Mathematical Modeling of Bivariate Distributions of Polymer Properties Using 2D Probability Generating Functions. Part II: Transformation of Population Mass Balances of Polymer Processes

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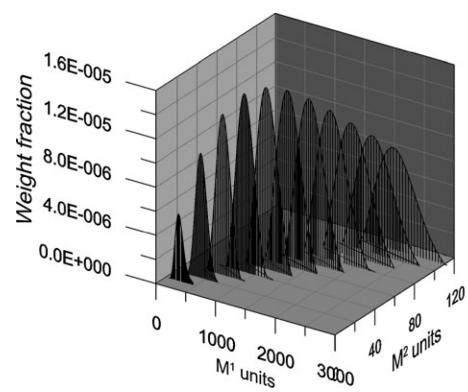
This is the second of two works presenting a new mathematical method for modeling bivariate distributions of polymer properties. It is based on the transformation of population balances using 2D probability generating functions (pgf) and *a posteriori* recovery of the distribution from the transform domain by numerical inversion. Part I of this work was devoted to the numerical inversion step. Here the transformation of the population balances to the pgf domain is analyzed. A 2D pgf transform table is developed, which allows a simple transformation of any typical polymer balance equation. Three copolymerization examples are used to show the application of the complete procedure of this modeling technique.



1. Introduction

Most common polymer synthesis methods produce resins that are composed by molecules which are not identical. This results from the random nature of the chain building process. At the very least, the resulting polymer chains vary in size. Hence, polymer samples are characterized by a distribution of chain length, or molecular weight. Molecular weight distributions (MWDs) may have very different shapes. Other polymer properties may also be described by a distribution. Branched polymers, for instance, present distributions of branch points and of crystallizable segments. Copolymers have chains with different amounts of each of the comonomers, and therefore they exhibit a composition distribution. Besides, the length of the comonomer sequences varies along the copolymer chains.

The polymer chain microstructure, including the MWD, the copolymer composition distribution (CCD), the long-chain branching distribution (LCBD), the short-chain branching distribution (SCBD), the sequence length distribution (SLD), etc., have a profound influence on the end-use properties of the material. For example, high molecular weight polyolefins exhibit improved mechanical properties, but on the other hand they have higher melt viscosities and therefore they are more difficult to process. Polyolefins with broad or bimodal MWD may present good mechanical properties due to the high molecular weight fraction, as

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well as improved processability thanks to its low molecular weight tail. The CCD also plays an important role in the applicability of copolymers, since it has influence on final properties such as stiffness, hardness, shrinkage, transparency, and optical properties.[1] The LCBD significantly influences the rheological properties of polymers, affecting the flow properties of the melted material, as well as solid state properties, like orientation effects and stressed induced crystallization.[2] The SCBD impacts on the polymer density. On its turn, the SLD affects the bulk and interfacial activity of copolymers, as well as the glass transition temperature and the lower critical solution temperature.[3] Due to the strong relationship between processing and end-use properties of polymers and their distributed molecular properties, a detailed knowledge of them is very important. In many cases, a proper characterization of a polymer sample will require simultaneous information on more than one property distribution. For instance, the joint MWD-CCD is important for copolymer systems; MWD-SCBD and/or LCBD are needed in the case of branched polymers. This requirement must be taken into account in the development of advanced mathematical models of polymer systems.

The prediction of a single property distribution, in most cases the MWD, has been extensively studied. However, the treatment of more than one independent property coordinate leads to highly complex problems for which seldom solution approaches have been developed. It is possible to divide reported modeling techniques into two major groups: stochastic methods and deterministic methods. Stochastic approaches are mainly represented by the Monte Carlo technique. The advantage of this approach is that it is relatively simple to implement and can provide extremely detailed information about the polymer microstructure and chain topological architecture that is not available with deterministic solvers. For example, Krallis et al.[4] applied a Monte Carlo Method to predict the bivariate MWD-CCD in a copolymerization system. Meimaroglou et al.[5] used a Monte Carlo technique for modeling the bivariate MWD-LCBD in the synthesis of highly branched polymers. Costeux[6] applied a Monte Carlo simulation for predicting the MWD-LCBD in the production of branched metallocene ethylene homopolymers using mixture of single-site catalysts. Soares and Hamielec[7] used Monte Carlo simulations to predict the MWD-LCBD-CCD of polyolefins produced under steady-state conditions with the mechanism of terminal branching. A significant drawback of this technique is the high computational cost required to obtain accurate results, even in modern, parallelized systems.[8]

Deterministic methods demand less computational time and storage capacity than stochastic methods. Besides, they are more appropriate for identification and optimization purposes, where it is necessary to deal with smooth, differentiable structures. These methods are based on the solution of the kinetic population balance equations. These balances are infinite in number, because the independent property coordinates (i.e., chain length of monomer/comonomer, number of short/long branches, etc.) are theoretically unbounded. The most straightforward solution approach is the direct numerical integration of the population balances of the polymer species. Under certain circumstances the infinitely sized system can be truncated by setting arbitrary upper bounds for the property variables and solving for all smaller values. Although this technique may demand solving a large system of equations, it is a simple and straightforward modeling approach. Zapata-González et al.[9] applied this approach to predict the bivariate MWD of an intermediate moiety in RAFT polymerizations. The quasi-steady state approximation was used in order to remove the stiffness of the system or equations. In earlier works, the numerical fractionation technique was used for predicting the bivariate MWD-LBCD.[2] This method consists in dividing the total population of polymer chains into classes according to the number of branching. Reconstruction of the MWD at high monomer conversions and high branching content may demanded a high computational load because a large number of classes is required in order to reduce approximation errors. More recently, Krallis et al.[4] and Meimaroglou et al.,[5] in parallel with their Monte Carlo model, applied a 2D sectional grid method for predicting the bivariate MWD-CCD and MWD-LCBD. In general, this method provided very accurate predictions of the molecular and branching characteristics of highly branched polymers in a relatively short time. Iedema et al.[10] developed a calculus method based on so-called distributed moments, in which the chain length distribution is obtained rigorously and the additional properties are computed as averages with respect to chain length. Recently, Schütte and Wulkow[11] presented a hybrid deterministic-stochastic method that combines advantages of both approaches. This hybrid method is based on computing the basic chain length distribution deterministically and adding further properties using a stochastic method based on relatively small ensembles of chains. This method was applied for predicting bivariate MWD-CCD and trivariate MWD-CCD-LCBDs in copolymerization systems.

In part I of this work,[12] we presented a new approach for the prediction of bivariate distributions of polymer properties, based on the transformation of population mass balances by means of probability generating functions (pgfs). Previously, our research group had employed the pgf technique as a comprehensive numerical tool for the prediction of the MWD in free radical polymer processes.[13,14] The pgf method was developed as a general modeling tool that can be applied to different systems. It provided excellent results in terms of accuracy, simplicity of implementation and computational effort, in models for simulation and optimization activities. In its previous state of the art, this technique employed univariate pgfs, which allowed modeling a single distribution. In parts I and II of this work, we present an extension of this technique to 2D pgfs, in order to model bivariate distributions. Briefly, the pgf technique consists of the following steps: (i) transformation of the polymer population balances to the pgf domain, (ii) solution of the transformed balances to compute pgf transforms of the distribution, and (iii) numerical inversion of the transforms obtained step (ii) to recover the bivariate distribution. In part I, the development of suitable numerical inversion algorithms of 2D pgf transforms was described. The purpose of part II of this work is to analyze comprehensively the transformation of the population balances to the pgf domain. A 2D pgf transform table is developed, which allows an easy and quick transformation of any typical polymer balance equation.

2. Pgf Modeling Method

Predicting a bivariate property distribution involves calculating the concentration of a chemical species $[S_{n,m}]$ for every possible value n and m of the two domains. If this operation were to be performed straightforwardly by solving the population balances of the chemical species present in the reacting system, an infinitely large system of equations would result. This is so because the random variables are usually unbounded (i.e., degrees of polymerization or number of branches range from 1 to infinity). Even though the upper limits were restricted to given maximum values based on previous knowledge of the system, the number of equations would be intractable in most cases for a bivariate distribution since an $n_{\max} \times m_{\max}$ grid, which easily involves thousands or millions of balance equations, needs to be computed. Different methods may be applied to this system in order to limit its size. One of them is the 2D pgf transform approach, which is appropriate for obtaining complete property distributions.

The 2D pgf transform is defined for a discrete bivariate probability distribution $p^S_{a_1,a_2}(n,m)$ as

$$\phi^S_{a_1,a_2}(z1,z2) = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m \, p^S_{a_1,a_2}(n,m) \tag{1}$$

In this expression, random variables identified by the indices n and m are the distributed properties, and $z1$ and $z2$ are the dummy variables of the pgf corresponding to the transformation on the variables idenfied by n and m, respectively. For the sake of clarity, the distributed properties will be referred as n and m, respectively, in the remainder of the paper. The notation employed in this article also uses a superscript to indicate the chemical species whose property is being considered, and the pgf order (a_1,a_2) to indicate different types of probabilities. The probability distribution $p^S_{a_1,a_2}(n,m)$ is related to the concentration of the chemical species by the following relationship:

$$p^S_{a_1,a_2}(n,m) = \frac{n^{a_1} m^{a_2} [S_{n,m}]}{\sum\limits_{p=0}^{\infty}\sum\limits_{q=0}^{\infty} p^{a_1} q^{a_2} [S_{p,q}]} \tag{2}$$

Examples of pairs (n,m) of distributed properties can be mentioned, such as (number of monomer 1, number of monomer 2) units in a copolymer chain, or the (chain length, number of branches) in a branched polymer, etc. The probability distribution has physical meanings for some combinations of (a_1,a_2). For instance, in the case of $a_1 = 0$, $a_2 = 0$ it represents the number fraction of species S.

Replacing Equation (2) in Equation (1), the following expression for the pgf definition is obtained:

$$\begin{aligned}\phi^S_{a_1,a_2}(z1,z2) &= \frac{1}{\sum\limits_{p=0}^{\infty}\sum\limits_{q=0}^{\infty} p^{a_1} q^{a_2} [S_{p,q}]} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m \, n^{a_1} m^{a_2} [S_{n,m}] \\ &= \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m \, n^{a_1} m^{a_2} [S_{n,m}]\end{aligned}$$

where $\lambda^S_{a_1,a_2} = \sum\limits_{p=0}^{\infty}\sum\limits_{q=0}^{\infty} p^{a_1} q^{a_2} [S_{p,q}]$is the double moment of order (a_1,a_2) of the bivariate distribution of species S.

It is interesting to note the resulting pgf expressions for particular values of the dummy variables $z1$ and $z2$ that are useful in the pgf transformation procedure:

$$\begin{aligned}\phi^S_{a_1,a_2}(0,0) &= \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} 0^n 0^m \, n^{a_1} m^{a_2} [S_{n,m}] \\ &= \begin{cases} \dfrac{[S_{0,0}]}{\lambda^S_{0,0}} & \text{if } a_1 = 0, a_2 = 0 \\ 0 & \text{otherwise} \end{cases}\end{aligned} \tag{4}$$

$$\begin{aligned}\phi^S_{a_1,a_2}(z1,0) &= \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n 0^m \, n^{a_1} m^{a_2} [S_{n,m}] \\ &= \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty} z1^n n^{a_1} \, 0^{a_2} [S_{n,0}] \\ &= \begin{cases} \dfrac{1}{\lambda^S_{a_1,0}} \sum\limits_{n=0}^{\infty} z1^n n^{a_1} [S_{n,0}] & \text{if } a_2 = 0 \\ 0 & \text{otherwise} \end{cases}\end{aligned} \tag{5}$$

Analogously,

$$\phi^S_{a_1,a_2}(0,z2) = \begin{cases} \dfrac{1}{\lambda^S_{0,a_2}} \displaystyle\sum_{m=0}^{\infty} z2^m m^{a_2}[S_{0,m}] & if\ a_1 = 0 \\ 0 & \text{otherwise} \end{cases} \quad (6)$$

$$\phi^S_{a_1,a_2}(z1,1) = \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n n^{a_1} m^{a_2}[S_{n,m}] \quad (7)$$

$$\phi^S_{a_1,a_2}(1,z2) = \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z2^m\, n^{a_1} m^{a_2}[S_{n,m}] \quad (8)$$

$$\phi^S_{a_1,a_2}(1,1) = \frac{1}{\lambda^S_{a_1,a_2}} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} n^{a_1} m^{a_2}[S_{n,m}] = 1 \quad (9)$$

Besides, Equation (10) and (11) present the derivatives of the pgf with respect to the dummy variables. These derivatives appear in the pgf transformation process.

$$\frac{\partial\phi^S_{a_1,a_2}(z1,z2)}{\partial z1} = \frac{1}{\lambda^S_{a_1,a_2} z1} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1+1} m^{a_2}[S_{n,m}] = \frac{\lambda^S_{a_1+1,a_2}\phi^S_{a_1+1,a_2}(z1,z2)}{\lambda^S_{a_1,a_2} z1} \quad (10)$$

$$\frac{\partial\phi^S_{a_1,a_2}(z1,z2)}{\partial z1} = \frac{1}{\lambda^S_{a_1,a_2} z2} \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1} m^{a_2+1}[S_{n,m}] = \frac{\lambda^S_{a_1,a_2+1}\phi^S_{a_1,a_2+1}(z1,z2)}{\lambda^S_{a_1,a_2} z2} \quad (11)$$

The pgf modeling method is based on the transformation of the infinite population mass balances governing the polymer process into the pgf domain, obtaining a system of equations in which the dependent variable is the pgf transform of the distribution. Pgf values are calculated by solving this system, from which the desired distribution is obtained by means of an inversion formula. The reason for this transformation is that pgf evaluations at a relatively coarse grid of its dummy variables $z1$ and $z2$ are required for recovering the distribution for a set of arbitrary values of the random variables. Hence, a finite and reasonably sized system of equations needs to be solved in order to predict the distribution.

Part I of this work[12] was focused on the development of suitable numerical inversion methods of 2D pgfs that allow recovering the distributions from the transformed domain. Efficient and accurate inversion methods were presented and thoroughly analyzed. This article, Part II of this work, is devoted to the mathematical procedures required to obtain the transformed equations. The development of a pgf transform table, likewise a Laplace transform table, that allows an easy transformation of the population balance equations, is shown.

3. Structure of the Population Balances from the Point of View of the Pgf Transformation

In a polymer reaction system, population balance equations are composed by an accumulation term (which is zero in the case of steady-state systems) and a sum of terms corresponding to the generation or consumption of the species due to each of the reaction steps and the contributions of the inputs to and outputs from the system. Table 1 shows a compilation of kinetic steps that are typical in polymerization systems, divided into linear copolymerization and homopolymerization with branching, two classic situations in which bivariate distributions appear. The terminal model is assumed for the copolymerization case, but the extension to the penultimate model is straightforward. This table is not intended as a complete collection of balance terms, but it provides a proper selection of the different balance term structures, from the point of view of the pgf transformation, that are likely to be found when applying the pgf technique to a polymer system.

From each one of the reaction steps in this table, reaction rate terms for the involved polymer species arise, as shown in the second column of this table. When a reaction step contributes in a different way to living polymer radical and to dead copolymer balance equations, reaction rate terms are preceded by the polymer species to whose balance equation they belong (i.e., $R^1_{n,m} : -\sum_{j=1}^{2} k_{tc,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$ means that the term $-\sum_{j=1}^{2} k_{tc,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$ belongs to the balance equation of species $R^i_{n,m}$). Accumulation and input/output terms are also shown in Table 1. Symbol k stands for a kinetic constant, I is an initiator molecule, θ is an integer number, Ri is an initiation radical, f is the initiator efficiency, M is a monomer (with a superscript indicating the monomer type in the copolymerization case), V is the reaction volume, $R_{n,m}$ is a homopolymer with n branches and chain length m, $R^i_{n,m}$ is a living copolymer radical with n units of monomer 1 and m units of monomer 2 with a monomer i final unit, $P_{n,m}$ is a dead copolymer with n units of monomer 1 and m units of monomer 2, or a dead homopolymer with n branches and chain length m, $S_{n,m}$ is any living or dead polymer species with n and m units of the first and second distributed properties, respectively, $\lambda^j_{a_1,a_2}$ is the double moment of order a_1,a_2 of the MWD of species j, and τ is the independent variable in the differential balance equation.

Table 1. Accumulation, input/output and kinetic steps in polymerization reactions. Contribution to population balances of polymer species and general structure of the balance terms.

Kinetic step	Population balance term	General structure
Accumulation	$\alpha \frac{\partial[S_{n,m}]}{\partial\tau}$	$\alpha \frac{\partial[S_{n,m}]}{\partial\tau}$
Input/output	$input: \sum_i F_{input_i}[S_{n,m}]_{input_i}$ $output: \sum_i F_{output_i}[S_{n,m}]_{output_i}$	$input: \alpha[S_{n,m}]$ $output: \alpha[S_{n,m}]$
Global cumulative distribution	$\alpha\sum_{i=0}^{n}\sum_{j=0}^{m}[S_{i,j}]$	$\alpha\sum_{i=0}^{n}\sum_{j=0}^{m}[S_{i,j}]$
Cumulative distribution in the first domain	$\alpha\sum_{i=1}^{n}[S_{i,m}]$	$\alpha\sum_{i=1}^{n}[S_{i,m}]$
Cumulative distribution in the second domain	$\alpha\sum_{i=1}^{m}[S_{n,i}]$	$\alpha\sum_{i=1}^{m}[S_{n,i}]$
	Copolymerization	
Initiation		
$I \xrightarrow{k_d} \theta Ri$		
$Ri + M^i \xrightarrow{f k_i} R^i_{2-i,i-1}, i = 1,2$	$R^i_{n,m}: \theta f\, k_d I \frac{[M^i]}{[M^1]+[M^2]} V\delta_{n,2-i}\delta_{m,i-1}$	$R^i_{n,m}: \alpha\delta_{n,2-i}\delta_{m,i-1}$
$R^i_{n,m} + M^j \xrightarrow{k_{p,ij}} R^j_{n+2-j,m+j-1}$, $i = 1,2,\ j = 1,2$	$R^i_{n,m}: \ -\sum_{j=1}^{2} k_{p,ij}[M^j][R^i_{n,m}] + \sum_{j=1}^{2} k_{p,ji}[M^i][R^j_{n+i-2,m+1-i}] (1-\delta_{n,2-i}\delta_{m,i-1})$	$R^i_{n,m}: \ \alpha[S_{n,m}], \alpha[S_{n-1,m}], \alpha[S_{n,m-1}]$ $\alpha[S_{n-1,m}]\delta_{n,1}\delta_{m,0}, \alpha[S_{n,m-1}]\delta_{n,0}\delta_{m,1}$
Termination by combination		
$R^i_{n,m} + R^j_{r,q} \xrightarrow{k_{tc,ij}} P_{n+r,m+q}$, $i = 1,2,\ j = 1,2$	$R^i_{n,m}: -\sum_{j=1}^{2} k_{tc,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$	$R^i_{n,m}: \alpha[S_{n,m}]$
	$P_{n,m}\ : k_{tc,12}\sum_{r=1}^{n}\sum_{s=0}^{m-1} R^1_{r,s}R^2_{n-r,m-s}$ $+\frac{1}{2}k_{tc,11}\sum_{r=1}^{n-1}\sum_{s=0}^{m} R^1_{r,s}R^1_{n-r,m-s}(1-\delta_{n,1})$ $+\frac{1}{2}k_{tc,22}\sum_{r=0}^{n}\sum_{s=1}^{m-1} R^2_{r,s}R^2_{n-r,m-s}(1-\delta_{m,1})$	$P_{n,m}\ : \alpha\sum_{r=1}^{n}\sum_{s=0}^{m-1} S^1_{r,s}S^2_{n-r,m-s}$, $\alpha\sum_{r=1}^{n-1}\sum_{s=0}^{m} S_{r,s}S_{n-r,m-s}$, $\alpha\sum_{r=1}^{n-1}\sum_{s=0}^{m} S_{r,s}S_{n-r,m-s}\delta_{n,1}$, $\alpha\sum_{r=0}^{n}\sum_{s=1}^{m-1} S_{r,s}S_{n-r,m-s}$ $\alpha\sum_{r=0}^{n}\sum_{s=1}^{m-1} S_{r,s}S_{n-r,m-s}\delta_{m,1}$
Termination by disproportionation		
$R^i_{n,m} + R^j_{r,q} \xrightarrow{k_{td,ij}} P_{n,m} + P_{r,q}$, $i = 1,2,\ j = 1,2$	$R^i_{n,m}: -\sum_{j=1}^{2} k_{td,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$	$R^i_{n,m}: \alpha[S_{n,m}]$
	$P_{n,m}: \sum_{i=1}^{2}\sum_{j=1}^{2} k_{td,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$	$P_{n,m}: \alpha[S_{n,m}]$

Table 1. (Continued)

