Topology Evolution in Polymer Modification

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A recent numerical method has opened new opportunities in multidimensional population balance modeling. Here, this method is applied to a full three-dimensional population balance model (PBM) describing branching topology evolution driven by chain end to backbone coupling. This process is typical for polymer modification reactions, e.g., in polyethylene, where initially linear polymer chains undergo hydrogen abstraction, and subsequent branching or scission. Topologies are distinguished by chain ends, number of branches, and number of reactive ends. The resulting time dependent trivariate distribution is utilized to extract various distributive properties of the polymer. The results exhibit excellent agreement with data from Monte Carlo simulations.

1. Introduction

Modeling of polymer systems has been approached in two different ways: stochastic or Monte Carlo (MC) simulations and deterministic population balance models (PBM). The first way produces a large amount of sample molecules and requires a generalization step to evaluate their properties statistically. The second describes a polymer system quantitatively on the basis of a few of the most important properties. The MC methods are strong in predicting morphology related properties, while various different implementations are available. In contrast, deterministic PBMs are focusing on a small number of properties and describe a polymer system by a compact and straightforward derived system of balance equations. From the viewpoint of optimizing the mass production of polymers and predicting physical properties, the deterministic methods are very attractive, as a high precision is often of high importance. Although the majority of the studies presented in literature refer to one dimensional PBMs, it is the numerical complexity one has faced when trying to solve the mathematical problem rather than a lacking demand for solutions, that have kept researchers out of investigations on multidimensional PBM. Indeed, tackling the problem of branched topologies deterministically makes unavoidable the consideration of at least two variables, chain length and amount of branches. Furthermore, the amount of reactive sites/reactive ends, also forms an essential dimension, as it affects the reactivity.

A lack of multidimensional PBM solvers on one hand, and attractiveness of the population palaces in a few dimensions on the other, has driven researchers into elaborate attempts to design hybrid methods. The hybrid methods, which combine PBM along one dimension and a method of moments or stochastic simulations along the others have been introduced at a price of complicated reasoning and analytical work. However, these attempts have remained case studies of single problems and are hardly transferable to other, even similar systems. The only attempt of developing a more general hybrid method has been done for the MC-Galerkin technique by Schütte and Wulkow. In previous work we have taken a different course. Instead of designing a hybrid method, we have invented a numerical approach capable of handling PBM in more than one dimension treating each of them equally. This permits not only an easy and transparent implementation, but also enables a better transferability to various PBM problems arising in polymer reaction engineering. The approach was successfully applied to polymerization and polymer modification problems in two dimensions.
The present paper widens the scope of application for the method to polymer modification problems in three-dimensional parametric space. Topologies of branched polymer are distinguished by chain length \( x \), amount of branch points \( y \), and amount of reactive ends \( z \). Three populations of linear chains are assumed to be present initially: chains with two non-reactive ends; chains with one reactive end; chains with two reactive ends. Such populations are typical for polymer chains undergoing scission or possessing reactive terminal double bonds. The chain coupling process is then integrated over time until all reactive ends are consumed. The final distribution, being two-dimensional only, as there are no reactive ends in the system, can be well validated by comparison with an MC simulation. The results of our new model are the first of their kind, not only for the studied system, but for three-dimensional PBM problems in general.

2. Random Process on Molecular Topologies and Reaction Mechanism

The polymer modification is represented by a random graph process. In the realm of this framework, the polymer molecules are represented by a collection of connected graphs of functionality at most three, see Figure 1. Some nodes of the graph are labeled with \( r, b \). The label \( b \) is always used for nodes of functionality three. All nodes of functionality two are unlabeled. Nodes of functionality one have either label \( r \) assigned or are left unlabeled, which is determined by the initial conditions. We distinguish topologies by only three parameters:

- \( x \): total amount of nodes (chain length);
- \( y \): total amount of branch points;
- \( z \): total amount of reactive ends.

