t < T$ is the interval in which $f(t)$ is to be recovered. Papoulis also mentions that if $f(t)$ is needed near the origin or for large values of t, $f(t)$ must be evaluated with different values of r. The latter is our situation, for values of the untransformed variable near and far from the origin correspond to low and high molecular weights, respectively, in an MWD.

In agreement with the comments made by Papoulis [8], our results show that a single value of r (calculated from Eq. (8)) is not adequate for the recovery of MWD(DP) for both small and large values of DP (DP = 1–300 000). In view of this result, we divided the DP range in a series of T_i (where T_i is the maximum DP value in the interval), and used a different value of r in each one of them. To recover MWD(DP) for DP between T_i and T_{i+1}, we calculated r_{i+1} with Eq. (8) and also with a variation of it, which also proved to be effective:

$$e^{-2rT} = \frac{1}{2} \quad (9)$$

In both expressions, we set $T = T_{i+1}$. We will show results with the DP range divided into six, 12 and 24 intervals. It must be remembered, however, that increasing the number of different values of r increases the number of transform evaluations needed.

Parameter N determines the number of terms to use in the summation in Eq. (3). Too small a value of N results in poor accuracy in the calculation of MWD(DP), but too large a value introduces noise due to error propagation. For the cases we tried, the system of equations from which the a_n are calculated became ill-conditioned for large values of N. The goodness of the solutions for the methods depends on the value of N. For this reason it is important to develop guidelines for the choice of N.

In the search of guidelines, it was necessary to quantify the error made in the recovery of particular MWDs. For this purpose two measures of error were evaluated. When experimental MWD are available for comparison, we defined SSQ as the sum of the squared differences between the true and the recovered MWDs, as indicated in Eq. (10)

$$\mathrm{SSQ} = \sum_{j=1}^{n_p} (x_{N,\mathrm{DP}_j} - y_{\mathrm{DP}_j})^2 \quad (10)$$

where n_p is the total number of DP points at which the distribution is being recovered; x and y are the calculated and true MWD in number ($\mathrm{MWD_n}$), weight ($\mathrm{MWD_w}$) or chromatographic ($\mathrm{MWD_c}$) basis.

A different measure of error is used for the situations where no experimental MWD is available for comparison. It is the sum of the squared differences between two curves calculated with successive values of N:

$$\mathrm{SSQ1} = \sum_{j=1}^{n_p} (x_{N,\mathrm{DP}_j} - y_{N+1,\mathrm{DP}_j})^2. \quad (11)$$

2.2. de Hoog's inversion method [9]

In this case, the computation of the inverse Laplace transform is based on the application of the epsilon algorithm [14] to the complex Fourier series obtained as a discrete approximation to the inversion integral. The initial algorithm was proposed by Crump [15] but was significantly improved by de Hoog et al. [9]. Given a complex-valued transform $F(s)$, the trapezoidal rule gives the

following approximation to the inverse transform:

$$f(t) = (\mathrm{e}^{\sigma t/T})\mathscr{R}\left\{\frac{1}{2}F(\alpha) + \sum_{k=1}^{\infty} F\left(\alpha + \frac{ik\pi}{T}\right)\exp\left(\frac{ik\pi t}{T}\right)\right\} \tag{12}$$

where $\mathscr{R}\{\ \}$ is the real part of the sum of a complex power series in $\exp(i\pi t/T)$, and T is the period. The algorithm accelerates the convergence of the partial sums of this power series by using the epsilon algorithm [14] to compute the corresponding diagonal Pade approximants. The algorithm attempts to choose the order of the Pade approximant to obtain the specified relative accuracy (ε) while not exceeding the maximum number of function evaluations allowed. The parameter α is an estimate for the maximum of the real parts of the singularities of F. An incorrect choice of α may give false convergence. Even in cases where the correct value of α is unknown, the algorithm will attempt to estimate an acceptable value.

In the original version of the method by Crump [15], the algorithm was tested with three analytical functions with accurate results. A small range of the independent variable was used: from 1 to 10. For the MWD recovery, we employ the algorithm implemented in the IMSL [12] subroutine DINLAP, which requires the user to specify the desired relative accuracy, the parameter α and the maximum number of iterations allowed ($k_{\max}$). Whenever the algorithm requires $F(s)$ the value of pgf evaluated at $z = \mathrm{e}^{-s}$ must be provided.

Parameter α of this method cannot be calculated if the analytical transform of the function to be recovered is not available. In this case, its value must be set to 0, as advised in Ref. [12]. This is our case, and it seems important to say that this will also be the case in the final application of the inversion methods, where the transforms are obtained through integration of the mass balance. The maximum number of iterations ($k_{\max}$) does not affect the quality of the inversion, it just determines the size of the problem to be solved. The user must specify the only remaining parameter, the relative accuracy. Its value will affect the quality of the inversion.

Preliminary numerical experiments with different polymer MWDs indicated that a high value of the relative tolerance led to inaccurate inversions. This is not surprising, but we also found that small values also led to unsatisfactory results. In order to select an appropriate value, a procedure equivalent to the one used to select N in Papoulis' method was followed. Fifteen values of the relative accuracy were considered, covering the range from 5×10^{-3} to 1×10^{-6}. The range and the number of different values of the parameter were selected after a trial and error procedure.

2.3. Garbow's inversion method [10,11]

The computation of the inverse Laplace transform is based on a modification of Weeks' method [16] due to Garbow et al. [10,11]. This method is suitable when $f(t)$ has continuous derivatives of all orders on $[0,\infty)$. It is especially efficient when multiple function values are desired. In particular, given a complex-valued function $F(s)$, we can expand f in a Laguerre series whose coefficients are determined by F. This is fully described in Garbow [10,11] and Lyness and Giunta [17].

