

## 분자 사슬의 무작위 절단 매카니즘으로 분해되는 고분자의 수평균 및 중량평균 중합도의 경시 변화

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### Prediction of the Number- and Weight-Average Degree of Polymerization of Polymers Subjected to Random Chain Scission Degradation

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**초록:** 분자 사슬의 무작위 절단 매카니즘으로 분해되는 고분자의 수평균( $\mu_n$ ) 및 중량평균 중합도( $\mu_w$ )를 예측할 수 있는 새로운 이론식을 유도하였다. 이전의 이론식들은 고분자의 분해 과정에서 생성되는 단량체를 포함하는 저분자량 물질이 제거되지 않고 고분자 시료 내에 모두 잔존한다고 가정한 상태에서 유도되었으나, 본 이론식은 중합도가 ( $m-1$ ) 보다 낮은 단량체 및 올리고머가 고분자 시료로부터 모두 제거되는 것을 고려하여 유도되었다. 이전의 이론식들은  $1/\mu_n$ 이 분해 시간에 따라 직선적으로 증가하며 분자량 분포 지수 ( $Q=\mu_w/\mu_n$ )가 2로 수렴한다고 예측하였으나 본 이론식에 의하면,  $m$  값이 커짐에 따라  $1/\mu_n$ 과 시간 사이의 관계가 직선으로부터 현저히 벗어나며  $Q$ 의 접근값이 2 보다 크게 낮아지는 것으로 예측되었다.

**Abstract:** New theoretical model equations were derived to predict the number- ( $\mu_n$ ) and weight-average degree of polymerization ( $\mu_w$ ) of polymers subjected to random chain scission degradation. Unlike previous theoretical equations, which were set up assuming that low molecular weight products, even including monomeric substances remain unrecovered in the polymer residue throughout degradation, the new model considered the concomitant removal of oligomers with a degree of polymerization  $\leq m-1$ . The previous models (corresponding to  $m=1$ ) predicted that  $1/\mu_n$  increases linearly with increasing degradation time and that the polydispersity ( $Q=\mu_w/\mu_n$ ) approaches asymptotically to 2. In contrast, as the value of  $m$  increases, the deviation from the linear relationship between  $1/\mu_n$  and time becomes increasingly significant, and the asymptotic value of  $Q$  becomes much less than 2.

**Keywords:** theoretical equations, random chain scission, removal of oligomers, thermal degradation, hydrolysis.

### Introduction

Synthetic commodity polymers, particularly polyethylene (PE), polypropylene (PP), polystyrene (PS), and poly(vinyl chloride) (PVC) are used worldwide owing to their versatile physical and chemical properties,<sup>1</sup> but cause huge municipal waste issues.<sup>2</sup> The thermal recycling of plastic waste has found increasing importance, in addition to material recycling, to address these serious issues by converting the plastic waste

into fuels.<sup>3</sup> Several reactions by different mechanisms, i.e., end-chain scission or unzipping, random-chain scission, chain stripping, and cross-linking can occur simultaneously during thermal pyrolysis of polymers.<sup>2</sup>

The thermal pyrolysis of PE and PP has attracted considerable attention,<sup>3-9</sup> because they are among the most abundant polymeric waste materials comprising 60-70% of municipal plastics waste, and because the degradation products could be of sufficient value to offset the collection and pyrolysis costs.<sup>7</sup>

The thermal degradation of PE and PP has been claimed to mainly follow the random chain scission route. On the other hand, direct evidence for random chain scission has not yet been presented.