Kinetic step	Population balance term	General structure
Reaction with terminal double bound		
$R^i_{n,m} + P_{r,q} \xrightarrow{k_{db,ij}} R^j_{n+r,m+q}$ $i = 1,2,\ j = 1,2$	$R^i_{n,m} \quad -\sum_{j=1}^{2} k_{db,ij}\left[R^i_{n,m}\right]\lambda^P_{0,0}$ $+k_{td,1i}\sum_{r=0}^{n-1}\sum_{s=0}^{m}\left[P_{r,s}\right]\left[R^1_{n-r,m-s}\right]$ $+k_{td,2i}\sum_{r=0}^{n}\sum_{s=0}^{m-1}\left[P_{r,s}\right]\left[R^2_{n-r,m-s}\right]$	$R^i_{n,m} \quad : \alpha\left[S_{n,m}\right], \alpha\sum_{r=0}^{n-1}\sum_{s=0}^{m} S^1_{r,s}S^2_{n-r,m-s},$ $\alpha\sum_{r=0}^{n}\sum_{s=0}^{m-1} S^1_{r,s}S^2_{n-r,m-s},$
	$P_{n,m} : -\sum_{i=1}^{2}\sum_{j=1}^{2} k_{db,ij}\left[P_{n,m}\right]\lambda^{R^i}_{0,0}$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Chain transfer to transfer agent		
$R^i_{n,m} + S \xrightarrow{k_{fsi}} R^i_{2-i,i-1}$ $+P_{n,m}, i = 1,2$	$R^i_{n,m} : k_{fsi}[S]\lambda^{R^i}_{0,0}\delta_{n,2-i}$ $\delta_{m,i-1} - k_{fsi}[S]\left[R^i_{n,m}\right]$	$R^i_{n,m} : \alpha\delta_{n,1}\delta_{m,0}, \alpha\delta_{n,0}\delta_{m,1}, \alpha\left[S_{n,m}\right]$
	$P_{n,m} : \sum_{i=1}^{2} k_{fsi}[S]\left[R^i_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Chain transfer to monomer		
$R^i_{n,m} + M^j \xrightarrow{k_{fmij}} R^i_{2-j,j-1}$ $+P_{n,m}, i = 1,2, j = 1,2$	$R^i_{n,m} : \sum_{j=1}^{2} k_{fmji}\left[M^i\right]\lambda^{R^j}_{0,0}\delta_{n,2-i}\delta_{m,i-1}$ $-k_{fmij}\left[M^j\right]\left[R^i_{n,m}\right]$	$R^i_{n,m} : \alpha\delta_{n,1}\delta_{m,0}, \alpha\delta_{n,0}\delta_{m,1}, \alpha\left[S_{n,m}\right]$
	$P_{n,m} : \sum_{i=1}^{2}\sum_{j=1}^{2} k_{fmij}\left[M^j\right]\left[R^i_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Chain transfer to polymer		
$R^i_{n,m} + P_{r,q} \xrightarrow{k_{fpij}} R^j_{r,q} + P_{n,m},$ $i = 1,2, j = 1,2$	$R^i_{n,m} : \sum_{j=1}^{2} k_{fpji} n^{2-i} m^{i-1}\lambda^{R^j}_{0,0} P_{n,m}$ $-k_{fpij}\lambda^P_{2-j,j-1}[R^i_{n,m}]$	$R^i_{n,m} : \alpha n\left[S_{n,m}\right],\ \alpha m\left[S_{n,m}\right],\ \alpha\left[S_{n,m}\right]$
	$P_{n,m} : \sum_{i=1}^{2}\sum_{j=1}^{2} k_{fpij}\lambda^P_{2-j,j-1}\left[R^i_{n,m}\right]$ $-k_{fpij}\lambda^{R^i}_{0,0} n^{2-j} m^{j-1}\left[P_{n,m}\right]$	$P_{n,m} : \alpha n\left[S_{n,m}\right],\ \alpha m\left[S_{n,m}\right],\ \alpha\left[S_{n,m}\right]$
	Branching	
Initiation		
$I \xrightarrow{k_d} \theta Ri$ $Ri + M \xrightarrow{f\,k_i} R_{1,1}$	$R_{n,m} : \theta f\ k_d[I][M]V\delta_{m,1}$	$R_{n,m} : \alpha\delta_{m,1}$
Propagation		
$R_{n,m} + M \xrightarrow{k_p} R_{n,m+1}$	$R_{n,m} : -k_p[M]\left[R_{n,m}\right]$ $+k_p[M]\left[R_{n,m-1}\right]\left(1-\delta_{m,1}\right)$	$R_{n,m} : \alpha\left[S_{n,m}\right], \alpha\left[S_{n,m-1}\right],$ $\alpha\left[S_{n,m-1}\right]\delta_{m,1}$
Termination by combination		
$R_{n,m} + R_{r,q} \xrightarrow{k_{tc}} P_{n+r-1,m+q}$	$R_{n,m} : -k_{tc}\lambda^R_{0,0}\left[R_{n,m}\right]$	$R_{n,m} : \alpha\left[S_{n,m}\right]$
	$P_{n,m} : \frac{1}{2}k_{tc}\sum_{r=1}^{n}\sum_{s=1}^{m-1} R_{r,s}$ $R_{n-r+1,m-s}\left(1-\delta_{m,1}\right)$	$P_{n,m} : \alpha\sum_{r=1}^{n}\sum_{s=1}^{m-1} S_{r,s}S_{n-r+1,m-s},$ $\alpha\sum_{r=1}^{n}\sum_{s=1}^{m-1} S_{r,s}S_{n-r+1,m-s}\delta_{m,1}$

Table 1. (Continued)

Kinetic step	Population balance term	General structure
Termination by disproportionation		
$R_{n,m} + R_{r,q} \xrightarrow{k_{td}} P_{n,m} + P_{r,q}$	$R_{n,m} : -k_{td}\lambda^R_{0,0}\left[R^i_{n,m}\right]$	$R_{n,m} : \alpha\left[S_{n,m}\right]$
	$P_{n,m} : k_{td}\lambda^R_{0,0}\left[R^i_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Reaction with terminal double bound		
$R_{n,m} + P_{r,q} \xrightarrow{k_{db}} R_{n+r,m+q}$	$R_{n,m} : -k_{db}\lambda^P_{0,0}\left[R_{n,m}\right] + k_{db}\sum_{r=1}^{n-1}\sum_{s=1}^{m-1}\left[P_{r,s}\right]\left[R_{n-r,m-s}\right] \left(1-\delta_{n,1}\right)\left(1-\delta_{m,1}\right)$	$R_{n,m} : \alpha\left[S_{n,m}\right], \alpha\sum_{r=1}^{n-1}\sum_{s=1}^{m-1} S^1_{r,s}S^2_{n-r,m-s}$ $\alpha\sum_{r=1}^{n-1}\sum_{s=1}^{m-1} S^1_{r,s}S^2_{n-r,m-s}\delta_{n,1},$ $\alpha\sum_{r=1}^{n-1}\sum_{s=1}^{m-1} S^1_{r,s}S^2_{n-r,m-s}\delta_{m,1},$ $\alpha\sum_{r=1}^{n-1}\sum_{s=1}^{m-1} S^1_{r,s}S^2_{n-r,m-s}\delta_{n,1}\delta_{m,1}$
	$P_{n,m} : -k_{db}\lambda^P_{0,0}\left[P_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Chain Scission		
$R_{n,m+1} \xrightarrow{k_s} P_{n,m} + R_{1,1}$	$R_{n,m} : -k_s\left[R_{n,m}\right]\left(1-\delta_{m,1}\right) + \left(\sum_{s=1}^{\infty}\sum_{t=2}^{\infty}\left[R_{s,t}\right]\right)\left(\delta_{n,1}\delta_{m,1}\right)$	$R_{n,m} : \alpha\left[S_{n,m}\right], \alpha\left[S_{n,m}\right]\delta_{m,1}, \alpha\delta_{n,1}\delta_{m,1}$
	$P_{n,m} : k_s\left[R_{n,m+1}\right]$	$P_{n,m} : \alpha\left[S_{n,m+1}\right]$
Chain transfer to transfer agent		
$R_{n,m} + S \xrightarrow{k_{fs}} R_{1,1} + P_{n,m}$	$R_{n,m} : k_{fs}[S]\lambda^R_{0,0}\delta_{n,1}\delta_{m,1} - k_{fs}[S]\left[R_{n,m}\right]$	$R_{n,m} : \alpha\delta_{n,1}\delta_{m,1}, \alpha\left[S_{n,m}\right]$
	$P_{n,m} : k_{fs}[S]\left[R_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Chain transfer to monomer		
$R_{n,m} + M \xrightarrow{k_{fm}} R_{1,1} + P_{n,m}$	$R_{n,m} : k_{fm}[M]\lambda^R_{0,0}\delta_{n,1}\delta_{m,1} - k_{fm}[M]\left[R_{n,m}\right]$	$R_{n,m} : \alpha\delta_{n,1}\delta_{m,1}, \alpha\left[S_{n,m}\right]$
	$P_{n,m} : k_{fs}[S]\left[R_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$
Chain transfer to polymer		
$R_{n,m} + P_{r,q} \xrightarrow{k_{fp}} R_{r+1,q} + P_{n,m}$	$R_{n,m} : k_{fp}m\lambda^R_{0,0}P_{n-1,m} - k_{fp}\lambda^P_{0,1}\left[R_{n,m}\right]$	$R_{n,m} : \alpha m\left[S_{n-1,m}\right], \alpha\left[S_{n,m}\right]$
	$P_{n,m} : -k_{fp}n\lambda^R_{0,0}P_{n,m} + k_{fp}\lambda^P_{0,1}\left[R_{n,m}\right]$	$P_{n,m} : \alpha\left[S_{n,m}\right]$

Different conventions are used in the literature for the minimum values of the chain lengths or number of branches. In this paper, it is considered that a copolymer has at least one unit of any of the comonomers, that is, for a copolymer $P_{n,m}$, $n \geq 0$, $m \geq 0$, and $n + m \geq 1$. This is further restricted for living radicals, since a living radical ending in a monomer i unit must have at least one unit of this monomer (i.e., for the living radical $R^1_{n,m}$, $n \geq 1$). In the case of branched homopolymers, the minimum number of branches is 1, which means that the main chain is regarded as a branch. Hence, for a homopolymer $S_{n,m}$ with n branches and chain length m, $n \geq 1$ and $m \geq 1$. Factor α stands for all the variables that are not themselves functions of the distributed domains. Examples would include concentrations of monomer, solvent or initiator, kinetic constants, and the like.

The balance terms shown in column 2 of Table 1 can be represented by a general structure. This structure is composed by the product of a factor α multiplied by the concentrations of polymer species with certain values of the two distributed domains that characterize them. The representation of the balance terms according to this general structure is shown in the third column of Table 1. From inspection of the balance terms, it can be seen that many of them share the same general structure. For instance, terms corresponding to the system input/output, termination by combination or disproportionation for radical species, reaction with terminal double bond for dead polymer species, and others, have the same structure $\alpha[S_{n,m}]$. The general structure is what matters when performing the 2D pgf transformation. Hence, all terms with the same general structure will have the same pgf transform, regardless the kinetic step they come from. This facilitates considerably the pgf transformation process and allows condensing information on the pgf transformation. The pgf transformation process is described in the next section.

4. Pgf Transformation

The pgf transform of a balance equation consists of the sum of the transforms of the individual terms comprising it. The general method to carry out the 2D pgf transformation consists in multiplying each term of the population balance equation, which is function of the concentrations of polymeric species characterized by the two distributed domains n and m, by $z1^n z2^m n^{a_1} m^{a_2}$ ($a_1 = 0, 1$, $a_2 = 0, 1$), and then performing a double summation for all possible values of n and m. The result is put in terms of the 2D pgfs by means of the definitions of the pgf and the different probabilities, obtaining an equation which is now function of the 2D pgf and moments of the bivariate distributions.

The transformation process can be tedious and time consuming. In order to aid in this procedure, the different general structures of the terms that may appear in population balance equations were collected and tabulated together with their 2D pgf transforms. This information is presented in Table 2. Comprehensiveness was sought when building this table. However, it should not be regarded as absolutely complete. Details on the transformation procedure to obtain the results shown in this table are given in the Appendix section. If a different kinetic step from those presented in Table 1 appears, its pgf transform can be derived following the procedures explained there.

Although powerful, the pgf method still cannot be used on every type of polymerization. So far we have been able to apply this method for the cases were termination constants are independent of chain length. The applicability of this technique to polymerization systems where the kinetic rate of termination depends on the chain length is not straightforward and it further requires an exhaustive mathematical work that is under way.

Three examples are presented in the next section in order to illustrate how to apply the previous derivations to transform the population balances of a polymer process into the 2D pgf domain.

5. Application Examples

This section illustrates the application of the pgf method for modeling bivariate polymer distributions. The pgf technique is applied for modeling the bivariate MWD in a copolymerization system.

A general kinetic scheme that collects the most usual reactions appearing in different copolymerization systems is shown in Table 3.

Symbols I, Ri, S*, and M^j ($j = 1,2$) denote, respectively, initiator, initiation radical from initiator decomposition, initiation radical from transfer to transfer agent, and monomers. The symbols $R^i_{n,m}$ and $P_{n,m}$ identify the live and dead copolymer chains, respectively, with n units of monomers M^1 and m units of monomers M^2, and a monomer M^i as final unit. Although this kinetic mechanism is not completely general, it allows most of the accepted kinetic phenomena. Extension to multiple transfer agents, capping reactions (i.e., in controlled living polymerization), etc., is trivial.

5.1. Case I

As a first case study, a hypothetical copolymerization reaction (system S1) described only by initiation, propagation, and termination by disproportionation steps will be considered. The corresponding population balances are shown in Table 4.

The first step of the pgf technique is transforming the population balances of the polymer species (Equation 24 and 25) into the pgf domain. In this case only the number distribution will be recovered from the transformed domain, so pgfs of order (0,0) will be computed. The pgf transform table (Table 2) can be used to perform this transformation. In order to use this table, first the general structure of each of the terms in the population balances has to be identified. For instance, the accumulation term $\frac{d[R^i_{n,m}]}{dt}$ in Equation (24) corresponds to the entry $\frac{d\alpha[S_{n,m}]}{d\tau}$ in row T2.1 of Table 2. Hence, the transform of this term is $\frac{\partial(\lambda^{R^i}_{0,0}\phi^{R^i}_{0,0}(z1,z2))}{\partial\tau}$. The term $2fk_d[I]\frac{[M^i]}{[M^1]+[M^2]}\delta_{n,2-i}\delta_{m,i-1}$ can be found in row T2.3 with the general structure $\alpha\delta_{n,u}\delta_{m,v}$, and its transform is $2fk_d[I]\frac{[M^i]}{[M^1]+[M^2]}z1^{2-i}z2^{i-1}$. The transform of the term $\sum_{j=1}^{2} k_{p,ji}[M^i]\left[R^j_{n+i-2,m+1-i}\right](1-\delta_{n,2-i}\delta_{m,i-1})$ is found, expanding the sum in j, in rows T2.6 and T2.8. From row T2.6 it can be seen that the transform of $\sum_{j=1}^{2} k_{p,ji}[M^i]\left[R^j_{n+i-2,m+1-i}\right]$ is, collecting again the sum in j, $\sum_{j=1}^{2} k_{p,ji}[M^i](zi)\left(\lambda^{R^i}_{0,0}\phi^{R^i}_{0,0}(z1,z2)\right)$. In the same way, row T2.8 tells that the transform of $\sum_{j=1}^{2} k_{p,ji}[M^i]\left[R^j_{n+i-2,m+1-i}\right]\delta_{n,2-i}\delta_{m,i-1}$ is $\sum_{j=1}^{2} k_{p,ji}[M^i](zi)\left[R^j_{0,0}\right]$. Species $R^j_{0,0}$ does not exist

Table 2. Terms of a population balance for $[S_{n,m}]$ and their corresponding transformed terms in a balance equation for $\lambda_{a1,a2}\phi_{a_1,a_2}(z1,z2)$.

Balance term	Pgf transform	
$\frac{\partial\alpha[S_{n,m}]}{\partial\tau}$	$\frac{\partial\alpha\left(\lambda^{S}_{a_1,a_2}\phi^{S}_{a_1,a_2}(z1,z2)\right)}{\partial\tau}$	T2. 1
$\alpha\delta_{n,j}(\alpha\delta_{m,j}),\quad j=0,1,2,\ldots$	$\alpha z1^{j} j^{a_1}\frac{\prod_{k=1}^{a_2}(z2+k-1)}{(1-z2)^{a_2+1}}\left(\alpha z2^{j} j^{a_2}\frac{\prod_{k=1}^{a_1}(z1+k-1)}{(1-z1)^{a_1+1}}\right)$	T2. 2
$\alpha\delta_{n,u}\delta_{m,v}, u,v=0,1,2,\ldots$	$\alpha z1^{u}z2^{v}u^{a_1}v^{a_2}$	T2. 3
$\alpha[S_{n,m}]\delta_{n,j}(\alpha[S_{n,m}]\delta_{m,j}),\ j=0,1,2,\ldots$	$\alpha j^{a_1}z1^{j}\left(\mu^{S_{j,*}}_{a_2}\varphi^{S_{j,*}}_{a_2}(z2)\right)\quad j=0,1,2,\ldots$ or $\alpha 0^{a_1}\left(\lambda^{S}_{0,a_2}\phi^{S}_{0,a_2}(0,z2)\right)\quad j=0$ $\left(\begin{array}{l}\alpha z2^{j} j^{a_2}\left(\mu^{S_{*,j}}_{a_1}\varphi^{S_{*,j}}_{a_1}(z1)\right)\quad j=0,1,2,\ldots\\ \text{or}\\ \alpha 0^{a_2}\left(\lambda^{S}_{a_1,0}\phi^{S}_{a_1,0}(z1,0)\right)\quad j=0\end{array}\right)$	T2. 4
$\alpha[S_{n,m}]$	$\alpha\left(\lambda^{S}_{a_1,a_2}\phi^{S}_{a_1,a_2}(z1,z2)\right)$	T2. 5
$\alpha[S_{n-1,m}](\alpha[S_{n,m-1}])$	$\alpha z1\sum_{r=0}^{a_1}\binom{a_1}{r}\left(\lambda^{S}_{r,a_2}\phi^{S}_{r,a_2}(z1,z2)\right)\left(\alpha z2\sum_{r=0}^{a_2}\binom{a_2}{r}\left(\lambda^{S}_{a_1,r}\phi^{S}_{a_1,r}(z1,z2)\right)\right)$	T2. 6
$\alpha[S_{n-1,m}]\delta_{n,j}(\alpha[S_{n,m-1}]\delta_{m,j}),\ j=0,1,2\ldots$	$\alpha z1^{j-1}(j-1)^{a_1}\left(\mu^{S_{j-1,*}}_{a_2}\varphi^{S_{j-1,*}}_{a_2}(z2)\right)\left(\alpha z2^{j} j^{a_2}\left(\mu^{S_{*,j-1}}_{a_1}\varphi^{S_{*,j-1}}_{a_1}(z1)\right)\right)$	T2. 7
$\alpha[S_{n-1,m}]\delta_{n,u}\delta_{m,v}(\alpha[S_{n,m-1}]\delta_{n,u}\delta_{m,v}),\ u,v=0,1,2\ldots$	$\alpha z1^{u}z2^{v}u^{a_1}v^{a_2}[S_{u-1,v}](\alpha z1^{u}z2^{v}u^{a_1}v^{a_2}[S_{u,v-1}])$	T2. 8
$\alpha[S_{n+1,m}](\alpha[S_{n,m+1}])$	$\frac{\alpha}{z1}\left(\sum_{r=0}^{a_1}\binom{a_1}{r}(-1)^{a_1-r}\left(\lambda^{S}_{r,a_2}\phi^{S}_{r,a_2}(z1,z2)\right)-(-1)^{a_1}\lambda^{S}_{0,a_2}\varphi^{S}_{0,a_2}(0,z2)\right)$ $\left(\frac{\alpha}{z2}\left(\sum_{r=0}^{a_2}\binom{a_2}{r}(-1)^{a_2-r}\left(\lambda^{S}_{a_1,r}\phi^{S}_{a_1,r}(z1,z2)\right)-(-1)^{a_2}\lambda^{S}_{a_1,0}\varphi^{S}_{a_1,0}(z1,0)\right)\right)$	T2. 9
$\alpha\sum_{i=1}^{n}\sum_{j=0}^{m-1}[S^{1}_{i,j}][S^{2}_{n-i,m-j}]$	$\alpha\left(\begin{array}{l}\sum_{r=0}^{a_1}\sum_{t=0}^{a_2}\binom{a_1}{r}\binom{a_2}{t}\left(\lambda^{S^1}_{r,t}\phi^{S^1}_{r,t}(z1,z2)\right)\left(\lambda^{S^2}_{a_1-r,a_2-t}\phi^{S^2}_{a_1-r,a_2-t}(z1,z2)\right)\\ -\sum_{l=0}^{a_2}\binom{a_2}{l}\left(\lambda^{S^l}_{0,a_2-l}\phi^{S^1}_{0,a_2-l}(0,z2)\right)\left(\lambda^{S^2}_{a_1,l}\phi^{S^2}_{a_1,l}(z1,z2)\right)-\\ \sum_{l=0}^{a_1}\binom{a_1}{l}\left(\lambda^{S^2}_{a_1-l,0}\phi^{S^2}_{a_1-l,0}(z1,0)\right)\left(\lambda^{S^l}_{l,a_2}\phi^{S^1}_{l,a_2}(z1,z2)\right)+\left(\lambda^{S^2}_{a_1,0}\phi^{S^2}_{a_1,0}(z1,0)\right)\left(\lambda^{S^1}_{0,a_2}\phi^{S^1}_{l,a_2}(0,z2)\right)\end{array}\right)$	T2. 10
$\alpha\sum_{i=0}^{n-1}\sum_{j=0}^{m}[S^{1}_{i,j}][S^{2}_{n-i,m-j}]$	$\alpha\left(\begin{array}{l}\sum_{r=0}^{a_1}\sum_{t=0}^{a_2}\binom{a_1}{r}\binom{a_2}{t}\left(\lambda^{S^1}_{r,t}\phi^{S^1}_{r,t}(z1,z2)\right)\left(\lambda^{S^2}_{a_1-r,a_2-t}\phi^{S^2}_{a_1-r,a_2-t}(z1,z2)\right)\\ -\sum_{l=0}^{a_2}\binom{a_2}{l}\left(\lambda^{S^2}_{0,l}\phi^{S^2}_{0,l}(0,z2)\right)\left(\lambda^{S^1}_{a_1,a_2-l}\phi^{S^1}_{a_1,a_2-l}(z1,z2)\right)\end{array}\right)$	T2. 11

