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Theoretical prediction of weight loss and molecular weight during random chain scission degradation of polymers

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The number-average molecular weight and weight loss of a polymer are predicted by considering that oligomeric substances are produced by random chain scission degradation and they are removed upon being formed. Model calculation shows that the higher the degree of polymerization of the extractable oligomers, the faster the rate of weight loss and the slower the rate of the decrease in the number-average molecular weight of the remaining polymer. When the weight change of poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) due to hydrolysis was monitored experimentally, it was found to be consistent with the theoretical prediction, only if the oligomers, whose degree of polymerization was less than 60, were dissolved. The observed weight loss of the polymer was interpreted to be caused by the fragmentation rather than the dissolution of the oligomers. As the number of broken bonds increased, the weight fraction of the monomer due to degradation approached one, while that of the oligomers due to degeneration approached zero after reaching a maximum. The lower the degree of polymerization of the oligomers, the higher the number of broken bonds of the maximum weight fraction. © 1997 Elsevier Science Ltd.

(Keywords: polymer degradation; random chain scission; simulation)

INTRODUCTION

Biodegradable polymers are widely used as environmentally friendly materials and for medical applications such as surgical sutures[1], implants for bone fixation, etc.[2]. Their biodegradability due to enzymes[3,4], micro-organisms[5,6] or hydrolysis[7–11] can be evaluated by monitoring of CO_2 generation, O_2 consumption, or the change in molecular weight, physical properties and weight with time.

It has been known[7,10,12] that when polymer molecules degrade via random chain scission, there is a linear relationship between the inverse of the number-average molecular weight and the degradation time. This can be satisfied only if the low molecular weight substances resulting from random chain scission degradation remain in the sample and the number-average degree of polymerization is far greater than 1[11]. However, as a result of degradation many types of low molecular weight substances are produced and they may be either volatile or water-soluble. A majority of the degradation studies failed to consider the production of these low molecular weight substances and they simply measured the change in the molecular weight as a function of time. While the degradation by enzymes or micro-organisms occurs preferentially on the polymer surface, hydrolytic degradation can proceed uniformly in the bulk of the specimen as long as the rate of polymer chain scission is lower than the diffusion rate of water into the bulk. However, for thick samples there would be an autocatalytic effect in the centre as a result of an increase in acidity when the degradation products are acidic and have limited diffusivity[13]. The reduction in the sample weight in hydrolysis is mainly caused by the dissolution of the water-soluble low molecular weight substances. However, as the sample hydrolyses, the mechanical strength of the degraded sample also decreases and many small fragments are separated from the sample resulting in the weight loss.

In this work a random chain scission model was developed which can predict the number-average molecular weight of the polymer subjected to the homogeneous hydrolytic degradation. The low molecular weight degradation products were assumed to be dissolved in water and they were removed from the sample during hydrolysis. And, by assuming the weight loss during hydrolysis was due to the formation of water-soluble oligomers, the weight change of the polymer was calculated as a function of the number-average degree of

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*To whom correspondence should be addressed polymerization of water-soluble oligomers. They were also compared with the experimental data reported previously by other researchers[10,14].

DESCRIPTION OF THE MODEL

The mechanism of the hydrolytic degradation of a polymer can be described as follows

$$\begin{aligned} &P_2 + W \rightarrow 2P_1 \\ &P_3 + W \rightarrow P_1 + P_2 \\ &\quad\vdots \\ &P_n + W \rightarrow P_{n-r} + P_r \qquad (r = 1, \ldots, n-1) \end{aligned} \tag{1}$$

where W is a water molecule and P_i is a polymer molecule of i repeat unit. If hydrolysis of each chain occurs with equal probability, the rate constants of all elementary reactions, k_h, can be assumed to be same. Then, the mole balance equations are

$$\begin{aligned} \frac{\mathrm{d}[P_1]}{\mathrm{d}t} &= 2k_h[W]\sum_{i=2}^{\infty}[P_i] \\ \frac{\mathrm{d}[P_2]}{\mathrm{d}t} &= -k_h[W][P_2] + 2k_h[W]\sum_{i=3}^{\infty}[P_i] \\ &\vdots \\ \frac{\mathrm{d}[P_n]}{\mathrm{d}t} &= -(n-1)k_h[W][P_n] + 2k_h[W]\sum_{i=n+1}^{\infty}[P_i] \end{aligned} \tag{2}$$