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Hydrolytic degradation is an important step for assimilating polymer molecules by microorganisms because large polymeric molecules should be fragmented into substances with a molecular weight less than 500 to pass through the cell membrane of the microorganisms.<sup>10</sup> Doi *et al.*<sup>11-14</sup> and Lauzier *et al.*<sup>15</sup> examined the hydrolytic degradation of poly(3-hydroxybutyrate), and its copolymers with 3-hydroxyvalerate and 4-hydroxybutyrate. They concluded that the hydrolysis of aliphatic polyesters took place through a random chain scission mechanism. Lin *et al.*<sup>16</sup> examined the hydrolysis of poly(lactic acid) (PLA) by comparing the molecular weight distribution of PLA with their results simulated using the Monte Carlo method. They reported that the hydrolysis reaction rate depended on the chain length of PLA. Therefore, PLA with a longer chain length had a larger reaction rate than that with a shorter chain length. Wadsö and Karlsson,<sup>17</sup> Codari *et al.*<sup>18</sup> and Pickett and Coyle<sup>19</sup> also examined the hydrolysis of other condensation polymers.

A linear relationship between  $1/\mu_n$  and time has been presented as direct evidence for the random chain scission degradation of polymeric materials. On the other hand, this linear relationship is valid only when all the degradation products, even monomeric substances, remain unremoved in the polymer residue throughout the degradation procedure, which is unreasonable, because a variety of volatile substances normally evaporated off during thermal degradation of polymers. During hydrolysis as well, oligomeric products may be removed from the mother polymeric substances depending on the solubility of the oligomeric products in the hydrolyzing medium.

In this study, theoretical equations were derived to predict  $\mu_n$  and  $\mu_w$  as a function of time taking into consideration the elimination of degradation products with a degree of polymerization  $\leq m-1$  from the polymer residue during degradation.

### Model Description

Previous equations of  $\mu_n$  as a function of time were derived for the random chain scission degradation defining the  $k^{\text{th}}$  moment, as shown in eq. (1).

$$\lambda_k = \sum_{n=1}^{\infty} n^k [P_n] \tag{1}$$

where  $[P_n]$  is the number of moles of molecules with a degree of polymerization,  $n$ .

The number average degree of polymerization was deter-

mined using eq. (2).

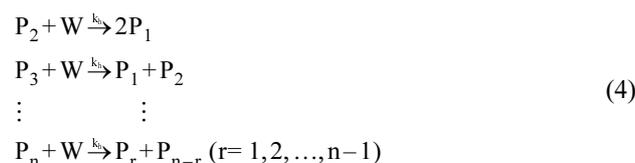
$$\mu_n = \frac{\lambda_1}{\lambda_0} \tag{2}$$

Using the moments in eq. (1), Yoon *et al.*<sup>20</sup> proved the linear relationship between  $1/\mu_n$  and time theoretically if the chain scission reaction proceeds isothermally in a random manner.

On the other hand, the moment equation should be redefined as eq. (3) instead of eq. (1) to take into account the removal of the oligomers up to a degree of polymerization,  $m-1$ .

$$\lambda_k = \sum_{n=m}^{\infty} n^k [P_n] \tag{3}$$

Based on the mechanism of the random chain scission degradation, as shown in eq. (4), Yoon *et al.*<sup>20</sup> derived eq. (5) using eq. (1). All the degradation products including the monomeric substances were considered to remain in the residue after degradation.



$$\frac{d\mu_n}{d\tau} = -\mu_n(\mu_n - 1) \tag{5}$$

where  $\tau = \int_0^t k_h [W] dt = k_h [W] t$  for isothermal hydrolysis.  $[W]$  and  $k_h$  are the water concentration and the hydrolysis reaction rate constant, respectively.

The integration of eq. (5) yields eq. (6).

$$\frac{1}{\mu_n} - \frac{1}{\mu_{n0}} = \left(1 - \frac{1}{\mu_{n0}}\right)(1 - e^{-\tau}) \tag{6}$$

When  $\mu_n \gg 1$ , eq. (6) becomes eq. (7), revealing a linear relationship between  $1/\mu_n$  and  $\tau$ .

$$\frac{1}{\mu_n} - \frac{1}{\mu_{n0}} = \tau \tag{7}$$

When the moment equation is redefined as eq. (3), the material balance equation for  $\mu_n$  based on the mechanism of the random chain scission degradation in eq. (4) becomes eq. (8), whose derivation is described in detail in the Appendix.