The algorithm attempts to return approximations $g(t)$ to $f(t)$ satisfying

$$\left|\frac{g(t) - f(t)}{\mathrm{e}^{\sigma t}}\right| < \varepsilon \tag{13}$$

where ε is the specified relative accuracy and $\sigma > \sigma_0$. σ_0 is the maximum of the real parts of the singularities of F. The expression on the left is called the pseudo error.

The first step in the method is to transform F to ϕ where

$$\phi(\zeta) = \frac{b}{1-\zeta}F\left(\frac{b}{1-\zeta} - \frac{b}{2} + \sigma\right) \tag{14}$$

In this expression, b is one of the algorithm's parameters. Then, if f is smooth, it is known that ϕ is analytic in the unit circle of the complex plane and hence has a Taylor series expansion

$$\phi(\zeta) = \sum_{l=0}^{\infty} a_l \zeta^l \tag{15}$$

which converges for all ζ whose absolute value is less than the radius of convergence R_c.

The coefficients of the Taylor series for f can be used to expand f in a Laguerre series

$$f(t) = \mathrm{e}^{\sigma t}\sum_{l=0}^{\infty} a_l\, \mathrm{e}^{-bt/2} L_l(bt) \tag{16}$$

In the original work [10,11], the algorithm was analysed by means of tests similar to those found in the work by Davies and Martin [3]. The authors mention (without quantifying) that for continuous functions their method gives results of comparable accuracy to those tested by Davies and Martin [3] but with much less computational effort. This method, however, presents poor results with discontinuous functions. The independent variable ranged from 1 to 30 in their work in order to agree with the examples given by Davies and Martin.

Here, we employed the algorithm implemented in the IMSL [12] subroutine DS2NLP, which requires the user to specify the value of ε, b, σ, σ_0 and m_{top}. With respect to $F(s)$ it is provided as the pgf evaluated at $z = \mathrm{e}^{-s}$, as in the other methods.

Parameter σ_0 of this method is equivalent to parameter α of de Hoog's method, and it must be also set to 0 if its actual value is unknown. The treatment of the remaining ones is explained later.

Table 1
SSQ values for MWD calculation with Papoulis' method

N	From pgf_n			From pgf_w			From pgf_c		
	MWD_n	MWD_w	MWD_c	MWD_n	MWD_w	MWD_c	MWD_n	MWD_w	MWD_c
11	**0.04338**	5.19301	6.44747	0.81663	**0.00647**	3.99794	6.76166	0.88829	**0.01134**
12	**0.04242**	5.25655	6.38695	0.18215	**0.00801**	4.69391	70.15241	0.15895	**0.00933**
13	**0.04096**	4.53500	11.94266	1.29358	**0.00586**	2.90307	3.22641	1.40775	**0.00602**
14	**0.04897**	30.60128	105.43150	2.24979	**0.00558**	11.71067	15.41539	2.09531	**0.00881**
15	**0.04807**	4.52860	8.57361	1.21358	**0.00498**	3.88632	3.17534	1.04186	**0.00416**
16	**0.05164**	4.74645	6.93323	0.41424	**0.00520**	4.23584	10.29978	0.23519	**0.00350**
17	**0.05311**	3.99048	6.25733	1.44903	**0.00506**	4.01037	6.36853	0.83347	**0.02403**
18	**0.06241**	10.35842	9.53245	1.44242	**0.00516**	4.65685	3.20439	1.32578	**1.23295**
19	**0.05477**	19.01860	114.60260	2.46592	**0.05840**	10.79333	534.35400	1.26652	**4.39494**
20	**0.08449**	875.36770	1.05×10^8	1.27037	**1.66207**	2.9×10^4	3.38171	0.90609	**872.09100**

2.3.1. Parameters b and σ

Garbow et al. [10,11] suggest calculation of these parameters in the following way:

$$\sigma - \sigma_0 = \frac{3}{T} \tag{17}$$

and

$$b = 2.5(\sigma - \sigma_0) \tag{18}$$

where $0 \le t \le T$.

Due to the wide range of DP in the function MWD(DP), this suggestion does not work properly. Completely erroneous MWD are predicted in this way. To solve this problem, the DP interval was subdivided and the parameters were calculated in each subinterval in the following fashion

$$\sigma_i - \sigma_0 = \frac{3}{T_i} \tag{19}$$

and

$$b_i = 2.5(\sigma_i - \sigma_0) \tag{20}$$

where

$$cT_{i-1} < \mathrm{DP} \le cT_i \tag{21}$$

and

$$T_i = 10^{-0.15+(0.25a)i} \tag{22}$$

From numerical simulations we found $c = 0.6$ and $a = 4$ to be suitable choices for most cases.

2.3.2. Parameters ε and m_{top}

Parameter m_{top} is required for the method to provide an upper limit to the summation of the Laguerre expansion [12]. As $k_{\max}$ in de Hoog's method, m_{top} determines the size of the problem and has no influence in the performance of the algorithm. With respect to ε, the minimum value that allows convergence appears to be a good choice. Here we used values ranging from 1×10^{-5} to 1×10^{-7}.

2.4. Method used for experimental validation

Five polyethylenes (PE1, PE2, M2, M3, M7) and two polystyrenes (PS4, PS8) of very different MWDs were used to carry out the experimental validation. The polydispersity of the various samples ranged from 1.1 to 69. These samples are the same used to validate other inversion methods reported in Brandolin et al. [2].

MWDs of the polymer samples were obtained by size exclusion chromatography (SEC) in a Waters 150C, according to standard procedures for each type of polymer.

