Towards the architectures of macromolecules: Modeling of multi-dimensional polymer chain distributions
Yaghini, N.

Citation for published version (APA):

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Modeling of ldPE molecular weight/branching distributions; topological scission and combination termination

In this chapter, a comprehensive model to predict the Molecular Weight Distribution (MWD), and branching distribution of low-density Polyethylene (ldPE), for free radical polymerization system in a Continuous Stirred Tank Reactor (CSTR) is presented. The model accounts for branching, by branching moment or pseudo-distributions. The common free radical polymerization reactions including chain scission have been considered in the model. Non-linear or the so-called topological scission has been modeled using approximate Fragment Length Distribution (FLD) derived from scission, applied to branching topologies. To model the distributions, the Galerkin-Finite Element Method (FEM) based on the same principles as PREDICI® has been applied and implemented in MATLAB©. The fundamental numerical problem arising from topological scission has been solved. Thus, the model provides more accurate results, allowing a precise comparison to earlier results and to Monte Carlo simulations.

2.1 Introduction

Properties such as rheological behavior, radius of gyration and morphology (Smagala and McCoy, 2006) strongly affect the quality of the final product and are closely related to microstructural properties as molecular weight distribution. According to Kim et al. (2004), and Kim and Iedema (2004), ldPE molecular weight distribution is strongly dependent on scission mechanism, being linear or topological. In addition, rheology and contraction factor are affected by branching architectures as well, and thus important for characterization besides weight distribution.

Studies on scission mechanism started around 2000 (Iedema et al. 2000), and progressed to the introduction and early implementations of the so-called “topological scission” (Iedema and Hoeofsloot, 2004a). The latter defined the topological scission by the FLD function, obtained from branched ldPE structures and from Monte Carlo simulations. FLD was defined to account for real random scission and was based on the idea that scission fragments of branched molecules could be only extremely long or remarkably short. However, assuming topological scission led to a paradoxical situation (Kim et al. 2004; Kim and Iedema, 2008), which the well-known shoulder experimentally observed in autoclave CSTR for ldPE (Tackx and Tacx, 1998) disappeared.

The focus of this chapter is on modeling MWD to be compared directly to the results from Size Exclusion Chromatography-Multi Angle Laser Light Scattering (SEC-
MALLS) and Monte Carlo (MC) simulations. The former deterministic studies of ldPE molecular weight distribution were mostly implemented in the software package PREDICI®, which all generated a series of serious modeling problems, since the implementation of the FLD for topological scission did not comply with the standard methods in the software and resulted in grid refinement problems.

Here, the same method as PREDICI® (Galerkin-FEM) is applied. The method is a finite element method used by Wulkow (2008) to solve polymerization Population Balance Equations (PBEs), and is especially preferred for polymerization reactions with chain-length-dependent rate coefficients such as scission and transfer to polymer. We apply the method of moments - the “pseudo-distributions” method - as reported in Kim et al. (2004) to reduce the dimensions of a 2-Dimensional (2D) problem into a 1-Dimensional (1D) one in order to fit it to the 1D Galerkin framework. The model accounts precisely for topological scission of ldPE chains. The obtained MWD are compared to the results of the earlier studies by PREDICI® and also for the first time to the results of MC simulations by Tobita (2001b).

2.2 Reaction equations

The polymerization of Ethylene starts with the decomposition of initiators at high temperature and high pressure (Kim et al., 2004):

initiation

\[ I_2 \rightarrow 2I^*, k_d, \]  
\[ I^* + M \rightarrow R_i, k_f, \]

where \( f \) is the initiator efficiency and assumed to be 0.7 (Busch, 2001a, 2001b).

The following relevant reaction steps are expressed in two dimensions: chain length (synonym to number of monomeric units), \( n \), and branching, \( i \):

propagation

\[ R_{nj} + M \rightarrow R_{n+i,j}, k_p, \]  

transfer to polymer

\[ P_{nj} + R_{mj} \rightarrow_{nk} P_{nj} + P_{m,j+1} \]

random scission

\[ R_{nj} + P_{r,j} \rightarrow_{nk} P_{nj} + R_{r-s,j-k-1} + P_{s,k} \]

termination by disproportionation

\[ R_{nj} + R_{r,j} \rightarrow_{k_t} P_{nj} + P_{r,j} \]

termination by combination

\[ R_{nj} + R_{r,j} \rightarrow_{k_c} P_{n+r+j, j} \]

transfer to chain transfer agent (Chain Transfer Agent (CTA))

\[ R_{nj} + S \rightarrow_{k} P_{nj} + R_{1j} \]

and transfer to monomer

\[ R_{nj} + M \rightarrow_{k} P_{nj} + R_{1j} \]

Here, \( I, M, S, R \) and \( P \) stand for initiator, monomer, chain transfer agent, living polymer chain and dead polymer chain concentrations, respectively. Terminal double bond
propagation and backbiting are not considered. To date most kinetic studies do not attribute a significant role to the former mechanism. The latter mechanism is very important indeed, leading to strong short chain branching, but this does not affect the chain length and long chain branching distributions.

2.3 Linear scission versus topological scission

Nowadays, random scission is generally accepted in ldPE modeling. With random scission, it is assumed that any C−C bond in any polymer molecule has the same probability to get broken. This assumption is as well valid for the stochastic models by Tobita (2001a, 2001b, 2014) that make use of linear ‘primary polymers’ as the building blocks of the polymer molecules. In these models the problem is treated in a straightforward manner, since the scission probability of a primary polymer only depends on its length. The probability of breaking any C−C bond in a chain with length \( n \) is exactly equal to \( \frac{n-1}{1} \) times the scission probability per bond. In addition, for a linear segment to be broken from a chain with length \( n \), the probability to get a fragment of certain size \( <n \) is a uniform distribution, \( \frac{1}{n-1} \), and hence independent of fragment length. For example, for a molecule with 1000 monomeric units, the probability of getting two fragments with 200 and 800 monomers would be \( \frac{1}{999} \).

The uniform distribution holds for linear structures, but for branched structures the reality is more complicated. In stochastic polymer processing and polymerization studies of branched systems, the scission essentially occurs to the bonds in linear primary polymers of which the branched architectures are built. In this type of models, scission process influences the size and the architecture of the resulting molecules locally, but the size and the architecture of the resulting molecules do not, reversely, affect the scission process. In contrast, in the population balance model no explicit information on primary polymer lengths is available. Instead, only the complete size \( s \) and, if branching is included, the total number of branch points of the molecules is accessible. Furthermore, in contrast to linear chains, it was observed (Iedema and Hoefsloot, 2001a, 2001b) that fragment sizes resulting from random scission of a branched polymer do depend on branching and branching architecture. Fragments have been found to be extremely long or notably short (Guidici and Hamielec, 1996; Iedema and Hoefsloot, 2001b). This is a direct consequence of scission statistics for branched structures (Kim et al., 2004). From Monte Carlo simulations of breaking architectures based on transfer to polymer as the branching mechanism (Iedema and Hoefsloot, 2001a), it was found that the fragment length distribution could be approximated by:

\[
f(n,m) = \frac{1}{\left(2\bar{s}(n) + m\right)^2} + \frac{1}{\left(2\bar{s}(n) + n - m\right)^2},
\]

\[
\frac{1}{\bar{s}^2} = \frac{1}{\frac{1}{2}n + \bar{s}} - \frac{1}{\left(2\bar{s}(n) + n\right)^2} + \frac{1}{\left(2\bar{s}(n)\right)^2}
\]

\( n \) is defined as the length of the initial polymer chain before scission reaction would take place and \( m \) is the scission fragment accordingly, while \( \bar{s} \) is the average length between two branch points or segment length after scission. Note that Equation 2.9 slightly differs from the fragment length expression in Kim and Iedema (2008). From the normalization factor in the denominator the term between brackets is subtracted accounting for the fact that the
minimum scission fragment size is 1 unit smaller than the original chain length instead of
equal to it. It was concluded that applying the FLD of the presented shape and parameters in
deterministic MWD modeling would give good agreement with molecular weight
distributions obtained with a stochastic approach (Tobita, 2001b).

In addition to the issue of the fragment size distribution, one has to answer the
question of the redistribution of branch points on scission fragments. Hutchinson (2001),
proposed a hypergeometric distribution for \( \beta(n,m,i,j) \):

\[
\beta(n,m,i,j) = \frac{{\binom{n-i}{j} \binom{m-j}{m-n}}}{\binom{n}{m}},
\]

(2.10)

This discussion on the FLD completes the description of the set of population balance
equations, which should be solved to calculate the polymer weight distributions for the free
radical polymerization system. In the next section, the Galerkin-FEM method will be
presented as a very efficient computational method to solve the population balance
equations of polymer reactions (Wulkow and Deufhard, 1990) – also used in PREDICI®.

