

# Modeling of Poly(L-lactide) Thermal Degradation: Theoretical Prediction of Molecular Weight and Polydispersity Index

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**ABSTRACT:** A mathematical model to describe the molecular weight and polydispersity index ( $Q$ ) in poly(L-lactide) (PLLA) thermal degradation has been developed. Based on the random chain scission mechanism, effects of temperature and time on the molecular weight and polydispersity index are included in this model. It incorporates the degradation and recombination reaction of PLLA thermal degradation, while taking into account the equal probability assumption. The developments of molecular weight and polydispersity index of PLLA polymer in the thermal degradation process were investigated at temperature ranging

from 180–220°C, the experimental data show PLLA reaches its thermal degradation equilibrium in 2 h. The simulated results of this model are compared with the measured molecular weight and polydispersity index of the PLLA polymer. The changes of the molecular weight and polydispersity index in the PLLA thermal degradation can be predicted by this model. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2557–2562, 2003

**Key words:** modeling; degradation; molecular weight distribution

## INTRODUCTION

Poly-L-lactide (PLLA) is a thermoplastic and biodegradable polyester. Its polymers and copolymers are currently receiving industrial attention for use as commodity resins.<sup>1</sup>

PLLA can be directly prepared by polycondensation of lactic acid; however, it is hard to increase the molecular weight enough due to the difficulty of removing the water from the system.<sup>2</sup> To achieve high molecular weight the preparation must be carried out by ring-opening polymerization of the cyclic dimer of lactic acid-lactide in the presence of various catalysts, which is relatively complicated and expensive.<sup>2</sup>

The ester linkages of PLLA tend to degrade during thermal processing or under hydrolytic conditions, and thus affect the final properties of the polymer, such as the mechanical strength and the rate of hydrolytic degradation. The PLLA undergoes thermal degradation at temperatures lower than the melting point of the polymer but the degradation rate rapidly increases above the melting point. It has been suggested that the thermal degradation of PLLA is a random main-chain scission reaction of first order.<sup>3</sup> According

to earlier reports, the reactions involved in the PLLA degradation can be hydrolysis, depolymerization,<sup>4</sup> oxidation degradation,<sup>3</sup> as well as intramolecular and intermolecular reactions.<sup>4</sup> Acidic end groups, residual catalyst, residual monomers, and other impurities have been reported to enhance the thermal degradation.<sup>4</sup> As the thermal processing of PLLA causes an undesired reduction of the molar mass,<sup>5</sup> it would be desired to suppress degradation in the melt.

As reported by Wachsen et al.,<sup>6</sup> the degradation of PLLA during thermal processing is mainly caused by intramolecular transesterification reactions leading to cyclic oligomers of lactic acid and lactide. Simultaneously, there is a combination of the cyclic oligomers with linear polyesters through insertion reactions. Doi and coworkers<sup>7</sup> claimed that thermal degradation and hydrolysis of microbial polyesters occurred via random chain scission regardless of the type and the chemical composition, by showing there was a linear relationship between the inverse of the number-average degree of polymerization and time.

Unfortunately, the literature on the kinetics of molecular weight and polydispersity index change during thermal processing of PLLA above the melting point is absent. Up to now the thermal degradation of PLLA in the melt has been described as a statistical process.<sup>6</sup> The changes in molecular weight were simulated by using a two-parameter model, consisting of

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TABLE I  
z-Transform Pairs

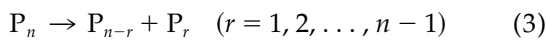
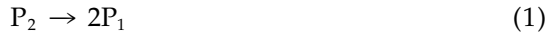
Original	Z-Transform	$z \rightarrow 1$
$-k\delta(n)$	$-kz^{-n}$	$-k$
$-k[P_n]$	$-kD(z,t)$	$-k\lambda_0$
$k \sum_{m=1}^{n-1} [P_{-m}][P_{n-m}]$	$kD^2(z,t)$	$k\lambda_0^2$
$k \sum_{m=n-1}^{\infty} [P_m]$	$\frac{k(D(1,t) - zD(z,t))}{z-1}$	$k(\lambda_1 - \lambda_0)$
$k(n-1)[P_n]$	$k \frac{\partial[-zD(z,t)]}{\partial z}$	$k(\lambda_1 - \lambda_0)$

a statistical degradation step and a recombination step.<sup>6</sup>

In this article, we attempted to theoretically calculate the changes in the molecular weight and polydispersity index of biodegradable PLLA during their thermal degradation by random chain scission mechanism. Experimental data were compared with our theoretical predictions.