$$\ln\left(1 - \frac{1}{\mu_n - m + 1}\right) - \ln\left(1 - \frac{1}{\mu_{n0} - m + 1}\right) = -\tau \tag{8}$$

Assuming the molecular weight distribution follows the Schulz-Zimm equation<sup>21</sup> as shown in eq. (9), Yoon *et al.*<sup>20</sup> derived eq. (10) for  $\mu_w$  of polymer molecules degrading in a random manner, when all the degradation products remain unremoved in the polymer residue.

$$\lambda_3 = \frac{\lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)}{\lambda_1\lambda_0} \quad (9)$$

$$\frac{1}{\mu_w} = \frac{1}{2} \left( \tau + \frac{1}{\mu_{n0}} \right) + \left( \frac{1}{\mu_{n0}} \right)^{1/3} \left( \frac{1}{\mu_{w0}} - \frac{1}{2\mu_{n0}} \right) \left( \tau + \frac{1}{\mu_{n0}} \right)^{-1/3} \quad (10)$$

When oligomeric substances with a degree of polymerization  $\leq m-1$  are removed from the polymer residue, eq. (11) holds instead of eq. (10).

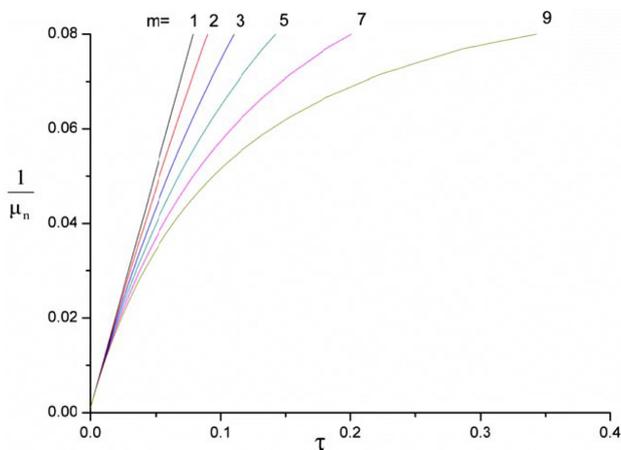
$$\frac{d\mu_w}{d\tau} = \frac{1}{3} \left\{ 1 - 2\mu_w^2 + \mu_w\mu_n - m(m-1)(2m-1) \frac{1}{\mu_n} \right\} + m(m-1) \frac{\mu_w}{\mu_n} \quad (11)$$

The derivation procedure of eq. (11) is shown in detail in the Appendix.

### Simulation Results

Figure 1 shows the variation of  $1/\mu_n$  as a function of  $\tau$  predicted using eq. (8) for  $m=1, 2, 3, 5, 7$ , and  $9$  when  $\mu_{n0}$  is 1000.

In the case when  $m=1$ , i.e., when all the hydrolysis products including monomeric substance remain unremoved in the residue, a plot of  $1/\mu_n$  vs.  $\tau$  yields a straight line with a slope of 1, irrespective of  $\mu_{n0}$ , with the intercept at the vertical axis of  $1/\mu_{n0}$ .



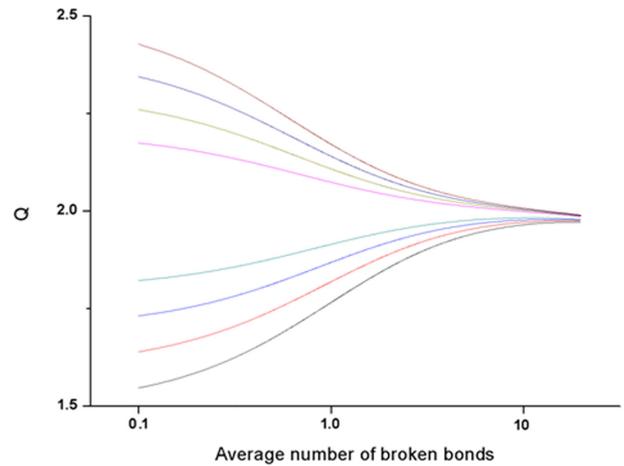
**Figure 1.** Plot of  $1/\mu_n$  vs.  $\tau$  for  $m=1, 2, 3, 5, 7$ , and  $9$ , when  $\mu_{n0}$  is 1000.