2.4 Population balance equations

The population balance equations of free radical polymerization problem are derived using
the reaction equations. A complete set of PBEs denotes the time–dependent concentration
variations for all existing species in the polymerization system. The following PBEs set is
derived for the free radical polymerization system of ldPE, as described by the reaction
equations in the previous section. Equations 2.11-2.16 indicate the population balances of
low molecular weight species. Equations 2.17 and 2.18 are the 2-dimensional population
balances (chain length and branching) for living chains and dead chains.

\[
\frac{dI_2}{dt} = -k_d I_2 + \frac{1}{\tau}(I_{20} - I_2),
\]

(2.11)

\[
\frac{dI^*}{dt} = 2k_d I_2 - k_f M I^* - \frac{1}{\tau} I^*,
\]

(2.12)

\[
\frac{dM}{dt} = -k_f M I^* - (k_p + k_m) M \lambda_0 + \frac{1}{\tau}(M_m - M),
\]

(2.13)

\[
\frac{dR}{dt} = k_f M I^* - k_p MR_1 - k_d R_1 \lambda_0 + k_n R_1 \lambda_0 - \frac{1}{\tau} R_1,
\]

(2.14)

\[
\frac{dS}{dt} = -k_s \lambda_0 S + \frac{1}{\tau}(S_{wa} - S),
\]

(2.15)

\[
\frac{d(LCB)}{dt} = k_{mp} \lambda_0 \mu_1,
\]

(2.16)

\[
\frac{dP_{n,i}}{dt} = k_d \lambda_0 R_{n,i} + \frac{1}{2} k_{m} \sum_{m=1}^{n-1} \sum_{j=0}^{i} R_{m,j} R_{n-m,j-i} + (k_{wp} + k_n) \left( \mu_1 R_{n,i} - n \lambda_0 P_{n,i} \right)
\]

\[
\quad + \left( k_m M + k_s S \right) \mu_1 R_{n,i} + k_x \lambda_0 \sum_{j=1}^{\infty} \sum_{i=1}^{\infty} f(m,n) \beta(m,n,j,i) m P_{m,j} - \frac{1}{\tau} P_{n,i},
\]

(2.17)
\[
\frac{dR_{n,i}}{dt} = k_p M \left( R_{n-1,i} - R_{n,i} \right) - (k_{id} + k_{i}) R_{n,i} \lambda_0 R_{n,i} + k_{ip} R_{n,i} \left( -\mu_i R_{n,i} + n \lambda_0 P_{i,n,i+1} \right) \\
- \left( k_m M + k_s S \right) \mu_i R_{n,i} - k_s \mu_i R_{n,i} \\
+ k_{rs} \lambda_0 \sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(m,n) \beta(m,n,j,i) m P_{m,j} \\
+ \{ [k_m M + k_s \lambda_0 S] \lambda_0 + k_s M I \} \delta(n-1) \delta(i-1) - \frac{1}{\bar{\tau}} R_{n,i},
\]

(2.18)

Here, \( P_{n,i} \) and \( R_{n,i} \) are the concentrations for a dead chain and a living chain with chain length equal to \( n \) and number of branch points equal to \( i \). \( \lambda_k \) and \( \mu_k \) are the \( k^{th} \) moments of living chains and dead chains distributions and are defined as \( \lambda_k = \sum_{n=0}^{\infty} n^k R_n \) and \( \mu_k = \sum_{n=0}^{\infty} n^k P_n \), respectively. The scission functions \( f(n,m) \) and \( \beta(n,m,i,j) \) represent, correspondingly, the aforementioned fragment length distribution and the distribution of branch points, \( j \), on fragments of length \( m \) from scission of chains of length \( n \) having \( i \) branch points. \( \bar{\tau} \) is the average residence time in the reactor and is defined as the volume of the reactor over the volume flow in and out of the reactor. Obviously, in a CSTR at steady state the Left-Hand Side (LHS) equals zero. As will be explained later, if the Right-Hand Side (RHS) is linear, in principle Equations 2.17 and 2.18 could be solved as a linear set.

As in previous work (Iedema et al., 2000; Kim et al., 2004; Kim and Iedema, 2008) a 2D problem has been reduced to a 1D problem by taking the moments over the branching distribution. For the first time, a grid refinement as required by the narrow shape of the fragment length distribution function in order to model the topological scission in a precise manner has been applied. The \( \theta^{th} \) moment results into equations expressed in the usual living and dead chain distributions, \( R_n \) and \( P_n \), while higher moments lead to equations in ‘pseudo-distributions’. They are defined as:

\[
P_n = \sum_{i=0}^{\infty} P_{n,i},
\]

(2.19)

\[
R_n = \sum_{i=0}^{\infty} R_{n,i},
\]

(2.20)

\[
\Psi^n = \sum_{i=0}^{\infty} \lambda^n P_{n,i},
\]

(2.21)

\[
\Phi^n = \sum_{i=0}^{\infty} i^n R_{n,i},
\]

(2.22)

The set of population balance equations for \( R_n \) and \( P_n \) thus would be:

\[
\frac{dR_n}{dt} = k_p M (R_{n-1} - R_n) - (k_{id} + k_{i}) R_n \lambda_0 R_n + k_{ip} R_n \left( -\mu_i R_n + n \lambda_0 P_{n,i+1} \right) \\
- \left( k_m M + k_s S \right) \mu_i R_n - k_s \mu_i R_n \\
+ k_{rs} \lambda_0 \sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(m,n) \beta(m,n,j,i) m P_{m,j} \\
+ \{ [k_m M + k_s \lambda_0 S] \lambda_0 + k_s M I \} \delta(n-1) \delta(i-1) - \frac{1}{\bar{\tau}} R_n,
\]

(2.23)
\[
\frac{dP_n}{dt} = k_d R_n \lambda_n - (k_{ip} + k_{rs}) \lambda_n P_n + (k_{ip} + k_{rs}) \mu_n R_n - \frac{1}{\tau} P_n + \frac{1}{2} k_c \sum_{m=1}^{n-1} R_m R_{n-m} + k_s \lambda_0 \sum_{m=n+1}^{\infty} mf(m,n)P_m + (k_m M + k_s S)R_n,
\]

The general form of the pseudo-distribution equations in the \(N\)th moment would be:

\[
\frac{d\Phi^N_n}{dt} = k_p M(\Phi^N_n - \Phi^N_n) - (k_m M + k_s S)\Phi^N_n - k_d \lambda_n \Phi^N_n - k_c \lambda_0 \Phi^N_n - k_s \mu_n \Phi^N_n + k_{tp} (n\lambda_0 \sum_{j=0}^{\infty} P_{n,j-1} - \mu_1 \Phi^N_n)
\]

\[
+k_{rs} \sum_{i=0}^{n-1} \sum_{j=1}^{\infty} \sum_{m=n+1}^{\infty} f(n,m)\beta(n,m,i,j)mP_{m,j} - \frac{1}{\tau} \Phi^N_n = 0,
\]

and

\[
\frac{d\Psi^N_n}{dt} = (k_m M + k_s S)\Phi^N_n + k_d \lambda_n \Phi^N_n + \frac{1}{2} k_c \sum_{i=0}^{n-1} \sum_{j=0}^{i} R_{m,j} R_{n-m,j-i} + (k_{tp} + k_{rs})(\mu_1 \Phi^N_n - n\lambda_0 \Psi^N_n)
\]

\[
+k_{rs} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(n,m)\beta(n,m,i,j)mP_{m,j} - \frac{1}{\tau} \Phi^N_n = 0,
\]

In Iedema et al. (2000) the combination terms were identified as:

\[
\sum_{j=0}^{\infty} \sum_{m=1}^{n-1} \sum_{j=0}^{i} R_{m,j} R_{n-m,j-i} = 2\sum_{m=1}^{n-1} \Phi^i_m R_{n-m},
\]

\[
\sum_{j=0}^{\infty} \sum_{m=1}^{n-1} \sum_{j=0}^{i} R_{m,j} R_{n-m,j-i} = \sum_{m=1}^{n-1} (\Phi^2_m R_{n-m} + \Phi^i_m \Phi^i_m)
\]

In Kim et al. (2008) the pseudo-distribution terms for the first and second branching moments, based on the hypergeometric function are derived as:

\[
\sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(n,m)h(n,m,i,j)mP_{m,j} = \sum_{m=n+1}^{\infty} f(n,m)n\Psi^i_m,
\]

\[
\sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(n,m)h(n,m,i,j)mP_{m,j} = \sum_{n=m+1}^{\infty} f(n,m)\frac{1}{m-1}\left\{n(n-1)\Psi^2_m + n(m-n)\Psi^i_m\right\},
\]
2.5 MWD modeling and the Galerkin method

Various research works address MWD calculations for LDPE: (Buback et al., 1996; Pladis and Kiparissides, 1998; Iedema et al., 1998; Tobita, 2001a, 2001b; Kim et al., 2004; Stickel and Griggs, 2012). Kim et al., 2004, lists a few of the mostly used methods: method of moments, continuous variable approximation, Monte Carlo simulation, numerical fractionation techniques, finite differences and finite element methods. Different ranges of authors have addressed scission in the polymer context. As early as 1940, Montroll and Simha derived an analytical solution for random scission of polymer chains with a monodisperse distribution by a statistical argument. Ziff and McGrady (1985, 1986) were able to develop analytical expressions for various scission processes, random or non-random, using the similarity approach to solve a set of population balance equations. Tobita (1992) introduced a Monte Carlo sampling method to deal with chain length and branching distribution, changing by simultaneous degradation and branching of a given polymer. In 2004, Bos and Git proposed a Monte Carlo algorithm, simulating the change of a chain length distribution over time due to various scission mechanisms. Tobita in 2010 has reviewed the analytical expressions found by Ziff and McGrady and applied them to polydisperse starting-length distributions and compared the results to a numerical scheme to solve the population balances for different scission mechanisms.

