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Recovery of molecular weight distributions from transformed domains. Part I. Application of pgf to mass balances describing reactions involving free radicals

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Abstract

We present a general framework for the application of a transform technique, probability generating functions (pgf), to mass balances that describe free radical reactions, in particular synthesis or modification of polyolefins. Contributions of specific reactions to the mass balances are identified and transformed separately, so that a modular approach is possible for the construction of the pgf balance equations for different free radical processes. This simplifies the transformation step hopefully making the method useful to more people. Three examples taken from the literature are transformed using this modular method showing its ease of use. In Part II of this work, the resulting transforms are inverted to recover the complete molecular weight distribution. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Probability generating functions; Polyolefins; Molecular weight distribution

1. Introduction

Polyolefins are among the commodities with largest production and sales volume. In view of their good properties and low cost, they are used in many applications, such as automotive parts, films and sheeting, bottles and housewares. The advances in the material and production technology of commodity plastics have improved their properties leading to an increasing trend to use some of them to replace engineering plastics. Among polyolefins, polypropylene offers an excellent cost/performance ratio, ease of processing, desirable inherent properties, good environmental image and the possibility of single-polymer applications [1]. Polyethylene is also characterised by its excellent impact strength, resistance to chemicals and by its low production costs.

Molecular weight and molecular weight distribution (MWD), among other molecular parameters, greatly affect solubility and mechanical properties such as hardness, impact strength, fatigue resistance and softening temperature. It is possible to produce polyolefins with specific final properties by performing the polymerisation under particular operating and design conditions. An alternative and economic way to expand the range of applications of the virgin resins obtained in a given reactor is modifying them chemically or physically in a post-reactor process. Mathematical models that represent these processes are powerful tools for predicting operating conditions for materials currently under production, for process optimisation and process control. These mathematical models must be able to solve the mass, momentum and energy balances that describe the process of interest. The simplest model will offer as results only species concentrations and process productivity while the most complex ones will also provide molecular information, such as molecular weight, MWD, and concentration of branches and insaturations.

Different approaches to modelling are possible. For example, deterministic mathematical models are based on the solution of balance equations for the reaction components. In systems involving polymer and radical reactions, balance equations are functions of a discrete variable that represents the degree of polymerisation of polymer species. As the degree of polymerisation can theoretically grow without bounds, the mass balances for all the polymerising species form an infinite set of equations. Several techniques are available to reduce their number. If the interest is on the calculation of average quantities, the moment method is appropriate [2–4]. Other techniques must be sought if the calculation of the MWD is necessary.

Some authors prefer to assume the shape of the MWD and

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calculate its parameters from the first few moments [5,6]. Others resort to divide the molecular weight range in regions and solve the corresponding distributions for a given number of molecular weights [7–10]. The statistical approach has also been employed [11], especially when dealing with prediction of final MWD and gel points. The application of Laplace transforms and generating functions to mass balance equations in radical systems has also been reported [12–14].

In this work, we demonstrate the use of probability generating functions (pgf) in the prediction of MWDs. These transforms represent an attractive alternative to the Laplace transform because they are defined for discrete distributions, as those found in polymer science. Besides, no information on the final distribution is needed. We have used pgf in the prediction of MWD in several free radical reaction systems [15–18]. Two basic steps are involved in the use of the method: first, transforming the mass balances that describe the process and solving the resulting finite system of equations; second, inverting the result to recover the MWD. The transformation step may be cumbersome and time-consuming if one applies it from the beginning for every single system. However, if one recognises that there are many common blocks to different free-radical systems, since some reactions appear in more than one system, it is possible to generalise the method. In this work we aim to give the reader the necessary tools to apply pgf transforms to mass balances in a generalised way. To this purpose, we consider that the following terms may appear in the mass balances: accumulation, input/output and reaction. With respect to the reaction terms, we take into account individual reactions that have been proposed to take part in polymerisation systems as well as in polyolefin reactive modification. We intend to cover as thoroughly as possible all the kinetic steps that may appear in these systems.

Finally, to illustrate the pgf application to mass balances, we selected three of the examples presented by Miller et al. [12], transformed them and solved for the corresponding pgf curves. The resulting MWD obtained by inversion of those pgf are discussed in Part II of this work [16].

2. Usage of the pgf transform

Given any discrete probability mass function $p(n)$, its pgf is defined as $\sum_{n=0}^{\infty} z^n p(n)$, where z is the pgf 'dummy' variable. If one wants to find the pgf of the MWD, this definition must be applied to the probability that the degree of polymerisation has a value of n. This probability measures the chance that a molecule of length n is being selected when looking at molecules according to their MWD. Three probabilities are the most common when working with MWDs. If all molecules have an equal chance of being selected, the number probability is used and the number MWD results. If all units of mass have an equal chance of selection, weight probability and weight MWD are involved. If the quantity with equal chance is the product of mass times molecular weight, the 'chromatographic' MWD and probability are to be used. Chromatographic distributions are what one gets as a result of analysis by chromatography such as size exclusion chromatography. Eqs. (1)–(3) define these probabilities in a general way, where T_n stands for a polymer (P_n) or radical (R_n) molecule.

Number probability:

$$P_0^{\oplus}(N=n) = \frac{[T_n]}{\sum_{n=0}^{\infty}[T_n]} = \frac{[T_n]}{U_0} \tag{1}$$

Weight probability:

$$P_1^{\oplus}(N=n) = \frac{n[T_n]}{\sum_{n=0}^{\infty}n[T_n]} = \frac{n[T_n]}{U_1} \tag{2}$$

Chromatographic probability:

$$P_2^{\oplus}(N=n) = \frac{n^2[T_n]}{\sum_{n=0}^{\infty}n^2[T_n]} = \frac{n^2[T_n]}{U_2} \tag{3}$$

Summarising Eqs. (1)–(3), it may be expressed generically as in Eq. (4)

$$P_a^{\oplus}(N=n) = \frac{n^a[T_n]}{\sum_{n=0}^{\infty}n^a[T_n]} = \frac{n^a[T_n]}{U_a}, \qquad \text{for } a = 0,1,2 \tag{4}$$

Eq. (4) may be applied both to polymer and radical distributions. $P_a^{\oplus}(N=n)$ stands for the probability—number ($a=0$), weight ($a=1$) or chromatographic ($a=2$)—that a polymer molecule or a radical molecule has degree of polymerisation n. The superscript is there to remind us of a previous notation convention, where probabilities for polymer molecules have no superscript (as in $P_a(N=n)$), while probabilities for radicals have a superscript (as in $P_a^{*}(N=n)$). U_0, U_1 and U_2 are the first three moments of the chain length distribution of polymer (M_0,M_1,M_2) or radicals (Y_0,Y_1,Y_2). Brackets are used to indicate molar concentrations of the different components.

Different conventions about the length of the smallest polymer molecule can be adopted and have been used in the literature. For example, it may be assumed that a molecule must have at least two monomer units in order to be counted as a polymer molecule, that is $n \geq 2$. If, however, the one-monomer molecule is considered as part of the polymer distribution then $n \geq 1$. This affects the summations in Eq. (4). In order to gain generality it is convenient to be able to perform the summations in Eq. (4) starting from $n=0$. In order to accommodate the different definitions of minimum polymer length, polymer molecules with chain length 0 (or 0 and 1) must be considered, whose concentrations are always equal to 0.

The situation for the radicals is different since radicals of chain length unity do exist. In some mathematical models of polymerisation reactions, radicals of chain length zero with nonzero concentration are also considered. They are derived from initiator species. If this is the case, the numerator in Eq. (4) must be changed for $(Mw_{R_0}/Mw_M)^a[R_0]$ when $n = 0$. Mw_{R_0} is the molecular weight of the radical of chain length 0, and Mw_M is the molecular weight of the repeat unit. Again, if the zero-length radical does not form part of the radical distribution in a given polymerisation, its concentration is considered to be 0. Later on we will multiply several equation terms by n^a and then add from $n = 0$ to ∞. We express this procedure as $\sum_{n=0}^{\infty} n^a$ for simplicity but, when the sum involves radicals the factor of the first term will be $(Mw_{R_0}/Mw_M)^a$ and not 0^a.