As shown in Figures 1, for  $m=2$ , corresponding to when only the monomer is removed from the polymer residue,  $1/\mu_n$  varies almost linearly with  $\tau$ . On the other hand, as  $m$  increases to 5, 7 and 9, i.e., when oligomers up to tetramer, hexamer and octamer, respectively, are removed from the residue after degradation, the deviation from the linear relationship between  $1/\mu_n$  and  $\tau$  becomes significant.

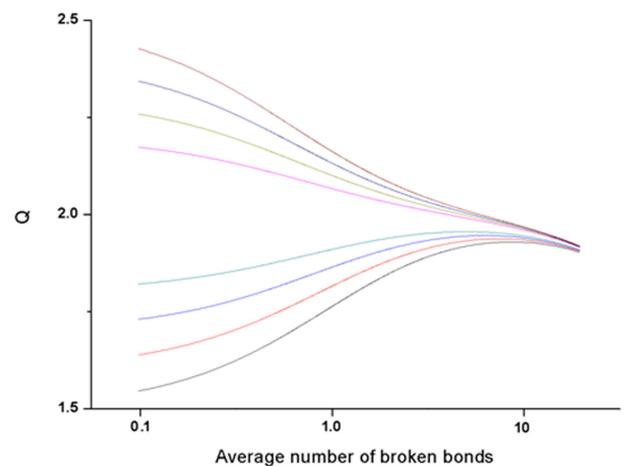
When  $m=1$ , Yoon *et al.*<sup>20</sup> obtained an analytical solution for  $\mu_w$  as eq. (10), approximating as  $|-2\mu_w^2 + \mu_w\mu_n| \gg 1$ .

On the other hand, when  $m \neq 1$ , it is practical to use the numerical integration method to integrate eq. (11).

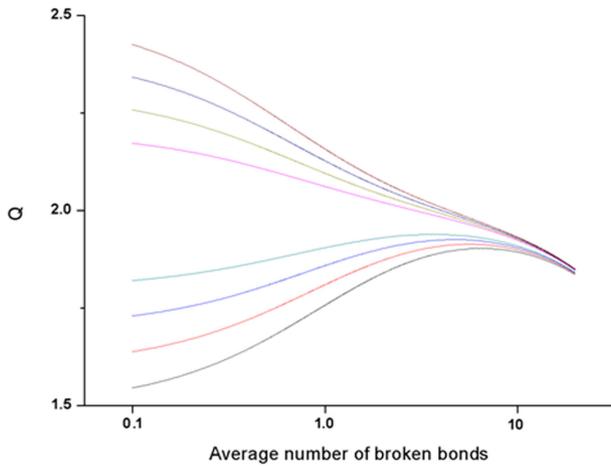
Figures 2, 3, 4, 5, and 6 show  $Q (\mu_w/\mu_n)$  as a function of the average number of broken bonds per molecule ( $B$ ) for  $m=1, 3, 5, 7$ , and  $9$ , respectively, which was predicted by the numerical



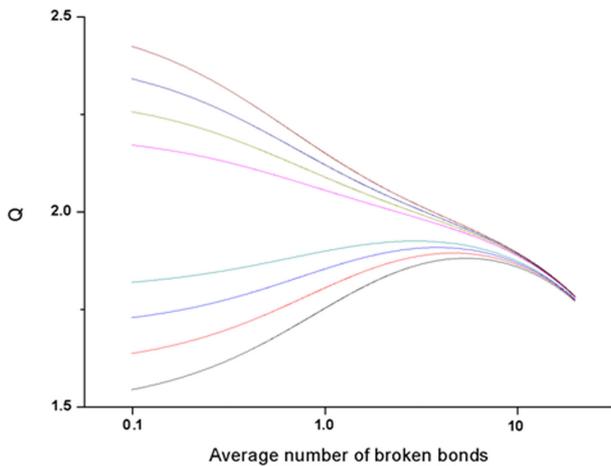
**Figure 2.**  $Q (\mu_w/\mu_n)$  as a function of the average number of broken bonds per molecule ( $B$ ) for  $m=1$ , when  $\mu_{n0}$  is 1000.



