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TOWARDS THE ARCHITECTURES OF MACROMOLECULES

Modeling of Multi-Dimensional Polymer Chain Distributions

NAZILA YAGHINI
TOWARDS THE ARCHITECTURES OF MACROMOLECULES
MODELING OF MULTI-DIMENSIONAL POLYMER CHAIN DISTRIBUTIONS

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1 Introduction

Control of end-use properties of polymers produced at industrial scale at the molecular level is difficult as experimental techniques fail to detect most of the decisive microstructural properties. Therefore, mathematical models have become increasingly important in predicting the interesting microstructural properties such as chain length distribution. Though, other properties of a polymer chain such as number of branch points, number of combination points, number of radical sites, number of terminal double bonds, etc., provide added valuable microstructural information, and hence are of great interest for industrial applications besides chain length.

To obtain reliable models of polymerization mechanisms and to interpret results appropriately, the outcome of all model assumptions should be followed closely. For example scission type (linear or random) and (dis)allowing for gelation are two key assumptions that require specific interpretations. To clarify the role of the influencing mechanisms in free radical polymerization process of branched molecules such as low-density Polyethylene (ldPE), the reminder of this chapter has been devoted mostly to an extensive explanation of the decisive reactions and the modeling assumptions to be made. Furthermore, the potential modeling schemes are briefly introduced; finally, the aims and the outline of the thesis are highlighted.

1.1 Decisive mechanisms and issues

1.1.1 Degree of branching

Knowledge of branched architectures improves the predictability of the end-use, and processability properties. Branching architectures are strongly correlated to rheology and contraction of the radius of gyration, important for characterization. For instance, for ldPE, the branched structure in relation to rheology and melt strength has been discussed recently in Science (Read et al., 2012). As branching is concerned, although no direct experimental method is capable of determining polymer branching architectures, it is possible to predict the architectures (Iedema and Hoefsloot, 2004a). Experimental studies of long chain branching of ldPE have been performed (Tackx and Tacx, 1998), employing Size Exclusion Chromatography-Multi Angle Laser Light Scattering (SEC-MALLS), and establishing a way to relate the radius of gyration and the molecular architecture of a polymer to its molar mass.

Examples of modeling studies accounting for branching are Teymour and Campbell (1994) as well Pladis and Kiparisssides (1998), which present numerical fractionation techniques and the method of moments applied to each class of branched molecules to compute the molecular weight and degree of branching where branching is caused by chain
transfer to polymer. Further predictions of Degree of Branching Distribution (DBD) and Molecular Weight Distribution (MWD) accounting for random scission, and thereby the exact architectures of the branched molecules by applying Monte Carlo (MC) simulations is provided by Tobita (1996a, 1996b and 1998b); Tobita and Saito (1999). From this information, the mean square radius of gyration could be obtained by explicitly constructing the conformations of the branched molecules. Instead in Iedema and Hoefsloot (2001c), a statistical mechanical theory on the basis of a graph theoretical representation of branched molecules to find the radius of gyration has been used. In Versluis and Hillegers (2002), the contraction factor for stars with arms with a Flory (1946) distribution is calculated, and a proof to show that the contraction factor distribution for this type of star molecules is the same as for stars with uniformly distributed arms that had been provided before by “Zimm and Stockmayer” (1949) is given.

1.1.2 Random scission

As it has been put forward before (Kim et al., 2004; Kim and Iedema, 2004), the molecular weight distribution of low-density polyethylene in both Continuous Stirred Tank Reactor (CSTR) and tubular reactor is strongly affected by the scission mechanism. Hence, better understanding of this mechanism may lead to improvement of the industrial production of ldPE.

Comprehensive studies over the impact of scission on ldPE polymerization had never been done before 2000. From that time on, a number of papers around this subject have been published and several new concepts have been provided. In the simple models of scission (linear scission), the length of fragments (the resulting shorter chains by scission) was not taken into the account for ldPE polymerization (Iedema et al., 2000). More advanced models made use of the “topological scission” concept, by introducing the “Fragment Length Distribution” (FLD) obtained from branched ldPE structures and from Monte Carlo simulations (Iedema and Hoefsloot, 2004a). They showed that topological scission (long/short scission fragments) as an attempt to account for real random scission of branched polymer molecules leads to a paradoxical situation (Kim et al., 2004; Kim and Iedema, 2008).

Experimental studies of the MWD and branching properties of ldPE have revealed a bimodal MWD, in particular for the IUPAC-Alpha standard for autoclave ldPE as shown in Figure 1.1(Tackx and Tacx, 1998). Assuming topological scission, in the MWD of ldPE one observes vanishing the well-known shoulder, experimentally observed in autoclave CSTR for ldPE (Tackx and Tacx, 1998). Assuming random scission for ldPE polymerization, which is a bad model for random scission, yields better agreement with the observed bimodal shape. It was also demonstrated that, in contrast, assuming mechanical (mid-chain) scission would enhance the MWD bimodality. In comparison to Monte Carlo simulations, where it is possible to exactly describe random scission, the deterministic model assuming topological scission gave a nearly perfect agreement. Evidently, real random scission, as appears either from MC simulations or the model with topological scission, turns out to give long-tailed but no bimodal MWD. The issue of which model is most representative for ldPE, random (topological) or linear scission, is not yet definitively resolved.
The presented models in the current study are implemented in MATLAB® using a Galerkin method, a finite element method allowing for the representation of population balance problem on a chain length grid. It represents a model of molecular weight and branching distribution, which is able to show how the MWD for random scission would shift towards the MWD with topological scission. The implementation of a correct FLD in the Galerkin scheme gave rise to a serious grid refinement problem, which was adequately dealt with. The new model now perfectly allows implementing a proper FLD, based on branched architectures and the average segment length after scission, into the population balance equations.

1.1.3 Combination termination

The termination by combination reaction is a well-known mechanism for radical polymerization in general and it is also assumed to be present under conditions of IdPE polymerization. Concerning branching topology, next to chain length and number of branch points, the number of combination points is an important attribute of a polymer molecule. The issue of trivariate Chain Length Distribution/Degree of Branching Distribution/Combination Points Distribution (CLD/DBD/CPD) in modeling the topological architectures of polymer molecules in the presence of termination by combination and transfer to polymer in radical polymerization has been clarified previously (Iedema and Hoefsloot, 2005). They applied a combination of the method of moments and deterministic 1-Dimensional (1D) approach to 3-Dimensional (3D) population balance equations to estimate the overall distributions without presenting the actual full 3D distributions. Implementing termination by combination mathematically implies dealing with a non-linearity on the one hand and a complex convolution problem at the other. Monte Carlo simulations include the termination by combination reaction in the modeling scheme by generating the expected architectures directly (Tobita, 1989, 2003, 2013; Tobita and Kawai, 2002; Neuhaus et al. 2014). Kim, et al. (2004), and Iedema and Hoefsloot (2005) utilized the so-called “pseudo-distributions method” by calculating moments over the number of combination points distribution. In this thesis, the focus will be on providing a solution that is one step further than Iedema and Hoefsloot (2005), since pseudo-distribution
model is now incorporated in a 2-dimensional model, with dimensions chain length and number of branch points.

1.1.4 Multiradicals

The problem of multiradicals – chains with multiple radical sites - is often addressed in relation to gel formation. The multiradical issue for radical polymerization in a CSTR with transfer to polymer with disproportionation termination only, without scission has been addressed before (Iedema and Hoefsloot, 2004b). It was shown that without combination termination the model would not require accounting for gel formation, but multiple radical sites turns out to be an issue indeed, which then could be properly dealt with by employing a multiradical model. The slightly bimodal MWD shape predicted by the mono-radical model was reproduced by the multiradical model, where a better agreement to MC simulations of this system were obtained than with the monoradical model (Iedema and Hoefsloot, 2004b). More recently, Lazzari and Storti (2014) and Hamzehlou et al. (2013) dealt with multiradical models in crosslinking polymerization.

1.1.5 Gelation

Gel formation in industrial polymerization processes is usually an undesired consequence of certain if not all-operating conditions of the process. Fouling in reactors for ldPE is often ascribed to gel formation (Schmidt and Harmon Ray, 1981; Spivey et al., 2012; Zacca and Debling, 2001).

Flory (1941a, 1941b, 1941c, 1942) and Stockmayer (1943, 1944), and Fox and Gratch (1953) were the first to address gelation in polymerization systems, followed by several studies (Charlesby and Pinner, 1959; Saito, 1972; Durand and Bruneau, 1982). The branching probability factor was used to predict the gelation behavior by applying a statistical method. These early statistical methods based on simplified kinetics were capable of calculating the gel-point and finding chain distributions in the pre-gel and post-gel regions (Zhu and Hamielec, 1992, 1993, 1994; Zhu, 1996; Tobita and Hamielec, 1989; Tobita, 1993; Mikos et al. 1986; Mullikin and Mortimer, 1970; Beasley, 1953; Barnford and Tompa, 1953; Nicolas, 1958; Small, 1972). Zhu and Hamielec (1994) as well Teymour and Campbell (1994) studied the gelation mechanism in free radical polymerization systems in a comprehensive manner. It was observed that radical polymerization with transfer to polymer and disproportionation only, will never lead to gelation (Zhu and Hamielec, 1993, 1994; Zhu, 1996; Tobita, 1993; Tobita and Zhu, 1996; Tobita, 1994, 1998; Dias and Costa, 2003; Wulkow, 1996), but with combination termination gel is readily formed. In the case of crosslinking gel formation even may occur without combination termination being present (Tobita, 1993; Tobita and Zhu, 1996; Tobita, 1994, 1998b). Gel formation in population balance modeling of radical polymerization with transfer to polymer has been addressed by introducing explicit gel moment terms for living and dead chains in the equations (Iedema and Hoefsloot, 2002).

Mathematical modeling studies of ldPE till now (Kim et al., 2004; Kim and Iedema, 2008) have attempted to explain various issues like the typical bimodal shape of the molecular weight distribution of ldPE produced in an autoclave reactor. However, to the best of our knowledge, no studies have been devoted to the possibility of gelation in ldPE, which is now fully done in Chapter 3.
1.1.6. Tubular reactor versus continuous stirred tank reactor

Tubular reactor represents the most modern reactor type for polymerization of low-density polyethylene. Although the autoclave reactors are still employed especially in ldPE film production, in the near future this older technology is expected to vanish. An important issue regarding the tubular reactors is to improve this technology in order to reproduce the desired properties of specific autoclave film grades of ldPE. Therefore, controlling molecular weight distribution and branching through better understanding the relation between kinetics and branching topology of tubular ldPE is of utmost importance (Larson, 2011).

Several authors have studied the modeling tubular reactors for ldPE, among them Goldstein and Amundson (1965), Zabisky et al. (1991) and Kiparissides (2010) studied the bivariate molecular weight, and branching for tubular ldPE polymerization. They applied the method of moments to model the molecular weight averages and branching frequency. To solve bivariate polymerization problems in autoclave and extend it to batch reactors Krallis et al. (2007, 2008), Krallis and Kiparissides (2007) applied 2-dimensional fixed pivot technique. Asteasuain and Brandolin (2009) proposed a comprehensive model for tubular polymerization of ethylene.

In chemical engineering, compartment models have been used earlier to investigate the influence of non-ideally mixed reactors on ldPE polymerization (Wells and Ray, 2005a, 2005c, 2005b; Villa et al., 1998). In compartment models, two or more CSTRs in series are considered altogether in such a way that the flow from the first reactor continues to the second reactor and eventually exits the final reactor. In general, compartment models provide an opportunity to model the polymerization systems without thermal runaway by adjusting the type and amount of the initiators for each reactor element (Villa et al., 1998). These models are very beneficial to study the residence time distribution since having more than one reactor enables the investigation of the effect of residence time variations in a wider range. For this purpose, Marini and Georgakis (1984) used three CSTRs in series to model an autoclave reactor. As well as, Pladis and Kiparissides (1998) applied a numerical fractionation technique to find a joint molecular weight and long chain branching distribution in a series of 2 CSTRs and investigated the effect of residence time on MWD.

1.2 Methods

1.2.1 Population balance modeling

Population balance modeling is one of the widely applicable methods to keep track of number of different entities in industrial processes, especially those that include entities of particle birth and death phenomena (Ramkrishna and Mahoney, 2002). Note that each entity in the population balances system could be a function of discrete or continuous variable(s). In deriving physical properties of polymers usually we deal with discrete variables (chain length, number of branch points, number of combination points, etc.).

Among chemical reactions, modeling polymerization reactions by population balances is favorable over many other methods as clarified in Yaghini and Iedema (2014a), although a very hard task even in one dimension. The challenge is in relation to the difficulties in population balance equations formulation, and their numerical solutions, which are excessively complex to be employed in more than two independent dimensions (Schutte and Wulkow, 2010). For this complexity, there are no more than few instances of population
balance based modeling in the literature reported for bivariate/multivariate distributions of chemical/polymerization reactions. Though, population balance models are computationally affordable if one could deal appropriately with the inherent complexity.

1.2.2 The Galerkin method

The Galerkin method was employed first by Wulkow (2008) to polymerization problems. As a finite element method, it allows for providing a solution without adding simplifying assumptions to the original problem in principle. Especially, it is preferred for polymerization reactions with chain-length-dependent rate coefficients (such as transfer to polymer and scission), in comparison to the method of moments. For such non-linear polymerization problems, the method of moments requires closure equations and hence introduces arbitrariness to the solution. Furthermore, the Galerkin method employs efficient size reduction techniques, which speeds up the calculations considerably. In this context, PREDICI® solves 1D population balances only accounting for chain length.

The present study is a necessary follow-up of earlier studies by Galerkin, as they generated a series of serious modeling problems. Until now, the software package PREDICI® has been used, to construct the models. The software package is based on the Galerkin-hp method. In the current research, the same method but without step size optimization (Galerkin method) has been used. In Chapter 2 a detailed description of the method in 1D is given. The 2-Dimensional (2D) Galerkin follows in Chapter 6.

1.2.3 Pseudo-distributions approach

The pseudo-distribution concept first applied by Iedema et al. (2000) to branching (Iedema et al. 2000). The model was then extended to a pseudo-distribution model of multiradicals (Iedema and Hoefsloot, 20004b) - previously used for the cases without scission- to account for scission, both linear and topological. The latter model is based on the notified empirical scission fragment length distribution in order to properly account for the special scission features of highly branched polymer chains (Iedema and Hoefsloot, 2001b).

The method of moments has also been applied to reduce the dimensions of a 2D problem (chain length and branching) into a 1D problem (only chain-length) and to fit it to the 1D algorithm of the PREDICI® by Kim et al. (2004). Using a binominal distribution for branching at a given chain length the authors were able to construct a full 2D distribution. However, the implementation of the fragment length distribution function to account for topological scission did not fully comply with the standard methods in the software and gave rise to grid refinement problems, which are being treated in the current study. Pseudo-distributions are employed and elucidated in deep in the upcoming chapters.

1.2.4 Monte Carlo simulations

Tobita (1989, 2003, and 2014) applied MC simulation techniques to deal with polymerization problems. Regarding ldPE the same author (Tobita, 2001b) was the first to account for simultaneous branching and random scission (equivalent to topological scission) in a batch reactor. Recently, he has further extended his method to a series of CSTRs (Tobita, 2014). In this thesis, MC method is extended to a CSTR (Yaghini and Iedema (2014a)), and all MC schemes implemented as a basis benchmark for the deterministic models throughout the
thesis. It has been noted that comparison of the results from the deterministic model show fair agreement to the MC schemes. Although such comparisons form a valuable check as a real validation of the models should be executed using MWD measured by SEC-MALLS. The main drawback of the stochastic methods is observed to be the large computation time required when analyzing properties of largest molecules that are only scarcely generated.

1.2.5 Multidimensional population balances

A multi-dimensional polymerization problem necessitates the application of advanced numerical techniques to multi-dimensional Population Balance Equations (PBEs). The known numerical methods fail in providing a solution for higher dimensional PBEs, especially when taking the computation time into account. Obviously, these numerical techniques are less developed to solve multi-dimensional PBEs in polymer reaction engineering field in comparison to the similar methods in other fields such as computational fluid dynamics. Further in this context, the nature of the properties of interest is usually discrete and requires a special treatment.

Higher dimensional population balance models have been applied very rarely to polymer reaction engineering problems due to their complexity. This complexity increases tremendously for 3D problems and even becomes prohibiting in higher dimensions (Schutte and Wulkow, 2010). Wulkow et al. (2003) applied the method of moments to reduce a 2D Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization problem to a 1D problem, which was accordingly solved in the PREDICI©. Immanuel and Doyle (2005) and Pinto et al. (2007, 2008) provided solutions to multi-dimensional population balances in the context of chemical particulate processes using the so-called two-tire hierarchical algorithm.

Krallis et al. (2007) have applied the so-called fixed pivot technique to PBEs in order to model the evolution of molecular weight-long chain branching distributions of ldPE. Krallis and Kiparissides (2007) applied the same technique as Krallis et al. (2007) to PBEs to find the bivariate molecular weight/long chain branching distribution for branched molecules and presented 2D distributions, this time only for polyvinyl acetate with maximum of 8 branch points, certainly not realistic enough for the ldPE case.

Meimaroglou et al. (2011) have applied a combined kinetic/topology MC method to model the ldPE bivariate chain length-long chain branching/short chain branching distributions. Iedema (2012) has followed a MC sampling technique to model the 2D chain length/number of branching points distribution of terminally branched polymers when scission reaction takes place.

Therefore, the main goal in this thesis is providing a reasonable solution for multi-dimensional PBEs in the framework of ldPE kinetics.

1.3 Aims and outline

In Chapter 2 on modeling MWD in CSTR (Yaghini and Iedema, 2014a), a recent overview about ldPE molecular weight and Long Chain Branching distribution modeling is given. Modeling MWD with the Galerkin is of main concern, which allows a direct comparison to SEC-MALLS data, and MC simulations. The focus of Chapter 3 is on possible gel formation, using a new model predicting the shape of the MWD under gelation or near-gelation conditions and allowing for multiradicals. For
the first time the possible occurrence and implications of multiradicals and gelation under circumstances that are typical for the ldPE process has been discussed. It has been shown in the context of full chain length distribution modeling, that assuming the overall moments of the general model to include gel is an effective manner of dealing with gel, as has already been shown for the moments-based study for batch and continuous reactors by Teymour and Campbell (1994). This assumption is also fully equivalent to the treatment of gel in MC simulations. In both model types, MC and deterministic, this treatment of gel implies that reactive groups in sol and gel (radical sites and backbone monomer units) are chemically behaving identically. The present study has also revealed a very important and elegant feature of the topological scission model regarding the difficult problem of gel undergoing scission.

Chapter 4 is concerned with modeling MWD in various reactor configurations; from CSTR to series of CSTRs and tubular reactors. To our knowledge CSTR compartment models have not been used in combination with deterministic methods to estimate molecular weights and to investigate the effect of multiradicals on different reactor configurations (a bivariate model), so far. In Chapter 4, for the first time a deterministic model of several CSTRs in series is provided as a model for a tubular reactor.

In Chapter 5 the famous Zimm and Stockmayer’s (1949) model of branching is revisited. Using the same concepts as Zimm and Stockmayer, it is demonstrated that more realistic architectures give rise to different contraction factors than those from the Zimm and Stockmayer’s model. This is exemplified by a radical polymerization system resembling ldPE with transfer to polymer as the branching mechanism and combination termination.

Chapter 6 reveals an advanced technique to solve full 2D population balance equations deterministically. The 2D Galerkin method is developed by extending the original 1D method to model the full 2D molecular weight CLD/DBD of ldPE, accounting for transfer to polymer and topological scission. 2D fragment length distribution functions are applied to model the topological scission. Further the limitations of implementing hypergeometric function to account for the distribution of branch points on the scission fragments are discussed.

Chapter 7 is indeed an extension to Chapter 6 by employing 3-dimensional pseudo-distributions along with 2D Galerkin to model the moment of combination points and to estimate the trivariate CLD/DBD/CPD. 2-dimensional convolution procedure in the modeling scheme is discussed in length.
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 Hoefsloot, 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 to 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**

\[ I_2 \rightarrow 2I^\cdot, k_d, \]

\[ I^\cdot + M \rightarrow R_i, k_i, \]

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**

\[ R_{nj} + M \rightarrow R_{nj+1}, k_p, \]

**transfer to polymer**

\[ P_{nj} + R_{mj} \rightarrow P_{nj} + P_{mj+1} \]

**random scission**

\[ R_{nj} + P_{rj} \rightarrow P_{nj} + P_{rj-k-1} + P_{rj+k} \]

**termination by disproportionation**

\[ R_{nj} + R_{rj} \rightarrow P_{nj} + P_{rj} \]

**termination by combination**

\[ R_{nj} + R_{rj} \rightarrow P_{nj+1} \]

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

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

**and transfer to monomer**

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

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 \( n−1 \) 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, \( 1/n−1 \), 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 \( 2/999 \).

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 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:

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

\( n \) 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 \( \beta(n,m,i,j) \):

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

(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.

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

(2.11)

\[
\frac{dI_1}{dt} = 2k_d I_2 - k_f M I_1 - \frac{1}{\tau} I_1,
\]

(2.12)

\[
\frac{dM}{dt} = -k_f M I_1 - (k_p + k_m) M \lambda_0 + \frac{1}{\tau} (M_m - M),
\]

(2.13)

\[
\frac{dR}{dt} = k_f M I_1 - k_p M R_i - k_d R_i \lambda_0 + k_r R_i \lambda_0 - \frac{1}{\tau} R_i,
\]

(2.14)

\[
\frac{dS}{dt} = -k_\lambda \lambda_0 S + \frac{1}{\tau} (S_m - S),
\]

(2.15)

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

(2.16)

\[
\frac{dP_{n,j}}{dt} = k_d R_{n,j} + \frac{1}{2} k_w \sum_{m=1}^{n-1} R_{m,j} R_{n-m,j} + (k_{wp} + k_{wi}) \left( \mu_{1,n,j} - n \lambda \lambda_0 P_{n,j} \right) + \left( k_m M + k_s S \right) \mu_1 R_{n,j} + k_r \lambda \sum_{j=1}^{\infty} \sum_{m=1}^{\infty} f(m,n,\beta(m,n,j,i)) m P_{m,j} - \frac{1}{\tau} P_{n,j},
\]

(2.17)
The set of population balance equations for distributions and dead chain distributions, manner fragment length distribution function in order to model the topological scission in a precise distribution. RHS is linear, in principle Equations state the Left the reactor over the volume flow in and out of the reactor. Obviously, branch points, correspondingly, the aforementioned fragment length distribution and the distribution of living chains and dead chains distributions and are defined as

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

\[ +\left\{ k_m M + k_r \lambda_0 \delta(n-1)\delta(i-1) - \frac{1}{\tau} R_{n,j} \right\} \]

(2.18)

Here, \( P_{n,j} \) and \( R_{n,j} \) 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 \( \beta(n,m,j,i) \) 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. \( \tau \) 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:

\[ P_n = \sum_{j=0}^{\infty} P_{n,j} \quad (2.19) \]

\[ R_n = \sum_{j=0}^{\infty} R_{n,j} \quad (2.20) \]

\[ \Psi_n^N = \sum_{j=0}^{\infty} i^N P_{n,j} \quad (2.21) \]

\[ \Phi_n^N = \sum_{j=0}^{\infty} i^N R_{n,j} \quad (2.22) \]

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

\[ \frac{dR_{n,j}}{dt} = k_p M \left( R_{n-1} - R_n \right) - (k_{ld} + k_s) R_n \lambda_0 + k_{rp} \lambda_0 nP_n - (k_r + k_0) R_{n,j} - \frac{1}{\tau} R_n - (k_m M + k_s) R_n + k_r R_n \sum_{m=n+1}^{\infty} mf(m,n)P_m \quad (2.23) \]
\[
\frac{dP_n}{dt} = k_{id} R_n \lambda_n - (k_{ip} + k_{rs}) \lambda_0 n P_n + (k_{ip} + k_{rs}) \mu_1 R_n - \frac{1}{\tau} P_n + \frac{1}{2} k_{ic} \sum_{m=1}^{\infty} R_m R_{n-m} + k_x \lambda_0 \sum_{n=1}^{\infty} mf(m,n) P_m + (k_M + k_S) R_n, \tag{2.24}
\]

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

\[
\frac{d\Phi_N}{dt} = k_p M (\Phi_N - \Phi_n) - (k_M + k_S) \Phi_N - k_{id} \lambda_0 \Phi_n - k_{ic} \lambda_0 \Phi_n - k_{rs} \mu_1 \Phi_n \\
+ k_{trp} (n \lambda_0 \sum_{j=0}^{\infty} i^N P_{n,j} - \mu_1 \Phi_n) \tag{2.25}
\]

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

and

\[
\frac{d\Psi_N}{dt} = (k_M + k_S) \Phi_N + k_{id} \lambda_0 \Phi_N + \frac{1}{2} k_{ic} \sum_{m=1}^{\infty} \sum_{j=0}^{\infty} R_{m,j} R_{n-m,j-j} \\
+ (k_{trp} + k_{rs}) (\mu_1 \Phi_n - n \lambda_0 \Psi_n) \\
+ k_{rs} \sum_{i=0}^{\infty} i^N \sum_{j=\infty}^{\infty} \sum_{m=\infty}^{\infty} f(n,m) \beta(n,m,i,j) m P_{m,j} - \frac{1}{\tau} \Phi_N = 0, \tag{2.26}
\]

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

\[
\sum_{j=0}^{\infty} \sum_{m=1}^{\infty} \sum_{i=0}^{\infty} R_{m,j} R_{n-m,j-j} = 2 \sum_{m=1}^{\infty} \Phi_i R_m, \tag{2.27}
\]

\[
\sum_{j=0}^{\infty} \sum_{m=1}^{\infty} \sum_{i=0}^{\infty} R_{m,j} R_{n-m,j-j} = \sum_{m=1}^{\infty} \left( \Phi_i R_m + \Phi_m \Phi_i \right). \tag{2.28}
\]

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

\[
\sum_{j=0}^{\infty} \sum_{m=\infty}^{\infty} \sum_{n=\infty}^{\infty} f(n,m) h(n,m,i,j) m P_{m,j} = \sum_{n=\infty}^{\infty} f(n,m) n \Psi_m^i, \tag{2.29}
\]

\[
\sum_{j=0}^{\infty} \sum_{m=\infty}^{\infty} \sum_{n=\infty}^{\infty} f(n,m) h(n,m,i,j) m P_{m,j} = \sum_{n=\infty}^{\infty} f(n,m) \frac{1}{m-1} \left\{ n(n-1) \Psi_m^2 + n(m-n) \Psi_m^i \right\}, \tag{2.30}
\]
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 \( P \) 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 \( T_k^M(s) \):

\[
P(s) = \sum_{k=0}^{r_M} a_k^M T_k^M(s)
\]

(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):
\[ T^M_0 (s) = 1 \]
\[ T^M_1 (s) = \frac{2}{d_m} \left( s - L_M - \frac{d_M - 1}{2} \right) \]
\[ d_M = U_M - L_M + 1 \]
\[ T^M_k(s) = \frac{2k + 1}{k + 1} T^M_1(s) T^M_k(s) \quad k = 0 : r_M \]  

For a known distribution \( P(s) \), the values of the coefficients \( a^M_k \) 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:

\[ a^M_k = \frac{1}{\gamma^M_k} \sum_s P(s) w^M_s(s) T^M_k(s) \quad k = 0 : r_M \]  

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

\[ \left< T^M_k, T^M_l \right> = \frac{1}{\gamma^M_k} \sum_s T^M_k(s) T^M_l(s) = \gamma^M_k \delta_{k,l} \]  

The term \( w^M_s(s) \) 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 \( T^M_{n+1} \) 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:

\[ \lambda_0 = \sum_I \sum_s w^M(s) R(s) \quad I = 1 : M, \quad s = 1 : N \]  

\[ \mu_1 = \sum_I \sum_s w^M(s) s R(s) \quad I = 1 : M, \quad s = 1 : N \]  

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 $a^p_k$ for dead chains and $a^p_{kr}$ 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 $w_1 T_0(s_k)$ through $w_n T_0(s_k)$ and summing them up, yielding the first equation. Subsequently, they are multiplied with $w_1 T_0(s_k)$ through $w_n T_0(s_k)$, 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>$\frac{dP(s_i)}{dt} = f\left(P(s_i),R(s_i)\right)$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$w_2$</td>
<td>$\frac{dP(s_j)}{dt} = f\left(P(s_j),R(s_j)\right)$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$s_N$</td>
<td>$w_N$</td>
<td>$\frac{dP(s_n)}{dt} = f\left(R(s_n),P(s_n)\right)$</td>
</tr>
</tbody>
</table>

Table 2.1.a. 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>$T_0(s_1) \frac{da^p_1}{dt} + T_1(s_1) \frac{da^p_2}{dt} + \ldots + T_n(s_1) \frac{da^p_n}{dt} = a^p_{01} f^p_1 \left(T_1(s_1)\right) + \ldots + a^p_{0n} f^p_n \left(T_n(s_1)\right) + b_1$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$w_2$</td>
<td>$T_0(s_2) \frac{da^p_1}{dt} + T_1(s_2) \frac{da^p_2}{dt} + \ldots + T_n(s_2) \frac{da^p_n}{dt} = a^p_{01} f^p_1 \left(T_1(s_2)\right) + \ldots + a^p_{0n} f^p_n \left(T_n(s_2)\right) + b_2$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$s_N$</td>
<td>$w_N$</td>
<td>$T_0(s_N) \frac{da^p_1}{dt} + T_1(s_N) \frac{da^p_2}{dt} + \ldots + T_n(s_N) \frac{da^p_n}{dt} = a^p_{01} f^p_1 \left(T_1(s_N)\right) + \ldots + a^p_{0n} f^p_n \left(T_n(s_N)\right) + b_n$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$N$ (or $r+1$) PB equations after Gauss quadrature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_0 \frac{da^p_{t_0}}{dt} = a^p_{0t_0} A^p_{t_0} + a^p_{1t_0} A^p_{t_1} + \ldots + a^p_{rt_0} A^p_{t_r} + a^p_{0t_1} A^p_{t_0} + a^p_{1t_1} A^p_{t_1} + \ldots + a^p_{rt_1} A^p_{t_r} + b^p_{t_0}$</td>
</tr>
<tr>
<td>$\gamma_1 \frac{da^p_{t_1}}{dt} = a^p_{0t_1} A^p_{t_1} + a^p_{1t_1} A^p_{t_1} + a^p_{0t_1} A^p_{t_0} + a^p_{1t_1} A^p_{t_1} + a^p_{1t_1} A^p_{t_1} + \ldots + a^p_{rt_1} A^p_{t_r} + b^p_{t_1}$</td>
</tr>
<tr>
<td>...</td>
</tr>
</tbody>
</table>

Table 2.1.c. PBEs in Table 2.1.b 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:

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

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 $a^2_k$, while only the diagonal elements contain the normalization factor $\gamma_k$ as well. The latter originates from the $-k_p M R(s_j)$ 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 $-k_p M R(s_j - 1)$ 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>$dR(s_1)/dt = k_p M \left[R(s_1 - 1) - R(s_1)\right]$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$w_2$</td>
<td>$dR(s_2)/dt = k_p M \left[R(s_2 - 1) - R(s_2)\right]$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$s_N$</td>
<td>$w_N$</td>
<td>$dR(s_N)/dt = k_p M \left[R(s_N - 1) - R(s_N)\right]$</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>$T_0(s_1)\frac{da^2_1}{dt} + T_1(s_1)\frac{da^2_1}{dt} + ... + T_j(s_1)\frac{da^2_1}{dt} = k_p M \left[T_0(s_1 - 1) - T_0(s_1)\right]a^2_1 + ... + k_p M \left[T_j(s_1 - 1) - T_j(s_1)\right]a^2_1$</td>
</tr>
<tr>
<td>$s_2$</td>
<td>$w_2$</td>
<td>$T_0(s_2)\frac{da^2_1}{dt} + T_1(s_2)\frac{da^2_1}{dt} + ... + T_j(s_2)\frac{da^2_1}{dt} = k_p M \left[T_0(s_2 - 1) - T_0(s_2)\right]a^2_1 + ... + k_p M \left[T_j(s_2 - 1) - T_j(s_2)\right]a^2_1$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$s_N$</td>
<td>$w_N$</td>
<td>$T_0(s_N)\frac{da^2_1}{dt} + T_1(s_N)\frac{da^2_1}{dt} + ... + T_j(s_N)\frac{da^2_1}{dt} = k_p M \left[T_0(s_N - 1) - T_0(s_N)\right]a^2_1 + ... + k_p M \left[T_j(s_N - 1) - T_j(s_N)\right]a^2_1$</td>
</tr>
</tbody>
</table>

Table 2.2b. Result of propagation equations after substitution of $R(s)$ by Chebyshev polynomials.
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 $k^h$ order Chebyshev polynomials (according to the Gauss quadrature), it appears on the $k^h$ line of $A'$. As well as, element $A_{ij}^{RP}$ after being multiplied with coefficient $a_i$ appears in the $l^h$ 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 ‘$R_1 \rightarrow P_1$’ 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 ‘$P_1 \rightarrow P_1$’, which is positioned on the same lines as the ‘$R_1 \rightarrow P_1$’ 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): $a_0^a, a_1^a, \ldots, a_n^a, a_{n+1}^a, \ldots, a_i^a$. Finally, the elements $b_0$ through $b_i$, 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.

![Matrix Representation of PBEs](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 \( 10^5 \)), 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, \( n > m \); for \( \delta \) different fragment lengths, \( m \) (from 1 to \( 10^4 \)). The multiplication factor has values both lower and higher than \( \ell \). The factor decreases sharply for long fragments. The factor has high values for contributions from long chains to short fragments, up to \( 10^5 \).

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 \( n \geq m + 1 \). 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 \( R(s_k)R(s_k-s_i) \) has to be made, where \( s_i \) is a ‘regular’ node from the aforementioned series, but \( s_k-s_i \) is a new complementary node. The concentration at this new node \( R(s_k-s_i) \) has to be calculated from the proper set of coefficients and Chebyshev polynomials belonging to the interval on which \( s_k-s_i \) 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 \( s_i - s_k \). 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 thus 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: Convolution matrix with $j = 2:s$ 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 $s$).](image)

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 \( \Psi_n^1, \Phi_n^1 \) and \( \Psi_n^2, \Phi_n^2 \), give rise to similar \( \mathbf{A} \)-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 \( \Psi_n^1, \Phi_n^1 \) appear in the equations for \( \Psi_n^2 \) and \( \Phi_n^2 \). These parts lead to the lower-left elements in Figure 2.8.

![Figure 2.8. Structure of the \( \mathbf{A} \)-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 \( ktp/k_p \) 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 Hoefsloot (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>Arhenius expression</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propagation</td>
<td>$k_p$</td>
<td>$k_p^0 = 1.88 \times 10^7 \exp \left( \frac{-4125 + 0.324 P}{T} \right)$</td>
<td>m$^{-3}$/(kmole.s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_p = k_p^0 / \left( 1 + \frac{k_p^0}{1.13 \times 10^{-1} \eta} \right)$</td>
<td></td>
</tr>
<tr>
<td>Termination</td>
<td>$k_{tc}$</td>
<td>$k_{tc}^0 = 8.11 \times 10^6 \exp \left( \frac{-553.26 - 0.19 P}{T} \right)$</td>
<td>m$^{-3}$/(kmole.s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\eta = 10^{0.17 \times (4.57 / T)}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{tc} = k_{tc}^0 \left( 1 + \frac{1}{\eta} + 8.04 \times 10^{-6} (1 - x) \kappa \right)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{tc} = 3.21 \exp \left( \frac{150.10 - 0.1086 P}{T} \right)$</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>m$^{-3}$/(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>m$^{-3}$/(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>m$^{-3}$/(kmole.s)</td>
</tr>
<tr>
<td>Scission</td>
<td>$k_{ss}$</td>
<td>$3.73 \times 10^4 \exp \left( \frac{-6357 - 0.0869 P}{T} \right)$</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 MIFD (from Busch, 2001a, 2001b). The reaction rate constants are based on $k = k_0 \exp (\beta + AV/P/RT)$.

<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>$0.3 \times 10^{-3}$ m$^3$</td>
</tr>
<tr>
<td>Feed condition</td>
<td>16.75 kmole/m$^3$</td>
</tr>
<tr>
<td>Monomer</td>
<td>16.75 kmole/m$^3$</td>
</tr>
<tr>
<td>Chain transfer agent</td>
<td>$1.00 \times 10^{-2}$ kmole/m$^3$</td>
</tr>
<tr>
<td>Initiator</td>
<td>$3.50 \times 10^{-3}$ kmole/m$^3$</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:

$$F(\theta) = \exp(-\theta), \quad \theta = \tau / \overline{\tau}$$  \hspace{1cm} (2.38)

Here, $\theta$ denotes the reduced residence time and $\overline{\tau}$ 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 $\theta_p$ 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:

$$\bar{n} = k_p \lambda_0 \left\{ (k_c + k_d) \lambda_0 + k_r u_1 + k_r' u_1 \right\}$$

(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’, $\rho_s(\theta)$:

$$\bar{n}_s(\theta) = \frac{1}{\rho_s(\theta)} = \frac{1}{\rho_s' \theta} = \frac{k_p(1-x)}{k_r x \theta}$$

(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, $CP_{r,s}(\theta_1 | \theta_0)$ is a uniform distribution, hence $\theta_1$ is an arbitrary time in that interval calculated by multiplying $\theta_1$ 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:

$$P_s = k_r u_1 \left\{ (k_c + k_d) \lambda_0 + k_r u_1 + k_r' u_1 \right\}$$

(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:

$$CP_{r,s}(\theta_2 | \theta_0) = \frac{1 - F(\theta_2)}{1 - F(\theta_0)}$$

(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:

\[
P_c = \frac{k_{ic}\lambda_0}{\{(k_{ic} + k_{im})\lambda_0 + k_{rs}\mu_1 + k_{rp}\mu_1\}}
\]  

(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:

\[
P_b = \frac{k_{rp}\mu_1}{\{(k_{ic} + k_{im})\lambda_0 + k_{rs}\mu_1 + k_{rp}\mu_1\}}
\]  

(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’ \(\rho_b(\theta)\) and length of each of the segments individually, where:

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

(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 \((k_{ad}/k_p = 2000)\) and high transfer to polymer rate \((k_{tp}/k_p = 0.0032)\), the second is with combination \((k_{ad}/k_p = k_{ic}/k_p = 1000)\) and lower \(k_p\) \((k_{tp}/k_p = 0.0006)\).

<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 of PE.
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: $s = i(n)$, where $i(n)$ is the average number of branch points at length $n$, equal to $\left( \Psi_n^1 + \Phi_n^1 \right)/\left( P_n + R_n \right)$. 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 $10^7$. 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](image.png)

Figure 2.10. Dead chain distributions for linear and topological scission from old and new model. Scission parameters: linear scission, $k_{rs} = 2 \text{ m}^3/(\text{kmole.s})$; topological scission, $k_{rs} = 30 \text{ m}^3/(\text{kmole.s})$, segment length $\sigma = \bar{T}(n)/n$. 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 $nP_c$. 
Figure 2.11. Average number of branch points, $\mathcal{T}(n) = \left(\Psi^1_n + \Psi^1_n\right) \left(\beta_n + \beta_n\right)$, 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, $\mathcal{T}(n) / n$, 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, $k_p/k_s = 0.0032$, 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.
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-MALS (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 ($k_{rs}/k_p = 1.6 \times 10^{-5}$); $k_p = 5000 \text{m}^{-1} \text{kmole}^{-1} \text{s}^{-1}$; conversion $x = 0.456$; $M_w = 36.75 \text{kmole/m}^3$; $\lambda_0 = 5.59 \times 10^{-6} \text{kmole/m}^3$.

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.
3 Modeling of molecular weight/branching distributions; under gel conditions and allowing for multiradicals

A population balance model for the prediction of Molecular Weight Distribution (MWD) in a Continuous Stirred Tank Reactor (CSTR) has been developed accounting for multiradicals and gel formation in the framework of Galerkin-Finite Element Method (FEM). In the absence of combination, gel does not form, but accounting for multiradicals leads to a better prediction of the long MWD tail. Results of the multiradical model with topological scission are well in line with Monte Carlo (MC) simulations. For the case of combination without scission the multiradical model leads to a perfect agreement with MC simulations as regards prediction of the gel fraction and chain length distribution. The classical monoradical model fails to describe the gel regime. Gel fragmentation is accounted in systems with gelation and scission. Results for this case are in agreement with MC simulations. A non-gel assuming variant allows properly detecting the gelpoint and the associated distribution. The scission model adopted, linear or topological scission, turns out to be of extreme importance for the gel regime prediction.

3.1 Introduction

In industrial processes, fouling in low-density Polyethylene (ldPE) reactors is usually attributed to gelation (Schmidt and Harmon ray, 1981; Spivey et al., 2012; Zacca, Debling, 2001), and is an undesired consequence of certain process conditions. Up until now, mathematical ldPE modeling studies of MWD have only aimed to analyze the common bimodality, without accordingly taking the gel formation possibilities and the effect of multiradicals into account. In this context, former mono-radical assumption based models have reported the typical shoulder of the ldPE molecular weight distribution with ignoring the eventual gelation prospects (Kim et al., 2004).

The very first studies of gelation date back to 1940s (Flory, 1941a, 1941b, 1941c, 1942; Stockmayer, 1943, 1944). Later, statistical methods based on simplified kinetics were used to predict the gelation behavior from branching probability factor. These models were able to find the gelation mechanism in free radical polymerization systems and to calculate the gel point (Zhu and Hamielec, 1992, 1993, 1994; Zhu, 1996; Tobita and Hamielec, 1989; Tobita, 1993; Mikos et al. 1986; Mullikin and Mortimer, 1970; Beasley, 1953; Bamford and Tompa, 1953; Nicolas, 1958; Small, 1972).