When dealing with a discrete distribution, such as the chain length distribution where the independent variable is the degree of polymerisation, Miller and Macosko [19] define the pgf for a distribution as the linear operation shown in Eq. (5)

$$\Phi_{N,a}(z) = \sum_{n=0}^{\infty} z^n P_a^{\oplus}(N = n), \qquad a = 0, 1, 2 \tag{5}$$

When applied to a polymer distribution, our previous notation stated $\Phi = \psi$, and $\Phi = \phi$ for a radical distribution.

Eq. (6) shows the pgf first derivative [20], which will be useful in the development of the pgf balances

$$\frac{\partial \Phi_{N,a}(z)}{\partial z} = \frac{1}{z} \sum_{n=1}^{\infty} n z^n P_a^{\oplus}(N = n), \qquad n = 0, 1, 2 \tag{6}$$

3. Structure of balance equations to be transformed

In a reacting system, component balance equations have a general structure. For example, one of the terms corresponds to the accumulation of the component. The others are composed by the sum of the contributions of the inputs and outputs of the component plus the net generation of the component due to each of the reaction steps.

Accumulation and input/output terms are shown in Table 1. Several usual kinetic steps (Eqs. (7)–(19)) that may appear in polymerisation systems are also listed in Table 1. The symbol k represents a kinetic rate constant. The requirement of length $n \geq 2$ for polymers is implicit in those kinetic steps.

The initiation reaction (Eq. (7)) corresponds to a first order, thermal peroxide (I) decomposition. Parameter θ indicates the number of initiation radicals into which the organic peroxide decomposes, which is usually 2 or 4. Parameter f is the initiation efficiency. The use of peroxides is common to initiate radical polymerisations and modification of polyolefins. If the initiation reaction consists of the direct reaction of monomer with initiator Eq. (8) results.

The propagation reaction (Eq. (9)) refers to the addition of a monomer unit (M) to a growing radical chain (R_n). This is a reaction that takes place in every addition polymerisation. No by-product results, so the mass of the repetitive unit is the same as that of the monomer. As customary in this field, we assume that radical reactivity is independent of chain length.

The growing radicals lose their activity when they react with each other to form a paired-electron covalent bond leading to a dead polymer molecule. A termination by combination occurs (Eq. (10)) if a coupling of the radicals takes place. This reaction may occur both in polymerisation processes and in post-reactor modifications. For systems where polyethylene or polystyrene is involved, this is the main termination step. Termination by disproportionation occurs (Eq. (11)) when two radical molecules react producing a hydrogen transfer. Both molecules lose their activity but remain separate, one with an unsaturated end and the other one with a saturated end. This reaction takes place in some polymerisation systems, for example when producing poly(methyl methacrylate). It has also been proposed to occur in post-reactor processes where polypropylene is modified.

More than one form of chain scission and thermal degradation have been proposed for polymerisation [21] and post-reactor modification reactions [9,10,22–24]. We present here three of them (Eqs. (12)–(14)). The reactions shown in Eqs. (12) and (13) are more likely to appear in post-reactor modification of polyolefins. The one shown in Eq. (14) has been proposed to take part in the high-pressure polymerisation of ethylene, where a backbiting reaction occurs. The presence of this mechanism is claimed to be crucial to be able to predict molecular weights in this process [21]. In this type of reaction, the kinetic constants are commonly reported per unit of reactive site. The total number of reactive sites that may react must multiply them, in each case. To maintain generality, for an R_n (or P_n) molecule we account for $(\beta n - \gamma)$ sites. β and γ are positive integers that allow for different molecule configurations.

Hydrogen abstraction (Eq. (15)) has been proposed to occur in reactive modification of polyethylenes [9]. In this reaction, initiation radicals randomly abstract protons on the polyethylene backbone. The kinetic constant for this step is commonly reported by reactive site unit. To keep generality we consider that the number of reactive sites in a polymer molecule P_n is proportional to $n(\mu n)$, and that the initiation radical R_0 belongs to the radical distribution. If this were not the case, R_0 would have its own balance, and its related terms would not appear in the general radical balance.

Solvents or chain transfer agents such as low molecular weight hydrocarbons (i.e. propene, butene) are used to control molecular weight in polymerisation reactions. It provides a way of deactivating radicals. Their presence affects mainly the number-average molecular weight. Eq. (16) represents the corresponding reaction. We assume that the resulting radical R_0 has the same reactivity as any of the macroradicals.

Table 1
Accumulation, input/output and kinetic steps in polymerisation reactions. Contribution to balances of radical and polymer of length n ($n = 0,\ldots,\infty$)

Kinetic step	Radical balance	Polymer balance
Accumulation	$\frac{\mathrm{d}\{V[R_n]\}}{\mathrm{d}t}$	$\frac{\mathrm{d}\{V[P_n]\}}{\mathrm{d}t}$
Input/output	$\sum_{i=1}^{N_{in}} [R_n]_{in_i} F_{Vin_i} - \sum_{i=1}^{N_{\mathrm{out}}} [R_n] F_{Vout_i}$	$\sum_{i=1}^{N_{in}} [P_n]_{in_i} F_{Vin_i} - \sum_{i=1}^{N_{\mathrm{out}}} [P_n] F_{Vout_i}$
Initiation $I \xrightarrow{fk_{\mathrm{d}}} \theta R_0$ (7)	$\theta f k_{\mathrm{d}} V[I]\delta_{n,0}$	–
$I + M \xrightarrow{fk_{\mathrm{d}}} R_1$ (8)	$fk_{\mathrm{d}} V[I][M]\delta_{n,1}$	–
Propagation $R_n + M \xrightarrow{k_{\mathrm{p}}} R_{n+1}$ $n = 0,\ldots,\infty$ (9)	$k_{\mathrm{p}} VM[-[R_n] + [R_{n-1}](1 - \delta_{n,0})]$	–
Termination by combination $R_n + R_r \xrightarrow{k_{\mathrm{tc}}} P_{n+r}$ $n = 1,\ldots,\infty;\ r = 1,\ldots,\infty$ (10)	$-k_{\mathrm{tc}} V(Y_0 - [R_0])[R_n](1 - \delta_{n,0})$	$\frac{1}{2} k_{\mathrm{tc}} V \sum_{r=1}^{n-1} [R_r][R_{n-r}](1 - \delta_{n,0} - \delta_{n,1})$
Termination by disproportionation $R_n + R_r \xrightarrow{k_{\mathrm{td}}} P_n + P_r$ $n = 2,\ldots,\infty;\ r = 2,\ldots,\infty$ (11)	$-k_{\mathrm{td}} V \begin{pmatrix} Y_0 - [R_0] \\ -[R_1] \end{pmatrix} [R_n](1 - \delta_{n,0} - \delta_{n,1})$	$k_{\mathrm{td}} V \begin{pmatrix} (Y_0 - [R_0] \\ -[R_1] \end{pmatrix} [R_n](1 - \delta_{n,0} - \delta_{n,1})$
Chain scission/thermal degradation $R_n \xrightarrow{k_{\mathrm{s}}} P_r + R_{n-r}$ $n = 2,\ldots,\infty$ (12)	$k_{\mathrm{s}} V \begin{bmatrix} -(\beta n - \gamma)[R_n] \\ + \sum_{r=n+1}^{\infty} [R_r] \end{bmatrix} (1 - \delta_{n,0} - \delta_{n,1})$	$k_{\mathrm{s}} V \sum_{r=n+1}^{\infty} [R_r](1 - \delta_{n,0} - \delta_{n,1})$
$P_n \xrightarrow{k_{\mathrm{td}}} R_r + R_{n-r}$ $n = 2,\ldots,\infty$ (13)	$k_{\mathrm{td}} V \sum_{r=n+1}^{\infty} [P_r](1 - \delta_{n,0})$	$-k_{\mathrm{td}} V(\beta n - \gamma)[P_n](1 - \delta_{n,0} - \delta_{n,1})$
$R_n \xrightarrow{k_{\mathrm{tdt}}} P_n + R_0$ $n = 2,\ldots,\infty$ (14)	$k_{\mathrm{tdt}} V \begin{bmatrix} -[R_n](1 - \delta_{n,0} - \delta_{n,1}) \\ +(Y_0 - [R_0] - [R_1])\delta_{n,0} \end{bmatrix}$	$k_{\mathrm{td}} V[R_r](1 - \delta_{n,0} - \delta_{n,1})$
Hydrogen abstraction $P_n + R_0 \xrightarrow{k_{\mathrm{ha}}} R_n$ $n = 2,\ldots,\infty$ (15)	$k_{\mathrm{ha}} V \begin{bmatrix} -\mu M_1 [R_n]\delta_{n,0} \\ +\mu n[P_n][R_0](1 - \delta_{n,0} - \delta_{n,1}) \end{bmatrix}$	$-k_{\mathrm{ha}} V \mu n[P_n][R_0](1 - \delta_{n,0} - \delta_{n,1})$
Chain transfer to solvent $R_n + S \xrightarrow{k_{\mathrm{trs}}} P_n + R_0$ $n = 2,\ldots,\infty$ (16)	$k_{\mathrm{trs}} VS \begin{bmatrix} -[R_n](1 - \delta_{n,0} - \delta_{n,1}) \\ +(Y_0 - [R_0] - [R_1])\delta_{n,0} \end{bmatrix}$	$k_{\mathrm{trs}} VS[R_n](1 - \delta_{n,0} - \delta_{n,1})$