![Figure 1](image1.png)

If all three properties coincide, then the molecules are treated as essentially the same. Obviously, \( x \), \( y \), and \( z \) are insufficient to fully describe the branched structure, and for full morphological information Monte Carlo based methods should be addressed. On another hand this is the most minimal data that captures reactivity exactly \((x,z)\) and contains information on branches \((y)\). The idea permits to describe the whole system consisting of a huge number of molecules, at time \( t \) by a trivariate distribution. The relative frequency of molecules (connected graph components) with parameters \( x,y,z \) is denoted by

\[
f(x,y,z,t) \in \mathbb{Z}^3 \times C[0, \infty]
\]

This distribution consists of all possible three-element vectors of integer positive numbers that continuously depend on time, \( t \in \mathbb{R}_0^+ \). The reaction mechanism can be described by a simple rule: An \( r \)-labeled node from one connected component obtains a new edge to an unlabeled node of another connected component at rate \( k_p \). Thus, the rule defines an intermolecular reaction that alternatively can be described with a diagram

\[
P_{x,y,z} + P_{x',y',z'} \xrightarrow{k_p y z} P_{x+y, y', z+z'}
\]

Here, the reactivity rate is proportional to the total number of nodes \( x \) and amount of reactive ends \( z \).

In order to perform a simulation we reformulate the reaction mechanism in terms of population balance equations and apply a suitable discretization technique. Three species of linear chains are present initially. Those, without, with one, or two \( r \)-labels, see Figure 1a. This formulation permits to cover a number of different polymer modification systems. In the case when reactive ends are introduced in a form of primary radicals created by a scission process, it is realistic to assume that the chain fragments of the three different classes have different length distributions. In this situation the initial condition as regards the chain populations with different numbers of reactive radical ends is artificial. In reality, scission events yielding reactive ends and coupling events take place throughout the whole reactive modification process. However, since all reacting units of the polymer are present during the whole process, the end result, at full conversion of the reactive ends, yet corresponds to the correct solution. In other words, in this case the assumption, that scission and coupling may be separated in time, is correct. If reactive ends are representing terminal double bonds not introduced by scission, than all three initial distributions will have equal shape (up to a scaling factor), unlike the “scission scenario” where the shape of starting chain length distribution are, no doubts, dependent on number of reactive ends. Then one might assume equal length
distributions. In this case the simulated coupling process more closely resembles the real time evolution. At the end the reactive ends need not wholly be depleted. Note that
this situation is usually in contrast with polymerization processes requiring the simultaneous treatment of scission and branching, leading to high complexity in solving PBM problems.\[11\]

3. Mathematical Model

\[
\frac{\partial f(x, y, z, t)}{\partial t} = \mathcal{L}(f(x, y, z, t))
\]

(3)

subject to the initial conditions

\[
f(x, y, z, t)|_{t=0} = f(x, y, z)
\]

(4)

Here \( \mathcal{L}(f) \) denotes the right-hand side of Equation 3,

\[
\mathcal{L}(f(x, y, z, t)) = k_p \left( T_{0, 1} \sum_{z=0}^{\infty} \left\{ \left( x f(x, y, z, t) + x f(x, y, z - z', t) \right) \right\} \right)
\]

(5)

which in turn is defined employing some custom notations; the operation of convolution (\( \cdot \)), shift operator \( T \), and partial moments \( \mu_{x,y,z} \) are to be explained below. The bilinear operation \( f(x, y, z) \cdot g(x, y, z) \) denotes the convolution over the three discrete variables

\[
f(x, y, z) + g(x, y, z) = \sum_{(x,y,z)=0}^{(x',y',z')} f(x', y', z') f(x - x', y - y', z)
\]

(6)

The role of the operation in Equation 6 is to account for all possible combinatorial possibilities when combining two components, so the conservation of the properties holds,

\[
(x', y', z') + (x - x', y - y', z - z') \rightarrow (x, y, z)
\]

(7)

The conservation law in Equation 7 is valid for the studied reaction mechanism from Equation 2 except for a small difference: exactly one end-point is consumed, \( z - 1 \), and one branch point is produced, \( y + 1 \), with each reaction firing. Therefore, we also need to employ the shift operator \( T_{0, 1} \) in the model of Equation 3,

\[
T_{x, y, z} f(x, y, z) = f(x - x', y - y', z - z')
\]

(8)

to correct for this small difference. In this particular case we set \( z' = 1 \), \( y' = -1 \). Many authors include the shift of

the distribution in the definition of the convolution. In contrast, we consider the two transformations separately in order to point out the similarity to other polymer systems. Thus, we put the current problem in the context of a more general theory for numerical treatment of multidimensional PBM's that was initiated in our previous works This concerned polymer modification resulting from crosslinking and tri-functional additive coupling,\[9\] and polymerization of \( AB_2 \) monomers,\[10\] which problems have been treated using an identical approach.