This chapter is based on N. Yaghini, P. D. Iedema, Macromolecules (2014), 47 (15) 4851-4863
According to several studies on gelation, radical polymerization will never lead to gel formation in the presence of transfer to polymer and termination by combination only (Zhu and Hamielec, 1993, 1994; Zhu, 1996; Tobita, 1993; Tobita and Zhu, 1996; Tobita, 1994, 1998b; Dias and Costa, 2003; Wulkow, 1996), but with termination by combination gel would form. Gelation in radical polymerization has been earlier studied in a population balance modeling framework by introducing explicit gel moments for living and dead chains (Iedema and Hoefsloot, 2002).

Gel formation problem is also described by multiradicals existence. This problem has been addressed for CSTR radical polymerization with transfer to polymer and termination by disproportionation without scission and combination reactions by Iedema and Hoefsloot (2004b). They reported the presence of multiradicals as a big issue even without termination by combination, which could be studied with the multiradical model.

In this chapter, for the first time the possible occurrence and the implications of multiradicals and gelation are discussed for the ldPE polymerization process circumstances. Similar to the previous chapter pseudo-distributions are employed, this time to compute the moments of multiradicals. In the context of modeling full distributions, it is shown that assuming the overall moments of the general model to include gel formation is indeed an effective manner in dealing with gel and is equivalent to the treatment of gel in MC simulations. In both model types, MC and deterministic, this treatment of gel implies that reactive groups in sol and gel (radical sites and backbone monomer units) are chemically behaving identically. The multiradical model did not reproduce the bimodal shape of the ldPE molecular weight distribution predicted by mono-radical model, which is confirmed by MC simulations of the system.

3.2 Multiradical pseudo-distribution model with linear and topological scission

3.2.1 Formulation of reaction and population balance equations

The reaction equations and the population balances are formulated in two dimensions: chain length and number of radical sites. Since some branching issues will be addressed, in principle a 3-dimensional formulation is required. However, as it will be shown in the paragraph on gelation, in the case where branching is discussed the classical mono-radical model yields the same results as the multiradical model. Therefore, the branching pseudodistribution equations derived before, based on the mono-radical model by Kim et al. (2004) have been utilized to study that case.

Dissociation of initiator and initiation:

\[ I_2 \xrightarrow{k_i} 2I \bullet \]  
\[ I \bullet + M \xrightarrow{k_i} R_{1,1} \] \hspace{1cm} (3.1)

Propagation

\[ R_{n,i} + M \xrightarrow{k_{pi}} R_{n+1,i} \] \hspace{1cm} (3.2)

Termination by disproportionation

\[ R_{n,i} + R_{m,j} \xrightarrow{k_{ij}} R_{n,j-1} + R_{m,j-1} \] \hspace{1cm} (3.3)
Termiination by combination

\[ R_{n,i} + R_{m,j} \xrightarrow{k_{ij}} R_{n+m,i+j-2} \]  
(3.4)

Transfer to polymer

\[ R_{n,i} + R_{m,j} \xrightarrow{k_{in}} R_{n,i+1} + R_{m,j-1} \]  
(3.5)

Random scission

\[ R_{n,i} + R_{m,j} \xrightarrow{\lambda R m} R_{n-k,i-p+1} + R_{k,p} + R_{m,j-1} \]  
(3.6)

Note that one of the fragments in Equation 3.6 has an extra radical site. The function \( f(n,k) \) denotes the fragment length distribution of scission fragments resulting from random scission.

With these reaction equations the initiator and initiator radical balances and the overall population balance equation in two dimensions, chain length and number of radical sites for an ideally mixed CSTR are obtained. The conditions of a CSTR are the most expected representative of an LDPE autoclave reactor, although non-ideal mixing effects might influence the final MWD. In the forthcoming chapter the results of the multiradical approach for a series of CSTRs and a tubular reactor are presented.

\[
\frac{dI_2}{dt} = -2k_dI_2 + \frac{1}{r}(I_0 - I_2) = 0 \]  
(3.7)

\[
\frac{dI}{dt} = 2k_dI_2 - k_i MI \bullet + \frac{1}{r}I_\bullet = 0 \]  
(3.8)

\[
\frac{dM}{dt} = -k_p\lambda_{01} - k_i MI \bullet + \frac{1}{r}(M_0 - M) = 0 \]  
(3.9)

\[
\frac{dR_{1,0}}{dt} = k_d\lambda_{01}R_{1,1} + k_p\lambda_{01}R_{1,1} + k_r\lambda_{1,0}R_{1,1} - \frac{1}{r}R_{1,0} \]

\[
\frac{dR_{n,0}}{dt} = k_d\lambda_{01}R_{n,1} + \frac{1}{2}k_n \sum_{m=1}^{n-1} R_{m,1}R_{n-m,1} + k_p\lambda_{1,0}R_{n,1} + k_r\lambda_{1,0}R_{n,1} - \frac{1}{r}R_{n,0}, \quad n \geq 2 \]  
(3.10)

\[
\frac{dR_{1,1}}{dt} = k_i MI \bullet - k_d\lambda_{01}R_{1,1} - k_p\lambda_{1,0}R_{1,1} - k_r\lambda_{1,0}R_{1,1} - \frac{1}{r}R_{1,1} \]

\[
\frac{dR_{n,i}}{dt} = k_p M \left\{ -iR_{n,i} + (i+1)R_{n-1,i+1} \right\} + k_d\lambda_{01} \left\{ (i+1)R_{n,i+1} - iR_{n,i} \right\} + \]  
(3.10)

\[
\frac{1}{2}k_c \sum_{j=1}^{n-1} \sum_{m=1}^{n-1} j(i-j+2)R_{m,j}R_{n-m,j+1} + \]  
(3.10)

\[
k_p \left\{ \lambda_{01}nR_{n,i+1} + \lambda_{01}(i+1)R_{n,i+1} - \lambda_{01}nR_{n,i} - \lambda_{01}iR_{n,i} \right\} + \]

\[
k_r \left\{ \lambda_{01}R_{n,i} + \lambda_{10}(i+1)R_{n,i+1} - \lambda_{10}nR_{n,i} - \lambda_{10}iR_{n,i} \right\} - \frac{1}{r}R_{n,i}, \quad n \geq 2, i \geq 1 \]

The total moments are defined as:

\[
\lambda_{10} = \sum_{n=1}^{\infty} \sum_{i=0}^{\infty} R_{n,i}; \quad \lambda_{01} = \sum_{n=1}^{\infty} \sum_{i=0}^{\infty} iR_{n,i} \]  
(3.11)

\( I_0 \) and \( M_0 \) represent the feed concentrations of initiator and monomer. In Equations 3.10
\( R^{\text{frag}}(n,i) \) denotes the contribution to the population balance of the scission fragments from the random scission reaction. The general expression for this term is:

\[
R^{\text{frag}}(n,i) = \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left\{ mf(n,m) \beta(n,i,m,j) \right\} R_{m,j} \\
R^{\text{frag}}(n,i) = \\
\sum_{m=n+1}^{\infty} \left\{ \frac{mf(n,m)}{i + 1} \right\} R_{m,j} + 2 \sum_{j=i}^{\infty} \left\{ mf(n,m) \beta(n,i,m,j) \right\} R_{m,j} \\
(3.12)
\]

In the fragment length distribution function \( f(n,m) \), \( n \) is fragment length and \( m \) chain length before scission. It equals \( 1/(m-1) \) for linear scission, and for topological scission it is given by the empirical equation (Kim et al., 2004):

\[
f(n,m) = \frac{1}{(2\bar{s}(n) + m)^2 + (2\bar{s}(n) + n - m)^2} \\
\frac{1}{\bar{s}} - \frac{1}{2} \frac{n + \bar{s}}{(2\bar{s}(n) + n)^2} - \frac{1}{(2\bar{s}(n))^2} \\
(3.13)
\]

Here, \( \bar{s}(m) \) represents the average length of a segment between two branch points for a branched molecule of size \( m \), calculated as \( 1/\rho_s(m) \), where \( \rho_s \) is the branching density. The function \( \beta(n,i,m,j) \) represents a model of the manner in which the radical sites are redistributed among the scission fragments. It represents the probability that \( j \) radical sites are found on a scission fragment of length \( m \), if \( n \) is the original chain length, and \( i \) is the number of radical sites on the original chain. A similar approach has been followed here as in Iedema and Hoefsloot (2001b) for the redistribution of branch points on scission fragments. The assumption that the number of radical sites on the fragments is independent of the size of the fragments corresponds to:

\[
\beta(i) = 1/(i + 1) \\
(3.14)
\]

It is more realistic to assume that the number of radical sites is higher on larger fragments. In fact, assuming that each monomer unit in a molecule has equal probability of undergoing a transfer to polymer reaction and thereby becoming a secondary radical site, the redistribution function should obey a hypergeometric distribution:

\[
\beta(n,i,m,j) = p^H(j \mid n,i,m) = \binom{i}{j} \binom{n - i}{m - j} / \binom{n}{m} \\
(3.15)
\]

Note that the average number of radical sites on a fragment of length \( m \) coming from a chain of length \( n \) with \( i \) radical sites equals \( im/n \), since the first radical site moment of the hypergeometric function is given by:
\[
\sum_{j=0}^{i} j p^H(j \mid n,i,m) = \frac{im}{n}
\]  

(3.16)

The two terms in the summation over \( m \) term of Equation 3.12 \((i > 0)\) originate from two different scission contributions to the population balance. The first reflects the fact that upon scission of a chain two fragments are created, of which one possesses an extra radical site. The second contribution describes the redistribution of radical sites on the fragments and consequently it contains the redistribution function \( \beta(n,i,m,j) \), whereas the first does not.

The simplest form the fragment contribution in the population balance assumes is obtained for linear scission and fragment size independent redistribution:

\[
R_{\text{frag}}^{n,i} = \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left( \frac{1}{j+1} \right) R_{m,j}^{i} \quad i = 0
\]

\[
R_{\text{frag}}^{n,i} = \sum_{m=n+1}^{\infty} \left[ \left( \frac{1}{i+1} \right) R_{m,j}^{i} + 2 \sum_{j=i}^{\infty} \left( \frac{1}{j+1} \right) R_{m,j}^{i} \right] \quad i > 0
\]

(3.17)

For linear scission and radical site redistribution obeying the hypergeometric function, we have:

\[
R_{\text{frag}}^{n,i} = \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} p^H(j \mid n,i,m) R_{m,j}^{i} \quad i = 0
\]

\[
R_{\text{frag}}^{n,i} = \sum_{m=n+1}^{\infty} \left[ \left( \frac{1}{i+1} \right) R_{m,j}^{i} + \sum_{j=i}^{\infty} p^H(j \mid n,i,m) R_{m,j}^{i} \right] \quad i > 0
\]

(3.18)

In the most comprehensive form including topological scission with the fragment length distribution as a function of fragment \((m)\) and chain length \((n)\) we have:

\[
R_{\text{frag}}^{n,i} = \sum_{m=n+1}^{\infty} \frac{m}{m} f(n,m) \sum_{j=0}^{\infty} p^H(j \mid n,i,m) R_{m,j}^{i} \quad i = 0
\]

\[
R_{\text{frag}}^{n,i} = \sum_{m=n+1}^{\infty} f(n,m) \left[ \left( \frac{1}{i+1} \right) R_{m,j}^{i} + \sum_{j=i}^{\infty} p^H(j \mid n,i,m) R_{m,j}^{i} \right] \quad i > 0
\]

(3.19)

The 2-dimensional population balance will be solved using the pseudo-distribution approach and applying it to the distribution of radical sites. As in Iedema and Hoefsloot (2004b) this involves taking the summation over the number of radical sites. The radical site moments are defined as:

\[
R_n = \sum_{i=0}^{\infty} R_{n,i}, \quad \Phi_{n}^{1} = \sum_{i=0}^{\infty} i R_{n,i}, \quad \Phi_{n}^{2} = \sum_{i=0}^{\infty} i^2 R_{n,i}
\]  

(3.20)
Note that physically $R_n$ and $\Phi_n^1$ represent the total concentration of polymer chains of length $n$ and the total concentration of radical sites on chains with length $n$, respectively.

Furthermore, we have:

$$\lambda_{01} = \sum_{n=1}^{\infty} \Phi_n^1$$  \hspace{1cm} (3.21)

Performing the summation over $i$ for the 0th radical sites moment yields the balance for $R_n$:

$$\frac{dR_n}{dt} = k_i M \Phi_i^1 - k_p M \Phi_n^1 - \frac{1}{\tau} R_n$$

$$\frac{dR_n}{dt} = k_p M (\Phi_n^1 - \Phi_n^0) + k_n \left[ \frac{1}{2} \sum_{m=1}^{n-1} \Phi_m^1 \Phi_{n-m}^1 - \lambda_{01} \Phi_n^1 \right] +$$

$$k_{rs} \lambda_{01} \left( 2 \sum_{n=1}^{\infty} f(n, m) mR_m - nR_n \right) - \frac{1}{\tau} R_n \quad n \geq 2$$  \hspace{1cm} (3.22)

The first radical site moment distribution follows after multiplying the 2-Dimensional (2D) population balance by $i$, and subsequently summing over $i$:

$$\frac{d\Phi_i^1}{dt} = k_i M \Phi_i^1 - k_p M \Phi_i^1 - \frac{1}{\tau} \Phi_i^1$$

$$\frac{d\Phi_n^1}{dt} = k_p M (\Phi_n^1 - \Phi_n^0) - k_n \lambda_{01} \Phi_n^1 +$$

$$k_n \left( \sum_{m=1}^{n-1} (\Phi_m^1 \Phi_{n-m}^1 - \Phi_m^0 \Phi_{n-m}^0) - \lambda_{01} \Phi_n^1 \right) +$$

$$k_{ip} \lambda_{01} \left( 2 \sum_{n=1}^{\infty} f(n, m) (R_m + \frac{2m}{n} \Phi_m^1) - \lambda_{01} n \Phi_n^1 - \lambda_{01} \Phi_n^1 \right) - \frac{1}{\tau} \Phi_n^1 \quad n \geq 2$$  \hspace{1cm} (3.23)

These expressions are valid for topological scission with fragment length distribution $f(n, m)$; for linear scission the factor $m * f(n, m)$ equals 1. It is obvious that this set leads to a closure problem, since the lower radical site moments are expressed in moments one higher. This problem is solved in the same manner as in Iedema and Hoefsloot (2004b) by assuming that the radical site distribution for a given chain length, $n$, obeys a binomial distribution. Thus, for the second radical site moment, $\Phi_n^2$:

$$\Phi_n^2 = (1 + \rho_{RS} n - \rho_{RS}) \rho_{RS} n$$  \hspace{1cm} (3.24)

With $\rho_{RS}$ the radical site ‘density’ defined as:

$$\rho_{RS} = \Phi_n^1 / (nR_n)$$  \hspace{1cm} (3.25)
It is evident that applying this closure relationship introduces an additional non-linearity, apart from the combination term, into the system.

### 3.2.2 Validity of the model in the gel regime

The simplest manner of addressing gel is assuming that its reactive groups in the gel behave in an identical way as these groups in the sol molecules. The calculation of gel fraction and properties under this assumption has been performed using Monte Carlo sampling by Tobita (1993, 1994, 1998b), and Tobita and Zhu (1996). Note that this sampling method essentially deals with units ('primary polymers') that may connect with other units according to probabilities that are indeed independent of the size of the molecule, be it sol or gel, of which they make part. Obviously, in reality the assumption of equal behavior of all groups is not valid, for instance since some reactive groups in the large gel molecule might be less accessible to other groups. However, assuming equal behavior in sol and gel in Monte Carlo simulations and in the proposed model for this reason is expected to lead to identical results.

In the present system the reactive groups involved are the radical sites and the monomer units in the polymer. The total amount of radicals in sol and gel are defined as \( \lambda_0^* \) and the total amount of monomer units in the polymer material in sol and gel as \( \lambda_1^* \). By replacing \( \lambda_0 \) and \( \lambda_1 \) in the population balance equations, Equations 3.22 and 3.23 by \( \lambda_0^* \) and \( \lambda_1^* \), respectively, and realizing that they might be larger than just the moments as defined in Equation 3.11, equations that are in principle able to cover the gel regime are obtained.

Note that the possibility of gel implies the following conditions:

\[
\begin{align*}
\lambda_0^* &\geq \lambda_{0l} = \sum_{n=1}^{\infty} \Phi_n^1, \\
\lambda_1^* &\geq \lambda_{10} = \sum_{n=1}^{\infty} nR_n
\end{align*}
\]  

(3.26)

The values of \( \lambda_0^* \) and \( \lambda_1^* \) are obtained by solving balances describing the creation and termination of radical sites:

\[
\begin{align*}
\frac{d\lambda_0^*}{dt} &= k_iM - (k_{id} + k_{tc})\left(\lambda_0^*\right)^2 - \frac{1}{r}\lambda_0^* = 0 \\
\lambda_1^* &= M_0 - M
\end{align*}
\]  

(3.27)

(3.28)

The use of \( \lambda_0^* \) and \( \lambda_1^* \) in Equations 3.22 and 3.23 reflects the notion that all the radical sites in the system, in sol and gel, react with the monomer units of the chains in the sol, with concentration distribution \( R_n \), and that all the monomer units react with radicals in the sol, with concentration distribution \( \Phi_n^1 \). It is evident that the inequalities, Equation 3.26, imply a 'deficit' in both radical sites and monomer units: the distributions of chains in the sol amount to less than what would follow from the balance Equations 3.22 and 3.23. Wattis et al. (2004) has discussed this deficit in the context of gel formation. At present, the idea that what is a deficit in the sol has been transferred to gel has been adopted.
Now, if scission occurs, an interesting problem arises regarding the interaction between sol and gel groups. The fact that both sol and gel radical sites, represented by $\lambda_0^*$, initiate the scission reaction taking place at any backbone unit, represented by $\lambda_1^*$, is correctly accounted for. However, it should be realized that both sol and gel produce scission fragments. The sol fragment production terms in the population balance are described by the linear and topological scission (Equation 3.13) models. Since the fragment length distribution functions for linear and topological scission contain the length of the chain before scission, it seems beforehand to consider these in the gel condition implying that this length goes to infinity, $m \to \infty$. For linear scission, independent of fragment length, the fragment length distribution equals $f(m,n) = 1/m$, which approaches zero as $m \to \infty$. However, in the population balance for $R_n$, Equation 3.22, in the summation over $m = n : \infty$, it is multiplied with $mR(m)$, so that we end up with the summation of $R(m)$ as $m \to \infty$. Obviously, this term would vanish as the concentration of the gel, expressed as the number of molecules per unit volume, goes to zero. In other words, the linear scission model does not allow accounting for a contribution of scission fragments from gel. In Section 3.3, the consequences of this situation are explored.

For topological scission the situation is different. We have to consider the fragment distribution, Equation 3.13, for $m \to \infty$. First, we note that the parameter $s(m)$, equal to $1/(2\rho_b m)$, in the ldPE system approaches a constant value as $m$ becomes larger, since the branching density does so (see e.g. branching density plots in Kim and Iedema (2008)). If we denote this asymptotic value by $s_\infty$, then the fragment length function for $m \to \infty$ becomes:

$$f(m \to \infty, n) = \frac{1}{(2s_\infty + n)^2} \left\{ \frac{1}{s_\infty} - \frac{1}{(2s_\infty)^2} \right\}$$

(3.29)

It is obvious that this expression no longer contains the size before scission $m$; hence $m$ is no longer present in the summation over $m$ in the population balance, Equation 3.22:

$$\sum_{m \to \infty} f(m,n)mR_m = \frac{1}{(2s_\infty + n)^2} \left\{ \frac{1}{s_\infty} - \frac{1}{(2s_\infty)^2} \right\} \sum_{m \to \infty} mR_m$$

(3.30)

In Equation 3.30 the remaining summation term evidently represents the number of monomer units in the gel, in agreement with Equation 3.26 equal to the difference $\lambda_1^* - \lambda_0^*$. Thus, we see that the fragment length expression leads to an elegant and mathematically sound expression for the contribution of fragments from the gel. Equation 3.30 has been added to the population balance equation, Equation 3.22, allowing gel formation and fragmentation becomes:
\[
\frac{dR_n}{dt} = k_p M (\Phi_{n-1} - \Phi_n^1) + k_{tc} \left[ \frac{1}{2} \sum_{m=1}^{n-1} \Phi_m^1 \Phi_{n-m}^1 - \lambda_{01} \Phi_n^1 \right] + k_{rs} \lambda_{01} \left( \frac{2}{(2s_\infty + n)^2} \right) \left[ \frac{1}{s_\infty} - \frac{1}{(2s_\infty)^2} \right] \left( \lambda_{10}^\Phi - \lambda_{10} \right) + 2 \sum_{m=n+1}^{\infty} f(m,n) m R_m - n R_n - \frac{1}{\tau} R_n
\]

(3.31)

Here, the summation term present in the contribution from scission denotes the first moment of the sol distribution \( R_n \), summed up over molecules of all lengths, corrected for the fragment length distribution \( f(m,n) \). Note finally that in the population balance for \( \Phi_n^i \) the gel fragmentation terms would vanish.

### 3.2.3 Model implementation

The model equations have been implemented in MATLAB® using a Galerkin numerical scheme comparable to the algorithm underlying the software package PREDICI® (Wulkow, 2008). As explained in the previous chapter, this requires the transformation of a set of population balance equations by a Gaussian quadrature operation to a set of differential equations. In the linear steady-state case, the solution of the linear set of equations is obtained as the coefficients \( a_i \) from:

\[
A a = b
\]

(3.32)

These coefficients are employed to represent the distributions using Chebyshev polynomials on chain length intervals up to a maximum chosen at a sufficiently high value; such that the second moment of the distribution is no longer affected by it (Wulkow, 2008). The block structure of matrix \( A \) is depicted in Figure 3.1. The vector \( b \) represents a vector of known numbers (Wulkow, 2008). In matrix \( A \), the 1\(^{st}\) moment contribution to the 0\(^{th}\) moment (Equation 3.22) is situated in the right-upper corner of the plot. The 2\(^{nd}\) moment contribution is calculated from Equation 3.23, and appears as a contribution to the right-hand side of the linear set of equations.

![Block structure of matrix A](image)

**Figure 3.1.** Block structure of matrix \( A \).

### 3.2.4 Monte Carlo simulations

A Monte Carlo sampling model has been employed as a reference to compare the results of the newly developed deterministic model. This model has been developed by Tobita (2001b),
and has been extended to series of CSTR (Tobita, 2014). An extensive description of the principles of this model may be found in these references. In the simulations transfer to polymer to propagation and random scission to propagation ratio’s, $k_{tp}/k_p$ and $k_{rs}/k_p$, are varied. This corresponds to changes in the specific MC parameters describing branching and scission (Tobita, 2014):

$$P_b = \frac{k_{tp}\lambda_1^*}{\left\{ (k_{tc} + k_{td})\lambda_0^* + k_{rs}\lambda_1^* + k_{tp}\lambda_1^* \right\}}$$

(3.33)

$$\rho_b(\theta) = \frac{\rho_b x \theta}{k_p (1 - x)}$$

(3.34)

$$P_s = \frac{k_{rs}\lambda_1^*}{\left\{ (k_{tc} + k_{td})\lambda_0^* + k_{rs}\lambda_1^* + k_{tp}\lambda_1^* \right\}}$$

(3.35)

$$\frac{1}{\rho_s(\theta)} = \frac{1}{\rho_s x \theta} = \frac{k_p (1 - x)}{k_{rs} x \theta}$$

(3.36)

The values of these parameters are given in the captions.

Referring to the aforementioned extensive descriptions only the manner has been discussed here, in which the production of scission fragments from gel is implicitly accounted for in the MC simulations. We may realize from Tobita (2001b) that the linear primary polymers may consist of several scission fragments that have grown and undergone scission with various residence times. In this procedure certain scission points are identified as the starting point for the growth of a new segment with a certain residence time. Such a scission event would have taken place on a second primary polymer with a longer residence time; thus the two segments become connected through a scission point. Then, with probability $1/2$ the second segment is identified as the head of the primary polymer before scission, or with the same probability as its tail. Now, in the case gel is present, the tails may originate both from sol and gel – the latter with a probability equal to the gel fraction. Thus, the transfer of scission fragments from gel to sol is implicitly, but properly accounted for.

### 3.3 Results

Calculations have been carried with various models for values of kinetic parameters, concentrations and reactor conditions as listed in Table 3.1. Eventual modifications in these values are mentioned in the captions to the figures showing results of the calculations.
<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
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<td>1/s</td>
</tr>
<tr>
<td>Initiation rate constant</td>
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<td>m$^3$/kmole.s</td>
</tr>
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<td>Propagation rate constant</td>
<td>$k_p$</td>
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</tr>
<tr>
<td>Termination by combination and disproportionation rate</td>
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<td>m$^3$/kmole.s</td>
</tr>
<tr>
<td>CSTR residence time</td>
<td>$\tau$</td>
<td>30</td>
<td>s</td>
</tr>
<tr>
<td>Feed concentration monomer</td>
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<td>kmole/m$^3$</td>
</tr>
<tr>
<td>Feed concentration initiator</td>
<td>$I_{20}$</td>
<td>$5 \times 10^{-3}$</td>
<td>kmole/m$^3$</td>
</tr>
</tbody>
</table>

Table 3.1. Parameters used in calculations.

### 3.3.1 Termination by disproportionation only

#### 3.3.1.1 Effect of scission

In the case of termination by disproportionation only, the present system of radical polymerization with transfer to polymer is not expected to lead to gelation. This has been confirmed (Iedema and Hoefsloot, 2004b), by a version of the multiradical model described above using the standard reaction steps of PREDICI®. Scission was assumed to be absent. We observed that the multiradical model yielded perfect agreement with Monte Carlo simulations up to chain lengths of $10^8$, whereas the classical monoradical model failed to describe the extremely long tail of this example. This result is shown in Figure 3 of the Reference (Iedema and Hoefsloot, 2004b).

In the present study, results of the multiradical model are shown accounting for random scission and again comparing to the results from Monte Carlo simulations. In a previous article (Kim et al., 2004), it has been shown that topological scission leads to better agreement with MC results than linear scission – typically yielding bimodal distribution shapes. However, still a discrepancy was observed in the tail of the distributions that turned out to be more extended according to the MC simulations. Hence, here it is checked whether multiradicals might be responsible for this discrepancy. The result is shown in Figure 3.2 for the same case as in Kim et al. (2004) of strong branching ($k_{tp}/k_p = 0.0032$) and mild scission ($k_{rs}/k_p = 1.6 \times 10^{-5}$). One observes a significantly better agreement with the MC simulations – perfect coincidence is seen – where the monoradical model deviates. Thus, we can conclude that multiradicals do play an important role.

![Figure 3.2. Termination by disproportionation only, strong branching ($k_{tp}/k_p = 0.0032$) and mild scission ($k_{rs}/k_p = 1.6 \times 10^{-5}$). Perfect agreement between multiradical model and MC simulations. Further kinetic data: $k_d/k_i = 2000$; $k_o = 0$; conversion $x = 0.456$; $k_{td}/k_p = 2000$; branching parameters: $\rho_b = 0.0027$; $P_b = 0.684$; branch parameters: $\rho_b = 1.34 \times 10^{-3}$, $P_b = 0.0034$.](image-url)
3.3.1.2 Role of multiradicals

To understand the role of multiradicals and the difference between the multiradical and the monoradical model, the average number of radical sites per molecule and the radical site density for both models has been computed – shown in Figure 3.3. The radical site density is calculated from the multiradical model using Equation 3.22, while the number of radical sites follows as \( \Phi_n/R_n \). In the monoradical model the number of radicals per molecules equals \( R_n/(P_n + R_n) \), where \( R_n \) and \( P_n \) are the concentrations of living and dead chains, respectively; for the radical site density we divide this quantity by \( n \). We clearly observe that according to the monoradical model the number of radical sites asymptotically nears 1 for long chains, which is logical, since the maximum number of radical sites is 1. Consequently, the radical site density drops to lower values for long chain lengths. In contrast, the radical site density from the multiradical model asymptotically goes to a value somewhat lower than \( 10^4 \) radical sites per monomer unit. Accordingly, the average number of radical sites per molecule rises to around 1000 for long chains.

![Figure 3.3. Average number of radical sites per molecule and radical site density from multiradical and monoradical model for strong branching and topological scission (\( k_{tp}/k_p = 0.0032, k_{rs}/k_p = 8 \times 10^5 \)). Further kinetic data as in Figure 3.2 and Table 3.1.](image)

3.3.1.3 Bimodal distributions from multiradical model

A further issue is concerned with the bimodal distribution shapes that have been observed in the models presented hitherto. Apparently, these shapes are never attained in the case of topological scission as assumed in deterministic modeling, nor have they ever appeared in results from MC simulations. The question to be answered next is whether the bimodal shape is retained, for the case of linear scission, if multiradicals are accounted for. This situation is tested for two values of the transfer to polymer coefficient, \( k_{tp}/k_p = 0.0032 \) and \( k_{tp}/k_p = 0.005 \) and mild scission, \( k_{rs}/k_p = 1.6 \times 10^5 \). The result is shown in Figure 3.4 and one clearly observes that the bimodality is retained indeed, and even slightly enhanced.
3.3.1.4 Behavior at higher scission rates

For the case of disproportionation only, it has been observed earlier that when comparing to Monte Carlo simulations, the linear scission model leads to large discrepancies, while the topological scission model leads to better, but not perfect agreement (Kim et al., 2004). When accounting for multiradicals, in the case without scission in Iedema and Hoefsloot (2004b), perfect agreement with MC simulations was observed. In the presented new multiradical model, it now is possible to account for linear and topological scission; Figure 3.2 also shows perfect agreement. This is a case of mild scission ($k_{rs}/k_p = 1.6 \times 10^{-5}$), which is a condition that is applicable to the ldPE polymerization process, since all models show that the broad MWD measured by Size Exclusion Chromatography- Multi Angle Laser Light Scattering (SEC-MALLS) is not attainable for strong scission. However, testing the new multiradical model for stronger scission is still desirable. Hence, for a constant high transfer to polymer rate, $k_{tp}/k_p = 0.005$, the scission rate $k_{rs}/k_p$ has been varied between $8 \times 10^{-5}$ and $0.0009$ in both the deterministic multiradical model and the MC sampling model. The results are shown in Figure 3.5a to 3.5c. For completeness, in Figure 3.5a, the distributions of the classical monoradical model and those resulting assuming linear scission are shown as well. We clearly observe that for mild scission, until $k_{rs}/k_p = 10^{-4}$, there is a good agreement between the multiradical model and MC simulations. However, for increasing scission rates $>10^{-4}$ one observes a growing deviation. The MC results show the Chain Length Distribution (CLD) peak slightly shifted to lower values, while the tail is somewhat more extended. Note that for the highest scission rate (Figure 3.5c) the multiradical and monoradical model yield coinciding distributions, hence for these relatively narrow distributions multiradicals do not play an important role. We can conclude that, although the multiradical model with topological scission always comes closest to the MC simulations, the agreement is no longer perfect for high scission rates. Evidently, the empirical fragment length distribution in the deterministic model fails to fully properly describe the precise random scission characteristics that are accurately accounted for by the MC sampling model.

3.3.2 Termination by combination and disproportionation, no scission

Under the circumstances of combination termination in a CSTR, gelation is expected. The important questions regarding the proposed models consequently are whether they correctly predict the gelpoint and, if in the gel regime, whether they accurately describe the chain length distributions of the sol fraction.
3.3.2.1 Behavior in sol and gel regime

The results of the multiradical model allowing for gel formation are presented, that is by solving the population balances, Equations 3.22 and 3.23, where \( \lambda_{0i} \) and \( \lambda_{10} \) are replaced by \( \lambda_{0i}^{*} \) and \( \lambda_{10}^{*} \). In accordance to the idea that sol and gel contain a fraction of the radical sites and the monomer units, we define two types of gel fractions, one based on the deficit in monomer units, the other based on the deficit in radical sites:

\[
\begin{align*}
 w_{g, \lambda_{i}^{*}} &= 1 - \frac{\lambda_{10}^{*}}{\lambda_{i}^{*}} \\
 w_{g, \lambda_{0}^{*}} &= 1 - \frac{\lambda_{0}^{*}}{\lambda_{0}^{*}}
\end{align*}
\]  

(3.37)

(3.38)

Figure 3.5. Comparison of multiradical and monoradical model to MC simulations for various scission rates. Transfer to polymer rate: \( k_{tp}/k_{p} = 0.005 \). Further kinetic data as in Figure 3.3 and Table 3.1. MC parameters: \( \bar{\Pi}_{pp} = 161.8 - 184.4 \); branching: \( \rho_{b} = 0.0042, P_{b} = 0.774 \); scission: \( \rho_{s} = 0 - 7.54 \times 10^{-4}, P_{s} = 0 - 0.122 \).

The population balance equations (Equations 3.22 and 3.23) are solved for various values of transfer to polymer coefficient, \( k_{tp} \), ranging from low values representative for the sol regime to much higher values to simulate the gel regime. The distributions and gel fractions obtained are compared to those from Monte Carlo simulations. The resulting dead chain distributions are shown in Figure 3.6 for the sol region and around the gelpoint and in Figure 3.7 for the gel regime. Figure 3.8 exhibits the gel fraction according to both definitions versus the transfer to polymer rate coefficient and Figure 3.9 the branching density as a
function of chain length. The distributions, gel fraction curves and branching distributions show excellent agreement with the MC simulations. The characteristic behavior around the gelpoint, a broadening in the dead chain distributions followed by a narrowing, is obvious from both MC simulations and population balances calculations. Both from deterministic model as from MC simulations, the average branching density of the gel turn out to be equal to the branching density of the largest sol molecules.

It could be concluded that in the case of combination termination and no scission the deterministic model correctly predicts the gelpoint and the associated chain length distribution as goes from the perfect agreement with the results from MC simulations. It turns out that under these conditions the role of multiradicals is only limited, since both the distributions and the gel fractions calculated using the monoradical model practically coincided to the ones shown in the figures of this paragraph. This is in contrast to what was observed for the case of disproportionation only, so evidently combination termination suppresses the effect of multiradicals to a certain extent.

![Graph](image1.jpg)  
**Figure 3.6.** Chain length distributions from Equations 3.22 and 3.23 and MC simulations (dots) in pre-gel regime and around gelpoint for various transfer to polymer rates. Kinetic data: \( k_0^* = 5.5885 \times 10^{-6} \), \( k_0/k_p = k_c/k_p = 1000 \); monomer conversion 0.456. Further data as in Table 3.1. MC parameters: \( R_{pp} = 104-717 \), \( \rho_b = 0.000168-0.00848 \), \( P_b = 0.12-0.87 \), \( P_c = 0.064-0.44 \).

![Graph](image2.jpg)  
**Figure 3.7.** Chain length distributions, \( R_n \), from Equations 3.22 and 3.23 and MC simulations (dots) in gel-regime. Kinetic data the same as in Figure 3.6 and Table 3.1.
Figure 3.8. Gel fractions based on monomer units and living chain concentration versus transfer to polymer rate coefficient from population balances and MC simulations. Kinetic data the same as in Figure 3.6 and Table 3.1.

Figure 3.9. Branching density versus chain length in the gel regime from population balances and MC simulations. The average gel branching density is equal to the plateau values of the sol branching density. Kinetic data the same as in Figure 3.6 and Table 3.1.

3.3.2.2 Assuming absence of gel

The results of the deterministic model in the gel regime are nicely in agreement with MC simulations and also in line with previous findings concerning radical polymerization with transfer to polymer and combination termination. However, the model has been adopted to possibly accommodate gel formation by replacing the moments $\lambda_{\text{w1}}$ and $\lambda_{\text{w0}}$ by $\lambda_0^*$ and $\lambda_1^*$, the total concentration of radical sites and monomer units in polymer, in Equations 3.22 and 3.23. One might wonder what would happen, if this aforementioned replacement were not carried out, which implies that no gel is formed. Mathematically speaking, the following question should be answered: do the population balances in their original form (with $\lambda_{\text{w1}}$ and $\lambda_{\text{w0}}$) have consistent solutions, even in a parameter range that is far into the gel regime? It should be emphasized that this is not a mere academic issue, since using $\lambda_{\text{w1}}$ and $\lambda_{\text{w0}}$ has been common practice in a number of ldPE modeling studies addressing full MWD, for instance: Asteasuain and Brandolin (2008) (using a generating function approach), Pladis and Kiparissides (1998) (using numerical fractionation), Kiparissides et al. (2010), Kim et al. (2004) and Kim and Iedema (2008). Moreover, using distribution moments $\lambda_{\text{w1}}$ and $\lambda_{\text{w0}}$ is also standard in the commercial PREDICI® package (Wulkow, 2008). It is not claimed here that the results of these modeling studies are all wrong, but they might be erroneous if the kinetic parameters used would imply gel formation. However, the issue has never been explicitly raised in ldPE modeling context, which is indeed the objective of this paragraph. In addition, doing so also implies a warning for those undertaking ldPE modeling under (possible) gel
conditions. Regarding the PREDICI® package, it is expected that allowing for gel by using \( \lambda_0^* \) and \( \lambda_1^* \) as calculated from Equations 3.27 and 3.28 may be easily introduced.

In the current study, solutions from deterministic models of population balances have been explored in their original form (with \( \lambda_0 \) and \( \lambda_1 \)), assuming no gel, by varying the rate coefficient for transfer to polymer. This exercise has been performed for both the multiradical model and the classical monoradical model. The same parameter settings have been applied as before, gelation is allowed. Note that the no gel assumption implies the equality, in contrast to the inequality, Equation 3.26:

\[
\lambda_{10} = M_0 - M
\]  

(3.39)

Obviously, increasing the \( k_{tp}/k_p \) up to the gelpoint at a value of 0.0004 gave the same results. However, at higher values and in the gel regime no convergence could be achieved for the multiradical model in the no gel mode. Hence, a clear conclusion may be driven that this model does not have a solution in the gel regime, if \( \lambda_0 \) and \( \lambda_1 \) are not replaced by \( \lambda_0^* \) and \( \lambda_1^* \) to accommodate gel formation. Nevertheless, although the model in its no gel formulation does not cover the gel regime, it may be used to detect the gelpoint by exploring the point, for which a solution is no longer attainable.

In a similar manner the monoradical model has been explored in the no gel mode. The classical population balance equations for living and dead chains, expressed by \( R_n^c \) and \( P_n^c \), may be recalled as in Kim and Iedema (2008) (only the relevant terms are shown):

\[
\frac{dR_n^c}{dt} = k_p M (R_{n-1}^c - R_n^c) - (k_{id} + k_{tc}) R_n^c \lambda_0 + k_{tp} \lambda_0 nP_n^c - k_{tp} R_n^c \mu_1 - \frac{1}{\tau} R_n^c = 0
\]  

(3.40)

\[
\frac{dP_n^c}{dt} = 2k_{td} R_n^c \lambda_0 - k_{tp} \lambda_0 nP_n^c + k_{tp} \mu_1 P_n^c - \frac{1}{\tau} P_n^c + k_{tc} \sum_{m=1}^{n-1} P_m^c P_{m-n}^c
\]  

(3.41)

Here, the moments are defined as usual in the monoradical model:

\[
\lambda_0 = \sum_{n=1}^{\infty} nR_n^c \quad \mu_1 = \sum_{n=1}^{\infty} nP_n^c \quad \lambda_1 = \sum_{n=1}^{\infty} n^2 R_n^c
\]  

(3.42)

The no gel condition accords to the equality:

\[
\mu_1 + \lambda_1 = M_0 - M
\]  

(3.43)

In this case of the monoradical model, it turns out that the population balance equations in the no gel form indeed have consistent solutions well within the gel regime that feature no deficit and hence represent solutions with zero gel formation! The fact that there is no deficit is in all cases confirmed as for all solutions the equality of Equation 3.43 holds. The reason, why the monoradical model behaves so differently, must be found in the different
assumptions concerning the transfer to polymer reactions. From Equations 3.40 and 3.41, it is clear that the transfer to polymer reaction is supposed to occur only to dead chains. This is consistent with the monoradical assumption, since a living chain undergoing transfer to polymer would yield a biradical, which cannot be accounted for in the monoradical model. Obviously, living chains do undergo transfer to polymer (and scission as well), which is correctly described by the multiradical model.

In this paragraph, the results of the monoradical model assuming no gel will be discussed and compared to the results accounting for gel in Figures 3.10 and 3.11. Figure 3.10 shows the dead and living chain distributions for \( k_{tp} \)-values that previously were shown to fall well within the gel regime, representing solutions for the population balance equations (Equation 3.22 and 3.23) with \( \lambda_0 \) and \( \mu_1 \) as defined as the living and dead chain length distributions moments defined above instead of \( \lambda_0^* \) and \( \lambda_1^* \). One observes a very important contribution from the living chains that seem to grow extremely long. These living chains also contain a considerable fraction of the overall monomer units present in all polymer chains, amounting to 50 % for the highest \( k_{tp} \)-value. Figure 3.11 shows the comparison of overall distributions, \( R_n = R_{nc} + P_{nc} \) for cases in the gel regime according to the model variant that does assume gel. It is obvious that the no gel distributions are extremely much broader than the distributions presented before. The contribution of the living chains is even leading to a pronounced bimodal overall distribution.

In conclusion, the no gel variant of the multiradical model is usable to detect the gelpoint as the limit at which still a solution is possible; the associated chain length distribution agrees to the result of MC simulations. In contrast, the monoradical model provides consistent solutions for the assumption of zero gel, even far in the gel regime and these solutions strongly deviate from those from the model variant allowing for gel. From a purely mathematical point of view, one might argue that the solutions without gel are not inferior to those with gel. However, the monoradical model is able to generate such solutions only due to the assumption that part of the chains, the living ones, does not undergo transfer to polymer, which is not a realistic assumption. Hence, we should reject these solutions, and instead properly apply the models in the form allowing for gel formation by the substitution of the sol moments by the overall amounts of monomer units in polymer and overall number of radical sites.

