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>$I^* + M \rightarrow R_{n_i}^f$</td>
</tr>
<tr>
<td>Propagation</td>
<td>$R_{n_i} + M \rightarrow R_{n+1}^f$</td>
</tr>
<tr>
<td>Transfer to monomer</td>
<td>$R_{n_i} + M \rightarrow R_{n+1} + R_j$</td>
</tr>
<tr>
<td>Transfer to CTA</td>
<td>$R_{n_i} + Y \rightarrow R_{n+1} + R_j$</td>
</tr>
<tr>
<td>Transfer to polymer</td>
<td>$R_{n_i} + R_{m_j} \rightarrow R_{n+1} + R_{m-1}$</td>
</tr>
<tr>
<td>Random scission</td>
<td>$R_{n_i} + R_{m_j} \rightarrow R_{n+1} + R_{m-1}$</td>
</tr>
<tr>
<td>Termination by disproportionation</td>
<td>$R_{n_i} + R_{m_j} \rightarrow R_{n+1} + R_{m-1}$</td>
</tr>
<tr>
<td>Termination by combination</td>
<td>$R_{n_i} + R_{m_j} \rightarrow R_{n+1} + R_{m-1}$</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 0th 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:

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

(4.1)

where $\rho_{RS}$ is the radical site density, defined as:

$$\rho_{RS} = \Phi_n^i / (n R_n)$$

(4.2)

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.
\[ \lambda^* \geq \lambda_{01} = \sum_{n=1}^{\infty} \Phi^1_n, \quad \lambda^* \geq \lambda_{00} = \sum_{n=1}^{\infty} nR_n \]

\[ \lambda^*_0 \quad \text{Total number of radical sites in sol and gel} \]

\[ \lambda^*_1 \quad \text{Total number of radical sites in sol} \]

\[ \lambda^*_1 \quad \text{Total number of monomer units in sol and gel} \]

\[ \lambda^*_1 \quad \text{Total number of monomer units in sol} \]

\[ \frac{dI}{dt} = -2k_d I \]

\[ \frac{dI}{dt} = 2k_d I - kMI \]

\[ \frac{dM}{dt} = -(k_p + k_w)M \lambda^*_0 - kMI \]

\[ \frac{dY}{dt} = -k_{CT,2} Y \lambda^*_0 \]

\[ \frac{d\lambda^*_0}{dt} = kMI - (k_w + k_m) (\lambda^*_0)^2 \]

\[ \lambda^*_0 = M_0 - M \]

\[ \frac{dR_n}{dt} = kMI \cdot n + k_m M \lambda^*_0 + k_{CT,2} Y \lambda^*_0 - k_p M \Phi^1_n \quad n = 1 \]

\[ \frac{dR_n}{dt} = k_p M (\Phi^{n-1}_n - \Phi^1_n) + k \left[ \sum_{n=1}^{\infty} \Phi^1_n \Phi^{n-1}_n - \lambda^*_0 \Phi^1_n \right] + k_m M \Phi^1_n - k_{CT,2} Y \Phi^1_n + k_{CT,2} \lambda^*_0 \left( 2 \sum_{m=1}^{\infty} f(n,m) mR_m - nR_n \right) \quad n \geq 2 \]

\[ \frac{d\Phi^1_n}{dt} = kMI \cdot n + k_m M \lambda^*_0 + k_{CT,2} Y \lambda^*_0 - k_p M \Phi^2_n \quad n = 1 \]

\[ \frac{d\Phi^2_n}{dt} = k_p M (\Phi^{n-1}_n - \Phi^2_n) - k_m M \Phi^1_n - k_m M \Phi^2_n - k_{CT,2} Y \Phi^2_n + k_m \left( \sum_{n=1}^{\infty} \Phi^1_n \Phi^{n-1}_n - \Phi^2_n \Phi^1_n - \lambda^*_0 \Phi^2_n \right) + k - \lambda^*_0 \Phi^2_n + \lambda^*_0 nR_n \]

\[ k_m \left( \sum_{n=1}^{\infty} \Phi^1_n \Phi^{n-1}_n - \Phi^2_n \Phi^1_n - \lambda^*_0 \Phi^2_n \right) + k - \lambda^*_0 \Phi^2_n + \lambda^*_0 nR_n \quad n \geq 2 \]

