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A GENERAL APPROACH TO DETERMINING THE EVOLUTION OF MOLECULAR WEIGHT DISTRIBUTION CURVES OF LINEAR POLYMERS UNDERGOING CHAIN SCISSION*

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Abstract A numerical method is developed to compute the development of molecular weight distribution (MWD) curves of linear polymers undergoing chain scission. The method can be applied to complex chain scission kinetics and for arbitrarily complex initial MWD curves. Our method is based on the method of lines (MoL). Different from the existing numerical scheme, we propose the use of logarithmically spaced points. This development ensures the accuracy of the computed MWD curves at low molecular weights, and it does not require a very fine discretization to produce an accurate result.

Keywords: Polymer degradation; Reaction kinetics; Molecular weight distribution; Modeling.

INTRODUCTION

Modeling the development of molecular weight distribution (MWD) of degradable polymers has received considerable attention because of its practical importance for the polymer industry and its potentially important role in the biomedical application of biodegradable polymers^[1–3]. Notably, polymer degradation has found applications in studies including the modification of MWD through chain scission, anti-fouling^[4], controlled drug delivery system^[5] and the recycling of waste plastics.

There are different types of polymer degradation such as photo, thermal, mechanical, chemical and biological degradation. Fundamentally speaking, polymer degradation is difficult to describe analytically or numerically because it involves complex physical and chemical mechanisms and can be influenced by a number of parameters^[1, 6–11], such as sample crystallinity^[9] and solution pH^[10] in the hydrolysis of polylactic acid.

In theoretical studies, polymer degradation is often simplified as a first-order process with a kinetic rate function that depends on the molecular weight of the degradation molecule and the scission site^[1, 11–19]. Under such circumstances, once the initial MWD and the kinetic rate function are known or assumed, one can in principle predict the time evolution of the MWD function by solving a set of population balance equations that describe the degradation process^[17, 18]. For simple forms of the kinetic rate function, the MWD development can be solved analytically. A variety of such analytically tractable cases have recently been summarized by

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Tobita^[17]. For general forms of the kinetic rate function, the MWD development can be solved by solving the population balance equations numerically using *e.g.* the Monte Carlo method^[11, 13, 15, 19]. Recently, Yeow *et al.*^[18] proposed a general numerical method for solving the integro-differential form of the population balance equations. The key step was the application of the Method of Lines (MoL) to convert the integro-differential equation into a set of ordinary differential equations which can then be solved using conventional time-stepping methods.

Experimentally, the MWD is commonly measured by gel permeation chromatography (GPC). In GPC measurements, the MWD data are usually given as a function of the logarithm of molecular weight^[17]. The original numerical scheme of Yeow *et al.* used linearly spaced discretization points, *i.e.* the range of molecular weight considered was discretized linearly into evenly distributed points^[18]. To compare the computed MWD curves against the corresponding experimental curves determined by GPC, especially in the low molecular weight ranges, the discretization step size has to be small, which will inevitably increase the number of equations as well as the computation cost.

In this work, we propose using logarithmically spaced points. With this idea, we derived a new numerical scheme from that of Yeow *et al.*, as is presented in the method section. This method can be applied to compute the time evolution of MWD curves of linear polymers for arbitrarily complex kinetic rate functions and initial MWD. In the results and discussion section, we present comparison of both methods for a simple test case of random degradation, which clearly demonstrates the advantage of using logarithmically spaced points in ensuring the numerical accuracy at low molecular weights.

METHOD

Consider the binary scission of a linear polymer chain of molecular weight m_r :

$$m_r \rightarrow m_s + (m_r - m_s) \quad (1)$$

where m_r is the molecular weight of the chain undergoing degradation, and m_s is the molecular weight of one of the degradation product. The other degradation product thus has molecular weight $(m_r - m_s)$. The kinetic rate coefficient for a chain scission is represented by $k(m_r, m_s)$, which is in principle a function of the molecular weight of the molecule under scission and the scission site. To be self-consistent, it is required that $k(m_r, m_s) = k(m_r, m_r - m_s)$. Under the continuum assumption^[17, 18], the evolution of MWD as a function of time t during chain scission reactions of the type of Eq. (1) is governed by the following integro-differential equation (also known as the population balance equation):

$$\frac{\partial c(m, t)}{\partial t} = - \int_{m_s=m_{\min}}^m k(m, m_s) c(m, t) dm_s + 2 \int_{m_r=m}^{m_{\max}} k(m_r, m) c(m_r, t) dm_r \quad (2)$$

where $c(m, t)$ is the number concentration of polymer with molecular weight m at time t . $m_{\min} \leq m \leq m_{\max}$ is the range of molecular weight under consideration, which typically spans several orders of magnitude.