Figure 3.10. Solutions for dead (black) and living (gray) chain distributions assuming absence of gel for two high values of the transfer to polymer coefficient. Living chain concentrations are extremely high and contain large fractions of the monomer units. Kinetic data the same as in Figure 3.6 and Table 3.1.
3.3.3 Termination by combination and disproportionation, scission effect

In this section the behavior of the entire gamut of model variants that were discussed before have been explored near and in the gel regime, accounting for the most important kinetic mechanisms usually assumed in the ldPE polymerization process: transfer to polymer, termination by disproportionation, termination by combination, and random scission. Since many authors have employed linear scission as the prevailing scission mechanism, this mechanism is discussed next to the topological scission. Even more important is the possibility that the prediction of the gelpoint might well be dependent on the scission model adopted. For similar reasons, both the non-gel and gel variants of the models are discussed as well. When revisiting examples in previous work, it is especially interesting, utilizing the newly developed model tools, to check their validity under possibly occurring gel conditions.

The possible role of multiradicals is checked again, and for all the conditions of the cases discussed in this paragraph this turns out to confirm what has been found for the case without scission, so a general conclusion may be drawn here already regarding the multiradical aspect. The multiradical model in the gel mode (Equation 3.31) could be used to predict the gelpoint and calculate the chain length distribution, if topological scission is assumed. In contrast, for linear scission the model can only be used in the non-gel mode, condition Equation 3.43, as in the gel regime this model fails to converge. Again, the monoradical model in the non-gel mode generated solutions in both sol and gel regime.

3.3.3.1 Topological scission

For the case of topological scission we have a model that is supposed to be valid in both sol and gel regime, as the population balance for $R_n$, Equation 3.31, accounts for eventual gel fragmentation. For a moderate value of the transfer to polymer reaction, $k_{tp}/k_p = 0.0012$, the scission rate is varied. In the case of no scission perfect agreement is found between the multiradical model and MC simulations, both regarding the shape of the chain length distribution as in the value of the gel fraction: 24.8 %. Figure 3.12 shows the result from the multiradical model for a moderate scission rate. In this case the gel fraction predicted by the multiradical model, 11.9 % is slightly lower than that from MC simulations, 13.9 %. The chain length distributions from both models are well in agreement. Figure 3.13 shows the result for the situation near the gelpoint. Again a fair agreement is observed between the deterministic model and the MC simulations. One observes a slightly longer tail in the chain...
length distribution from MC, while the gel fraction from the multiradical is slightly lower here. As becomes clear from the gel fraction versus scission rate plot of Figure 3.14, fair agreement exists regarding the gel fraction, although over the largest range the multiradical model seems to over-estimate gel by 2% maximum. Figures 3.12 through 3.14 show that if the gel content is under-estimated the CLD tail is over-estimated in comparison to MC simulations, and vice versa.

These findings are very interesting and important result, since they imply that the apparently difficult problem of gel fragmentation in deterministic modelling is surprisingly well solved by the asymptotical variant of the fragment length distribution model, Equation 3.13, for $m \rightarrow \infty$ leading to Equation 3.31. Obviously, the remaining small differences should be attributed to the fact that the deterministic model employs an empirical approach to real random scission of branched molecules after all.

Figure 3.12. Results of the multiradical model and MC simulations in the gel regime. Scission rate: $k_{rs}/k_p = 0.00012$. Good agreement between multiradical model and MC simulations; gel fraction predicted slightly lower by multiradical model. Further kinetic and MC data as in Figure 3.2 and Table 3.1.

Figure 3.13. Results of the multiradical model and MC simulations practically at the gel point. Scission rate: $k_{rs}/k_p = 0.00028$. Slightly higher gel prediction by multiradical model, while CLD tail is longer from MC simulations. Further kinetic and MC data as in Figure 3.2 and Table 3.1.

Figure 3.14. Gel fraction as a function of scission rate. Same conditions as in Figure 3.12. Fair agreement between multiradical model and MC simulations - multiradical model over estimates the gel fraction by one or two percent.
3.3.3.2 Linear scission

Here, an example is revisited that has been discussed before in the context of ldPE polymerization process (Kim et al., 2004), where transfers to monomer and transfer to chain transfer agent were involved. The kinetic parameters are given in the caption of Figure 3.15. Assuming fairly weak linear scission (rate $k_{ns}/k_p = 4 \times 10^{-5}$) the classical monoradical model in the non-gel mode proved to yield a strongly bimodal distribution, see Figure 3.16. In this case also a dominant combination termination was assumed ($k_{tc}/k_p = 744; k_{td}/k_p = 244$). Now, in view of the results observed in the previous section one might expect these conditions to lead to gel formation. Indeed, in absence of scission, as shown in Figure 3.15 and 3.16, a gel fraction of 35.4 % is present, as was calculated from both the multiradical model in the gel mode and MC simulations. For the aforementioned low scission rate the MC simulations reveal a slightly lower gel fraction. A much higher scission rate is required to arrive at the gelpoint under these conditions: $k_{ns}/k_p = 0.0014$. This result could be obtained from MC simulations and from the multiradical model in the non-gel mode. The associated CLDs from both models are shown in Figure 3.15. A similar, but stronger discrepancy between these is observed as in Figure 3.13, to be attributed again to the incomplete representation of random scission by the topological scission model. One may conclude that for topological scission the weak scission condition would lead to strong gel formation.

In the case of linear scission we get a completely different picture. Here, the gelpoint is achieved at a much lower scission rate, $k_{rs}/k_p = 1.2 \times 10^{-5}$, as has been calculated using the non-gel mode of the multiradical model with linear scission. Thus, one may observe a remarkable difference in the prediction of the gel regime between linear and topological scission. Assuming topological scission gel is obtained at scission rates $k_{ns}/k_p < 0.0014$, while assuming linear scission gel will only exist for $k_{ns}/k_p < 1.2 \times 10^{-5}$ – a much narrower gel regime. Now, it is clear that under the conditions, for which the strongly bimodal distribution was obtained, $k_{ns}/k_p = 4 \times 10^{-5}$, is not falling in the gel regime indeed. The multiradical model exactly confirms the CLD from the monoradical model, both in non-gel mode. Right at the gelpoint, as shown by Figure 3.16, the chain length distribution turns out to possess an even more extended bimodal shape.

In conclusion, the scission mechanism adopted is very important for both the prediction of the gelpoint and the chain length distribution. This is not fully unexpected, since we have observed before that linear scission tends to lead to bimodal but less tailed distributions, while with topological scission much longer tails are predicted. Evidently, the systems featuring longer tails are more prone to gelation. It should be realized that these solutions are obtained from the multiradical model assuming linear scission and absence of gel, according to Equation 3.39, and they must be considered as the only rigorous and consistent solution of the set of population balance equations describing this particular kinetic system. For a system like ldPE it is possible that the linear scission mechanism is the best approximation of the true scission process. Hence for such systems this model is most appropriate. Model variants with other assumptions, like the existence of gel or living chains not undergoing transfer to polymer or scission (monoradical model), should be considered as less representative. Note, for instance, that the gel-assuming model even with linear scission still yields 35 % gel fraction at the earlier defined gelpoint ($k_{rs}/k_p = 1.2 \times 10^{-5}$). In contrast to the case of topological scission, where the MC sampling model acts as a reference, no other models are currently available to verify the multiradical model in non-gel mode with linear scission.
Figure 3.15. Termination by combination and disproportionation and topological scission. Kinetic data: $k_2 = 25,000 \text{ m}^3/\text{(kmole.s)}$; $k_0^* = 3.0654 \times 10^{-7}$; $k_{ccl}/k_2 = 244$; $k_c/k_2 = 744$; $k_d/k_2 = 0.014984$; $k_{md}/k_2 = 0.000624$; $k_{md}/k_2 = 0.006186$; $S_0 = 0.017 \text{ kmole/ m}^3$; monomer conversion 0.1807. MC parameters: $\beta_{pp} = 223.1$, $\rho_b = 0.00321$, $\rho_s = 0.000322$, $P_b = 0.762$, $P_s = 0.0719$, $P_c = 0.00374$.

Figure 3.16. Termination by combination and disproportionation and assuming linear scission. Same kinetic data as Figure 3.15. Zero scission CLD with gel fraction 35.4% (same as Figure 3.15). Gelpoint for linear scission at very low scission rate: $k_2/k_2 = 1.2 \times 10^{-5}$ (from multiradical model not allowing for gel). CLD at gelpoint and in sol regime, $k_2/k_2 = 4 \times 10^{-5}$ (multiradical model not allowing for gel).

3.4 Conclusions

In this chapter, a series of new population balance models for radical polymerization in a CSTR are constructed in order to explore the possible effects of multiradicals and gel formation, under conditions typical for the ldPE process. To have a better overview over all model variants tested; a ‘model tree’ in Figure 3.17 is presented.

In the case of termination by disproportionation only (no gelation) the importance of multiradicals is shown, for linear and topological scission, as was observed in earlier work (Iedema and Hoefsloot, 2004b), not yet allowing for scission. Good agreement was found with MC simulations for mild scission, but larger discrepancies for strong scission. In all cases the monoradical model turned out to lead to larger differences when comparing to MC simulations.

In the case of strong or dominant termination by combination (gel formation), in absence of scission both the mono- and multiradical model yield perfect agreement with MC simulations concerning the CLD and gel fraction. If the no gel condition is imposed, the multiradical model is only able to generate a solution in the pre-gel regime. In contrast, the no-gel variant of the monoradical model features a continuous range of solutions in sol and gel regime, and is therefore not suited to detect the gelpoint. This mathematically correct, but chemically strange behavior is explained by the assumption in the monoradical model, that...
living chains do not undergo transfer to polymer. The multiradical model does not suffer from this assumption.

The introduction of scission in all the models in general yields results that for topological scission again agree fairly well to those produced by MC simulations, even in the gel regime. Under gel conditions a gel fragmentation model is employed, which is directly derived from the empirical expression for the scission fragment length distribution. Thus, using the deterministic multiradical model a close correspondence is found, both in predicting the gelpoint as in the CLD, with results from MC simulations that must be considered as the exact solution to the problem at hand, with random scission allowing for gel formation.

In the non-gel regime, under the circumstances of combination termination and scission the non-gel assuming variant of the multiradical model yields consistent results. Remarkably, the linear scission model leads to a much narrower gel regime than topological scission. The chain length distributions obtained are strongly bimodal, especially at the gelpoint. Evidently, the linear scission mechanism is much more effective in preventing gel formation than topological scission.

Thus, we see that adopting a scission model that does not at all represent full random scission represents a kinetic system with completely different behavior. Regarding the ldPE process, where bimodal distributions are often measured by SEC-MALLS in Kim et al. (2004), the scission mechanism is not known certainly, whether it is mainly random (chemical action) or non-random, possibly caused by mechanical stress. In the latter case linear scission is a better model of reality than random scission. This solution cannot be verified with MC simulations. The multiradical model shows that for this type of scission for dominant combination termination no gelation occurs even if the scission rate is low, leading to bimodal distributions. Note besides that the fact that linear and mechanical scission best reproduce the measured MWD bimodality must be considered as a direct proof of their validity. However, until now the bimodality has not been explained by other mechanisms, like strong temperature or concentration gradients, nor by any non-ideal (micro- or macro-) mixing effect. Still, the impact of non-ideal mixing on MWD in the case of ldPE is not exhaustively investigated.

Finally, regarding the performance of the proposed models we can conclude that for full random scission the deterministic multiradical model assuming topological scission comes close to the exact solution from MC simulations. In contrast, for linear scission the implementation in our deterministic model is simple and straightforward, while – vice versa - not at all attainable in MC simulations.
Figure 3.17. Overview and performance of all model variants.
4 Modeling of molecular weight/branching distribution, series of continuous stirred tank reactors versus tubular reactor

In this chapter, modeling Molecular Weight Distribution (MWD) under the circumstances of low-density Polyethylene (ldPE) has been tackled for a tubular reactor with realistic non-isothermal conditions and for a series of Continuous Stirred Tank Reactors (CSTRs). The existence of multiradicals and the occurrence of gelation are allowed. The presented deterministic model is based on the Galerkin finite element method and employs the pseudodistribution concept to address the number of radical sites per chain as the second dimension next to chain length. For reference, Monte Carlo (MC) simulations have been carried out for the same reactor configurations. Assuming ‘topological scission’, accounting for the highly branched character of the system, good agreement was found between the multiradical model and MC simulations. As conditions of ldPE polymerization lead to broad MWD and are close to gelation, allowing for gel turns out to be crucial. Not allowing for gel leads to extremely broad bimodal MWD, which with the present set of models, is identified now as an artifact. A bimodal MWD was indeed obtained for a single CSTR, but the bimodality decreases as the number of CSTRs in series increases and it disappears in the batch reactor.

4.1 Introduction

Currently, for ldPE polymerization, tubular reactor is of more use than CSTR, although autoclave reactors are still widely applied in ldPE film production. Improving the tubular technology to reproduce the desired properties of specific ldPE film grades is of utmost concern via controlling MWD and branching architectures. This chapter is dedicated to model MWD in CSTR, series of CSTRs and tubular reactor, all operating under isothermal or more realistic temperature profiles. The basic idea is to study the impact of these reactor configurations on the MWD and allowing for gel formation.

Furthermore, the recent modeling studies of random scission mechanism, which account for the branched structure of ldPE by using an improved ‘topological scission’ concept (Kim et al., 2004, Yaghini and Iedema, 2014a) are the only ones in their kind in deterministic modeling and have been applied only to CSTR. The same holds for the possible effect of multiradicals in the near gel regime, which is also addressed in the context of a CSTR. The present study for the first time deals with the modeling of other reactor configurations including improved topological scission and multiradicals. Thus, the main focus is modeling the molecular weight distributions of tubular free radical ldPE polymerization, accounting for topological scission and the effect of multiradicals.
Two different modeling strategies have been followed to reproduce a tubular reactor model. Firstly, a tubular model consisting of several continuous batch reactors and three downstream feeding points has been introduced. Secondly, a model of CSTRs in series with several initiator insertion points without back streaming has been proposed as an extendible model of a tubular reactor. Since a comprehensive model for single CSTR distributions (Yaghini and Iedema, 2014a, 2014b) has been presented in the former chapters, the explanation of the modeling scheme is being skipped in this chapter.

4.2. Reaction mechanisms and Population Balance Equations (PBEs)

4.2.1 Reaction equations

The reaction mechanism has been formulated by the reactions in two dimensions shown in Table 4.1. The first dimension \( n \) accounts for chain length, while the second dimension \( i \) denotes the number of radical sites per polymer chain. \( f(n,k) \) is the fragment length distribution function. Note that one of the fragments resulting from scission would get one extra radical site.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation</td>
<td>( \text{I} \cdot + M \rightarrow R_{n},k,f )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( R_{n,i} + M \xrightarrow{k_{p,i}} R_{n+1,i} )</td>
</tr>
<tr>
<td>Transfer to monomer</td>
<td>( R_{n,i} + M \xrightarrow{k_{m,i}} R_{n,i+1} + R_{3} )</td>
</tr>
<tr>
<td>Transfer to CTA (CTA)</td>
<td>( R_{n,i} + Y \xrightarrow{k_{CTA,i}} R_{n+1,i} + R_{3} )</td>
</tr>
<tr>
<td>Transfer to polymer</td>
<td>( R_{n,i} + R_{m,j} \xrightarrow{k_{p,j}} R_{n+1,i} + R_{m,j-1} )</td>
</tr>
<tr>
<td>Random scission</td>
<td>( R_{n,i} + R_{m,j} \xrightarrow{k_{rs}(n,k)} R_{n-k,i-p} + R_{k,p} + R_{m,j-1} )</td>
</tr>
<tr>
<td>Termination by disproportionation</td>
<td>( R_{n,i} + R_{m,j} \xrightarrow{k_{dt}} R_{n+1,i} + R_{m,j-1} )</td>
</tr>
<tr>
<td>Termination by combination</td>
<td>( R_{n,i} + R_{m,j} \xrightarrow{k_{dt}} R_{n+1,i} + R_{m,j-2} )</td>
</tr>
</tbody>
</table>

Table 4.1. Reaction mechanism for ldPE polymerization.

4.2.2 Population balance model

Previously, in Chapters 2 and 3 molecular weight/branching modeling of a single CSTR has been discussed. In Chapter 2, a Finite Element Method (FEM) called Galerkin was applied to 1-Dimensional (1D) population balance equations including pseudo (moment)-distributions for the number of branch points, to model the molecular weight and branching distributions for free radical polymerization of ldPE in CSTR. An empirical scission fragment length distribution function was used to model random scission of the strongly branched ldPE chains. The grid refinement difficulties arising from the scission function in the framework of the Galerkin-FEM method, for which ultimately a rigorous solution could be provided was presented. In Chapter 3, the number of radicals was chosen as the second dimension. This multiradical model proved to be successful not only describing multiradical chains, but also extended the applicability of the deterministic model to cover the gel regime. The present chapter is also based on the multiradical model.
4.2.2.1 Multiradical model

For a detailed description of the population balance equations formulation in a 2-Dimensional (2D) setting with the dimensions chain length and number of radical sites per polymer chain, and the solution method applied to these PBEs see Chapter 3. The procedure of applying pseudo-distributions to 2D population balance equations and transforming them to the 1D space of only chain length has been explained comprehensively in this chapter. In Table 4.2 and Table 4.3 the equations for the chain length, \(R_n\), and the number of radicals pseudo-distributions, \(\Phi_n^i\) (first moment), and \(\Phi_n^2\) (second moment) are listed. The balance equations for \(R_n\) have been obtained from the full 2D formulation in Yaghini and Iedema (2014b), by summing up over \(i\) for the \(0^{th}\) radical site moment, and the first and second radical site moment distributions have been acquired by multiplying with \(i\) and \(i^2\) respectively, followed by summing up over \(i\). The same terminology as in previous chapter has been used, distinguishing between total moments, \(\lambda_0^*\) and \(\lambda_1^*\), for sol and gel together, and \(\lambda_{0i}\) and \(\lambda_{1i}\), for sol only. Note that in absence of gel these quantities are identical. The equations previously derived for a single CSTR to a batch reactor (Table 4.2a) and to a series of CSTRs (Table 4.2b) are applied. In the latter case, the upper index, \(k\), refers to the \(k^{th}\) CSTR of the series. As before, the second radical moment, \(\Phi_n^2\), follows from the closure relation:

\[
\Phi_n^2 = (1 + \rho_R s n - \rho_R s) \rho_R s n
\]

where \(\rho_R s\) is the radical site density, defined as:

\[
\rho_R s = \frac{\Phi_n^i}{(nR_n)}
\]

These relations hold for a batch reactor, but identical equalities hold for each of the reactors of a series of CSTRs. Note finally, that this closure relation imposes an extra non-linearity to the equations besides the one from the convolution terms arising from combination termination.
\[ \lambda_0^* \geq \lambda_{01} \quad \lambda_1^* \geq \lambda_{11} = \sum_{n=1}^{\infty} nR_n \]

\[ \lambda_0 \quad \text{Total number of radical sites in sol and gel} \]

\[ \lambda_{01} \quad \text{Total number of radical sites in sol} \]

\[ \lambda_1^* \quad \text{Total number of monomer units in sol and gel} \]

\[ \lambda_{10} \quad \text{Total number of monomer units in sol} \]

\[ \frac{dI}{dt} = -2k_{r1}I_2 \]

\[ \frac{dI}{dt} = 2k_dI_2 - k_MI^* \]

\[ \frac{dM}{dt} = -(k_p + k_m)M\lambda_0^* - k_MI^* \]

\[ \frac{dY}{dt} = -k_{CTA}Y\lambda_0^* \]

\[ \frac{d\lambda_0^*}{dt} = k_MI - (k_{w1} + k_w)\left(\lambda_0^*\right)^2 \]

\[ \lambda_0^* = M_0 - M \]

\[ \frac{dR_n}{dt} = k_MI^* + k_{w1}M\lambda_{01} + k_{CTA}Y\lambda_{01} - k_pM\Phi_n^1 \quad n = 1 \]

\[ \frac{dR_n}{dt} = k_pM(\Phi_n^1 - \Phi_n^2) + k_m\left[\frac{1}{2}(\sum_{m=n}^{\infty} \Phi_m^1 \Phi_m^1 - \lambda_{01} \Phi_n^1)\right] + \]

\[ -k_{w1}M\Phi_n^1 - k_{CTA}Y\Phi_n^1 + k_m\lambda_{01}\left(2 \sum_{m=1}^{n} f(n, m)R_m - nR_n\right) \quad n \geq 2 \]

\[ \frac{d\Phi_n^1}{dt} = k_MI^* + k_{w1}M\lambda_{01} + k_{CTA}Y\lambda_{01} - k_pM\Phi_n^1 \quad n = 1 \]

\[ \frac{d\Phi_n^1}{dt} = k_pM(\Phi_n^1 - \Phi_n^2) - k_{w1}M\lambda_{01} - k_{CTA}Y\Phi_n^2 + \]

\[ k_m\left[\sum_{m=n}^{\infty} \Phi_m^1 \Phi_m^1 - \Phi_n^1 \Phi_n^1 - \lambda_{01} \Phi_n^1\right] + k_m\left[-\lambda_{01} \Phi_n^1 + \lambda_{01} R_n\right] + \]

\[ k_m\left[\lambda_{01} \sum_{m=1}^{n} f(n, m)\left(R_m + \sum_{m=1}^{\infty} \Phi_m^1\right) - \lambda_{01} \Phi_n - \lambda_{01} \Phi_n^1\right] \quad n \geq 2 \]

Table 4.2. Population balance equations and first radical site moment distributions for a batch reactor.
\[ \tau' = \frac{\tau}{\text{number of CSTRs}} \]

\[
\frac{dI^k_i}{dt} = -2k_j I^k_i + \frac{1}{\tau} (I_{20} - I^k_i) = 0; \quad \frac{dI^k_{i+1}}{dt} = -2k_j I^k_{i+1} + \frac{1}{\tau} (I_{20} - I^k_{i+1}) = 0; \quad k \geq 2
\]

\[
\frac{dI^k}{dt} = -2k_j I^k + k^2 M^k I^k + \frac{1}{\tau} \left[ \left( 1 - \delta(k-1) \right) I^{k-1} - I^k \right] = 0
\]

\[
\frac{dM^k}{dt} = -k^2 M^k I^k - k^2 M^k I^k - k^2 M^k \lambda^k_0 + \frac{1}{\tau} (M_0 - M^k) = 0
\]

\[
\frac{dM^k}{dt} = -k^2 M^k \lambda^k - k^2 M^k \lambda^k - k^2 M^k \lambda^k_0 + \frac{1}{\tau} (M^k - M^k) = 0; \quad k \geq 2
\]

\[
\frac{dY^k}{dt} = -k^2 M^k I^k \lambda^k_0 + \frac{1}{\tau} (Y_0 - Y^k) = 0; \quad \frac{dY^{k+1}}{dt} = -k^2 M^k \lambda^k_0 + \frac{1}{\tau} (Y^{k+1} - Y^k) = 0
\]

\[
\lambda^k = M_0 - M^k; \quad \lambda^k = M^k - M^k; \quad k \geq 2
\]

\[
\frac{dR^k}{dt} = k^2 M^k I^k + (k^2 M^k + k^2 C^k Y^k) \lambda^k_0 - k^2 M^k R^k +
\]

\[
\frac{1}{\tau} \left[ \left( 1 - \delta(k-1) \right) R^{k-1} - R^k \right]
\]

\[
\frac{dR^{k+1}}{dt} = k^2 M^{k+1} (\Phi^{k+1} - \Phi^{k+1}) + k^2 \left[ \sum_{n=1}^{N} \Phi^{k+1} - \lambda^k_0 \Phi^{k+1} \right] +
\]

\[
-(k^2 M^k + k^2 C^k Y^k) \Phi^{k+1} + k^2 \lambda^k_0 \left[ \sum_{n=1}^{N} f(n,m) R^n - nR^n \right] - \frac{1}{\tau} R^n \quad n \geq 2
\]

\[
\frac{d\Phi^{k+1}}{dt} = k^2 M^k I^k + (k^2 M^k + k^2 C^k Y^k) \lambda^k_0 - k^2 M^k \Phi^{k+1} +
\]

\[
+ \frac{1}{\tau} \left[ \left( 1 - \delta(k-1) \right) \Phi^{k+1} - \Phi^{k+1} \right]
\]

\[
\frac{d\Phi^{k+1}}{dt} = k^2 M^k (\Phi^{k+1} - \Phi^{k+1}) - k^2 \lambda^k_0 \Phi^{k+1} - (k^2 M^k + k^2 C^k Y^k) \Phi^{k+1} +
\]

\[
k^2 \left[ \sum_{n=1}^{N} \Phi^{k+1} - \lambda^k_0 \Phi^{k+1} \right] + k^2 \left[ -\lambda^k_0 \Phi^{k+1} + \lambda^k_0 R^n \right] +
\]

\[
k^2 \lambda^k_0 \left[ \sum_{n=1}^{N} f(n,m) (R^n + nR^n) - \lambda^k_0 R^n - \lambda^k_0 \Phi^{k+1} \right] +
\]

\[
+ \frac{1}{\tau} \left[ \left( 1 - \delta(k-1) \right) \Phi^{k+1} - \Phi^{k+1} \right]
\]

\[
\text{Table 4.5. Population balance equations and first radical site moment distributions for the } k^2 \text{ CSTR of a series of CSTRs.}
\]

4.2.2.2 Numerical implementation

4.2.2.2.1 Galerkin-FEM scheme

The Galerkin is a numerical method, which has been proven to be a powerful method to deal with this type of equation sets in Chapter 2. To solve the equations by this method either for a series of CSTRs or for a batch reactor, \( R^k \), \( \Phi^i \) and \( \Phi^j \) terms in the population balances are replaced by summations of polynomial terms:
\[ X(n) = \sum_{k=0}^{M} a_k^{M} T_k^M(n) \] (4.3)

where \( T_k^M(n) \) is defined as a Chebyshev polynomial for a chain with length \( n \), and is a polynomial of order \( k \). In the Galerkin-FEM framework chain length nodes \( n \) are selected in a way that exploits the orthogonality property of Chebyshev polynomials, which allows the evaluation of the coefficients \( a_k^{M} \) for a number of intervals \( M \) as in Chapter 2. According to this procedure the many original equations for each chain length are replaced by much fewer number of equations for the chain length nodes on intervals. The estimated coefficients are used to interpolate the whole MWD for the entire chain length domain.

**4.2.2.2 Implementation of series of CSTRs**

In the case of a single CSTR without combination termination the set of equations resulting from applying the Galerkin-FEM procedure to the population balance equations is linear and may be solved by a single matrix inversion step. In the case of combination termination the multiplication of the concentrations in the convolution forms a non-linearity. As discussed in the previous chapters, this problem is solved by moving the convolution term to the right hand side of the equations and adopting a dynamic solution scheme. According to this CSTR is simulated from a zero conversion starting point to a steady state, using the standard MATLAB® solver ode15s.m. Note that the differential equations describing the radical species give rise to stiffness of the set to be solved.

**4.2.2.3 Weighting procedure**

We are often interested in the shape and in particular the tail of the chain length distribution \( R(n) \) as represented in the ‘Gel Permeation Chromatography mode’ (GPS), which scales with \( n^2 R(n) \). For linear (multi-) CSTR problems, mostly those without scission, the coefficients of the Chebyshev polynomials are directly obtained by matrix inversion. Thus, accurate results are obtained for the whole chain length ranging up to very high chain lengths. However, for nonlinear problems, those with combination termination, CSTR problems are solved as dynamic systems, starting at zero conversion and using an ode-solver (the ode15s.m from MATLAB®) until steady state is achieved. For broad distributions, operation in the \( R(n) \) domain gives rise to inaccuracies, especially in the Chain Length Distribution (CLD) tails, that even prevents reaching a steady state solution. To improve this situation, a weighting procedure has been developed that allows weighting the distribution \( R(n) \) with a weighting factor \( n^i \). Thus, solutions in the \( n^i R(n) \) domain are obtained. It turns out that with \( i = 2 \) both accuracy and computational efficiency are significantly enhanced and it provides us with converged solutions for all conditions. Note that the commercial software package PREDICI® possesses a similar weighting option that is also recommended for broad distributions.

Operating in the \( n^i R(n) \) domain implies that the coefficients of the Chebyshev polynomials calculated for each chain length interval describe the weighted distribution. The
relation between the weighted and non-weighted coefficients, \( a^w_i \) and \( a_i \), respectively follows from the equality:

\[
R^w(s) = s^2 R(s) = \sum_{k=0}^{r} a^w_k T_k(s) = s^2 \sum_{k=0}^{r} a_k T_k(s)
\]  

(4.4)

Here, the nomenclature used by Wulkow (2008) and by, Yaghini and Iedema (2014a) is employed; \( T_k(s) \) represents the Chebyshev polynomial of the \( k \)th order at node \( s \). Where Equation 4.4 holds for each node in an interval, the system of equations for each interval may be written in matrix form:

\[
T^w \times a^w = T \times a
\]  

(4.5)

Here, \( T \) and \( T^w \) represent the sets of un-weighted and weighted Chebyshev polynomials, respectively, while \( a \) and \( a^w \) are the corresponding column vectors of coefficients per interval. For \( T^w \) we have:

\[
T^w = S^i \times T
\]  

(4.6)

With \( S^i \) the diagonal matrix with the nodes to the power \( i \) of the interval:

\[
S^i = \begin{bmatrix}
  s_1^i & 0 & \ldots & 0 \\
  0 & s_2^i & \ldots & 0 \\
  0 & 0 & \ldots & s_N^i
\end{bmatrix}
\]  

(4.7)

From the equality above we infer the following relation between the weighted and un-weighted sets of coefficients per interval, using a ‘transformation matrix’ \( U \):

\[
a^w = U \times a = \left( T^w \right)^{-1} T \times a
\]  

(4.8)

This weighting procedure has been implemented in the integration scheme using MATLAB®, ode15s.m. At each time step the non-weighted coefficients \( a \) are inferred from the weighted coefficients \( a^w \) using Equation 4.8 \((a = U^{-1} \times a^w)\). Then the RHS values of the Galerkin-FEM equations are calculated on non-weighted basis from \( a \), as described in Yaghini and Iedema (2014a). This yields a column vector of function values, \( F \), in the non-weighted domain. Subsequently, this vector is transformed back to the weighted domain by multiplying with the transformation matrix \( U \). Thus, at each time step the finite difference scheme is solved effectively:

\[
\Delta a^w = U \times F
\]  

(4.9)
4.2.2.4 Numerical implementation of series of CSTRs

A schematic compartment model consisting of \( n \) CSTRs in series is given further in this chapter. The Galerkin-FEM scheme of the proposed approach to model this type of compartment models only with two CSTRs in series is illustrated in Figure 4.1. The upper right block matrix shows the solution matrix for the first reactor and is identical to that for the single CSTR. This block matrix is resulting from the dead and living chains population balances for the first reactor. The matrix is in fact the complete left hand side matrix of a single CSTR. The lower right block matrix is similar to the upper left matrix and represents the second CSTR. The lower left block matrix contains the terms to connect the two CSTRs, and the upper right block matrix is basically a zero sub-matrix. Two separate Right-Hand Side (RHS) vectors, \( B_1 \) and \( B_2 \), are defined for the two CSTRs separately, and are both originating from the initiation of macroradicals in the reactors. Thus, the Galerkin-FEM method to solve the set of population balance equations for dead and living chains of the two CSTRs is represented as a single mathematical system. In absence of combination termination the set is solved with a single matrix inversion step, while the non-linear problem with combination is again treated as a dynamic system integrated using MATLAB® ode15s.m.

![Figure 4.1. Schematic representation of the solution scheme for two CSTRs in series as a compartment base-model for a tubular reactor.](image)

The sub-blocks show the contributions of all chains to a specific chain within a population balance equation and each block receives a contribution from other blocks.
4.2.3 Monte Carlo simulations

Monte Carlo simulations are carried out for both tubular reactor, under isothermal conditions and for a realistic temperature profile, and for a series of CSTRs. The concept of the tubular or batch reactor has been introduced for complete ldPE kinetics by Tobita (2001b) and has been applied for mostly constant probability parameters. Recently, Tobita (2014) has formulated a Monte Carlo scheme for series of CSTRs. This sophisticated algorithm allows defining different reaction conditions in each CSTR as expressed by different values of the probability parameters. The sampling procedure representing the growth of a molecule may be distributed between various CSTRs. The algorithm explicitly attributes the construction of various parts to various reactors by sampling from a probability density function expressing the distribution of conversion increments in all of the reactors. For both tubular reactor and for CSTR series the algorithm has been implemented in MATLAB® as described in the aforementioned chapters. Thus, an extensive description of the principles of this model is not provided here. In the simulations the transfer to polymer rate, scission rate, and combination termination rate are varied, which corresponds to changes in the specific MC parameters (Tobita, 2014):

Branching probability:
\[ P_b = \frac{k_p \lambda^*}{(k_c + k_d) \lambda_0^* + k_p \lambda_1^* + k_p \lambda_1^* + k_m M + k_S S} \]  

Branching density:
\[ \rho_b(\theta) = \rho_b' \theta = \frac{k_p \lambda^*}{k_p' (1-x)} \]  

Scission probability:
\[ P_s = \frac{k_r \lambda_1^*}{(k_c + k_d) \lambda_0^* + k_p \lambda_1^* + k_p \lambda_1^* + k_m M + k_S S} \]  

Branching density:
\[ \frac{1}{\rho_s(\theta)} = \frac{1}{\rho_s' \theta} = \frac{k_s(1-x)}{k_p' x \theta} \]  

Combination probability:
\[ P_C = \frac{k_c \lambda^*_0}{(k_c + k_d) \lambda_0^* + k_p \lambda_1^* + k_p \lambda_1^* + k_m M + k_S S} \]  

Average primary polymer length:
\[ \bar{n}_{pp} = \frac{k_p M}{(k_c + k_d) \lambda_0^* + k_p \lambda_1^* + k_p \lambda_1^* + k_m M + k_S S} \]

It should be noted that in contrast to Tobita’s papers, realistic profiles of the probability parameters for tubular reactor and series of CSTRs have been applied. The present study is the first to apply the MC method on a real ldPE system. The rate coefficients and the concentrations in these equations vary with time in the batch reactor, with length in the non-isothermal tubular reactor and are also different for each reactor in the series of CSTRs, according to the equations in Table 4.2 and Table 4.3. This also implies, for instance, that the average primary polymer length varies. With respect to the sampling of ‘birth conversions’ in the tubular reactor case the varying conditions no longer allow using simple algebraic expressions for the Cumulative Distribution Functions (CDF) to sample from. Instead, a
CDF on grid points is required, with numerical values of the CDF of the remaining birth conversion interval for each birth conversion. The sampling is carried out using a 2D interpolation routine in MATLAB®. To illustrate the variability in the results section, the time profile for some of the important MC parameters, like average primary polymer length are shown.

In the recent treatment of CSTRs in series (Tobita, 2014), a different sampling scheme of the branch points on a linear primary polymer is employed. Rather than sampling all the branch points at once using a binomial distribution, an average branching density of the primary polymer (segment) and the lengths of the segments, a 'block' approach is used. A branch point that is selected in an identical manner as a scission point separates each linear block. In MATLAB® implementation of this method, the method with the binomial distribution has been employed, which is fully equivalent with the newer one.

4.3 Reactor configuration and kinetic data

4.3.1 Sources of kinetic data

The same kinetic data set has been applied as in the papers by Yaghini and Iedema (2014a, 2014b), and Kim et al. (2004). Table 4.4 lists the reaction rate coefficients for the calculations of all models, except for the specified values in the figure’s captions. Table 4.5 and Table 4.6 show the reaction rates and the reactor configuration for tubular reactor, respectively.

<table>
<thead>
<tr>
<th>Parameter/ Mechanism</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator dissociation rate constant</td>
<td>$k_d$</td>
<td>0.5</td>
<td>1/s</td>
</tr>
<tr>
<td>Initiation rate constant</td>
<td>$k_i$</td>
<td>5000</td>
<td>m$^3$/(kmole.s)</td>
</tr>
<tr>
<td>Propagation rate constant</td>
<td>$k_p$</td>
<td>5000</td>
<td>m$^3$/(kmole.s)</td>
</tr>
<tr>
<td>Termination by combination and disproportionation rate constant</td>
<td>$k_{tc} + k_{td}$</td>
<td>10$^7$</td>
<td>m$^3$/(kmole.s)</td>
</tr>
<tr>
<td>CSTR residence time</td>
<td>$\tau$</td>
<td>30</td>
<td>s</td>
</tr>
<tr>
<td>Feed concentration monomer</td>
<td>$M_0$</td>
<td>16.75</td>
<td>kmole/ m$^3$</td>
</tr>
<tr>
<td>Feed concentration initiator</td>
<td>120</td>
<td>5 10-3</td>
<td>kmole/ m$^3$</td>
</tr>
</tbody>
</table>

Table 4.4. Parameters used in calculations.
Investigating the impact of different reactor types on MWD of ldPE free radical polymerization accounting for various types of reaction mechanisms and allowing for gel is the main goal of this chapter.

Figure 4.2 displays a simple compartment model consisting of \( n \) CSTRs in series. Initiator 1 and ethylene monomers are the inputs to the first CSTR. The polymer/monomer mixture flow proceeds through further reactor elements, while receives downstream injections of initiator and chain transfer agent. A series of a few CSTRs only may be viewed
to come close to the back-mixing regime of an ldPE autoclave reactor. For \( n \) CSTRs when \( n \) approaches to infinity, the series would behave as a tubular reactor.

A schematic model of an industrial tubular reactor with three downstream injection points has been shown in Figure 4.3. The figure illustrates a tubular reactor as a long tube with additional injection points to add high temperature initiators and chain transfer agents to the flow down the polymer/monomer stream. Obviously, the properties of the polymer melt such as molecular weight and number of radical sites per chain vary along the tube, which should be accounted for in the model. In the simulations, the temperature and the associated tube length profiles are applied the same as a solution previously obtained in PREDICI® (Kim and Iedema, 2004) with equal reaction kinetics. It is obvious that temperature along the tubular reactor varies as the polymerization proceeds. Hence, a temperature profile over the length of the tube is imposed as has been performed in the aforementioned publication.

![Figure 4.2](image1)

**Figure 4.2.** Schematic illustration of \( n \) CSTRs in series, initiator1 and ethylene monomers are injected to the first CSTR and initiator \( n \) is being injected to the \( n^\text{th} \) CSTR.

![Figure 4.3](image2)

**Figure 4.3.** Schematic configuration of tubular reactor with three downstream initiator-feeding points.

### 4.4 Results

#### 4.4.1 Outline

In the first part of this section the results for various reactor configurations are presented, in the second part, the outcomes of a realistic non-isothermal tubular reactor plus a series of CSTRs with and without intermediate initiator feeds are reported. The behavior of the
MWD as reactor configuration changes from a single CSTR, via series of increasing numbers of CSTRs to tubular reactor – essentially an infinite series of CSTRs is an interesting issue. Therefore, resulting MWDs of all configurations will be mostly presented in one plot, while the kinetic conditions are varied. Where it is relevant, a comparison is made between the deterministic model and Monte Carlo simulations. Finally, the deterministic and MC simulation models are subjected to realistic conditions regarding temperature profiles and feed positions and concentrations of initiator and chain transfer agent for industrial tubular reactors.

The reactor configurations are investigated under isothermal conditions assuming different kinetics: absence or presence of random scission, modeled as topological scission, sometimes linear scission; absence or presence of combination termination, the latter in relation to possible gel formation. The main aim is comparing the different reactor configurations for the same final monomer conversion, assuming a single initiator feed at the first CSTR and kinetic parameters remaining constant, while also the total residence time in all CSTRs stays the same, so $\tau = \tau_{total}/n_{CSTR}$. To ensure this, the feed concentration of initiator as is shown is Figure 4.4 has been adjusted. Note that increasing the number of CSTRs asymptotically approaches the limit of initiator feed concentration for a batch reactor, apparently. Batch residence time equals the total residence time in CSTRs, $\tau_{total}$.

![Figure 4.4. Initiator feed concentration as a function of number of CSTRs, n CSTR yielding the same monomer conversion of 0.456, assuming a single initiator feed at the first CSTR.](image)

### 4.4.2 Various reactor configurations under different kinetic conditions

#### 4.4.2.1 Disproportionation only, no scission

The results for the case of termination by disproportionation only, no combination and no scission, are shown in Figure 4.5. There is a remarkable narrowing of the distribution as the number of CSTRs increases until the narrowest CLD for the batch reactor. Figure 4.6 indicates that a similar trend is seen for the intermediate chain length distributions between the various CSTRs, going from the first to the last, as in those for the batch reactor at various time instants. It is expected that for an infinite number of CSTRs the plots would be identical to that of the batch reactor.

In this case of disproportionation only and no scission the agreement between the deterministic and MC simulations is perfect. This also holds for the intermediate results for various numbers of CSTRs and times. These are directly available from the deterministic model. Intermediate results from the MC simulations are obtained after
separate runs for specified intermediate numbers of CSTRs (with the same residence time per CSTR) or specified intermediate time.

Note that an isothermal condition for all reactor configurations has been assumed. It is interesting to observe that even under these conditions the values of the MC parameters change significantly, as is shown in Figure 4.7. This clearly illustrates how the MC simulation method indeed well accommodates realistic changes in the profiles of these parameters, where earlier studies (Tobita, 2001b, 2014) usually were performed with constant parameter values.

Figure 4.5. Chain length distributions from multiradical model and MC simulations for the case without scission and combination for series of CSTRs and batch reactor; conversion $x = 0.456$, kinetic data from Table 4.4, initiator feed according to Figure 4.4. Perfect agreement for all configurations.

Figure 4.6. Chain length distribution for series of CSTRs from multiradical model for the case without scission and combination for series of CSTRs at intermediate points between CSTR (left) and batch reactor at intermediate time points (right); conversion $x = 0.456$, kinetic data from Table 4.4, initiator feed according to Figure 4.4. Development of CLD over CSTR number and time are similar.
Figure 4.7. MC parameters for 8 CSTRs in series (left) and batch reactor (right), no scission, no combination, kinetic data in Table 4.4. Total residence time in CSTRs, $\tau_{\text{total}} = 30 \ s$; conversion in batch reactor after $30 \ s$ equal to CSTRs, $x = 0.456$.