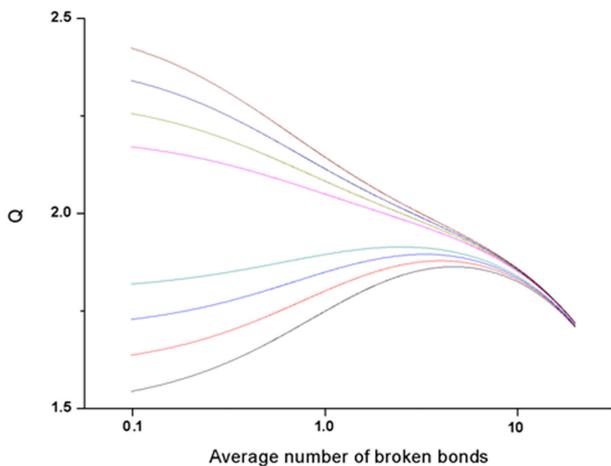
**Figure 3.**  $Q (\mu_w/\mu_n)$  as a function of the average number of broken bonds per molecule ( $B$ ) for  $m=3$ , when  $\mu_{n0}$  is 1000.



**Figure 4.**  $Q (\mu_w/\mu_n)$  as a function of the average number of broken bonds per molecule ( $B$ ) for  $m=5$ , when  $\mu_{n0}$  is 1000.



**Figure 5.**  $Q (\mu_w/\mu_n)$  as a function of the average number of broken bonds per molecule ( $B$ ) for  $m=7$ , when  $\mu_{n0}$  is 1000.



**Figure 6.**  $Q (\mu_w/\mu_n)$  as a function of the average number of broken bonds per molecule ( $B$ ) for  $m=9$ , when  $\mu_{n0}$  is 1000.

integration of eq. (11) and using eq. (8). The initial  $\mu_{n0}$  was set to 1000.

$$B = \frac{\mu_{n0} - \mu_n}{\mu_n} \tag{12}$$

When  $m=1$ ,  $Q$  approaches 2 asymptotically with increasing  $B$ , irrespective of the initial value of  $Q$ . In contrast, as the value of  $m$  increases, the asymptotic value of  $Q$  becomes less than 2. Moreover,  $Q$  increases and then decreases after showing a maximum when the initial value of  $Q$  is less than 2. At higher value of  $m$ , the maximum  $Q$  appears at a smaller  $B$ .

Therefore, eqs. (8) and (11) should be tested in lieu of eqs. (7) and (10) to determine if degradation proceeds in a random manner throughout the thermal degradation, because the  $m$  value should be much larger than 1. For hydrolysis, the same is true, particularly at later stages of hydrolysis, corresponding to large  $B$  value. Oligomers with a high degree of polymerization can also be eluted from the polymer sample during hydrolysis despite their poor solubility because the hydrolysis experiment is normally carried out by immersing a small quantity of the polymer sample into a large amount of hydrolyzing medium.

### Conclusions

The number- and weight-average degree of polymerization as a function of time could be predicted more accurately for random chain degradation by eqs. (8) and (11) rather than by eqs. (7) and (10), respectively. The thermal degradation of PE and PP is particularly the case, because, it proceeds at temperatures higher than 400 °C so that the degradation products with a high degree of polymerization may be devolatilized off from the polymer residue. The same situation may also be applicable to the hydrolysis of polymers, because hydrolysis experiments are normally carried out by immersing a very small amount of polymer sample in a large amount of hydrolyzing medium. Hence, the  $m$  value could be much larger than 1, even though oligomers with a high degree of polymerization may be sparingly soluble in the hydrolyzing medium. A plot of  $1/\mu_n$  vs.  $\tau$  yielded a straight line with a slope of 1 when the polymeric chain cleavage occurs in a random manner if all the degradation products including monomeric substances remain unremoved in the residue. On the other hand, as  $m$  increases, the deviation from the linear relationship between  $1/\mu_n$  and  $\tau$  becomes significant. The polydispersity,  $Q$ , approaches 2 asymptotically with increasing number of broken bonds,  $B$ ,

irrespective of the initial value of  $Q$  when  $m=1$ . On the contrary, as the value of  $m$  increases, the asymptotic value of  $Q$  goes far below 2.

