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Three-dimensional chain-length-branching-combination points distribution modeling of low density polyethylene in a continuous stirred tank reactor allowing for gelation

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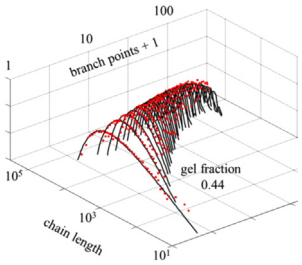
HIGHLIGHTS

- Rigorous 3D model of chain length-branching-combination points distribution for ldPE.
- 'Combinatorial Explosion' as a result of termination by combination.
- Successful implementation of the combination termination reaction in the Galerkin–FEM.
- Correctly accounting for gel formation in comparison to the Monte Carlo simulations.

GRAPHICAL ABSTRACT



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ABSTRACT

The focus of this paper is especially on the role of combination termination in the context of 3-dimensional population balance modeling of trivariate chain length/number of branch points/number of combination points distribution for low-density Polyethylene. Termination by combination is a well-known termination mechanism in radical polymerization and regarding low-density Polyethylene many authors have assumed this mechanism to be present. The ratio between disproportionation and combination termination in the previous studies varies, but usually the two mechanisms are thought of equal importance.

Full 3-dimensional population balance equations are solved by a combination of the 2-dimensional Galerkin–finite element method and the pseudo distributions method to estimate chain length/branching/number of combination points distributions. Termination by combination is treated in a different scheme than the framework employed for other kinetic reactions. Good agreement with Monte Carlo results has been observed for low-density Polyethylene-like kinetics.

1. Introduction

Architectures of large hyper-branched molecules even in low concentrations play a dominant role in determining the physical properties of polymers such as rheology and also in polymer characterization by size exclusion chromatography (Yaghini and Iedema, 2015a). Predicting these architectures by mathematical modeling is therefore highly interesting and many researchers have been engaged in such an activity. In a previous paper (Yaghini and Iedema, 2015d) we have addressed the 2-Dimensional (2D) [1]

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[1] 2-Dimensional.

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population balance problem concerning low-density Polyethylene (ldPE)[2], assuming disproportionation as the sole termination mechanism. The present paper is especially devoted to investigate the role of combination termination in the context of 3-Dimensional (3D)[3] chain length/branching population balance modeling.

Combination termination is a common termination type in radical polymerization and several authors have presumed this mechanism to be present in ldPE polymerization. Tobita (2013, 2014) has applied a Monte Carlo (MC)[4] simulation technique to deal with the problem at hand, where combination termination is correctly allowed for. Krallis et al. (2007a, 2007b) have applied the so-called fixed pivot technique to Population Balance Equations (PBEs)[5] in order to model the evolution of molecular weight-long chain branching distributions of low-density Polyethylene (ldPE) under combination termination conditions. Meimaroglou et al. (2011) have applied a Gillespie MC method to model the ldPE bivariate chain length-long chain branching/short chain branching distributions. In the studies mentioned above as well the studies by Busch (2001a, 2001b), the ratio between disproportionation and combination termination is supposed to be a key parameter and usually the two mechanisms are thought to have equal importance.

As has been noticed by many authors on radical polymerization and discussed in Yaghini and Iedema (2014b), the polymerization system with chain transfer to polymer and combination termination may lead to gelation. The question rises then is whether the developed 2D model would also work in the gel regime. This problem has been treated in the same manner as it was realized for the 1-Dimensioanl (1D)[6] problem in the aforementioned reference. Our solution and conclusions concerning the gelation issue will shed a new and interesting light on previous works, where combination was assumed to play an important role.

Furthermore, 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)[7] in modeling topological architectures of polymer molecules in the presence of termination by combination and chain transfer to polymer in radical polymerization has been clarified previously (Iedema and Hoefsloot, 2005). These authors have applied a combination of the method of moments and deterministic 1D approach to 3D population balance equations to estimate the overall distributions without presenting the actual full 3D distributions. In this paper we will provide 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 free radical polymerization with chain transfer to polymer, topological scission and termination by combination as the most influencing reactions in ldPE polymerization, and employ the moments of combination points to allow for the effect of the third dimension.