Table 2. (Continued)

Balance term	Pgf transform	
$\alpha \sum_{i=0}^{n} \sum_{j=0}^{m-1} \left[S_{i,j}^1\right]\left[S_{n-i,m-j}^2\right]$	$\alpha \left(\begin{array}{l} \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r}\binom{a_2}{t} \left(\lambda_{r,t}^{S1}\phi_{r,t}^{S1}(z1,z2)\right)\left(\lambda_{a_1-r,a_2-t}^{S2}\phi_{a_1-r,a_2-t}^{S2}(z1,z2)\right) \\ -\sum_{l=0}^{a_1}\binom{a_1}{l}\left(\lambda_{l,0}^{S2}\phi_{l,0}^{S2}(z1,0)\right)\left(\lambda_{a_1-l,a_2}^{S1}\phi_{a_1-l,a_2}^{S1}(z1,z2)\right) \end{array} \right)$	T2. 12
$\alpha \sum_{i=1}^{n-1} \sum_{j=1}^{m-1} \left[S_{i,j}^1\right]\left[S_{n-i,m-j}^2\right]$	$\alpha \left(\begin{array}{l} \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r}\binom{a_2}{t} \left(\lambda_{r,t}^{S1}\phi_{r,t}^{S1}(z1,z2)\right)\left(\lambda_{a_1-r,a_2-t}^{S2}\phi_{a_1-r,a_2-t}^{S2}(z1,z2)\right) \\ -\sum_{l=0}^{a_2}\binom{a_2}{l}\left(\lambda_{0,a_2-l}^{S1}\phi_{0,a_2-l}^{S}(0,z2)\right)\left(\lambda_{a_1,l}^{S2}\phi_{a_1,l}^{S2}(z1,z2)\right)+\left(\lambda_{0,a_2}^{S1}\phi_{0,a_2}^{S1}(0,z2)\right)\left(\lambda_{a_1,0}^{S2}\phi_{a_1,0}^{S2}(z1,0)\right) \\ -\sum_{l=0}^{a_2}\binom{a_2}{l}\left(\lambda_{a_1,a_2-l}^{S1}\phi_{a_1,a_2-l}^{S1}(z1,z2)\right)\left(\lambda_{0,l}^{S2}\phi_{0,l}^{S2}(0,z2)\right)+\left(\lambda_{a_1,0}^{S1}\phi_{a_1,0}^{S1}(z1,0)\right)\left(\lambda_{0,a_2}^{S2}\phi_{0,a_2}^{S2}(0,z2)\right) \\ -\sum_{l=0}^{a_1}\binom{a_1}{l}\left(\lambda_{a_1-l,0}^{S1}\phi_{a_1-l,0}^{S1}(z1,0)\right)\left(\lambda_{l,a_2}^{S2}\phi_{l,a_2}^{S2}(z1,z2)\right) \\ -\sum_{l=0}^{a_1}\binom{a_1}{l}\left(\lambda_{a_1-l,a_2}^{S1}\phi_{a_1-l,a_2}^{S1}(z1,z2)\right)\left(\lambda_{l,0}^{S2}\phi_{l,0}^{S2}(z1,0)\right) \end{array} \right)$	T2. 13
$\alpha \sum_{i=1}^{n-1} \sum_{j=0}^{m} \left[S_{i,j}\right]\left[S_{n-i,m-j}\right]$	$\alpha \left(\begin{array}{l} \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r}\binom{a_2}{t} \left(\lambda_{r,t}^{S}\phi_{r,t}^{S}(z1,z2)\right)\left(\lambda_{a_1-r,a_2-t}^{S}\phi_{a_1-r,a_2-t}^{S}(z1,z2)\right) \\ -\sum_{l=0}^{a_2}\binom{a_2}{l}\left(\lambda_{0,a_2-l}^{S}\phi_{0,a_2-l}^{S}(0,z2)\right)\left(\lambda_{a_1,l}^{S}\phi_{a_1,l}^{S}(z1,z2)\right) \\ -\sum_{l=0}^{a_2}\binom{a_2}{l}\left(\lambda_{0,a_2}^{S}\phi_{0,a_2}^{S}(0,z2)\right)\left(\lambda_{a_1,a_2-l}^{S}\phi_{a_1,a_2-l}^{S}(z1,z2)\right) \end{array} \right)$	T2. 14
$\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} \left[S_{i,j}\right]\left[S_{n-i,m-j}\right]$	$\alpha \left(\begin{array}{l} \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r}\binom{a_2}{t} \left(\lambda_{r,t}^{S}\phi_{r,t}^{S}(z1,z2)\right)\left(\lambda_{a_1-r,a_2-t}^{S}\phi_{a_1-r,a_2-t}^{S}(z1,z2)\right) \\ -\sum_{l=0}^{a_1}\binom{a_1}{l}\left(\lambda_{a_1-l,0}^{S}\phi_{a_1-l,0}^{S}(z1,0)\right)\left(\lambda_{l,a_2}^{S}\phi_{l,a2}^{S}(z1,z2)\right) \\ -\sum_{l=0}^{a_1}\binom{a_1}{l}\left(\lambda_{l,0}^{S}\phi_{l,0}^{S}(z1,0)\right)\left(\lambda_{a_1-l,a_2}^{S}\phi_{a_1-l,a_2}^{S}(z1,z2)\right) \end{array} \right)$	T2. 15
$\alpha \sum_{i=1}^{n-1} \sum_{j=1}^{m-1} \left[S_{i,j}^1\right]\left[S_{n-i,m-j}^2\right]\delta_{n,1}\delta_{m,1}$	0	T2. 16
$\alpha \sum_{i=1}^{n-1} \sum_{j=0}^{m} \left[S_{i,j}\right]\left[S_{n-i,m-j}\right]\delta_{n,j},\ j=0,1$	0	T2. 17
$\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} \left[S_{i,j}\right]\left[S_{n-i,m-j}\right]\delta_{m,j},\ j=0,1$	0	T2. 18

Table 2. (Continued)

Balance term	Pgf transform	
$\alpha \sum_{i=m+1}^{\infty} [S_{n,i}]$	$\alpha\left(\frac{1}{(1-z2)}\left(\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,1)\right)-\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)\right)\right)\right)$ if $a_2=0$ $\alpha\left(-\frac{1}{(1-z2)}\left(\lambda^S_{a_1,1}\phi^S_{a_1,1}(z1,z2)\right)+\frac{z2}{(1-z2)^2}\left(\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,1)\right)-\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)\right)\right)$ if $a_2=1$	T2. 19
$\alpha \sum_{i=n+1}^{\infty} [S_{i,m}]$	$\alpha\left(\frac{1}{(1-z1)}\left(\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(z1,1)\right)-\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(z1,z2)\right)\right)\right)$ if $a_1=0$ $\alpha\left(-\frac{1}{(1-z1)}\left(\lambda^S_{1,a_2}\phi^S_{1,a_2}(z1,z2)\right)+\frac{z1}{(1-z1)^2}\left(\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(1,z2)\right)-\lambda^S_{0,a_2}\phi^S_{0,a_2}(z1,z2)\right)\right)$ if $a_1=1$	T2. 20
$\alpha \sum_{i=n}^{\infty}\sum_{j=m}^{\infty} [S_{i,j}]$	$\alpha\left(\frac{1}{(1-z1)(1-z2)}\left(\begin{array}{l} z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)-z1\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right) \\ -z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)+\lambda^S_{0,0}\end{array}\right)\right)$ *if* $a_1=0$ *and* $a_2=0$ $\alpha\left(\begin{array}{l}\frac{1}{(1-z1)(1-z2)}\left(z1z2\left(\lambda^S_{1,0}\phi^S_{1,0}(z1,z2)\right)-z1\left(\lambda^S_{1,0}\phi^S_{1,0}(z1,1)\right)+\right. \\ \frac{1}{(1-z1)^2(1-z2)}\left(\begin{array}{l} z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)-z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)- \\ z1\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right)+z1\lambda^S_{0,0}\end{array}\right)\end{array}\right)$ *if* $a_1=1$ *and* $a_2=0$ $\alpha\left(\begin{array}{l}\frac{1}{(1-z1)(1-z2)}\left(z1z2\left(\lambda^S_{0,1}\phi^S_{0,1}(z1,z2)\right)-z2\left(\lambda^S_{0,1}\phi^S_{0,1}(1,z2)\right)\right)+ \\ \frac{1}{(1-z1)(1-z2)^2}\left(\begin{array}{l} z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1z2)\right)-z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right)- \\ z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)+z2\lambda^S_{0,0}\end{array}\right)\end{array}\right)$ *if* $a_1=0$ *and* $a_2=1$	T2. 21
$\alpha \sum_{i=1}^{m} [S_{n,i}]$	$\frac{\alpha}{(1-z2)}\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)-\lambda^S_{a_1,0}\varphi^S_{a_1,0}(z1,0)\right)$ *if* $a_2=0$ $\frac{\alpha}{(1-z2)}\left(\lambda^S_{a_1,1}\phi^S_{a_1,1}(z1,z2)+\frac{z2}{(1-z2)}\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)-\lambda^S_{a_1,0}\varphi^S_{a_1,0}(z1,0)\right)\right)$ *if* $a_2=1$	T2. 22
$\alpha \sum_{i=1}^{n} [S_{i,m}]$	$\frac{\alpha}{(1-z1)}\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(z1,z2)-\lambda^S_{0,a_2}\varphi^S_{0,a_2}(0,z2)\right)$ *if* $a_1=0$ $\frac{\alpha}{(1-z1)}\left(\lambda^S_{1,a_2}\phi^S_{1,a_2}(z1,z2)+\frac{z1}{(1-z1)}\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(z1,z2)-\lambda^S_{0,a_2}\phi^S_{0,a_2}(0,z2)\right)\right)$ *if* $a_1=1$	T2. 23
$\alpha \sum_{i=0}^{n}\sum_{j=0}^{m} [S_{i,j}]$	$\alpha\frac{\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)}{(1-z1)(1-z2)}$ *if* $a_1=a_2=0$ $\alpha\left(\frac{1}{(1-z1)(1-z2)}\left(\lambda^S_{1,0}\phi^S_{1,0}(z1,z2)\right)+\frac{z1}{(1-z1)^2(1-z2)}\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)\right)$ *if* $a_1=1$ *and* $a_2=0$ $\alpha\left(\frac{1}{(1-z1)(1-z2)}\left(\lambda^S_{0,1}\phi^S_{0,1}(z1,z2)\right)+\frac{z2}{(1-z1)(1-z2)^2}\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)\right)$ *if* $a_1=0$ *and* $a_2=1$	T2. 24
$\alpha \sum_{i=n+1}^{\infty} [S_{i,m}]\delta_{n,0}$	0 *if* $a_1=1$ $\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(1,z2)\right)-\left(\lambda^S_{0,a_2}\varphi^S_{0,a_2}(0,z2)\right)$ *if* $a_1=0$	T2. 25
$\alpha \sum_{i=m+1}^{\infty} [S_{n,i}]\delta_{m,0}$	0 *if* $a_2=0$ $\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,1)\right)-\left(\lambda^S_{a_1,0}\varphi^S_{a_1,0}(z1,0)\right)$ *if* $a_2=0$	T2. 26
$\alpha \sum_{i=n}^{\infty}\sum_{j=m}^{\infty} [S_{i,j}]\delta_{n,0}$	0 *if* $a_1=1$ $\frac{1}{(1-z2)}\left(\lambda^S_{0,0}-z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)\right)$ *if* $a_1=0$ *and* $a_2=0$ $-\frac{z2}{(1-z2)}\left(\lambda^S_{0,1}\phi^S_{0,1}(1,z2)\right)+\frac{z2}{(1-z2)^2}\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)$ *if* $a_1=0$ *and* $a_2=1$	T2. 27

Table 2. (Continued)

Balance term	Pgf transform	
$\alpha\sum_{i=n}^{\infty}\sum_{j=m}^{\infty}\left[S_{i,j}\right]\delta_{m,0}$	$0 \quad if\ a_2=1$ $\frac{1}{(1-z1)}\left(\lambda^S_{0,0}-z1\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right)\right) \quad if\ a_1=0\ and\ a_2=0$ $-\frac{z1}{(1-z1)}\left(\lambda^S_{1,0}\phi^S_{1,0}(z1,1)\right)+\frac{z1}{(1-z1)^2}\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right) \quad if\ a_1=1\ and\ a_2=0$	T2. 28
$\alpha n^{2-i}m^{i-1}\left[S_{n,m}\right],\ i=1,2$	$\alpha\frac{zi\partial\left(\lambda^S_{a_1,a_2}\phi^S_{a_1,a_2}(z1,z2)\right)}{\partial zi} \quad i=1,2$	T2. 29
$\alpha n^{2-i}m^{i-1}\left[S_{n,m}\right]\delta_{n,0}\left(\alpha n^{2-i}m^{i-1}\left[S_{n,m}\right]\delta_{m,0}\right),\ i=1,2$	$0 \quad if\ i=1\, or\, a_1=1$ $\alpha\left(\lambda^S_{0,a_2+1}\phi^S_{0,a_2+1}(0,z2)\right)=\alpha z2\frac{\partial\left(\lambda^S_{0,a_2}\phi^S_{0,a_2}(0,z2)\right)}{\partial z2} \quad if\ i=2\, and\, a_1=0$ $\left(\begin{array}{l}0 \quad if \quad i=2\, or\, a_2=1\\ \alpha\left(\lambda^S_{a_1+1,0}\phi^S_{a_1+1,0}(z1,0)\right)=\alpha z1\frac{\partial\left(\lambda^S_{\alpha_1,0}\phi^S_{\alpha_1,0}(z1,0)\right)}{\partial z1} \quad if\ i=2\, and\, a_2=0\end{array}\right)$	T2. 30
$\alpha(n-1)\left[S_{n,m}\right]\left(\alpha(m-1)\left[S_{n,m}\right]\right)$	$\alpha\left(z1\frac{\partial\left(\left(\lambda_{a_1,a_2}\phi_{a_1,a_2}(z1,z2)\right)\right)}{\partial z1}-\left(\lambda_{a_1,a_2}\phi_{a_1,a_2}(z1,z2)\right)\right)$ $\left(\alpha\left(z2\frac{\partial\left(\left(\lambda_{a_1,a_2}\phi_{a_1,a_2}(z1,z2)\right)\right)}{\partial z2}-\left(\lambda_{a_1,a_2}\phi_{a_1,a_2}(z1,z2)\right)\right)\right)$	T2. 31
$\alpha(n-1)\left[S_{n,m}\right]\delta_{n,1}\left(\alpha(m-1)\left[S_{n,m}\right]\delta_{m,1}\right)$	0	T2. 32
$\alpha n\left[S_{n,m-1}\right]\left(\alpha m\left[S_{n-1,m}\right]\right)$	$\alpha z1z2\sum_{r=0}^{a_2}\binom{a_2}{r}\frac{\partial\left(\lambda^S_{a_1,r}\phi^S_{a_1,r}(z1,z2)\right)}{\partial z1}\left(\alpha z1z2\sum_{r=0}^{a_1}\binom{a_1}{r}\frac{\partial\left(\lambda^S_{r,a_2}\phi^S_{r,a_2}(z1,z2)\right)}{\partial z2}\right)$	T2. 33
$\alpha n\left[S_{n,m-1}\right]\delta_{n,0}\delta_{m,0}\left(\alpha m\left[S_{n-1,m}\right]\delta_{n,0}\delta_{m,0}\right)$	0	T2. 34
$\alpha\sum_{i=1}^{n}\sum_{j=1}^{m-1}\left[S_{i,j}\right]\left[S_{n-i+1,m-j}\right]$	$\frac{\alpha}{z1}\left(\begin{array}{l}\sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\sum_{x=0}^{a_1-u}\binom{a_1}{u}\binom{a_2}{v}\binom{a_1-u}{x}(-1)^{a_1-u-x}\left(\lambda^S_{u,v}\phi^S_{u,v}(z1,z2)\right)\left(\lambda^S_{x,a_2-v}\phi^S_{x,a_2-v}(z1,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{a_2}(-1)^{a_1-u}\left(\lambda^S_{0,a_2-v}\phi^S_{0,a_2-v}(0,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\binom{a_1}{u}\binom{a_2}{v}(-1)^{a_1-u}\left(\lambda^S_{u,v}\phi^S_{u,v}(z1,z2)\right)\left(\lambda^S_{0,a_2-v}\phi^S_{0,a_2-v}(0,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{u}\binom{a_1}{u}\binom{u}{v}(-1)^{u-v}\left(\lambda^S_{a_1-u,0}\phi^S_{a_1-u,0}(z1,0)\right)\left(\lambda^S_{v,a_2}\phi^S_{0,a_2}(z1,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{u}\binom{a_1}{u}\binom{u}{v}(-1)^{u-v}\left(\lambda^S_{v,0}\phi^S_{v,0}(z1,0)\right)\left(\lambda^S_{a_1-u,a_2}\phi^S_{a_1-u,a_2}(z1,z2)\right)\end{array}\right)$	T2. 35
$\alpha\sum_{i=1}^{n}\sum_{j=1}^{m-1}\left[S_{i,j}\right]\left[S_{n-i+1,m-j}\right]\delta_{n,0}$	0	T2. 36
$\alpha\sum_{i=1}^{n}\sum_{j=1}^{m-1}\left[S_{i,j}\right]\left[S_{n-i+1,m-j}\right]\delta_{m,1}$	0	T2. 37

Table 3. Kinetic mechanism.

Step	Equation	
Initiation	$I \xrightarrow{efic,k_d} 2Ri$	(12)
	$Ri + M^j \xrightarrow{k_i} R^j_{2-j,j-1}$	(13)
	$S^* + M^j \xrightarrow{k_{is}} R^j_{2-j,j-1}$	(14)
Propagation	$R^i_{n,m} + R^j_{r,q} \xrightarrow{k_{p,ij}} R^j_{n+2-j,m+j-1}$	(15)
Termination by combination	$R^i_{n,m} + R^j_{r,q} \xrightarrow{k_{tc,ij}} P_{n+r,m+q}$	(16)
Termination by disproportionation	$R^i_{n,m} + R^j_{r,q} \xrightarrow{k_{td,ij}} P_{n,m} + P_{r,q}$	(17)
Chain transfer to monomer	$R^i_{n,m} + M^j \xrightarrow{k_{trm,ij}} P_{n,m} + R^j_{2-j,j-1}$	(18)
Chain transfer to transfer agent	$R^i_{n,m} + S \xrightarrow{k_{trs,i}} P_{n,m} + S^*$	(19)
Chain transfer to polymer	$R^i_{n,m} + P_{r,q} \xrightarrow{k_{trp,ij}} P_{n,m} + R^j_{r,q}$	(20)
Reaction of terminal double bond	$R^i_{n,m} + P_{r,q} \xrightarrow{k_{db,ij}} R^j_{n+r,m+q}$	(21)

Table 4. Population balances for system S1.