The measured average molecular weights were reported in a previous work [2], while measured MWDs are shown in Section 3. These distributions are expressed mostly in chromatographic basis (MWD_c). The distributions are also expressed in number (MWD_n) or weight basis (MWD_w). The number (n_i), weight (w_i) and chromatographic (c_i) fractions of molecules in the ith fraction of the chromatogram are obtained by manipulation of measured data as reported elsewhere [2].

To calculate the pgfs of number, weight and chromatographic distributions Eqs. (23)–(25) were employed. These are an adaptation of Eq. (2) to the experimental distributions. Here, and from now on, the untransformed variable t of Eq. (2) is the chain length or degree of polymerisation, DP.

$$\phi_{N,0}(z) = \sum_{i=1}^{i_{\max}} n_{\mathrm{DP}_1+i-1} z^{\mathrm{DP}_1+i-1} \tag{23}$$

$$\phi_{N,1}(z) = \sum_{i=1}^{i_{\max}} w_{\mathrm{DP}_1+i-1} z^{\mathrm{DP}_1+i-1} \tag{24}$$

$$\phi_{N,2}(z) = \sum_{i=1}^{i_{\max}} c_{\mathrm{DP}_1+i-1} z^{\mathrm{DP}_1+i-1} \tag{25}$$

To accomplish the summations indicated in Eqs. (23)–(25) it was necessary to evaluate the distributions beginning at the lowest available DP (DP_1) and advance with

Table 2
SSQ values obtained at the value of N at which either SSQ1 or SSQ is minimum, for different interval partitions

MWD	SSQ	$N_{SSQ1_{min}}$	SSQ_{min}	$N_{SSQ_{min}}$
$i_{max} = 6$				
Number	0.05311	17	0.04096	13
Weight	0.00506	17	0.00498	15
Chromatographic	0.00933	12	0.00350	16
$i_{max} = 12$				
Number	0.05127	15	0.04980	14
Weight	0.00231	17	0.00231	17
Chromatographic	0.00880	15	0.00552	15
$i_{max} = 24$				
Number	0.06854	17	0.05109	13
Weight	0.00226	17	0.00167	14
Chromatographic	0.00908	15	0.00338	12
$i_{max} = 24'$				
Number	0.06467	16	0.04929	9
Weight	0.00227	16	0.00180	13
Chromatographic	0.00583	16	0.00491	9

step one up to $DP_1 + i_{max} - 1$. Cubic splines [18] were applied to the experimental data to obtain all the information needed to calculate Eqs. (23)–(25).

It is always possible to go from one type of MWD (MWD_n, MWD_w or MWD_c) to any one of the other two by direct calculation. Thus, we not only recovered each MWD from its own transform, but also calculated it by manipulating the inversions of the other two. All calculated values were then compared with the experimental data. This comparison was carried out using as index the value of SSQ (Eq. (10)).

3. Results and discussion

3.1. Experimental validation

3.1.1. Papoulis' inversion method

First we analysed which pgf is the best to employ in the recovery of each type of MWD. Table 1 shows the values of SSQ that result when MWD_n, MWD_w and MWD_c are obtained from each pgf in the case of polyethylene M7. The remaining polymers present equivalent results. For these results, the DP interval was divided into six parts in the following way:

$$T_i = 10^{-0.15+(0.25a)i} \qquad i = 1, 2, \ldots, i_{top} = 6 \;\; a = \frac{24}{i_{top}} \quad (26)$$

Similar behaviours are observed when the interval is divided in 12 or 24 parts (setting the range of variable i from 1 to 12 or from 1 to 24 in Eq. (26), respectively).

It may be observed that lower errors are obtained when each distribution is recovered from its corresponding pgf.

The values in Table 1 also show that different errors are obtained with different values of N. If the experimental distribution is not known, as is the case when the transform is obtained from a polymerisation model, it is necessary to have an approach to select a good value of N.

In a previous work by the authors [2], other methods for the numerical inversion of Laplace transforms were studied. These methods were similar to the one by Papoulis in that they also performed a sum were the number of terms (N) had to be determined. The same approach that was suggested there for the estimation of an optimum N is used here: performing the inversion for different values of N, and then selecting the curve that presents the lowest SSQ1 (Eq. (11)).

Table 2 shows the results obtained with this procedure for six, 12 and 24 partitions of the interval, when inverting MWDs of polyethylene M7 (each MWD is recovered from its corresponding pgf). The numbers under the $24'$ were obtained using Eq. (8) to calculate r. For the other cases, Eq. (9) was used.

The columns labelled $SSQ1_{min}$ give the values of the selected Ns and the SSQ of the curves obtained with them. The columns labelled SSQ_{min} give the value of N for which the lowest SSQ results, and this SSQ value.

It can be observed that the selected N is generally different from the actual optimum N. However, the SSQ corresponding to the selected N is similar to the lowest SSQ. This means that the procedure to select N gives a good value of this parameter. The values of N that cause important errors are eliminated in this way.

It may also be observed that there appears to be no differences in the accuracy of the inversions when the interval is divided into six, 12 or 24 subintervals, nor with the equation selected to calculate r, for similar SSQ values are obtained in these situations.

Figs. 1 and 2 show the MWDs of the six different polymers, calculated with the above technique (▲ symbols), compared with the respective measured MWD (lines).

3.1.2. de Hoog's inversion method

As in the analysis of the previous method, one must find out from which type of pgf (number, weight or chromatographic) is it better to recover each type of MWD. For polymers M2, M3, PE1 and PE2 only when inverting from the pgf_c the method converges with values of the relative accuracy less than 1×10^{-4}. Besides, the SSQ1 method for selecting the optimum relative accuracy fails when working with pgf_n and pgf_w. On the other hand, the SSQ1 method works well with the pgf_c of all polymers. This implies that pgf_c should be used with this method for recovering the three types of distributions from the transform domain.