### DESCRIPTION OF THE MODEL

Supposedly with all the bonds in PLLA polymer with equal probability to degrade, the mechanism of the thermal degradation can be written as:



where  $P_n$  is the PLLA polymer with a number-average degree of polymerization of  $n$ . If the rate constant of the thermal degradation of each step is  $k_d$ , the rate equation for each species is as follows:

$$\begin{aligned} \frac{d[P_1]}{dt} &= 2k_d[P_2] + 2k_d[P_3] + \dots + 2k_d[P_n] \\ &= 2k_d\{[P] - [P_1]\} \end{aligned} \quad (4)$$

$$\frac{d[P_2]}{dt} = -k_d[P_2] + 2k_d \sum_{i=3}^{\infty} [P_i] \quad (5)$$

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

where  $[P] = \sum_{i=1}^{\infty} [P_i]$ . Although there is only one way for  $P_2$  degrades into  $P_1$ , the number of the resulting  $P_1$  is 2; there are also two ways that  $P_n$  can produce  $P_1$ .

TABLE II  
Rate Equations in Terms of Moments for PLLA Thermal Degradation

$\frac{d\lambda_0}{dt} = k_d(\lambda_1 - \lambda_0) - \frac{k_c\lambda_0^2}{2}$
$\frac{d\lambda_1}{dt} = k_d(\lambda_1 - \lambda_0)$
$\frac{d\lambda_2}{dt} = \frac{k_d(\lambda_1 - \lambda_0)}{3} + k_c\lambda_1^2$

Thus, a factor of 2 is required in eqs. (4), (5), and (6). On the other hand, there are  $(n-1)$  ester bonds in the chain of  $P_n$ ,  $(n-1)$  ways exist for  $P_n$  to degrade, and a factor of  $(n-1)$  appears in eq. (6).

Taking into account of the inverse recombination reaction with rate constant each step is  $k_c$ , the rate equation can be given:

$$\frac{d[P_n]}{dt} = \frac{1}{2}k_c \sum_{i=1}^{n-1} [P_i][P_{n-r}] - k_c[P_n] \sum_{i=1}^{\infty} [P_i] \quad (n = 2, 3, \dots) \quad (7)$$

Summing all equations in eqs. (6) and (7), the total equation for  $P_n$  is summarized as eq. (8):

$$\begin{aligned} \frac{d[P_n]}{dt} &= -(n-1)k_d[P_n] + 2k_d \sum_{i=n-1}^{\infty} [P_i] \\ &+ \frac{1}{2}k_c \sum_{i=1}^{n-1} [P_i][P_{n-r}] - k_c[P_n] \sum_{i=1}^{\infty} [P_i] \quad (n = 2, 3, \dots) \end{aligned} \quad (8)$$

### Z-TRANSFORM

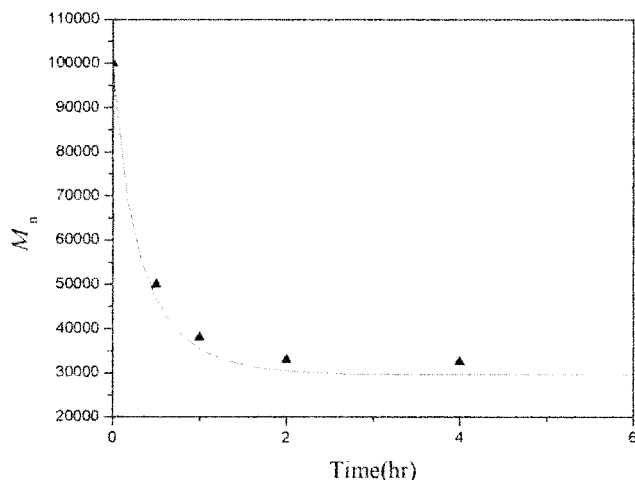
The numerical integration of eq. (8) for the individual molecular species is extremely cumbersome and time consuming. To simplify the analysis, it is possible to study the molecular weight distribution (MWD) in terms of different orders of moments defined as:

$$\lambda_i = \sum_{n=1}^{\infty} n^i [P_n] \quad i = 0, 1, 2, 3 \quad (9)$$

Associating z-transform with the time-varying concentrations  $[P_n]$  as:

TABLE III  
Preexponential Constant  $A$  and energies of activation  $E_a$  for Recombination ( $k_c$ ) and Degradation ( $k_d$ ) in the case of Purified PLLA Polymer

$A_c/10^3 \text{ mol} \cdot \text{s}^{-1}$	$E_c/\text{kJ} \cdot \text{mol}^{-1}$	$A_d/10^6 \text{ s}^{-1}$	$E_d/\text{kJ} \cdot \text{mol}^{-1}$
$2.2 \pm 0.2$	$49 \pm 15$	$7.0 \pm 0.3$	$120 \pm 20$



**Figure 1** Plot of  $M_n$  vs. time at 200°C in  $N_2$  atmosphere: (▲) experimental, — simulated.

$$D(z, t) = \sum_{n=1}^{\infty} z^{-n} [P_n] \quad (10)$$

We can find the following relationship between  $\lambda_i$  and  $D(z,t)$ :

$$\lambda_i = \left. \frac{\partial^i D(z, t)}{(\partial \ln z^{-1})^i} \right|_{z=1} \quad (11)$$

Using the above eq. (11), the following  $z$ -transform pairs are got as shown in Table I.

On the basis of Table I, a set of rate equations in terms of moments for PLLA thermal degradation has been well established, as shown in Table II, wherein various orders of moments  $\lambda_i$  appear, for instance,  $\lambda_0$  corresponding to the number of molecules,  $\lambda_1$  to their mass, etc.

To solve the rate equations of Table II, it is required to “break” the hierarchy of equations. The following approximations<sup>8</sup> are used for this purpose:

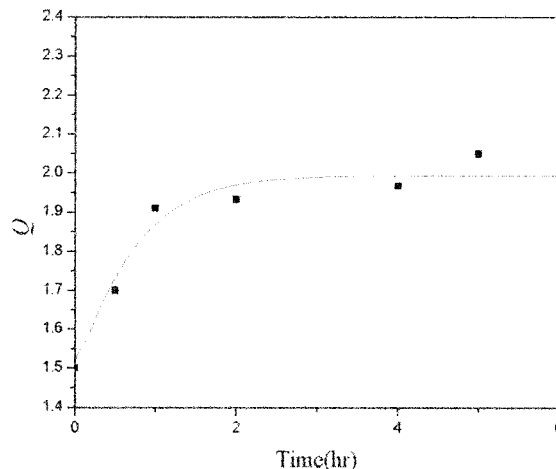
$$\lambda_3 = \frac{\lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)}{\lambda_1\lambda_0} \quad (12)$$

The recombination and degradation rate constant,  $k_c$  and  $k_d$ , which depends on temperature, can be described by an Arrhenius equation.

$$k_c = A_c \exp\left(\frac{-E_c}{RT}\right) \quad (13)$$

$$k_d = A_d \exp\left(\frac{-E_d}{RT}\right) \quad (14)$$

The activation energy ( $E_d$ ) and preexponential constant ( $A$ ) are shown in Table III given by Wachsen.<sup>6</sup>