Table 4.2. Population balance equations and first radical site moment distributions for a batch reactor.
balances are replaced by summations of polynomial terms:

\[
\frac{dI_1}{dt} = -2k_{f,d}I_1 + \frac{1}{\tau}(I_{20} - I_1) = 0; \quad \frac{dI_2}{dt} = -2k_{f,d}I_2 + \frac{1}{\tau}(I_{21} - I_2) = 0; \quad k \geq 2
\]

\[
\frac{dI^{(*)}}{dt} = -2k_{f,d}I^{(*)} - k_dM^{(*)}I^{(*)} + \frac{1}{\tau}\left[\left(1 - \delta(k - 1)\right)I_{k-1}^{(*)} - I^{(*)}\right] = 0
\]

\[
\frac{dM_1}{dt} = -k_{p,d}M_1\lambda_0 - k_{f,d}M_1I^{(*)} - k_{d}M_1\lambda_0 + \frac{1}{\tau}(M_0 - M_1) = 0
\]

\[
\frac{dM_k}{dt} = -k_{p,d}M_k\lambda_0 - k_{f,d}M_kI^{(*)} - k_{d}^{k-1}M_k\lambda_0^k + \frac{1}{\tau}(M^{k-1} - M^k) = 0; \quad k \geq 2
\]

\[
\frac{dY_1}{dt} = -k_{C,T}\lambda_0 Y_0 + \frac{1}{\tau}(Y_0 - Y_1) = 0; \quad \frac{dY_k}{dt} = -k_{C,T}Y^k\lambda_0^k + \frac{1}{\tau}(Y^{k-1} - Y^k) = 0
\]

\[
\frac{d\lambda_0^k}{dt} = k_d^k M^kI^{(*)} - \left(k_{p,d} + k_{f,d}\right)\left(\lambda_0^k\right)^2 + \frac{1}{\tau}\left[\left(1 - \delta(k - 1)\right)\lambda_0^{k-1} - \lambda_0^k\right] = 0
\]

\[
\lambda_0^k = M_0 - M_1; \quad \lambda_0^{k-1} = M^{k-1} - M_1; \quad k \geq 2
\]

\[
\frac{dR^k}{dt} = k_{p,d}M^kI^{(*)} + (k_{p,d} + k_{C,T}Y^k)\lambda_0^k - k_{p,d}M^kR^k + \frac{1}{\tau}\left[\left(1 - \delta(k - 1)\right)R^{k-1} - R^k\right] \quad n = 1
\]

\[
\frac{dR_k}{dt} = k_{p,d}M^k(\Phi^k_{n+1} - \Phi^k_n) + k_{f,d}\left[\sum_{n=m}^{N} \Phi^k_{n+1} - \Phi^k_n - \lambda_0^k \Phi^k_n\right] + \left(-k_{p,d}^k + k_{C,T}Y^k\right)\Phi^k_n + k_d^k \lambda_0^k \left(2 \sum_{n=m}^{N} f(n,m)R^k_n - nR^k_n\right) - \frac{1}{\tau}R^k_n \quad n \geq 2
\]

\[
\frac{d\Phi^k_n}{dt} = k_{p,d}^k M^{k-1}(\Phi^k_{n+1} - \Phi^k_n) - (k_{p,d} + k_{C,T}Y^k)^k\lambda_0^k - k_{p,d}^k M^{k-1}\Phi^k_n + \frac{1}{\tau}\left[\left(1 - \delta(k - 1)\right)\Phi^k_{n-1} - \Phi^k_n\right] \quad n = 1
\]

\[
\frac{d\Phi^k_n}{dt} = k_{p,d}^k M^{k-1}(\Phi^k_{n+1} - \Phi^k_n) - (k_{p,d} + k_{C,T}Y^k)^k\lambda_0^k - (k_{p,d}^k + k_{C,T}Y^k)^k\Phi^k_n + k_{f,d}\left[\sum_{n=m}^{N} \Phi^k_{n+1} - \Phi^k_n - \lambda_0^k \Phi^k_n\right] + k_{f,d}\left[\lambda_0^k \left(2 \sum_{n=m}^{N} f(n,m)R^k_n - nR^k_n\right) - \frac{1}{\tau}R^k_n\right] \quad n \geq 2
\]