Table 1 (*continued*)

Kinetic step	Radical balance	Polymer balance
Chain transfer to monomer $R_n + M \xrightarrow{k_{\mathrm{trm}}} P_n + R_1$ (17) $n = 2, \ldots, \infty$	$k_{\mathrm{trm}}VM\left[\begin{array}{c} -[R_n](1-\delta_{n,0}-\delta_{n,1}) \\ +(Y_0-[R_0]-[R_1])\delta_{n,1} \end{array}\right]$	$k_{\mathrm{trm}}VM[R_n](1-\delta_{n,0}-\delta_{n,1})$
Chain transfer to polymer $P_n + R_r \xrightarrow{k_{\mathrm{trp}}} R_n + P_r$ $n = 2, \ldots, \infty \; r = 2, \ldots, \infty$ (18)	$k_{\mathrm{trp}}V\left[\begin{array}{c} -[R_n](\beta M_1-\gamma M_0) \\ +(\beta n-\gamma)[P_n](Y_0-[R_0]-[R_1]) \end{array}\right](1-\delta_{n,0}-\delta_{n,1})$	$k_{\mathrm{trp}}V\left[\begin{array}{c} -(\beta n-\gamma)[P_n](Y_0-[R_0] \\ -[R_1])+[R_n](\beta M_1-\gamma M_0) \end{array}\right](1-\delta_{n,0}-\delta_{n,1})$
$P_n + R_r \xrightarrow{k_{\mathrm{ct}}} R_s + P_{n-s} + P_r$ $n = 3, \ldots, \infty,\ r = 2, \ldots, \infty,$ $s = 1, \ldots, \infty$ (19)	$k_{\mathrm{ct}}V\left[\begin{array}{c} -[R_n]\left(\begin{array}{c} \beta M_1-\gamma M_0 \\ -(2\beta-\gamma)[P_2] \end{array}\right)(1-\delta_{n,0}-\delta_{n,1}) \\ +(Y_0-[R_0]-[R_1])\sum_{r=n+2}^{\infty}[P_r](1-\delta_{n,0}) \end{array}\right]$	$k_{\mathrm{ct}}V\left[\begin{array}{c} -(Y_0-[R_0]-[R_1])(\beta n-\gamma)[P_n] \\ (1-\delta_{n,0}-\delta_{n,1}-\delta_{n,2}) \\ [R_n]\left(\begin{array}{c} \beta M_1-\gamma M_0 \\ -(2\beta-\gamma)[P_2] \end{array}\right)(1-\delta_{n,0}-\delta_{n,1}) \\ +(Y_0-[R_0]-[R_1])\sum_{r=n+1}^{\infty}[P_r](1-\delta_{n,0}-\delta_{n,1}) \end{array}\right]$

The transfer to monomer reaction (Eq. (17)) is also a reaction associated with polymerisation processes. Depending on the particular polymer being produced, and the temperature and pressure conditions of the process, this reaction will be more or less important.

The first of the chain transfer to polymer reactions presented (Eq. (18)) is the one that most often appears in literature. This reaction has been used to be able to predict long-chain branching and high polydispersities typical of polyethylene processes [21]. However, some authors have proposed that in the reactive modification of polyolefins, chain transfer to polymer occurs together with a scission step [25], as Eq. (19) shows. Every time a chain transfer to polymer occurs, a new long branch is formed. The kinetic constant for this reaction is usually reported per unit of reactive site, so we made the same assumptions here that were made for the chain scission reaction.

From each one of the reaction steps in Table 1, terms for the polymer and/or radical mass balances arise, as shown in the last two columns of this table. From inspection of these balance terms, it appears that it is possible to group them in some general structures. All of these structures are represented in the first column of Table 2. They are represented as the product of a factor α times a function of radical and/or polymer concentrations of certain chain lengths. α stands for all the variables that are not themselves functions of chain length n. Examples would include monomer, solvent or initiator concentration, kinetic constants, and the like. As already explained, concentrations $[R_n]$ and $[P_n]$ are represented in a general way by $[T_n]$. By these means, we only present the terms with different structure, without discriminating from which kinetic step they come from. Structure is what matters when performing the pgf transformation. Note that accumulation and input/output terms are also shown in the first two rows of Table 2.

4. pgf transformation

The general method to carry out the pgf transformation consists in multiplying the balance terms by $n^a z^n$, $a = 0$, 1 or 2, and adding for all possible values of n. The result is reorganised in terms of the various pgf by means of the definitions of the pgf and the different probabilities. This reorganisation may lead to moment definitions for radical and polymer distributions, which are presented in Eqs. (20) and (21)

$$Y_a = \sum_{n=1}^{\infty} n^a [R_n] + \left(\frac{Mw_{R_0}}{Mw_M}\right)^a [R_0], \qquad a = 0, 1, 2 \tag{20}$$

$$M_a = \sum_{n=0}^{\infty} n^a [P_n], \qquad a = 0, 1, 2 \tag{21}$$

For the remainder of this work, $\psi_{N,a}(z)$, $P_a(N = n)$ and M_a will stand for the pgf, probabilities and moments of the dead polymer distribution $\phi_{N,a}(z)$, $P_a^*(N = n)$ and Y_a will stand for the pgf, probabilities and moments of the radical distribution. When we deal with the generic species that represent polymer or radical the corresponding nomenclature will be $\Phi_{N,a}(z)$, $P_a^{\oplus}(N = n)$ and U_a.

The process of obtaining the pgf transform of balance equations can rather be tedious and time-consuming. Table 2 (second column) presents the pgf transforms of

Table 2
Balance terms and their corresponding pgf transforms

Balance term, $n \geq 0$	pgf transform	Row
$\frac{\mathrm{d}\{V[T_n]\}}{\mathrm{d}t}$	$U_a \Phi_{N,a}(z) \frac{\mathrm{d}(V)}{\mathrm{d}t} + V \frac{\mathrm{d}(U_a \Phi_{N,a}(z))}{\mathrm{d}t}$	2.1
$\alpha[R_n]_{\mathrm{in}}$	$\alpha(U_a \Phi_{N,a}(z))_{\mathrm{in}}$	2.2
$\alpha\delta_{n,0}$	$\alpha\left(\frac{Mw_{T_0}}{Mw_M}\right)^a$	2.3
$\alpha\delta_{n,1}$	αz	2.4
$\alpha[T_n]\delta_{n,0}$	$\alpha\left(\frac{Mw_{T_0}}{Mw_M}\right)^a [T_0]$	2.5
$\alpha[T_n]\delta_{n,1}$	$\alpha z[T_1]$	2.6
$\alpha[T_n]\delta_{n,2}$	$\alpha 2^a z^2 [T_2]$	2.7
$\alpha[T_n]$	$\alpha U_a \Phi_{N,a}(z)$	2.8
$\alpha[T_{n-1}](1 - \delta_{n,0})$	$\mathrm{gpt}(a) = \begin{cases} \alpha z U_0 \Phi_{N,0}(z) & a = 0 \\ \alpha z[U_0 \Phi_{N,0}(z) + U_1 \Phi_{N,1}(z)] & a = 1 \\ \alpha z[U_0 \Phi_{N,0}(z) + 2U_1 \Phi_{N,1}(z) + U_2 \Phi_{N,2}(z)] & a = 2 \end{cases}$	2.9
$\alpha[T_{n-1}]\delta_{n,1}$	$\alpha z[T_0]$	2.10
$\alpha \sum_{r=1}^{n-1} [T_{n-r}][T_r]$	$\mathrm{tct}(a) - 2\alpha[T_0] U_a \Phi_{N,a}(z) \text{ with } \mathrm{tct}(a) = \begin{cases} \alpha(U_0 \Phi_{N,0}(z))^2 & a = 0 \\ 2\alpha(U_0 \Phi_{N,0}(z))(U_1 \Phi_{N,1}(z)) & a = 1 \\ 2\alpha(T_0 \Phi_{N,0}(z))(U_2 \Phi_{N,2}(z)) + 2\alpha(U_1 \Phi_{N,1}(z))^2 & a = 2 \end{cases}$	2.11
$\alpha \sum_{r=1}^{n-1} [T_{n-r}][T_r]\delta_{n,0}$	0	2.12
$\alpha \sum_{r=1}^{n-1} [T_{n-r}][T_r]\delta_{n,1}$	0	2.13