In this section, the numerical aspects of the model applied to this problem are discussed. An introduction to the Galerkin method is given. It is shown how the primary set of population balance equations could be rewritten in a system of linear equations with a ‘block structure’. Then the numerical issues concerning the implementation of the fragment length distribution and the required grid refinement are presented. Further, it is discussed how the combination termination mechanism introduces a non-linear element in the PBEs, which leads to a stiff ode-problem. Finally, it is shown how the pseudo-distribution equations are placed in the block structure of the set of equations.

2.5.1 Description of the Galerkin method

According to Wulkow (2008), we represent the concentrations distribution $P_s$ at chain length intervals $M$ with chain length nodes $s$, running from a lower limit of chain length $L_M$ to an upper limit $U_M$ (Figure 2.1). When addressing LDPE, all intervals together should cover an appropriate domain of chain lengths, typically from $1$ to $10^7$. At each interval $M$, the concentration of a polymer chain at chain length node $s$ is approximated by a combination of discrete Chebyshev polynomials denoted by $T_k^M(s)$:

$$P(s) = \sum_{k=0}^{r_M} a_k^M T_k^M(s)$$  \hspace{1cm} (2.31)

Here, $r_M$ shows the order of Chebyshev polynomial. A Chebyshev polynomial of order $r_M \geq 0$ is defined as (Gil et al., 2007):
\[ T_0^M(s) = 1 \]
\[ T_1^M(s) = \frac{2}{d_m} \left\{ s - L_M - \frac{1}{2}(d_M - 1) \right\} \quad d_M = U_M - L_M + 1 \]
\[ T_{k+1}^M(s) = \frac{2k+1}{k+1} T_k^M(s) T_1^M(s) \quad k = 0 : r_M \]

For a known distribution \( P(s) \), the values of the coefficients \( a_k^M \) are obtained by computing the \( P \)-values at the nodes \( s \) at interval \( M \). Calculating the \( P(s) \) and applying the relationship is based on the orthonormality of the polynomials for each coefficient:

\[ a_k^M = \frac{1}{\gamma_k^M} \sum_s P(s)w_M(s)T_k^M(s) \quad k = 0 : r_M \] (2.33)

The summation is taken over all the nodes, \( s \), on the interval \( M \). The normalization factor \( \gamma_k^M \) is directly associated to the orthonormality condition of the discrete Chebyshev polynomials (again with the summation over all nodes \( s \)):

\[ \left\langle T_k^M, T_l^M \right\rangle = \frac{1}{\gamma_k^M} \sum_s T_k^M(s)T_l^M(s) = \gamma_k^M \delta_{k,l} \] (2.34)

The term \( w_M(s) \) is the weight belonging to node \( s \) on interval \( M \). The system of nodes for an arbitrary interval \( M \) is illustrated in Figure 2.1. The values of the nodes may be calculated from the roots of the Chebyshev polynomial \( T_{n+1} \), or using standard algorithms (Deuflhardt and Hohmann, 2003). Note that the lower and upper interval edges, \( L_M \) and \( U_M \), are integer numbers, however, the nodes \( s \) are not necessarily so. An example of a series of 200 nodes and weights covering a chain length axis between 1 and \( 10^7 \) is given in Figure 2.2.

Further convenient properties of the Galerkin approach are that they allow fast evaluations of moments. The zeroth moment of living chains, \( \lambda_0 \), and the first moment of dead chains, \( \mu_1 \), follow as:

\[ \lambda_0 = \sum_I \sum_s w_M(s)R(s) \quad I = 1 : M, \quad s = 1 : N \] (2.35)
\[ \mu_1 = \sum_I \sum_s w_M(s)sR(s) \quad I = 1 : M, \quad s = 1 : N \] (2.36)

Thus, we see that the contributions to these moments per interval \( I \) are simply the weighted sum of the concentrations at the nodes \( s \), eventually multiplied by the node value.
2.5.2 Mathematical modeling of ldPE molecular weight distribution with Galerkin-FEM

The idea of defining the specific number of nodes per each interval is essential to reduce the number of total required calculations. Accordingly, instead of accounting for all chain lengths of the chain length domain, only the selected nodes are considered. Indeed, the nodes are the chain length values that the exact concentrations are calculated for. Obviously, the molecular weight distribution could be estimated at any chain length \( n \) by interpolation and using Equation 2.31 for \( P(n) \).

The main task now is calculating the concentrations of polymer chains at the previously defined nodes. The procedure starts with the population balances and use of Equation 2.31 to substitute all the concentrations by the Chebyshev series expansion. There are two different groups of equations to be solved: those describing dead chains (Equation 2.24) and the ones for the living chains (Equation 2.23), to be called ‘P-equations’ and ‘R-equations’, hereafter. Thus, all \( P_n \) and \( R_n \) terms in the PBEs set could be replaced by combinations of the Chebyshev polynomials and \( a_k^M \) coefficients (the unknowns system).

The transformed equations in matrix form constitute a new set of equations with one unknown column of \( a_k^M \) coefficients to be found. In Tables 2.1a-2.1c it is shown that the transformation of the PBEs in a number of steps. Table 2.1.a gives the nodes, \( s_j \), of an interval with the associated weights, \( w_j \), and PBEs for dead chains at each node. On this interval there are \( N \) nodes, the maximum order of the polynomials is \( r \); note that \( N = r + 1 \), while the nodes, \( j \), range from 1: \( N \), and the order, \( k \), from 0: \( r \). Table 2.1.b shows the result after insertion of the Chebyshev polynomial.
approximations into the population balance equations with the unknown coefficient $a_k^{n}$ for dead chains and $a_k^{n}$ for living chains (note that the upper index $M$, has been dropped for interval, and replaced by $R$ and $P$). Finally, Table 2.1.c shows the PBEs from Table 2.1.b after Gauss quadrature. These are obtained by multiplying all left and right-hand side elements of the PBEs in Table 2.1.b at lines 1 through $n$ with $w_{1}T_{0}(s_{1})$ through $w_{n}T_{n}(s_{n})$ and summing them up, yielding the first equation. Subsequently, they are multiplied with $w_{n}T_{n}(s_{n})$ through $w_{n}T_{n}(s_{n})$, etc., which results in the 2nd equation, and so on until reaching to $N$ new equations, which are shown in Table 2.1.c.

<table>
<thead>
<tr>
<th>node</th>
<th>weight</th>
<th>$N$ (or $r+1$) original PB equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_1$</td>
<td>$w_1$</td>
<td>$\frac{dP(s_1)}{dt} = f (P(s_1), R(s_1))$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$w_2$</td>
<td>$\frac{dP(s_2)}{dt} = f (P(s_2), R(s_2))$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$s_N$</td>
<td>$w_N$</td>
<td>$\frac{dP(s_N)}{dt} = f (R(s_N), P(s_N))$</td>
</tr>
</tbody>
</table>

Table 2.1a. Nodes, weights and original PBEs for dead chains $P$, at one interval; order is $r$ and number of nodes is $N = r+1$. A similar system describes living chains, $R$.