Let us define $[P] = \sum_{i=1}^{\infty}[P_i]$ and $\tau = \int_0^t k_h[W]\,\mathrm{d}t$, then equation (2) becomes

$$\begin{aligned} \frac{\mathrm{d}[P_1]}{\mathrm{d}\tau} &= 2([P] - [P_1]) \\ \frac{\mathrm{d}[P_2]}{\mathrm{d}\tau} &= -[P_2] + 2\sum_{i=3}^{\infty}[P_i] \\ &\vdots \\ \frac{\mathrm{d}[P_n]}{\mathrm{d}\tau} &= -(n-1)[P_n] + 2\sum_{i=n+1}^{\infty}[P_i] \end{aligned} \tag{3}$$

The number-average degree of polymerization, μ_n, can be obtained by using equation (3)[11]

$$\frac{\mathrm{d}\mu_n}{\mathrm{d}\tau} = -\mu_n(\mu_n - 1) \tag{4}$$

For $\mu_n \gg 1$, integration of equation (4) yields

$$\frac{1}{\mu_n} - \frac{1}{\mu_{no}} = \tau \tag{5}$$

which indicates a linear relationship between $1/\mu_n$ and τ. Many researchers obtained degradation reaction rate constants from the slope of such plots[7,10,12].

Meanwhile, if degradation proceeds to such an extent that μ_n becomes closer to 1, the number-average degree of polymerization becomes

$$\frac{1}{\mu_n} - \frac{1}{\mu_{no}} = \left(1 - \frac{1}{\mu_{no}}\right)(1 - \mathrm{e}^{-\tau}) \tag{6}$$

In order to determine the hydrolysis rate many people measured the change in the molecular weight and the sample weight. Weight loss as a result of hydrolysis may be due to the dissolution of oligomers in water and also due to the fragmentation of the sample. If the weight loss is assumed to be due to the dissolution of oligomers without any resistance to diffusion, it is possible to theoretically predict the weight loss of the sample. From equation (3) the following equations are obtained

$$\begin{aligned} \frac{\mathrm{d}\lambda_0}{\mathrm{d}\tau} &= (\lambda_1 - \lambda_0) \\ \frac{\mathrm{d}[P_1]}{\mathrm{d}\tau} &= 2(\lambda_0 - [P_1]) \\ \frac{\mathrm{d}[P_2]}{\mathrm{d}\tau} &= -3[P_2] + 2([\lambda_0] - [P_1]) \\ \frac{\mathrm{d}[P_3]}{\mathrm{d}\tau} &= -4[P_3] + 2([\lambda_0] - [P_1] - [P_2]) \\ &\vdots \\ \frac{\mathrm{d}[P_n]}{\mathrm{d}\tau} &= -(n+1)[P_n] + 2\left([\lambda_0] - \sum_{i=1}^{n-1}[P_i]\right) \end{aligned} \tag{7}$$

where the moment, λ_k is $\sum_{n=1}^{\infty} n^k[P_n]$. They are integrated by using Laplace transformation to give

$$\begin{aligned} \frac{[P_1]}{\lambda_1} &= 1 - 2\left(1 - \frac{1}{\mu_{no}}\right)\mathrm{e}^{-\tau} + \left(1 - \frac{2}{\mu_{no}}\right)\mathrm{e}^{-2\tau} \\ \frac{[P_2]}{\lambda_1} &= \left(1 - \frac{1}{\mu_{no}}\right)\mathrm{e}^{-\tau} - 2\left(1 - \frac{2}{\mu_{no}}\right)\mathrm{e}^{-2\tau} + \left(1 - \frac{3}{\mu_{no}}\right)\mathrm{e}^{-3\tau} \\ &\vdots \\ \frac{[P_k]}{\lambda_1} &= \left(1 - \frac{(k-1)}{\mu_{no}}\right)\mathrm{e}^{-(k-1)\tau} - 2\left(1 - \frac{k}{\mu_{no}}\right)\mathrm{e}^{-k\tau} \\ &\quad + \left(1 - \frac{(k+1)}{\mu_{no}}\right)\mathrm{e}^{-(k+1)\tau} \end{aligned} \tag{8}$$