4.4.2.2 Disproportionation only, topological and linear scission

Here, the issue of the mode of scission is addressed, either topological scission or linear scission. Figure 4.8 shows a range of CLDs for both scission cases for all reactor configurations from CSTR to batch reactor, at moderate scission rate ($k_{cs}/k_p = 1.6 \times 10^5$). Remarkably, the characteristic bimodal shape of the CLD for the CSTR assuming linear scission upon changing the configuration has completely vanished for the batch reactor. In fact, the curves already coincide for 4 CSTRs in series, apart from the CLD tail. Note that for this case of moderate (realistic) scission the results for a batch reactor are completely insensitive to the scission mode. For higher scission rates the impact is still very limited.

For the present scission rates the agreement between the multiradical model assuming topological scission and the MC simulations is perfect. The lower part of Figure 4.8 shows that for 2 CSTRs in series assuming linear scission a bimodal CLD shape is still present according to the deterministic model from PREDICI®, clearly deviating from the CLD from MC simulations and multiradical model.
Figure 4.10 displays the decreasing trend of gel fraction as a function of number of CSTRs in series with a mild transfer to polymer ($k_{tp}/k_p = 0.005$) and no scission while the rates for combination and disproportionation are supposed to be the same. The development of the living chain length distributions over time with strong transfer to polymer ($k_{tp}/k_p = 0.012$), equal combination and disproportionation rates without scission is illustrated in Figure 4.11. The gelpoint, which is characterized by strong tailing of the chain length distributions, is visible only between 2 and 3 seconds from the beginning of the polymerization. In Figure 4.12 the evolution of conversion and polydispersity index from multiradical model and MC simulation, and two types of gel fractions based on the loss of monomer units and radical sites from multiradical model over time for a batch reactor are
compared. The two types of gel fractions are defined according to the idea that sol and gel accommodate both the radical sites and the monomer unites. The sharp peak in the polydispersity index depicts the gelpoint, which takes place at 2.3 s and in 20% conversion. Figure 4.13 shows a perfect agreement between the final resulting living chain length distribution from Figure 4.11 and the resulting distribution from MC simulations.

Figure 4.9. Chain length distributions from multiradical model and MC simulations for the case without scission, mild transfer to polymer and combination for series of CSTRs and batch reactor; conversion \( x = 0.456 \), kinetic data from Table 4.4, initiator feed according to Figure 4.4. Gel fraction decreases from 24 % for 1 CSTR to 0 for 4 CSTRs and batch reactor. Perfect agreement between deterministic model and MC simulations for all configurations.

Figure 4.10. Gel fraction as a function of number of CSTRs for the case without scission and with combination (as in Figure 4.9). Gel fraction decreasing with number of CSTRs.
Figure 4.11. Chain length distributions over time from multiradical model without scission, with high transfer to polymer and combination for batch reactor; conversion $x = 0.456$, kinetic data from Table 4.4, initiator feed according to Figure 4.4. Between 2 and 3 s the gelpoint is reached accompanied by a strong tailing of the CLD that reduces afterwards.

Figure 4.12. Development of conversion, polydispersity index and gel fraction over time for the batch reactor according to multiradical model and MC simulations; conditions of Figure 4.11. Radical site gel fraction from multiradical model. At the gelpoint, at 2.3 s and 20 % conversion, the system reaches the gelpoint, which is accompanied by a sharp peak in the polydispersity index.

Figure 4.13. Chain length distributions from multiradical model and MC simulations for batch reactor for the case of Figure 4.11. Time profiles of MC parameters not shown, but comparable to RHS of Figure 4.7. Exact agreement between deterministic multiradical model and MC simulations.
4.4.2.4 Combination termination, with topological scission

In this section the presence of termination by combination is assumed, a mechanism commonly accepted for ldPE. According to Chapter 2 on single CSTR, the fragment length distribution function describing the topological scission allows inferring a proper expression for the scission contribution from gel within the multiradical model, where the linear scission model failed to do so (Yaghi and Iedema, 2014b). In this section, only the topological scission in the tubular reactor under possible gel conditions is discussed. Due to the empirical nature of the fragment length distribution function assumed in the deterministic approach, a small deviation from real random scission of branched molecules, as correctly described by MC simulations, is expected, however.

In Figure 4.14 we compare the chain length distributions for a series of 2 and 4 CSTRs and a batch reactor as obtained from MC simulations with outcomes from the multiradical model for moderate rates of transfer to polymer and scission ($k_p/k_p = 0.0012$, $k_c/k_p = 0.00012$), and equal combination and disproportionation rates ($k_c/k_p = k_d/k_p = 1000$). For this kinetic data set, gelation has not been observed and a fair agreement has been obtained for the resulting distributions from the deterministic model and MC simulations. The results from both models show that increasing the number of CSTRs narrows the chain length distributions, making them closer to the distribution of an ideal batch reactor.

Figure 4.15 shows close ups of the chain length distributions tails of Figure 4.14. Given that MC simulations are most adequate in describing random scission, discrepancies with the deterministic model are expected (Yaghi and Iedema, 2014b). However, it might appear strange that in the single CSTR case the deterministic model over-estimates the tail, while in the 2 CSTR case it under-estimates the tail extension. This must be explained by the ‘turning’ of the CLD at the gel point: upon increasing of branching before the gel point the CLD broadens, after the gel point it narrows again. The 2 CSTR case is in a pre-gel situation. Here, the deterministic model describing gel fragmentation leads to under-estimation of the tail. The single CSTR case is in post-gel; here the gel fragmentation model leads to under-estimating of the gel (11.9 % instead of the 13.9 % from MC simulations). This behavior is consistent with the aforementioned turning phenomenon that lower gel content leads to a longer tail. Hence, the inadequacy of the multiradical model in computing scission fragments in both cases is the source of the deviation with the results from MC simulations.

Figure 4.14. Chain length distributions from multiradical model and MC simulations for series of 2 and 4 CSTRs and batch reactor assuming equal combination and disproportionation and topological scission. No gelation, fair agreement between multiradical model and MC simulations.
4.4.3 More realistic reactor configurations for ldPE

Here, the results for more realistic ldPE reactor conditions, all on the basis of the multiradical model and MC simulations are presented. First an ldPE autoclave being mimicked by a series of 4 CSTRs with and without intermediate initiator injection point is discussed. Then the results of simulations of a tubular ldPE reactor with realistic temperature profile, under identical conditions as described in Kim et al. (2004) are presented.

4.4.3.1 Autoclave reactor simulated as series of 4 CSTRs

The simulations with the series of 4 CSTRs have been carried out to demonstrate the effect of different feed strategies. In principle, the deterministic model allows configuring any compartmentalization of a real (autoclave) reactor by selecting the number of compartments (CSTRs), the temperatures at which they operate as well as the flows to (monomer, initiator, transfer agent) and in between compartments. For instance, ‘back-mixing’ is easily introduced by a flow from a downstream compartment to one or more upstream compartments. Note that MC simulations according to the description given above also allow specifying any condition for each of the compartments, but back-mixing is not so easily implemented.

In this section an exhaustive survey of all the compartment configurations possible with the deterministic model is not given, but just a proof of principle in one example. Here, a series of 4 CSTRs with a single injection of initiator in the first CSTR to such a series with equally shared multiple initiator injection – single and multiple injections leading to the same overall conversion are compared. Kinetic conditions in all the reactors are assumed to be the same – those listed in Table 4.4 – with mild scission, $k_{sc}/k_p = 4 \times 10^{-5}$. The results are shown, as double chain length weighted concentrations, in Figure 4.16 for both deterministic model and MC simulations. The single injection case leads to a narrow chain length distribution and no gel is formed. The multiple injection leads to a much broader distribution and also gel formation, 7.1 % both from multiradical model and from MC simulations. Note that under these conditions the deterministic model perfectly coincides with MC simulations. This example shows the strong impact of the initiator feed strategy on the quality of the ldPE produced.
4.4.3.2 Non-isothermal tubular reactor under realistic conditions

To account for the influence of the strongly varying temperature, the best-known Arrhenius parameters for all the reactions are employed; as in Kim and Iedema (2004), see Table 4.5. A realistic mild scission reaction rate is assumed. The flow conditions are listed in Table 4.6. Figure 4.17 shows the resulting development of chain length distribution with tube length, clearly showing the discontinuities at the initiator feed points. Figure 4.18 compares the chain length distribution at the end of the tubular reactor as obtained by the multiradical model, by the monoradical model (Kim and Iedema, 2004) and by MC simulations. The parameter profiles for the latter have been calculated for the temperature profile and the kinetic equations given in Table 4.5; these profiles are shown in Figure 4.19. It turns out that the distributions from the deterministic multiradical model show a perfect agreement with MC simulations. The chain length distribution resulting from the monoradical model, as shown in Kim and Iedema, 2004, features a less extended tail. This agrees with findings in Yaghini and Iedema (2014b), where often chain length tails from the multiradical model were found to be more extended.

Finally, here in the context of a non-isothermal tubular reactor the issue of either or not assuming gel as has been done for a single steady-state CSTR in Yaghini and Iedema (2014b) is raised. Figure 4.20 presents chain length distributions for the non-isothermal tubular reactor with strong transfer to polymer (50 % higher than value of Table 4.4), no scission and no CTA injection, from deterministic monoradical and multiradical models and from MC simulations. The monoradical model – as in Kim and Iedema (2004) - shows a strong bimodality when assuming no gel. This solution is mathematically correct, but must nevertheless be considered erroneous, since it is based on the no gel assumption, while in reality the operating point falls into the gel regime. This is proved by the results of both the multiradical model and the MC simulations that indicate a gel fraction of 28.5 %. The bimodality, also shown in Kim and Iedema, 2004, is obviously an artifact due to the no gel assumption, as similar to the artificial broad and bimodal distributions for the same assumption in the single CSTR case (Yaghini and Iedema, 2014b).
Figure 4.17. Development of CLD along tube length for realistic \( \text{ldPE} \) temperature profile and intermediate initiator feed points (Kim and Iedema, 2004), see Table 4.6.

Figure 4.18. CLD at the end of the \( \text{ldPE} \) tubular reactor (same as in Figure 4.17) from new multiradical model and monoradical model (Kim and Iedema, 2004) and from MC simulations. Exact agreement between multiradical model and MC simulations (mild scission).

Figure 4.19. MC parameters for realistic \( \text{ldPE} \) tubular reactor, same as Figure 4.17 and Figure 4.18. Discontinuities at intermediate initiator feed points clearly observed.
Figure 4.20. Comparison of monoradical and multiradical model with MC simulations for non-isothermal tubular reactor assuming no scission and no CTA addition and 59% higher transfer to polymer rate than according to Table 4.4. Assuming no gel monoradical model gives solution with strong bimodality (see Kim and Iedema, 2004). This operating point (non-realistic for ldPE) falls in the gel regime, according to both MC and multiradical model; CLD’s from these perfectly agree.

4.5 Conclusions

A pseudo-2D population balance modeling framework to determine the MWD of ldPE free radical polymerization in various reactor configurations like a tubular reactor and a series of CSTRs is provided. The first dimension, chain length, is fully dealt with, the second, number of radical sites, is accounted for by a pseudo-distribution (moment) approach that was successfully applied to a single CSTR (Yaghini and Iedema, 2014b). This multiradical model includes the topological scission and termination by combination. The effect of multiradicals and reactor configurations (isothermal) on the behavior of MWD has been investigated under different assumptions concerning the kinetics of the system.

Assuming termination by disproportionation only and no scission it is observed that by increasing the number of CSTRs, chain length distributions started to narrow down until reaching the chain length distribution from a batch reactor. Perfect agreement with MC simulations has been found for the case of no scission. With termination by disproportionation and linear scission when changing the reactor configuration from a single CSTR to batch, the bimodality of chain length distribution that is measured by Size Exclusion Chromatography- Multi Angle Laser Light Scattering (SEC-MALLS) in some autoclave grades of ldPE disappeared for the batch reactor. It turned out that the distribution shapes obtained in a batch reactor are almost insensitive to scission model assumed (linear or topological).

Introducing combination termination – as expected - gave rise to gel formation in the CSTR series and batch reactor – albeit less so in the latter. Indeed, increasing the number of CSTRs in series caused a significant decrease in gel fraction, eventually leading to low amounts or total absence of gel in the batch reactor. All results agreed perfectly well with MC results for all reactor configurations, if no scission was assumed. In the presence of scission, due to a less than ideal approximation of random scission in the deterministic model, less perfect agreement is observed, but still quite satisfactory for realistic scission rates.

More realistic reactor configurations for ldPE, a series of 4 CSTRs with different initiator feed strategies, and a tubular reactor with a realistic temperature profile over tube length have also been tested. The resulting distributions from deterministic models always...
showed perfect agreements with MC simulations for the case of no scission and satisfactory agreement for mild scission. For a non-isothermal tubular setting with strong transfer to polymer the strong bimodality detected in a previous publication (Kim et al., 2004) proved to be a complete artifact due to the no gel assumption of the monoradical model. Hence once more, as shown previously for a single CSTR (Yaghini and Iedema, 2014b), now for a batch reactor and CSTR series the importance of the gel assumption in combination with the presence of multiradicals is demonstrated.
5 Branching determination from radius of gyration contraction factor

In this chapter we propose a set of models to calculate contraction factor, the kinetics of a radical polymerization with transfer to polymer and combination termination to maximum extent are accounted for. The models are alternatives to the Zimm and Stockmayer’s (1949) analytical expression of contraction factor for molecules with terminal branching. The results, being representative for molecules such as low-density Polyethylene (ldPE), show significantly stronger contraction than predicted by the model of Zimm and Stockmayer. In the case of termination by disproportionation only, molecular sizes turn out to be smaller by a factor of almost two. In presence of combination termination molecules are less compact. It is shown that the interpretation of contraction factors as measured by the Size Exclusion Chromatography – Multi Angle Laser Light Scattering to find the branchedness of ldPE, with the new model leads to a considerably lower estimate of branching than by using the standard Zimm and Stockmayer’s model.

5.1 Introduction

It is well known that the degree of branching and thus radius of gyration has a strong effect on microstructural properties of polymer (Tackx and Tacx, 1998), such as rheology and melt strength (Read et al., 2011). The question we desire to answer in this chapter is essentially the same as Zimm and Stockmayer’s in 1949: how could we relate long chain branching to radius of gyration contraction factors (Zimm and Stockmayer, 1949)? This has obvious practical relevance in characterization of branched polymers by Size Exclusion Chromatography–Multi Angle Laser Light Scattering (SEC-MALLS), since up until today the theory of Zimm and Stockmayer is used to estimate branching from the observed contraction factor. Note that Zimm and Stockmayer just claimed the validity of their model for a simple end-to-end branching structure. After more than 60 years with powerful computers and good mathematical models we are now able to predict branched architectures based on the real polymerization kinetics. Applying the same concepts as Zimm and Stockmayer, it is shown in this chapter that these more realistic architectures give rise to different contraction factors than those from the old model and exemplified for an ldPE radical polymerization with transfer to polymer and combination termination. The latter mechanism introduces an extra connectivity element, since parts of a molecule are not only connected by branch points, but also by combination points. It is shown that absence or presence of combination termination is strongly influencing the compactness of the molecules.

This chapter is based on N. Yaghini, P. D. Iedema, Polymer (2015), 59 166-179
5.2 Zimm and Stockmayer revisited

Here we briefly discuss the early paper by Zimm and Stockmayer (1949). They provided a classical estimation to the branching by using the radius of gyration. According to the usual definition (see Figure 5.1), the radius of gyration is defined as the sum of the distances between each monomer unit, \( r_k \), and the center of mass, \( \mathbf{r} \). For larger molecules, they adopt Kramers theorem (Kramers, 1946):

\[
R_g = \left\langle n_{1c} n_{2c} \right\rangle / n = \sum_{c=1}^{n} n_{1c} n_{2c} / n^2
\]

(5.1)

According to this concept a (branched) molecule of \( n \) monomeric units is considered being cut into two parts of \( n_{1c} \) and \( n_{2c} \), where \( n_{1c} + n_{2c} = n \), and \( \left\langle n_{1c} n_{2c} \right\rangle \) represents the average value of the product of \( n_{1c} \) and \( n_{2c} \) obtained by averaging over all possible ways, \( c \), of cutting the molecule. This situation is represented in Figure 5.1, where the size of the molecule is \( n \), while the fragments are \( n_{1c} = m \) and \( n_{2c} = n - m \). For a large linear molecule, Equation 5.1 is easily shown to reproduce the well-known result for such chains, again with \( n_{1c} = m \) and \( n_{2c} = n - m \), since:

\[
R_{g,\text{linear}} = \sum_{c=1}^m n_{1c} n_{2c} / n^2 = \int_0^\infty m(n-m)dm / n^2 = n / 6
\]

(5.2)

For a population of molecules of size \( n \) with different architectures the fragment sizes have to be multiplied with the probabilities \( p(n_{1c}) \) and according to which the fragment sizes occur, such that:

\[
R_g = \sum_{c=1}^n p(n_{1c}) n_{1c} p(n_{2c}) n_{2c} / n^2
\]

(5.3)

Figure 5.1. Radius of gyration from distances to center of mass and from products of distances between monomer units.
Zimm and Stockmayer apply this concept to an example introduced by them as: “… we study only an idealized example, which may, however, not be so different from actuality as to be useless” (Zimm and Stockmayer, 1949). This example refers to a branched structure created by linear segments connected at their end points with connection probability $\beta$ at either side, Iedema (2012) has referred to earlier as ‘terminal branching’, see Figure 5.2. Regarding the probability distribution of numbers of branch points in the part of the network connected at one side of an arbitrary unit in the whole molecule, they employ an expression, derived earlier by Flory (1946):

$$p_i = \frac{(2i)!}{(i+1)!i!} \beta^i (1-\beta)^{i+1}$$

(5.4)

where $i$ denotes the number of branch points. For a molecule with $i$ branch points, where the segment lengths follow the most probable distribution, Zimm and Stockmayer use another result obtained by Flory (1946):

$$p_{nj} = \frac{(n-1)!(1-\alpha)^{2i+2}}{(n-2i-2)!} \alpha^{n-2i-2} \frac{1}{(2i+2)!}$$

(5.5)

Here, $\alpha$ is the Flory parameter:

$$\alpha = 1 - 1/\bar{n}$$

(5.6)

with $\bar{n}$ the number average segment length. Equation 5.1 now used to form the product of probabilities in Equation 5.3, yielding Equation 5.7. This product is dependent on both the numbers of monomer units on fragments, $m$ and $n-m$, as on the numbers of branch points on fragments, $j$ and $i-j$. Here $n$ and $i$ represent the overall numbers of monomer units of a molecule and the number of branch points, respectively.

$$P(n,m,i,j) = (1-\beta)^2 \frac{\beta(1-\beta)^j}{j!} \frac{m^{(j-1)!}(n-m)^{(j-1)(i-j)}}{(f-2)!} \alpha^{(1-\alpha)/\alpha} \frac{1}{(f-2)(i-j+1)!}$$

(5.7)

Thus, formulating the radius of gyration of the branched molecule according to Equation 5.3 by taking the sum and normalizing and subsequently dividing by the radius of gyration of a linear molecule, $n/6$, Zimm and Stockmayer find the radius of gyration contraction factor as:

$$g_f(n,i) = \frac{6 \sum_{m=1}^{n} \sum_{j=0}^{n} P(n,m,i,j) m(n-m)/n \sum_{m=1}^{n} \sum_{j=0}^{n} P(n,m,i,j)}{\sum_{n=1}^{n} \sum_{j=0}^{n} P(n,m,i,j)}$$

(5.8)

By an elaborate algebraic procedure, they are able to derive the famous expression for the radius of gyration contraction factor for a molecule with $i$ branch points:
\[ g_f(i) = \frac{3}{(f-1)i+3} \left[ 1 + \sum_{j=1}^{i} (f-1)^j \prod_{k=0}^{i} \frac{i-k}{(f-1)i+2-k} \right] \] (5.9)

where, \( f \) is the branching functionality of a molecule with \( i \) branch points. (Note that the original publication by Zimm and Stockmayer uses \( n \) for the number of branch points and \( N \) for the number of monomer units). The both number of monomer units, \( n \), and the connection probability, \( \beta \), are absent in Equation 5.9, so that under the prevailing assumptions the contraction factor exclusively depends on the number of branch points. Equation 5.9, obtained in 1949, is still widely used in characterization of branched polymers – in spite of the modest claim of the authors cited above!

It is instructive to see the result of Equation 5.9 practically reproduced by directly enumerating Equation 5.8, Equation 5.9 for the case of \( i = 250 \) branch points and for \( n = 5000 \) underestimates the \( g_f \) by 2% and for \( n = 100,000 \) by 0.2%. Thus, the fact that the radius of gyration contraction factor is practically independent on the size of the molecule, for the case of terminal branching under the conditions considered, is confirmed.

![Figure 5.2. Construction of one-sided branched polymer architecture distributions, \( \beta \) is defined as in Equation 5.4.](image)

### 5.3 Radius of gyration distribution for terminal branching

Obviously, Equations 5.8 and 5.9 predict the average of all possible topologies within populations of terminally branched molecules of given dimensions, \( n \) and \( i \). It should be realized that such populations possess a wide variety of different topologies (see Figure 5.2) for the given dimensions, having varying contraction factors as well. In this paragraph we will present a Monte Carlo algorithm to find the distribution of radius of gyration contraction factors for terminal branching using identical assumptions as in Zimm and Stockmayer’s derivation (Zimm and Stockmayer, 1949).

The task of the algorithm is to find explicit architectures for polymer molecules with terminal branch points given the number of branch points, \( i \), and the branching probability,
\( \beta \), as defined above. Again, the number of branch points distribution is given by Equation 5.4. The first step of the algorithm is shown in Figure 5.3. An arbitrary free dangling segment (not connected on one end) is picked, which as a part of a molecule with \( i \) branch points is certainly connected to two other fragments at its other end. The numbers of branch points on either of the fragments, \( j \) and \( i - j - 1 \), may vary between 0 and \( i - 1 \). Obviously, these numbers are complementary adding up to \( i - 1 \), since neither fragment contains the first branch point (black dot in Figure 5.3). Because of the self-similar nature of the architecture, Equation 5.4 also holds for the fragments. This implies that the conditional probability of finding \( j \) given \( i \), \( \Re(j|i) \), is given by:

\[
\Re(j|i) = \frac{p(j)p(i-j-1)}{\sum_{j=0}^{i} p(j)p(i-j-1)}
\]

Here, \( p(j) \) and \( p(i-j-1) \) are given by Equation 5.4. Inspection of the product of probabilities \( p(j)p(i-j-1) \) indicates that the factors containing \( \beta \) lead to a product that is independent of \( j : \beta^j (1-\beta)^{i-j-1} (1-\beta)^{i-j} = \beta^j (1-\beta)^{i-j} \). In Equation 5.10 this constant term appears in both numerator and denominator, so it will be canceled out upon division. The interesting consequence is that the conditional probability function, Equation 5.10, becomes independent of \( \beta \) ! Hence, the shape of the function that is symmetrical around \( j = i/2 \) and has the maxima at \( j = 0 \) and \( j = i - 1 \) is identical for all \( \beta \)-values and only depends on \( i \). Note that a similar independency of the contraction factor (Equation 5.9) had already been observed in the discussion about the Zimm and Stockmayer model (Zimm and Stockmayer, 1949), where Equation 5.7 expresses a similar operation as Equation 5.10. This outcome may seem logical, if one realizes that irrespective of the average connectivity value \( \beta \) imposed on a system of segments, an architecture of given number of branch points, \( i \), always possesses \( i \) connected ends and \( i+1 \) non-connected ends. Hence, the average connection probability simply equals \( i/(2i+1) \).

Sampling from the probability density function, Equation 5.10, yields values for the numbers of branch points in one particular molecule. For each of the fragments the algorithm proceeds in exactly the same manner as before with the lower numbers \( j \), respectively \( i-j-1 \), each of which may split up in the next step. This is repeated until the last fragment is found having zero branch points, representing the last free dangling end. To perform this series of sampling steps, we have employed the recursive algorithm developed for the similar, but slightly more complex problem of branching architectures arising from insertion of vinyl-ended segments using Constrained Geometry Catalyst in metallocene-based polymerization of ethylene (Hoefsloot and Iedema, 2003). The algorithm performs the sampling steps and generates the connectivity pattern in a graph theoretical representation, an incident matrix. This forms the basis to infer the radius of gyration contraction factor from, as will be explained in section 5.5.
First step in algorithm to find architectures for a polymer molecule with terminal branching having \( j \) branch points.

Radius of gyration contraction factor dependent on kinetics

Measuring the contraction factor has been so far the best applicable method to determine branching in the presence of long and short chain branching together. The contraction factor or shrinkage of a branched polymer chain, \( g \), is defined as the ratio of its radii of gyration to the radii of gyration of a linear polymer of the same mass. Zimm and Stockmayer (1949) have derived their well-known expression, Equation 5.9, for the case of terminal branching. The relationship between contraction factor and kinetics has been discussed before (Iedema and Hoefsloot, 2004b; Iedema et al. 2007).

Branched polyethylene made using metallocene catalysts turned out to possess less important contraction than radical systems with transfer to polymer as the branching mechanism. Here, we will focus on radical polymerization again and explore the effect of termination mechanism on the radius of gyration contraction: disproportionation and combination termination. In order to realize this we have to find the equivalents of Equations 5.4 -5.5 and 5.7 above, especially that describing the probability distributions of numbers of monomer units connected to the networks at either side of an arbitrary monomer unit in the whole branched molecule, as shown in Figure 5.1. It will turn out that we are not able to derive an analytical expression like equation 5.7 for more realistic but complex kinetics. Instead, we have to create populations of explicit branched topologies, by Monte Carlo simulation, from which to derive the connectivity to the networks at either side of an arbitrary monomer unit in each of the branched topologies generated. In order to create the populations of topologies, we have employed a Monte Carlo algorithm, the ‘history backtracking’ method (Iedema et al., 2007), while graph theory is used to represent the connectivity pattern of the networks generated.

5.4.1 Reaction and population balance equations, various distributions

A solution for 3- Dimensional (3D) population balances describing Chain Length Distribution/Degree of Branching Distribution/Combination Points Distribution (CLD/DBD/CPD) in a Continuous Stirred Tank Reactor (CSTR) has been presented by Iedema and Hoefsloot (2005). This solution was obtained using a direct computation method, recursively enumerating the concentrations of dead and living chains at all combinations of the first two dimensions, chain length and number of branch points, 1, 2, 3, \( \ldots \), 300 000; and 0, 1, 2, \( \ldots \), 1 000, respectively. The number of combination points
dimension; the 3rd dimension, were found using the pseudo-distribution approach. At present, this computationally expensive method has been replaced by a much more efficient Galerkin-Finite Element Method (FEM) algorithm in the full 2 dimensions of chain length and number of branch points, while treating number of combination points with pseudo-distributions. This full 2-Dimensional (2D) Galerkin-FEM approach will be presented in a forthcoming chapter. Under the present kinetic conditions, without random scission, the 3D results from the old direct computation method and the full 2D Galerkin-FEM method turns out to practically coincide. Therefore, the same 3D solution for CLD/DBD/CPD as in Iedema and Hoefsloot (2005) is used. Note that from the CPD moments obtained using the pseudo-distributions method (both for the direct and full 2D method) the full CPD are inferred assuming that this distribution obeys a binomial distribution. The reaction and population balance equations describing the radical polymerization process with transfer to polymer and termination by disproportionation and combination are presented in Table 5.1. Furthermore, Table 5.2 gives the kinetic parameter settings together with the reaction rates and the relevant concentrations.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator dissociation</td>
<td>( I_2 \xrightarrow{k_d} 2I )</td>
</tr>
<tr>
<td>Initiation</td>
<td>( I + M \xrightarrow{k_i} R_{100} )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( R_{n+i,j,k} + M \xrightarrow{k_p} R_{n+i,j,k} )</td>
</tr>
<tr>
<td>Termination by disproportionation</td>
<td>( R_{n+i,j,k} + R_{m+j,l} \xrightarrow{k_t} P_{n+i,j,k} + P_{m+j,l} )</td>
</tr>
<tr>
<td>Termination by combination</td>
<td>( R_{n+i,j,k} + R_{m+j,l} \xrightarrow{k_t} P_{n+i,j,k+l+1} )</td>
</tr>
<tr>
<td>Transfer to polymer</td>
<td>( R_{n+i,j,k} + P_{m+j,l} \xrightarrow{k_t} P_{n+i,j,k} + R_{m+j+l+1} )</td>
</tr>
</tbody>
</table>

Population balance equations:

\[
\frac{dR_{n+i,j,k}}{dt} = k_p M (R_{n+i,j,k} + R_{n-i,j,k}) - (k_d + k_i) \lambda_\nu R_{n+i,k} + k_p (\mu R_{n+i,j,k} + \lambda_\nu n P_{n-i,k}) - \frac{1}{\tau} R_{n+i,j,k} \\
\frac{dP_{n+m,j,k}}{dt} = k_p \lambda_\nu R_{n+i,k} + \frac{1}{2} k_p \sum_{m=1}^{n+i} \sum_{j=1}^{n+j} R_{n+j,k} R_{n+m-j,k-l-1} + k_p (\mu R_{n+i,j,k} - \lambda_\nu n P_{n-j,k}) - \frac{1}{\tau} P_{n+i,j,k}
\]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>m, n</td>
<td>chain length</td>
</tr>
<tr>
<td>i, j</td>
<td>number of branch points per chain</td>
</tr>
<tr>
<td>k, l</td>
<td>number of combination sites per chain</td>
</tr>
</tbody>
</table>

Table 5.1. Polymerization reactions and the associated population balance equations.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation</td>
<td>$k_d$</td>
<td>0.5 [s$^{-1}$]</td>
</tr>
<tr>
<td>Propagation</td>
<td>$k_p$</td>
<td>5000 [m$^3$kmole$^{-1}$s$^{-1}$]</td>
</tr>
<tr>
<td>Disproportionation termination</td>
<td>$k_d$</td>
<td>$5 \times 10^5$ [m$^3$kmole$^{-1}$s$^{-1}$]</td>
</tr>
<tr>
<td>Combination termination</td>
<td>$k_c$</td>
<td>$5 \times 10^6$ [m$^3$kmole$^{-1}$s$^{-1}$]</td>
</tr>
<tr>
<td>Transfer to polymer</td>
<td>$k_p^T$</td>
<td>1.5 [m$^3$kmole$^{-1}$s$^{-1}$]</td>
</tr>
<tr>
<td>Average residence time CSTR</td>
<td>$\tau$</td>
<td>30 [s]</td>
</tr>
<tr>
<td>Feed monomer concentration</td>
<td>$M_f$</td>
<td>16.75 [kmole.m$^{-3}$]</td>
</tr>
<tr>
<td>Feed initiator concentration</td>
<td>$I_{2,f}$</td>
<td>$5 \times 10^{-3}$ [kmole.m$^{-3}$]</td>
</tr>
<tr>
<td>Monomer concentration</td>
<td>$M$</td>
<td>9.1067022 [kmole.m$^{-3}$]</td>
</tr>
<tr>
<td>Macroradical concentration</td>
<td>$\lambda_0$</td>
<td>5.58850 10$^{-6}$ [kmole.m$^{-3}$]</td>
</tr>
<tr>
<td>Incorporated monomer concentration</td>
<td>$\mu_1$</td>
<td>7.638741575 [kmole.m$^{-3}$]</td>
</tr>
</tbody>
</table>

Table 5.2: Kinetic and concentration data.

5.4.2 Generating architectures by conditional Monte Carlo sampling

Here, the main features of the ‘history backtracking’ and architectures construction algorithms that have been introduced in Iedema et al. (2007) are resumed. This conditional Monte Carlo algorithm is based on the chemistry of the radical polymerization system as briefly summarized in the reaction and population balance equations of Table 5.1. The solution of balance equations using the 2D Galerkin approach employing pseudo-distributions (moments) for the distributions of combination points provides the 3-dimensional chain length, $n$, number of branch points, $i$, number of combination points, $k$, distribution of dead and living chains, $P(n,i,k)$ and $R(n,i,k)$, respectively. In the algorithm length, $n$, number of primary polymers, $n_p$, and number of combined parts, $n_c$, are used instead of branch points and combination points. The relations between the number of combination points, $k$, and number of branch points, $i$, as appearing in the population balances, and the number of combined parts, $n_c$, and number of primary polymers, $n_p$, are, respectively:

$$n_c = k + 1$$

(5.11)

$$n_p = i + k + 1$$

(5.12)

5.4.2.1 The algorithm to generate architectures and branching determination

5.4.2.1.1 Outline of the algorithm

A branched molecule is created from linear segments, or primary polymers, that are assumed to grow instantaneously in a certain time order and a certain length. The algorithm first identifies the time sequences and lengths of the primary polymers as well as their connectivity to other primary polymers, and then secondly builds up the architectures. The
first task is performed by the **history backtracking algorithm**. The process of the latter task is schematically shown in Figure 5.4. Typically, in the case of combination termination, the creation of one molecule may start at more than one initial primary polymers being formed at different instants of time.

The growth history backtracking algorithm is now demonstrated on a molecular example as shown in Figure 5.5. The idea behind this algorithm is to consider a molecule of given dimensions, in this example \( n \) (not specified in this demonstration), \( n_p = 15 \), \( n_c = 7 \), and find the answer to the following question: “what was the last reaction step that created the dead molecule of these dimensions”? We realize that this must have been a termination reaction of a living chain end by either disproportionation or transfer to polymer on the one hand or combination on the other. The probability that the last step was combination is \( \mathbb{R}_c(n, n_p, n_c) \), the probability for one of the two other reactions is \( 1 - \mathbb{R}_c(n, n_p, n_c) \). This probability is inferred from the solution of the 3D population balance, as we will see later.

The combination test for this molecule, performed by requiring \( \mathbb{R}_c(n, n_p, n_c) > r \) (random number \( 0 < r < 1 \)), in this example revealed that the last event was a combination step indeed. As this combination has occurred between two fragments of the molecule, we now should find the fragment dimensions. This proceeds by subsequently applying three further Probability Density Functions (PDFs):

1. \( \mathbb{R}(n_1 | n, n_p, n_c) \), probability distribution of numbers of combination parts on fragment 1, \( n_1 \), given the dimensions of the whole molecule \( (n_2 = n_c - n_1) \).

2. \( \mathbb{R}(n_p | n, n_p, n_c, n_2) \), probability distribution of numbers of primary polymers on fragment 1, \( n_p \), given the dimensions of the whole molecule and the numbers of combination parts on both fragments \( (n_p = n_p - n_1) \).

3. \( \mathbb{R}(n_c | n, n_p, n_p, n_2, n_c, n_2) \), probability distribution fragment 1 size, \( n_1 \), given the dimensions of the whole molecule and numbers of combination parts and primary polymer on fragments \( (n_2 = n_c - n_1) \).

These PDFs also follow from the population balance solution. The result is shown for the example in cartoon 2 from Figure 5.5: one fragment is a single primary polymer with length \( n_1 \) that is now fully identified; the other fragment is a larger structure of dimensions \( (n_2, 14, 6) \).

Next, as shown in cartoon 3, the lengths of the last grown primary polymer, \( n_1 \), and that of the structure on which it grows, \( n_2 \), are determined, using the PDF \( \mathbb{R}_p(n_1 | n, n_p, n_c) \), fragment 1 size distribution given the whole molecule’s dimensions. This yields a fully identified primary polymer again and a structure of dimensions \( (n_2, 13, 6) \). At this point the algorithm returns to the combination test and a new round is entered.

As shown in cartoon 4, again the last step turns out to be combination, this time resulting in two larger structures of dimensions \( (n_1, 7, 3) \) and \( (n_2, 6, 3) \). Now, the algorithm branches into two paths that are worked through one after another. Figure 5.5 shows only one of these parts, that of structure \( (n_2, 6, 3) \). Note that ultimately as many paths are tracked
as there are initial primary polymers as each path should end in an initial primary polymer—hence the example has 5 paths.

Figure 5.4. Construction of branched polymer architecture with \( n_p = 15 \) primary polymers and \( n_c = 6 \) combined parts from 5 initial primary polymers connected by combination and branching points.

5.4.2.1.2 Probability density functions

Here, it is shown how one of the probability density functions, \( \mathbb{W}_t(n_1|n,n_p,n_c) \), is inferred from the solution of the 3D population balances. The derivation of the other PDFs is given in Appendix 1. This PDF denotes the probability distribution of lengths \( n_1 \) of single chains becoming connected to the larger fragment, given the dimensions of the whole molecule, which is the result of the connection process. This happens by a transfer to polymer step, where the living molecule \((n,n_p,n_c)\) is created from a smaller dead molecule with \( n_p - 1 \) primary polymers, and a consecutive growth step producing a new primary polymer of length \( n_1 \), whose length is sought. In the first step from a dead chain of dimensions \((n-n_1,n_p-1,n_c)\) a living chain of the same dimensions is created with probability \( p_1 \):

\[
p_1(n-n_1,n_p-1,n_c) \sim (n-n_1)P(n-n_1,n_p-1,n_c)
\]

(5.13)

Here, \( p \) represents the solution of the 3D population balances for dead molecules. In \( p_1 \), the multiplication by \( n-n_1 \) arises from the fact that any of the \( n-n_1 \) units of the molecule can undergo this step. The second step is growth of a new arm by propagation at the new branch point to length \( n_1 \) until termination. The probability, \( p_2 \), of creating an arm length \( n_1 \) obeys the Flory distribution:

\[
p_2(n_1) \sim p_p(n_1) = (1 - 1/\bar{n})^{(n_1-1)}/\bar{n}
\]

(5.14)

where the average primary polymer length \( \bar{n} \) is given in Iedema and Hoefsloot (2007):
\[
\bar{\eta} = \frac{k_p M I + k_p \mu \lambda_0 + k_M \lambda_0}{\lambda_0 (k_p \mu + k_d \lambda_0 + k_c \lambda_0 + 1/\tau)}
\]  

(5.15)

Figure 5.5. Example of history backtracking starting from \( n_p = 15 \) and \( n_c = 7 \). Cartoons through 9 only show the 'paths' following the structure \((n_2, 6, 3)\) ending in the two initial primary polymers shown in cartoon 9.

Thus the probability of creating a dead molecule of total length \( n \) and \( n_p \) primary polymers is simply the product of \( p_1 \) and \( p_2 \), since length \( n_1 \) is independent of length \( n - n_1 \). Hence, the normalized PDF is:

\[
\mathcal{R}_{n_1}(n_1 | n, n_p, n_c) = \frac{p_2(n_1) P(n - n_1, n_p - 1, n_c) (n - n_1)}{\sum_{n_1=1}^{n_p} p_2(n_1) P(n - n_1, n_p - 1, n_c) (n - n_1)}
\]  

(5.16)

Flowcharts of history backtracking and architecture algorithm are provided in Figure 5.6.
Figure 5.6. Flowcharts of the history backtracking algorithm (left) and the architecture generation algorithm (right). The backtracking algorithm provides time sequences, lengths and connectivity of the \( n_p \) primary polymers. The architecture algorithm selects these primary polymers one by one (counter \( N = 1:n_p \)) in proper time order and performs the connecting process.

5.5 Determination of radius of gyration using graph theory

Kramers theorem (Kramers, 1946) will be employed to obtain the radius of gyration from the sizes of molecules at either side of all the monomer units, by Equation 5.1, but now from representations of explicit topologies. According to these representations, any branched architecture is characterized by a set of branch points connected by a specific pattern as well as the lengths of the segments between branch points and the lengths of free dangling segments. A feature from graph theory is chosen, the adjacency matrix, to represent the connectivity of branch points \( A \), as shown in Figure 5.7. Each element \( A_{ij} \) that is equal to one represents a segment; in the example of Figure 5.7, 10 branch points are connected by 9 ‘inner’ segments. Thus, a molecule of \( N \) branch points generated by Conditional Monte Carlo (CMC) is represented by an adjacency matrix of size \( N \times N \) and a list of \( N-1 \) inner segment lengths and \( N+1 \) lengths of free dangling segment. It should be realized that such representations of branched topologies are applicable to all architectures, irrespective of the manner in which they are created. In the present study topologies of terminally branched
molecules are considered and created by the CMC method fully accounting for the kinetics of a radical polymerization system as described above.

To infer the number of monomer units in the networks connected at either side of an arbitrary monomer unit in a branched molecule, an algorithm based on the graph representation and using segment ‘balances’ as shown in Figure 5.8 has been developed. Note that it only holds for branched architectures without cycles. Here, present vertices are connected by inner or by free dangling segments; former vertices represent branch points, latter ones terminal vertices (last monomer unit of a free dangling segment). A branched structure may have branch points connected to two terminal vertices (e.g. branch point 1 in Figure 5.7) or to just one (e.g. branch point 5). The pairs of sizes directly follow from the balance of segment lengths at either side of that position. As shown in Figure 5.8, these balances are constructed twice for each segment, that is, in two directions. The reference segment is defined between two vertices $\alpha^*$ and $\beta^*$ with length $L_i$. One or both of the vertices may be branch points. Thus, we have:

Terminal segment from right to left:  
\[ n_{2i} = L_i \] (5.17)

Terminal segment from left to right:  
\[ n_{1i} = n_{1j} + n_{1k} + L_i \] (5.18)

Intermediate segment from right to left:  
\[ n_{2i} = n_{2m} + n_{2p} + L_i \] (5.19)

Intermediate segment from left to right:  
\[ n_{1i} = n_{1j} + n_{1j} + L_i \] (5.20)

Here, $n_{2i}$ is the total number of monomer units at the $\beta^*$-side (right side in Figure 5.8) of segment $I$ plus the number of monomer units $L_i$ in the segment itself, and $n_{1i}$ at $\alpha^*$-side (left side in Figure 5.8). For $N$ branch points Equations 5.20 form a set of $2(2N+1)$ linear equations, which we may write as:

\[ \mathbf{B} \times \mathbf{n} = \mathbf{l} \] (5.21)

$\mathbf{n}$ is a vector of size $2(2N+1)$ with the $n_{1i}$ and $n_{2i}$ as defined in Equations 5.21 and $\mathbf{l}$ is a vector of the same size, where the segment lengths $L_i$ appear twice. Segment connectivity matrix $\mathbf{B}$ is a matrix with elements consist of only 0 and 1 and is derived from the adjacency matrix $\mathbf{A}$ as shown in Appendix 2; this matrix $\mathbf{B}$ contains the connectivity information of the segments. Equation 5.21 may now be solved to yield the $\{n_{1i}, n_{2i}\}$ pairs of sizes at both sides of each segment:

\[ \mathbf{n} = \mathbf{B}^{-1} \times \mathbf{l} \] (5.22)

The pair of sizes at either side of a monomer unit on segment $I$ may now be calculated from $\mathbf{n}$, since:

\[ n_{1,2i} = n_{2i} - L \] (5.23)
\[ n_{Li} = n_{li} - L_i + L \]  

(5.24)

Here \( L \) denotes the position of the monomer unit with respect to vertex \( i : 1 \leq L \leq L_i \). Thus, with the solution of Equation 5.22 for all the segments and with Equations 5.24 for all monomer units on segments finally the pair of sizes at either side of it has been obtained for each monomer unit. According to Kramer’s rule, the radius of gyration contraction factor then follows by summation of the products of size pairs for all monomer units, all with probability equal to one:

\[ g = \frac{1}{n^2} \sum_{j=1}^{2N+1} \sum_{j=1}^{L_i} n_{ji} n_{j2i} \]  

(5.25)

Figure 5.7. Graph representation of branched molecule with \( N = 10 \) (numbered) branch points and 22 connecting ‘vertices’ (segments). Matrix \( A \) is the adjacency matrix based on the branch points as the vertices with \( A_{\alpha\beta} = A_{\beta\alpha} = 1 \) if branch points \( \alpha \) and \( \beta \) are connected, and zero otherwise.