<table>
<thead>
<tr>
<th>node</th>
<th>weight</th>
<th>$N$ (or $r+1$) PB equations in Chebyshev polynomial terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_1$</td>
<td>$w_1$</td>
<td>$T_0(s_1) \frac{da_0^P}{dt} + T_1(s_1) \frac{da_1^P}{dt} + ... + T_n(s_1) \frac{da_n^P}{dt} = a_0^P f^P(T_0(s_1)) + ... + a_n^P f^P(T_n(s_1)) + b_1$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$w_2$</td>
<td>$T_0(s_2) \frac{da_0^P}{dt} + T_1(s_2) \frac{da_1^P}{dt} + ... + T_n(s_2) \frac{da_n^P}{dt} = a_0^P f^P(T_0(s_2)) + ... + a_n^P f^P(T_n(s_2)) + b_2$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$s_N$</td>
<td>$w_N$</td>
<td>$T_0(s_N) \frac{da_0^P}{dt} + T_1(s_N) \frac{da_1^P}{dt} + ... + T_n(s_N) \frac{da_n^P}{dt} = a_0^P f^P(T_0(s_N)) + ... + a_n^P f^P(T_n(s_N)) + b_N$</td>
</tr>
</tbody>
</table>

Table 2.1b. Result after substitution of $P(j)$ and $R(j)$ by Chebyshev polynomials. Coefficients $a_k^P$ denote the $k$th order coefficient for the $P$-distribution, $a_k^R$ for the $R$-distribution.

<table>
<thead>
<tr>
<th>$N$ (or $r+1$) PB equations after Gauss quadrature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_0 \frac{da_0^P}{dt} = a_0^P A_0^P + a_1^P A_1^P + ... + a_n^P A_n^P + a_0^R A_0^R + a_1^R A_1^R + ... + a_n^R A_n^R + b_0$</td>
</tr>
<tr>
<td>$\gamma_1 \frac{da_1^P}{dt} = a_0^P A_0^P + a_1^P A_1^P + ... + a_n^P A_n^P + a_0^R A_0^R + a_1^R A_1^R + ... + a_n^R A_n^R + b_1$</td>
</tr>
<tr>
<td>...</td>
</tr>
<tr>
<td>$\gamma_r \frac{da_r^P}{dt} = a_0^P A_0^P + a_1^P A_1^P + ... + a_n^P A_n^P + a_0^R A_0^R + a_1^R A_1^R + ... + a_n^R A_n^R + b_r$</td>
</tr>
</tbody>
</table>

Table 2.1c. PBEs in Table 2.1b after applying the Gauss quadrature.
An illustration of the generalized procedure is shown in Tables 2.1a through 2.1c for the contribution of the propagation terms to the population balance. The propagation contribution is written using the \(+ =\) sign, as:

\[
\frac{dR_n}{dt} = k_p M (R_{n+1} - R_n)
\]  \(2.37\)

The corresponding equations for the \(N\) nodes of interval \(M\) are listed in Table 2.2a. Note that these RHS terms only contain concentrations of living chains, no dead chains. Furthermore, no \(b\)-terms would arise from propagation. By replacing the living chain concentrations, \(R(s_j)\), by the Chebyshev polynomials Table 2.2b is obtained. Gauss quadrature finally yields the \(r+1\) linear equations for the present interval as shown in Table 2.2c. All RHS terms contain Chebyshev polynomial terms in front of each coefficient \(a_i^2\), while only the diagonal elements contain the normalization factor \(\gamma_s\) as well. The latter originates from the \(-k_p MR(s_j)\) term in the population balances. Similarly, all terms in the population balances containing \(R(s_j)\) such as disproportionation termination and transfer to monomer lead to diagonal elements in the \(A\)-matrix (\(N\) for each interval), due to the orthogonality property. In contrast, the terms arising from \(-k_p MR(s_j-1)\) lead to a full \(N \times N\) block in the \(A\)-matrix for each interval.

<table>
<thead>
<tr>
<th>node</th>
<th>weight</th>
<th>(N) (or (r+1)) original PB equations for propagation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s_1)</td>
<td>(w_1)</td>
<td>(\frac{dR(s_1)}{dt} = k_p M { R(s_1-1) - R(s_1) } )</td>
</tr>
<tr>
<td>(s_2)</td>
<td>(w_2)</td>
<td>(\frac{dR(s_2)}{dt} = k_p M { R(s_2-1) - R(s_2) } )</td>
</tr>
<tr>
<td>(\ldots)</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>(s_N)</td>
<td>(w_N)</td>
<td>(\frac{dR(s_N)}{dt} = k_p M { R(s_N-1) - R(s_N) } )</td>
</tr>
</tbody>
</table>

Table 2.2a. Original propagation terms for each node.

<table>
<thead>
<tr>
<th>node</th>
<th>weight</th>
<th>(N) (or (r+1)) propagation equations in Chebyshev polynomial terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s_1)</td>
<td>(w_1)</td>
<td>(T_0(s_1) \frac{da_1^0}{dt} + T_1(s_1) \frac{da_1^1}{dt} + \ldots + T_r(s_1) \frac{da_1^r}{dt} )</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td>(= k_p M { T_0(s_1-1) - T_0(s_1) } a_1^0 + \ldots + k_p M { T_r(s_1-1) - T_r(s_1) } a_1^r )</td>
</tr>
<tr>
<td>(s_2)</td>
<td>(w_2)</td>
<td>(T_0(s_2) \frac{da_1^0}{dt} + T_1(s_2) \frac{da_2^1}{dt} + \ldots + T_r(s_2) \frac{da_2^r}{dt} )</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td>(= k_p M { T_0(s_2-1) - T_0(s_2) } a_2^0 + \ldots + k_p M { T_r(s_2-1) - T_r(s_2) } a_2^r )</td>
</tr>
<tr>
<td>(\ldots)</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>(s_N)</td>
<td>(w_N)</td>
<td>(T_0(s_N) \frac{da_1^0}{dt} + T_1(s_N) \frac{da_N^1}{dt} + \ldots + T_r(s_N) \frac{da_N^r}{dt} )</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td>(= k_p M { T_0(s_N-1) - T_0(s_N) } a_N^0 + \ldots + k_p M { T_r(s_N-1) - T_r(s_N) } a_N^r )</td>
</tr>
</tbody>
</table>

Table 2.2b. Result of propagation equations after substitution of \(R(j)\) by Chebyshev polynomials.
N(or r+1) propagation equations after Gauss quadrature

\[
\gamma_0 \frac{da_0^k}{dt} = k_p M \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j-1) \right] a_0^k + k_p M \left[ \sum_{j=1}^{N} w_j T_1(s_j) T_0(s_j-1) \right] a_0^k + \ldots + k_p M \left[ \sum_{j=1}^{N} w_j T_l(s_j) T_0(s_j-1) \right] a_0^k
\]

\[
\gamma_1 \frac{da_1^k}{dt} = k_p M \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j-1) \right] a_1^k + k_p M \left[ \sum_{j=1}^{N} w_j T_1(s_j) T_0(s_j-1) \right] a_1^k + \ldots + k_p M \left[ \sum_{j=1}^{N} w_j T_l(s_j) T_0(s_j-1) \right] a_1^k
\]

\[
\gamma_r \frac{da_r^k}{dt} = k_p M \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j-1) \right] a_r^k + k_p M \left[ \sum_{j=1}^{N} w_j T_1(s_j) T_0(s_j-1) \right] a_r^k + \ldots + k_p M \left[ \sum_{j=1}^{N} w_j T_l(s_j) T_0(s_j-1) \right] a_r^k
\]

Table 2.2c. Result of propagation terms after Gauss quadrature. The factors in front of the coefficients \(a_0^k\) finally appear in the \(A\)-matrix.

The final resulting PBEs set in a big matrix \(A\) is illustrated schematically in Figure 2.3. The elements of matrix \(A\) are the multiplication factors with coefficients as shown in Table 2.1c. Here, \(A_{ij}^{RP}\) denotes the element of a sub-matrix \(A'\) for the \(R\)-equations, which is obtained for the interval considered, after multiplication with \(k^a\) order Chebyshev polynomials (according to the Gauss quadrature), it appears on the \(k^a\) line of \(A'\). As well as, element \(A_{ij}^{PP}\) after being multiplied with coefficient \(a^k\) appears in the \(i^a\) column of \(A'\). The superscript \(RP\) indicates that it originates from a living chain, hence the \(R\)-term in the population balance equations from dead chains \(P\). In Figure 2.3 sub-matrix \(A'\) is shown as the block ‘\(R_i \rightarrow P_i\)’ for the first interval. Likewise, \(A_{ij}^{PP}\) as an element of \(A''\) for dead chains originates from a \(P\)-term in the \(P\)-balance equations; in Figure 2.3 it appears as the block ‘\(P_i \leftarrow \)’, which is positioned on the same lines as the ‘\(R_i \rightarrow P_i\)’ block and at columns to the right.

Hence, in matrix notation the multiplication of the \(A\) elements with the coefficients is performed as the matrix multiplication of matrix \(A\) with coefficient column \(a\) with the (top-down) sequence (see Table 2.1c): \(a_0^k, a_1^k, \ldots, a_r^k\). Finally, the elements \(h_0\) through \(h_r\), being known values originating from PBEs terms not containing living or dead chain concentrations, appear in a column vector \(b\) at RHS. Note that, if the system of equations for a CSTR is solved as a linear set, the time difference terms at LHS in Table 2.1c are set to zero.