At the outset of hydrolysis it is assumed that there is no water-soluble oligomer in the sample. The solubility depends upon the degree of polymerization of the oligomer, and if oligomers, whose degree of polymerization is not greater than k, are assumed to be water-soluble, then

$$[P_1]_0 = [P_2]_0 = \cdots = [P_k]_0 = 0 \tag{9}$$

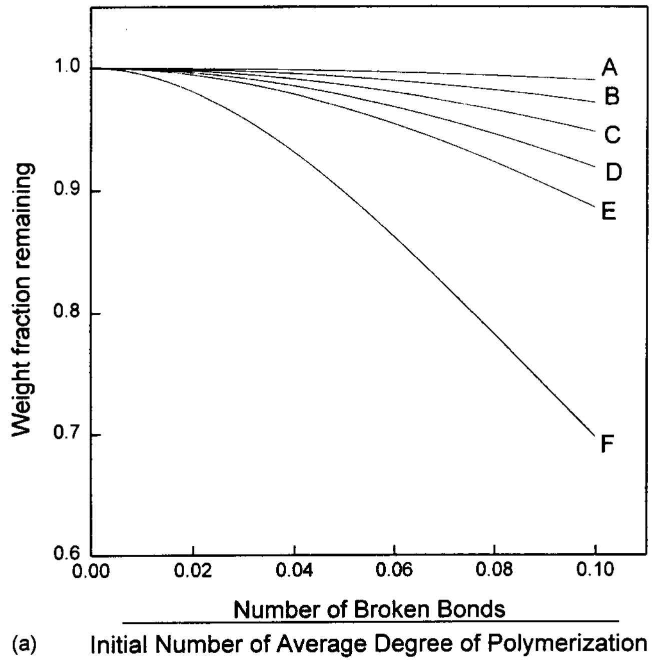
In fact, equation (9) was used as initial conditions in deriving equation (8). $[P_k]/\lambda_1$ $(k = 1, 2, \ldots, \infty)$ in equation (8) can be verified easily by the induction method.

COMPARISON OF MODEL CALCULATION WITH EXPERIMENTAL DATA

The rate of the hydrolytic degradation of polymers can be described by the change in the average molecular weight, the weight change, and so on. Doi *et al.* studied hydrolytic degradation of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV)) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-*co*-4HB))[10] and found that the molecular weight decreased rapidly with time but the change in weight was negligible. Kanesawa and Doi reported that hydrolysis of P(3HB-*co*-3HV) fibres at 37°C and 60°C caused a decrease in the molecular weight with no measurable weight loss[15]. However, at 70°C they found about 59% of weight loss after 91 days of hydrolysis. Doi and his coworkers found for P(3HB-*co*-4HB) films that at 70°C and pH 7.4 the molecular weight began to decrease rapidly from the beginning and the weight of the sample remained almost constant until the number of broken bonds reached 16[14]. However, the sample weight decreased quite rapidly afterwards. According to Arvanitoyannis *et al.*, when poly(lactic acid) was hydrolysed in basic solutions, the weight decreased steadily from the beginning, yet the molecular weight remained rather constant[9]. In fact, when water-soluble oligomers are produced from the hydrolytic degradation, they are dissolved in the buffer solution and removed from the sample. However, the papers cited above seem to have failed to take the formation of the water-soluble oligomers into consideration. They simply measured the molecular weight and the sample weight on a dry basis by taking an insoluble portion out of the solution. In equation (8) $\lambda_1 = \sum_{n=1}^{\infty} n[P_n]$, which is the total number of the monomer unit, and can be assumed to be constant regardless of the degradation time. Thus, $k[P_k]/\lambda_1$ becomes the weight fraction of k mer. If oligomers, whose degree of polymerization is equal to or less than k, are soluble in the buffer solution, the reduction in weight due to the dissolution of oligomers would amount to $\sum_{n=1}^{k} n([P_n]/\lambda_1)$. The number-average degree of polymerization of the sample, μ_n', excluding the water-soluble oligomers, whose number-average degree of polymerization is not greater than k, can be easily obtained by μ_n, the number-average molecular weight including the extractable substances, using equation (6) as follows.