Following Yeow *et al.*^[18], Eq. (2) can be made dimensionless by introducing a set of dimensionless quantities: rate constant K , molecular weight M , concentration distribution θ , and dimensionless time τ

$$K(M_r, M_s) = \frac{k(m_r, m_s)}{k_{\max}}, \quad M = \frac{m - m_{\min}}{m_{\max} - m_{\min}}, \quad \theta = \frac{c(m)}{c_{\max}}, \quad \tau = k_{\max} (m_{\max} - m_{\min}) t \quad (3)$$

in these equations, $k_{\max}$ is the maximum value of the function $k(m_r, m_s)$ for $m_{\min} \leq m_r \leq m_{\max}$, $c_{\max}$ is the maximum value of the initial concentration distribution. With these dimensionless variables, Eq. (2) becomes

$$\frac{\partial \theta(M, \tau)}{\partial \tau} = - \left[\int_{M_s=0}^M K(M, M_s) dM_s \right] \theta(M, \tau) + 2 \int_{M_r=M}^1 K(M_r, M) \theta(M_r, \tau) dM_r \quad (4)$$

This makes it convenient for numerical handling since the reduced molecular weight $0 \leq M \leq 1$.

Yeow *et al.* reported a numerical procedure to solve Eq. (4) using the MoL^[18]. In their original development, the molecular weight range was discretized evenly into N_k points, $0(M_1)$, M_2 , M_3 , ..., M_{N_k-1} , $1(M_{N_k})$. The trapezoidal rule was used to approximate the integrals on the right hand side (RHS) of Eq. (4), resulting in a set of ordinary differential equations of the form^[18]:

$$\frac{d\theta_i}{d\tau} = - \left\{ \sum_{j=1}^i \alpha_{i,j} K_{i,j} \right\} \theta_i \Delta M + 2 \left\{ \sum_{p=i}^{N_k} \beta_{i,p} K_{p,i} \theta_p \right\} \Delta M \quad (5)$$

where $\theta_i \equiv \theta(M_i, \tau)$, $K_{i,j} \equiv K(M_i, M_j)$, and similarly $\theta_p \equiv \theta(M_p, \tau)$, $K_{p,i} \equiv K(M_p, M_i)$. ΔM is the discretization step size. $\alpha_{i,j}$ and $\beta_{i,p}$ are the numerical coefficients which are 1/2 for the upper and lower limits of the integrals and 1 for all the interior discretization points. As shown by Tobita^[17], in order for this numerical scheme to be accurate, the discretization step size ΔM should be smaller than about one half of the number-average molecular weight of the resulting MWD. To overcome this constraint, we propose here using logarithmically spaced points, *i.e.* $\lg m$ is discretized evenly instead of the M . This is in line with the distribution of the logarithm of molecular weight obtained in GPC experiments. Based on this idea and again using the trapezoidal rule to approximate the integrals on the RHS of Eq. (4), we obtain

$$\frac{\partial \theta_i}{\partial \tau} = \begin{cases} -\frac{1}{2} \Delta M_i K_{i,i} \theta_i + \sum_{p=i}^{N_k-1} \Delta M_p \left[(K_{p,i} \theta_p) + (K_{p+1,i} \theta_{p+1}) \right] & i = 1 \\ -\frac{1}{2} \sum_{j=1}^{i-1} \Delta M_j \left[K_{i,j} + K_{i,j+1} \right] \theta_j + \sum_{p=i}^{N_k-1} \Delta M_p \left[(K_{p,i} \theta_p) + (K_{p+1,i} \theta_{p+1}) \right] & 1 < i < N_k \\ -\frac{1}{2} \sum_{j=1}^{i-1} \Delta M_j \left[K_{i,j} + K_{i,j+1} \right] \theta_j + \Delta M_{i-1} K_{i,i} \theta_i & i = N_k \end{cases} \quad (6)$$

where $\Delta M_i = M_{i+1} - M_i$ is now a variable and increases with the increment of i . Note that using the MoL (Eqs. (5) or (6)), the number of evaluated molecular weight variables, N_k , is only a small fraction of the total number of reacting species in the system. This speeds up the calculation greatly.