Thus, the set consists of a big block matrix \(A\), and a column of unknown coefficients \(a\) at the left-hand side, and a known column in the right-hand side. Each sub-block in the block matrix has a specific type of contribution to the PBEs set, and thus to the final distribution. There are distinct sub-blocks for the contribution of \(P\)-terms to the \(R\)-equations and vice versa, also sub-blocks for the contribution of \(R\)-terms to the \(R\)-equations, and sub-blocks for the contribution of \(P\)-terms to the \(P\)-equations. Scission
terms are shown separately in the right half of the big block matrix. The solution for this system of PBEs as a linear set directly results into the polymer chains concentrations.

![Population balance equation in a matrix form with the associated sub-blocks.](image)

**Figure 2.3.** Population balance equation in a matrix form with the associated sub-blocks.

### 2.5.3 Implementation of topological scission using fragment length distribution; FLD

Introducing the FLD according to Equation 2.9 with a proper value for the average segment length, in the order of 100, gives rise to a numerical difficulty. This originates from the steep gradient of the FLD, which is not captured by the normal grid. This grid problem has already been discussed in Kim and Iedema (2008). Previously, the problem is only partially dealt with in the PREDICI context, by replacing the standard scission step by a standard depropagation step. But some of the distributions obtained still featured spikes and other irregularities. Here, a grid refinement technique that solves the problem entirely is presented.

Note that the problem arises from the scission terms in Equation 2.23 and Equation 2.24. These terms refer to the contributions to the population balances of living and dead chains of length \( m \) from scission of chains with evidently larger lengths, \( n > m \). Figure 2.4 illustrates the problem for 6 fragment lengths, \( m \) (from 1 to \( 10^3 \)), for varying chain lengths, \( n \), starting at \( m + 1 \). One observes that the fractional distribution according to Equation 2.9 for varying fragment length \( m \) given the chain length \( n \) now from the different perspective of a given fragment length \( m \) and varying \( n \) turns into a multiplication factor with values both lower and higher than 1. For long fragments the function is descending rapidly, which requires grid refinement. Note also, for short fragment lengths, there is a large multiplication factor for contributions from large molecules – up to \( 10^4 \).
Figure 2.4. The fragment length distribution (Equation 2.9) from the perspective of a given fragment length, \( m \), as a function of chain length, \( n \geq m \); for \( \delta \) different fragment lengths, \( m \) (from 1 to 10). The multiplication factor has values both lower and higher than 1. The factor decreases sharply for long fragments. The factor has high values for contributions from long chains to short fragments, up to \( 10^6 \).

A gridding problem would arise here if we keep the original grid nodes and then apply the Galerkin method; the previously assigned nodes might not be feasible to cover the sharpness of the fragment length distribution functions as shown in Figure 2.4. This happens when the very sharp beginning of a function falls into an interval between two regular nodes, so that the estimation of the concentration based on those two nodes is not accurate enough. This complication has been observed for higher fragment lengths and so for higher intervals of the chain length domain, strongly.

The problem is solved by a new grid refinement strategy; an example is depicted in Figure 2.4. The refinement procedure starts with the starting point \( m \) of a specific interval. For the amount of scission fragments of length \( m \) we need to consider chain lengths \( n \simeq m+1 \). Consequently, we need to apply a routine starting from chain length \( n_{\text{start}} = m+1 \) to find out the problematic area of the chain length domain, with end-point of the grid refinement range, \( n_{\text{end}} \). From Figure 2.4, it is clear that no longer grid refinement is necessary.
after the FLD has reached its minimum value, which chain length location then determines this end-point. Doing so, the refinement zone is identified to be between \( n_{\text{start}} \) and \( n_{\text{end}} \), demanding the insertion of extra nodes. After locating the refinement zone, it is critical to define a sufficiently finer system of new intervals that are smaller as the gradient of the FLD is steeper. The refinement now takes the start point \((n_1, f_1)\) as the initial estimate of the end-point, so initially \( n_1 = n_{\text{start}} \). The end of each new interval is determined as the chain length, \( n_2 \), at which the estimated value of the FLD multiplication factor, \( f_2 \), equals a critical fraction \( \delta \). The estimate is based on the slope of the FLD function at \( n_1 \). A value for \( \delta \) equal to 0.25 turns out to be satisfactory. New and increasingly larger (due to the shape of the FLD function) intervals are found by repeating this procedure until the new interval edge falls beyond the position of the minimum FLD. Thus, this refinement zone is covered by the newly defined intervals. Figure 2.5 shows an example interval of chain lengths (10 000:60 000) with the original nodes (upper edge) on a logarithmic scale. The refined new interval edges are illustrated with the numbers on the function’s curve. These are the intervals, to which grid refinement should be applied to, implying to calculate series of nodes, weights and Chebyshev polynomial values on these intervals according to the usual Galerkin-FEM method.

2.5.4 Implementation of combination termination

Combination termination is one of the commonly accepted mechanisms in ldPE polymerization. Accounting for this mechanism requires the implementation of the convolution term in Equation 2.17, \( \sum_{m=1}^{n-1} R_m R_{m-m} \), in the Galerkin FEM framework. In solving this problem the option that the living chain concentration \( R(s_k) \) is explicitly available on the series of nodes constructed as described above, \( s_k \) is chosen. In the following paragraphs we will first discuss the procedure to find the convolution term in an efficient and sufficiently accurate manner – apparently a difficult problem for broad distributions as in ldPE. Furthermore, we will discuss the treatment of the inherent non-linearity.

2.5.4.1 Procedure to compute the convolution term and grid refinement

For each of these nodes, \( s_k \), a summation of a range of concentration products \( R(s_k)R(s_k-s_k) \) has to be made, where \( s_k \) is a ‘regular’ node from the aforementioned series, but \( s_k-s_k \) is a new complementary node. The concentration at this new node \( R(s_k-s_k) \) has to be calculated from the proper set of coefficients and Chebyshev polynomials belonging to the interval on which \( s_k-s_k \) is located.

For narrow distributions a simple procedure gives sufficiently accurate results for the convolution term: for each regular node, \( s_k \), the convolution is constructed from the lower regular nodes < \( s_k \) and their new complementary counterparts, \( s_k-s_k \). However, for the broad distributions typical for ldPE this procedure fails, as exemplified in Figure 2.6. This shows the case of obtaining the convolution for node \( s_k = 1.7 \times 10^5 \). According to the simple
procedure, the first summation term is constructed at the adjacent lower node, \( s_k = 1.58 \times 10^5 \) and the subsequent terms for all lower nodes. In Figure 2.6 the concentration distribution for the complementary nodes is also shown. Clearly, it falls drastically in the range between the two adjacent nodes. If we would take the regular first node, as indicated in the figure, as the first convolution term, the summation procedure fails to cover the much higher values close to \( s_k = 1.7 \times 10^5 \). Hence, the regular grid is too coarse to capture the steep concentration gradient at the complementary nodes. Evidently, a grid refinement to cover the steep gradient is required.

The convolution operation is carried out for all of the nodes (1 to \( s \)) on all intervals using a summation grid and a convolution matrix. The latter matrix is depicted in Figure 2.7. In the standard operation for a given node \( s \) a summation has to be performed using a summation grid using the standard nodes only. At each node \( s_j \) of the summation grid the product of the concentrations at complementary points is evaluated, \( R(s_j)R(s-s_j) \). The sum is calculated per interval using the nodes on that interval with the associated weights. Nodes and weights are calculated employing the same procedure as explained before (Deuflhardt and Hohmann, 2003).

Figure 2.7 shows the elements of the convolution matrix, of which the rows are the nodes on all intervals, \( j = 2 : s \), and the columns represent the summation grid, \( j' = 1 : j-1 \). The actual nodes are indicated as encircled dots, the summation nodes as black dots. Typically, the distance between the summation nodes increases exponentially with chain length as is shown in the figure. The positions of the regular (counting from LHS) summation nodes at the same time represent the positions of the complementary nodes if counted from RHS. Obviously, the pairs of regular and complementary nodes fall in different intervals. For instance, for the last node, \( s \) (bottom row in Figure 2.7), the first regular node \( (j = 1) \) sits in interval 1, while its complementary counterpart falls in interval \( M \); the last regular node \( (j = s-1) \) sits in interval \( M \), the complementary node in interval 2. The last example illustrates the problem: no complementary nodes are present in interval 1.