Figure 5.8. Segment lengths \( L_a \), etc., and vertices \( \alpha, \beta, \gamma \), etc. Left: terminal segment; right: intermediate segment. A branched structure may have branch points connected to two terminal vertices (e.g. branch point 1 in Figure 5.7) or to just one (e.g. branch point 5).

5.6 Results

Here, the results concerning the radius of gyration contraction factors for several cases, including terminal branching, and radical polymerization with transfer to polymer and termination by disproportionation either or not accompanied by combination termination are presented.
5.6.1 Comparison kinetic-based to terminal branching-based contraction factors

Simulations are carried out with the architecture-generating algorithm for terminal branching presented in section 5.3 and the kinetics-based algorithm of section 5.4. Thus populations of both types of architectures for the molecular dimensions, number of monomer units $n = 200,000$ and number of branch points $i = 100$ have been generated. After applying the procedure explained in the section 5.5 to these populations, the radius of gyration contraction factor distributions as shown in Figure 5.9 is ultimately found. Note that for the terminal branching population, the average radius of gyration coincides to that predicted by Equation 5.9 (Zimm and Stockmayer, 1949): $c_f = 0.236$. The figure clearly demonstrates that there is a considerable difference between the two populations. This is especially so for the radical polymerization case without combination termination. The chains produced with only disproportionation termination and transfer to polymer turn out to be much more compact than the ones with terminal branching. This confirms the expectation of Zimm and Stockmayer in their paper that their formula might not be valid for systems that go beyond the assumptions that they had to make to arrive at their formula. Although it does not well apply to a radical polymerization system with transfer to polymer, closely resembling for instance ldPE, it does provide a far better prediction in the case of metalloocene-based polymerization of ethylene with Constrained Geometry Catalyst (Hoefsloot and Iedema, 2003). Evidently, the terminal branching model best describes the nature of the branching of the latter system. Finally, we may state that we have clearly shown that architectures based on a realistic kinetic description of radical polymerization with transfer to polymer as the branching mechanism are significantly more compact than architectures with terminal branching. However, an intuitive explanation for this finding is hard to provide, which implies that we indeed needed a model to show us this phenomenon.

Figure 5.9. Radius of gyration contraction factor distribution, due to variations in branched architectures, for terminal branching (from Monte Carlo simulations) and for the radical polymerization case without combination termination. The average of the terminal branching values coincides with the Zimm and Stockmayer model, Equation 5.9.
5.6.2 Effect of termination mode on radius of gyration contraction factor

The effect of absence and presence of combination termination on the contraction factor distribution are compared for molecules of the same number of monomer units and number of branch points; \( n = 255 \, 000 \) and \( i \) is chosen as a few values between 200 and 300. As shown in Figure 5.10 due to the larger molecules created in presence of combination termination, everything else being the same, the selected point on the chain length axis in the tails of the chain length distributions, corresponds to a much lower concentration in the disproportionation only case than in the combination case. Also shown is the distribution for the specific chosen value of the number of branch points (270) as obtained from the 2D chain length/number of branch points solutions for the case of disproportionation only. In the case of combination, the distribution shown is even more specific, since it holds for 270 branch points and 135 combination points; this curve is obtained from the 2D solution with pseudo-distributions for the combination points, as explained in section 5.4.1. These distributions are much narrower having a maximum near \( n = 255 \, 000 \).

Populations of branched architectures are generated for the given number of monomer units, 255 000 and a few values of the numbers of branch points. In the case of combination termination (see Figure 5.11), a number of points are selected on the number of combination points axis with appreciable concentrations on a few cross sections at \( i \) between 200 and 300, and 100 molecules for each \( i, c \) combination using the history backtracking algorithm are generated. For these populations, the radius of gyration contraction factors is calculated using the algorithm described in section 5.5. The resulting distributions are shown for two values of the numbers of branch points, 210 and 270 in Figure 5.12. In the case of combination we have taken the concentration weighted average of the results originating from the various values of combination point numbers.

Note, in Figure 5.12, that the variation in contraction factor in both cases is wholly due to the variations in architectures. The contraction factor distribution is at a higher range for the case with combination termination, so evidently, but remarkably, such molecules are less compact than those created in the case of disproportionation only. Concluding, the model clearly shows the strong effect of the termination mode on the contraction factor. However, again it seems hard to give an intuitive explanation – one would not on beforehand expect molecules only having undergone disproportionation to be more compact. Again, a model is required to show this effect.

Figure 5.10. Molecular size distributions of dead chains (\( P_n \)) for cases with disproportionation without and with combination. Drawn curves represent overall distributions, linear (inset) and logarithmic concentration scales. Dashed curves represent specific size distribution for a sample molecule of 255 000 monomer units with 270 branch points (without combination) and 270 branch points and 135 combination points (with combination).
Figure 5.11. 2-dimensional concentration distribution of number of branch points, \( i \), and number of combination points, \( c \), for the sample molecule of 255,000 monomer units (same case as Figure 5.10). For \( i = 255,000 \) and \( c \) values with appreciable concentration, \( P(i,c) \), populations of 100 branched architectures are generated.

Figure 5.12. Distributions of radius of contraction factors for samples of branched architectures of molecules with dimensions, \( n = 255,000 \) and 210 or 270 branch points. For the case of combination termination populations averages over varying numbers of combination points were taken, using weights according to the cross sections of the 2D concentration distribution \( P(i,c) \) shown in Figure 5.11, at \( i = 210 \) and \( i = 270 \).

Figure 5.13 shows the average radius of contraction factor at each number of branch points obtained by averaging the results from the populations with varying branching architectures as shown in Figure 5.12, using weights according to the concentration distribution of the different numbers of combination points (Figure 5.10). We see the observation confirmed that molecules of the same number of monomer units and branch points are less compact, if combination termination is occurring. Once more, as in section 5.6.1, it is clearly demonstrated that the Zimm and Stockmayer formula (Zimm and Stockmayer, 1949), Equation 5.9, applied with the numbers of branch points on the horizontal axis, underestimates the contraction effect. Yet, quite remarkably, the contraction factors for the combination case are considerably closer to the Zimm and Stockmayer outcome than those assuming just disproportionation.
In view of the fact that polymer molecules having undergone combination termination are less compact, it seems interesting to investigate the effect of the number of combination points – keeping number of monomer units and branch points constant. This is shown in Figures 5.14 and 5.15 for two values of the number of branch points, 210 and 270. Comparing the contraction factor distributions in Figure 5.14 and the average factors in Figure 5.15 for two different numbers of combination points in each case, we now see that the molecules become more compact as the number of combination points increases. Evidently, a higher number of connections between the various parts of the molecule make it more compact.

Figure 5.13. Average radius of contraction factor as a function of number of branch points for samples of branched architectures of molecules with $n = 255,000$. Molecules of the same number of monomer units and branch points are less compact, if combination termination is occurring.

Figure 5.14. Distributions of radius of gyration contraction factors for four populations of molecules with size $n = 255,000$. Those with $i = 270$ branch points have either 105 or 130 combination points, those with 210 branch points 75 or 90 combination points. Architectures having more combination points are more compact.
Figure 5.15. Average radius of gyration contraction factor as a function of number of combination points for \( n = 255,000 \) and number of branch points, \( i = 210 \) and \( i = 270 \). Same conditions as Figure 5.14. Molecules of given number of monomer units and branch points become more compact as the number of combination points increases.

### 5.6.3 Consequences for interpreting measured contraction factors

The differences in contraction factors due to branching type and kinetic conditions has significant consequences as regards the interpretation of measured contraction factors (e.g. by SEC-MALLS) to find the degree of branching of a polymer. In Table 5.3 for a contraction factor of \( g_f = 0.08 \), with the value falling in the range of typical values measured for ldPE, the branching density is found to be between 0.00082 and 0.0025, depending on the type of branching and kinetic conditions. If hitherto the measured contraction factor has been interpreted using the Zimm and Stockmayer model giving a certain branching density, then with the presented model we would see that this branching density might be no less than a factor of 3 too high! Assuming the occurrence of combination termination, the overestimation is still more than a factor of 2. It should be noted that in the present kinetic example transfer to monomer and chain transfer agent reactions have not been taken into account. As such reactions imply a termination mechanism resembling that of disproportionation, their presence is therefore expected to reduce the impact of combination termination. Finally, as regards ldPE, a polymer for which finding the branching density is an important issue indeed, it should be noted that one essential kinetic feature is still missing in presented architecture prediction model: the random scission mechanism. Implementing this in the model is though possible.

<table>
<thead>
<tr>
<th>Branching type</th>
<th>Number of branch points, ( i )</th>
<th>Branching density, ( i/n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal (Zimm and Stockmayer, 1949)</td>
<td>645</td>
<td>0.00253</td>
</tr>
<tr>
<td>Disproportionation termination</td>
<td>210</td>
<td>0.00082</td>
</tr>
<tr>
<td>Disproportionation + combination termination</td>
<td>290</td>
<td>0.00114</td>
</tr>
</tbody>
</table>

Table 5.3. Interpretation of a measured contraction factor \( g_f = 0.08 \) for a molecular size of \( n = 255,000 \) according to various models.

### 5.6.4 Computational considerations

It should be realized that the computational procedure followed to obtain samples of populations that are sufficiently large to infer distributions caused by topological variation only, as shown in the last figures, is apparently complex, but yet highly efficient. This is due
to the ‘conditional’ character of the procedure to generate architectures, meaning that the computational effort is fully spent on molecules of the desired dimensions: number of monomer units, number of branch points and number of combination points. Using alternative Monte Carlo methods to detect the effect of topological variation would require the generation of whole populations of molecules, very few of which satisfy the predefined dimensions. This may be quantified by exploring the Figure 5.9, where we see that the concentration of the sample molecule of 255 000 monomer units is a factor $4 \times 10^8$ lower than the maximum concentration (small molecules), which implies that a Monte Carlo (MC) method would have to generate the same number of molecules to obtain just one of the desired size. Since furthermore, in the example, samples of 100 molecules were generated for each of the combinations of branch and combination points ($i$ and $c$) – also around 100 – 10 000 molecules are required at $n = 255 000$, hence $4 \times 10^{12}$ in total, which is virtually impossible.

Even in a chain length weighted MC procedure, like those introduced by Tobita (1995), generating $10^{10}$ molecules is necessary. As the implementation of Tobita’s MC method here on average requires $0.0075$ s per molecule for the kinetic conditions displayed in Table 5.1, without accounting for the time needed to construct graphs, the generation of such a sample would take a year of CPU-time. Limiting the radius of gyration calculation to a selection of molecules of the desired dimensions would still imply a post-processing procedure for the construction of the graphs similar to the one explained in section 5.3.2. As all the steps of the procedure introduced in the present chapter may be performed in a few hours CPU-time, it is possible to conclude that the described procedure is very efficient indeed.

5.7 Conclusions

The fundamental work of Zimm and Stockmayer (1949) on the relation between branching and radius of gyration contraction factor has been reviewed by acknowledging that they intended it to apply to an ‘idealized example’ only. This example in fact turns out to be a very specific type of branching architecture, namely terminal or end-to-end branching. In this chapter it has been demonstrated that the Zimm and Stockmayer theory, nowadays still widely in use for characterization of branched polymers, is indeed limited to this type of branching only. At the same time it has been shown how to exploit a kinetically realistic model predicting the required microstructural properties in order to arrive at better estimates of the radius of gyration contraction factor for the case of radical polymerization with transfer to polymer as the branching mechanism, a model more or less representative for low-density Polyethylene.

A number of modeling tools have been applied to provide descriptions of branched architectures based on realistic kinetics using Monte Carlo simulations, the ‘growth history backtracking’ method. The architectures thus generated are represented with the help of graph theory, allowing to apply the ‘Kramers rule’ (Kramers, 1946) – the same concept as employed by Zimm and Stockmayer – to find the radius of gyration contraction factor. The first important finding is that molecules with architectures as predicted by the presented model are significantly compacter than Zimm and Stockmayer’s theory would predict – based on a comparison between molecules with identical numbers of branch points. This leads to the conclusion that evidently the type of branching assumed is decisive in determining the contraction level. Furthermore, the effect of the termination mode, disproportionation or
combination, has been investigated. It turns out, unexpectedly, that molecules having undergone termination by disproportionation only are most compact, while combination termination leads to less compact molecules. Both the higher compactness of the molecules generated assuming realistic kinetics as compared to the terminal branched structures according to Zimm and Stockmayer, and the difference in compactness caused by the termination mechanism seem to be unattainable by intuitive reasoning. Finally, within the class of polymers made under combination circumstances those with a higher number of combination points are more compact. This seems to be in line with intuitive expectations.
A full extensive 2-Dimensional (2D) model of low-density Polyethylene (ldPE) chain length/branching distribution is provided in this chapter. Full 2D Population Balance Equations (PBEs) are solved by Galerkin-Finite Element Method (FEM) to obtain the distributions, accounting for 2D ‘topological scission’, a manner to approximate random scission by an estimated Fragment Length Distribution (FLD). It turns out that explicit assumptions have to be made concerning the redistribution of the branch points on scission fragments and thus this model of scission can only lead to successful estimation of overall chain-length distributions. The description of the problem relies on assuming that the redistribution of branch points on scission fragments is independent of the lengths of the fragments.

It was observed with pseudo-distribution model that hypergeometric function is more realistic than fragment length distribution function to estimate the branching on scission fragments. However, in this chapter, it is shown that employing hypergeometric function to account for number of branch points according to scission fragment lengths is not a straightforward task with the current solution strategy. Thus the 2D model of this chapter is based on the simpler assumption of fragment length distributions.

The calculations without scission show that in 2D case a finer grid of chain length is required comparing to the 1-Dimensional (1D) case because of the narrow shape of the branching distribution at the given chain length. These results are in exact agreement to Monte Carlo (MC) simulations, which shows the success of the implementation. Including random scission to the scheme results to 1D branching densities that are different than the former results with pseudo-distributions and MC simulations, while the branching density at high chain lengths should attain a constant value, the 2D solution shows a maximum at medium chain lengths and a decrease afterwards. This incorrect result is a direct consequence of the scission fragment length independent redistribution of branch points.

6.1 Introduction

The most important property of polymer molecules is assumed to be chain length in many modeling schemes. However, other microstructural properties such as number of branch points, number of combination points, number of radical sites, number of terminal double bounds, etc. provide interesting information on processability, and thus are of concern in most industrial applications in addition to the chain length. The properties of interest in modeling physical properties of polymers are usually with a discrete nature (chain length,
number of branch points, number of combination points, etc.) and need to be encountered in special ways. Including any of the above-mentioned properties as extra dimension coordinates along with chain length into PBEs, gives rise to multi-dimensional population balance equations that are excessively complex to be solved in more than two independent dimensions (Schutte and Wulkow, 2010). However, among all other applications, modeling polymerization reactions by population balances is beneficial in many ways as clarified in Yaghini and Iedema (2014a). Furthermore, population balance equations provide advantageous possibilities to deal with discrete properties.

This chapter is devoted to investigate the feasibility of 2D Galerkin method to model the bivariate ldPE chain length/branching distributions. A comprehensive framework is applied to extend the original 1D Galerkin to a 2D method capable of solving full 2D polymerization population balances, accounting for 2D topological scission. The possibility of implementing hypergeometric function to estimate the distribution of branch points on scission segments in accordance to their lengths is explored and an alternative assumption is presented, which is less realistic in comparison to the hypergeometric distribution, but is compatible with the current numerical strategy.

6.2 Two-dimensional population balance equations

The reaction equations in the full 2 dimensions chain length \((n)\) and number of branch points \((i)\) are listed in Table 6.1. The corresponding population balances for living and dead chains for the case of a Continuous Stirred Tank Reactor (CSTR) read as follows:

\[
\frac{dR_{n,i}}{dt} = k_p M (-R_{n,i} + R_{n-1,i}) - k_p \lambda P_{n-1,i} + k_p (-\mu R_{n,i} + \lambda n P_{n,i-1})
\]

\[
- k_p \mu R_{n,i} + k_p \sum_{m=1}^{\infty} \sum_{j=1}^{\infty} \beta(n,m,i,j) P_{m,j} - \frac{1}{\tau} R_{n,i}
\]

\[
\frac{dP_{n,i}}{dt} = k_p \lambda P_{n,i} + k_p (\mu R_{n,i} - \lambda n P_{n,i-1}) -
\]

\[
- k_p \mu P_{n,i} + k_p \sum_{m=1}^{\infty} \sum_{j=1}^{\infty} \beta(n,m,i,j) P_{m,j} - \frac{1}{\tau} P_{n,i}
\]

Note that this set describes chains with one radical site at maximum; hence polyradicals are not accounted for. In calculations, the kinetics are chosen in such that neglecting polyradicals is indeed allowed. The set of equations (Equations 6.1 and 6.2) form the basis of all subsequent sets to be derived of real and pseudo-distributions of lower dimension are obtained by summation over one or two indices. The interpretation of the scission functions \(f(n,m)\) and \(\beta(n,m,i,j)\), and assumptions concerning them are discussed below.

6.2.1 Scission aspects

6.2.1.1 Linear and topological scission

Random scission is considered to take place randomly independent of the architecture of a molecule on any location of a chain with the same probability for each bond to be broken. The same assumption underlies the work by Tobita (2001a, 2001b and 2014). Where it is
straightforward to obey this assumption in the stochastic method, in deterministic modeling an extra model is required to approximate random scission as closely as possible to this definition (Yaghini and Iedema, 2014a). Earliest 1-dimensional ldPE models in treating scission, simply ignored branching and assumed scission to take place as if it happens to linear chains -this has been called ‘linear scission’. The 2D approach by Krallis et al. (2007) also employs the linear scission model. A better though not perfect model for random scission is the ‘topological scission’ model, which was developed for 1-dimensional models (Yaghini and Iedema, 2014a). Applying topological scission in 2D is discussed in this chapter. It should be realized based on outcomes from 1D models, that both stochastic models and deterministic models using topological scission are correctly representing random scission. However, the bimodality of the ldPE molecular weight distribution that is observed experimentally (Tackx and Tacx, 1998) has never been reproduced when applying it, while the linear scission model does generate the bimodality. This may cast doubt on the assumption that scission in ldPE is fully random.

\[

definition{I_2} \xrightarrow{k_j \rightarrow 2I} 2I
\]

Initiation
\[
I + M \xrightarrow{k_b \rightarrow R_{i,0}}
\]

Propagation
\[
R_{n,i} + M \xrightarrow{k_j \rightarrow R_{n+1,i}}
\]

Termination by disproportionation
\[
R_{n,i} + R_{n,j} \xrightarrow{k_{dp}} P_{n,i} + P_{n,j}
\]

Random scission
\[
R_{n,i} + P_{r,j} \xrightarrow{k_{rs}} P_{n,i} + R_{n,k-1} + P_{k}
\]

Transfer to polymer
\[
R_{n,i} + P_{m,j} \xrightarrow{k_{tp}} P_{n,i} + R_{m,j+1}
\]

<table>
<thead>
<tr>
<th>Initiator dissociation</th>
<th>( I_2 \xrightarrow{k_j \rightarrow 2I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation</td>
<td>( I + M \xrightarrow{k_b \rightarrow R_{i,0}} )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( R_{n,i} + M \xrightarrow{k_j \rightarrow R_{n+1,i}} )</td>
</tr>
<tr>
<td>Termination by disproportionation</td>
<td>( R_{n,i} + R_{n,j} \xrightarrow{k_{dp}} P_{n,i} + P_{n,j} )</td>
</tr>
<tr>
<td>Random scission</td>
<td>( R_{n,i} + P_{r,j} \xrightarrow{k_{rs}} P_{n,i} + R_{n,k-1} + P_{k} )</td>
</tr>
<tr>
<td>Transfer to polymer</td>
<td>( R_{n,i} + P_{m,j} \xrightarrow{k_{tp}} P_{n,i} + R_{m,j+1} )</td>
</tr>
</tbody>
</table>

Table 6.1.Polymerization reaction equations

The concept of topological scission is introduced and tackled by using an FLD function (Iedema and Hoefsloot, 2001a; Kim et al. 2004; Yaghini and Iedema, 2014a). The FLD function is an empirical function and describes the distribution of fragment lengths caused by random scission of topologies that were generated by MC simulations. An extensive discussion is given in Chapter 2 concerning the necessity of employing the topological scission model and FLD in the context of modeling ldPE (1D) molecular weight distributions, also in (Yaghini and Iedema, 2014a). Here the focus is on presenting and implementing a 2D fragment length function that explicitly incorporates the chain length and branching mechanisms. A framework to apply a hypergeometric function to model the distribution of branch points on scission fragments is also provided.

A 2D fragment length distribution function is defined as the following approximation (see Chapter 2):

\[
f(n,m) = \frac{1}{(2\overline{s}(n)+m)^2} + \frac{1}{(2\overline{s}(n)+n-m)^2} - \frac{1}{\overline{s}} \left\{ \frac{1}{(2\overline{s}(n)+n)^2} + \frac{1}{(2\overline{s}(n))^2} \right\}, \tag{6.3}
\]
Here, \( n \) and \( m \) are the length of the original chain, and the length of the fragment after scission, respectively. The parameter \( s \) denotes the average segment length between branch points. In the 1-dimensional model the parameter \( s \) had to be estimated by taking the inverse of branching density. However, we are able to realize a parameter-free formulation, since the segment length simply follows from the combination of the chain length, \( n \), and the number of branch points, \( i \), of the chain is undergoing scission:

\[
\bar{s}(n,i) = \frac{n}{2i+1} \quad (6.4)
\]

### 6.2.1.2 2-dimensional branch points redistribution on scission fragments

In the population balance equations (Equations 6.1 and 6.2), the function \( \beta(n,m,i,j) \) describes the redistribution of the number of branch points on the scission fragment. Hutchinson (2001) approximated the distribution of scission fragment size and the redistribution of the branch points on the scission fragments by defining a hypergeometric distribution:

\[
\beta(n,m,i,j) = \binom{i}{j} \binom{n-i}{m-j} \binom{n}{m} \quad (6.5)
\]

Thus, the branch point redistribution is a function of original chain length \( (n) \), scission fragment length \( (m) \), number of branch points on the original polymer chain \( (i) \) and number of branch points on the fragment after scission \( (j) \). Note that the hypergeometric function also has been employed in the pseudo-distribution approach of the chain length-branching problem (Kim and Iedema, 2008, Yaghini and Iedema, 2014a). In Kim and Iedema (2008) the pseudo-distribution terms for the first and second branching moments, based on the hypergeometric function has been formulated as:

\[
\sum_{j=0}^{\infty} \sum_{i=0}^{n} f(n,m)\beta(n,m,i,j) mP_{m,j} = \frac{1}{2} \sum_{m=n+1}^{\infty} f(n,m)mn\Psi_{1}^{1},
\]

\[
(6.6)
\]

\[
\sum_{j=0}^{\infty} \sum_{i=0}^{n} f(n,m)\beta(n,m,i,j) mP_{m,j} =
\]

\[
\sum_{m=n+1}^{m} f(n,m) \frac{1}{m-1} \{ n(n-1)\Psi_{1}^{2} + n(m-n)\Psi_{2}^{1} \},
\]

\[
(6.7)
\]

Here, \( \Psi_{1}^{1} \) and \( \Psi_{2}^{2} \) represent the first and second branching moments, defined as:
\[ \Psi_m^1 = \sum_{j=0}^{\infty} j P_{m,j} \quad ; \quad \Psi_m^2 = \sum_{j=0}^{\infty} j^2 P_{m,j} \] (6.8)

The implication of assuming the hypergeometric function in a full 2D formulation is that the contribution to the scission term in population balances (Equations 6.1 and 6.2) at a given combination of fragment dimensions, length \( m \) and number of branch points \( j \), originating from chains with longer lengths, \( n > m \), and higher number of branch points, \( i > j \), is a function of all 4 dimensions. The behavior of this function for longer lengths and higher numbers of branch points has been inspected as shown in Figure 6.1. It turns out that the resulting distribution as a function of original chain length \( (n) \) is a function of increasing sharpness as the number of branch points on the original fragment \( (i) \) is lowered to near the value of \( j \). It should be realized that the scission contribution due to the hypergeometric distribution is an even sharper function of the original chain length than the contribution from topological scission. The latter problem has been satisfactorily solved by a grid refinement strategy as described in Yaghini and Iedema (2014a). However, due to the difference in shape and the sharper form, this numerical strategy cannot be applied to the present problem caused by the shape of the hypergeometric function. A completely different numerical approach of calculating scission contributions has to be developed. This will be the topic of a future work.

As it is not possible to realize a proper numerical implementation of the hypergeometric function, a simpler model to describe the redistribution of branch points on scission fragments is applied. In fact, the assumption made earlier in Iedema et al. (2000) is adopted here, so the number of branch points on fragments is presumed to be independent of the length of these fragments. This implies that the redistribution function \( \beta(n,m,i,j) \) is simply:

\[ \beta = \frac{1}{i+1} \] (6.9)

Thus, the redistribution function is totally independent on fragment dimensions and chain length and is a function of the number of branch points on the original chain only.

Accounting for this assumption then leads to a new form of the population balance equations (Equations 6.1 and 6.2).

Note that Krallis et al. (2007) do not discuss this issue in their paper. However, their equations also contain the factor \( \frac{1}{i+1} \) of Equation 6.9, hence it is obvious that they also assume fragment length independent redistribution of branch points.

\[
\frac{dR_{n,i}}{dt} = k_p M (-R_{n,i} + R_{n-1,i}) - (k_{td} + k_{tc}) \lambda_0 R_{n,i} + k_r (-\mu R_{n,i} + \lambda_0 p P_{n-1,i}) + \\
- k_{rs} \mu R_{n,i} + k_{rs} \sum_{m=n+1}^{\infty} \sum_{j=1}^{\infty} \left( \frac{f(m,n)}{j+1} \right) P_{m,j} - \frac{1}{\tau} R_{n,i} 
\] (6.10)
\[
\frac{dP_{n,i}}{dt} = k_d \lambda_0 R_{n,i} + \frac{1}{2} k_{ic} \sum_{m=1}^{\infty} \sum_{j=0}^{i-1} R_{m,j} R_{n-m,j-i} + k_{sp} (\mu_1 R_{n,i} - \lambda_0 nP_{n,i}) +
\]

\[
+ k_{rs} \mu_1 R_{n,i} - k_{rs} \lambda_0 nP_{n,i} + k_{rs} \sum_{m=1}^{\infty} \sum_{j=1}^{i} \left( \frac{f(m,n)}{j+1} \right) P_{m,j} - \frac{1}{\tau} P_{n,i}
\]

(6.11)

Later a comparison will be made between the 2D results concerning branching and the ones from the pseudo-distribution approach, thus, the expressions for the scission contribution assuming \( \beta = \frac{1}{i+1} \) in that approach is recalled here, as derived in Iedema et al. (2000):

\[
\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(n,m)\beta(n,m,i,j) mP_{m,j} = 0.5 \sum_{m=n+1}^{\infty} f(n,m) m^2 \Psi_{m}^1
\]

(6.12)

\[
\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{m=n+1}^{\infty} f(n,m)\beta(n,m,i,j) mP_{m,j} = \sum_{m=n+1}^{\infty} f(n,m) m \left( \frac{1}{3} \Psi_{m}^2 + \frac{1}{6} \Psi_{m}^1 \right)
\]

(6.13)

The above-mentioned equations form the equivalent of the Equations 6.6 and 6.7 are derived using the hypergeometric distributions for the redistribution of branch points on scission fragments.

![Hypergeometric Distribution](image)

Figure 6.1. Shape of the hypergeometric distribution \( \beta(n,m,i,j) \) from the perspective of the fragments of given dimensions (chain length \( m = 10^5 \), number of branch points \( j = 1000 \)), in the population balances (Equations 6.1 and 6.2) receiving contributions from longer chains having dimensions as chain length \( n \) and number of branch points \( i \), both varying in this plot. As the number of branch points on the original chain before scission nears that on the fragment, the hypergeometric distribution grows narrower. This poses a grid refinement problem.

6.3 The 2D Galerkin method

The 1D Galerkin-FEM has been presented by Wulkow (2008), and has been employed to model Molecular Weight Distribution (MWD) of CSTR by Yaghini and Iedema (2014a). In this chapter the original 1D method has been extended to cover the second dimension and
to solve full 2D population balance equations of ldPE free radical polymerization. The dimensions for the deterministic modeling with Galerkin-FEM are assumed to be chain length \( (n) \) and number of branch points \( (i) \).

Hereafter, 2D consternations are represented as \( P_{n,i} \) at chain length intervals \( N \) with chain length nodes \( n \) and branching intervals \( I \) with branching nodes \( i \). Chain length for ldPE molecules vary between 1 and \( 10^7 \), and each polymer chain may receive number of branch points (maximum of \( 10^4 \)) or grow as a linear chain with 0 branch points.

### 6.3.1 Galerkin representation

\( P_{n,i} \) for a polymer chain at each 2D interval element is represented by a combination of discrete Chebyshev polynomials for any of the two dimensions. Note that applying discrete polynomials to model the chain length and branching as discrete attributes of polymer chains is essential. Chebyshev polynomials for chain length dimension with nodes \( s \) from chain length interval \( M \) and for branching dimension with nodes \( s' \) from branching interval \( H \) are indicated as \( T_{l_{M}}^{u_{M}}(s) \) and \( T_{l_{H}}^{u_{H}}(s') \), respectively. \( l_{M} \) \( u_{M} \) \( l_{H} \) \( u_{H} \) are the lower and upper limits of chain length (number of branch points) values. The 2-dimensional \( P_{n,i} \) at chain length node \( s \) and branching node \( s' \) from 2D interval element \( MH \) is defined in terms of Chebyshev polynomials as:

\[
\sum_{l_{M} = l_{H}}^{r_{M}} \sum_{l_{H} = l_{H}}^{r_{H}} a_{l_{M}l_{H}}^{MH} T_{l_{M}}^{u_{M}}(s)T_{l_{H}}^{u_{H}}(s')
\]

where \( r_{M} \) is the order of Chebyshev polynomial in the chain length dimension and \( r_{H} \) is the order of Chebyshev polynomial in the branching dimension. Chebyshev polynomials are defined as in Gil et al. (2007).

The exact values for 2D coefficients \( a_{l_{M}l_{H}}^{MH} \) could be obtained for any arbitrary pair of \( (s,s') \) from any 2D interval element for known 2D concentrations \( P(s,s') \). \( P(s,s') \) could be calculated by Equation 6.14 and applying the orthonormality property of Chebyshev polynomials. As the 1D case, although the upper and lower limits for all intervals are integer numbers for both dimensions, the intermediate nodes might not be so.

\[
a_{l_{M}l_{H}}^{MH} = \frac{1}{l_{M}l_{H}} \sum_{s} \sum_{s'} P(s,s')w_{M}(s)w_{M}(s')T_{l_{M}}^{u_{M}}(s)T_{l_{H}}^{u_{H}}(s')
\]

where \( l'_{H} = 0 : r'_{H} \), \( l_{M} = 0 : r_{M} \), \( w_{M}(s) \) is the correlated weight of the node \( s \) from interval \( M \) in chain length dimension and \( w_{M}(s') \) is the weight of node \( s' \) on interval \( H \) of branching.
dimension. Figure 5 shows the distribution of weights for all chain length and branching intervals in the form of weights products, thus the form they appear in the equations. The nodes in each interval are obtained from the roots of Chebyshev polynomials for each dimension individually. An example of a 2D interval element is given in Figures 6.2, indicating a chain length and branching interval with the upper and lower limits and intermediate nodes. Further, an illustration of an exemplified 2D interval in chain length and branching dimensions with associated nodes in each dimension is given in Figure 3. The possible contribution types from the nodes of one 2D interval to other 2D intervals are presented in Figure 4. In this figure, shades of gray indicate the contribution type, for example the nodes in dark gray contribute to the population balance equations of the nodes of other intervals only in the branching dimension.

Figure 6.2. Example of 2D interval element indicating the interval $M$ of chain length and interval $H$ of branching dimensions with the associated nodes in each dimension. The lower and upper limits of intervals are shown with $l$ and $u$ for both dimensions.

Figure 6.3. Example of 2D chain length/branching intervals of exponentially increasing size. The shown interval has 8 nodes in chain length dimension and 3 in branching dimension. Upper chain length edges: \{8 17 35 57 92 150 245 \ldots 1000\}; upper branching edges: \{2 5 8 12 15 19 24 \ldots 1000\};
Figure 6.4. Schematic representation of chain length and branching intervals. Nodes in grey shades specify the type of contribution to the concentration of other nodes. The concentration of nodes in black have no contributions to the concentration of other nodes while the ones in two shades of gray contribute to the concentrations of nodes in both dimensions. The dark gray nodes contribute to the concentration of other nodes only in branching dimension and the light gray nodes have contributions only in the chain length dimension.

Figure 6.5. Example of weights distribution, product of chain length and branching weights for all chain length/branching nodes on the 2D grid. Inset shows a part of the weight distribution in details.

6.3.2 Implementation of the bivariate LDPE molecular weight/branching distribution into a 2D Galerkin-FEM scheme

To solve full 2D population balance equations with chain length \((1 \leq n \leq 10^7)\) and branching \((1 \leq n \leq 10^4)\) as the dimensions, we would need to solve a system of \(10^7 \times 10^4\) differential equations. Most known numerical methods fail to deal with such a system of differential equations, especially if we consider the computation time. Alike the 1D model from Yaghini and Iedema (2014a), the number of necessary calculations is reduced by defining specific nodes on chain length intervals \(M\) and branching intervals \(H\). The nodes are indicated as pair nodes \((s,s')\), and are selected in a way that satisfies the orthonormality of Chebyshev polynomials. The calculation of exact concentration for any combination of \(s\) nodes from intervals \(M\) and \(s'\) nodes from intervals \(H\) is done by applying Equation 6.14. Eventually, the exact concentrations \(P(s,s')\) at pair nodes \((s,s')\) are interpolated to obtain the full 2D distributions of chain length and branching.

In order to calculate the concentrations at the selected pair nodes, \(P(s,s')\) are replaced by Chebyshev expansions from Equation 6.14 in the population balance equations. This
replacement is indeed the transformation of PBEs to the Chebyshev polynomials space with the unknowns indicated as $a^{MH}_{i,H}$. The solution procedure is very similar to the one of the 1D solution (Yaghini and Iedema, 2014a), except that the PBEs should be multiplied with both types of Chebyshev polynomials at pair nodes $(s,s')$, thus $T_{i}^{H}(s')$ and $T_{i}^{M}(s)$.

### 6.3.3 Transformation by expansion into 2D Chebyshev polynomials

In this section, the transformation of 2D population balance equations is presented. The general form of the equations for the dead chains is:

$$
\frac{dP(s',s)}{dt} = f\left(P(s',s), R(s',s)\right)
$$

(6.16)

The nodes $s_j$ on a chain length interval and $s'_i$ on a branching interval correspond to weights $w_j$ and $w'_i$. Equation 6.16 expresses the population balance equation at the node pair $(s,s')$. Using the Chebyshev expansion:

$$
\sum_{k=0}^{r} \sum_{k'=0}^{r'} a_{i,k}^{p} f^{p} \left(T_{k}(s_{j})T_{k'}^{'}(s'_{i})\right) + \sum_{k=0}^{r} \sum_{k'=0}^{r'} a_{i,k}^{p} f^{p} \left(T_{k}(s_{j})T_{k'}^{'}(s'_{i})\right) + b_{i,k}^{p} =
$$

(6.17)

The maximum order of Chebyshev polynomials are $r (N = r + 1)$ and $r' (I = r' + 1)$ for chain length and branching, accordingly. The range of nodes $j$ is $1:N$ and the range of nodes $i$ is $1:I$. The orders $k$ and $k'$ are assumed to vary as $0:r$ and $0:r'$ for chain length and branching dimensions.

### 6.3.4 Gauss quadrature operation in two dimensions

The procedure starts with the representation as given in Equation 6.16. Any chain length/branching interval element (block interval) refers to the equations describing the concentrations at all the $N \times I$ combinations of chain length and branching nodes in that block, so $N \times I$ equations. In the 2-dimensional Gauss quadrature operation these equations are first multiplied with products of Chebyshev polynomial terms of all orders, $T_{k}(s_{j})T_{k'}^{'}(s'_{i})$, $T_{k}(s_{j})T_{k'}^{'}(s'_{i})$, etc., where the $j,i$ pair refer to the chain length/branching node combination. A 2-dimensional Gauss quadrature subsequently prescribes two summation procedures: one over the branch point nodes and the other over the chain length nodes. This would ultimately lead to $N \times I$ equations for the $N \times I$ coefficients $a_{i,k}^{p}$. The procedure then could be described in two steps, first a Gauss quadrature operation for the branch points, and then a
Gauss quadrature operation for the chain length dimension. Hence, first branch points and then chain length, however, the reverse order might have been chosen.

The intermediate result after multiplication with Chebyshev terms for the branching dimension only, \( T_0(s_i) \), \( T_1(s_i) \), etc., and the summation over the branch point \( j \) nodes are shown in below. For the sake of the presentation, the function \( f^x(T_0(s_i), T_0'(s_i)) \) has been separated into a product of two distinct functions, \( f(T_0(s_i))f'(T_0'(s_i)) \), while dropping the reference to the chain type, living or dead (upper index). For the first chain length node \( s_{i}' \), the multiplication by the \( 0^{th} \) order terms \( T_0(s_i) \), weighted summation over the \( j \) -nodes \( (s_j) \) and collecting all the terms containing the coefficients \( a_{u} \) in accolades, leads to an equation with the following Right-Hand Side (RHS).

\[
\begin{align*}
&f\left(T_0'(s_i')\right) \left\{ \sum_{j=1}^{N} w_j f\left(T_1(s_j)\right) T_0(s_j) \right\} a_{00} + \\
&+ f\left(T_0'(s_i')\right) \left\{ \sum_{j=1}^{N} w_j f\left(T_0(s_j)\right) T_0(s_j) \right\} a_{01} + \ldots + f\left(T_0'(s_i')\right) \left\{ \sum_{j=1}^{N} w_j f\left(T_0(s_j)\right) T_0(s_j) \right\} a_{0r} + \\
&\quad + f\left(T_1'(s_i')\right) \left\{ \sum_{j=1}^{N} w_j f\left(T_0(s_j)\right) T_0(s_j) \right\} a_{10} + A_{01} a_{11} + \ldots + A_{0r} a_{r1} + \ldots + \\
&\quad + f\left(T_r'(s_i')\right) \left[ A_{00} a_{0r} + A_{01} a_{1r} + \ldots + A_{0r} a_{rr} \right]
\end{align*}
\]

Anew for the first chain length node \( s_i \), the multiplication by the \( 1^{st} \) order branching Chebyshev elements \( T_i(s_j) \) and summation over the \( j \) -nodes \( (s_j) \) leads to a \( 2^{nd} \) equation, having RHS:
Thus, for the whole set of vectors $\text{Equa}$ corresponds to the chain length (first) index of the coefficient Chebyshev term which has been multiplied with in the Gauss quadrature, while indicated in Equations 6.18 and 6.19. Together they form the 2 intermediate set of equations we obtain coefficients, $(\text{shown above})$, all for the first branching node, summations over the nodes Doing what is explained above for $f_0'$ $(= T_0')$ (see $\text{Equation 6.18}$). We define the following $a_0$ $(1)$. $r (\text{order of the } \text{Chebyshev term which has been multiplied with in the Gauss quadrature, while } l \text{ corresponds to the chain length (first) index of the coefficient } a_w \text{ from the element } A_{w_l} \text{ (see Equation 6.18). We define the following } I = r' + 1 \text{ (number of branching nodes) by a column vectors } a_k \text{ containing coefficients } a_{w_l}$.

\[
\begin{bmatrix}
  a_{00} \\
  a_{01} \\
  \vdots \\
  a_{kl}
\end{bmatrix}
\quad a_0 =
\begin{bmatrix}
  a_{00} \\
  a_{01} \\
  \vdots \\
  a_{kl}
\end{bmatrix}
\quad a_1 =
\begin{bmatrix}
  a_{00} \\
  a_{01} \\
  \vdots \\
  a_{kl}
\end{bmatrix}
\quad \ldots
\quad \begin{bmatrix}
  a_{00} \\
  a_{01} \\
  \vdots \\
  a_{kl}
\end{bmatrix}
\quad a_r =
\begin{bmatrix}
  a_{00} \\
  a_{01} \\
  \vdots \\
  a_{kl}
\end{bmatrix}
\quad (6.20)
\]

Thus, for the whole set of equations and for the first branching nodes, the repetitive structure of the RHS in terms of $\begin{bmatrix} \text{2A} \end{bmatrix}$ and $a_k$ is written as:

\[
f''\left(T_0'(s')\right)\begin{bmatrix} \text{2A} \end{bmatrix} \times a_0 + f''\left(T_1'(s')\right)\begin{bmatrix} \text{2A} \end{bmatrix} \times a_1 + \ldots + f''\left(T_r'(s')\right)\begin{bmatrix} \text{2A} \end{bmatrix} \times a_r
\]

(6.21)
Equations 6.18 and 6.19 are derived from the first two instances of the RHS. It should be noted that this intermediate result resembles the end result of the Gauss quadrature in the 1-dimensional problem addressed in Yaghini and Iedema (2014a), where there was obviously just one of the terms of Equation 6.21 as the ultimate RHS: \( \left( \frac{1}{2} A \right) \times a \). As in the 1D case, depending on the form of the chain length functions \( f(T_k(s_j)) \), the orthogonality properties of the Chebyshev series may lead to (partly) full or diagonal matrices \( \frac{1}{2} A \).