Table 3 shows the results obtained for polymer M7. Figs. 1 and 2 show the MWDs of the six different polymers calculated with the above technique (○ symbols) compared with the measured ones (lines).

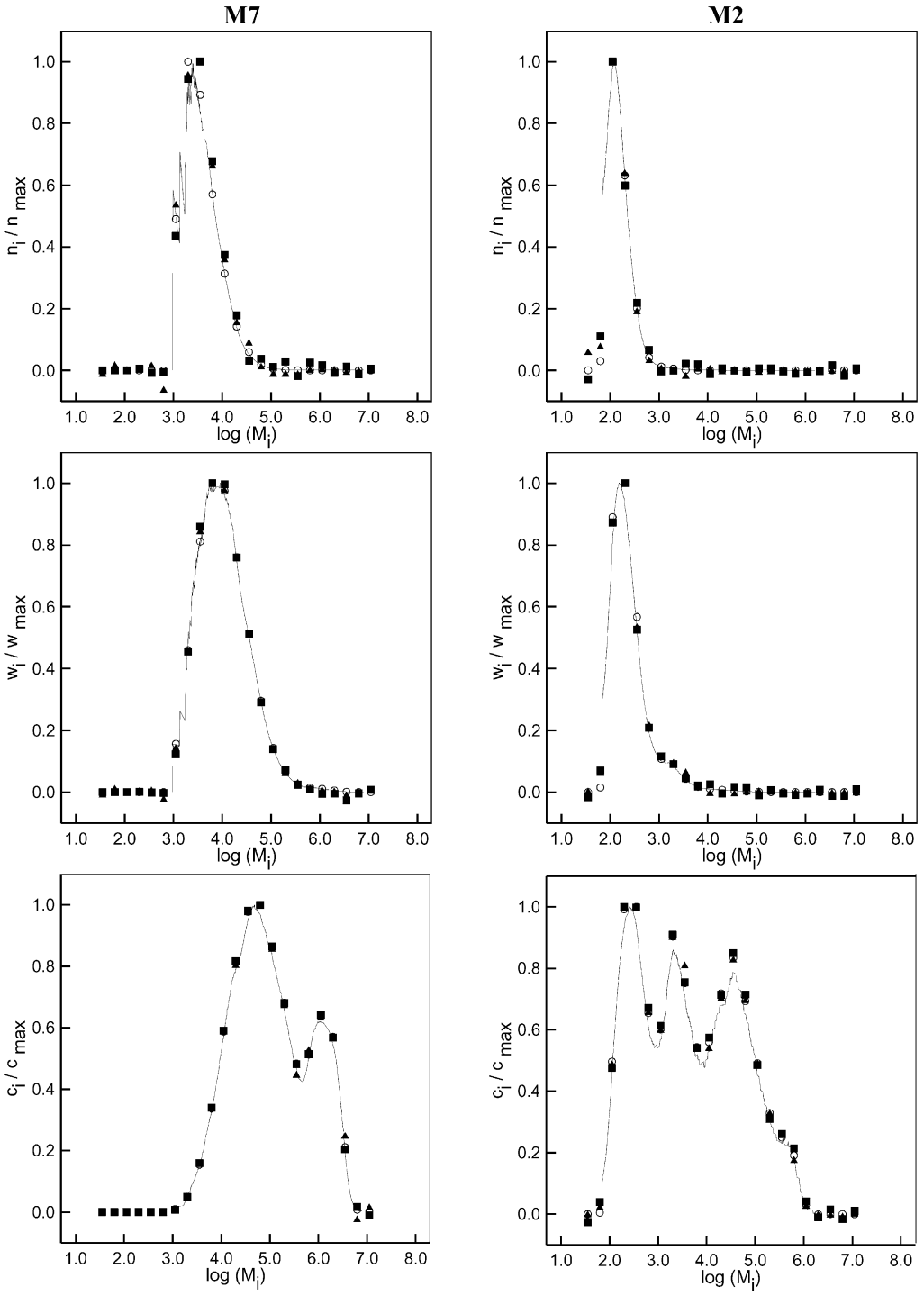

Fig. 1. Experimental and calculated distributions for polymers M7 and M2. Lines: experimental; ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion.

3.1.3. Garbow's inversion method

Table 4 shows the SSQ values when the three MWDs are obtained from the three pgfs. In this case, we present results for all the polymers used in the validation.

As shown in the table, the best results are obtained when each MWD is recovered from its corresponding pgf.

Figs. 1 and 2 show the graphs of the MWDs corresponding to the cases highlighted in 'bold' in Table 4 (■ symbols).

The three methods are able to recover the MWDs from the pgf transform domain with good accuracy. Papoulis' method is the one that demands less computational effort, because it uses only real values of the transformed variable. Methods that use a complex transformed variable double the