**Figure 2**  $Q$  vs. time at 200°C in  $N_2$  atmosphere: (■) experimental, — simulated.

The number- and weight-average degree of polymerization ( $i_n$  and  $i_w$ ) can be computed at any stage as follows:

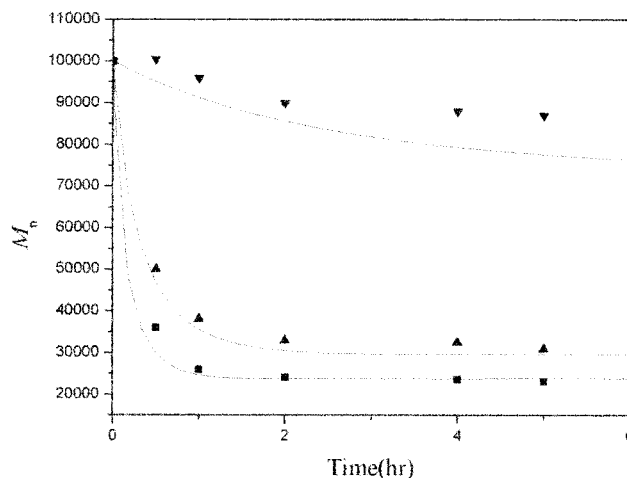
$$\mu_n = \frac{\lambda_1}{\lambda_0} \quad (15)$$

$$\mu_w = \frac{\lambda_2}{\lambda_1} \quad (16)$$

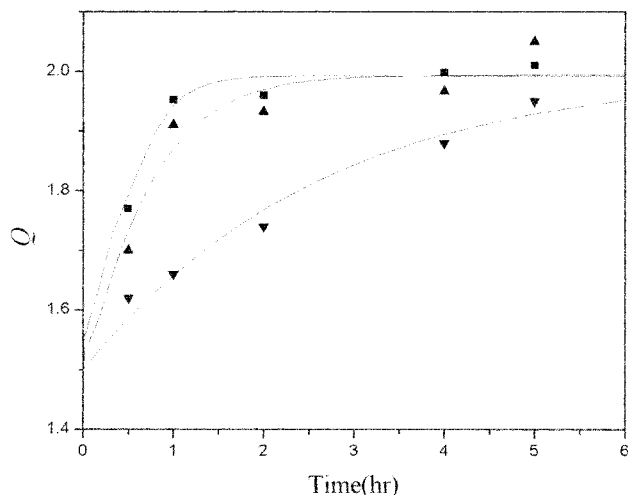
The polydispersity index,  $Q$ , is given by

$$Q = \frac{\mu_w}{\mu_n} = \frac{\lambda_2\lambda_0}{\lambda_1^2} \quad (17)$$

The differential equations in Table II are solved by the Runge-Kutta method of fourth order (ODE45) in Matlab5.3.



**Figure 3** Changes in  $M_n$  of PLLA at different temperatures in  $N_2$  atmosphere: (▼) 180°C, (▲) 200°C, (■) 220°C experimental, — simulated.



**Figure 4** Changes in  $Q$  of PLLA at different temperatures in  $N_2$  atmosphere: (▼) 180°C, (▲) 200°C, (■) 220°C experimental, — simulated.

## EXPERIMENTAL

### Materials

Poly(L-lactide) was prepared by ring-opening polymerization in the melt using stannous octoate (0.04 wt %) as a catalyst, the initial number-average molecular weight ( $M_{n0}$ ) was about 108,000 kg/mol. Samples for thermal degradation process were dissolved in chloroform and precipitated in methanol. The precipitated polymer powder was dried under vacuum to a constant weight for 36h at 45°C.

### Thermal degradation process

The thermal degradation was carried out in a four cylindrical, glass reaction vessel of 100-mL capacity, equipped with  $N_2$  flowmeter with a range from 30 to 300 mL/min. The vessel was charged by 3.0–5.0g of the PLLA precursor, the temperature was increased to

180–220°C, depending on the melting temperature of the PLLA sample. The thermal degradation process was carried out for 0.5–6 h, after defined time, taking a 0.5-g sample of the PLLA polymer to denote a molecular weight and polydispersity index.