The Left-Hand Side (LHS) of the equations is addressed here, which after the above-performed Gauss quadrature, have exactly the same structure as the RHS, except that the coefficients are replaced by their time derivatives, \( \frac{d(a_k)}{dt} \). Since the functions here are simply the Chebyshev terms themselves, \( f(T_k(s_j)) = T_k(s_j) \), the quadrature yields diagonal \( A \)-matrices containing the normalization factors for the Chebyshev terms for branching, \( \gamma_k \), defined as (Yaghini and Iedema, 2014a):

\[
\langle T_k, T_l \rangle = \sum_j w(s_j) T_k(s_j) T_l(s_j) = \gamma_k \delta_{k,l}
\] (6.22)

In matrix notation, the vector of normalization factors \( \mathbf{Y} \) is derived using the vector of weights, \( \mathbf{w} \):

\[
\mathbf{Y} = \text{inv}(\mathbf{W}) \times \text{diag}(\mathbf{w}) \times \mathbf{T}
\] (6.23)

Hence:

\[
A_y = \begin{bmatrix}
\gamma_0 & \gamma_1 & \ldots & \gamma_r \\
\gamma_1 & \gamma_2 & \ldots & \gamma_r \\
\vdots & \vdots & \ddots & \vdots \\
\gamma_r & \gamma_r & \ldots & \gamma_r 
\end{bmatrix}
\] (6.24)

The Gauss quadrature operation is completed by performing the multiplication with Chebyshev terms from the chain length dimension, \( T_k(s'_i) \), and subsequent summation over the chain length nodes, \( s'_i \). The starting point for this operation is different than for the 1D case since quadrature is applied to the results after being applied to the branching dimension. The set of \( N \) equations represented by Equation 6.21 is one part of these results holding for the first chain length node. Clearly, similar sets may be derived for all the \( I \) branching nodes, so the start is with \( I \) sets of \( N \) equations.

It should be realized that the summation part of the quadrature operation is not to be applied to the all sets of \( N \) equations simultaneously, but to the single equations for a particular chain length order, only. Note that in the 1D case as well, the summation was performed over single equations – one equation per node. For the present 2D case this implies that the operation should be repeated \( r+1 \) times. Therefore, all equations with the same branching order from the set of RHS as represented by Equations 6.18, 6.19 and 6.21
should be collected, for node $i = 1$ to $i = I$. Thus, for the $0$th chain length order the following set for the RHS is assembled:

$$
\begin{align*}
&f'(T_0'(s'_j)) \{ A_{00}a_{00} + A_{01}a_{10} + \ldots + A_{0r}a_{r0} \} \\
&\quad + f'(T_1'(s'_1)) \{ A_{00}a_{01} + A_{01}a_{11} + \ldots + A_{0r}a_{r1} \} + \ldots \\
&\quad + f'(T_r'(s'_r)) \{ A_{00}a_{0r} + A_{01}a_{1r} + \ldots + A_{0r}a_{rr} \} \\
&f'(T_0'(s'_j)) \{ A_{10}a_{00} + A_{11}a_{10} + \ldots + A_{1r}a_{r0} \} \\
&\quad + f'(T_1'(s'_1)) \{ A_{10}a_{01} + A_{11}a_{11} + \ldots + A_{1r}a_{r1} \} + \ldots \\
&\quad + f'(T_r'(s'_r)) \{ A_{10}a_{0r} + A_{11}a_{1r} + \ldots + A_{1r}a_{rr} \} \\
&\ldots \\
&f'(T_0'(s'_j)) \{ A_{I0}a_{00} + A_{I1}a_{10} + \ldots + A_{Ir}a_{r0} \} \\
&\quad + f'(T_1'(s'_1)) \{ A_{I0}a_{01} + A_{I1}a_{11} + \ldots + A_{Ir}a_{r1} \} + \ldots \\
&\quad + f'(T_r'(s'_r)) \{ A_{I0}a_{0r} + A_{I1}a_{1r} + \ldots + A_{Ir}a_{rr} \} \\
\end{align*}
$$

(6.25)

Likewise, for the $1$st chain length order the RHS set is assembled as:

$$
\begin{align*}
&f'(T_0'(s'_j)) \{ A_{i0}a_{00} + A_{i1}a_{10} + \ldots + A_{ir}a_{r0} \} \\
&\quad + f'(T_1'(s'_1)) \{ A_{i0}a_{01} + A_{i1}a_{11} + \ldots + A_{ir}a_{r1} \} + \ldots \\
&\quad + f'(T_r'(s'_r)) \{ A_{i0}a_{0r} + A_{i1}a_{1r} + \ldots + A_{ir}a_{rr} \} \\
&f'(T_0'(s'_j)) \{ A_{i0}a_{00} + A_{i1}a_{10} + \ldots + A_{ir}a_{r0} \} \\
&\quad + f'(T_1'(s'_1)) \{ A_{i0}a_{01} + A_{i1}a_{11} + \ldots + A_{ir}a_{r1} \} + \ldots \\
&\quad + f'(T_r'(s'_r)) \{ A_{i0}a_{0r} + A_{i1}a_{1r} + \ldots + A_{ir}a_{rr} \} \\
&\ldots \\
&f'(T_0'(s'_j)) \{ A_{ir}a_{00} + A_{i1}a_{10} + \ldots + A_{ir}a_{r0} \} \\
&\quad + f'(T_1'(s'_1)) \{ A_{ir}a_{01} + A_{i1}a_{11} + \ldots + A_{ir}a_{r1} \} + \ldots \\
&\quad + f'(T_r'(s'_r)) \{ A_{ir}a_{0r} + A_{i1}a_{1r} + \ldots + A_{ir}a_{rr} \} \\
\end{align*}
$$

(6.26)

The process should be repeated to the $r$th chain length order. Note that the sets of equations, such as displayed in Equations 6.25 and 6.26, contain $I$ equations for the $I$ different $i$-nodes, while each set refers to the same chain length order as is reflected by the appearance of the elements of matrix $A$ of one line only: $A_{00}, A_{01}, \ldots, A_{0r}$ for the $0$th order, $A_{I0}, A_{I1}, \ldots, A_{Ir}$ for the $1$st order, etc.

As before for the chain length quadrature, first the multiplication by the $0$th order Chebychev terms for the branching $T_0'(s'_j)$ is carried out, followed by summing up over the $i$-nodes ($s'_j$) and collecting again all the terms containing the coefficients $a_{0r}$ in accolades. Applying this to the RHS terms for the $0$th branching order first (Equation 6.25, with only coefficients $A_{0r}$)

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leads to the following expression for the RHS terms (empty accolade pairs denote repetition of the previous term within accolades):

\[
\begin{align*}
\left\{ \sum_{i=1}^l w_i f'\left(T_0'(s'_i)\right) T_0'(s'_i) \right\} A_{000} a_{00} + \left\{ \ldots A_{010} a_{10} + \ldots \right\} A_{000} a_{00} + \\
\left\{ \sum_{i=1}^l w_i f'\left(T_1'(s'_i)\right) T_0'(s'_i) \right\} A_{001} a_{00} + \left\{ \ldots A_{010} a_{10} + \ldots \right\} A_{001} a_{00} + \\
\left. \ldots \vphantom{ \right\} \right. \\
\left\{ \sum_{i=1}^l w_i f'\left(T_r'(s'_i)\right) T_0'(s'_i) \right\} A_{00r} a_{00} + \left\{ \ldots A_{010} a_{10} + \ldots \right\} A_{00r} a_{00} + \\
\left. \right. \\
\end{align*}
\tag{6.27}
\]

Note that thus, for each chain length/branching interval element, a 4-dimensional matrix \( f_4 A \) with elements \( A_{ijkl} \) is introduced. The first two indices, \( k \) and \( l \), exactly correspond to the two indices of the elements from matrix \( f_4 A \) and refer to the orders of the chain length dimension. The latter two indices, \( k' \) and \( l' \), denote the branching orders. The same subscript assignment convention is applied as before for the chain length indices: \( k' \), corresponding to the order of the Chebyshev element it has been multiplied with, and \( l' \) being equal to the branching index (last index) of the coefficient \( a_{kl} \) with which it forms a product. For instance, in Equation 6.27 the element \( A_{ijkl} = A_{00r} \) has the same \( k' \) and \( l' \) as element \( A_{ijkl} \), while \( k = 0 \) originates from the Gauss multiplication with the 0th order term \( T_0(s_j) \) and \( l \) is equal to the first index of coefficient \( a_{ikl} \).

The procedure leading to Equation 6.27 has been applied in a similar manner, but for the 1st branching order (Equation 6.26) and higher branching orders instead of the 0th, with multiplication by the 0th and higher order chain length Chebyshev terms. This is discussed in the Appendix A.3. Finally, it is explained how the elements of the 4-dimensional matrix \( f_4 A \) are constructed for all combinations of \( k, l, k' \) and \( l' \). As in the 1D case, depending on the form of the chain length functions, \( f_T(s_j) \), the orthogonality properties of the Chebyshev series may lead to cancellation of many terms in \( f_4 A \). Also as before, the LHS of the equations containing the elements of \( f_4 A \), of which Equation 6.27 (and Equations A.3.1-A.3.3) form the RHS, possess the same structure as the RHS – with the coefficients replaced by their time derivatives. All multiplication terms within the accolades in the equations reduce to zeros and normalization factors, since:

\[
\left\{ T_k'(s_j), T_l'(s_j) \right\} = \sum_{i=1}^l w_i(s_i') T_k'(s_i') T_l'(s_i') = \gamma_{kl} \delta_{ij}
\tag{6.28}
\]
Once again in the matrix notation, the vector of normalization factors \( \mathbf{Y}' \) is derived using the vector of weights, \( \mathbf{w}' \):

\[
\mathbf{Y}' = \text{inv}(\mathbf{T}') \times \text{diag}(\mathbf{w}') \times \mathbf{T}'
\]  

(6.29)

(Note that \( \mathbf{w}' \), \( \mathbf{Y}' \) and \( \mathbf{T}' \) refer to the vectors and matrix with elements \( w'_i \), \( y'_i \) and \( T'_i(s'_i) \), not to their transpose). Hence, similar to Equations 6.24, the LHS is a full diagonal matrix, \( \mathbf{A}_{\mathbf{Y}}' \) of size \((N \times I) \times (N \times I)\) with the products of the normalization factors on the diagonal positions.

\[
A_{(k-1)r+k',(k-1)r+k} = y_k y'_k
\]  

(6.30)

Henceforth, the product of normalization factors is denoted simply by \( \mathbf{Y}_{kk} \). Back to the nomenclature used in Equation 6.16, where contributions to the population balance equations from living and dead chains were distinguished, and applying the result from the double Gauss quadrature as described above, a general expression for all the \( N \times I \) equations for one 2-dimensional interval is obtained:

\[
\frac{\partial a_{lk}}{\partial t} = a_{00}^R A_{kk}^0 + a_{01}^R A_{kk}^1 + ... + a_{(l-1)R}^R A_{kk}^{l-1} + a_{00}^R A_{kk}^{l+1} + ... + a_{(I-1)R}^R A_{kk}^{I-1} + \gamma_k
\]

\[
\begin{align*}
\gamma_k & = a_{00}^R A_{kk}^0 + a_{01}^R A_{kk}^1 + ... + a_{(l-1)R}^R A_{kk}^{l-1} + a_{00}^R A_{kk}^{l+1} + ... + a_{(I-1)R}^R A_{kk}^{I-1} + \\
& \quad + a_{00}^R A_{kk}^{2l} + a_{01}^R A_{kk}^{2l+1} + ... + a_{(l-1)R}^R A_{kk}^{2l-1} + a_{00}^R A_{kk}^{2l+2} + ... + a_{(I-1)R}^R A_{kk}^{2I-1} + b_m
\end{align*}
\]  

(6.31)

An illustration of a 4-dimensional matrix \( \mathbf{A} \) with its 4 dimensions \( k, l, k', l' \) is shown in Figure 6.6. The figure represents a ‘space’ containing all \( \mathbf{A} \) matrices for all block intervals, where each chain length interval has 5 nodes and each branching interval 6 nodes (arbitrary values). The matrix for one block interval is drawn with bold lines. In principle, the values of the elements of the \( \mathbf{A} \) matrices for all blocks may be stored in a 4-dimensional matrix, which is throughout feasible in MATLAB® in which the solution is implemented. However, in view of the fact that the set of linear equations as represented by Equation 6.30 has to be solved by a 2-dimensional matrix-inversion, a rearrangement is required to transform the 4-dimensional matrix into a 2-dimensional matrix with a substructure for one dimension and a superstructure for the other. As Figure 6.6 suggests, the two sets of dimensions of \( \mathbf{A} \) are independent, allowing several rearrangement options. However, here the chain length dimension is chosen arbitrarily as the substructure and the branching dimension as the superstructure.

Note that a 2-dimensional matrix \( \mathbf{A} \) has been introduced as an intermediate result in the 2-dimensional quadrature operations, a 4-dimensional matrix \( \mathbf{A} \) as the final result after quadrature, and finally, a 2-dimensional matrix \( \mathbf{A} \) as a 2-dimensional representation of \( \mathbf{A} \). In the reminder when discussing matrix \( \mathbf{A} \), the latter 2-dimensional representation is meant.
6.3.5 An example for propagation terms

In this section, an exemplified procedure will be shown, demonstrating the contribution of propagation reaction to the population balances in order to clarify the operations reported in the previous section. Similar steps have been applied to model the other reaction types of free radical polymerization. The contributions of propagation are indicated as \( += \) sign in the following equations. This contribution to the PBEs is defined as:

\[
\frac{dR_{n,i}}{dt} = k_p M \left( R_{n-1,i} - R_{n,i} \right) \tag{6.32}
\]

The related 2D equations for the pair nodes of intervals \( M \) (chain length) and \( H \) (branching) are reported below. The RHS equations from propagation reaction incorporate the concentration of living chains only as shown in Equation 6.32. According to the Galerkin method, it is formulated for all nodes in chain length and branching dimensions as:

\[
\frac{dR(s_j,s'_j)}{dt} = k_p M \left\{ R(s_j,s_j - 1) - R(s_j,s'_j) \right\} \tag{6.33}
\]

After Chebyshev expansion:

\[
\sum_{k'=0}^{r'} \sum_{k=0}^{r} T_k(s_j)T'_k(s'_j) \frac{da^R_{k,k'}}{dt} = k_p M \sum_{k'=0}^{r'} \sum_{k=0}^{r} \left\{ T_k(s_j - 1) - T_k(s_j) \right\} T'_k(s'_j) a^R_{k,k'} \tag{6.34}
\]

Note that the propagation terms contain factors \( T_k(s_j) \) and \( T_k(s_j - 1) \) for the chain length dimension, whereas there are only simple \( T'_k(s'_j) \) terms for the branching dimension. This has consequences for the contribution to the matrix \( A \), as will be seen later.
\[ k_p M \times \left( \begin{array}{c} 
T_0'(s_1') \\
T_1'(s_1') \\
T_r'(s_1') 
\end{array} \right) \]

\[
\left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) - \gamma_0 \right\} a_{00} + \\
\left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) \right\} a_{01} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_r(s_j - 1) \right\} a_{0r} + \\
\left\{ \sum_{j=1}^{N} w_j T_1(s_j) T_0(s_j - 1) - \gamma_0 \right\} a_{10} + \\
\left\{ \sum_{j=1}^{N} w_j T_1(s_j) T_1(s_j - 1) \right\} a_{11} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_1(s_j) T_r(s_j - 1) \right\} a_{1r} + \\
\left\{ \sum_{j=1}^{N} w_j T_r(s_j) T_0(s_j - 1) \right\} a_{r0} + \\
\left\{ \sum_{j=1}^{N} w_j T_r(s_j) T_1(s_j - 1) \right\} a_{r1} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_r(s_j) T_r(s_j - 1) \right\} a_{rr} \right\} 
\]

(6.35)

Due to orthogonality the product sum terms \( T_i(s_j) T'_i(s_j) \) lead to the normalization factor \( \gamma_0 \) as defined by Equation 6.23, while other terms disappear. Hence, this factor is appearing in the terms with coefficients \( a_{00}, \ldots, a_{0r} \). Obviously, products containing \( T_0'(s_j - 1) \) are not vanishing. Thus, the multiplication with \( T_i(s_j) \) and summation yields:

\[
\left( \begin{array}{c} 
T_0'(s_1') \\
T_1'(s_1') \\
T_r'(s_1') 
\end{array} \right) \times \left( \begin{array}{c} 
\left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) \right\} a_{00} + \\
\left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) \right\} a_{01} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_r(s_j - 1) \right\} a_{0r} + \\
\left\{ \sum_{j=1}^{N} w_j T_1(s_j) T_0(s_j - 1) - \gamma_0 \right\} a_{10} + \\
\left\{ \sum_{j=1}^{N} w_j T_1(s_j) T_1(s_j - 1) \right\} a_{11} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_1(s_j) T_r(s_j - 1) \right\} a_{1r} + \\
\left\{ \sum_{j=1}^{N} w_j T_r(s_j) T_0(s_j - 1) \right\} a_{r0} + \\
\left\{ \sum_{j=1}^{N} w_j T_r(s_j) T_1(s_j - 1) \right\} a_{r1} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_r(s_j) T_r(s_j - 1) \right\} a_{rr} \right\} \right) \right) + \ldots 
\]

(6.36)

The empty square brackets in Equation 6.36 after \( k_p MT'_i(s'_i) \) refer to a similar series of summations as the one shown for \( k_p MT'_i(s'_i) \), but obviously with different coefficients \( a_{00}, a_{11}, \ldots, a_{rr} \); they are followed by similar terms until \( k_p MT'_r(s'_r) \). This procedure is repeated for all chain length orders up to \( r \), yielding similar sets of RHS as above, all for one branching node, \( s'_r \). Then, such sets are generated for all other branching nodes, up to \( s'_i \). As in the general description, for the second Gauss quadrature step, all the RHS expressions are collected with the same chain length order after multiplication with Chebyshev terms for branching of various orders and after summation. Hence, for the 0th chain length with order \( I \), RHS terms to be collected are:
Likewise, for the Note that due to orthogonality only the terms are compiled in front of the coefficients employing orthogonality properties, the terms are compiled in front of the coefficients $a_0, a_0, \ldots$. For branching order $0$ this leads to the following set of $N$ RHS expressions, one for each chain length order:

$$
\begin{align*}
&M T'(s_1) \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) - \gamma_0 \right] a_{00} + \\
&+ \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) a_{01} + \ldots + k_p M T'(s_1) \right] + \ldots
\end{align*}
$$

... 

$$
\begin{align*}
&M T'(s_i) \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) - \gamma_0 \right] a_{00} + \\
&+ \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) a_{01} + \ldots + k_p M T'(s_i) \right] + \ldots
\end{align*}
$$

(6.37)

After multiplication with branching Chebyshev terms $T_k(s_i)$, subsequent summation and employing orthogonality properties, the terms are compiled in front of the coefficients $a_0, a_0, \ldots$. For branching order $0$ this leads to the following set of $N$ RHS expressions, one for each chain length order:

$$
\begin{align*}
&M T'(s_1) \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) - \gamma_0 \right] a_{00} + \\
&+ \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) a_{01} + \ldots + k_p M T'(s_1) \right] + \ldots
\end{align*}
$$

... 

$$
\begin{align*}
&M T'(s_i) \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) - \gamma_0 \right] a_{00} + \\
&+ \left[ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) a_{01} + \ldots + k_p M T'(s_i) \right] + \ldots
\end{align*}
$$

(6.38)

Note that due to orthogonality only the $0^\text{th}$ branching order terms are retained, containing the normalization factor $\gamma_0$ as defined in Equation 6.29, while the higher orders are canceled. Likewise, for the $k^\text{th}$ branching order:
\[
\begin{align*}
\kappa \gamma_i' & \left( \left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_0(s_j - 1) - \gamma_0 \right\} a_{k0} + \\
+ & \left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_1(s_j - 1) \right\} a_{k1} + \ldots + \left\{ \sum_{j=1}^{N} w_j T_0(s_j) T_r(s_j - 1) \right\} a_{kr} \right)
\end{align*}
\]

These sets form the end point of the double Gauss quadrature for the contribution of propagation to the RHS. These contributions for each 2-dimensional interval lead to sub-blocks in the 2-dimensional matrix \( \mathbf{A} \) consisting of \( r \times r \) sub-matrices for the chain length dimension. Each sub-block corresponds to a specific branching order being, so there is a superstructure of \( r' \times r' \) sub-blocks. For the propagation contribution, the branching superstructure has only non-zero sub-blocks at the diagonal positions, while the off-diagonal sub-blocks are zero.

### 6.3.6 Structure of the two-dimensional \( \mathbf{A} \)-matrix

The general structure of the 2-dimensional \( \mathbf{A} \)-matrix is shown in Figure 6.7. In section 6.3.4 the structure of sub-blocks of \( \mathbf{A} \), each associated to a 2-dimensional interval (see Figure 6.6), having a substructure for the chain length dimension and a superstructure for the branching dimension is presented. The sub-blocks for the intervals are organized in the same manner, consistent with this choice, although not necessarily. In Figure 6.8, a sub-block of the \( \mathbf{A} \)-matrix is provided, which indicates the superstructure of an \( \mathbf{A} \)-matrix arranged in a 2D manner for an interval element. At the lowest sub-structural level, each 2D block includes the sub-blocks of the whole chain length spectra and a single branching index. As in the case of 1D solution (Yaghini, Iedema, 2014a), every lower level sub-block receives contributions from living and dead chains population balances (\( R \) and \( P \) contributions). These contributions to the sub-blocks are indicated by arrow marks in Figure 6.8.

The elements of \( \mathbf{A} \) sub-blocks are the factors, which should be multiplied to the coefficients shown in Equation 6.17. \( A_{ij}^{RP} \) signifies an element of an \( \mathbf{A} \) sub-block, standing for the \( i^{th} \) chain length interval and \( j^{th} \) branching interval after multiplication with \( k^a \) and \( k^b \) order Chebyshev polynomials from chain length and branching dimensions. It shows the contribution of living chains and is located on the \( k^a \) line and \( k^b \) column of that specific sub-block \( (i,j)^{th} \) sub-block of \( \mathbf{A} \) after being multiplied by the associated unknown coefficient, \( a_{ij}^b \). The superscript \( RP \) shows that the term is derived from the living chains incorporation to the dead chains population balance equations. Likewise, the superscript \( PP \) indicates incorporation of dead chains to the dead chains population balance equations. Note
that the multiplication of matrix $\mathbf{A}$ with the column of unknown coefficients, $a_0^a, a_1^a, \ldots, a_0^b, a_1^b, \ldots$ for living chains PBEs, and $a_0^c, a_1^c, \ldots, a_0^n, a_1^n, \ldots$ for dead chains PBEs, in fact is a matrix multiplication. The right-hand side of the population balance equations forms a column $\mathbf{b}$. Column $\mathbf{b}$ is a sequence of known values emerging from population balance equations of dead and living chains represented as $b_0, b_1, \ldots, b_0, b_1, \ldots, b_0, b_1, \ldots$. Accordingly, the system of 2-dimensional PBEs could be indicated in a matrix notation as following:

$$\mathbf{A} \times \mathbf{a} = \mathbf{b}$$  \hspace{1cm} (6.40)

where $\mathbf{a}$ is the column of unknowns. For CSTR the equations set in Equation 6.18 is solved under steady state assumption by setting the time difference terms in Equation 6.18 to zero in the LHS matrix. Eventually, the solution for unknown coefficients is replaced in Equation 6.14 and interpolated to obtain full 2D chain length and branching distributions.

As mentioned, the diagonal sub-blocks shown by number 1 in Figure 6.7 are the main sub-blocks and each is consisting of a complete solution for all chain length nodes and a specific branching interval. This is the superstructure. Each block of size $(r+1)(r'+1)H$ represents one branching interval. Diagonal sub-blocks (1) are composed of contributions from all mechanisms. Chain transfer to polymer gives rise to a transfer term between adjacent sub-blocks in branching dimension from lower to higher branching intervals: the ‘connection’ sub-blocks 2. The upper diagonal sub-blocks represented by number 3 are the contributions of higher branching nodes from higher branching intervals to the scission of diagonal blocks at the same block-row. In total, the size of the matrix $\mathbf{A}$ for all intervals together is $(r+1)(r'+1)MH \times 2(r+1)(r'+1)MH$.

Figure 6.8 shows the substructure of each of the blocks in Figure 6.7. Each $2 \times 2$-block contains the R- and $P$ -equations (after double quadrature) for a certain chain length interval, ranging from 1 to $n$. The size of one $2 \times 2$ block is $(r+1)(r'+1) \times (r+1)(r'+1)$. Most diagonal blocks contain contributions from all mechanisms; $P$ -blocks do not contain propagation, but do have termination by disproportionation, scission and outflow from CSTR. The ‘connecting’ blocks, $R_v \rightarrow R_v, R_1 \rightarrow R_1$, etc. arise from propagation requiring a transfer from lower to higher chain length intervals. Upper-right blocks originate from random scission.
Figure 6.7. 2D population balance equations transformed to the 2-dimensional matrix $\mathbf{A}$ having a superstructure with sub-blocks associated to specific kinetic mechanisms. Each block of size $2(r+1)(r'+1)M \times 2(r+1)(r'+1)M$ represents one branching interval. Diagonal sub-blocks (1) are composed of contributions from all mechanisms. Chain transfer to polymer gives rise to a transfer term between adjacent sub-blocks in branching dimension from lower to higher branching intervals: the 'connection' sub-blocks (2). The upper-left sub-blocks (3) all arise from random scission. In total, the size of the matrix $\mathbf{A}$ for all intervals together is $2(r+1)(r'+1)MH \times 2(r+1)(r'+1)MH$.

Figure 6.8. Substructure of the main diagonal blocks in 2-dimensional matrix $\mathbf{A}$ as shown in Figure 6.7. Each 2x2 block contains the $R$- and $P$-equations (after double quadrature) for a certain chain length interval, ranging from $l$ to $n$. The size of one 2x2 block is $(r+1)(r'+1) \times (r+1)(r'+1)$. Most diagonal blocks contain contributions from all mechanisms; $P_l$-blocks do not contain propagation, but do have termination by disproportionation, scission and outflow from CSTR. The 'connecting' blocks, $R_1 \rightarrow R_2$, $R_2 \rightarrow R_3$, etc. here arise from propagation requiring a transfer from lower to higher chain length intervals. Upper-right blocks originate from random scission.

### 6.3.7 Implementation of topological scission by 2D fragment length distribution functions

Equations 6.3 and 6.4 express the fragment length distribution in the 2 dimensions, chain length $n$ and branch points $i$, without the parameter $\Sigma$ that was required in the 1D expression, as this parameter is replaced by equation 6.4. The function is known to be very
steep in chain length dimension, giving rise to a serious grid refinement problem that was solved as explained in Chapter 2. Here, it is explored whether a grid refinement is required in the branching dimension as well. Figure 6.9 shows a piece of the 2D distribution, $P_{n,i}$, at a chain length/branching interval (left) and the same piece but multiplied with the fragment length distribution from Equations 6.3 and 6.4 (right). It is clear that the distribution $P_{n,i}$ is well represented on the original coarse grid in both chain length and branching dimension. The product $f_{n,i}P_{n,i}$, however, is badly represented in chain length dimension and requires grid refinement. Here, in the 2D model the same algorithm has been applied as before for the 1D model (Chapter 2). Figure 6.9 also reveals that in branching dimension the product $f_{n,i}P_{n,i}$ is not a steep function and is well represented on the original grid. Hence, no grid refinement in branching dimension is required.

![Figure 6.9](image)

Figure 6.9. At left-hand side a piece of the 2D distribution $P_{n,i}$ is shown on a certain 2D interval. The original, coarse grid describes the distribution well in both dimensions. At right-hand side the same piece of $P_{n,i}$ is shown multiplied with the fragment length distribution function according to Equations 6.3 and 6.4. In chain length dimension the resulting function is very steep and is badly represented on the original grid – a much finer grid is required. In branching dimension not much difference exists in steepness between $P_{n,i}$ and the product $f_{n,i}P_{n,i}$ – grid refinement in branching dimension is not needed.

### 6.4 Results

Simulations have been carried out with the new 2D model and with the Monte Carlo model described in Chapter 2, serving as a reference. Concentrations and kinetic coefficients are listed in Table 6.2. The Monte Carlo parameters are mentioned in the captions to the figures.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Unity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTR feed concentration monomer</td>
<td>$M_0$</td>
<td>16.75</td>
<td>kmole.m$^{-3}$</td>
</tr>
<tr>
<td>CSTR feed concentration initiator</td>
<td>$I_0$</td>
<td>5 $\times$ 10$^{-3}$</td>
<td>kmole.m$^{-3}$</td>
</tr>
<tr>
<td>CSTR residence time</td>
<td>$\tau$</td>
<td>30</td>
<td>s</td>
</tr>
<tr>
<td>Initiator dissociation coefficient</td>
<td>$k_{di}$</td>
<td>0.5</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>Initiation coefficient</td>
<td>$k_i$</td>
<td>5000</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Propagation coefficient</td>
<td>$k_p$</td>
<td>5000</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Disproportionation termination coefficient</td>
<td>$k_{dt}$</td>
<td>10$^7$</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Combination termination coefficient</td>
<td>$k_{tc}$</td>
<td>0</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Transfer to polymer coefficient</td>
<td>$k_{tp}$</td>
<td>0 - 16</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Conversion</td>
<td>$\eta$</td>
<td>45.7</td>
<td>%</td>
</tr>
<tr>
<td>Macroradical concentration</td>
<td>$\lambda_0$</td>
<td>5.59 $\times$ 10$^6$</td>
<td>kmole.m$^{-3}$</td>
</tr>
</tbody>
</table>

Table 6.2. Simulation data 2D model
6.4.1 Choice of numbers of intervals and nodes in relation to accuracy

In the Galerkin implementation of the 1D chain length problem, it should be recalled that a proper solutions has been obtained by choosing a sufficiently high maximum chain length and equally sufficient numbers of intervals and nodes per interval. A ‘numerically proper’ solution is obviously defined by a solution, where changing either of these numerical parameters does no longer change the shape of the distribution obtained. In the 1D case typically 20 chain length intervals and 8 nodes per interval, i.e. 160 coefficients for each distribution was used.

A similar test has been performed for the 2D case, the simplest one: without combination termination and without random scission, for a moderate branching level, \( k_{np}/k_p = 0.0012 \) and further using the data of Table 6.2. Exact solutions using a direct calculation method (Iedema and Hoesloot, 2002) for this simple problem are available, being in full agreement with Monte Carlo results, may act as a reference. Interestingly, the shape of the branching distribution at a given chain length turns out to obey a binomial distribution with the average branching density, \( \rho_b \), as the parameter. Since this is a relatively narrow distribution, one might expect that a fine grid is required for the branching dimension.

Indeed, it turns out that in order to obtain numerically proper solutions, finer grids in both branching and chain length dimensions are required. The narrow binomial-like shape of the distribution at constant chain length in combination with the fact that the average branching level varies approximately linearly with chain length, evidently lead to very narrow distributions of chain length at constant number of branch points as well. This implies that the location of the 2D solution in the chain length-branching plane is confined to a very narrow area towards higher chain length and branching values. This is illustrated in the double-logarithmic contour plot of Figure 6.10, showing branching intervals as a function of chain length where the concentration is higher than 50 % of the maximum of the distribution at those intervals. Although the 50 % criterion somewhat under-estimates the area of meaningful solutions, it shows that the solution at higher chain length and branching is limited to a very narrow area, in Figure 6.10 pointing in upper-right dimension.

Thus, it is clear that in both chain length and branching dimension a finer grid is required for proper solutions in 2D than in 1D. Figure 6.10 and also the 2D plot of Figure 6.12 have been obtained for a chain length range from 1 to \( 2 \times 10^6 \), a branching range of 0 to \( 10^3 \), while taking 20 chain length and 49 branching intervals, with respectively 8 and 3 nodes per interval. This leads to a large problem size with 47040 coefficients \( a \) and a matrix \( A \) of \( 47040 \times 47040 \). Since in this case without scission \( A \) is a sparse matrix, inverting it to find the coefficients \( a \) according to Equation 6.18 is only moderately time consuming. However, in the case of scission and especially topological scission, the upper-right part of \( A \) is no longer sparse, making the inversion a prohibitive factor.

It may be concluded that proper 2D solutions of the type at hand are feasible and that the numerical procedure is adequate. However, as proper solutions only are found at the expense of a large problem size due to grid refinement requirements, in the future additional options have to be developed, especially when dealing with mechanisms causing fuller \( A \)-matrices. One of the options could be confining the \( A \)-matrix to non-zero sub-blocks in the narrow space of meaningful solutions as depicted in Figure 6.10. Even when accounting for scission, the matrix would be considerably sparser. A further improvement could be attained...
by constructing a local grid refinement similar to the one we already have developed for
topological scission. This will probably be in line with the new strategy of finding the scission
contribution terms arising from the assumption of the hypergeometric distribution to
describe the branch points redistribution on scission fragments.

**Figure 6.10.** Contour plot of 2D solution for case with moderate branching ($k_b/k_p = 0.0012$), disproportionation termination only, without scission and combination. Shown in grey are branching intervals as a function of chain length where the concentration is higher than 50 % of the maximum of the distribution at those intervals. This shows that the solution at higher chain length and branching is becoming confined to a very narrow area pointing in upper-right dimension.

### 6.4.2 Branching distribution

In this section the second dimension of the 2D solution will be explored, the branching
distribution. Figure 6.11 shows the branching density calculated for the standard data in
Table 6.2 in various ways as a function of chain length, $n$. The average branching density at
$n$, $\rho_b(n)$, is obtained from the 2D solution by:

$$\rho_b(n) = \frac{\sum_{i=0}^{\infty} P(n,i)i}{\sum_{i=0}^{\infty} P(n,i)}$$  \hspace{1cm} (6.41)

The average branching density per chain length is inferred from the Monte Carlo results
allowing for the fact that MC generates the weighted chain length distribution, proportional to
$nP(n)$. Figure 6.11 shows that according to the MC simulations the branching density
should near a constant value of almost 0.003 at long chain lengths. This is in perfect
agreement with the pseudo-distribution results presented in Yaghini and Iedema (2014a). It
should be recalled, however, that it was assumed a hypergeometric distribution as to account
for the redistribution of branch points on chain fragments. The constant branching density
at long chain lengths is observed by MC simulations.

In the present 2D model it is not possible to implement the hypergeometric function
being a very sharp function of chain length. Instead, fragment length is assumed to be an
independent redistribution of branch points, similar to an earlier pseudo-distribution
approach (Iedema et al., 2000) and also similar to the work of Krallis et al. (2007). The effect
of this assumption is clearly visible as a decrease of the branching density towards larger
chain lengths. This effect has already been observed using the pseudo-distribution approach
in Iedema et al. (2000), where linear scission was presumed. It is also visible in the branching
density as a function of chain length as calculated by the 2D model of Krallis et al. (2007),
which equally clearly shows a maximum. Note that the decrease towards higher \( n \) has the same origin as the considerable increase as \( n \to 1 \). The fragment length independent redistribution implies that large fragments receive a relatively small number of branch points, while simultaneously small fragments receive relatively many branch points. Figure 6.11 shows that the full 2D result is in exact agreement to the 1-dimensional pseudo-distribution model. The decrease of \( \rho_b \) is even more pronounced in the case of topological scission. The results from the 2D model and pseudo-distribution approach are similar, though not exactly equal. Thus, it turns out that a constant \( \varpi \) (equal to 200) for all chain lengths in the pseudo-distribution model leads to a different result than assuming \( \varpi \) equal to \( n/(2i+1) \) as is in the 2D model.

In conclusions, the simplifying assumption of fragment length independent branch point redistribution leads to a strongly deviating course of the branching density varying with chain length. In addition, it has been observed that the branching distribution for a given chain length is considerably broader than the one predicted by the pseudo-distribution approach and assuming hypergeometric redistribution. In agreement with Monte Carlo results for the branching distribution, this is expected to be very closely shaped as a binomial distribution. The 2D solution yields much wider branching distributions than the expected binomial shapes, especially for longer chain lengths. For this reason, the number of intervals required for the branching dimension and the number of nodes per interval to achieve a proper solution also turned out to be smaller.

![Figure 6.11. Branching distribution. Reference solution for branching density versus chain length given by Monte Carlo simulations and pseudo-distribution approach assuming hypergeometric redistribution of branch points on scission fragments (dark gray). Branching density as obtained from 1D pseudo-distribution and full 2D models assuming fragment length independent branch point redistribution both show a maximum and an increase to lower \( n \). This is an artificial effect caused by this assumption, which is even more pronounced for topological scission.](image)

**6.4.3 Results in 2D**

**6.4.3.1 No scission, no combination**

For the case without scission and combination, with disproportionation only and moderate branching level, \( k_{tp}/k_p = 0.0012 \) the 2D model has been run with a sufficient resolution in both chain length and branching dimensions, 20 and 49 intervals, respectively. The order of the polynomials in the chain length dimension was equal to 7 for all intervals (8 nodes), while in view of the shorter branching-intervals a lower order has been chosen as 2. The results from the 2D model are compared to those from Monte Carlo simulations in Figure 6.12.
The MC simulations generate both the number of monomer units and number of branch points for each chain and the 2D distribution is obtained by taking histograms in both chain length and branching dimensions. As MC provides chain length weighted distributions, at each chain length interval of the histogram the numbers of molecules found with a certain number of branch points are corrected for chain length weighting. Figure 6.12 shows excellent agreement between the deterministic 2D model and the MC simulations.

Figure 6.12. 2-dimensional chain length/branching distribution for moderate branching ($k_{dp}/k_p = 0.0012$), disproportionation only, without scission. Further kinetic data: standard from Table 6.2. Numerical parameters: chain length range: $1 - 5 \times 10^5$; branching range: $0 - 10^3$; number of chain length intervals: 20; number of chain length nodes: 8; number of branching intervals: 49; number of branching nodes: 3. Size of matrix $A$: $47,040 \times 47,040$. Dots from Monte Carlo simulation, $\rho_b = 0.001; \rho_l = 0.45; n_p = 448$; sample size: 250,000. Exact agreement between deterministic 2D model and MC simulations.

6.4.3.2 No combination, linear and topological scission

Next, the 2D solution for a case of disproportionation only, with strong branching $k_{dp}/k_p = 0.002$, and mild scission, $k_{rs}/k_p = 1.6 \times 10^{-5}$ is discussed, further data from Table 6.2. First, in Figure 6.13, the 1D chain length distribution as obtained from the 2D solution is shown, for both linear and topological scission. In agreement to Yaghini and Iedema (2014a), the tail of the distribution with topological scission is longer. It should be noted, however, that for this relatively high level of branching multiradicals are becoming important. In Yaghini and Iedema (2014b), it was shown that accounting for multiradicals in this area leads to even longer distribution tails, especially in the case of topological scission. The multiradical solutions agree best to Monte Carlo results. In the present 2D model multiradicals are not accounted for – thus the model is a monoradical model. Hence, the distributions in Figure 6.13 should be compared to those generated by the 1D versions of the mono-radical models, and indeed, they are exactly coinciding.

The full 2D solution is shown in Figure 6.14, for both linear and topological scission. The latter shows a 2D distribution more extended in the high region. As compared to the distributions in Figure 6.12, without scission, one observes that they are significantly broader in branching dimension. This is even more clearly seen when comparing the 2D distribution for topological scission to that resulting from Monte Carlo simulations, Figure 6.15. As it has been shown in 1D models, topological scission is the model that comes closest to exact random scission as described by MC. Hence, also for 2D it would make sense to compare the 2D distribution to that from MC. However, as it was already noted when discussing the branching density (Figure 6.11), the present implementation of the 2D model fails to correctly predict the branching density and the shape of the branching distribution at given
chain length. This is due to the assumption of scission fragment length independent redistribution of branch points. Obviously, the Monte Carlo simulation does not suffer from this condition and yields the correct higher branching values and narrower branching distribution, practically having the shape of binomial distributions. This explains the discrepancy one may observe in Figure 6.15, where for longer chains and higher branch point number, the peaks of the distributions from MC are higher. Obviously, this illustrates the necessity of a future implementation of the hypergeometric distribution as the proper description of redistribution of branch points over scission fragments.

It should finally be noted that the 2D solutions shown are numerically proper solutions, even with a limited number of intervals in both chain length and branching dimension. This is a direct consequence of the broadening of the branching distribution due to scission fragment length independent branch point redistribution, also causing a broadening in chain length dimension.

Figure 6.13. 1-dimensional chain length distribution obtained from 2D solution for disproportionation only, with strong branching $k_p/k_b = 0.002$, and mild scission, $k_r/k_b = 1.6 \times 10^4$. Further kinetic data: standard from Table 6.2. Numerical parameters: chain length range: $1 - 2 \times 10^6$; branching range: $0 - 10^3$; number of chain length intervals: 22; number of chain length nodes: 8; number of branching intervals: 26; number of branching nodes: 3. Size of matrix $A$: $27 \times 27$. Distributions coincide exactly with 1D solutions from Yaghini and Iedema (2014a).