## Appendix

### Derivation of Equations Correlating $\mu_n$ with Time Taking into Account the Removal of Oligomers

If oligomers  $\leq (m-1)$ -mer are removed from the polymer residue during degradation, the moment equation should be redefined as eq. (3).

From the mechanism in eq. (4), the material balance becomes

$$\frac{d[P]}{d\tau} = - \sum_{n=m}^{\infty} (n-1)[P_n] + 2 \sum_{n=m}^{\infty} \sum_{i=n+1}^{\infty} [P_i] \quad (A1)$$

$$\text{where } [P] = \sum_{n=m}^{\infty} [P_n]$$

According to Gupta *et al.*,<sup>21</sup>

$$\sum_{n=m}^{\infty} \sum_{i=n+1}^{\infty} [P_i] = \sum_{n=m}^{\infty} (n-m)[P_n] \quad (A2)$$

Therefore, eq. (A3) holds.

$$\frac{d\lambda_0}{d\tau} = \lambda_1 + (1-2m)\lambda_0 \quad (A3)$$

In addition, eqs. (A4) and (A5) can be proved inductively.

$$\frac{d}{d\tau} \sum_{n=m}^{\infty} n[P_n] = - \sum_{n=m}^{\infty} n(n-1)[P_n] + 2 \sum_{n=m}^{\infty} n \sum_{i=n+1}^{\infty} [P_i] \quad (A4)$$

$$\sum_{n=m}^{\infty} n \sum_{i=n+1}^{\infty} [P_n] = \sum_{n=m}^{\infty} \frac{(n+m-1)(n-m)}{2} [P_n] \quad (A5)$$

Therefore,

$$\frac{d\lambda_1}{d\tau} = -m(m-1)\lambda_0, \quad (A6)$$

Because

$$\frac{d\mu_n}{d\tau} = \frac{d}{d\tau} \left( \frac{\lambda_1}{\lambda_0} \right) = \frac{\lambda_0 \left( \frac{d\lambda_1}{d\tau} \right) - \lambda_1 \left( \frac{d\lambda_0}{d\tau} \right)}{\lambda_0^2} \quad (A7)$$

the following equation holds.

$$\frac{d\mu_n}{d\tau} = -m(m-1) - (1-2m)\mu_n - \mu_n^2 \quad (A8)$$

The integration of eq. (A8) yields eq. (A9), which correlates  $\mu_n$  with  $\tau$ .

$$\ln \left( 1 - \frac{1}{\mu_n - m + 1} \right) - \ln \left( 1 - \frac{1}{\mu_{n0} - m + 1} \right) = -\tau \quad (A9)$$

If  $\frac{1}{\mu_n - m + 1}$  and  $\frac{1}{\mu_{n0} - m + 1}$  are  $\ll 1$ , eq. (A9) can be approximated to eq. (A10),

$$\frac{1}{\mu_n - m + 1} - \frac{1}{\mu_{n0} - m + 1} = \tau, \quad (A10)$$

because  $\ln(1-x) = -\sum_{n=1}^{\infty} \frac{x^n}{n} \doteq -x$  when  $x \ll 1$ .

Of course, when  $m-1 \ll \mu_n$ , eq. (A10) approaches eq. (7).