$$\mu_n' = \frac{\sum_{n=1}^{\infty} n[P_n] - \sum_{n=1}^{k} n[P_n]}{\sum_{n=1}^{\infty} [P_n] - \sum_{n=1}^{k} [P_n]} = \frac{1 - \frac{1}{\lambda_1}\sum_{n=1}^{k} n[P_n]}{\frac{1}{\mu_n} - \frac{1}{\lambda_1}\sum_{n=1}^{k} [P_n]} \qquad (10)$$

When the weight loss in hydrolytic degradation is assumed to be due to the dissolution of oligomer in water, the weight loss can be predicted as shown in *Figure 1a*. Each curve corresponds to different water-soluble oligomers: for Curve A, only monomer is soluble; for Curve B, monomer and dimer are soluble; for Curve C, monomer, dimer and trimer are soluble; and so on. *Figure 1b* depicts the calculation of the number-average degree of polymerization for the polymer, whose initial degree of polymerization is 2000. As the degradation reaction rate constant increases, the number-average degree of polymerization and the sample weight change more rapidly. However, they could be described by the same curve, regardless of the degradation reaction rate constant, when they were plotted as a function of the number of broken bonds. Sample weight decreased faster, if the degree of polymerization of the water-soluble oligomers were higher, which was anticipated. We also analysed the simulation results for the samples of lower initial degree of polymerization. The lower the initial degree of polymerization of the sample, the faster the rate of weight decrease. When only the monomeric species are water-soluble, the weight change was so small that it would be measured only after the number of broken bonds per initial number-average degree of polymerization far exceeds 0.08. It is shown that the number-average degree of polymerization decreased much faster than the weight of the insoluble portion of the sample. Also, the higher the degree of polymerization of the soluble oligomers, the slower the rate of reduction in the number-average degree of polymerization of the remaining portion. Polymers having different initial degree of polymerizations followed the same weight change curves independent of the initial degree of polymerization as in *Figure 1a*, when the sample weight was plotted as a function of the number of broken bonds per initial number-average degree of polymerization.



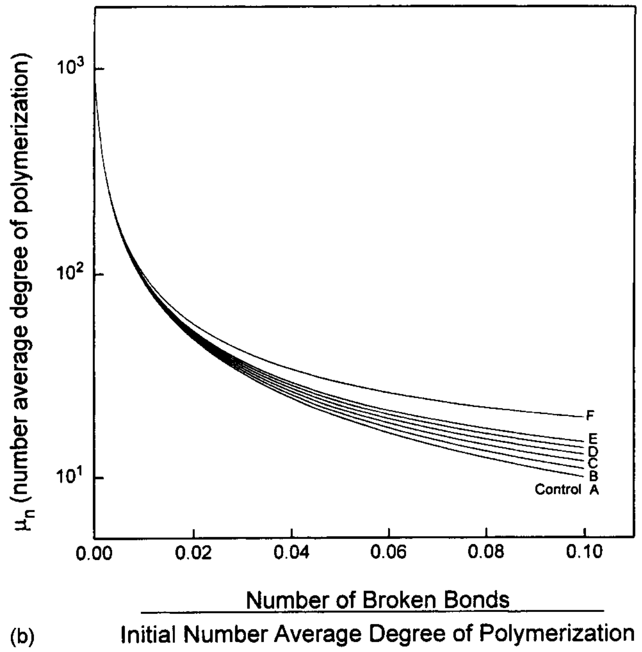


Figure 1 Weight (a) and the number-average degree of polymerization (b) of a polymer calculated by random chain scission model. (Initial number-average degree of polymerization = 2000.) Degree of polymerization of water-soluble oligomer: $A = 1$, $B = 2$, $C = 3$, $D = 4$, $E = 5$, and $F = 10$. Control includes the extractable substances

