



On the modeling of number and weight average molecular weight of polymers

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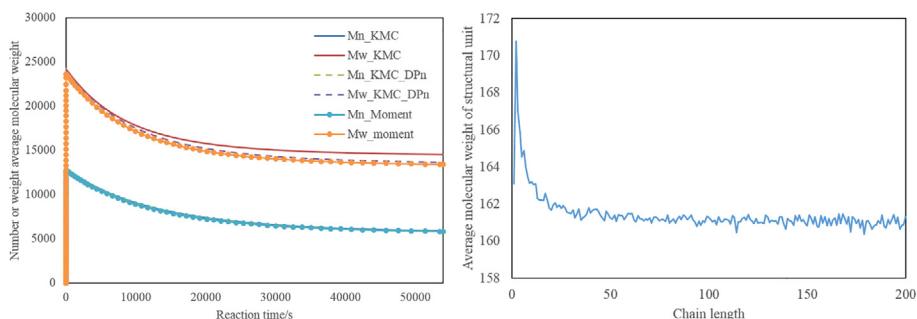
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HIGHLIGHTS

- Demonstrated the importance of monitoring each type of monomer in simulating Mw.
- Quantitatively analyzed the dependence of monomer composition on chain length.
- Derived an explicit moment-based model that describes the full MWD.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form 22 June 2017

Accepted 23 June 2017

Available online 27 June 2017

Keywords:

Kinetic Monte Carlo

Moment-based methods

Weight average molecular weight

Explicit sequence

ABSTRACT

The modeling of the molecular weight distribution of polymers is critical in polymerization modeling. Moment-based models and kinetic Monte Carlo are two methods used to calculate the number and weight average molecular weight during simulation of polymerization. While these two methods are commonly considered to yield equivalent results in the molecular weight distribution, we show that there can be significant differences between these two methods when copolymerization of multiple monomers is modeled. In particular, clear differences in results exist for low molecular weight polymers where the molar mass of one monomer is two or more times greater than the others. Detailed analysis is provided for the cause of the difference, and we demonstrate the importance of tracking the exact number of each type of monomer in every polymer chain when calculating the moments of molecular weight.

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1. Introduction

Polymers are an important class of material in the chemical and consumer products industries. Depending on their size and composition, they have significant ranges over which their properties can be adjusted, because of the broad variability of the microstructures for different polymer chains. The modeling of polymerization continually attracts research interest, as it is crucial for tuning the

properties of polymer products and controlling polymerization processes [1–19]. Most modeling techniques for polymerization not only track the concentration of polymer, but also focus on the distributions of the polymer chains. Molecular weight distribution is one of the most important and frequently modeled properties of polymers, and new techniques for modeling molecular weight distributions continue to emerge [20,21]. The molecular weight distribution is closely related to physical and mechanical properties of polymers, including glass transition temperature, elasticity modulus, etc [22,23].

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Molecular weight distribution is commonly characterized by two average quantities – number-average molecular weight (M_n) and weight-average molecular weight (M_w), both of which can be calculated from the moments of the molecular weight distribution. Because of this, different methods have been developed for modeling moments of molecular weight (or M_n and M_w), including continuum models and stochastic models. Among continuum modeling techniques, the most extensively used are moment-based models [24–31]. This formulation uses differential equations to describe the change of moments of molecular weight and is able to calculate M_n and M_w in a computationally efficient way. Most moment-based models do not keep track of the exact number of different types of monomers in the polymer [25]. Instead, they calculate the moments of chain length and multiply them by the molecular weight of an average structural unit to obtain moments of molecular weight.

Alternatively, moment-based models that do keep track of the exact number of each type of monomer in each polymer chain when calculating the moments of molecular weight have been developed. For example, Keramopoulos and Kiparissides [32] developed a model for terpolymerization. Three indices are used to denote the number of the three types of monomers in the radical and polymer chains, which is then used to calculate the moments of molecular weight distribution. To differentiate from other moment-based models, we will refer to the Keramopoulos and Kiparissides method as the explicit moment-based model. The derivation and programming are more complicated for the explicit moment-based model, which is the tradeoff required for the enhanced accuracy in tracking molecular weight values. Furthermore, the complexity of the model and computational cost increase if additional types of monomers are included or more complicated reaction mechanisms are considered.