Table 2 (*continued*)

Balance term, $n \geq 0$	pgf transform	Row
$\alpha \sum_{r=0}^{n-1} [T_{n-r}][T_r]$	$\mathrm{tct}(a) - \alpha[T_0]U_a \Phi_{N,a}(z)$	2.14
$\alpha n[T_n]$	$\alpha\left[z\dfrac{\partial(U_a \Phi_{N,a}(z))}{\partial z} + \left(\dfrac{Mw_{T_0}}{Mw_M}\right)^{a+1}\right]$	2.15
$\alpha n[T_n]\delta_{n,0}$	$\alpha\left(\dfrac{Mw_{T_0}}{Mw_M}\right)^{a+1}[T_0]$	2.16
$\alpha n[T_n]\delta_{n,1}$	$\alpha z[T_1]$	2.17
$\alpha n[T_n]\delta_{n,2}$	$\alpha 2^{a+1} z^2 [T_2]$	2.18
$\alpha \sum_{m=n+1}^{\infty} [T_m]$	$\mathrm{gst}(a) = \begin{cases} \dfrac{\alpha}{1-z}[U_0 - (U_0 \Phi_{N,0}(z))] & a = 0 \\ \dfrac{\alpha}{(1-z)^2}[(z-1)(U_1 \Phi_{N,1}(z)) + z(U_0 - (U_0 \Phi_{N,0}(z)))] & a = 1 \\ \dfrac{\alpha}{(1-z)^3}[-(z-1)^2(U_2 \Phi_{N,2}(z)) + 2z(z-1)(U_1 \Phi_{N,1}(z)) - z(z+1)(U_0 \Phi_{N,0}(z)) + z(z+1)U_0] & a = 2 \end{cases}$	2.19
$\alpha \sum_{m=n+j}^{\infty} [T_m]\delta_{n,0}$	$\alpha\left(\dfrac{Mw_{T_0}}{Mw_M}\right)^{a}\left(U_0 - \sum_{k=0}^{j-1}[T_k]\right)$	2.20
$\alpha \sum_{m=n+j}^{\infty} [T_m]\delta_{n,1}$	$\alpha z\left(U_0 - \sum_{k=0}^{j}[T_k]\right)$	2.21
$\alpha \sum_{m=n+2}^{\infty} [T_m]$	$\mathrm{gctt}(a) = \begin{cases} \dfrac{\alpha}{z-1}\left[\dfrac{1}{z}((U_0 \Phi_{N,0}(z)) - [T_0] - z[T_1]) - (U_0 - [T_0] - [T_1])\right] & a = 0 \\ \dfrac{\alpha}{(1-z)^2}\left[\dfrac{(z-1)}{z}(U_1 \Phi_{N,1}(z)) - \dfrac{(2z-1)}{z}(U_0 \Phi_{N,0}(z)) + zU_0\right] & a = 1 \\ \dfrac{\alpha}{(z-1)^3}\left[\dfrac{(z-1)^2}{z}(U_2 \Phi_{N,2}(z)) - \dfrac{(4z^2-6z+2)}{z}(U_1 \Phi_{N,1}(z)) + \dfrac{(4z^2-3z+1)}{z}(U_0 \Phi_{N,0}(z)) - z(z+1)U_0\right] & a = 2 \end{cases}$	2.22

each of the terms that contributes to the mass balances. Although we have tried to be comprehensive, Table 2 should not be regarded as absolutely complete.

Details on the transformation procedure performed to obtain the results shown in Table 2 are given in Appendix A. If a different kinetic step from those presented in Table 1 appears, its pgf transform will have to be deduced following the procedures explained there.

To illustrate a practical application of this technique we present some polymerisation examples in Section 5.

5. Polymerisation examples

We have chosen three of the theoretical examples presented by Miller et al. [12] to illustrate how to apply the previous derivations to transform the mass balance equations of a polymerisation reaction into the pgf domain. The resulting sets of differential equations are solved using the standard available numerical methods for stiff systems [26]. The recovery of MWDs from the resulting pgf is discussed in Part II of this work.

5.1. Living polymerisation

This simple system presents only one reaction, propagation and is described by Eq. (9) in Table 1. For simplicity, monomer concentration is considered constant. Introducing the dimensionless time, $\tau = k_p[M]t$, the resulting mass balance equations for an isothermal batch reactor are

$$\frac{d[R_0]}{d\tau} = -[R_0] \tag{22}$$

$$\frac{d[R_n]}{d\tau} = -([R_n] - [R_{n-1}]), \qquad n \geq 1 \tag{23}$$

These two equations may be condensed into just one by using Kronecker's delta $\delta_{n,0}$ as:

$$\frac{d[R_n]}{d\tau} = -[R_n] + [R_{n-1}](1 - \delta_{n,0}), \qquad n \geq 0 \tag{24}$$

where $[R_0]$ is the initiator concentration. The initial conditions are $[R_0]_{\tau=0} = R_0^{(0}$ and $[R_n]_{\tau=0} = 0\ n \geq 1$.

To transform this equation into the pgf domain, we take advantage of the information presented in Table 2. The accumulation term transform can be found in row 2.1 of this table keeping in mind that the volume is constant in this model. The right hand side terms of Eq. (24) match the ones in rows 2.8 and 2.9 of Table 2, with $\alpha = -1$ and $\alpha = 1$, respectively. Therefore, the transform of this equation will be

$$\frac{d(Y_0\phi_{N,0}(z))}{d\tau} = -(Y_0\phi_{N,0}(z)) + z(Y_0\phi_{N,0}(z)) \tag{25}$$

To obtain the initial condition for this equation, Eqs. (4) and (5) are applied to the initial conditions of the original system obtaining the result $(Y_0\phi_{N,0}(z))_{\tau=0} = R_0^{(0}$.

Eq. (25) may be solved analytically for the given initial condition, obtaining:

$$(Y_0\phi_{N,0}(z)) = R_0^{(0}\, e^{(z-1)\tau} \tag{26}$$

As Y_0 is equal to $R_0^{(0}$ in this system, the value of $\phi_{N,0}(z)$ is readily available to be used in the subsequent inverting steps used in Part II.

For comparison purposes we also consider the case presented by Miller, where Eq. (22) is neglected. The analytical solution for this system [12] is:

$$[R_n](\tau) = \begin{cases} R_0^{(0}\, e^{n-\tau} & n < \tau \\ 0 & n > \tau \end{cases} \tag{27}$$

Miller found the value of $[R_0]$ by extrapolation. This particular expression may not be found in the table. Hence, we apply pgf and probability definitions (Eqs. (4) and (5)) to Eq. (27) to obtain an analytical expression for the pgf transform. Only the number pgf is needed in order to compare with Miller's results, that is for $a = 0$ in Eqs. (4) and (5). The resulting transform is

$$(Y_0\phi_{N,0}(z)) = R_0^{(0}\left(\frac{z^{\tau+1}\, e - e^{-\tau}}{z\, e - 1}\right) \tag{28}$$

The results of its inversion are shown in Part II.