It shows that the standard convolution procedure misses a complete interval – for very broad distributions even the first few intervals altogether - which nevertheless would
contribute significantly to the sum accounted for. The grid refinement procedure consists of creating extra summation nodes indicated as grey bullets in the lower part of Figure 2.7. The extra summation nodes are created for each node separately by subtracting the regular nodes from the node at hand. Thus, it is ensured that complementary nodes are placed in the lower intervals as well. In the case of the example of Figure 2.6, one would obtain around 100 extra nodes between $s_k = 1.58 \times 10^5$ and $s_k = 1.7 \times 10^5$. In this manner, convolutions are accurately obtained for very broad distributions.

![Figure 2.7](image.png)

Figure 2.7. Convolution matrix with $j = 2s$ nodes (encircled dots) as rows and for each node $j' = 1:j-1$ nodes on the regular summation grid (black dots). Regular nodes are counted from LHS, complementary nodes from RHS. Pairs of regular and complementary nodes are placed in different intervals. For last node ($j$) first complementary node ($s-1$) is in interval 2, interval 1 has no complementary nodes. In refined grid sufficient nodes (grey dots) are placed in lowest intervals (as indicated for last 3 nodes, $s-2$, $s-1$, and $s$).

### 2.5.4.2 Addressing the non-linearity due to combination termination

Accounting for this type of termination also implies introducing a strong non-linearity in the model. Several options have been explored to deal with this non-linearity using standard tools in MATLAB®. One is the non-linear solver based on a Newton-Raphson method that allows the solution of the steady-state version of the population balance equations – i.e. taking the left-hand sides of Equations 2.17 and 2.18 equal to zero. Thus, solutions for cases, where the obtained distributions are not very broad, meaning that concentrations in the significant part of the MWD are not very low are found readily. However, broader distributions could much less easily be computed, probably because of the very low concentrations for long chain lengths. A more successful approach proved to be solving the dynamic variant of the model, starting from zero conversion, using the standard MATLAB® ODE-solver ‘ode15s.m’. Thus, the time profiles of the coefficients are calculated together with the concentrations of low-molecular species initiator, initiator radicals, monomer and chain transfer agent. The routine offers the possibility of additionally supplying an analytical model for calculating the Jacobian matrix in order to accelerate the integration procedure.

The afore-described A-matrix is employed as such, including a set of equations to calculate the partial derivatives of the low-molecular species. Obviously, the Jacobian would not include terms coming from the convolution in Equation 2.18. Still, a considerable speed up
could be attained in this way. Depending on the number of pseudo-distributions taken into account calculation runs typically ranged from 5 to 30 s CPU-time.

### 2.5.5 Implementation of branching pseudo-distribution approach

Equations 2.25 and 2.26 describe the branching pseudo-distributions. Each set of higher moment distributions, here \( \Psi^N_n, \Phi^1_n \) and \( \Psi^2_n, \Phi^2_n \) give rise to similar \( A \)-matrices as the \( P_n, R_n \) do, which is illustrated in Figure 2.8. The parts of the equations that relate \( \Psi^N_n \) and \( \Phi^N_n \) to themselves appear as the diagonal blocks. In addition, we see that \( P_n, R_n \) appear in the equations for both higher moments, while \( \Psi^1_n, \Phi^1_n \) appear in the equations for \( \Psi^2_n \) and \( \Phi^2_n \). These parts lead to the lower-left elements in Figure 2.8.

![Figure 2.8. Structure of the A-matrix with contributions from branching pseudo-distributions.](image)

### 2.6 Kinetic data and parameter setting

The ldPE free radical polymerization is a complex polymerization process. Due to this fact, there exist several apparently dissimilar kinetic data sets in the literature. However, coefficient ratios like \( k_{tp}/k_p \) do not turn out to be very different. Here, the same kinetic data set as in former studies (Iedema et al., 2000) is used. Table 2.3 demonstrates the kinetic data set that is applied to calculate the distributions in this chapter, while Table 2.4 presents the presumed reaction conditions for CSTR low-density polyethylene polymerization. Regarding the concentration and kinetic coefficient of the chain transfer agent the values are supposed to be representative of species like isopropylene being used in industrial practice.

The number of intervals is set to be fifteen and the number of nodes per each primary interval and any sub-interval is set to be eight in the modeling scheme. It means Chebyshev polynomials of order eight are used in the Galerkin-FEM method.

### 2.7 Monte Carlo sampling procedure

The Monte Carlo sampling procedure to obtain chain length and branching distributions for radical polymerization with branching by transfer to polymer, random scission and combination termination has been developed for a batch reactor by Tobita (2001b). The method has been adapted to a CSTR, where the residence time of individual primary polymers takes the role of the ‘birth conversion’ in the batch reactor (Tobita, 2001b).
that the MC sampling method has been utilized for radical polymerization in a CSTR with transfer to polymer without scission by Tobita (1994) and also by Iedema and Hoeftsloot (2004b). A brief description of the newly developed MC method follows here, with emphasis on the residence time effects.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Kinetic coefficients</th>
<th>Arrhenius expression</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propagation</td>
<td>$k_p$</td>
<td>$k_p^0 = 1.88 \times 10^7 \exp\left(\frac{-4125 + 0.324P}{T}\right)$</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_p = \frac{k_p^0}{1 + \frac{k_p^0}{1.13 \times 10^9 \eta}}$</td>
<td></td>
</tr>
<tr>
<td>Termination</td>
<td>$k_{sc}$</td>
<td>$k_{sc}^0 = 8.11 \times 10^9 \exp\left(\frac{-553.26 - 0.19P}{T}\right)$</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\eta = 10^{0.15 P + 1.7 \sqrt{P}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{sc} = k_{sc}^0 \left[0.832 \frac{1}{\eta} + 8.04 \times 10^{-5} (1 - \lambda) k_p\right]$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{uc} = 3.32 \exp\left(\frac{150.10 - 0.1086 P}{T}\right)$</td>
<td></td>
</tr>
<tr>
<td>Transfer to monomer</td>
<td>$k_{tm}$</td>
<td>$3.42 \times 10^4 \exp\left(\frac{-9135 + 0.0674 P}{T}\right)$</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td>Transfer to polymer (long chain branching formation)</td>
<td>$k_{tp}$</td>
<td>$2.15 \times 10^4 \exp\left(\frac{-5921.9 + 0.04059 P}{T}\right)$</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td>Transfer to CTA</td>
<td>$k_s$</td>
<td>$1.99 \times 10^4 \exp\left(\frac{-5499 + 0.3253 P}{T}\right)$</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td>Scission</td>
<td>$k_{ss}$</td>
<td>$3.7 \times 10^4 \exp\left(\frac{-6357 - 0.0869 P}{T}\right)$</td>
<td>s⁻¹</td>
</tr>
</tbody>
</table>

Note 1) For the conversion ranging 0 to 0.35, propagation rate constant can be assumed as being independent of conversion ($k_p = k_p^0$).

Note 2) Termination rate considers gel-effect.

Table 2.3. Kinetic data set applied to model MFIP (from Busch, 2001a, 2001b). The reaction rate constants are based on $k = k_0 \exp \left(\frac{E}{RT}\right)$.

<table>
<thead>
<tr>
<th>Reactor condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>1850 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>260°C</td>
</tr>
<tr>
<td>Volume</td>
<td>0.3 x 10⁻³ m³</td>
</tr>
<tr>
<td>Feed condition</td>
<td>16.75 kmole/m³</td>
</tr>
<tr>
<td>Monomer</td>
<td>16.75 kmole/m³</td>
</tr>
<tr>
<td>Chain transfer agent</td>
<td>1.00 x 10⁻² kmole/m³</td>
</tr>
<tr>
<td>Initiator</td>
<td>3.50 x 10⁻³ kmole/m³</td>
</tr>
</tbody>
</table>

Table 2.4. Reaction configuration and reaction conditions, note that the monomer concentration is assumed to be valid at reaction temperature.