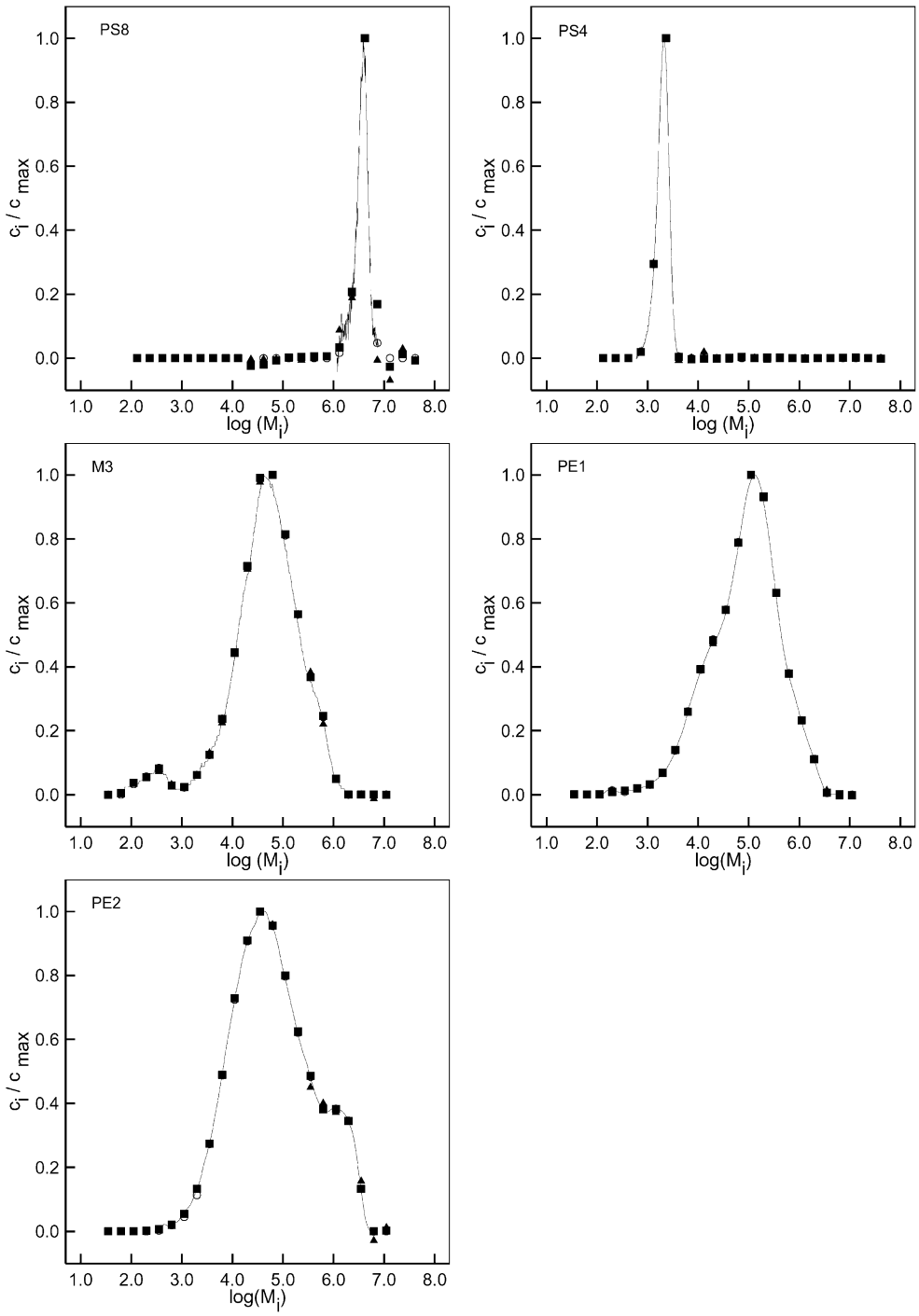

Fig. 2. Experimental and calculated chromatographic distributions for polymers PS8, PS4, M3, PE1 and PE2. Lines: experimental; ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion.

Table 3
SSQ values obtained at the value of relative accuracy (ε) at which either SSQ1 or SSQ is minimum, for M7 MWD calculated with de Hoog's method

MWD	$\varepsilon_{SSQ1_{min}}$	SSQ	$\varepsilon_{SSQ_{min}}$	SSQ_{min}
Number	7.5×10^{-5}	0.01712	5.0×10^{-5}	0.01661
Weight	7.5×10^{-4}	0.12140	5.0×10^{-6}	0.00154
Chromatographic	2.5×10^{-6}	0.00580	1.0×10^{-6}	0.00572

size of the problem to solve, as the real and imaginary parts of the transformed variable must be treated as two different variables (when the pgfs are obtained through integration of mass balance equations). However, de Hoog's method appears to be more accurate at degrees of polymerisation where the distributions start to vanish. As an extra advantage, assigning a suitable value to its parameter is a simple matter. Garbow's method also uses complex values of the

Table 4
SSQ values for MWDs calculated with Garbow's method

Polymer	MWD	Recovered from		
		pgf_n	pgf_w	pgf_c
M2	Number	**0.01770**	6.31194	8.24223
	Weight	0.02484	**0.01507**	8.03267
	Chromatographic	0.35930	0.04345	**0.03758**
M7	Number	**0.05702**	6.79040	6.79115
	Weight	0.04680	**0.00880**	6.46249
	Chromatographic	0.08182	0.00372	**0.00654**
PS8	Number	**0.20742**	0.04828	0.41546
	Weight	5.81754	**0.08252**	0.02308
	Chromatographic	276 498.40000	21.33983	**0.02449**
PS4	Number	**0.20732**	16.87743	150.19330
	Weight	0.20655	**0.04446**	16.92283
	Chromatographic	0.20729	0.04439	**0.00657**
PE2	Number	**0.83145**	5.37322	6.23501
	Weight	0.91824	**0.00953**	5.62563
	Chromatographic	1.30702	0.01854	**0.00041**
PE1	Number	**0.18335**	63.06179	1250.78100
	Weight	1.08270	**0.09744**	3.59725
	Chromatographic	1.24818	1.87269	**0.00115**
M3	Number	**0.17101**	6.45783	5.53822
	Weight	0.17615	**0.69897**	51.36684
	Chromatographic	0.30494	0.06119	**0.00828**

transformed variable. In addition to this, it has more parameters than the others, which complicates the process of finding suitable values for them. Nevertheless, it is always advisable to use several inversion methods to compare results, in order to keep anomalous behaviour or numerical problems with one particular method from obscuring the real nature of the MWD [3].