The operators \( \mu_{x,y,z} \) denote partial moments

\[
\begin{align*}
(\mu_x f(x, y, z))(t) &= \sum_{(x,y)=0}^{(x,y)} x f(x, y, z, t) \\
(\mu_y f(x, y, z))(t) &= \sum_{(x,y)=0}^{(x,y)} y f(x, y, z, t) \\
(\mu_z f(x, y, z))(t) &= \sum_{(x,y)=0}^{(x,y)} z f(x, y, z, t)
\end{align*}
\]

(9)

which are used to express the total amount of monomers \( \mu_x f(x, y, z, t) \), branch points \( \mu_y f(x, y, z, t) \), and reactive ends \( \mu_z f(x, y, z, t) \); this represents essential information when calculating the consumption rate for a particular topology \( (x,y,z) \). In Equation 9, the summation should be performed over two indices \( x, y \) starting from zero vector \( \overrightarrow{0} = (0, 0, 0) \).

Finally, the initial conditions in Equation 4 contain information on three types of linear components, and constitute the chain length distribution for

fragments without end points: \( f(x, 0, 0) \)

fragments with one end point: \( f(x, 0, 1) \)

fragments with two end points: \( f(x, 0, 2) \)

This simple setting allows to implicitly account for the post-scission effect in the model.\[11\] An obvious approach for the numerical treatment of the model in Equation 3 would be the trimming of coordinates \( x, y, z \) to a finite domain and considering a system of dependent ordinary differential equations (ODEs), but this is not of practical interest. Indeed, a huge number of equations would make the computational procedure extremely expensive. As opposed to simulations of the full model of Equation 3, we efficiently parametrize the multidimensional distribution \( f(x, y, z, t) \) with a relatively small number of coefficients. The coefficients are computed rapidly by solving the discretized equation. As can be seen from the numerical experiments presented further in Table 1, the number of approximation coefficients employed represents only 0.0014% of the full set of discrete values of the model.
4. Approximation Scheme

According to the chosen approximation scheme we replace \( f(x,y,z,t) \) by a sum of two-dimensional Gaussian basis functions,

\[
\tilde{f}(x,y,z,t) = \sum_{i=1}^{n} \alpha_{x,i}(t)\phi_i(x,y) \tag{10}
\]

\[
\phi_i(x,y) = e^{-\sigma_x(x-x_i)^2-\sigma_y(y-y_i)^2}, \sigma_z > 0, i = 1, 2, \ldots, n \tag{11}
\]

It is convenient to refer to the expansion coefficients \( \alpha_{x,i}(t) \) as a column vector \( (\alpha_z(t))_i = \alpha_{z,i}(t) \). This allows, e.g., to consider an interpolation matrix

\[
(A)_{ij} = \phi_j(x_i,y_i) \tag{12}
\]

used to obtain coefficients of the distribution that have known values at points \((x_i,y_i,z)\). As we will see further, the parametrization enables replacing the functional differential Equation 3 with a set of ODEs for time-dependent column vectors \( \alpha_z(t) \). The transition from a population balance to a set of ODEs was discussed for a few different cases in refs.\[9,10\].

In this paper we present an approximated form of the population balance Equation 3 and focus on the discrete nature of the problem. Regardless of the preferred time integration scheme the most important question is: what is the discretized form for the right hand side of the nonlinear equation? Although, the original Equation 3 is already discrete, we employ a commonly used term discretization, denoting the reduction of the degrees of freedom to an acceptable from a computational point of view. The original population balance Equation 3 is replaced by an ODE that defines how the vector of expansion coefficients from Equation 10 evolves in time

\[
\frac{\partial \alpha_{z,i}(t)}{\partial t} = \hat{L}(\alpha_{z,i}(t)) \tag{13}
\]

where \( \hat{L} \) is a discretized right-hand side of Equation 3,

\[
\hat{L}(\alpha_z(t)) = k_p (T_{0,1} - 3A^{-1} \gamma_z - \alpha_z \cdot \sum_{z=0}^{2m} (W_x \mu z + z \mu W_x) \alpha_z). \tag{14}
\]

One can see that Equation 14 can be easily derived from formulation of the specific problem in Equation 5. However, the building blocks for Equation 14, \( \mu, W_q(x,y) \), \( T \), \( \gamma_z \) are not problem specific but common for a broad spectrum of polymer problems. Row vectors of weights \( \mu \) are used to express a summation in terms of coefficient columns \( \alpha_z \)

\[
(\mu)_i = \sum_{(x,y) \in S} \phi(x,y) \tag{15}
\]

The matrix \( W_q(x,y) \) is used to obtain expansion coefficients of a distribution with the weight \( q(x,y) \),

\[
W_{q(x,y)} = A^{-1} \text{diag} \{q(x_i,y_i)\} \tag{16}
\]

Primarily, to discretize Equation 5, we adopt \( q(x,y) = x \) to obtain expansion coefficients of the weighted chain-length distribution \( x f(x,y,z) \), or \( q(x,y) = z \) for weighted reactive ends distribution \( z f(x,y,z) \).