In *Figure 2* the theoretical calculations based on equations (8) and (10) were compared with the experimental data obtained by Doi *et al.* for the hydrolytic degradation of P(3HB-*co*-10 wt%-4HB)[10]. Although the initial number-average degree of polymerization of their sample was relatively high, the number of broken bonds

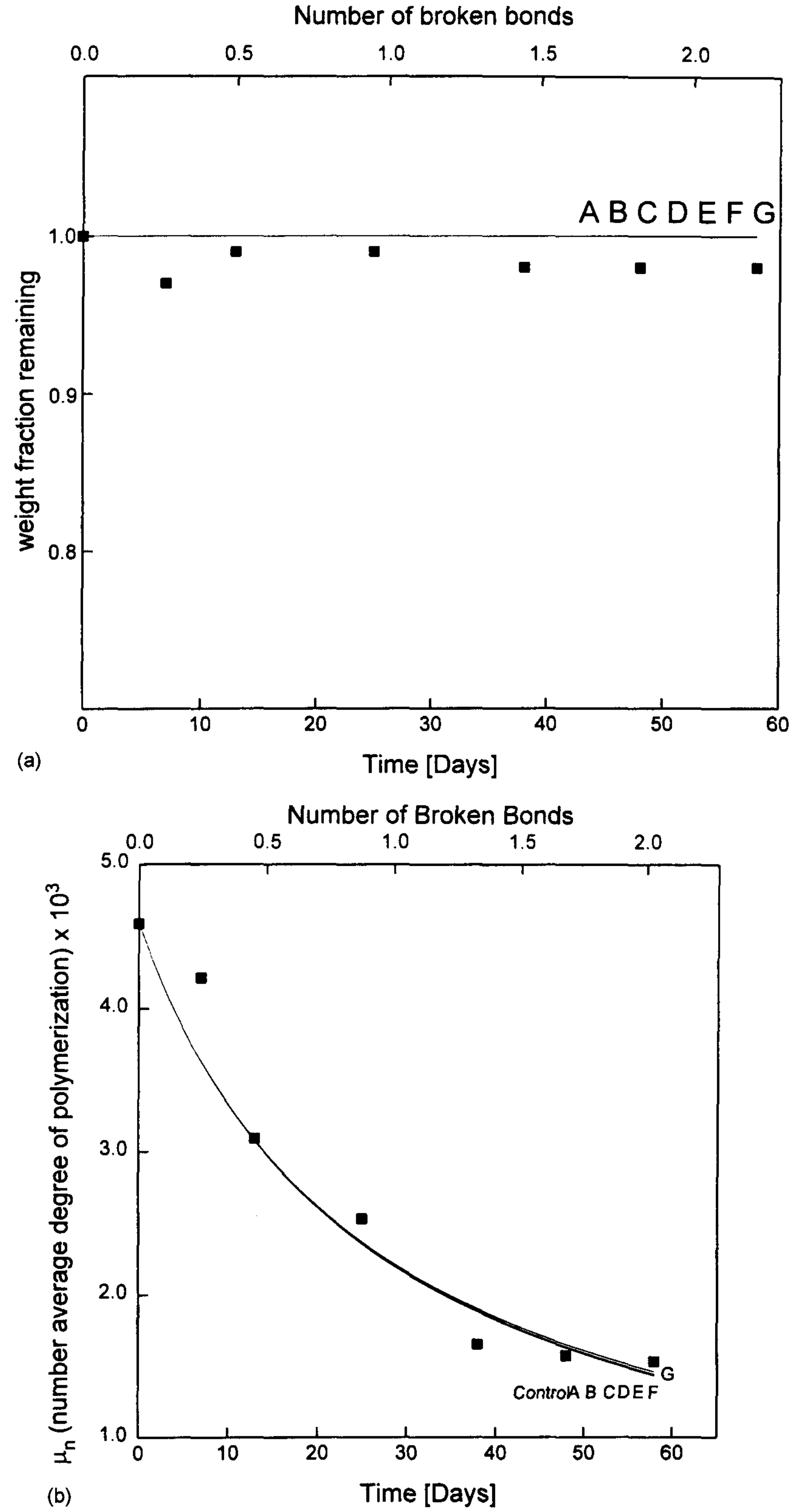


Figure 2 Weight (a) and the number-average degree of polymerization (b) of P(3HB-*co*-10 wt%-4HB) subjected to hydrolysis at 55°C and pH 7.4 (■: data taken from Doi *et al.*'s work[10]). Degree of polymerization of water-soluble oligomer: $A = 1$, $B = 2$, $C = 3$, $D = 5$, $E = 10$, $F = 20$ and $G = 60$. Control includes the extractable substances

reached only 2. *Figures 2a* and *b* clearly demonstrate that as long as the number of broken bonds is low (that is, around 2), the change in weight or the number-average degree of polymerization is somewhat independent of the presence of the water-soluble oligomers. Indeed the experimental results in *Figure 2* are in good agreement with our model predictions. A majority of the papers dealing with the hydrolytic degradation investigated the weight change up to a point where the number of broken bonds is not very high. Therefore, they found that the weight change due to hydrolysis was not significant[10,15]. Doi and his collaborators, however,