### Measurements

For the PLLA polymer after thermal degradation process, the weight- and number-average molecular weight ( $M_w$  and  $M_n$ ), the polydispersity index were obtained by Gel Permeation Chromatograms (GPC), using four columns of Microstyrogel<sup>®</sup> and tetrahydrofuran as the mobile phase.

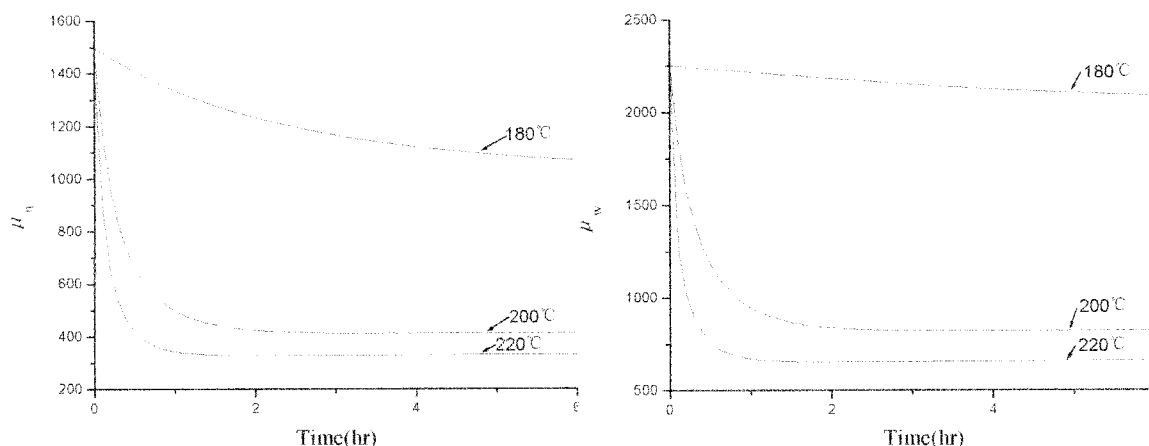
## RESULTS AND DISCUSSION

Utilizing the kinetic data given by Wachsen,<sup>6</sup> simulations by the rate equations (Table II) were executed to demonstrate the continuous responses to each reaction. Figures 1–4 demonstrates a fairly good agreement between the simulation curves and the experimental data.

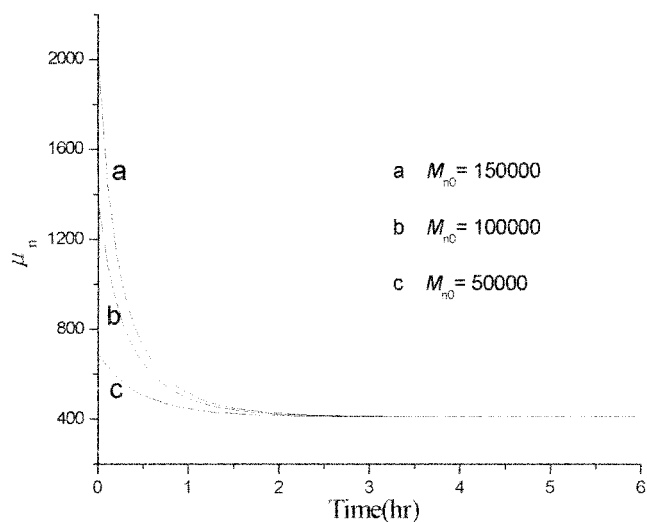
As observed in Figure 1, it is found that the number-average molecular weight of PLLA decrease quickly with the increase of time at 200°C in  $N_2$  atmosphere, and reaches its equilibrium in 2 h. The experimental data show the similar trend, though which are relative slowly than the simulation curve.