Figure 6.14. 2-dimensional chain length/branching distribution for system with strong branching, mild scission (linear and topological) and no combination for identical systems as Figure 6.13. In agreement to the 1D solution the tail of the 2D distribution in the case of topological scission extends to longer chains and higher number of branch points. In the tail region distributions in branching dimension are relatively broad (see Figure 6.12) due to the assumption of scission fragment length independent redistribution of branch points.
Figure 6.15. 2-dimensional chain length/branching distribution for system with strong branching, mild topological scission and no combination with identical parameters to those in Figure 6.13. Dots are from Monte Carlo simulations, $\rho = 0.00168; \beta = 0.575; P_{\text{br}} = 343$; sample size: $250,000$. At small chain length and few branch points good agreement between deterministic 2D model and MC simulations. At the higher end agreement is lacking due to the assumption of scission fragment length independent redistribution of branch points. MC simulations show higher branching values and narrower branching distributions.

Finally, the full chain length/branching distributions corresponding to the famous bimodal chain length distribution that has also been found from Size Exclusion Chromatography-Multi Angle Laser Light Scattering (SEC-MALLS) for an industrial ldPE grade, Alpha IUPAC (Tacz and Taczx, 1998) are of interest. This shape is found for even higher branching levels, $k_{\text{br}}/k_p = 0.0032$, and mild linear scission, $k_n/k_p = 1.6 \times 10^{-3}$, further data according to Table 6.2. Note that disproportionation is the only present termination reaction since for high branching levels even weak combination would immediately result in gel formation, as it was shown in Yaghini and Iedema (2014b). Furthermore, it has been observed earlier (Yaghini and Iedema, 2014a, 2014b) that only with linear scission bimodal distributions are possible to be obtained. The 2D solution is shown in Figure 6.16, while the numerical parameters are given in the caption. One may observe the broadness of the distribution in both chain length and branching dimensions. Once again, this must be attributed to the previously discussed issue of the scission fragment length independent redistribution of branch points. Comparing our results to that generated by the 2D model of Krallis et al. (2007), we see that they arrive at a bimodal MWD as well. This is logical since the linear scission assumption is known to lead to this bimodality. However, Krallis et al. (2007) find their result by assuming a considerable combination termination rate, in fact equal to disproportionation. We know that combination may lead to gel formation (Yaghini and Iedema, 2014b).
6.5 Conclusions

The challenging task of solving full 2D population balance equations in the dimensions chain length and number of branch points has been successfully performed, although a number of concessions had to be made while transforming the problem into the format required by the Galerkin method. The Galerkin method proved to be feasible and the transformation is resulting in an ordered structure, the 2-dimensional matrix $A$, which is the end point of the transformation resulting in a simple linear set of equations. In $A$ the positions of blocks and sub-blocks are clearly and in a straightforward manner associated to the contributions of the various kinetic mechanism, both in chain length and branching dimensions. For example, propagation terms are found around the diagonal of $A$, while scission contributions are found in the upper-right part.

The 2D implementation of topological scission, already causing grid refinement problems in the 1D problem, was also successful in the sense that the overall chain length distribution could be correctly reproduced. In the 1D case it is necessary to rely on the average segment length, $\overline{s}$, which although being related to the average branching density, is acting as an empirical parameter. In contrast, the 2D implementation is parameter-free, since the parameter $\overline{s}$ is now explicitly given by the number of branch points and chain length.

However, with respect to random scission, both linear and topological, it was required to do concessions to the adequacy of the model employed. It was simply assumed that the redistribution of branch points on scission fragments is independent of the lengths of the fragments. In the pseudo-distribution approach based on moments of the branching distribution, it was observed that assuming a hypergeometric distribution instead is more realistic. According to this assumption the number of branch points on fragments is proportional to their length. Branching distribution thus obtained were fully in line with Monte Carlo simulations. However, in 2D it turned out to be impossible to implement the hypergeometric function within the existing numerical strategy, since it gives rise to a serious grid refinement problem. Properly accounting for the hypergeometric function requires a new strategy. Hence, simulations had to be performed with the fragment length independent redistribution.
A series of calculations with the 2D model have been carried out and the results were compared, where relevant, with Monte Carlo simulations. As regards accuracy, simulations with a kinetically simple system without scission and combination termination proved that in chain length dimension a finer grid (more intervals) is required than in 1D. This is caused by the narrow shape of the branching distribution at given chain length, practically equal to a binomial distribution. Numerically proper solutions were obtained by increasing the number of chain length intervals from 15 in the 1D case to 20 in 2D, for branching we need 60 intervals. Thus, the size of the problem (size of $A_{50000 \times 50000}$) rapidly grows as prohibiting, in particular for non-sparse $A$ due to scission. Several options exist, for the future, to solve these problems.

Furthermore, the results of the kinetically simple case without scission provided the grid resolution was sufficient and were in an exact agreement to Monte Carlo simulations. This proves the success of the implementation. When random scission, linear or topological is assumed, the overall 1D distribution of branching density turns out to deviate from earlier solutions obtained with the pseudo-distribution approach or Monte Carlo simulation results. Whereas the branching density at high chain length should attain a constant value, the 2D solution shows a maximum at medium chain length and a decrease afterwards. This incorrect result is a direct consequence of the scission fragment length independent redistribution of branch points. This was confirmed by comparing the branching density results to those from the pseudo-distribution approach also assuming fragment length independent redistribution. Obviously, in 2D this problem should be solved by finding a proper strategy to implement the hypergeometric function. The 2D solutions not only proved to under-estimate the branching at long chain lengths, but also to give much broader branching distributions at constant chain length. Regarding accuracy and grid requirements, due to the fact that in both chain length and branching dimension the distribution is more spread out, numerically proper solutions could be obtained with coarser grids and smaller problem size. Comparing the full 2D chain length/branching distribution assuming topological scission to Monte Carlo simulations nevertheless showed good agreement at the lower chain length and branching region.
Modeling of 3D molecular weight/branching/combination points distribution

The focus of this chapter is especially on the role of combination termination in the context of 3-Dimensional (3D) population balance modeling. Termination by combination is a well-known termination mechanism in radical polymerization and regarding low-density Polyethylene (ldPE) many authors (for instance Krallis et al., 2007) have assumed this mechanism to be present. The ratio between disproportionation and combination termination that is assumed in these studies varies, but usually the two mechanisms are thought of equal importance.

Full 3D Population Balance Equations (PBEs) are solved by a combination of the (2D) Galerkin–Finite Element Method (FEM) and the pseudo-distributions method to estimate the trivariate chain length/branching/number of combination points distribution. Termination by combination is treated in a scheme different than the ones employed for other kinetic reactions. Good agreement with Monte Carlo (MC) results has been observed for ldPE –like kinetics.

7.1 Introduction

Chain length, number of branch points and number of combination points are the important attributes of a polymer chain that together define the topological architecture of the polymer molecule. The importance of trivariate Chain Length Distribution/Degree of Branching Distribution/Combination Points Distribution (CLD/DBD/CPD) in modeling the topological architectures of polymer molecules in the presence of termination by combination and transfer to polymer in radical polymerization has been clarified previously (Iedema and Hoefsloot, 2005). Despite of the decisive effect of the trivariate CLD/DBD/CPD on the generated polymer chain architectures, to our knowledge Iedema and Hoefsloot are the only ones, who have addressed it. They have applied a combination of the method of moments and deterministic 1-Dimensional (1D) approach to 3D population balance equations to estimate the overall distributions without presenting the actual full 3D distributions.

The focus of this chapter will be on providing a solution that is one step further than Iedema and Hoefsloot (2005). We present full 2D distributions of chain length and degree of branching for a free radical polymerization with transfer to polymer, topological scission and termination by combination as the most affecting reactions in ldPE polymerization, and employ the moments of combination points to cast the effect of the third dimension. The numerical implementation in the Galerkin scheme that proved to be successful in the 2D
model discussed in the previous chapter is applied here as well. However, the combination termination reaction introduces a non-linearity in the system that will be dealt with in a different scheme than the other kinetic mechanisms. In addition, a serious problem is encountered by the 2D convolution arising from the combination termination reaction as implemented in the Galerkin framework.

Furthermore, as has been noticed by many authors on radical polymerization before and has been discussed in Chapter 3, this polymerization system with transfer to polymer and combination termination may lead to gelation. The question then rises whether the 2D model developed also would work in the gel regime. This problem has been treated in the same manner as it was realized for the 1D problem in Chapter 3.

### 7.2 Reaction and Population balance equations in full 3 dimensions

#### 7.2.1 Reaction equations and 3D formulation

The 3D reaction equations and 3D population balances with regard to chain length \( (n) \), number of branch points \( (i) \) and number of combination points \( (k) \) have to be defined on the basis of the reaction equations. Table 7.1 shows the entire reaction equations system for ldPE free radical polymerization.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator dissociation</td>
<td>( I \rightarrow I )</td>
</tr>
<tr>
<td>Initiation</td>
<td>( I + M \rightarrow R_{0,j,k} )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( R_{i,j,k} + M \rightarrow R_{i+1,j,k} )</td>
</tr>
<tr>
<td>Random scission</td>
<td>( R_{i,j,k} + P_{i,j,l} \rightarrow P_{i,j,k} + P_{i,j,l} + R_{i,j,s} )</td>
</tr>
<tr>
<td>Termination by disproportionation</td>
<td>( R_{i,j,k} + R_{i,m,j} \rightarrow P_{n+m,i,j,k+l} )</td>
</tr>
<tr>
<td>Termination by combination</td>
<td>( R_{i,j,k} + R_{i,m,j} \rightarrow P_{i,n,j,k+l} )</td>
</tr>
<tr>
<td>Transfer to polymer</td>
<td>( R_{i,j,k} + P_{i,j,l} \rightarrow P_{i,j,k} + R_{m,j+l} )</td>
</tr>
</tbody>
</table>

| \( m, n \) | chain length; |
| \( i \) | number of branch points per chain |
| \( k, l \) | number of combination sites per chain |

Table 7.1 3D reaction equations of ldPE free radical polymerization

The general population balance equations for free radical polymerization in Continuous Stirred Tank Reactor (CSTR), for living chains and dead chains are indicated as below:

\[
\frac{dR_{n,i,k}}{dt} = k_p M (-R_{n,i,k} + R_{n-1,i,k}) - (k_{rd} + k_{tr}) R_{n,i,k} +
\]

\[
- k_{rs} \mu R_{n,i,k} + k_{rs} \sum_{m=0}^{\infty} m f(n,m) \sum_{j=i}^{\infty} \beta^b(n,m,i,j) \sum_{l=k}^{\infty} \beta^c(n,m,k,l) P_{m,j,l} +
\]

\[
+ k_{rp} (-\mu R_{n,i,k} + \lambda_0 n P_{n,i-1,k}) - \frac{1}{\tau} R_{n,i,k}
\]  

(7.1)
\[ \frac{dP_{n,j,k}}{dt} = k_i \frac{\lambda_0}{\rho} R_{n,j,k} + \frac{1}{2} k_i \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \sum_{l=0}^{\infty} R_{n,j,l} R_{n-m,j-k-l-1} + \]
\[ - k_i \lambda_0 nP_{n,j,k} + k_i \mu_i R_{n,j,k} + k_i \sum_{n=1}^{\infty} \sum_{n+i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{l=0}^{\infty} m_f(n,m) \beta^i(n,m,i,j) \sum_{l=0}^{\infty} \beta^j(n,m,k,l) P_{m,j,l} + \]
\[ + k_i (\mu_i R_{n,j,k} - \lambda_0 n P_{n,j,k}) - \frac{1}{\tau} P_{n,j,k} \]

\( (7.2) \)

In Equations 7.1 and 7.2, chains with more than one radical site per molecule have not been taken into account, in other words multiradicals are supposed to be negligible. The scission contribution containing the 3 summations over the 3 dimensions possess the scission fragment length distributions \( f(n,m) \) and functions \( \beta^i(n,m,i,j) \) and \( \beta^j(n,m,k,l) \) that describe the redistribution of branch points and combination points over scission fragments, respectively. The form of these will be discussed below.

### 7.2.2 3D pseudo-distributions of combination points distribution-moments

With respect to the full 3-dimensional CLD/DBD/CPD-problem, the pseudo-distribution method is employed in such a way that a full solution in two distribution variables, chain length \( n \) and number of branch points \( i \) is computed, while computing only the moments of the third variable, number of combination points \( k \). The usual moments \( \lambda_0 \) and \( \mu_i \) and the 2-dimensional moments in number of combination points (including the ‘zeroth’ moments \( R_{n,j} \) and \( P_{n,j} \)) are defined as:

\[ \lambda_0 = \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \sum_{l=0}^{\infty} R_{n,j,k} \]
\[ \mu_i = \sum_{n=1}^{\infty} \sum_{j=0}^{\infty} \sum_{l=0}^{\infty} n P_{n,j,k} \]
\[ R_{n,j} = \sum_{k=0}^{\infty} R_{n,j,k} \]
\[ P_{n,j} = \sum_{k=0}^{\infty} P_{n,j,k} \]
\[ R_{n,k} = \sum_{j=0}^{\infty} R_{n,j,k} \]
\[ P_{n,k} = \sum_{j=0}^{\infty} P_{n,j,k} \]
\[ \Phi^{c1}_{n,j} = \sum_{k=0}^{\infty} k R_{n,j,k} \]
\[ \Phi^{c2}_{n,j} = \sum_{k=0}^{\infty} k^2 R_{n,j,k} \]
\[ \Phi^{cN}_{n,j} = \sum_{k=0}^{\infty} k^N R_{n,j,k} \]
\[ \Psi^{c1}_{n,j} = \sum_{k=0}^{\infty} k P_{n,j,k} \]
\[ \Psi^{c2}_{n,j} = \sum_{k=0}^{\infty} k^2 P_{n,j,k} \]
\[ \Psi^{cN}_{n,j} = \sum_{k=0}^{\infty} k^N P_{n,j,k} \]

The combination point density at given chain length \( n \) and number of branches \( i \), \( \rho_{n,j}^c \), is defined in terms of the zeroth and first moments: \( \rho_{n,j}^c = \Phi^{c1}_{n,j} / P_{n,j} \), while the polydispersity \( D_{n,j}^c \) follows from moments 0, 1 and 2: \( D_{n,j}^c = \Psi^{c2}_{n,j} / \left( \Phi^{c1}_{n,j} \right)^2 \).
7.2.3 Zeroth CPD-moment: CLD/DBD-balances

The 2D combination points pseudo-distribution problem is solved for the case of random scission, either linear or topological scission, which determines the shape of the fragment length distribution \( f(n,m) \) (Yaghini and Iedema, 2014a). In the previous chapter the issue of redistribution of branch points on scission fragments has been extensively discussed. In this 3D formulation, the additional concern is with redistribution of combination points over scission fragments. In Yaghini and Iedema (2014a), it is argued that for branch points redistribution a hypergeometric distribution is the best model, thus the number of branch points on a scission fragment is proportional to its length. The same reasoning is valid for combination points. Hence, both \( \beta \)-functions in the population balances should be hypergeometric distributions.

However, as discussed in the previous chapter accounting for the full hypergeometric distribution in the branch points dimension leads to a grid refinement problem that could not be solved using the present numerical strategy. Therefore, for branching, as before, the assumption is made that the redistribution of branch points on scission fragments is independent of fragment length, hence \( \beta^b = i/(i+1) \). In contrast, since the pseudo-distributions method will be employed for the combination points dimension, only the implement of combination moment expression arising from a hypergeometric combination points distribution assumption is required. This proceeds in the same manner exactly as for branching in the pseudo-distribution approach discussed in Yaghini and Iedema (2014a), yielding similar expressions. The 2D balances describing the Chain Length Distribution/Degree of Branching Distribution (CLD/DBD) are obtained by taking the sums over the number of combination points index, \( k \). In the zeroth combination moment expression, the \( \beta^c \)-function, would disappear.

\[
\frac{dR_{n,i}}{dt} = k_p M (-R_{n,i} + R_{n-1,i}) - (k_{id} + k_{ic}) \lambda_0 R_{n,i} + k_y (-\mu_1 R_{n,i} + \hat{\lambda}_0 n P_{n-1,i}) +
- k_{r_1} \mu_1 R_{n,i} + k_{r_2} \sum_{m=i}^{n+1} \sum_{j=0}^{m-i} \left( \frac{1}{j+1} \right) f(n,m) m P_{m,j} R_{n,i} - \frac{1}{\tau} R_{n,i}
\]

(7.4)

\[
\frac{dP_{n,j}}{dt} = k_{id} \lambda_0 R_{n,j} + \frac{1}{2} k_{ic} \sum_{m=1}^{n-j} R_{m,j} R_{n-m,j} + k_y (\mu_1 R_{n,j} - \lambda_0 n P_{n,j}) +
+ k_{r_1} \mu_1 R_{n,j} - k_{r_2} \lambda_0 n P_{n,j} + k_{r_2} \sum_{m=1}^{n-j} \sum_{j=0}^{m-i} \left( \frac{1}{j+1} \right) f(n,m) m P_{m,j} R_{n,j} - \frac{1}{\tau} P_{n,j}
\]

(7.5)

Note that the shift of the second index in the CLD/DBD balances (denoting the number of branches) is located in the transfer to polymer production term in the living chain equation, Equation 7.3. This obviously reflects that this mechanism is responsible for the branch formation. Evidently, in these equations all information about the number of combination points is lost.
7.2.4 First and second CPD-moments

Population balances of 2D distributions of the leading moments in the combination points could be obtained by performing multiplications with \( k \) and \( k^2 \), and summing up over the number of combination points index \( k \). With the assumptions concerning the branch points and combination points redistribution functions, \( \beta^+ = \sqrt{(i+1)} \) and \( \beta^c \) as hypergeometric functions, in the expressions for the first and second combination moments, the followings are obtained for scission terms:

\[
\sum_{k=0}^{\infty} \sum_{m=n+1}^{\infty} m \Phi^b(n,m,i,j) \sum_{l=0}^{\infty} \beta^c(n,m,k,l) P_{m,j} = \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left( \frac{1}{j+1} \right)^2 f(n,m) m \Psi^{c1}_{m,j}
\]

\[
\sum_{k=0}^{\infty} \sum_{m=n+1}^{\infty} m \Phi^b(n,m,i,j) \sum_{l=0}^{\infty} \beta^c(n,m,k,l) P_{m,j} = \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left( \frac{1}{j+1} \right)^2 f(n,m) m \Psi^{c1}_{m,j}
\]

Thus, the full population balance expression in the pseudo-distribution formulation is:

\[
\frac{d\Phi^{c1}_{n,j}}{dt} = k_p M (\Phi^{c1}_{n,j} + \Phi^{c1}_{n-1,j}) - (k_m + k_c) \lambda_0 \Phi^{c1}_{n,j} + k_p (\mu_1 \Phi^{c1}_{n,j} + \lambda_0 n \Psi^{c1}_{n,j})
\]

\[
- k_m \mu_1 \Phi^{c1}_{n,j} + k_n \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left( \frac{1}{j+1} \right)^2 f(n,m) m \Psi^{c1}_{m,j} - \frac{1}{\tau} \Phi^{c1}_{n,j}
\]

\[
\frac{d\Psi^{c1}_{n,j}}{dt} = k_n \lambda_0 \Phi^{c1}_{n,j} + k_p (\mu_1 \Phi^{c1}_{n,j} - \lambda_0 n \Psi^{c1}_{n,j})
\]

\[
k_n \left( \sum_{m=1}^{\infty} \sum_{j=0}^{\infty} \Phi^{c1}_{m,j} R_{m-j,n-j} + \frac{1}{2} \sum_{m=1}^{\infty} \sum_{j=0}^{\infty} \Phi^{c1}_{m,j} R_{n-j,m-j} \right)
\]

\[
+ k_n \mu_1 \Phi^{c1}_{n,j} - k_n \lambda_0 n \Psi^{c1}_{n,j} + k_n \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left( \frac{1}{j+1} \right)^2 f(n,m) m \Psi^{c1}_{m,j} - \frac{1}{\tau} \Psi^{c1}_{n,j}
\]

\[
\frac{d\Phi^{c2}_{n,j}}{dt} = k_p M (\Phi^{c2}_{n,j} + \Phi^{c2}_{n-1,j}) - (k_m + k_c) \lambda_0 \Phi^{c2}_{n,j} + k_p (\mu_1 \Phi^{c2}_{n,j} + \lambda_0 n \Psi^{c2}_{n,j})
\]

\[
- k_m \mu_1 \Phi^{c2}_{n,j} + k_n \sum_{m=n+1}^{\infty} \sum_{j=0}^{\infty} \left( \frac{1}{j+1} \right)^2 f(n,m) m \Psi^{c2}_{m,j} - \frac{1}{\tau} \Phi^{c2}_{n,j}
\]
Chains are not separated as in the 2D model, but with the number of radical sites in sol and gel, react with the monomer units of the polymer chains in the sol, with concentration distribution. 

Employing moments in Equation 7.3. In fact, the following conditions are posed by gelation possibility: of covering the gel regime by definition. Note that equations, Equation 7.5 to Equation 7.10 to polymer material in sol and gel. Changing radicals in sol and gel, and radical sites and the monomer units in the polymer. 

The same as the 1D model, the involved reactive groups are assumed to be the radical sites and the monomer units in the polymer. $\lambda_0^*$ is defined as the total amount of radicals in sol and gel, and $\mu_1^*$ is defined as the total amount of monomer units in the polymer material in sol and gel. Changing $\lambda_0$ and $\mu_1$ respectively in the population balance equations, Equation 7.5 to Equation 7.10 to $\lambda_0^*$ and $\mu_1^*$, equations are obtained that are cable of covering the gel regime by definition. Note that $\lambda_0^*$ and $\mu_1^*$ could be larger than the moments in Equation 7.3. In fact, the following conditions are posed by gelation possibility:

$$\lambda_0^* \geq \lambda_0 = \sum_{n=1}^{\infty} \sum_{i=0}^{\infty} \sum_{k=0}^{\infty} R_{n, i, k} \quad \mu_1^* \geq \mu_1 = \sum_{n=1}^{\infty} \sum_{i=0}^{\infty} \sum_{k=0}^{\infty} nP_{n, i, k}$$

By solving balance equations including creation and termination of radical sites:

$$\frac{d\lambda_0^*}{dt} = k_\lambda M - (k_{\lambda_0} + k_{\lambda_c}) \left( \lambda_0^* \right)^2 - \frac{1}{t} \lambda_0^* = 0$$

$$\lambda_0^* = M_0 - M$$

Employing $\lambda_0^*$ and $\lambda_1^*$ in the 2D population balance equations indicates that all the radical sites in sol and gel, react with the monomer units of the polymer chains in the sol, with concentration distribution $P_{n, j, k}$, and that all the monomer units react with radicals in the sol, with concentration distribution $R_{n, j, k}$. Note that in the multiradical model, dead and living chains are not separated as in the 2D model, but with the number of radical sites per
molecule as an extra dimension. This implies a slightly different definition of the moments addressed above. However, the principle of allowing the total monomer units and radical sites in the polymer to be shared between sol and gel in the 2D formulation is fully equivalent.

7.3 The 2D Galerkin method and modeling molecular weight/branching distribution

7.3.1 Galerkin method

The 2D model equations derived above are implemented in the Galerkin scheme in exactly the same manner as described in Chapter 6, with the exception of the combination termination that has to be treated in a different manner. This treatment is using the concepts and practically the same nomenclature as the 2D Galerkin scheme of the previous chapter, but for the sake of completeness the basics are repeated here.

All the 2D concentrations introduced above including the pseudo-distributions are represented by the discrete Chebyshev polynomials at the non-equidistant nodes of the so-called “interval elements” (2D intervals with respect to chain length and branching). Assuming \( s \) as a chain length node of the interval element \( MH \) (chain length interval \( M \) and branching interval \( H \)), and \( s' \) as a branching node of the same interval element, the 2D concentration at these nodes is defined as:

\[
P(s,s') = \sum_{i_H=0}^{r_H} \sum_{i_M=0}^{r_M} a_M^{i_M} T_M^{i_M}(s) T_H^{i_H}(s')
\]

(7.15)

and thus:

\[
a_M^{i_M} = \frac{1}{l_H^{i_H} l_M^{i_M}} \sum_s \sum_{s'} P(s,s') w_H^{i_H}(s') w_M^{i_M}(s) T_M^{i_M}(s) T_H^{i_H}(s')
\]

(7.16)

The variables and coefficients used in this chapter are the same as in Chapter 6.

Replacing the 2D concentration terms in population balances by their equivalent in the Galerkin representation, we come up with a set of differential equations. In the case of CSTR, the set of differential equations is transformed to a set of algebraic equations by applying the steady state assumption. The general form of the equations for the dead chains is:

\[
\frac{dP(s',s_j)}{dt} = f\left( P(s',s_j), R(s',s_j) \right)
\]

(7.17)

The weights corresponding to the nodes \( s_j \) on a chain length interval and on a branching interval \( s' \) are \( w_j \) and \( w_i' \). Equation 7.17 is the population balance equation at \( (s,s') \). \( r \) \( (N = r + 1) \) and \( r' \) \( (I = r' + 1) \) are the maximum order of Chebyshev polynomials for chain
length and branching, \( j \) is 1: \( N \) and \( i \) is 1: \( I \), \( k \) and \( k' \) vary as 0: \( r \) and 0: \( r' \) accordingly for chain length and branching dimensions.

Applying the Chebyshev polynomials:

\[
\sum_{s=0}^{r} \sum_{k=0}^{r'} T_k(s_j) T_{k'}(s_i') \frac{da_{k,k'}^{r'}}{dt} = \sum_{s=0}^{r} \sum_{k=0}^{r'} a_{k,k'}^{r} R(k) + \sum_{s=0}^{r} \sum_{k=0}^{r'} a_{k,k'}^{r} \left( T_k(s_j) T_{k'}(s_i') \right) + b_{kk'}
\]  

(7.18)

Similar representations hold for the other 2D distributions: \( R_{m,j}, \Psi_{n,i}, \Phi_{n,i} \).

Finally, as extensively has been described in the previous chapter, the system of 2D PBEs after transformation results into a set of linear equations:

\[
A \times a = b
\]

(7.19)

with \( a \) as the column of unknown coefficients. The structure of \( A \) contains the contributions of all 2D distributions.

In the present implementation of the 2D problem all kinetic mechanisms are accounted for in matrix \( A \), except the convolution terms arising from combination termination. The various convolutions terms are appearing in the population balance equations associated with dead chains: Equations 7.5, 7.9 and 7.11. In fact, the convolution terms will form non-linear terms as part of the vector \( b \). This problem is solved as a dynamic simulation starting at zero conversion and proceeding by updating the vector \( b \) at each time step with new values of the convolution terms. The efficient computation of the convolution terms requires an elaborate algorithm, as is explained in the next section.

### 7.3.2 Convolution procedure in two dimensions

#### 7.3.2.1 Principle of treating convolution in Galerkin scheme

The 2D distributions are expressed in Chebyshev polynomials in the chain length and number of branch points dimensions and are specified by the indexes \( n \) (chain length) and \( i \) (branch points). The maximum order of the polynomials in the chain length and branching dimensions are indicated as \( r_n \) and \( r_i \), respectively. Accordingly, the number of intervals on the chain length and branch points axes are represented by \( M_n \) and \( M_i \). Thus, there are \((r_n+1)M_n\) nodes in the chain length dimension and \((r_i+1)M_i\) in the branching dimension.

Regarding the required convolution operation to address combination termination, the convolution procedure described in Yaghini and Iedema (2014a) has been extended using two convolution matrices. Note that a distribution, \( P(s) \), could be convoluted with itself or with another distribution \( Q(s) \), where the second distribution may or may not be equal to the first one. The basic idea is that at each node \( s \), a summation of products of concentrations as \( \sum P(s)Q(s) \) is to be performed such that \( s+s' \) equals \( s \), requiring function evaluations of \( P(s) \) and \( Q(s) \). In order to reduce the number of function
evaluations, which may be extremely high in the 2D case, the choice of the summation grid \( s_i \), for each node is highly important. The summation grid for all nodes is represented by a ‘regular’ and a ‘complementary’ convolution matrices, \( \mathbf{Z}_1 \) and \( \mathbf{Z}_2 \), respectively. In Figure 7.1 some parts of the convolution matrices for one dimension (chain length or number of branch points) are shown. Each row of the matrices corresponds to either \((r_e + 1)M_s\), or \((r_i + 1)M_t\) nodes. The column positions of \( \mathbf{Z}_1 \) (upper part of Figure 7.1) refer to the ‘regular’ summation nodes and the column positions \( \mathbf{Z}_2 \) (lower part of Figure 7.1) refer to the ‘complementary’ nodes. As a starting point for the summation grid \( s_i \), the regular nodes \( s \) from the Galerkin procedure are taken, from which for each node the complementary nodes \( s_i \) are calculated. As explained in Yaghini and Iedema (2014a) for broad distributions a refinement of the summation grid is required, by introducing extra grid points \( s_i \) at the range with lowest values, Right-Hand-Side (RHS) in Figure 7.1. These extra nodes \( s_i \), invoke the extra nodes \( s_i \) as well, complementary to \( s_i \). The node values \( s_i \) and \( s_i \) for all \( s \) are then collected and stored in two vectors, \( \mathbf{s}_1 \) and \( \mathbf{s}_2 \). It is obvious from Figure 7.1 that some node values, for instance the first node of the first interval, appear many times. To reduce the size of the vectors only unique values are stored. Convolution matrices \( \mathbf{Z}_1 \) and \( \mathbf{Z}_2 \) then contain the position numbers of the nodes in vectors \( \mathbf{s}_1 \) and \( \mathbf{s}_2 \), such that \( s_i(z(i,j)) + s_j(z(i,j)) = s \), where \( s_i \) and \( s_j \) are then the elements of the vectors \( \mathbf{s}_1 \) and \( \mathbf{s}_2 \), while \( z(i,j) \) and \( z(i,j) \) are the elements on the \( i^{th} \) row and \( j^{th} \) column of matrices \( \mathbf{Z}_1 \) and \( \mathbf{Z}_2 \). The concentrations belonging to the regular and complementary nodes are denoted by \( p(z(i,j)) \) and \( q(z(i,j)) \). For each node \( s(i) \) the convolution follows as a summation of products \( p_i p_j \) over the elements of row \( i \):

\[
p(s(i)) = \sum_{j=1}^{J} w_i(i,j) p_1(z_1(i,j)) p_2(z_2(i,j)) \quad (7.20)
\]

Here, \( w_i(i,j) \) is the weight belonging to the node \( s_i(z(i,j)) \) of the summation grid and it is calculated in an identical way as the regular weights of the Galerkin approach (Yaghini and Iedema, 2014a). The number of rows in convolution matrices \( \mathbf{Z}_1 \) and \( \mathbf{Z}_2 \) always equals to the total number of nodes, \((r_e + 1)M_s\), or \((r_i + 1)M_t\). In the absence of grid refinement the number of columns is the same, while with grid refinement is roughly twice as many; then the rows of \( \mathbf{Z}_1 \) and \( \mathbf{Z}_2 \) are practically mirrored images of each other. The values of \( p_i(z(i,j)) \) and \( q_i(z(i,j)) \) are calculated using the proper coefficients at each interval and as well as the values of the Chebyshev polynomials of various order. The latter are stored in matrices \( \mathbf{T}_1 \) and \( \mathbf{T}_2 \) with elements \( t_1(z_1(i,j),1:1 + 1) \) and \( t_1(z_2(i,j),1:1 + 1) \), having the same sequence and length in the direction of the rows as the vectors \( \mathbf{s}_1 \) and \( \mathbf{s}_2 \). In contrast to the row positions, the column positions correspond to order of the polynomials.
7.3.2.2 Extension of convolution algorithm to 2 dimensions

Without further debate, it is stated that for a 2D convolution all the possible combinations of summation nodes for chain length and number of branch points have to be evaluated. This would imply that the sizes of the 2D convolution matrix equivalents are $(r_0+1)M_0(r_0+1)M_0 \times 2(r_0+1)M_0(r_0+1)M_0$. In a realistic case for ldPE with orders of $r_0 = 7, r_1 = 2$, and numbers of intervals $M = 15, M_0 = 14$, the size of $Z_1$ and $Z_2$ is $5040 \times 10080$. As explained above, for the function evaluations that are required for all the elements of the matrices $p_1(z_i)$ and $q_2(z_j)$, $(r_0+1)M_0$ number of Chebyshev polynomial values for each point has to be evaluated; in the provided example this number is equal to 24. In the case of a 1D convolution these polynomial values are calculated just once, and are stored in $T$, and $T_2$, since during the necessary integration procedure to solve the dynamic population balances, these values could be reused as long as the grid of Galerkin nodes is not changed. However, in the 2D case one would have to store $2(r_0+1)^1(M_0)^1(r_0+1)^1(M_0)^2$ function values, in the example $2 \times 10^9$ numbers, which requires 20 GB of internal memory storage space for the 2D equivalents of $T$ and $T_2$. Since this is not feasible, the idea of calculating the Chebyshev polynomials beforehand was abandoned and an alternative procedure was taken.

7.3.2.3 Saving of storage requirement in convolution procedure

Instead of storing the 2D equivalents of $T$ and $T_2$, the 2D Chebyshev elements are calculated at each time step of the integration for the elements in the whole series of regular and complementary blocks for each node.

In the 2D convolution procedure, the function evaluations are performed for all the nodes per interval elements, as shown in Figure 7.2. 2D summation grids are constructed on nodes in interval blocks, yet a series of ‘regular’ and a series of ‘complementary’ blocks. The convolution matrices, summation node vectors and Chebyshev polynomial matrices are calculated separately for chain length and branch points

$Z_1^{n}, Z_2^{n}, Z_1^{s}, Z_2^{s}, S_1^{n}, S_1^{s}, S_2^{n}, S_2^{s}, T_1^{n}, T_1^{s}, T_2^{n}, T_2^{s}$. These values are stored, while the 2D Chebyshev elements are calculated at each time step of the integration for the elements in the whole series of regular and complementary blocks for each node by multiplying elements from $T_1^{n}, T_1^{s}, T_2^{n}, T_2^{s}$, respectively. For each interval block $(r_0+1)(r_1+1)$ nodes are selected from $S_1^{n}, S_1^{s}, S_2^{n}, S_2^{s}$, and for each node all the combinations are taken, $(r_0+1)$ selected rows from $Z_1^{n}, Z_2^{n}$ with $(r_1+1)$ selected rows from $Z_1^{s}, Z_2^{s}$. Since each combination of rows produces $2(r_0+1)M_0(r_0+1)M_1$ elements, the total size of the summation grid amounts to $2(r_0+1)^1M_0(r_0+1)^1M_1$, which is equal to 483 840 points for both the regular and complementary part in the example. Since for each summation grid point the multiplication of Chebyshev elements has to be carried out, each block of nodes requires around one million multiplications.

In order to reduce the number of multiplications even further, the fact that a large part of the multiplications within one interval element turned out to be identical has been
considered. An algorithm has been constructed that strictly restricts the number of multiplications to the uniquely different ones. The values of all selected summation nodes on the chain length axis are multiplied by the values of those on the branch points axis. Before multiplication an arbitrary high number is added to either chain length or branch point node values. This produces a series of additional $2(r_n + 1)^2M_n(r_i + 1)^2M_i$ numbers that are equal for equal multiplications. These numbers are stored in a vector called $v$. Using the MATLAB® routine “unique.m” both the unique multiplications are identified and stored in a new vector, $v'$, which is much shorter if many repetitions are present, as well as a vector $u$ with the same length as $v$ containing the positions in $v'$, at which the values should appear in the original vector $v$. This allows calculating the uniquely different Chebyshev products just once, while $u$ is used to assign multiple products to the proper positions in the summation grid. The multiplication of the Chebyshev elements with the proper coefficients is also subjected to this procedure. This requires similar vectors as $v'$ and $u$, where the interval numbers of the summation grid nodes are stored. The example shows that instead of one million, just around 80 000 function evaluations are required. Since for a fixed summation grid the positions of multiple products remains unaltered, the reduction algorithm has to be carried out just once for each dynamic simulation. This requires the storage of the vectors $u_1$ and $v'_1$, $u_2$ and $v'_2$ for the regular and complementary nodes from each interval block. The vectors $u_1$ and $u_2$ have the full length of $2(r_n + 1)^2M_n^2(r_i + 1)^2M_i^2$, which is $4 \times 10^8$ in the example and requires in total 0.8 GB of internal storage capacity.

Figure 7.1. Part of convolution matrix $C_1$ for one dimension with $j = 2$ nodes (encircled dots) as rows and for each node $j' = 1: j - 1$, nodes on the regular summation grid (black dots). Regular nodes in $C_1$ (upper part) are counted from left hand side, complementary nodes in $C_1$ (lower part) from right hand side. Pairs of regular and complementary nodes are placed in different intervals. For last node ($s$) 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 the last 3 nodes, $s-2$, $s-1$, and $s$).
7.3.3 Implementation of combination points pseudo-distribution approach

Equations 7.8 through 7.11 describe the combination points pseudo-distributions. Each set of higher moment distributions, here $\Psi_{nj}^1$, $\Phi_{nj}^1$ and $\Psi_{nj}^2$, $\Phi_{nj}^2$ give rise to similar $A$-matrices as the $P_{nj}$, $R_{nj}$ do, which is illustrated in Figure 7.3. Thus, one observes that in a pseudo-distribution model with $N$ moments (0,1 or 2) the size of the matrix $A$, being $s_A \times s_A$ for $N = 0$, is $(N+1)s_A \times (N+1)s_A$. Furthermore, the parts of the equations, which relate $\Psi_{nj}^{1/N}$ and $\Phi_{nj}^{1/N}$ to themselves appear as the diagonal blocks. In addition, $\Psi_{nj}^{2/N}$, $\Phi_{nj}^{2/N}$ appear in the equations for $\Psi_{nj}^{1/N}$ and $\Phi_{nj}^{1/N}$. These parts lead to a lower-left element in Figure 7.3. Note that in this pseudo-distribution model, this term originates from the scission contribution. In fact, the combination terms in the higher moment population balance equations all contain lower moment terms too. However, since in the convolution procedure described in Section 7.3 the combination terms are dealt with in the RHS of the equations as a part of vector $b$ in equation 7.19, they do not appear at all in matrix $A$.

As the size of the complete matrix $A$ is $(N+1)s_A \times (N+1)s_A$ for a 2D pseudo-distribution approach, the dynamic solution procedure requiring the inversion of $A$ at each time step might be very time consuming. It was decided to adopt a sequential solution procedure, where $N+1$ dynamic simulation runs with a $0$-size matrix $A(s_A)$ is performed. The proper matrix $A$ of a particular run according to the diagonal block in Figure 7.3 is employed, while an eventual contribution of the lower moment is transferred to the right-hand side, and is incorporated in vector $b$. This is possible in the present pseudo-distribution problem, since the solution of lower moments does not depend on higher moments. Otherwise, this separation would not have been possible.
Figure 7.3. Structure of matrix $\mathbf{A}$ in 2D pseudo-distribution approach with 2 higher moments, $N = 2$. If the size of one block is $s_A \times s_A$, the overall size is $3s_A \times 3s_A$. In the dynamic simulation solution the diagonal blocks of size $s_A \times s_A$ are solved in $J$ separate runs. The non-diagonal, lower-left block is incorporated in vector $\mathbf{b}$, Equation 7.19.

7.4 Results

Model simulations have been performed with various values for kinetic parameters (see Table 7.2), without and with gel formation, both with the 2D model and with the 2D combination points pseudo-distribution model. The main objective of these calculations was to demonstrate the feasibility of the elaborate convolution procedure explained in the previous sections. In none of these cases random scission was assumed to take place, although this is technically completely possible. The results were compared to Monte Carlo simulations performed with a model described in Yaghini and Iedema (2014a, 2014b). The Monte Carlo parameters are mentioned in the captions of the figures.

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<th>Name</th>
<th>Symbol</th>
<th>Value</th>
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<td>kmole.m$^{-3}$</td>
</tr>
<tr>
<td>CSTR feed concentration initiator</td>
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<td>5 $10^{-3}$</td>
<td>kmole.m$^{-3}$</td>
</tr>
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<td>CSTR residence time</td>
<td>$\tau$</td>
<td>30</td>
<td>s</td>
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<td>Initiator dissociation coefficient</td>
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<td>s$^{-1}$</td>
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<tr>
<td>Initiation coefficient</td>
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<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Propagation coefficient</td>
<td>$k_p$</td>
<td>5000</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Disproportionation termination coefficient</td>
<td>$k_{d}$</td>
<td>5 $10^6$</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Combination termination coefficient</td>
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<td>5 $10^6$</td>
<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Transfer to polymer coefficient</td>
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<td>m$^3$kmole$^{-1}$s$^{-1}$</td>
</tr>
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<td>%</td>
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<td>Gel content</td>
<td>$\lambda_0$</td>
<td>0 - 44</td>
<td>%</td>
</tr>
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<td>Macroradical concentration</td>
<td>$\lambda_0$</td>
<td>5.59 $10^6$</td>
<td>kmole.m$^{-3}$</td>
</tr>
</tbody>
</table>

Table 7.2. Simulation data 2D model

7.4.1 2D model without and with gel formation

Simulations have been performed for relatively strong combination termination: $k_{ct}/k_p = k_{d}/k_p = 1000$, while a low branching level has been assumed, $k_{tp}/k_p = 0.0003$. As it was already shown in Yaghini and Iedema (2014b), strong combination very easily leads to gel formation, even for relatively weak branching – the gelpoint is at around twice the present...
branching level. The full 2D solution is shown in Figure 7.4. Obviously, there is no gel formation! Note that the 1D chain length distribution is a not very broad and uni-modal distribution (Yaghini and Iedema, 2014b). The 2D solution has been obtained using a fairly coarse grid of maximum chain length $3 \times 10^5$ and maximum branch points 500; number of chain length intervals 15; number of chain length nodes 8; number of branching intervals 14; number of branching nodes 3. This gives rise to a size of matrix $A$ equal to $10,080 \times 10,080$. The preparation of the convolution matrices and vectors as described in the previous section for a problem of this size takes around one minute CPU-time. The whole dynamic simulation is completed in around 30 minutes of CPU-time.