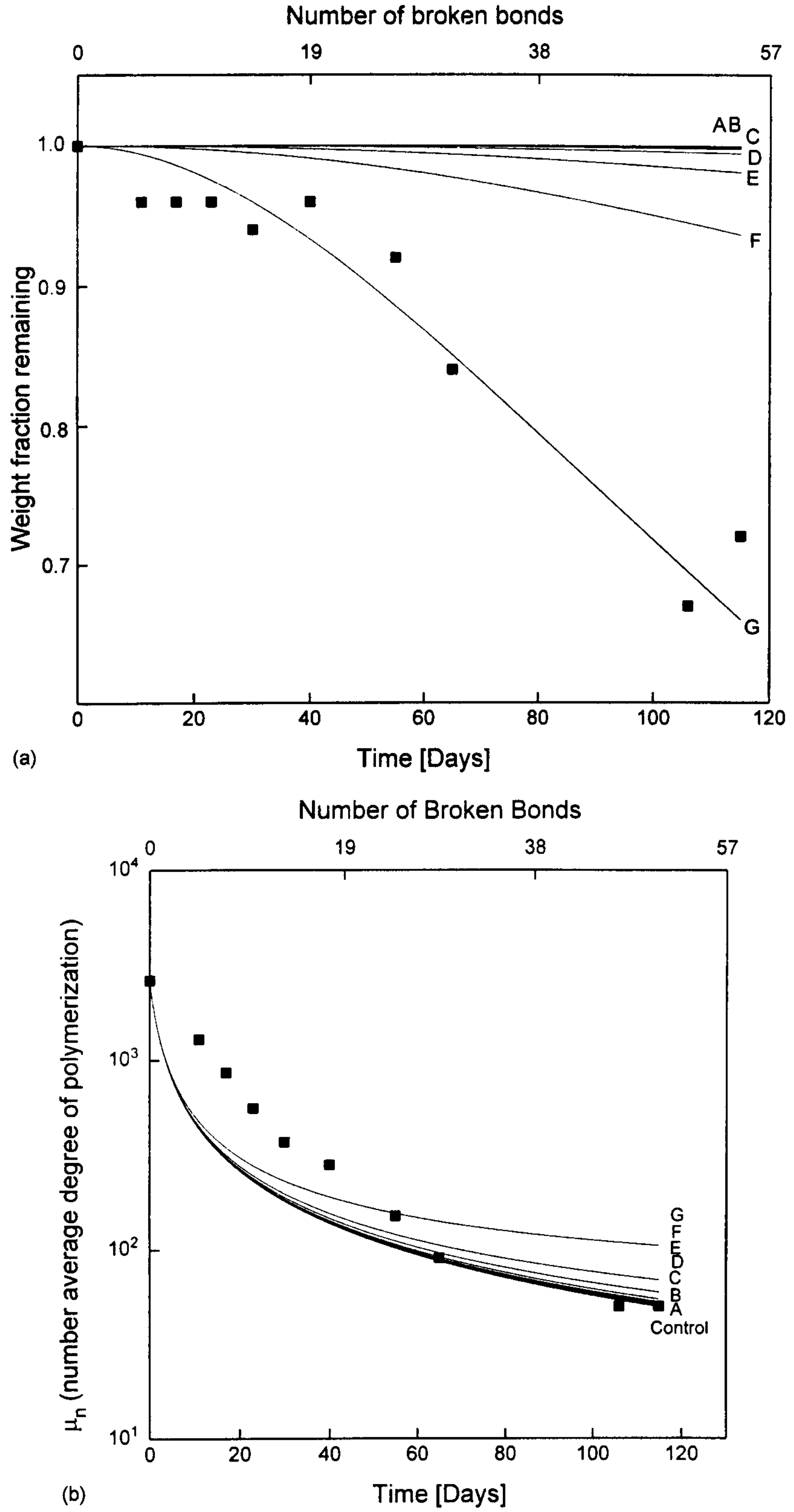


Figure 3 Weight (a) and the number-average degree of polymerization (b) of P(3HB-*co*-9 wt%-4HB) subjected to hydrolysis at 70°C and pH 7.4 (■: data taken from Doi *et al.*'s work[14]). Degree of polymerization of water-soluble oligomer: $A = 1$, $B = 2$, $C = 3$, $D = 5$, $E = 10$, $F = 20$ and $G = 60$. Control includes the extractable substances

studied the hydrolytic degradation of P(3HB-*co*-9 wt%-4HB) at pH 7.4 and 70°C until the number of broken bonds reached 55[14]. Their results are compared with our theoretical calculations using equations (8) and (10) in *Figure 3*. Calculation required the degradation rate constant which was obtained by the least square analysis using their experimental data[14]. In *Figure 3a* it should be noted that equation (8) can effectively predict the weight change of P(3HB-*co*-9 wt%-4HB), only if the oligomers, whose degree of polymerization are up to 60, are water-soluble. However, when the calculated number-average degree of polymerization is compared with the

Table 1 Alkali hydrolysis (10% NaOH w/v, 80°C) of poly(L-lactic acid-*co*-glycerol)[9]

LLA/GL mole ratio	$\bar{M}_n \times 10^{-4}$		$\bar{M}_n \times 10^{-4}$		Weight loss (%)	
	5 h	40 h	5 h	40 h	5 h	40 h
100/0	4.1	4.0	8.3	8.5	2.6	13.0
100/1	1.2	0.9	2.1	2.0	3.9	19.6
70/1	1.1	0.9	2.3	2.2	5.5	33.9