Species	Equation	
Initiator	$\frac{d[I]}{dt} = -k_d[I]$	(22)
Monomers	$\frac{d[M^i]}{dt} = -2fk_d[I]\frac{[M^i]}{[M^1]+[M^2]} - \sum_{j=1}^{2} k_{p,ji}[M^i]\lambda^{R^j}_{0,0}$	(23)
Live copolymer	$\frac{d[R^i_{n,m}]}{dt} = 2fk_d[I]\frac{[M^i]}{[M^1]+[M^2]}\delta_{n,2-i}\delta_{m,i-1} + \sum_{j=1}^{2} k_{p,ji}[M^i][R^j_{n+i-2,m+1-i}](1-\delta_{n,2-i}\delta_{m,i-1}) - \sum_{j=1}^{2} k_{p,ij}[M^j][R^i_{n,m}] - \sum_{j=1}^{2} k_{td,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$ $i = 1, 2;\ n = 2-i, \ldots, \infty;\ m = i-1, \ldots, \infty$	(24)
Dead copolymer	$\frac{dP_{n,m}}{dt} = \sum_{i=1}^{2}\sum_{j=1}^{2} k_{td,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}](1-\delta_{n,0}\delta_{i,1}-\delta_{m,0}\delta_{i,2}) \quad n = 0, \ldots, \infty;\ m = 0, \ldots, \infty$	(25)

because any polymer radical has at least one monomer unit of any of the monomers. Hence, it can be considered that $[R^j_{0,0}] = 0$ and therefore the transform of $\sum_{j=1}^{2} k_{p,ji}[M^i][R^j_{n+i-2,m+1-i}]\delta_{n,2-i}\delta_{m,i-1}$ is 0. Finally, the transforms of the terms $-\sum_{j=1}^{2} k_{p,ij}[M^j][R^i_{n,m}] - \sum_{j=1}^{2} k_{td,ij}\lambda^{R^j}_{0,0}[R^i_{n,m}]$ can be found in row T2.5 with the general structure $\alpha[S_{n,m}]$. The transforms of these terms are $-\sum_{j=1}^{2} k_{p,ij}[M^j]\left[\lambda^{R^i}_{0,0}\phi^{R^i}_{0,0}(z1,z2)\right]$ $-\sum_{j=1}^{2} k_{td,ij}\lambda^{R^j}_{0,0}\left(\lambda^{R^i}_{0,0}\phi^{R^i}_{0,0}(z1,z2)\right)$. Concluding, the transformed equation of Equation (24) is the collection of the transforms of its individual terms shown above and is presented in Equation (26) in Table 5.

Following the same procedure, the pgf transforms of the terms in Equation (25) can be found in rows T2.1, T2.4, and T2.5, previous expansion of the double sum in i and j. It should be noted that, since R^1 has at least one

Table 5. Pgf equations for system S1.

Variable	Equation	
Pgf of the live copolymer MWD	$\frac{d\psi^{R^i}(z1,z2)}{dt} = 2fk_d[I]\frac{[M^i]}{[M^1]+[M^2]}z1^{2-i}z2^{i-1} + \sum_{j=1}^{2} k_{p,ji}[M^i](zi)\psi^{R^j}(z1,z2) - \sum_{j=1}^{2} k_{p,ij}[M^j]\psi^{R^i}(z1,z2) - \sum_{j=1}^{2} k_{td,ij}\lambda_{0,0}^{R^j}\psi^{R^i}(z1,z2) \quad i=1,2$	(26)
Pgf of the dead copolymer MWD	$\frac{d\psi^{P}(z1,z2)}{dt} = \sum_{i=1}^{2}\sum_{j=1}^{2} k_{td,ij}\lambda_{0,0}^{R^j}\psi^{R^i}(z1,z2)$ *with* $\psi^{\bullet}(z1,z2) = \lambda_{0,0}^{\bullet}\phi_{0,0}^{\bullet}(z1,z2)$	(27)

unit of M_1 and R^2 has at least one unit of M_2, $\left[R_{0,m}^1\right] = 0$ and $\left[R_{n,0}^2\right] = 0$. Therefore, the pgfs involved in row T2.4 are equal to zero according to their definitions in Equation (5) and (6). The pgf transform of Equation (25) is built collecting these terms, and is shown in Equation (27) in Table 5.

The pgf technique requires the inversion of the pgf transforms obtained from the solution of Equation (26) and (27). The pgf inversion method employed here is the adaptation of Papoulis' method for 2D pgf inversion developed in Part I of this work.[12] According to this method the MWD is obtained from the transform domain as:

$$\mathrm{MWD}_{\text{number fraction}}(n,m) = \frac{(\ln(2))^2}{n\,m}\mathbf{v}^T.\hat{\hat{\phi}}^{\bullet}(\mathbf{z1},\mathbf{z2}).\mathbf{v} \quad (28)$$

where $\hat{\hat{\phi}}^{\bullet}(\mathbf{z1},\mathbf{z2})$ is a matrix of 2D pgf transforms defined as

$$\hat{\hat{\phi}}^{\bullet}(\mathbf{z1},\mathbf{z2}) = \begin{bmatrix} \hat{\hat{\phi}}^{\bullet}(z1_0,z2_0) & \hat{\hat{\phi}}^{\bullet}(z1_0,z2_2) & \dots & \hat{\hat{\phi}}^{\bullet}(z1_0,z2_N) \\ \hat{\hat{\phi}}^{\bullet}(z1_1,z2_0) & \dots & \dots & \hat{\hat{\phi}}^{\bullet}(z1_1,z2_N) \\ \vdots & \vdots & \vdots & \vdots \\ \hat{\hat{\phi}}^{\bullet}(z1_N,z2_0) & \dots & \dots & \hat{\hat{\phi}}^{\bullet}(z1_N,z2_N) \end{bmatrix},$$
$$zi_j = e^{-(2j+1)\ln(2)/n_i} \quad (29)$$

and $\mathbf{v}$ is a constant vector that is obtained by solving the linear system

$$\mathbf{A}^T\cdot\mathbf{v} = \mathbf{p} \quad (30)$$

where $\mathbf{A}$ and $\mathbf{p}$ are defined as follows:

$$A_{i,j} = \frac{(i-j+1)_j}{2(i+1/2)_{j+1}} \qquad i=0,\dots,N, j=0,\dots,i$$
$$\text{with}$$
$$(k)_l = \begin{cases} 1 & l=0 \\ k(k+1)\dots(k+l-1) & l>0 \end{cases} \quad (31)$$

$$\begin{aligned} & p_i = h(2i) \\ & \text{with} \\ & h(0) = 1 \\ & h(1) = 1/2 \\ & (i+1)h(i+1) = (2i+1)\frac{1}{2}h(i) - ih(i-1) \end{aligned} \quad (32)$$

Variable N appearing in Equation (29) and (31) is a parameter of this inversion method. Guidelines for setting the value of this parameter can be found elsewhere.[12] It can be noted from Equation (29) that the inversion method determines the values of the dummy variables $z1$ and $z2$ for which the pgf is required, which are $zi_j = e^{-(2j+1)\ln(2)/n_i}$, $i=1,2$, $j=0,\dots,N$. The number of pgf values, and hence the number of pgf equations in the model, is $(N+1)^2$ per pair of (n,m) values for which the MWD is to be computed. The pgf values for each (n,m) pair are independent of each other, which means that the grid of the MWD can be made as scarce as desired, and that this grid can be divided into separate subsections for calculating the complete MWD. This allows adjusting the size of the mathematical model.

The MWD expressed in weight fraction can be calculated from the MWD expressed in number fraction recovered from the transform domain as

$$\mathrm{MWD}_{\text{weight fraction}}(n,m) = \frac{(\mathrm{Mw}_1 n + \mathrm{Mw}_2 m)\mathrm{MWD}_{\text{number fraction}}(n,m)}{\mathrm{Mw}_1\lambda_{1,0}^S + \mathrm{Mw}_2\lambda_{0,1}^S} \quad (33)$$

Moments of the MWD are required to solve Equation (26), (27), and (33). Moment equations can be obtained from the polymer population balances using well-know techniques. These equations are shown in Table 6.

Table 6. Moment equations for system S1.

Variable	Equation
Moment of order (a_1,a_2) of the live copolymer MWD	$$\frac{d\lambda^{\mathrm{R}^i}_{a_1,a_2}}{dt} = 2f\,k_{\mathrm{d}}[\mathrm{I}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}(2-i)^{a_1}(i-1)^{a_2} + \sum_{j=1}^{2} k_{\mathrm{p},ji}[\mathrm{M}^i]\sum_{s=0}^{{a_1}^{2-i}{a_2}^{i-1}}\binom{{a_1}^{2-i}{a_2}^{i-1}}{s}\lambda^{\mathrm{R}^j}_{{a_1}^{i-1}s^{2-i},{a_2}^{2-i}s^{i-1}} - \sum_{j=1}^{2} k_{\mathrm{p},ij}[\mathrm{M}^j]\lambda^{\mathrm{R}^i}_{a_1,a_2} - \sum_{j=1}^{2} k_{\mathrm{td},ij}\lambda^{\mathrm{R}^j}_{0,0}\lambda^{\mathrm{R}^i}_{a_1,a_2} \quad (34)$$ $i = 1, 2; (a_1, a_2) = (0,0), (1,0), (0,1)$
Moment of order (a_1,a_2) of the dead copolymer MWD	$$\frac{d\lambda^{\mathrm{P}}_{a_1,a_2}}{dt} = \sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{td},ij}\lambda^{R^j}_{0,0}\lambda^{R^i}_{a_1,a_2} \quad (a_1,a_2) = (0,0),\ (1,0),\ (0,1) \quad (35)$$

The whole mathematical model consists of the pgf equations (Equation 26 and 27) parameterized for the set of values of $z1$ and $z2$ required by the inversion method, the moment equations (Equation 34 and 35), initiator and monomers' balances (Equation 22 and 23), the algebraic equations of the inversion method (Equation 28--32), and Equation (33) for computing the weight fraction MWD. This model was solved for the set of parameters' values and initial conditions shown in Table 7. For comparison purposes, the bivariate MWD was also computed by direct integration of the population balances shown in Equation (24) and (25). In order to predict a MWD grid from ($n = 0$, $m = 0$) to ($n = n_{\max}$, $m = m_{\max}$) with the direct integration method, all points in the grid need to be computed because the corresponding balance equations are coupled. On the other hand, the pgf technique allows fixing the density of the MWD grid and hence adjusting the size of the mathematical model according to the preferred level of detail. Although inefficient, the direct integration is possible in this case because the molecular weight of the system is low enough so as to allow a reasonable number of balance equations for the polymer species.

Table 7. Parameters and initial conditions used in the simulation of system S1.

Parameter/Initial condition	Value	Units	Ref.
k_{d}	1×10^{-5}	s^{-1}	[15]
$k_{\mathrm{p},11}$	705	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{p},12}$	35.25	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{p},21}$	2.4×10^5	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{p},22}$	3600	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{td},11}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{td},12}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{td},21}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{td},22}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{tc},12}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	
$k_{\mathrm{tc},21}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	
$k_{\mathrm{tc},22}$	1×10^7	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	
$k_{\mathrm{fp},11}$	0	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{fp},12}$	0	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[15]
$k_{\mathrm{fp},21}$	$2.36 \times 10^{-4}{\cdot}k_{\mathrm{p},21}$	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[16]
$k_{\mathrm{fp},22}$	$2.36 \times 10^{-4}{\cdot}k_{\mathrm{p},22}$	$\mathrm{L{\cdot}s{\cdot}mol^{-1}}$	[16]
f	1	–	–
[I](0)	0.06	$\mathrm{mol{\cdot}L^{-1}}$	–
$[\mathrm{M}_1](0)$	4	$\mathrm{mol{\cdot}L^{-1}}$	–
$[\mathrm{M}_2](0)$	4	$\mathrm{mol{\cdot}L^{-1}}$	–
$\lambda^{\bullet}_{a,b}$ (0)	0	$\mathrm{mol{\cdot}L^{-1}}$	–
$\psi^{\bullet}(z1, z2)$ (0)	0	$\mathrm{mol{\cdot}L^{-1}}$	–

The direct integration solution can be regarded as a reference MWD since this method does not perform any manipulation of the balance equations. Figure 1 shows the

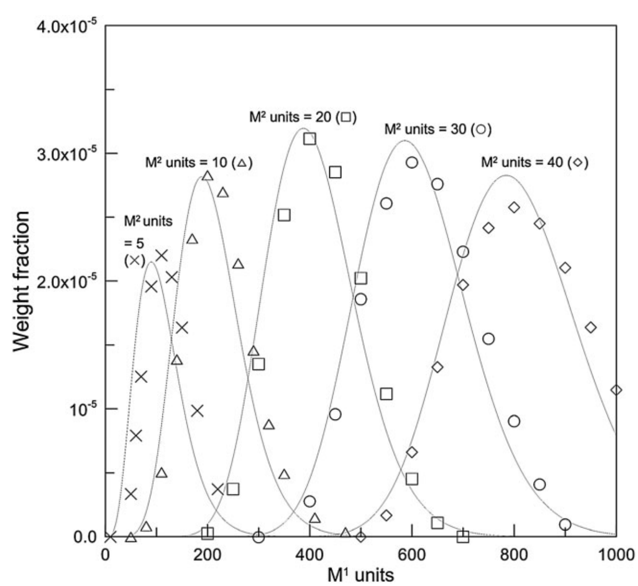

Figure 1. Bivariate MWD calculated with the pgf technique (symbols) and by the direct integration method (lines) for Case I.

Table 8. Comparison between leading moments and number-average molecular weight calculated from the recovered MWD and by the method of moments for system S1.

Moment	From the recovered MWD	Using method of moments
$\lambda_{0,0}^{P}$	1.7699×10^{-4}	1.7952×10^{-4}
$\lambda_{1,0}^{P}$	1.3908×10^{-1}	1.5068×10^{-1}
$\lambda_{0,1}^{P}$	7.1036×10^{-3}	7.4950×10^{-3}
$\overline{M_n}$	82130	87629

bivariate MWD calculated both with the pgf technique and by the direct integration method. It can be seen that an accurate prediction is achieved with the pgf technique.

In order to further validate the MWD calculated with the pgf technique, the leading moments and the number-average molecular weight obtained from this distribution were compared with the ones computed using the method of moments. The results are presented in Table 8. It can be seen that the values computed from the calculated MWD are very close to the ones obtained using the method of moments.

It should be remarked that the pgf method is not efficient for computing moments. These are calculated from the MWD by applying their definition, $\lambda_{a_1,a_2}^{S} = \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} p^{a_1} q^{a_2} [S_{p,q}]$, already introduced in

Table 9. Population balances for system S2.

Species	Equation
Initiator	$\dfrac{d[I]}{dt} = -k_d[I]$ (36)
Monomers	$\dfrac{d[\mathrm{M}^i]}{dt} = -2f\,k_\mathrm{d}[\mathrm{I}]\dfrac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]} - \sum_{j=1}^{2} k_{\mathrm{p},ji}\mathrm{M}_i\lambda_{0,0}^{\mathrm{R}^j} - \sum_{j=1}^{2} k_{\mathrm{trs},j}\lambda_{0,0}^{\mathrm{R}^j}[\mathrm{S}]\dfrac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]} - \sum_{j=1}^{2} k_{\mathrm{trm},ji}\lambda_{0,0}^{\mathrm{R}^j}[\mathrm{M}^i] \quad i=1,2$ (37)
Transfer agent	$\dfrac{d[S]}{dt} = -\sum_{i=1}^{2} k_{\mathrm{trs},i}[S]\lambda_{0,0}^{\mathrm{R}^i}$ (38)
Live copolymer	$\dfrac{d\left[\mathrm{R}_{n,m}^i\right]}{dt} = 2f\,k_\mathrm{d}[\mathrm{I}]\dfrac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}\delta_{n,2-i}\delta_{m,i-1} + \sum_{j=1}^{2} k_{\mathrm{p},ji}[\mathrm{M}^i]\left[\mathrm{R}_{n+i-2,m+1-i}^j\right](1-\delta_{n,2-i}\delta_{m,i-1}) - \sum_{j=1}^{2} k_{\mathrm{p},ij}[\mathrm{M}^j]\left[\mathrm{R}_{n,m}^i\right] - \sum_{j=1}^{2} k_{\mathrm{tc},ij}\lambda_{0,0}^{\mathrm{R}^j}\left[\mathrm{R}_{n,m}^i\right] - k_{\mathrm{trs},i}\left[\mathrm{R}_{n,m}^i\right][\mathrm{S}] - \sum_{j=1}^{2} k_{\mathrm{trm},ij}\left[\mathrm{R}_{n,m}^i\right][\mathrm{M}^j] + \sum_{j=1}^{2} k_{\mathrm{trs},j}\lambda_{0,0}^{\mathrm{R}^j}[\mathrm{S}]\dfrac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}\delta_{n,2-i}\delta_{m,i-1} + \sum_{j=1}^{2} k_{\mathrm{trm},ji}\lambda_{0,0}^{\mathrm{R}^j}[\mathrm{M}^i]\delta_{n,2-i}\delta_{m,i-1} \quad i=1,2;\, n=2-i,\ldots,\infty;\, m=i-1,\ldots,\infty$ (39)
Dead copolymer	$\dfrac{d[\mathrm{P}_{n,m}]}{dt} = k_{\mathrm{tc},12}\sum_{r=1}^{n}\sum_{s=0}^{m-1}\left[R_{r,s}^1\right]\left[R_{n-r,m-s}^2\right](1-\delta_{n,0}-\delta_{m,0}+\delta_{n,0}\delta_{m,0}) + \dfrac{1}{2}k_{\mathrm{tc},11}\sum_{r=1}^{n-1}\sum_{s=0}^{m}\left[R_{r,s}^1\right]\left[R_{n-r,m-s}^1\right](1-\delta_{n,0}-\delta_{n,1}) + \dfrac{1}{2}k_{\mathrm{tc},22}\sum_{r=0}^{n}\sum_{s=1}^{m-1}\left[R_{r,s}^2\right]\left[R_{n-r,m-s}^2\right](1-\delta_{m,0}-\delta_{m,1}) + \sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{trm},ij}\left[R_{n,m}^i\right][\mathrm{M}^j](1-\delta_{n,0}\delta_{i,1}-\delta_{m,0}\delta_{i,2}) + \sum_{i=1}^{2} k_{\mathrm{trs},i}\left[R_{n,m}^i\right][\mathrm{S}](1-\delta_{n,0}\delta_{i,1}-\delta_{m,0}\delta_{i,2}) \quad n=0,\ldots,\infty;\; m=0,\ldots,\infty$ (40)

Equation (3). The increment step of this double sum is one, which requires a full grid of MWD points. Even though numerical techniques can be used to "fill" missing data, like gridding or bivariate interpolation techniques, the source of MWD data (provided by the pgf method) still needs to be very detailed for a good performance. Therefore, a sparse grid of points is no longer enough but a quite full grid is needed, which results in a large number of model equations. The well-known method of moments is more suitable for this operation.

5.2. Case II

The purpose of the last two case studies, Case II and Case III, is to illustrate that the pgf technique can be easily applied to systems of different complexity, taking advantage of previous works on other systems. Case II differs from Case I in that the termination reaction is by combination instead of disproportionation. Besides, transfer to transfer agent and transfer to monomer reactions are added. The population equations that describe this system are shown in Equation (36)–(40) in Table 9.

As in the previous case, the balances of the polymer species (Equation 39 and 40) have to be transformed into the pgf domain. However, as the transformation is carried out term by term, only the contributions of the new reactions have to be taken into account, while the others are the same as in the transforms of the balance equations corresponding to the previous case. Hence, the first three terms of the transform of the balance equation for the live copolymer species (Equation 39) are the same as in Equation (26), because they correspond to the contribution of the initiation and propagation reactions, which are the same as in Case I. The next three terms in Equation (39), corresponding to the live copolymer consumption in termination by combination, transfer to transfer agent and transfer to monomer belong to the general structure $\alpha[S_{n,m}]$, whose transform is found in row T2.5 of the Transform Table. Similarly, the last two terms that correspond to the production of live copolymer chains by transfer to transfer agent and to monomer have the general structure $\alpha\delta_{n,u}\delta_{m,v}$ whose transform is in row T2.3 of the Transform Table. The final transformed equation for Equation (39) is shown in Equation (41) in Table 10. In a similar way, the pgf transform of Equation (40) is obtained, which is shown in Equation (42) in Table 10. Moment equations are also needed, which are presented in Table 11.

Figure 2 shows the bivariate MWD calculated using the pgf technique. It can be seen that the system has shifted to higher molecular weights in comparison to Case I, due to the combination process of the termination reaction. A 3D view of the bivariate MWD is shown in Figure 3. The model was solved with the same set of parameters and initial conditions shown in Table 7. Like in Case I, the number of model equations was approximately 300 per pair of (n,m)

Table 10. Pgf equations for system S2.