Change of polydispersity index of PLLA at 200°C in  $N_2$  atmosphere is shown in Figure 2. The polydispersity index asymptotically approaches a value of 2 in 2 h, where the simulated curve is based on the set of equations of Table II. This conclusion is theoretically compatible with that of Flory's statistical theory,<sup>9</sup> which predicts that the value of polydispersity index of polymer without regulator is about 2.

According to random chain scission model, if the polydispersity index of the initial PLLA is less than 2,



**Figure 5** Changes in number- and weight-average degree of polymerization ( $i_{\mu_n}$  and  $i_{\mu_w}$ ) of PLLA at 180, 200, and 220°C in  $N_2$  atmosphere: — simulated.

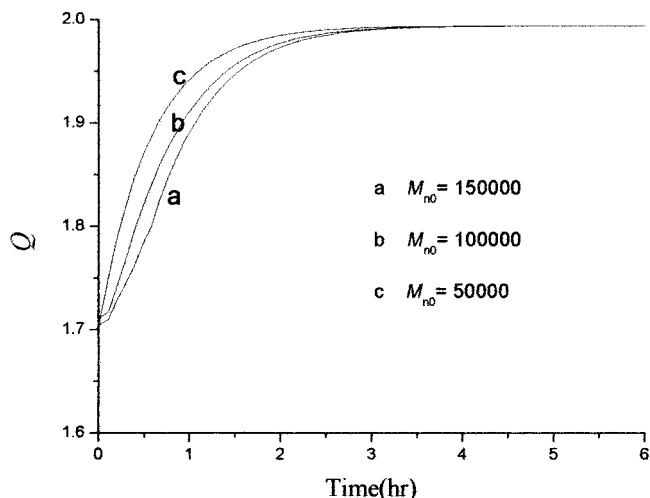


**Figure 6**  $\bar{i}_n$  vs. time of PLLA with different  $M_{n0}$  at 200°C in  $N_2$  atmosphere: — simulated.

it will increase up to a value of 2 as random chain scission progressing. However, if  $Q$  is greater than 2 initially, it will decrease to 2. And the value of  $Q$  is expected to remain constant, if the initial value is around 2. However, as PLLA polymer degrades to monomeric species completely,  $Q$  should approach 1.

As shown in Figures 3 and 4, both the number-average molecular weight and the polydispersity index are sensitive to the increase or decrease of temperature. The influence of varying the temperature on the number-average molecular weight is obvious.

The simulated result of the changes in number-average and weight-average degree of polymerization of PLLA at 180, 200, 220°C in  $N_2$  atmosphere are also shown in Figure 5. From Figure 5, we can find the similar trend as shown in Figure 3: as the temperature is higher, the thermal degradation velocity of PLLA is