Table 4.3. Population balance equations and first radical site moment distributions for the \(k^{\text{th}}\) 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, \( R_n \), \( \Phi^i_n \) and \( \Phi^\beta_n \) 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 \( n^2 R(n) \) 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:

$$R^w(s) = s^2 R(s) = \sum_{k=0}^{r} a^w_k T_k(s) = s^2 \sum_{k=0}^{r} a_k T_k(s)$$  \hspace{1cm} (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:

$$T^w \times a^w = T \times a$$ \hspace{1cm} (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:

$$T^w = S^i \times T$$ \hspace{1cm} (4.6)

With $S^i$ the diagonal matrix with the nodes to the power $i$ of the interval:

$$S^i = \begin{bmatrix} s^i_1 & 0 & \ldots & 0 \\ 0 & s^i_2 & \ldots & 0 \\ 0 & 0 & \ldots & 0 \\ 0 & 0 & \ldots & s^i_N \end{bmatrix}$$ \hspace{1cm} (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’ $U$:

$$a^w = U \times a = \left( T^w \right)^{-1} T \times a$$ \hspace{1cm} (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:

$$\Delta a^w = U \times F$$ \hspace{1cm} (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.

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 in 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:

\[ P_b = \frac{k_n \lambda_0^*}{(k_c + k_{id}) \lambda_0^* + k_{rs} \lambda_0^* + k_{tp} \lambda_0^* + k_m M + k_S S} \]  

Branching density:

\[ \rho_b(\theta) = \frac{k_n x \theta}{k_p (1-x)} \]  

Scission probability:

\[ P_s = \frac{k_r \lambda_1^*}{(k_c + k_{id}) \lambda_0^* + k_{rs} \lambda_0^* + k_{tp} \lambda_0^* + k_m M + k_S S} \]  

Branching density:

\[ \frac{1}{\rho_s(\theta)} = \frac{1}{\rho_s' \theta} = \frac{k_s (1-x)}{k_{rs} x \theta} \]  

Combination probability:

\[ P_C = \frac{k_c \lambda_0^*}{(k_c + k_{id}) \lambda_0^* + k_{rs} \lambda_0^* + k_{tp} \lambda_0^* + k_m M + k_S S} \]  

Average primary polymer length:

\[ \bar{n}_{pp} = \frac{k_p M}{(k_c + k_{id}) \lambda_0^* + k_{rs} \lambda_0^* + k_{tp} \lambda_0^* + k_m M + k_S S} \]  

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>$k_{sc} + k_{sd}$</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.
Table 4.5. Kinetic data (from Busch, 2001a, 2001b).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Kinetic coefficient</th>
<th>Arrhenius expression</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation</td>
<td>( k_{DS} )</td>
<td>( 1.35 \times 10^9 \exp\left(\frac{-14130 - 0.03374P}{T}\right) )</td>
<td>m³/s</td>
</tr>
<tr>
<td>Dissociation</td>
<td>( k_{DC} )</td>
<td>( 2.89 \times 10^4 \exp\left(\frac{-16627 - 0.1217P}{T}\right) )</td>
<td>m³/s</td>
</tr>
<tr>
<td>Propagation</td>
<td>( k_p )</td>
<td>( k_p' = 1.88 \times 10^9 \exp\left(\frac{-4125 + 0.324P}{T}\right) )</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_p = \frac{k_p'}{1 + 1.13 \times 10^8 \eta} )</td>
<td></td>
</tr>
<tr>
<td>Termination</td>
<td>( k_{nc} )</td>
<td>( k_{nc}' = 8.11 \times 10^9 \exp\left(\frac{-555.26 - 0.19P}{T}\right) )</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \eta = 10^{0.06555 \exp e^{-0.0125}} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_p = k_p' \left(0.832 \frac{1}{\eta} + 8.04 \times 10^{-4} - X \right) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{nc} = 3.321 \exp\left(\frac{150.10 - 0.1086P}{T}\right) )</td>
<td></td>
</tr>
<tr>
<td>Transfer to monomer</td>
<td>( k_m )</td>
<td>( 3.42 \times 10^8 \exp\left(\frac{-9135 + 0.0674P}{T}\right) )</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td>Transfer to polymer (long chain</td>
<td>( k_{tp} )</td>
<td>( 2.15 \times 10^5 \exp\left(\frac{-5921.9 + 0.04059P}{T}\right) )</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td>branching formation)</td>
<td></td>
<td>( k_{CTA} = 1.99 \times 10^5 \exp\left(\frac{-5499 + 0.3253P}{T}\right) )</td>
<td>m³/(kmole.s)</td>
</tr>
<tr>
<td>Scission</td>
<td>( k_{rs} )</td>
<td>( 3.7 \times 10^8 \exp\left(\frac{-6357 - 0.08696P}{T}\right) )</td>
<td>sec⁻¹</td>
</tr>
</tbody>
</table>