3.1.4. Influence of the degree of polymerisation range

Setting the molecular weight range may result crucial to the success of the recovery procedure, especially for narrow distributions [2]. The results which are shown in Figs. 1 and 2 were obtained assuming a wide molecular weight range ($1.45 < \log(Mi) < 7.10$). The calculated distributions which are shown in Fig. 3 for the polystyrene standards were obtained assuming $2.5 < \log(Mi) < 3.7$ for PS4 and $6. < \log(Mi) < 7.$ for PS8. This range was 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. In the case of narrow distributions such as PS4 and PS8 the problem is more evident. In Figs. 2 and 3, 23 points of the distribution were evaluated. For the distributions shown in Fig. 2, only around four points lie on the curves, while the others are outside the actual distribution ranges. As the range narrows (Fig. 3), more calculated points lie on the actual distribution. It is surprising to find that the experimental distribution is recovered correctly from points calculated using different molecular weight ranges. But when using an inappropriate range, computational effort is being wasted. This may become a particularly bad problem when the inversion process is rather time-consuming. In addition to this, avoiding the calculation of the MWD at values of DP where the distribution is close to vanishing improves the convergence of de Hoog's and Garbow's methods.

3.1.5. Inversion of 'noisy' pgfs

In all the cases presented so far, the pgfs were calculated directly from the actual experimental information. The small numerical error associated with any ordinary algebraic calculation was considered unimportant, and so the pgfs were regarded as numerically noise-free. Nevertheless, 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. We have previously shown [2] that an error with rapidly fluctuating sign, such as random error, could emulate the error due to the numerical integration of mass balance equations. So, in order to estimate the influence of noise on the quality of the recovered MWD curves, we added random noise to the clean pgfs in different levels (0.1 and 0.5% of the pgf clean value) and then inverted the resulting pgfs using all the inversion methods. As an example, the MWD_c calculated in this way for polymer M7 is shown in Fig. 4. Similar results were obtained for the other polymers.

From these results it can be concluded that noise, in the levels added to the pgfs, has little influence in the performance of these methods. The algorithms analysed in Ref. [2] also could reproduce appropriately MWDs from noisy pgf, but they incorporated some 'bumps' to the curves.

3.2. Polymerisation examples

The inversion methods validated as explained before were also applied to the calculation of MWDs from the mass balance equations of polymerisation reactions. With this purpose we chose some of the examples presented by Miller et al. [13]. Miller calculates the MWDs by applying the Laplace transform to the mass balance equations, and then performs the inversion with an adapted version of Garbow's modification of Weeks' method [10,11], and by Talbot's method [19], but the latter failed in all his examples. In Part I of this work [1], we derived the pgf equations that describe these polymerisation systems. Here we also present the solution analytically or by direct integration whenever possible for comparison purposes. For details about the pgf transformation of the mass balance equations, the reader is referred to Part I of this work [1].

Gear's method for stiff problems [20] was used to solve the systems of differential equations.

The cases considered are described in what follows.

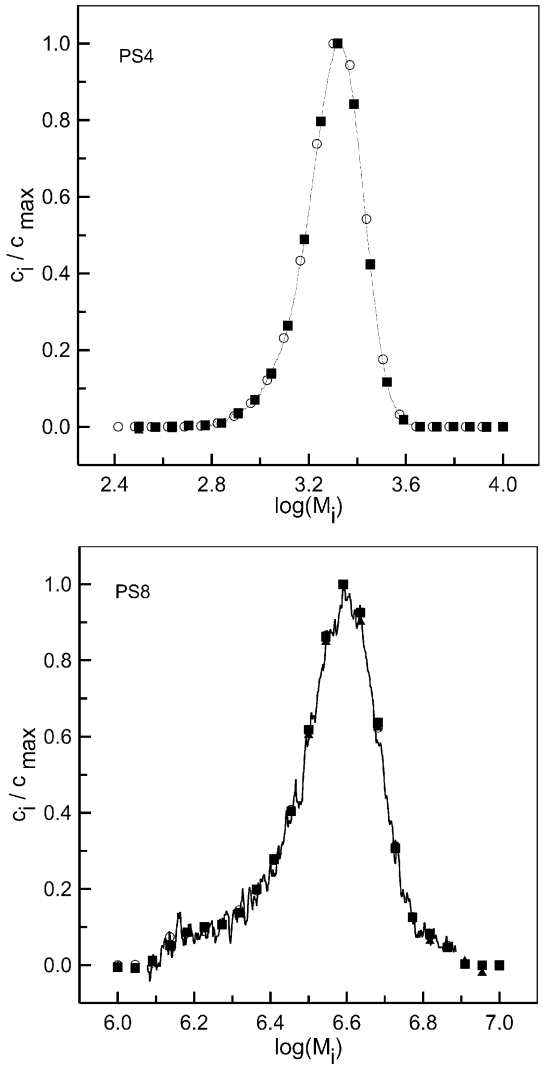

Fig. 3. Chromatographic distributions calculated with reduced rank. Lines: experimental; ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion.

3.2.1. Living polymerisation

A batch isothermal living polymerisation where monomer concentration remains constant is considered here. This simple system is described by the propagation reaction only. The pgf equations were obtained in Part I of this work [1]. We considered two possible cases, the first one where zero-length radicals were taken into account through extrapolation and a second one where they were calculated separately. The resulting pgf for each case were inverted using the methods proposed in this work. For comparison purposes we also integrated the mass balances for molecules with up to 100 monomer units, as described elsewhere [1]. The chain length distributions obtained in this way are compared with the ones recovered from the transform domain.