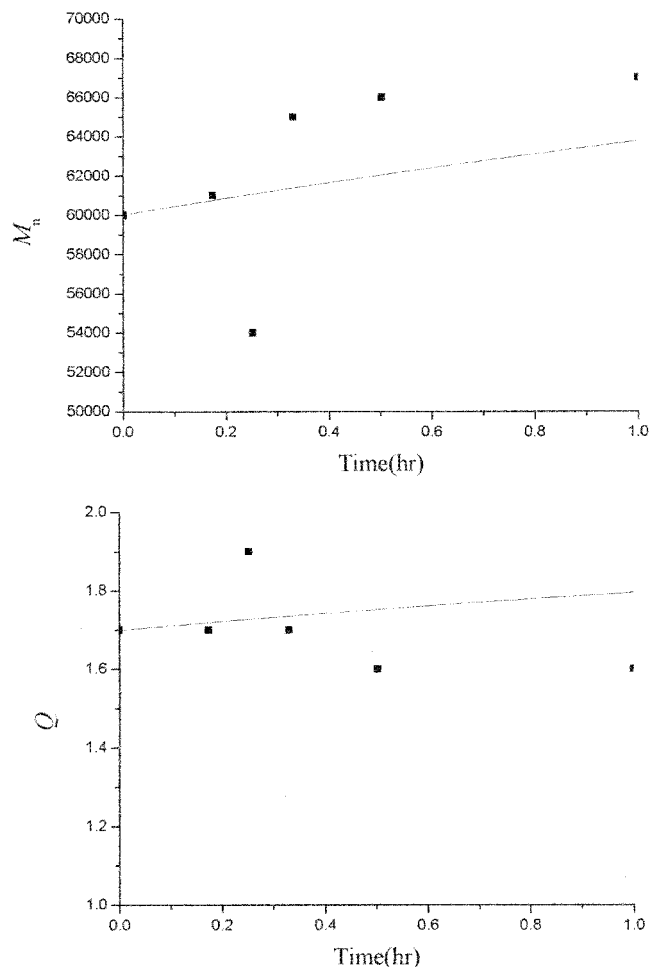


**Figure 7**  $Q$  vs. time of PLLA with different  $M_{n0}$  at 200°C in  $N_2$  atmosphere: — simulated.

faster, the final number-average or weight-average degree of polymerization of PLLA is lower, the time to reach its thermal degradation equilibrium is shorter. It is easy to see the difference among the PLLA's thermal degradation velocity and the final number- or weight-average degree of polymerization at different temperatures. The number-average degree of polymerization is sensitive to the presence of low molecular weight species, while the weight-average degree of polymerization is sensitive to the presence of high molecular weight species.

Changes in number-average degree of polymerization and  $Q$  of PLLA with different  $M_{n0}$  at 200°C in  $N_2$  atmosphere are shown in Figure 6, at the same temperature (200°C). Although the thermal degradation curve is sharper with the larger  $M_{n0}$  PLLA than that of the smaller  $M_{n0}$  PLLA (Fig. 6), the larger  $M_{n0}$  PLLA needs more time to reach its thermal degradation equilibrium (Fig. 7).

Figure 8 shows the changes in the number-average molecular weight and polydispersity index of PLLA polymer, which was obtained by Wachsen.<sup>6</sup> Both the



**Figure 8** Plots of  $M_n$  and  $Q$  vs.time for PLLA at 180°C. Data obtained by Wachsen et al.<sup>6</sup> (— simulated).

number-average molecular weight and the polydispersity index agree with the prediction of eqs. (15) and (17) based on the random chain scission degradation model in the first 30 min. The agreement between the prediction and the experimental result is poor in the next 30 min.

### CONCLUSION

Based on the random chain scission mechanism, the changes of the molecular weight and polydispersity index in the PLLA thermal degradation process can be predicted by this mathematical model, including a degradation reaction and its inverse reaction. The rate equations in terms of moments were derived by applying the *Z*-transform technique and solved by the Runge-Kutta method. The results from this new model were found to be quite consistent with the experimental data. Both the number-average molecular weight and the polydispersity index of purified PLLA polymer are sensitive to the increase or decrease of temperature, and reach its equilibrium in 2 h.

### NOMENCLATURE

$P_1$  L-lactide  
 $P_2$  linear dimer  
 $P_3$  linear trimer  
 $P_n$  polymer chain with *n* monomeric units  
*A* preexponential constant

$A_c$  preexponential constant of recombination reaction ( $\text{mol} \cdot \text{s}^{-1}$ )  
 $A_d$  preexponential constant of degradation reaction ( $\text{s}^{-1}$ )  
 $E_a$  activation energies ( $\text{kJ} \cdot \text{mol}^{-1}$ )  
 $E_c$  activation energies of recombination reaction ( $\text{kJ} \cdot \text{mol}^{-1}$ )  
 $E_d$  activation energies of degradation reaction ( $\text{kJ} \cdot \text{mol}^{-1}$ )  
 $k_c$  recombination rate constant ( $\text{kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ )  
 $k_d$  degradation rate constant ( $\text{kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ )  
*Q* polydispersity index  
 $\lambda_i$  the *i*th order moment of all polymer molecules  
 $i_n$  number-average degree of polymerization  
 $i_w$  weight-average degree of polymerization  
 $[\ ]$  square brackets stand for concentration ( $\text{mol} \cdot \text{kg}^{-1}$ )

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