### Derivation of Equations Correlating $\mu_w$ with Time Taking into Account the Removal of Oligomers

According to the hydrolysis mechanism (4), the material balance becomes eq. (A11)

$$\frac{d}{d\tau} \left( \sum_{n=m}^{\infty} n^2 [P_n] \right) = - \sum_{n=m}^{\infty} n^2 (n-1) [P_n] + 2 \sum_{n=m}^{\infty} n^2 \sum_{i=n+1}^{\infty} [P_i] \quad (A11)$$

Because eq. (A12) can be proved inductively,

$$\sum_{n=m}^{\infty} n^2 \sum_{i=n+1}^{\infty} n^2 [P_i] = \sum_{n=m}^{\infty} \frac{n(n-1)(2n-1) - m(m-1)(2m-1)}{6} [P_n] \quad (A12)$$

eq. (A11) becomes eq. (A13).

$$\begin{aligned} \frac{d}{d\tau} \left( \sum_{n=m}^{\infty} n^2 [P_n] \right) &= - \sum_{n=m}^{\infty} n^2 (n-1) [P_n] \\ &+ \frac{1}{3} \sum_{n=m}^{\infty} \{ n(n-1)(2n-1) - m(m-1)(2m-1) \} [P_n] \end{aligned} \quad (A13)$$

Adopting the moments in eq. (3), eq. (A13) can be arranged as eq. (A14)

$$\frac{d\lambda_2}{d\tau} = -\frac{1}{3}\lambda_3 + \frac{1}{3}\lambda_1 - \frac{1}{3}m(m-1)(2m-1)\lambda_0 \quad (A14)$$

Therefore, the time derivative of  $\mu_w$  can be expressed as eq. (A15)

$$\frac{d}{d\tau}(\mu_w) = \frac{d}{d\tau}\left(\frac{\lambda_2}{\lambda_1}\right) = \frac{\lambda_1 \frac{d\lambda_2}{d\tau} - \lambda_2 \frac{d\lambda_1}{d\tau}}{\lambda_1^2} \quad (\text{A15})$$

Placing eq. (A6) and (A14) into eq. (A15) and assuming the molecular weight distribution to follow the Schulz-Zimm equation,<sup>21</sup> eq. (A15) can be simplified as eq. (A16).

$$\frac{d\mu_w}{d\tau} = \frac{1}{3} \left\{ 1 - 2\mu_w^2 + \mu_w \mu_n - m(m-1)(2m-1) \frac{1}{\mu_n} \right\} + m(m-1) \frac{\mu_w}{\mu_n} \quad (\text{A16})$$

Modification of the equations proposed by Lin *et al.*<sup>7</sup>

Lin *et al.*<sup>7</sup> obtained an analytical solution for the variation of  $\mu_n$  as a function of time for the random chain scission hydrolysis of polymers possessing one COOH group per molecule, such as PLA, so that the rate of ester bond cleavage is equal to the rate of generation of PLA molecules.

$$\frac{d[\text{COOH}]}{dt} = k_h[\text{ester}][W] \quad (\text{A17})$$

Lin *et al.*<sup>7</sup> assumed that [ester] is constant.

Integration of eq. (A17) was successful even though Lin *et al.*'s assumption was alleviated as follows:

eqs. (A18) and (A19) are valid for polymers possessing one COOH group per molecule.

$$[\text{COOH}] = \sum_{n=m}^{\infty} [P_n] \quad (\text{A18})$$

$$[\text{COOH}]_0 = \sum_{n=1}^{\infty} [P_n]_0 \quad (\text{A19})$$

Therefore, the decrease in the ester bond concentration is equal to the increase in COOH group concentration.

$$[\text{ester}] = [\text{ester}]_0 - ([\text{COOH}] - [\text{COOH}]_0) \quad (\text{A20})$$

If all the degradation products remain in the polymer residue, then

$$\sum_{n=1}^{\infty} n[P_n]_0 = \sum_{n=1}^{\infty} n[P_n] \quad (\text{A21})$$

and thus eq. (A22) holds.

$$[\text{COOH}] = [\text{COOH}]_0 \frac{\mu_{n0}}{\mu_n} \quad (\text{A22})$$

By placing the relations of eqs. (A18)–(A22) into eq. (A17), the integration to yield eq. (6) is straightforward.

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