Variable	Equation
Pgf of the live copolymer MWD	$$\begin{aligned}\frac{d\psi^{R^i}(z1,z2)}{dt} &= 2f\,k_d[I]\frac{[M^i]}{[M^1]+[M^2]}z1^{2-i}z2^{i-1}+\sum_{j=1}^{2}k_{p,ji}[M^i](zi)\psi^{R^j}(z1,z2)\\ &-\sum_{j=1}^{2}k_{p,ij}[M^j]\psi^{R^i}(z1,z2)-\sum_{j=1}^{2}k_{td,ij}\lambda_{0,0}^{R^j}\psi^{R^i}(z1,z2)\\ &-k_{trs,i}[S]\psi^{R^i}(z1,z2)-\sum_{j=1}^{2}k_{trm,ij}[M^j]\psi^{R^i}(z1,z2)\\ &+\sum_{j=1}^{2}k_{trs,j}\lambda_{0,0}^{R^j}[S]\frac{[M^i]}{[M^1]+[M^2]}z1^{2-i}z2^{i-1}\\ &+\sum_{j=1}^{2}k_{trm,ji}\lambda_{0,0}^{R^j}[M^i]\,z1^{2-i}z2^{i-1}\\ &i=1,2;(a,b)=(0,0),(1,0),(0,1)\end{aligned} \qquad (41)$$
Pgf of the dead copolymer MWD	$$\begin{aligned}\frac{d\psi^{P}(z1,z2)}{dt} &= k_{tc,12}\psi^{R^1}(z1,z2)\psi^{R^2}(z1,z2)+\frac{1}{2}k_{tc,11}\left(\psi^{R^1}(z1,z2)\right)^2\\ &+\frac{1}{2}k_{tc,22}\left(\psi^{R^2}(z1,z2)\right)^2+\sum_{i=1}^{2}\sum_{j=1}^{2}k_{trm,ij}[M^j]\psi^{R^i}(z1,z2)\\ &\sum_{i=1}^{2}k_{trs,i}[S]\psi^{R^i}(z1,z2)\end{aligned} \qquad (42)$$

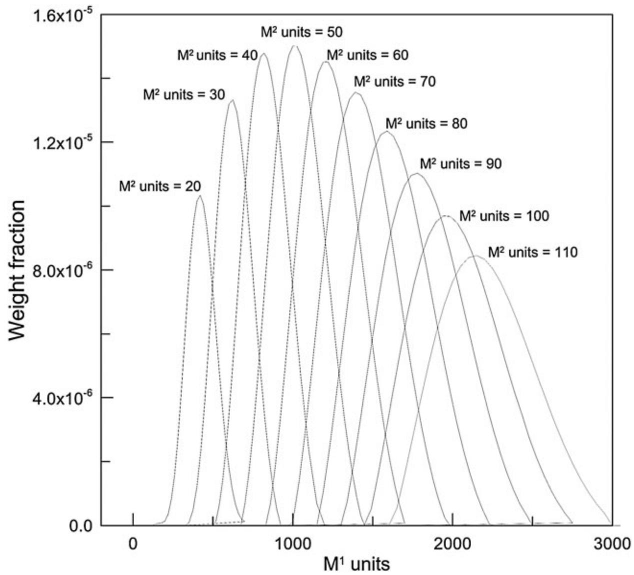

Figure 2. Bivariate MWD calculated with the pgf technique for Case II.

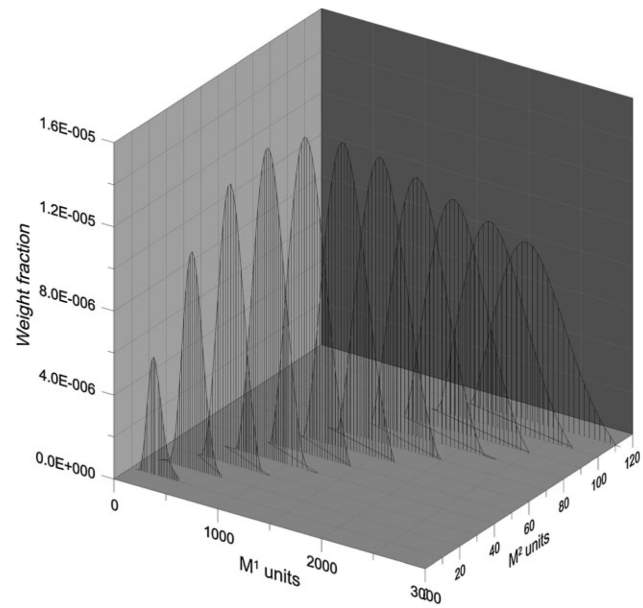

Figure 3. 3D view of the bivariate MWD calculated with the pgf technique for Case II.

points of the MWD grid. As the pgf method allows it, the MWD was computed sequentially for each of the parameterized values of $m = M^2$ units, for computational efficiency. In this way about 9 500 equations were solved per model run. Besides, solving the model equations presented no difference in complexity compared to Case I. On the other hand, direct integration of the population balances was not feasible in this case. Firstly, all combinations of chain lengths values in the significant ranges for St and MMA had to be computed in a single model simulation because the population balances are interdependent. This implied increasing the number of

Table 11. Moment equations for system S2.

Variable	Equation	
Moment of order (a_1,a_2) of the live copolymer MWD	$\begin{aligned} \frac{d\lambda^{\mathrm{R}^i}_{a_1,a_2}}{dt} &= 2f\,k_{\mathrm{d}}[\mathrm{I}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}(2-i)^{a_1}(i-1)^{a_2} + \sum_{j=1}^{2} k_{\mathrm{p},ji}[\mathrm{M}^i] \sum_{s=0}^{{a_1}^{2-i}{a_2}^{i-1}} \binom{{a_1}^{2-i}{a_2}^{i-1}}{s} \lambda^{\mathrm{R}^j}_{{a_1}^{i-1}s^{2-i},{a_2}^{2-i}s^{i-1}} \\ &- \sum_{j=1}^{2} k_{\mathrm{p},ij}[\mathrm{M}_j]\lambda^{\mathrm{R}^i}_{a_1,a_2} - \sum_{j=1}^{2} k_{\mathrm{td},ij}\lambda^{\mathrm{R}^j}_{0,0}\lambda^{\mathrm{R}^i}_{a_1,a_2} \\ &- k_{\mathrm{trs},i}[\mathrm{S}]\lambda^{\mathrm{R}^i}_{a_1,a_2} - \sum_{j=1}^{2} k_{\mathrm{trm},ij}[\mathrm{M}^j]\lambda^{\mathrm{R}^i}_{a_1,a_2} \\ &+ \sum_{j=1}^{2} k_{\mathrm{trs},j}\lambda^{\mathrm{R}^j}_{0,0}[\mathrm{S}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}(2-i)^{a_1}(i-1)^{a_2} \\ &+ \sum_{j=1}^{2} k_{\mathrm{trm},ji}\lambda^{\mathrm{R}^j}_{0,0}[\mathrm{M}^i](2-i)^{a_1}(i-1)^{a_2} \qquad i=1,2;(a_1,a_2)=(0,0),(1,0),(0,1) \end{aligned}$	(43)
Moment of order (a_1,a_2) of the dead copolymer MWD	$\begin{aligned} \frac{d\lambda^{\mathrm{P}}_{a_1,a_2}}{dt} &= k_{\mathrm{tc},12}\sum_{i=0}^{a_1}\sum_{j=0}^{a_2}\binom{a_1}{i}\binom{a_2}{j}\lambda^{\mathrm{R}^1}_{i,j}\lambda^{\mathrm{R}^2}_{a_1-i,a_2-j} + \tfrac{1}{2}k_{\mathrm{tc},11}\sum_{i=0}^{a_1}\sum_{j=0}^{a_2}\binom{a_1}{i}\binom{a_2}{j}\lambda^{\mathrm{R}^1}_{i,j}\lambda^{\mathrm{R}^1}_{a_1-i,a_2-j} \\ &+ \frac{1}{2}k_{\mathrm{tc},22}\sum_{i=0}^{a_1}\sum_{j=0}^{a_2}\binom{a_1}{i}\binom{a_2}{j}\lambda^{R^2}_{i,j}\lambda^{R^2}_{a_1-i,a_2-j} + \sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{trm},ij}[\mathrm{M}^j]\lambda^{R^i}_{a_1,a_2} \\ & \sum_{i=1}^{2} k_{\mathrm{trs},i}[\mathrm{S}]\lambda^{R^i}_{a_1,a_2} \qquad (a_1,a_2)=(0,0),(1,0),(0,1) \end{aligned}$	(44)

Table 12. Population balances for system S3.

Species	Equation	
Initiator	$\frac{d[I]}{dt} = -k_d[I]$	(45)
Monomers	$\frac{d[M^i]}{dt} = -2f\,k_d[I]\frac{[M^i]}{[M^1]+[M^2]} - \sum_{j=1}^{2} k_{p,ji}[M^i]\,\lambda_{0,0}^{R^j} - \sum_{j=1}^{2} k_{trs,j}\lambda_{0,0}^{R^j}[S]\frac{[M^i]}{[M^1]+[M^2]} - \sum_{j=1}^{2} k_{trm,ji}\lambda_{0,0}^{R^j}[M^i] \qquad i=1,2$	(46)
Transfer agent	$\frac{d[S]}{dt} = -\sum_{i=1}^{2} k_{trs,i}[S]\lambda_{0,0}^{R^i}$	(47)
Live copolymer	$\frac{d\left[R^i_{n,m}\right]}{dt} = 2f\,k_d[I]\frac{[M^i]}{[M^1]+[M^2]}\delta_{n,2-i}\delta_{m,i-1} + \sum_{j=1}^{2} k_{p,ji}[M^i]\left[R^j_{n+i-2,m+1-i}\right](1-\delta_{n,2-i}\delta_{m,i-1}) - \sum_{j=1}^{2} k_{p,ij}[M^j]\left[R^i_{n,m}\right] - \sum_{j=1}^{2} k_{tc,ij}\lambda_{0,0}^{R^j}\left[R^i_{n,m}\right] - k_{trs,i}\left[R^i_{n,m}\right][S] - \sum_{j=1}^{2} k_{trm,ij}\left[R^i_{n,m}\right][M^j] + \sum_{j=1}^{2} k_{trs,j}\lambda_{0,0}^{R^j}[S]\frac{[M^i]}{[M^1]+[M^2]}\delta_{n,2-i}\delta_{m,i-1} + \sum_{j=1}^{2} k_{trm,ji}\lambda_{0,0}^{R^j}[M^i]\,\delta_{n,2-i}\delta_{m,i-1} + \sum_{j=1}^{2} k_{fpji}n^{2-i}m^{i-1}\lambda_{0,0}^{R^j}[P_{n,m}] - k_{fpij}\lambda^{P}_{2-j,j-1}[R^i_{n,m}]$ $\quad i=1,2;\, n=2-i,\ldots,\infty;\, m=i-1,\ldots,\infty$	(48)
Dead copolymer	$\frac{d[P_{n,m}]}{dt} = k_{tc,12}\sum_{r=1}^{n}\sum_{s=0}^{m-1}\left[R^1_{r,s}\right]\left[R^2_{n-r,m-s}\right](1-\delta_{n,0}-\delta_{m,0}+\delta_{n,0}\delta_{m,0}) + \frac{1}{2}k_{tc,11}\sum_{r=1}^{n-1}\sum_{s=0}^{m}\left[R^1_{r,s}\right]\left[R^1_{n-r,m-s}\right](1-\delta_{n,0}-\delta_{n,1}) + \frac{1}{2}k_{tc,22}\sum_{r=0}^{n}\sum_{s=1}^{m-1}\left[R^2_{r,s}\right]\left[R^2_{n-r,m-s}\right](1-\delta_{m,0}-\delta_{m,1}) + \sum_{i=1}^{2}\sum_{j=1}^{2} k_{trm,ij}\left[R^i_{n,m}\right][M^j](1-\delta_{n,0}\delta_{i,1}-\delta_{m,0}\delta_{i,2}) + \sum_{i=1}^{2} k_{trs,i}\left[R^i_{n,m}\right][S](1-\delta_{n,0}\delta_{i,1}-\delta_{m,0}\delta_{i,2}) + \sum_{i=1}^{2}\sum_{j=1}^{2}\left(k_{fpij}\lambda^{P}_{2-j,j-1}[R^i_{n,m}] - k_{fpij}\lambda_{0,0}^{R^i}n^{2-j}m^{j-1}[P_{n,m}]\right) \quad n=0,\ldots,\infty;\, m=0,\ldots,\infty$	(49)

simultaneous model equations from approximately 80 000, for the direct integration approach in Case I, to 660 000 in Case II. Besides, the extensive double sums involved in termination by combination reaction terms of the dead polymer balance equation (first three terms in Equation 40), caused the evaluation of the derivatives to be prohibitively time-consuming.

5.3. Case III

In this case study, the reaction step transfer to polymer has been added to the kinetic mechanism of Case II. The main effect of this reaction on the MWD is a broadening of the distribution. From the point of view of the mathematical treatment of the system, this kinetic step introduces some modeling issues that are described below. The population balance equations that describe this system, designated as S3, are shown in Table 12. It can be noticed that the difference between these balances and those of system S2 is only in the last term of the live and of the dead copolymer balances, Equation (48) and (49), respectively. These terms represent the contributions of the transfer to polymer reaction. Hence, the pgf transform equations of the live and dead polymer balances are obtained by just adding the pgf

Table 13. Pgf equations for system S3.

Variable	Equation
Pgf of the live copolymer MWD	$$\frac{d\psi^{R^i}(z1,z2)}{dt} = 2f\,k_d[\mathrm{I}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}z1^{2-i}z2^{i-1} + \sum_{j=1}^{2}k_{p,ji}[\mathrm{M}^i](zi)\psi^{R^j}(z1,z2) - \sum_{j=1}^{2}k_{p,ij}[\mathrm{M}^j]\psi^{R^i}(z1,z2) - \sum_{j=1}^{2}k_{td,ij}\lambda_{0,0}^{R^j}\psi^{R^i}(z1,z2) - k_{trs,i}[\mathrm{S}]\psi^{R^i}(z1,z2) - \sum_{j=1}^{2}k_{trm,ij}[\mathrm{M}^j]\psi^{R^i}(z1,z2) + \sum_{j=1}^{2}k_{trs,j}\lambda_{0,0}^{R^j}[\mathrm{S}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}z1^{2-i}z2^{i-1} + \sum_{j=1}^{2}k_{trm,ji}\lambda_{0,0}^{R^j}[\mathrm{M}^i]z1^{2-i}z2^{i-1} + \sum_{j=1}^{2}\left(k_{fpji}\lambda_{0,0}^{R^j}\frac{zi\,\partial(\psi^P(z1,z2))}{\partial zi} - k_{fpij}\lambda_{2-j,j-1}^{P}\psi^{R^i}(z1,z2)\right) \quad (50)$$ $i=1,2;(a,b)=(0,0),(1,0),(0,1)$
Pgf of the dead copolymer MWD	$$\frac{d\psi^P(z1,z2)}{dt} = k_{tc,12}\psi^{R^1}(z1,z2)\psi^{R^2}(z1,z2) + \frac{1}{2}k_{tc,11}\left(\psi^{R^1}(z1,z2)\right)^2 + \frac{1}{2}k_{tc,22}\left(\psi^{R^2}(z1,z2)\right)^2 + \sum_{i=1}^{2}\sum_{j=1}^{2}k_{trm,ij}[\mathrm{M}_j]\psi^{R^i}(z1,z2) \sum_{i=1}^{2}k_{trs,i}[\mathrm{S}]\psi^{R^i}(z1,z2) + \sum_{i=1}^{2}\sum_{j=1}^{2}\left(k_{fpij}\lambda_{2-j,j-1}^{P}\psi^{R^i}(z1,z2) - k_{fpij}\lambda_{0,0}^{R^i}\frac{zj\,\partial(\psi^P(z1,z2))}{\partial zj}\right) \quad (51)$$

transforms of those terms to the pgf equations of system S2. The resulting pgf balances for the system of Case III are shown in Table 13. As previously, moment equations are needed, which are presented in Table 14.

One of the distinct features that introduce the transfer to polymer reaction is the presence of the derivatives of the dead polymer pgf with respect to the dummy variables zi (see last term of Equation 50 and 51). These derivatives were computed using backwards finite differences as follows

$$\left.\frac{\partial(\psi^P(z1,z2))}{\partial zi}\right|_{z1_k,z2_l} \cong \frac{\psi^P(z1_k,z2_l) - \psi^P(z1_{k+0^{i-1}},z2_{l+0^{2-i}})}{zi_{0^{i-1}k+0^{2-i}l} - zi_{0^{i-1}(k+1)+0^{2-i}(l+1)}} \quad (55)$$

where $\psi^P(z1_k,z2_l)$ is the (k,l) element of the dead polymer pgf matrix defined as in Equation (29). It should be noted that, as shown in Equation (29), zi_j decreases as j increases. The boundary condition used is

$$\psi^P(0,z2) = \psi^P(z1,0) = 0 \quad (56)$$

This condition assumes that $[\mathrm{P}_{0,m}]=[\mathrm{P}_{n,0}]=0$, which is a very reasonable approximation for the typical shapes of copolymer MWDs.

The second particularity that the transfer to polymer reaction introduces is that moment equations depend on higher order moments. In order to break-down this dependence, the "bulk moment" closure method was applied. According to this closure method,[16,17] a "bulk moment" $\lambda_{\bullet}^{B} = \lambda_{\bullet}^{P} + \lambda_{\bullet}^{R^1} + \lambda_{\bullet}^{R^2}$ is defined which includes the contribution of the live copolymer chains. It should be noted that the term $\lambda_{\bullet}^{B} = \lambda_{\bullet}^{P} + \lambda_{\bullet}^{R^1} + \lambda_{\bullet}^{R^2}$ is approximately equal to $\lambda_{\bullet}^{P}$ due to the very low contribution of $\lambda_{\bullet}^{R^1}$ and $\lambda_{\bullet}^{R^2}$. Balance equations corresponding to these "bulk moments" do not depend on higher order moments and hence provide a closed system of equations. The actual moment equations were applied to moments of order (0,0), (1,0), and (0,1), and "bulk moments" were defined for orders (2,0), (1,1), and (0,2), as shown in Table 14.

The model was solved with the set of parameters and initial conditions shown in Table 7. The details of the numerical solution are the same as in Case II. Figure 4 shows the bivariate MWD for system S3. It can be seen that, as expected, the MWD is broader that the one of Case II as a

Table 14. Moment equations for system S3.