5.2. Simple addition polymerisation

The kinetic equations that describe this process are initiation as described in Eq. (8), propagation as in Eq. (9) with $n \geq 1$, and a termination by transfer to monomer similar to Eq. (17), where the outcome of the reaction is a single molecule P_{n+1}. The mass balance equations for this system are

Monomer

$$\frac{d[M]}{dt} = -k_i[M] - (k_p + k_t)Y_0[M] \tag{29}$$

Radical R_n

$$\frac{d[R_n]}{dt} = k_i[M]\delta_{n,1} - k_t[R_n][M](1 - \delta_{n,0}) - k_p[M]([R_n](1 - \delta_{n,0}) - [R_{n-1}](1 - \delta_{n,1} - \delta_{n,0})) \quad n = 0, \ldots, \infty \tag{30}$$

Radical moment

$$\frac{dY_0}{dt} = k_i[M] - k_t Y_0[M] \tag{31}$$

Polymer P_n

$$\frac{d[P_n]}{dt} = k_t[R_{n-1}][M(1 - \delta_{n,0} - \delta_{n,1}) \qquad n = 0, \ldots, \infty \tag{32}$$

Polymer moment

$$\frac{dM_0}{dt} = k_t Y_0[M] \tag{33}$$

with the following supplementary conditions: $[M]_{t=0} = M_0^{(0}$, $[R_n]_{t=0} = 0\ n \geq 1$, $[P_n]_{t=0} = 0\ n \geq 2$, $[R_0]_{\forall t} = 0$, $[P_0]_{\forall t} = 0$ and $[P_1]_{\forall t} = 0$.

The pgf transforms of these equations are built matching each of their terms with their equivalents in Table 2 (see rows 2.4, 2.5, 2.8, 2.9, 2.10). It must be kept in mind that as the radical of chain length 0 as well as polymer of chain lengths 0 and 1 do not exist in this model, they must be assigned a concentration of 0 in the expressions in Table 2. Then, the pgf transform of the radical and polymer balance are:

$$\frac{d(Y_0\phi_{N,0}(z))}{dt} = k_i[M]z + k_p[M](z-1)(Y_0\phi_{N,0}(z)) - k_t[M] \times (Y_0\phi_{N,0}(z)) \tag{34}$$

$$\frac{d(M_0\psi_{N,0}(z))}{dt} = k_t[M]z(Y_0\phi_{N,0}(z)) \tag{35}$$

As there is neither polymer nor radical at the beginning of the reaction, the initial conditions for the differential equations of the pgf transforms will be zero. The transformed system of equations to be solved is then composed of Eqs. (29), (31), (33)–(35), with the initial conditions: $[M]_{t=0} = M_0^{(0}$, $Y_0|_{t=0} = 0$, $M_0|_{t=0} = 0$, $Y_0\phi_{N,0}(z)|_{t=0} = 0$ and $M_0\psi_{N,0}(z)|_{t=0} = 0$. This system was solved with an appropriate numerical method for ordinary differential equations [26].

Miller et al. [12] use a slightly different approach. They consider the monomer as a polymer of chain length 1, and include it in the polymer chain length distribution. In this case, the polymer mass balance equation changes to

$$\frac{d[P_n]}{dt} = k_t[R_{n-1}][P_1](1-\delta_{n,0}) - k_i[P_n]\delta_{n,1} - (k_p + k_t)Y_0[P_n]\delta_{n,1} \qquad n = 0,\ldots,\infty \tag{36}$$

The pgf transform of this equation is

$$\frac{d(M_0\psi_{N,0}(z))}{dt} = k_t[M]z(Y_0\phi_{N,0}(z)) - k_i z[P_1] - (k_p + k_t)Y_0 z[P_1] \tag{37}$$

with initial conditions $[P_1]_{t=0} = P_1^{(0}$, $Y_0|_{t=0} = 0$, $(Y_0\phi_{N,0}(z))|_{t=0} = 0$, and $(M_0\psi_{N,0}(z))|_{t=0} = zP_1^{(0}$.

However, this methodology introduces an important discontinuity in the polymer chain length distribution, since the concentrations of monomer and polymer of two or more monomer units differ in several orders of magnitude. This appears to be unsuitable for the method of pgf transformation of the balance equations. As we show in Part II of this work, only one of the inversion methods tested can overcome this problem.

In all cases a suitable numerical method was used to solve the system [26].

Both the living polymerisation and simple addition polymerisation examples present two features that allow the direct integration of the mass balance equations without any transformation: (a) the balance equation for component n depends on components of smaller length, and (b) the entire distribution can be described with values of n up to approximately 100. Therefore, the distributions can be obtained by solving about 200 differential equations, a reasonable number. We take advantage of these features to obtain nearly exact distributions that may be used to compare with the ones recovered through inversion.

5.3. Linear free radical polymerisation

This polymerisation is described by the following kinetic system, which is essentially included in Table 1. It considers initiation (Eq. (7)), which leads to two ($\theta = 2$) initiation radicals R_0. It also includes propagation (Eq. (10)), chain transfer to solvent and monomer (Eqs. (17) and (18)), and termination by combination and disproportionation (Eqs. (11) and (12)). The smallest radical and polymer both have unit length.

To be consistent with Miller's approach we only consider the number distribution. Assuming quasi-stationary state for the concentration of initiation radicals, the resulting mass balance equation system is:

$$\frac{d(V[I])}{dt} = -k_d[I]V \tag{38}$$

$$\frac{d(V[M])}{dt} = -(2fk_dV[I] + (k_p + k_{trm})V[M]Y_0) \tag{39}$$

$$\frac{d(V[S])}{dt} = -k_{trs}V[S]Y_0 \tag{40}$$

$$\frac{d(V[R_n])}{dt} = 2fk_dV[I]\delta_{n,0} + k_pV[M][R_{n-1}](1-\delta_{n,0}) - k_pV[M][R_n] - (k_{trs}[S] + k_{trm}[M])V[R_n] + (k_{trs}[S] + k_{trm}[M])VY_0\delta_{n,0} - k_tY_0V[R_n] \qquad n \geq 0 \tag{41}$$

$$\frac{d(V[P_n])}{dt} = (k_{trs}[S] + k_{trm}[M])V[R_n] + k_{td}V[R_n]Y_0 + \frac{k_{tc}}{2}V\sum_{r=0}^{n-1}[R_{n-r}][R_r] \tag{42}$$

$n \geq 0$

$$\frac{d(VY_0)}{dt} = 2fk_dV[I] - k_tVY_0^2 \tag{43}$$

Here k_t is the sum of the rate constants for termination by combination and by disproportionation, k_{tc} and k_{td}, respectively. The rate of change of volume (dV/dt) is given by

$$\frac{dV}{dt} = \frac{\epsilon V(2fk_d[I] + (k_p + k_{trm})[M]Y_0)}{[M]|_{t=0}} \tag{44}$$

where ϵ is the volume contraction factor. The initial conditions are $V_{t=0} = V_0^{(0}$, $[M]_{t=0} = M_0^{(0}$, $[I]_{t=0} = I_0^{(0}$, $[S]_{t=0} = S_0^{(0}$, $[Y_0]_{t=0} = 0$, $[R_n]_{t=0} = 0$, and $[P_n]_{t=0} = 0$. For all species, $n \geq 0$.