Fig. 5a shows the chain length distribution for the first case of the living polymerisation at a value of the dimensionless time $\tau = 100$, for the three inversion methods. It

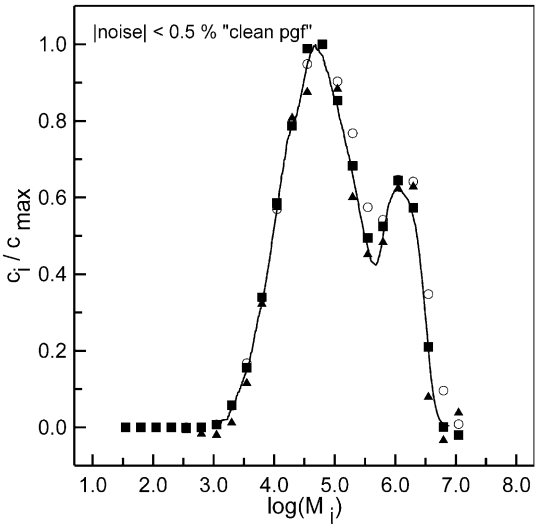

Fig. 4. Inversion from noisy pgfs. Lines: experimental; ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion.

may be observed that only the inversion with de Hoog's method follows the analytical solution accurately. The curve obtained with Garbow's method is identical to the one obtained by Miller with his adapted version of Garbow's modification of Week's method [13]. It is not surprising that Garbow's method failed, as it is not suitable

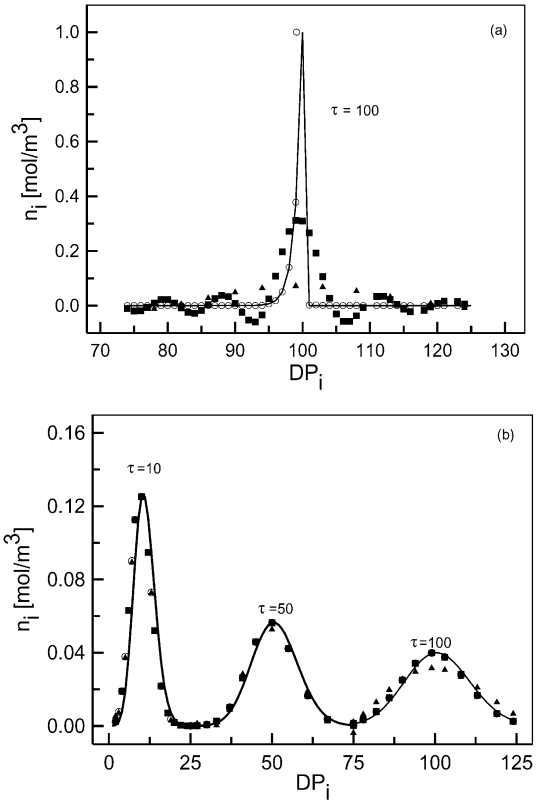

Fig. 5. Chain length distribution for the living polymerisation. Lines: analytical solution; ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion. (a) R_0 calculated by extrapolation, (b) R_0 calculated separately.

Table 5
Rate constants and initial conditions for the simple addition polymerisation

Parameter	Value
Initiation rate constant	0.15 1/h
Propagation rate constant	500 l/mol h
Termination rate constant	5.0 l/mol h
Initial monomer concentration	1.0 mol/l
Initial radical concentration	0
Initial radical pgf_n	0
Initial polymer pgf_n	0

for sharp, discontinuous functions [10,13]. Papoulis' method appears to have difficulties with this kind of function, too, as the distribution it predicts is very different from the analytical one.

Fig. 5b presents results for different residence times τ for the second case. The three inversion methods produce almost identical results for the distributions, which are in agreement with Miller's results. However, Papoulis' method predicts a slightly broader distribution at $\tau = 100$.

3.2.2. Simple addition polymerisation

The kinetic equations that describe this process correspond to initiation, propagation, chain transfer, and termination by combination and disproportionation. Initial conditions and balances for chemical species, and pgf transforms were obtained in Part I of this work [1].

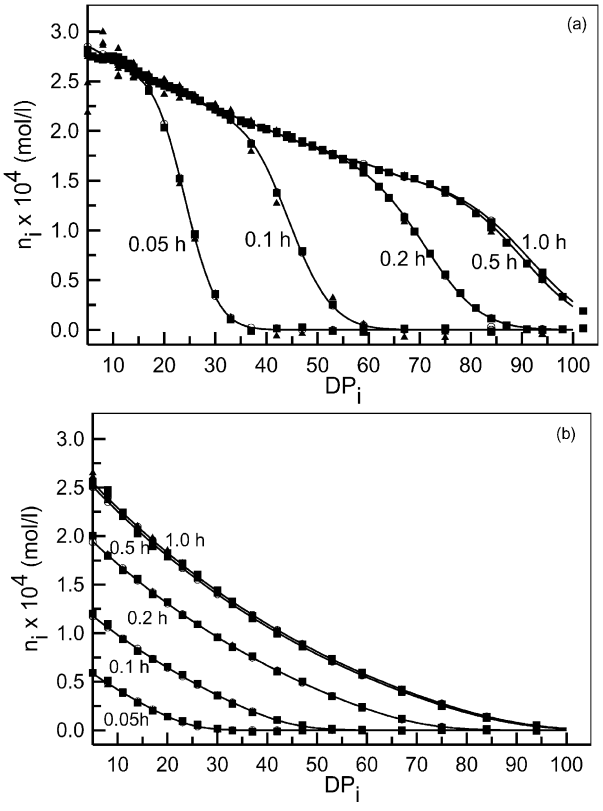

Fig. 6. (a) Polymer and (b) radical chain length distributions for the simple addition polymerisation. Lines: analytical solution; ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion.