The residence time distribution in a CSTR is:

$$F(\theta) = \exp(-\theta), \quad \theta = \tau / \bar{\tau}$$

(2.38)

Here, $\theta$ denotes the reduced residence time and $\bar{\tau}$ is the average residence time. As in the batch case, linear primary polymers may be created by several scission and combination events, as is illustrated in Figure 2.9. The initially selected unit (black square) sits on the first primary polymer with residence time $\theta_x$ and is obtained by two times sampling from a
number length distribution (Flory, average \( \bar{n} \)) and aligning them with the initial unit as the connection-equivalent to sampling once from a weighted distribution and choosing an arbitrary unit. The average primary polymer length is:

\[
\bar{n} = k_p \lambda_0 \left/ \left\{ \left( k_c + k_{al} \right) \lambda_0 + k_{rr} \mu_1 + k_{gr} \mu_1 \right\} \right.
\]

(2.39)

The usual (Tobita) scission test is performed at RHS and LHS of the first primary polymer (Seg-0) by comparing the chain lengths to the ‘scission lengths’, also Flory distributed, with average \( \bar{n}_s(\theta) \), which are related to the ‘scission density’, \( \rho_s(\theta) \):

\[
\bar{n}_s(\theta) = \frac{1}{\rho_s(\theta)} = \frac{1}{k_p (1 - x)} = \frac{k_p (1 - x)}{k_{rs} x \theta}
\]

(2.40)

In the example scission happened, obviously at a time instant, \( \theta_1 \), during the residence time of the first primary polymer in the CSTR, so between 0 and \( \theta_0 \). Since conditions do not change in a CSTR, the conditional probability, \( CP_{rr}(\theta_1 | \theta_0) \) is a uniform distribution, hence \( \theta_1 \) is an arbitrary time in that interval calculated by multiplying \( \theta_0 \) by an arbitrary number between 0 and 1. Since half of the scission fragments end as a living chain growing further, the scission point may with probability 0.5 become an initiation point for a new chain, as is the case in Figure 2.9 (Seg-1). This chain fragment may again undergo scission, which is determined by the scission check. In the example no scission happens, the fragment ends by its termination point. This may be a combination point, leading to further extension, but here it turns out to be a disproportionation point, which is the real end-point at RHS of the primary polymer.

At LHS of the initially selected unit the scission test reveals, in the example that no scission has occurred. So this chain fragment has grown from an initiation point according to 3 different possible ways: from an initiator radical, from a backbone radical or from a scission point. The probability that it is a scission point is given by:

\[
P_s = k_{rr} \mu_1 \left/ \left\{ \left( k_c + k_{al} \right) \lambda_0 + k_{rr} \mu_1 + k_{gr} \mu_1 \right\} \right.
\]

(2.41)

In the example it is a scission point indeed, meaning that scission took place on time \( \theta_0 \) of a new chain fragment (Seg-2”) that obviously has longer residence time, \( \theta_2 > \theta_0 \), with probability distribution:

\[
CP_{rr}(\theta_2 | \theta_0) = \frac{1 - F(\theta_2)}{1 - F(\theta_0)}
\]

(2.42)

Sampling from this distribution is exactly identical to sampling from the exponential residence time distribution and adding \( \theta_0 \). The growth direction of the primary polymer grown at \( \theta_1 \) is either equal or opposite of the first one, with identical probabilities, so either its ‘tail’ or the ‘head’ fragment is connected at the scission point (Tobita, 2001b). In the example a tail fragment is present, which again undergoes a scission check. Since no scission
occurs this time, a termination point is identified, here a combination point, according to the probability:

\[ P_c = \frac{k_{tc} \lambda_0}{(k_{tc} + k_{tw}) \lambda_0 + k_{sc} \mu_1 + k_{sp} \mu_1} \]  

(2.43)

Thus, the chain is extended further with a fragment with the same residence time (Seg-2”). No scission happens; hence an initiation point is identified, having the same three birth options as described above. This time from sampling it follows that it did not grow from a scission point. This then concludes the construction of the segmented primary polymer at LHS. Note that in this example the primary polymer ends with one ‘free’ end (RHS) and one initiation point (LHS), but primary polymers may also end up with two free ends or two initiation points.

The MC algorithm constructs several primary polymers for each ‘generation’ as has been described before (Tobita, 2001a, 2001b; Iedema and Hoefsloot, 2004b). The possible connections at initiation points, branch points, follow from the probability that an initiation takes place at the backbone of another primary polymer:

\[ P_b = \frac{k_{tp} \mu_1}{(k_{tc} + k_{td}) \lambda_0 + k_{rs} \mu_1 + k_{tp} \mu_1} \]  

(2.44)

The possible branch points on the backbones of the segmented primary polymers follow by the usual sampling from a binomial distribution for the scission ‘density’ \( \rho_s(\theta) \) and length of each of the segments individually, where:

\[ \rho_b(\theta) = \rho_b ' \theta = \frac{k_{tp} x \theta}{k_p (1 - x)} \]  

(2.45)

The values of these parameters used for two sets of MC simulations are listed in Table 2.5; the first run is without combination termination \( (k_{td}/k_p = 2000) \) and high transfer to polymer rate \( (k_{tp}/k_p = 0.0032) \), the second is with combination \( (k_{td}/k_p = k_{tw}/k_p = 1000) \) and lower \( k_{tp} \) \( (k_{tp}/k_p = 0.0006) \).

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Equation</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average residence time</td>
<td>( \tau )</td>
<td>42</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Average primary polymer length</td>
<td>( \pi )</td>
<td>43</td>
<td>254.7</td>
<td>566.7</td>
</tr>
<tr>
<td>Scission density</td>
<td>( \rho_s )</td>
<td>44</td>
<td>1.341 ( 10^{-5} )</td>
<td>3.353 ( 10^{-5} )</td>
</tr>
<tr>
<td>Branching density</td>
<td>( \rho_b )</td>
<td>49</td>
<td>0.00268</td>
<td>0.000503</td>
</tr>
<tr>
<td>Scission probability</td>
<td>( P_s )</td>
<td>45</td>
<td>0.00342</td>
<td>0.01903</td>
</tr>
<tr>
<td>Combination probability</td>
<td>( P_c )</td>
<td>47</td>
<td>0</td>
<td>0.348</td>
</tr>
<tr>
<td>Branching probability</td>
<td>( P_b )</td>
<td>48</td>
<td>0.68401</td>
<td>0.285</td>
</tr>
</tbody>
</table>

Table 2.5: Monte Carlo sampling parameters dPP.
2.8 Results

For industrial ldPE free radical polymerization, mostly CSTR and tubular reactors are used. Since CSTR is a simpler case study comparing to a tubular reactor, the modeling was started with molecular weight/branching distribution of ldPE for a CSTR. The tubular reactor case will be addressed in Chapter 4, as well. The provided molecular weight distribution for CSTR with topological scission does not show bimodality as the linear scission model does, and it exhibits a tailing effect, which has not been observed in the Monte Carlo models.

2.8.1 Comparison to the previous model

The mathematical formulation of the model presented is essentially identical to the one published before in Kim and Iedema (2008). In the previous work the model has been implemented in PREDICI®. It showed that topological scission according to the fragment length distribution given before requires a specific combination of standard reaction steps in the package, like a series of depropagation steps instead of scission steps. This older approach has produced results that now for the first time can be validated with the new model with a more straightforward, rigorous and precise manner of programming the fragment length distribution. The results from the new model to those from the old model have been compared using the same kinetic data for both linear and topological scission – except the scission parameters, see Table 2.3; for linear scission $k_{rs} = 2 \text{ m}^3/(\text{kmole.s})$ is assumed, while for topological scission $k_{rs} = 30 \text{ m}^3/(\text{kmole.s})$ and a varying segment length: $s = \bar{n} / n$, where $\bar{n}$ is the average number of branch points at length $n$, equal to $(\Psi_i^1 + \Phi_i^1) / (P_n + R_n)$. Note that in the old model a chain length independent of segment length is applied. This turned out to have a small effect on the branching distributions only.

Figure 2.10 shows the dead chain distributions in SEC-MALLS mode, meaning that the surface under the distribution curve is normalized to one, while the concentration (vertical axis) scales with $n^2 P_n$. The bimodal distributions for linear scission from old and new model...
perfectly agree. For topological scission the old model produced a wavy distribution, since evidently the stiffness of the fragment length distribution could not be captured in a sufficient way in PREDICI®. The new model clearly overcomes this problem yielding a smooth distribution and a slightly longer tail. The average numbers of branch points and branching density versus chain length plots of Figures 2.11 and 2.12 show similar trends. The results for linear scission completely coincide, whereas the old model for topological scission produces wavy curves. Moreover, at the high chain length side the old model over-estimates the branching, which is most clearly visible in the branching density. This discrepancy must be wholly ascribed to the insufficient capturing of the fragment length distribution.

It should also be noted that the branching density as calculated from the new model does not approach zero towards small chain lengths, which should be expected. This is likely an artifact of the model, due to the shape of the fragment length distribution. This correctly describes the fact that highly branched molecules predominately break into small and large fragments. This is clearly visible in Figure 2.4, where the multiplication factor due to the FLD for the smallest chains is considerably larger than one, up to $10^4$ for breaking chains of length $10^3$. If it is realized that these large molecules have high branching densities, it is expected that the small fragments originating from scission of these large molecules contribute to the higher branching density obtained at low $n$. In addition, from Monte Carlo simulations of scission of branched molecules (Iedema and Hoefsloot, 2001b) we know that small fragments possess slightly lower numbers of branch points than predicted by the hypergeometric distribution. Both effects are absent in this model for linear scission; hence a non-zero branching density at low $n$ in that case is not observed.