If we match the terms in Eq. (41) with their equivalent ones in Table 2 (rows 2.1, 2.3, 2.8 and 2.9) we can build the transform of this balance, which is

$$\begin{aligned} V\frac{d\lfloor(Y_0\phi_{N,0}(z))\rfloor}{dt} &= 2fk_d V[I] + (k_{trs}[S] + k_{trm}[M])VY_0 \\ &\quad - [k_p[M](1-z) + k_{trs}[S] + k_{trm}[M] \\ &\quad + k_t Y_0]V(Y_0\phi_{N,0}(z)) - (Y_0\phi_{N,0}(z))\frac{dV}{dt} \end{aligned} \tag{45}$$

Following a similar procedure with Eq. (42) one obtains the transform of the polymer balance

$$\begin{aligned} V\frac{d\lfloor(M_0\psi_{N,0}(z))\rfloor}{dt} &= (k_{trs}[S] + k_{trm}[M] + k_{td}Y_0)V(Y_0\phi_{N,0}(z)) \\ &\quad + \frac{k_{tc}}{2}V[(Y_0\phi_{N,0}(z))^2 - [R_0](Y_0\phi_{N,0}(z))] \\ &\quad - (M_0\psi_{N,0}(z))\frac{dV}{dt} \end{aligned} \tag{46}$$

The initial conditions for Eqs. (45) and (46) are: $(Y_0\phi_{N,0}(z))|_{t=0} = 0$ and $(M_0\psi_{N,0}(z))|_{t=0} = 0$, respectively.

Finally, the system of differential equations to be solved is composed of Eqs. (38)–(40) and (43)–(46). A suitable numerical method was used to obtain the solution [26]. The obtained pgf values are used as data for the inversion methods tested in Part II of this work.

6. Conclusions

The pgf transforms of different balance equations corresponding to polymerisation reactions were deduced. By these means we develop a general framework for the use of pgf in prediction of MWDs

The results are presented in a way that will allow a quick transformation of most new balance equations provided their terms belong to any of the general expressions we summarise in this paper. However, if this is not the case, we intended our deductions to be detailed enough to guide the reader in performing his or her own transformations without serious difficulties.

The pgf transforms of the balance equations constitute a very promising tool for calculating MWD. In Part II of this work, we analyse the capabilities of some of the available numerical inversion techniques obtaining very good MWD recoveries.

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Appendix A. Calculation of pgf transforms

A.1. Accumulation term

Row 2.1 in Table 2 show the accumulation term for a polymerising species $[T_n]$ for the general case where volume (V) is variable as

$$\frac{d\{V[T_n]\}}{dt} \qquad n = 0, 1\ldots, \infty \tag{A1}$$

This expression is multiplied by $n^a z^n$ and then a summation for all n from zero to infinity is performed. These two steps will be referred to as 'multiplying by $\sum_{n=0}^{\infty} n^a z^n$' in the remainder of the appendix.

$$\frac{d\sum_{n=0}^{\infty} n^a z^n\{V[T_n]\}}{dt} \tag{A2}$$

Recalling the definition of derivative of a product and making the appropriate substitutions so that probability definitions appear Eq. (A3) is obtained. Note that from Eq. (4), it is possible to show that $U_a P_a^{\oplus}(N = n) = n^a[T_n]$

$$\begin{aligned} &\sum_{n=0}^{\infty} n^a z^n [T_n]\frac{dV}{dt} + V\frac{d\left\{\sum_{n=0}^{\infty} n^a z^n [T_n]\right\}}{dt} \\ &= \sum_{n=0}^{\infty} U_a z^n P_a^{\oplus}(N = n)\frac{dV}{dt} + V\frac{d\left\{\sum_{n=0}^{\infty} U_a z^n P_a^{\oplus}(N = n)\right\}}{dt} \\ &= \left\{U_a\sum_{n=0}^{\infty} z^n P_a^{\oplus}(N = n)\frac{dV}{dt} + V\frac{d\left\{U_a\sum_{n=0}^{\infty} z^n P_a^{\oplus}(N = n)\right\}}{dt}\right\} \end{aligned} \tag{A3}$$

for U_a is independent of n. Recalling the definition of pgf given by Eq. (5) the accumulation term transform is finally expressed as

$$U_a\Phi_{N,a}(z)\frac{d(V)}{dt} + V\frac{d(U_a\Phi_{N,a}(z))}{dt} \tag{A4}$$

A.2. $\delta_{n,j}$ ($j = 0, 1, 2$) terms

Terms where Kronecker's delta appears are used to subtract some of the first terms in an infinite sum. For example terms like the ones in row 2.3 and 2.4 in Table 2 may represent the contribution of the initiation reaction to radical balances. Kronecker's delta $\delta_{n,j}$ only allow the term corresponding to $n = j$.

If all variables that do not depend on chain length are included in constant αthen the term has the general form

$$\alpha\delta_{n,j} \tag{A5}$$

After applying the operation $\sum_{n=0}^{\infty} n^a z^n$ $a = 0, 1, 2$, to Eq. (A5), Eq. (A6) is obtained

$$\sum_{n=0}^{\infty} n^a z^n \alpha\delta_{n,j} = \alpha z^j j^a \tag{A6}$$

Keep in mind that in all the cases where $j = 0$, j^a should be replaced by $(Mw_{T_0}/Mw_M)^a$ as already indicated in the text.

To obtain the pgf transforms of terms shown in rows 2.5–2.7 and 2.16–2.18 in Table 2, the same procedure should be followed obtaining

$$\sum_{n=0}^{\infty} n^a z^n \alpha n^b [T_n]\delta_{n,j} = \alpha z^j j^{a+b}[T_j] \tag{A7}$$

where $b = 0$ in rows 2.5–2.7 and $b = 1$ in rows 2.16–2.18. The same considerations apply for j^a and for j^{a+b}.

For the terms with the structure shown in rows 2.20 and 2.21, we start from:

$$\alpha\sum_{n=0}^{\infty} n^a z^n \sum_{m=n+j}^{\infty} [T_m]\delta_{n,t} = \alpha t^a z^t \sum_{m=t+j}^{\infty} [T_m] \tag{A8}$$

Replacing the definitions of moments given in Eqs. (20) and/or (21) into Eq. (A8), Eq. (A9) is obtained

$$\alpha t^a z^t \sum_{m=t+j}^{\infty} [T_m] = \alpha t^a z^t \left(U_0 - \sum_{k=0}^{t+j-1} [T_k] \right) \tag{A9}$$

Again, if $t = 0$ one should act with t^a as already explained for $j = 0$.

The results shown in rows 2.10, 2.12 and 2.13 were obtained similarly.

A.3. $[T_n]$, $n[T_n]$ and $[T_{n-1}]$ terms

Terms proportional to $[T_n]$ (row 2.8) and $[T_{n-1}]$ (row 2.9) appear in the contribution of propagation reactions to the mass balance of radicals. The term in row 2.8 also appears frequently in the contribution to radical and/or polymer balances of termination, chain scission, hydrogen abstraction and chain transfer reactions. Terms proportional to $n[T_n]$ (row 2.15) appear in the contributions to radical or polymer balances of chain scission, hydrogen abstraction and chain transfer to polymer reactions where the kinetic constants are given per unit of reactive site. First, we consider the derivation of term in row 2.8

$$\alpha[T_n] \tag{A10}$$

Following the procedure used in the previous section this term transforms into

$$\alpha\sum_{n=0}^{\infty} n^a z^n [T_n] = \alpha U_a \sum_{n=0}^{\infty} z^n P_a^{\oplus}(N = n) = \alpha(U_a \Phi_{N,a}(z)) \tag{A11}$$

Now we consider the term in row 2.9:

$$\alpha[T_{n-1}](1 - \delta_{n,0}) \tag{A12}$$

Multiplying Eq. (A12) by $\sum_{n=0}^{\infty} n^a z^n$ yields

$$\alpha\sum_{n=0}^{\infty} n^a z^n [T_{n-1}](1 - \delta_{n,0}) = \alpha\sum_{n=1}^{\infty} n^a z^n [T_{n-1}] \tag{A13}$$

At this point, it is convenient to make a change of variables. Taking $r = n - 1$, Eq. (A14) results

$$\alpha\sum_{r=0}^{\infty} (r + 1)^a z^{r+1} [T_r] = \alpha z \sum_{r=0}^{\infty} (r + 1)^a z^r [T_r] \tag{A14}$$

This transform will have different forms depending on the value of a. It will be called gpt(a), and is found as follows. Here we make use of probability and pgf definitions as in the previous cases.