Equation (6) is the key result of this work. To examine its validity and also to demonstrate its efficiency over the existing method (Eq. (5)), we applied both Eq. (5) and Eq. (6) to determine the MWD during a simple test case of random degradation where $k(m_r, m_s) = k_0$ is a constant. This case was chosen because it has a known analytical solution^[17]. For the initial weight-fraction MWD, we used the most probable distribution with an initial number-average chain length of 10^3 . In our numerical implementation, the molecular weight range considered was set to $[1, 3 \times 10^4 + 1]$. We used $N_k = 1501$ for the numerical scheme of Yeow *et al.*^[18] (Eq. (5)), corresponding to a discretization step size of $\Delta m = 20$. For our newly developed numerical scheme (Eq. (6)), we used a fine mesh of $N_k = 1501$ (corresponding to $\Delta \lg m = 2.98 \times 10^{-3}$) and a coarser mesh of $N_k = 301$ (corresponding to $\Delta \lg m = 1.49 \times 10^{-2}$), respectively. The computed MWD curves were represented using the weight fraction distribution function of the logarithm of molecular weight^[17], *i.e.* $W(\Delta \lg m)$ as a function $\Delta \lg m$, the same as that obtained in conventional GPC measurements.

RESULTS AND DISCUSSION

Figure 1 shows the calculated MWD curves at three reduced occasions (τ) using the numerical scheme of Yeow *et al.* (Eq. (5)) and that developed in this work (Eq. (6)) in comparison with the analytical results by Tobita (labeled as “Theory”)^[17]. Using a total number of $N_k = 1501$ grid points, the numerical method of Yeow *et al.* agrees very well with theory at $\tau = 30$. However, deviation from theory appears at low molecular weights at $\tau = 300$, and clear deviation is observed at $\tau = 1500$. As pointed out by Tobita^[17], the deviation is because the number-average chain length at $\tau = 1500$ is as small as $M_n = 20.6$, which is too small for the

discretization step size of $\Delta m = 20$ to be accurate. In contrast, using logarithmically spaced discretization points, our results fully agree with theory, not only the one using $N_k = 1501$ but also the one with a much coarser discretization $N_k = 301$. Thus, our development ensures the accuracy of the computed MWD curves at low molecular weights using the MoL, and it does not require a very fine discretization to produce an accurate result.

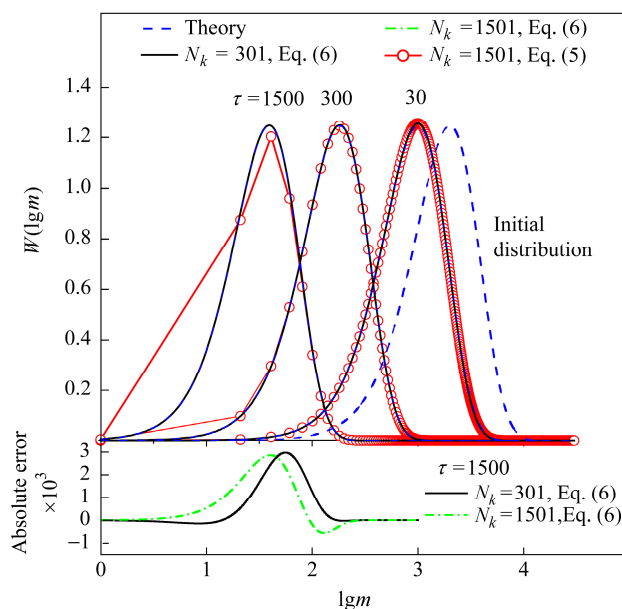


Fig. 1 Upper panel: numerical results (circles with solid lines: $N_k = 1501$, constant Δm based on Eq. (5); dotted line: $N_k = 1501$, constant Δlgm based on Eq. (6); solid line: $N_k = 301$, constant Δlgm based on Eq. (6)) compared with the theoretical (dashed line) molecular weight distributions for random degradation of linear polymer chains with the initial most probable distribution (From right to left: the reduced degradation time τ is 0 (initial distribution), 30, 300 and 1500. The numerical results using logarithmically spaced points (Eq. (6)) nearly overlap with theory at all simulated occasions, and therefore their differences are difficult to see in the upper panel of the figure); Lower panel: absolute error (numerical results-theoretical results) of our numerical results at $\tau = 1500$

While we considered here a simple case of random degradation, the numerical scheme (Eq. (6)) proposed can be applied to determine the MWD development for more general cases of polymer degradation and for arbitrarily complex initial MWD curves.

CONCLUSIONS

A numerical method is developed for calculating the evolution of MWD curves of linear polymers undergoing chain scission. The method is based on the method of lines. Different from the existing numerical scheme in which linearly spaced discretization points were used, we propose using logarithmically spaced points. We show that this development ensures the accuracy of the computed MWD curves at low molecular weights, and it does not require a very fine discretization.

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