Table 4.6. Tubular reactor configuration and reaction conditions (Kim and Iedema, 2004), subscript, T2 shows the initial injection point and T1; T2 show the downstream injection points, initiator C is a high temperature initiator for downstream injection points.

### 4.3.2 Various reactor configurations

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. 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 \( n^{th} \) CSTR.](image)

![Figure 4.3. Schematic configuration of tubular reactor with three downstream initiator-feeding points.](image)

### 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 \( \tau = \tau_{\text{total}} / n_{\text{CSTR}} \). To ensure this, the feed concentration of initiator as is shown in 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, \( \tau_{\text{total}} \).

![Figure 4.4](image)

Figure 4.4. Initiator feed concentration as a function of number of CSTRs, \( n_{\text{CSTR}} \) yielding the same monomer conversion of 0.456, assuming a single initiator feed at the first CSTR.

### 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 $x = 0.456$,
kineic data from Table 4.4, initiator feed according to Figure 4.4. Development of CLD over CSTR number and time are similar.
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 ($k_{rs}/k_p = 1.6 \times 10^5$). 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 4.8. Chain length distributions from multiradical model and MC simulations for the case with moderate scission ($k_{rs}/k_p = 1.6 \times 10^{-5}$), topological (top) and linear (bottom), and no 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. Bimodality from linear scission vanishes as number of CSTRs increases, until complete coinciding for batch reactor. Perfect agreement between deterministic model with topological scission and MC simulations for all configurations.

### 4.4.2.3 Combination termination, no scission

With combination termination and transfer to polymer, in principle gel formation is possible in a CSTR. Chain length distributions for the gel regime have been derived from multiradical model allowing for gel formation by solving the equations of Table 4.2 and Table 4.3 (Yaghini and Iedema, 2014b), and are depicted in Figure 4.9 through Figure 4.16. Figure 4.9 shows the outcomes from the multiradical model and MC simulations for moderate transfer to polymer ($k_{tp}/k_p = 0.0012$) and equal combination and disproportionation rates for a single CSTR, two different configurations of CSTRs in series and a batch reactor. The results from the deterministic model agree very well with the ones from MC simulations for all configurations. The gel fraction, 24.9% for a single CSTR, turns out to decrease significantly with the number of CSTRs: 7.9% for 2 CSTRs and finally 0% for 4 CSTRs and batch reactor. Thus we can conclude that the deterministic model with combination termination and no scission predicts the gelpoint, the gel fraction and the chain length distributions properly.

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 $\times = 0.456$, 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 Monte Carlo 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 Monte Carlo 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 iDPE. 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 \((k_p/k_p = 0.0012, k_{sc}/k_p = 0.00012)\), and equal combination and disproportionation rates \((k_{cc}/k_p = k_{ap}/k_p = 1000)\). 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.](image-url)
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, $k_\text{rs}/k_\text{p} = 4 \times 10^{-5}$. 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 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 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 ldPE tubular reactor, same as Figure 4.17 and Figure 4.18. Discontinuities at intermediate initiator feed points clearly observed.
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.