Finally, in Figure 2.13 the branching polydispersity is depicted. Here also, the old model shows a wavy pattern. In all cases however, confirming observations in the previous work (Kim and Iedema, 2008), the polydispersity practically coincides with that predicted assuming that branch points for all chain lengths follow a binomial distribution.

Figure 2.10. Dead chain distributions for linear and topological scission from old and new model. Scission parameters: linear scission, $k_m = 2 m^3/(kmole.s)$; topological scission, $k_m = 30 m^3/(kmole.s)$, segment length $\tau = I(\theta)/n$. For linear scission results coincide. Wavy distribution from old model for topological scission attributed to insufficient capture of fragment length distribution. The CLD representation is in SEC-MALLS mode, scaling with $nP_n$. 

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Figure 2.11. Average number of branch points, $\mathcal{T}(n) = \frac{\Psi_n + \Phi_n}{(P_n + R_n)}$, as a function of chain length for linear and topological scission from old and new model. Same scission parameters as in Figure 2.10. For linear scission results coincide. Wavy pattern and very high branching numbers at high $n$ from old model for topological scission both attributed to insufficient capture of fragment length distribution.

Figure 2.12. Branching density, $\mathcal{B}(n)/n$, as a function of chain length for linear and topological scission from old and new model. Same scission parameters as in Figure 2.10. For linear scission results coincide. Wavy pattern and very high branching density at high $n$ from old model for topological scission attributed to insufficient capture of fragment length distribution. Non-zero density at low $n$ caused by fragment length function (Equation 2.9) yielding relatively many short fragments from breaking large molecules with high branching density.

Figure 2.13. Branching polydispersity, as a function of chain length for linear and topological scission from old and new model. Same scission parameters as in Figure 2.10. For linear scission results coincide. Wavy pattern and very high branching density at high $n$ from old model for topological scission attributed to insufficient capture of fragment length distribution. All curves practically coincide with those based on a binomial shape of the branching distribution.
2.8.2 Comparison to Monte Carlo simulations

The results of the deterministic model are compared, both with linear scission and topological scission, to the outcomes from the Monte Carlo simulations for two cases, one without combination termination, strong transfer to polymer \((k_{tp}/k_p = 0.0032)\) and relatively weak scission \((k_{rs}/k_p = 1.6 \times 10^{-5})\), the other with combination \((k_{tc}/k_p = k_{td}/k_p = 1000)\), lower \(k_{tp} (k_{tp}/k_p = 0.0006)\) and stronger scission \((k_{rs}/k_p = 4 \times 10^{-5})\). The sample size of the MC simulations was \(10^6\) in both cases. The first case, with stronger branching, yields the typical bimodal shape that is also observed in practice for autoclave ldPE (Tackx and Tacx), if linear scission is assumed.

Figures 2.14 through 2.16 show the results of the comparison for the strong branching case. One observes that the bimodal shape is completely absent in the outcomes from the deterministic model with topological scission and from the MC simulations. This confirms what has been observed before concerning topological scission (Kim et al., 2004): a bimodal MWD is not found, if scission is assumed to occur according to a scission fragment length distribution resembling that of scission of highly branched polymers. Now, for the first time, because of the availability of an accurate solution of the population balance with such a fragment length distribution, it is possible to compare this solution to the MC simulation results. As shown by Figure 2.14 and the double-log plot of Figure 2.15, one observes smooth, non-bimodal tails in chain length distributions from the deterministic model assuming topological scission and from MC simulations. However, the tail is longer in the MC results. The double-log plot of Figure 2.15 reveals an almost linear descending of the concentration with length for the MC results, whereas the curves from the deterministic solutions decay much more rapidly.

The branching density as a function of chain length is depicted in Figure 2.16. All models show the typical S-shaped form leveling off to a constant value at long lengths. The results of all models almost coincide.

Figures 2.17 and 2.18 show the results for the case with less branching and including significant combination termination. The deterministic model assuming linear scission does not possess a bimodal shape. The differences with the situation of topological scission and with the MC results are less pronounced than those observed in the case without combination. This also holds for the comparison of the branching density results.

Concluding, one observes that introducing a correction to the linear scission function by means of a fragment length distribution function inferred from random scission of branched architectures (Iedema et al., 2000) leads to a better approximation of the proper random scission result only attainable by MC simulations. However, a small but clear difference with the ‘true’ random scission result from MC still remains. On the other hand, the experimentally observed MWD bimodality proves that complete randomness of the scission process is not adequately describing reality either. In addition, the results of the MC simulations may have a modeling error due to the assumption of instantaneous growth of the primary polymers. In Chapter 3 it is shown that this is related to the issue of multiradicals. These are only implicitly dealt with in MC simulations, but from an explicit treatment in a deterministic approach they appear to play a significant role around gel point conditions.
Figure 2.14. Chain length distribution from deterministic model (linear and topological scission) and from MC sampling (run 1, no combination, $k_p/k_t = 0.0032$, sample size $10^6$). No bimodal shape for topological scission in agreement with MC simulations.

Figure 2.15. Double-log plot of chain length distribution from deterministic model and from MC sampling (run 1) – same as Figure 2.14.

Figure 2.16. Branching density versus chain length from deterministic model (pseudo-distributions) and MC sampling.
Figure 2.17. Chain length distribution from deterministic model (linear and topological scission) and from MC sampling (run 2, with combination, $k_p/k_s = 0.0006$, sample size 10^6). Better agreement between topological scission and MC sampling.

Figure 2.18. Double-log plot of chain length distribution from deterministic model and from MC sampling (run 2) – same as Figure 2.17.

2.8.3 Comparison to experimental data from SEC-MALLS

Figure 2.19 shows an experimental molecular weight distribution for ldPE from SEC-MALLS (Tackx and Tacx, 1998) in comparison to the distribution resulting from the modeling with linear scission and disproportionation only. This is meant to illustrate that the provided model in here reproduces a similar bimodality as observed experimentally, if linear scission is assumed. For topological scission the bimodality disappears altogether (Figure 2.14). No exact agreement is obtained from the present set of kinetic conditions. In Chapter 4, the reactor configuration and kinetic parameters have been varied in order to find the optimal fit to more recent industrial MWD data.
Figure 2.19. Bimodal molecular weight distribution (expressed as chain length distribution) as measured by SEC-MALLS (Tackx and Tacx, 1998) and predicted by the new model assuming linear scission. Both feature a bimodal shape. Kinetic data: termination by disproportionation only ($k_{td}/k_p = 2000$; $k_{td} = 0$); strong branching ($k_{tp}/k_p = 0.0032$) and mild scission ($k_{rs}/k_p = 1.6 \times 10^{-5}$); $k_p = 5000 \text{ m}^3/\text{(kmole.s)}$; conversion $x = 0.436$; $M_0 = 16.75 \text{ kmole/m}^3$; $\lambda_0 = 5.39 \times 10^6 \text{ kmole}^2/\text{m}^4$.

2.9 Conclusions

A rigorous model predicting molecular weight distribution including branching, scission and combination termination reactions is provided for ldPE free radical polymerization in CSTR. The model employs fragment length distributions to deal with topological scission. A Galerkin-FEM algorithm similar to one used in PREDICI® is constructed and implemented in MATLAB® to solve the 1D population balance equations, including pseudo-distribution equations to deal with branching. A crucial grid refinement problem arising from the steep FLD addressed earlier is now fully and ultimately solved.

The resulting smooth distributions with those of the old model (Kim and Iedema, 2008) are compared. Firstly, chain distributions are modeled, which are in a perfect agreement with the distributions from an earlier model for linear scission. In the case of topological scission, where the old model still featured spiky distributions, perfectly smooth distributions with the new model are obtained. Also improved plots of the average number of branch points and branching density versus chain length are observed. In addition, the new model shows that the old model over-estimates the branching density for long chains due to the insufficient capturing of fragment length distribution.

A comparison has also been made to the MWD and branching distributions obtained from Monte Carlo simulations using a newly constructed MC sampling code. The MWD resulting when assuming topological scission with the empirical fragment length distribution, Equation 2.9, is better in line with the MC results than that by assuming linear scission. Both topological scission and MC fail to give the typical bimodal shape obtained with linear scission. However, since it is possible now to dispose of a more accurate implementation of topological scission, we are able to observe small but clear differences. The MC results show longer tails, both in cases with and without combination termination.

In conclusion, the population balance model developed forms a sound basis for further investigations of MWD and degree of branching distribution of ldPE. In Chapter 4 the model is employed and validate with the kinetic parameters using SEC-MALLS data for ldPE from both autoclave and tubular reactors. Furthermore, the model is utilized to explore the behavior of the ldPE system under varying conditions eventually leading to gel formation.