Dealing with higher dimensional polymerization problems, necessitates the application of advanced numerical techniques to multi-dimensional population balance equations. In Yaghini and Iedema (2015d) we have introduced a new 2D Galerkin method with an elaborate but straightforward scheme to transcribe the original 2D population balance equations into a linear set of equations. Where 1-dimensional population balances require a 2D matrix forming the heart of the Galerkin representation, with a 2D problem a 4-dimensional matrix has to be generated to find the coefficients of the representation. We will use the same methodology here, but extend it to allow for combination termination. This implies adding a non-linear term to the linear 2D problem of disproportionation only, which requires non-linear solving techniques. Furthermore, a huge challenge consists in the 2D convolution problem that has to be solved as a consequence of combination termination. To deal with this inherent 'combinatorial explosion' with a minimum of CPU and memory requirements, we adopted a scheme within the Galerkin context that was already successful in the 1-dimensional problem.

The reminder of this paper is organized as follows. First, the trivariate PBEs are introduced and several assumptions concerning the issue of random scission are discussed. Then the pseudo-distribution equations are derived accounting for various scission assumptions. An extensive discussion is given next of the treatment of the convolution problem in 2 dimensions. Finally, results of a number of simulations under non-gelling conditions and in the gel regime are discussed and compared to those from Monte Carlo simulations.

2. Reaction and population balance equations in full 3 dimensions

2.1. Reaction equations and 3D formulation

The 3D reaction equations and 3D population balances with regards 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 1 shows the entire reaction equations system for ldPE free radical polymerization.

The general population balance equations for free radical polymerization in Continuous Stirred Tank Reactor (CSTR)[8] for living chains and dead chains are indicated as below

$$\begin{aligned}\frac{dR_{n,i,k}}{dt} &= k_p M(-R_{n,i,k}+R_{n-1,i,k})-(k_{td}+k_{tc})\lambda_0 R_{n,i,k}\\ &\quad -k_{rs}\mu_1 R_{n,i,k}+k_{rs}\sum_{m=n+1}^{\infty} mf(n,m)\sum_{j=i}^{\infty}\beta^b(n,m,i,j)\\ &\quad \sum l = k\infty\beta^c(n,m,k,l)P_{m,j,l}\\ &\quad +k_{tp}(-\mu_1 R_{n,i,k}+\lambda_0 nP_{n,i-1,k})-\frac{1}{\tau}R_{n,i,k}\end{aligned} \tag{1}$$

$$\begin{aligned}\frac{dP_{n,i,k}}{dt} &= k_{td}\lambda_0 R_{n,i,k}+\tfrac{1}{2}k_{tc}\sum_{m=1}^{n-1}\sum_{j=0}^{i}\sum_{l=0}^{k-1}R_{m,j,l}R_{n-m,i-j,k-l-1}\\ &\quad -k_{rs}\lambda_0 nP_{n,i,k}+k_{rs}\mu_1 R_{n,i,k}+k_{rs}\sum_{m=n+1}^{\infty}mf(n,m)\\ &\sum j = i\infty\beta^b(n,m,i,j)\sum_{l=k}^{\infty}\beta^c(n,m,k,l)P_{m,j,l}\\ &\quad +k_{tp}(\mu_1 R_{n,i,k}-\lambda_0 nP_{n,i,k})-\frac{1}{\tau}P_{n,i,k}\end{aligned} \tag{2}$$

M is the monomer concentration. $P_{n,i,k}$ and $R_{n,i,k}$ show the concentrations for a dead chain and a living chain of chain length n with i number of branch points and k number of combination points. λ_0 and μ_1 are respectively the 0th and 1st moments of living chains and dead chains and have been defined as $\lambda_0=\sum_{n=0}^{\infty}n^0R_n$ and $\mu_1=\sum_{n=0}^{\infty}n^1P_n$. In Eqs. (1) and (2), chains with more than one radical site per molecule have not been taken

[2] Low-density polyethylene.
[3] 3-Dimensional.
[4] Monte Carlo.
[5] Population Balance Equations.
[6] 1-Dimensioanl.
[7] Chain Length Distribution /Degree of Branching Distribution/Combination Points Distribution.
[8] Continuous Stirred Tank Reactor.