The matrix \( T_v \) is used to obtain expansion coefficients of a shifted distribution,

\[
T_v A^{-1} = A^{-1} v, \quad (A_v)_{ij} = \phi(x_{i-v}, y_{i-v}) \tag{17}
\]

The bilinear form \( C_k \) is used to obtain a value of two convoluted distributions at \( k^{th} \) basis function center \( (x_k,y_k) \),

\[
(C_k)_{ij} = \phi(x,y) \cdot \phi(x,y) \mid (x_k,y_k) \tag{18}
\]

Although the components of the summation quadrature in Equation 15 may be computed directly, a considerable speedup in the computation time may be achieved by employing a short analytical equation

\[
(\mu)_i = \frac{\pi}{\sqrt{\sigma_x \sigma_y}} \tag{19}
\]
that reproduces the original values approximately. The fast summation in Equation 19 tends to produce more accurate results as $s_i \rightarrow 0$ and to converge more rapidly to machine precision accuracy, Figure 2. Thus one may consider employing Equation 19 for those basis functions that are broader than a desired threshold.

Now, the multidimensional distribution and the reaction mechanism are expressed in terms of a small number of ODEs to be integrated numerically. There are no limitation on the shape of the initial distribution by design. Similarly to Finite Elements like methods, the present method is quite universal, and can handle arbitrary distributions including those of binomial, multimodal, or rectangular nature. The only limiting factor on the accuracy of the method is amount of basis functions, and it is left for user to specify as a parameter by setting a desired tolerance. Since the polymer modification problems tend not to be stiff, the 13th order Gear’s multistep method was employed for time integration. In view of the high accuracy of this method, the end of the integration was reached in 15 time steps. The full set of method parameters is given in Table 1.

### 5. Simulation Results and Discussion

We present the results of the simulation of a polymer modification process that is initiated with three species of linear chains with $z = 0, 1, 2$ reactive ends. The initial distributions are set by analytical formulas for scission fragments derived by us before\cite{9}:

\[
\begin{align*}
  f(x, 0, 0, 0) & = (1 - \rho_1)x^{-1}p(x) \\
  f(x, 0, 1, 0) & = 2(1 - \rho_1)x^{-1} \sum_{k=x+1}^{\infty} p(k) \\
  f(x, 0, 2, 0) & = \rho_1^2(1 - \rho_1)x^{-1} \sum_{k=x+1}^{\infty} (k - x)p(k)
\end{align*}
\]

![Figure 2](image-url) The error of fast summation formula as a function of grid step.

![Figure 3](image-url) Reactive ends present in the system initially fully convert into branch points as reaction converge.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>zeroth moment $\mu_0$</td>
<td>1</td>
</tr>
<tr>
<td>number-average chain length $\mu_1$</td>
<td>200</td>
</tr>
<tr>
<td>weighted average $\mu_2/\mu_1$</td>
<td>600</td>
</tr>
<tr>
<td>scission probability, $\rho_i$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

![Table 2](image-url) Parameters used to define initial conditions for chain end to backbone branching mechanism.

![Figure 4](image-url) The one-dimensional marginals of the full distribution $f(x, y, z, t)$: (a) the three starting and the final chain length distributions (b) the final chain length distribution as compared to MC data.
which are defined in terms of the scission probability $\rho$. The linear chain length distribution is an artificial one as given by a two-parametric distribution expression based on the three leading moments

$$
p(x) = (1 - \rho)^{1+\alpha}
\left(\frac{x - 1 + \alpha}{x - 1}\right)^{\rho - 1}
$$

$$
\rho = \frac{\mu_0\mu_2 - \mu_1^2 - \mu_1\mu_0 + \mu_2^2}{\mu_0\mu_2 - \mu_1^2}
$$

$$
\alpha = \frac{2\mu_1^2 - \mu_3\mu_0 - \mu_0\mu_2}{\mu_0\mu_2 - \mu_1^2 - \mu_1\mu_0 + \mu_2^2}
$$

(21)

The relation to the moments $\mu_0, \mu_1$ and $\mu_2$ given in Table 2.