Kinetic Monte Carlo (KMC) is a stochastic simulation algorithm that has become increasingly popular in recent years [2,3,33–50]. KMC tracks explicitly the monomer sequence in all polymer chains, which is not possible to obtain using moment-based models. The full molecular weight distribution is available, and the values of the M_n and M_w can be calculated from the distribution. Generally, due to the higher level of detail involved in explicitly tracking individual chains, KMC simulations are computationally more expensive than moment-based models, and simulation time can reach hours or days. Nevertheless, recently there have been methods developed that have greatly improved the efficiency of KMC simulations and render them more competitive [37,40,47,51], with the simulation time brought down to the scale of minutes or even seconds.

Despite the vast difference in how these models are formulated and how they are executed, they are generally considered equivalent in the quality of the results, i.e. they give the same prediction of M_n and M_w for the same reaction system. These approaches have been validated for homopolymerization [47], and Storti et al. reported a good match for copolymerization between results calculated from a theoretical MWD and using the pseudo-homopolymerization approach [52,53]. However, they did not rule out the possibility for discrepancies and encouraged further comparisons. To the best of our knowledge, detailed quantitative comparisons for systems with more than two monomers have not been reported to gauge the extent to which the different methods differ. In this work, we used these three methods to model M_n and M_w for a terpolymerization system as a function of reaction conditions, and show that these methods can yield significant differences in weight-average molecular weight. The origin of these differences is revealed in detail, demonstrating under what circumstances it is important to keep track of the explicit number of each type of monomer in each polymer chain.

2. Methods

2.1. Reaction system

In this work, we model a terpolymerization system using a terminal model. Solution polymerization up to moderate conversion values is modeled, and effects of diffusion limitations on any of the kinetic parameters are neglected. The reactions included in the mechanism are listed in Table 1.

The monomers used in the simulation are termed generically as A, B and C, and the initiator is denoted as I. The physical properties and rate coefficients are listed in Table 2. The values are chosen to represent typical values of an acrylate polymer system, but sensitivity tests with respect to these parameters to demonstrate the general prevalence of this phenomenon are conducted.

2.2. Moment-based model

The moment-based model for batch, semi-batch, or steady state plug flow reactors is a differential equation system that can be described as consisting of two parts. The first part is the differential equations that describe the mole balance of all the reacting species, and the second part is the balance equations that describe the change of the moments. For polymerization with more than one type of monomer (e.g., copolymerization, terpolymerization, etc.), a common practice is to use the concept of pseudo-kinetic parameters [54,55]. This approach is widely applied and summarized in academic research (e.g. Penlidis et al. Chapter 12 in Handbook of Polymer Synthesis, Characterization and Processing [56]) and in commercial software like PREDICI [2,57–65]. The pseudo-kinetic parameters manifest as a single propagation and termination rate coefficient that are derived from the collection of the kinetic parameters of different propagation and termination steps based on the fraction of radicals and monomers. As a result, these systems can be treated in the same way as a homopolymerization system, with the reaction mechanism simplified to:

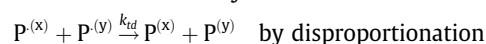
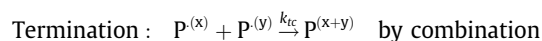
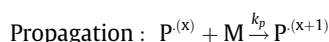
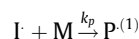
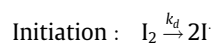


Table 1

Free radical polymerization steps incorporated into the models of this work.

Reaction events	
Initiation	
Initiator decomposition	$I_2 \rightarrow 2I\cdot$
Chain initiation	$I\cdot + M_i \rightarrow P_i^{(1)}$
Propagation	
Terminal effect	$P_i^{(x)} + M_j \rightarrow P_j^{(x+1)}$
Termination	
By recombination	$P_i^{(x)} + P_j^{(y)} \rightarrow P^{(x+y)}$
By disproportionation	$P_i^{(x)} + P_j^{(y)} \rightarrow P^{(x)} + P^{(y)}$

I_2 denotes initiator, $I\cdot$ represents initiator radical, M_i represents monomer i , $P_i^{(x)}$ is a polymeric radical of chain length x ending with monomer i , and $P^{(x)}$ is a dead polymer chain of length x .

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