40/1	0.86	0.72	1.5	1.3	6.4	45.8
20/1	0.68	0.53	1.0	1.1	10.3	56.2
10/1	0.49	0.38	0.67	0.65	13.0	63.5
3/1	0.13	0.10	0.16	0.18	19.6	78.0

experimental data in *Figure 3b*, the agreement is very poor. Here, the number-average degree of polymerization was obtained for the insoluble portion of the sample and the oligomers with $\mu_n \leqq 60$ were assumed to be completely dissolved. In reality, the degree of polymerization of water-soluble P(3HB-*co*-9 wt%-4HB) oligomers is expected to be far less than 60. Thus the decrease in the sample weight was caused by not only the dissolution of the low molecular weight oligomers but also the fragmentation of the film into many small pieces. For thick samples autocatalytic effect accelerating hydrolysis can be induced by the formation of α,ω-hydroxy acids in the bulk as a result of hydrolysis and by the concomitant decrease in pH in the neighbourhood[13]. In that case the weight change in the hydrolytic degradation might occur much faster than it is predicted to occur by homogeneous random chain scission model. However, in *Figure 3* the autocatalytic effect was believed to be minimal because 70 μm thick films were used by Doi *et al.*[14]. It is also possible that bonds near the end of the chain have greater reactivity than those in the centre, hence violating the random chain scission model[16].