Variable	Equation	
Moment of order (a_1,a_2) of the live copolymer MWD	$\begin{aligned} \frac{d\lambda^{\mathrm{R}^i}_{a_1,a_2}}{dt} &= 2f\,k_{\mathrm{d}}[\mathrm{I}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}(2-i)^{a_1}(i-1)^{a_2} + \sum_{j=1}^{2} k_{\mathrm{p},ji}[\mathrm{M}^i] \sum_{s=0}^{{a_1}^{2-i}{a_2}^{i-1}} \binom{{a_1}^{2-i}{a_2}^{i-1}}{s} \lambda^{\mathrm{R}^j}_{{a_1}^{i-1}s^{2-i},{a_2}^{2-i}s^{i-1}} \\ &- \sum_{j=1}^{2} k_{\mathrm{p},ij}[\mathrm{M}^j]\lambda^{\mathrm{R}^i}_{a_1,a_2} - \sum_{j=1}^{2} k_{\mathrm{td},ij}\lambda^{\mathrm{R}^j}_{0,0}\lambda^{\mathrm{R}^i}_{a_1,a_2} - k_{\mathrm{trs},i}[\mathrm{S}]\lambda^{\mathrm{R}^i}_{a_1,a_2} - \sum_{j=1}^{2} k_{\mathrm{trm},ij}[\mathrm{M}^j]\lambda^{\mathrm{R}^i}_{a_1,a_2} \\ &+ \sum_{j=1}^{2} k_{\mathrm{trs},j}\lambda^{\mathrm{R}^j}_{0,0}[\mathrm{S}]\frac{[\mathrm{M}^i]}{[\mathrm{M}^1]+[\mathrm{M}^2]}(2-i)^{a_1}(i-1)^{a_2} \\ &+ \sum_{j=1}^{2} k_{\mathrm{trm},ji}\lambda^{\mathrm{R}^j}_{0,0}[\mathrm{M}^i](2-i)^{a_1}(i-1)^{a_2} + \sum_{j=1}^{2}\left(k_{\mathrm{fp}ji}\lambda^{\mathrm{R}^j}_{0,0}\lambda^{\mathrm{P}}_{a_1+0^{i-1},a_2+0^{2-i}} - k_{\mathrm{fp}ij}\lambda^{P}_{2-j,j-1}\lambda^{\mathrm{R}^i}_{a_1,a_2}\right) \\ & i=1,2;(a_1,a_2)=(0,0),(1,0),(0,1) \end{aligned}$	(52)
Moment of order (a_1,a_2) of the dead copolymer MWD	$\begin{aligned} \frac{d\lambda^{\mathrm{P}}_{a_1,a_2}}{dt} &= k_{\mathrm{tc},12}\sum_{i=0}^{a_1}\sum_{j=0}^{a_2}\binom{a_1}{i}\binom{a_2}{j}\lambda^{R^1}_{i,j}\lambda^{R^2}_{a_1-i,a_2-j} + \frac{1}{2}k_{\mathrm{tc},11}\sum_{i=0}^{a_1}\sum_{j=0}^{a_2}\binom{a_1}{i}\binom{a_2}{j}\lambda^{R^1}_{i,j}\lambda^{R^1}_{a_1-i,a_2-j} \\ &+ \frac{1}{2}k_{\mathrm{tc},22}\sum_{i=0}^{a_1}\sum_{j=0}^{a_2}\binom{a_1}{i}\binom{a_2}{j}\lambda^{R^2}_{i,j}\lambda^{R^2}_{a_1-i,a_2-j} + \sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{trm},ij}[M^j]\lambda^{R^i}_{a_1,a_2} \\ &+ \sum_{i=1}^{2} k_{\mathrm{trs},i}[\mathrm{S}]\lambda^{R^i}_{a_1,a_2} + \sum_{i=1}^{2}\sum_{j=1}^{2}\left(k_{\mathrm{fp}ij}\lambda^{\mathrm{P}}_{2-j,j-1}\lambda^{R^i}_{a_1,a_2} - k_{\mathrm{fp}ij}\lambda^{\mathrm{R}^i}_{0,0}\lambda^{\mathrm{P}}_{a_1+0^{i-1},a_2+0^{2-i}}\right) \\ (a_1,a_2) &= (0,0),(1,0),(0,1) \end{aligned}$	(53)
	$\begin{aligned} \frac{d\left(\lambda^{\mathrm{P}}_{a_1,a_2}+\lambda^{R^1}_{a_1,a_2}+\lambda^{R^2}_{a_1,a_2}\right)}{dt} &= 2f\,k_{\mathrm{d}}[\mathrm{I}]\sum_{i=1}^{2}\frac{[M^i]}{[M^1]+[M^2]}(2-i)^{a_1}(i-1)^{a_2} \\ &+ \sum_{i=1}^{2} k_{\mathrm{trs},i}[\mathrm{S}]\lambda^{R^i}_{0,0}\sum_{j=1}^{2}\frac{[M^j]}{[M^1]+[M^2]}(2-j)^{a_1}(j-1)^{a_2} + \sum_{i=1}^{2}\sum_{j=1}^{2} k_{\mathrm{trm},ij}[M^j]\lambda^{R^i}_{0,0}(2-j)^{a_1}(j-1)^{a_2} \\ &+ \sum_{i=1}^{2}\left(k_{\mathrm{p},i1}[\mathrm{M}^1]\left(\lambda^{\mathrm{R}^i}_{0,0}+2\lambda^{\mathrm{R}^i}_{1,0}\right)\delta_{a_1,2}\delta_{a_2,0} + k_{\mathrm{p},i2}[\mathrm{M}^2]\left(\lambda^{\mathrm{R}^i}_{0,0}+2\lambda^{\mathrm{R}^i}_{0,1}\right)\delta_{a_1,0}\delta_{a_2,2}\right) \\ &+ \sum_{i=1}^{2}\left(k_{\mathrm{p},i1}[\mathrm{M}^1]\lambda^{\mathrm{R}^i}_{0,1} + k_{\mathrm{p},i2}[\mathrm{M}^2]\lambda^{\mathrm{R}^i}_{1,0}\right)\delta_{a_1,1}\delta_{a_2,1} \\ & \sum_{i=1}^{2} k_{\mathrm{tc},ii}\left(\left(\lambda^{\mathrm{R}^i}_{1,0}\right)^2\delta_{a_1,2}\delta_{a_2,0} + \left(\lambda^{\mathrm{R}^i}_{0,1}\right)^2\delta_{a_1,0}\delta_{a_2,2} + \lambda^{\mathrm{R}^i}_{1,0}\lambda^{\mathrm{R}^i}_{0,1}\delta_{a_1,1}\delta_{a_2,1}\right) \\ &+ k_{\mathrm{tc},12}\left(2\lambda^{\mathrm{R}^1}_{1,0}\lambda^{\mathrm{R}^2}_{1,0}\delta_{a_1,2}\delta_{a_2,0} + \left(\lambda^{\mathrm{R}^1}_{0,1}\lambda^{\mathrm{R}^2}_{1,0}+\lambda^{\mathrm{R}^1}_{1,0}\lambda^{\mathrm{R}^2}_{0,1}\right)\delta_{a_1,1}\delta_{a_2,1} + 2\lambda^{\mathrm{R}^1}_{0,1}\lambda^{\mathrm{R}^2}_{0,1}\delta_{a_1,0}\delta_{a_2,2}\right) \\ \lambda^{\mathrm{P}}_{a_1,a_2} &\cong \lambda^{\mathrm{P}}_{a_1,a_2}+\lambda^{R^1}_{a_1,a_2}+\lambda^{R^2}_{a_1,a_2};(a_1,a_2)=(2,0),(1,1),(0,2) \end{aligned}$	(54)

result of the contribution of the transfer to polymer reaction.

6. Conclusion

The transformation step of the 2D pgf method for modeling bivariate distributions of polymer properties was analyzed comprehensively. The transformation of the mass balances of the polymeric species to the 2D pgf domain was systematized by the breakdown of this procedure into the transformation of the individual terms that make up the balance equations. Individual terms arising from the kinetic steps most commonly found in different polymer processes, were classified in common structures from the point of view of the transformation. This allowed compiling a collection of balance equation terms along with their corresponding pgf transforms. The results were presented in a way that allows a quick transformation of most new balance equations provided that their terms belong to any of the general expressions summarized in this paper. However, if this is not the case, deductions were intended to be detailed enough to guide the reader in performing their own transformations without serious difficulties. The complete 2D pgf technique was applied to three examples that showed the potential of this method for modeling bivariate distributions of polymer properties.

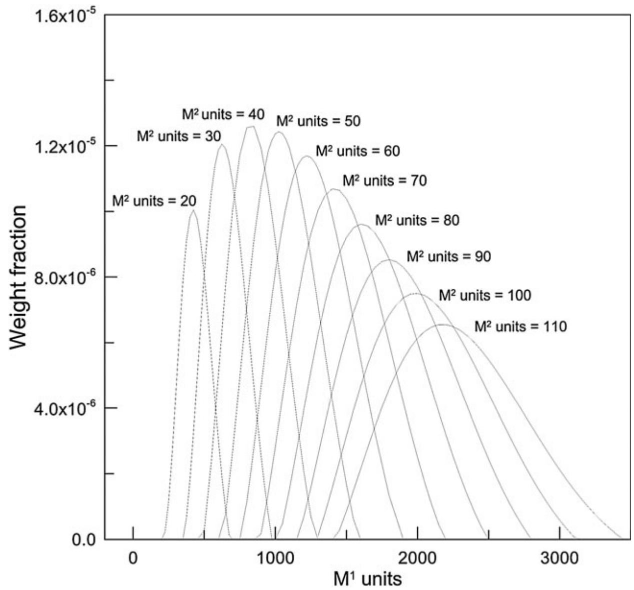

Figure 4. Bivariate MWD calculated with the pgf technique for Case III.

Appendix

In this section, we detail the transformation process that leads to the different transform terms shown in Table 1. The method to carry out the 2D pgf transformation consists in multiplying each term, which is function of the concentration of polymeric species characterized by two distributed domains n and m, by $z1^n z2^m n^{a_1} m^{a_2}$ ($a_1 = 0$, 1, $a_2 = 0$, 1), and then performing a double summation for all possible values of n and m. The result is put in terms of the 2D pgfs by means of the definitions of the pgf and the different probabilities.

A.1. $\alpha[S_{n,m}]$, $\frac{\partial \alpha[S_{n,m}]}{\partial \tau}$ Terms

Multiplication of the expression $\alpha[S_{n,m}]$ by $z1^n z2^m n^{a_1} m^{a_2}$ and summation for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$ leads to

$$\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \alpha z1^n z2^m n^{a_1} m^{a_2} [S_{n,m}] = \alpha \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1} m^{a_2} [S_{n,m}] \quad \text{(A1)}$$

Using the 2D pgf definition given in Equation (3), the double sum in Equation (A1) can be substituted in terms of the double moment and 2D pgf leading to the final transformed term

$$\alpha\left(\lambda^S_{a_1} \phi^S_{a_1,a_2}(z1, z2)\right) \quad \text{(A2)}$$

In a similar way the pgf transform of the term $\frac{\partial \alpha[S_{n,m}]}{\partial \tau}$ is obtained, taking into account that $\sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1} m^{a_2}$ $\frac{\partial \alpha[S_{n,m}]}{\partial \tau} = \frac{\partial \alpha \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1} m^{a_2} [S_{n,m}]}{\partial \tau}$

A.2. $\alpha[S_{n-1,m}]$, $\alpha[S_{n,m-1}]$ Terms

Multiplying $\alpha[S_{n-1,m}]$ by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$ leads to

$$\alpha \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1} m^{a_2} [S_{n-1,m}] \tag{A3}$$

Taking $n-1 = l$ and replacing in Equation (A3),

$$\begin{aligned}\alpha \sum_{l=-1}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m (l+1)^{a_1}\, m^{a_2}[S_{l,m}] &= \alpha \begin{cases} \sum\limits_{m=0}^{\infty} z1^n z2^m 0^{a_1} m^{a_2}[S_{-1,m}] \\ +\sum\limits_{l=0}^{\infty}\sum\limits_{m=0}^{\infty} z1^n z2^m (l+1)^{a_1} m^{a_2}[S_{l,m}] \end{cases} \\ &= \alpha \sum_{l=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m (l+1)^{a_1} m^{a_2}[S_{l,m}]\end{aligned} \tag{A4}$$

In the previous derivation it was considered that $[s_{-1,m}] = 0$ since the species $[s_{-1,m}]$ does not exist in the system. Recalling the binomial formula for $(l+1)^{a_1}$, $(l+1)^{a_1} = \sum\limits_{r=0}^{a_1}\binom{a_1}{r} l^r$ and replacing in Equation (A4),

$$\begin{aligned}\alpha \sum_{l=0}^{\infty}\sum_{m=0}^{\infty} z1^{l+1} z2^m \sum_{r=0}^{a_1}\binom{a_1}{r} l^r\, m^{a_2}[S_{l,m}] &= \alpha z1 \sum_{r=0}^{a_1}\binom{a_1}{j}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty} z1^l z2^m l^r m^{a_2}\,[S_{l,m}] \\ &= \alpha z1 \sum_{r=0}^{a_1}\binom{a_1}{r}\left(\lambda^S_{r,a_2}\phi^S_{r,a_2}(z1,z2)\right)\end{aligned} \tag{A5}$$

In a similar way the transform for $\alpha[S_{n,m-1}]$ is obtained.

A.3. $\alpha[S_{n+1,m}]$, $\alpha[S_{n,m+1}]$ Terms

Starting with

$$\alpha \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} z1^n z2^m n^{a_1} m^{a_2}[S_{n+1,m}] \tag{A6}$$

Taking $l = n+1$ and replacing in Equation (A6),

$$\alpha \sum_{l=0}^{\infty}\sum_{m=0}^{\infty} z1^{l-1} z2^m (l-1)^{a_1} m^{a_2}[S_{l,m}] \tag{A7}$$

$$\alpha \sum_{l=0}^{\infty}\sum_{m=0}^{\infty} z1^{l-1} z2^m (l-1)^{a_1} m^{a_2}[S_{l,m}] - \frac{1}{z1}(-1)^{a_1}\sum_{m=0}^{\infty} z2^m m^{a_2}[S_{0,m}] \tag{A8}$$

Applying the binomial formula to $(l-1)^{a_1}$ to the first term and rearranging,

$$\frac{\alpha}{z1}\left(\sum_{r=0}^{a_1}\binom{a_1}{r}(-1)^{a_1-r}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty} z1^l z2^m l^r m^{a_2}[S_{l,m}] - (-1)^{a_1}\lambda^S_{0,a_2}\varphi^S_{0,a_2}(z1,z2)\right) \tag{A9}$$

Replacing by the pgf definition,

$$\frac{\alpha}{z1}\left(\sum_{r=0}^{a_1}\binom{a_1}{r}(-1)^{a_1-r}\left(\lambda^S_{r,a_2}\phi^S_{r,a_2}(z1,z2)\right) - (-1)^{a_1}\lambda^S_{0,a_2}\varphi^S_{0,a_2}(0,z2)\right) \tag{A10}$$

In a similar way the transform for $\alpha[S_{n,m+1}]$ is obtained.

A.4. $\boldsymbol{\alpha \sum_{i=1}^{n} \sum_{j=0}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]}$, $\boldsymbol{\alpha \sum_{i=0}^{n-1} \sum_{j=0}^{m} [S^1_{i,j}][S^2_{n-i,m-j}]}$, $\boldsymbol{\alpha \sum_{i=0}^{n} \sum_{j=0}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]}$, $\boldsymbol{\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]}$, $\boldsymbol{\alpha \sum_{i=1}^{n-1} \sum_{j=1}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]}$, $\boldsymbol{\alpha \sum_{i=1}^{n-1} \sum_{j=0}^{m} [S_{i,j}][S_{n-i,m-j}]}$, $\boldsymbol{\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i,m-j}]}$ **Terms**

Let us consider the term $\alpha \sum_{i=1}^{n} \sum_{j=0}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]$. Multiplying by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$ it is obtained

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{i=1}^{n} \sum_{j=0}^{m-1} n^{a_1} m^{a_2} z1^n z2^m [S^1_{i,j}][S^2_{n-i,m-j}] \tag{A11}$$

The sums in i and j can be extended to 0 and m as

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \left(\sum_{i=0}^{n} \sum_{j=0}^{m} [S^1_{i,j}][S^2_{n-i,m-j}] - \sum_{j-1}^{m} [S^1_{0,j}][S^2_{n,m-j}] - \sum_{i=1}^{m} [S^1_{i,m}][S^2_{n-i,0}] - [S^1_{0,0}][S^2_{n,m}] \right) \tag{A12}$$

The last term in Equation (A12) vanishes because $[S^1_{0,0}] = 0$. For the first term, rearranging sums leads to

$$\alpha \sum_{n=0}^{\infty} \sum_{i=0}^{n} \sum_{m=1}^{\infty} \sum_{j=0}^{m} n^{a_1} m^{a_2} z1^n z2^m [S^1_{i,j}][S^2_{n-i,m-j}] \tag{A13}$$

Then, the identity $\sum_{l=0}^{\infty} \sum_{k=0}^{l} \ldots = \sum_{k=0}^{\infty} \sum_{l=k}^{\infty} \ldots$ is applied to the previous expression, giving

$$\alpha \sum_{i=0}^{\infty} \sum_{n=i}^{\infty} \sum_{j=0}^{\infty} \sum_{m=j}^{\infty} n^{a_1} m^{a_2} z1^n z2^m [S^1_{i,j}][S^2_{n-i,m-j}] \tag{A14}$$

Taking $s = n-i$ and $t = m-j$ and operating,

$$\alpha \sum_{i=0}^{\infty} \sum_{u=0}^{\infty} \sum_{j=0}^{\infty} \sum_{v=0}^{\infty} (i+u)^{a_1} (j+v)^{a_2}\, z1^{i+u} z2^{j+v} [S^1_{i,j}][S^2_{u,v}] \tag{A15}$$

$$\alpha \sum_{i=0}^{\infty} \sum_{u=0}^{\infty} \sum_{j=0}^{\infty} \sum_{v=0}^{\infty} \left(\sum_{r=0}^{a_1} \binom{a_1}{r} i^r u^{a_1-r} \right) \left(\sum_{t=0}^{a_2} \binom{a_2}{t} j^t v^{a_2-t} \right) z1^{i+u} z2^{j+v}\, [S^1_{i,j}][S^2_{u,v}] \tag{A16}$$

$$\alpha \sum_{r=0}^{a_1} \sum_{r=0}^{a_2} \binom{a_1}{r} \binom{a_2}{t} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} i^r j^t z1^i z2^j\, [S^1_{i,j}] u^{a_1-r} v^{a_2-t} z1^u z2^v [S^2_{u,v}] \tag{A17}$$

$$\alpha \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r} \binom{a_2}{t} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} i^r j^t z1^i z2^j\, [S^1_{i,j}] \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} u^{a_1-r} t^{a_2-t} z1^u z2^v [S^2_{u,v}] \tag{A18}$$

$$\alpha \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r} \binom{a_2}{t} \left(\lambda^{S^1}_{r,t} \phi^{S^1}_{r,t}(z1, z2) \right) \left(\lambda^{S^2}_{a_1-r,a_2-t} \phi^{S^2}_{a_1-r,a_2-t}(z1, z2) \right) \tag{A19}$$

The transform of the second term in Equation (A12) is deduced as follows. From

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{j=1}^{m} [S^1_{0,j}][S^2_{n,m-j}] \tag{A20}$$

Extending the sum in j from 0 since $[S^1_{0,0}] = 0$ and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{j=0}^{m} [S^1_{0,j}][S^2_{n,m-j}] \tag{A21}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} \sum_{m=j}^{\infty} n^{a_1} m^{a_2} z1^n z2^m [S^1_{0,j}][S^2_{n,m-j}] \tag{A22}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} n^{a_1} (k+j)^{a_2} z1^n z2^{k+j} [S^1_{0,j}][S^2_{n,k}] \tag{A23}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} n^{a_1} \left(\sum_{l=0}^{a_2} \binom{a_2}{l} k^l j^{a_2-l} \right) z1^n z2^{k+j} [S^1_{0,j}][S^2_{n,k}] \tag{A24}$$

$$\alpha \sum_{l=0}^{a_2} \binom{a_2}{l} \left(\sum_{j=0}^{\infty} z2^j j^{a_2-l} [S^1_{0,j}] \right) \left(\sum_{n=0}^{\infty} \sum_{k=0}^{\infty} n^{a_1} k^l z1^n\, z2^k) [S^2_{n,k}] \right) \tag{A25}$$

Equation (A25) can be put in terms of the pgf definition using Equation (3) and (6):

$$\alpha \sum_{l=0}^{a_2} \binom{a_2}{l} \left(\lambda^{S^1}_{0,a_2-l} \phi^{S^1}_{0,a_2-l}(0, z2) \right) \left(\lambda^{S^2}_{a_1,l} \phi^{S^2}_{a_1,l}(z1, z2) \right) \tag{A26}$$

Following a similar procedure, the transform of the third term in Equation (A12) is

$$\alpha \left(\sum_{l=0}^{a_1} \binom{a_1}{l} \left(\lambda^{S^2}_{a_1-l,0} \phi^{S^2}_{a_1-l,0}(z1, 0) \right) \left(\lambda^{S^1}_{l,a_2} \phi^{S^1}_{l,a_2}(z1, z2) \right) - \left(\lambda^{S^2}_{a_1,0} \phi^{S^2}_{a_1,0}(z1, 0) \right) \left(\lambda^{S^1}_{0,a_2} \phi^{S^1}_{l,a_2}(0, z2) \right) \right) \tag{A27}$$

It should be noted that the contribution of Equation (A26) and (A27) is usually zero because species S^1 and S^2 can be chosen so as that $[S^1_{0,j}] = 0$ and $[S^2_{i,0}] = 0$.

The final expression for the pgf transform is

$$\alpha \left(\begin{array}{l} \sum_{r=0}^{a_1} \sum_{t=0}^{a_2} \binom{a_1}{r} \binom{a_2}{t} \left(\lambda^{S^1}_{r,t} \phi^{S^1}_{r,t}(z1, z2) \right) \left(\lambda^{S^2}_{a_1-r,a_2-t} \phi^{S^2}_{a_1-r,a_2-t}(z1, z2) \right) \\ - \sum_{l=0}^{a_2} \binom{a_2}{l} \left(\lambda^{S^1}_{0,a_2-l} \phi^{S^1}_{0,a_2-l}(0, z2) \right) \left(\lambda^{S^2}_{a_1,l} \phi^{S^2}_{a_1,l}(z1, z2) \right) - \\ \sum_{l=0}^{a_1} \binom{a_1}{l} \left(\lambda^{S^2}_{a_1-l,0} \phi^{S^2}_{a_1-l,0}(z1, 0) \right) \left(\lambda^{S^1}_{l,a_2} \phi^{S^1}_{l,a_2}(z1, z2) \right) + \left(\lambda^{S^2}_{a_1,0} \phi^{S^2}_{a_1,0}(z1, 0) \right) \left(\lambda^{S^1}_{0,a_2} \phi^{S^1}_{l,a_2}(0, z2) \right) \end{array} \right) \tag{A28}$$

The pgf transform of the remaining expressions, $\alpha \sum_{i=0}^{n-1} \sum_{j=0}^{m} [S^1_{i,j}][S^2_{n-i,m-j}]$, $\alpha \sum_{i=0}^{n} \sum_{j=0}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]$, $\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]$, $\alpha \sum_{i=1}^{n-1} \sum_{j=1}^{m-1} [S^1_{i,j}][S^2_{n-i,m-j}]$, $\alpha \sum_{i=1}^{n-1} \sum_{j=0}^{m} [S_{i,j}][S_{n-i,m-j}]$, $\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i,m-j}]$, are deduced likewise.

