



Method of moments: A versatile tool for deterministic modeling of polymerization kinetics



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ABSTRACT

Method of moments is a simple deterministic method widely applicable in modeling various polymerization processes. This method is easy to use and computationally inexpensive. Although the mathematics involved is simple and elementary, the derivation step is often lengthy and thus it may be intimidating. This paper aims to serve as a tutorial by providing step-by-step guide on how to apply the method of moments to different polymerization and polymer modification systems. The basics behind method of moments, the limitation related to it, and common problems encountered in derivation with ways to counter them are described in details. Several examples are presented to clearly elucidate these concepts.

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1. Introduction

Research on polymer modeling is essential in precisely tuning the properties of polymers produced, and in industrial process control for safety and quality assurance. Polymerization modeling methods can be divided into two major classes, deterministic (or kinetic) and statistical (or stochastic). The general characteristics of these two approaches are compared as shown in Table 1. Statistical modeling (e.g., Monte Carlo) involves the use of probabilistic theory by reconstructing the problem at hand. While this is a powerful method, it ignores the history of reaction, which may result in significant discrepancies from the reality. On the other hand, deterministic modeling (e.g., method of moments) is a kinetic-based approach. This method usually involves derivation from the mass balances of reactants. Unlike the statistical approach, this method has a “memory” of the reaction history. Therefore, deterministic modeling is more appropriate for kinetically-controlled processes. The combination of statistical and deterministic approaches gives rise to powerful methods, such as kinetic Monte Carlo (Gillespie's algorithm) [1,2].

Modeling polymerization processes using kinetic-based approach involves writing the mass balances for all chain types and for all possible chain lengths. These balances can then be simultaneously solved to obtain the properties of each individual chain, which can give information such as full molecular weight distribution (or equivalently chain length distribution), and branching density distribution. However, theoretically this requires simultaneously solving an infinite number of equations. While the possible chain lengths can be truncated to a certain number, this still involves a huge number of equations. For example, if we consider the polymers to possess a maximum of 10,000 monomer units and we have two types of polymers, radical and dead, we need to solve 20,000 differential equations in order to obtain the properties of these chains.

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Table 1
General comparison of the deterministic and statistical modeling approaches.

Deterministic modeling	Statistical modeling
Generally based on mass balance Kinetically derived, preserve reaction history	Generally based on probabilistic theories Reconstructed problem, no reaction history

Solving such a large system is not impossible, but it is still computationally expensive. Discretization method such as fixed pivot can be used to group the chain lengths into finite intervals, thus greatly reducing the number of equations to be solved.

Another popular kinetic-based approach is the method of moments. Method of moments is a powerful tool in modeling polymerization processes. The use of moments to model polymerization system was pioneered by Bamford and Tampa [3,4]. This method has been widely used by many research groups to develop kinetic models for conventional free radical polymerization, coordination polymerization, controlled radical polymerization, and others, for linear and branched polymers, homo and copolymerization, solution and surface polymerization, batch and continuous processes [5–31]. In addition, method of moments has also been used to model the kinetics of polymer modification such as crosslinking and degradation of prepolymers [32–36]. The evidences of the versatility of method of moments are abundant in literature [37–39].

One of the major advantages of method of moments is that it simplifies a theoretically infinite number of the mass balance equations for chain species into a much smaller and more manageable set of equations. In this method, the information about individual chains is sacrificed for faster computation, thus it is only capable of predicting average properties of the polymers. For example, method of moments cannot predict the full molecular weight distribution and branching density distribution. Rather, it predicts the molecular weight and branching density averages. Even though method of moments does not provide prediction of the full distribution, there are many cases where the information on average chain properties suffices, especially in an industrial setting. Moreover, for cases where the distribution type is known, the average properties can be used to construct the full distribution. In addition, method of moments can predict the average properties of each chain population, not just the whole population. This allows comparison of the properties between different chain populations (e.g., properties of dead vs. dormant chains) One of the limitations of method of moments is that it does not account for chain length dependence of reaction rate constants. However, there are many modifications proposed in the literature to overcome this limitation [7,40–42]. The chain length dependent rate constants will not be discussed in this paper in order to keep the focus on the method of moments itself.

Another major advantage of the method of moments is its simplicity involved in derivation process. Albeit the simple derivation, the process is often lengthy, which may be confusing at first. When there is a chain combination/coupling reaction, the derivation of moment balances will involve double summations that may not be intuitively expressed as existing moments. On the other hand, when there is a chain breaking/scission reaction, method of moments will run into closure problem, where a lower order moment is a function of a higher order moment. Various empirical closure conditions must be introduced to counter this problem [34].

In this work, we present an easy-to-follow tutorial to elucidate the use of method of moments to model polymerization processes, at the invitation of the editor. This tutorial includes the introduction of method of moments with the relevant physical implications to relate the calculated variables with experiment data. To further clarify the derivation process, various polymerization systems are modeled using the method of moments as examples. In the derivation for these examples, the step-by-step guide illustrated in Fig. 1 will be followed. Moreover, commonly encountered problems will be explained and tackled in these examples. While the examples given here are of chain-growth polymerization types, the method of moments are also applicable for step-growth polymerization systems.

2. Mathematical formulations

The definitions of the i th moments for propagating radical and dead polymer in radical polymerization are given by Y_i and Q_i in Eqs. (1) and (2), respectively. The same concept can be extended to other polymer populations, such as dormant chains, intermediate radical chains, and others. In most cases, due to their highly reactive nature, the propagating radical moments are much smaller than those of dead chains and other polymer chain populations (equivalent to quasi-steady state assumption, QSSA). Therefore, the overall polymer moments can be assumed to be equal to the dead chain moments for systems involving only dead and radical chains ($Y_i \ll Q_i$ and thus $Y_i + Q_i \cong Q_i$).

$$Y_i \equiv \sum_{r=0}^{\infty} r^i [P_r^*] \quad (1)$$

$$Q_i \equiv \sum_{r=0}^{\infty} r^i [P_r] \quad (2)$$

From the definition, it can be seen that the zeroth order moment physically represents the concentration of polymer chains in the system. On the other hand, the first order moment represents the concentration of monomeric units that have been incorporated into the polymer chains. The zeroth and first moments can be related to the number-fraction and

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