A check of the overall chain length distribution obtained from the 2D solution showed perfect agreement with the 1D multiradical model (Yaghini and Iedema, 2014b) and with Monte Carlo simulations. Figure 7.4 shows that for the 2D solution there is a good agreement with the Monte Carlo simulations, especially for smaller chains. At the higher chain lengths and number of branch points, there is a larger discrepancy. This is completely attributable to the coarse grid used in the 2D model. Increasing grid resolution ultimately leads to the sharp distribution shapes for constant chain length and number of branch points. The shapes of the distributions in branch points dimension very closely resemble binomial distributions, for the case with combination termination.

Recombination, no scission, $k_{tp}/k_p = 0.0003$, $k_q/k_p = k_{cq}/k_p = 1000$

![Figure 7.4. 2-dimensional chain length/branching distribution from combinations moments pseudo-distribution model for weak branching ($k_d/k_p = 0.0003$), equal combination and disproportionation, $k_c/k_p = k_{cd}/k_p = 1000$, without scission. Further kinetic data: standard from Table 7.2. Numerical parameters: chain length range: $1 - 3 \times 10^5$; branching range: $0 - 500$; number of chain length intervals: 15; number of chain length nodes: 8; number of branching intervals: 14; number of branching nodes: 3. Size of matrix $A$: $10,080 \times 10,080$. Dots from Monte Carlo simulation, $\rho = 0.000251$; $P_b = 0.17$; $P_c = 0.415$; $n_p = 677$; sample size: 500,000. No gel formation. Good agreement between deterministic 2D model and MC simulations.](image)

A case of strong gel formation has been studied assuming strong branching: $k_{tp}/k_p = 0.002$, at the same level of combination termination as before. The same numerical parameters determining the grid resolution have been applied. Also CPU- and storage requirements were similar as in the case without gelation. Note, interestingly, the Monte Carlo simulations took much more time in the gelation case. This is due to the fact that the individual molecules that turn out to be part of the gel first have to be very large in order to make decision about if they...
belong to gel. Both the Monte Carlo simulation and the 2D model reveal a gel fraction of 0.44. The overall chain length distribution obtained from the 2D solution is in perfect agreement with the 1D solution of the multiradical model and with Monte Carlo results. The full 2D solution is shown in Figure 7.5. Good agreement is again observed. The same remarks concerning the limited accuracy of the solution shown due to the fairly coarse grid as made before for the no-gel case do apply here as well.

It is concluded that the 2D model with the elaborated convolution procedure as explained previously works well and within reasonable CPU-time and storage requirements.

Figure 7.5. 2-dimensional chain length/branching distribution from combinations moments pseudo-distribution model for weak branching \( (k_b/k_p = 0.0003) \), equal combination and disproportionation, \( k_c/k_p = k_d/k_p = 1000 \), without scission. Further kinetic data: standard from Table 7.2. Numerical parameters: chain length range: \( 1 \times 10^5 \); branching range: \( 0 \sim 500 \); number of chain length intervals: 15; number of chain length nodes: 8; number of branching intervals: 14; number of branching nodes: 3. Size of matrix \( A \): \( 10 \, 080 \times 10 \, 080 \). Dots from Monte Carlo simulation, \( \rho_b = 0.00168; P_b = 0.578; P_c = 0.211; \pi_{pp} = 345 \); sample size: 70,000. Strong gel formation: 44%. Good agreement between deterministic 2D model and MC simulations.

### 7.4.2 2D model with combination points pseudo-distribution approach

The case without gel formation that was discussed in section 7.4.1 has been used to demonstrate the combination points pseudo-distribution approach. Simulations have been performed for the non-gelling conditions as in Section 7.4.1 with weak branching and strong combination. The full 2D distribution \( P_{n,i} \), shown in Figure 7.4, has already been discussed.

The availability of solutions of the first and second combination points moments, \( \Psi_{n,i}^{(1)}, \Phi_{n,i}^{(1)}, \Psi_{n,i}^{(2)}, \Phi_{n,i}^{(2)} \) at each combination of chain length \( n \) and number of branch points \( i \) allows for computing various combination point related properties. Figure 7.6 shows the combination point density versus chain length, calculated from the first moment, \( \Psi_{n,i}^{(1)} \), and averaged over all numbers of branch points. The lowest plot shows the ratio of numbers of combination points to numbers of branch points as a function of chain length. From this plot one may conclude that the largest molecules are so large because of being strongly branched rather than having undergone combination.
The full 3-dimensional distribution of chain length, number of branch points and number of combination points of dead chain may be reconstructed from the moments \( P_n, \Psi^\alpha_n, \Psi^\beta_n \) assuming a certain shape for the combination points distribution at given \( n \) and \( i \). To do this a 3-parameter distribution has been taken (Iedema and Hoefsloot, 2005). In Chapter 2 we have seen that the branching distribution for constant chain length practically coincides to a binomial distribution around the average number of branch points at that chain length. It is expected that this also would hold for the combination points distribution. However, since the task is to reconstruct this distribution at certain fixed values of both chain length and number of branch points, there are two options possible to perform it. The first is to take the probability of a monomer unit of being a combination point, \( \rho_c \), on a chain of given length, \( n \), and apply the binomial distribution with these parameters: \( p_B(n, \rho_c(n)) \). Note that \( \rho_c(n) \) is shown as the 3rd plot in Figure 7.6. The second option is based on the consideration that a molecule with \( i \) branch points consists of \( i-1 \) linear chains that each has either been created by disproportionation or by combination. The average probability of a linear chain of carrying a combination point as a function of \( i, \rho_c(i) \), is directly linked to the ratio of combination and branch points inferred from the branching and combination point density as a function of \( n \), as shown in the bottom plot of Figure 7.6. The corresponding binomial distribution then would possess parameters: \( p_B(i-1, \rho_c(i)) \). The latter option seems to be the most correct, since the theoretical maximum number of combination points in this case correctly equals \( i-1 \), whereas in the first option it might exceed \( i-1 \). Thus, one might expect the distribution in the latter case to be narrower, which indeed turns out to be the case from a comparison of the two options for chain length \( n = 123,650 \).

Choosing a binomial distribution, \( p_B(i-1, \rho_c(i)) \), based on the number of linear chain segments in the molecule, \( i-1 \), is not necessarily the best possible approximation of the true distribution, since it would use only two out of the three available combination points moments. In fact, a 3-parameter distribution based on the binomial distribution is required. Therefore, a method based on Krawtchouk polynomials is adopted, similar to Iedema and Hoefsloot (2005). The approximated distribution, \( p \), is constructed as the product of the binomial distribution, \( p_B \), and a linear combination of these (orthogonal) polynomials of order \( N \):

\[
p = p_B \left( 1 + \sum_{N=2}^{N} k_N L_N \right) \tag{7.21}
\]

A general expression for these polynomials is:

\[
L_N^{(\nu)}(k,i) = \sum_{\nu=0}^{N} (-1)^{N-\nu} \binom{i-1-k}{N-\nu} \binom{k}{\nu} \rho^{N-\nu}(1-\rho)^\nu \tag{7.22}
\]

where \( N \) is the order of the polynomial, \( k \) is the number of combination points, \( i-1 \) is the maximum of \( k \) and \( \rho \) is the combination point density. The first three Krawtchouk polynomials are:
\[ L_0^{(r)}(k,i) = 1 \]
\[ L_1^{(r)}(k,i) = -(i-1)\rho + k \]
\[ L_2^{(r)}(k,i) = \frac{1}{2} \left[ (i-1)^2 \rho^2 + k(2\rho + k - 1) - (i-1)\rho(\rho + 2k) \right] \] (7.23)

In view of the fact that we need just one extra parameter, the highest order of the required polynomials is \( N = 2 \). Thus, the approximation in Equation 7.21 only employs the second order polynomial, \( L_2^{(r)}(k,i) \). The coefficient \( k^2 \) in fact represents the extra parameter sought after. It is obtained from the second combination points moment \( \Psi_{n,i}^{r^2} \) from the definition of this moment in terms of the approximation:

\[ \Psi_{n,i}^{r^2} = \sum_{k=0}^{\infty} p_B(n,i,k) \left( 1 + k_2 L_2 \right) k^2 \] (7.24)

Note that \( p_B(n,i,k) \) represents the binomial distribution for the given chain length, \( n \), and number of branch points, \( i \), using the combination points density \( \rho_c(n,i) \) as defined above. Thus, the approximation becomes:

\[ P(n,i,k) = p_B(n,i,k) \left\{ 1 + k_2(n,i)L_2(n,i,k) \right\} \] (7.25)

Figure 7.7 shows, for a chain length of \( n = 123650 \), the 2D branch points/combination points distribution obtained from Equation 7.25. It was observed that the value of the 3rd parameter, \( k^2 \), was so low that the distribution \( P(i,k) \) in \( k \)-dimension was hardly distinguishable from a binomial distribution. However, due to the relatively coarse grid that has been applied (15 chain length, 14 branching intervals) the distribution in branching direction was fairly broad, having a polydispersity of 1.032. The true distribution is expected to be, again, very close to a binomial distribution, with polydispersity of 1.0088. In principle, by tracking the occurrence of combination points in Monte Carlo simulations, it should be possible to construct a 2D distribution like the one in Figure 7.7. However, a proper comparison would require excessively large populations of Monte Carlo molecules to suppress the scattering of such data.
Figure 7.6. Branching and combination point density versus chain length as extracted from combinations moments pseudo-distribution model for weak branching, equal combination and disproportionation, without scission, same kinetic and numerical conditions as Figure 7.4. The lowest plot shows that largest molecules are so large because of being strongly branched rather than having undergone combination.

Figure 7.7. 2D distribution of branching and combination points at chain length 123 650 as extracted from combinations moments pseudo-distribution model for weak branching, equal combination and disproportionation, without scission, same kinetic and numerical conditions as Figure 7.4.

7.5 Conclusions

The problem of finding the 3-dimensional distribution of chain length, branch points and combination points for conditions of ldPE polymerization has been addressed. The full 3D formulation has been reduced to 2D by using the pseudo-distribution approach for the combination points dimension, up to two higher combination points moments. The 2D population balance equations have been implemented using a Galerkin scheme that proved to be successful in a 2D model, where combination termination was not yet accounted for.
The implementation of the combination mechanism was the most difficult task. This is partly due to the fact that termination causes a non-linearity in the system that could be previously reduced to a linear set of equations. This could be solved, as in the 1D case, by using a dynamic simulation scheme and updating the combination termination term. However, the main difficulty turned to arise from the convolution problem, since especially in 2D an extremely large number of multiplication operations have to be performed. An algorithm to deal with the 2D convolution has been designed based on the principles of a 1D convolution scheme as described in Chapter 2. To avoid excessive computer memory usage, the algorithm does not store the Chebyshev polynomial term products of the multiplications, but rather performs the multiplications in each time step using a smaller set of elements. This way memory usage could be drastically reduced.

The pseudo-distribution model has been tested using ldPE-like kinetic data and the results were compared to Monte Carlo simulations. As the mix of transfer to polymer and combination termination is known to possibly lead to gel formation, the model was also tested in the gel regime. A similar approach to account for gelation has been used as for the 1D model (Chapter 3). It turned out, for an acceptable grid resolution of 15 chain length intervals of 8 nodes and 14 branching intervals of 3 nodes, good agreement could be obtained with Monte Carlo simulations. The gel content was correctly predicted and the 2D distributions of chain length and branching were well in line. Finally, it is demonstrated that a full 3-dimensional distribution of chain length/branch points and combination points could be generated from the solution in terms of pseudo-distributions. The combination points distribution was calculated from the moments using a two-parameter standard distribution. The results prove that the implementation of this considerable multidimensional population model in the Galerkin scheme was successful. The critical factor was the convolution operation, but this turned out to perform satisfactorily. The results shown were obtained in a reasonable time: 30 CPU-minutes.
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Appendix

A.1 Derivation of further probability density functions

In order to determine whether the last chemical event has occurred in a dead molecule before leaving the reactor was a termination by combination or another termination step, the reaction rates of both termination possibilities have to be known. According to the reaction mechanisms in Table 5.1 from the main text, living chains may terminate by disproportionation/combination or by transfer to polymer. The reaction rate of combination termination for molecules of dimensions \( n, n_p \) and \( n_c \) is given by the following sum:

\[
\begin{align*}
    r_c(n, n_p, n_c) &= k_c \sum_{n_1=1}^{n} \sum_{n_{p1}=1}^{n_p} \sum_{n_{c1}=1}^{n_c} R(n_1, n_{p1}, n_{c1}) R(n_2, n_{p2}, n_{c2}); \\
    n_2 &= n - n_1 \\
    n_{p2} &= n_p - n_{p1} \\
    n_{c2} &= n_c - n_{c1}
\end{align*}
\]  
\[\text{(A.1.1)}\]

Here, \( R \) is the 3-dimensional distribution of length, number of primary polymers and number of combination parts of living molecules as calculated from the population balance solution in Chapter 5. The total rate of reaction for termination by disproportionation and transfer to polymer for molecules of the same dimensions follows as:

\[
\begin{align*}
    r_{dl}(n, n_p, n_c) &= (k_d \lambda_n + k_p \mu_1) R(n, n_p, n_c)
\end{align*}
\]  
\[\text{(A.1.2)}\]

The probability that a dead molecule of these dimensions is created by combination follows from the ratio between these two rates:

\[
\begin{align*}
    \mathcal{R}_c(n, n_p, n_c) &= \frac{1}{1 + \frac{r_c(n, n_p, n_c)}{r_{dl}(n, n_p, n_c)}}
\end{align*}
\]  
\[\text{(A.1.3)}\]

Next follows the derivation of the probability density function describing the characteristics of the pairs of molecular parts involved in a combination step. The probability density function describing the probability that a dead molecule of dimensions \( n, n_p, n_c \) is the product of the reaction between two living molecules, of which one has \( n_i \) combination parts (and the other \( n_i - n_{i1} \)) is given by:

\[
\begin{align*}
    \mathcal{R}(n_{i1} | n, n_p, n_c) &= \frac{\sum_{n_1=1}^{n} \sum_{n_{p1}=1}^{n_p} \sum_{n_{c1}=1}^{n_c} R(n_{i1}, n_{p1}, n_{c1}) R(n_{i2}, n_{p2}, n_{c2})}{\sum_{n_1=1}^{n} \sum_{n_{p1}=1}^{n_p} \sum_{n_{c1}=1}^{n_c} R(n_{i1}, n_{p1}, n_{c1}) R(n_{i2}, n_{p2}, n_{c2}); \\
    n_2 &= n - n_1 \\
    n_{p2} &= n_p - n_{p1} \\
    n_{c2} &= n_c - n_{c1}
\end{align*}
\]  
\[\text{(A.1.4)}\]

The following probability density function defines the probability that given \( n \) and \( n_p \) of the complete molecule and \( n_{i1} \) and \( n_{i2} \) of the parts the number of primary polymers of part 1 equals \( n_{i1} \) (and the complementary number \( n_{p2} = n_p - n_{p1} \) on part 2):
The segment connectivity matrix \( B \) is derived from the adjacency matrix \( A \) based on both branch points and end points of free dangling segments as the vertices; if the number of branch points is \( N \), then the number of vertices for a 3-functional branched molecule is \( 2N+2 \). The algorithm consists of the following steps:

1. Take the lower triangular part of \( A \) and assign segment order numbers from 1 to \( 2N+1 \) to the non-zero elements of it.
2. Take the upper triangular part of \( A \) and assign segment order numbers from \( 2N+2 \) to \( 2(2N+1) \), to the non-zero elements of it.
3. Assemble the matrix parts from 1 and 2 to one matrix, \( B' \), of size \( 2N+2 \times 2N+2 \).
4. Construct 2 segment order vectors \( v_1 = 1 : 2(2N+1) \), and a ‘mirrored’ one:
   \[
v_2 = [2N+2 : 2(2N+1) 1 : 2N+1].
   \]
5. Sweep through the rows \( r \) of \( B' \) to find the non-zero segment numbers, \( k_i : k_j \).
6. For each segment number, \( k_i \), identify the other (connected) segment numbers \( (c) \) in the same row \( r \) of \( B' \); \( c = k_i : k_j \).
7. Start constructing \( B \) by assigning values -1 on row positions \( v_1(r) \) and column positions \( v_2(c) \), \( r \) and \( c \) as obtained in 5 and 6.
8. Complete \( B \) by assigning the value 1 to all the diagonal positions.
A.3 2D RHS equations

If the procedure leading to Equation 6.27 of the main text is applied in a similar manner but for the 1st chain length order (starting from Equation 6.26, main text) instead of the 0th, but still doing the multiplication by the 0th order chain length Chebyshev terms, $T'_0(s'_i)$, it would result to:

\[
\begin{align*}
\sum_{i=0}^{l} f_i(T'_0(s'_i)) T'_0(s'_i) \frac{A_{i0} a_{i0} + \cdots + \{A_{i1} a_{i1} + \cdots + \{A_{in} a_{in}\}}{A_{i0}} \\
\left(\frac{\sum_{i=0}^{l} f_i(T'_0(s'_i)) T'_0(s'_i) \frac{A_{i0} a_{i0} + \cdots + \{A_{i1} a_{i1} + \cdots + \{A_{in} a_{in}\}}{A_{i0}}}{A_{i0}}\right)
\end{align*}
\]  

(A.3.1)

Applying the procedure to the highest chain length order ($r$), still multiplied with $T'_0(s'_i)$ yields:

\[
\begin{align*}
\sum_{i=0}^{l} f_i(T'_0(s'_i)) T'_0(s'_i) \frac{A_{i0} a_{i0} + \cdots + \{A_{i1} a_{i1} + \cdots + \{A_{in} a_{in}\}}{A_{i0}} \\
\left(\frac{\sum_{i=0}^{l} f_i(T'_0(s'_i)) T'_0(s'_i) \frac{A_{i0} a_{i0} + \cdots + \{A_{i1} a_{i1} + \cdots + \{A_{in} a_{in}\}}{A_{i0}}}{A_{i0}}\right)
\end{align*}
\]  

(A.3.2)

Multiplication by the 1st and higher order Chebyshev terms $T'_1(s'_i)$, respectively $T'_i(s'_i)$, followed by summation and assembly of all the terms with $a_{ik}$ in accolades leads to similar expressions as Equations A.3.1-A.3.2, with $T'_0(s'_i)$ replaced by $T'_1(s'_i)$, respectively $T'_i(s'_i)$ and different elements of $\mathbf{A}$. The result for multiplication with the highest order branching Chebyshev terms, $T'_r(s'_i)$ is given as:
\[
\frac{\sum_{i} f(P_{i}(s_{i}'))P_{i}(s_{i}')}A_{i0} + \frac{\ldots A_{i1} + \ldots}{A_{i0}}\]

\[
\frac{\sum_{i} f(P_{i}(s_{i}'))P_{i}(s_{i}')}A_{i1} + \frac{\ldots A_{i2} + \ldots}{A_{i1}}\]

\[
\ldots
\]

\[
\frac{\sum_{i} f(P_{i}(s_{i}'))P_{i}(s_{i}')}A_{i_{m-1}} + \frac{\ldots A_{im} + \ldots}{A_{im}}\]

\text{(A.3.3)}
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>1-Dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>2-Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>3-Dimensional</td>
</tr>
<tr>
<td>CDF</td>
<td>Cumulative Distribution Function</td>
</tr>
<tr>
<td>CLD</td>
<td>Chain Length Distribution</td>
</tr>
<tr>
<td>CLD/DBD/CPD</td>
<td>Chain Length Distribution/Degree of Branching Distribution/Combination Points Distribution</td>
</tr>
<tr>
<td>CMC</td>
<td>Conditional Monte Carlo</td>
</tr>
<tr>
<td>CSTR</td>
<td>Continuous Stirred Tank Reactor</td>
</tr>
<tr>
<td>CTA</td>
<td>Chain Transfer Agent</td>
</tr>
<tr>
<td>DBD</td>
<td>Degree of Branching Distribution</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>FLD</td>
<td>Fragment Length Distribution</td>
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<tr>
<td>GPS</td>
<td>Gel Permeation Chromatography</td>
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<tr>
<td>ldPE</td>
<td>low-density Polyethylene</td>
</tr>
<tr>
<td>LHS</td>
<td>Left-Hand Side</td>
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<tr>
<td>MC</td>
<td>Monte Carlo</td>
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<tr>
<td>MWD</td>
<td>Molecular Weight Distribution</td>
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<tr>
<td>PBEs</td>
<td>Population Balance Equations</td>
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<tr>
<td>PDF</td>
<td>Probability Density Function</td>
</tr>
<tr>
<td>RAFT</td>
<td>Reversible Addition-Fragmentation chain Transfer</td>
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<tr>
<td>RHS</td>
<td>Right-Hand Side</td>
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<tr>
<td>SEC_MALLS</td>
<td>Size Exclusion Chromatography-Multi Scale Laser Light Scattering</td>
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Summary

"Towards the architectures of macromolecules, modeling of multi-dimensional polymer chain distributions"

Control of end use properties of branched polymers such as low-density Polyethylene (ldPE) produced at industrial scale is difficult at the molecular level since experimental techniques fail to detect the most decisive microstructural properties. Therefore, mathematical models are important in predicting the interesting microstructural properties of polymers. Besides chain length, properties such as number of branch points, number of combination points, number of radical sites, number of terminal double bonds, etc., also provide valuable microstructural information, and hence are of great interest for industrial applications. Thus, the main goal of this thesis was to provide reliable multi-dimensional models of ldPE accounting for chain length, degree of branching and combination points as dimensions. Obviously, to obtain reliable models of polymerization mechanisms and to interpret results appropriately, the outcomes of all model assumptions are followed closely. Key assumptions are related to the random scission reaction (breaking can take place in any random position of the chain), being modeled as linear or ‘topological’ scission, and to allowing/disallowing gelation.

An extensive explanation of the decisive reactions, modeling assumptions and the potential modeling schemes is given in Chapter 1. All the provided models in this thesis are more or less resembling the free radical polymerization condition of ldPE, while the implementations of the models have been done in MATLAB®. In Chapter 2, the developed population balance model forms a sound basis for further investigations of molecular weight and degree of branching distribution of ldPE. The 1-dimensional chain length-model, accounts for degree of branching by branching moments or pseudo distributions of branch points. The common free radical polymerization reactions including chain scission have been considered in the model. The scission reaction is modeled by either the linear or the topological scission model. The latter takes (in comparison to linear chains) the varying scission length distributions into account by applying an empirical Monte Carlo based function of fragment lengths resulting from random scission of branched topologies. Regarding the numerical treatment of the distributions, the Galerkin-finite element method has been applied, which is based on the same principles as PREDICI®. The fundamental numerical problem arising from topological scission has been solved by developing a special method to deal with grid refinement problems. Thus, the model provides more accurate results, allowing a precise comparison to earlier results of Molecular Weight Distribution (MWD) by Size Exclusion Chromatography- Multi Angle Laser Light Scattering (SEC-MALLS) data, and to Monte Carlo simulations.

In Chapter 3, the model from Chapter 2 has been developed further to investigate the effect of multiradicals (multiple radical sites on a chain) and gelation on the molecular weight distribution of ldPE. The number of radical sites dimension is treated by pseudo-distributions. The model shows that in the absence of combination, gel does not form, but that accounting for multiradicals leads to a better prediction of the long molecular weight distribution tail. Results of the multiradical model with topological scission are well in line with Monte Carlo simulations, which implicitly but properly accounts for multiradicals. For the case of combination without scission, the multiradical model gave a perfect agreement
with Monte Carlo simulations as regards prediction of the gel fraction and chain length distribution of sol molecules. The classical monoradical (maximum of one radical site per chain) model failed to describe the gel regime. A remarkable outcome of this model is that the classic model under the conditions of strong branching and combination termination gives rise to extremely broad and bimodal distributions, which according to the multiradical model is an absolute artifact, although mathematically correct. This effect is entirely due to the assumptions stating that gel is absent and transfer to polymer is exclusively occurring to dead chains. The multiradical model does not have to apply these erroneous assumptions. A non-gel assuming variant of this model allowed us to properly detect the gelpoint and the associated distribution. The scission model adopted, linear or topological scission, was also of extreme importance for the gel regime prediction. Regarding the performance of the proposed models, we could conclude that for full random scission the (deterministic) multiradical model assuming topological scission was the closest to the exact solution from Monte Carlo simulations.

In Chapter 4, we provide a model of the molecular weight distribution under circumstances of ldPE for a tubular reactor with realistic non-isothermal (industrial) conditions and for a series of Continuous Stirred TankReactors (CSTRs). The existence of multiradicals and the occurrence of gelation were allowed. The presented deterministic model is based on the Galerkin method and employed the moments of the radical sites distribution using pseudo distributions to model the second dimension next to the chain length for several CSTRs in series and a batch reactor. For reference, Monte Carlo simulations have been carried out for the same reactor configurations. Assuming topological scission to account for the highly branched characteristic of the system, good agreement was found between the multiradical model and Monte Carlo simulations. As conditions of ldPE polymerization lead to broad molecular weight distributions being close to gel point, allowing for gel turned out to be crucial. Not allowing for gel resulted into extremely broad bimodal distributions, which with the present set of models were identified as an artifact. The experimentally observed bimodal distribution was indeed obtained for a single tank reactor, but the bimodality decreased as the number of the reactors in series increased and it finally disappeared in batch reactor. The resulting distributions from deterministic models always showed perfect agreement with Monte Carlo simulations for the case of no scission and satisfactory agreement for mild scission.

A set of models to calculate the contraction factor of the radius of gyration (compactness), which to maximum extent account for the kinetics of a radical polymerization closely resembling ldPE, is presented in Chapter 5. The models provide an alternative to the Zimm and Stockmayer's (1949) analytical expression of contraction factor for molecules with terminal branching. The new models take more realistic kinetics-branching due to chain transfer to polymer and termination by combination reactions-into account and are based on the results of a 3-dimensional population balance model of chain length, number of branch points and number of combination points. The results, being representative for branched molecules such as ldPE, show significantly stronger contraction than those predicted by the model of Zimm and Stockmayer. In the case of termination by disproportionation only, the calculated molecular sizes were smaller by a factor of almost two. It was shown that the interpretation of contraction factor as measured by SEC-MALLS to find the branchedness of ldPE leads to a considerably lower estimate of branching with the new model than by using the standard Zimm and Stockmayer model.

A full 2-dimensional model of ldPE chain length/branching distribution is provided in Chapter
6. This chapter is limited to model the linear problem of termination by disproportionation only, without recombination. Full 2-dimensional population balance equations were solved by the Galerkin method to obtain the distributions, accounting for 2-dimensional topological scission. It was concluded that besides the fragment length distribution as discussed before, explicit assumptions have to be made concerning the redistribution of the branch points on scission fragments. In earlier studies with pseudo distribution models, it was observed that the hypergeometric function is the best model for estimating the branching on scission fragments, since it allows for allocating the branch points on fragments in proportion to the fragment lengths. However, employing the hypergeometric function to this end is not a straightforward task with the presented solution strategy in the Galerkin scheme, since it leads to an even more serious grid refinement problem than implementing the fragment length distribution (Chapter 2). Thus, the full 2-dimensional model was based on the simpler assumption of branching redistribution, where the number of branch points on the fragment is independent of fragment length. The results of the 2-dimensional model without scission are in line with the results of 1-dimensional models that are addressed in the previous chapters, under conditions where the effect of multiradicals may assumed to be negligible.

The provided 2-dimensional distributions are also in perfect agreement with Monte Carlo simulations, if the resolution of the grid nodes on chain length dimension is high enough. It is remarkable that the required resolution of grid points in chain length dimension turned out to be higher in the 2-dimensional model in comparison to the 1-dimensional models. In the results with scission, the effect of applying the simplifying assumption of redistributing branch points on scission fragments is visible in the plot of branching distribution, which shows a maximum. It differs to the results of pseudo-distribution models with hypergeometric distribution and Monte Carlo simulation showing constant values for higher chain lengths. In the case of linear scission the bimodal MWD was exactly reproduced by the 2-dimensional model, but in the case of topological scission, disagreements with MWD from 1-dimensional models have been observed when a parameter-free variant was applied for fragment length distribution.

The focus of Chapter 7 was especially on the role of combination termination in the context of 2- and 3-dimensional population balance models, implying that a mathematically non-linear problem had to be addressed in those modeling schemes. Termination by combination is assumed to be present in most ldPE-modeling studies. Full 3-dimensional population balance equations were solved by the 2-dimensional Galerkin implementation presented in Chapter 6 to estimate trivariate chain length/branching/number of combination points distribution. Accordingly, the third dimension- the combination points- was treated using the pseudo-distributions framework. In the case without scission, good agreements with Monte Carlo simulations as well as with results from lower-dimensional models were observed with sufficiently enough grid resolution. In the case with scission, some deviations were seen as in Chapter 6 due to the way of implementing number of branch points redistribution on scission fragments.
Samenvatting

"Op weg naar macromoleculaire architecturen, modelleren van multidimensionale verdelingen van polymeerketens"

De beheersing van de kwaliteit van vertakte polymeren zoals lage-dichtheid Polyethyleen (ldPE) wordt bemoeilijkt door het ontbreken van experimentele technieken om de essentiële micro-structurele eigenschappen te meten. Dat maakt wiskundige modellen belangrijk, die deze eigenschappen kunnen voorspellen. De micro-structurele eigenschappen van belang voor industriële toepassingen zijn naast de ketenlengte van het polymeer, het aantal vertakkingspunten, verbindingspunten tussen lineaire ketenfragmenten, radicaalposities en (eindstandige) dubbele bindingen. Derhalve was het voornaamste doel van dit proefschrift om betrouwbare multidimensionele modellen voor ldPE te ontwikkelen, vooral voor de verdelingen van ketenlengte, vertakkingspunten en verbindingspunten als de dimensies.

Uiteraard is met het oog op betrouwbaarheid van de modellen en de juiste interpretatie van de uitkomsten ervan het effect van de aannames nauwkeurig nagegaan. Belangrijke aannames betreffen de wijze waarop random ketenbreuk (breuk op willekeurige posities in de polymeerketens) gemodelleerd wordt, lineair (zoals gebruikelijk in de literatuur) of ‘topologisch’, en of al dan niet ‘gel’ gevormd kan worden.

Een uitvoerige beschrijving van de relevante reacties, de model-aannames en de mogelijke uitvoeringsvormen van de modellen is te vinden in Hoofdstuk 1. Alle modellen betreffen meer of minder complete beschrijvingen van radicaal-polymerisatie van ldPE, terwijl in alle gevallen de modellen geïmplementeerd zijn in MATLAB®. In Hoofdstuk 2 wordt de basis gelegd voor het populatiebalansmodel voor ketenlengte en vertakkingspunten van ldPE, dat het vertrekpunt vormt voor de verdere ontwikkelingen. Dit één-dimensionale ketenlengte-model verdisconteert de verdeling van vertakkingspunten door middel van de momenten van deze verdeling, ofwel ‘pseudo-verdelingen’ van vertakkingspunten. Alle gebruikelijke vrije radicaal-polymerisatie reacties zijn in het model opgenomen, inclusief random ketenbreuk. De ketenbreuk-reactie is gemodelleerd met zowel het lineaire als het niet-lineaire ketenbreuk-model, ofwel ‘topologische ketenbreuk’. Bij de laatste is rekening gehouden met de afwijkende (ten opzichte van lineaire ketens) verdeling van breukfragmentlengtes ten gevolge van de vertakkingen door middel van een empirische vergelijking van de fragmentlengte-verdeling, gebaseerd op Monte Carlo simulaties van random ketenbreuk van vertakte polymeerketens. Om de verdelingen te beschrijven is gebruik gemaakt van een Galerkin eindige elementenmethode, gebaseerd op dezelfde principes als het commerciële pakket PREDICI®. Een speciale methode is ontwikkeld om het numerieke probleem op te lossen, dat veroorzaakt wordt door topologische ketenbreuk, door een fijnmaziger resolutie van de elementen toe te passen, dan die vereist voor de andere reacties. Zo wordt een nauwkeurige vergelijking mogelijk met eerdere resultaten, met experimentele (SEC-MALLS) metingen van de molecuulgewichtsverdeling (MWD) en met resultaten van Monte Carlo simulaties.

In Hoofdstuk 3 wordt het in Hoofdstuk 2 ontwikkelde model uitgebreid om het effect van multiradicalen (meerdere radicaalposities op één keten) en formatie van gel op de ketenlengte-verdeling van ldPE na te gaan. De dimensie van het radicalen-aantal wordt behandeld met behulp van het pseudo-distributie concept. Het model toont aan, dat in afwezigheid van terminatie door recombinatie van macro-radicalen geen gel gevormd wordt,
maar dat multiradicalen een belangrijke rol spelen en dat door daarmee rekening te houden de lange ‘staart’ van de ketenlengteverdeling beter voorspeld wordt. Dat laatste blijkt uit een perfecte overeenkomst met resultaten van Monte Carlo simulaties, die impliciet, maar correct rekening houden met multiradicalen. In het geval van terminatie door recombinatie wordt inderdaad gel gevormd, wat door het multiradicaal-model correct voorspeld wordt, weer in perfecte overeenstemming met Monte Carlo simulaties, zowel wat betreft de voorspelde gelfractie als de bijbehorende ketenlengteverdeling van de sol-moleculen. Dit terwijl het klassieke monoradicaal-model (maximaal één radicaal-positie per keten) niet in staat is het gedrag in het gel-regime correct te beschrijven. Een frappante uitkomst is, dat het klassieke model onder condities van sterke vertakking en recombinatie-terminatie extreem brede en bimodale verdelingen voorspelt, die mathematisch correct zijn, terwijl die volgens het multiradicaal-model een compleet artefact blijken te zijn. Deze zijn namelijk volledig te wijten aan de aanname van de afwezigheid van gel in combinatie met de veronderstelling dat de vertakkingsreactie uitsluitend plaatsvindt aan dode ketens. Het multiradicaal-model hoeft van deze niet algemeen-geldige aannames geen gebruik te maken. Een variant van het model, dat geen aanwezigheid van gel veronderstelt, bleek wel in staat het gel-punt en de bijbehorende verdeling correct te voorspellen. Tevens kwam naar voren, dat het gebruikte ketenbreuk-model, lineair of topologisch, van cruciaal belang is voor de voorspelling van het gel-regime. Met betrekking tot de prestaties van de onttwikkelde model-varianten kon de conclusie getrokken worden, dat het (deterministische) multiradicaal-model de beste benadering geeft van de exacte oplossing gegenereerd door de Monte Carlo simulaties.

In Hoofdstuk 4 wordt een model gepresenteerd voor de moleculegewichtsverdeling van ldPE geproduceerd in een buisreactor onder representatieve, industriële condities qua temperatuurprofiel over de buis en in een serie van ideaal-gemengde reactoren (CSTRs). Daarbij werd rekening gehouden met multiradicalen en de mogelijkheid van het ontstaan van gel. Het deterministische model is weer gebaseerd op de Galerkin-methode en de radicalen worden verdisconteerd met behulp van pseudo-distributies, evenals bij de enkele CSTR. Ter vergelijking zijn Monte Carlo simulaties uitgevoerd voor exact dezelfde reactor-configuraties. Ook hier werd goede overeenkomst gevonden, indien het topologische ketenbreuk-model werd toegepast. Wanneer de condities van de ldPE-polymerisaties in de bestudeerde reactor-configuraties tot brede MWDs leiden, dan bleek het belangrijk rekening te houden met gelformatie. Evenals bij de enkele CSTR blijken extreem brede MWDs verkregen uit het klassieke model een artefact. De typische brede, bimodale verdeling, die in de praktijk voor ldPE uit een autoclaaf-reactor met SEC-MALLS gemeten is en die door de modellen gereproduceerd wordt voor een enkele CSTR (lineaire ketenbreuk), blijkt langzamerhand te verdwijnen naarmate het aantal CSTRs in serie groter wordt, onder gelijke kinetische condities, terwijl de MWD het smalst is voor een buisreactor. In vergelijking met Monte Carlo simulaties werd perfecte gelijkenis gevonden voor het multiradicaal-model in afwezigheid van ketenbreuk en acceptabele overeenkomst ingeval van milde ketenbreuk. Een set van verschillende modellen om de contractie van de gyratiestraal van (compactere) vertakte polymeer-moleculen ten opzichte van lineaire moleculen te berekenen wordt gepresenteerd in Hoofdstuk 5. Deze modellen vormen een alternatief voor de analytische uitdrukking van Zimm en Stockmayer (1949), die blijkt alleen geldig te zijn voor eindstandige vertakkingen. In de nieuwe modellen wordt rekening gehouden met meer realistische kinetiek – vertakkingen ten gevolge van een ketenoverdrachtsreactie naar polymeer en recombinatie-terminatie – en is gebaseerd op de uitkomsten van een populatiebalansmodel, dat de 3-dimensionale verdeling van ketenlengte, vertakkingspunten
en verbindingspunten beschrijft. De resultaten, die representatief zijn voor vertakt polymeer als ldPE, laat een aanzienlijke sterkere contractie zien dan het model van Zimm en Stockmayer. In het geval van terminatie door uitsluitend disproportionering bleken de moleculen een factor twee kleiner te zijn. Aangetoond wordt, dat de interpretatie van contractie-factoren gemeten met behulp van SEC-MALLS voor vertakt polymeer als ldPE met de nieuwe modellen tot veel lagere schattingen van de vertakkingsgraad leidt dan de veelgebruikte methode van Zimm en Stockmayer.

Een compleet 2-dimensionaal model van de verdelingen ketenlengte en vertakkingsgraad voor ldPE wordt gepresenteerd in Hoofdstuk 6. Dit Hoofdstuk beperkt zich tot het lineaire probleem van terminatie door uitsluitend disproportionering. De gehele set 2-dimensionale populatiebalans-vergelijkingen wordt opgelost met de Galerkin-methode, waarbij een eveneens 2-dimensionaal model voor topologische ketenbreuk gehanteerd wordt. Aangetoond wordt, dat – naast de eerder gesignaleerde noodzaak om de fragmentlengte-verdeling te verdisconteren - de herverdeling van vertakkingspunten over ketenbreuk-fragmenten expliciet mee gemodelleerd moet worden. In eerdere studies gebaseerd op de pseudo-distributie methode was reeds opgemerkt, dat de hypergeometrische verdeling daartoe het meest geschikt is, omdat deze op correcte wijze het aantal vertakkingspunten evenredig laat zijn aan de lengte van de ketenfragmenten. De implementatie van een herverdeling gebaseerd op een hypergeometrische verdeling in het Galerkin-schema roept echter een nog sterker resolutie-probleem op, dan de fragmentlengteverdeling, waarvoor de oplossing in Hoofdstuk 2 beschreven wordt. Derhalve is gekozen voor een meer eenvoudig te implementeren herverdeling, namelijk dat het aantal vertakkingspunten onafhankelijk is van de fragment-lengte. De resultaten van het 2-dimensionale model zonder ketenbreuk zijn in overeenstemming met die van de 1-dimensionale modellen beschreven in de eerdere Hoofdstukken, voor zover daar geen rekening gehouden is met multiradicalen. De gegenereerde 2-dimensionele verdelingen zijn in perfecte overeenstemming met Monte Carlo simulaties, mits de resolutie van de roosterpunten in zowel ketenlengte- als vertakkingsgraadrichting voldoende hoog gekozen wordt. Opmerkelijk is, dat de resolutie in ketenlengte groter dient te zijn dan in het 1-dimensionale model. In de resultaten met ketenbreuk is het effect van de simplificatie van de herverdeling van vertakkingspunten zichtbaar op het verloop van de vertakkings-dichtheid, die een maximum vertoont. Dit wijkt af van resultaten uit het pseudo-distributie model met hypergeometrische verdeling en uit Monte Carlo-simulaties, die een constante waarde laten zien bij hogere ketenlengte. In het geval van lineaire ketenbreuk wordt de bimodale MWD door het 2-dimensionale exact gereproduceerd, maar in het geval van topologische ketenbreuk worden verschillen gezien met de MWD uit 1-dimensionale modellen, indien een parametervrije variant van de fragmentlengte-verdeling toegepast wordt.

De focus van Hoofdstuk 7 ligt op recombinatie-terminatie in 2- en 3-dimensionale populatiebalansmodellen, waarmee mathematisch gezien een niet-lineariteit geïntroduceerd wordt. In de meeste ldPE-modellen wordt dit mechanisme als relevant beschouwd. De complete set 3-dimensionale populatiebalansvergelijkingen in termen van ketenlengte, vertakkingsgraad en verbindingspunten, wordt opgelost met behulp van de in Hoofdstuk 6 geïntroduceerde 2-dimensionale Galerkin-implementatie. Daarbij wordt de derde dimensie, de verbindingspunten, behandeld met behulp van pseudo-distributies. Weer wordt ingeval van afwezigheid van ketenbreuk goede overeenkomst opgemerkt met lager-dimensionale modellen en met Monte Carlo simulaties, indien de resolutie voldoende hoog gekozen wordt. Ook de gelfractie wordt correct voorspeld. Wanneer ketenbreuk meegenomen wordt,
worden er afwijkingen gesignaleerd, evenals in Hoofdstuk 6 als gevolg van de wijze waarop de herverdeling van vertakkingspunten over fragmenten behandeld wordt.
Publications

N. Yaghini, P.D. Iedema  
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*New models of radical polymerization with branching and scission predicting molecular weight distribution in tubular and series of continuous stirred tank reactors allowing for multiradicals and gelation, accepted in Chemical Engineering Science*

N. Yaghini, P.D. Iedema  
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*Molecular weight/branching /combination points distribution modeling of low-density polyethylene in continuous stirred tank reactor, submitted to Chemical Engineering Science*

N. Yaghini, P.D. Iedema  
*Determination of low-density polyethylene molecular structure; a hybrid modeling scheme plus experiments, in preparation to be submitted to Polymer*
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