A.5. $\alpha \sum_{i=m+1}^{\infty} S_{n,i}$ and $\alpha \sum_{i=n+1}^{\infty} S_{i,m}$ Terms

Applying to this term the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0, \ldots, \infty$ and $m = 0, \ldots, \infty$ it is obtained

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{i=m+1}^{\infty} [S_{n,i}] \tag{A29}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \left(\sum_{i=m}^{\infty} [S_{n,i}] - [S_{n,m}] \right) \tag{A30}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{i=m}^{\infty} [S_{n,i}] - \alpha \left(\lambda^{S}_{a_1,a_2} \phi^{S}_{a_1,a_2}(z1, z2) \right) \tag{A31}$$

Now, operating with the first term in Equation (A31),

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{i=m}^{\infty} [S_{n,i}] \tag{A32}$$

$$\alpha \sum_{n=0}^{\infty} n^{a_1} z1^n \sum_{m=0}^{\infty} \sum_{i=m}^{\infty} m^{a_2} z2^m [S_{n,i}] \tag{A33}$$

$$\alpha \sum_{n=0}^{\infty} n^{a_1} z1^n \sum_{i=0}^{\infty} \sum_{m=0}^{i} m^{a_2} z2^m [S_{n,i}] \tag{A34}$$

$$\alpha \sum_{n=0}^{\infty} n^{a_1} z1^n \sum_{i=0}^{\infty} [S_{n,i}] \sum_{m=0}^{i} m^{a_2} z2^m \tag{A35}$$

The sum $\sum_{m=0}^{i} m^{a_2} z2^m$ can be shown to yield

$$\sum_{m=0}^{i} m^{a_2} z2^m = \begin{cases} \dfrac{1 - z2^{i+1}}{1 - z2} & if\ a_2 = 0 \\ \dfrac{z2^{i+2} i - z2^{i+1} i - z2^{i+1} + z2}{(1 - z2)^2} & if\ a_2 = 1 \end{cases} \tag{A36}$$

Replacing the expression for $a_2 = 0$ in Equation (A35),

$$\alpha \sum_{n=0}^{\infty} n^{a_1} z1^n \sum_{i=0}^{\infty} [S_{n,i}] \frac{1 - z2^{i+1}}{1 - z2} \tag{A37}$$

$$\frac{\alpha}{(1 - z2)} \left(\sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} z1^n [S_{n,i}] - z2 \sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} z1^n z2^i [S_{n,i}] \right) \tag{A38}$$

$$\frac{\alpha}{(1 - z2)} \left(\left(\lambda^S_{a_1,0} \phi^S_{a_1,0}(z1, 1) \right) - z2 \sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} m^0 z1^n z2^i [S_{n,i}] \right) \tag{A39}$$

$$\frac{\alpha}{(1 - z2)} \left(\left(\lambda^S_{a_1,0} \phi^S_{a_1,0}(z1, 1) \right) - z2 \left(\lambda^S_{a_1,0} \phi^S_{a_1,0}(z1, z2) \right) \right) \tag{A40}$$

Now, adding the second term in Equation (A31) and operating, the final expression for the pgf transform of the term $\alpha \sum_{i=m+1}^{\infty} S_{n,i}$ when $a_2 = 0$ is obtained:

$$\alpha \left(\frac{1}{(1 - z2)} \left(\left(\lambda^S_{a_1,0} \phi^S_{a_1,0}(z1, 1) \right) - \left(\lambda^S_{a_1,0} \phi^S_{a_1,0}(z1, z2) \right) \right) \right) \tag{A41}$$

In the case of $a_2 = 1$, replacing the corresponding expression in Equation (A36) into Equation (A35), it is obtained

$$\alpha \sum_{n=0}^{\infty} n^{a_1} z1^n \sum_{i=0}^{\infty} [S_{n,i}] \frac{m z2^{m+2} - m z2^{m+1} - z2^{m+1} + z2}{(1 - z2)^2} \tag{A42}$$

$$\frac{\alpha}{(1 - z2)^2} \begin{pmatrix} z2^2 \sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} z1^n m z2^m [S_{n,i}] - z2 \sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} z1^n m z2^m [S_{n,i}] \\ -z2 \sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} z1^n z2^m [S_{n,i}] + z2 \sum_{n=0}^{\infty} \sum_{i=0}^{\infty} n^{a_1} z1^n [S_{n,i}] \end{pmatrix} \tag{A43}$$

$$\frac{\alpha}{(1-z2)^2}\begin{pmatrix} z2^2\left(\lambda^S_{a_1,1}\phi^S_{a_1,1}(z1,z2)\right)-z2\left(\lambda^S_{a_1,1}\phi^S_{a_1,1}(z1,z2)\right)-z2\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)\right)\\ +z2\left(\lambda^S_{a_1}\phi^S_{a_1,0}(z1,1)\right)\end{pmatrix} \tag{A44}$$

Adding to Equation (A44) the second term in Equation (A31) and operating, the final expression for the pgf transform of the term $\alpha\sum_{i=m+1}^{\infty}S_{n,i}$ when $a_2=1$ is obtained

$$\alpha\left(-\frac{1}{(1-z2)}\left(\lambda^S_{a_1,1}\phi^S_{a_1,1}(z1,z2)\right)+\frac{z2}{(1-z2)^2}\left(\left(\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,1)\right)-\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)\right)\right) \tag{A45}$$

In a similar way the transform of the term $\alpha\sum_{i=n+1}^{\infty}S_{i,m}$ is obtained.

A.6. $\alpha\sum_{i=n}^{\infty}\sum_{j=m}^{\infty}[S_{i,j}]$ Term.

Starting with

$$\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}n^{a_1}m^{a_2}z1^n z2^m\sum_{i=m}^{\infty}\sum_{j=m}^{\infty}[S_{n,i}] \tag{A46}$$

Rearranging sums,

$$\alpha\sum_{n=0}^{\infty}\sum_{i=n}^{\infty}\sum_{m=0}^{\infty}\sum_{j=m}^{\infty}n^{a_1}m^{a_2}z1^n z2^m[S_{i,j}] \tag{A47}$$

Applying the identity $\sum_{l=0}^{\infty}\sum_{k=0}^{l}\ldots=\sum_{k=0}^{\infty}\sum_{l=k}^{\infty}\ldots$ to the two first and two second sums,

$$\alpha\sum_{i=0}^{\infty}\sum_{n=0}^{i}\sum_{j=0}^{\infty}\sum_{m=0}^{j}n^{a_1}m^{a_2}z1^n z2^m[S_{i,j}] \tag{A48}$$

Rearranging sums again,

$$\alpha\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}[S_{i,j}]\sum_{n=0}^{i}n^{a_1}z1^n\sum_{m=0}^{j}m^{a_2}z2^m \tag{A49}$$

The last two sums in Equation (A49) yield the following expressions depending on the values of a_1 and a_2:

$$\sum_{n=0}^{i}n^{a_1}z1^n\sum_{m=0}^{j}m^{a_2}z2^m=\begin{cases}\dfrac{z1z2z1^iz2^j-z1z1^i-z2z2^j+1}{(1-z1)(1-z2)} & if\ a_1=0\ \text{and}\ a_2=0\\ \dfrac{\begin{array}{c}-z1z2^{j+1}+z1-iz1^{i+2}z2^{j+1}+iz1^{i+2}\\ +z1^{i+1}z2^{j+1}-z1^{i+1}+iz1^{i+1}z2^{j+1}-iz1^{i+1}\end{array}}{(1-z1)^2(1-z2)} & if\ a_1=1\ \text{and}\ a_2=0\\ \dfrac{\begin{array}{c}-z2z1^{i+1}+z2-jz1^{i+1}z2^{j+2}+jz2^{j+2}\\ +z1^{i+1}z2^{j+1}-z2^{j+1}+jz1^{i+1}z2^{j+1}-jz2^{j+1}\end{array}}{(1-z1)(1-z2)^2} & if\ a_1=0\ \text{and}\ a_2=1\end{cases} \tag{A50}$$

Replacing Equation (A50) into Equation (A49) and rearranging sums seeking pgf definitions, like in A.5, yields the following final expressions:

$$\begin{array}{ll} \alpha\left(\frac{1}{(1-z1)(1-z2)}\left(\begin{array}{l} z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)-z1\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right)\\ -z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)+\lambda^S_{0,0}\end{array}\right)\right) & \text{if } a_1=0 \text{ and } a_2=0\\ \alpha\left(\begin{array}{l} \frac{1}{(1-z1)(1-z2)}\left(z1z2\left(\lambda^S_{1,0}\phi^S_{1,0}(z1,z2)\right)-z1\left(\lambda^S_{1,0}\phi^S_{1,0}(z1,1)\right)\right)+\\ \frac{1}{(1-z1)^2(1-z2)}\left(\begin{array}{l} z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)-z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)-\\ z1\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right)+z1\lambda^S_{0,0}\end{array}\right)\end{array}\right) & \text{if } a_1=1 \text{ and } a_2=0\\ \alpha\left(\begin{array}{l} \frac{1}{(1-z1)(1-z2)}\left(z1z2\left(\lambda^S_{0,1}\phi^S_{0,1}(z1,z2)\right)\right)-z2\left(\lambda^S_{0,1}\phi^S_{0,1}(1,z2)\right)+\\ \frac{1}{(1-z1)(1-z2)^2}\left(\begin{array}{l} z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,z2)\right)-z1z2\left(\lambda^S_{0,0}\phi^S_{0,0}(z1,1)\right)-\\ z2\left(\lambda^S_{0,0}\phi^S_{0,0}(1,z2)\right)+z2\lambda^S_{0,0}\end{array}\right)\end{array}\right) & \text{if } a_1=0 \text{ and } a_2=1 \end{array} \quad \text{(A51)}$$

A.7. $\alpha\sum_{i=1}^{m}[S_{n,i}]$ and $\alpha\sum_{i=1}^{n}[S_{i,m}]$ Terms

Starting with

$$\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}n^{a_1}m^{a_2}z1^n z2^m\sum_{i=1}^{m}[S_{n,i}] \quad \text{(A52)}$$

$$\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}n^{a_1}m^{a_2}z1^n z2^m\left(\sum_{i=0}^{m}[S_{n,i}]-[S_{n,0}]\right) \quad \text{(A53)}$$

$$\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}n^{a_1}m^{a_2}z1^n z2^m\sum_{i=0}^{m}[S_{n,i}]-\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}n^{a_1}m^{a_2}z1^n z2^m[S_{n,0}] \quad \text{(A54)}$$

Operating with the first term of Equation (A54),

$$\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{i=0}^{m}n^{a_1}m^{a_2}z1^n z2^m[S_{n,i}] \quad \text{(A55)}$$

$$\alpha\sum_{n=0}^{\infty}n^{a_1}z1^n\sum_{m=0}^{\infty}\sum_{i=0}^{m}m^{a_2}z2^m[S_{n,i}] \quad \text{(A56)}$$

$$\alpha\sum_{n=0}^{\infty}n^{a_1}z1^n\sum_{i=0}^{\infty}[S_{n,i}]\sum_{m=i}^{\infty}m^{a_2}z2^m \quad \text{(A57)}$$

The sum $\sum_{m=i}^{\infty}m^{a_2}z2^m$ yields

$$\sum_{m=i}^{\infty}m^{a_2}z2^m=\begin{cases}\dfrac{z2^i}{1-z2} & \text{if } a_2=0\\ \dfrac{z2^i(z2-iz2+i)}{(1-z2)^2} & \text{if } a_2=1\end{cases} \quad \text{(A58)}$$

Hence, replacing Equation (A58) in Equation (A57) and rearranging in terms of the pgf definitions, yields

$$\begin{array}{ll} \dfrac{\alpha}{(1-z2)}\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2) & \text{if } a_2=0\\ \alpha\left(\dfrac{1}{(1-z2)}\lambda^S_{a_1,1}\phi^S_{a_1,1}(z1,z2)+\dfrac{z2}{(1-z2)^2}\lambda^S_{a_1,0}\phi^S_{a_1,0}(z1,z2)\right) & \text{if } a_2=1\end{array} \quad \text{(A59)}$$

On the other hand, the second term of Equation (A54) is rearranged into

$$\alpha \sum_{n=0}^{\infty} n^{a_1} z1^n [S_{n,0}] \sum_{m=0}^{\infty} m^{a_2} z2^m = \begin{cases} \dfrac{\alpha}{(1-z2)} \sum\limits_{n=0}^{\infty} n^{a_1} z1^n [S_{n,0}] & \text{if } a_2 = 0 \\ \dfrac{z2}{(1-z2)^2} \sum\limits_{n=0}^{\infty} n^{a_1} z1^n [S_{n,0}] & \text{if } a_2 = 1 \end{cases} \tag{A60}$$

Recalling Equation (5), it can be seen that $\sum\limits_{n=0}^{\infty} n^{a_1} z1^n [S_{n,0}] = \lambda^S_{a_1,0} \varphi^S_{a_1,0}(z1, 0)$. Therefore, the final expression for the pgf transform of the term $\alpha \sum\limits_{i=1}^{m} [S_{n,i}]$ is

$$\begin{matrix} \dfrac{\alpha}{(1-z2)} \left(\lambda^S_{a_1,1} \phi^S_{a_1,1}(z1, z2) - \lambda^S_{a_1,0} \varphi^S_{a_1,0}(z1, z2) \right) & \textit{if } a_2 = 0 \\ \dfrac{\alpha}{(1-z2)} \left(\lambda^S_{a_1,1} \phi^S_{a_1,1}(z1, z2) + \dfrac{z2}{(1-z2)} \left(\lambda^S_{a_1,0} \phi^S_{a_1,0}(z1, z2) - \lambda^S_{a_1,0} \varphi^S_{a_1,0}(z1, 0) \right) \right) & \textit{if } a_2 = 1 \end{matrix} \tag{A61}$$

In a similar way the pgf transform of the term $\alpha \sum\limits_{i=1}^{n} [S_{i,m}]$ is obtained.

A.8. $\alpha \sum\limits_{i=0}^{n} \sum\limits_{j=0}^{m} [S_{i,j}]$ Term

Applying to this term the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0, \ldots, \infty$ and $m = 0, \ldots, \infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{i=0}^{n} \sum_{j=0}^{m} [S_{i,j}] \tag{A62}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{i=0}^{n} \sum_{m=0}^{\infty} \sum_{j=0}^{m} n^{a_1} m^{a_2} z1^n z2^m [S_{i,j}] \tag{A63}$$

$$\alpha \sum_{i=0}^{\infty} \sum_{n=i}^{\infty} \sum_{j=0}^{\infty} \sum_{m=j}^{\infty} n^{a_1} m^{a_2} z1^n z2^m [S_{i,j}] \tag{A64}$$

$$\alpha \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} [S_{i,j}] \sum_{n=i}^{\infty} n^{a_1} z1^n \sum_{m=j}^{\infty} m^{a_2} z2^m \tag{A65}$$

The last two sums in Equation (A65) lead the following expressions according to the values of a_1 and a_2:

$$\sum_{n=i}^{\infty} n^{a_1} z1^n \sum_{m=j}^{\infty} m^{a_2} z2^m = \begin{cases} \dfrac{z1^i z2^j}{(1-z1)(1-z2)} & \text{if } a_1 = a_2 = 0 \\ \dfrac{(z1 - iz1 + i) z1^i z2^j}{(1-z1)^2 (1-z2)} & \text{if } a_1 = 1 \text{ and } a_2 = 0 \\ \dfrac{(z2 - jz2 + j) z1^i 2^j}{(1-z1)(1-z2)^2} & \text{if } a_1 = 0 \text{ and } a_2 = 1 \end{cases} \tag{A66}$$

Replacing Equation (A66) into Equation (A65) and operating seeking for the pgf definitions yield the final expressions for the pgf transforms:

$$\begin{matrix} \alpha \dfrac{\left(\lambda^S_{0,0} \phi^S_{0,0}(z1, z2) \right)}{(1-z1)(1-z2)} & \text{if } a_1 = a_2 = 0 \\ \alpha \begin{pmatrix} \dfrac{1}{(1-z1)(1-z2)} \left(\lambda^S_{1,0} \phi^S_{1,0}(z1, z2) \right) \\ + \dfrac{z1}{(1-z1)^2 (1-z2)} \left(\lambda^S_{0,0} \phi^S_{0,0}(z1, z2) \right) \end{pmatrix} & \text{if } a_1 = 1 \text{ and } a_2 = 0 \\ \alpha \begin{pmatrix} \dfrac{1}{(1-z1)(1-z2)} \left(\lambda^S_{0,1} \phi^S_{0,1}(z1, z2) \right) \\ + \dfrac{z2}{(1-z1)(1-z2)^2} \left(\lambda^S_{0,0} \phi^S_{0,0}(z1, z2) \right) \end{pmatrix} & \text{if } a_1 = 0 \text{ and } a_2 = 1 \end{matrix} \tag{A67}$$

A.9. $\alpha n^{2-i} m^{i-1}[S_{n,m}]$, $i = 1, 2$ Term

Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m n^{2-i} m^{1-i} [S_{n,m}] \quad i = 1, 2 \tag{A68}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1+2-i} m^{a_2+1-i} z1^n z2^m [S_{n,m}] \quad i = 1, 2 \tag{A69}$$

$$\alpha \left(\lambda^S_{a_1+2-i,a_2+i-1} \phi^S_{a_1+2-i,a_2+i-1}(z1, z2) \right) \quad i = 1, 2 \tag{A70}$$

The previous expression adopts the following outputs for each value of i:

$$\begin{aligned} &\alpha \left(\lambda^S_{a_1+1,a_2} \phi^S_{a_1+1,a_2}(z1, z2) \right) \quad \text{if } i = 1 \\ &\alpha \left(\lambda^S_{a_1,a_2+1} \phi^S_{a_1,a_2+1}(z1, z2) \right) \quad \text{if } i = 2 \end{aligned} \tag{A71}$$

Recalling Equation (10) and (11), the pgf of orders $a_i + 1$ can be put in terms of the derivative of the pgf with respect to their dummy variables as shown in Equation (A72), which is the final form of the pgf transform.

$$\alpha \frac{zi \partial \left(\lambda^S_{a_1,a_2} \phi^S_{a_1,a_2}(z1, z2) \right)}{\partial zi} \quad i = 1, 2 \tag{A72}$$

A.10. $\alpha(n-1)[S_{n,m}]$, $\alpha(m-1)[S_{n,m}]$ Terms

Let us consider the term $\alpha(n-1)[S_{n,m}]$. Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m (n-1)[S_{n,m}] \tag{A73}$$

$$\alpha \left(\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1+1} m^{a_2} z1^n z2^m [S_{n,m}] - \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m [S_{n,m}] \right) \tag{A74}$$

$$\alpha \left(\lambda^S_{a_1+1,a_2} \phi^S_{a_1+1,a_2}(z1, z2) - \lambda^S_{a_1,a_2} \phi^S_{a_1,a_2}(z1, z2) \right) \tag{A75}$$

Finally, expressing the pgf of order a_1+1 in terms of the derivative with respect to the dummy variable $z1$,

$$\alpha \left(\frac{z1 \partial \left(\lambda^S_{a_1,a_2} \phi^S_{a_1,a_2}(z1, z2) \right)}{\partial z1} - \lambda^S_{a_1,a_2} \phi^S_{a_1,a_2}(z1, z2) \right) \tag{A76}$$

Likewise, the transform of the term $\alpha(m-1)[S_{n,m}]$ can be obtained.

A.11. $\alpha n[S_{n,m-1}]$, $\alpha m[S_{m-1,m}]$ Terms

Let us consider the term $\alpha n[S_{n,m-1}]$. Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m n [S_{n,m-1}] \tag{A77}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1+1} m^{a_2} z1^n z2^m [S_{n,m-1}] \tag{A78}$$

Letting $r = m-1$ and substituting,

$$\alpha \sum_{n=0}^{\infty} \sum_{r=-1}^{\infty} n^{a_1+1}(r+1)^{a_2} z1^n z2^{r+1} [S_{n,r}] \tag{A79}$$

Since $z2$ is independent of the summation variables and $[S_{n,-1}] = 0$,

$$\alpha z2 \sum_{n=0}^{\infty} \sum_{r=0}^{\infty} n^{a_1+1}(r+1)^{a_2} z1^n z2^r [S_{n,r}] \tag{A80}$$

$$\alpha z2 \sum_{n=0}^{\infty} \sum_{r=0}^{\infty} n^{a_1+1} \left(\sum_{t=0}^{a_2} \binom{a_2}{t} r^t \right) z1^n z2^r [S_{n,r}] \tag{A81}$$

$$\alpha z2 \sum_{t=0}^{a_2} \binom{a_2}{t} \sum_{n=0}^{\infty} \sum_{r=0}^{\infty} n^{a_1+1} r^t z1^n z2^r [S_{n,r}] \tag{A82}$$

$$\alpha z2 \sum_{t=0}^{a_2} \binom{a_2}{t} \left(\lambda^S_{a_1+1,t} \phi^S_{a_1+1,t}(z1, z2) \right) \tag{A83}$$

$$\alpha z2 \sum_{t=0}^{a_2} \binom{a_2}{t} \frac{z1 \partial \left(\lambda^S_{a_1,t} \phi^S_{a_1,t}(z1, z2) \right)}{\partial z1} \tag{A84}$$

$$\alpha z1 z2 \sum_{t=0}^{a_2} \binom{a_2}{t} \frac{\partial \left(\lambda^S_{a_1,t} \phi^S_{a_1,t}(z1, z2) \right)}{\partial z1} \tag{A85}$$

In a similar way, the pgf transform of the term $\alpha m[S_{n-1,m}]$ is obtained.

