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Predicting molecular weight distribution by deterministic modeling and Monte Carlo simulations of radical polymerization with branching and scission allowing for multiradicals and gelation in various reactor configurations

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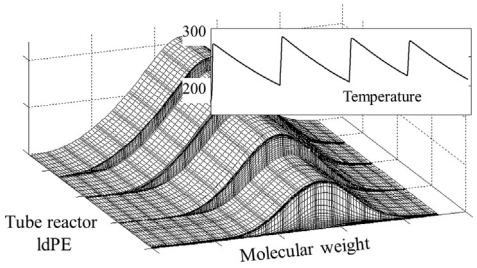
HIGHLIGHTS

- ldPE molecular weight distribution modeling for tubular free radical polymerization by Galerkin-FEM.
- Tubular reactor model as a batch reactor and as a compartment model of *n*CSTRs.
- Effect of multiradicals and kinetics on molecular weight distributions.
- Good agreement with MC results.

GRAPHICAL ABSTRACT



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ABSTRACT

Modeling of the molecular weight distribution (MWD) under circumstances of low-density polyethylene (ldPE) has been carried out for a tubular reactor under realistic non-isothermal conditions and for a series of CSTR's (Yaghini and Iedema, in press). The model allows for the existence of multiradicals and the occurrence of gelation. This model is based on a Galerkin finite element approach (FEM) and employs the pseudo distribution 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 we could now identify as an artefact.

1. Introduction

This paper is concerned with the application of a newly developed multiradical model (Yaghini and Iedema, in press) for low-density Polyethylene (ldPE) predicting MWD in various reactor configurations, from continuous stirred tank reactor (CSTR)[1] to series of CSTRs and tubular reactors all operated under isothermal or more realistic temperature gradient conditions. The basic idea is to study the impact of these reactor configurations on the MWD and allowing for gel

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[1] Continuous stirred tank reactor.

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Table 1
Reaction mechanism for ldPE polymerization. Same nomenclature as used in Yaghini and Iedema, in press.

Initiator dissociation	$I_2 \xrightarrow{k_d} 2I\bullet$	(1.1)
Initiation	$I\bullet + M \xrightarrow{k_i} R_{1,1}$	(1.2)
Propagation	$R_{n,i} + M \xrightarrow{k_p i} R_{n+1,i}$	(1.3)
Transfer to monomer	$R_{n,i} + M \xrightarrow{k_m i} R_{n,i-1} + R_{1,1}$	(1.4)
Transfer to CTA	$R_{n,i} + Y \xrightarrow{k_{CTA} i} R_{n,i-1} + R_{1,1}$	(1.5)
Transfer to polymer	$R_{n,i} + R_{m,j} \xrightarrow{k_{tp} nj} R_{n,i+1} + R_{m,j-1}$	(1.6)
Random scission	$R_{n,i} + R_{m,j} \xrightarrow{k_{rs}(n-1)jf(n,k)} R_{n-k,i-p+1} + R_{k,p} + R_{m,j-1}$	(1.7)
Termination by disproportionation	$R_{n,i} + R_{m,j} \xrightarrow{k_{td} ij} R_{n,i-1} + R_{m,j-1}$	(1.8)
Termination by recombination	$R_{n,i} + R_{m,j} \xrightarrow{k_{tc} ij} R_{n+m,i+j-2}$	(1.9)

formation. The results of the deterministic model will be compared to those from Monte Carlo simulations.

In Yaghini and Iedema (in press) a recent overview about ldPE molecular weight and long chain branching (LCB)[2] distribution modeling has been provided. Regarding Monte Carlo (MC) simulations, Tobita (2001) was the first to account for simultaneous branching and random scission in a batch reactor. In Yaghini and Iedema (2014a) we have extended this to a CSTR. The comparison to results from our deterministic model with topological scission showed fair agreement. Recently, Tobita (2014) has further extended his method to a series of CSTRs. For the present study we have implemented all these MC schemes as a reference basis for our deterministic models.

The paper will continue as follows. The reaction mechanisms accounted for are presented. A description of the deterministic model is not given as it may be found in Yaghini and Iedema (in press). Also a short explanation is given of the Monte Carlo simulation scheme. The main part consists of a discussion on the results of various kinetic effects, absence or presence of scission and gelation in several different reactor configurations. In most cases comparisons between the results of the deterministic model and MC simulations are given.

2. Reaction mechanisms and population balance equations

The reaction mechanism has been formulated by the reactions shown in Table 1 in two dimensions. 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.

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 (2001) 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 we have implemented the algorithm in MATLAB® as described in the aforementioned papers. We do not provide an extensive description of the principles of this model here, since this may be found in these references. In the simulations we varied the transfer to polymer rate, scission rate, and recombination termination rate, which corresponds to changes in the specific MC parameters (Tobita, 2014, using the same notation as in Yaghini and Iedema, in press):

$$\text{Branching probability}: \quad P_b = \frac{k_{tp}\lambda_1^*}{(k_{tc}+k_{td})\lambda_0^* + k_{rs}\lambda_1^* + k_{tp}\lambda_1^* + k_m M + k_{CTA} Y} \tag{1}$$

$$\text{Branching density}: \quad \rho_b(\theta) = \rho_b'\theta = \frac{k_{tp} x\theta}{k_p(1-x)} \tag{2}$$

$$\text{Scission probability}: \quad P_s = \frac{k_{rs}\lambda_1^*}{(k_{tc}+k_{td})\lambda_0^* + k_{rs}\lambda_1^* + k_{tp}\lambda_1^* + k_m M + k_{CTA} Y} \tag{3}$$

$$\text{Branching density}: \quad \frac{1}{\rho_s(\theta)} = \frac{1}{\rho_s'\theta} = \frac{k_p(1-x)}{k_{rs} x\theta} \tag{4}$$

Recombination probability :

$$P_C = \frac{k_{tc}\lambda_0^*}{(k_{tc}+k_{td})\lambda_0^* + k_{rs}\lambda_1^* + k_{tp}\lambda_1^* + k_m M + k_{CTA} Y} \tag{5}$$

Average primary polymer length :

$$\overline{n}_{pp} = \frac{k_p M}{(k_{tc}+k_{td})\lambda_0^* + k_{rs}\lambda_1^* + k_{tp}\lambda_1^* + k_m M + k_{CTA} Y} \tag{6}$$

It should be noted that in contrast to Tobita's papers we have applied realistic profiles of the probability parameters for tubular reactor and series of CSTRs. 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 model equations in Yaghini and Iedema (in press). 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 we show the time profile for some of the important MC parameters, like average primary polymer length.

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 our MATLAB® implementation of this method, we have employed the method with the binomial distribution, which is fully equivalent with the newer one.

4. Reactor configuration and kinetic data

4.1. Sources of kinetic data

The same kinetic data set has been applied as in our earlier papers (Yaghini and Iedema, 2014a, 2014b; Kim et al, 2004). Table 2 lists the reaction rate coefficients for the calculations of all models, except for

[2] Long chain branching.