Table 1 summarizes the hydrolysis results poly(L-lactic acid-*co*-glycerol) obtained by Arvanitoyannis *et al.*[9]. The number-average and weight-average degree of polymerization of P(LLA-*co*-GL) changed very little with time irrespective of the copolymer composition, while the weight changed significantly with degradation time. When compared with P(3HB), P(HB-*co*-4HB), or P(3HB-*co*-3HV), the degree of polymerization of water-soluble oligomers of P(LLA-*co*-GL) is believed to be much higher. In *Figure 1b* the decrease in the number-average degree of polymerization became smaller as the degree of polymerization of water-soluble oligomers increased. The average molecular weight of P(LLA-*co*-GL) changed very little with time in *Table 1*, even though the average degree of polymerization was relatively high. Since the hydrolytic degradation of Arvanitoyannis *et al.* was done in basic condition[9], the hydrolysis rate was so fast that hydrolysis occurred preferentially on the sample surface to bring about the decrease in weight. However, in the bulk of the sample hydrolysis occurred negligibly and so the average molecular weight remained nearly constant.

Figure 4 plots the weight fraction of the monomer unit in monomer, dimer, trimer, tetramer, pentamer, and decamer ($k[P_k]/\lambda_1$) vs the extent of the hydrolytic degradation. Monomer weight fraction increased monotonically to 1, as the number of broken bonds approached $\mu_{no} - 1$. The weight fraction of the oligomers longer than monomer slowly increased to a maximum and decreased to 0. The number of broken bonds required to reach the maximum weight fraction decreased as the degree of polymerization of the oligomer increased. Oligomer weight fraction was dependent upon the initial number-average degree of polymerization and the degradation reaction rate constant. However, if the oligomer weight fraction is plotted against the number of broken bonds per initial number

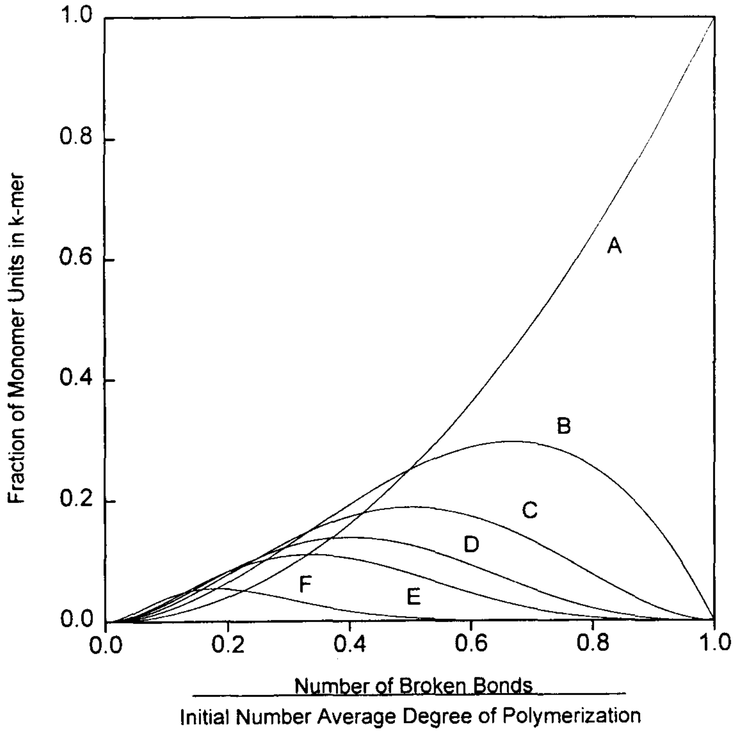


Figure 4 Weight fraction of monomer in oligomers produced during hydrolysis. Degree of polymerization of water-soluble oligomers: $A = 1$, $B = 2$, $C = 3$, $D = 4$, $E = 5$, $F = 10$

average degree of polymerization, the effect of the initial number-average degree of polymerization and the degradation rate constant can be neglected and the same curves as in *Figure 4* are obtained.

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