A.12. $\alpha \sum_{i=1}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i+1,m-j}]$ Term

Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for n=0,. . .,∞ and m=0,. . .,∞, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{i=1}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i+1,m-j}] \tag{A86}$$

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \left(\begin{array}{c} \sum_{i=0}^{n} \sum_{j=0}^{m} [S_{i,j}][S_{n-i+1,m-j}] - \sum_{j=1}^{m-1} [S_{0,j}][S_{n+1,m-j}] \\ - \sum_{i=0}^{n} \left([S_{i,0}][S_{n-i+1,m}] + [S_{i,m}][S_{n-i+1,0}] \right) \end{array} \right) \tag{A87}$$

Taking the first term in Equation (A87) and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{i=0}^{n} \sum_{j=0}^{m} n^{a_1} m^{a_2} z1^n z2^m [S_{i,j}][S_{n-i+1,m-j}] \tag{A88}$$

$$\alpha \sum_{i=0}^{\infty} \sum_{n=i}^{\infty} \sum_{j=0}^{\infty} \sum_{m=j}^{\infty} n^{a_1} m^{a_2} z1^n z2^m [S_{i,j}][S_{n-i+1,m-j}] \tag{A89}$$

Applying the substitutions $p=n-i$ and $q=m-s$ and operating,

$$\alpha\sum_{i=0}^{\infty}\sum_{p=0}^{\infty}\sum_{j=0}^{\infty}\sum_{q=0}^{\infty}(i+p)^{a_1}(j+q)^{a_2}z1^{i+p}z2^{j+q}[S_{i,j}][S_{p+1,q}] \tag{A90}$$

$$\alpha\sum_{i=0}^{\infty}\sum_{p=0}^{\infty}\sum_{j=0}^{\infty}\sum_{q=0}^{\infty}\left(\sum_{u=0}^{a_1}\binom{a_1}{u}i^u p^{a_1-u}\right)\left(\sum_{v=0}^{a_2}\binom{a_2}{v}j^v q^{a_2-v}\right)z1^i z1^p z2^j z2^q[S_{i,j}][S_{p+1,q}] \tag{A91}$$

$$\alpha\sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\binom{a_1}{u}\binom{a_2}{v}\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}i^u j^v z1^i z2^j[S_{i,j}]\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}z1^p z2^q p^{a_1-u}q^{a_2-v}[S_{p+1,q}] \tag{A92}$$

$$\alpha\sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\binom{a_1}{u}\binom{a_2}{v}\left(\lambda_{u,v}^S\phi_{u,v}^S(z1,z2)\right)\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}z1^p z2^q p^{a_1-u}q^{a_2-v}\ [S_{p+1,q}] \tag{A93}$$

From the derivation in section A.3 of this appendix, it can be seen that $\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}z1^p z2^q p^{a_1-u}q^{a_2-v}[S_{p+1,q}]=\frac{1}{z1}\left(\sum_{x=0}^{a_1-u}\binom{a_1-u}{x}\right.$ $\left.(-1)^{a_1-u-x}\left(\lambda_{x,a_2-v}^S\phi_{x,a_2-v}^S(z1,z2)\right)-(-1)^{a_1-u}\left(\lambda_{0,a_2-v}^S\phi_{0,a_2-v}^S(0,z2)\right)\right)$, and hence the expression in Equation (A93) results

$$\frac{\alpha}{z1}\left(\begin{array}{l}\sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\sum_{x=0}^{a_1-u}\binom{a_1}{u}\binom{a_2}{v}\binom{a_1-u}{x}(-1)^{a_1-u-x}\left(\lambda_{u,v}^S\phi_{u,v}^S(z1,z2)\right)\left(\lambda_{x,a_2-v}^S\phi_{x,a_2-v}^S(z1,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{a_2}(-1)^{a_1-u}\left(\lambda_{0,a_2-v}^S\phi_{0,a_2-v}^S(0,z2)\right)\end{array}\right) \tag{A94}$$

Following a similar procedure the pgf transforms of the last three terms in Equation (A87) can be obtained, yielding the final expression

$$\frac{\alpha}{z1}\left(\begin{array}{l}\sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\sum_{x=0}^{a_1-u}\binom{a_1}{u}\binom{a_2}{v}\binom{a_1-u}{x}(-1)^{a_1-u-x}\left(\lambda_{u,v}^S\phi_{u,v}^S(z1,z2)\right)\left(\lambda_{x,a_2-v}^S\phi_{x,a_2-v}^S(z1,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{a_2}(-1)^{a_1-u}\left(\lambda_{0,a_2-v}^S\phi_{0,a_2-v}^S(0,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{a_2}\binom{a_1}{u}\binom{a_2}{v}(-1)^{a_1-u}\left(\lambda_{u,v}^S\phi_{u,v}^S(z1,z2)\right)\left(\lambda_{0,a_2-v}^S\phi_{0,a_2-v}^S(0,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{u}\binom{a_1}{u}\binom{u}{v}(-1)^{u-v}\left(\lambda_{a_1-u,0}^S\phi_{a_1-u,0}^S(z1,0)\right)\left(\lambda_{v,a_2}^S\phi_{0,a_2}^S(z1,z2)\right)-\\ \sum_{u=0}^{a_1}\sum_{v=0}^{u}\binom{a_1}{u}\binom{u}{v}(-1)^{u-v}\left(\lambda_{v,0}^S\phi_{v,0}^S(z1,0)\right)\left(\lambda_{a_1-u,a_2}^S\phi_{a_1-u,a_2}^S(z1,z2)\right)\end{array}\right) \tag{A95}$$

A.13. $\alpha\delta_{n,j}$, $\alpha\delta_{m,j}$, $j=0,1,2$ Terms

Let us consider the term $\alpha\delta_{n,j}$, the transform for the term $\alpha\delta_{m,j}$ is derived in the same way. Applying the multiplication by $z1^n z2^m n^{a_1}m^{a_2}$ and summing for $n=0,\ldots,\infty$ and $m=0,\ldots,\infty$, and operating,

$$\alpha\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}n^{a_1}m^{a_2}z1^n z2^m\delta_{n,j} \tag{A96}$$

$$\alpha\sum_{n=0}^{\infty}n^{a_1}z1^n\delta_{n,j}\sum_{m=0}^{\infty}m^{a_2}z2^m \tag{A97}$$

$$\alpha j^{a_1}z^j\sum_{m=0}^{\infty}m^{a_2}z2^m \tag{A98}$$

$$\begin{array}{ll}\alpha j^{a_1}z1^j\dfrac{1}{(1-z2)} & \text{if } a_2=0\\ \alpha j^{a_1}z1^j\dfrac{z2}{(1-z2)^2} & \text{if } a_2=1\end{array} \tag{A99}$$

The expression in Equation (A99) can be compacted as function of a_2 in the following way, which is the final form of the pgf transform of this term:

$$\alpha j^{a_1} z1^j \frac{\prod_{k=1}^{a_2} (z2 + k - 1)}{(1 - z2)^{a_2+1}} \tag{A100}$$

A.14. $\alpha\delta_{n,u}\delta_{m,v}, \alpha[S_{n-1,m}]\delta_{n,u}\delta_{m,v}, \alpha[S_{n,m-1}]\delta_{n,u}\delta_{m,v}, u, v = 0, 1, 2, \ldots$ Terms

Let us consider the term $\alpha\delta_{n,u}\delta_{m,v}$ since the other ones are transformed likewise applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0$,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \delta_{n,u}\delta_{m,v} \tag{A101}$$

Since the only non-zero term in the previous sums is that with n equal to u and m equal to v simultaneously, the expression yields

$$\alpha u^{a_1} v^{a_2} z1^u z2^v \tag{A102}$$

A.15. $\alpha[S_{n,m}]\delta_{n,j}, \alpha[S_{n,m}]\delta_{m,j}, \alpha[S_{n-1,m}]\delta_{n,j}, \alpha[S_{n,m-1}]\delta_{m,j}\, j = 0, 1, 2, \ldots$ Terms

Let us consider the term $\alpha[S_{n,m}]\delta_{n,j}$ since the other ones are transformed likewise. Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m [S_{n,m}]\delta_{n,j} \tag{A103}$$

$$\alpha j^{a_1} z1^j \sum_{m=0}^{\infty} m^{a_2} z2^m [S_{j,m}] \tag{A104}$$

The sum $\sum_{m=0}^{\infty} m^{a_2} z2^m [S_{j,m}]$ is the univariate pgf transform of the distribution of the property represented by the second subscript, of the polymer molecules with a j value of the first distributed property. Examples of this could be the chain length distribution of branched macromolecules with j branches, or the distribution of the second comonomer content in a copolymer with j units of the first comonomer. More details about univariate pgf can be found elsewhere. Besides, in the case of $j = 0$, this univariate pgf coincides with the bivariate pgf evaluated at $z1 = 0$. Hence, the final expression of the 2D pgf transform of the term $\alpha[S_{n,m}]\delta_{n,j}$ is

$$\begin{aligned} &\alpha j^{a_1} z1^j \left(\mu_{a_2}^{S_{j,*}} \varphi_{a_2}^{S_{j,*}}\right) \qquad j = 0, 1, 2, \ldots \\ &\text{or} \\ &\alpha 0^{a_1} \left(\lambda_{0,a_2}^{S} \phi_{0,a_2}^{S}(0, z2)\right) \quad j = 0 \end{aligned} \tag{A105}$$

where $\left(\mu_{a_2}^{S_{j,*}} \varphi_{a_2}^{S_{j,*}}(z2)\right)$ is the univariate pgf transform mentioned before.

A.16. $\alpha \sum_{i=1}^{n-1} \sum_{j=1}^{m-1} [S_{i,j}^1][S_{n-i,m-j}^2]\, \delta_{n,1}\delta_{m,1}$, $\alpha \sum_{i=1}^{n-1} \sum_{j=0}^{m} [S_{i,j}][S_{n-i,m-j}]\, \delta_{n,j}, j = 0, 1$, $\alpha \sum_{i=0}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i,m-j}]\, \delta_{m,j}, j = 0, 1$ Terms

Let us consider the term $\alpha \sum_{i=1}^{n-1} \sum_{j=1}^{m-1} [S_{i,j}^1][S_{n-i,m-j}^2]\, \delta_{n,1}\delta_{m,1}$ as example, since the procedure with the other ones is similar. Keeping only the nonzero terms in these sums, the result is

$$\alpha \sum_{i=1}^{0} \sum_{j=1}^{0} [S_{i,j}^1][S_{1-i,1-j}^2] = 0 \tag{A106}$$

Therefore, applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m 0 = 0 \tag{A107}$$

which means that the pgf transform of this term is 0.

A.17. $\alpha \sum_{i=n+1}^{\infty} [S_{i,m}]\,\delta_{n,0}$, $\alpha \sum_{i=m+1}^{\infty} [S_{n,i}]\,\delta_{m,0}$ Terms

Let us consider the term $\alpha \sum_{i=n+1}^{\infty} [S_{i,m}]\,\delta_{n,0}$. Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots,\infty$ and $m = 0,\ldots,\infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{\alpha_1} m^{a_2} z1^n z2^m \sum_{i=n+1}^{\infty} [S_{i,m}]\delta_{n,0} \tag{A108}$$

$$\alpha \sum_{m=0}^{\infty} 0^{a_1} m^{a_2} z1^0 z2^m \sum_{i=1}^{\infty} [S_{i,m}] = \begin{cases} 0 & \text{if } a_1 = 1 \\ \sum_{m=0}^{\infty} m^{a_2} z2^m \sum_{i=1}^{\infty} [S_{i,m}] & \text{if } a_1 = 0 \end{cases} \tag{A109}$$

Additional operation with the expression $\sum_{m=0}^{\infty} m^{a_2} z2^m \sum_{i=1}^{\infty} [S_{i,m}]$ gives

$$\sum_{m=0}^{\infty} \sum_{i=0}^{\infty} m^{\alpha_2} z2^m [S_{i,m}] - \sum_{m=0}^{\infty} m^{a_2} z2^m [S_{0,m}] \tag{A110}$$

Recalling the 2D-pgf definition given in Equation (3), it can be seen that the previous expression results

$$\left(\lambda^S_{0,a_2} \phi^S_{0,a_2}(1, z2)\right) - \left(\lambda^S_{0,a_2} \varphi^S_{0,a_2}(0, z2)\right) \tag{A111}$$

Therefore, the pgf transform of the term is

$$\begin{array}{ll} 0 & \text{if } a_1 = 1 \\ \left(\lambda^S_{0,a_2} \phi^S_{0,a_2}(1, z2)\right) - \left(\lambda^S_{0,a_2} \varphi^S_{0,a_2}(0, z2)\right) & \text{if } a_1 = 0 \end{array} \tag{A112}$$

The pgf transform of the other term is deduced likewise.

A.18. $\alpha \sum_{i=n}^{\infty} \sum_{j=m}^{\infty} [S_{i,j}]\,\delta_{n,0}$, $\alpha \sum_{i=n}^{\infty} \sum_{j=m}^{\infty} [S_{i,j}]\,\delta_{m,0}$ Terms

Let us consider the term $\alpha \sum_{i=n}^{\infty} \sum_{j=m}^{\infty} [S_{i,j}]\,\delta_{n,0}$, the other one is deduced likewise. Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0,\ldots, \infty$ and $m = 0,\ldots, \infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m \sum_{i=n}^{\infty} \sum_{j=m}^{\infty} [S_{i,j}]\,\delta_{n,0} \tag{A113}$$

$$\alpha \sum_{m=0}^{\infty} 0^{a_1} m^{a_2} z1^0 z2^m \sum_{i=0}^{\infty} \sum_{j=m}^{\infty} [S_{i,j}] = \begin{cases} 0 & \textit{if } a_1 = 1 \\ \alpha \sum_{m=0}^{\infty} m^{a_2} z2^m \sum_{i=0}^{\infty} \sum_{j=m}^{\infty} [S_{i,j}] & \textit{if } a_1 = 0 \end{cases} \tag{A114}$$

Proceeding with the expression for $a_1 = 0$,

$$\alpha \sum_{i=0}^{\infty} \sum_{m=0}^{\infty} \sum_{j=m}^{\infty} m^{a_2} z2^m [S_{i,j}] \tag{A115}$$

$$\alpha \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} [S_{i,j}] \sum_{m=0}^{j} m^{a_2} z2^m \tag{A116}$$

The sum in m in the previous expression has the following results according to the value of a_2:

$$\sum_{m=0}^{j} m^{a_2} z2^m = \begin{cases} \dfrac{1 - z2^{j+1}}{1 - z2} & \text{if } a_2 = 0 \\ \dfrac{jz2^{j+2} - jz2^{j+1} - z2^{j+1} + z2}{(1 - z2)^2} & \text{if } a_2 = 1 \end{cases} \tag{A117}$$

Replacing these expressions into Equation (A116) and using the pgf definition, the following expression is obtained for the pgf transform of this term:

$$\begin{array}{ll} 0 & \textit{if } a_1 = 1 \\ \dfrac{1}{(1 - z2)} \left(\lambda_{0,0}^S - z2 \left(\lambda_{0,0}^S \phi_{0,0}^S(1, z2) \right) \right) & \textit{if } a_1 = 0 \textit{ and } a_2 = 0 \\ -\dfrac{z2}{(1 - z2)} \left(\lambda_{0,1}^S \phi_{0,1}^S(1, z2) \right) + \dfrac{z2}{(1 - z2)^2} \left(\lambda_{0,0}^S \phi_{0,0}^S(1, z2) \right) & \textit{if } a_1 = 0 \textit{ and } a_2 = 1 \end{array} \tag{A118}$$

A.19. $\alpha n^{2-i} m^{i-1} [S_{n,m}] \delta_{n,0}$, $\alpha n^{2-i} m^{i-1} [S_{n,m}] \delta_{m,0}$, $i = 1, 2$ Terms

Let us consider the term $\alpha n^{2-i} m^{i-1} [S_{n,m}] \delta_{n,0}$, since the other one is derived likewise. Applying the multiplication by $z1^n z2^m n^{a_1} m^{a_2}$ and summing for $n = 0, \ldots, \infty$ and $m = 0, \ldots, \infty$, and operating,

$$\alpha \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^{a_1} m^{a_2} z1^n z2^m n^{2-i} m^{i-1} [S_{n,m}] \, \delta_{n,0} \tag{A119}$$

$$\alpha 0^{a_1+2-i} z1^0 \sum_{m=0}^{\infty} m^{a_2+i-1} z2^m [S_{0,m}] \tag{A120}$$

$$\alpha 0^{a_1+2-i} z1^0 \left(\lambda_{0,a_1+i-1}^S \phi_{0,a_2+i-1}^S(0, z2) \right) \tag{A121}$$

$$\begin{cases} 0 & \textit{if } i = 1 \textit{ or } a_1 = 1 \\ \alpha \left(\lambda_{0,a_2+1}^S \phi_{0,a_2+1}^S(0, z2) \right) = \alpha z2 \dfrac{\partial \left(\lambda_{0,a_2}^S \phi_{0,a_2}^S(0, z2) \right)}{\partial z2} & \textit{if } i = 0 \textit{ and } a_1 = 0 \end{cases} \tag{A122}$$

A.20. $\alpha(n - 1)[S_{n,m}]\delta_{n,1}$, $\alpha(m - 1)[S_{n,m}]\delta_{m,1}$ Terms

Any of these terms are always zero for any value of n or m. For instance, the term $\alpha(n - 1)[S_{n,m}]\delta_{n,1}$ is 0 for $n \neq 1$ because of the Kronecker delta factor, and also for $n = 1$ because of the (n–1) factor. Therefore, the pgf transform of this term is 0.

A.21. $\alpha n[S_{n,m-1}]\delta_{n,0}\delta_{m,0}$, $\alpha m[S_{n-1,m}]\delta_{n,0}\delta_{m,0}$ Terms

As in the previous case, these terms are always zero for any value of n or m. For the first one, the multiplication of Kronecker deltas extract as the only potentially nonzero expression, among all the possible ones for the different combinations of n and m, the one $\alpha 0[S_{0,-1}] = 0$. Therefore, the pgf transform of this term is 0.

A.22. $\alpha \sum_{i=1}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i+1,m-j}]\delta_{n,0}$, $\alpha \sum_{i=1}^{n} \sum_{j=1}^{m-1} [S_{i,j}][S_{n-i+1,m-j}]\delta_{m,1}$ Terms

The pgf transforms of these terms are zero because the Kronecker deltas determine meaningless sums, i.e., $\sum_{i=1}^{n(=0)}$ or $\sum_{j=1}^{m-1(=0)}$.

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[1] C. Chatzidoukas, V. Kanellopoulos, C. Kiparissides, *Macromol. Theory Simul.* **2007**, *16*, 755.
[2] P. Pladis, C. Kiparissides, *Chem. Eng. Sci.* **1998**, *53*, 3315.
[3] L. Wang, L. J. Broadbelt, *Macromolecules* **2009**, *42*, 7961.
[4] A. Krallis, D. Meimaroglou, C. Kiparissides, *Chem. Eng. Sci.* **2008**, *63*, 4342.
[5] D. Meimaroglou, A. Krallis, V. Saliakas, C. Kiparissides, *Macromolecules* **2007**, *40*, 2224.
[6] S. Costeux, *Macromolecules* **2003**, *36*, 4168.
[7] J. B. P. Soares, A. E. Hamielec, *Macromol. Theory Simul.* **1997**, *6*, 591.
[8] M. Wulkow, *Macromol. React. Eng.* **2008**, *2*, 461.
[9] I. Zapata-González, E. Saldívar-Guerra, J. Ortiz-Cisneros, *Macromol. Theory Simul.* **2011**, *20*, 370.
[10] P. D. Iedema, M. Wulkow, H. C. J. Hoefsloot, *Macromolecules* **2000**, *33*, 7173.
[11] C. Schütte, M. Wulkow, *Macromol. React. Eng.* **2010**, *4*, 562.
[12] M. Asteasuain, A. Brandolin, *Macromol. Theory Simul.* **2010**, *19*, 342.
[13] M. Asteasuain, A. Brandolin, C. Sarmoria, *Polymer* **2002**, *43*, 2529.
[14] M. Asteasuain, C. Sarmoria, A. Brandolin, *Polymer* **2002**, *43*, 2513.
[15] W. H. Ray, T. L. Douglas, E. W. Godsalve, *Macromolecules* **1971**, *4*, 166.
[16] A. Baltsas, D. S. Achilias, C. Kiparissides, *Macromol. Theory Simul.* **1996**, *5*, 477.
[17] D. J. Arriola, Ph. D. Thesis, University of Wisconsin, Madison 1989.