Table 5 shows the values for the rate constants and parameters of this model, which were taken from Miller et al. [13]. Fig. 6a and b shows the radical and polymer chain length distributions, respectively, for the simple addition polymerisation when considering monomer as a different species. For the polymer distribution, the three methods provide results that coincide with the distribution obtained from the direct integration of the balance equations. For the radical distribution, Garbow's method presents slight oscillations at low degrees of polymerisation, and Papoulis' method shows stronger oscillations.

If the terms corresponding to monomer are included when performing the transformation of the polymer balance equation (i.e. $M = P_1$), Papoulis' and Garbow's methods fail. This is probably because of the discontinuity of several orders of magnitude between the concentrations of monomer (polymer of chain length 1), and polymer of chain length 2. On the contrary, de Hoog's method gives satisfactory results with both approaches. A relative tolerance of 5×10^{-5} was used with de Hoog's method, and values of 14 and 5×10^{-7} were assigned to parameters a and the relative tolerance, respectively, in Garbow's method.

3.2.3. Linear free radical polymerisation

This reaction is described by a kinetic system that includes initiation, propagation, chain transfer and termination. Its pgf equations were deduced in Part I of this work.

Table 6 shows the values for rate constants and initial concentrations for this system.

In Fig. 7a and b we show the calculated polymer number and weight MWDs for this case. Papoulis' and de Hoog's methods show similar results, in agreement with those published by Miller. The results obtained with Garbow's method are also good, but present slight oscillations.

To achieve accurate results, the error tolerance used with de Hoog's and Garbow's method had to be much lower than the ones used in the validation, 1×10^{-9} and 5×10^{-12}, respectively. Parameter a of Garbow's method was set to 8 to allow convergence with the error tolerance used.

For Papoulis' method, Eq. (8) was used to calculate r, and the number of subintervals in the DP range was equal to the number of values of DP at which the MWDs were calculated. This means that r was recalculated for each DP. All these changes with respect to the validation part of the work stress the importance of having a method for the selection of parameter values.

4. Conclusions

This work provides a demonstration of the recovery of experimental MWDs from pgfs. Three methods for the numerical inversion of Laplace transforms were adapted to be used with pgfs.

Table 6
Rate constants and initial conditions for the linear free radical polymerisation

Parameter	Value
Initiator decomposition rate constant	1.5×10^{-5} s^{-1}
Propagation rate constant	7.594×10^{2} l/mol s
Transfer to solvent rate constant	3.31×10^{-2} l/mol s
Transfer to monomer rate constant	1.78×10^{-2} l/mol s
Termination rate constant (k_t)	3.45×10^{7} l/mol s
Termination by combination rate constant	$0.7k_t$
Termination by disproportionation rate constant	$0.3k_t$
Volume contraction factor	-0.11
Initiation efficiency	0.3
Initial initiator concentration	0.01508 mol/l
Initial monomer concentration	4.32 mol/l
Initial solvent concentration	4.91 mol/l

An experimental validation was successfully performed for the three inversion methods. Techniques for setting values to the method parameters were developed, comparing calculated with real polymer MWDs.

On the whole, the results are of the same degree of accuracy when using either of the three inversion methods. Each of them has particular advantages and disadvantages from the operational point of view. Papoulis' method is the most economical one in computational effort. However, de Hoog's method appears to be more accurate, especially at the low and high molecular weight tails of the distributions. Furthermore, it is easy to find appropriate values for its parameter. Garbow's method has more parameters than the other two, making it harder to find suitable values for all of them. As an added difficulty, de Hoog's and Garbow's methods use complex values of the transformed variable, leading to a larger system of equations since the real and the complex parts must be treated separately.

The addition of noise to the original pgfs and the subsequent inversion of the noisy transforms show that error propagation has little effect on the performance of the studied inversion methods.

We have also shown that the three methods can be successfully applied to the calculation of MWD through the inversion of pgfs obtained through the integration of mass balance equations. In these cases, de Hoog's method gave the best results with respect to accuracy, showing good performance with MWDs of 'difficult' shapes. However, it requires integrating twice as many differential equations as those required by Papoulis' method, something that may be a serious shortcoming for some systems.

Work is under way in the application of pgf transforms to mass balances that describe more realistic systems, such as reactive extrusion of high density polyethylene [21] and controlled rheology of polypropylene.

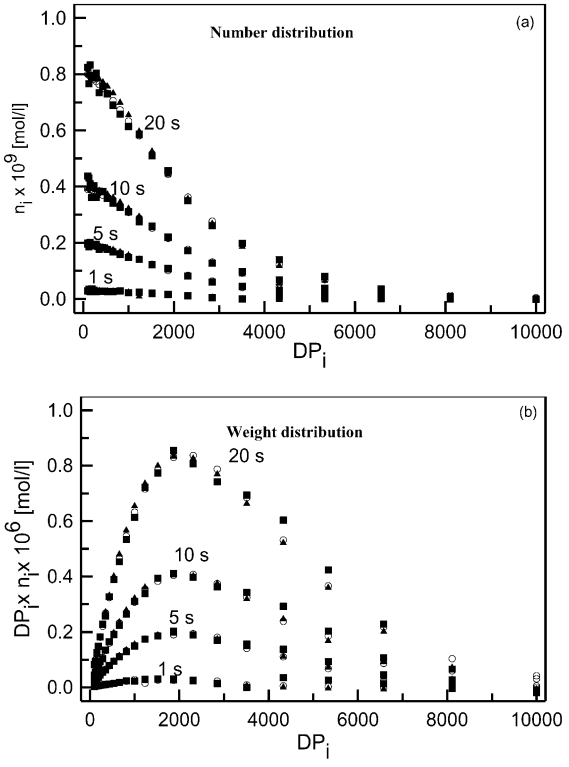

Fig. 7. Polymer length distributions for the linear free radical polymerisation. ▲: Papoulis inversion; ○: de Hoog inversion; ■: Garbow inversion.

Acknowledgements

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