The chain end to backbone reaction consumes reactive ends, that are initially present in the system and converts them into branch points, Figure 3. The double weighted plots $x^2f(x, 0, z, 0), z = 0, 1, 2$ of the one-dimensional starting distributions in Equation 20 are shown in Figure 4a. Their representation in the three-dimensional parametric space $x, y, z$ is depicted in Figure 5, $t = 0$.

As time progress, new molecules with a higher number of reactive ends are formed. This results in the evolution of the three-dimensional distribution $f(x, y, z, t)$ into a tube-shaped structure pointing diagonally toward longer chain length $x$ and higher number of branch points $y$, Figure 4a. Note that the three-dimensional distribution never represents an end point as the reaction proceeds as long as there are molecules with a non-zero number of reactive ends. Therefore, eventually the distribution shifts toward a region with lower numbers of reactive ends $z$, up to full convergence into a flat two-dimensional plane $x, y$, as shown in Figure 5. This implies that the end point distribution as depicted in Figure 4 corresponds to molecules with no reactive ends. Although the plane $z = 0$ acts as a two dimensional attractor, in order to reach it from the initial conditions in Equation 20, the integration trajectory has to pass through domains of full three-dimensional distributions. The end point of the distribution, being only two-dimensional, is compared with data from a Monte Carlo simulation, described in more details in ref. [9] A good agreement was found considering $2 \times 10^6$ Monte Carlo generated topologies as depicted in Figure 6 and also in chain length marginal distribution, Figure 4b.

The time profile of the concentration of molecules with different numbers of reactive ends obtained as partial moments of the distribution $f(x, y, z, t)$ clearly illustrates how the process of polymer modification evolves over time. During the whole reaction period the concentration of molecules with $z = 1.2$ is monotonically decreasing contributing either to class $z = 0$ or to $z > 2$. This produces a
rapid increase in the concentration of molecules with a number of reactive ends $z > 2$ at the beginning. Eventually, the contribution to lower classes takes over, and molecules with $z = 0$ significantly dominate in concentration. As time approaches infinity, the reaction leads to the final state: zero concentration of all molecules except those with no reactive ends $z = 0$.

In contrast to the reactive ends dimension, $z$, the number of branches $y$, and chain length $x$ is monotonically increasing with time. The distribution of branches at different time points is depicted in Figure 7. In this double-log plot it can be observed that the branching distribution approaches an algebraic decay with slope $-2.80$ in the limit case. Figure 8 shows that the branching density, defined as the ratio of numbers of branch points to the chain length of a molecule, is not constant for all chain lengths. It can be seen that the branching density of larger molecules is more affected by the reaction. As the reaction approaches full conversion all large molecules tend to gain similar branching.

6. Conclusion

We have presented a mathematical model describing the evolution of distributive properties of molecular topologies induced by a chain end to backbone coupling reaction, representative of a polymer modification process, where simultaneous scission and branching takes place. The model is presented as a population balance equation in three-dimensional parametric space: chain length, branches, reactive ends. Three species of linear chains are considered to be present initially, containing zero, one, and two reactive ends. The novel method developed in our previous work, the approximation on Gaussian basis functions, has opened new horizons in modeling of multidimensional nonlinear population balances. This permits to solve the mathematical model numerically without any additional assumptions or simplifications. We successfully applied the method yielding the full time profile of a three-dimensional distribution leading to full conversion of the all reactive end points. We were able to extract detailed information on microstructural and distributive properties, namely:

- chain length distribution
- branching distribution
- branching density versus chain length
• dynamics for species with different numbers of reactive ends
• two-dimensional distribution for chain length and branches
• three-dimensional distribution for chain length, branches, and reactive ends at different stages of the reaction.

The numerical results were confirmed by Monte Carlo data obtained for $2 \times 10^6$ sample molecules. This result constitutes the first successful full solution to a three-dimensional time dependent PBM in the area of polymer reaction engineering.

The present paper contributes to better understanding of reactive modification processes, for instance that of high-density polyethylene. Although the chain end of backbone reaction takes place with possibly a number of side reactions, it is the most influential one as it is responsible for the branching structure. While the topic of numerically solving even a two-dimensional population balance has remained almost untouched in the literature, we have made a significant step forward by demonstrating the power of our numerical method in the framework of a complex three-dimensional population balance problem. We also expect the numerical techniques to be easily transferable to other multidimensional, non-linear PBM’s arising in polymer reaction engineering.

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