1. $a = 0$

$$\alpha z \sum_{r=0}^{\infty} z^r [T_r] = \alpha z \sum_{r=0}^{\infty} z^r (U_0 P_0^{\oplus}(N = r)) \tag{A15}$$

$$\mathrm{gpt}(0) = \alpha z (U_0 \Phi_{N,0}(z)) \tag{A16}$$

2. $a = 1$

$$\begin{aligned} \alpha z \sum_{r=0}^{\infty} (r + 1) z^r [T_r] &= \alpha z \left[\sum_{r=0}^{\infty} r z^r [T_r] + \sum_{r=0}^{\infty} z^r [T_r] \right] \\ &= \alpha z \left[\sum_{r=0}^{\infty} z^r \left(U_1 P_1^{\oplus}(N = r) \right) + \sum_{r=0}^{\infty} z^r \left(U_0 P_0^{\oplus}(N = r) \right) \right] \end{aligned} \tag{A17}$$

$$\mathrm{gpt}(1) = \alpha z [(U_1 \Phi_{N,1}(z)) + (U_0 \Phi_{N,0}(z))] \tag{A18}$$

3. $a = 2$

$$\begin{aligned}
&\alpha z \sum_{r=0}^{\infty} (r+1)^2 z^r [T_r] \\
&= \alpha z\left[\sum_{r=0}^{\infty} r^2 z^r [T_r] + 2\sum_{r=0}^{\infty} r z^r [T_r] + \sum_{r=0}^{\infty} z^r [T_r]\right] \\
&= \alpha z\left[\sum_{r=0}^{\infty} z^r \left(U_2 P_2^{\oplus}(N=r)\right) + 2\sum_{r=0}^{\infty} z^r \left(U_1 P_1^{\oplus}(N=r)\right) \right. \\
&\quad \left. + \sum_{r=0}^{\infty} z^r \left(U_0 P_0^{\oplus}(N=r)\right)\right]
\end{aligned} \tag{A19}$$

$$\mathrm{gpt}(2) = \alpha z[(U_2 \Phi_{N,2}(z)) + 2(U_1 \Phi_{N,1}(z)) + (U_0 \Phi_{N,0}(z))] \tag{A20}$$

In what follows we proceed to obtain the transform term shown in row 2.16 starting from Eq. (A21)

$$\alpha n[T_n] \tag{A21}$$

Multiplying Eq. (A21) by $\sum_{n=0}^{\infty} n^a z^n$ and then expressing explicitly the term corresponding to $n = 0$ gives

$$\alpha \sum_{n=0}^{\infty} n^{a+1} z^n [T_n] = \alpha \sum_{n=1}^{\infty} n^{a+1} z^n [T_n] + \alpha\left(\frac{Mw_{T_0}}{Mw_M}\right)^{a+1} [T_0] \tag{A22}$$

After rearranging we obtain:

$$\begin{aligned}
&\alpha \sum_{n=1}^{\infty} n^{a+1} z^n [T_n] + \alpha\left(\frac{Mw_{T_0}}{Mw_M}\right)^{a+1} [T_0] \\
&= \alpha \sum_{n=1}^{\infty} n z^n \left(U_a P_a^{\oplus}(N=n)\right) + \alpha\left(\frac{Mw_{T_0}}{Mw_M}\right)^{a+1} [T_0] \\
&= \alpha z\left(\frac{\partial(U_a \Phi_{N,a}(z))}{\partial z}\right) + \alpha\left(\frac{Mw_{T_0}}{Mw_M}\right)^{a+1} [T_0]
\end{aligned} \tag{A23}$$

A.4. Combination terms

The contribution of the termination by combination term to the polymer P_n balance gives a term of the form shown in row 2.11 in Table 2:

$$\alpha \sum_{r=1}^{n-1} [T_{n-r}][T_r] \tag{A24}$$

The transform is deduced as follows. We start from

$$\alpha \sum_{n=0}^{\infty} n^a z^n \sum_{r=1}^{n-1} [T_{n-r}][T_r] \tag{A25}$$

Now we extend the sum for r from 0 to n and subtract the terms corresponding to $r = 0$ and n

$$\begin{aligned}
&\alpha\left[\sum_{n=0}^{\infty} n^a z^n \sum_{r=0}^{n} [T_{n-r}][T_r](1 - \delta_{r,0} - \delta_{r,n})\right] \\
&= \alpha\left[\sum_{n=0}^{\infty} n^a z^n \sum_{r=0}^{n} [T_{n-r}][T_r] - 2[T_0]\sum_{n=0}^{\infty} n^a z^n [T_n]\right]
\end{aligned} \tag{A26}$$

Next we invert the order of the summations remembering that $\sum_{x=0}^{\infty}\sum_{y=x}^{\infty} = \sum_{y=0}^{\infty}\sum_{x=0}^{y}$ and then performing the change of indexes $t = n - r$. The result is

$$\begin{aligned}
&\alpha\left[\sum_{r=0}^{\infty}\sum_{n=r}^{\infty} n^a z^n [T_{n-r}][T_r] - 2[T_0]\sum_{n=0}^{\infty} n^a z^n [T_n]\right] \\
&= \alpha\left[\sum_{r=0}^{\infty}\sum_{t=0}^{\infty} (t+r)^a z^{t+r} [T_t][T_r] - 2[T_0]\sum_{n=0}^{\infty} n^a z^n [T_n]\right]
\end{aligned} \tag{A27}$$

The transform of the last sum in Eq. (A27) is simply $2[T_0]U_a \Phi_{N,a}(z)$. The first term will yield different results depending on the value of a. Therefore, the transform of this term will be called tct(a) and is deduced in the following way:

1. $a = 0$

$$\alpha \sum_{r=0}^{\infty} z^r [T_r] \sum_{t=0}^{\infty} z^t [T_t] = \alpha \sum_{r=0}^{\infty} z^r P_0^{\oplus}(N=r) \sum_{t=0}^{\infty} z^t P_0^{\oplus}(N=t) \tag{A28}$$

$$\mathrm{tct}(0) = \alpha(U_0 \Phi_{N,0}(z))^2 \tag{A29}$$

2. $a = 1$

$$\alpha\left[\sum_{r=0}^{\infty} z^r [T_r] \sum_{t=0}^{\infty} z^t t [T_t] + \sum_{r=0}^{\infty} z^r r [T_r] \sum_{t=0}^{\infty} z^t [T_t]\right] \tag{A30}$$

$$\begin{aligned}
&\alpha\left[\sum_{r=0}^{\infty} z^r U_0 P_0^{\oplus}(N=r) \sum_{t=0}^{\infty} z^t U_1 P_1^{\oplus}(N=t) \right. \\
&\quad \left. + \sum_{r=0}^{\infty} z^r U_1 P_1^{\oplus}(N=r) \sum_{t=0}^{\infty} z^t U_0 P_0^{\oplus}(N=t)\right]
\end{aligned} \tag{A31}$$

$$\mathrm{tct}(1) = 2\alpha(U_0 \Phi_{N,0}(z))(U_1 \Phi_{N,1}(z)) \tag{A32}$$

3. $a = 2$

$$\alpha\left[\sum_{r=0}^{\infty} z^r [T_r] \sum_{t=0}^{\infty} z^t t^2 [T_t] + 2\sum_{r=0}^{\infty} z^r r [T_r] \sum_{t=0}^{\infty} z^t t [T_t] + \sum_{r=0}^{\infty} z^r r^2 [T_r] \sum_{t=0}^{\infty} z^t [T_t]\right] \tag{A33}$$

$$\alpha\left[\sum_{r=0}^{\infty} z^r U_0 P_0^{\oplus}(N = r) \sum_{t=0}^{\infty} z^t U_2 P_2^{\oplus}(N = n - r) + 2\sum_{r=0}^{\infty} z^r U_1 P_1^{\oplus}(N = r) \sum_{t=0}^{\infty} z^t U_1 P_1^{\oplus}(N = n - r) + \sum_{r=0}^{\infty} z^r U_2 P_2^{\oplus}(N = r) \sum_{t=0}^{\infty} z^t U_0 P_0^{\oplus}(N = n - r)\right] \tag{A34}$$

$$\mathrm{tct}(2) = 2\alpha[(Y_0 \phi_{N,0}(z))(Y_2 \phi_{N,2}(z)) + (Y_1 \phi_{N,1}(z))^2] \tag{A35}$$

Finally, Eq. (A36) summarises the transform of the term in row 2.11 of Table 2

$$\mathrm{tct}(a) - 2\alpha[T_0](U_a \Phi_{N,a}(z)) \tag{A36}$$

To obtain the pgf transform of the analogous term in row 2.14, the same steps must be followed.

A.5. Terms of the form $\sum_{m=n+j}^{\infty} [T_m]$ $j = 1$ or 2

These terms appear as part of the contribution of chain scission and transfer to polymer reactions to mass balances. The pgf transforms of these terms are presented in rows 2.19 and 2.22 of Table 2. In what follows we show the deduction of the pgf transform of row 2.19

$$\alpha \sum_{m=n+1}^{\infty} [T_m] \tag{A37}$$

Multiplying this term by $\sum_{n=0}^{\infty} n^a z^n$

$$\alpha \sum_{n=0}^{\infty} n^a z^n \sum_{m=n+1}^{\infty} [T_m] \tag{A38}$$

To transform the second summation, the relationship

$$\sum_{x=0}^{\infty} \sum_{y=x+1}^{\infty} = \sum_{y=1}^{\infty} \sum_{x=0}^{y-1}$$

is used giving as a result

$$\alpha \sum_{n=0}^{\infty} n^a z^n \sum_{m=n+1}^{\infty} [T_m] = \alpha \sum_{m=1}^{\infty} \sum_{n=0}^{m-1} n^a z^n [T_m] \tag{A39}$$

Substituting with the probability and moment definitions and extending the sum for m to 0, this expression turns into

$$\alpha \sum_{m=0}^{\infty} \sum_{n=0}^{m-1} n^a z^n U_0 P_0^{\oplus}(N = m) \tag{A40}$$

This yields different transforms depending on the value of a. This term will be called gst(a).

1. $a = 0$

$$\alpha U_0 \sum_{m=0}^{\infty} P_0^{\oplus}(N = m) \sum_{n=0}^{m-1} z^n = \alpha U_0 \sum_{m=0}^{\infty} P_0^{\oplus}(N = m) \frac{(1 - z^m)}{1 - z} = \alpha \frac{U_0}{1 - z}\left(\sum_{m=0}^{\infty} P_0^{\oplus}(N = m) - \sum_{m=0}^{\infty} z^m P_0^{\oplus}(N = m)\right) \tag{A41}$$

$$\mathrm{gst}(0) = \alpha \frac{1}{(1 - z)}(U_0 - (U_0 \Phi_{N,0}(z))) \tag{A42}$$

2. $a = 1$

$$\alpha\left(\sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N = m) \sum_{n=0}^{m-1} n z^n\right) = \alpha\left(U_0 \sum_{m=0}^{\infty} P_0^{\oplus}(N = m)\left(\frac{z^{m+1} m - z^m m - z^{m+1} + z}{(1 - z)^2}\right)\right) \tag{A43}$$

From Eqs. (1)–(4), it is possible to show that $U_1 P_1^{\oplus}(N = n) = n U_0 P_0^{\oplus}(N = n)$ and $U_2 P_2^{\oplus}(N = n) = n^2 U_0 P_0^{\oplus}(N = n)$. By using these equalities in Eq. (A43), Eq. (A44) is obtained

$$= \alpha \frac{1}{(1 - z)^2}\left(z \sum_{m=0}^{\infty} z^m U_1 P_1^{\oplus}(N = m) - \sum_{m=0}^{\infty} z^m U_1 P_1^{\oplus}(N = m) - z \sum_{m=0}^{\infty} z^m U_0 P_0^{\oplus}(N = m) + z U_0 \sum_{m=0}^{\infty} P_0^{\oplus}(N = m)\right) \tag{A44}$$

$$\mathrm{gst}(1) = \alpha \frac{1}{(1 - z)^2}[(z - 1)(U_1 \Phi_{N,1}(z)) + z(U_0 - (U_0 \Phi_{N,0}(z)))] \tag{A45}$$

3. $a = 2$

$$
\begin{aligned}
&\alpha\left(\sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N=m) \sum_{n=0}^{m-1} n^2 z^n \right) \\
&\quad = \alpha\left(\sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N=m) \right. \\
&\quad \left. \frac{(-2z^{m+2}m + 2z^{m+1}m + z^{m+2} + z^{m+1} + z^{m+2}m^2 - 2z^{m+1}m^2 + z^m m^2 - z^2 - z)}{(z-1)^3} \right)
\end{aligned}
\tag{A46}
$$

$$
\begin{aligned}
&\alpha\left(\sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N=m) \sum_{n=0}^{m-1} n^2 z^n \right) \\
&\quad = \alpha\left(\frac{1}{(z-1)^3} \left(-2 \sum_{m=0}^{\infty} z^{m+2} m U_0 P_0^{\oplus}(N=m) \right.\right. \\
&\qquad + 2 \sum_{m=0}^{\infty} z^{m+1} m U_0 P_0^{\oplus}(N=m) \\
&\qquad + \sum_{m=0}^{\infty} z^{m+2} U_0 P_0^{\oplus}(N=m) \\
&\qquad + \sum_{m=0}^{\infty} z^{m+1} U_0 P_0^{\oplus}(N=m) \\
&\qquad + \sum_{m=0}^{\infty} z^{m+2} m^2 U_0 P_0^{\oplus}(N=m) \\
&\qquad - 2 \sum_{m=0}^{\infty} z^{m+1} m^2 U_0 P_0^{\oplus}(N=m) \\
&\qquad + \sum_{m=0}^{\infty} z^{m} m^2 U_0 P_0^{\oplus}(N=m) \\
&\qquad - \sum_{m=0}^{\infty} z^2 U_0 P_0^{\oplus}(N=m) \\
&\qquad \left.\left. - \sum_{m=0}^{\infty} z U_0 P_0^{\oplus}(N=m) \right)\right)
\end{aligned}
\tag{A47}
$$

Proceeding again as with $a = 1$, we obtain Eq. (A48)

$$
\begin{aligned}
&\alpha\left(\sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N=m) \sum_{n=0}^{m-1} n^2 z^n \right) \\
&\quad = \alpha \frac{1}{(z-1)^3} \left(-2z^2 \sum_{m=0}^{\infty} z^m U_1 P_1^{\mp\oplus}(N=m) \right. \\
&\qquad + 2z \sum_{m=0}^{\infty} z^m U_1 P_1^{\oplus}(N=m) \\
&\qquad + z^2 \sum_{m=0}^{\infty} z^m U_0 P_0^{\oplus}(N=m) + z \sum_{m=0}^{\infty} z^m U_0 P_0^{\oplus}(N=m) \\
&\qquad + z^2 \sum_{m=0}^{\infty} z^m U_2 P_2^{\mp\oplus}(N=m) \\
&\qquad - 2z \sum_{m=0}^{\infty} z^m U_2 P_2^{\oplus}(N=m) + \sum_{m=0}^{\infty} z^m U_2 P_2^{\oplus}(N=m) \\
&\qquad \left. - z^2 \sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N=m) - z - \sum_{m=0}^{\infty} U_0 P_0^{\oplus}(N=m) \right) \\
&\quad = \alpha \frac{1}{(z-1)^3} \left(-2z^2 U_1 \Phi_{N,1}(z) + 2zU_1 \Phi_{N,1}(z) \right. \\
&\qquad + z^2 U_0 \Phi_{N,0}(z) + zU_0 \Phi_{N,0}(z) + zU_2 \Phi_{N,2}(z) \\
&\qquad \left. - 2zU_0 \Phi_{N,0}(z) + U_2 \Phi_{N,2}(z) - z(z+1)U_0 \right)
\end{aligned}
\tag{A48}
$$

Rearranging Eq. (A48):

$$\begin{aligned}\mathrm{gst}(2) = \alpha \frac{1}{(1-z)^3}[&-(z-1)^2(U_2\Phi_{N,2}(z))\\ &+2z(z-1)(U_1\Phi_{N,1}(z)) - z(z+1)(U_0\Phi_{N,0}(z))\\ &+z(z+1)U_0]\end{aligned} \quad (\mathrm{A49})$$

To obtain the transform of the term in row 2.22, a totally analogous procedure must be followed. In this case, one uses the property that $\sum_{x=0}^{\infty}\sum_{y=x+2}^{\infty} = \sum_{y=2}^{\infty}\sum_{x=0}^{y-2}$.

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